

**The Atmospheric Chemical
Vapour Deposition Of Coatings
On Glass.**

by

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Abstract:

The deposition of thin films of indium oxide, tin doped indium oxide (ITO) and titanium nitride for solar control applications have been investigated by Atmospheric Chemical Vapour Deposition (APCVD).

Experimental details of the deposition system and the techniques used to characterise the films are presented. Results from investigations into the deposition parameters, the film microstructure and film material properties are discussed.

A range of precursors were investigated for the deposition of indium oxide. The effect of pre-mixing the vaporised precursor with an oxidant source and the deposition temperature has been studied. Polycrystalline In_2O_3 films with a resistivity of $1.1 - 3 \times 10^{-3} \Omega \text{ cm}$ were obtained with $\text{In}(\text{thd})_3$, oxygen and nitrogen.

The growth of ITO films from $\text{In}(\text{thd})_3$, oxygen and a range of tin dopants is also presented. The effect of the dopant precursor, the doping concentration, deposition temperature and the effect of additives on film growth and microstructure is discussed.

Control over the preferred orientation growth of ITO has been achieved by the addition of acetate species during film growth. Insitu infra-red spectroscopy has been used to identify the gas phase species and identify the species responsible for the film modification. ITO films with a resistivities of $1.5 - 4 \times 10^{-4} \Omega \text{ cm}$ have been achieved.

The deposition of titanium nitride by the APCVD of $\text{Ti}(\text{NMe}_2)_4$ and a mixture of $\text{Ti}(\text{NMe}_2)_4$ and ammonia is reported. Contamination of the films and pre-reaction between the precursors in the gas phase is discussed, and the synthesis of new precursors for the deposition of titanium nitride is reported.

New precursors have been synthesised under anaerobic conditions and characterised by infra-red spectroscopy, ^1H and ^{13}C NMR, mass spectrometry, thermal gravimetric analysis and three by single crystal X-ray diffraction.

Deposition of titanium nitride utilising two new precursors is reported.

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Abbreviations Used:

acac	2,4-pentanedione
AFM	Atomic Force Microscopy
APCVD	Atmospheric Pressure Chemical Vapour Deposition
BuOAc	Butylacetate
CVD	Chemical Vapour Deposition
DBTDA	Diacetatodibutyltin
DMT	Dichlorodimethyltin
DMTDA	Diacetatodimethyltin
FTIR	Fourier Transform Infra Red Spectroscopy
ITO	Tin Doped Indium Oxide
NMR	Nuclear Magnetic Resonance Spectroscopy
PVD	Physical Vapour Deposition
SEM	Scanning Electron Microscopy
SV	Set Point
TCO	Transparent Conducting Oxide
TGA	Thermal Gravimetric Analysis
thd	2,2,6,6-tetramethylheptanedione
THF	Tetrahydrofuran
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

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1. Introduction

1.1 Background

With the use of ceramic materials many new applications in both the electrical and optical industries have been developed, including high Tc superconductors such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, piezo electrics such as BaTiO_3 and titania based materials for optoelectrical purposes.¹ Many of these new ceramics are still in the development stage and are being designed to fulfil the future requirements of a variety of industries from aerospace to electronics. Many of these developing ceramics are based on metal oxides, nitrides, borides and carbides. Due to their many unique combinations of properties, such as mechanical strength, hardness, wear resistance, chemical stability and low density, they present exciting new chemical possibilities. These new materials require strict chemical control of purity and stoichiometry and therefore rigorous and careful preparations are required if their optimum properties are to be achieved.²

In the electronics industry a strong demand for compounds which exhibit high electrical conductivities exists. In many applications, especially in microelectronics, thin film technology is required to build the devices. The use of thin film technology is not only limited to the electronics industry, however, and the optical properties of certain thin films, has lead to an interest in this technology from other industries, e.g. glass manufacturers.

A variety of techniques are available to deposit thin films, and these can be broadly split into two classes:^{3,4}

1. Physical Thin Film Deposition
2. Chemical Thin Film Deposition

Physical methods include evaporation and sputtering. Evaporation involves the transfer of species evaporated from a heated source to the substrate, where condensation of the species and subsequent film formation occurs. This transfer is carried out under vacuum conditions of around 10^{-5} torr. A variety of materials can be deposited using this

technique, e.g. metals, alloys, oxides and nitrides, and resistive heating of the species to be evaporated is usually sufficiently efficient. Problems with this technique include interaction of the evaporant with materials in the reactor, and also alloys rarely evaporate concurrently and thus films result which are richer in the more volatile constituent.

Sputtering is also carried out under vacuum conditions and involves the bombardment of target materials with energetic particles of the positive ions of heavy neutral gases such as argon. This bombardment results in a number of surface processes, including the ejection of surface atoms from the target, which can then condense on a nearby substrate to give a thin film of the target material. The methods by which the bombarding species are produced include creating a glow discharge between electrodes (where one electrode is the target), and direct formation of ions using an ion gun. As with evaporation a wide variety of species can be deposited using this technique, such as metals, metal oxides and nitrides.⁵

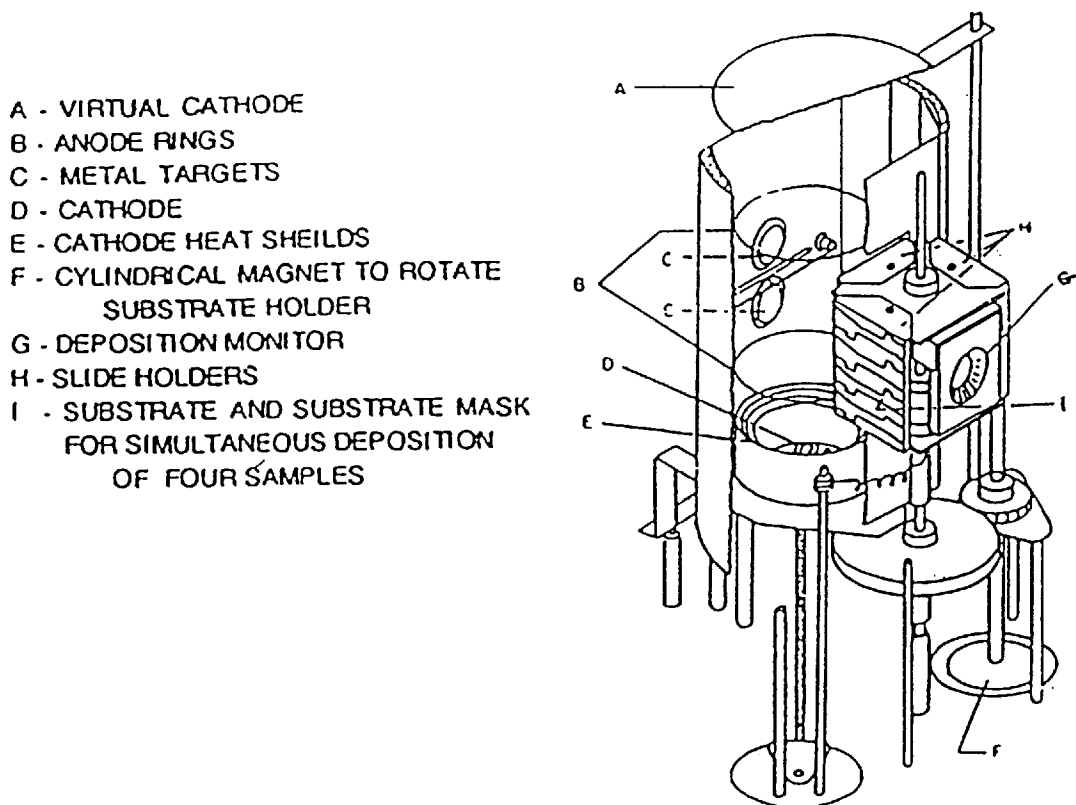


Figure 1-1 Diagram Of A Typical Sputtering Reactor.⁵⁴

Newer techniques have developed based around these two physical deposition techniques such as molecular beam epitaxy, which is a ultra high vacuum (UHV, 10^{-10} torr) technique and involves the generation of molecular beams of various layer constituents. However, all these techniques are very expensive due to the large amounts of specialist vacuum equipment associated with them.⁶

A wide number of chemical deposition techniques also exist. The most basic of these is thermal growth, whereby thin films usually of oxides or nitrides are deposited onto a heated substrate. An example of this technique is the deposition of SiO_2 which is routinely deposited onto Si in the semiconductor industry by this method.⁷

Sol-gel is another chemical deposition technique that is widely used. This method consists of dipping a substrate into a sol, which is a solution containing the constituents of the film in a metastable suspension. The substrate is then withdrawn from the sol and the film is allowed to gel via reaction with the atmosphere (usually a hydrolysis step). Subsequent processing of the film by drying and then heating to densify the material is then carried out. A variety of materials such as TiO_2 can be prepared by this method. Sol-gel derived films are relatively cheap to prepare, but problems with film uniformity and the requirement for large amounts of solvent in the process, are two of its biggest disadvantages.⁸

Anodisation and electroplating which involve the transfer of ionic species to and from electrodes immersed in an electrolyte are two other chemical deposition techniques. Anodisation is carried out under aqueous conditions resulting in oxide growth whereas electroplating is used for the deposition of metallic elements. The major disadvantage of this technique arises from the cost of the large amount of electricity required.⁹

One of the most important chemical deposition techniques is chemical vapour deposition (CVD). Chemical vapour deposition can be split into several types: ultra high vacuum chemical vapour deposition (UHVCVD), low pressure chemical vapour deposition (LPCVD), and atmospheric pressure chemical vapour deposition (APCVD). As their names suggest, UHVCVD and LPCVD are carried out under vacuum conditions and this means that the techniques are expensive, requiring specialist vacuum apparatus similar to that required for sputtering. Atmospheric pressure CVD, however, is not done under vacuum, but just under the flow of gases. This results in the technique being:^{10,11,12}

1. Relatively cheap
2. It can be used as an on-line (i.e. continuous process) technique as no vacuum is required.

The method involves the transport of a vaporised or gaseous precursor over a heated substrate, onto which the film deposition occurs. The technique is described in more detail below.

1.2 Chemical Vapour Deposition:

Chemical vapour deposition involves a change in state, i.e. the initial reactant gases or vaporised precursors are changed to another state, i.e. a solid film on the substrate and the gaseous reaction products which are released.

The general steps involved in chemical vapour deposition are described below:¹³

1. Transport of the reactants from a bubbler, or gas cylinder to the reaction zone.
2. Chemical reactions in the gas-phase, leading to a multitude of new reactive species and by-products referred to as intermediates.
3. Transport of the initial reactants or intermediates formed from gas phase reaction to the substrate surface.
4. Adsorption or chemisorption of these species on the substrate surface.
5. Surface diffusion of the adsorbed species over the substrate surface.
6. Heterogeneous reactions on the substrate surface, leading to solid film formation.
7. Desorption of gaseous reaction by-products.
8. Diffusive transport of the gaseous by-products away from the substrate surface.
9. Transport of the reaction products and unreacted chemicals from the reaction zone and to the outlet of the reactor.

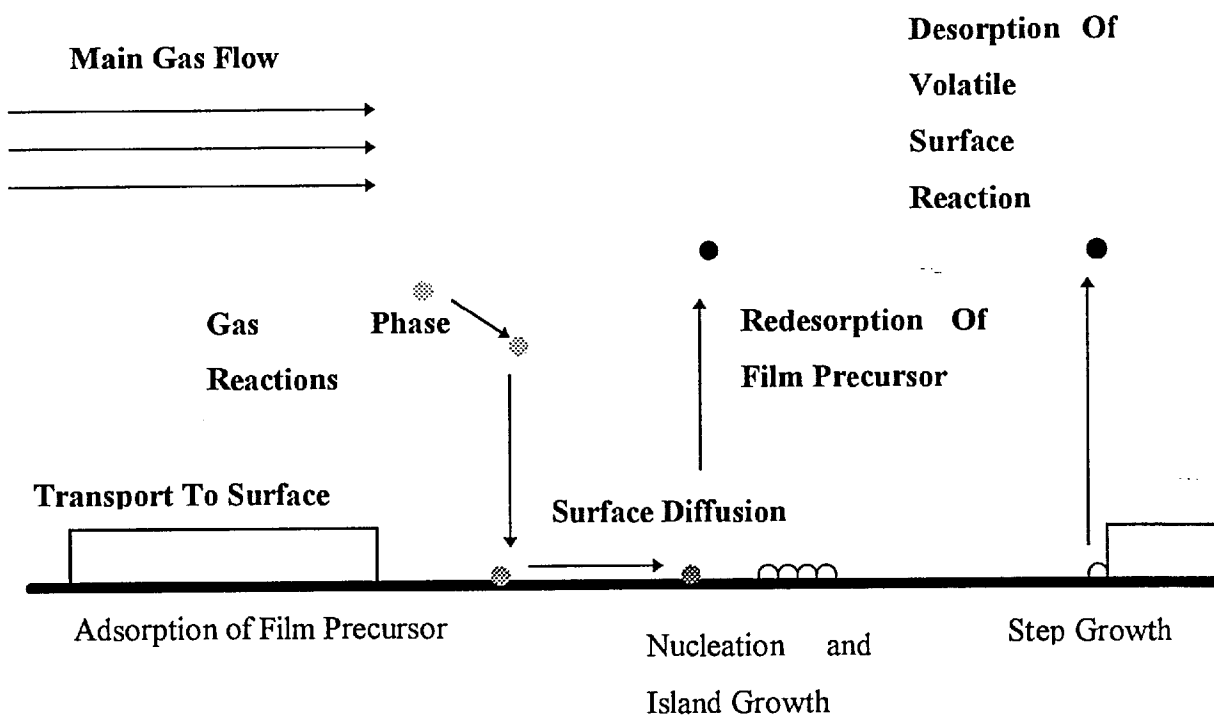


Figure 1-2 Diagram Of Process's Occurring During Chemical Vapour Deposition.¹³

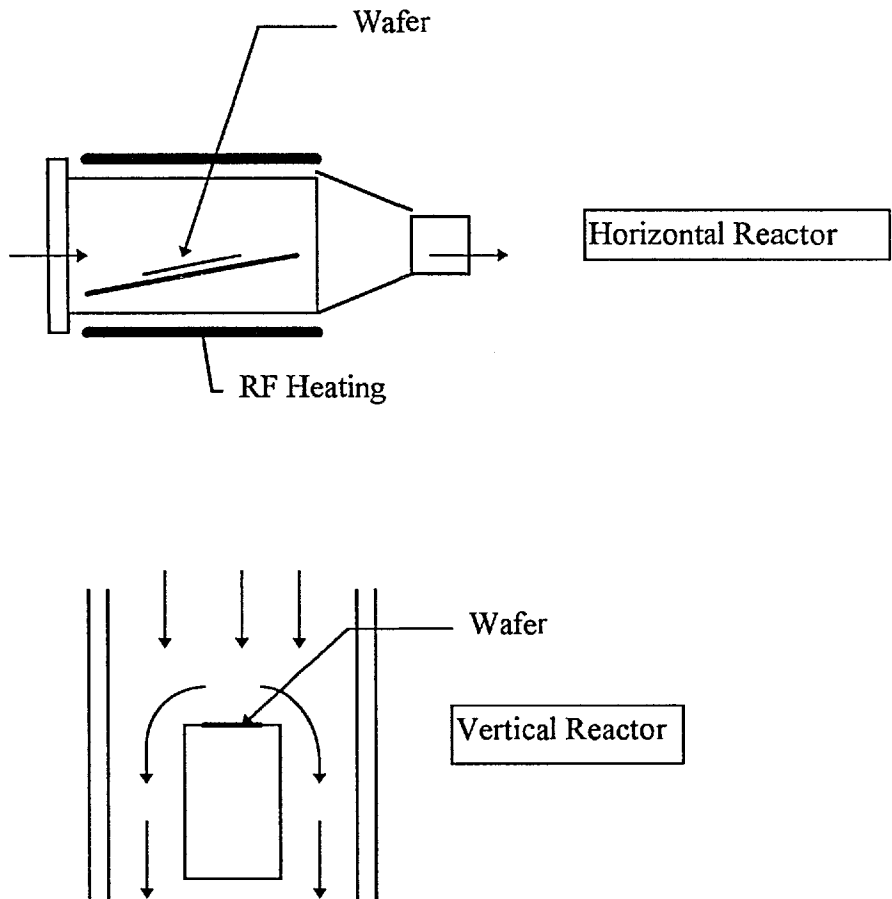
In certain processes the reaction of the chemicals in the vapour phase prior to reaching the surface is avoided, making the processes truly heterogeneous.

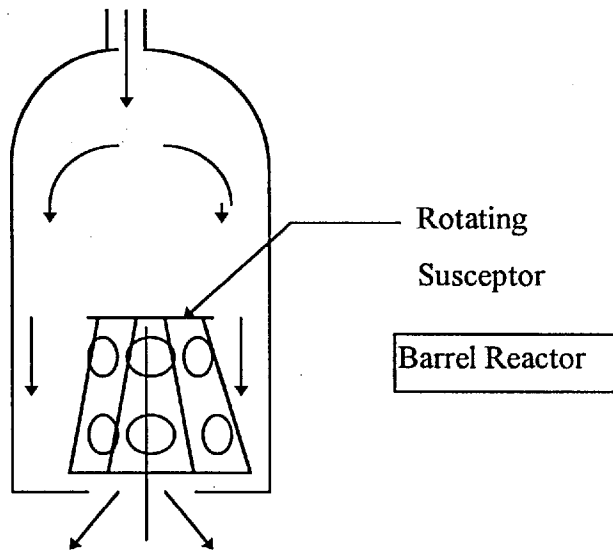
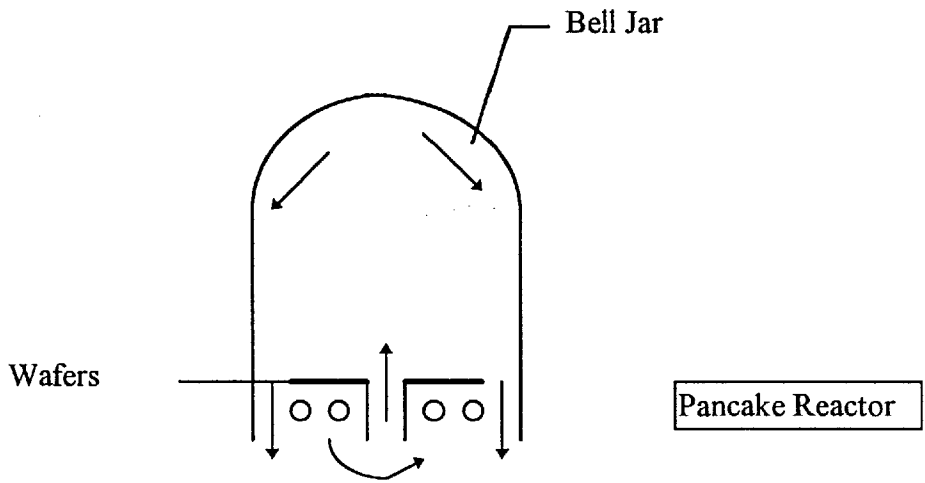
The process requires a precursor, which has a sufficiently high vapour pressure (i.e. is volatile enough) to be picked up in a gas stream and transported in the gas phase to a reactor vessel. This very simplistic view of the CVD process does not completely define the very complex nature of process. In order for uniform film thickness and thin films of uniform composition to be obtained by such a process, the equipment involved is very complex, and factors such as gas hydrodynamics, gas purity, precursor decomposition mechanisms and the solid state processes that occur on the substrate must be taken into consideration.

The precursor transport to the reactor, is determined by the type of source compound used. If a gaseous source material is used, then the material can be delivered direct from the cylinder and metered by flow controllers. If solid or liquid precursors are

used, then a bubbler system is used with a gas flow being used to sweep the precursor into the reactor. The amount of carry-over of the precursor using bubbler delivery techniques depends upon the source temperature, gas flow rate in the bubbler and the total pressure over the source.

The reactor chamber design is also of great importance in chemical vapour deposition. Careful control of the gas flows over the heated substrates must be achieved, if good film uniformity and composition are to be attained. If this is not achieved the onset of turbulence in the reactor can affect both the film uniformity and composition. A range of reactor configurations have been reported in the literature and some of these are illustrated in Figure 1-3.





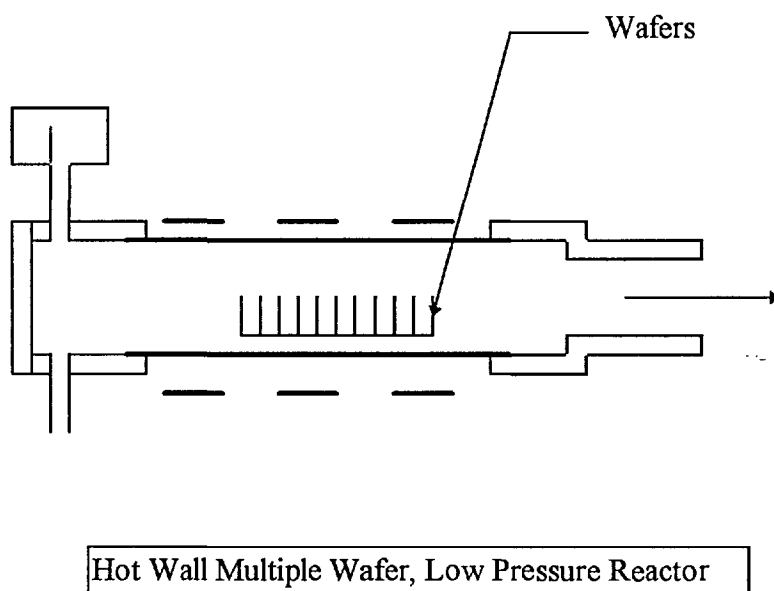


Figure 1-3 Diagrams Of Typical Reactor Chamber Designs Used in Chemical Vapour Deposition.¹³

The horizontal and vertical flow reactors are classical configurations for atmospheric and reduced pressure growth. The barrel reactors are utilised in the growth of GaAs and silicon epitaxy, whilst the pancake reactor is used in other systems where thermal gradients are required in the system to achieve reproducible film growth. The multiple wafer reactor is used at low pressures of approximately 0.5 Torr, and is used to achieve simultaneous growth on a number of substrates.^{14,15}

The initial step in film growth is often the adsorption of the initial precursor or one of the intermediates formed in the gas phase on the surface, and subsequently the precursor reacts to form the solid film. This deposition process can be described by two different mechanisms using general concepts of catalysis:^{16,17}

1. Bimolecular Eley-Rideal Mechanism

The adsorbed molecule reacts directly with a molecule in the gas phase, i.e. only one type of molecule is adsorbed. In this mechanism, the growth rate saturates for high mass transport of the reactant gas or the vaporised precursor.

2. Bimolecular Langmuir-Hinshelwood Mechanism

The precursor and the reactant are adsorbed on the substrate and the reaction takes place between those two adsorbed molecules. The growth rate increases with increasing flow rates of both molecules until a limit is reached. It decreases for larger flow rates, because the species in excess occupies vacant sites which the other molecule would have utilised at lower flow rates.

The resulting growth and microstructure of the coating is determined by surface diffusion and nucleation processes on the growth surface. These processes have been shown to be influenced by the substrate temperature, reactor pressure and gas-phase composition during film growth.¹⁸

Amorphous films tend to be formed at low substrate temperatures (and high growth rates), when the surface diffusion is slow compared with the rate of delivery of the precursor to the surface. At high growth temperatures (and low growth rates), surface diffusion is fast compared with the rate of precursor delivery to the surface, allowing the adsorbed species to diffuse to step growth and form epitaxial layers which replicate the underlying substrate lattice. At intermediate temperatures nucleation occurs at many points on the substrate surface. The adsorbed species then diffuse to islands which grow and eventually coalesce to form a polycrystalline film.

The growth rate of the coating is primarily determined by the substrate temperature, reactor pressure and gas phase composition. The dependence of film growth on these parameters has been most extensively studied for the deposition of GaAs by CVD and Figure 1-4, shows the growth rate dependence on substrate temperature for the deposition of GaAs from trimethylgallium and arsine.

Deposition Rate Variation With Reciprocal Growth Temperature

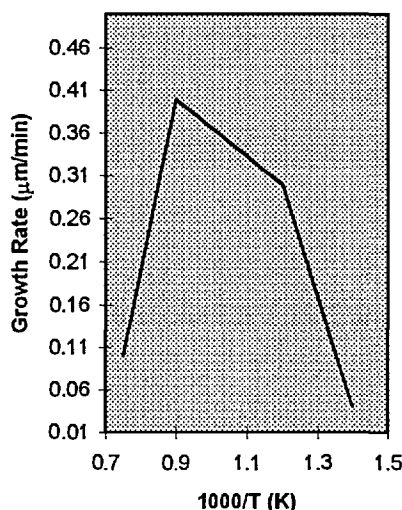


Figure 1-4 Typical Deposition Rate Variation With Reciprocal Growth Temperature (Example Shown Is For GaAs growth From Me_3Ga and AsH_3).¹³

Three growth regimes can be seen to exist for CVD processes:

1. At low temperatures the growth rate is kinetically controlled, with the rate of reaction at the surface determining the growth rate. This implies that the diffusion of the reactive species to the surface is faster than the reaction at the surface to produce the film. In the deposition of GaAs, the reduced growth rate is believed to be a result of either the incomplete pyrolysis of AsH_3 limiting the nucleation or due to cracking of the TMGa being reduced as a result of the low temperature.^{19,20} The increase in growth rate observed as the temperature is increased is consistent with both explanations, with growth increasing as more cracking / pyrolysis of the precursor chemicals occurs.

2. At a certain substrate temperature the growth becomes mass transport limited. Under this regime all the precursor reaching the surface is reacting, and the growth is limited by the transport of the vaporised precursor to the surface. For GaAs growth mass transport limited growth has been observed between 550 and 850°C.²¹
3. As the temperature is further increased decomposition of the precursor occurs in the gas phase prior to reaching the substrate surface. This results in a decrease in growth rate as the decomposition of the precursor leads to less precursor being available for reaction at the substrate surface. In GaAs growth the reduced growth rate observed at temperatures above 850°C, is reported to be a result of homogeneous gas-phase nucleation or premature decomposition.^{22,23} Both processes compete with film growth, depleting the precursor concentration and thus resulting in a diminished growth rate.

Understanding of the way that deposition parameters such as substrate temperature, reactor pressure and gas-phase composition affect film growth, has been crucial in the application of CVD for thin film growth, as the deposition of thin films by CVD need to fulfil a range of requirements if they are to be utilised by industry.

The required properties generally reflect the specific needs of the particular industry. For example in the semiconductor and electronics industries the general requirements for films are:²⁴

1. High purity coatings.
2. Uniform deposition.
3. Good step coverage (conformality).
4. No reaction of the deposited film with the underlying layer.
5. Low stresses in the film.
6. Minimal particulate generation and inclusion in the film.
7. Good adhesion of the film.
8. Economic use of reactants.

A vast range of materials are now widely deposited by CVD for the semiconductor and electronics industries. Due to the nature of this industry slow growth rates and expensive starting materials can be tolerated if the demand for the product exists, and there is little limitation on the type of CVD used, with both LPCVD and APCVD being used. Examples of some of the deposited films and their applications are shown in the Table 1-1.

Table 1-1 Materials Deposited By CVD.

General Type of Material	Type of Layer	Examples
Conductors	Metals	Al, ^{26,27} Cu, ²⁸ W, ^{29,30} Ta, ³¹ Mo. ³²
	Silicides	MoSi ₂ , TaSi ₂ , TiSi ₂ , ⁴⁶ WSi _x
	Doped Semiconductors	P/Si, B/Si
	Transparent	In ₂ O ₃ , SnO ₂ ³³⁻³⁵
	Superconductors	YBa ₂ Cu ₃ O _{7-x} , ³⁶ Bi-Sr-Ca-Cu-O, Tl ₂ Ba ₂ Ca _{n-1} Cu _n O _{4+2n} . ²⁵
Semiconductors	Elemental	Si, ³⁷ Ge
	III-V	GaAs ³⁸
	II-VI	ZnS, CdTe, ZnSSe ⁴⁵
	IV-IV	SiC ³⁹
Insulators and Dielectrics	Single Oxides	SiO ₂ , ^{40,41} Al ₂ O ₃ , TiO ₂ ^{42,43}
	Mixed Oxides	Aresenosilicate Glasses, Borosilicate Glasses, Phosphosilicate Glasses, Aluminosilicate Glasses
	Nitrides	Si ₃ N ₄ . ⁴⁴
	Oxynitrides	Si _x O _y N _z

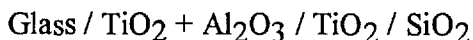
As a result of the wide range of materials that can be deposited by CVD, there is a great deal of interest in CVD deposition of other coatings for other industrial applications, for example the use of CVD to deposit wear resistant coatings such as metal carbides, borides and nitrides on tool bits, and the deposition of optical coatings on glass. This last area is of particular importance due to the high volumes of products involved.

1.3 Chemical Vapour Deposition In The Glass Industry:

CVD of thin films on glass is of particular importance as the function of the glass can be modified by the application of a range of thin coatings on the glass. Whilst glass in its standard (flat glass) form is a useful material with its transparency to visible radiation, the addition of coatings can greatly expand its uses. A range of coatings can be applied to glass to serve a range of applications:

1.3.1 Anti-Reflection Coatings:

Soda lime glass produced in sheets by the Float Glass Process has approximately 4% reflection from each face. Whilst this does not prevent its use in applications such as shop windows, this reflection can reduce its appeal for applications such as picture glasses. By the addition of anti-reflective coatings this reflection can be significantly reduced. Anti-reflection coatings usually consist of alternate layers of high and low refractive index coatings e.g. $\text{TiO}_2/\text{SiO}_2$.⁴⁸ At present no such coating is commercially put down by on-line CVD, but Schott glass plc. deposit a sol-gel derived coating which consists of:



Where / signifies an interface between the two materials.

1.3.2 Liquid Crystal / Electrochromics:

The “Smart Window” would be a glazing unit that would enable a variable degree of transparency to be achieved depending upon external conditions. At present two possibilities exist for such coatings:

a. Liquid Crystal Smart Windows:

This consists of two pieces of glass each of which have electrically conductive coatings. Sandwiched between these two glass plates is a polymer which contains a dispersion of liquid crystals. This polymer can change between transparent and translucent. The change between translucency and transparency is caused by polarisation

of the liquid crystal molecules dispersed in the polymer. The polarisation is obtained by the application of an electric field. The liquid crystals have an ordinary refractive index when the crystals are perpendicular to their symmetry axis, but have a high refractive index parallel to this axis. When unpolarised, the optical axes of the droplets are randomly distributed and the system is light diffusive. When polarised, the droplets become parallel to the electric field and the device becomes transparent.⁴⁹

b. Electrochromic Smart Windows:

These are based on the potential for transition metal oxides to change colour reversibly by the extraction or injection of mobile ions. The devices consist of two outer transparent conductors required for setting up an electric field, an electrochromic layer, an ion conductor and an ion storage layer. Colour changes occur when ions are moved from (or to) the ion storage electrode, via the ion conductor, into (or from) the electrochromic layer.⁵⁰ The deposition of the conducting oxides may be achieved by CVD, but the production of the device will be an off line process, due to the need to stack the required layers.

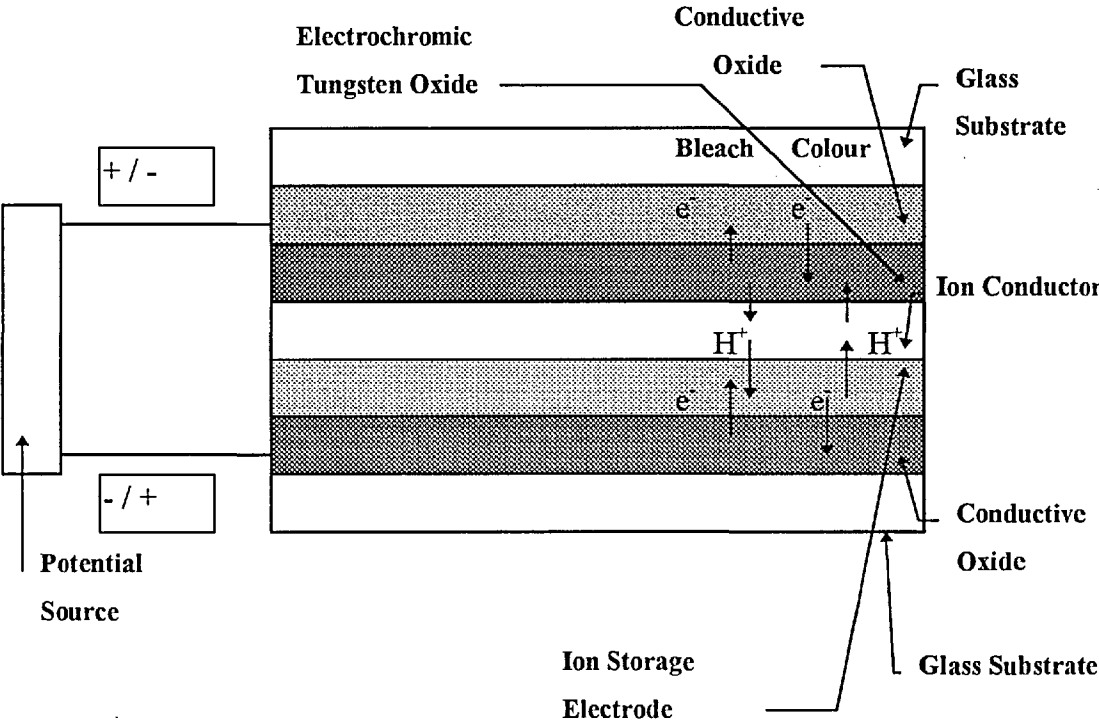


Figure 1-5 Diagram Showing The Construction Of a Typical Electrochromic Device.⁵⁰

1.3.3 Solar Control Films:

Solar control is required where there is a need for a high cooling effect in summer months. Using such coatings it is possible to vary the degree of wavelength selectivity.⁵¹ Ideally such films would:

1. Minimise solar transmittance beyond $0.7\mu\text{m}$
2. Reduce visible transmittance to a level which would provide adequate illumination during daylight hours, whilst limiting the total solar radiant load or have a high transparency to visible light in the case of Clear Solar Control Coatings.

Achieving such properties can be done by:

- a. Increasing the reflectance by use of a single layer with a high refractive index dielectric coating, e.g. TiO_2
- b. Creating an increase in absorption by the use of a single layer absorbing film, e.g. TiN/TiON . However, no wavelength selectivity is possible with such coatings.
- c. Multilayer metal-dielectric coatings which have a selective increase in the infrared reflectance, e.g. Cu, Ag, Au

1.3.4 Low Emissivity Coatings:

Low Emissivity coatings are ideal for cold climate countries. By applying a low emissivity coating, and placing such a piece of coated glass into a double glazing unit, insulation equivalent to triple glazing can be achieved. This can result in a reduction in the energy bill for domestic and industrial buildings.

Ordinary glass has a high emissivity ($E=1-\langle R \rangle$), (where $\langle R \rangle =$ Reflectance) of circa 0.85-0.88. By the application of a low emissivity coatings this can be reduced to <0.3 . The properties required for such a film are high reflectance and therefore low emittance

of room temperature radiation whilst having maximum transmittance over the solar spectral range.⁵² Two types of coating exist for this application:

- a. Extrinsic Semi-conductors, e.g. transparent conducting oxides (TCO)
- b. Multilayer silver based systems

Low emissivity coatings are one of the largest uses of on-line CVD and this technique is employed by many of the worlds glass manufacturers.

The deposition of low emissivity coatings and solar control coatings on-line is therefore of great commercial importance, and improvement of their properties to lower the emissivity and increase the visible transmission is vital.

As mentioned previously the on-line deposition of coatings onto glass substrates is increasing. Deposition on such a large scale, rather than smaller batch processes requires several specific requirements to be met:

1. High efficiency of conversion of reactants to solid film.
2. Very high growth rates (at least a factor of ten better than any current semi-conductor process).
3. Film properties including electrical properties and film durability
4. Low haze levels, i.e. low particulate formation, low surface roughness.
5. Low cost precursors.

In large scale CVD on glass substrates, thin coatings are being deposited on a continually moving glass substrate, which is being produced on a float line. As the glass is continually moving, technology has been developed to coat the glass as it is produced. As the glass moves across the tin bath, it is coated on the top surface by passing under a coating head. The time spent under the coating head is determined by the speed at which the glass is moving, which in turn is determined by the thickness of the glass being produced.

The deposition occurs on the float line itself and Figure 1-6 shows a typical set-up:

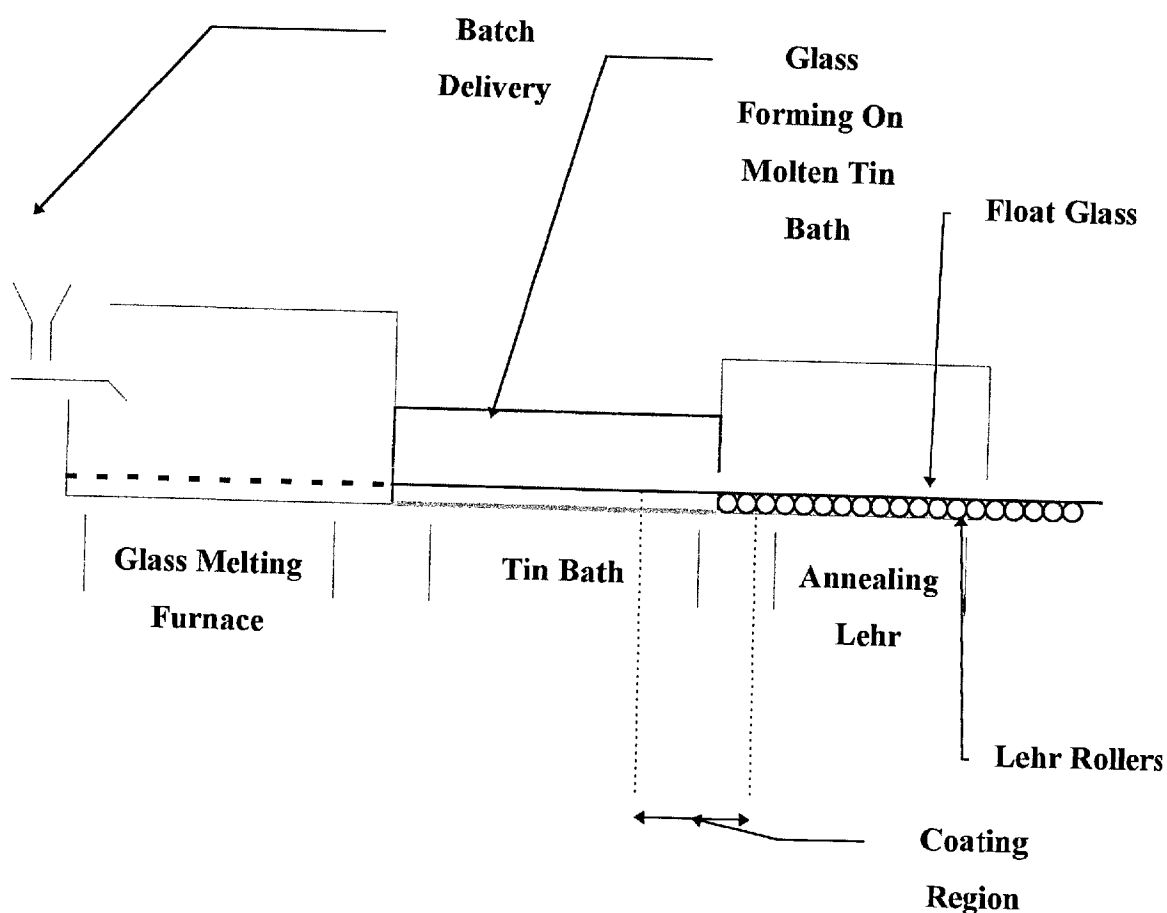


Figure 1-6 Diagram Of A Float Line Production Facility For Glass.⁵³

As the glass has been formed on the tin bath it is coated whilst still at a temperature of approximately 600°C. The glass then cools down as it travels along the Lehr before packaging occurs.

The continual movement of the glass substrate means that the growth rates must be far higher than those used for the deposition of thin films in the semiconductor industry. In the semiconductor industry growth rates are typically several thousand Å per hour, compared with 500-800 Å per second in on-line glass coating. A further complication of this system is that growth must be carried out at atmospheric pressure, due to the high temperatures involved and the physical constraints of a float line.

Therefore all coatings on-line must be deposited by atmospheric chemical vapour deposition (APCVD).⁵³

In order to achieve fast enough deposition of the film in an on-line situation, growth in a mass transport limited growth regime where reaction at the surface is fast compared with the diffusion of the precursor to the surface is preferable, otherwise insufficient film growth is likely to occur in the limited deposition period. This puts two further limitations on the process:

1. The precursors used must have sufficient volatility to deliver enough vaporised precursor to the reaction zone.
2. The kinetics of the process at the surface must be sufficiently fast to allow conversion of the precursor to the required film at a sufficiently high rate.

Efficiency of the process is also important in such a large scale process. If a process is to be economically viable, the conversion of the input chemicals to the product must be relatively high especially if the cost of the precursor is high. In order to achieve high efficiency usage of precursor chemicals turbulent flow systems are poor, with the bulk of the chemicals not reacting at the surface and being swept out of the reactor. A system in which the chemicals mix in the delivery lines leading to the reactor is beneficial as such a system results in more efficient mixing of the chemicals and a laminar flow system can be used. In order to be able to mix the chemicals in the delivery lines, however, the vaporised precursors and carrier gases used in the process must not react or any reaction must not be detrimental to the process. This feature of the process will be discussed in more detail in the design of the equipment along with the types of reactor that can be used.

1.4 Scope Of This Study

The research presented in this thesis, is an investigation of the Atmospheric Chemical Vapour Deposition of coatings on glass such as those used for Low Emmissivity and Solar Control purposes. The deposition of indium oxide, tin doped indium oxide and titanium nitride has been investigated by APCVD. The following chapters describe the apparatus used during the study and the experimental detail.

1.5 References:

1. W. Schauerle, H. U. Shulse, N. Knof and R. Muller, *Z. Anorg. Allg. Chem.*, **1992**, 616, 186
2. J. Williams, *Angew. Chem. Int. Ed.*, **1989**, 28(8/9), 1110
3. D. S. Campbell, *Chapter 2 of Active and Passive Thin Film Devices*, **1978**, Academic Press
4. L. F. Maissel and R. Glang, *Handbook of Thin Film Technology*, **1970**, Sections 1-7, McGraw Hill, New York
5. W. D. Manz, D. Hoffmann and K. Hartig, *Thin Solid Films*, **1982**, 96, 79
6. J. C. Brice, *Crystal Growth Processes*, **1986**, Blackie, Glasgow
7. J. Livage and C. Sanchez, *J. Non-Cryst. Solids*, **1992**, (145), 11
8. C. Sanchez and M. In, *J. Non-Cryst. Solids*, **1992**, (145), 11
9. G. Wang, S. Groves, S. Palnatee, D. Weyburne and R. Brown, *J. Cryst. Growth.*, **1986**, 77, 136
10. C. H. Winter, P. H. Sheidon, T. S. Lewsebandara, M. Heg and J. S. Porscia, *J. Am. Chem. Soc.*, **1992**, **114**, 1095
11. W. Gladfeller, D. Boyd and K. Jensen, *Chem. Mater.*, **1984**, 1, 339
12. R. H. Moss and E. White, *Brit. Telecom Tech. J.*, **1984**, 2(4), 74
13. M. L. Hitchman and K. F. Jensen, *Chemical Vapour Deposition Principles and Applications*, **1993**, Academic Press, London
14. G. W. Cullen, J. F. Corboy and R. Metzl, *RCA Review*, **1983**, 44, 187
15. M. L. Hammond, *Solid State Technol.*, **1988**, 31(5), 159 and 31(6), 103
16. P. W. Atkins, *Physical Chemistry*, **1982**, 2nd Edition, Oxford University Press, Oxford
17. G. C. Bond, *Heterogeneous Catalysis*, **1990**, 2nd Edition, Clarendon Press, Oxford
18. A. Madhukar and S. A. Chaisas, *CRC Crit. Rev. Solid State Mater. Sci.*, **1988**, 14, 1
19. H. Krautler, H. Rochle, A. Escobosa and H. Beneking, *J. Electron. Mater.*, **1983**, 12, 215

20. R. Bhat, *Electronics Material Conference, Santa Barbara CA, 1984*, Paper J-1
21. D. W. Shaw, in *Crystal Growth Vol. 1*, 1978, C. H. C. Goodman eds, Plenum Press, New York
22. W. H. Petzke, V. Gottschalch and E. Butler, *Krist. Technol.*, **1974**, 9, 763
23. M. R. Leys and H. Veenvliet, *J. Cryst. Growth*, **1981**, 55, 145
24. C. Kleijn, *Transport Phenomena In Chemical Vapor Deposition Reactors*, Ph.D Thesis 1991
25. B. J. Hinds, D. B. Studebaker, J. Chen, R. J. McNeely, B. Han, J. L. Schindler, T. P. Hogan, C. R. Kannewurf and T. J. Marks, *J. De Physique IV*, **1995**, 5, C5-391
26. I. P. Herman, *Chem. Rev.*, **1989**, 89, 1323
27. K. F. Jensen and W. Kern, *In Thin Film Processes II (J. L. Vossen and W. Kern, eds.)*, **1991**, 283, Academic Press, Orlando Fl. (Review of various CVD Processes)
28. T. Kodas and M. Hampden-Smith, *The Chemistry of Metal CVD*, Weinham; New York, **1994**
29. J. Ammerlaan, *Kinetics and Characterisation of Tungsten CVD Processes*, Ph.D Thesis, Delf University of Technology, Delft university Press, **1994**
30. J. Schmitz, *Chemical Vapour Deposition of Tungsten and Tungsten Silicides*, Noyes, Park Ridge New Jersey, **1991**
31. F. A. Glaski, *Proceedings IV th Int. Conf. CVD Conf.*, G. F. Wakefield and J. M. Blocher eds., **1973**, 521, Electrochemical Soc. America, Princeton NJ
32. W. Abrams, A. Gerg, S. Gonella, J. Harding and R. Kaplan, *Proceedings of Euro CVD 10*, **1985**, J. O. Carlsson and J. Lindstron eds, Uppsala Univ. Sweden, 293
33. R. G. Livesey, E. Lyford and H. Moore, *J. Phys. E. Ser.*, **1968**, 2.1, 947
34. J. A. Aboaf, V. C. Marcotile and N. J. Chou, *J. Electrochem. Soc.*, **1973**, 120, 701
35. K. Akiyoshu, K. Yamamoto and H. Yoshikawa, *Jpn. Patent 7214593*, **May 1 1972**
36. B. Schilte, M. Maul, P. Haussler, W. Becker, M. Schmelz, M. Steins and H. Adrian, *J. Of Alloys and Compounds*, **1993**, 195, 299

37. Pilkington Pilkington Bros. Ltd., *Ger Offenlagungssehr* 2626118, **December 30 1976**
38. F. Maury, A. Talin, H. Kaesz and R. Williams, *Chem. Mater.*, **1993**, 5, 84
39. J. Brokos, *Chem. Phys. Carbon*, **1969**, 5, 1
40. R. Levy, J. Grow and G. Chakravarthy, *Chem. Mater.*, **1993**, 5, 1710
41. N. Archer, *Proceedings of Conference on Surface, Treatment, Techniques and Processes*, **1982**, Paper 19, 1, Metals Society
42. A. E. Badyer, *U.S. Patent* 2991566, **April 14 1959**
43. Z. Chen, A. Derking, *J. Mater. Chem.*, **1993**, 3(11), 1137
44. R. Gordon, D. Hoffman and U. Riaz, *Chem. Mater.*, **1990**, 2, 480
45. D. Cole, *Chem. In Britain*, **1990**, (September), 852
46. M. Mendicino and E. Seebauer, *J. Of Cryst. Growth*, **1993**, 134, 377
48. I. Chambouleyron and E. Saucedo, *Sol. Energy Mater.*, **1979**, 1, 299
49. L. A. Goodman, *RCA Rev.*, **1974**, 35, 613
50. C. G. Granqvist, *Appl. Phys.*, **1993**, A57, 19
51. G. Frank, E. Kauer and H. Kostlin, *Thin Solid Films*, **1981**, 77, 107
52. C. G. Granqvist, *Arkhimedes*, **1994**, 2, 95
53. R. B. Nikodem, *J. Vac. Sci. Technol. A.*, **1992**, 10(4), 1884
54. H. Bell, Y. M. Shy and D. E. Anderson, *J. Appl. Phys.*, **1965**, 39, 1450

2. Apparatus Design and Description.

2.1 Introduction

The design of the CVD rig has taken into careful consideration the eventual aim of the project, which was to develop an APCVD process for the deposition of solar control and low emissivity thin films onto an on-line float glass coating apparatus. The equipment was designed to give an idea of the potential for coating on-line.

All the In_2O_3 and ITO film depositions were carried out on the same CVD equipment. The TiN / TiON depositions were deposited on a similar system, but designed and built as part of the work program at Imperial College. In any APCVD process consideration of factors such as temperature control, distribution of reactant gases, and powder formation must be made as these can effect the growth rate, uniformity and morphology of the film. The important features of the CVD equipment are described below and their relevance are discussed.

2.2 Gas Handling System:

The equipment is housed in a purpose built extraction hood in order to minimise risk to the user. Due to the toxic and corrosive nature of the chemicals used in the film deposition process, all the pipework was 1/4" stainless steel, with Swagelok couplings. The gases used in the deposition process are monitored using a panel of ten Platon rotameter type flow meters. These allow individual control over the process parameters. Figure 2-1, shows the pipework used in the equipment.

The diagram illustrates a vacuum furnace system for extraction. It features a main horizontal line at the top with a vacuum pump connected to the left. A series of vertical lines branch off from this main line, each leading to a rectangular component (likely a reactor tube or incinerator). These components are connected to a common horizontal line on the right, which then leads to a vertical line labeled 'EXTRACTION'. The system includes various pipe sizes (e.g., 1/2 inch 316, 1/2 inch Monel 400) and a section for a nebuliser, bubbler, or syringe. The diagram is titled 'EXTRACTION' and 'VACUUM FURNACE'.

The apparatus has the capacity to deliver three separate precursors, two by conventional bubbling techniques and the third by utilisation of an evaporator, all using nitrogen gas lines to sweep the precursor into the mixing chamber. Each of the bubblers can be isolated by the use of a shut-off valve placed on the inlet and outlet lines of the bubblers. This prevents leakage of the precursor into the delivery lines when not required. The bubbler delivery lines can also be isolated from the mixing chamber by a shut-off valve placed at the entry of the bubbler line into the mixing chamber. The evaporator consists of a spiralled piece of stainless steel tubing, that is heated and swept with gas. This can also be isolated from the mixing line by the use of a shut-off valve placed at the entry of the evaporator to the mixing chamber. All three of the delivery systems meet at a ½" piece of pipe used as a mixing chamber. This mixing chamber is approximately 50-80cm long. The nitrogen carrier gas and oxygen, are mixed immediately downstream of the flow meters, and then meet the other reactant gases that have already mixed in the ½" mixing line, just prior to a four way valve.

A four way valve is used in the system, to allow the reactor chamber to be either flushed out with pure nitrogen, or to allow the reactant gases to be diverted into the reactor chamber. Whilst heating the equipment, the reactor is constantly flushed with nitrogen in order to prevent oxidation of the carbon block in the reactor. This system also allows the reactant gases to be stabilised prior to coating. Before deposition, the reactant gases can be stabilised by flowing the gases down a waste line. This passes the chemicals through a tube furnace (Carbolite Model) which pyrolyses the chemicals prior to introducing them into the extraction system. In order to ensure complete pyrolysis of the precursor chemicals this waste furnace is held at a constant 700°C. Once stabilisation of the precursor flows has been achieved through this waste line, (typically after 60 seconds), the four way valve can be turned, diverting the reactant gases into the reactor, and the purge gas down the waste line. After deposition has occurred, the four way valve is turned back to its original position, again sending the reactant species down the waste lines. This also has the advantage of flushing out the reactor chamber, as the nitrogen purge gas is diverted back through the reactor and forces any remaining reactants downstream and out of the reactor chamber.

The four way valve used contains teflon inserts and allows rapid change between the reactant and purge gas flows whilst preventing any leakage between the two gas streams.

In order to prevent condensation of any of the precursors in the delivery lines, and to provide sufficient heat to the evaporator each of the gas lines is heated using Eurotherm heater tapes. The delivery lines are each controlled from a separate temperature controller to allow accurate temperature control of the precursors, with a control thermocouple being attached to each of the delivery lines to provide control of the heater tape temperature. Just prior to entry into the reactor chambers the gases pass through a “Baffle Pack”. This is a “tortuous” path type of device and is illustrated in Figure 2-2.

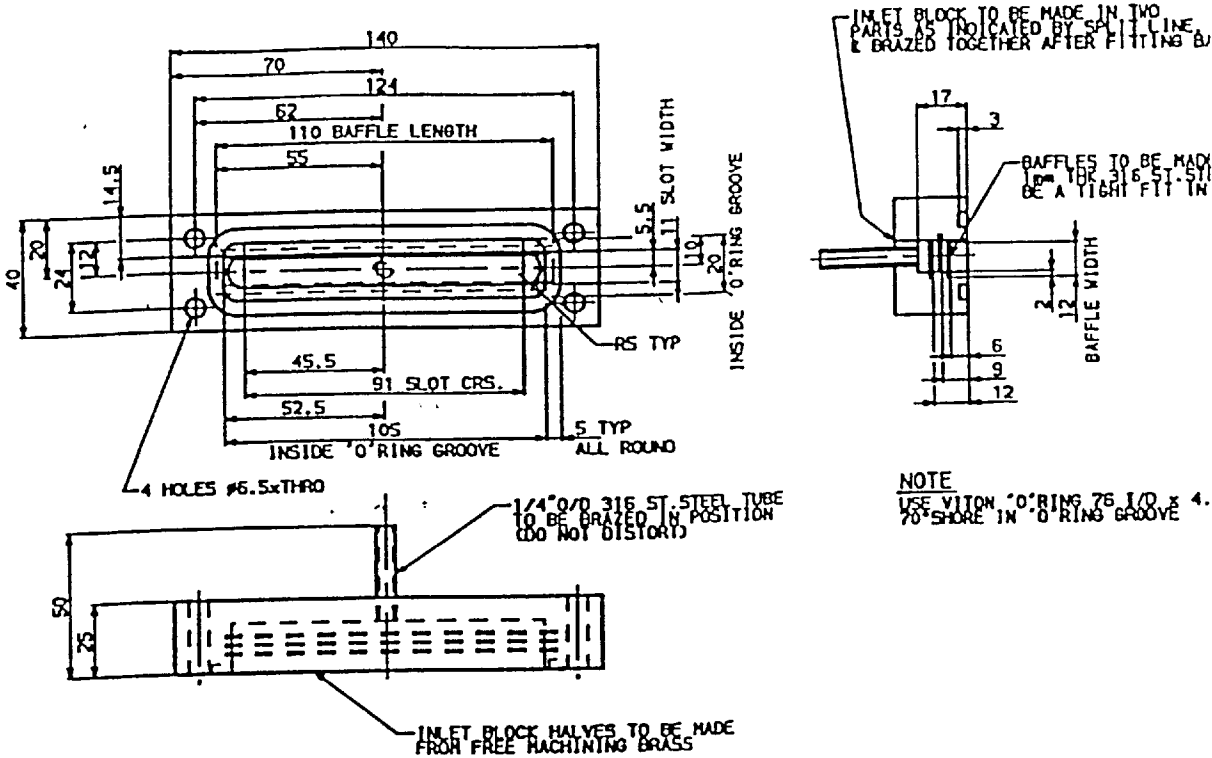


Figure 2-2 Diagram Of Baffle Pack, Gas Distribution Device

By passing the gases through this device, they are spread out so that the velocity of the gases is equal across the 5-7cm width of the baffle exit. The gases then pass into the CVD reactor tube. The mixing of the chemicals prior to delivery to the reactor

chamber is of particular importance, with the precursors all mixing together before they are delivered into the reactor. This mixing of the chemicals in the delivery lines is an important parameter as mixing of the chemicals prior to entry into the reactor, removes the need for the chemicals to be delivered separately and then mixed in the coating chamber. Mixing in the coating chamber would require turbulent flows to exist in order to mix the chemicals and to initiate reaction. If the chemicals are mixed prior to delivery into the chamber a laminar flow system can be utilised where turbulence is deliberately prevented.

The following section describes the reactor chamber.

2.3 CVD Reactor.

The CVD reactor is also designed to emulate the coating of glass on-line. On a float line the glass is moving under a coating head continually and as such is a dynamic system. The CVD reactor used in the course of this investigation is of a static design, but gives an indication of the compatibility of chemicals for the deposition of films on a dynamic system. The temperature at which coatings are deposited was also determined by the necessity to coat glass on-line. On-line processes deposit on the glass as it is formed. The temperature at which the coating is deposited is determined by the temperature of the glass surface at the position of the coating head in the float line, this is estimated at approximately 600°C.

The CVD reactor is of a cold wall design and its components and structure are shown in Figure 2-3.

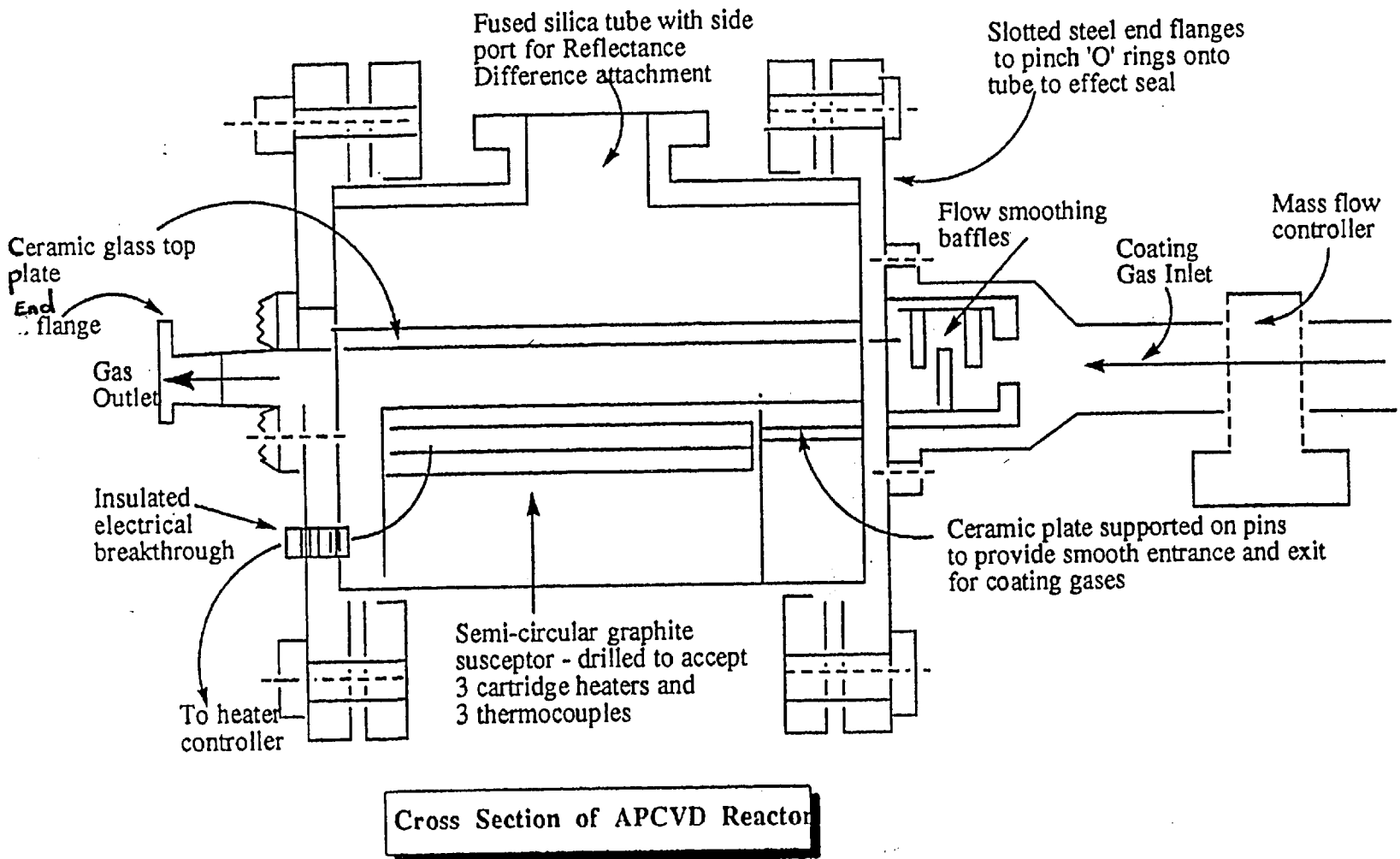


Figure 2-3 Diagram of Components and Construction of Reactor Chamber of CVD Equipment

The reactor chamber consists of a quartz glass tube which has dimensions of:

Length: approximately 330mm
Diameter: approximately 100mm

At each end of the silica tube there are metal flanges which seal the quartz tube. Each metal flange consists of two sections sealed by a sealing Viton O ring, and the two flanges screw together sealing the silica tube. On the entrance flange there are electrical through ports for heating cartridges and the baffle pack is screwed onto this flange. This allows effective gas distribution of the reactant gases into the reactor tube. On the exit flange a fish tail device allows funnelling of the exhaust gases out of the reactor and into the waste line. This exit flange also contains thermocouple junctions for the heating block temperature control. The fish tail exit flange can be removed from the end flanges to allow input and removal of the glass substrate.

The inside of the reactor consists of a graphite block, which contains three Watlow Firerod cartridge heaters each rated at 1600W, and three thermocouple holes. The three cartridge heaters are connected in parallel and the electrical connections pass out through ports in the inlet flange. The heated graphite block holds the glass substrate, and is of a semicircular design with approximate dimensions 230mm long by 100mm wide. The semicircular design allows it to sit in the quartz tube without moving and forms a flat base. At the front end there is a levelling plate, and a top plate which is held by slots in the inlet flange and a hollow circular metal device with slots at the exit end of the reactor, completes a tunnel inside the quartz tube. The tunnel created is of a rectangular cross section with dimensions of:

Height approximately 11mm
Width approximately 100mm
Length approximately 330mm

One of the most crucial aspects in the reactor set-up is the levelling plate at the front edge of the reactor. This is used to complete the tunnel and ensure that there is a level base along the length of the reactor, when the glass substrate of dimensions 9cm x 22cm x 0.4cm is placed on the graphite block. If this is not placed correctly and the glass substrate is higher or lower than the levelling plate, there is no longer a flat base to

the tunnel. This results in non-laminar flow being created inside the reactor and the extra turbulence created may result in particulate formation and poor film deposition.

The heating of the cartridge heaters in the graphite block is regulated by a Eurotherm PID temperature controller, which allows ramping of the temperature at 9°C a minute. Attempts at increasing this ramp rate resulted in thermal stressing of the glass substrate and subsequent glass breakage. A “policeman” is also employed, to ensure user safety by cutting power input if a substrate temperature greater than 700°C is achieved. The control inputs to the “policeman” and temperature controller are supplied from separate thermocouples inserted into the graphite block at approximately 0.2cm below the base of the substrate. The set-point of the reactor is therefore, the temperature at which the graphite block is held. This set-point will always be higher than the temperature of the glass substrate surface due to both heat loss during the radiative heating of the substrate and cooling of the substrate due to a gas flow through the reactor.

This reactor design is described as a cold wall, laminar flow reactor. The cold wall designation is used as only the substrate is heated, and the rest of the reactor wall is cool, only being heated by radiation from the substrate heating. This reactor system provides a good laminar flow, and temperature investigations have been carried out on the reactor to investigate the temperature of the substrate at a range of set-points. This also gives us information about the temperature uniformity of the reactor chamber.

2.4 Temperature Profile Of Reactor:

In order to investigate the uniformity of the substrate temperatures, nine twist wire thermocouples were fixed to a glass substrate using Auto-Stick, a ceramic cement, which was cured with a heat-gun. The wires from the thermocouples were run out of the exit flange of the reactor. This was then placed in the reactor and the reactor set-point increased. The reactor was heated up with a nitrogen gas flow equal to the total gas flow of a normal run. The delivery lines were also maintained at an operating temperature of 180°C to simulate growth conditions, and to ensure the nitrogen gas used was heated prior to entry into the reactor.

Tables 2-1, 2-2 and 2-3 summarise the temperature profile of the reactor. The positions of the thermocouples are shown in the Figure 2-4

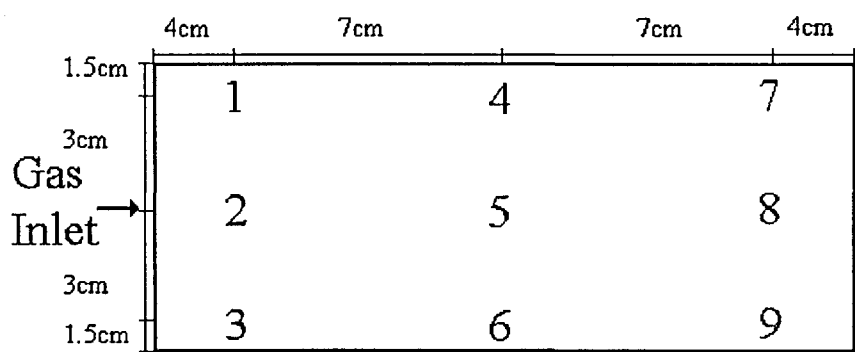


Figure 2-4 Diagram Showing Position Of Thermocouples on Glass Substrate

Table 2-1 Thermocouple Readouts At Set-Point of 565°C, With 6.5 l of N₂ Over Glass

Thermocouple	Temperature 1 min After Attaining Set Point °C	Temperature 5 mins After Attaining Set Point °C	Temperature 10mins After Attaining Set Point °C
1	503	507	509
2	526	529	531
3	495	501	502
4	536	537	537
5	551	552	552
6	534	536	536
7	506	510	510
8	528	530	531
9	504	507	508

Table 2-2 Thermocouple Readouts At Set-Point of 625°C, With 6.5 l of N₂ Over Glass

Thermocouple	Temperature 1 min After Attaining Set Point °C	Temperature 5 mins After Attaining Set Point °C	Temperature 10mins After Attaining Set Point °C
1	560	572	574
2	583	596	598
3	541	557	563
4	592	595	596
5	607	610	610
6	590	596	597
7	559	570	571
8	585	595	596
9	554	568	569

An investigation of the effect of gas flow on the temperature of the glass substrate at a particular set point has also been investigated, with the glass plate being allowed to thermally soak for 10 minutes after attaining the set-point:

Table 2-3 Thermocouple Readouts At a Set-point of 625°C as Gas Flow Varied

Thermocouple	Temperature of Substrate With Flow of 2.5 litres	Temperature of Substrate With Flow of 6.5 litres	Temperature of Substrate With Flow of 11.5 litres
1	584	574	547
2	602	598	580
3	580	563	544
4	598	596	592
5	612	610	604
6	598	597	592
7	572	571	572
8	597	596	595
9	570	569	570

From the results shown above it can be seen that 5-10 mins after reaching the set-point the glass substrate temperature equilibrates. It can also be seen that the set-point temperature is approximately 10°C above the temperature of the centre of the glass substrate at both 565 and 625°C set-points.

The temperature profile of the reactor at a set-point of 625°C is shown in Figure 2-5:

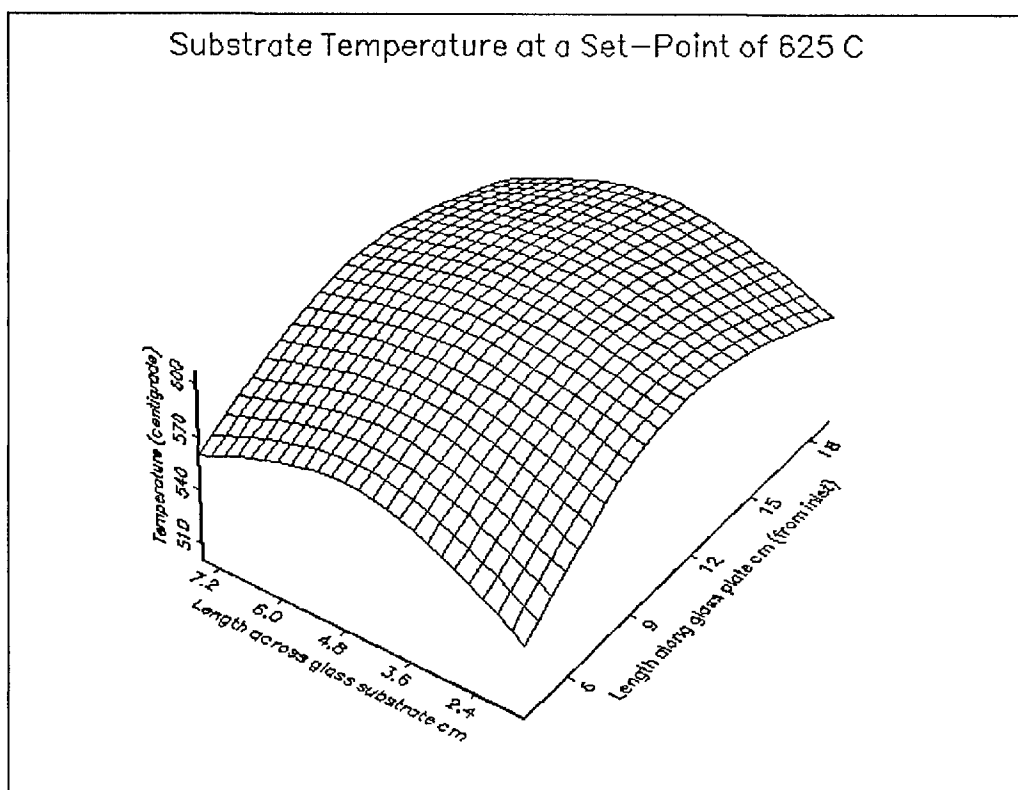


Figure 2-5 Diagram of Temperature Profile Of Reactor at a set-point of 625°C

The lower temperature at the front (i.e. inlet) of the reactor, is most likely due to the cooling effect of the inlet gasses. But the lateral temperature gradient across the 9cm substrate is good at circa 10°C . This lateral temperature gradient, is likely to be due to slight uneven heating of the carbon block, but is unlikely to affect film growth adversely. From 6cm - 20 cm along the glass substrate the temperature is quite uniform with only a small change being observed of circa $8-10^{\circ}\text{C}$.

The temperature of the top-plate, was also measured during the course of these experiments, to determine the temperature difference between the set-point of the reactor, and the top of the reactor. The temperature of the top plate was found to be

approximately 100°C below the substrate temperature at both a set-point of 565°C, and 625°C. This 100°C temperature drop between the top-plate and the substrate is believed to be due to poorer radiative heating of the top-plate due to the air gap present and also due to a cooling effect due to the gas flow through the reactor.

2.5 Reactor Hydrodynamics.

The design of the reactor chamber is of vital importance in obtaining good film growth. In order to get good film growth with efficient use of the precursor chemicals the use of turbulent flow reactors is not ideal. In such systems turbulence is deliberately induced to mix the chemicals and initiate gas phase reaction. If a laminar flow system is used, whereby the chemicals are pre-mixed, far more efficient use of the chemicals is achieved and equivalent if not better film uniformity and growth rates are obtained.

In order to have a laminar flow system, turbulence inside the reactor chamber has to be kept to a minimum. The reactors heating system is an important consideration in reducing turbulence. Whilst hot wall systems can have laminar flow, they are not ideal as deposition occurs on all surfaces and not just the substrate. The system used was therefore a cold wall reactor, where only the substrate was heated.¹

Due to the cold wall design of the reactor there is little temperature variation along or across the substrate, but there is a vertical temperature gradient in the reactor. This arises because the top plate of the reactor is only heated by radiated heat from the heating block. Whilst such a temperature gradient is not ideal, as it could induce convection resulting in a disturbance in the gas flow, such a temperature gradient can be advantageous.

A small temperature gradient in the reactor can produce thermophoresis. The thermophoretic force produced by this effect is advantageous as it results in any powder or particulate matter caused by gas phase nucleation being lifted away from the substrate surface, and prevents incorporation of the particles in the final film.

The Rayleigh(Ra) number is used to characterise convective motion in a reactor tube and thus give an idea of the amount of convection induced turbulence in the reactor.²

$$Ra = Gr \times Pr$$

Where:³

$$Gr = \frac{g \rho_{ref}^2 L^3 (T_h - T_c)}{\mu_{ref}^2 T_{ref}}$$

$$Pr = \frac{\mu_{ref} C_{p_{ref}}}{\lambda_{ref}}$$

Where Gr=	Grashof Number
Pr=	Prantl Number
g=	acceleration due to gravity
ρ_{ref} =	Density of gas at reference temperature assuming that

$$\rho_{ref} = \rho_{298} \times \frac{273}{T_{ref}}$$

μ_{ref} =	Viscosity of gas at reference temperature assuming that
---------------	---

$$\mu_{ref} = \mu_{298} \times \left(\frac{T_{ref}}{298} \right)^{0.7}$$

T_h =	Temperature of Substrate	(898K)
T_c =	Temperature of Top-Plate	(798K)
$C_{p_{ref}}$ =	Heat Capacity of gas at reference temperature	
λ_{ref} =	Heat Conductivity of gas at reference temperature	
L=	Height between substrate and top plate of reactor	(0.01m)

Assuming that the reference temperature is the temperature of the gas stream then:

$$T_{ref} = T_h - \left(\frac{T_h - T_c}{2} \right)$$

$$Ra = \frac{g \rho_{ref}^2 L^3 (T_h - T_c) C_{p_{ref}}}{\mu_{ref} T_{ref} \lambda_{ref}}$$

For a substrate temperature of 625°C and a total gas flow of 5.5 litres/ min, (assumed to be all nitrogen for the purpose of these calculations), this gives the values of:

$$Ra = 293$$

$$Pr = 1.8$$

$$Gr = 163$$

Literature suggests that the onset of convection occurs at a Rayleigh number of circa 2300.³ The reactor has a far lower Rayleigh number than 2300 under the highest flow rates and temperature regime used, suggesting that convection in the reactor is not a significant problem.

Whilst the temperature of the reactor and uniform heating of the substrate are important if uniform films are to be attained, and convection is to be prevented, gas flow dynamics are also important if uniform growth is to be achieved.

As mentioned earlier the reactor was designed as a pre-mixed laminar flow reactor. The laminarity of the flow in the reactor is expressed by the Reynolds number. The Reynolds number must be below 2300 in pipe flow for laminarity.⁴

The Reynolds number for the reactor can be calculated from:⁵

$$Re = \frac{\rho_{ref}VL}{\mu_{ref}}$$

Where L= Linear Dimension = $4 \times (\text{Height} \times \text{Width}) / 2 \times (\text{Width} + \text{Height})$

V= Velocity of Gas (at reference temperature)

For the conditions used for deposition the Reynolds number for the reactor was determined to be 40. This is well below the value of 2300 at which laminarity is lost. It can therefore be assumed that the reactor has a good laminar flow regime under all the growth conditions used.⁶

$$\rho_{848} = 0.439 \text{ Kg m}^{-3}$$

$$\mu_{848} = 370.33 \times 10^{-7} \text{ Kg sec}^{-1} \text{ m}^{-1}$$

$$\lambda_{848} = 24 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-1}$$

Note all at T_{ref} of 848K (Assumed temperature of gas in reactor)

The calculations above, are for the highest temperature and flow rates used during experimentation. As such it can be assumed that behaviour of the reactor during lower temperature and flow rate experiments are also within a laminar flow regime.

The cleanliness of the reactor also has a bearing on film quality. Deposition on the sidewalls and top plate were observed during deposition runs. In order to prevent contamination of the film with particles from these areas the apparatus was routinely cleaned to remove these deposits before they resulted in turbulence or contamination of the grown film.

Apparatus cleaning was carried out by rinsing the reactor tube and top plate in alcohol solvents and dilute acid. Periodically the outer tube and top plate were replaced, when deposits were not easily removed by simple cleaning. Abrasive solvents and etching were not used to clean the tube and top plate as this may damage the polished surfaces of the top plate and reactor tube.

2.6 Substrates:

The coatings have been deposited onto glass substrates containing a coating that had previously been deposited onto the bare glass by an APCVD process. For the purposes of this thesis the glass substrates used will be referred to as undercoated glass. The undercoat layer on the glass has two major roles:

1. It acts as a blocking layer.⁷ Sodium migration in hot glass is a significant problem, with the migration of the sodium to the top surface of the glass resulting in NaCl being observed on the top surface of the glass. This is a particular problem at temperatures above the softening point of glass. Contamination of the glass surface with NaCl is a major problem for coating glass, because haze and deterioration of electrical properties of any subsequent coating is observed. For example in coatings such as F:SnO₂, the sodium can act as a poison for the conduction mechanism of the coating.
2. The undercoat acts as a colour suppressant for the coating. Coatings on non-undercoated glass exhibit a number of interference fringes, as a result of variations in the thickness of the coating. This problem is reduced to an extent by the use of a

colour suppressant. The theory of colour suppression is described in the patent by R. Gordon.⁸

The SEM micrograph in Figure 2-6 shows the colour suppression underlayer. The small lumps visible on the top surface of the coating are due to imperfections in the layer and are likely to be due to NaCl leeching from the glass and disturbing the coating. The composition of the undercoat is shown in the Auger depth profile trace shown in Figure 2-7.

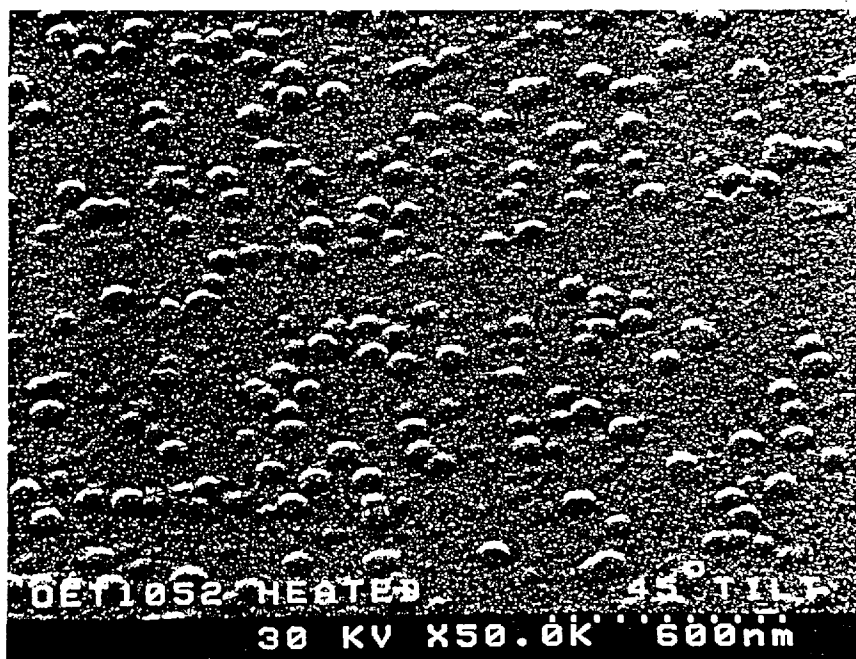


Figure 2-6 SEM Micrograph Of Undercoated Glass Used As Substrates.

Profile: UCASR Scan range: 1 - 20 OET1053 U/C AS REC

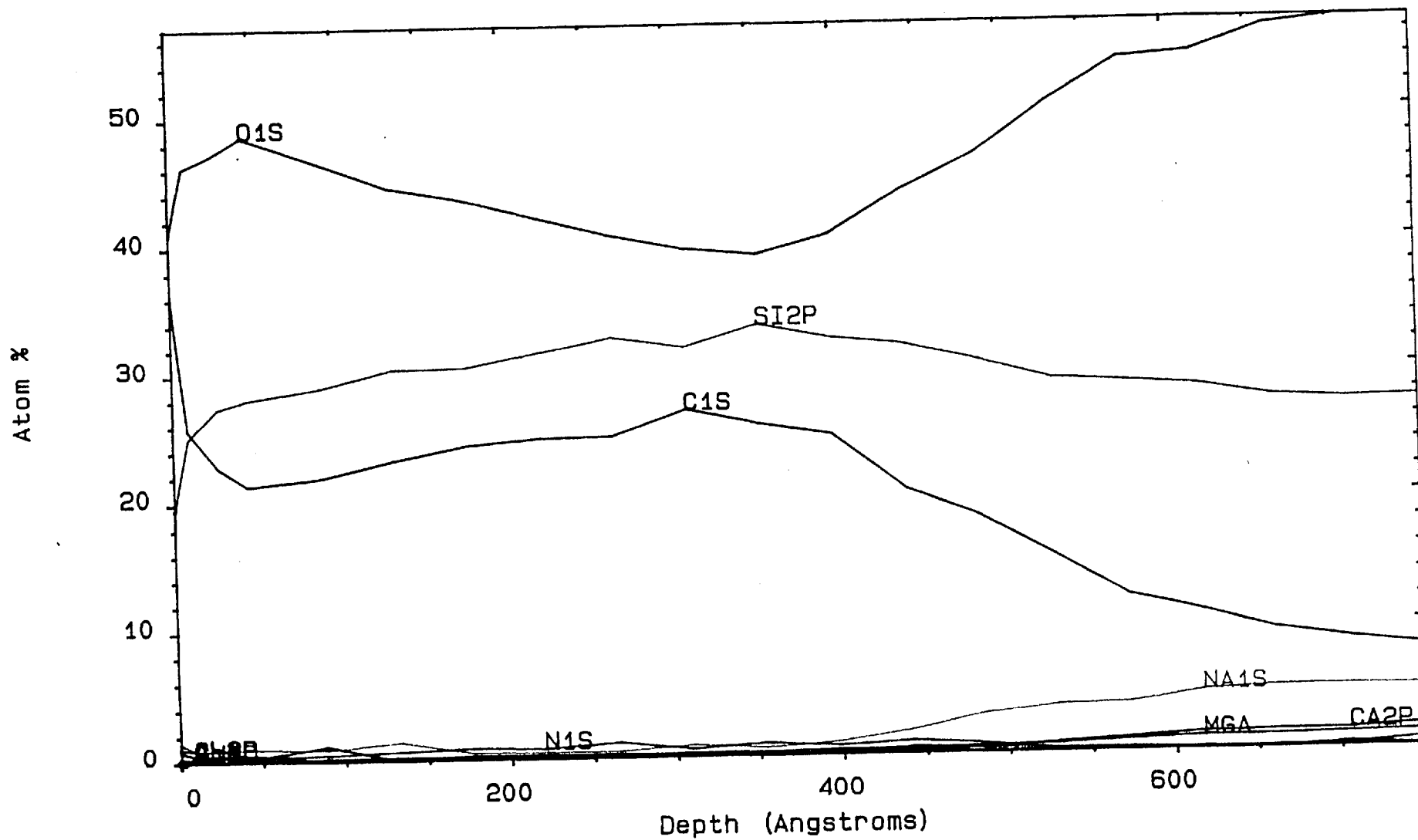


Figure 2-7 Auger Depth Profile Analysis of Undercoat

Confidential

Before coating, the glass substrate had to be prepared and cleaned. The glass substrates used were of dimensions 4mm thick, 220 long and 90 mm wide. The glass substrates were edgeworked to prevent breakage of the glass substrate due to imperfections and stresses.

Cleaning of the glass substrate was carried out in three stages:

1. The glass was soaked in a 0.002% Decon 90 detergent solution with slight agitation of the glass surface being carried out by use of a glove. The detergent solution was then removed from the surface of the glass under flowing tap water.
2. The surfaces of the glass were thoroughly rinsed with deionised water.
3. The surfaces of the glass were rinsed with iso-propanol and the glass substrate was then left to dry.

The cleaned glass substrate was then placed into the reactor chamber, ensuring that the front edge of the glass substrate sat flush up against the levelling plate at the inlet to the reactor.

2.7 Film Analysis:

A standard form of analysis was carried out on each sample grown, in order to get comparable analyses between coatings produced. After removal from the reactor and subsequent cooling to room temperature, circles of 14mm diameter were scribed onto the coating at 1-10cm and 12,14,16,18 and 20 cm from the gas inlet (front) edge of the substrate. These circles were marked as close to the centre of the piece of glass without overlapping. This allowed positions on the film to be known accurately, and also provided small pieces of electrically isolated coating for analysis. This is particularly important for sheet resistance and resistivity measurements.

The piece of glass was then analysed by a variety of methods.

2.7.1 Electrical and Thickness Characterisation:

All coatings grown had the sheet resistance measured within the circles scribed onto the coating. This measurement was done using a 4 point probe. In order to get

accurate sheet resistance measurements it has been calculated that the a 14mm circle of coating must be electrically isolated from the bulk of the film. The four point probe is then used to measure the sheet resistance inside this circle. The sheet resistance is defined as the resistance that would be measured between two electrodes placed on opposite edges of a square of film. It is given the units $\Omega / \square$. In order to get the true sheet resistance, a correction factor is applied to this measured value, this is to account for the distance between the measuring probes not being infinitely small compared with the dimensions of the measured circle.⁹

$$\text{Sheet Resistance} = \text{Measured Sheet Resistance Within 14mm circle} \times 0.9577$$

The bulk resistivity of the film is then calculated by measuring the thickness (d) of the film, and assuming the bulk resistivity is constant throughout the thickness of the coating:

$$\text{Bulk Resistivity} = \text{Sheet Resistance} \times \text{Thickness}$$

In order to measure the thickness of the coating, an etching technique is used. Firstly the film is masked using electrical insulation tape to cover the entire coating, except a 2-3 mm thick line that goes through the centre of the scribed circles at 2,4,6,8,10,12,14,16,18 and 20 cm along the glass plate. An etching solution of zinc dust and 50 % hydrochloric acid is used to etch a line in the coating.¹⁰ This provides a step in the film, on careful removal of the insulation tape. The thickness of the coating at these points on the film is then measured using a Sloan DekTak stylus profilometer. These thickness measurements are then used to calculate the bulk resistivity of the coating at 2,4,6,8,10,12,14,16,18 and 20cm along the coating.

Certain samples are then further analysed to obtain values of the conduction mobility and the number of carriers, by use of the Hall Effect.

2.7.2 Hall Effect Measurements:

Electron density can be found from Hall effect measurements. In this experiment, the sample is placed in a magnetic field with the film surface perpendicular to the faces of the poles of the magnet. A current is passed through the film inducing an electric field

that is perpendicular to both the magnetic field and the current. This transverse field, E, is simply:¹¹

$$E = -\frac{1}{en_e} jB$$

where j = current density and

B = magnetic field strength

The quantity $R_H=1/en_e$, is referred to as the Hall coefficient. In terms of experimentally determined quantities:

$$R_H = \frac{E}{jB} = \frac{V/w}{I/wd B} = \frac{Vd}{IB}$$

In more convenient units this is:

$$R_H (cm^3/C) = \frac{V(mV)d(\mu m)}{I(ma)B(Kg)} \times 10$$

Where, V = measured voltage

I = measured current

w = width of film

The electron density of the film is given by:

$$n_{eH} (cm^{-3}) = \frac{f_H}{eR_H}$$

$$n_{eH} (cm^{-3}) = \frac{1}{1.6 \times 10^{-19} C R_H (cm^3/C)}$$

where f_H is a scattering factor which is 1 for completely degenerate semiconductors). The Hall mobility μ_H which is analogous to the conduction mobility above, and is obtained from:¹²

$$\mu_H = \frac{R_H}{\rho}$$

In order to measure the Hall effect, a square sample of the coating of dimensions 3cm x 3cm was cut out of the substrate at the best position of the film. A template sticker of the type shown in the Figure 2-8 was stuck onto the coated side of the substrate. The template sticker allowed the film to be etched with the required pattern without affecting the rest of the coating. The sample was then etched by sand blasting the coating. This left a template on the coating, with a section of the film being completely etched off. To ensure that the pattern provided an electrically isolated section, an electronic voltmeter was used to check that no conduction occurred across the electrically isolating area of the sample.



Figure 2-8 Diagram of Template Used For Hall Effect Measurement

Electrical connections for the Hall effect apparatus were put onto the film using silver dag paint on the six connection points. This was painted directly onto the coated film.

The film was then placed into the apparatus to supply a current. The current supply was then set at 5mA and an electrometer with an offset nulling control was used to measure the transverse voltage across the film. Before the sample was placed between the poles of the magnet (0.7T), the Hall voltage was then zeroed and the sample put in the magnetic field. The Hall voltage was then recorded. This process was repeated at two different sample currents of 10 and 15mA. Hysteresis was prevented in the magnet by cycling between +1 and -1 T several times before measurements were made. The thickness of the coating, in the Hall Effect region, was examined using Dektak measurements after the Hall Effect measurements had been carried out.

2.7.3 X-Ray Diffraction (XRD).

Samples of coating for XRD were of approximate dimensions 1.5 x 2cm, and were cut from the glass plate to the left or right of the scribed circles.

The X-ray diffraction equipment consists of a Philips PW1130 generator operating at 45KV and 40 mA to power a copper long fine focus X-ray tube. A PW 1820 goniometer fitted with "thin film optics" and proportional X-ray detector is used. The non focusing thin film optics employs a ¼ degree primary beam slit to irradiate the specimen at a fixed incident angle of 1.5°. Diffraction radiation from the sample is collimated with a flat plate collimator and passed through a Graphite flat crystal monochromator to isolate diffracted Copper K α peaks onto the detector. The equipment is situated in a total enclosure to provide radiation safety for the highly collimated narrow beams of X-rays. Data is acquired by a PW1710 microprocessor and processed using Philips APD VMS software on a Micro VAX computer. Crystalline phases are identified from the International Centre for Diffraction Data (ICDD) database held on CD-ROM. Crystallite size is determined from line broadening using the Scherrer equation. The instrumental effect is removed using the NIST SRM660 lanthanum hexaboride standard. These operating conditions are used in preference to conventional

Bragg-Brentano optics for thin films to give an order of magnitude increased count rates from a fixed volume of coating with little contribution from the substrate.

2.7.4 Auger Analysis.

Samples for Auger depth profiling were of dimensions 0.5cm^2 and were cut from within the scribed circles. The samples were examined by depth profiling Auger Electron Spectroscopy on a Kratos machine. Analysis of the coating from the top surface to the glass interface was carried out, with analysis for Na, K, Ca, In, Ti, N, O, S, C being carried out.

2.7.5 X-Ray Fluorescence.

The apparatus used for the analysis is a Philips PW1400 machine fitted with a Scandium Target X-ray tube. The penetration depth achieved on the equipment is between 9 and 10 microns, so the result obtained is throughout the thickness of the coating. The analysis was carried out on an approximate 1 inch square of material and provides an average ratio over an irradiated area of the sample (a 25mm circle).

Theory predicts that the response of indium and tin to XRF analysis using the $L\alpha$ line should be very similar. In order to calibrate the apparatus the response of In and Sn in a 2% by weight sample of SnO_2 and In_2O_3 in glass. This resulted in the counts: In 16.77 Kcps, Sn 16.52 Kcps. These values show that a ratio of the observed countrates, give a good approximation of the weight ratio of the two elements in the coating.

The test is destructive, however, resulting in brown discoloration of the submitted sample.

2.7.6 Optical Measurements.

2.7.6.1 Haze Test:

A sample of glass 3cm x 3cm was cleaned using iso-propanol and allowed to dry to remove dust from the surface of the glass, prior to analysis.

The haze of the sample was then measured on a Pacific Scientific Hazeguard meter. The sample is placed against a barium fluoride detector and the machine is started.

The calculation of haze is carried out by measurement of the specular light and diffusive light. The specular light is defined as light transmitted straight through the sample within $\pm 2.5^\circ$ of normal incidence, the diffusive light is defined as light scattered beyond 2.5° . The initial measurement, is carried out with the specular detector slot closed, and therefore a value of Specular light + diffusive light is obtained. The specular light slot is then opened and a measurement of the diffusive light is obtained.

$$\% \text{ Haze} = \{\text{Diffusive Light} / (\text{Diffusive} + \text{Specular Light})\} \times 100$$

2.7.6.2 Infrared Reflectance and Visible Reflectance Spectra:

Infrared reflectance spectra are measured using a 2 beam Perkin Elmer 883 machine. The spectra is measured against a rhodium mirror standard.

Emissivity data are also calculated from this infra red reflectance spectra, using the formula.¹³

$$Emissivity = 1 - \frac{\int_{5\mu}^{50\mu} R_{\lambda} P_{\lambda} d\lambda}{\int_{5\mu}^{50\mu} P_{\lambda} d\lambda}$$

i.e. Integral of total emittance between 5 and 50 μ m divided by the integral from 5-50 μ m of the total emittance of a black body at room temperature

2.8 Chemicals Used For In₂O₃/ITO Work:

The precursors used for the deposition of In₂O₃ and the tin dopant materials used in the deposition of ITO were all purchased. The bulk of the precursors were purchased from Epichem Ltd. These precursors included:

1. Trimethyl-indium adducts, Me₃InL (where L= OEt₂ and THF). These precursors were made from Me₃In with a slight stoichiometric excess of the adduct.
2. Dimethyl(methoxide)indium. This was made from the Me₃In, with a stoichiometric amount of the alcohol added to an ether solution of Me₃In.
3. Diacetatodimethyltin. This was made from DMT.

These precursors were supplied in stainless steel bubblers.

Other precursors were purchased from the suppliers listed below and were supplied in non-bubbler containers:

1. Tris(acetylacetonate)indium - Aldrich Chemicals.
2. Tris(tetramethylheptanedionato)indium - Inorgtech.
3. Diacetatodibutyltin - Aldrich Chemicals.
4. Tetrachlorotin - BDH Chemicals.
5. Tin(II) salt of ethyl-hexanoic acid - Aldrich Chemicals.

All the chemicals supplied were of > 90% purity except 3 and 5 which were technical grade. The chemicals were all used as received without further purification.

Solvents used in the film deposition were GPR grade and all purchased from BDH chemicals and used as supplied, except for the acetates and tetrahydrofuran which were HiperSolv grade.

2.9 Chemicals Used For the Titanium Nitride Work:

The chemicals used for the titanium nitride work were obtained from a range of sources. The $\text{Ti}(\text{NMe}_2)_4$ was kindly supplied by Inorgtech, and was used as supplied. The solvents and other chemicals used in the synthetic work were purchased from Aldrich Chemicals and were further purified prior to use. The solvents were all dried and distilled by standard methods prior to use, whilst all other chemicals were dried using hot molecular (4A) sieves prior to use.

NMR solvents were also dried prior to use and were obtained from Goss Scientific.

2.10 Chemical Analysis Techniques:

2.10.1 Mass Spectrum:

This was carried out on by Kratos MS 30 (University of London Mass Spectroscopy Service at the School of Pharmacy) operating in Electron Impact (positive) mode using a direct insertion probe over the temperature range 50-200°C. Sample submission was carried out using micro sure-seal bottles.

2.10.2 ^1H and ^{13}C NMR Spectroscopy:

NMR data were recorded on either a Jeol GS 270 NMR spectrometer, using the protio impurities of the deuterated solvent as a reference for ^1H spectra and the ^{13}C resonance of the solvent as a reference for the ^{13}C spectra. Chemical shifts were also independently referenced to tetramethylsilane (<1%) added by volume. All chemical shifts are positive to high frequency of the standard.

2.10.3 Microanalyses:

Analyses for the elements nitrogen, hydrogen and carbon were carried out by the micro analytical service of Imperial College London. Combustion aids were used during the analyses in an effort to discourage carbide formation.

2.10.4 TGA/DSC:

This was carried out on a PL Scientific DSC/TGA. The apparatus was microprocessor controlled, and a temperature ramp rate of 5°C per minute from room temperature up to a maximum temperature of 1500°C was carried out. During heat-up and cool down, a nitrogen flow through the apparatus was used of circa 50%.

2.10.5 Single Crystal X-ray Structure Determination:

These were kindly carried out by Professor M.B Hursthouse, University of Wales Cardiff. Samples were submitted in sealed sample containers with a small amount of the crystallisation liquor left with the sample.

2.10.6 Infra-Red Spectroscopy

Infrared spectra were recorded on a Perkin Elmer FTIR 1720 spectrometer as Nujol or hexachlorobutadiene mulls or as neat materials between 25 x 4 KBr plates. The solvents were pre-dried with 4A molecular sieves prior to use, and the samples were prepared under glove-box conditions and were protected from the atmosphere by an O-ring sealed Presslock holder.

2.11 References

1. H. O. Pierson, *Handbook of CVD Principles Technology and Applications*, 1992, Noyes Publications and R. F. Bانشah, *Handbook of Deposition Technologies For Films and Coatings, Science, Technology and Applications*, 1994, 2nd Edition, Noyes Publications
2. G. H. Westphal, *J. Cryst. Growth.*, 1983, 65, 105
3. B. J. Curtis and J. P. Dismukes, *J. Cryst. Growth.*, 1972, 17, 128
4. L. J. Giling, *J. Electrochem Soc.*, 1982, 129, 637
5. H. Schlichting, *Boundary Layer Theory 7th Ed.*, 1979, McGraw Hill, New York
6. The Handbook of Chemistry and Physics, Forty-sixth addition, 1965

7. J. Kane, H. Schwizer and W. Kerr, *J. Electrochem. Soc., Solid State Science and Technology*, **1976**, 123, 270
8. R. Gordon, US Patent 4, 308, 316, **1981**
9. J. van der Pauw, *Philips Research Reports*, **1958**, 13, 1
10. Ya. Kuznetsov, *Sov. Phys.-Solid State*, **1960**, 2, 30
11. J. W. Orton and M. J. Powell, *Rep. Prog. Phys.*, **1980**, 43, 1267
12. S. M. Sze, *Physics of Semiconductor Devices*, 2nd Ed., **1981**, (Wiley and Sons, New York)
13. M. Bass, *Handbook of Optics Vol. 2*, **1995**, 2nd Edition, McGraw Hill Inc.

3. Growth Of In_2O_3 By Atmospheric Pressure Chemical Vapour Deposition.

3.1 Background:

One of the most interesting classes of coatings for the glass industry is that based on transparent conducting oxides (TCO's), as these can be used as low emissivity energy saving coatings on glass. The first reported observation of both transparency in the visible range and high electrical conductivity was found by Badeker in 1907 for CdO .¹ The first commercial use of such coatings in aircraft windscreens occurred in the 1940's. The literature of these coatings up to 1955 has been reviewed by Holland,² and from 1955-1977 by Vossen.³

The properties of transparency and high electrical conductivity are mutually exclusive, because charge carriers in the valence or conduction band absorb light from the infrared to the visible region and lead to a significant decrease in transparency. Despite this, two ways of achieving transparent films are possible:

1. Very thin metal films (i.e. $<5\text{nm}$ thick)
2. Heavily doped wide-band semi-conductors, the most widely reported being doped tin, indium and zinc oxides. These are referred to as TCO's.

Deposition of thin metal films has been widely reported, and aluminium, copper and other metal films have been studied intensively because of their applications in the semi-conductor industry. These applications have been reviewed and the problems in achieving the necessary film purity have been described.⁴ Deposition of thin metal films on glass substrates at high temperatures, appears particularly problematical. Poor film quality arises from problems associated with both the composition and adhesion of the films. The relative ease of deposition of transparent conductive oxides on glass, has therefore lead to an interest in these materials.

3.2 Transparent Conducting Oxides TCO's

Several metal oxides with optical band gaps of 2.5 to 4eV have been identified as suitable TCO coatings.^{5,6} The most commonly reported are:

1. Fluorine or antimony doped tin oxide
2. Fluorine or aluminium doped zinc oxide
3. Tin doped indium oxide (ITO)

Of these materials only one is currently put down by large scale APCVD onto a glass substrate. This material is fluorine doped tin oxide and is marketed by several international companies including PPG, Glaverbel, Libbey Owen Ford and Pilkington.⁷

The application of TCO's as good low emissivity coatings on glass, require three properties to be achieved. Firstly the films must be highly transparent to visible light, with at least 80% transmittance. Secondly, the films must be highly electrically conducting, as this determines the degree of infra-red reflectance that occurs. Typically the films must have a resistivity in the range of $1.8-3.9 \times 10^{-4} \Omega \text{ cm}$. Finally the coatings must not appear hazy, because of particulate incorporation in the film, or high surface roughness of the coating, otherwise the visual appeal of the coating is diminished. Typical infra-red reflectance and visible transmittance spectra for a low emissivity coating are shown in Figure 3-1. Further details of the requirements of coatings for energy saving applications are summarised in chapter 6.

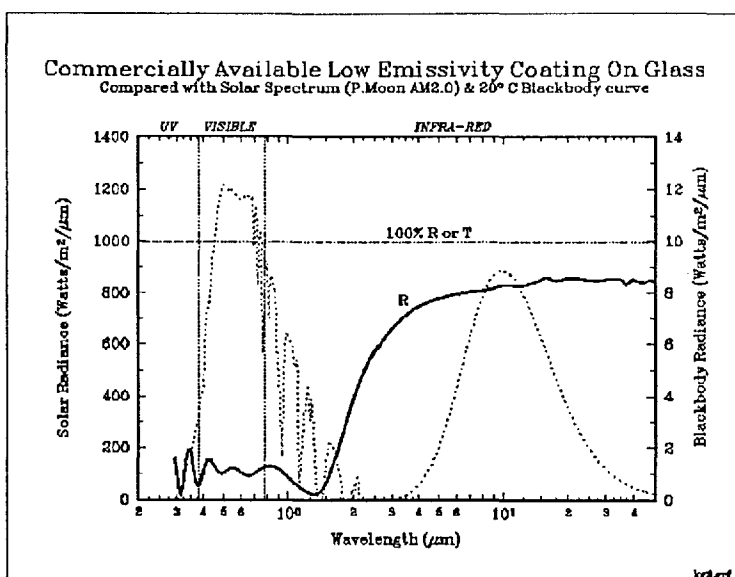


Figure 3-1 Reflectance Spectra Of a Typical Low Emissivity Coating Compared With the Solar Spectrum and a Blackbody

The literature on the deposition of TCO coatings is vast. In particular the growth and properties of ITO and aluminium doped zinc oxide have been studied in detail by Granqvist and co-workers by sputtering deposition techniques.⁸ The deposition of SnO₂ doped films by both sputtering and CVD has also been widely studied. Excellent reviews on both of these areas are available.^{9,10,11}

As with all three of the systems many dopants have been studied. The best dopant materials appear to have been identified for each of the materials and the best properties achievable are summarised in Table 3.1.

Table 3-1 Electrical Properties of TCO's

Properties	SnO ₂ F ¹²	ITO ¹³	ZnO ₂ Al ¹⁴
Resistivity (Ω cm)	Approximately 4-5x10 ⁻⁴	Approximately 1.5 x10 ⁻⁴	5-6x10 ⁻⁴
Transmission	>75-85%	90-95%	<85%

The superior electrical properties of doped tin and indium oxide make them the best optical materials.

The bulk of reports on the growth of doped and undoped In_2O_3 films are based around two techniques:

1. Sputtering
2. Spray Pyrolysis

The deposition of ITO by sputtering is a vast subject and excellent reviews have been published.^{15,16,17} Whilst the electrical properties of these coatings are excellent, two major problems with this deposition technique exist:

1. It is a batch process technique, requiring substrates to be prepared prior to deposition. This is mainly because it is a vacuum technique.
2. The coating is soft. Handling of the coated material is difficult because it is soft and easily damaged.

The use of spray pyrolysis techniques for the deposition of this material is also widespread, because the technique is fast, and cheap due to the low cost of the precursors required. Unlike CVD the precursors do not have to be volatile. However, the coatings produced by this technique suffer from high haze, which is a major limitation to their use.¹⁸

While doped tin oxide is the only material currently deposited by large scale CVD in an on-line situation, the better electrical properties of indium oxide which are outlined in Table 3-2 make the investigation of an APCVD process for its deposition important:

Table 3-2 Comparison of Electrical and Optical Properties Of ITO and $\text{SnO}_2\text{:F}$

Properties	$\text{SnO}_2\text{:F}$	ITO
Resistivity ($\Omega \text{ cm}$)	$4\text{-}5 \times 10^{-4}$	$1.5\text{-}3 \times 10^{-4}$
Mobility ($\text{cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$)	approximately 20-30	approximately 45
Carrier Concentration (cm^{-3})	approximately $3\text{-}5 \times 10^{20}$	approximately $5\text{-}10 \times 10^{20}$
Haze	< 0.2%	< 0.2%
Emissivity	0.12	0.08
Thickness ($\text{\AA}$)	3200	1800-2500

3.3 Indium Oxide and ITO Deposition

Metal oxides are usually electrical insulators, e.g. tin oxide and indium oxide. However, if there is an oxygen deficiency in a thin film of a metal oxide, such as indium oxide, this results in a degree of electrical conductivity in the deposited film. This makes undoped In_2O_3 an n-type, wide band-gap semiconductor. This conduction is due to oxygen vacancies in the deposited film and the number of vacancies can depend on the method by which the film is deposited. Control of this conduction is very difficult, because the level of oxygen deficiency in the film introduced by the manufacturing process is variable.

Better electrical properties are obtained if a dopant material is added. As described previously, the two major dopants for indium oxide are fluorine, which has only been briefly reported on in the literature, and secondly tin, which makes ITO. The addition of these dopants allows the conductivity of the film to be controlled within a useful range, by substitutional doping in the film.

When fluorine is added as a dopant material to the film, it acts as an anion electron donor, substituting for oxygen atoms in the film producing a material of the general stoichiometry: $\text{In}_2\text{O}_{3-y}\text{F}_y$.

If tin is added as the dopant material to the film then the tin acts as a cation electron donor, substituting for indium atoms in the coating, and producing a film of the general stoichiometry: $\text{In}_{2-x}\text{Sn}_x\text{O}_3$

Some reports of dual doping using both fluorine and tin dopants have been reported. In this case, the tin substitutes for indium, and fluorine substitutes for oxygen as a system of dual electron donors. This dual doping results in a film of the general stoichiometry: $\text{In}_{2-x}\text{Sn}_x\text{O}_{3-y}\text{F}_y$.

The use of ITO is the most widespread, because of the range over which conductivity can be controlled. The applications for which ITO coatings have been used include optical coatings and electrical circuits. A sheet resistance range from 5 to $150\ \Omega/\square$ is required to fill the requirements of these applications. Alteration of the thickness of the coatings and doping level can be used to control the conductivity between these two levels.

The deposition of undoped and doped indium oxide by CVD has been reported in the literature using a range of indium and dopant precursors. The bulk of this literature, however, has concentrated on the properties achievable from the coatings with equipment design and deposition parameters being altered to achieve the best properties from a particular precursor system. A typical deposition system used in CVD of ITO is shown in Figure 3-2.^{19,30,34,37,38}

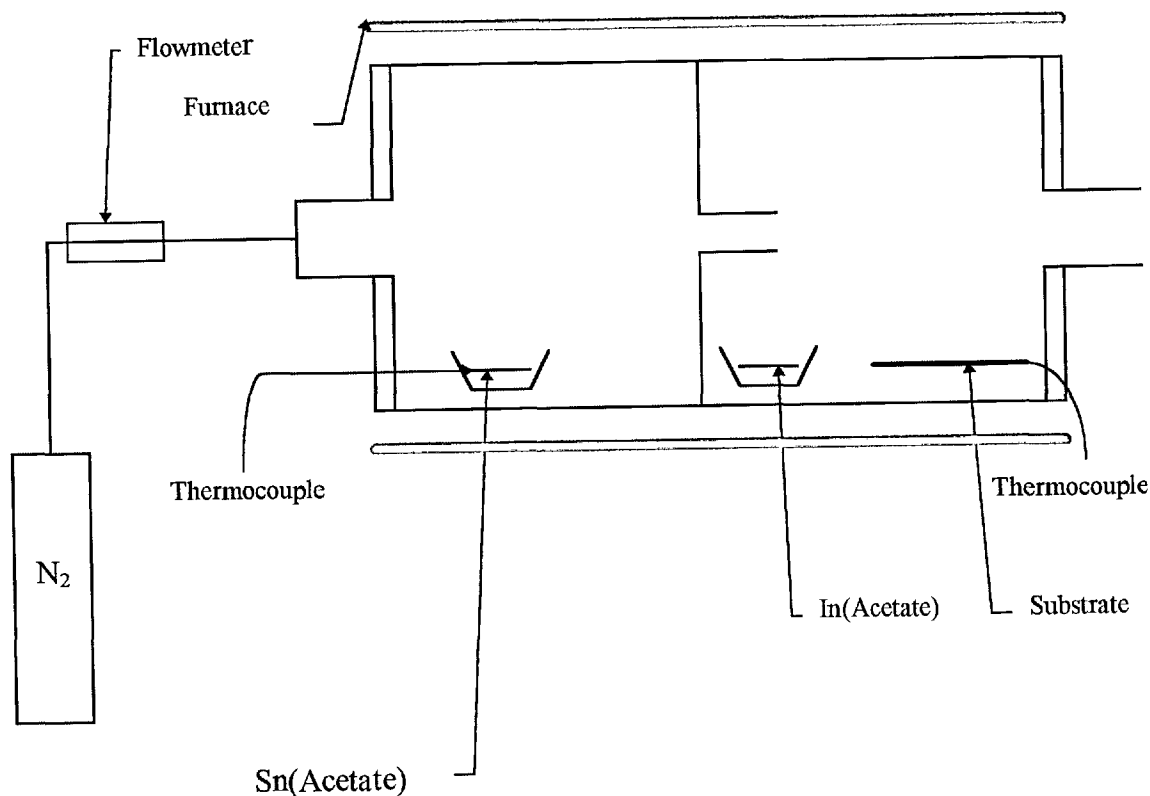
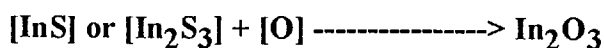
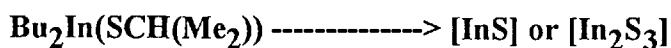


Figure 3-2 Deposition Rig Used By Marayuma *et. al.* For ITO Deposition.^{19,30,34,37,38}

Whilst good film properties have been achieved from such a set-up, little information about the gas phase stability of the precursors, or their mass transport characteristics can be derived from this design of equipment. Other literature reports have used more conventional CVD equipment, but again deposition conditions have been altered to obtain the best properties. These studies have concentrated on the achievable properties of the films and little information is available on the effect of deposition parameters. The precursors deposition characteristics have not usually been defined.

Kinetic studies of the deposition of ITO and undoped In_2O_3 by CVD have not generally been made and only two papers on the decomposition mechanisms by which coatings are achieved have been published. Maruyama *et. al.* have suggested that no oxygen is required during the deposition of In_2O_3 from indium acetate, implying some In-O bonds are not decomposed during the deposition,¹⁹ and Nomura *et. al.* proposed the decomposition of the butylindium thiolate goes via indium sulphides:²⁰



This study set out to investigate the growth of both doped and undoped In_2O_3 on a particular deposition system, and a range of precursors was compared. As described previously, the apparatus and growth conditions as a function of substrate temperature, flow rates and reactor design have all been set for the particular application of film growth on glass substrates. This Chapter describes the study of a range of indium precursors, either commercially available or synthesised specifically for the study, on the growth of undoped In_2O_3 . Investigation of the mass transport characteristics of the precursors and their ability to grow films in a pre-mixed laminar flow reactor has been completed and the effect of variations in the deposition parameters on the film properties is discussed.

Table 3-3 Review Of Precursors Used Previously For Deposition Of ITO

Precursor	Evaporation Temperature	Reactant	Deposition Temperature	Resistivity ($\times 10^{-4}$) Ω cm	Dopant Material	Comments
InCl_3 . ²¹	Spraying	Air	350-480°C	-	-	
InCl_3 . ^{22-24,27}	Spraying	Air	300-500°C	-	SnCl_4	
InCl_3 . ²⁵	Spraying	Air	350-500°C	10	NH_4F	Fluorine Doped
InCl_3 . ²⁶	Spraying	Air	270-330°C	-	TbCl_3	
$\text{In}(\text{ac})_2(\text{OH})$. ¹⁹	300°C	-	300°C	2.2-7.1	$\text{Sn}(\text{ac})_2$	
$\text{In}(\text{acac})_3$. ²⁸	-	O_2	270-520°C	-	-	
$\text{In}(\text{acac})_3$. ²⁹	150-200°C	-	350-450°C	1.6-1.8	$\text{Sn}(\text{acac})_2$	
$\text{In}(\text{acac})_3$. ³⁰	180°C	O_2	350-550°C	1.8	$\text{Sn}(\text{acac})_2$	
$\text{In}(\text{acac})_3$. ³¹	-	O_2	410-500°C	2.2-7.1	$\text{Sn}(\text{Me})_4$	
$\text{In}(\text{thd})_3$. ³²	220°C	O_2	375-550°C	2.2-7.1	$\text{Bu}_2\text{Sn}(\text{ac})_2$	
$\text{In}(\text{thd})_3$. ³³	155°C	O_2	50-400°C	-	-	
$\text{In}(\text{Me})_3$. ³⁴	-	O_2	130-330°C	-	-	Plasma enhanced CVD
$\text{In}(\text{Me})_3$. ³³	12-20°C	O_2	50-°C	-	-	
$(\text{Me})_3\text{In}(\text{OEt}_2)$. 35	40-80°C	O_2	508°C	3.5	$\text{Sn}(\text{Me})_4$ CF_3Br	
$\text{In}(\text{C}_7\text{H}_{15}\text{COO})_3$. 36	280°C	-	330-430°C	-	InF_3	
$\text{In}(\text{C}_7\text{H}_{15}\text{COO})_3$. 37	280°C	-	400°C	2.9	SnCl_4	
$(\text{C}_7\text{H}_{15}\text{COO})_2\text{In}$ $(\text{OOC}(\text{CF}_2)_4\text{H})$. 38	280°C	-	350-450°C	4.4	Single Source	

Bu ₂ InSPri. ²⁰	60°C	O ₂	200-400°C	1.2 at 300°C 5.2 at 400°C	Single Source Sulphur Doping	Resistivity very temperature dependant.
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Where ac= acetate, acac=2,4 pentadione, thd=2,2,6,6-tetramethylheptanedione

3.4 Experimental:

The growth of indium oxide has been carried out on the equipment described previously in Chapter 2, in the temperature range 565-625°C onto undercoated glass substrates.

A range of indium compounds were investigated to determine the best precursor for the deposition of indium oxide before a study of the deposition of doped indium oxide was undertaken. The precursors investigated were:

1. Trimethyl-indium adducts (Me₃InL where L=THF, Et₂O)
2. Tris(acetylacetonato)indium
3. Tris(2,2,6,6, tetramethyl 3,5, heptanedionato)indium
4. Dimethyl(methoxy)indium

If a precursor is to be of use for growth of indium oxide and ITO by APCVD it is important that three factors are considered. Firstly the thermal stability of the precursor when held at a temperature sufficient to obtain a high enough vapour pressure to allow mass transport of the precursor. If standard bubbling techniques are used for the delivery of the precursor decomposition of the material on standing at this temperature would prevent its use. The second important factor considered is pre-reaction of the precursor. Investigation of the growth of In₂O₃ has been confined to the use of a pre-mixed precursor system, where the vaporised precursor mixes with the oxygen prior to reaching the glass substrate. Therefore, any pre-reaction which occurs is only acceptable if the intermediates formed are volatile and will act as precursors for film growth. Due to

the complex nature of the possible intermediates, and the high possibility of particulate formation it is beneficial to have a pre-mixed system in which no pre-reaction occurs. The third factor is the growth rate achievable from the precursor. If the growth rate is too slow due to the precursors involatility then the precursor cannot be considered for use in a conventional APCVD system.

A reliable comparison of the growth of In_2O_3 from these precursors has previously not been achieved as literature reports have used widely differing apparatus and techniques for the growth of these materials. Previous studies have also used significantly lower deposition temperatures of $< 550^\circ\text{C}$, $565\text{--}625^\circ\text{C}$ deposition temperatures were used in this study. This study also details the effect of deposition parameters on the growth of In_2O_3 .

3.5 Results and Discussion:

3.5.1 The Growth of In_2O_3 From Trimethylindium-adducts

3.5.1.1 Background

The growth of In_2O_3 from trimethylindium is widely reported in the literature (for the semi-conductor industry) by low pressure chemical vapour deposition.^{33,34} The use of trimethylindium as a precursor in the apparatus used in this study was not undertaken. Although the precursor has sufficient volatility to be transported to the reactor chamber, its high reactivity towards oxygen would not allow pre-mixing of the precursor with an oxidant. As such this would require a two feed delivery system, keeping the precursor away from any oxidant source until reaction was required in the reactor chamber. This precursor was not therefore studied because of the potential hazards in the pre-reaction step which would result in involatile intermediates. These could block the delivery lines and cause a dangerous pressurisation of the system.

The use of the trimethylindium adducts for the growth of both doped and undoped In_2O_3 has been reported in the literature with $\text{Me}_3\text{In}(\text{OEt}_2)$ having been used for the growth of In_2O_3 , ITO and $\text{In}_2\text{O}_3\text{:F}$ by chemical vapour deposition.³⁵ However, whilst film growth was achieved using this system, the adducted Me_3In precursor was

not pre-mixed with the oxidant source, with the precursor and oxidant being fed separately into the reaction zone and only mixed just above the substrate surface. This study has investigated the use of trimethyl-indium adducts on a premixed system.

It was hoped that adduct formation would allow pre-mixing of the precursor with the oxidant by reducing pre-reaction of the precursor and oxidant in the gas phase. As part of the investigation of In_2O_3 growth, two Me_3In adducts have been studied; firstly the diethyletherate adduct and secondly a tetrahydrofuran adduct which has not previously been reported as a CVD precursor. These materials were both supplied by Epichem, and are both pyrophoric liquids at room temperature. Decomposition of both materials occurs at $>100^\circ\text{C}$ to Me_3In and the Lewis base,³⁹ therefore the materials were held below this temperature during all deposition experiments.

These materials were both used by standard bubbling techniques, with the materials held in sealed stainless steel bubblers, with all gas lines thoroughly purged to remove water and oxygen prior to opening the bubblers. Typical growth conditions used for the deposition of In_2O_3 from these materials are shown in Table 3-4.

Table 3-4 Growth Conditions For In_2O_3 Film Growth From The Trimethylindium adducts

Substrate Temperature:	515-615°C
Nitrogen Carrier Gas Flow:	4.7 l / min
Oxygen Carrier Gas Flow:	600 cc / min
Bubbler Temperature:	75-80°C
Bubbler Flow:	200 cc / min
Run Time:	2.5 mins

3.5.1.2 Growth From $\text{Me}_3\text{In}(\text{OEt}_2)$:

Initial film growth using the diethyletherate adduct under the above growth conditions was not encouraging, with a white powder being formed in the gas delivery lines and only a slight powdery coating was obtained on the glass substrate. This powdery material was not possible to collect, but it is believed to be due to a pre-reaction occurring between the oxygen in the carrier gas and the vaporised precursor resulting in the formation of In_2O_3 .

This pre-reaction was still significant, if the oxygen concentration in the carrier gas was reduced. Film growth of this material without oxygen, was also not effective, with a dark powdery coating being obtained on the glass plate, indicative of the precursor thermally decomposing on the surface of the glass, rather than being oxidised to In_2O_3 .

From this film growth study it was clear that the precursor $\text{InMe}_3(\text{OEt}_2)$ was not suitable for the deposition of In_2O_3 by pre-mixture of the vaporised precursor and oxygen.

Attempts at reducing the degree of pre-reaction, by the use of different oxygen sources was also investigated, with vaporised iso-propanol, and water both being used as alternative oxygen sources. The alternative oxygen sources were added to the reaction, by syringe injection at a rate of 0.75-2.5 ml / min and were then evaporated prior to mixing with the other materials. Experiments with each of the alternative oxygen sources, still resulted in significant pre-reaction between the oxidant and precursor in the gas delivery lines and a white material was observed in the delivery lines.

This work appears to support the conclusion that successful growth from this material would require a different type of precursor delivery system, whereby the vaporised precursor and the oxidant are kept separate until just prior to the glass surface. This type of system is by its very nature less efficient than a system in which all the sources are mixed prior to the reactor chamber, due to turbulent flows being required to obtain adequate mixing of the chemicals. The turbulence induced would probably result in less uniform films. The investigation of In_2O_3 growth from this precursor was

therefore not continued, as a major redesign of the reactor and the gas handling lines would be required for successful film growth.

The high levels of pre-reaction observed during this study, are believed to be a result of rapid pre-reaction between the precursor and the oxidant in the gas phase. This pre-reaction may be due to either:

1. The precursor dissociating into Me_3In and Et_2O in the gas delivery lines, which were held at approximately 120°C to prevent condensation of the precursor, or
2. The adduct did not provide sufficient protection for the metal centre from attack by the oxidant.

Lowering the temperature of the delivery lines to $< 100^\circ\text{C}$, was therefore investigated in an attempt to determine whether dissociation of the adduct during transport to the reactor chamber was responsible for the pre-reaction. Significant pre-reaction was still observed under these growth conditions, however, suggesting rapid formation of In_2O_3 was responsible for the pre-reaction observed. Therefore an investigation of other Me_3In adducts was carried out.

3.5.1.3 Growth of In_2O_3 From $\text{Me}_3\text{In}(\text{THF})$:

In order to reduce the pre-reaction between the precursor and the oxygen source, a precursor which undergoes less pre-reaction with the formation of In_2O_3 is required. An investigation of the $\text{Me}_3\text{In}(\text{THF})$ adduct was conducted to see if this precursor fulfilled this requirement.

Initial growth studies using this material were very encouraging, with good film growth of In_2O_3 occurring along the whole length of the glass plate at a deposition temperature of 565°C , with no sign of pre-reaction of the precursor in the gas delivery lines. This suggests that the tetrahydrofuran adduct was protecting the metal centre from attack more effectively than the diethyletherate adduct. The reason for the improved stability to attack by the oxygen source is unclear. One possible explanation is that the THF ligand prevents facile attack of the oxygen source at the metal centre, and thus reduces the degree of pre-reaction observed by sterically blocking the approach of the oxidant.

Growth rates of approximately $200 \text{ \AA min}^{-1}$ were obtained at a deposition temperature of 565°C and the films had a resistivity of $1.76 \times 10^{-3} \text{ } \Omega \text{ cm}$. The films also exhibited a low haze, although the emissivity of the films was poor at 0.88.

Analysis of a typical film grown using this precursor by SEM, AFM and X-ray diffraction is shown in Figures 3-3, 3-4 and 3-5. The SEM micrographs of films grown at a deposition temperature of 565°C , show the film to be continuous, with small crystallites on the surface.

AFM analysis of the coating shows the film to be relatively smooth with a mean roughness (R_a) of 2.35 nm, calculated over a $2 \text{ } \mu$ region of the coating. The X-ray diffraction of the film, confirmed the presence of polycrystalline In_2O_3 , but the signal strength was weak due to the thin nature ($300 \text{ \AA}$) of the film.

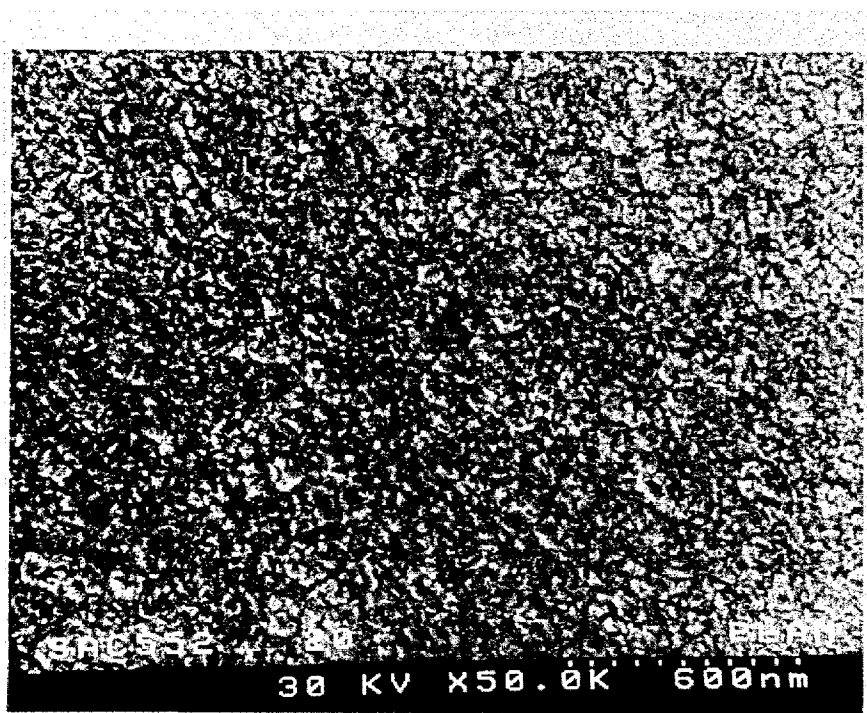


Figure 3-3 SEM Micrograph of In_2O_3 Grown From $\text{Me}_3\text{In}(\text{THF})$ and O_2

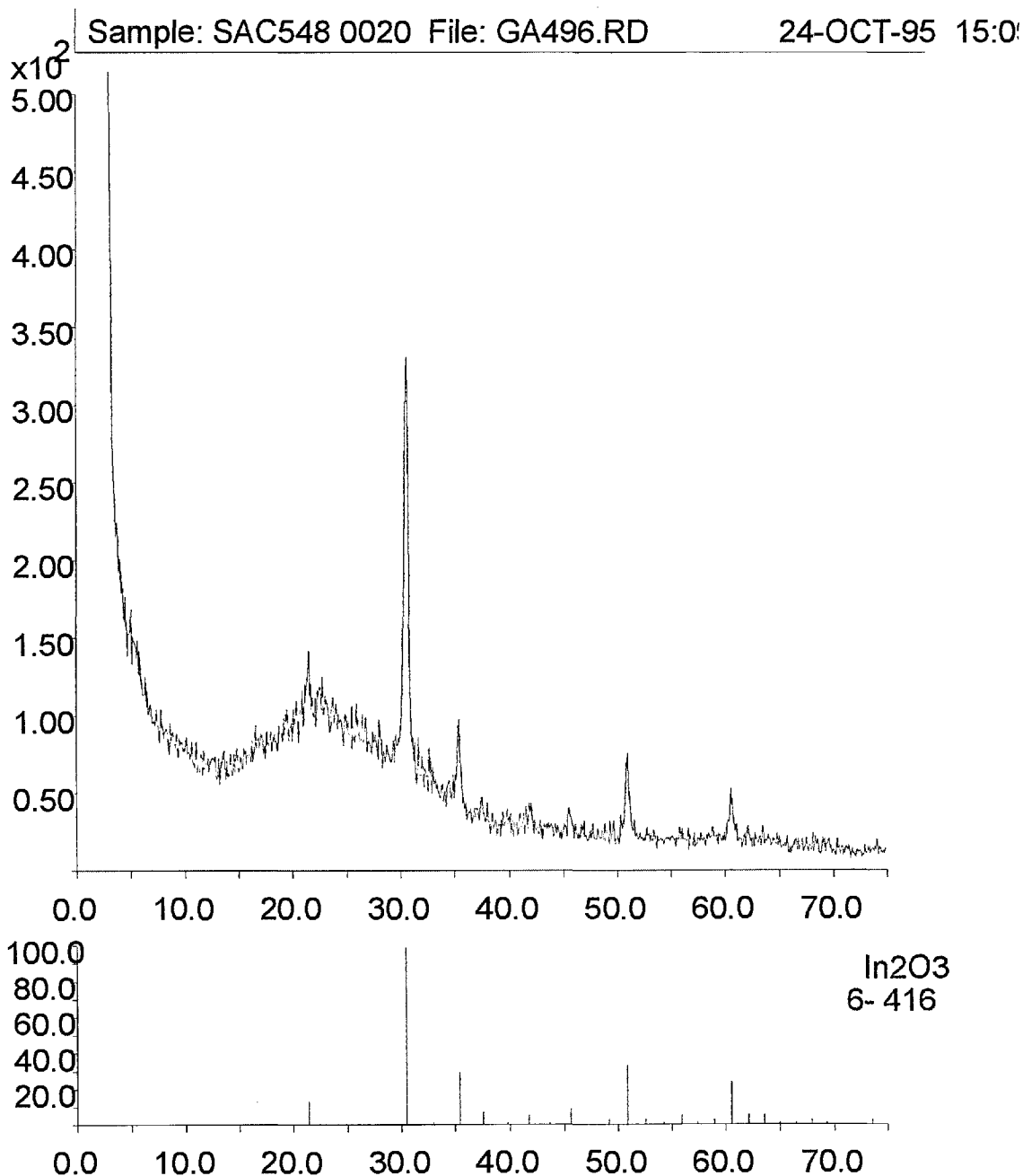


Figure 3-4 Glancing Angle X-Ray Diffraction of In₂O₃ Grown From Me₃In(THF)

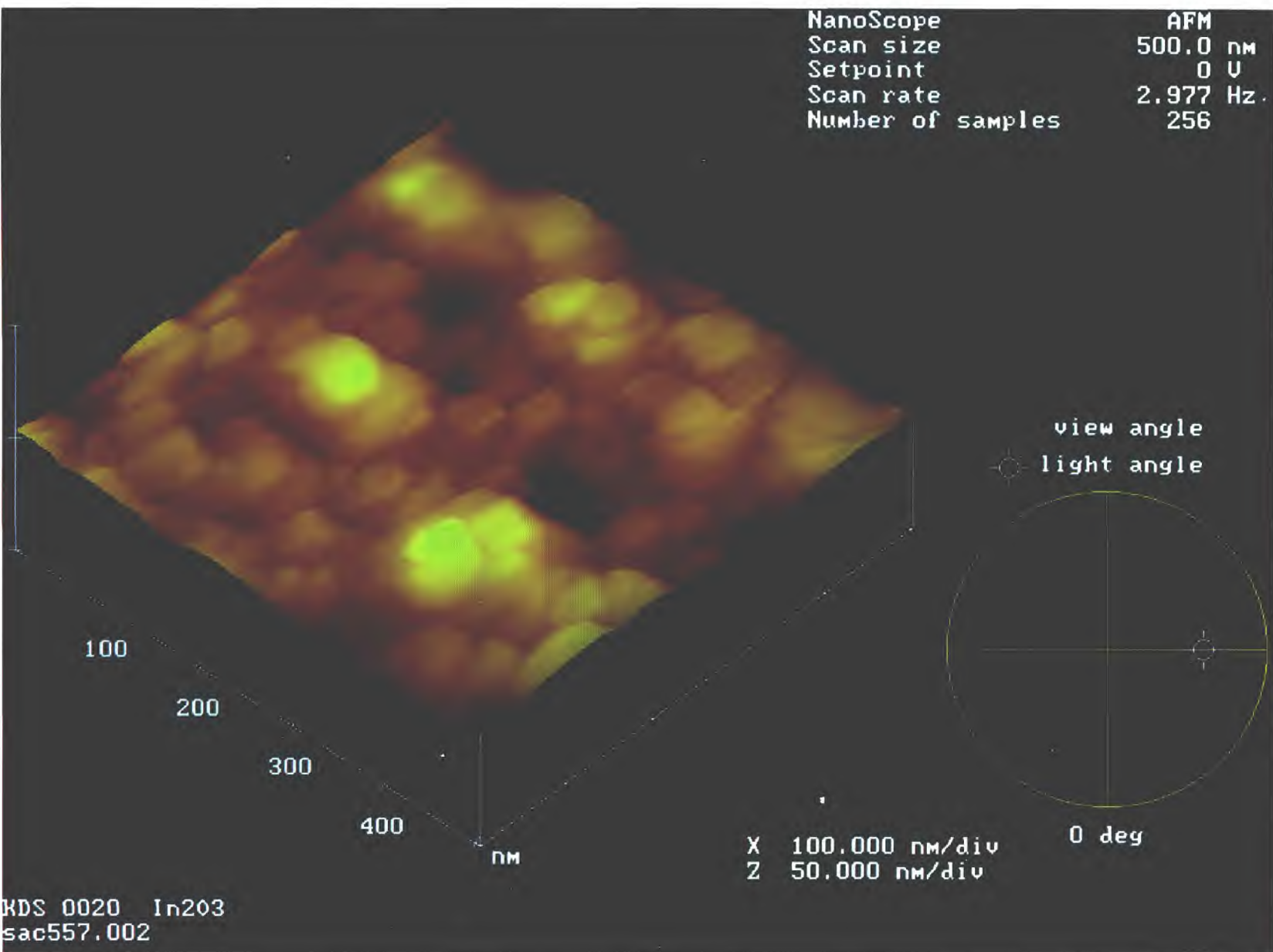


Figure 3-5 AFM Micrograph of In_2O_3 Grown From $\text{Me}_3\text{In}(\text{THF})$

3.5.1.3.1 Effect of Substrate Temperature On In_2O_3 Growth:

An investigation to determine the effect of the deposition temperature on the properties of the coating was carried out. Depositions were carried out in the temperature range 400-615°C.

Film growth at 565°C, resulted in good film growth covering the whole substrate, with the film thickness increasing to a maximum at approximately 6 cm from the inlet end of the substrate before decreasing again as depletion of the precursor in the gas phase occurred.

On increasing the deposition temperature it was noticeable that the profile of film growth altered considerably. As the deposition temperature was increased the thickest part of the film moved closer to the front edge of the glass plate and film growth terminated earlier. Films grown at 615°C, exhibited a rapid increase in film thickness at the inlet end of the substrate, with the maximum film thickness being achieved approximately 3cm along the substrate.

Decreasing the deposition temperature, however, had the opposite effect, with the film growth appearing to be moved back towards the exhaust end of the reactor. At 515°C, the maximum thickness of the film was achieved at approximately 8-9 cm along the substrate, whilst at a deposition temperature of 400°C, no film growth was seen at the very front of the substrate, with film growth only commencing 3-5cm from the front of the glass plate and reaching a maximum thickness 10-12 cm along the substrate.

This study indicates that film growth from this precursor system is very temperature dependant. The movement of film growth towards the front of the substrate as the deposition temperature is increased is likely to be a result of the gas phase temperature in the deposition zone being higher. As a result of this, oxidation of the precursor occurs earlier resulting in the maximum film thickness occurring at the front of the glass plate. Conversely, as the deposition temperature is decreased, the gas phase temperature decreases and oxidation of the precursor occurs further along the reactor.

The mechanism for the deposition is unclear, but the temperature dependency of the process, may indicate that the initial step in the process is the decomposition of the adduct into Me_3In and THF, followed by rapid oxidation of Me_3In to In_2O_3 . This would

explain the temperature dependency of the process, as it has been seen that very little if any pre-reaction occurs between $\text{Me}_3\text{In}(\text{THF})$ and oxygen in the delivery lines, but the oxidation of the Me_3In is rapid. The shift in the growth profile, may therefore be an indication of the position at which the $\text{Me}_3\text{In}(\text{THF})$ decomposes in the gas phase.

3.5.1.3.2 Effect Of Oxygen Concentration On In_2O_3 Growth:

Investigation of the effect of oxygen concentration on film growth was carried out at a deposition temperature of 565°C , at oxygen concentrations in the gas stream from 4 to 24% (i.e. 4-24% of total flow).

Alteration of the oxygen concentration, during film growth did not have an effect on the maximum thickness of the film, with the maximum thickness observed being similar at $500\text{-}600\text{\AA}$ at all oxygen concentrations. The similar thickness of the coatings, suggests that no increase in the growth rate is observed on increasing the oxygen concentration.

Alteration of the oxygen concentration between 10 and 20% also had little effect on the growth profile of the film. As the oxygen concentration was reduced, a similar growth profile was observed to that obtained at a 12% oxygen concentration, with film thickness increasing to a maximum approximately 6cm along the glass plate before diminishing. If the oxygen concentration was reduced too much, however, to approximately 4% of the total gas stream the films began to darken suggesting that incomplete oxidation or some thermal decomposition of the precursor was occurring on the substrate resulting in some carbon incorporation. Increasing the oxygen concentration above 20% also resulted in a detrimental effect with some powder generation in the coater. This may imply that gas phase production of some In_2O_3 occurred which did not result in film growth.

This study suggests that film growth from this precursor is oxygen dependant, but successful film growth can be achieved at an oxygen concentration of between 10 and 20% of the total gas stream.

3.5.1.3.3 Effect Of Precursor Stability On In_2O_3 Growth:

On continued use of the precursor, film growth at all deposition temperatures deteriorated, with less coverage of the glass plate being observed. This deterioration in the growth profile was accompanied by an increase in the haze level of the deposited films, with powder inclusion being observed in the coating.

It is believed that the deterioration in the growth profile of the deposited films is a result of increased pre-reaction of the precursor with the oxidant in the delivery lines prior to the deposition chamber. A similar degradation in the films properties also occurred if the $\text{Me}_3\text{In}(\text{THF})$ was heated over 75°C , with fresh batches of the material degrading rapidly if the material was held at circa 100°C for 2-3 hours.

This deterioration appears to be due to decomposition of the precursor occurring when the bubbler is held at elevated temperatures. This decomposition may be dangerous since some metallic indium was obtained from a bubbler after it had been held at 95°C for a period of time. As a result the bubblers were held at a maximum temperature of 80°C , in order to prevent a potentially dangerous explosion due to the decomposed precursor.

This study indicates that initial decomposition of the precursor into its constituents, THF and Me_3In , may be occurring in the bubbler. The addition of THF in the vapour phase during film deposition, from a bubbler of the deteriorating precursor was investigated in an attempt to confirm this hypothesis.

It was found that the performance of the precursor growth could initially be improved close to the levels obtained from the fresh precursor, by the addition of THF into the vapour phase. The investigation showed, however, that it was necessary to add the THF in excess prior to the mixing of the indium precursor with oxygen to achieve this improvement. Addition of an excess of THF after the mixing of the precursor with the oxidant had no effect on the film growth, with excessive pre-reaction observed.

These results are consistent with the THF acting to reduce the pre-reaction with oxygen. This is likely to occur by the THF shifting the equilibrium towards the re-formation of $\text{Me}_3\text{In}(\text{THF})$ in the gas phase.

After extended periods of time with the precursor held at a temperature of 80°C, the film growth further deteriorated, with the addition of THF no longer effective. This implies that the precursor continues to degrade whilst being held at this temperature, until it eventually reaches a point where film growth is very poor. This may indicate that complete decomposition of the precursor with the formation of an involatile indium species has occurred. This is consistent with the observation of indium metal in the bubbler.

3.5.1.3.4 Summary of Me₃In Adduct Precursors

The thermal stability of the adducts of Me₃In on bubbling are clearly questionable. Whilst no film growth from the diethyletherate adduct was possible due to rapid pre-reaction between the precursor and the oxidant in the delivery lines, the tetrahydrofuran adduct did appear to be better, with no pre-reaction in the delivery lines observed. Film growth from the tetrahydrofuran adduct was very temperature dependent, however, and at high deposition temperatures film growth occurred rapidly at the inlet of the reactor suggesting the material had a limited thermal stability.

Both precursors when held at elevated temperatures in the bubbler for any period of time also exhibited decomposition which is believed to result in the initial formation of Me₃In and the free ligand. Such decomposition of the precursor is consistent with the increase in pre-reaction between the oxygen source and precursor that is observed from materials when they have been held at elevated temperatures for a period of time. The decomposition of the precursors in the bubblers does not appear to stop at this stage, however, with further decomposition possibly by a radical mechanism to form indium metal in the bubbler occurring.

The limited thermal stability of these precursors prevented attempts at further increasing the mass transport of the precursor by the use of elevated temperatures and as such limited the application of these precursors in systems where high growth rates are required.

3.5.2 Growth Of In_2O_3 From Indium Tris- β -diketonates

3.5.2.1 Background

The second class of indium precursor used for the deposition of In_2O_3 were the indium β -diketonates, $\text{In}(\text{acac})_3$ and $\text{In}(\text{thd})_3$. It was hoped the β -diketonates may have the advantage of having a higher thermal stability than the methylindium compounds at the high deposition temperatures used in this study.

The biggest disadvantage of these materials is their comparatively low volatilities compared with the trimethylindium adducts and thus the problems associated with transporting these materials in the vapour phase in sufficiently high concentrations to achieve fast growth.

Whilst both materials have been previously reported as CVD precursors, these studies have been limited with no investigation of the pre-mixed delivery of the precursor with an oxidant and only limited studies of the effect of deposition parameters on film growth have been made.²⁸⁻³³

The high melting points of these materials $\text{In}(\text{acac})_3$, (approximately 194°C) and $\text{In}(\text{thd})_3$, (approximately 184°C), required high bubbler temperatures in order to get a sufficiently high vapour pressure for mass transport of the material to occur. These materials have been studied for the growth of In_2O_3 but extended run times of 10 - 30 minutes were required in order to get coatings on the glass.

Table 3-5 Growth Conditions For In_2O_3 Film Growth From $\text{In}(\beta\text{-diketonate})_3$

Substrate Temperature	515-625°C
Bubbler Temperature	approximately 200°C
Bubbler Gas Flow:	200 cc / min
Nitrogen Carrier Gas Flow:	4.7 litres / min
Oxygen Gas Flow:	600 cc / min
Nitrogen Flush:	5.5 litres / min
Run Time:	10 - 30 mins

3.5.2.2 Growth of In_2O_3 From $\text{In}(\text{acac})_3$:

Growth of In_2O_3 from the precursor $\text{In}(\text{acac})_3$, was investigated in a deposition temperature range of 515-625°C. Very low growth rates were achieved using this precursor despite it being held above its melting point at a temperature of 200°C.

Holding the precursor above its melting point also resulted in a slight decomposition of the precursor being observed in the bubbler, with the initial white powdery $\text{In}(\text{acac})_3$ precursor, turning to an orange colour on heating. Volatilisation of the bulk of the precursor was still possible, however, which is consistent with only partial decomposition of the precursor occurring. Surface oxidation of the top surface of the precursor is a possible explanation for the colour change observed. The rate of precursor delivery was not effected by this slight decomposition, however, with reproducible carryover attained.

Extended growth times of up to 15 minutes were required to get any coating using this precursor at substrate temperatures from 515 to 625°C. The films produced were of a gold colour, but non-conductive.

The SEM micrograph of a typical film grown at 565°C, for 15 minutes, is shown in Figure 3-6 and shows the film to be non-continuous, with small islands of film growth being visible on the glass substrate. Closer examination of the SEM micrographs at a magnification of 50000x, shows these particles to be of very similar sizes, and to be spread across the whole substrate. The SEM micrographs also show smaller “humps” in the undercoat, but these do not appear to have affected the In_2O_3 growth, and no replication of these defects was observed. The non-continuous nature of the films explains the non-conductance of the films, with the conduction mechanism being prevented by the gaps in the coating.

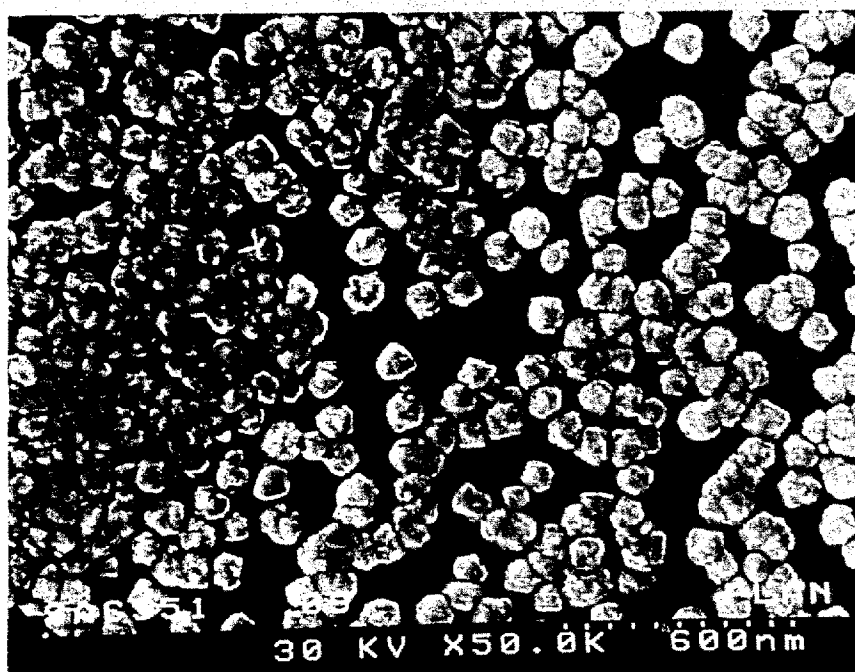
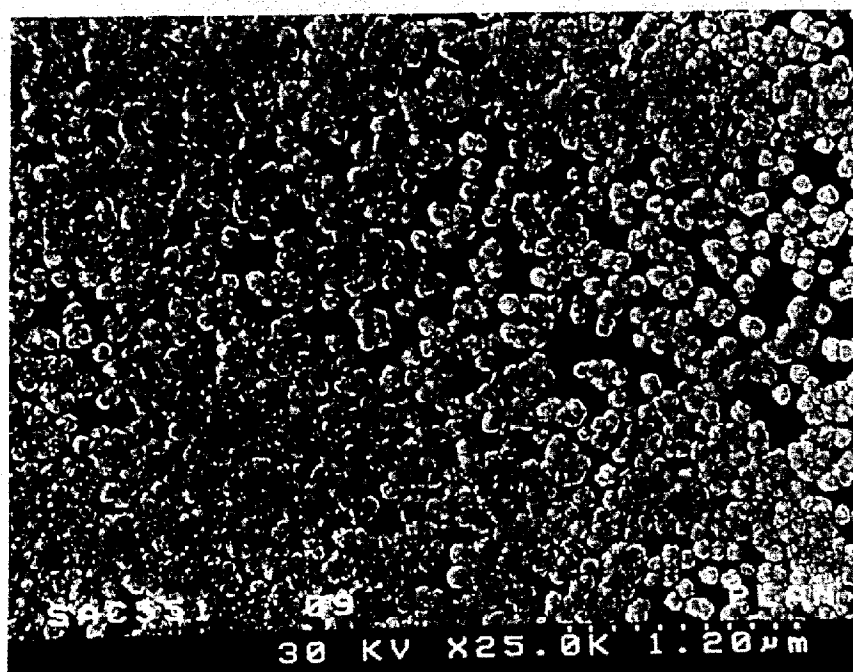


Figure 3-6 SEM Micrographs of In_2O_3 Growth From $\text{In}(\text{acac})_3$ and O_2 at 565°C

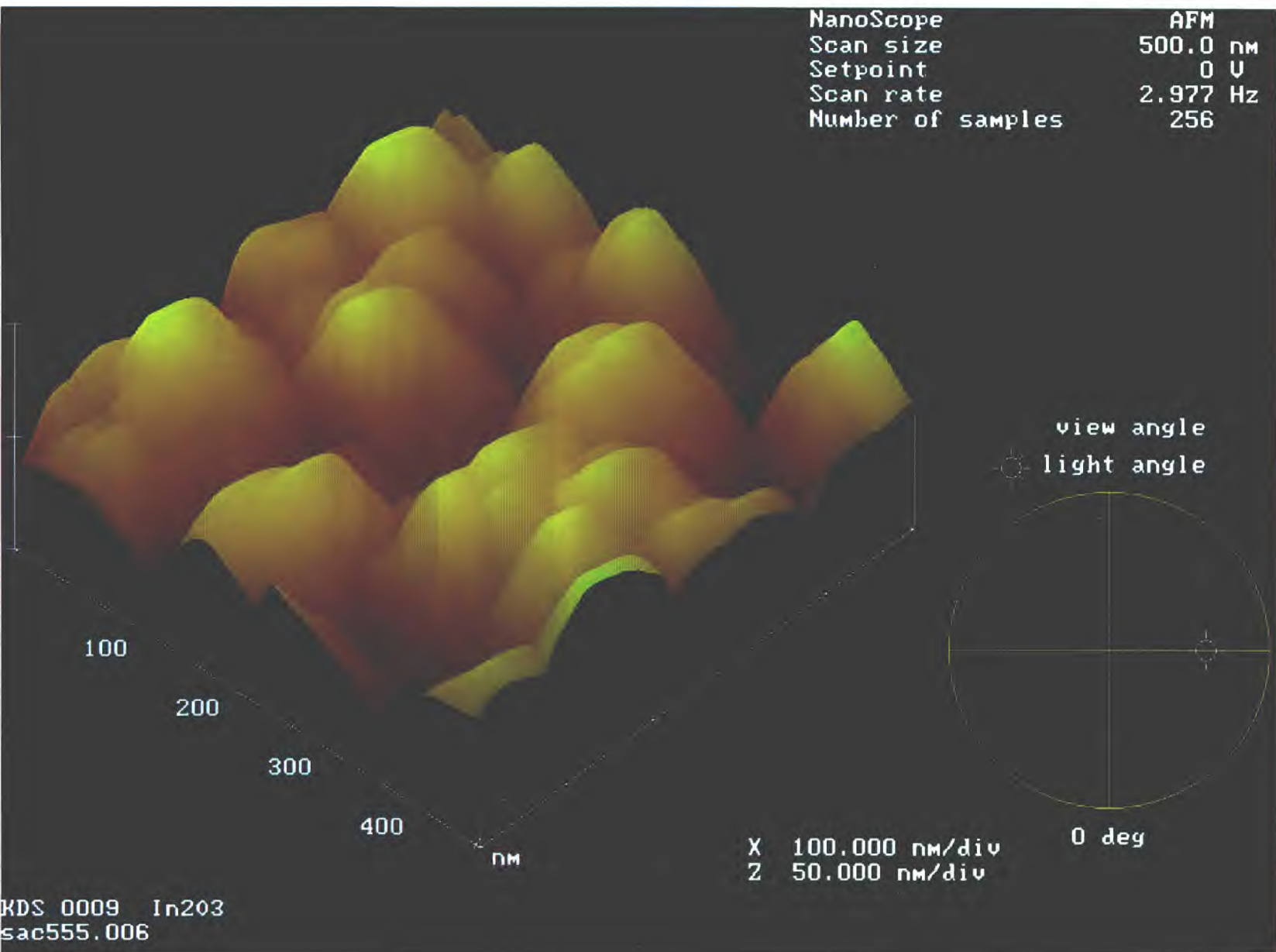


Figure 3-7 AFM Micrograph of In_2O_3 Growth From $\text{In}(\text{acac})_3$ and O_2 at 565°C

AFM analysis of films deposited under these conditions (Figure 3-7) confirmed the non-continuous nature of the coatings, with islands of film growth visible. The non-continuous nature of the film growth also resulted in the film being rougher than that seen for In_2O_3 growth from $\text{Me}_3\text{In}(\text{THF})$ and oxygen, with a mean roughness (Ra) of 10.1 nm over a 2μ area of the coating.

The formation of islands on the substrate would be consistent with the formation of polycrystalline In_2O_3 , with coalescence of these islands required before a continuous In_2O_3 film is produced.

Glancing angle X-ray diffraction of the films failed to confirm the polycrystalline nature of the film, with no crystalline In_2O_3 observed, although this is likely to be a result of the very thin and non-continuous nature of the film achieved.

Extending the deposition time from 15 to 30 minutes did result in the growth of conductive films of approximately 500Å in thickness. Studies on the effect of deposition parameters on film growth were therefore undertaken.

3.5.2.2.1 Effect Of Deposition Temperature On Film Growth

Film growth was achieved in the temperature region 515 - 615°C with continuous films being deposited after extended run times of 30 minutes. The study indicated that increasing the deposition temperature resulted in a slight increase in the growth rate of In_2O_3 , with a growth rate of approximately 10 Å min^{-1} at 515°C, increasing to 15-20 Å min^{-1} at 615°C.

The increased growth rate observed is likely to be due to an increase in the efficiency of the deposition process, with more of the precursor being utilised in film growth. The higher efficiency of precursor usage may be due to the increased gas phase temperature resulting in more gas phase reaction between the precursor and the oxidant forming the intermediate species responsible for film growth.

A similar relationship between the growth rate and deposition temperature has previously been observed for the growth of SnO_2 from a range of precursors including DMT and SnCl_4 .

Increasing the deposition temperature had little effect, however, on the growth profile of the indium oxide with only a slight alteration in the position of maximum thickness being observed. As the deposition temperature was increased the position at which maximum thickness was achieved on the glass substrate was moved only slightly towards the inlet of the reactor.

These results are in contrast to those obtained for the deposition of In_2O_3 from $\text{Me}_3\text{In}(\text{THF})$ and O_2 , which showed a strong dependency between the growth profile and the deposition temperature. This may indicate that the $\text{In}(\text{acac})_3$ is more thermally stable. As the temperature is increased the position at which maximum thickness occurs would be expected to move towards the reactor inlet and therefore the initial oxidation reactions would be expected to commence earlier. The fact that this change in the growth profile is only small, however, suggests that the precursor is more thermally stable and does not undergo rapid decomposition and oxidation under these deposition conditions.

The poor vapour pressure of this precursor, was a limiting factor, as the poor growth rate achievable limits its applicability for use by APCVD. As a result a more volatile indium β -diketonate, based on the ligand 2,2,6,6-tetramethyl-heptanedione (thd) has been investigated.

3.5.2.3 Growth of In_2O_3 From $\text{In}(\text{thd})_3$:

Tris(tetramethylheptanedionato)indium is believed to be a monomeric species and has a melting point of 184°C . This material has been used to grow In_2O_3 using the same pre-mixed route as with $\text{In}(\text{acac})_3$, but the higher vapour pressure associated with this material allowed growth of the material at higher growth rates. The thermal gravimetric analysis (TGA) of $\text{In}(\text{thd})_3$ is shown in Figure 3-8.

Method: TGA Ramp 20°C/400°C
Comment: HELIUM PURGE 8 INDIUM THD

Run Date: 26-Jul-95 16:26

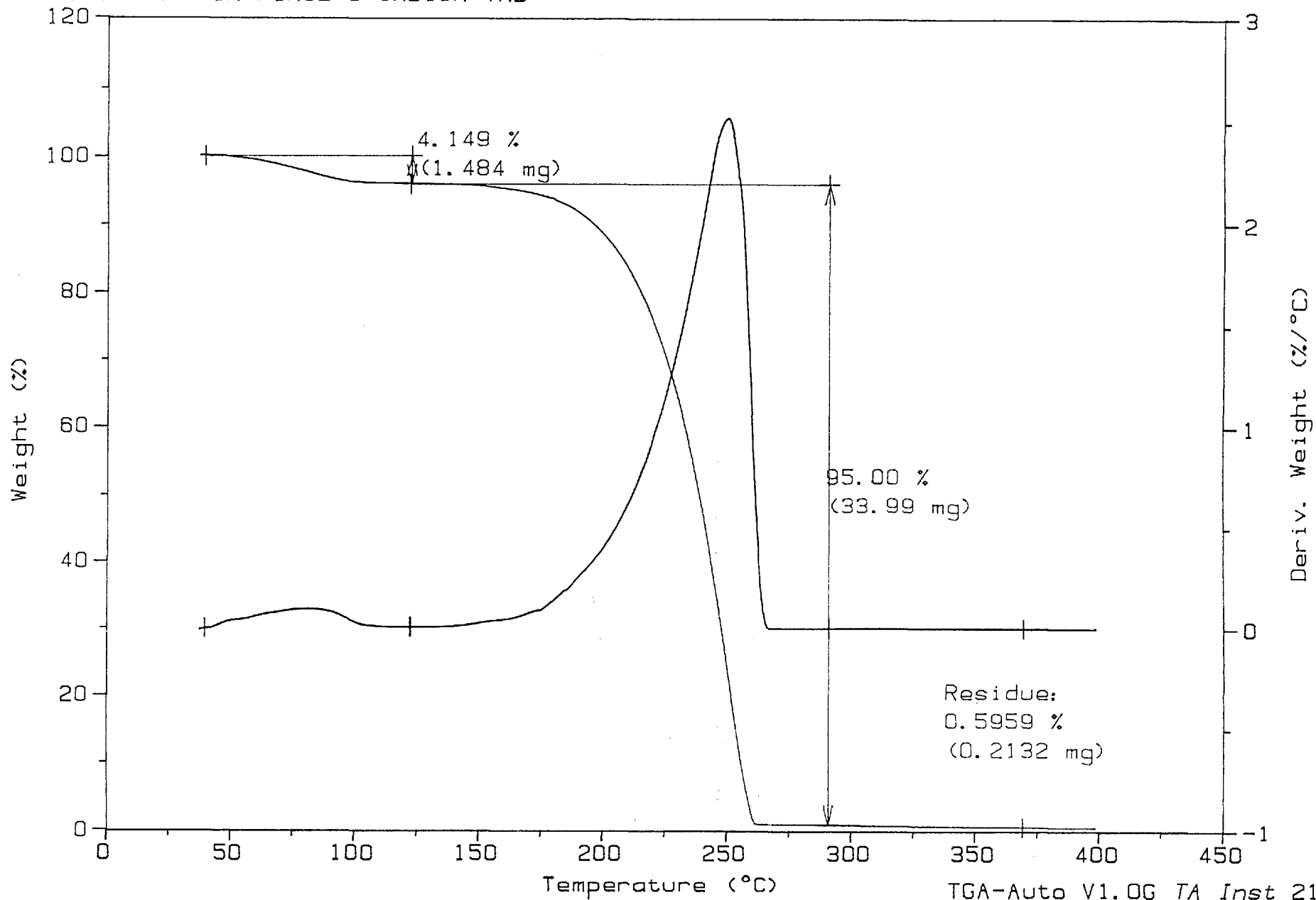


Figure 3-8 Thermal Gravimetric Analysis of $\text{In}(\text{thd})_3$

The TGA of the precursor shows a single weight loss commencing at approximately 180°C and finishing at approximately 250°C. The small residue left (3%), indicates that the bulk of the material sublimed, and the isothermal TGA of the material at 80, 150 and 200°C, indicates that mass transport of this material should be acceptable at a precursor temperature of 200°C.

As with the $\text{In}(\text{acac})_3$ this material showed some signs of slight decomposition to In_2O_3 when held at a temperature of 200°C for extended periods of time. This can be seen from the XRD patterns of the precursor taken before and after being held at temperature for approximately 10 hrs at 230°C. The XRD pattern shows a peak due to In_2O_3 becoming clearly visible after the precursor had been held at elevated temperatures and suggests that the decomposition is due to oxidation of some of the precursor. Subsequent volatilisation of the precursor, however, shows this to be a minor impurity, with growth of In_2O_3 from the precursor not adversely affected by the In_2O_3 impurity. This suggests that the decomposed precursor remains as an involatile decomposition product in the bubbler and does not disturb transport of the intact precursor.

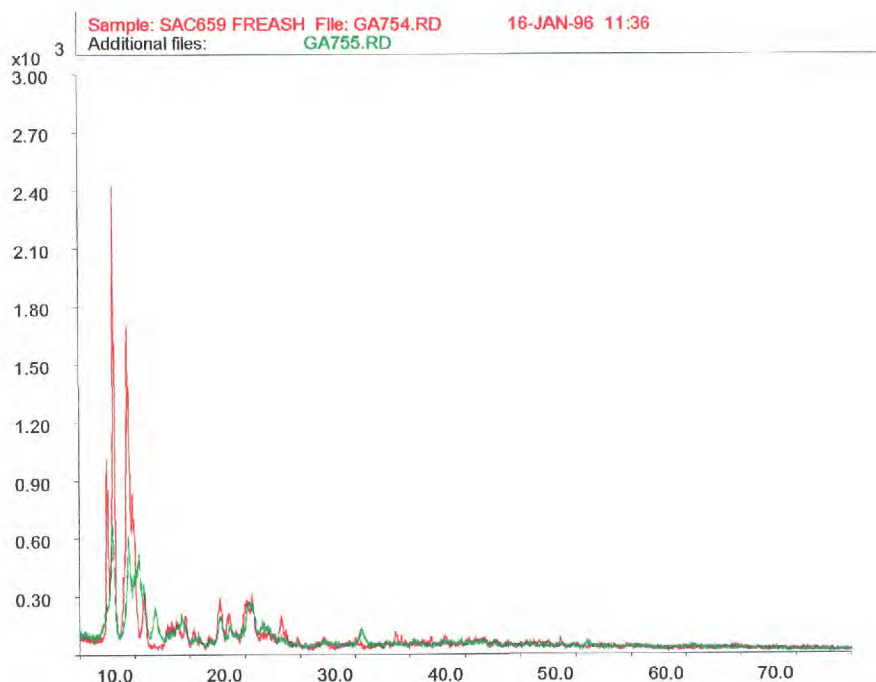


Figure 3-9 XRD Of $\text{In}(\text{thd})_3$ When Fresh (Red) and After Being Held at 300°C For 10 hours (Green)

Typical growth rates of $70\text{-}150\text{ \AA min}^{-1}$ have been achieved using this precursor held at 200°C , at a deposition temperature of 565°C . The films produced under these conditions showed similar properties to those obtained from $\text{In}(\text{acac})_3$, with a resistivity of $1.1\text{-}1.5 \times 10^{-3}\text{ }\Omega\text{ cm}$.

3.5.2.3.1 Effect of Temperature on Film Growth:

Studies of film deposition were carried out at a range of substrate temperatures from 515 to 625°C .

The growth profile of In_2O_3 from $\text{In}(\text{thd})_3$ at $515\text{-}565^{\circ}\text{C}$, was similar to that seen for the growth of In_2O_3 from $\text{In}(\text{acac})_3$ and to that of SnO_2 deposition from the DMT and oxygen system by Strickler, with a gradual increase in the film thickness along the substrate until a maximum thickness was observed at $8\text{-}12\text{ cm}$ from the inlet, before the thickness decreased due to depletion of the precursor from the gas phase. The increase in thickness along the glass plate is likely to be due to a gradual increase in the gas phase temperature along the reactor resulting in a change in the deposition rate along the reactor.

Increasing the deposition temperature resulted in both an increase in growth rate and also a slight change in the growth profile of the film with the film growth moving slightly towards the inlet of the reactor.

These results are similar to those observed for the precursor $\text{In}(\text{acac})_3$ and suggest that the precursor is more thermally stable than the trimethylindium adducts. As the deposition temperature is increased the gas phase temperature also increases, resulting in a higher growth rate by increasing the rate of oxidation of the precursor.

3.5.2.3.2 Effect of Oxygen Concentration:

The effect of oxygen concentration on film growth was also studied. If oxygen was not added to the gas stream during film growth, the result was a marked decrease in the growth rate of the In_2O_3 , but a thin film was still produced. This result is similar to that of Sugiyama *et. al.* who have grown $\text{In}_2\text{O}_3\text{:F}$ from a fluorinated acetylacetonate

without the addition of oxygen to the gas stream, but at a low growth rate.³⁸ Film growth under these conditions is a result of the thermal decomposition of the precursor, with loss of the carbon containing species as by-products of the thermal decomposition of the precursor. Films produced by the thermal decomposition of the $\text{In}(\text{thd})_3$, exhibited poorer electrical properties than those grown with the addition of oxygen in the gas stream, with resistivities of circa $3\text{--}4 \times 10^{-3} \Omega \text{ cm}$ being achieved. The deterioration in the electrical properties of the coating is likely to be a result of impurities in the film, causing scattering of the carriers and thus reducing their mobility.

The addition of oxygen to the gas stream at a level of between 10 and 25% of the total gas stream, resulted in good film growth of In_2O_3 at a far higher growth rate than that obtained with no oxygen addition. Films grown under these conditions all exhibited a similar growth profile, however, unless the oxygen concentration in the gas stream was increased beyond 25%, under which conditions a deterioration in the growth profile of the precursor was observed, with In_2O_3 growth moving towards the inlet of the reactor. From this study the optimum film growth has been identified to occur at an oxygen concentration of circa 10–25 %, with film growth at lower oxygen concentrations exhibiting slightly inferior electrical properties.

The similar growth profile observed at a range of oxygen concentrations, indicates that unlike the $\text{Me}_3\text{In}(\text{OEt}_2)$ adduct reported earlier in this study, the precursor does not significantly pre-react in the gas delivery lines. This indicates that whilst the addition of oxygen is beneficial to film growth, aiding the oxidation of the precursor, film growth is not as reliant on the oxygen concentration as that from the trimethyl-indium adducts.

3.5.2.3.3 Nature of Film Growth

SEM analysis of film growth after 5 minute and 12 minute runs was carried out to investigate the nature of film growth. As with the $\text{In}(\text{acac})_3$ precursor, initially the films produced were non-continuous with small islands of growth seen on the glass substrate. However, with increased growth times, the films became continuous, with no individual islands of growth being visible any more. The SEM micrographs of the film

surface show small crystals on the surface. This initial island growth followed by the coalescence to form a continuous film is the classical deposition mechanism for the formation of polycrystalline films and glancing angle X-ray diffraction of the continuous film confirms the material to be polycrystalline In_2O_3 .

Atomic force microscopy of the polycrystalline films show the film to be fairly smooth with an Ra(mean roughness) of 3.52 nm. This is far lower than the roughness of the incontinuous films grown using this precursor which have a roughness of approximately 5.4 - 10 nm. The lower roughness of the continuous films indicates that the initial island growth is not replicated by continued film growth, and coalescence of the islands results in a smoother coating. This is an important consideration in obtaining good optical coatings, as increased surface roughness can result in a higher haziness in the coating as a result of diffusive scattering of light.

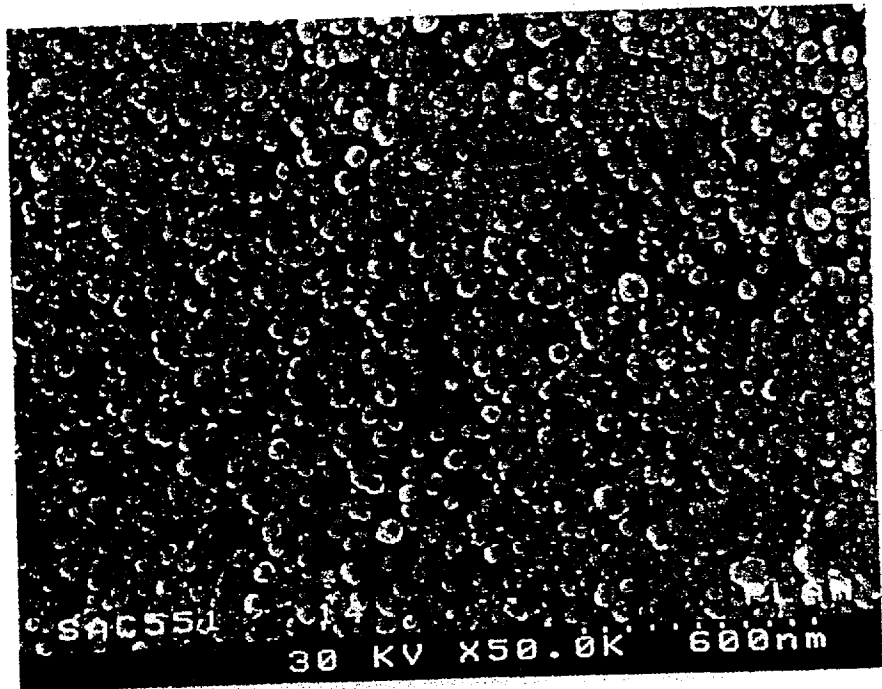


**Figure 3-10 SEM Analysis Of In_2O_3 Film Growth From $\text{In}(\text{thd})_3$ and O_2 at 565°C
After 5 mins**

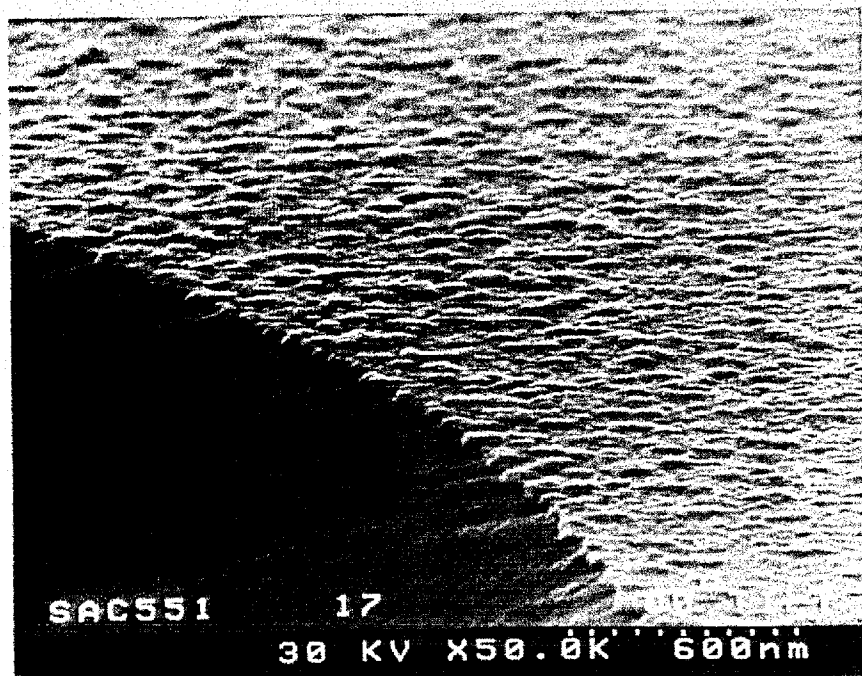
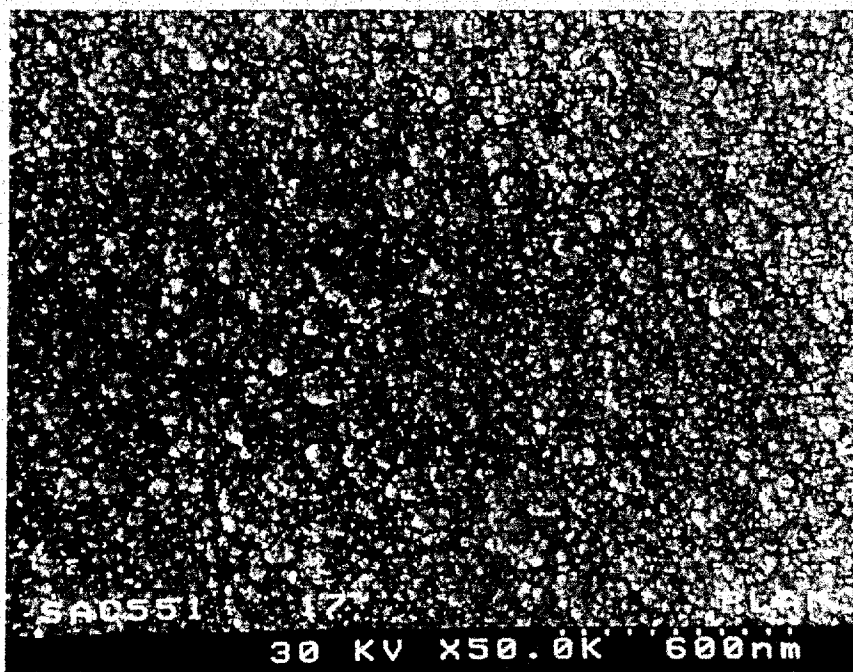


Figure 3-11 SEM Micrographs of In_2O_3 Film Growth From $\text{In}(\text{thd})_3$ and O_2 at 565°C After 12 mins

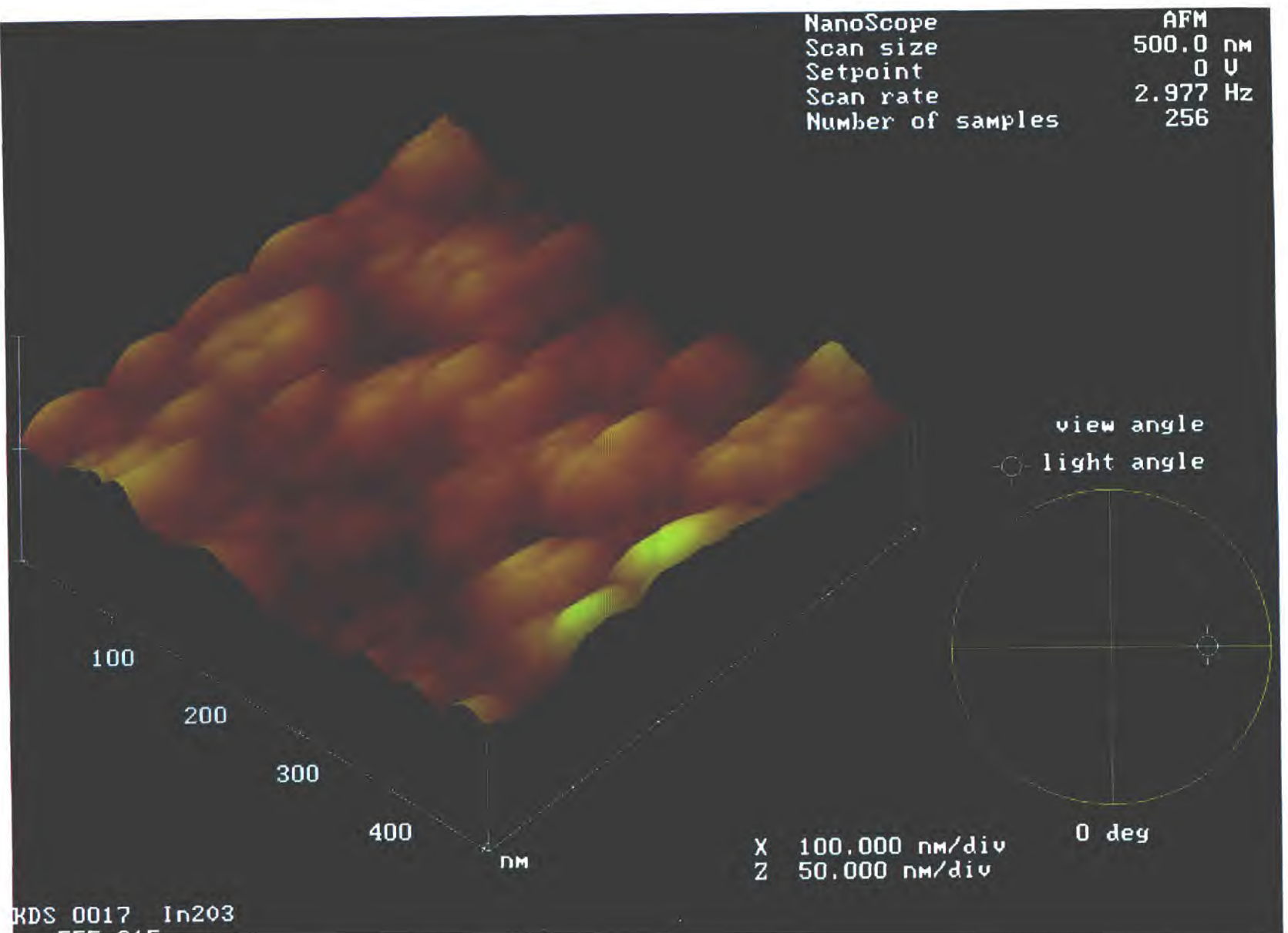


Figure 3-12 AFM Micrograph of In_2O_3 Film Growth From $\text{In}(\text{thd})_3$ and O_2 at 565°C After 12 mins

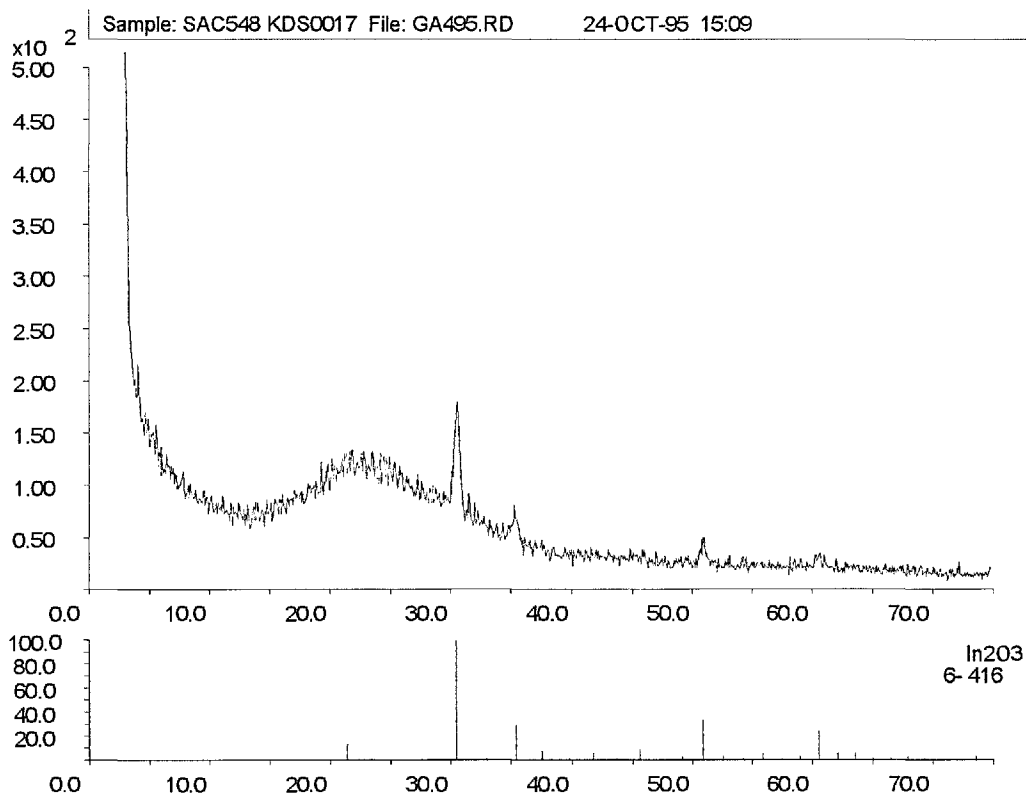


Figure 3-13 Glancing Angle XRD Pattern Of In_2O_3 Grown From $\text{In}(\text{thd})_3$

3.5.2.4 Summary of In_2O_3 Growth From Indium- β -diketonates

The indium- β -diketonates exhibited far better thermal stabilities when stored at temperatures in a bubbler than the trimethyl-indium adducts. Both $\text{In}(\text{acac})_3$ and $\text{In}(\text{thd})_3$ exhibited good deposition profiles, with no sign of pre-reaction of the precursor and the oxidant source in the gas delivery lines. These precursors, and particularly the more volatile $\text{In}(\text{thd})_3$, are therefore highly compatible with a pre-mixed APCVD system.

Both precursors also exhibited far better gas phase stability in the required deposition temperature region, with the growth profile of the coatings not being highly temperature dependant.

Unfortunately the high melting points of the materials is a disadvantage, requiring considerable heating of all delivery lines to prevent condensation. An investigation of other novel indium compounds was therefore carried out to determine if a material showing a similar gas phase stability to the indium- β -diketonates but with a higher volatility existed.

3.5.3 Growth Of In_2O_3 From Dimethylindium compounds.

3.5.3.1 Growth of In_2O_3 From $\text{Me}_2\text{In}(\text{OMe})$:

The compound $\text{Me}_2\text{In}(\text{OMe})$ has been investigated for the growth of In_2O_3 by conventional CVD using the same pre-mixing arrangement with oxygen that has previously been used for the indium chelates and the trimethylindium adducts. The growth of In_2O_3 using this precursor at a substrate temperature of 565°C was investigated.

Table 3-6 Growth Conditions For In_2O_3 Film Growth From $\text{Me}_2\text{In}(\text{OMe})$

Substrate Temperature	565-625°C
Bubbler Temperature	80°C
Bubbler Gas Flow	200 cc / min
Nitrogen Carrier Gas	4 litres / min
Oxygen Flow	0.6 litre / min
Delivery Line Temperature	150°C
Run Time	2.5 minutes

At a deposition temperature of 565°C film growth was carried out with similar flow rates to those used for the growth of In_2O_3 from the indium chelates, but with a reduced growth period of 2.5 minutes.

Under these conditions the film coverage of the glass substrate was relatively poor with only the front 4-5 cm of the glass showing signs of a conductive coating. By reducing of the oxygen concentration by a factor of three, to 4% of the total gas stream, an improvement in the film coverage was obtained, producing a conductive coating along

the whole length of the film, with the coatings having a resistivity of approximately $1 \times 10^3 \Omega \text{ cm}$.

The poor film coverage obtained using this precursor and the high dependency of film growth on the oxygen concentration in the gas stream suggest that the precursor is pre-reacting in the gas phase in a similar way to the trimethylindium adduct $\text{Me}_3\text{In}(\text{OEt}_2)$.

The addition of solvent additives was therefore investigated in an attempt to produce a more thermally stable gas phase intermediate.

The addition of butyl-acetate, water and iso-propanol were all unsuccessful, however, with powdery coatings and signs of In_2O_3 particulates being formed in the reactor chamber.

After a series of deposition experiments, the quality of the deposited films also deteriorated, with the mass transport of the precursor diminishing, despite the bubbler temperature never exceeding 80°C .

Analysis of the bubbler residues, showed the precursor had decomposed producing indium metal in the bubbler. Repeated examination of the precursor $\text{Me}_2\text{In}(\text{OMe})$ showed this decomposition to be accelerated by increasing the temperature at which the material was held, with lifetime of the precursor diminishing to less than 1 hour if the bubbler was held at 100°C . The decomposition of this material is likely to occur by a radical mechanism, and this is consistent with the formation of indium metal in the bubbler.

As with the trimethylindium compounds the long term thermal stability of this precursor in a bubbler held at temperature is questionable. Further study of this precursor was as a result not attempted due to its poor deposition characteristics and its poor thermal stability.

3.6 Conclusions:

The growth of satisfactory In_2O_3 films has been achieved using a wide range of precursors.

Some of the precursors have been identified as unsuitable for use in a pre-mixed reactor system because they exhibited pre-reaction in the gas phase, resulting in involatile intermediates which either drop out in the delivery lines or result in a powder being blown through the reactor which produces little film deposition.

Of the chemicals investigated the $\text{Me}_3\text{In}(\text{OEt}_2)$ compound appears to be the worst for pre-reaction with the compound appearing to pre-react completely before it enters the reactor chamber. This is a very similar result to that seen previously for Me_3In suggesting that the adducted compound may be breaking down or is behaving in a similar fashion to the non-adducted compound. This pre-reaction has been overcome, to an extent by the use of the tetrahydrofuran adduct which appears to protect the metal centre from premature attack by the oxidant source. Film growth from this precursor is highly temperature dependant, and whilst good films can be achieved at lower deposition temperatures of $400\text{--}450^\circ\text{C}$, at higher deposition temperatures film growth is concentrated near the reactor inlet.

The thermal stabilities of these materials in a bubbler are also poor, and significant signs of thermal decomposition are observed on holding the bubbler at a sufficiently high temperature to obtain a usable vapour pressure. The maximum temperature of 80°C (to prevent potentially dangerous decomposition) at which the material can be held also seriously reduces the vapour pressure of the material achievable.

The dimethylindium compound $\text{Me}_2\text{In}(\text{OMe})$ also suffers from similar problems to the trimethylindium compounds, with thermal decomposition problems being observed when the material is held at an elevated temperature in the bubblers. The thermal stability of this material in the gas phase is also questionable, and it is unclear whether transport of the intact precursor is occurring.

The indium β -diketonates exhibit significantly better stabilities in the bubblers, with the materials capable of being held at elevated temperatures for a significant period of time with only small thermal decomposition of the material being observed. Whilst the low volatilities of the precursors present problems, the materials also exhibit far better gas phase stability than the methylindium compounds with no signs of pre-reaction of the precursors with oxygen being observed. This results in film growth from these materials having little dependency upon the growth temperature and oxygen concentration of the gas stream.

From the studies of the growth of In_2O_3 it was decided to carry out doping studies on the most promising precursor. The precursor chosen for an investigation of doping was $\text{In}(\text{thd})_3$, because it showed no sign of pre-reaction in the delivery lines, and was thermally stable when held at elevated temperatures in the bubbler.

The following Chapter will describe the effects of doping studies carried out using this indium precursor.

3.7 References

1. K. Badeker, *Ann. Phys.(Leipzig)*, **1907**, 22, 749
2. L. Holland, *Vacuum Deposition Of Thin Films*, Wiley, New York, **1958**
3. J. L. Vossen, *Physics of Thin Films*, **1977**, 9, 1
4. T. T. Kodas and M. Hampden-Smith, *The Chemistry of Metal CVD*, **1994**, VCH, Weinheim and references therein
5. W. Spence, *J. Appl. Phys.*, **1967**, 38, 3767
6. K. B. Sundaram and G. K. Bhagavat, *J. Phys. D.*, **1981**, 14, 333
7. R. Terneu and A. Van Cauter, *Uk Patent No. GB 2026454B*, **1979**, J. F. Thomas, R. Terneu, A. Van Cauter and R. Laethem, *UK Patent No. GB 2185250A*, **1985**, F. B. Ellis Jr., *United States Patent No. 5393563*, **1995**, G. H. Lindner, *United States Patent No. 4788079*, **1988**, Elf Atochem, *International Patent No. WO 93/12934*, **1993**, V. A. Henry, *United States Patent 4853257*, **1989**
8. I. Hamberg and C. Granqvist, *J. Appl. Phys.*, **1986**, 60, 123
9. Z. Jin, I. Hamberg and C. Granqvist, *J. Appl. Phys*, **1988**, 64, 5117

10. K. L. Chopra, S. Major and D. Pandya, *Thin Solid Films*, **1983**, 102, 1
11. A. Dawar, J. Joshi, *J. Mater. Sci.*, **1984**, 19, 1
12. Sputtered Example: C. Geoffroy, G. Campet, F. Menil, J. Portier, J. Salardienne and G. Couturier, *Active Passive Elect. Comp.*, **1991**, 14, 111. CVD Example: W. Luo and Z. Tan, *J. Phys (Paris)*, **1989**, C5, 773
13. M. Higuchi, S. Uekusa, R. Nakano and K. Yokogawa, *J. Appl. Phys.*, **1993**, 74(11), 6710
14. Z. Jin, I. Hamberg and C. Granqvist, *J. Appl. Phys.* , **1988**, 64(10), 5118
15. A. Dawar and J. Joshi, *J. Mater. Sci.*, **1984**, 19, 1
16. I. Hamberg, and C. Granqvist, *J. Appl. Phys.*, **1986**, 60(11), R123
17. G. Frank, E. Kauer and H. Kostlin, *Thin Solid Films*, **1981**, 77, 107
18. P. Balian, G. Zagdoun and M. Trouve, US Patent 5, 387, 433, **1995**
19. T. Maruyama and K. Fukui, *Jpn. J. Appl. Phys., Part 2*, **1990**, 29, L1705
20. R. Nomura, K. Kohinishi and H. Matsuda, *J. Electrochem. Soc.*, **1991**, 138, 631
21. S. Mirzapour, S. M. Rozati, M. G. Takwale, B. R. Marathe and V. G. Bhide, *Mater. Lett.*, **1992**, 13, 1357
22. M. G. Mikhailov, T. M. Ratcheva and M. D. Nanova, *Thin Solid Films*, **1987**, 146, L23
23. W. Siefert, *Thin Solid Films*, **1984**, 121, 275
24. S. Kulaszewicz, W. Jarmoc, I. Lasocka, Z. Lasocki, C. Michalski and K. Turowska, *Thin Solid Films*, **1987**, 148, L55
25. S. Mirzapour, S. M. Rozati, M. G. Takwale, B. R. Marathe and V. G. Bhide, *J. Mater. Sci.*, **1994**, 29, 700
26. A. Oritz, M. Garcia, S. Lopez and C. Falcony, *Thin Solid Films*, **1988**, 165, 249
27. T. Ishida, H. Kouno, H. Kobayashi and Y. Nakato, *J. Electrochem. Soc.* , **1994**, 141, 1357
28. V. F. Korzo and V. N. Chernayaev, *Phys. Stat. Sol.(a)*, **1973**, A20, 695
29. L. A. Ryabova, V. S. Salun and I. A. Serbinov, *Thin Solid Films*, **1982**, 92, 327
30. T. Maruyama and K. Fukui, *J. Appl. Phys.*, **1991**, 70(7), 3848
31. W. Luo, P. Ren, C. Tan and Z. Tan, *J. Phys. II, Coll. C2*, **1991**, 1, C2-961
32. J. Kane, H. P. Schweizer and W. Kern, *Thin Solid Films*, **1975**, 29, 155
33. S. Reich, H. Suhr and B. Waimer, *Thin Solid Films*, **1990**, 189, 293

34. T. Maruyama and T. Kitamura, *Jpn. J. Appl. Phys., Part 2*, **1989**, 28, L1096
35. B. Mayer, *Thin Solid Films*, **1992**, 221, 166 and US Patent 5, 122, 391, **1992**
36. T. Maruyama and K. Fukui, *Jpn. J. Appl. Phys., Part 2*, **1990**, 29, L1705
37. T. Maruyama and K. Fukui, *Thin Solid Films*, **1991**, 203, 297
38. T. Maruyama and T. Nakai, *J. Appl. Phys.*, **1992**, 71, 2915
39. Safety Data Sheet Supplied by Epichem

4. Growth Of ITO From $\text{In}(\text{thd})_3$ and a Range of Tin Dopants

4.1 Aim:

The growth of ITO from the precursor $\text{In}(\text{thd})_3$ and a range of tin dopant precursors has been investigated. The films have been grown onto an undercoated glass substrate in the temperature range 565-625°C. The optical and electrical properties of the films have been investigated.

4.2 Experimental:

The films have been grown using the equipment that has been described previously in Chapter 2, onto an undercoated glass, to obtain an understanding of the effect of a range of tin dopants on the growth ITO from $\text{In}(\text{thd})_3$ and oxygen. The tin dopants investigated include:

1. Dichlorodimethyltin (DMT)
2. Diacetatodimethyltin (DMTDA)
3. Tetrachlorotin
4. Diacetatodibutyltin
5. Di(ethylhexanato)tin(II)

For all the experiments the growth of In_2O_3 was carried out using standard conditions. The tin dopant was then added to the system either by bubbler or syringe injection.

4.3 Results and Discussion:

4.3.1 Effect of Solvent on the growth of In_2O_3

Initially an investigation of the effect on In_2O_3 film growth from $\text{In}(\text{thd})_3$ and oxygen of gas phase additives was carried out in order to determine the best solvent for the transport of tin dopant materials via syringe injection. In order to allow a range of tin dopant materials to be investigated, it was important to have a range of solvents which dissolved the tin precursors. Various solvents were used as additives, with the additives

being vaporised and added to the gas streams leading to the reactor. An investigation of the effect on film growth of the addition of water, cyclohexane, tetrahydrofuran, ethanol and butylacetate was carried out.

The additives were added by syringe injection and evaporation at a rate of 0.75 ml / min.

The addition of water and ethanol had a detrimental effect on film growth, with signs of severe pre-reaction being observed and resulted in powder formation both in the delivery lines and the reactor chamber. The addition of these solvents without the addition of oxygen as a co-reactant, also resulted in poor film growth, suggesting these solvents were not ideal for the transport of tin dopants.

Many metal beta-diketonates have been reported for the deposition of oxide films mainly by the use of LPCVD.^{1,2} In these systems the addition of water vapour in the gas stream has been reported to be beneficial particularly when fluorinated beta-diketonates have been used.³ Whilst the exact role of the water is not fully understood it is believed the water vapour aids the clean breakdown of the precursor. The water vapour may result in the displacement of the beta-diketonate ligand from the metal centre, with the subsequent formation of hydroxy intermediates in the gas phase. The deposition of In_2O_3 from $\text{In}(\text{thd})_3$ is likely to follow a similar decomposition pathway to these other metal beta-diketonates. The signs of pre-reaction observed in the gas delivery lines when water is added to the reaction are consistent with this, with hydroxy species possibly being formed on mixing the precursors. Unlike in the LPCVD from these metal beta-diketonates, however, the resulting intermediates appear to be insufficiently volatile to be transported in the gas phase and result in powder formation in the gas delivery lines.

The use of cyclohexane and tetrahydrofuran, did not have a detrimental effect on film growth and the growth appeared to be similar to that achieved without any solvent addition.

The addition of butylacetate to the reaction mixture had the most beneficial effect with two clear advantages being observed:

- A spreading of the growth profile towards the exhaust of the reactor.

- An increase in the crystallite size in the coating and an increase in the crystallinity of the film.

Table 4-1 Comparison of In₂O₃ Film Growth With and Without BuOAc Addition

Angle	(hkl)	In(thd) ₃ , O ₂ and BuOAc	In(thd) ₃ and O ₂
21.5°	(211)	210	56
30.6°	(222)	2372	262
33.1°	(321)	17	-
35.5°	(400)	48	62
37.7°	(411)	21	10
39.8°	(420)	-	-
41.8°	(332)	53	10
43.8°	(422)	10	-
45.7°	(310)	69	12
49.3°	(521)	16	-
51.0°	(440)	246	59
60.7°	(622)	146	31
Total Diffraction Counts		3208	502
(222) Divided by Total as Percentage		73.9	52.2
Crystallite Size Angstroms		735	402
FWHM		0.306	0.338

The increase in the crystallite size, observed in the grown coating has an important influence on the electrical properties of the grown film. Increasing the crystallite size results in fewer grain boundaries in the coating, and consequently scattering of the carriers in the coating is reduced, and their mobility increases.

The changes in film growth observed may indicate a change in the deposition mechanism involved in the reaction, either with the formation of a more thermally stable

gas phase intermediate resulting in the improved growth profile or with a change in the surface reaction involved. From this study the exact role of the butylacetate is unclear, but further investigation of its role during film deposition is described in Chapter 5 of this thesis.

Table 4-2 Typical Growth Conditions For Growth Of In_2O_3 From $\text{In}(\text{thd})_3$

In(thd) ₃ bubbler	200°C and 200 cc/min through precursor
Substrate temperature	565-625°C
Oxygen Flow	600 cc/min
Nitrogen Carrier Flow	4.5 litres/min
Reactor flush flow	5.5 litres/min
Growth Time	12 minutes

4.3.2 ITO Growth From $\text{In}(\text{thd})_3$ and DMT:

The growth of ITO from the reaction of $\text{In}(\text{thd})_3$ with DMT and oxygen has been investigated. Standard conditions for the growth of In_2O_3 from $\text{In}(\text{thd})_3$ and oxygen were used, and the tin dopant was delivered via a bubbler. The chemicals were then all pre-mixed prior to entry into the reactor chamber.

4.3.2.1 Effect of Dopant Concentration on Film Properties:

The effect of dopant concentration on film growth has been investigated in the deposition temperature range 565-625°C

4.3.2.1.1 Effect of dopant concentration on the film's electrical properties

An investigation of the effect of the tin dopant concentration on the films electrical properties was initially carried out at a growth temperature of 565°C. The amount of dopant added to the films was determined by the amount of carrier gas passed through the tin precursor bubbler, and the temperature at which the bubbler was maintained.

Initial growth studies using this material were carried out using the conditions outlined in Table 4-3.

Table 4-3 Typical Growth For ITO From In(thd)₃ and DMT

In(thd) ₃	200°C, 200 ml / min through precursor
DMT:	75°C, 60 ml / min passed over precursor
Substrate Temperature	565°C
Carrier Gas Flow:	Nitrogen 4.5 l/ min
Oxygen Gas Flow:	600 ml / min
Growth Time:	12mins

Films grown under these conditions exhibited poor electrical properties with resistivities of 4.5×10^{-4} - $6.5 \times 10^{-4} \Omega \text{ cm}$ being achieved. These results are poor compared with previous literature reports of CVD and PVD deposited ITO which exhibit a resistivity of approximately $2 - 3.5 \times 10^{-4} \Omega \text{ cm}$.^{4,5}

Analysis of films deposited under these conditions by X-ray fluorescence determined the Sn:In ratio in the coatings to be approximately 1:1. This suggests that the doping level was far above the optimum level of tin doping previously reported for ITO produced by PVD and CVD techniques, which exhibit the best electrical properties at a doping level of approximately 23 weight % tin : indium (8 atom % tin) in the coating.^{4,5} Further analysis of the films produced under these growth conditions by Auger depth profiling confirmed the average Sn:In ratio in the coatings to be approximately 1:1 but also indicated that the film had a variable composition.

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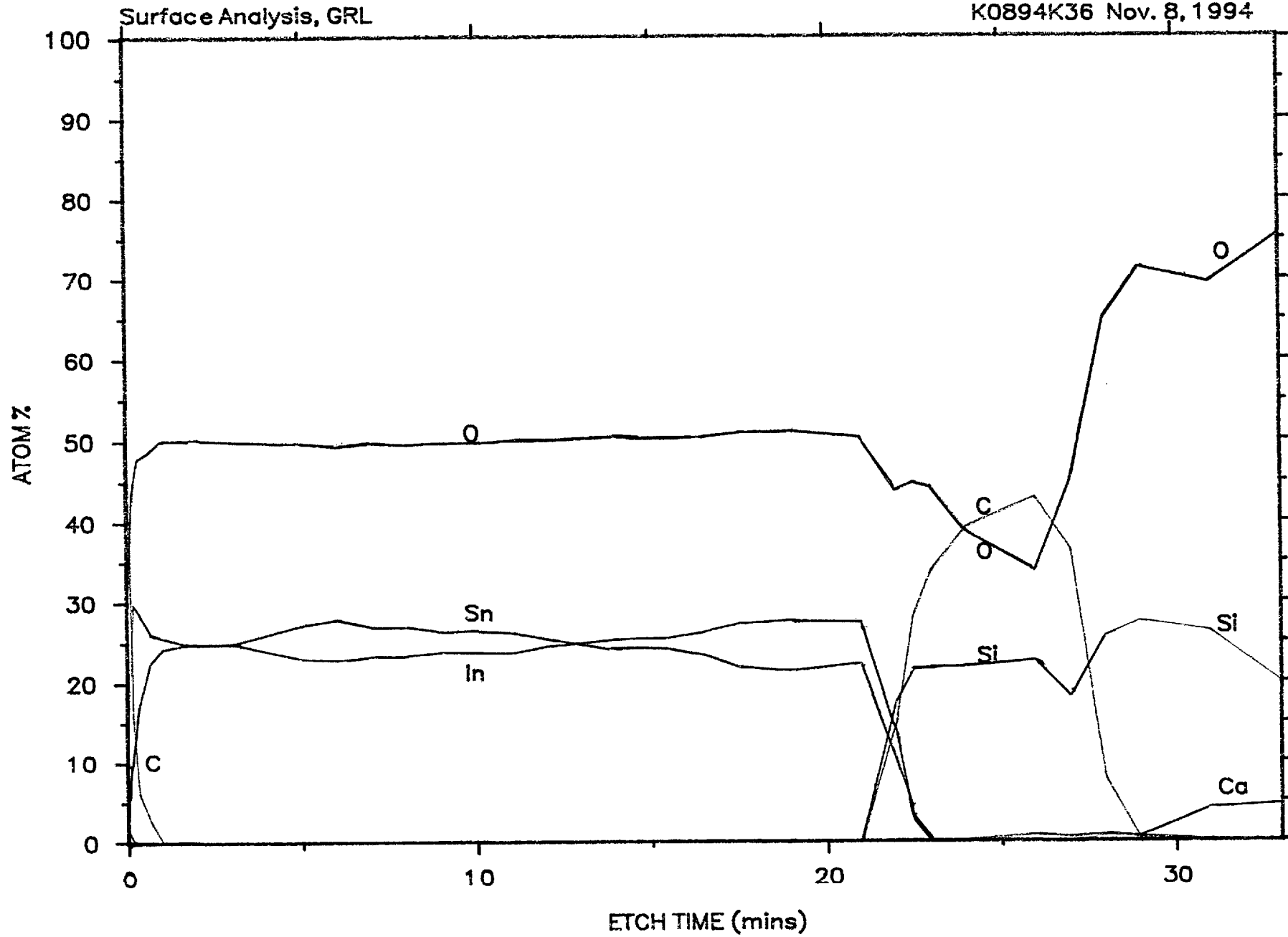


Figure 4-1 Auger Depth Profile Of Overdoped ITO

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Auger analysis showed the films to have low contamination levels of carbon and chlorine, except on the top surface and at the interface between the top coating of ITO and the undercoated glass substrate.

The impurities present at the surface of the coating, are probably a result of atmospheric contamination of the coating surface, whereas impurities at the interface between the undercoat layer and the ITO are more likely to be a result of contaminants in the glass leaching out of the bulk glass. This phenomenon is well documented, particularly for sodium diffusing out of glass. It results in the formation of film defects, and affects the films electrical properties by acting as scattering sites, which reduce the mobility of the films electrical carriers.^{7,8}

The variation in doping level throughout the thickness of the coatings, is consistent with the material not being a single phase material, and this is supported by glancing angle X-ray diffraction results.

The XRD patterns of the overdoped films exhibited a halo at around 20° due to amorphous material in the film. This is believed to be amorphous tin oxide in the film due to an excess of tin in the vapour phase during the deposition process. The excess tin which is unable to incorporate into the In_2O_3 lattice as a substitutional dopant therefore results in separation of the coating into a two phase material, consisting of doped indium oxide and tin oxide. The presence of a two phase material at such high doping levels is consistent with literature reports which indicate that the In_2O_3 lattice can accommodate approximately 50% doping of tin before separating into a two phase material.⁹

Etching of this overdoped material was also more difficult than PVD ITO, with an extended Zn:HCl etch being required to remove all the film from the glass surface.¹⁰ The increased etch time is further evidence for the existence of a two phase material, with amorphous tin oxide material in the coating being more etch resistant than the bulk of the polycrystalline film. The excess tin oxide and the two phase nature of the coating accounts for the poor electrical properties of the coatings, with the amorphous tin oxide reducing the mobility of the carriers by acting as scattering sites.

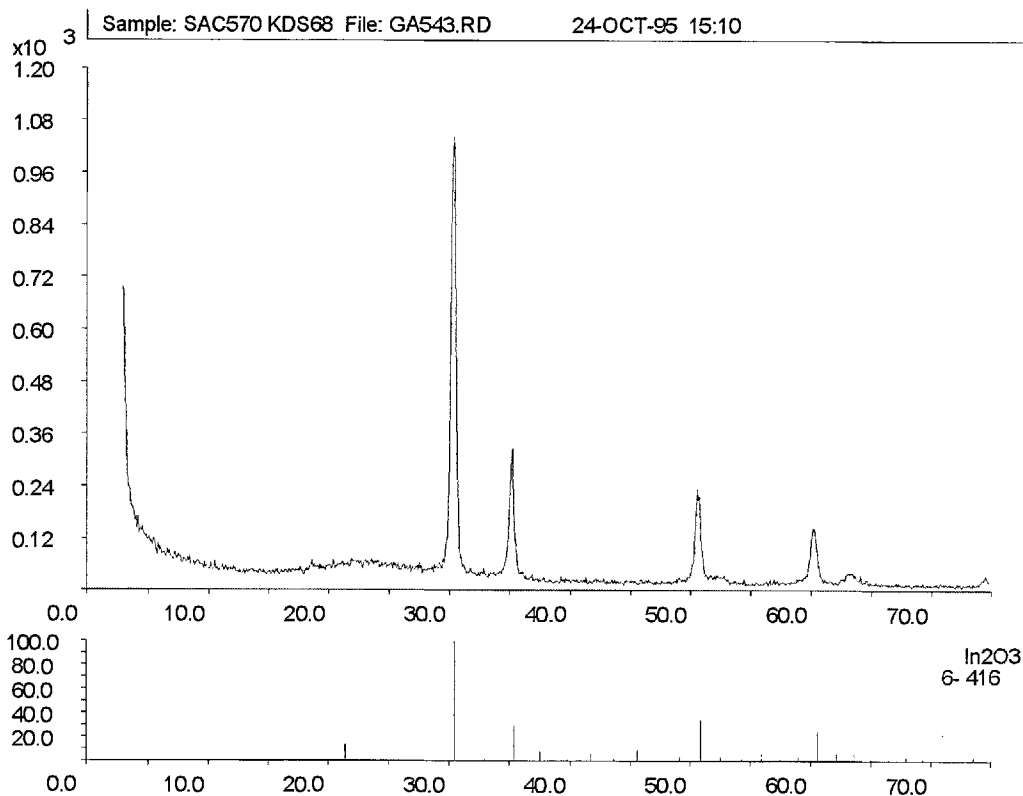


Figure 4-2 Glancing Angle XRD Pattern Of Overdoped ITO Grown From $\text{In}(\text{thd})_3$, O_2 and DMT

The SEM micrograph shown in Figure 4-3 of the overdoped In_2O_3 shows the presence of a crystalline coating, although the surface is also covered with dark areas of what is believed to be an amorphous material. Previous studies of the growth of amorphous SnO_2 , have shown similar images.¹¹

The AFM micrograph in Figure 4-4 of a typical overdoped film shows the surface of the coating to be relatively rough with a mean roughness of 5.42 nm over a 2μ square of the coating. The roughness of these film compared with that of In_2O_3 may be a result of the amorphous material at the surface.

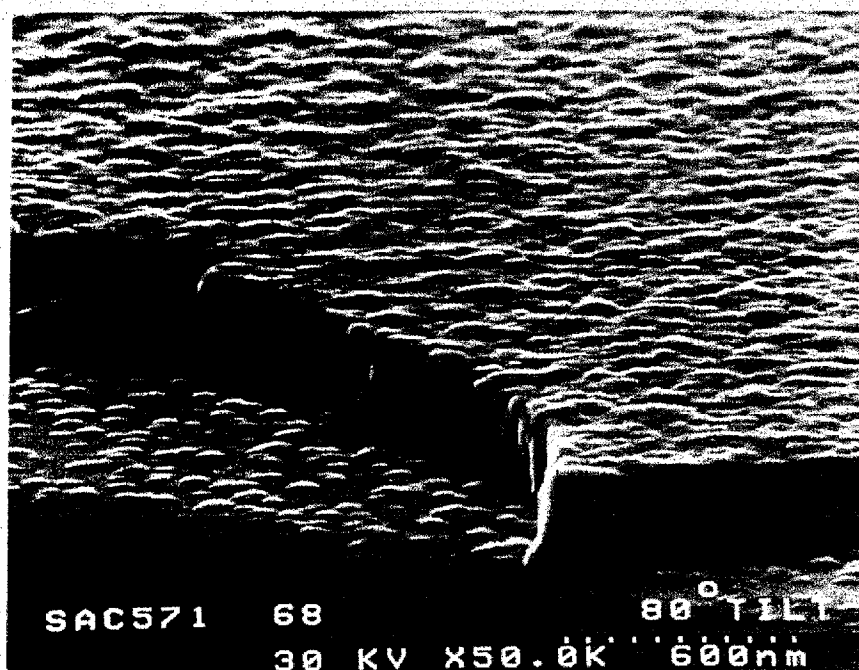
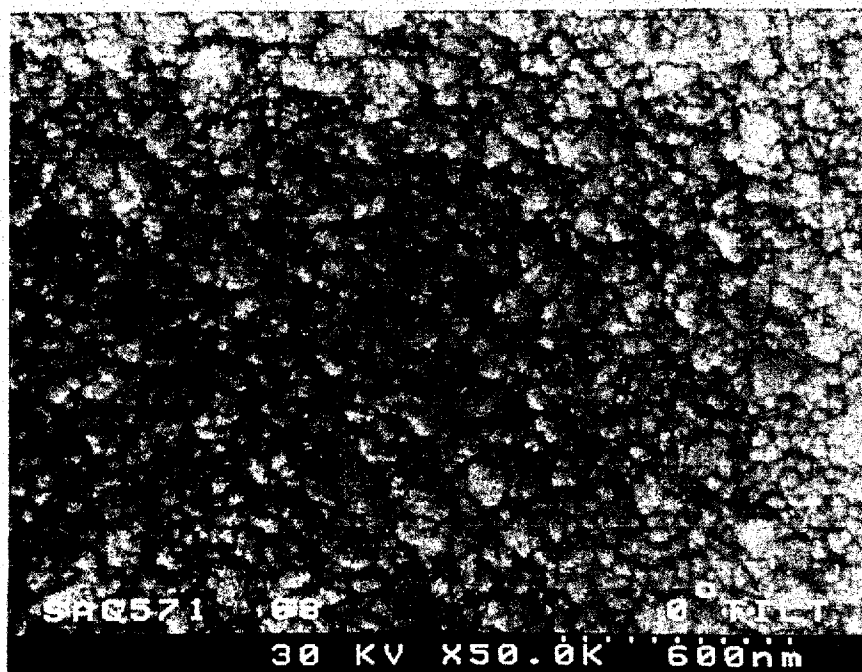


Figure 4-3 SEM Micrographs of Overdoped ITO Grown From In(thd)₃, DMT and O₂ at 565°C

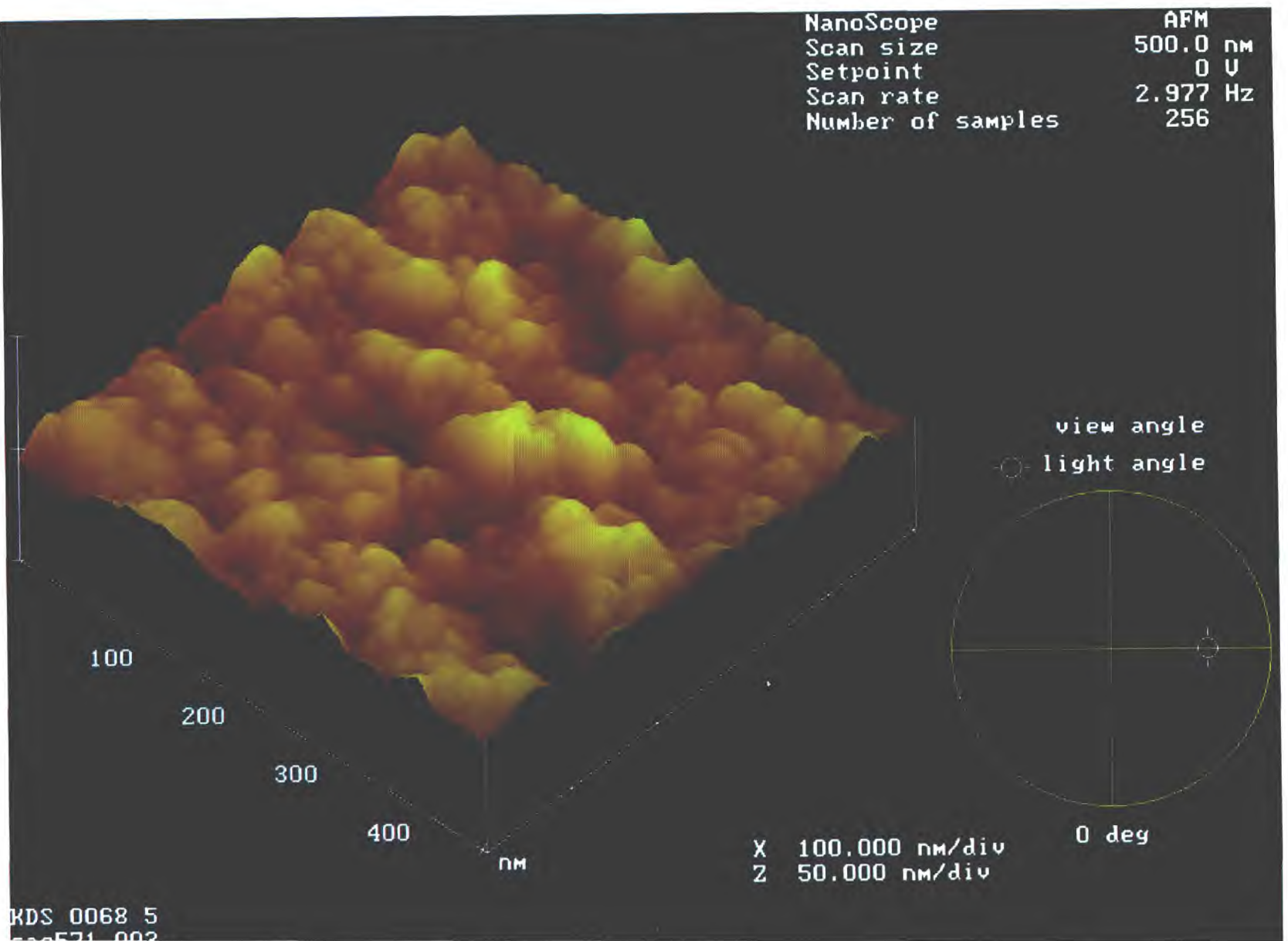


Figure 4-4 AFM Micrograph Of Overdoped ITO Grown From In(thd)₃, DMT and O₂ at 565°C

In order to reduce the tin doping level, the temperature of the DMT was reduced to lower its vapour pressure and reduce the carryover of precursor. It was found that by holding the DMT bubbler at 28°C and passing the gas over the top of the precursor, the films exhibited better electrical properties, with resistivities of approximately $2.0\text{-}5 \times 10^{-4} \Omega \text{ cm}$ being achieved. By altering the gas flow over the precursor, control over the exact doping level in the film could be achieved. Alteration of the doping level to achieve the optimum electrical properties was therefore investigated.

The tin doping level has been shown to drastically affect the conductivity of the film obtained, with too low and too high a doping level resulting in films with poor electrical properties.

The results of this doping study are outlined in the Table 4-4.

Table 4-4 Effect Of Doping Concentration On Electrical Properties Of Coating

Weight Sn:In	%	Ratio (222):(400) From XRD*	Resistivity ($\times 10^{-4} \Omega \text{ cm}$)	Mobility (V^{-1} $\text{cm}^2 \text{ sec}^{-1}$)	Carrier Concentration $\times 10^{20} (\text{cm}^{-3})$
2.7		86:912	5.43	25.1	4.62
5.6		108:713	2.97	28.46	7.31
5.7		404:380	1.72	48.05	7.46
9.6		357:361	2.00	46.01	6.79
92.7		999:286	5.7	-	-

* Ratio (222):(400) For Random ITO = 3.5:1.¹²

The best electrical properties were attained at a doping level of approximately 6-8 weight % tin : indium at a growth temperature of 565°C, with resistivities as low as $1.72 \times 10^{-4} \Omega \text{ cm}$ being achieved. The results of this study are similar to those observed for other doped oxides such as antimony doped tin oxide and ITO deposited by other techniques, with the electrical properties improving with increased doping until a point is reached above which further increases in the doping concentration result in a deterioration in the films properties.¹²⁻¹⁵ This has been explained by in terms of an increased disorder at high dopant concentrations.¹⁶ Kostlin *et. al.*¹⁷, suggested that tin atoms surrounded by In_2O_3 act as donors improving the films properties, but if the tin's nearest neighbour is another tin atom the donor action is compensated and no increase in

the carrier concentration in the film is observed. If the films are even more heavily doped, however, the excess tin can then also act as a scattering site reducing the mobility of the carriers.

In order to investigate further the effect of dopant concentration on the electrical properties of the films, ITO films were grown at a temperature of 625°C, with the dopant concentration varying from 2 to 10 weight % tin to indium.

The best electrical properties for films grown at 625°C were achieved at a dopant concentration of approximately 3 weight % tin, well below the best doping level of approximately 8 weight % tin : indium required at 565°C.

The electrical properties achieved in this study are comparable with films grown by the industrially standard PVD technique,⁵ and are better than those achieved by previous reports of CVD ITO. The tin dopant level required to achieve equivalent properties to previously reported ITO by both CVD and PVD techniques is significantly lower in this study. The films had electrical properties equivalent to films deposited by other techniques although the doping level was typically less than 50%. The results obtained in this study therefore suggest that there is a relationship between the optimum doping level and the deposition temperature.

Whilst previous literature reports have reported that electrical properties of films are dependant upon the doping level, no dependency upon the deposition temperature has been reported for ITO deposited by CVD. Nath *et. al.*,¹⁸ reported the electrical properties of ITO deposited by activated reactive sputtering to be dependant upon the deposition temperature. They showed that for ITO films with a tin dopant concentration of 18 weight % tin to indium, the electrical resistivity of the films reduced monotonically with increasing temperature up to 250°C. Above this temperature, however, the electrical resistivity of the deposited film decreased rapidly.

The dependency of the electrical properties on the deposition temperature could be due to either an increase in the oxygen vacancies in the film, or an increase in the crystallinity occurring in films deposited at higher deposition temperatures.

Both of these factors would explain the higher conductivity, with increases in the number of oxygen vacancies leading to more carriers in the films whilst increased

crystallinity would decrease the scattering of carriers from grain boundaries resulting in improved mobility of the carriers. This is in general agreement with the standard conduction mechanisms for semiconductors^{19,20} and with studies carried out on sputtered and reactively evaporated ITO.²¹⁻²³

In order to determine which of these factors is likely to be responsible for the improved electrical properties of films, the number and mobility of the carriers in films deposited at 565 and 625°C and exhibiting similar electrical properties was investigated.

Figure 4-5 Comparison of films deposited at 565 and 625°C, exhibiting similar electrical properties.

Growth Temperature °C	Tin Dopant Concentration Weight %	(222):(400) Ratio**	Resistivity $\times 10^{-4} \text{ } (\Omega \text{ cm})$	Mobility $(\text{V}^{-1} \text{ cm}^2 \text{ sec}^{-1})$	Carrier Concentration $\times 10^{20} (\text{cm}^{-3})$
565	5.7	404:380	1.72	48.05	7.46
625	2.2	666:590	1.80	43	8.07

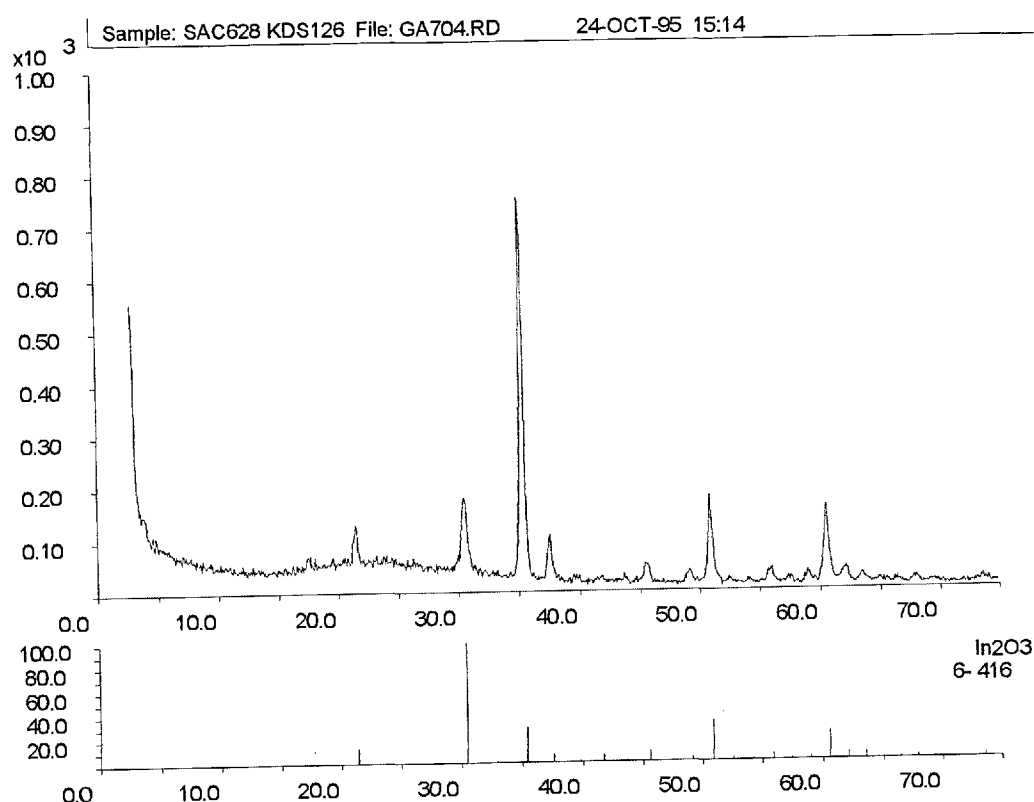
** Random In_2O_3 has a ratio of (222) : (400) of 3.5 : 1

Table 4-5 shows that whilst the mobility of the carriers remains fairly constant at approximately $45 \text{ V}^{-1} \text{ cm}^2 \text{ sec}^{-1}$, the number of carriers is increased in films exhibiting similar electrical properties. This is unexpected as the films deposited at a higher deposition temperature contain a lower level of tin dopant, and would therefore be expected to have a lower number of carriers. The increase in carriers is therefore likely to be due to an increase in the oxygen deficiency in the coating deposited at 625°C. As the oxygen deficiency of the coatings increases a lower amount of tin is likely to be required to achieve the optimum electrical properties. If the carrier concentration is too high the mobility of the carriers will begin to decrease as a result of collisions between the carriers. This study therefore suggests that there is a relationship between the amount of tin dopant and the degree of oxygen deficiency in the coating. If optimum electrical properties are to be achieved a balance between these must be achieved.

4.3.2.1.2 Effect of Dopant Concentration on Film Crystallinity

The dopant concentration not only influenced the electrical properties of the films, but also effected the crystallinity of the coatings.

Whilst XRD analysis of all the films grown at 565°C with a tin dopant level of 2-10 weight % tin to indium exhibited some (400) preferred orientation (as revealed by comparison of the XRD pattern of the coating with the XRD pattern of a randomly orientated sample of In_2O_3). They showed a similar level of crystallinity to ITO grown by other deposition techniques and the amount of dopant appeared to effect the extent of the preferred orientation. At low tin dopant concentrations of approximately 2 weight % tin, the films showed highly preferred growth of the (400) plane, but as this dopant level increased, the degree of (400) preferred orientation diminished. The decrease in (400) preferred orientation continued as the doping level increased until randomly orientated films were obtained when overdoping occurred. This change in the degree of (400) preferred orientation as the doping level in the film is modified can be seen in Figure 4-6.



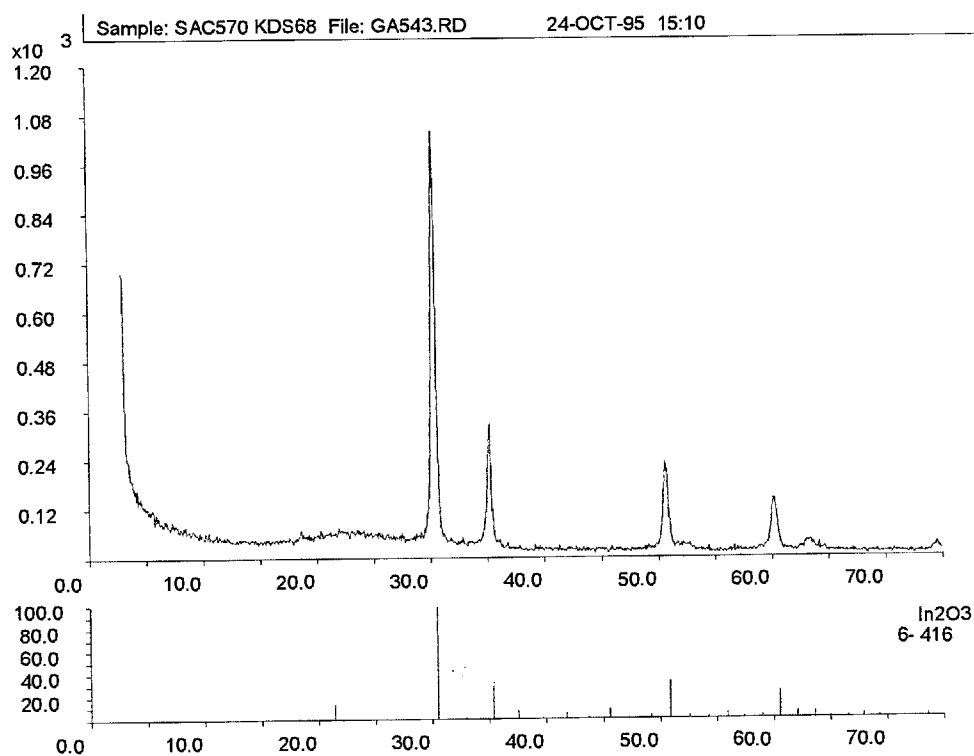
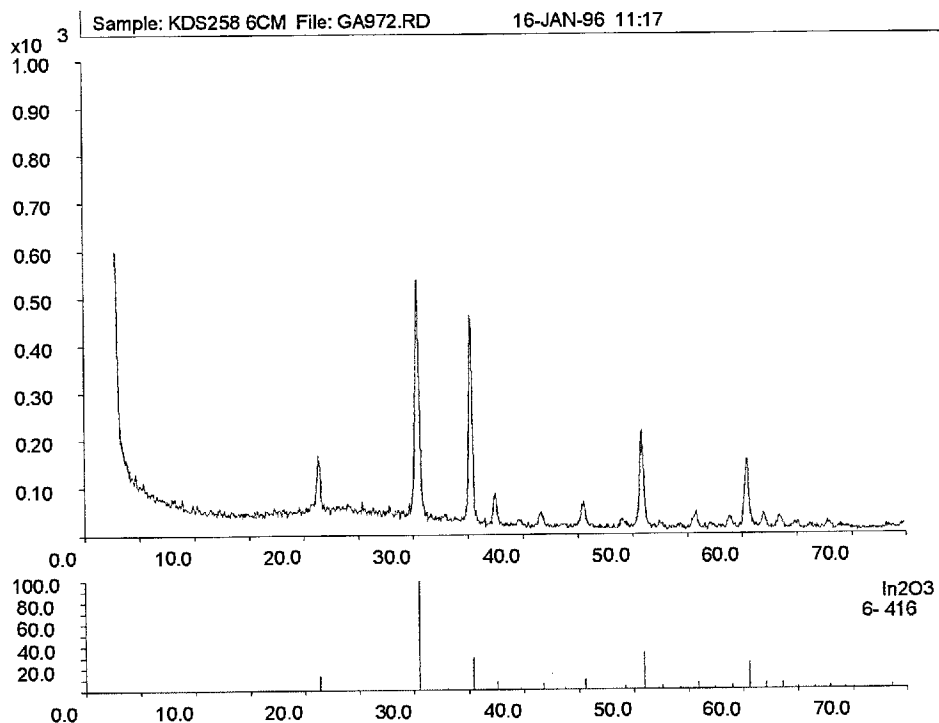


Figure 4-6 Glancing Angle XRD of ITO Grown From In(thd)₃ and DMT showing a. Highly Preferred Growth, b. Some Preferred Growth, c. Low Preferred Growth

Two further observations can be noted from the data:

1. As the extent of (400) preferred orientation diminished, the mobility of the carriers increased, until overdoping was observed at > 10 weight % tin.
2. The crystallite size in the films increased from approximately 200 Å in a highly preferred (400) film, to 360-380 Å in films exhibiting less preferred orientation.

The SEM micrograph analyses of films grown from $\text{In}(\text{thd})_3$ and DMT at different doping levels are shown in Figures 4-7 and 4-8. SEM micrographs of coatings with highly preferred growth in the (400) plane (Figure 4-7) show small crystallites, and appear to have resulted in a rough surface to the coating. This is confirmed by AFM analysis of the coating, with the mean roughness over a $2\ \mu$ square of coatings grown under these conditions being 8.9-10 nm., far higher than that observed for the In_2O_3 grown from $\text{In}(\text{thd})_3$ and oxygen. SEM micrographs of coatings grown with less preferred orientation in the (400) plane (Figure 4-8) show the presence of larger crystallites and AFM analysis of these films show them to be smoother.

Maruyama and Fukui reported a similar reduction in the degree of preferred orientation of film growth in ITO deposited by CVD from indium acetate and tin acetate,²⁴ but no relationship between this and the electrical properties of the films was reported.

As the dopant level is increased it is expected that the electrical properties of the coating will improve as the number of carriers increases due to substitutional doping of tin for indium, but the mobility of these carriers would be expected to remain fairly constant. As the dopant concentration is increased, the number of carriers does increase as expected, but the mobility of the carriers also changes. In films exhibiting a high degree of (400) preferred orientation the mobility of the carriers is low at approximately $28\ \text{V}^{-1}\ \text{cm}^2\ \text{sec}^{-1}$, whilst in films with less preferred orientation the mobility of the carriers is higher, reaching $40\text{-}48\ \text{V}^{-1}\ \text{cm}^2\ \text{sec}^{-1}$. This suggests that the structural properties of the film are affecting the mobility of the carriers.

The effect of preferred orientation on the electrical properties of the films has not previously been reported for ITO, but work carried out on SnO_2 deposited by CVD,²⁵ has shown that certain preferred orientations can be detrimental to the electrical

properties of coating, with reports suggesting that best electrical properties are obtained for films exhibiting a degree of (200) preferred orientation.

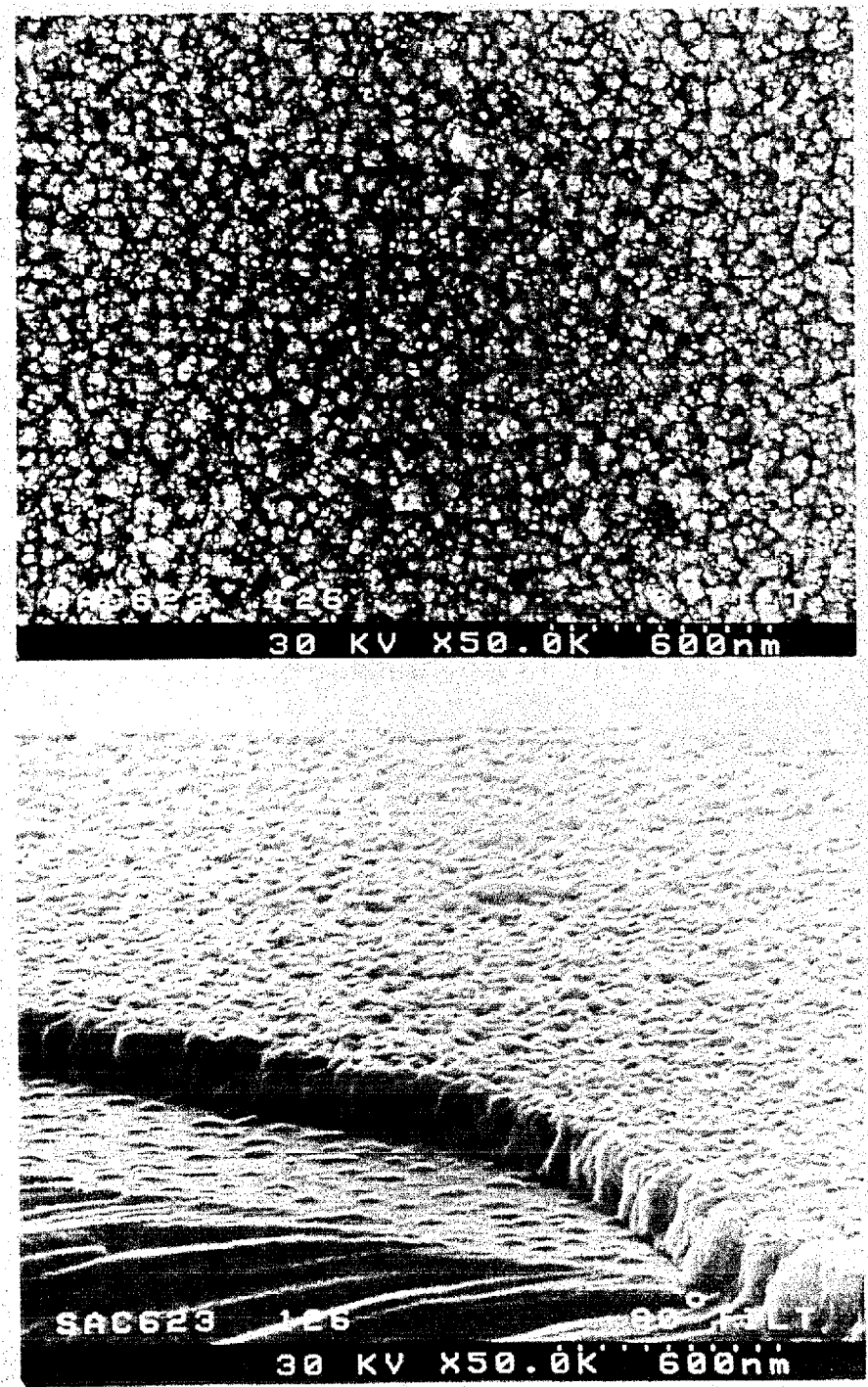


Figure 4-7 SEM Micrographs Of ITO Grown From In(thd)₃, DMT and O₂ Exhibiting Preferred Growth In The (400) plane.

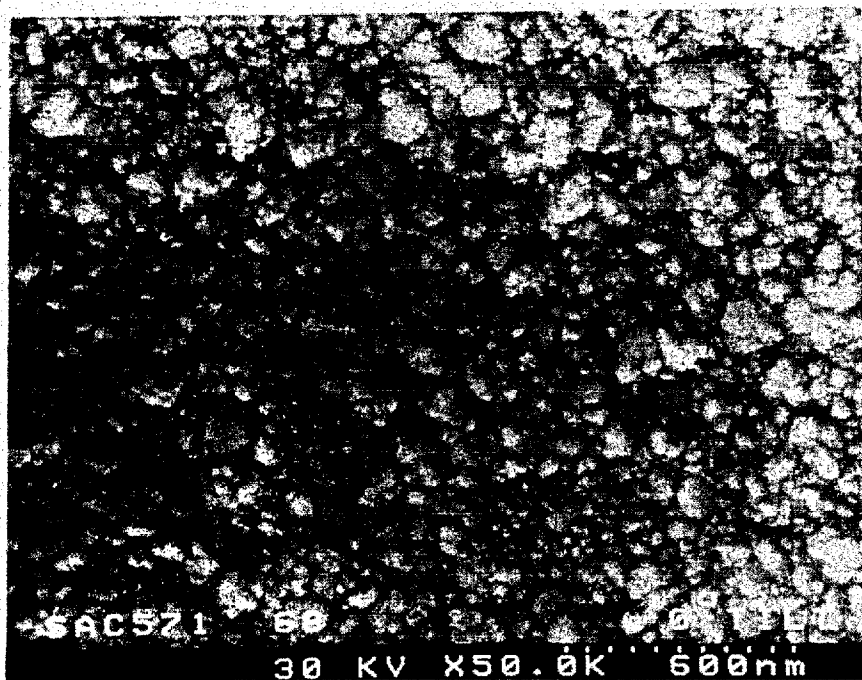


Figure 4-8 SEM Micrographs Of ITO Grown From $\text{In}(\text{thd})_3$, DMT and O_2 Exhibiting Little Preferred Orientation Growth.

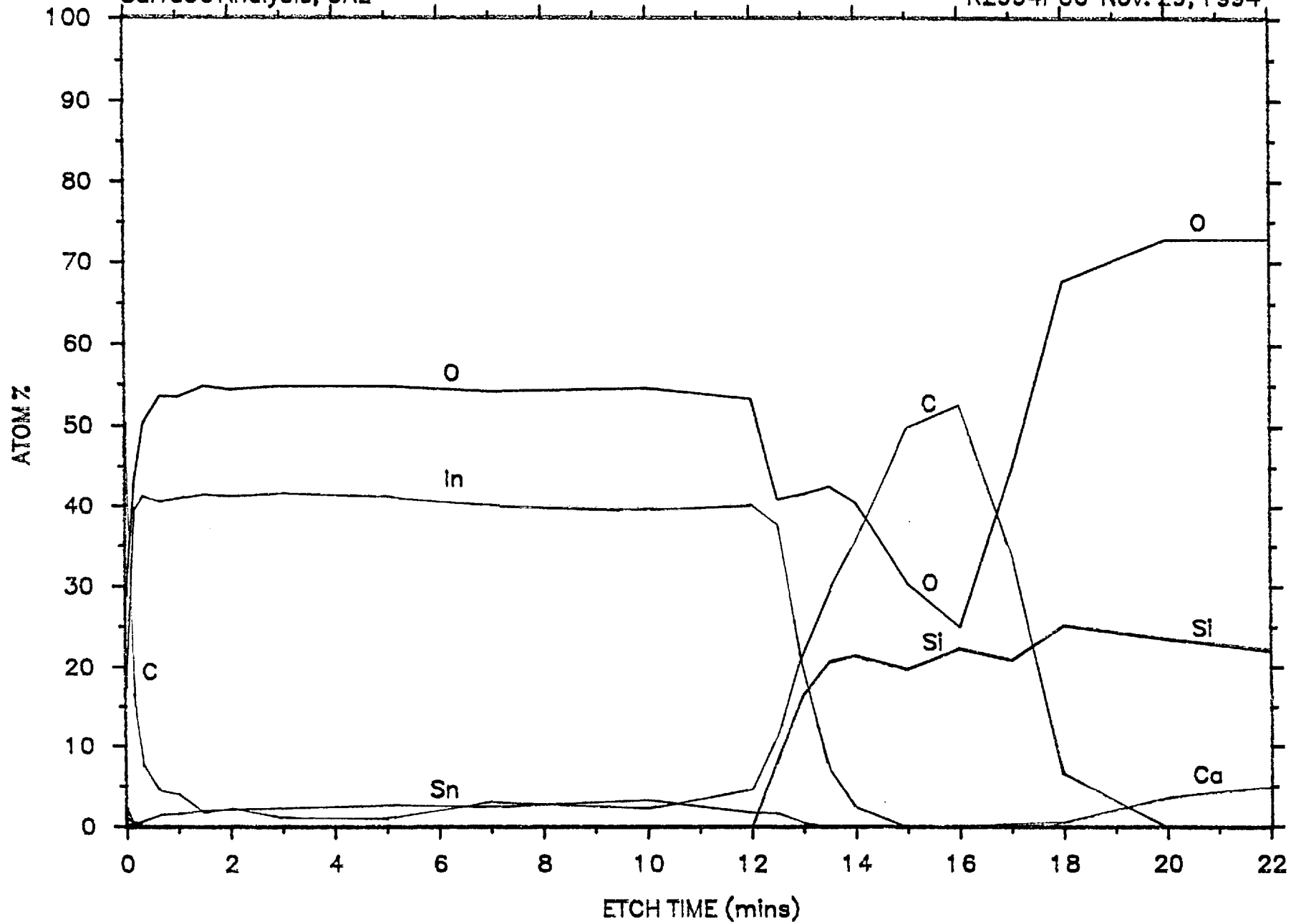


Figure 4-9 Auger Depth Profiles Of ITO Grown From In(thd)₃, DMT and O₂

The lower mobility observed in coatings showing preferred growth in the (400) plane may be due to crystal growth in this plane resulting in increased carrier scattering. The smaller crystallite size observed for coatings exhibiting a degree of (400) rather than (222) preferred orientation growth is consistent with this, with the smaller crystallite size resulting in an increase in the number of grain boundaries in the coating.

The results suggest that the degree of preferred orientation has an important influence on the electrical properties of the coating. The preferred orientation towards the (400) plane being detrimental to the electrical properties of the film, reducing the mobility of the carriers.

XRD analysis of the films deposited at a higher deposition temperature of 625°C, showed the films to be similar to those grown at 565°C, exhibiting preferred growth in the (400) plane. The films, however, had a lower degree of preferred orientation in the (400) plane, and unlike those grown at 565°C, no relationship between the dopant level and the degree of preferred orientation was observed. The reduction in the degree of preferred orientation observed in the films grown at higher deposition temperatures, may indicate that an increase in the nucleation at the surface is occurring and there is no preference towards growth in either the (222) or (400) plane. This has been seen for a wide range of CVD systems with the increased nucleation resulting in the crystal growth on top of the existing growth. As a result of the increased nucleation a tendency to form less preferred films occurs.

The effect of growth temperature on the films is shown in Table 4-6.

Table 4-6 Comparison Of Film Growth At 565 and 625°C

Growth Temperature °C	Tin Dopant Concentration Weight %	(222):(400) Ratio**	Resistivity $\times 10^{-4}$ (Ω cm)	Mobility ($V^{-1} cm^2 sec^{-1}$)	Carrier Concentration $\times 10^{20}$ (cm^{-3})
565	2.7	86:912	5.43	25.1	4.62
625	2.2	666:590	1.80	43	8.07

** Random In_2O_3 has a ratio of (222) : (400) of 3.5 : 1

This study has shown that the crystallinity of APCVD ITO is dependant upon the doping level and the deposition temperature. A similar relationship has been observed

for indium doped zinc oxide (ZnO:In), by Olvera *et. al.*²⁶, who observed that the crystallinity of films deposited by spray pyrolysis, was dependant upon the deposition temperature and also the indium dopant precursor used, although at higher deposition temperatures the degree of preferred orientation growth diminished.

4.3.2.2 *Effect of Growth Temperature:*

The effect of growth temperature on film properties of the films has been investigated between 400 and 625°C.

Below 400°C film growth was very slow with no observable coating obtained after a 12 minute deposition period. Film growth at 450°C, for the same time resulted in conductive films but the electrical properties of the coating were very poor with resistivities of approximately $7 \times 10^{-4} \Omega \text{ cm}$ being achieved. Alteration of the doping concentration at this deposition temperature, had little effect on the film properties, with X-ray analysis of coatings showing them to be less crystalline than those achieved at higher deposition temperatures.

The poor crystallinity of these coatings, may indicate that the films contain an increased number of impurities, due to incomplete oxidation of the precursor. The impurities in the coatings are likely to result in increased carrier scattering, and this would be consistent with the poor electrical properties observed in these coatings.

As previously described, film growth at 565°C, was good, with coatings having a resistivity of approximately $2 \times 10^{-4} \Omega \text{ cm}$ being achieved at a doping level of approximately 8 weight % tin : indium. An investigation of film growth at a higher deposition temperature of 625°C was therefore undertaken, in order to determine whether such properties could be achieved at higher deposition temperatures. An investigation of the effect of dopant concentration on the electrical properties of the film has already been discussed (4.3.2.1.1)

Whilst the best electrical properties of the films grown at 625°C were equivalent to those for films grown at 565°C with resistivities of approximately $2 \times 10^{-4} \Omega \text{ cm}$ being achieved, this was accompanied by a deterioration in the coverage of the glass plate at higher deposition temperatures, with the position at which maximum film thickness

moving closer to the inlet of the reactor. This indicates that the gas phase species are reacting at the substrate earlier as a result of the higher deposition temperature and as a result depletion of the gas phase precursor concentration is accelerated and the substrate coverage diminishes. The fact that the tin doping of the films was still as effective at 625°C as at 565°C, however, indicates that an equivalent change in the growth profile of the tin dopant is occurring. If the tin dopant profile had changed more or less than the indium precursors at the higher deposition temperature, the doping of the film and the films electrical properties would have been poorer at the higher deposition temperature.

A further effect of higher deposition temperatures was an increase in the efficiency of tin dopant incorporation, with a lower flow through the bubbler required to achieve a particular doping level, for example 500 cc / min over DMT at 28°C resulted in a 5-6 weight % tin film at a growth temperature of 565°C, but resulted in 10-12 weight % tin : indium at a growth temperature of 625°C. This indicates that the growth rate of tin oxide from DMT is enhanced more than the deposition of In_2O_3 from $\text{In}(\text{thd})_3$ by the increase in the deposition temperature. This is consistent with the work of Strickler,²⁷ on the growth of SnO_2 from DMT, which showed a marked increase in the growth rate occurs at deposition temperatures of >600°C for this system.

This study has shown that the properties of ITO are highly dependant upon the deposition temperature and the dopant concentration. The effect of other additives to the system was therefore investigated to determine if more accurate control over the deposited film and optimisation of the films electrical properties could be obtained .

4.3.2.3 Effect of Solvent Addition:

An investigation to determine the effect of additive addition on preferred growth was therefore undertaken to see if control over the preferred orientation of film growth could be achieved.

4.3.2.3.1 Effect of Solvent Addition at 565°C

Previously in an attempt to determine suitable solvents for the addition of tin dopants by syringe injection and evaporation the effect of solvents on In_2O_3 growth was investigated (Section 4.3.1). This study identified that butylacetate had a beneficial effect when added during film growth. This is believed to be due to a change in the deposition chemistry during film growth and therefore the addition of butylacetate to the vapour phase during the growth of ITO was investigated.

Butylacetate was added at a rate of 0.75 ml / min via syringe injection into an evaporator and then mixed with the precursors prior to contact with oxygen. This mixture resulted in a marked change in the grown film at a growth temperature of 565°C. The most marked effect was a change in the growth profile of the film, with the best conductivity of the film moving towards the exhaust end of the reactor. This is shown in the Figure 4-10.

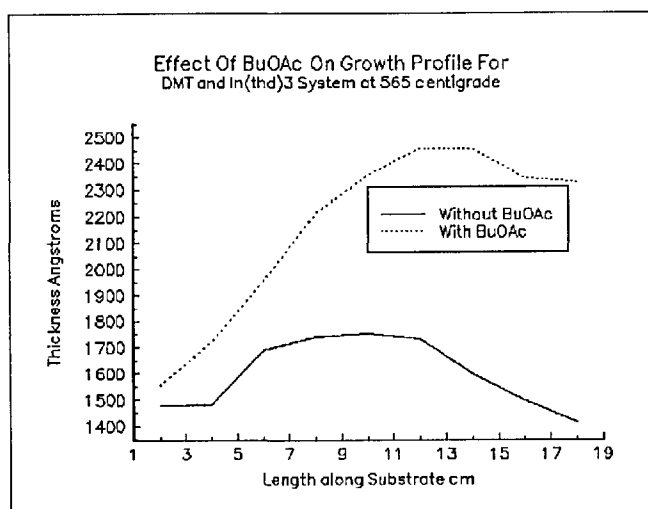


Figure 4-10 Graph Showing the Effect of Butylacetate Addition on the Growth Profile of ITO From $\text{In}(\text{thd})_3$ and DMT at 565°C

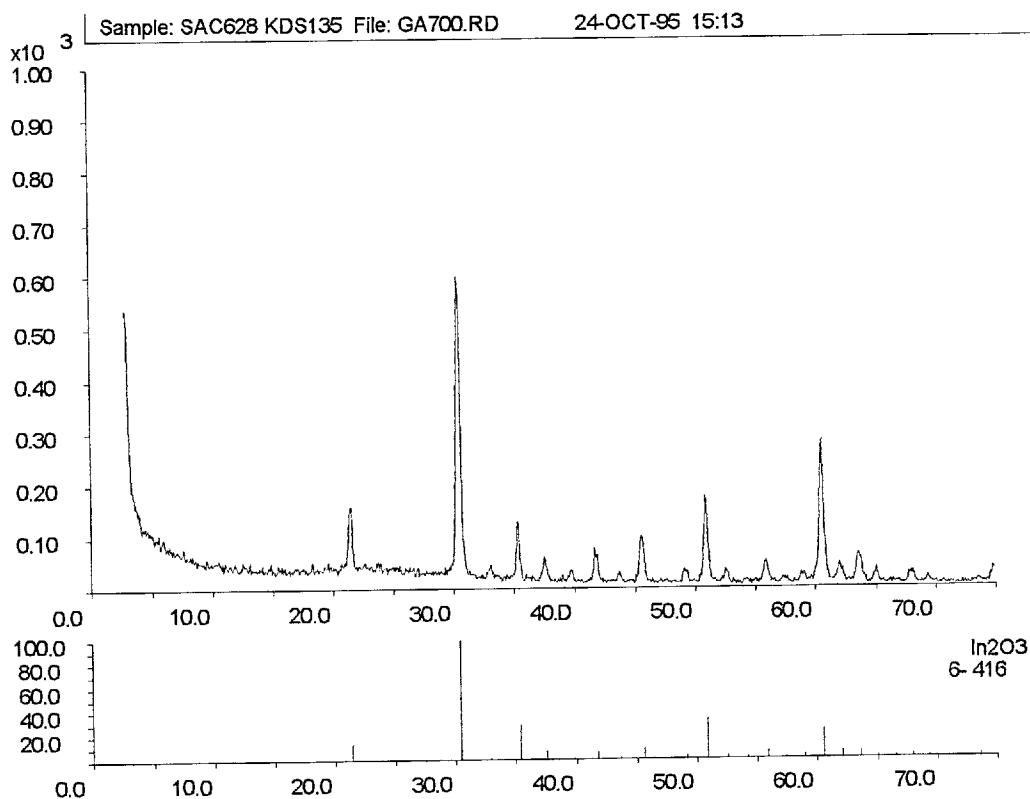


Figure 4-11 Glancing Angle XRD Pattern Of ITO Growth From $\text{In}(\text{thd})_3 + \text{DMT} + \text{BuOAc}$

The crystallinity of the films was also changed with the films exhibiting (222) preferred orientation growth rather than the (400) preferred growth seen under similar conditions without the addition of butyl-acetate. The properties of ITO growth with and without BuOAc addition at a substrate temperature of 565°C are summarised in Table 4-

6

Table 4-7 Table Comparing Properties Of Coatings Grown From In(thd)₃ and DMT With and Without Butylacetate Addition

Angle	(hkl)	In(thd) ₃ and DMT Without BuOAc Addition	In(thd) ₃ and DMT With BuOAc Addition
21.5°	(211)	71	193
30.6°	(222)	130	1521
33.1°	(321)	-	15
35.5°	(400)	713	151
37.7°	(411)	67	41
39.8°	(420)	10	13
41.8°	(332)	10	53
43.8°	(422)	10	10
45.7°	(310)	38	79
49.3°	(521)	23	19
51.0°	(440)	144	256
60.7°	(622)	144	166
Total Diffraction Counts		1360	2517
(222) Divided by Total as Percentage		9.6	60.4
Crystallite Size (Å)		231	Approx. 600
FWHM		0.451	0.306
Sn:In Ratio By XRF		0.055	0.026
Resistivity (Ω cm)		2.97×10^{-4}	2.38×10^{-4}
Mobility ($V^{-1} cm^2$ sec^{-1})		28.46	44.08
Carrier Concentration $\times 10^{20} (cm^{-3})$		7.31	5.71

The resistivity of the films also improved on the addition of butylacetate with films of 2.2 weight % Sn resulting in films with a resistivity as low as $2.2 \times 10^{-4} \Omega cm$ at

a thickness of 2000 Å. This is more in the expected region for the resistivity of ITO. Two possible explanations for the improvement in the films properties are:

1. The growth of the film in a different preferred orientation is responsible for the improvement, with the carriers being more mobile in the film deposited with the addition of butylacetate. This would suggest that the (400) orientation has a detrimental effect on the resistivity of the film, whereas the (222) preferred orientation improves the properties of the film.
2. An increased number of oxygen vacancies may occur in the film. This would result in an increase in the carrier concentration in the coating, thus resulting in improved electrical properties in the film.

Both of these effects are likely to be contributing to the improved properties of the grown film. This is supported by measurement of the carrier concentration and mobility in films grown with, and without the addition of butylacetate in the gas stream which are shown in Table 4-6. In both coatings the carrier concentration is relatively high at $> 5 \times 10^{20} \text{ cm}^{-3}$, despite the doping level being significantly lower in films deposited with the addition of butylacetate. This suggests that in films with butylacetate added, an increase in the number of oxygen vacancies is occurring, and resulting in an increase in the carrier concentration. The increase in the number of oxygen deficiencies in films grown with the addition of butylacetate, however, does not account for the increased mobility of the carriers. The increased mobility in films grown with the addition of butylacetate is therefore likely to be due a change in the crystallinity of the films when butylacetate is added.

The addition of butylacetate therefore has two clear effects on the structure of the film:

1. The crystallite size has increased by a factor of three from that obtained at 565°C from $\text{In}(\text{thd})_3$ and DMT.
2. The preferred orientation has changed from (400) to (222).

The relationship between the preferred orientation of the coating and the electrical properties has been previously noted for SnO_2 deposited by CVD,²⁵ with films

exhibiting preferential growth in the 200 crystal plane exhibiting better electrical properties than other tin oxide films.

SEM and AFM pictures of the films grown at 565°C with the addition of butylacetate are shown in Figure 4-12 and 4-13. The SEM micrograph shows the presence of much larger crystallites than those previously observed in the SEM micrographs of films grown without the addition of butyl acetate (Figure 4-7). AFM analysis of these films (Figure 4-13) also show them to be much smoother with a mean roughness over a 2 μ square of 3.9nm compared with approximately 10nm for the films grown without BuOAc (Figure 4-14). The smoothness of these films is beneficial to the optical properties of the coating, resulting in lower haziness of the film as less diffusive light scattering occurs at the films surface.

Auger results on films grown at 565°C with the addition of butylacetate (Figure 4-15) do not show any significant increase in impurity content over those grown with no BuOAc addition (Figure 4-9), suggesting that whilst the butylacetate has resulted in a change in the deposition mechanism, no increase in the carbon content is observed due to less efficient oxidation of the intermediates formed by butylacetate addition during the deposition process.

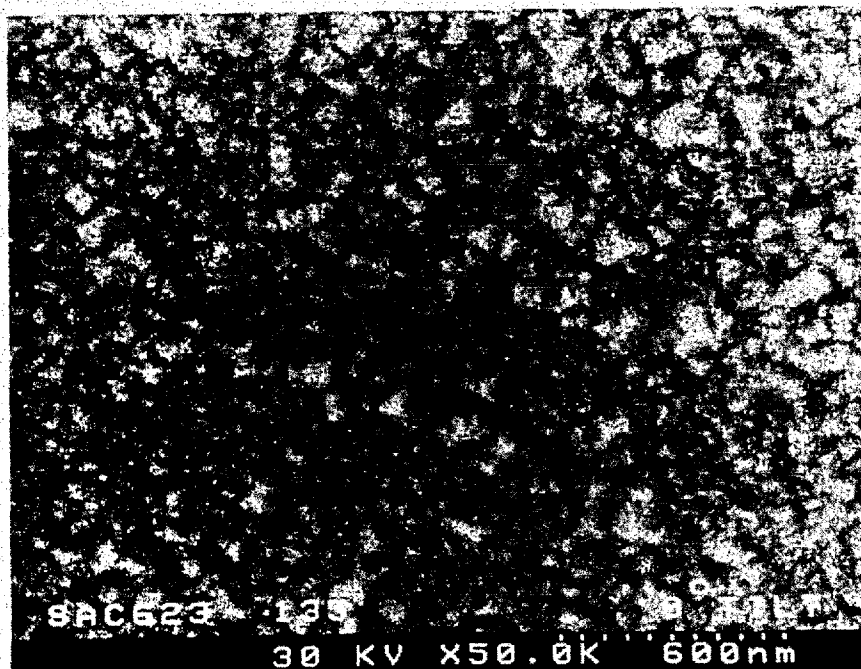


Figure 4-12 SEM Micrographs Of Film Grown From $\text{In}(\text{thd})_3$ and DMT with BuOAc Addition

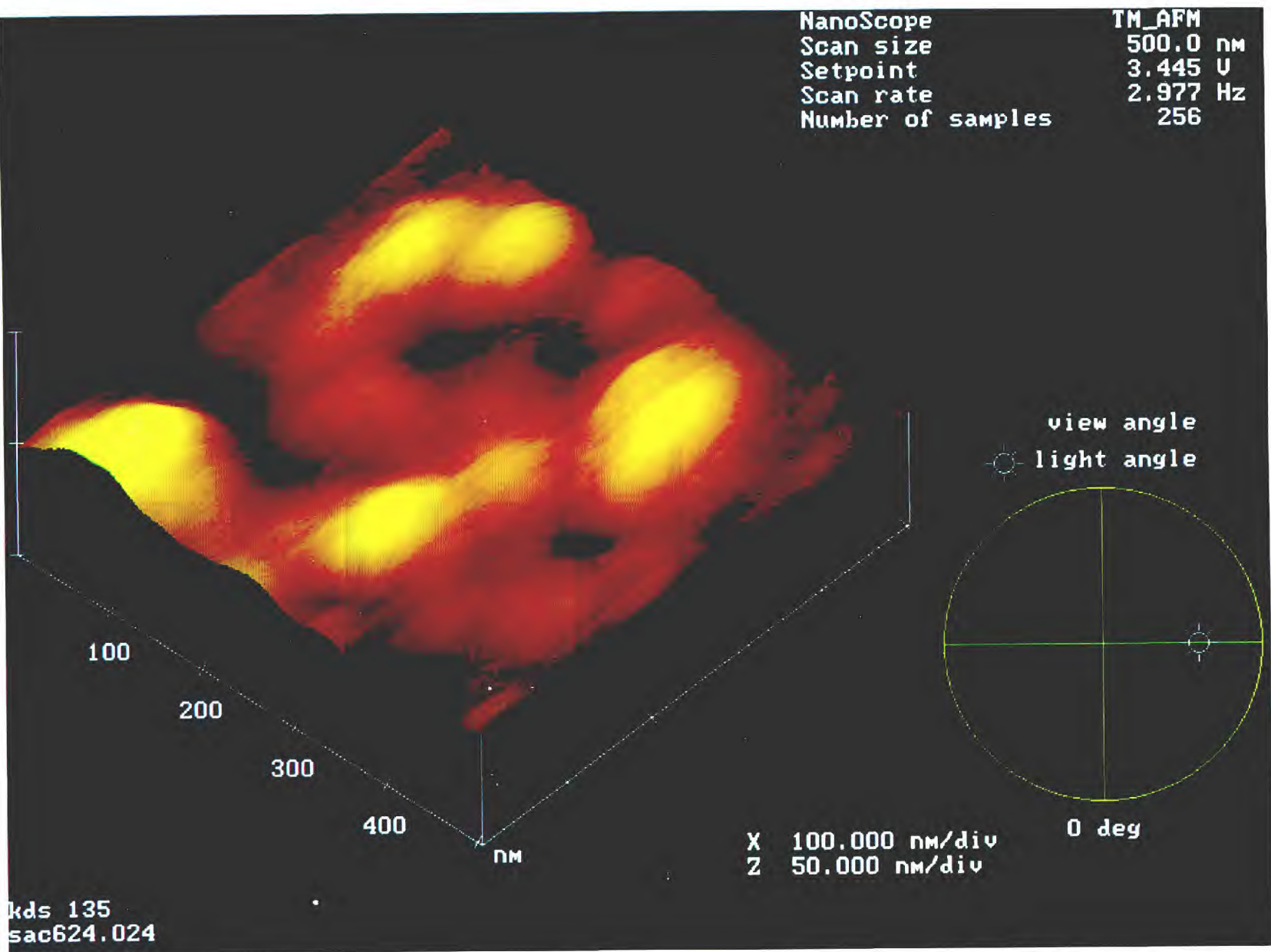


Figure 4-13 AFM Micrograph of ITO Grown From $\text{In}(\text{thd})_3$ and DMT With BuONc Addition

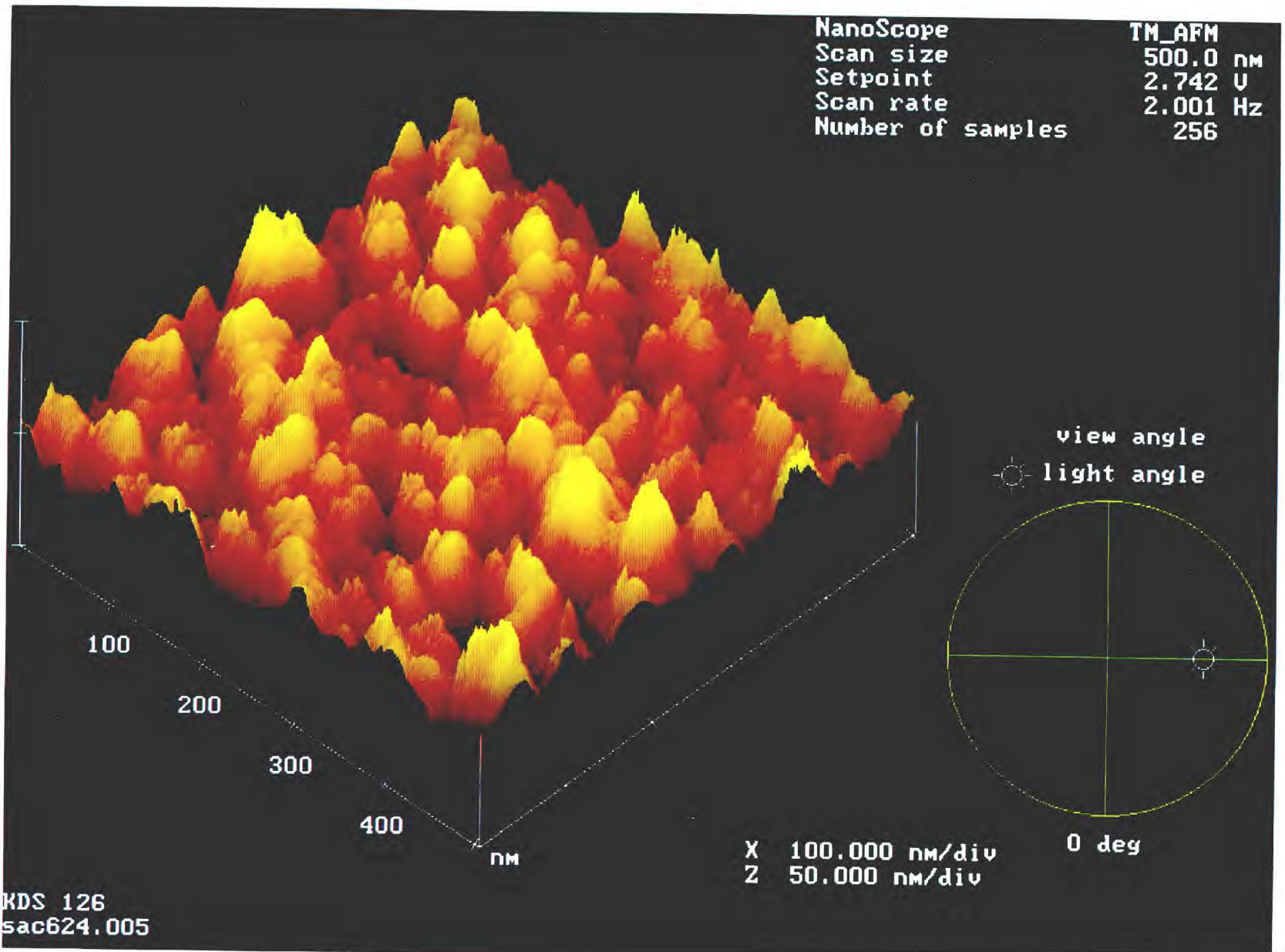


Figure 4-14 AFM Micrographs of ITO Grown From In(thd)₃ and DMT Without BuOAc Addition

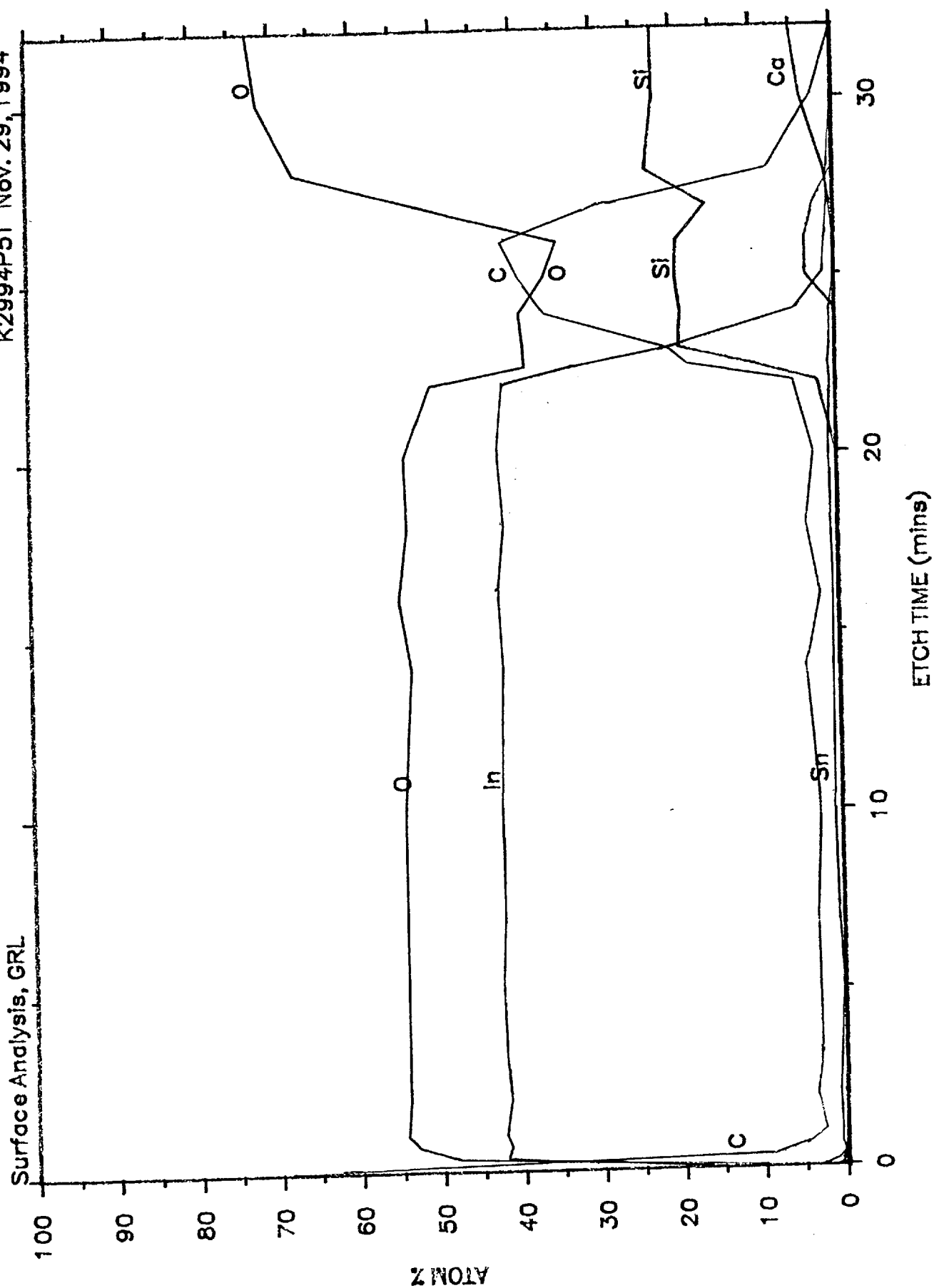


Figure 4-15 Auger Depth Profile Of ITO Grown From $\text{In}(\text{thd})_3$ and DMT with BuOAc Addition

4.3.2.3.2 Effect of Solvent at 625°C

An investigation of growth patterns using the $\text{In}(\text{thd})_3$, DMT, O_2 and $\text{In}(\text{thd})_3$, DMT, O_2 , BuOAc systems has also been carried out at 625°C. As discussed earlier for the growth of ITO from $\text{In}(\text{thd})_3$ and DMT without butylacetate addition, films grown at 625°C have a greater doping efficiency than those grown at 565°C, and showed less preferred orientation than films grown at 565°C.

Addition of butylacetate during film growth at both temperatures resulted in a change to the growth profile of the film and caused a change in preferred orientation. The thickness profiles along the glass plate, show that the addition of butylacetate has a different effect on the growth profile at 625°C, than that observed at 565°C.

At 565°C the addition of butylacetate resulted in the best conductivity of the film being obtained further back on the coating, suggesting that a gas phase reaction may have produced a more thermally stable intermediate, which takes longer to decompose, or resulted in a change in the deposition mechanism at the surface, resulting in the improvement in film properties towards the rear of the glass plate. However, at 625°C the improved film properties occur at the front of the film, and tail off markedly towards the rear. This profile is in marked contrast to that observed for film growth at 565°C. A comparison of the two growth profiles can be seen by comparing Figures 4-10 and 4-16.

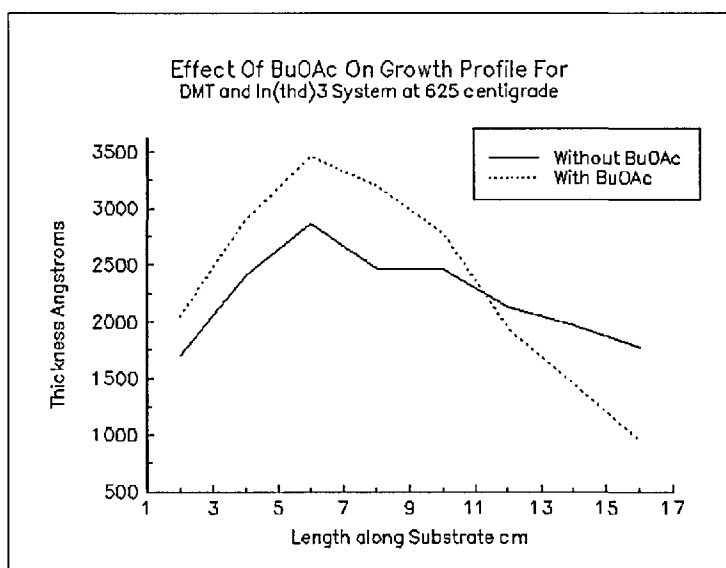


Figure 4-16 Effect of Butylacetate Addition on the Growth Profile of ITO from $\text{In}(\text{thd})_3$ and DMT at 625°C

This suggests that the gas phase species are decomposing more rapidly at 625°C, resulting in a good film properties at the front of the glass substrate.

At both deposition temperatures, the addition of butylacetate resulted in a marked change in the preferred orientation, when compared to films grown at the same temperature without the addition of butylacetate, with the films changing from having a slight preference for the (400) plane to having a preference for the (222) orientation. This is consistent with the butylacetate resulting in a similar change in the deposition mechanism at both deposition temperatures.

The exact role of butylacetate on the gas phase or surface chemistry of the system has not been defined by this study. Nevertheless, its addition has several beneficial effects. Film growth was therefore conducted with the use of other acetate solvents as additives. Film growth with methyl, ethyl and propyl acetate was carried out to determine if these acetates had a similar effect. Each acetate gave a similar beneficial effect on film growth to that obtained with butylacetate. Therefore to probe the role of the butylacetate, and in particular the acetate group which is most likely to be responsible, it was decided to investigate a tin dopant containing an acetate group. The most closely related precursor to dichlorodimethyltin containing an acetate group is diacetatodimethyltin (DMTDA). Therefore an investigation of the growth of ITO using this dopant has been investigated.

4.3.3 ITO Film Growth From In(thd)₃ and DMTDA:

4.3.3.1 Effect of Dopant Concentration on Film Properties:

Film growth using this precursor system in the temperature range 565 to 625°C has been investigated.

Initially films were grown at 565°C, with both materials held in stainless steel bubblers. Pre-mixing the precursors with oxygen was carried out prior to the reaction chamber. As with the DMT system, in order to match the vapour pressures of the two materials and obtain films with resistivities in the region $2-5 \times 10^{-4} \Omega \text{ cm}$, it was necessary

to hold the DMTDA at 28°C and to pass the carrier gas over the top of the precursor rather than through it. Film growth using this system resulted in good film coverage on the glass plate.

Alteration of the amount of carrier gas blown over the top of the DMTDA allowed control over the doping level to be achieved. As with the use of DMT as a dopant, the doping level had an affect on the resistivity of the coatings. If the dopant level was too low the resistivity of the coating was poor, and the carrier concentration in the coating was low. By increasing the dopant level, the resistivity of the coatings improved, with the best electrical properties were achieved at a doping concentration of between 8 and 12 weight % tin to indium at a growth temperature of 565°C. Increasing the doping level beyond this level appeared to have a detrimental effect on film properties, with the resistivity of the coating deteriorating. This deterioration in the electrical properties as the doping level was further increased was previously observed for ITO from $\text{In}(\text{thd})_3$ and DMT and is likely to be due to excess tin being incorporated into the film in a non-active role and acting as a carrier scattering point.

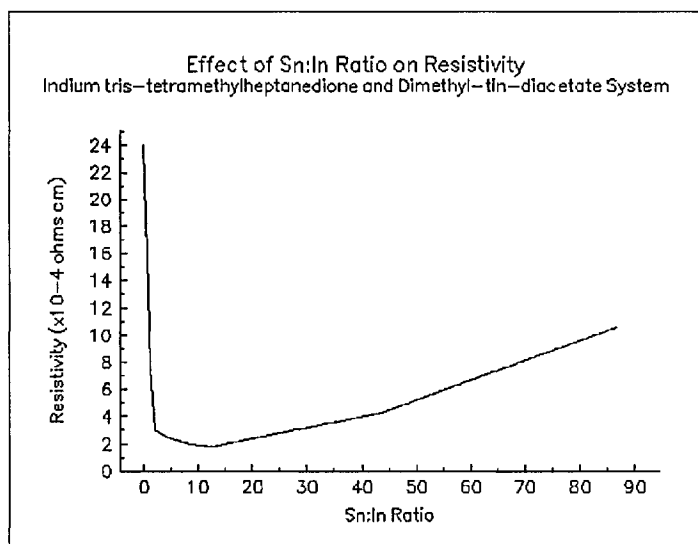


Figure 4-17 Graph Showing Effect of Doping Level on Resistivity of ITO Film For Film Growth From $\text{In}(\text{thd})_3$ and DMTDA

Unlike the $\text{In}(\text{thd})_3$ and DMT system, however, no relationship between the dopant level in the coating and the degree of preferred orientation in the grown film was observed for this system, and all the films grown at this temperature exhibited a (222) preferred orientation.

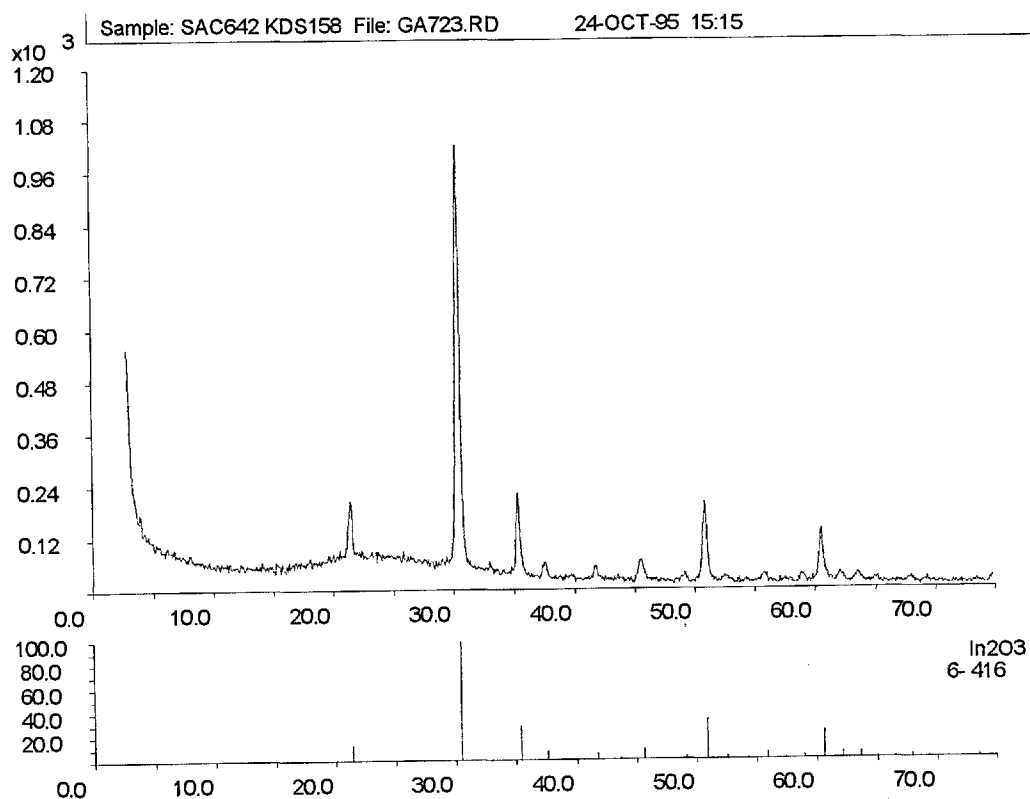


Figure 4-18 Glancing Angle XRD Pattern Of ITO Grown at 565°C From $\text{In}(\text{thd})_3$ and DMTDA

4.3.3.2 Effect of deposition temperature on film growth:

Films grown at 565°C with a doping level of approximately 8-10 weight % tin to indium had good electrical properties, and showed a similar growth profile to that observed for the growth of ITO at 565°C using the precursor system $\text{In}(\text{thd})_3$ with DMT and BuOAc addition. The films grown also exhibited similar structural properties to those grown using this system, with a preferred orientation of (222) being observed. These results are summarised in Table 4-8.

Table 4-8 Comparison of Film Properties of ITO Grown From In(thd)₃ + DMT + BuOAc and In(thd)₃ + DMTDA

Angle	(hkl)	In(thd) ₃ + DMT + BuOAc	In(thd) ₃ + DMTDA
21.5°	(211)	193	128
30.6°	(222)	1521	942
33.1°	(321)	15	-
35.5°	(400)	151	174
37.7°	(411)	41	35
39.8°	(420)	13	10
41.8°	(332)	53	29
43.8°	(422)	10	-
45.7°	(310)	79	46
49.3°	(521)	19	13
51.0°	(440)	256	180
60.7°	(622)	166	106
Total Diffraction Counts		2517	1553
(222) Divided by Total as Percentage		60.4	60.7
Crystallite Size Angstroms		*	577
FWHM		0.306	0.326
Sn/In Ratio By XRF		2.6	2.2
Resistivity Ω cm		2.52x10 ⁻⁴	2.8x10 ⁻⁴

*= No Determination Possible

SEM micrographs of films grown from In(thd)₃ and DMTDA at 565°C show the presence of large crystallites on the surface of the films. These appear similar to those obtained with the In(thd)₃, DMT and BuOAc system.

Auger analysis of the coating, shows the composition to be very similar to that obtained using the DMT and In(thd)₃ and BuOAc system, with only small amounts of carbon incorporated in the film. The low level of carbon incorporation in the final film is

consistent, with the acetate grouping attached to the tin precursor acting in a similar fashion to butylacetate added in the vapour phase.

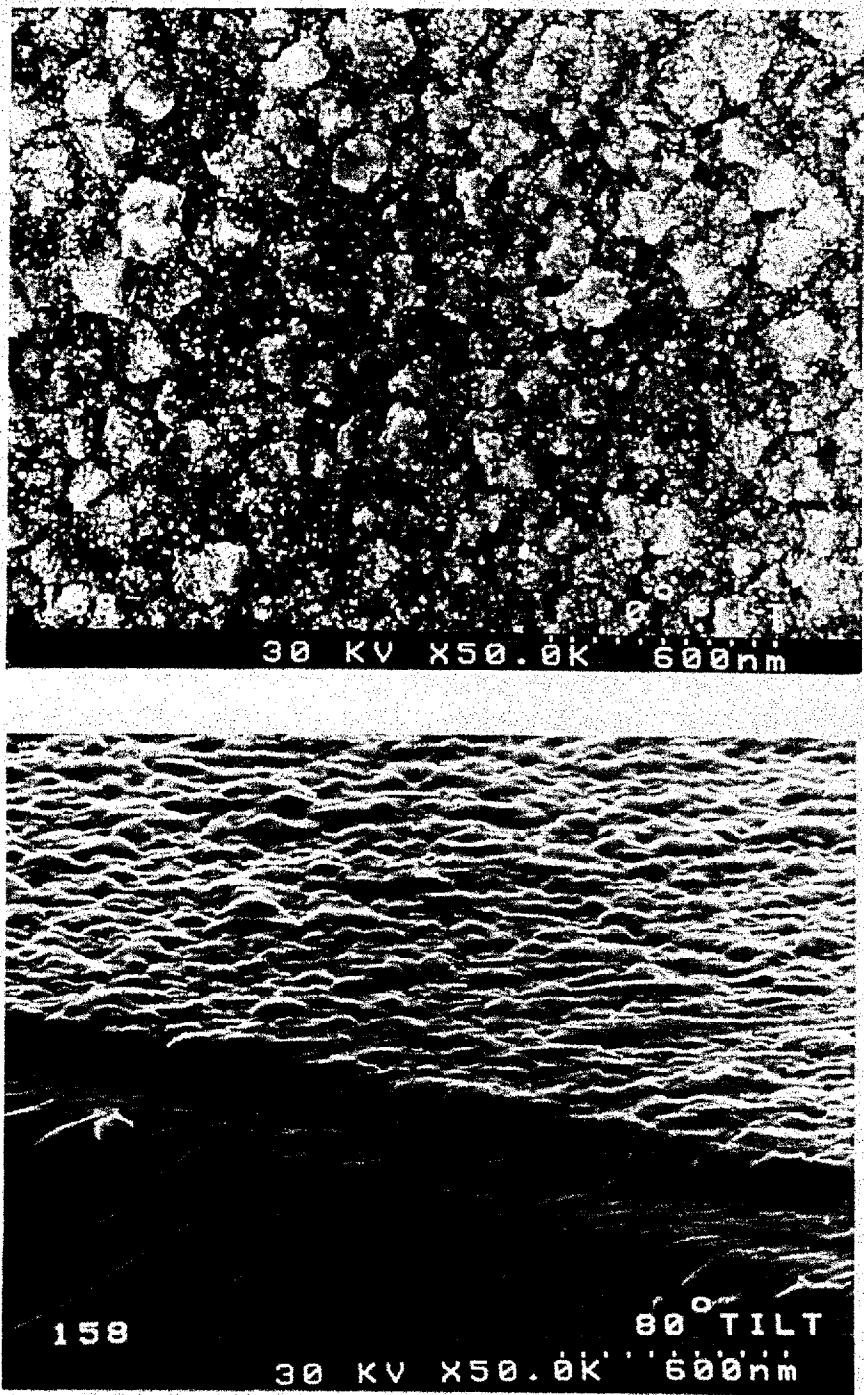


Figure 4-19 SEM Micrographs of Coating Grown From $\text{In}(\text{thd})_3$ and DMTDA at 565°C

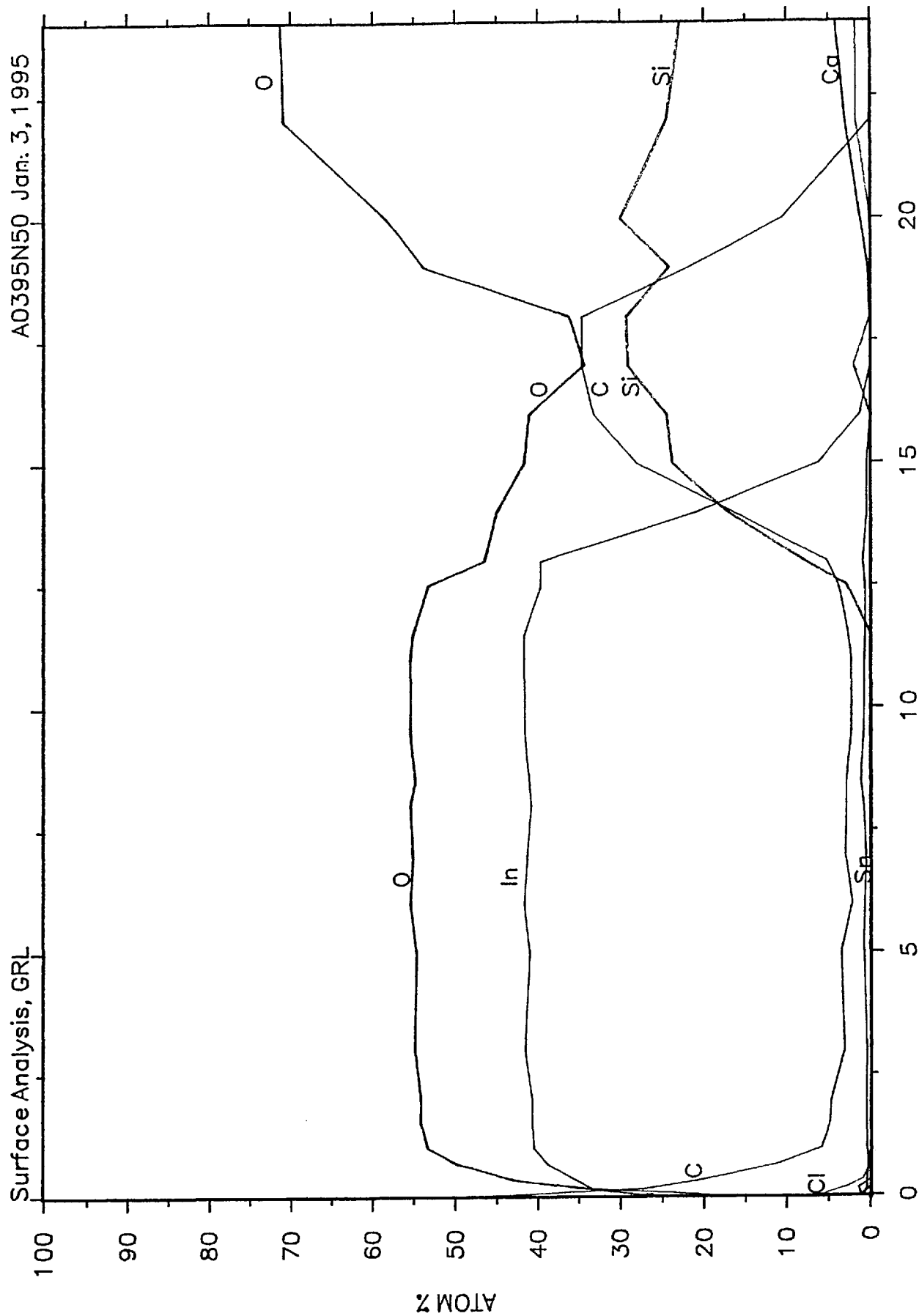


Figure 4-20 Auger Depth Profile Of ITO Grown From $\text{In}(\text{thd})_3$, DMTDA and O_2 at 565°C

On increasing the growth temperature to 625°C, the two systems no longer behaved in a similar fashion. Previously film growth using the $\text{In}(\text{thd})_3 + \text{DMT} + \text{BuOAc}$ system, at 625°C resulted in (222) preferred orientation films with film growth concentrated at the inlet of the reactor. However, the use of DMTDA as the dopant at 625°C, whilst resulting in film growth concentrated at the inlet end of the reactor as in the $\text{In}(\text{thd})_3 + \text{DMT} + \text{BuOAc}$ system, resulted in films with a preferred orientation towards the (400) plane, similar to that seen for films grown using $\text{In}(\text{thd})_3$ and DMT at both 565 and 625°C without the addition of acetate. The change in preferred orientation implies that the acetate grouping on the ligand is no longer behaving in a similar fashion to that of butylacetate added as a separate constituent. A different decomposition mode of the precursor's acetate group compared to the butylacetate additive would explain why the films' preferred orientation reverts back to a (400) preferred plane. This indicates that the preferred orientation of the film is dependant upon the presence of the acetate group or one of its decomposition products. The exact role of the acetate group cannot be defined by this study, however, and therefore the addition of butylacetate to this system was studied.

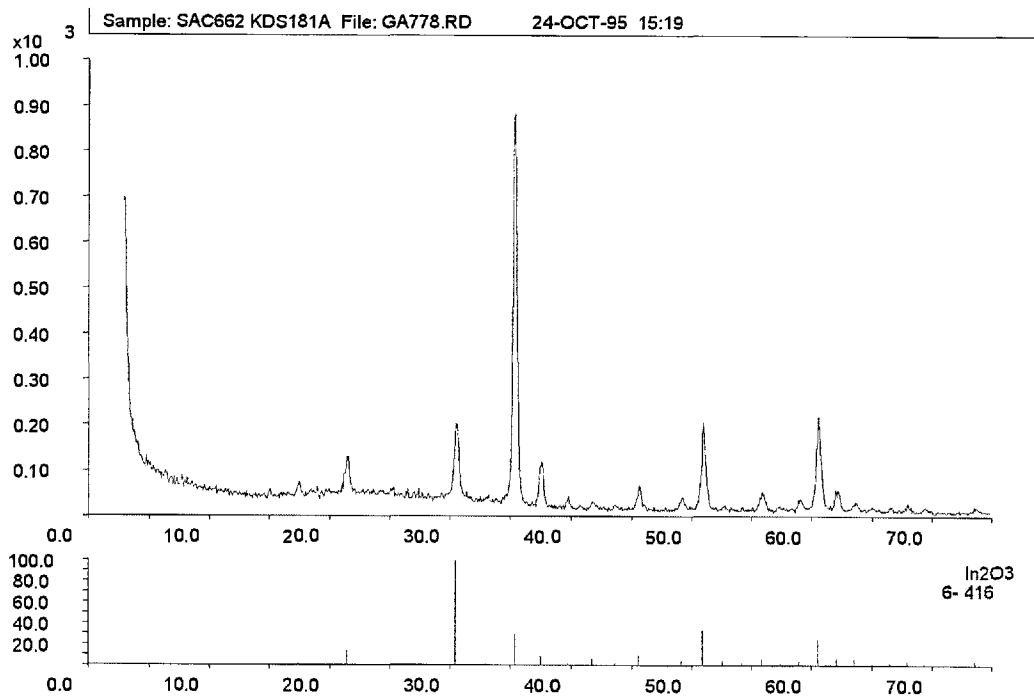


Figure 4-21 Glancing Angle XRD Pattern Of ITO Growth From $\text{In}(\text{thd})_3$ and DMTDA at 625°C

4.3.3.3 Effect of butylacetate addition on film growth

Addition of butylacetate to the reaction of $\text{In}(\text{thd})_3$ and DMTDA on films grown at 565°C , had no further effect on the properties of the ITO coating.

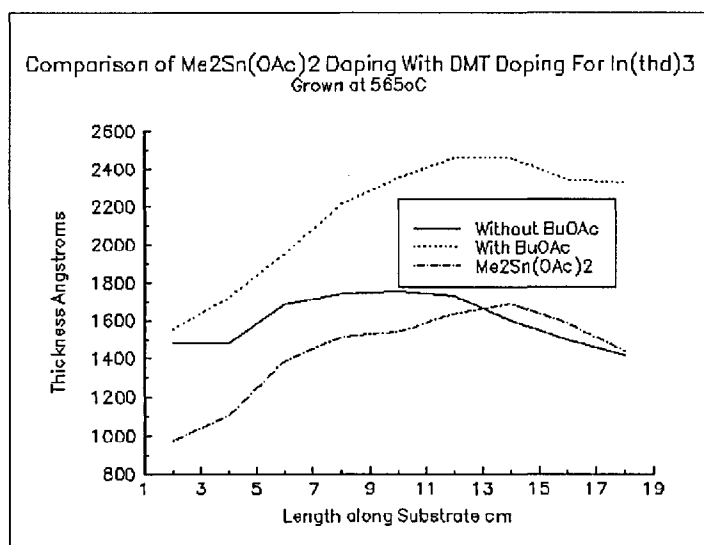


Figure 4-22 Comparison Of Growth Profiles Of Film Growth From In(thd)₃ With the Doping Systems 1. DMT, 2. DMTDA, 3. DMT+ BuOAc at 565°C

As described above, increasing the substrate temperature from 565°C to 625°C, had previously been seen to have a significant effect on the film growth, resulting in a change in the preferred orientation of the film growth, from the (222) preferred orientation seen at 565°C, to a (400) preferred orientation, previously seen for the DMT and In(thd)₃ system for films grown at 565 and 625°C.

Addition of butylacetate to the DMTDA + In(thd)₃ reaction mixture during film deposition, at 625°C, however, resulted in a switch to the (222) preferred orientation, suggesting that the butylacetate may be more thermally stable than the acetate of the DMTDA and as such can create the change in the preferred orientation of the film even at the higher temperature.

Table 4-9 Effect of the Addition of BuOAc on Film Properties Of ITO Grown at 625°C From In(thd)₃ and DMTDA

Angle	(hkl)	In(thd) ₃ + DMTDA at 625°C	In(thd) ₃ + DMTDA + BuOAc at 625°C
21.5°	(211)	86	190
30.6°	(222)	161	1369
33.1°	(321)	10	13
35.5°	(400)	858	180
37.7°	(411)	88	41
39.8°	(420)	17	10
41.8°	(332)	12	46
43.8°	(422)	10	13
45.7°	(310)	48	67
49.3°	(521)	26	18
51.0°	(440)	161	225
60.7°	(622)	180	135
Total Diffraction Counts		1657	2307
(222) Divided by Total as Percentage		9.7	59.3
Crystallite Size (Å)		270	Insufficient Line Broadening To Determine
FWHM		0.363	0.328

Whilst it has been found that the addition of butylacetate in both the DMT doping study and DMTDA doping study can have an effect on the properties of the coating, the reasons for this are not fully understood. An investigation by infrared spectroscopy has been used to investigate this further in an attempt to identify the species responsible for the observed changes in preferred orientation. The results of this study are detailed in Chapter 5.

An investigation of other tin dopants has also been investigated in order to determine if other dopants behave in a similar fashion.

4.3.4 ITO Film Growth From In(thd)₃ and Sn(II) Salt of Ethyl-hexanoic Acid

A study of ITO growth using the indium precursor In(thd)₃ and the tin(II) salt of ethyl-hexanoic acid as the tin dopant has been carried out. The high viscosity of this tin material, prevented the use of a bubbler delivery for this material, so delivery of the dopant, was therefore carried out by syringe injection of a dopant solution.

4.3.4.1 Effect of Tin Dopant Concentration

An investigation of the effect of tin dopant concentration on film properties was initially carried out. Solutions of the tin dopant were made in butylacetate and delivered via syringe injection into an evaporator at a delivery rate of 0.75ml / min.

The study has shown that the tin dopant concentration in the film is related to the concentration of the dopant solution used and therefore changing the tin dopant concentration has resulted in a variations in the dopant level in the coatings.

Films have been deposited at 565°C with a tin dopant concentration in the film varying from 2-20 weight % tin to indium. The study has identified that the best electrical properties are achieved at a tin dopant level of approximately 6-8 weight % tin : indium. Table 4-9 shows the effect of different dopant levels on the physical properties of the film.

Table 4-9 Effect of Doping Concentration on Electrical Properties Of ITO Grown From In(thd)₃ and Tin(II) Salt Ethylhexanoic Acid

Tin Dopant Level (weight %)	Sheet Resistance (Ω /□)	Thickness (Å)	Resistivity (Ω cm)
1.6	45	958	4.3×10^{-4}
5.4	15.8	1180	1.86×10^{-4}
6.3	14.6	1085	1.58×10^{-4}
8.0	16.8	1341	2.25×10^{-4}
22.0	35.3	975	3.6×10^{-4}

In overdoped films (>8 weight % tin : indium) the electrical properties were poor, with the resistivities of the films increasing. This suggests that the excess tin is

having a detrimental effect on the conductivity. The nature of the excess tin in the films is unclear, but as in other overdoped films a halo due to amorphous material in the film is observed in the XRD pattern of these coatings, which is believed to be due to amorphous tin oxide incorporated in the coating. This amorphous material is probably SnO_2 which increases the sheet resistance of the film by increasing the scattering of the films carriers. These results are consistent with the deposition of a two phase material consisting of ITO and amorphous tin oxide.

By lowering the dopant level good films were obtained with resistivities of approximately $2 \times 10^{-4} \Omega \text{ cm}$ being achieved. Lowering the dopant level further towards 2 weight % tin : indium, resulted in a deterioration in the film properties, suggesting that at this doping level the films are underdoped. This underdoping of the films is consistent with the electrical properties of the deposited films which are similar to those of pure In_2O_3 .

4.3.4.2 Effect of Solvent On Dopant Solution and Film Properties

Care had to be taken in handling the tin dopant solution, since they degraded with time if left open to the air. This decomposition of the dopant solution resulted in the formation of a white powdery material being precipitated on standing. Attempts at film deposition from these decomposed solutions were unsuccessful, with no doping achieved and only In_2O_3 deposited, suggesting that the white material precipitated out is an involatile tin compound such as a hydroxide which cannot be volatilised in the evaporator. The growth profile of the film is also affected by the type of solvent used in the tin dopant solution. The effect of the solvent used for the tin dopant solution on the films growth profile is seen in Figure 4-23.

The best results were obtained with acetate solvents such as ethyl and butylacetate. Films grown using acetate containing dopant solutions resulted in good film growth, with a good electrical properties being observed along the length of the glass plate.

If cyclohexane was used as a solvent, the growth profile was poorer with the plate coverage deteriorates and the bulk of the film growth moves towards the inlet end of the reactor.

These results may imply that the butylacetate is reacting in the gas phase to produce a more thermally stable intermediate which is improving the growth profile of the film. This clearly does not occur with cyclohexane and the less thermally stable dopant solution appears to result in a change in the deposition mechanism.

Whilst the effect of the cyclohexane appears to result in the best resistivity at the front of the coating, this does not appear to be due to a change in the doping profile, with XRF analysis of films grown using butylacetate and cyclohexane dopant solutions showing the dopant level along the film to be similar in both cases. The role of the cyclohexane therefore may be to increase the carbon impurity levels in the coating. Carbon impurity in the coating would be consistent with the deterioration in the resistivity of the coating, increasing the scattering of the carriers in the film and as a result reducing their mobility.

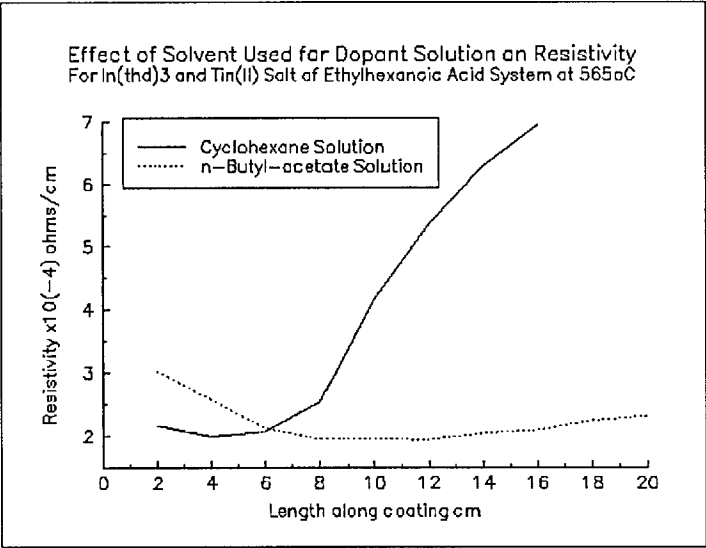


Figure 4-23 Effect of Different Solvents On ITO Growth Profile From $\text{In}(\text{thd})_3$ and Tin(II) Salt Ethylhexanoic Acid

The beneficial effect of the presence of acetate during film growth at 565°C , is clear, resulting in films with a resistivity of approximately $2 \times 10^{-4} \Omega \text{ cm}$ at a thickness of $1500 \text{\AA}$.

4.3.4.3 Effect of Temperature.

The effect of substrate temperature on film growth has been investigated for this precursor system. As the substrate temperature was increased the growth profile of the film deteriorated, with the film growth moving towards the front of the plate. This effect can be seen in the graph below.

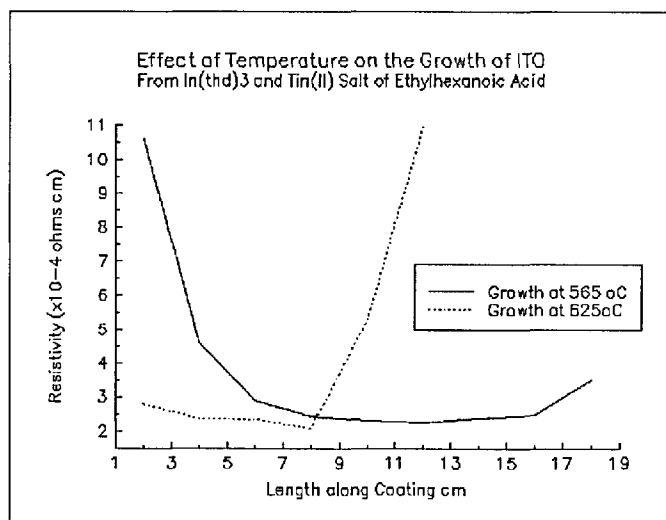


Figure 4-24 Effect of Substrate Temperature On Film Growth For In(thd)₃ and Tin(II) Salt Ethylhexanoic Acid System

XRF analysis of the films grown at 565 and 625°C was used to determine the composition of the films along the length of the glass substrate and to determine the effect of temperature on the coating. At 565°C the doping level along the length of the glass substrate was found to be similar, but at 625°C the doping level was found to be significantly higher at the inlet of the reactor, and then dropped off rapidly along the length of the substrate. This suggests that the increased deposition temperature has resulted in premature decomposition of the tin dopant. This suggests that the tin(II) salt of ethylhexanoic acid has insufficient thermal stability to dope effectively along the length of the substrate at a deposition temperature of >600°C, resulting in overdoping at the front of the glass plate. Good electrical properties could be achieved at a higher deposition temperatures if the dopant solution concentration was reduced, but the coverage of the glass plate was still poor. This is consistent with premature decomposition of the tin dopant which results in heavier doping at the front of the glass plate.

The films obtained using this precursor had a (222) preferred orientation at all deposition temperatures. SEM micrographs of films grown at 565°C using this precursor show the presence of small crystallites on the coating surface, which is consistent with line broadening determination of the crystallite size from XRD indicating a crystallite size of approximately 350Å.

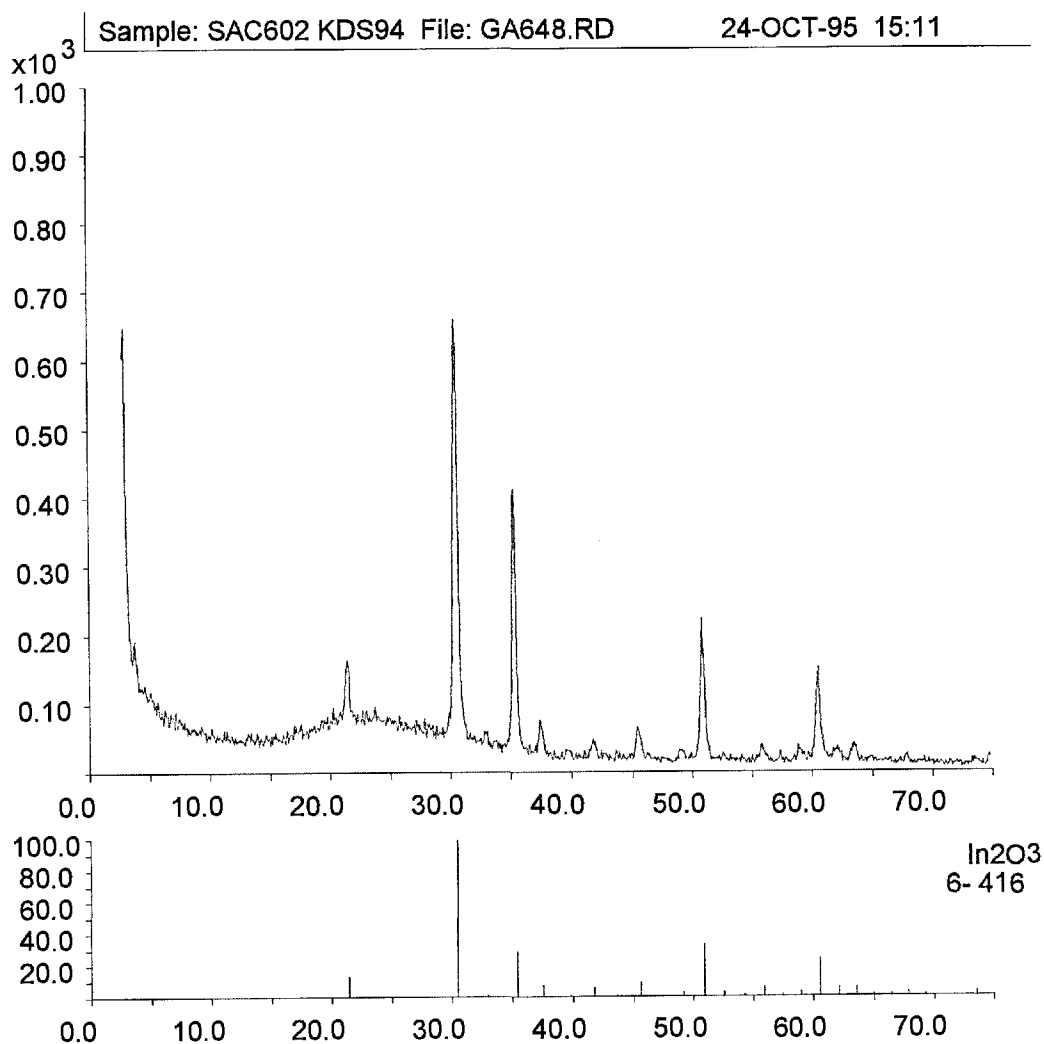


Figure 4-25 Glancing Angle XRD Pattern Of ITO Growth From In(thd)₃, O₂ and Tin(II) Salt of Ethylhexanoic Acid at 565°C

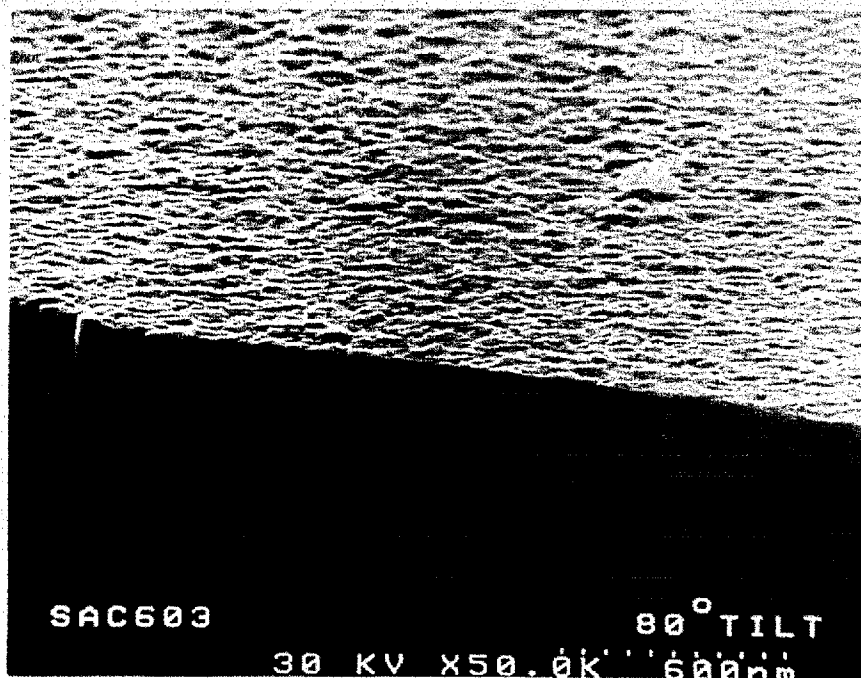
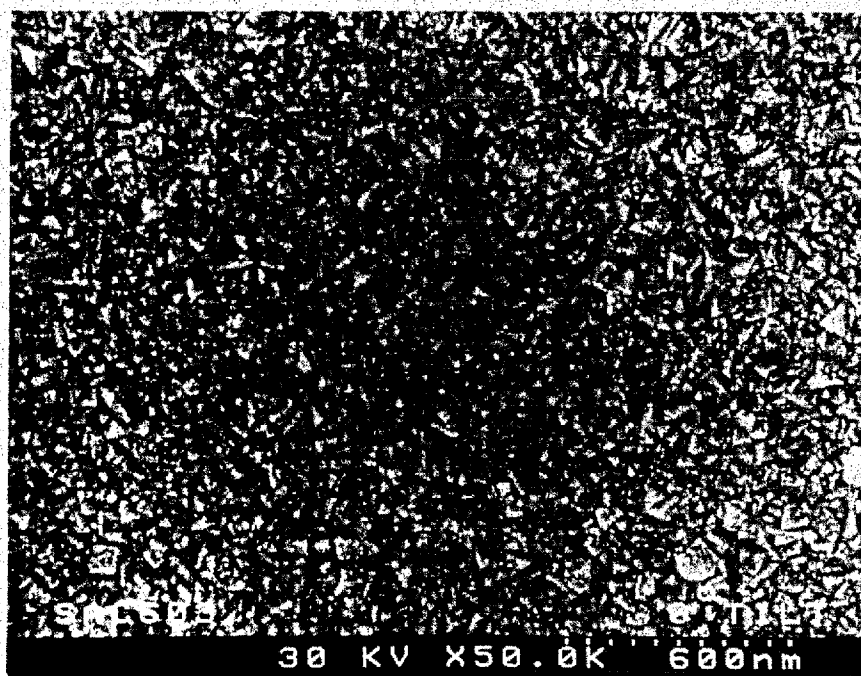


Figure 4-26 SEM Micrographs Of Film Growth From $\text{In}(\text{thd})_3$, O_2 and Tin(II) salt of ethylhexanoic acid.

4.3.4.4 Effect of Oxygen Concentration

The effect of changing the oxygen concentration used during film deposition has been found to have little effect on the film, provided that the concentration was not increased above 20-30% of the total gas stream, although a slight change in the growth profile was observed. As the oxygen concentration was increased, a gradual movement of the growth profile towards the front of the glass plate was observed. This is believed to be due to an increase in pre-reaction of the precursors in the gas phase. If the oxygen concentration was increased to approximately 20-30%, pre-reaction become excessive, with powder formation being observed. At times the powder collected in both the baffle pack gas distribution system at the reactor inlet and in the reactor chamber itself.

The removal of oxygen from the system completely, however, resulted in powdery coatings, indicating that there was insufficient oxygen to allow complete oxidation of the precursors to occur. As reported in Chapter 3 film growth of In_2O_3 without oxygen, from $\text{In}(\text{thd})_3$ is possible without an increase in the haze of the coatings. The increased haze seen during deposition of ITO without oxygen, therefore suggests that the tin dopant is responsible for the powder formation, possibly due to incomplete oxidation of the tin precursor.

The growth of highly conductive films of ITO using this system was encouraging, but the poor film growth achieved at higher temperatures with the doping moving towards the front edge of the plate, suggested that this is not an ideal dopant for the $\text{In}(\text{thd})_3$. Ideally a more thermally stable precursor is required.

4.3.4.5 Effect of Film Thickness:

Using this precursor system the electrical properties of the coatings for a range of film thickness' was investigated. Alteration of the film thickness was achieved by variation of the deposition time, using standard growth conditions for ITO. The effect of growth time on film thickness was found to be nearly linear within experimental error.

Table 4-11 Effect of Growth Time On Film Properties For In(thd)₃ and Tin(II) Salt Ethylhexanoic Acid System

Growth Time (minutes)	Thickness (Å)	Resistivity ($\times 10^{-4}$ Ω cm)
4	624	10.1
6	900	5.7
12	1937	1.86
24	3546	1.29

From the results it can be seen that the initial film growth exhibits very poor electrical properties. As the coating thickness increases, however, the resistivity of the coating improves significantly. This is unexpected as the resistivity of a coating should be independent of film thickness.

The initial 400 Å of the coating have very poor electrical properties, suggesting that as with previous deposition of In₂O₃ from In(thd)₃ the films are non-continuous below a thickness of 600-800 Å. This is common for the growth of many polycrystalline materials, with the initial island growth resulting in non-continuous insulating films, until coalescence of the individual islands occurs.

The electrical properties of the coatings did not significantly improve, until the film thickness reached approximately 900-1000 Å. This has previously been reported to be the case for SnO₂ films deposited by APCVD on glass substrates, but no reports of this phenomenon have been reported for CVD ITO. The poor electrical properties of the first 600 Å of the coating are also in contrast to ITO deposited by sputtering techniques, which show both continuous films at < 600 Å, and the film resistivity to be independent of thickness over a wide range of film thickness'.

The poor electrical properties of continuous thin APCVD films therefore, appear to suggest that the first several hundred angstroms of the coating provide only a small contribution to the electrical properties of the coating. Depth profiling analysis of the coatings, does not show any change in stoichiometry in the coatings in this region, however. This suggests that increased scattering of the carriers due to impurities in the film (so called ionized impurity scattering) is unlikely to be responsible for the poor conduction in thin films. One explanation for the poor electrical properties in this region of the coating, may therefore be that the initial nucleation and island growth in this

region, results in an increased number of grain boundaries and imperfections in the film growth. As such the carriers in this region of the coating would have a low mobility and would account for the poor electrical properties observed. Subsequent film growth, however, does not appear to replicate the initial defects in the film and the electrical properties of the coating improve significantly.

The initial 'dead' layer observed in the first 400-800Å of ITO film growth on glass, would be a significant disadvantage for its use as an electrical coating, as coatings of approximately 1000Å are used in these applications. For optical applications, however, where 3000Å thick coatings are utilised, the initial poor film growth is not a major problem.

4.3.5 Doping With Diacetatodibutyltin (DBTDA).

Diacetatodibutyltin is a liquid material at room temperature. It has been used for the deposition of SnO_2 by atmospheric chemical vapour deposition by bubbling techniques,²⁹ but due to its high solubility, delivery was via syringe injection and subsequent evaporation of a solution of DBTDA in butylacetate.

4.3.5.1 Effect of Dopant Concentration on Film Properties:

Solutions of DBTDA have been made up in butylacetate, and are more stable than equivalent solutions made with the tin(II) salt of ethyl-hexanoic acid, showing no decomposition over 2-3 hours in air. This is a significant advantage as long term stability would be required for large scale applications using such a system.

Film growth with a range of different doping levels has been carried out in order to investigate the effect of the dopant level on the electrical properties of the resulting film.

Table 4-12 Effect of dopant concentration on the electrical properties of the coating For In(thd)₃ and DBTDA System

Tin Dopant Level (Weight % tin to indium)	Resistivity (Ω cm)
13.7	7.97×10^{-4}
10.3	7.62×10^{-4}
9.2	2.84×10^{-4}
8.0	1.99×10^{-4}
4.7	4.44×10^{-4}
3.5	5.25×10^{-4}

As with the other tin dopants studied the best electrical properties are achieved at a doping level of approximately 8 weight % tin to indium at a growth temperature of 565°C.

A clear disadvantage of this tin dopant, is that the doping concentration along the length of a film varied quite markedly. It is expected that the doping level will decrease slightly towards the back of the coating plate, as depletion of the tin dopant material occurs in the gas phase. With other tin dopant materials this effect is quite small, unless the film is significantly overdoped, typically resulting in a drop in dopant concentration over a 10 cm region of 0.5-0.8 weight % tin to indium. However, the drop in doping level along the film when DBTDA solutions were used as the dopant source was significantly higher, with a drop over the same 10 cm region of approximately 5 weight % tin to indium being observed. This suggests that a significant proportion of the dopant being carried in the lines is reacting early on, and only a small amount is being carried towards the back of the reactor. This implies that the thermal stability of the precursor may be poorer than that of the others used, and this would explain the poor dopant profile seen for this material, with the front of the coating being heavily doped, and little if any dopant towards the exhaust end of the reactor. As a result a uniformly doped region of only 4-5 cm exists at the front of the substrate.

Due to the problem of thermal stability of DBTDA the films grown have a poorer doping uniformity than those seen for the precursors used so far. The electrical properties of the films in the uniform region, however, appear to be very similar to those

obtained for the other precursors, with resistivities of approximately $2 \times 10^{-4} \Omega \text{ cm}$ being obtained.

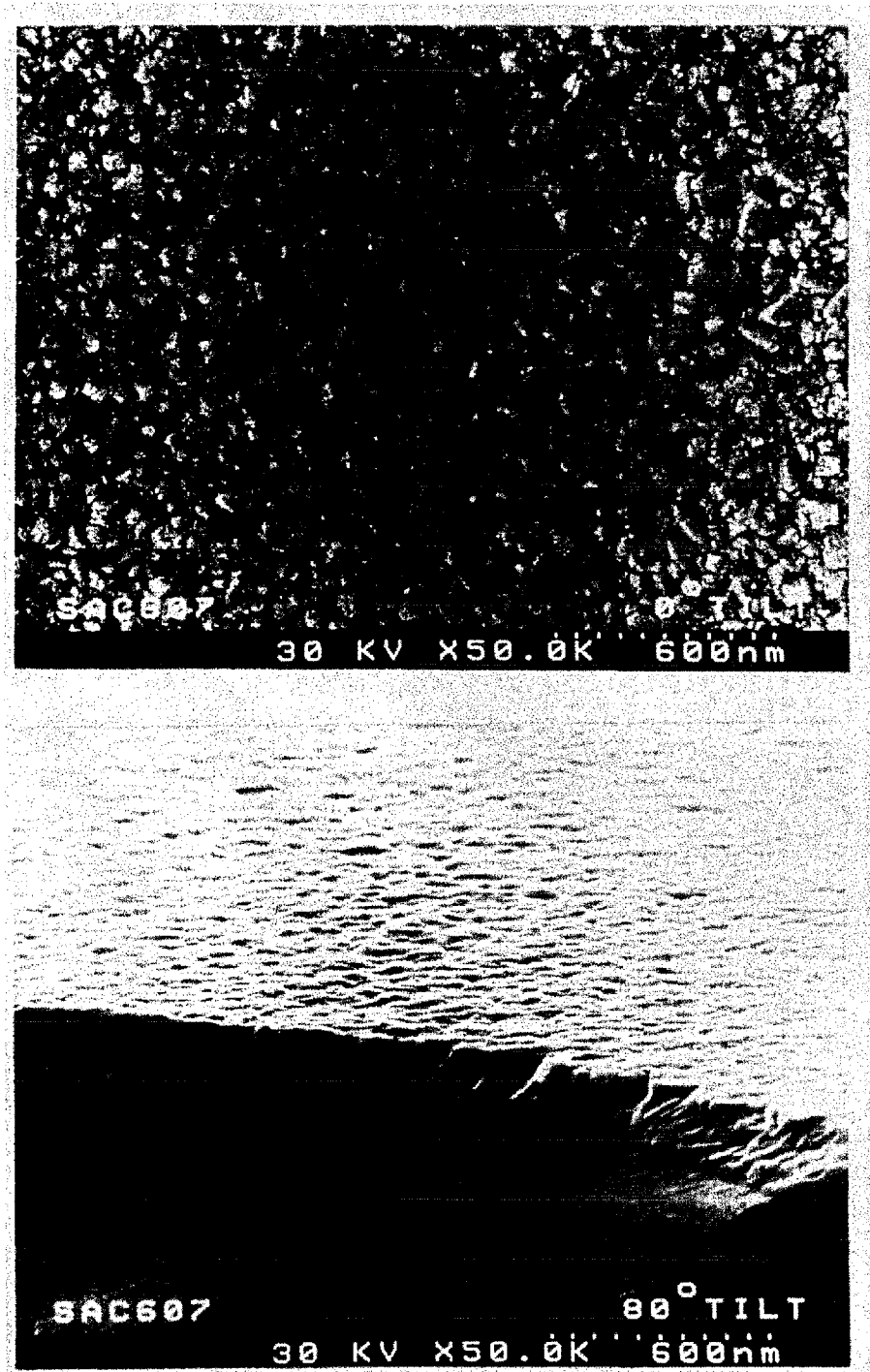


Figure 4-27 SEM Micrographs Of ITO Growth From $\text{In}(\text{thd})_3$, O_2 and DBTDA

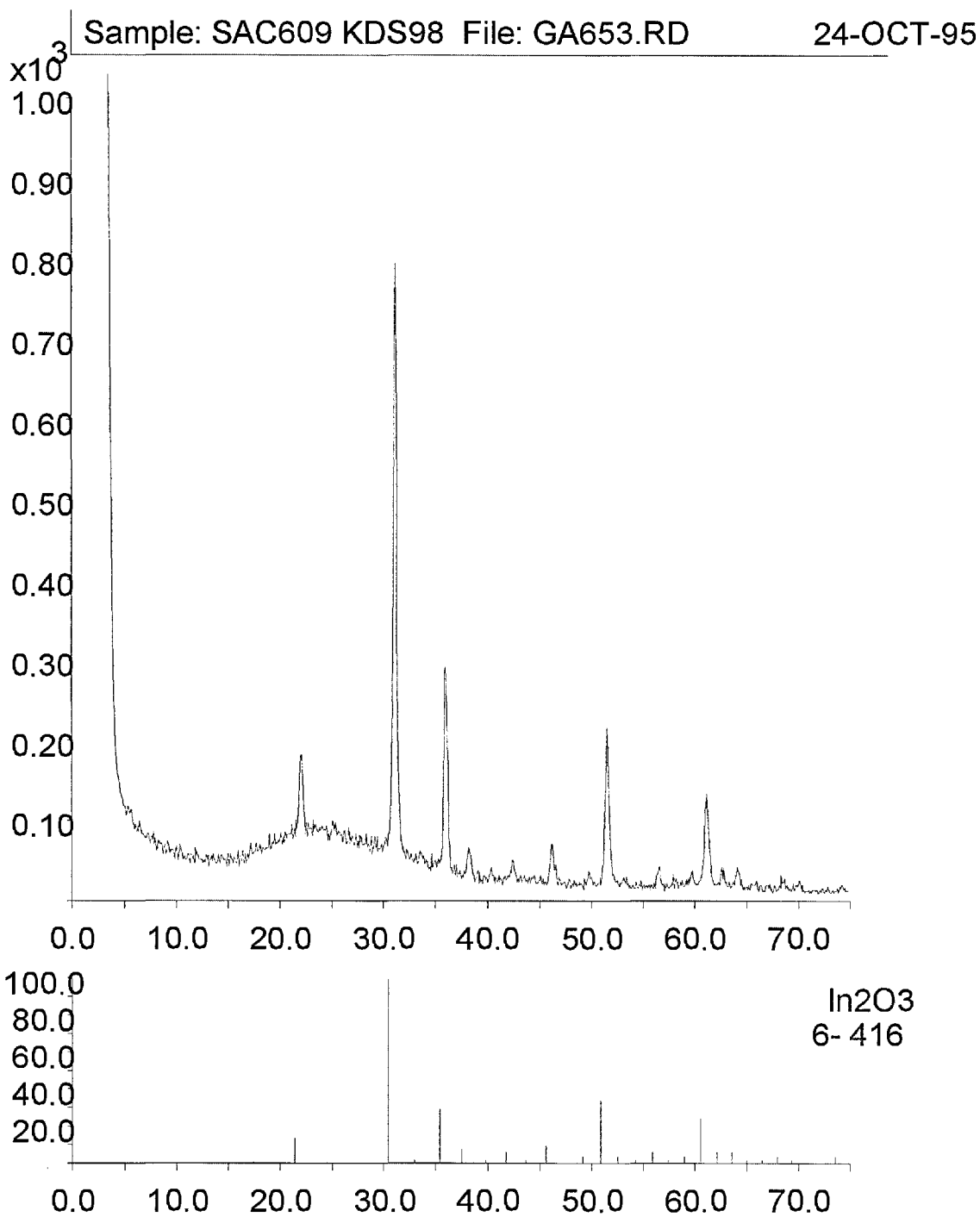


Figure 4-28 Glancing Angle XRD Pattern Of ITO Growth From $\text{In}(\text{thd})_3$, O_2 and DBTDA at 565°C

The effect of using a THF solution of DBTDA was also been investigated, to see how film growth was affected. The use of THF instead of butylacetate had little effect with this precursor, with the doping still concentrated towards the front of the substrate, suggesting that the thermal stability of the precursor had not been improved.

4.3.5.2 Effect of Temperature on Film Growth:

If the growth temperature of the coating was increased a further deterioration in the film properties is observed, with more doping occurring at the front of the coating.

This suggests the dopant lacks sufficient thermal stability to dope the whole film. This results in a degree of initial overdoping followed by a very rapid drop off in the dopant concentration towards the end of the film.

4.3.6 Tin Tetrachloride Doping Of In(thd)₃

4.3.6.1 Effect of Dopant Concentration on Film properties:

A doping study of In(thd)₃ with anhydrous tin tetrachloride as the tin dopant material was carried out. The anhydrous tin tetrachloride was delivered into the reaction as an evaporated solution, using butylacetate as the diluting solvent.

A range of tin concentrations in the delivered solution have been used to investigate the effect of the tin dopant level on the resistivity of the coating.

Table 4-13 Effect of changing the tin concentration in the solution, on the films resistivity for films grown at 565°C:

Concentration of Dopant Solution (mls of SnCl ₄ in 200 ml BuOAc)	Weight % Tin: Indium in Coating	Resistivity of Coating ($\times 10^{-4} \Omega \text{ cm}$)
0.67	11.6	2.72
0.8	24.0	3.75
1	58.2	6.78
2	>70	approximately 9.0 *

* Denotes that film properties are variable suggesting doping level varies from point to point on coating.

Using this precursor as a dopant, films with reasonable properties were achieved, but difficulties with achieving reproducible doping were experienced, as films showed initial signs of overdoping at the front of the plate, and a rapid drop off in the dopant concentration was seen towards the back of the reactor.

This suggests that the precursor is pre-reacting in the chamber and resulting in overdoping of the film at the front edge. The problem appears to be worse than that observed with other dopant precursors, and the reduction in dopant concentration along the length of the coating is not consistent with the usual depletion of chemicals in the gas phase as the precursors traverse the reactor. The explanation for the large change in dopant concentration along the film length is therefore likely to be due to the poor thermal stability of the dopant precursor in the gas phase in this system. The high dopant concentrations at the front of the coating implies that the bulk of the dopant precursor is being incorporated into the first 4-5 cm of the coating. The dopant concentration then drops off rapidly towards the back of the coating.

Good film properties could be achieved using this system, by reducing the concentration of the tin dopant solution, to a level, where the initial doping seen was at a correct level of 5-8 weight %. However, this had the effect that rapid depletion of the tin precursor lead to poor properties being achieved at the back edge of the coating, due

to underdoping of the film. Properties of $< 2.7 \times 10^{-4} \Omega \text{ cm}$ could therefore be achieved, but only at the expense of a deterioration in the coverage of the substrate.

The graph below shows the variation in the resistivity of the coating with length along the glass plate. This is compared with a film grown with the dopant tin(II) ethylhexanoic acid salt, with a similar dopant level in the coating.

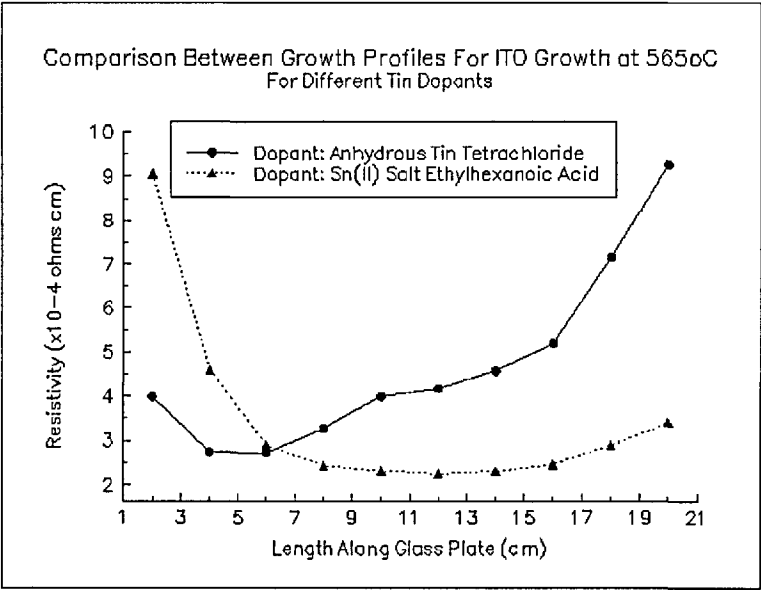


Figure 4-29 Graph Comparing Growth Profiles Of ITO Grown From In(thd)₃ and DBTDA and In(thd)₃ and Tin(II) Salt Ethylhexanoic Acid

The large increase in the resistivity towards the back of the plate with the SnCl₄ dopant is due to the reduction in the dopant concentration in the coating.

The films grown under these conditions exhibit preferred orientation in the (400) plane. This is similar to the preferred orientation observed for the growth of ITO from In(thd)₃ and DMT.

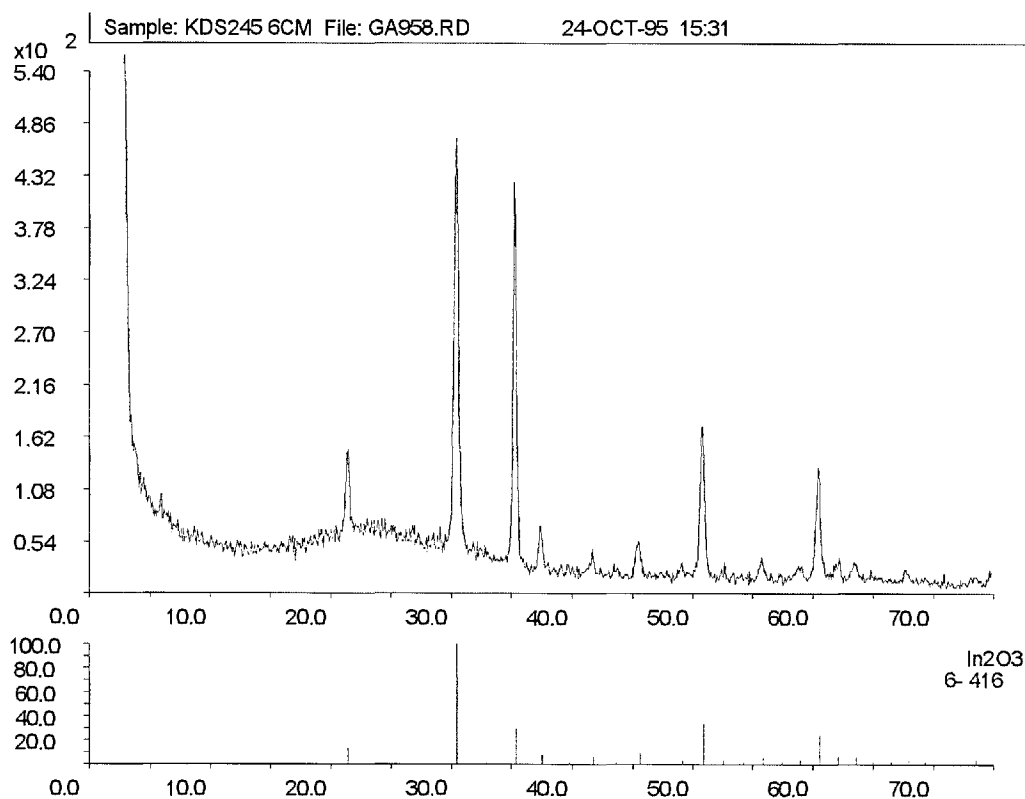


Figure 4-30 Glancing Angle XRD Pattern Of Film Growth From $\text{In}(\text{thd})_3$, O_2 and SnCl_4 at 565°C

4.3.6.2 Temperature Effect:

Film growth at 565°C using this precursor system showed problems with the thermal stability of the mixture, with signs of initial overdoping of the coating evident. If the growth temperature is increased from 565 to 625°C , the problem appears to be exacerbated, with the initial doping being even higher at the front of the film. As with other dopant precursors the film coverage also deteriorates.

As a result of the thermal stability problems associated with this precursor, the film growth was not studied further.

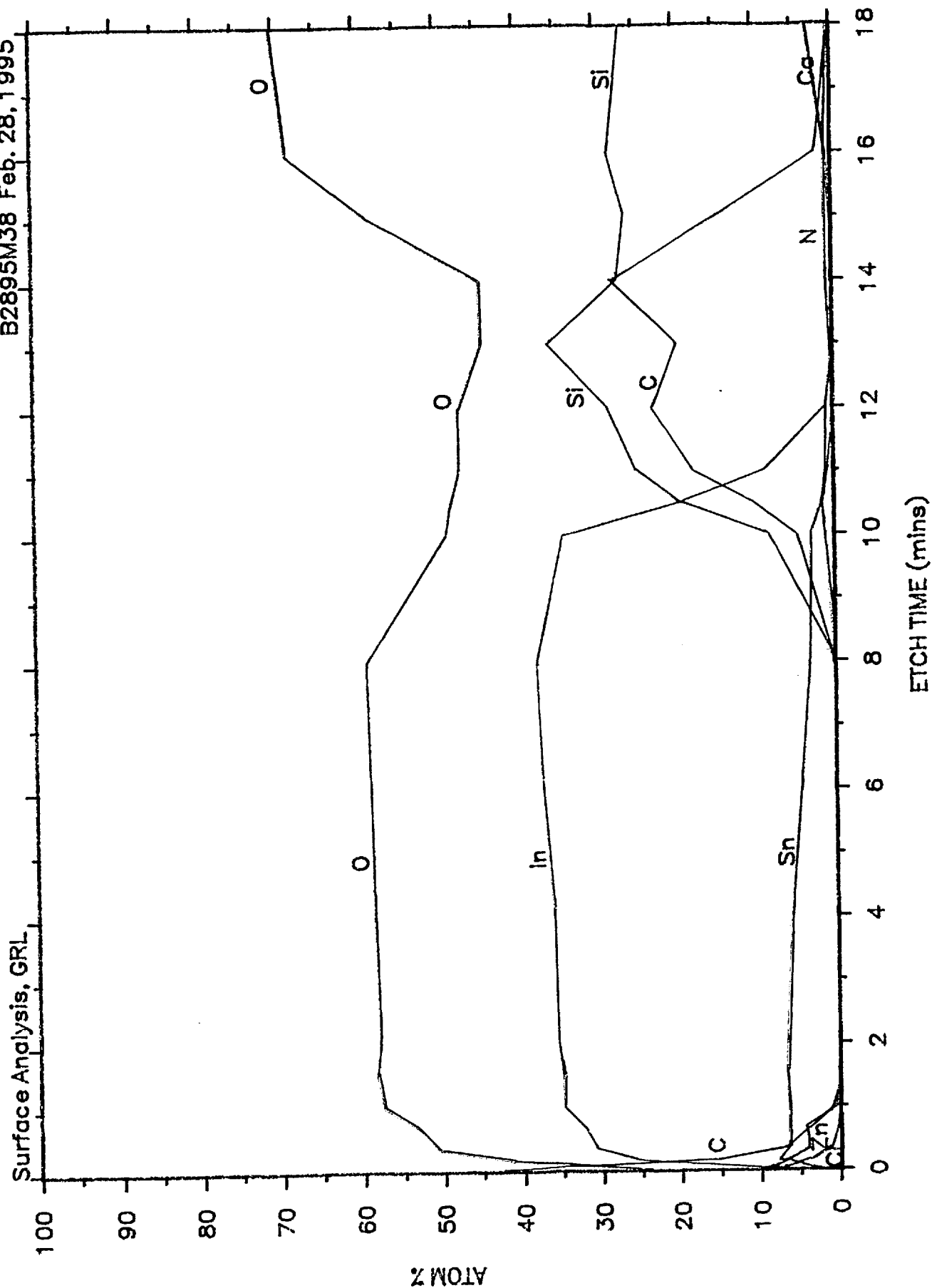


Figure 4-31 Auger Depth Profile Of ITO Growth From $\text{In}(\text{thd})_3$, SnCl_4 and BuOAc

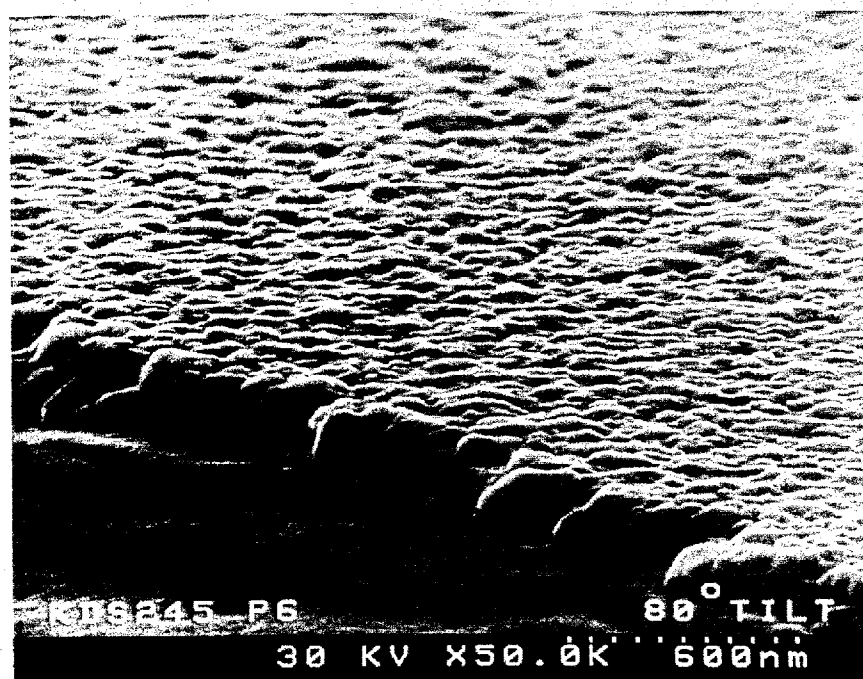
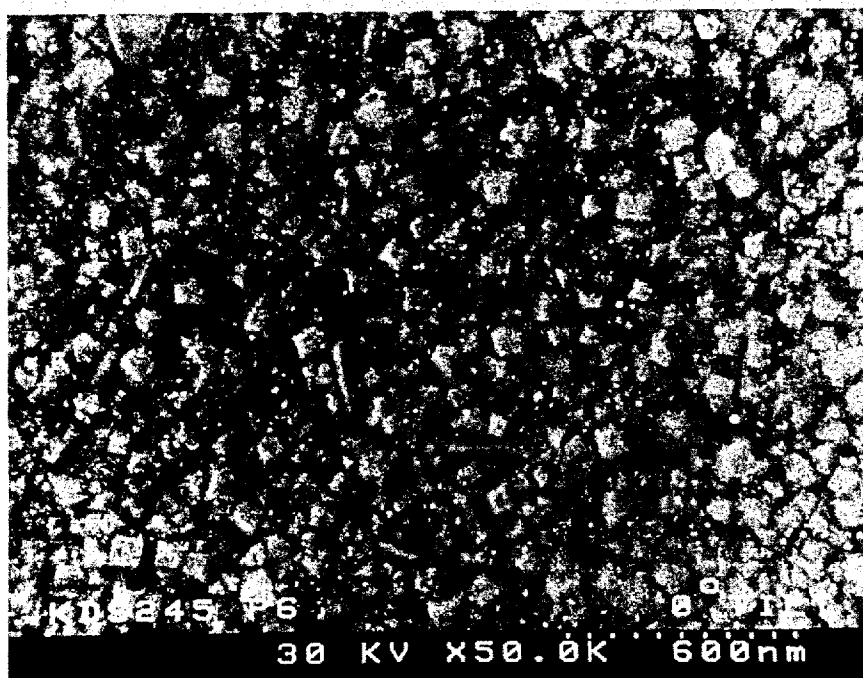


Figure 4-32 SEM Micrographs Of ITO Growth From In(thd)₃, SnCl₄ and BuOAc

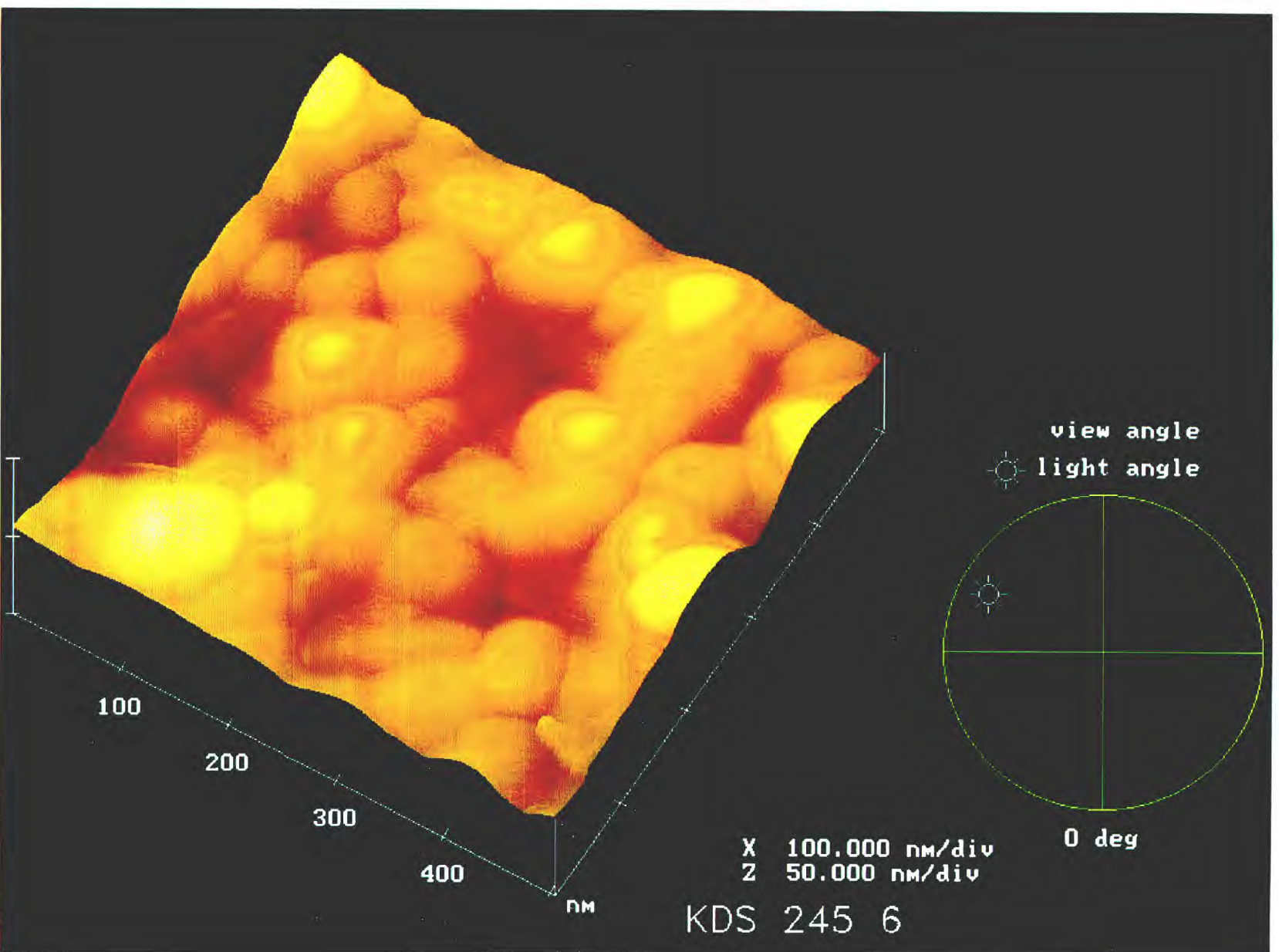


Figure 4-33 AFM Micrographs Of ITO Growth From $\text{In}(\text{thd})_3$, SnCl_4 and BuOAc

4.4 Conclusions:

The study of the growth of ITO from $\text{In}(\text{thd})_3$ and a range of tin dopants has shown good quality ITO films are obtained only when the growth profiles of the In_2O_3 precursor and the tin dopant precursor are matched. The materials DBTDA and tetrachlorotin are poor dopant precursors because they fail to produce a good film of ITO along the length of the glass plate. They produce heavily doped films at the front of the glass plate, but the dopant level drops away significantly towards the back end of the glass plate. The reason for this is believed to be the poor thermal stabilities of these dopant precursors. This is exacerbated by increasing the growth temperature of the precursor. The precursor tin(II) salt of ethylhexanoic acid is an efficient dopant at a growth temperature of 565°C , producing well doped films along the whole length of the plate. However, this precursor deteriorates as the growth temperature is increased. The two best dopant materials appear to be DMT and DMTDA which give good doped ITO at both 565 and 625°C .

The advantageous effect that the acetate group appears to have on film growth is novel.

ITO films with highly preferred (400) orientation have far poorer electrical properties. This preferred growth decreases the mobility of the carriers. A reduction of approximately 50% being seen between highly orientated and random films. The origin for this effect is not clear, but may be due to the preferred growth resulting in scattering of the carriers.

The growth temperature and dopant concentration have an effect on the degree of orientation. Accurate control of the orientation of the film has been achieved by the addition of butylacetate to the reaction and has resulted in the best electrical properties.

The properties achieved are comparable with those obtained by PVD and are better than those reported in the literature for CVD ITO with resistivities of as low as $1.29 \times 10^{-4} \Omega \text{ cm}$ being achieved from a $3000 \text{ \AA}$ film.

Whilst comparable properties to PVD ITO can be achieved for films of approximately $1500\text{-}3000 \text{ \AA}$, the first several hundred angstroms of the CVD films

appears to contribute very little to the electrical properties of the final film. This phenomenon whilst being recognised for some other CVD systems on glass substrates, has not been previously been reported for CVD ITO. The poor electrical properties of these thin films represents a potential disadvantage for CVD ITO in applications where film thickness of $< 1000 \text{ \AA}$ are required. The poor properties of the thin films appear to be associated with poor mobility of the carriers in this region of the coating. It is believed this is due to the island growth mechanism observed for these polycrystalline coatings. Alteration of the substrate material or pre-treatment of the substrate prior to coating may be required to modify this initial nucleation mechanism and thereby eliminate this problem.

4.5 References

1. R. Sievers, S. Turnipseed, L. Huang and A. Lagalanle, *Coord. Chem. Reviews*, **1993**, 128, 285
2. E. Mazureto and A. Gerasimuk, *J. de Physique IV*, **1995**, 5, C5-547
3. I. M. Watson, M. P. Atwood, D. A. Cardwell and T. J. Cumberbatch, *J. Mater. Chem.*, **1994**, 4(9), 1393 and S. J. Duray, D. B. Buchholz, S. N. Song, J. B. Ketterson, T. J. Marks and R. P. H. Chang, *Appl. Phys. Lett.*, **1991**, 59, 1503
4. See Chapter 3 Of this work references 20-38
5. I. Hamberg and C. G. Granqvist, *J. Appl. Phys.*, **1986**, 60(11), R123
6. J. M. Jarzebski, *Phys. Stat. Sol. A*, **1982**, 71, 13
7. S. E. Johnson and J. R. Owen, *J. de Physique IV*, **1995**, 5, C5-871
8. K. Arnold, *Weathering Processes at Glass Substrates*, **1995**, Bsc. Report, John Moors University Liverpool
9. I. Elfallal, R. D. Pilkington and A. E. Hill, *J. Mater. Science*, **1991**, 26, 6203
10. Ya. Kuznetsov, *Sov. Phys.-Solid State*, **1960**, 2, 30
11. Private Communication, Mike Bains
12. E. Shanthi, A. Banjeree, V. Dutta and K. L. Chopra, *J. Appl. Phys.*, **1982**, 53, 1615
13. E. Shanthi, A. Banjeree and K. L. Chopra, *Thin Solid Films*, **1982**, 88,93
14. R. Groth, *Phys. Status Solid*, **1966**, 14, 69

15. A. Rohatgi, T. Viverito and L. H. Slack, *J. Am. Chem. Soc.*, **1974**, 57, 278
16. A. F. Carrol and L. H. Slack, *J. Electrochem. Soc.*, **1976**, 123, 1889
17. H. Kostlin, R. Jost and W. Lems, *Phys. Status Solidi A*, **1975**, 29, 87
18. P. Nath, R. F. Bushah, B. M. Basol and O. M. Statssud, *Thin Solid Films*, **1980**, 72, 463
19. F. A. Kroger, *Chemistry of Imperfect Crystals*, **1964**, Chapt. 7 and 16, North-Holland, Amsterdam
20. C.A. Vincent, *J. Electrochem. Soc.*, **1972**, 119, 515
21. J. C.C. Fan and J. B. Goodenough, *J. Appl Phys.*, **1977**, 48, 239
22. S. Noguchi and H. Sakata, *J. Phys. D*, **1980**, 69, 63
23. J. C. Manificier, L. Szepessy, J. F. Breese, M. Perotin and R. Stuck, *Mater. Res. Bull.*, **1979**, 14, 163
24. T. Marayama and K. Tabata, *Jap. J. Appl. Phys.*, **1990**, 29(2), L355
25. J. Bruneaux, H. Cachet, M. Froment and A. Messad, *Thin Solid Films*, **1991**, 197, 129
26. M. L. Olvera, A. Maldonado, T. Assomoza, M. Konagai and M. Asomoza, *Thin Solid Films*, **1993**, 229, 196

5. Investigation of the Role of Solvents in The Deposition of ITO By Gas Phase IR Spectroscopy.

5.1 Background:

From the study of the growth of ITO using the precursor $\text{In}(\text{thd})_3$ with a range of tin dopant sources it has been observed that the addition of acetate containing groups has a beneficial effect on film growth, resulting in an improvement in the growth profile of the coating and improving the film's electrical properties.

Previous work on the deposition of ITO by APCVD by Maruyama *et. al.* has reported that a degree of (400) preferred orientation is achieved from the precursors indium acetate or indium 2-ethylhexanoate,¹ using the tin dopant tin diacetate. However, whilst this work related the degree of preferred orientation observed to the level of tin doping in the coating, no control over the preferred orientation was reported. In fact other literature reports of CVD ITO observe (222) preferred orientation in APCVD ITO films using the alternative precursor system $\text{In}(\text{acac})_3$ and tin acetylacetonate as the tin dopant.²

The work reported in this thesis correlates with these results, with the preferred orientation appearing to be related to the precursor system used for the deposition and the substrate temperature employed. Methods for controlling the preferred orientation obtained during film growth from a particular precursor system has not previously been reported. This work has shown that the addition of acetate species can result in a degree of control of the preferred growth between the (222) and (400) planes. A summary of the precursors used and the preferred growth achieved is shown in Table 5-1.

Table 5-1 Precursor System Effect On Preferred Orientation Growth

Indium Precursor	Tin Dopant Source	Deposition Temperature °C	Plane of Preferred Orientation
In(thd) ₃	Sn(II) Salt Ethylhexanoic Acid in Butyl or Ethyl- Acetate	565 and 625	(222) / Random
In(thd) ₃	DMT	565 and 625	(400), extent dependant upon doping level
In(thd) ₃	DMT and butyl, ethyl or methyl- acetate	565 and 625	(222)
In(thd) ₃	DMTDA	565	(222)
In(thd) ₃	DMTDA	625	(400)
In(thd) ₃	DMTDA and butyl, ethyl or methyl- acetate	625	(222)
In(thd) ₃	Tetrachlorotin and butylacetate	565 and 625	(400)

Attempts have been made at controlling the preferred orientation by the addition of butylacetate to the reaction mixture and also by the addition of the acetate grouping as part of the tin dopant precursor in the form of DMTDA and DBTDA.

The control of the preferred orientation obtained in the film is of particular importance to the electrical properties of the films, as this work has shown that films exhibiting a preference for the (222) plane have better electrical properties, due to the carriers in these films having a higher mobility than those with a preference for the (400) plane. This is clearly seen for the In(thd)₃ and DMT system where films grown with a similar doping level have very different electrical properties depending upon the preferred orientation of the coating.

Table 5-2 Effect of Preferred Orientation Growth On Electrical Properties Of Films

Doping Level Sn In Weight Ratio	Ratio (222):(400) Counts*	Resistivity $\times 10^{-4} \Omega$ cm
5.6	108:713	2.97
5.7	404:380	1.70

* For Random In_2O_3 (222):(400) ratio is 3.5:1

In order to further investigate the role of the acetate grouping and to obtain an understanding of which is the active species responsible for the observed change in preferred orientation of the coating, the stability of a range of acetate additives and precursors used during film deposition have been investigated by infrared absorbance spectroscopy.

5.2 Experimental:

Infrared data has been collected using the flow furnace / FTIR (Fourier Transform Infrared) system which is shown in Figure 5-1.

The species under investigation was held in a stainless steel bubbler, with the facility to blow carrier gas either over the top or through the precursor. The vapourised precursor was then passed via ¼" stainless steel pipework, which was held at approximately 180°C using heater tapes, into the furnace and interrogating infra-red beam. Just prior to entry into the furnace, the precursor flow was mixed with a nitrogen diluent stream with a flow rate of 6 litres / min. The nitrogen flow through the bubbler was held constant throughout the experiments at a flow rate of litres / min.

The infrared data was taken at 8cm^{-1} resolution and collected over a 1.5 minute period.

The interrogating IR beam was supplied by a commercial infrared spectrometer, with an external beam passing through KBr windows fitted with a nitrogen flush to prevent condensation on the windows themselves. The infra-red detector was of an MCT (mercury-cadmium-telluride) type.

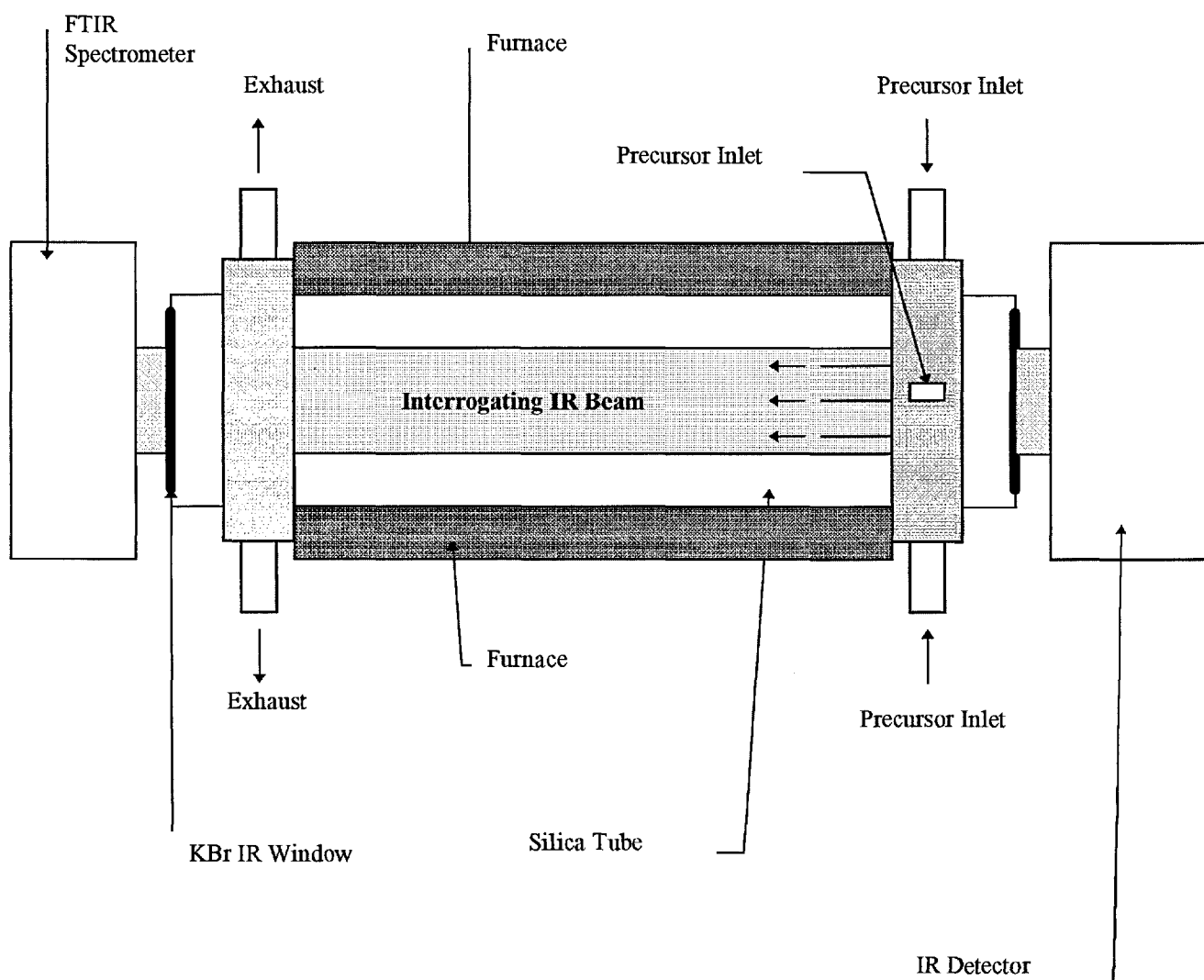


Figure 5-1 Diagram Of FTIR Equipment

The thermal decomposition of the organotin precursors diacetatodimethyltin, diacetatodibutyltin and the additive butylacetate has been studied using infrared

absorption spectroscopy under flow conditions. The interaction of butylacetate and acetic acid with the organotin compound dichlorodimethyltin was also investigated.

Standard organic reaction kinetics predict that the breakdown mechanism for n-butylacetate under static conditions follows the following decomposition route.³

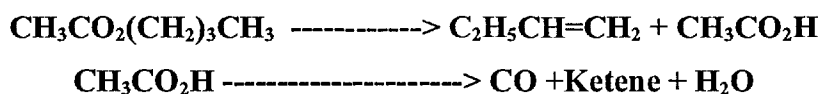


Figure 5-2 Breakdown mechanism of butylacetate under static conditions

Whilst a similar decomposition is expected under flow conditions, an investigation to obtain a direct comparison between the organo-tin and butylacetate decomposition under flow conditions, similar to those in the deposition experiments, was carried out to determine the active species responsible for the film modification observed.

5.3 Study of The Thermal Stability of Butylacetate:

The thermal stability of n-butylacetate in the gas phase was investigated over the temperature range of 200-800°C, to determine the species that are likely to be present in the gas phase under typical deposition conditions for ITO and In₂O₃.

Figures 5-3 and 5-4 show the infra-red of the butylacetate at a range of furnace temperatures.

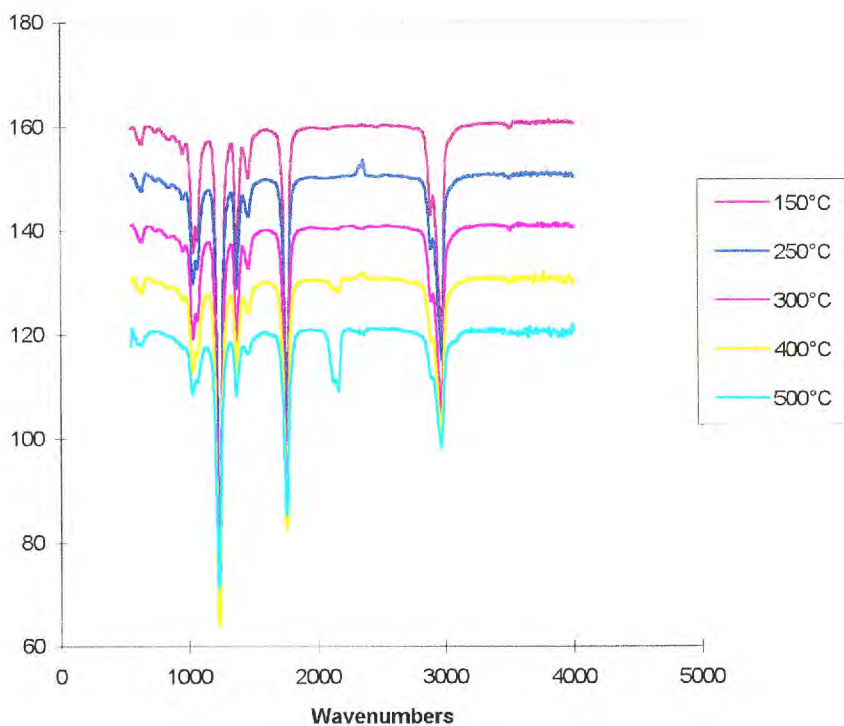


Figure 5-3 Spectra of Butylacetate at a range of furnace temperatures from 150-500°C

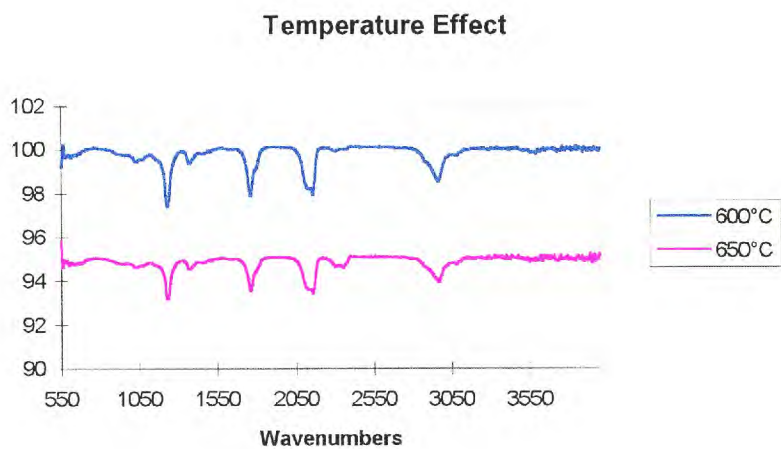


Figure 5-4 Spectra of Butylacetate at furnace temperature from 600-650°C

At a gas phase temperature of 200°C, which is the temperature at which the vapourised acetate was transported in the gas phase to the reaction vessel during film deposition, the butylacetate appeared to relatively intact, with the spectra similar to that of a vapour phase infrared reference spectrum.⁴

As the temperature of the furnace was increased, no significant change in the IR spectra was observed, apart from a general decrease in the band intensity of the butylacetate, due to line broadening effects as a result of the increased temperature at which data collection was taken.⁵ It was only at a temperature of approximately 450-500°C, that the decomposition of the butylacetate increased significantly. This can be seen in figure 5-5 which shows the integrated absorbance of the bands due to the C-O, C=O and C-H of the intact butylacetate. Whilst the band intensity gradually decreased, due to a line broadening effect caused by the temperature increase, it can be seen that the initial breakdown of the butylacetate became significant only at temperatures above 500°C, when the absorbance intensity of the bands due to butylacetate decreased significantly.

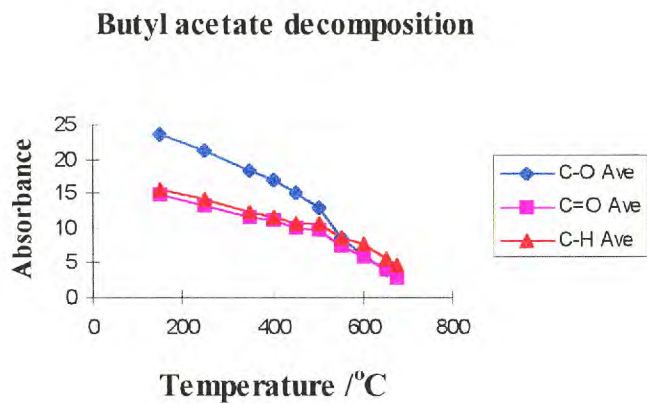


Figure 5-5 Graph Showing Level Of Intact Butylacetate With Respect To Temperature (Measured from absorbance of the C-O, C=O and C-H stretches)

From the spectra it can be seen that the decrease in intact butylacetate is accompanied by the occurrence of an absorbance at approximately 1800 cm⁻¹, due to the production of acetic acid in the gas phase.^{10, 11}

The production of acetic acid was accompanied by a large increase in the CO production, this suggesting that breakdown of the acetic acid occurs to produce CO. A maximum in the amount of CO produced due to the decomposition of the acetic acid occurred at a temperature of approximately 550°C. Above a temperature of 550°C, the amount of CO decreased, due to the conversion of CO to CO₂.

From the temperature study it can be seen that the breakdown of the material in the gas phase is consistent with that expected from literature reports. Initial breakdown of the butylacetate to acetic acid and but-1-ene being observed. The subsequent decomposition to CO is also observed, although the presence of but-1-ene in the gas phase can be difficult to detect because the bands characteristic of but-1-ene at 3080 and 1640 cm⁻¹ being obscured by other species.^{6, 12}

In order to determine the difference in stability between the acetate grouping in butylacetate and the acetate group in DMTDA and DBTDA, the thermal stability of these precursors were also investigated.

5.4 Investigation of Thermal Stability of DMTDA:

The precursor DMTDA, was held in a stainless steel bubbler, and the material heated upto approximately 60°C. A gas flow of 200 cc/min was then passed over the top of the precursor and the material swept down lines held at 200°C, into the flow furnace. Figure 5-6 shows the infra-red of the material at a range of furnace temperatures.

Temperature Effect on DMTDA

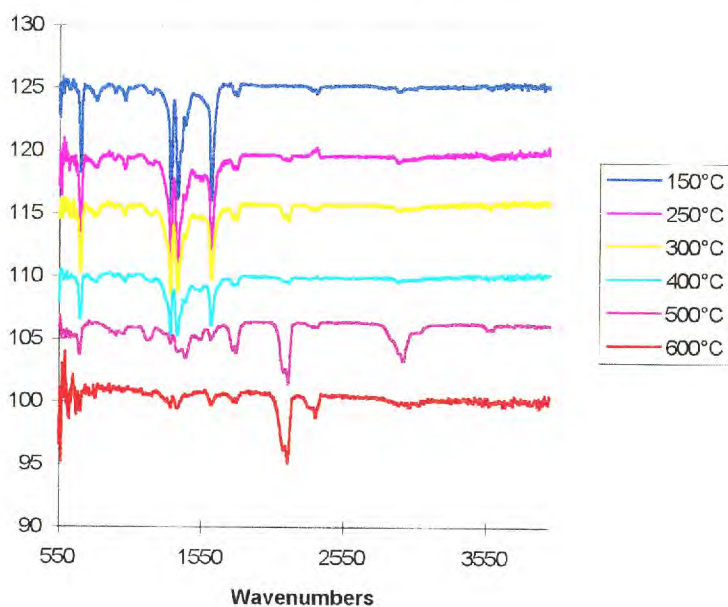


Figure 5-6 IR Spectra Of DMTDA At A Range of Furnace Temperatures From 150-600°C

At a temperature of approximately 200-300°C the precursor appeared intact, although there was a small amount of free acetate visible that is likely to be due to a small amount of free acetic acid impurity in the initial precursor.

As the reactor temperature was further increased to approximately 450°C, the precursor decomposed, with the production of acetic acid, which appeared as a doublet possibly due to dimerisation, producing acetic anhydride which is characterised by the band seen at 1800cm⁻¹.

This implies that significant breakdown of the tin precursor with release of the acetic acid has occurred, with this breakdown to the acetic acid being accompanied by the production of CO.

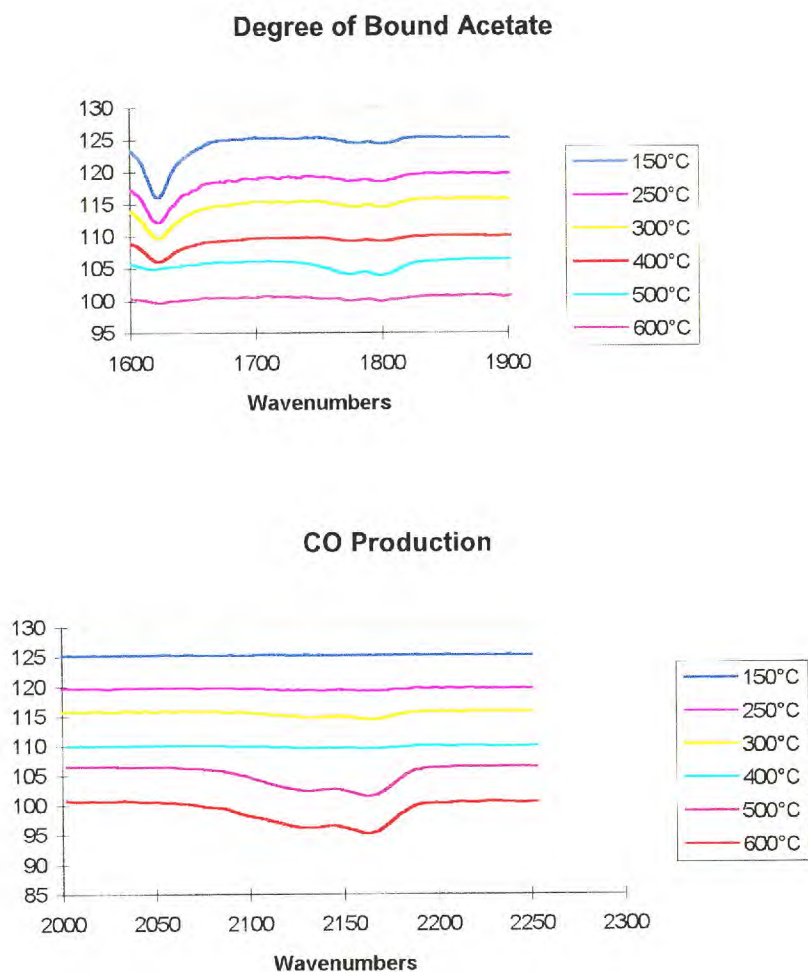


Figure 5-7 FTIR spectra showing the amount of intact acetate and evolution of CO at a range of furnace temperatures

As the temperature increased further the level of CO increased, which is consistent with the acetic anhydride further decomposing to liberate CO. The CO production reached a maximum at a temperature of approximately 450°C, which is significantly lower than that seen for the butylacetate, which had a maximum CO

production at a temperature of approximately 550°C. As the temperature was increased further, the level of CO began to diminish as the CO was converted to CO₂.

From these results it appears that the stability of the acetate grouping in the tin precursor is lower than that of the acetate group of butylacetate, as the production of CO due to the breakdown of the acetate to acetic anhydride / acid and then to CO occurs at a lower temperature in the DMTDA than in butylacetate. In the tin dopant material the loss of the acetate from the tin centre appears to occur at a temperature of approximately 450°C, followed by rapid decomposition of this acetate to acetic anhydride and subsequently to CO. The decomposition of the acetate grouping, is therefore occurring at a significantly lower temperature than observed in the case of the butylacetate, in which the acetate does not appear to decompose until a temperature of >500°C.

The difference in the decomposition temperature of the acetate to acetic anhydride or acetic acid and its subsequent decomposition to CO, therefore appears to be a result of the different thermal stability of the initial precursor.

5.5 Thermal stability of DBTDA.

This precursor was held in a stainless steel bubbler held at 80°C and 200 cc/min of gas was passed over the top of this precursor. Figure 5-8 shows the infra-red of the compound at a range of furnace temperatures.

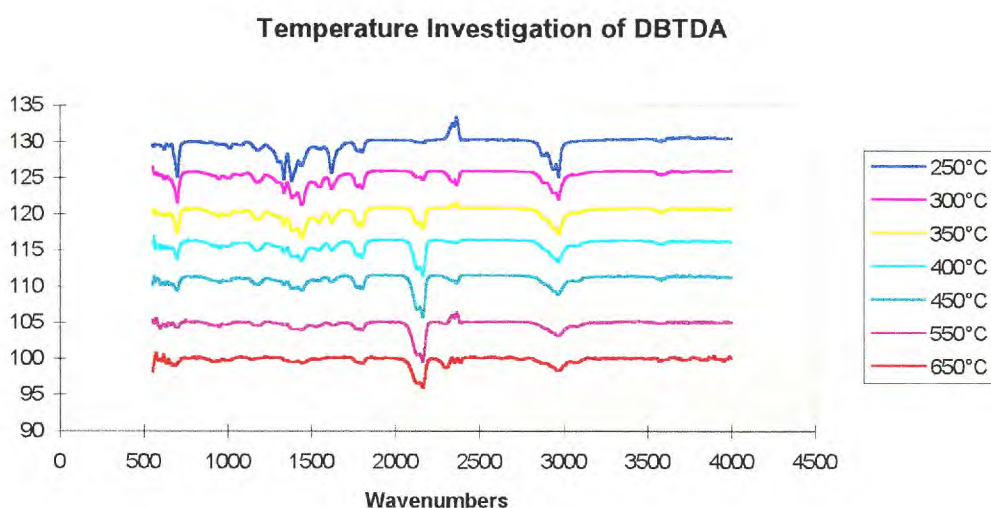


Figure 5-8 FTIR Spectra Of DBTDA At A Range Of Temperature

As with the precursor DMTDA this precursor appeared to remain intact upto a temperature of 300-350°C, although some evidence of free acetate due to impurity in the precursor was observed.

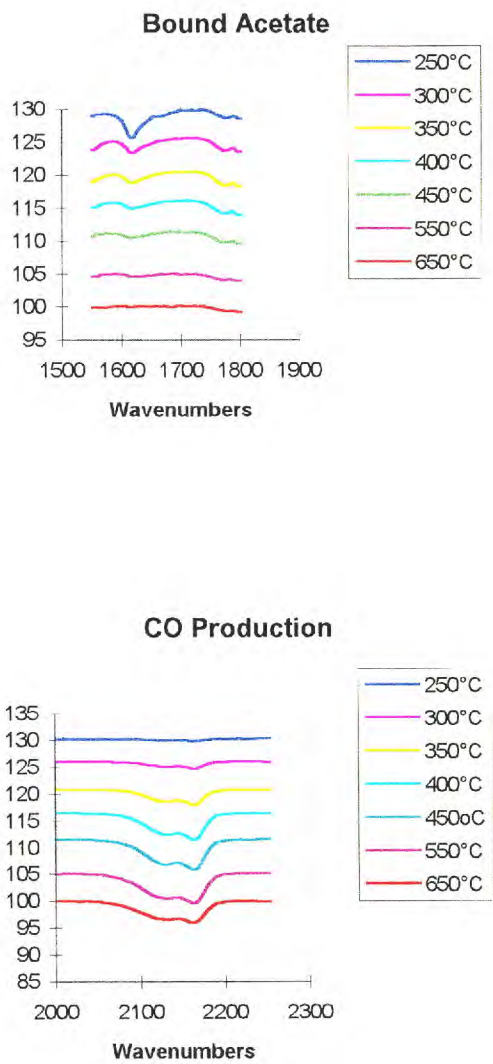


Figure 5-9 FTIR spectra showing amount of intact DBTDA and amount of CO evolution at different furnace temperatures

As the temperature was increased, evidence of breakdown of the tin precursor to the acetic acid was seen, with the maximum production occurring at a similar temperature to that in DMTDA at approximately 400°C.

The formation of CO due to the breakdown of the acetic acid was also observed.

5.6 Discussion:

From the study of the thermal stabilities of these materials it appears that the thermal stability of the acetate group is determined by the stability of the initial precursor. In each case, as soon as decomposition of the initial precursor occurred, resulting in the formation of free acetate, further decomposition to acetic acid (observed as acetic anhydride in the case of DMTDA) and then CO occurred. The thermal stability of the initial precursors is therefore important in determining which species are present in the gas phase at a particular temperature.

Figure 5-10 shows the level of acetic acid formation as a function of temperature, for the precursors DMTDA and DBTDA. This shows the formation of acetate due to decomposition of the tin precursors is occurring at approximately 400-450°C. No results for the production of free acetate from butylacetate have been possible, due to an overlap of the bands from the free and co-ordinated acetate.

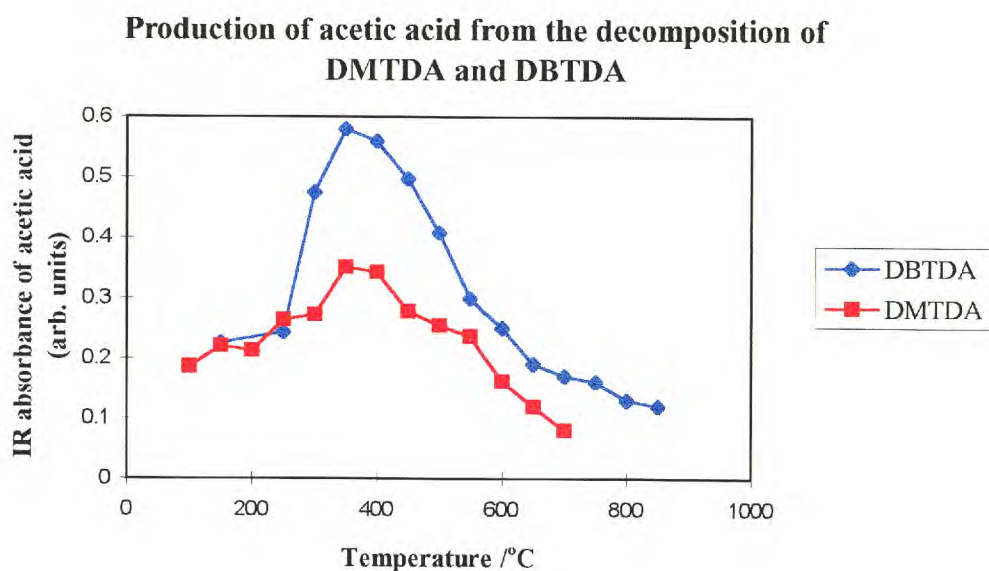


Figure 5-10 Graph illustrating the level of acetic acid production from the thermal decomposition of DMTDA and DBTDA as a function of temperature. Infrared absorbance of the C=O stretch of acetic acid at $\sim 1800\text{ cm}^{-1}$ is used as a measure of concentration

These experiments suggest that the stability of the acetate group with respect to Sn-O cleavage is similar in both DBTDA and DMTDA. This is a surprising result as film growth using these dopants is significantly different, with the tin dopant DMTDA produces films with an even doping profile along the glass plate, whilst DBTDA appears to dope preferentially at the front of the glass plate. This therefore suggests that it is the stability of the alkyl group which is responsible for the difference in the doping profile of these two precursors.

The poor doping profile obtained from DBTDA doping of indium oxide from $\text{In}(\text{thd})_3$ and oxygen is therefore likely to be a result of the hydrocarbon n-butyl group being less stable to loss from the tin metal centre than the methyl group in DMTDA. A facile route for n-butyl loss via β -hydride elimination, producing but-1-ene, is available for the alkyl group of DBTDA to decompose, whereas no facile route is available for the methyl group of DMTDA. The Sn-Me bond in DMTDA is likely to break homolytically at a much higher temperature, with the formation of a methyl radical which would then further react to form methane or ethene. As a result the lower thermal stability of DBTDA is likely to be responsible for its poor doping profile, with rapid decomposition of the precursor resulting in the preferential tin doping at the front of the film that is observed.

Subsequent decomposition of the acetic acid to CO has been observed for all the precursors investigated. Figure 5-11 shows the formation of CO as a function of temperature for BuOAc, DMTDA and DBTDA.

The production of CO from the decomposition of DMTDA, DBTDA and butyl acetate as a function of temperature

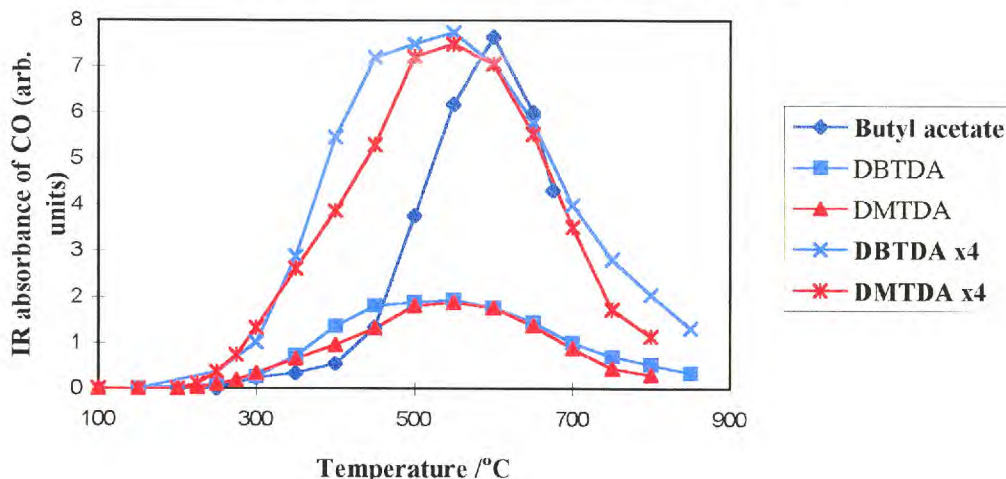


Figure 5-11 Graph illustrating the level of CO production from the thermal decomposition of DMTDA, DBTDA and BuOAc as a function of temperature. The concentration of CO from DBTDA and DMTDA is lower, and has therefore been scaled by a factor of 4.

As the formation of the free acetate is the initial decomposition step, and the subsequent decomposition to acetic anhydride (or acetic acid) and CO appears to be rapid at temperature above 400°C, this provides an indication of the thermal stability of the initial precursor, suggesting that the relative thermal stabilities of the acetate grouping in the investigated precursors is:



Whilst this is important for determining the species likely to be present in the gas phase, it does not in itself explain the variation in preferred growth seen when using these precursors.

Of the decomposition products identified several species could be responsible for changing the preferred orientation observed in the final coating including:

1. The intact acetate grouping
2. The acetic acid produced due to the decomposition of the acetate
3. The unsaturated hydrocarbon, but-1-ene, produced from the initial decomposition of butylacetate
4. The CO produced during the decomposition of the acetic acid.

Unsaturated hydrocarbons have been reported to modify film growth in CVD systems,⁷ therefore to investigate whether the active species in film growth was the unsaturated hydrocarbon produced during the decomposition of the acetates, growth of ITO using methyl-acetate was carried out. Film growth using this system was very similar to that obtained using BuOAc, with control over the preferred orientation being possible in a similar fashion to that found when BuOAc is used. This suggests that the unsaturated hydrocarbon is not the active species as unlike the BuOAc the decomposition of methylacetate does not result in the production of an unsaturated hydrocarbon. This is consistent with the results obtained using the tin dopant dimethyl-tin-diacetate, which does not result in an unsaturated hydrocarbon on decomposition, but does result in changes in the film properties.

In order to isolate the species responsible for the film modification, investigation of the interaction of the tin dopant DMT, which had been seen to result in both (222) and (400) preferred orientation growth, with butylacetate and acetic acid was investigated.

5.6.1 Interaction of Acetic Acid and Butylacetate With DMT

The interaction of DMT with butylacetate and acetic acid was investigated in the temperature range 200-550°C. Figure shows the spectra of a DMT and acetic acid mixture at 200°C. The main features of the spectra correlate with the presence of gas phase DMT and acetic acid. The band at 1600 cm⁻¹, however, is characteristic of a coordinated acetate;⁸ and was previously observed in DMTDA and DBTDA. This implies that a small amount of a new species is present, containing at least one bound acetate ligand. Figures 5-12 (a), (b) and (c) show the infrared spectra with the characteristic tin acetate species present at 1600 cm⁻¹.

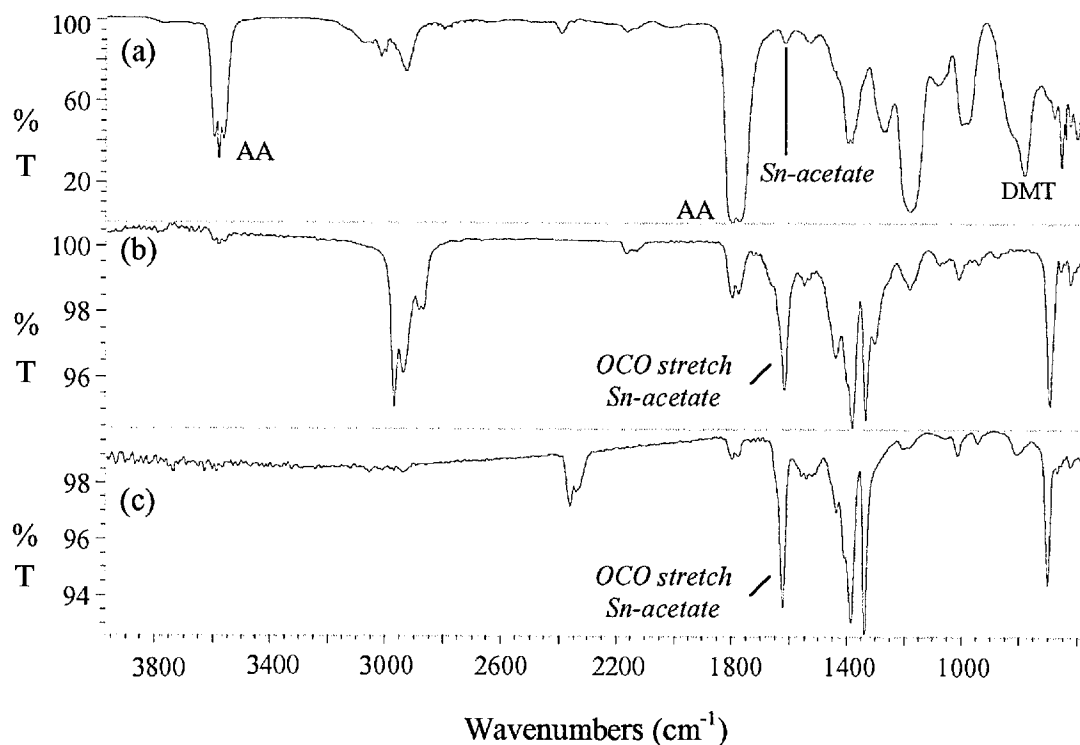


Figure 5-12 Infrared Spectra of a) Acetic acid and DMT at 200°C (AA= Features due to acetic acid, DMT= Features due to DMT). b) diacetatodibutyltin, c) diacetatodimethyltin. Features at $\sim 1600\text{cm}^{-1}$ are characteristic of a bidentate acetate co-ordinated at a tin centre

The interaction of butylacetate and DMT at 200°C does not produce this species, although at higher temperatures of approximately 400°C, when the acetate group has partially decomposed to acetic acid the presence of this species was detected.

The presence of this tin acetate species as a function of reactor temperature for DMT and 1. butylacetate and 2. acetic acid is shown in Figure 5-13.

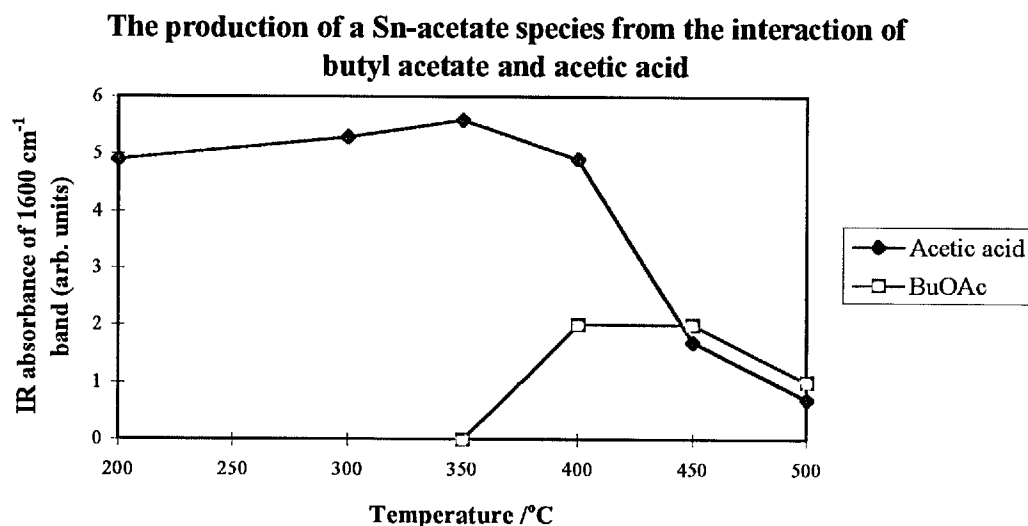


Figure 5-13 The production of a co-ordinated acetate species from the interaction of butylacetate and acetic acid with DMT as a function of temperature. Band at 1600cm^{-1} is used as a measure of the concentration of the acetate species

The formation of the tin acetate species with the DMT and butylacetate system correlates with the production of acetic acid from the thermal decomposition of butylacetate, and therefore suggests that the formation of the tin acetate species is dependant upon the presence of acetic acid in the gas phase. This is further confirmed by the reduction in the amount of tin acetate species as the temperature is further increased, as further decomposition of the acetic acid to CO and CO₂ occurs, reducing the amount of acetic acid present.

During the formation of the tin acetate species from both DMT and either acetic acid or butylacetate, very little formation of methane or HCl was observed. This suggests that the acetate species is formed by co-ordination of the acetate without hydrolysis of the DMT occurring.

This study suggests that the difference in the behaviour of butylacetate and acetic acid interaction with DMT as a function of temperature, is a result of the temperature range over which the acetic acid is present. Butylacetate which only produces acetic acid at approximately 400-500°C, forms the tin-acetate species only at these elevated temperatures, whereas acetic acid itself forms a tin-acetate species at lower temperatures as well.

In order to obtain a better correlation with the conditions used during film growth, the interaction of DMT with butylacetate and acetic acid was studied under oxidising conditions.

5.6.2 Interaction of DMT with acetic acid and butylacetate under oxidising conditions

The decomposition of butylacetate was initially studied under oxidising conditions. Comparison of the decomposition of butylacetate under non-oxidising and oxidising conditions is shown in Figure 5-14. The temperature at which the decomposition of butylacetate to acetic acid occurred was significantly reduced, suggesting the presence of oxygen accelerates the decomposition of the butylacetate.

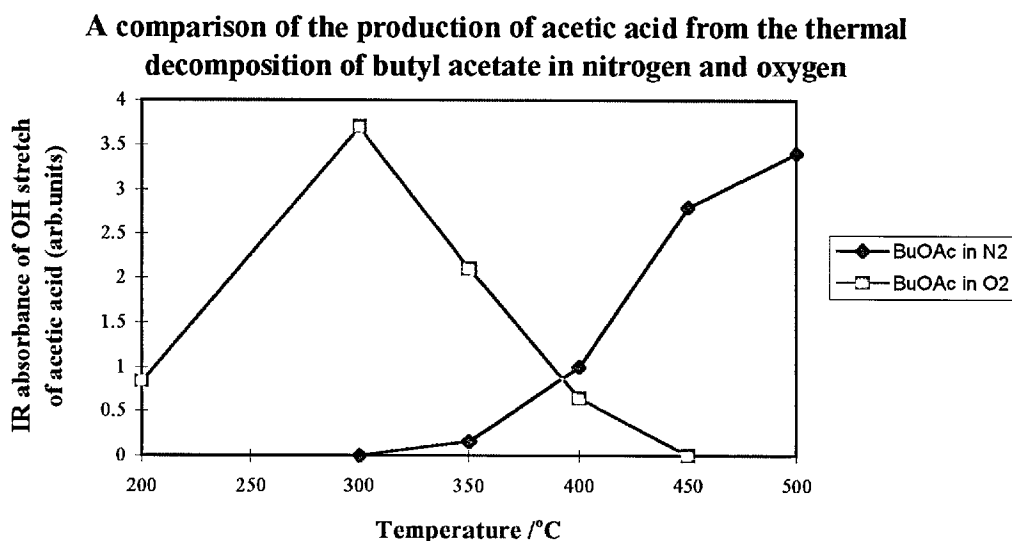


Figure 5-14 Graph comparing the production of acetic acid from butylacetate in the presence of oxygen with the production of acetic acid from the thermal decomposition of butylacetate in nitrogen. The absorbance of the OH stretch of acetic acid is used as a relative measure of the acetic acid concentration.

The study of the interaction of butylacetate and DMT under oxidising conditions was also seen to change significantly. The temperature range over which the tin acetate species produced from the interaction of butylacetate and DMT shifted to lower temperatures. This shift correlates to the production of acetic acid from the decomposition of butylacetate occurring at lower temperatures. At higher temperatures

of 400-500°C, the tin acetate species stability was also reduced, probably a result of the oxidising conditions resulting in fast oxidation of the acetic acid.

The interaction of acetic acid and DMT under oxidising conditions closely resembled that of the interaction of butylacetate with DMT.

These results imply that the active species, responsible for the change in preferred orientation when butylacetate is added is either the tin acetate species formed due to the interaction of acetic acid with the tin dopant to form a tin acetate species or acetic acid or a combination of the two.

Given that both DMTDA and a mixture of DMT and butylacetate have been shown to result in film modification, and from the infrared study carried out *in-situ*, production of acetic acid appears to play a key role in the mechanism of film modification.

The infrared study has clearly shown that the interaction of butylacetate and DMT produces a tin acetate species which in the absence of hydrolysis is likely to be of the form $\text{Me}_2\text{SnCl}_2(\text{HOAc})$ or $\text{Me}_2\text{SnCl}(\text{OAc})$, where the acetate acts in a bidentate fashion to produce a six co-ordinate tin centre. Whilst this species may be a more stable gas phase intermediate produced during deposition, and would explain the observed broadening of the doping profile observed when butylacetate is added during ITO growth from $\text{In}(\text{thd})_3$ and DMT, there is no evidence from the infrared study to show that DMT is stabilised by the formation of the co-ordinated acetate species. This is clearly shown in Figure 5-15 which shows the thermal decomposition of DMT in nitrogen and in the presence of butyl acetate and acetic acid.

Variation of DMT with temperature on interaction with acetic acid and butyl acetate

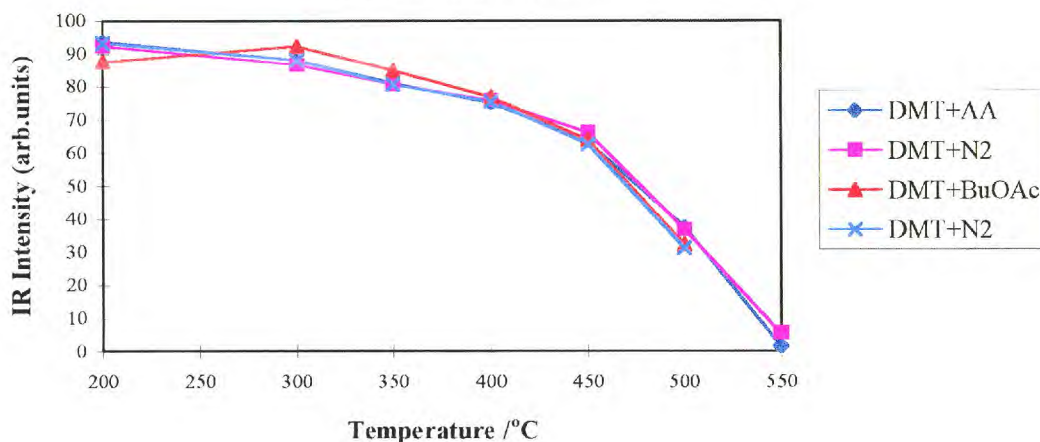


Figure 5-15 Decomposition of DMT in the presence of acetic acid and butylacetate. The graphs are labelled as to the gas phase composition. The IR absorbance of a band characteristic of DMT was used as a measure of its concentration

Moreover, since butylacetate causes a similar broadening of the growth profile for pure In_2O_3 , the formation of a more stable tin intermediate is unlikely to be responsible for the film modification.

DMT does appear to have a significant stabilisation effect on the thermal stability and decomposition mechanism of acetic acid, however. Figure 5-16 illustrates the stabilisation effect of DMT on the decomposition of acetic acid under oxidising conditions. A reduction in the rate of loss of acetic acid due to oxidation is observed in the presence of DMT in the temperature range 200-400°C, suggesting DMT allows the concentration of acetic acid to be kept high.

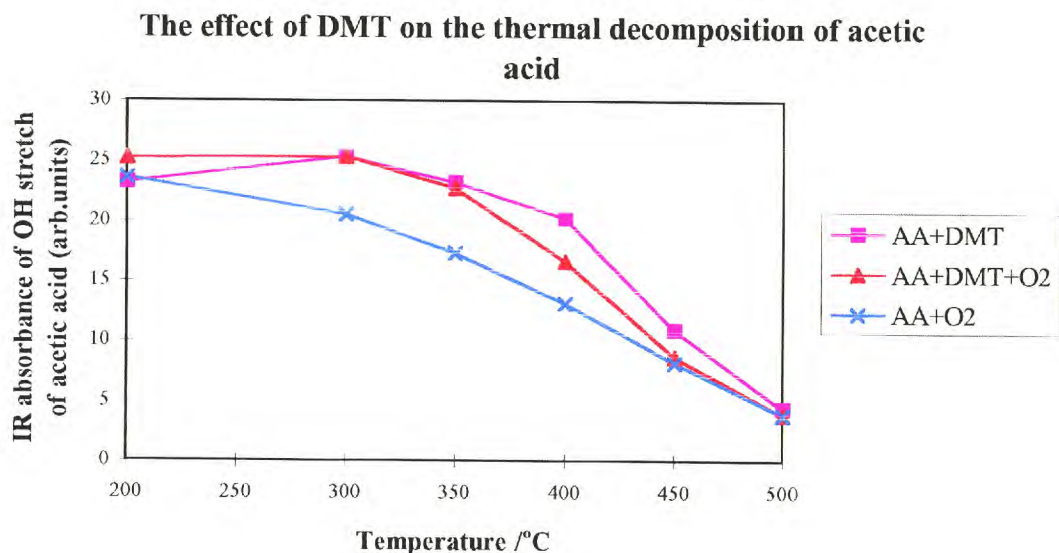


Figure 5-16 Graph illustrating the effect of DMT on the thermal stability of acetic acid in oxidising conditions. The IR absorbance of the OH stretch of acetic acid was used as a measure of its concentration.

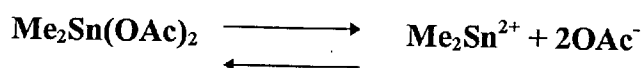
The interaction between acetic acid and DMT appears to result in a high concentration of acetic acid at or near the substrate. This is consistent with the result that no modification of film growth has been observed during growth using the alternative tin dopant SnCl_4 , with butyl acetate. The fact that there is a strong interaction between DMT and acetic acid without hydrolysis is significant; tetrachlorotin is more susceptible to hydrolysis, so that on co-ordination of acetic acid, significant hydrolysis at the tin centre is likely to occur. This also correlates with the experimental finding that the partially hydrolysed tin tetrachloride derivatives which are non-volatile result in overdoping at the front of the glass plate.

Since only small levels of the tin acetate species are detected, yet there is a large excess of acetic acid in the gas phase, it is possible further interactions between the acetic acid and DMT produce other intermediate species. Detection of these other species particularly if they are a result of the acetate acting in a monodentate mode, may not be possible, because their absorption bands would not be shifted sufficiently from that of the free acid.

This study therefore suggests that a strong interaction between the DMT and acetic acid (produced from the decomposition of butylacetate) without hydrolysis occurring, is required for film modification to occur.

If the key to film modification is in the first instance the production of acetic acid *in-situ*, followed by the maintenance of a steady state concentration of acetic acid at high temperatures via complexation / interaction with the tin precursor, then it is possible to explain why DMTDA produces film modification only at a lower deposition temperature of 565°C. The *in-situ* production of acetic acid from DMTDA occurs at a lower temperature than from butylacetate, and in addition, a proportion will further decompose to CO even at low temperatures. This coupled with the small doping levels of DMTDA used, results in a concentration of *in-situ* produced acetic acid, at or near the surface which is likely to be much smaller than produced from butylacetate. Therefore whilst there are sufficient active species present to allow film modification at 565°C, at a higher substrate temperature the higher rate of thermal decomposition of the DMTDA results in an insufficient steady state concentration of acetic acid to allow film modification.

Indeed these results are consistent with two further experimentally observed phenomenon. Firstly it has been observed that film modification from the DMT / butylacetate system is dependant upon the amount of butylacetate added, with insufficient addition of butylacetate resulting in no film modification. Secondly film modification from DMTDA can be achieved at 625°C with the addition of butylacetate. Butylacetate addition to DMTDA may serve two purposes. Firstly increasing the *in-situ* production of acetic acid and secondly influencing the steady state concentration of intact DMTDA by influencing the equilibrium:



Whilst a strong link between the *in-situ* production of acetic acid and film modification has been established, attempts at replacing butylacetate by 100% acetic acid during film growth were unsuccessful with no film of In₂O₃ or ITO being produced. In fact only an oily deposit was deposited.

This surprising result is likely to be a result of interaction between the indium precursor and the acetic acid occurring, resulting in pre-reaction of the precursors in the

gas phase to yield involatile species. This study has already shown (Chapter 3), that the indium precursors are susceptible to hydrolysis, with water causing pre-reaction. The failure of film growth when acetic acid is used as the additive therefore suggests that hydrolysis is occurring, possibly as a result of decomposition of the acetic acid with the production of water. This is not likely to occur with butylacetate as significant acetic acid formation is unlikely to occur until the hotter deposition zone.

Whilst the species most likely to cause surface modification has been isolated, the mechanism for the change is unclear. The addition of butylacetate during ITO film growth results in both a change in the preferred orientation growth from (400) to (222) and also broadens the growth profile of the ITO. It is postulated that the surface modification is a surface modulated process rather than a gas phase one. It is less likely that surface modification is a result of a gas phase effect, due to a change in the gas phase reaction rate for example. In fact it is widely accepted that reaction rate changes are rarely responsible for modification of the preferred orientation growth in the tin oxide system, with changes in the film growth generally only caused by vast changes in the precursor chemistry.

A surface modulated mechanism therefore appears most likely, and additives in other CVD systems have been seen to effect crystallite growth, for example trifluoroacetic acid modifies tin oxide crystallite growth in the DMT / O₂ system and phosphine effects crystallite growth in the deposition of polysilicon and tungsten.⁹ These effects are believed to be a result of a surface modulated effect. In the DMT / O₂ system the acid is believed to adsorb on the surface and provide nucleation sites for film growth, thus refining the grain size in the polycrystalline film. In tungsten and polysilicon deposition the phosphine is believed to preferentially adsorb on the substrate surface, poisoning the adsorption of the tungsten and silicon precursors, thus affecting film growth. A similar surface modulated mechanism may occur for the ITO growth, where adsorption of acetic acid may provide nucleation sites at which growth of a (222) orientated surface is more energetically favoured than (400) growth.

5.7 Conclusions:

This investigation has determined that control over the preferred orientation of ITO can be achieved between the (222) and (400) planes. Control over the preferred orientation has been related to several factors:

1. The thermal stability of the acetate precursor used
2. The temperature of deposition
3. The growth rate of the coating.

The investigation has shown that the active species present in the gas phase is likely to be acetic acid and that this can be supplied to the reaction vessel by *in-situ* formation either from part of the tin dopant or as a separate additive in the form of solvent addition.

This is believed to be the first report of control of the preferred orientation of ITO growth by APCVD. Whilst control over growth in any CVD system is advantageous in terms of film reproducibility, it is of particular importance due to the change in properties that is observed between the two preferred orientations. The low mobility (approximately 25-30) observed in (400) preferred films is detrimental to its electrical properties, compared with the higher mobility (40-45) seen for (222) preferred films. Such a relationship between the mobility of the carriers and the preferred orientation of the coating is highly important if the films properties are to be optimised.

The lower mobility of the (400) preferred coatings appears to be associated with more scattering of the carriers, as in both coatings the carrier concentrations are similar at $6 \times 10^{20} \text{ V}^{-1} \text{ cm}^{-2}$.

These results have indicated that control over the preferred orientation and thereby the electrical properties of the coating are achievable. The surface modification is believed to be a surface modulated process, with adsorption of acetic acid producing additional nucleation sites for ITO which favour the growth of (222) orientated films.

5.8 References

1. T. Maruyama and T. Tabata, *Jpn. J. Appl. Phys., Part 2*, **1990**, 29, L355
2. T. Maruyama and T. Tabata, *Jpn. J. Appl. Phys.*, **1991**, 70, 3848 and L. A. Ryabova, V. S. Salun and I. A. Serbinov, *Thin Solid Films*, **1982**, 92, 327
3. J. Marsh, *Advanced Organic Chemistry*, **1985**, 3rd Edition, John Wiley and Sons, New York
4. *The Aldrich Library of FT-IR Spectra*, C. J. Pouchert, Aldrich Chemicals Milwaukee, **1985**
5. C. N. Banwell, *Fundamentals of Molecular Spectroscopy*, **1983**, 3rd Edition, McGraw-Hill Book Company, London and J. M. Hollas, *Modern Spectroscopy*, **1987**, Wiley
6. J. Sheppard, *J. Chem. Phys.*, **1952**, 6, 1
7. T. Takahashi, Y. Egashira and H. Komiyama, *Appl. Phys. Lett.*, **1995**, 66, 2858
8. K. Nakamoto, *Infra Red Spectra of Inorganic and Co-Ordination Compounds*, **1963**, 1st Edition, Wiley
9. B. S. Meyerson and W. Olbricht, *J. Electrochem. Soc.*, **1984**, 131, 2361 and M. L. Yu, D. J. Vitkavage and B. S. Meyerson, *J. Appl. Phys.*, **1986**, 59, 4032
10. Hartwell and Thompson, *J. Chem. Soc.*, **1948**, 1436
11. L. J. Bellamy, *The Infrared Spectra of Complex Molecules Vol.1*, **1975**, 3rd Edition, Chapman and Hall, London
12. G. Socrates, *Infrared Characteristic Group Frequencies*, **1980**, John Wiley and Sons Ltd.

6. Properties Of APCVD Deposited ITO.

6.1 Introduction

Sheet glass is a widely used architectural material that is transparent to the solar radiation and completely opaque to the ambient thermal radiation spectrum. Each face of the glass has a reflectivity of approximately 4% in the visible region, and 15% in the thermal spectrum, which results in a glass sheet facing air having a high emissivity of circa 0.85 (Where Emissivity = $1 - \langle R \rangle$). These properties, whilst not preventing their use in a range architectural applications, can be a disadvantage in hot and cold climatic conditions.

In hot climates, the high transmittance of glass in the solar range is a disadvantage as all the energy from the sun (radiation spectrum extends from 0.3 to 2.2 μm) is transmitted into a room. The bulk of the solar energy is then absorbed by objects in the room (e.g. furniture) which re-emit the energy at a longer wavelength of circa 10 μm . Due to the low transmittance of glass at longer wavelengths the energy is therefore trapped in the room and results in heating of the interior of the building.

In cold climates the use of glass is also a disadvantage as the glass acts as a source of heat loss by conduction, convection and radiation due to the high emissivity value of glass. Whilst losses due to convection and conduction can be reduced by the use of multiple glazing, heat loss by radiation emittance cannot be reduced due to the high transparency of glass to emitted radiation from bodies in the room.

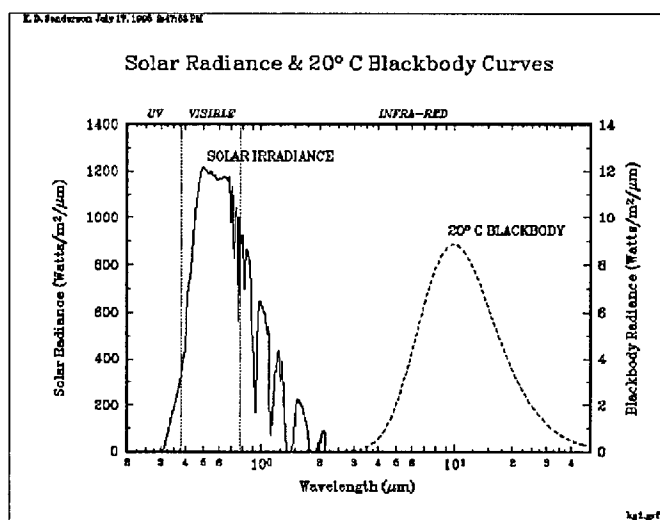


Figure 6-1 Spectrum of Solar Radiance and a Blackbody.

Investigation of the effectiveness of APCVD ITO coatings as solar control coatings for reducing heat gain and as low emissivity coatings for cold climatic conditions has been investigated.

6.2 Requirements For Solar Control Coatings

In order to reduce heat gain in the room, reflection of solar radiation from the sun is required. In order to maintain visual appeal, transmittance in the visible region must be maintained, however, and a visible transmittance of $>65\%$ is ideally required. Therefore reflection of the solar spectrum must be at wavelengths above 780 nm. In order to get maximum effect reflection must be increased to a maximum value as rapidly as possible. In order to achieve reflection in this region a conductive film is required. Figure 6-2 and 6-3 show the effect of mobility and carrier concentration on the reflectance in this region for thin films of approximately $3000\text{\AA}$. The curves which illustrate the effect of carrier concentration and mobility on the reflectance of the coating are the result of model calculations based on the Drude model.

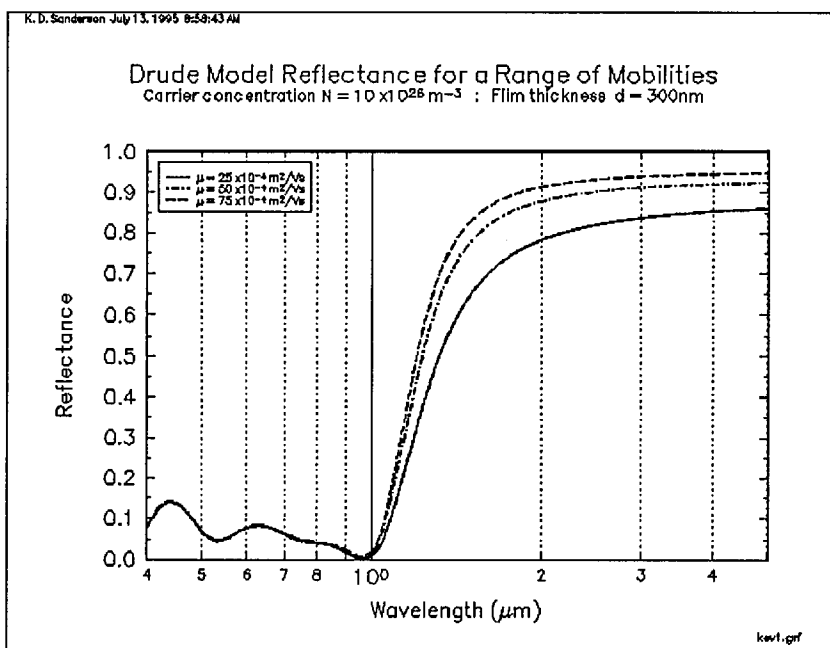


Figure 6-2 Effect Of Mobility On Reflectance At A Set Carrier Concentration

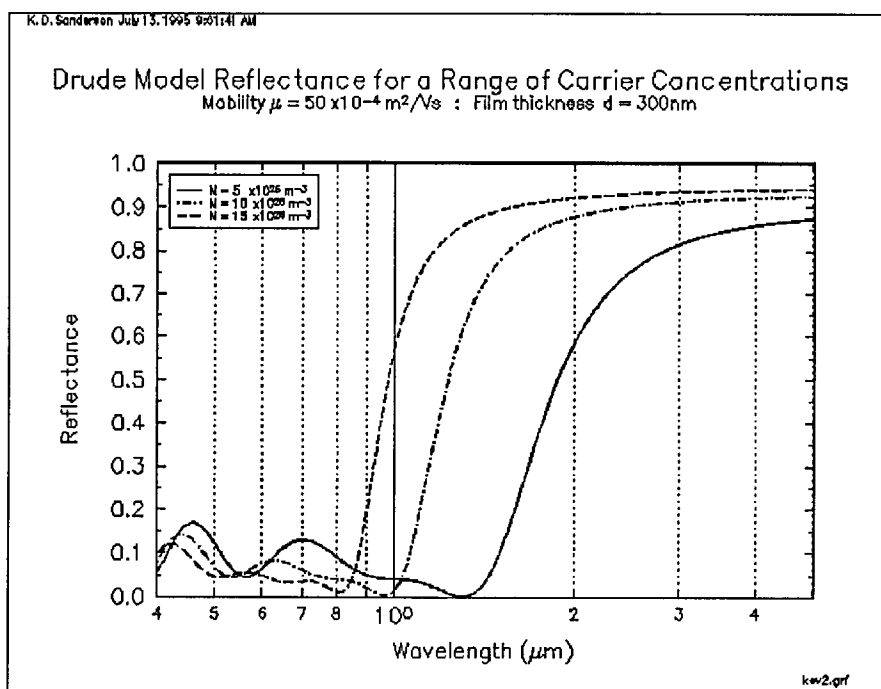


Figure 6-3 Effect Of Carrier Concentration On Reflectance At A Set Mobility

The Drude model is a relatively simple model which allows modelling of the optical constants.¹

The carrier concentration affects the wavelength at which reflectance starts, and increasing the carrier concentration, reduces the wavelength at which reflectance occurs. Ideally a carrier concentration of approximately $10 \times 10^{20} \text{ V}^{-1} \text{ cm}^2 \text{ sec}^{-1}$ is required if reflectance at circa 780nm is to occur.

The figures also show that a high mobility is required if maximum reflectance is to be achieved at 780nm, because the mobility of the coating determines the rate at which reflectance increases, (i.e. the gradient of the plasma edge).

The high optical transparency in the visible and near IR, results because ITO is a wide band gap semiconductor. The absorption edge which generally lies in the UV, but moves to shorter wavelengths with increasing carrier concentration is a result of the filling of the states at the bottom of the conduction band and is referred to as the Moss-Burstein shift.²

In theory the reflectance of a solar control coating does not need to extend beyond circa 2500 nm, as beyond this wavelength there is little radiation from the sun. However, most coatings that reflect at circa 780-2000nm also reflect at longer wavelengths and the reflection at longer wavelengths has the added advantage of reflecting re-emitted radiation from objects in the room.

6.3 Requirements For a Low Emissivity Coating.

In order to reduce heat losses caused by radiation emittance, reflectance of longer wavelength radiation (circa 10000 nm) resulting from re-emittance of transmitted solar radiation from bodies in the room is required. Coatings which reflect from circa 3000 - 5000nm are therefore required.

In order to achieve these properties a coating with similar properties to that required for a lower performance Solar Control Film is required. Lower mobility and carrier concentrations are acceptable as reflection does not need to occur at such low wavelengths and the reflectance need not maximise as rapidly, with maximum reflection only required at circa 5000-10000nm in order to reflect the bulk of re-radiated energy

from a room's interior. In order to achieve this reflectance the emissivity of glass must be reduced from its float glass value of circa 0.88 down to approximately 0.1-0.2.

The reflectance spectrum of a typical coating required for a low emissivity product is shown below. This clearly shows the reflectance begins at a longer wavelength and the increase in reflectance is fairly gradual.

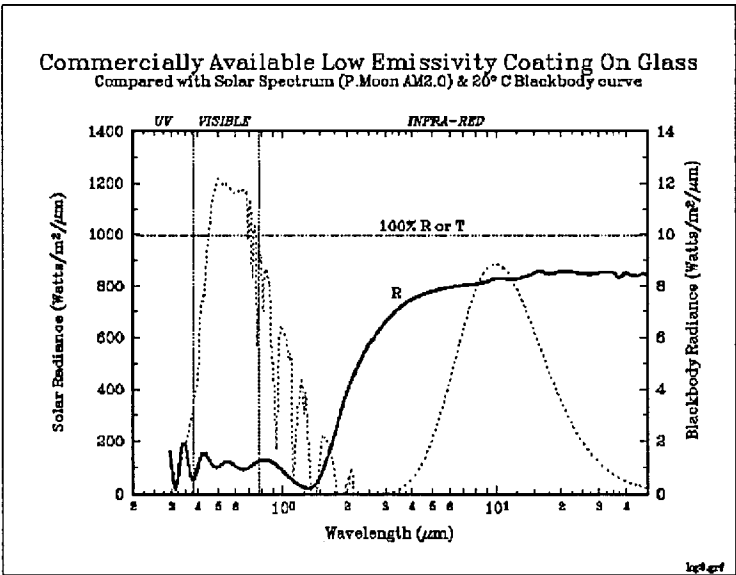


**Figure 6-4 Reflectance Spectra Of A Low Emissivity Coating On Glass,
Compared With the Solar Spectrum and That of A Blackbody**

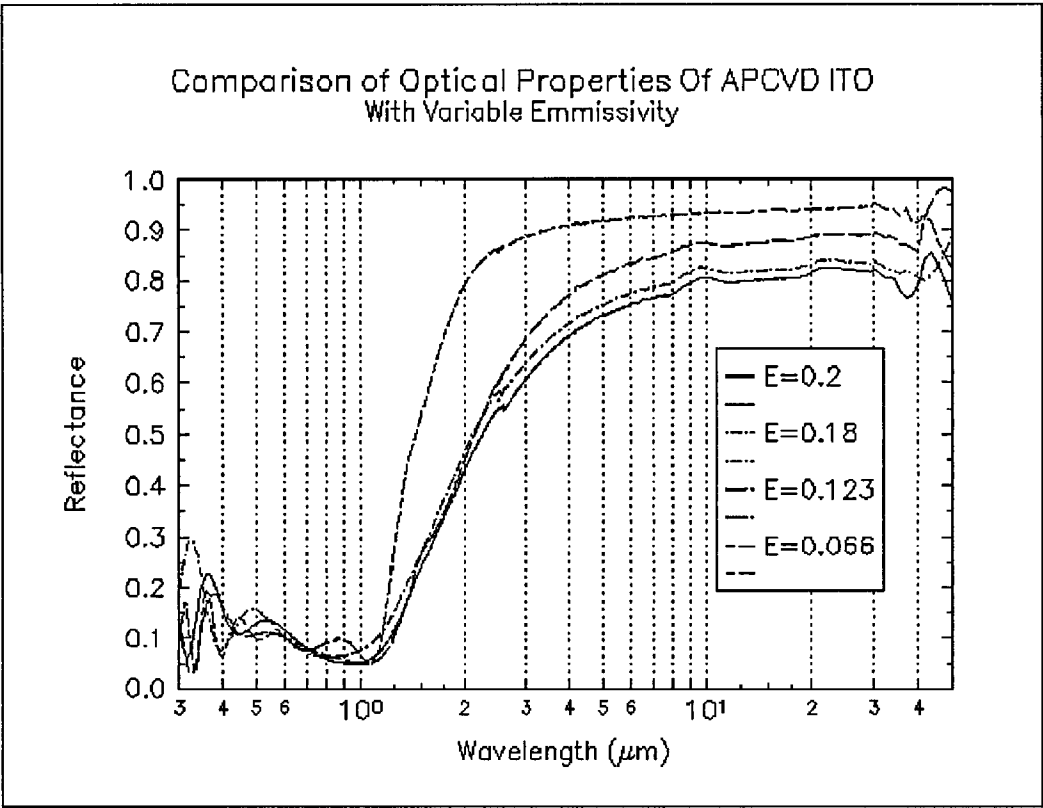
The reflectance spectra above shows the typical reflectance spectra of a commercially available fluorine doped tin oxide coating.³ The coating results in a reduction of the emissivity of glass from 0.88 to 0.15.

As part of this investigation, the growth of ITO coatings by APCVD onto glass has been investigated for the production of both low emissivity and solar control coatings. The following section describes the properties of the coatings grown using these products and evaluates them as low emissivity products.

6.4 APCVD ITO as a Low Emissivity Coating.

The ITO deposited from a range of precursors by APCVD in this study has shown good electrical properties varying in the range $3.5-1.3 \times 10^{-4} \Omega \text{ cm}$ and with carrier concentrations and mobility's varying from $6-10 \times 10^{20} \text{ V}^{-1} \text{ cm}^2 \text{ sec}^{-1}$ and $25-45 \text{ cm}^{-3}$ respectively.

By alteration of the growth conditions it has been possible to control the electrical properties of these coatings. In order to get comparable results with the optical properties of commercially available low emissivity coatings on glass, optical measurements of $2000-3000\text{\AA}$ thick APCVD ITO coatings with a range of electrical properties have been investigated. Figure 6-5 shows the reflectance spectra of a range of these coatings.



Where E= Emmissivity

Figure 6-5 Reflectance Spectra Of APCVD ITO Samples

Analysis of the electrical properties of these films shows that the results compare well with those predicted by the Drude model, with the higher carrier concentration and mobility resulting in films with a lower emissivity.

Emissivity	Resistivity (Ω cm)	Mobility ($V^{-1} cm^2 sec^{-1}$)	Carrier Concentration (cm^{-3})
0.065	1.26×10^{-4}	49.54	10.0×10^{20}
0.129	1.94×10^{-4}	47.57	6.19×10^{20}
0.18	2.17×10^{-4}	31.998	8.99×10^{20}
0.2	2.97×10^{-4}	28.46	7.31×10^{20}

From the spectra it can be seen that the APCVD ITO coatings are successful low emissivity coatings, reflecting the bulk of radiation in 5000nm region. The emissivity of the ITO coated glass has also been significantly reduced with values of 0.065-0.1 common for 3000Å thick coatings. The application of these coatings as low emissivity coatings therefore provides improved properties compared with any commercial CVD deposited low emissivity coating.

An investigation of the effect of film thickness on the optical properties of the coating has also been carried out. In theory the electrical properties of the coating are independent of the film thickness. This work, however, has demonstrated that there is a poorly conducting layer in the first 400-600Å of film growth, which appears to provide little contribution to the electrical properties of the coating and is a result of initial island growth resulting in an increased number of defects in the coating. As a result the resistivity of the film only appears to be independent of thickness for films of > 1000Å.

An investigation of a range of films with thicknesses from 1200-3500Å with similar resistivities was investigated.

Thickness (Å)	Emissivity	Sheet Resistance $\Omega / \square$
500*	0.691	195
1000	0.184	15
2000	0.129	10
3200	0.065	5

Resistivity of all coatings 2.0×10^{-4} ohms cm except * = circa $2 \times 10^{-3} \Omega \text{ cm}$

Table 6-1 Emissivity of Coatings With Variation in Thickness For $\text{In}(\text{thd})_3$ and $\text{Sn}(\text{II})$ Salt of Ethylhexanoic Acid

It can be seen from the table that the emissivity of the coating is not independent of the film thickness. As the thickness increases the emissivity of the coatings become smaller. As low thermal emissivity implies high IR reflectivity due to Kirchoff's Law,⁴ this implies that increased film thickness is advantageous in low emissivity coatings. Such a relationship between emissivity and film thickness has previously been observed for sputtered ITO with the emissivity being related to the sheet resistance of the coating by: $\text{Emissivity} = 1 - (1 + 0.00533R_{\text{sh}})^{-2}$.⁵ Whilst this work is in general agreement with this, because the thinner films with a higher sheet resistance have poorer emissivities. The dead layer at the base of CVD coatings further complicates the relationship between thickness and emissivity.

By altering the ITO thickness a range of low emissivity products can be derived. One potential advantage of the use of ITO instead of the currently used $\text{SnO}_2 \cdot \text{F}$, is that similar optical properties can be achieved from thinner coatings, with a potential 50% decrease in film thickness possible, whilst maintaining similar IR reflectance properties.

6.5 APCVD ITO As A Solar Control Material

As described in the previous chapters, ITO deposited by APCVD has resulted in films with good electrical properties. The performance of these coatings as Solar Control coatings has been investigated. The spectra in figure 6-5 show the visible transmittance and infra red reflectance spectra of deposited ITO. The sets of data are for ITO deposited with typical electrical properties and illustrate some of the best properties achieved.

It can be seen from the spectra, that typical ITO does not quite attain the required properties for a solar control product. The spectra shows that reflection does not occur until circa 1500nm and as a result reflection of the solar radiation between 780 and 1500nm does not occur. This is a significant proportion of the solar radiation and as a result the coatings effectiveness as a solar control coating is diminished.

The poor solar control properties of these coatings is a result of the carrier concentration and mobility of these coatings, which results in the reflection only increasing at 1500nm.

The ITO deposited with the best electrical properties can be seen to show far better solar control properties. The increased carrier concentration and mobility in these coatings has resulted in the reflection commencing at a lower wavelength and the reflection increasing to a maximum more rapidly. From the spectra it can be seen that whilst the solar control properties are improved, the properties are still not ideal.

Reflection at approximately 780 nm is still poor and as a result some of the solar radiation above the visible is not reflected and still reaches the interior of the room. The coating does, however, behave in a solar control fashion and the high visible transmittance is advantageous providing visual appeal.

6.6 Durability of ITO Produced By APCVD

Whilst the growth studies of ITO have shown that the achievable electrical properties are similar to that of ITO produced by other deposition techniques such as PVD, it was not clear whether the durability of the ITO was any different. One of the

areas of interest is how ITO withstands temperature exposure, as many process's particularly in the glass industry, such as toughening require a reheat of the glass after coating.

During the deposition of the ITO by APCVD, the samples were removed from the coater at approximately 300°C, and allowed to cool in air. The properties of the ITO removed at this temperature do not deteriorate compared to samples cooled to <100°C, under an inert atmosphere, suggesting that the material is stable at float line temperatures, and do not undergo any reaction due to air contact on removal. An investigation to determine, whether reheating of the material to its original deposition temperature or higher would result in a improvement or a deterioration in properties was therefore carried out.

ITO deposited by sputtering techniques is often annealed to improve the properties of the material. This is most commonly done under vacuum conditions, under which it is believed that extra oxygen vacancies are created. These result in an increase in the carrier concentration in the film which improve the electrical properties of the films.⁶⁻⁸

It was decided to reheat a series of samples to 625°C, this temperature being chosen as this is the temperature required for glass toughening. The effect of exposure of reheated ITO to an oxygen containing environment was studied to determine whether toughening in air or an inert atmosphere is possible. As a comparison ITO deposited by a PVD technique (Sputtering) was used as a comparison for the ITO coatings grown by the two different deposition methods.

6.6.1 Experimental Detail:

Samples of the APCVD and PVD deposited ITO of approximate dimensions 2.5 cm² were cut and the deposited surface cleaned using an iso-propanol rinse. The sheet resistance of each sample was recorded in set positions on each of the samples, before they were loaded into the reactor chamber used for the original deposition of the coatings. The samples were then heated upto 625°C under an inert nitrogen atmosphere at a ramp rate of 9°C per minute. On achieving the required temperature, a 1:1 nitrogen:oxygen gas stream of total flow 5 litre / min was introduced into the reactor

chamber. The gas stream was allowed to pass over the samples for 2 hours, before the temperature of the samples was reduced to 300°C. The cooldown from 625°C to 300°C took 23 minutes, and the oxygen:nitrogen gas stream was passed over at all times. The samples were then removed at 300°C, and allowed to cool to room temperature in air. The sheet resistance of the samples was then remeasured at the known position and the thickness of the samples measured at this point.

This experiment was repeated with fresh samples being held for 1 hr, 0.5 hrs and 1 min at the 625°C. One final experiment was then run where a sample was heated up under an inert atmosphere and then recooled under an inert atmosphere, without exposure to oxygen. The results of these experiments are summarised in Table 6-2.

Table 6-2 Effect of Variable Time Exposure Of APCVD ITO To Oxygen On The Electrical Properties Of Films.

Time Held at 625°C Under O ₂ :N ₂	Sheet Resistance of Sample Prior to Run (Ω/ □)	Sheet Resistance of Sample After Exposure (Ω/ □)	Change in Resistivity Of Sample (Ω cm)
0	9.3	9.5	-
1	13.1	45.9	6.2
30	9.3	34.2	5.6
60	8.0	27.7	4.4
120	12.4	43.4	5.9

Table 6-3 Effect of Variable Time Exposure Of PVD ITO To Oxygen On The Electrical Properties Of Films.

Time Held at 625°C Under O ₂ :N ₂	Sheet Resistance of Sample Prior to Run (Ω / □)	Sheet Resistance of Sample After Exposure (Ω/ □)	Change in Resistivity Of Sample (Ω cm)
0	10.8	10.8	-
1	10.8	32.9	6.6
30	10.6	30.3	5.91
60	10.3	27.9	5.28
120	11.0	33.0	6.6

From these results it can clearly be seen that exposure of both ITO samples to oxygen at a temperature of 625°C results in a marked deterioration in the electrical properties of the ITO. Typically this results in a deterioration in the sheet resistance of the sample from circa 2×10^{-4} to circa 8×10^{-4} Ω cm, in both types of ITO.

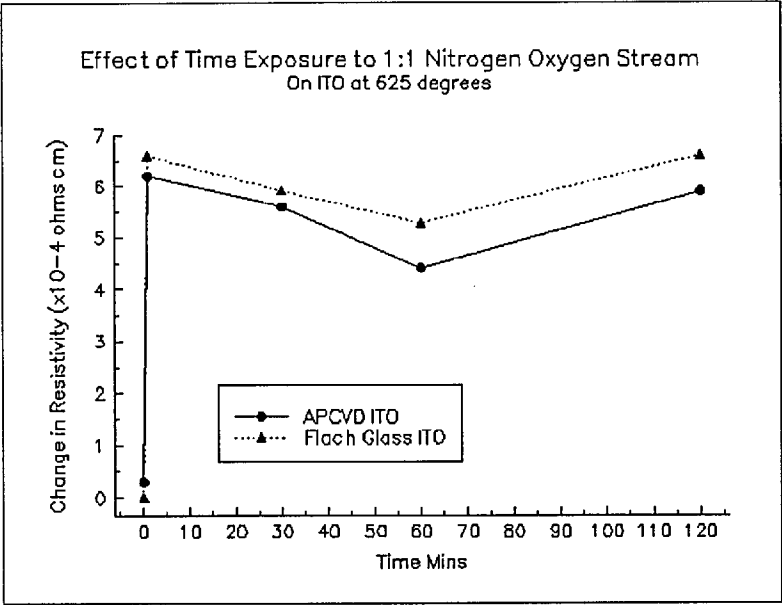


Figure 6-6 The Effect of the Length Variable Time Exposure to Oxygen at 625°C on the resistivity:

The initial deterioration in film properties appears to be severe in both cases. The deterioration occurs even after a short exposure time of 1 min, although the level of deterioration does not appear to increase if the time of exposure is increased. In contrast samples which were reheated and cooled under a nitrogen atmosphere showed little if any deterioration in the electrical properties of these coatings.

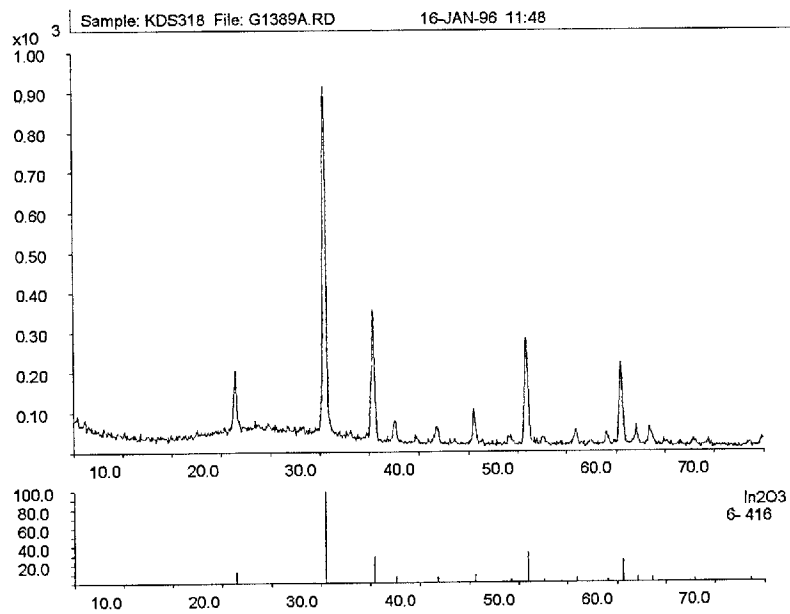
Analysis of the electrical properties of the coating showed that the mobility and carrier concentration of the coatings depended upon the treatment of the sample. Table 6-4 shows the effect of exposure to a 1:1 O₂:N₂ gas stream at 625°C, for both APCVD ITO and secondly for PVD ITO:

Table 6-4 Effect Of Time Exposure On Mobility and Carrier Concentration of APCVD ITO

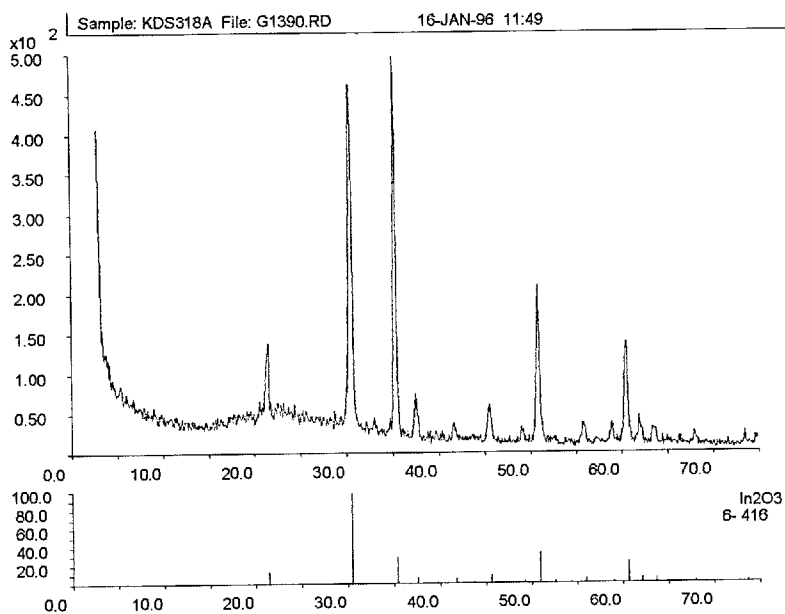
Time of Exposure to 50% O ₂	Resistivity (x10 ⁻⁴ Ω cm)	Mobility (V ⁻¹ cm ² sec ⁻¹)	Carrier Concentration (x10 ²⁰ cm ⁻³)
0, No Reheat	2.14	34.0	8.54
0, Reheated Under N ₂	2.38	43.6	6.01
1 min	8.33	37.7	1.99
30 min	5.65	38.54	2.87
120 min	8.13	32.0	2.38

From the results it can be seen that reheating of the ITO under an inert atmosphere has only a slight detrimental effect on the electrical properties of the ITO. On reheating the crystallinity is seen change, with the preferred orientation of the coating changing from being almost random, to having a degree of (400) preferred orientation. Changes in the crystallite size are hard to determine due to the line broadening being affected by both strain and the crystallite size, but it appears that a general increase in the crystallites in the (400) plane is observed. This change, however, appears to occur whether the sample is reheated under an inert nitrogen gas stream or under an oxygen stream, and as such this would not alone explain the change in resistivity upon exposing the films to oxygen.

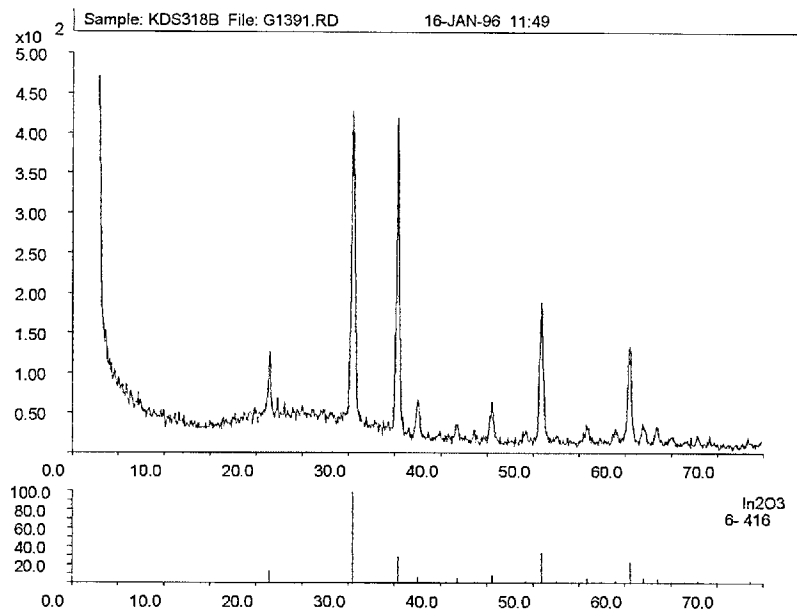
A) Film As Grown



B) Film After Reheat and Cool In Nitrogen



C) Film After Reheat and Exposure to 1:1 Nitrogen : Oxygen For 1 min at 625°C



D) Film After Reheat and Exposure to 1:1 Nitrogen : Oxygen For 2 hours at 625°C

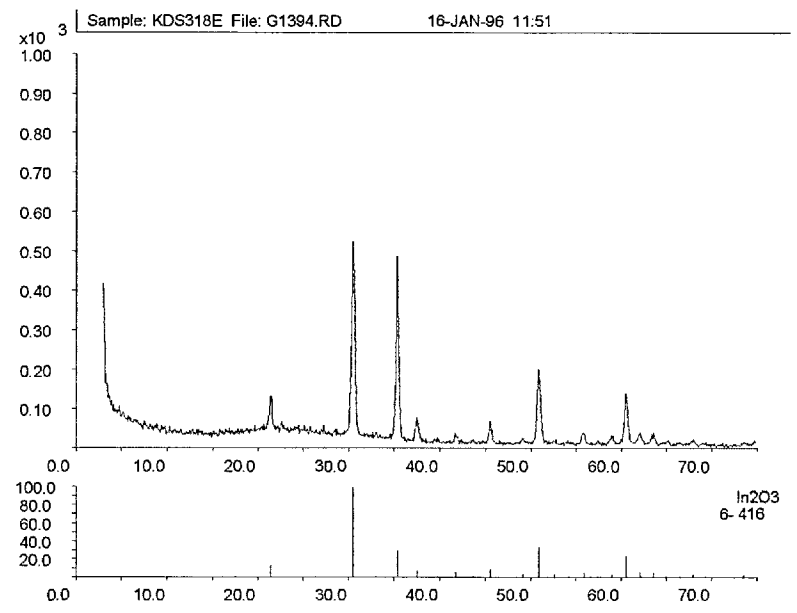


Figure 6-7 Glancing Angle XRD Pattern Of ITO Before And After Reheat.

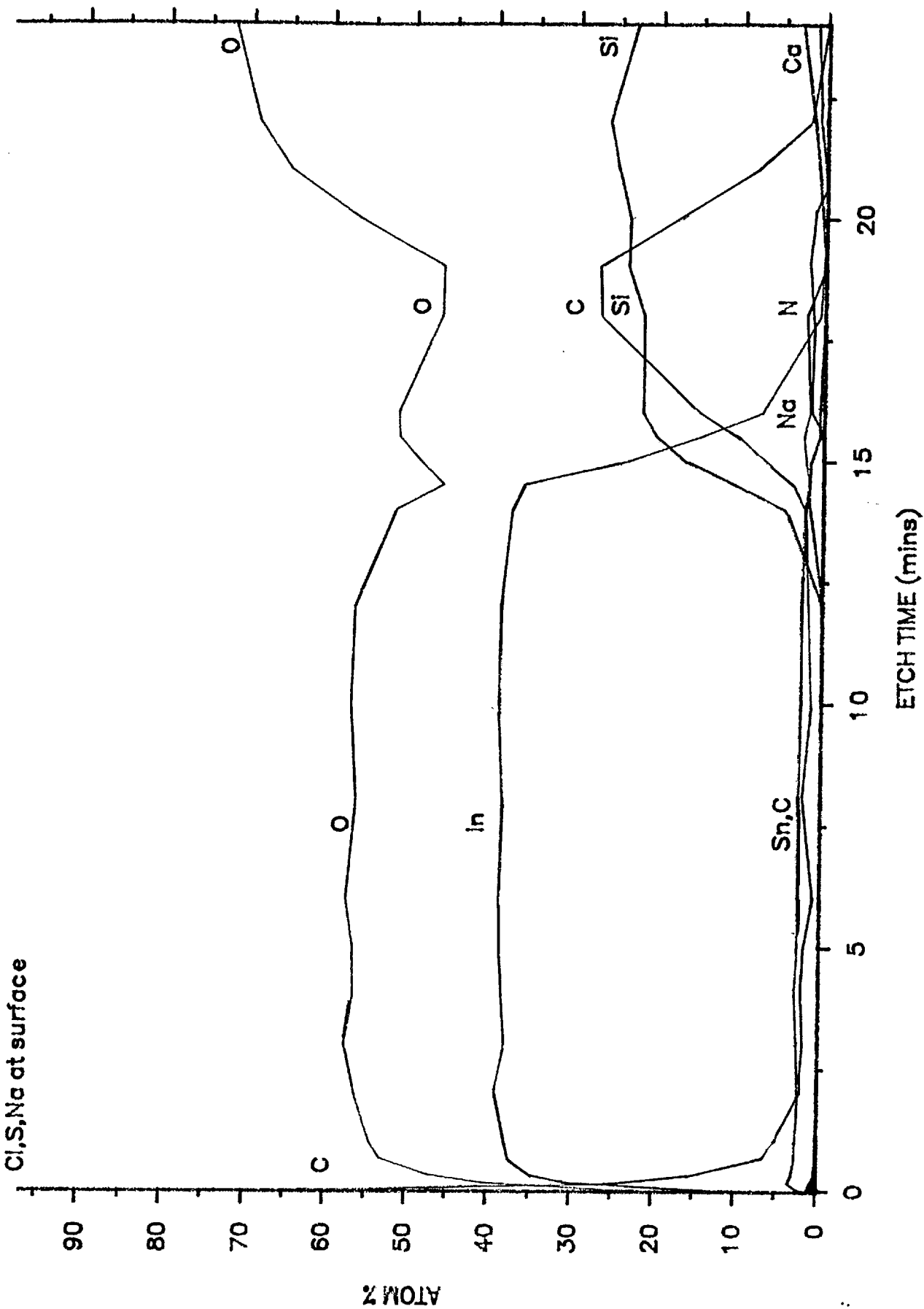
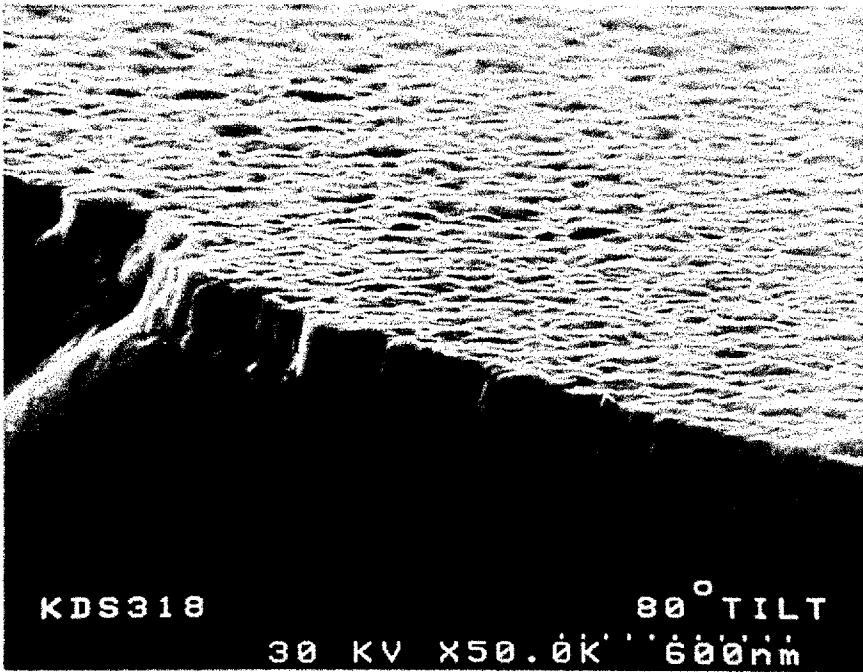
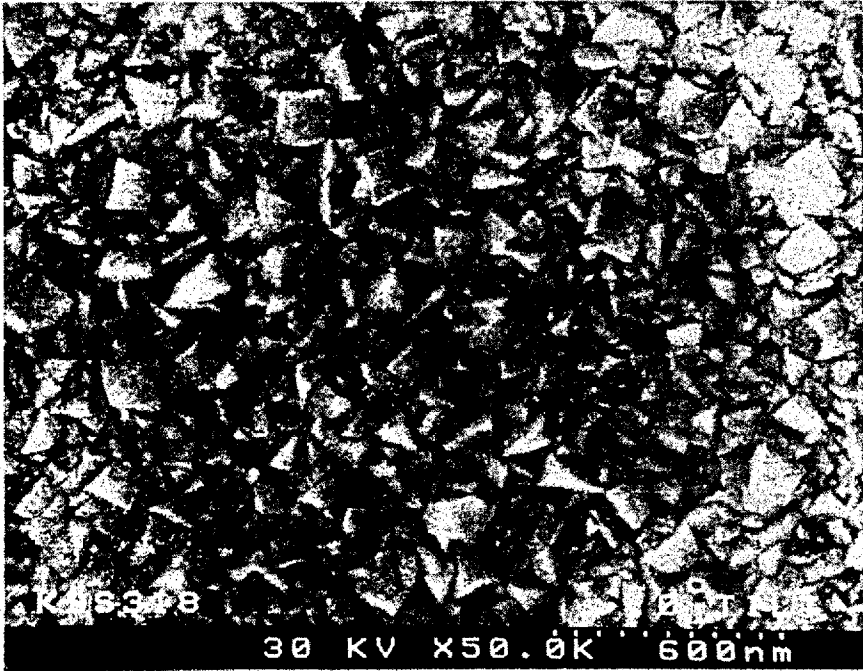


Figure 6-8 Auger Depth Profile of an Annealed ITO Sample



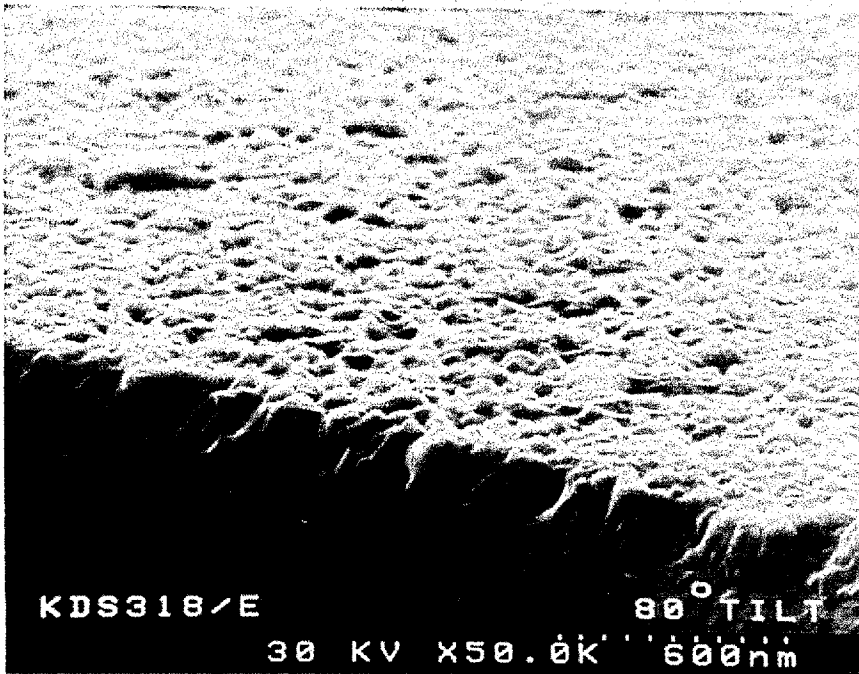
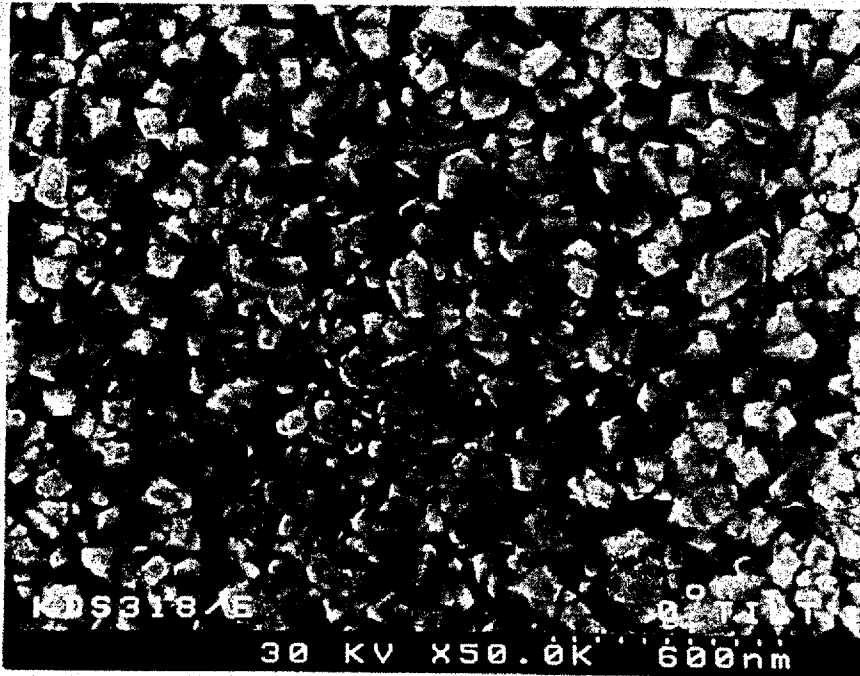


Figure 6-9 SEM Micrographs Of ITO Before and After Reheat

The increase in mobility in these samples may be due to:

1. Loss of volatile impurities in the coating which were acting as scattering sites for the carriers.
2. The change in preferred orientation may have resulted in less scattering of the carriers.

On exposure of the reheated film to oxygen, however, the resistivity of the coating deteriorates significantly, but there is no apparent further change in the crystallinity of the coating. This deterioration appears to be due to a large reduction in the number of carriers in the coating on exposure to oxygen, with the number of carriers being reduced from circa 6×10^{20} down to approximately $2 \times 10^{20} \text{ V}^{-1} \text{ cm}^2 \text{ sec}^{-1}$. This is believed to be due to a decrease in the number of oxygen vacancies.

On extending the period of time the film is exposed to oxygen to between 30 and 60 minutes, little further change was seen in the electrical properties of the ITO, with the carrier concentration and mobility remaining almost constant. However, after 2 hours of exposure the film appears to deteriorate further. This additional deterioration, does not result in a change in the number of carriers, but is due to a reduction in the mobility of the carriers. This implies that this second deterioration is no longer due to the oxygen vacancies in the coating being filled, but due to increased carrier scattering. The exact reason for this deterioration in mobility is unknown but may indicate that a further structural change in the coating is occurring.

Similar results were observed for PVD ITO.

Table 6-5 Effect Of Time Exposure On Mobility and Carrier Concentration of PVD ITO

Time of Exposure to 50% O ₂	Resistivity (x10 ⁻⁴ Ω cm)	Mobility (V ⁻¹ cm ² sec ⁻¹)	Carrier Concentration (x10 ²⁰ cm ⁻³)
0, No Reheat	3.28	23.0	8.21
0, Reheated Under N ₂	3.75	27.3	6.16
1 min	9.10	30.6	2.21
30 min	8.53	31.87	2.29
60 min	8.87	29.75	2.36
120 mins	18.3	15.72	2.16

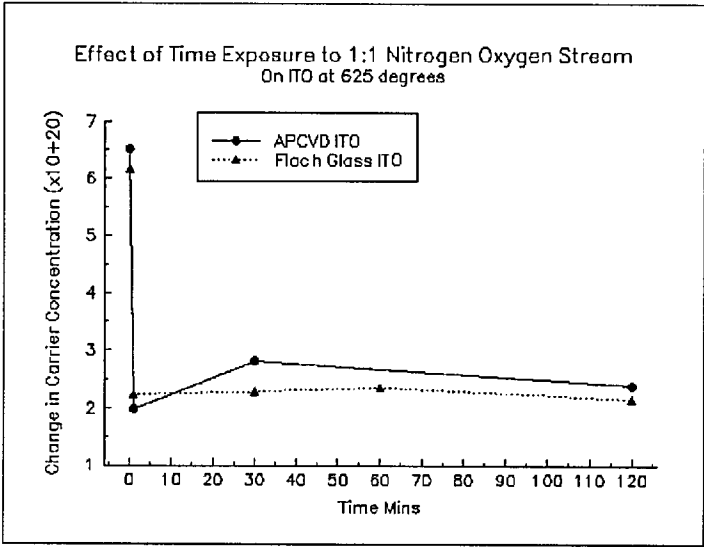


Figure 6-10 Effect Of Variable Time Exposure On Carrier Concentration In PVD and CVD ITO

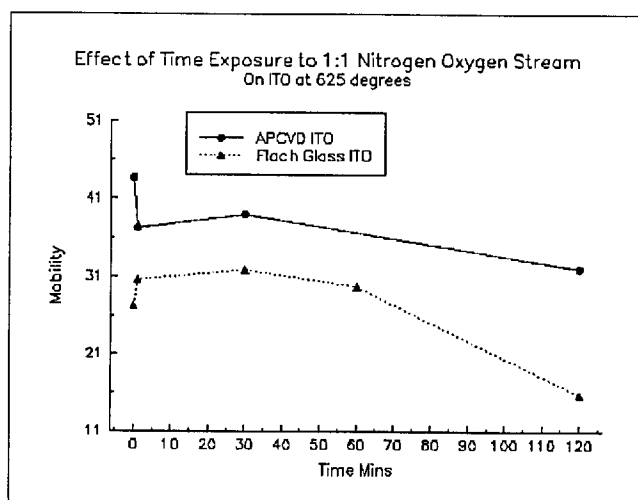


Figure 6-11 Effect Of Variable Time Exposure On Mobility In PVD and CVD ITO

As with CVD ITO, the reheating of PVD ITO in an inert atmosphere resulted in only a slight deterioration in electrical properties of the ITO, although as with CVD ITO, exposure to oxygen results in a large deterioration in the films electrical properties. The deterioration, as with the APCVD ITO, is initially related to a reduction in the number of carriers, but after 2 hours, as with CVD ITO, the mobility deteriorates and the film properties deteriorate further.

One anomaly between the CVD and PVD ITO is the initial change in mobility on reheating the samples under an inert atmosphere. In the APCVD ITO an initial deterioration in the mobility is observed, whilst in the PVD ITO, an increase is observed. The reason for this change may be due to a slight change in the crystallinity of the film, which results in more scattering of the carriers in CVD ITO, whilst in the PVD ITO the scattering appears to diminish, suggesting the change in crystallinity is beneficial.

The results of this study are consistent with Martinez *et. al.* who examined the effect of annealing on RF reactive magnetron sputtered ITO.⁹ On vacuum annealing it was found that the resistivity of films decreased up to an annealing temperature of 420°C. Above this temperature, however, no improvement was observed, suggesting that above 400°C, no more oxygen vacancies are created in the films. Increasing the annealing temperature, however also resulted in a change in the crystallinity of the film, with the (222) peak intensity increasing at the expense of the (400) reflection. This indicates a preferred orientation film developed on annealing.

Annealing in oxygen, however, did not result in large improvements in the resistivity of the films. At low oxygen concentrations slight changes were observed, with similar changes in the film crystallinity to those occurring under vacuum conditions occurring. The oxygen atmosphere is likely to result in these oxygen deficiencies being filled, however, and would account for only small changes being observed in the films properties due to the change in crystallinity of the film. At higher oxygen concentrations, however, the resistivity of the films were poor compared with those that were vacuum annealed (5×10^{-4} compared with $1.9 \times 10^{-4} \Omega \text{ cm}$). This is likely to be a result of the higher oxygen concentrations filling the films oxygen deficiencies and lowering the number of carriers in the films.

The exposure of the films to oxygen in the previous experiments were carried out with a high $\text{O}_2:\text{N}_2$ ratio of 1:1. An investigation to determine the extent of deterioration as a function of oxygen concentration in the gas stream was also investigated. Samples of APCVD ITO of 2 cm^2 of known sheet resistance, were reheated under a nitrogen atmosphere to 625°C , under a nitrogen atmosphere and were then exposed to an oxygen:nitrogen gas stream for 1 min at 625°C and cooled to 300°C over a 23 min period, at which time the samples were removed. On cooling to room temperature the sheet resistance of the samples were remeasured and the thickness of the coatings determined.

The results below show the effect of variations in the oxygen concentration on the coating. All the samples were held at 625°C in the gas stream for the same period of time and cooled over the same time period.

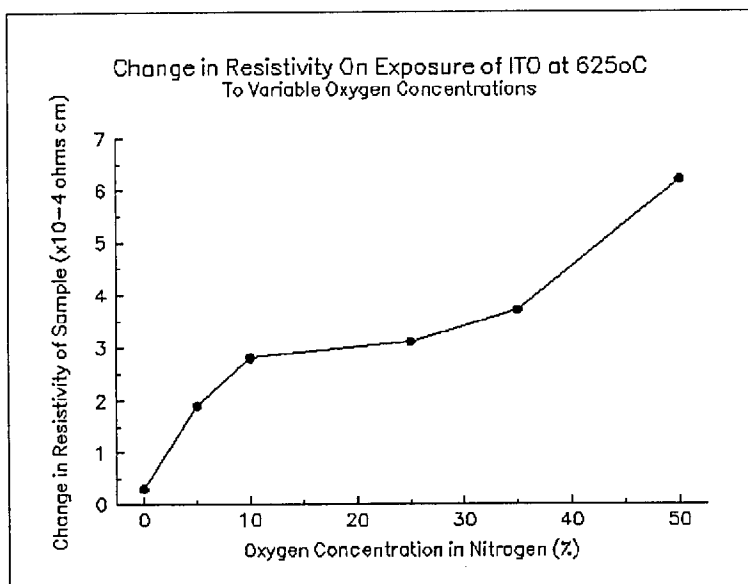


Figure 6-12 Effect of Oxygen Concentration During Annealing on the resistivity of APCVD ITO

The study has shown that the deterioration in the resistivity of the ITO coatings is not time dependant, occuring rapidly at a set oxygen concentration. The deterioration is dependant upon the concentration of the oxygen in the gas stream, however. At lower oxygen concentrations, the deterioration in the resistivity of the coating is low, gradually increasing as the oxygen concentration increases.

These results suggest that the rate of deterioration depends on both thermodynamic and diffusion processes.

The electrical properties of the films after exposure to the oxygen for 1 min at 625°C then on cool-down to 300°C have been measured:

Table 6-6 Effect Of Variable Oxygen Concentration On Carrier Concentration and Mobility In APCVD ITO

Oxygen Concentration Of Gas Stream	Resistivity ($\times 10^{-4} \Omega \text{ cm}$)	Mobility ($\text{V}^{-1} \text{ cm}^2 \text{ sec}^{-1}$)	Carrier Concentration ($\times 10^{20} \text{ cm}^{-3}$)
0% i.e. 100% N_2	2.38	43.6	6.01
35%	5.6	39.0	2.80
50%	8.33	37.7	1.99

The results show that as the oxygen concentration in the gas stream is increased the deterioration increases. The deterioration in the electrical properties of the films are a result of a decrease in the number of carriers in the coating. This is consistent with the oxygen vacancies being filled and causing a reduction in the carrier concentration in the coating. These results have shown that reheating ITO has a significant effect on the coating and its properties.

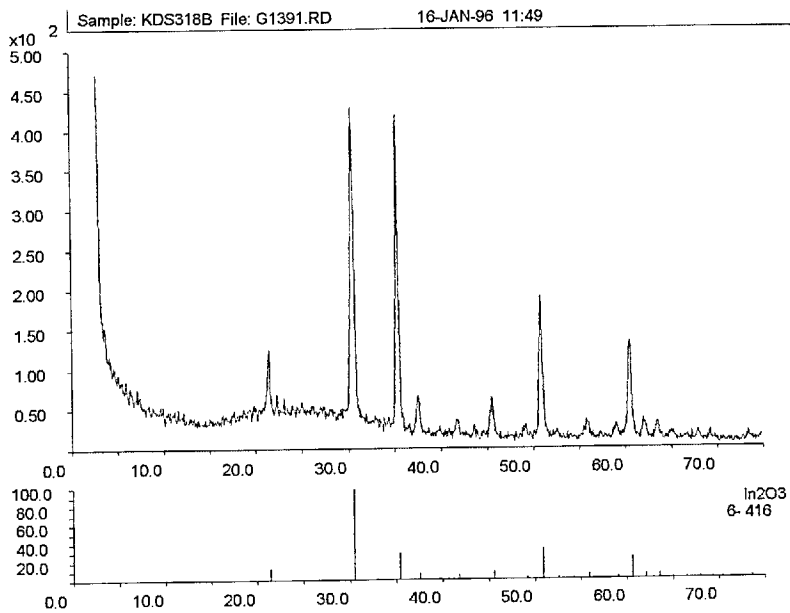
Growth of ITO and then cooling in oxygen prior to removal was also investigated to determine if freshly grown ITO behaves similarly on exposure to oxygen at high temperatures. After growth of the film the unreacted precursors were flushed out with nitrogen, then a 1:1 gas stream of $\text{O}_2:\text{N}_2$ was passed over the film for 1 minute and then the coating was cooled over a 20 minute period under the same gas stream. This was compared with a coating grown under the same conditions but cooled under nitrogen. The effect of cooling the coating under oxygen instead of under an inert nitrogen atmosphere was to increase the resistivity of the coating slightly from 1.93 to $2.2 \times 10^{-4} \Omega \text{ cm}$.

However, no significant change in the structure of the film was observed under these conditions.

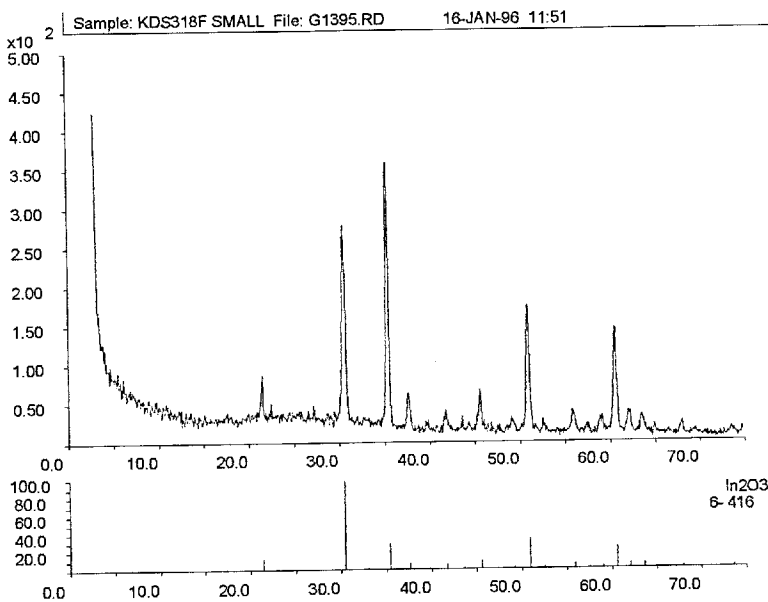
This suggests that the bulk of the deterioration seen in the ITO coatings is due to the reheating of the material. This implies that on reheating the coating becomes more susceptible to oxygen attack and the oxygen vacancies may be filled more easily.

The change in crystallinity of ITO on reheating is consistent with this, and may be facilitating the quenching of oxygen vacancies on exposure to a gas stream containing oxygen.

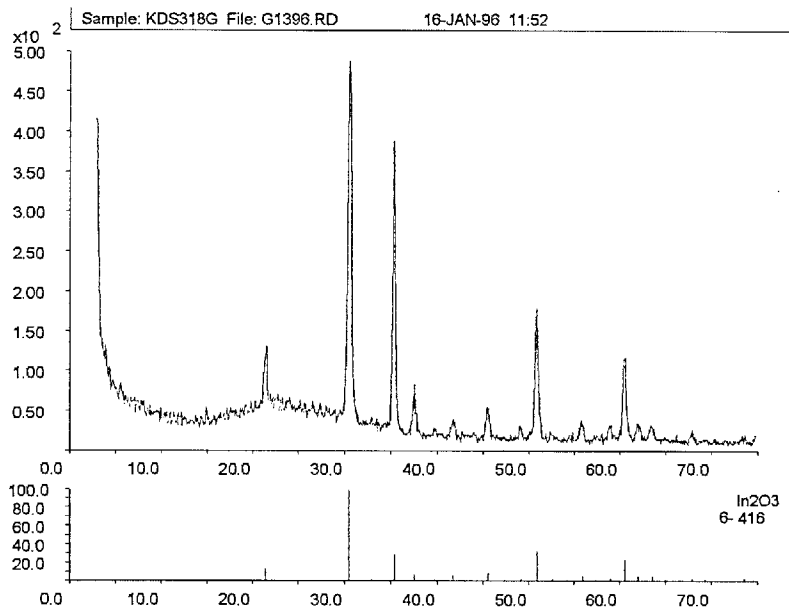
A) Reheat and Cooldown in 50% O₂, 50% N₂



B) Reheat and Cooldown in 5% O₂, 95% N₂



C) Reheat and Cooldown in 10 % O₂, 90 % N₂



D) Reheat and Cooldown in 35% O₂, 65 % N₂

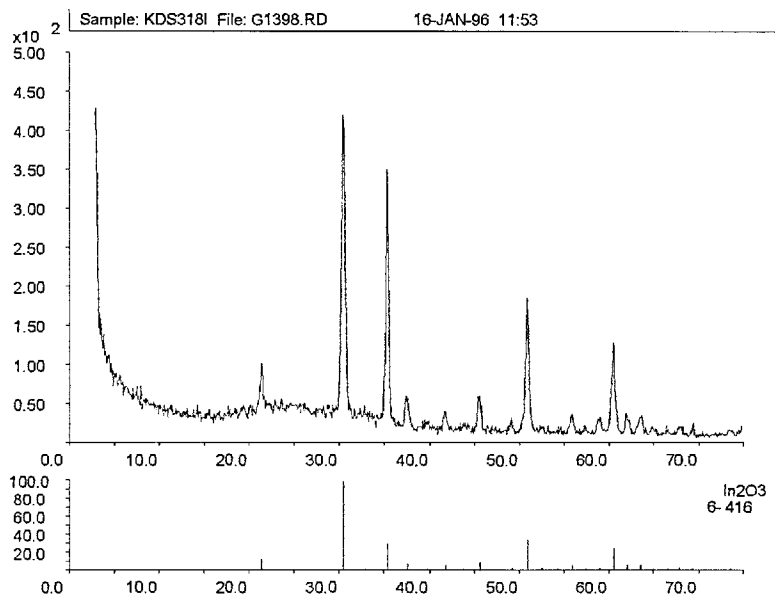


Figure 6-13 Glancing Angle XRD of ITO After Exposure to Variable Oxygen Concentrations

6.7 Conclusions:

The ITO deposited by APCVD has been investigated as a potential Solar Control and Low Emissivity coating on glass. The ITO deposited as part of this project has been seen to have a resistivity range varying from $1.5\text{-}3.5 \times 10^{-4}$ ohms cm and the carrier concentration and mobility ranges have been seen to be from $5\text{-}10 \times 10^{20} \text{ cm}^{-3}$ and $25\text{-}50 \text{ V}^{-1} \text{ cm}^2 \text{ sec}^{-1}$ respectively. This range has resulted in coatings which have a range of emissivities from 0.06-0.17. Whilst this range has a large effect on the reflectance properties of the film, the properties are still good compared with that of other transparent conducting oxide films with F:SnO₂ having the general properties:

Resistivity	Mobility	Carrier Conc.
$5\text{-}6.7 \times 10^{-4} \Omega \text{ cm}$	$29\text{-}40 \text{ cm}^2 \text{ V}^{-1} \text{ Sec}^{-1}$	$2.9\text{-}3.8 \times 10^{20} \text{ cm}^{-3}$

The application of the APCVD ITO is therefore better than commercially available CVD low emissivity products.

The APCVD ITO deposited as part of this study, does not fulfil all the requirements of a solar control coating. The best properties of the deposited ITO are a resistivity of approximately $1.5 \times 10^{-4} \Omega \text{ cm}$, emissivity of 0.06, mobility $50 \text{ V}^{-1} \text{ cm}^2 \text{ sec}^{-1}$ and carrier concentration of $10 \times 10^{20} \text{ cm}^{-3}$, from In(thd)₃ and DMT with BuOAc. The coatings would, however, show some solar control properties and would certainly be better than ordinary glass or a standard low emissivity coating. Further increases in the mobility and carrier concentrations are required if the properties are to be further improved, with a higher degree of reflectivity of the solar spectrum.

The study has shown, however, that APCVD ITO shows better properties than current CVD low emissivity products and is comparable with PVD coatings. Further development of ITO to increase the carrier concentration and crystallinity of the coating to reduce carrier scattering is required. The carriers' mobility needs to be increased if all requirements for a solar control products are to be achieved.

Overall the work has shown, however, that a degree of control over the plasma reflection edge and IR reflectivity can be achieved by APCVD ITO. The increased performance of this coating over other CVD deposited low emissivity coatings allows a degree of solar control to be achieved from this coating.

It has also been shown that APCVD ITO has similar durability to that of PVD ITO. Whilst APCVD as prepared has been shown to be resistant to oxygen vacancies being filled, on reheating the crystallinities of the films of both APCVD and PVD ITO change. Whilst such a change is observed even under an inert atmosphere, exposure of the films to oxygen during annealing results in a deterioration in the resistivity of ITO which has been shown to be related to the concentration of the oxygen vacancies. At a temperature of 625°C, it has been shown that the deterioration in the resistivity of ITO is complex being related to both the oxygen concentration and time of exposure, and this may be due to a filling of the oxygen vacancies in the coating. This has important implications if the films are to be heat treated after preparation; although the study has shown that reheating in an inert atmosphere has a negligible effect on the films electrical properties.

6.8 References

1. P. Drude, *Z. Phys.*, **1900**, 1, 161
2. E. Burstein, *Phys. Rev.*, **1954**, 93, 632
3. A Commercial Product, Measured For Comparison. Produced by a CVD Deposition Technique.
4. G. Kirchhoff, *On the Relation between the Radiative and Absorbing Powers of Different Bodies for Light and Heat*, *Phil. Mag.*, **1860**, 20:1, described in P. M. Whelan and M. J. Hodgson, *Essential Principles of Physics*, **1989**, 2nd Edition, Hazell Watson and Virey Ltd., UK.
5. G. Frank, E. Kauer and H. Kostlin, *Thin Solid Films*, **1981**, 77, 107
6. F. T. J. Smith and S. L. Lyu, *J. Electrochem. Soc.*, **1981**, 128(11), 2388
7. C. H. L. Weijtens, *J. Electrochem. Soc.*, **1991**, 138(11), 3432
8. H. W. Zhang and W. Xu, *Vacuum*, **1992**, 43(8), 835
9. M. A. Martinez, J. Herrero and M. T. Gutierrez, *Solar Energy Materials and Solar Cells*, **1992**, 26, 309

7. Nebulization Assisted APCVD.

7.1 Aim:

Many materials that would be of use as CVD precursors, have insufficient thermal stability to be held at temperature in a conventional bubbler without considerable thermal decomposition of the material being observed. This prevents their use as the vapour pressure is not sufficient to allow their mass transport. In an attempt to further study deposition from these materials, alternative methods for delivery of the precursors have been investigated. One of the most promising new methods of delivery appears to be the use of nebulization of a precursor solution. A study of the deposition of In_2O_3 and ITO by nebulization delivery of a range of indium precursors has been carried out.

7.2 Theory:

Nebulization is a relatively new method for the delivery of precursors, but has been reported in the literature for the deposition of metal films such as copper, and certain oxide coatings such as tin oxide.¹⁻⁴ The theory of nebulization is that a fine mist of a precursor solution is produced and this mist can then be used to deliver the precursor to the reactor chamber as each particle in the mist should contain some precursor. If the droplet size in the mist is sufficiently small, < 5 microns, coagulation of the droplets to form condensation of the mist should not occur, and the mist can thus be transported down pipework. The formation of the mist is achieved by excitation of the precursor solution by a piezoelectric device. This excitation of the solution can be carried out by direct or indirect methods.

In direct nebulization, the precursor solution is in direct contact with the piezoelectric device. In indirect nebulization, the precursor solution is not in direct contact with the piezoelectric, but is placed on a membrane. In order to transfer the power from the piezoelectric device a coupling solution is used which when agitated by the device, transmits the power to the membrane which in turn agitates the solution.

Indirect nebulization has the advantage over direct nebulization that the lifetime of the piezoelectric device is enhanced as the latter is not in contact with either the precursor or any solvents used in the system. However, this indirect method of nebulization is less effective than direct nebulization as power loss appears to occur in transferring the power through the coupling solution to the membrane.

Once the fine mist of the precursor solution has been generated, it can then be used to transfer the precursor to the reactor chamber. This can be done by two methods.

The first method involves the mist being swept from above the agitated precursor solution into a hot zone using a gas stream. There the large surface area of the droplets allows efficient vaporisation of the precursor to occur along with the solvent sheath that surrounds the precursor particles. The vaporised precursor is then transported into the reactor chamber. This method has been used for the deposition of various materials including CeO_2 , although it is more common for an ultrasonic spray nozzle to be employed for the generation of a mist of the precursor solution, rather than an ultrasonic transducer plate.⁵

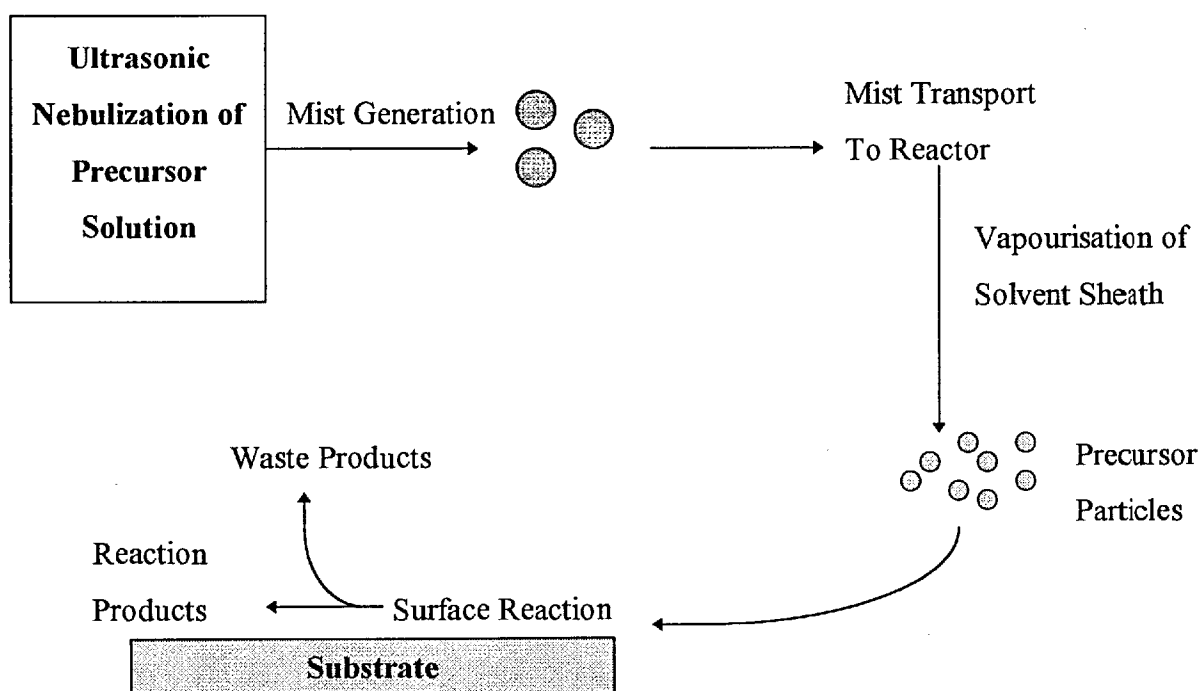
The second method involves the mist being swept in a similar fashion from above the precursor solution, but the mist is then delivered down cold pipework, into the reaction chamber.

The experiments carried out have used the second method of delivery. This method has two significant advantages over vaporisation of the generated mist in an evaporator and subsequent delivery of this vaporised material into the reactor. Firstly, this method allows the study of precursors that have been seen to be insufficiently thermally stable to be transported intact or to be stored at temperature in a bubbler, as no heat is used until the precursor reaches the reactor chamber. This is of particular importance for compounds such as Me_3In adducts, where decomposition of the adduct, results in materials that show significant pre-reaction with oxidant sources. Secondly this method can be used for the investigation of materials that have little if any vapour pressure such as InCl_3 . These materials could not be vaporised even with the aid of mist formation, and as such, can only be investigated by this method.

Once the mist enters the hot reactor zone, the solvent sheath that surrounds the precursor can then be vapourised, leaving small particulates of the precursor. The small

particulates of the precursor can then be vapourised above the glass surface prior to impinging on the substrate. Film growth should then occur in a similar fashion to that seen for conventional APCVD techniques that have been described previously, where the precursor is transported in a vapourised form.⁶

Figure 7-1 Summary Of Nebulization Process.⁴



Using this nebulization method of delivery a wide range of precursors have been studied for the growth of In_2O_3 , and some doping of the films has been attempted. The precursors studied include:

1. Tetrahydrofuran adduct of trimethylindium
2. Dimethyl(methoxy)indium
3. Tris(tetramethylheptandionato)indium $\text{In}(\text{thd})_3$
4. Tris(acetylacetonato)indium $\text{In}(\text{acac})_3$
5. Trichloroindium

7.3 Experimental techniques:

The equipment used for the nebulization studies is shown in diagram 7-2. The nebulizer consists of a B50 pyrex glass tube, which has the piezoelectric attached to the base by the use of a silicon sealing paste. This provides a solvent and air tight seal for the piezoelectric. A top cone is attached to this tube by a ground glass tube. The top cone has a long dip leg with a spiralled end, for the sweeping gas to be introduced and a take-off port with a dog-leg located at the top of the cone. This take-off allows the mist to be swept out of the nebulizing zone, whilst the dog-leg allows any liquid formed by coalescence of the mist to drop back down into the nebulization chamber. The piezoelectric is then connected by two leads to the driving electronics for the nebulizer.

The mist that is swept out of the nebulization chamber was then passed into stainless steel ¼" pipework, where the precursor passed into the reactor chamber. The following section describes the precursors investigated and the results obtained.

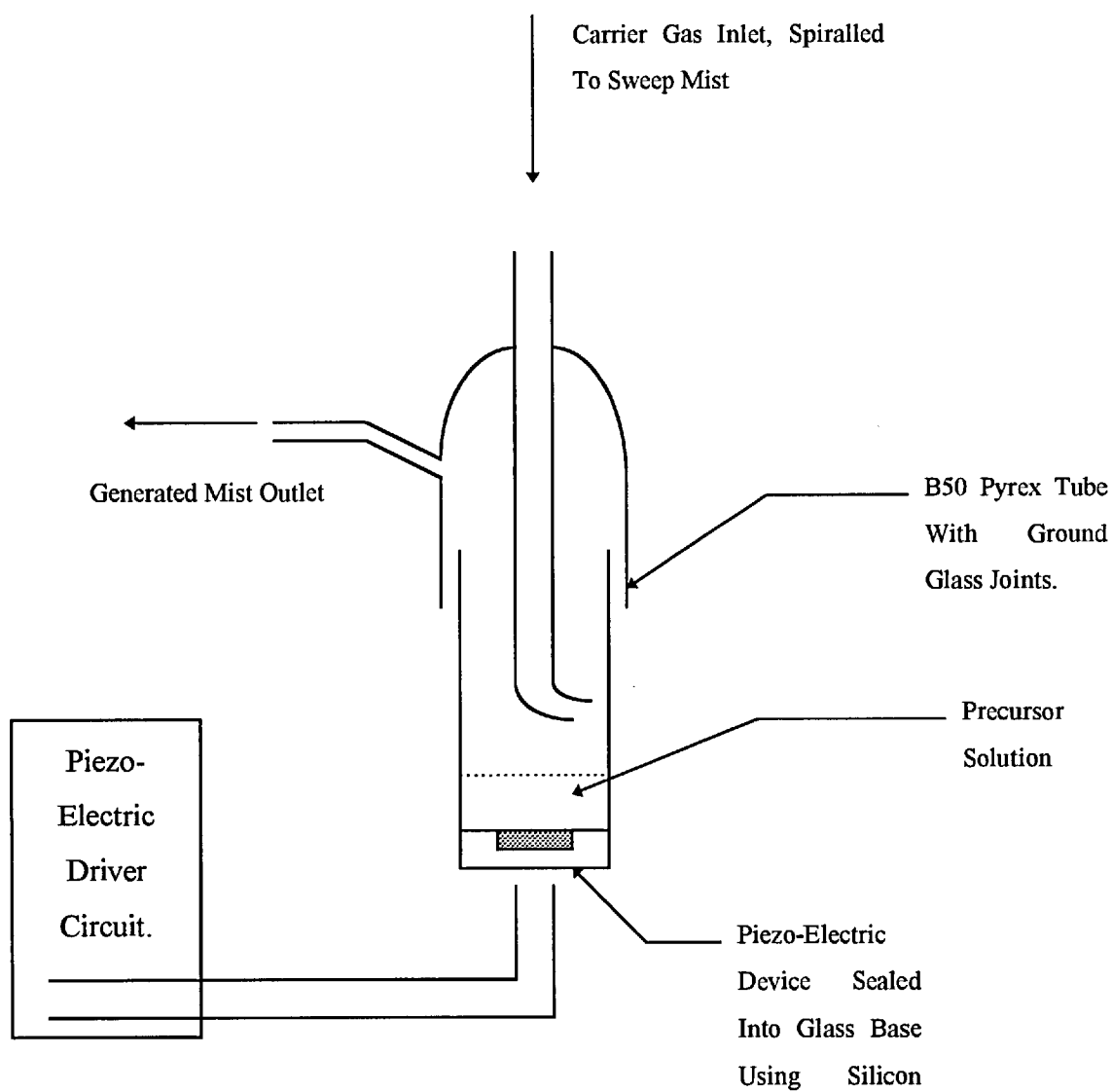


Figure 7-2 Diagram of Nebulizer Device

7.4 Deposition From Trimethylindium-tetrahydrofuran adduct.

This precursor is a pyrophoric and moisture sensitive liquid at room temperature, and as such, to prevent decomposition of the precursor careful handling of the precursor under a nitrogen atmosphere is required.

Previous attempts at growing In_2O_3 films from this precursor have been attempted using bubbling techniques for the delivery of the precursor and were described previously in Chapter 3. As described previously the poor thermal stability of the precursor when held at high temperatures leads to its gradual decomposition in the bubbler and deposition experiments resulted in severe pre-reaction between the oxidant and the precursor. Due to these problems, it was decided to attempt nebulization of the pure precursor and to carry the generated mist into the reactor chamber without pre-vapourization.

Due to the pyrophoric nature of the chemical, the nebulizer had to be filled and assembled in the glove-box under a nitrogen atmosphere. The nebulizer was filled with 20ml of the indium precursor and sealed prior to removal from the glove-box. The nebulizer was then attached to the chemical vapour deposition rig in place of a bubbler. The gas inlet to the nebulizer was therefore from the bubbler line and the mist generated was swept out of the reactor and into the mixing pipe of the CVD rig. The mist was then carried down the pipeline before mixing with the nitrogen and oxygen carrier gas approximately a metre before entry into the reactor chamber.

On direct nebulization of the neat precursor, a good mist was generated which was successfully carried down the pipe lines and into the reactor. No improvement was seen in the quality of the generated mist if the neat precursor was dissolved in a dry solvent prior to nebulization.

Careful handling of the precursor is required, as oxygen ingress into the nebulizer unit, results in an increase in the viscosity of the precursor. The ingress of oxygen also appears to result in decomposition of the precursor, as the initial increase in viscosity of the precursor, is followed by the formation of a white solid. This decomposition results in a decrease in the mist generation as the viscosity increases, eventually resulting in a failure to generate a mist.

Several factors were found to be of considerable importance if successful nebulization was to occur of the precursor.

1. Level of the precursor in the nebulizer.

This must be at between 25 and 15ml. If the level is higher or lower than this mist generation appears to deteriorate. If the level is too high nebulization fails to occur due to the guezzer of agitated precursor being suppressed. If the level is too low, the piezo-electric device rapidly overheats and results in a terminal failure of the device.

2. Viscosity of the solution.

If the viscosity is too high, the fountain created by the piezoelectric appears to have a lower amplitude, and mist generation is also reduced.

3. Sweeping Gas.

The quantity and position of the sweeping gas inlet is of importance. If wrongly positioned, the spiralled end of the inlet gas line, results in the gas flow impinging on the fountain created by the piezoelectric, which in turn decreases the mist generation and if the inlet gas flow is too high, mist generation can be inhibited by quenching of the guezzer.

In order to obtain good film growth, $800 \text{ cm}^3 / \text{min}$ of nitrogen was used to sweep the generated mist into the mixing chamber. This mist was then mixed with $4.5 \text{ l} / \text{min}$ of nitrogen and $600 \text{ cc} / \text{min}$ of oxygen about 1 metre prior to entry into the reactor chamber.

7.4.1 Results and Discussion:

The growth of In_2O_3 films was successful using this precursor and a nebulization delivery system with the growth rate achieved being comparable to that achieved by conventional bubbling techniques at approximately $250\text{-}400 \text{ \AA}$ per minute. As the precursor was cold at all times until entering the reactor zone, no problem was observed with thermal decomposition of the precursor.

Film growth using this delivery method, resulted in the thickest coating at the front edge of the glass plate, with the film thickness then reducing in thickness towards the back of the glass substrate, in a similar fashion to that obtained during film growth by

conventional bubbler delivery. Significantly better coverage of the glass plate was observed with the nebulization delivery, suggesting that pre-reaction of the precursor in the hot zone was less of a problem. The reduction in the degree of pre-reaction of the precursor with the oxidant source may be a consequence of the precursor vaporising intact on seeing the hot zone, in contrast to conventional bubbler delivery techniques, where the precursor is already vaporised and may have decomposed and undergone pre-reaction prior to entry into the reactor chamber. The vaporisation of the intact precursor would explain the better coverage of the plate, as it is believed that the THF adduct, prevents pre-reaction of the precursor with the oxygen co-reactant, by protecting the metal centre from attack by the oxidant.

The films obtained by this method of delivery appeared to have similar roughness values to those obtained by bubbling techniques with no signs of particulate contamination of the coating surface, and similar haze levels to those produced by bubbling techniques were achieved. This suggests that no problems with the mist impinging on the glass surface as a liquid material is occurring and that precursor particles are vaporising in the gas phase prior to hitting the glass substrate. The coating, however, is still very thin at approximately 800 Å. X-ray analysis of the coating shows the material to be polycrystalline In_2O_3 (Figure 7-3), and the sheet resistance measurements, suggest that the film is continuous.

The resistivity of the films was also similar to films produced by bubbling techniques at approximately $1.5 \times 10^{-3} \Omega \text{ cm}$

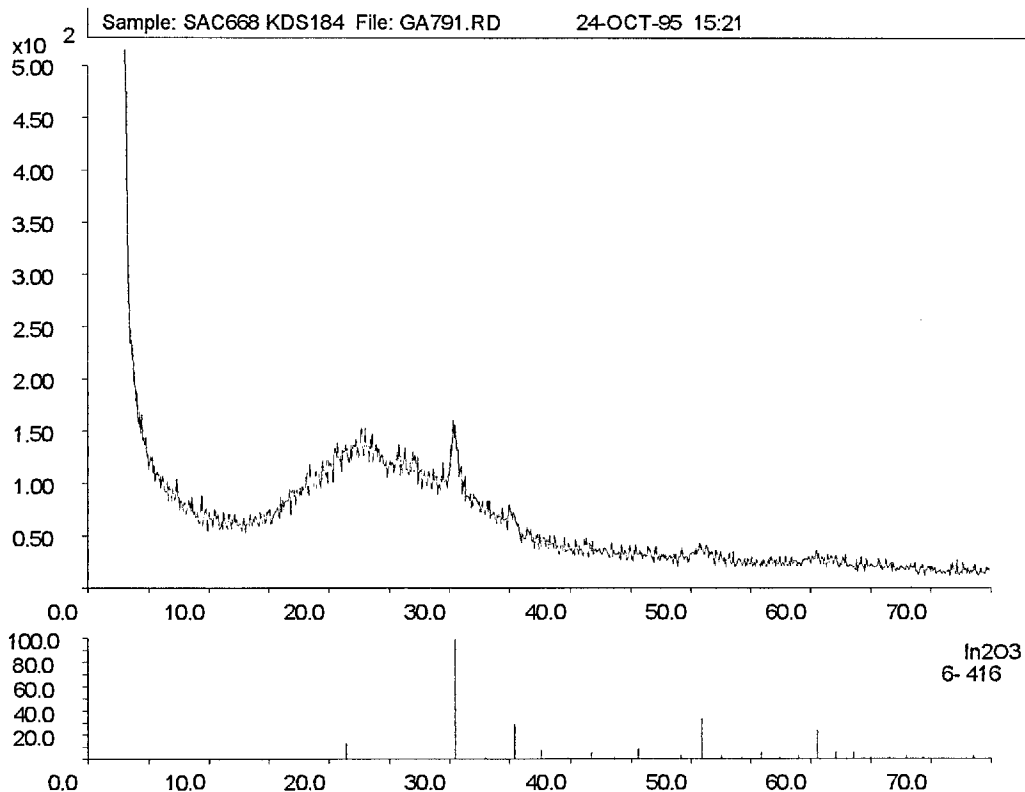


Figure 7-3 Glancing Angle XRD Pattern Of In_2O_3 Growth From $\text{Me}_3\text{In}(\text{thf})$ and O_2

The coatings produced using this precursor were encouraging due to the fact that provided oxygen was prevented from ingressing into the nebulizer, no decomposition of the precursor was seen. This is a big advantage over conventional bubbling techniques which showed a considerable deterioration in the precursor on heating the precursor to improve its vapour pressure and increase mass transport.

This method of delivery of precursors is clearly more successful than bubbling techniques for thermally sensitive materials. However, the handling of pyrophoric materials in a nebulizer is not trivial and the high reactivity of the material, also prevented investigation of the nebulization of this material by indirect nebulization, as leakage of the membrane would have resulted in direct contact between the precursor and the water used as a coupling fluid. Investigation of other coupling solutions, which would not have reacted dangerously with the precursor, has been carried out. These alternative coupling

solutions, however, further reduced the amount of nebulization, and the mist generation was considered too poor for further investigation.

Carry-over rates may be improved if more than one piezoelectric device is used. However, careful consideration of the air sensitivity of the precursor would have to be undertaken if this precursor was to be studied.

7.5 Growth of In_2O_3 From Dimethyl(methoxy)indium.

The precursor $\text{Me}_2\text{In}(\text{OMe})$ is a liquid precursor at room temperature, which is air and moisture sensitive as well as being potentially pyrophoric. As with the trimethyl-indium-tetrahydrofuran adduct, the material must therefore be handled under glove-box conditions and oxygen ingress into the nebulizer prevented.

Oxygen ingress into the nebulizer, resulted in a vigorous reaction, with the formation of a white solid and large amounts of effervescence being observed in the nebulizer.

Unlike the trimethyl-indium-tetrahydrofuran adduct, attempts at nebulizing this precursor as a neat material were not successful with very little mist generation, due to the high viscosity of the precursor, preventing formation of a geyser in the solution. In order to obtain mist generation, the viscosity of the precursor was reduced by the addition of a small amount of solvent to the precursor. The most successful solvent identified tetrahydrofuran, with dilution of the precursor with dried THF, in a ratio $\text{Me}_2\text{In}(\text{OMe})$: THF of 5:1 resulted in a solution which produced a good mist on nebulization.

Growth of In_2O_3 from this precursor was successful with good mist transport of the precursor achieved. As with the trimethyl-indium adduct no signs of droplet formation on the glass plate was observed. This suggests that the precursor mist is evaporated prior to hitting the glass substrate. However, the film quality produced using this technique was poor, with powdery films obtained. Variation of the partial pressure of oxygen during the deposition was investigated. Increasing the oxygen partial pressure failed to improve the film quality, with growth being observed to increase at the front of

the plate, and the coverage deteriorating, although the coatings were still powdery, consistent with pre-reaction of the precursor in the gas phase.

Reduction of the oxygen partial pressure did improve film quality, with the thickest growth, achieved at the front edge of the coating. These results were consistent with the previous studies of this precursor by conventional bubbling techniques. Whilst no advantage in the film growth over conventional bubbling techniques was observed as with the $\text{Me}_3\text{In}(\text{THF})$ the precursor did not decompose on nebulization.

7.6 Summary of Nebulization of Liquid Compounds:

The use of nebulization delivery techniques has been shown to be successful for the delivery of air sensitive precursors. Its biggest advantage is that precursors can be delivered without heating. As such the lifetime of the precursor is increased using this delivery technique and no decomposition of the bulk precursor is observed after nebulization. This is a significant change to bubbling, which resulted in a gradual decomposition of the precursor over relatively short periods of time.

Whilst this method of precursor delivery improves the lifetime of the precursor, no advantage in the properties of the films obtained was observed, implying that the precursors limited thermal stability and high reactivity in the gas phase are the limiting factors on the quality of the films. The delivery of chemicals by nebulization, whilst promising for thermally sensitive materials, cannot compensate for the poor gas phase stability of the precursor.

7.7 Nebulization of Low Volatility Precursors.

A range of precursors with low volatilities have been investigated by nebulization delivery. These precursors have been investigated in an attempt to increase the precursor carry-over without the need for heating the compounds to attain a sufficiently high vapour pressure to enable mass transport of the precursor. Unlike the methyl-indium

compounds these precursors are solids at room temperature, and have high melting points of between 180-330°C. In order to perform nebulization a suitable solvent for dissolving the precursors was required. Several factors were considered important in the choice of solvent for the system:

1. The precursor must be soluble with high concentration solutions of the material being attainable, without the precursor precipitating from the solution.
2. The solvent chosen must produce solutions of an acceptable viscosity to allow good mist generation when nebulized.
3. The solvent must not adversely effect the deposition of the coating.

Two solvents were identified as suitable for this purpose, tetrahydrofuran and n-butyl-acetate. Both of these solvents fulfilled the requirements for the range of solid indium precursors investigated.

The delivery system for the precursors had to be redesigned for the delivery of nebulized solutions of these low volatility solids. Unlike the liquid precursors, whereby the liquid could be nebulized and then mixed with the carrier gas, this was not possible with these low volatility precursors, as attempts at mixing the generated mist with the carrier gas resulted in blocking of the delivery lines, due to loss of the solvent sheath from the precursor particles. The resulting formation of solid particles in the delivery lines, caused line blockages. This was a potential hazard as significant back-pressures in the delivery line can occur resulting in possible failure under pressure of the weakest parts of the sealed delivery system, i.e. the nebulization vessel. This was more of a problem with tetrahydrofuran solutions than butylacetate solutions, due to the higher volatility of the tetrahydrofuran solvent, which resulted in premature loss of the solvent sheath around the precursor particles.

To solve this problem, all the carrier gas and oxygen was used to sweep the nebulized mist, and this was passed straight into the baffle system of the reactor. Using this system, blocking of the lines was significantly reduced as the distance over which the mist was transported was significantly reduced.

7.7.1 Growth of In_2O_3 from the Nebulization of $\text{In}(\text{thd})_3$:

The precursor $\text{In}(\text{thd})_3$ is a white crystalline material with a melting point of 184°C . The precursor was highly soluble in tetrahydrofuran, with 10g of precursor soluble in 30 ml of thf, without any signs of precipitation occurring in the solution. Nebulization of the THF solutions resulted in good mist generation, and film growth was achieved onto a glass substrate at a deposition temperature of 565°C . The large amount of carrier gas being required to sweep the generated mist into the reactor, resulted in significant solvent loss from the nebulizer due to evaporation. This resulted in a reduction in the mist generation as precipitation of the precursor occurred and the viscosity of the solution increased. Whilst reduction of the total flow through the nebulizer did result in a reduction in solvent loss, precipitation of the precursor in the delivery lines was still a significant problem due to the formation of solid particulates in the delivery lines.

The coatings produced were shown to be polycrystalline, and had a resistivity in the range $1\text{-}2 \times 10^{-3} \Omega \text{ cm}$. This is comparable to the results obtained for films grown by conventional bubbling techniques. The growth profile of the film was also comparable to that seen for bubbling techniques, and no difference in haze levels were seen, with typical values of $< 0.2\%$ being observed. The low haze values obtained were consistent with, no particulate incorporation in the film was occurring as such inclusion would have resulted in increased haze. These results are consistent with the $\text{In}(\text{thd})_3$ precursor was being successfully vapourised in the gas phase above the glass surface.

In an attempt to prevent solvent loss from the system, nebulization of butyl-acetate solutions of $\text{In}(\text{thd})_3$ were attempted. Whilst the boiling point of this solvent is higher and as such solvent loss due to evaporation of the precursor solution is reduced, the solubility of the precursor in the solvent was lower, being reduced by approximately 50% compared with THF solutions. Typical solutions used for film deposition were 5g of $\text{In}(\text{thd})_3$ dissolved in 30-40 ml of butyl-acetate. The mist generation from this system was also poorer than the THF precursor solution, due to the higher viscosity of the precursor solution.

The resulting films were similar to those produced by the nebulization of THF solutions and conventional bubbling techniques, however, no observable condensation of particulates in the delivery lines was observable using this solution.

Typical delivery rates using this system were the transport of 5-10 ml of the precursor solution in a 10 minute run. This implies that the precursor carryover was approximately 0.05-0.1 g / min. Whilst this is low, it is believed that the use of more than one nebulizer in series would enable an increase in the carryover rate of the precursor and as such increase the growth rate. The nebulization of $\text{In}(\text{thd})_3$ is therefore a viable possibility for the delivery of $\text{In}(\text{thd})_3$ and the growth of In_2O_3 .

7.7.2 Growth of In_2O_3 and ITO from the precursor $\text{In}(\text{acac})_3$:

The growth of In_2O_3 has also been investigated from the indium chelate $\text{In}(\text{acac})_3$ by nebulization. Unlike the $\text{In}(\text{thd})_3$, however, attempts at growing this material by conventional bubbling techniques were relatively unsuccessful due to the very poor vapour pressure of the $\text{In}(\text{acac})_3$ and its tendency to decompose in the bubbler when held at temperatures of approximately 200°C.

Whilst the use of THF as a solvent would have been advantageous for this precursor due to the high solubility of this precursor, the problems with premature solvent loss in the delivery lines would have resulted in blockages as observed with $\text{In}(\text{thd})_3$. Solutions of $\text{In}(\text{acac})_3$ in butyl-acetate were therefore used for nebulization studies. Slow growth rates equivalent to the growth of In_2O_3 by conventional bubbling techniques of 50 angstroms min^{-1} have been achieved, by nebulization of a saturated solution of $\text{In}(\text{acac})_3$ in butyl-acetate. The SEM micrograph (Figure 7-4) of a film grown from this precursor, shows the film to have no signs of particulate incorporation, suggesting that the precursor is volatilising prior to reaching the substrate. Films grown using this technique were polycrystalline, with the XRD pattern shown in Figure 7-5.

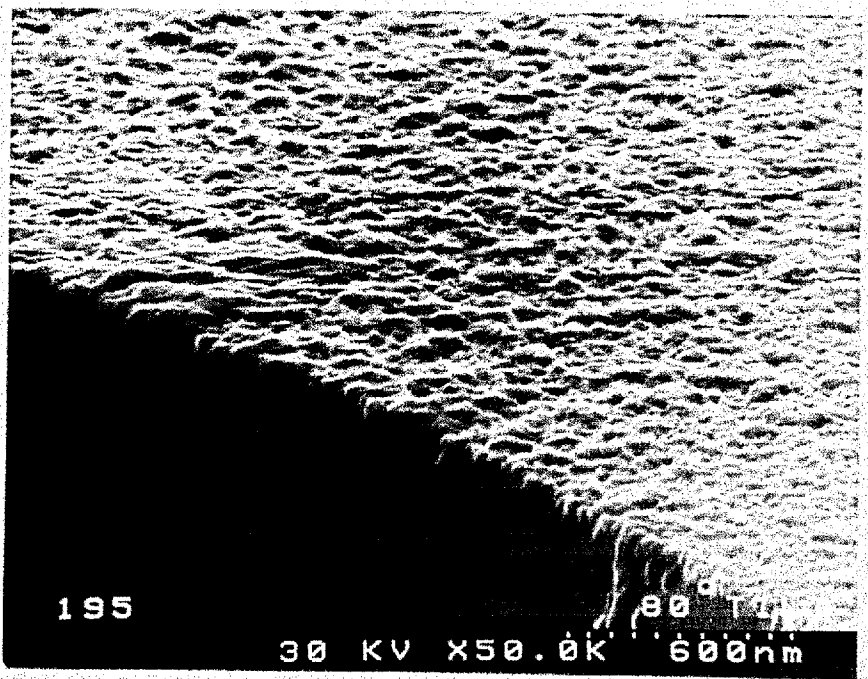
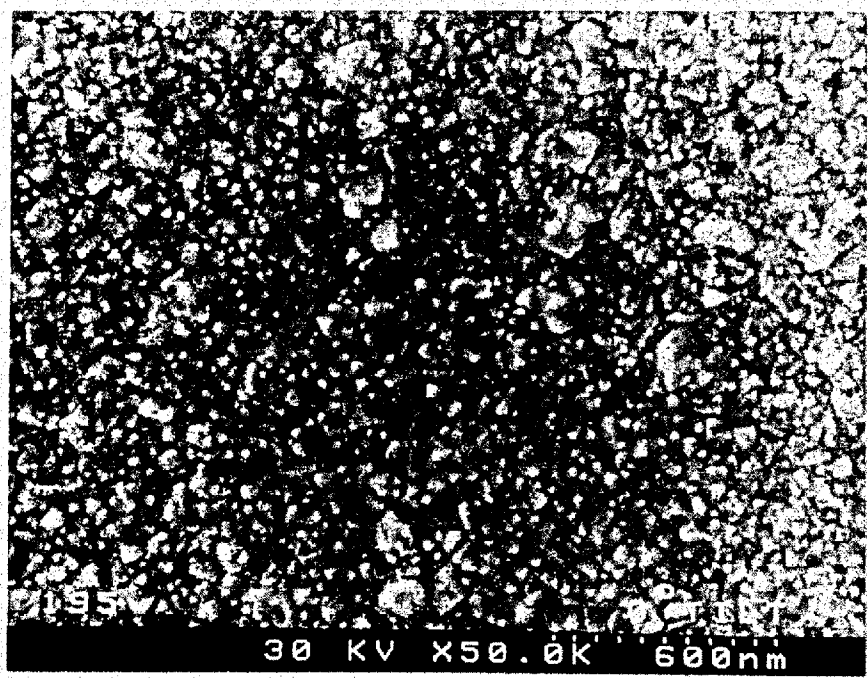


Figure 7-4 SEM Micrograph of In₂O₃ Grown From In(acac)₃ and O₂

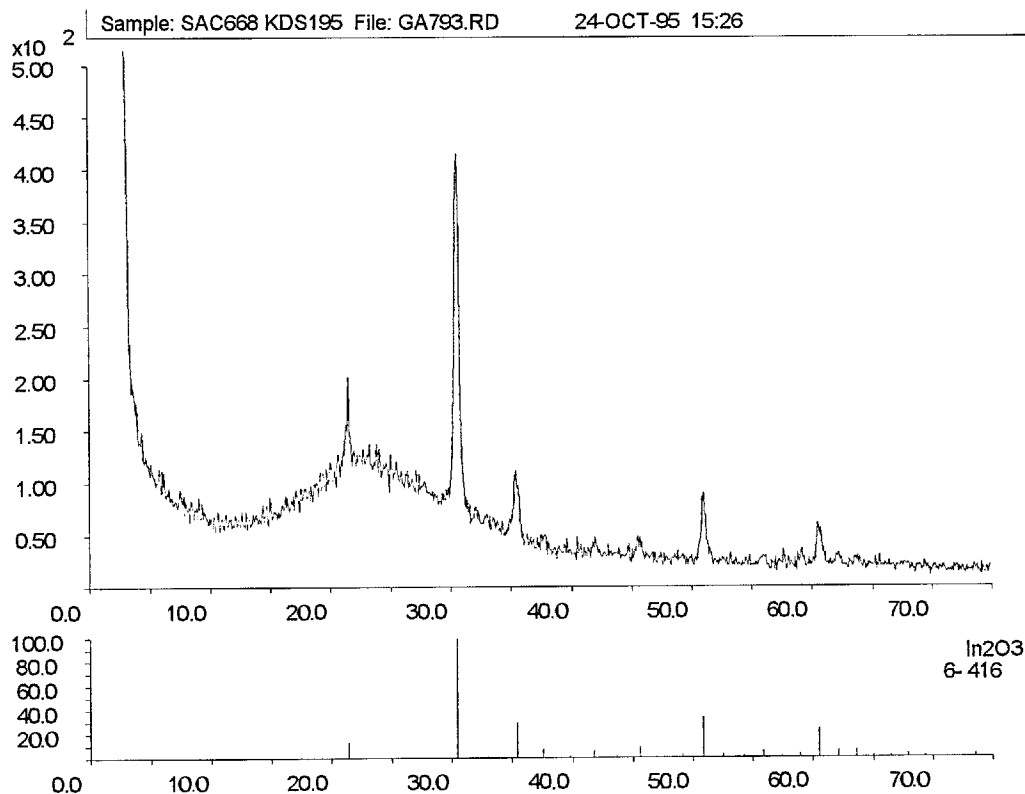


Figure 7-5 Glancing Angle XRD of In_2O_3 Growth From $\text{In}(\text{acac})_3$ and oxygen

The resistivity of the coatings were of the order of $1 \times 10^{-3} \Omega \text{ cm}$.

These coatings again showed no sign of particulate formation in the films, suggesting that the nebulized precursor has not resulted in powder formation in the gas phase, and that the precursor mist has not impinged on the glass surface.

7.7.3 Doping Studies of $\text{In}(\text{acac})_3$:

Attempts have also been made at tin doping of In_2O_3 films by nebulization. The advantage of nebulization for doping, is that a single solution can be used for deposition provided that both precursors are soluble in the common solvent. This technique also allows for far better control over the stoichiometry of the film, as in theory the relative concentrations of the precursors in the solution, should be identical to that in the generated mist. The final stoichiometry of the film can therefore be determined by the stoichiometry of the initial solution.

Initial attempts at doping concentrated on the use of solutions of $\text{In}(\text{acac})_3$ and diacetatodibutyltin. This tin dopant was chosen because at room temperature it is a liquid of similar viscosity to the $\text{In}(\text{acac})_3$ solution, and is soluble in butyl-acetate. However, on commencing nebulization, mist generation fell rapidly, and the viscosity of the solution increased, as a white solid was produced inside the nebulizer. The nature of this white solid is unknown, but reaction between the tin dopant and the $\text{In}(\text{acac})_3$ appears to have been initiated by nebulization resulting in a white polymeric material.

Studies of the growth of ITO from the precursor system $\text{In}(\text{acac})_3$ and dichlorodimethyltin were attempted, by the addition of DMT to a saturated solution of $\text{In}(\text{acac})_3$ in butylacetate. By altering the amount of added DMT the dopant concentration in the final film was changed. An investigation of a range of dopant concentrations of the indium solution showed that the best properties were achieved from the mixture, 0.1g DMT in 40ml of a saturated solution of $\text{In}(\text{acac})_3$ in butyl-acetate. This film had a resistivity of approximately $4.5 \times 10^{-4} \Omega \text{ cm}$. Unfortunately attempts at further improving these properties were hindered by poor reproducibility, with the film composition varying from run to run. This is believed to be a result of changes in the carry-over rates of the precursors from run to run. The variable delivery rate of the precursor is likely to be due to preferential solvent loss during nebulization. Due to the saturated nature of the solution, any solvent loss led to precipitation in the nebulizer, which affected the nebulization and mist generation. It was therefore decided to investigate doping of other precursor solutions which did not exhibit this problem.

7.8 Growth of In_2O_3 and ITO From InCl_3 :

Attempts at the growth of In_2O_3 from anhydrous InCl_3 by conventional bubbling techniques failed due to the involatility of the precursor. Studies on the growth of In_2O_3 using this precursor were therefore attempted using nebulization delivery.

Solutions of 5g anhydrous InCl_3 dissolved in 50ml of butyl-acetate were made up and placed into the nebulizer. Direct nebulization of the solution with the carrier gas and oxygen being passed over the nebulized precursor was utilised. Using this precursor

system film growth of In_2O_3 has been achieved, with polycrystalline In_2O_3 being deposited with a growth rate of $170 \text{ \AA min}^{-1}$ at a substrate temperature of 565°C . However, whilst the resistivity of these films is comparable to that obtained by from other precursors at approximately $2 \times 10^{-3} \Omega \text{ cm}$, the haze of the films is high at approximately 1-2%. The films show signs of particulate dropout on the surface of the glass. This was not apparent to the same extent with the other precursors and would explain the high haze of the coatings.

This is consistent with spray deposition of In_2O_3 from InCl_3 solutions, which also results in hazy films.⁷⁻¹²

Particulate incorporation in the films using both spray and nebulization delivery techniques may be explained by the mist of the precursor being carried into the hot reactor chamber, where the solvent sheath around the precursor vaporises resulting in small particulates of InCl_3 . Due to the very high melting point of InCl_3 , the gas phase temperature may be insufficiently high for the precursor to react or vaporise before hitting the surface of the glass and this explains the particulates seen on the glass surface, and the unreacted precursor being incorporated in the film.

Despite the high haze levels obtained for the In_2O_3 films, it was decided to investigate the doping of the coatings with tin. In order to dope the films, to the standard solution of 5g InCl_3 in 50ml BuOAc, DMT was also added to the solution.

Films grown using these solutions had significantly lower haze values than those obtained for In_2O_3 growth. This may suggest that the precursors are interacting prior to deposition to produce a more volatile intermediate species that undergoes vaporisation before hitting the surface of the glass.

Different doping levels were achieved by changing the amount of dimethyltin dichloride added to the solution. The properties of the coatings are consistent with ITO coatings produced by other precursors. Resistivities of between $3.7 \times 10^{-4} \Omega \text{ cm}$ and insulating films were obtained by alteration of the tin dopant concentration in the solution. The lowest resistivities were obtained at a doping concentration of approximately 18 weight % tin to indium, although this may indicate the films are overdoped with tin as ITO from other precursor systems has shown the best electrical

properties are achieved at lower doping levels of approximately 8 weighth % tin : indium. The other surprising feature is the amount of tin incorporation from the solutions used

Number of grams of DMT in Solution (5g InCl3 in 40ml BuOAc)	Expected Doping Level From Solution Tin Weight %	Doping Level in Film Weight % Tin : Indium	Resistivity (Ω cm)
0	0	0	2×10^{-3}
0.2	4	18.2	3.7×10^{-4}
0.7	14	35	6×10^{-4}
1.4	28	120	Insulating

From these results it can be seen that the level of doping achieved in the final film is far higher than that predicted by theory. The reason for the discrepancy between the experimental results and the theory is likely to be due to the growth rates of the materials being different. The theoretical doping level predicted assumes that the growth rate of the indium oxide is the same as the dopant growth rate. This is clearly not the case as the doping level is consistently higher than that predicted, suggesting that the rate of the tin precursors growth exceeds that of the indium precursor and as such the doping level is not as predicted. The tin dopant growth rate appears to be approximately 3-4 times faster than the theory predicts.

Analysis of the ITO coatings produced using this nebulization technique show slightly preferred growth towards the (222) orientation, with alteration in the doping level not changing this preferred orientation.

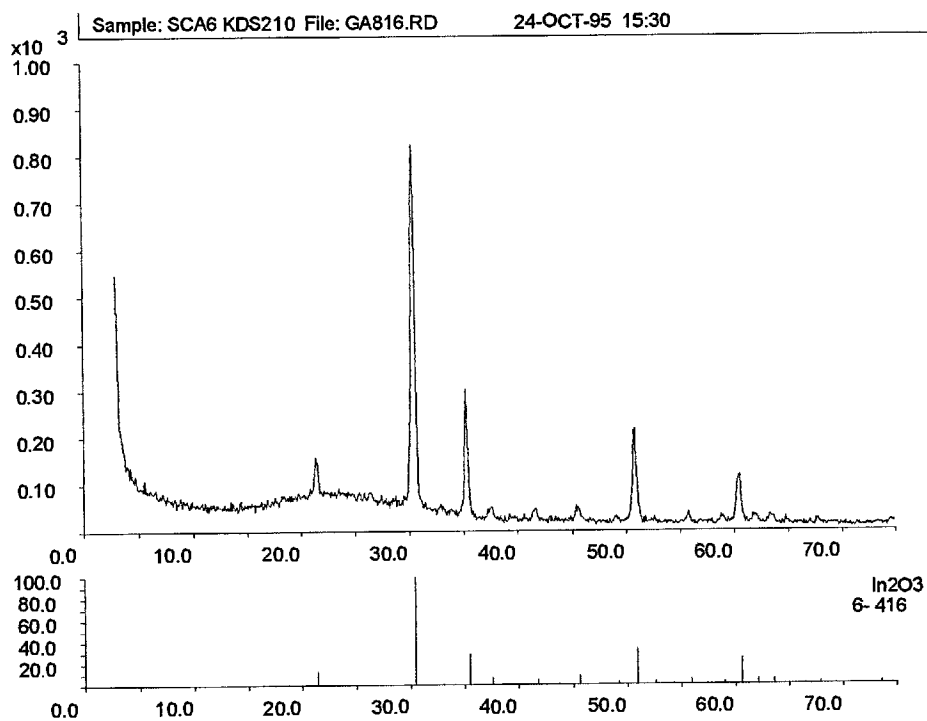
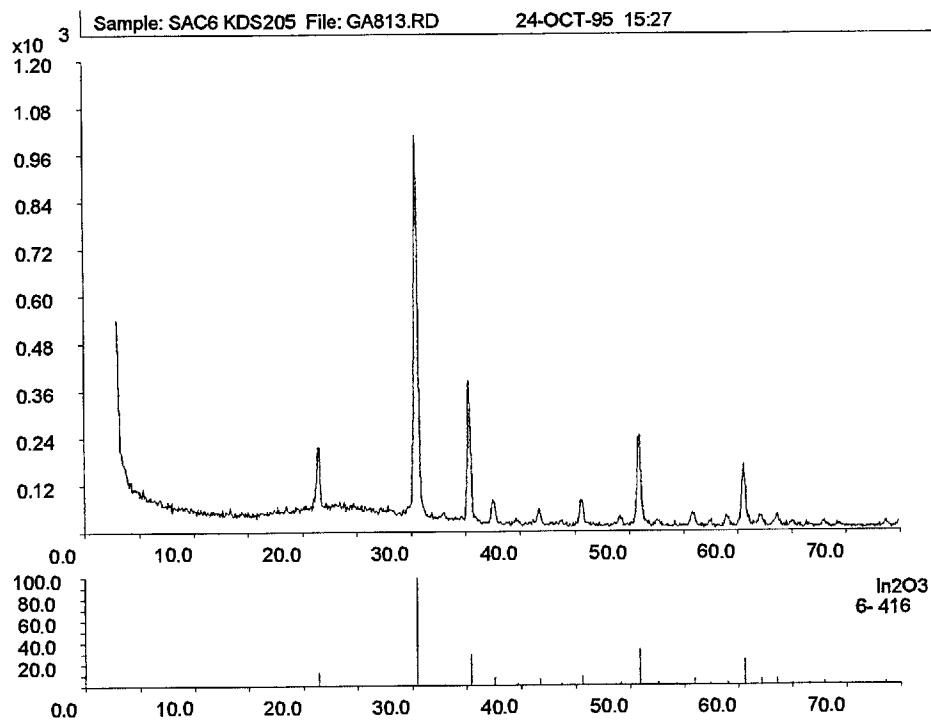


Figure 7-6 Glancing Angle XRD of (a) Undoped In₂O₃ and (b) ITO Grown From InCl₃ and DMT

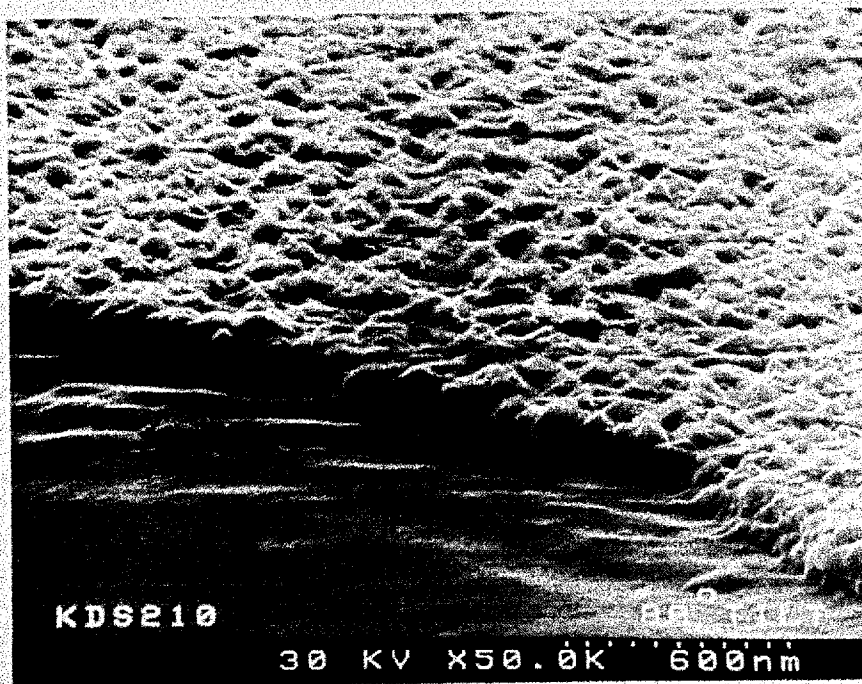
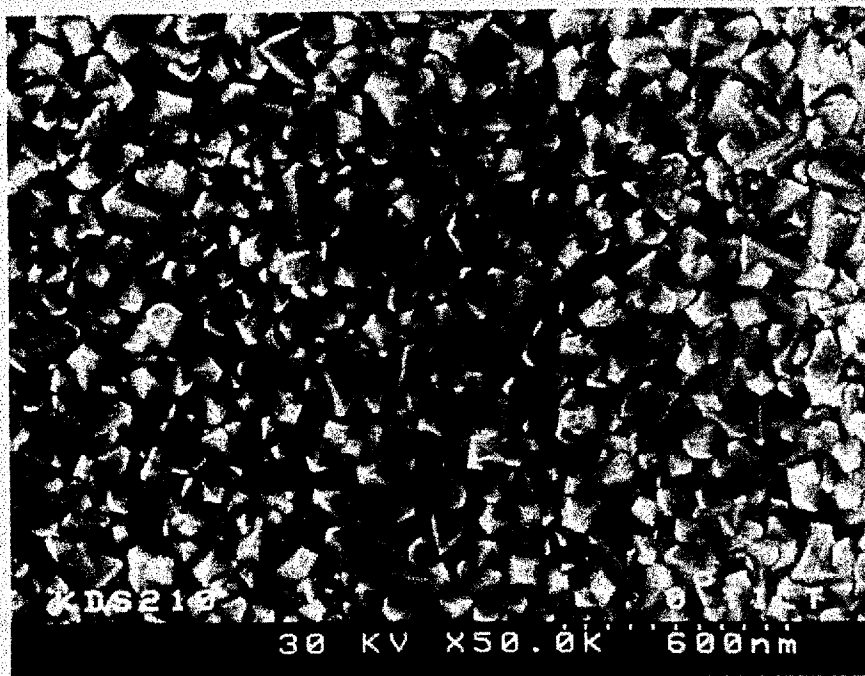


Figure 7-7 SEM Micrograph of an ITO Film Grown From InCl_3 and DMT

7.9 Conclusions:

This study has shown that nebulization is a viable alternative to the use of bubblers for the delivery of precursors in APCVD. It has been shown that In_2O_3 can be grown from a range of precursors using the nebulized mist to carry the precursor over into the reactor. It has the following advantages over conventional delivery techniques:

1. Thermally sensitive precursors can be delivered as no heating of the precursor is required.
2. No heating of the delivery lines is required so pre-reaction of the precursors in heated delivery lines is eliminated
3. Delivery of materials which have low vapour pressures can be achieved.

Film growth using this delivery method is comparable to that achieved with other delivery techniques. However, if the material carried in the mist has too high a melting or sublimation point, contamination of the film with powder can result, leading to hazy coatings. This appears to occur due to the solvent sheath of the precursor being evaporated and leaving small particulates, typically <10 microns. These small particles can then fall onto the growing surface if the precursor has insufficient volatility, to be vapourised in the gas phase prior to contact with the glass.

This study has also shown, the viability of single source delivery of a two component film, i.e. tin and indium precursors in one solution. However, whilst it has been shown that growth of ITO can be achieved, the ratio of precursors used in the solution is not reflected in the resulting film. In order to calculate the correct concentration required careful consideration of the growth rates of the two precursors is required.

In order to achieve higher growth rates from nebulization, a bank of piezoelectric devices could be used. This would increase the mist generation of the precursor solution, thus allowing greater carry-over of the precursor resulting in a higher growth rate. This technology would then only be limited by the amount of mist that the carrier gas can transport before coagulation of droplet particles occurs.

7.10 References

1. Personal Communication, C. Roger, T. Corbitt, C. Xu, D. Zeng, Q. Powell, C. D. Chandler, M. Nyman, M. J. Hampden-Smith and T. T. Kodas, *Submitted to Nanostructured Materials*.
2. T. T. Kodas and M. Hampden-Smith, *The Chemistry of Metal CVD*, 1994, VCH, Weinheim
3. C. Roger, T. Corbitt, M. Hampden-Smith and T. Kodas, *Appl. Phys. Lett*, 1994, 65, 1021
4. C. Xu, M. Hampden Smith and T. Kodas, *Advanced Materials*, In Press
5. K. Frohlich, J. Souc, D. Machajdik, A. P. Kobzev, F. Weiss, J. P. Senateur and K. H. Dahmen, *J. De Physique IV*, 1995, 2, C5-533
6. M. L. Hitchman and K. F. Jensen, *Chemical Vapor Deposition Principles and Applications*, 1993, Academic Press
7. S. Mirzapour, S. M. Rozati, M. G. Takwale, B. R. Marathe and V. G. Bhide, *Mater. Lett.*, 1992, 13, 1357
8. M. G. Mikhailov, T. M. Ratcheva and M. D. Nanova, *Thin Solid Films*, 1987, 146, L23
9. W. Siefert, *Thin Solid Films*, 1984, 121, 275
10. S. Kulaszewicz, W. Jarmoc, I. Lasocka, Z. Lasocki, C. Michalski and K. Turowska, *Thin Solid Films*, 1987, 148, L55
11. S. Mirzapour, S. M. Rozati, M. G. Takwale, B. R. Marathe and V. G. Bhide, *J. Mater. Sci.*, 1994, 29, 700
12. A. Ortiz, M. Garcia, S. Lopez and C. Falcony, *Thin Solid Films*, 1988, 165, 249

8. APCVD of Titanium Nitride

8.1 Introduction

In the bulk phase titanium nitride has a golden yellow colour, and up-to eight different phases have been reported. The two most widely studied of these phases are TiN and Ti₂N. The TiN phase has a NaCl type structure (B1). In this structure the metal atoms are arranged in a face centred cubic arrangement with the nitrogen atoms filling the octahedral interstitial sites.

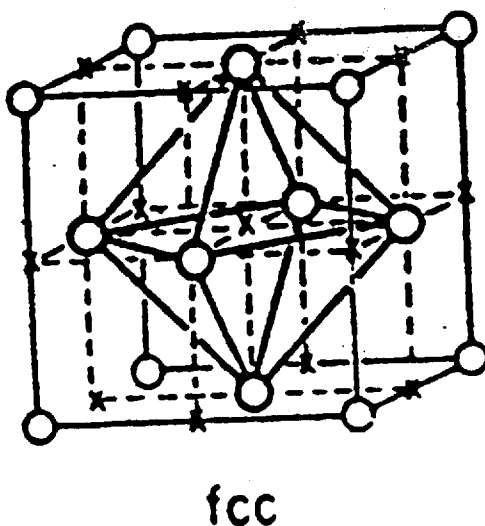


Figure 8-1 NaCl Type Structure Of Titanium Nitride.³⁸

Although the stoichiometry in this compound appears to be 1:1, this is not really the case, with vacancy concentrations being present, and the homogeneity range of the material extends from TiN_{0.6} to TiN_{1.0}. This range gives the metal nitride a lattice parameter of 4.240Å and a density of 5.39 gcm⁻³.¹ The non-stoichiometric phases of titanium nitride are less well understood, with Ti₂N being the most studied. The Ti₂N phase is synthesised by either condensing titanium into a controlled pressure nitrogen plasma or by heating titanium to 900-1000°C in a nitrogen atmosphere. Due to the

difficulty of these synthetic methods, this material has no current applications, but has either an ordered NaCl or an anti-rutile structure.

The hardness of titanium nitride when deposited as a thin film is one of the properties which makes it of interest to industry. It has a micro-hardness of 2000 kg mm⁻², which is comparable with that of tungsten carbide (2100 kg. mm⁻²).² This hardness, coupled with the high melting point of 2949°C, (which is almost twice that of the pure metal, and higher than tungsten carbide), ensures it has a considerable market for coating tool bits and machine tools.

The electrical properties possessed by titanium nitride thin films also have industrial applications. Stoichiometric titanium nitride has a bulk resistivity of 22 $\mu\Omega$ cm⁻¹, which is very different to that of thin films of titanium nitride, which varies from 200 to 6000 $\mu\Omega$ cm⁻¹.³ The range of resistivities achievable from titanium nitride films has resulted in many electrical applications such as in Schottky diodes, electrical contacts and other circuit board applications. Care has to be taken with the preparation of thin films of this material for such exact uses, however, as contamination in the films has a detrimental effect on the resistivity of the film, increasing it considerably.

Titanium nitride films have also been shown to exhibit superconductivity below the critical temperature of 5.49 K, but unlike its other properties this is of little interest to industry, due to the development of chemical vapour deposition routes to thin films of mixed metal oxides such as YBa₂Cu₃O_{7-x} and TlBa₂Cu₂O₅. These oxides have much higher critical temperatures of approximately 78K and 128K respectively, and are therefore of far more interest to industry, because of their wider commercial applications.⁴

The optical properties that titanium nitride thin films possess are very interesting and as such there is a potential large market for these coatings. Thin films (approximately 1 micron) of titanium nitride show a high degree of reflectance of electromagnetic radiation in the infra red region above 700 nm, but show a change in properties between 650 and 750 nm, when they begin to transmit a small amount of visible light. Studies of this phenomenon with thin films of approximately 0.1 microns in

thickness have shown 60-80% reflectance of infra-red radiation whilst transmitting 10-20% of visible light.. These properties make the material a type of heat mirror, allowing heat to be deflected, whilst transmitting a significant amount of visible light. The energy saving potential of these coatings as Solar control coatings on glass has lead to an interest in film deposition of titanium nitride.⁵

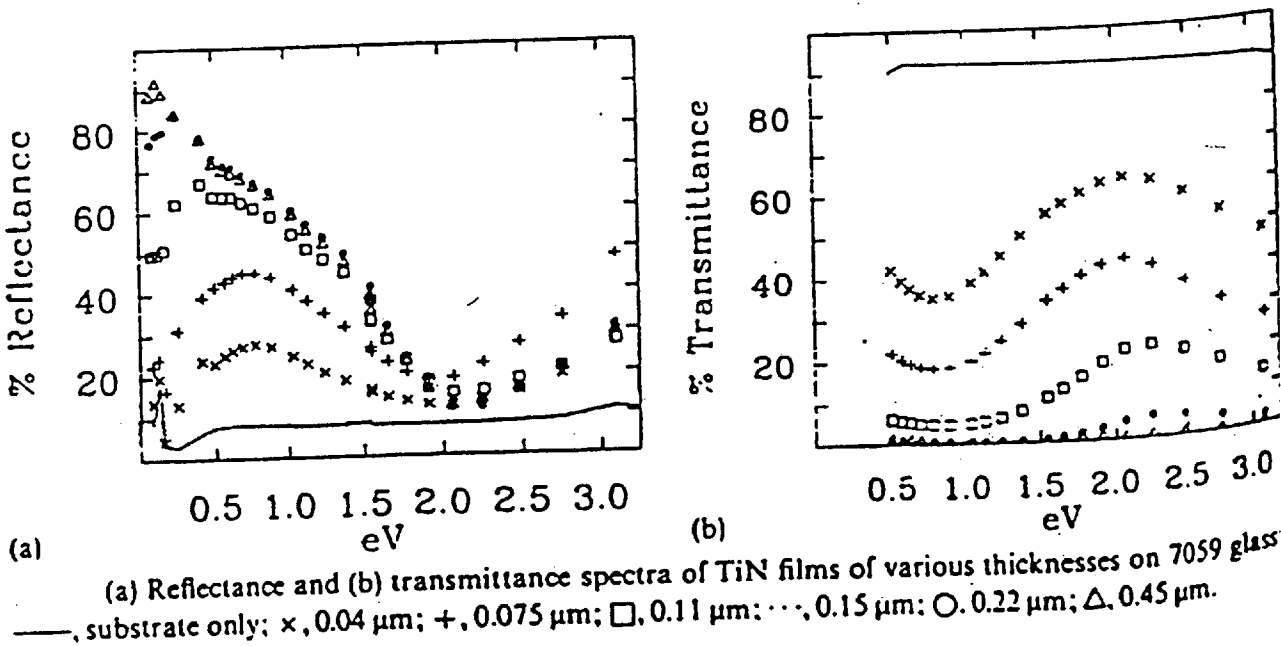


Figure 8-2 Optical Characterisation of a TiN Thin Film.⁵

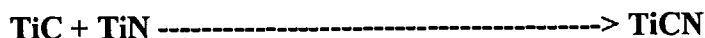
As mentioned previously titanium nitride thin films, are very difficult to make in a pure form with contamination by C, H and O being commonly reported in films of titanium nitride on a variety of substrates. These impure materials whilst of little interest to the electronics industry due to the variable nature of the films electrical properties, are still of interest as optical coatings. Whilst the properties are not the optimum achievable from the pure material, they are still comparable with other materials that are more expensive to deposit e.g. multi-layer and metal coatings . Some examples of the types of contaminated films produced are:

1. Titanium Carbo Nitride

Three types are known:

- a. TiCN .⁶

RF or Microwave Plasma



- b. Ti_2CN .⁷

Found in some types of steel and is orthorhombic

- c. Ti_4CN_3 .⁸



2. Titanium Halide Nitrides

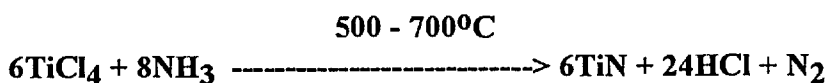
TiNF .⁹

280°C



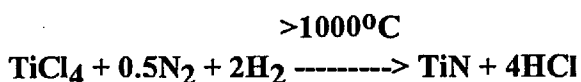
Many deposition techniques have been used for the deposition of titanium nitride and oxy-nitride thin films including sol-gel, sputtering and chemical vapour deposition. As described previously the relative low cost of CVD and its potential for large scale production make it particularly attractive as a deposition method.¹⁰

There are at present a wide variety of precursors which are used for the deposition of titanium nitride by CVD techniques. The first precursor reported for the APCVD of titanium nitride thin films was titanium tetrachloride. This material is reacted with ammonia in the gas phase at temperatures of between 500°C and 700°C to deposit TiN .¹¹



Deposition by this process occurs at temperatures as low as 500°C, but in order to ensure good quality films with minimal halide impurities resulting from incomplete reaction of the precursor, a deposition temperature in excess of 650°C is required.

The deposition of TiN from titanium tetrachloride has also been done in a nitrogen / hydrogen atmosphere without the use of ammonia, but higher temperatures of approximately 1000°C are required to initiate this reaction.^{5,12,22}



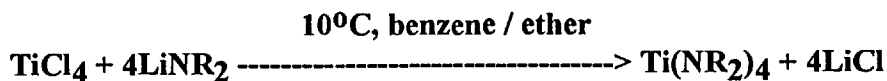
Neither of these processes are ideal on an industrial scale with the ammonia process considered “environmentally unfriendly” due to the large amounts of HCl produced and problems with halide impurities. The high temperature required for the second process has the disadvantage that thermally sensitive substrates such as glass and electronic devices cannot be coated.

As a result of the problems associated with the use of these precursors, alternative organometallic precursors have been developed.

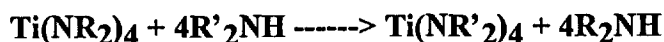
The tetrakis(dialkylamido)titanium compounds are the most widely reported and have been used for titanium nitride deposition by CVD. Whilst these precursors have the advantage of requiring a lower deposition temperature of approximately 400°C, they have the disadvantage of incorporating carbon containing ligands, which introduce the possibility of carbon contamination of the film during deposition. The precursors Ti(NMe₂)₄ and Ti(NEt₂)₄ were first used and growth has been reported by both the thermal decomposition of the precursor and by deposition using ammonia as an additive in the gas phase during deposition.

Preparation of these compounds has been reported via a range of synthetic methods including:

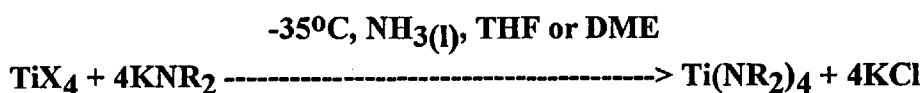
1. From the Chloride.¹³



2. Aminolysis of a lower secondary amine by a higher secondary amine.¹³



3. Liquid ammonia route



Where X= halide, nitrate or acetate

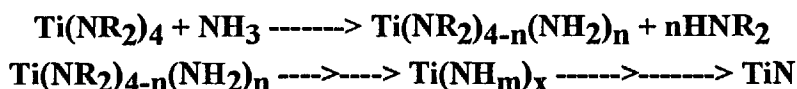
4. Metallation of HNR_2 by titanium organometallics



Where TiR_4 is alkyl or aryl

Film deposition by the reaction of $\text{Ti}(\text{NMe}_2)_4$ with ammonia occurs at temperatures as low as 150°C , with growth rates of upto $2000 \text{ \AA} / \text{min}$ and C / Ti ratios as low as 0.02 achieved.¹⁴

The mechanism involved in the deposition of TiN is believed to follow a similar pathway to reactions that occur in solution and were studied by Bradley and co-workers in the 1960's.¹³ These studies suggest that the reaction of $\text{Ti}(\text{NMe}_2)_4$ with primary amines results in the formation of imido bridged oligomers when the alkyl substituent is small,^{15,16} whilst resulting in dimer formation if a larger alkyl substituent is used e.g. Bu^tNH_2 .^{15,17} The deposition process is therefore believed to be:



This pathway suggests that the first stage of the reaction is the replacement of one or more of the NR_2 ligands by NH_2 groups via a transamination reaction with ammonia. The NH_2 substituted products then eliminate the remaining NR_2 groups, via alpha-hydrogen elimination reactions involving the NH_2 ligands, resulting in imido $\text{Ti}=\text{NH}$ groups being formed, which subsequently further react to yield nitrido TiN linkages. During this reaction the titanium metal is reduced from oxidation state four to three, but no mechanism for this reduction has been reported. Similar thermal decomposition studies on niobium(V) dialkylamido complexes have also been reported to result in reduction. This is believed to occur by homolytic M-N bond cleavage, and suggests a similar process may occur for titanium.^{18,19}

The level of carbon contamination in the deposited films appears to be related to the deposition temperature. At lower deposition temperatures, the carbon contamination is at a minimum,²⁰ but increasing the deposition temperature results in higher carbon contamination. The increased contamination is believed to be a result of intramolecular dimethylamido beta-hydrogen elimination, which occurs more readily at higher temperatures and this would effectively compete with intermolecular (ammonia transamination) and intramolecular (α -hydrogen elimination) deposition chemistry.

A further problem with these compounds is that hydrogen contamination of the films often occurs. Hydrogen contamination of up to 33% is observed at deposition temperatures of approximately 150°C, although this contamination in contrast to carbon contamination, is seen to reduce as the deposition temperature increases. The hydrogen contamination in these films is thought to be in the form of NH and NH_2 groups. Studies have shown that these groups are most likely located at the grain boundaries between the crystallites of TiN . The lower levels of hydrogen contamination observed at higher deposition temperatures, are consistent with the liberation of volatile hydrogen containing species as the deposition temperature is increased.

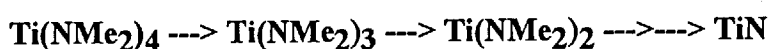
Deposition of titanium nitride films by the thermal decomposition of $\text{Ti}(\text{NMe}_2)_4$ and $\text{Ti}(\text{NEt}_2)_4$ has also been reported. Deposition temperatures for the thermal decomposition route, are higher than those used for the ammonia process, at 350-500°C, and the films produced have significant higher carbon and oxygen contamination levels.

Deposition using this process with the $\text{Ti}(\text{NMe}_2)_4$ at substrate temperatures of approximately 350°C , results in reddish-brown coatings which have been found to be $\text{Ti}(\text{C}, \text{N}, \text{H})$. Higher temperature deposition at approximately 450°C , produce yellowish coatings, which are more consistent with the usual properties of TiN .

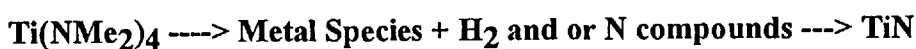
Studies of the films produced by this thermal decomposition of $\text{Ti}(\text{NR}_2)_4$, (Where $\text{R}=\text{Me}, \text{Et}$) at 400°C have been found to have average contents of Ti 25 atom %, N 25 atom %, O 15 atom % and C 35 atom %. Variations of the deposition temperature vary these values, but as the temperature is lowered the N / Ti ratio reaches 1.3, suggesting that the films become nitrogen rich.²¹

The reason for the change in composition of the coatings with changes in the deposition temperature is believed to be due to different decomposition pathways occurring. At low temperatures it has been found from mass spectral analysis that amines exist in the effluent gases, but at high temperatures, full degradation of the complex is seen. The two mechanisms are therefore thought to be:²²

Low Temperature:



High Temperature:



The low temperature route, therefore consists of a stepwise decomposition of the precursor, to give a low valent metal amide, which yields the nitride, by elimination of the alkyl group. In contrast to this the high temperature route sees a complete degradation of the amide. The metallic species, hydrogen and nitrogen compounds produced then further react to yield the titanium nitride. These pathways are consistent with different film stoichiometries being observed in the final film. The preference for nitrogen rich films at lower temperatures, is consistent with the incorporation of some nitrogen containing decomposition products in the coating.

The biggest advantage of these precursors is the lower substrate temperature that is required during the deposition process compared to that used in the $\text{TiCl}_4 / \text{NH}_3$

process, which is a result of the Ti-N bonds being weaker than the Ti-Cl bonds (20kcal/mol stronger), and as such the $Ti(NR_2)_4$ compounds thermodynamically favour nitride formation relative to $TiCl_4$. The reactions of $Ti(NR_2)_4$ with ammonia are also more kinetically labile than the $TiCl_4 / NH_3$, with these species rapidly reacting in the gas phase to generate $Ti-NH_2$ species. The high impurity levels of the films produced is the biggest disadvantage of these precursors and has lead to the synthesis of a range of alternative precursors, aimed at reducing these impurity levels.

The compounds that have been tried are listed in the table along with their properties. The general method for the preparation is similar to that used for the production of $Ti(NMe_2)_4$ and $Ti(NEt_2)_4$:

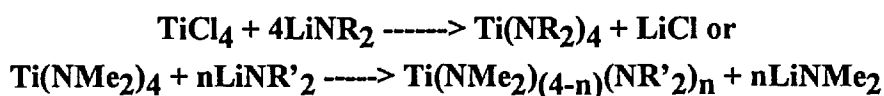


Table 8-1 Compounds Used For APCVD Of Titanium Nitride Thin films

Compound	Properties
$Ti(NMe_2)_4$. ²³	Yellow Liquid B.pt. 50°C at 0.05 mmHg
$Ti(NEt_2)_4$. ²³	Orange Liquid B.Pt. 112°C at 0.1 mmHg
$Ti(NMe_2)_3^tBu$. ²⁴	Orange Oil B.pt. 80°C at 0.1 mmHg
$Ti(NC_4H_8)_4$. ²⁴	Orange-Yellow Oil B.pt. 160°C at 0.05 mmHg
$Ti(NC_5H_{10})_4$. ²⁵	Red Solid M.pt. 70°C, B.pt. 180°C at 0.05 mmHg
$[Ti(N^tBu)(NMe_2)_2]_2$. ²⁶	Red Solid Sublimes at 140°C at 0.1 mmHg
$[TiCl_2(NHBU^t)_2(NH_2BU^t)_2]_n$. ²⁷	Solid. Sublimed at LPCVD

As with the tetrakis-dimethyl-amido and diethyl-amido compounds, deposition using these alternative precursors has resulted in high carbon impurity levels in the films. Attempts at providing a facile decomposition route for the carbon in the precursor, in the form of ring compounds or as stable radical species such as the tert-butyl radical having

failed to reduced the contamination levels. This can clearly be seen from results obtained for the deposition of titanium nitride from the precursor $\text{Ti}(\text{NMe}_2)_3^t\text{Bu}$. Films deposited using this precursor resulted in similar carbon impurity levels to those obtained using the precursor $\text{Ti}(\text{NMe}_2)_4$. This failure to reduce the carbon level in the films suggests that whilst the ^tBu group cleaves cleanly via alkyl-beta-hydrogen elimination or homolytic $\text{Ti}-\text{CMe}_3$ bond cleavage,²⁸⁻³⁰ common intermediates appear such as ' $\text{Ti}(\text{NMe}_2)_2$ ' or ' $\text{Ti}(\text{NMe}_2)$ ' in the subsequent decomposition of the precursor. The similar carbon impurity levels in films grown from the other precursors is also consistent with common intermediates being involved in the deposition process. Improvement in the impurity levels obtained will therefore require a better understanding of the decomposition pathway and also the prevention of by-product incorporation in the final film.

This project had two major aims. Firstly, to investigate the deposition of TiN onto a glass substrate, and secondly to attempt to improve the existing precursors to reduce the problems associated with impurities in the coating.

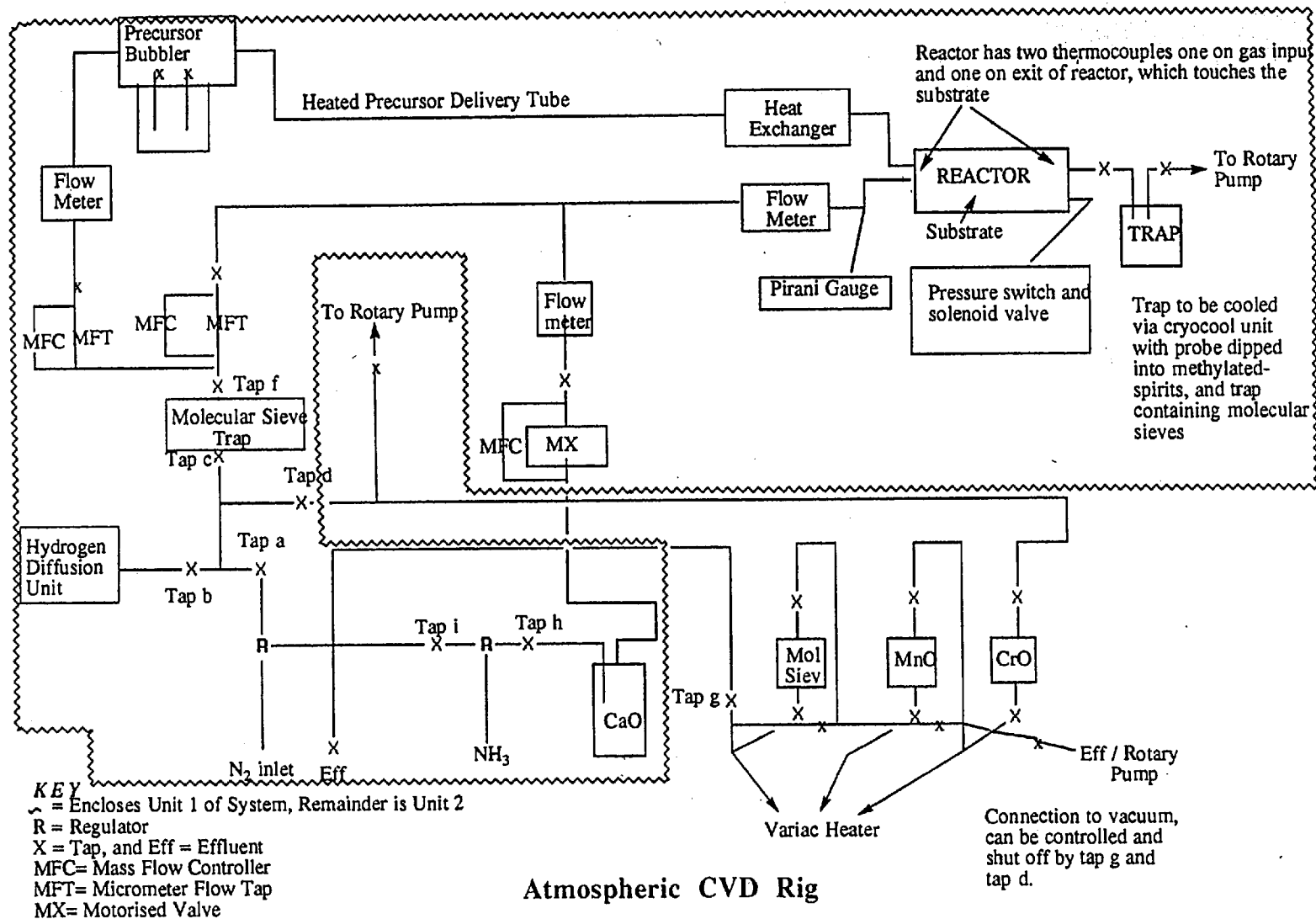
The synthesis of titanium nitride by lower temperature "molecular precursor" routes is clearly advantageous. For many of the metal nitrides, the currently preferred route of film formation is via chemical vapour deposition. The fabrication of such materials by metallo-organic chemical vapour deposition techniques (MOCVD) has allowed the preparation of thin films and semiconductors. However, few studies on the deposition of thin films of main group metals have been reported, (except AlN and GaN).^{31,32} This is primarily due to a lack of suitable precursors. The design of a precursor that is sufficiently volatile to be transported in the vapour phase to the reactor and then breakdown cleanly to the desired product either by thermal decomposition routes, or by reacting in the gas phase is required. Whilst sufficiently volatile precursors have been isolated, the problems associated with deposition from these precursors limits their current applications. The advantage of such low temperature "molecular precursor" routes is the possibility of tailoring the precursors volatility and breakdown mechanism by modification of the ligand arrangement around the metal centre.

8.2 Equipment Design:

The equipment used for the deposition of titanium nitride on glass was essentially identical to that previously described for the deposition of ITO by APCVD,³³ except that the apparatus was designed and built specifically for the deposition of TiN / TiON. The gas handling lines and precursor delivery system were designed and built as part of the project, and coupled to a reactor provided by Pilkington Ltd. Several differences to the apparatus used for the deposition of In₂O₃ and ITO existed.

1. The gas handling lines used were fitted with Brookes mass flow controllers rather than Platon rotameters. Mass flow meters were used to provide vacuum tight seals, so that evacuation of the apparatus could be achieved.
2. The four way valve was removed from the system, allowing a shorter distance for the precursor to travel prior to entry into the reaction chamber.
3. No mixing chamber was used. Instead the precursor met the ammonia and nitrogen carrier gas stream just prior (3 cm) to the inlet to the distribution baffle.
4. Instead of a waste furnace to decompose any unreacted precursor, a vacuum pump was attached to the outlet of the reactor. This allowed the system to be evacuated prior to deposition. A 3 way valve system allowed the reaction gases to be vented during the deposition procedure.
5. VLSI gases were used as the ammonia and nitrogen source gases.
6. The bubbler was designed to be filled in a glove-box and the heating of the material designed for more accurate control at temperatures below 80°C, by the use of a Watlow band heater wrapped around the bubbler. The temperature of the bubbler was controlled by a Fuji temperature controller, with the control temperature readout being taken from a type K thermocouple inserted through the top of the bubbler into the precursor.

Figure 8-3 Diagram Of Titanium Nitride APCVD Equipment



8.3 Deposition Procedures:

Undercoated glass samples of dimensions 4mm x 9cm x 22 cm were first cleaned by the previously described method (see chapter 2). The substrate was loaded into the reactor, and gas lines evacuated using the vacuum pump. The system was evacuated to 0.1 Torr and the reactor heated to 350°C. The system was left to evacuate for 4-5 hours at this temperature. On cooling the reactor nitrogen carrier gas was used to backfill the reactor and gas lines and the reactor was then reheated to the deposition temperature under a continual flow of nitrogen.

On reaching the desired deposition temperature the carrier flow rates were set and the bubbler opened. After a timed deposition period the bubbler was closed and the reactor allowed to cool to room temperature under a flow of nitrogen. The glass sample was then removed from the reactor for analysis.

In order to test the equipment and establish an understanding of the deposition process, initial investigation of the deposition of titanium nitride utilised the precursor $\text{Ti}(\text{NMe}_2)_4$.

8.4 The Deposition of Titanium Nitride By the Thermal Decomposition of $\text{Ti}(\text{NMe}_2)_4$

An investigation of the deposition of titanium nitride by the thermal decomposition of the organometallic precursor $\text{Ti}(\text{NMe}_2)_4$, under a nitrogen carrier flow was conducted.

Table 8-2 Typical Growth Conditions Used For the Deposition of TiN By Thermal Decomposition.

Precursor Used:	[Ti(NMe ₂) ₄]
Substrate Used:	SICO Undercoated Glass
Gas Used:	Nitrogen.
Regulator Pressure:	0.5 bar
Substrate Temperature:	ca. 400°C
Inlet Gas Temperature:	ca. 23-25°C
Bubbler Temperature:	ca. 80-100°C
Main Gas Flow Rate:	ca. 800-1600 cc / min
Bubbler Gas Flow Rate:	ca. 250 cc / min
Heater Tape Setting:	Maximum (approximately 100-130°C)
Number Of Bakeout Cycles Used:	3
Time Of Coating Run:	15 Minutes

8.4.1 Discussion:

Initial runs were carried out with a total gas flow through the reactor of approximately 2-2.5 l / min. These low flows were used to provide a long residence time for the precursor in the reactor. However, the low flow rates resulted in significant reaction of the precursor on the sidewalls of the reactor chamber and poor coverage of the glass substrate with a coating, resulting in thick coatings at the front (inlet) end of the glass plate.

Increases in the total flow rate through the reaction chamber resulted in a reduction in this sidewall contamination of the reactor chamber. Better coverage of the glass substrate with a more uniform coating along the glass plate was also observed, although a reduction in the coating thickness was observed along the length of the glass plate, consistent with precursor depletion in the gas phase.

These results suggest that the thermal decomposition of the precursor occurs rapidly at the deposition temperature of 400°C. The change in the growth profile observed as the gas flow through the reactor was increased appears to be a result of a

more gradual thermal gradient in the gas phase, resulting in the precursor reaching a sufficiently high temperature for decomposition to occur further along the reactor.

Film growth at a range of deposition temperatures was conducted to confirm this. Alteration of the deposition temperature was observed to have a significant effect on the growth of films. Reduction of the substrate temperature below 350°C resulted in no film deposition on the substrate over a thirty minute growth period. The reduction in growth rate observed with the reduction in substrate temperature, suggests that thermal decomposition of the precursor is very slow at temperatures below 300°C, and most of the precursor is exhausted intact from the reactor under these deposition conditions.

Increasing the deposition temperature resulted in an increase in the growth rate, although the growth profile of the deposited film deteriorated at temperatures above 450-500°C, with the growth being concentrated towards the front edge of the glass plate, suggesting that thermal decomposition of the precursor is occurring rapidly at these temperatures. The best results were obtained at a growth temperature of 400°C, with the resulting films having a good film thickness uniformity along their length. The typical film thickness of the coatings grown under these conditions was 3000Å.

These results are consistent with previous work carried out by Suigiyama on quartz glass substrates, who observed that below 250°C no deposition occurs and that a peak growth rate is achieved at 400-500°C.²⁰ The change in the growth profile observed during this study, however, gives a clear indication that there is a clear temperature window in which uniform film growth can be achieved from this precursor.

All the films grown using the thermal decomposition of $\text{Ti}(\text{NMe}_2)_4$ had a black, blue coloration. This coloration is believed to be due to carbon impurities in the coating. Analysis of the coatings by Auger analysis confirmed this with a general composition of the coating being confirmed as, $\text{TiON}_{0.33}\text{C}_{0.67}$.

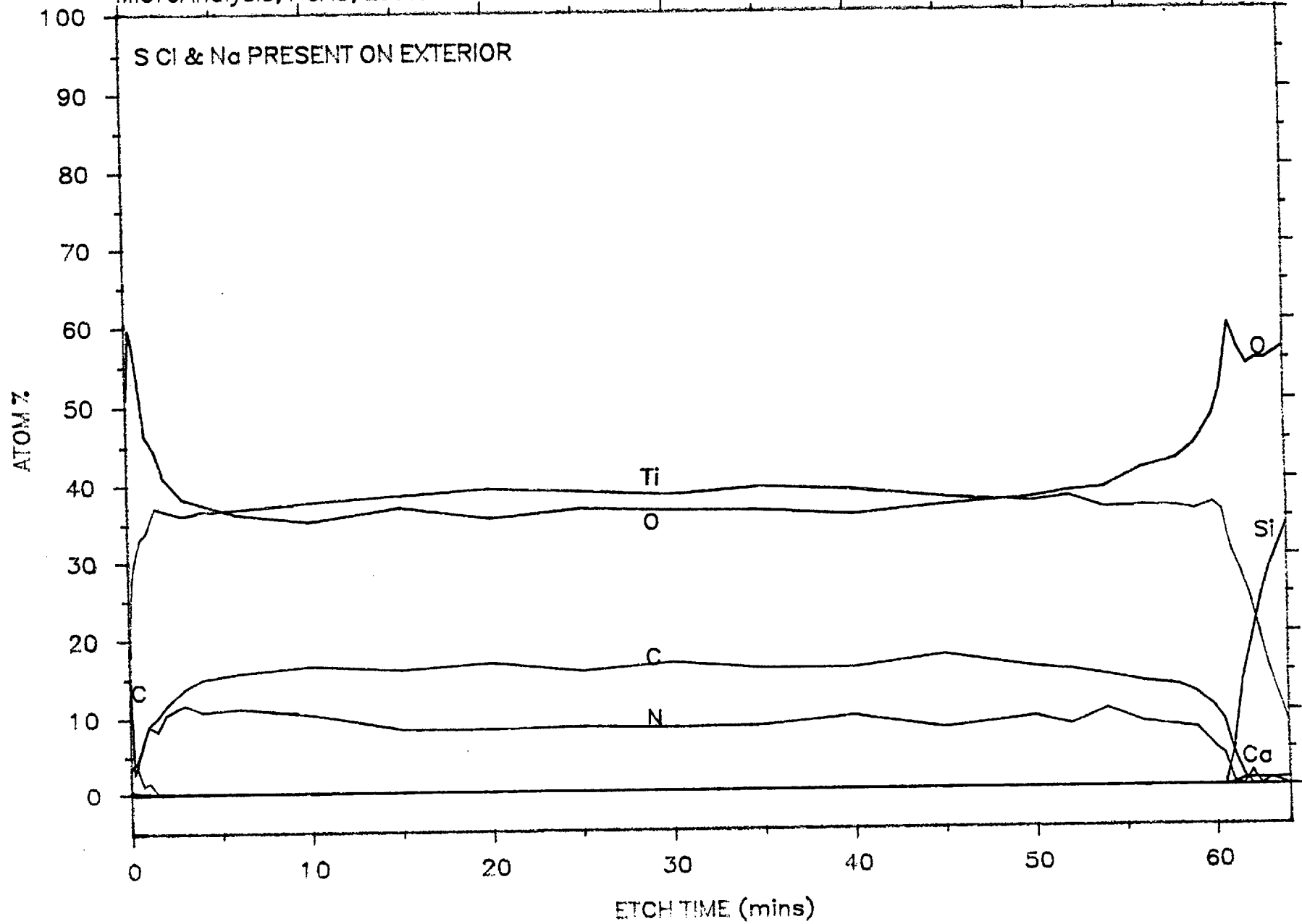


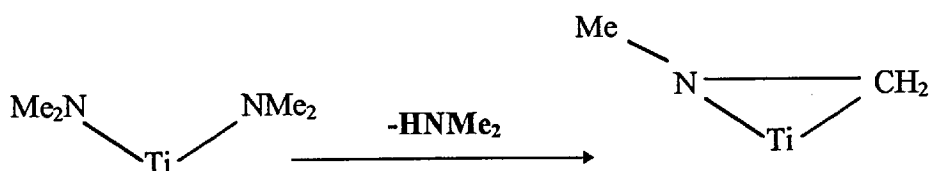
Figure 8-4 Auger Analysis Of Coating

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Careful examination of the coating showed that the top surface of the coating was more heavily oxygen contaminated than the bulk of the film, with the top surface having a composition of closer to TiO_2 and as such is very different to that of the bulk composition of the film.

Deterioration of the film due to oxygen attack at the surface of the film was not anticipated, since there were no reports in the literature for such an occurrence for MOCVD titanium nitride. The higher oxygen levels are believed to be due to either the incorporation of oxygen into the coatings structure, because of its porosity, or due to surface oxidation of the coating. Similar results have been observed for other metal nitrides such as aluminium nitride, and surface oxidation of the material was found to be responsible. The affinity of titanium for oxygen is consistent with surface oxidation being responsible for the higher oxygen levels at the top surface of the coating.

The high levels of carbon impurity observed during this study are consistent with previous work carried out on this precursor.^{22,24} The carbon incorporation is likely to be a result of β -hydride activation occurring and resulting in the incorporation of both organic and titanium bound carbon.



Analysis of the coatings produced using this deposition process, were all amorphous materials, and the SEM micrographs show the surface to be relatively flat consistent with an amorphous coating. The AFM spectra of the coating are complimentary also showing a very flat coating exists with low surface roughness.

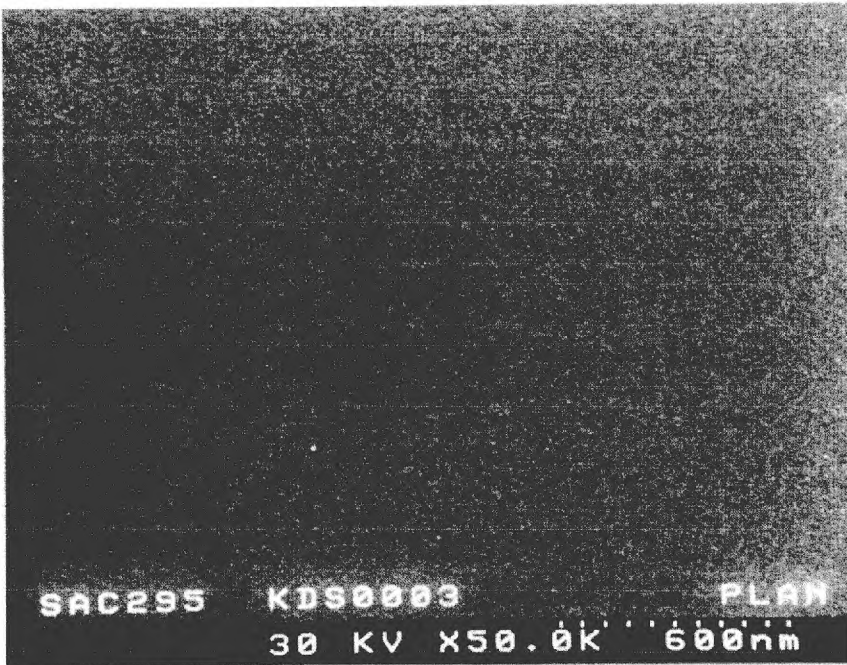


Figure 8-5 SEM Micrograph of TiN Coating

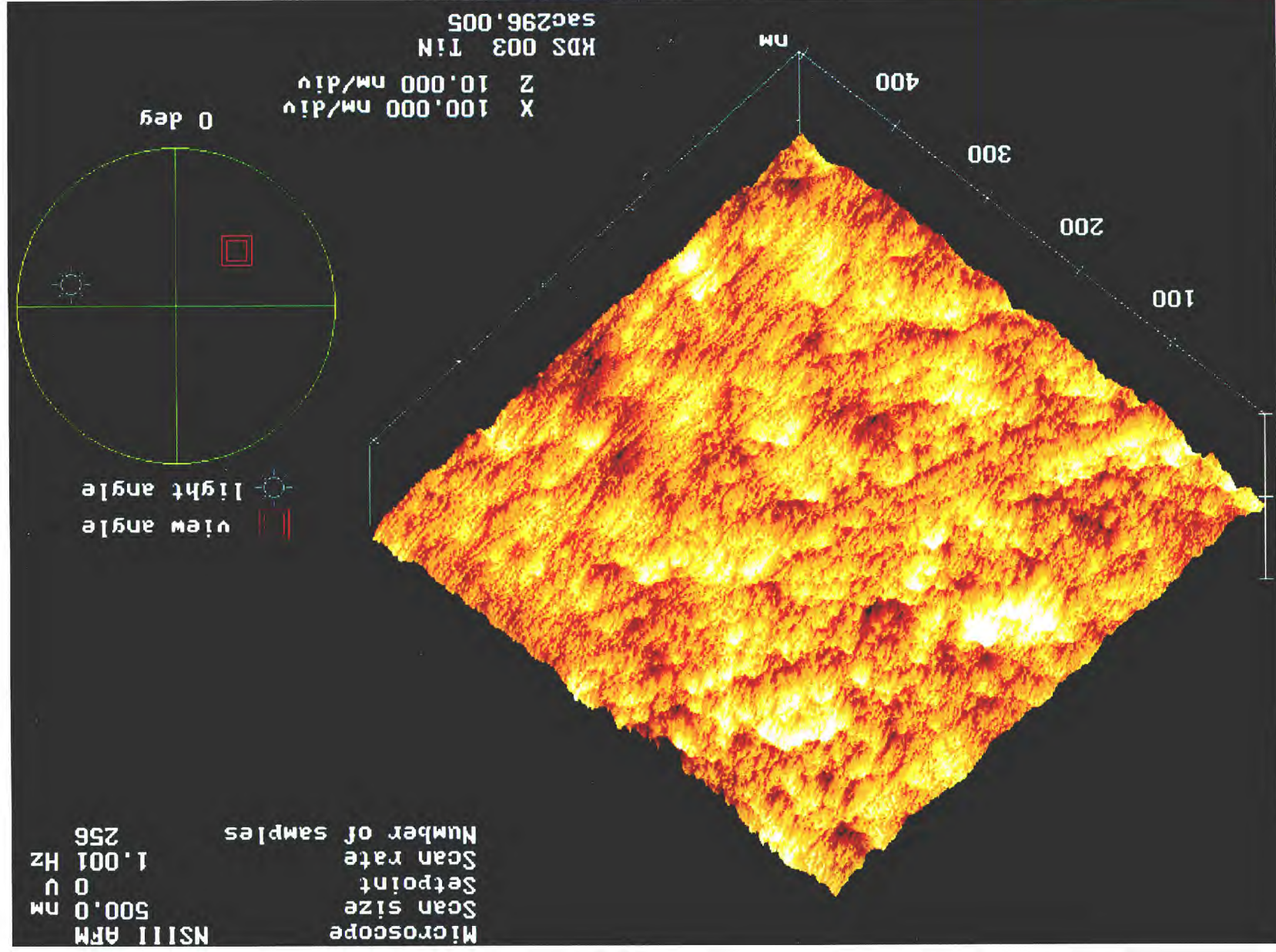


Figure 8-6 AFM Analysis of TiN Coating.

The amorphous nature of these materials is surprising, as previous reports of film deposition at these temperatures using the thermal decomposition of $\text{Ti}(\text{NMe}_2)_4$ have reported polycrystalline films grown on quartz substrates.²⁰ The polycrystalline nature of the films grown on quartz substrates may be due to either the change in substrate material, or due to a slight difference in the composition of the deposited material with increased impurity levels in the coating, resulting in the amorphous nature of the coating.

Despite the amorphous nature of the films produced, the films are relatively conductive with the graphs below showing the sheet resistance of a typical coating as it varies along the length and across the width of the glass plate.

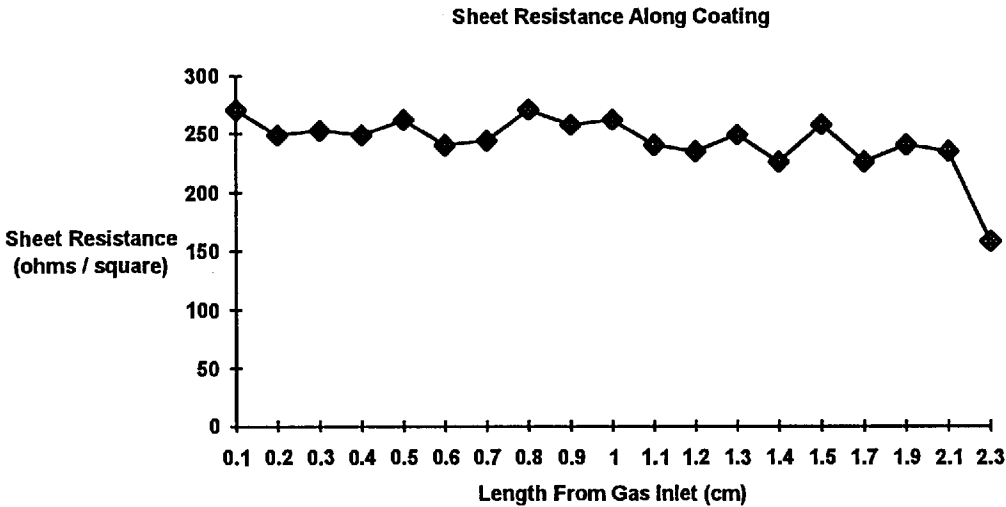


Figure 8-7 Variation of Sheet Resistance Along Coating of TiN

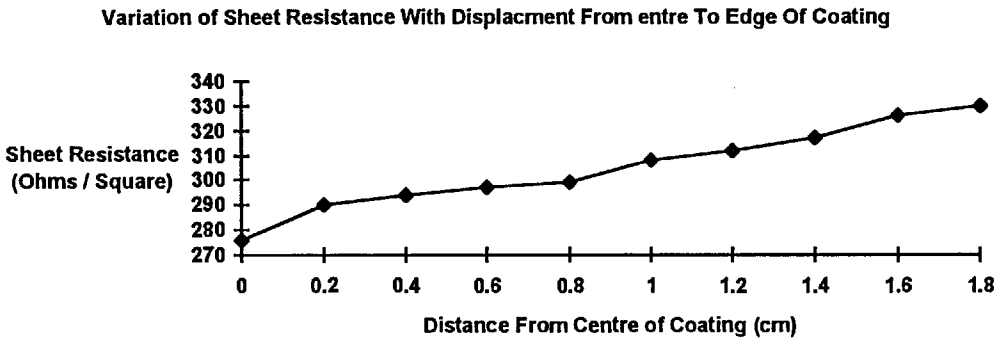


Figure 8-8 Variation of Sheet Resistance Across Coating of TiN

The above results show that the film uniformity is relatively good with a conductive film being obtained over the entire substrate. The first graph shows that the sheet resistance of the coating is approximately constant over the first 2cm of the film.

Whilst constant for the first two centimetres, it has been observed that the films then show a reduction in the sheet resistance to a minimum value at approximately 5-6 cm from the gas inlet, before increasing again towards the back of the coating. This is consistent with the growth profile, with the thickness gradually increasing to a maximum at approximately 6 cm from the front of the substrate before diminishing towards the gas exit.

The sheet resistance across the film is also consistent with the growth profile of the coating, with the lowest values coinciding with the thickest sections of the coating at the centre of the substrate and then increasing as the thickness of the coating diminishes towards the edges of the substrate.

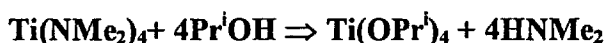
Whilst the presence of carbon and nitrogen in the coating can be expected as a result of the thermal decomposition of the precursor, the existence of oxygen in the coating cannot. The significant amounts of oxygen in the bulk material may only have come from:

1. Carrier gases used.
2. Oxygen impurity in the precursor.
3. Leaks in the reactor.
4. The glass substrate or sidewalls of the reactor chamber.

Whilst the first three of the potential problems were unlikely the fourth was not. Therefore it was believed that despite significant care being taken to remove water vapour and oxygen in the reactor, some oxygen donor was still present. It is believed that this oxygen source is water leeching from the glass substrate and reactor sidewalls at the deposition temperature.^{34,35} This is resulting in the significant oxygen incorporation in the bulk coating. The nature of the resulting reaction for the incorporation of oxygen in the final film could be initiated by a reaction of the type:



This reaction is likely to occur rapidly, with the amido complexes being known to react rapidly with compounds having weakly acidic hydrogen such as in alcohols and thiols.³⁶

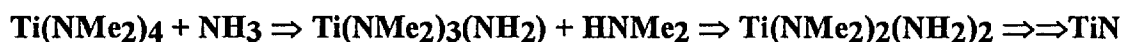


Such reactions are well known to occur in solution and have recently been utilised in CVD with oxide growth from $\text{M}(\text{NR}_2)_n / \text{O}_2$.³⁷

The poor quality of the films produced using this deposition technique, particularly with respect to the high levels of carbon impurity in the final coating made the coatings of little use for their optical properties. Therefore, an investigation of the addition of ammonia in the gas phase was conducted.

8.5 Growth of TiN From $\text{Ti}(\text{NMe}_2)_4$ and Ammonia

The addition of ammonia to the vapourised precursor has been seen from the literature to result in a reduction in the carbon content in the final film. The mechanism by which this reduction in carbon content is achieved is by the ammonia resulting in a transamination reaction occurring in the gas phase.



The intermediates then decompose to produce a TiN film with a lower carbon content.

8.5.1 Effect of Temperature on Film Growth.

Film growth of TiN from the $\text{Ti}(\text{NMe}_2)_4$ and NH_3 system, was investigated on glass substrates in the temperature range 150-450°C.

Table 8-3 Typical conditions used for film growth.

Precursor Used:	[Ti(NMe ₂) ₄]
Substrate Used:	Glass
Gas Used:	VLSI
Regulator Pressure:	0.5 bar
Substrate Temperature:	150-400°C
Inlet Gas Temperature:	ca. 23-25°C
Bubbler Temperature:	ca. 80-85°C
Main Gas Flow Rate:	ca. 1400-1600 cc / min
Bubbler Gas Flow Rate:	ca. 250 cc / min
Ammonia Gas Flow Rate:	ca. 10-20 cc/ min
Heater Tape Setting:	Maximum (100-120°C)
Number Of Bakeout Cycles Used:	Overnight Bakeout
Time Of Coating Run:	30 Minutes and 60 Minutes

As the deposition temperature was increased under identical gas flow rates, the coverage of the glass substrate with a coating was reduced. With increasing temperature the film growth consistently moved closer to the gas inlet of the reactor, until at a temperature of >400°C no coating on the substrate was observed, although some decomposed material was observed on the levelling plate of the reactor. This suggested that the precursor was pre-reacting and resulting in the poorer film growth. At all deposition temperatures a brown powder was observed to be formed and was blown through the reactor chamber. On removal of the substrate from the reactor, this material changed rapidly forming a whitish powder believed to be TiO₂. These results indicate that pre-reaction of the precursor with ammonia to form gas phase particulates is occurring.

The best films were achieved at a fairly low growth temperature of approximately 200°C, although film growth could be achieved at deposition temperatures as low as 150°C, if extended growth times were used, suggesting that the growth rate diminishes when the deposition temperature is decreased. Attempts at film growth at temperatures below this were unsuccessful, with no film being observed on the glass plate. It is believed that below 150°C the deposition temperature was too low to allow decomposition of the precursor or intermediates in the reaction.

One common feature of all the films grown under these conditions was the high contamination levels in the coatings. Analysis of a coatings grown under these conditions is shown below.

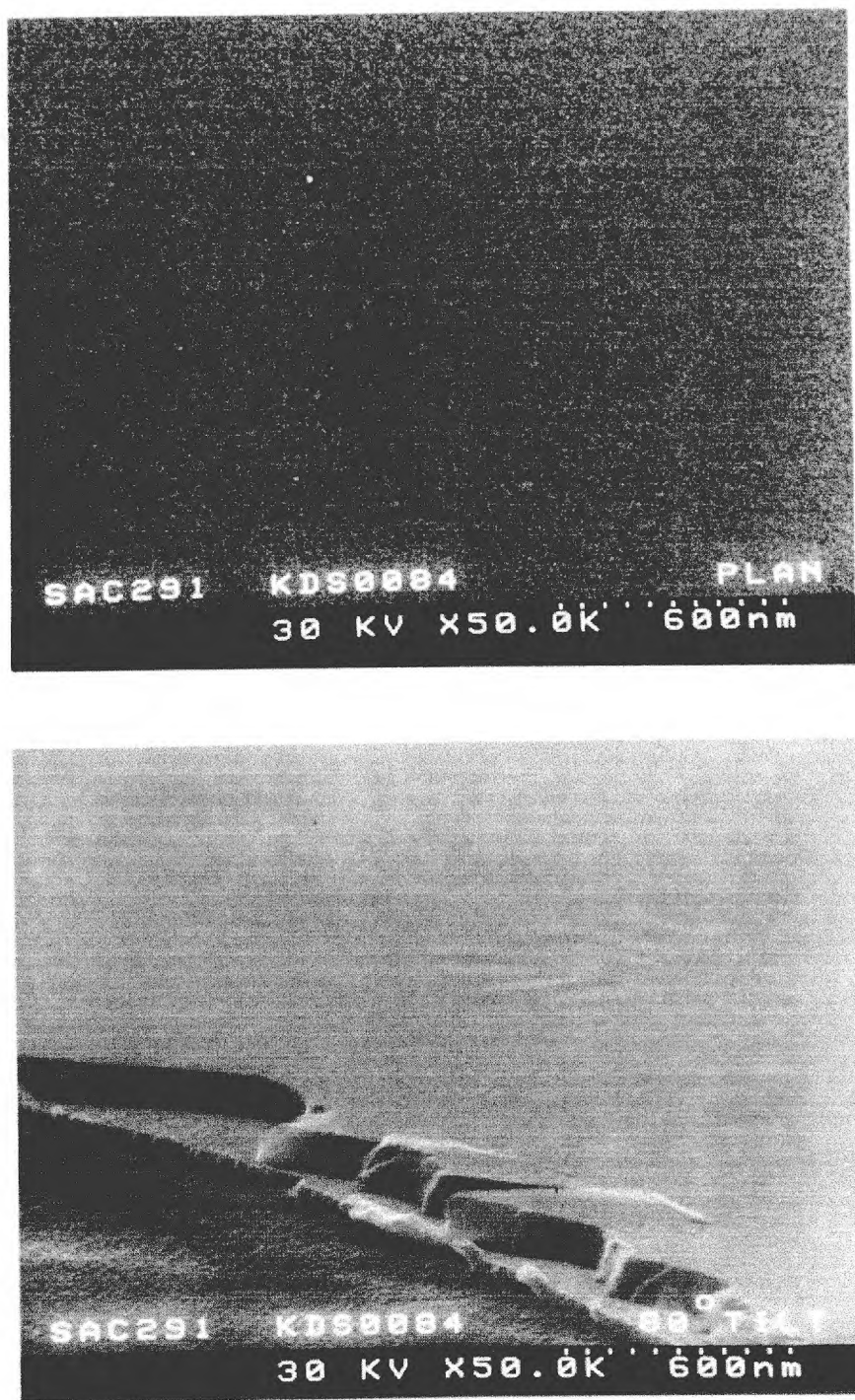
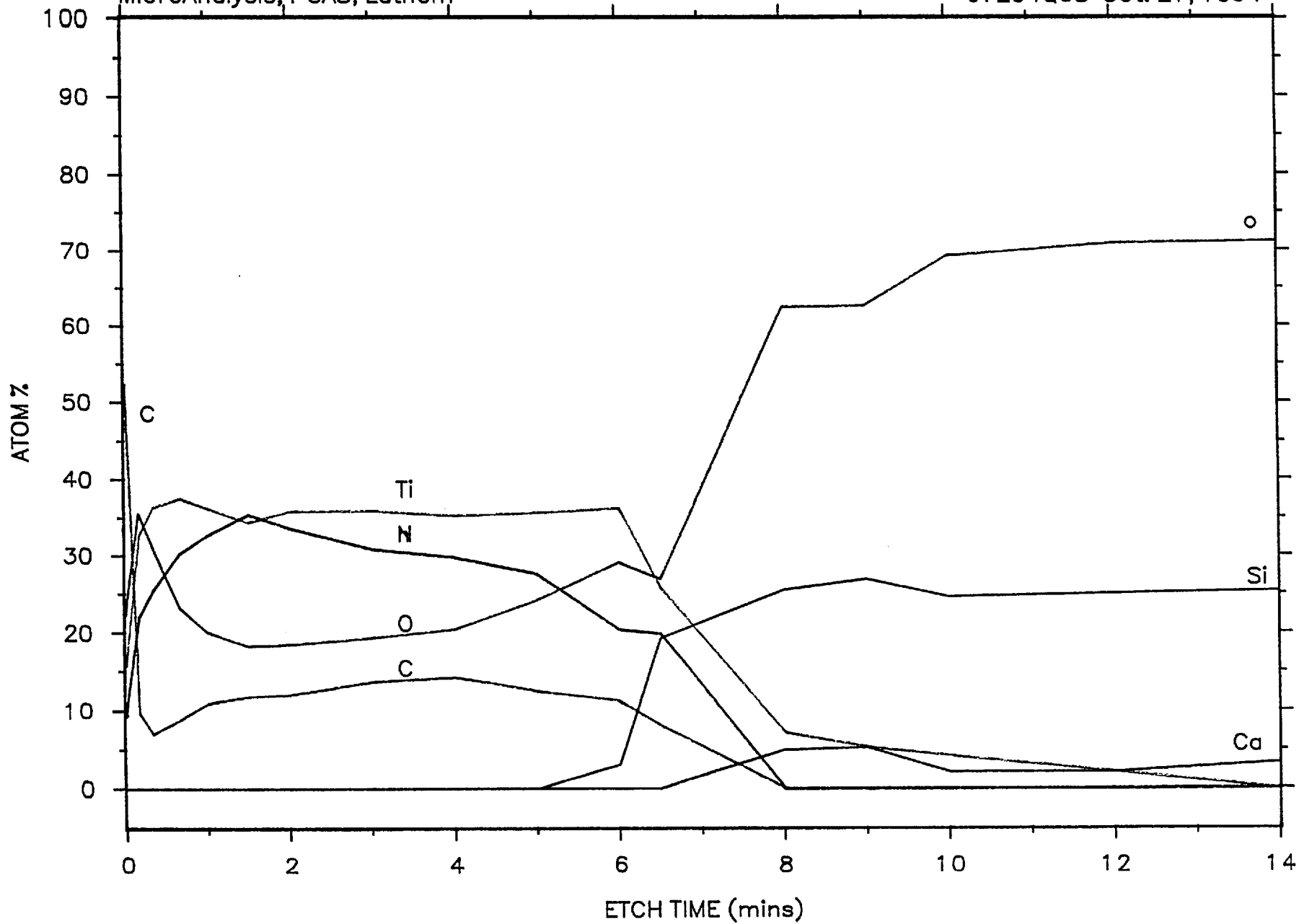


Figure 8-9 SEM Micrographs of Coating From $\text{Ti}(\text{NMe}_2)_4 + \text{NH}_3$

Figure 8-10 Auger Analysis of Coating From $\text{Ti}(\text{NMe}_2)_4 + \text{NH}_3$

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Both the carbon and oxygen impurity levels in the coatings were observed to increase as the deposition temperature was raised. Whilst previous reports have observed an increase in the carbon impurity levels as the deposition temperature was raised, due to competition between transamination reactions and thermal decomposition of the precursor by β -hydride elimination, the increase in oxygen impurity levels has not been observed.

The source of the oxygen contamination in the coating is unclear, but the successful transport of the precursor down the delivery lines into the reactor without the decomposition of the precursor to an oxide, suggests that the gases used and the delivery lines are free of oxygen contamination. This suggests that the bulk of the oxygen contamination of the film is occurring in the reactor chamber.

Previous literature reports have not reported oxygen contamination levels as high as those obtained in this study, although deposition was mainly on silicon rather than glass substrates. The oxygen contamination in the coatings may therefore be due to water leeching from the glass surfaces of the substrate and reactor. This is consistent with the results obtained, as a general increase in the oxygen contamination level in the film is observed as the deposition temperature is increased and more water leeches out of the substrate and reactor surfaces.

A similar result was previously observed for the deposition of titanium nitride by the thermal decomposition of $\text{Ti}(\text{NMe}_2)_4$. The failure of the ammonia to reduce the oxygen contamination in the film can be explained by the greater affinity of the titanium metal centre to the oxygen containing ligand. As such the level for oxygen incorporation in the final film would be expected to be related to the partial pressure of water vapour in the reactor tube.

Further evidence for the oxygen contamination of the film resulting from impurities in the glass, can be seen in the Auger analysis of the films obtained with and without the addition of ammonia. These exhibit higher oxygen impurity levels at the glass-coating interface. Water diffusing out of the glass, would attack the growing film, resulting in the higher oxygen contamination levels observed.

As with the thermal decomposition experiments the coatings also exhibit higher oxygen levels at the top surface than in the bulk of the coating, consistent with there being a degree of surface oxidation of the coating occurring deposition.

Whilst the films all exhibited oxygen contamination, reproducible coatings were not possible, suggesting that the impurity levels in the coater varied from run to run, with only general trends in the level of impurity being observed.

Analysis of the films by XRD again showed that the coatings were amorphous.

8.5.2 Effect of Ammonia Concentration.

At a set growth temperature of 250°C an investigation of the effect of ammonia concentration on the film growth was investigated.

Changing the ammonia concentration had several effects on film growth. Firstly it was observed that as the ammonia concentration in the gas stream was increased a clear deterioration in the growth profile of the films was observed. The film growth moved towards the inlet of the reactor, until above an ammonia concentration of 30% of the total gas stream no film growth on the glass substrate was observed. As the ammonia concentration was increased, it was also observed that a brown solid material was formed in the inlet baffle of the reactor. Isolation of this brown solid was not achieved, with the material changing colour to a whitish solid on exposure to air. This material is believed to be some form of titanium hydroxy or oxide species. The brown material is believed to be an intermediate formed in the gas phase which has insufficient volatility to be transported into the reactor. The intermediate is likely to be a result of transamination reactions in the gas phase resulting in a $\text{Ti}(\text{NMe}_2)_{4-x}(\text{NH}_2)_x$ species.

This investigation suggests that the ammonia results in pre-reaction of the precursors. Care must be taken therefore to prevent the formation of non-volatile intermediates by too much pre-reaction occurring in the gas phase prior to arrival at the deposition zone.

Previous reports of deposition using this precursor system have overcome this problem by minimising the distance over which the ammonia and precursor are pre-mixed to <5cm. Whilst this is convenient on a laboratory scale, any large scale process could not accommodate such a short pre-mixed distance without switching to a turbulent flow system, which would result in a reduction in the efficiency of the deposition process, and make it uneconomical.

A second effect of increasing the ammonia concentration, was that the degree of oxygen contamination in the films grown was reduced, although an increase in the pre-reaction between the precursor and ammonia was observed.

Low ammonia levels in the carrier gas stream resulted in coatings with high oxygen levels and poor electrical properties.

The reduction in the oxygen level with increasing ammonia concentration may be due to:

1. The production of a more stable intermediate, which does not react with any background oxygen as readily as the lone precursor.
2. The ammonia and oxygen are undergoing competing reactions.

The exact mechanism for the reduction in the oxygen contamination level is not clear, but even at high ammonia concentrations significant oxygen impurity levels in the coatings were observed compared with sputtered TiN. As a result of this contamination the coatings had poor optical and electrical properties.

8.6 Conclusions on the Growth of TiN From $Ti(NMe_2)_4$:

The APCVD of TiN thin films on glass substrates has been shown to be far more difficult than the deposition of oxide materials. The investigation of titanium nitride deposition has identified that film growth using the precursor $Ti(NMe_2)_4$ is extremely sensitive to oxygen contamination from sources such as diluent gases and reactor surfaces. As a result the deposited films have been seen to exhibit poor electrical and optical properties.

Both deposition from the thermal decomposition of the precursor and the deposition from a pre-reacted mixture of the precursor with ammonia has been investigated and these methods both produce films highly contaminated with oxygen. Initial studies with the thermal decomposition route have also been shown to result in high carbon contamination in the film, with this lowering the transmission of light through the coating.

The use of ammonia as a co-reactant whilst resulting in a reduction in the amount of carbon impurity and oxygen levels did not produce highly conductive titanium nitride comparable with that deposited by techniques such as sputtering. The poorer properties of the films are a result of impurities in the coating.

The investigation of titanium nitride deposition from $\text{Ti}(\text{NMe}_2)_4$ has highlighted three major problems. Firstly, the depositions have shown that reproducible coatings are difficult to obtain, due to varying levels of impurity incorporation in the films and this problem is believed to be associated with the apparatus design used for the experiments. The oxygen contamination has been seen to be the most variable, and is likely to be a result of water diffusing out of the glass substrate and reactor.

The second problem is associated with the growth profile. Film growth using the $\text{Ti}(\text{NMe}_2)_4$ both with and without ammonia has been shown to result in a poor growth profile, with most of the film growth occurring early on the glass plate. This suggests that the thermal stability of the precursors is poor at the deposition temperature. This problem is exacerbated by increases in the deposition temperatures in both systems.

The third potential problem, is the incompatibility of the system to a pre-mixed design. Mixing of the precursors with any reactive gas has been shown to be crucial, for both efficient use of chemicals and good film uniformity for CVD systems such as tin oxide deposition. In the investigation of the deposition of TiN from $\text{Ti}(\text{NMe}_2)_4$ and ammonia, pre-mixing has been observed to result in involatile intermediates being produced, which fail to deposit TiN. The precursors appear to react instantaneously on contact to form intermediates, which is believed to be a $\text{Ti}(\text{NMe}_2)_x(\text{NH})_y$ type species. Control of this pre-reaction appears necessary for good film growth. If too much pre-reaction occurs the involatile intermediates are formed and these result either in line blockage of the delivery system, or the intermediates pass through the reactor as a

powder without decomposing to give film growth. On the other hand if insufficient pre-reaction occurs, film deposition fails to occur, unless a deposition temperature of greater than 400°C is attained.

The deposition of TiN on glass substrates using a pre-mixed system therefore presents many problems. One of the most crucial requirements has been shown to be control of the degree of pre-reaction of the precursor with the ammonia carrier gas. The following sections describe the synthesis of new precursors for titanium nitride deposition. This study aimed to design novel molecular precursors for the deposition of TiN which provide a degree of control over the pre-reaction of the precursor with ammonia by tailoring the ligand sets used around the titanium metal centre. The by-products produced in the reactor from the thermal decomposition of the precursor have also been considered in an attempt to reduce contamination levels in the final film.

8.7 References

1. B. Holmberg, *Acta. Chem. Scand.*, **1962**, 16, 255
2. L. E. Toth and J. L. Margrave, *Transition Metal Carbides and Nitrides, Refractory Materials Vol. 7*, **1971**, Academic Press, New York
3. J. E. Sundgren, B. O. Johansson, S. E. Karlsson and H. T. Hentzell, *Thin Solid Films*, **1983**, 105, 367
4. M. K. Wu, O. Wang, J. Ashburn, C. Toring, R. Hor, R. Meng, L. Gao and Z. Huang, *Phys. Rev. Letts.*, **1987**, 58, 908
5. S. R. Kurtz and R. G. Gordon, *Thin Solid Films*, **1983**, 140, 277
6. A. V. Bolotov, *Symp. Proc. Int. Symp. Plasma Chem. 5th Ed.*, **1981**, 2, 850
7. H. Fabritius, *Arch. Eisenhuettenwer.*, **1974**, 45, 231
8. L. Maya, *Mater. Res. Soc. Symp. Proc.*, **1986**, 73, 401
9. W. Wuestefeld, *Angew. Chem. Int. Ed.*, **1988**, 27, 929
10. See Chapter 1 of this work
11. A. Sherman, *J. Electrochem. Soc.*, **1990**, 130(6), 1892
12. M. Kim and J. Chun, *Thin Solid Films*, **1983**, 107, 129
13. D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, **1960**, 3857
14. R. Fix, R. G. Gordon and D. M. Hoffman, *Chem. Mater.*, **1991**, 3, 1138
15. D. C. Bradley and E. G. Torrible, *Can. J. Chem.*, **1963**, 41, 134
16. R. K. Bartlett, *J. Inorg. Nucl. Chem.*, **1979**, 18, 2030
17. W. A. Nugent and R. L. Harlow, *Inorg. Chem.*, **1979**, 18, 2030
18. D. C. Bradley and I. M. Thomas, *Can. J. Chem.*, **1962**, 40, 449
19. D. C. Bradley and I. M. Thomas, *Can. J. Chem.*, **1962**, 40, 1355
20. K. Sugiyama, S. Pac, Y. Takahashi and S. Motojima, *J. Electrochem. Soc.*, **1975**, 1545
21. R. J. Schlutz, *Thin Solid Films*, **1983**, 104, 89
22. W. Schintlmeister, O. Pacher, K. Pfuffinger and J. Raine, *J. Electrochem. Soc.*, **1976**, 123, 924 and A. Schlegel, P. Wachter, J. NiNictel and H. Liugg, *J. Phys. C. Solid State Phys.*, **1977**, 10, 4889
23. L. H. Dubois, B. R. Zegraski and G. S. Girolami, *J. Electrochem Soc.*, **1992**, 139, 3603 and D. M. Hoffman, *Polyhedron*, **1994**, 13(8), 1169

24. R. Fix, R. G. Gordon and D. M. Hoffman, *Chem. Mater.*, **1990**, 2, 235
25. R. Fix, R. G. Gordon, D. M. Hoffman and S. Kurtz, *Thin Solid Films*, **1986**, 140, 277
26. W. A. Nugent and R. L. Harlow, *Inorg. Chem.*, **1979**, 2030
27. C. H. Winter, P. H. Sheridan, T. S. Lewkebandara, M. J. Hegg and J. W. Proscia, *J. Am. Chem. Soc.*, **1992**, 114, 1095
28. Y. Takahashi, N. Onoyama, Y. Ishikawa, S. Motojima and K. Sugiyama, *Chem. Lett.*, **1978**, 525
29. H. Burgend and H. Neese, *J. Organomet. Chem.*, **1970**, 21, 381
30. G. S. Girolami, J. A. Jensen and D. M. Pollina, *Mater. Res. Soc. Proc.*, **1988**, 121, 429
31. M. Morita, U. Norihiko, S. Isogai, K. Tsubouchi and N. Mikoshiba, *Jpn. J. Appl. Phys.*, **1981**, 20, 17 and Y. Chubachi, K. Sato and K. Kojima, *Thin Solid Films*, **1984**, 122, 259
- 32.. S. Lee, S. Park, P. Chong, *J. Mater. Chem.*, **1993**, 3(4), 347
- 33 See Chapter 2 of this work
34. C. G. Pantano, J. K. Kelso and M. J. Suscavage, *J. Am. Ceramic Soc.*, **1981**, 60, 1154 and in *Advances in Materials Characterisation*, **1983**, 15, Plenum, New York
35. H. Scholze, *J. Of Non-Crystalline Solids*, **1983**, 58, 295
36. M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides.*, **1980**, John Willey and Sons, New York
37. T. Tabuchi, Y. Sawado, K. Uematsu and S. Koshiba, *Jap. J. Appl. Phys.*, **1991**, 30, L1974
38. F. A. Cotton, G. Wilkinson and P. Gaus, *Basic Inorganic Chemistry*, **1987**, 2nd Edition, John Wiley and Sons, New York

9. Reaction of titanium tetrachloride with primary amines

9.1 Introduction

If a compound is to be a successful molecular precursor for APCVD, then it should have the following properties. Firstly the precursor should contain (or be able to react in the gas phase to produce a species which contains) the constituent elements of the film required. Secondly the precursor should have a sufficiently high vapour pressure to allow mass transport of the material in the gas phase to the reactor. A suitable vapour pressure would be approximately 1.2 kPa at 20°C ($\text{TiCl}_4(\text{liq})$).¹ Thirdly the precursor should decompose cleanly to produce the desired film, with minimal carbon, oxygen or halogen contamination. Finally the material should be available on a large scale, and be made from readily available (i.e. cheap) reagents, such as titanium tetrachloride. If the source chemicals are not readily available, the cost of the precursor production may become uneconomical.

In order to produce a suitable precursor, several important parameters have been considered:

1. Ease of preparation.

If the product is to be of use to industry, it must be easily manufactured, by a route that can be readily scaled up to industrial manufacturing levels.

2. Sensitivity of the compounds to air and moisture.

These materials are always likely to be air and moisture sensitive, but the materials must be sufficiently to have a usable shelf life. The effect of saturating the co-ordination sphere on the air sensitivity and volatility have to be considered.

3. Potential volatility.

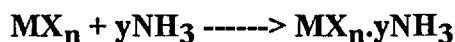
The following groups of ligands appear to be worth investigation.

- a. **Chelates** - e.g. thd. These are favored as chelated compounds are sufficiently volatile for CVD, e.g. $\text{Ba}_4(\text{thd})_8$, which is a precursor for BaO .²
- b. **Bulky ligands** - These appear to breakdown better in the CVD process, although have the disadvantage of increasing the carbon content
- c. **Hindered ligands** - These tend to favor monomeric species, which have a higher volatility than oligomeric species
- d. **Fluorinated Ligands** -. These ligands can give rise to more volatile compounds than their non-fluorinated equivalents.

Tailoring the use of these types of ligands should reduce aggregate growth and hence increase the volatility and mass transport of these materials. Therefore the reactions of TiCl_4 with these types of amines were investigated.

The reactions of metal halides with ammonia have been known for many years, and it is believed that these may involve the formation of two types of compounds:

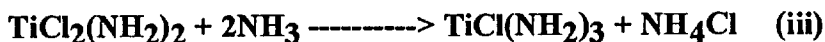
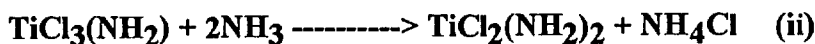
1. Addition Compounds



2. Solvolysis (Ammonolysis) Type Reactions



This later reaction has been extensively studied for titanium tetrachloride and the reactions that occur are believed to be:³



No Further Reaction

Many workers have shown that only three of the Ti-Cl bonds are solvolysed due to the increasing ionic nature of the remaining Ti-Cl bonds, preventing further reaction. The steps (i) - (iii) are likely to be reversible reactions, although it is believed that the ammonia co-ordinates to the titanium chloride, before solvolysis of the Ti-Cl bond occurs, i.e. $\text{TiCl}_4(\text{NH}_3)_x$.

The reaction of aliphatic amines with titanium tetrachloride have been less extensively studied than those with ammonia, but are seen to follow the same pattern, with both addition and solvolysis (ammonolysis) compounds being observed. Several differences have been noted though. Firstly, as you cross the series NH_3 , NH_2R , NHR_2 , NR_3 , the amines get progressively less ionising as a solvent, and as a result the extent of solvolysis is reduced, until no ammonolysis occurs and only addition compounds are formed with tertiary amines e.g.



Secondly, with increasing numbers of alkyl groups, the steric volume of the amine is increased, which results in the base strength of the amine (with a metal halide as the reference Lewis acid) decreasing.

Thirdly with secondary and tertiary amines problems due to reduction of the metal can occur.

Finally many of the products formed, unlike those with ammonia, are soluble in organic solvents and as such can be more readily purified.

It has been shown that various addition compounds and solvolysis compounds can be made from the reaction of titanium tetrachloride with the pure amine.^{5,6,7}

Table 9-1 Examples Of Various Materials Prepared By Solvolysis and Addition Reactions.

Reaction Mixture	Product
$\text{TiCl}_4 + \text{NMe}_3$	$\text{TiCl}_4 \cdot \text{NMe}_3 + \text{TiCl}_3 \cdot 2\text{NMe}_3$
$\text{TiCl}_4 + \text{NEt}_3$	$\text{TiCl}_4 \cdot \text{NEt}_3$
$\text{TiCl}_4 + \text{NHR}_2$ (R=Me, Et, Pr ⁿ)	$\text{TiCl}_3(\text{NR}_2) \cdot \text{NHR}_2$
$\text{TiCl}_4 + \text{NH}_2\text{R}$ (R=Me, Et, Pr ⁿ , Bu ⁿ)	$\text{TiCl}_2(\text{NHR})_2 \cdot 4\text{NH}_2\text{R}$

These compounds suggest that the alkyl group present on the amine affects the co-ordinating ability in two ways:

1. The donor power of the nitrogen is increased due to the inductive effect of the alkyl groups.
2. Increased size of the groups bound to nitrogen may result in steric strain which either weakens the donor-acceptor bond or results in a lower co-ordination number.

These factors appear to result in a variety of reactions being possible, with the amines steric bulk and nature (i.e. primary or secondary) determining the type of reaction that will occur.

The compounds of this type produced so far have not been fully investigated with regard to applications as precursors for chemical vapour deposition (CVD), with many having been produced in the 50's and early 60's before the recent interest in CVD. Only the ammonia adduct $\text{TiCl}_4(\text{NH}_3)_2$ has been studied for the deposition of titanium nitride by low pressure CVD.⁸ It was therefore decided to investigate the reaction of titanium tetrachloride with various new amines to find a sufficiently volatile compound for use as a precursor for the deposition of titanium nitride. The amines have been chosen for their ability to either protect the metal centre and as such reduce the degree of pre-reaction observed with a reactive gas such as ammonia e.g. the chelate $\text{HNMeCH}_2\text{CH}_2\text{NMe}_2$, or to breakdown cleanly to reactive by-products whilst still providing some steric bulk e.g. H_2NCMe_3 .

9.2 Experimental

9.2.1.1 Synthesis of $[\text{TiCl}_4(\text{HNMeCH}_2\text{CH}_2\text{NMe}_2)]$ (1)

In a flame dried Schlenk (1.5 ml, 11.8 mmol) of N,N,N-trimethylethylenediamine was dissolved in 20 ml of toluene, to yield a colourless solution. To the stirred solution 1.12ml (10.17 mmol) of TiCl_4 was added. This produced an exothermic reaction, with the solution turning a yellow / brown colour with some precipitate forming and white fumes of HCl evolved. The reaction mixture was then cooled using a cold water bath until the evolution of HCl had ceased. On heating the reaction mixture to approx. 50°C , the precipitate dissolved leaving a light brown solution, with a dark brown oil in the bottom of the Schlenk. 20ml of THF was added to the solution, and the solution was stirred at 70°C for 4 hours. This still failed to dissolve the oil completely, but a small amount of a fluffy brown precipitate was seen in solution. The solvent was then removed under vacuum to yield a light tan coloured precipitate, and taken up in 40ml of dichloromethane. On stirring at room temperature a large amount of the precipitate dissolved. The solution was then filtered to remove a small amount of undissolved precipitate, and the brown filtrate was cooled to -25°C for 72 hours. This produced a crop of brown crystals (2.07g, yield 82.3%) which were collected by filtration. **Melting Point:** 182°C ; **Infra Red:** (Nujol mull $\nu\text{ cm}^{-1}$) 3230(m), 1456(s), 1403(s), 1378(s), 1347(m), 1288(m), 1280(s), 1262(m), 1229(m), 1212(m), 1183(m), 1153(m), 1107(m), 1096(m), 1070(s), 1031(s), 1012(s), 930(s), 850(s), 802(m), 779(s), 728(m), 656(w), 584(m); **Infra Red:** (Hexa chloro butadiene mull $\nu\text{ cm}^{-1}$) 3231(m), 3021(w), 2989(w), 2934(w), 1634(w), 1612(m), 1564(s), 1454(s), 1419(m), 1403(w), 1288(m), 1229(w), 1212(w), 1184(w), 1070(m), 1031(m), 1011(s), 984(s), 943(s), 851(s), 794(s), 656(s), 584(w), 354(s), 286(s), 247(m), 241(m); **^1H NMR:** (90 MHz in $\text{d}_6\text{-DMSO}$ at 25°C): δ 2.51(s, 3H, CH_3), 2.65 s, 6H, CH_3), 3.52 (s, 2H, CH_2), 3.78 (s, 2H, CH_2), 10.97 (br.s, NH); **^{13}C NMR:** (22.61 MHz in $\text{d}_6\text{-DMSO}$ at 25°C): δ 33.91 (s, CH_3), 35.45 (s, CH_3), 53.01 (s, CH_2), 55.38 (s, CH_2); **Micro Analyses:** Calculated $[\text{TiCl}_4(\text{NHMeCH}_2\text{CH}_2\text{NMe}_2)]$; C: 20.56%, H: 4.80%. Found C: 20.72%, H: 4.95%; **Mass Spectrometry:** 351 $[\text{TiCl}_4\text{L}(\text{NMe}_3)]^+$, 321 $[\text{TiCl}_4(\text{NHMe})]^+$, 291 $[\text{TiCl}_4\text{L}]^+$, 276 $[\text{TiCl}_4(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NH})]^+$, 255 $[\text{TiCl}_3\text{L}]^+$, 221 $[\text{TiCl}_2\text{L}]^+$, 190 $[\text{TiCl}_4]^+$, 102 L, where L is

(Me₂NCH₂CH₂NHMe); TGA / DSC: 1 major weight loss of 71%, commencing at 320 and ending by 555°C

9.2.1.2 Synthesis Of [TiCl₄(C₆H₁₁NH₂)]_n (2)

In a flame dried Schlenk (3ml, 26.22 mmol) of cyclohexylamine was dissolved in 50ml of dichloromethane, producing a colourless solution. This solution was then cooled to -78°C, and (2.5ml, 22.7 mmol) of titanium tetrachloride was added. This produced an immediate exothermic reaction producing a purple / brown coloured solution, which on slowly warming to room temperature began to turn to a red colour, with an orange/red precipitate in it. The solution was too viscous to stir, however, so a further 30ml of dichloromethane was added. The solution was then filtered 3 times through very fine filter sticks and 5.9g of a red/orange precipitate was collected.

Melting Point: Decomposes 195°C, Melts 265°C; **Infra Red:** (Nujol mull ν cm⁻¹) 3414(m), 3396(m), 1771(w), 1583(s), 1572(s), 1281(m), 1263(m), 1168(m), 1055(s), 1029(s), 939(m), 917(m), 889(m), 865(m), 844(m), 795(m), 740(s), 614(m), 562(m), 481(w), 449(m); **Infra Red:** (Hexachlorobutadiene mull ν cm⁻¹) 3400(m), 3213(s), 3147(s), 2939(s), 2854(s), 1779(w), 1469(s), 1460(s), 1447(s), 1383(w), 1281(w), 1261(m), 1218(w), 1065(m), 1029(m), 741(w), 449(w), 369(m) cm⁻¹; **Micro Analyses:** Expected [TiCl₄(NHC₆H₁₁)]_n; C: 24.91%, H: 3.81%, N: 4.84%. Found C: 26.49%, H: 4.96%, N: 5.32%; **Mass Spectrometry:** [TiCl₄(NHC₆H₁₁)] 288, [TiCl(NHC₆H₁₁)] 183, [TiCl₂(NHC₆H₁₁)] 217, [NHC₆H₁₁]⁺ 98

9.2.1.3 Synthesis Of [TiCl₄(H₂NC(CH₃)₃)]_n (3)

In a flame dried Schlenk (2 ml, 19.03 mmol) of t-butylamine was dissolved in 30ml of dichloromethane, producing a colourless solution. This solution was then cooled to -78°C and (1.81 ml, 16.44 mmol) of titanium tetrachloride was added. This produced an immediate exothermic reaction, producing a orange/brown solid in an orange solution. On slowly warming to room temperature, and then stirring for 30 minutes, an orange precipitate in a dark red/orange solution is seen. The orange precipitate was then filtered off (3.5g) and the precipitate was cooled to -25°C, in order to see if crystals appear. No crystals appeared after 72 hours, and therefore the solvent was removed under vacuum to produce to a red/orange solid in approximately 5ml of solution. This solution was then dissolved in 40ml toluene and brought to boiling point. Some precipitate was formed and filtered off.

Melting Point: Decomposes 196°C, although gives off yellow gas 128°C. Does not melt at 330°C; **Micro Analyses:** Found C 18.51%, H 4.32%. Expected TiCl₄((CH₃)₃CNH₂) C 18.25%, H 4.18%;

Infra Red: (Nujol mull cm^{-1}) 3350(w), 1587(w), 1463(s), 1404(m), 1364(m), 1292(w), 1264(w), 1217(w), 1160(m), 1025(w), 918(w), 788(w), 737(w), 674(m), 500(w), 451(w), 387(s), 337(m), 303(w), 254(w), 227(m) cm^{-1} ; **Infra Red:** (Hexachlorobutadiene mull cm^{-1}) 3400 (w), 3350(w), 3197(m), 3072(m), 3044(m), 2969(m), 2934(m), 1587(m), 1470(m), 1405(m), 1363(w), 1292(m), 1261(m), 1217(w), 1095(m), 1024(m), 982(s), 942(m), 794(s); **Infra Red of Ligand:** 3352, 3281, 2959, 1868, 1732, 1682, 1471, 1385, 1245, 1228, 1117, 1036, 946, 847, 744 cm^{-1} ; **Mass Spectrometry:** 343 $[\text{Ti}_2\text{Cl}_6\text{L}]^+$ 100%, 309 $[\text{Ti}_2\text{Cl}_5\text{L}]^+$ 8%, 274 $[\text{Ti}_2\text{Cl}_4\text{L}]^+$ 3%, where $\text{L} = (\text{H}_2\text{NC}(\text{CH}_3)_3)$

9.2.1.4 Synthesis Of $[\text{TiCl}_2(\text{NMeCH}_2\text{CH}_2\text{NMe}_2)_2]_n$ (4)

In a flame dried Schlenk containing 30ml of toluene, (1.12 ml, 10.17 mmol) of titanium tetrachloride was added producing an orange coloured solution. This solution was then cooled to -78°C and (1.5 ml, 11.8 mmol) of N,N,N-trimethylethylenediamine was added. This produced an immediate exothermic reaction giving an oily black/brown solution, which was slowly warmed to room temperature. The solution was then recooled to -78°C and a further (1.5ml, 11.8 mmol) of N,N,N-trimethylethylenediamine was added. On slowly warming to room temperature, the solution began to precipitate a green coloured solid. The solution was then stirred at 55°C for 3 hours. The solution was then stripped to a third volume, and 25ml of dichloromethane was added. On stirring the green precipitate mostly dissolved, producing a black/brown solution. This was filtered and 1g of the green precipitate was collected.

Melting Point: $159-162^\circ\text{C}$; **Micro Analyses:** Found C: 37.63%, H 8.44%; expected $\text{TiCl}_2(\text{NMe}_2\text{CH}_2\text{CH}_2\text{NMe})_2$ C 37.38%, H 8.10%; **Infra Red of Initial Precipitate:** (Nujol mull cm^{-1}) 3400(m), 1936(w), 1868(w), 1733(w), 1683(w), 1652(w), 1607(m), 1590(m), 1457(s), 1406(m), 1377(s), 1338(m), 1286(m), 1262(m), 1240(m), 1224(m), 1194(m), 1153(m), 1133(m), 1119(m), 1077(m), 1039(m), 1086(m), 978(m), 948(m), 877(m), 850(m), 728(s), 694(m), 622(w), 549(w), 499(w), 464(w), 346(m), 280(m), 275(m) cm^{-1} ; **Infra Red of Initial Precipitate:** (Hexachlorobutadiene mull cm^{-1}) 2962(s), 2692(s), 2513(m), 2442(s), 1489(m), 1339(w), 1286(w), 1261(w), 1076(w), 1039(m), 1006(m), 854(s), 335(w) cm^{-1} . ^1H NMR: (90 MHz in C_7D_8 at 20°C): δ 2.0 (m, CH_3), 2.3 (m, CH_3), 2.5 (br. m, CH_2), 2.6 (m, CH_2); ^{13}C NMR: No Spectra as not sufficiently soluble; **Mass Spectrometry:** 321 $[\text{TiCl}_2(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)_2]$ 3%, 280 $[\text{TiCl}_2(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe})(\text{NMe}_3)]$ 18%, 220 $[\text{TiCl}_2(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe})]$ 5%, 207 $[\text{TiCl}_2(\text{MeNCH}_2\text{CH}_2\text{NMe})]$ 100%, 148 $[\text{TiCl}_2(\text{NMeH})]$ 12%; **TGA/DSC:** 1 major weight loss of 92.8%, commencing at 255 and ending by 315°C

9.2.1.5 Synthesis Of $[\text{TiCl}_2(\text{C}_6\text{H}_{11}\text{NH})_2]$ (5)

In a flame dried Schlenk 30ml of dichloromethane and (1 ml, 9.08 mmol) of titanium tetrachloride was added producing a pale yellow coloured solution. The solution was then cooled to -78°C and then (3.61 ml, 31.56 mmol) of cyclohexylamine was added. This gave an immediate very exothermic reaction, with a red/brown solution being produced. The solution was then allowed to warm to room temperature. This produced a very thick unfilterable solution. The solvent was therefore removed under vacuum, producing a reddish coloured solid. To this solid 40ml of toluene was added. This produced a red solution with an amount of red solid in the solution. The solution was then filtered and 3.41g of a red precipitate was collected. The red filtrate was then cooled, but no product appeared.

Melting Point: Decomposes 110°C , Melts $193\text{--}195^\circ\text{C}$; **Infra Red:** (Nujol mull $\nu\text{ cm}^{-1}$) 3227(w), 1587(w), 1465(s), 1405(m), 1292(m), 1197(w), 1161(m), 1094(m), 1028(m), 955(w), 918(m), 801(m), 737(m), 676(m); **Infra Red:** (Hexachlorobutadiene mull $\nu\text{ cm}^{-1}$) 3227(w), 29224(s), 2861(s), 1496(w), 1484(w), 1449(m), 1377(w), 1260(w), 1100(w), 1030(w), 729(w), 695(w), 501(w), 475(w), 465(w), 422(w), 354(m), 281(w), 227(w) cm^{-1} ; **^1H NMR:** (90 MHz in deuterated pyridine 25°C) 1.1 (quartet, CH_2), 1.6 (quartet, CH_2), 2.35 (doublet, CH_2), 3.3 (doublet, NH), 3.5 (multiplet, NH), 7.1 (multiplet); **^{13}C NMR:** (22.61 MHz in deuterated pyridine 25°C) 21.3 (s, CH_2), 24.6 (d, CH_2), 24.7 (s, CH_2), 26.2 (s, CH_2), 32.2 (s, CH_2), 34.5 (s, CH_2), 50.6 (s, CH_2), 74.8 (s, CH_2), 125.8 (s, NCH_2), 128.7 (s, NCH_2), 129.4 (s, NCH_2); **Mass Spectrometry:** 293 $[\text{TiCl}_2(\text{NMeCH}_2\text{CH}_2\text{NMe}_2)_2]$, 220 $[\text{Ti}(\text{NMeCH}_2\text{CH}_2\text{NMe}_2)]$, 264 $[\text{TiCl}_2(\text{NMeCH}_2\text{CH}_2\text{NMe}_2)(\text{NMeCH}_2\text{NMe})]$, 221 $[\text{TiCl}_2(\text{NMeCH}_2\text{CH}_2\text{NMe}_2)(\text{NMe}_2)]$, 134 $[\text{Ti}(\text{NMeCH}_2\text{CH}_2\text{NMe}_2)]$; **TGA/DSC:** 1 major weight loss of 92.8%, commencing at 255°C and ending by 315°C

9.2.1.6 Synthesis Of $[\text{TiCl}_2(\text{NHCMe}_3)_2]$ (6)

In a flame dried Schlenk, 40ml of dichloromethane and (2 ml, 18.17 mmol) of titanium tetrachloride was added producing a pale yellow coloured solution. This solution was then cooled to -78°C and (6.64 ml, 63.19 mmol) of t-butylamine was added. This produced an immediate, very exothermic reaction which produced a brown/red solution with the first few drops but as more amine was added the solution turned an orange colour and a precipitate was seen in the solution. On slowly warming to room temperature over 48 hours, this precipitate was seen to change colour to a dark red colour. The solution was then filtered with 8g of the red solid being collected.

Melting Point: Looses initial red colour $158\text{--}160^\circ\text{C}$. Melts $228\text{--}232^\circ\text{C}$; **Infra Red:** (Nujol mull $\nu\text{ cm}^{-1}$) 3300(w), 3124(m), 2600(m), 2501(m), 2079(w), 1962(w), 1612(w), 1511(m), 1460(s), 1403(m), 1377(s), 1356(m), 1294(m), 1217(m), 1167(m), 1092(m), 1027(m), 995(m), 800(m), 723(w), 618(m), 508(w), 451(m), 390(m), 346(m), 298(m), 261(m), 246(w); **Infra Red:** (Hexachlorobutadiene mull $\nu\text{ cm}^{-1}$) 2969(s), 2897(s), 2805(s), 2711(m), 2601(m), 2502(m), 2080(m), 1962(w), 1779(w), 1511(s), 1479(m), 1458(m), 1403(m), 1378(m), 1356(m), 1295(m), 1261(m), 1217(s), 1092(m), 1027(m), 610(s); **^1H NMR:** (270MHz CDCl_3 at 20°C) 1.4 (Me, 9H), 7.6 (br. NH, 1H); **^{13}C NMR:** 20.4(CH_3), No quaternary carbon observable; **Mass Spectrometry:** 263 $[\text{TiCl}_2(\text{NHCMe}_3)_2]$, 190 $[\text{TiCl}_2(\text{NHCMe}_3)]$, 176 $[\text{TiCl}_2(\text{NHCMe}_2)]$; **Micro Analyses:** Expected $\text{TiCl}_2(\text{NHCMe}_3)_2$ C: 36.50, H: 7.60, N: 10.65%. Found: C: 36.52%, H: 8.94, N: 10.60%

9.3 Results and Discussion:

9.3.1 Synthesis Route:

The synthetic route used for the reactions described in this section was the addition of neat TiCl_4 to a cooled solution of the amine in a dried organic solvent (toluene or dichloromethane). This has resulted in either addition or solvolysis reactions depending upon the stoichiometry of the reaction.

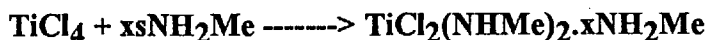
The reaction of one equivalent of the pure amine with titanium tetrachloride results in the formation of addition compounds of the general formula TiCl_4L (where $\text{L}=\text{diamine}$). If an excess of the amine is added, then solvolysis of one or more Ti-Cl

occurs with the liberation of HCl, and the formation of a Ti-N bond. These reaction types have both been previously reported.

Addition Reaction:⁹



Solvolysis Reaction:



The addition compounds previously reported in the literature have a six coordinated titanium metal centre, with the adducted material filling the space around the metal centre to produce an octahedral or distorted octahedral compound.

The addition of the titanium tetrachloride to the amine solution in this investigation was carried out at -78°C, in order to slow down the exothermic reaction between the titanium tetrachloride and the amine. All the synthesis was performed under an inert atmosphere using standard vacuum line techniques and Schlenk glassware, due to the air and moisture sensitivity of the products produced. All the manipulations of the products were then carried out in an argon filled glovebox to ensure that no decomposition of the product occurred.

9.3.2 Melting Point Data:

Compounds 1-6 are all solid materials that exhibit a wide range of colours. The materials all have relatively high melting / decomposition points, suggesting that they are fairly stable, despite their air and moisture sensitivity. The melting / decomposition points and colours of the compounds are listed in Table 9-2.

Table 9-2 Physical Properties and Characteristics of Compounds (1) - (6)

Compound	Colour	Melting Point
[TiCl ₄ (NMe ₂ (CH ₂) ₂ NMeH)] (1)	Yellow Crystals	Melts 182°C
[TiCl ₄ (NH ₂ C ₆ H ₁₁)] (2)	Red Solid	Dec. 195°C, Melts 265°C
[TiCl ₄ (NH ₂ CMe ₃)] (3)	Orange Solid	Dec. 196°C,
[TiCl ₂ (NMe ₂ (CH ₂) ₂ NMe) ₂] _n (4)	Green Solid	Melts 159 - 162°C
[TiCl ₂ (NHC ₆ H ₁₁) ₂] _n (5)	Red Solid	Dec. 110°C, Melts 193-195°C
[TiCl ₂ (NHCMe ₃) ₂] _n (6)	Red / Orange Solid	Melts 228 - 232°C

Table 9-2 illustrates that these compounds have melting / decomposition points in excess of 150°C. Due to the high melting points of these materials it is unlikely that they would be of use as precursors for the APCVD of TiN thin films, because with such high melting points the mass transport of these materials in the gas phase in sufficient quantity for film growth would be very difficult. Ideal precursors would be liquids with high vapour pressures which would allow easy mass transport in the gas phase.

These materials also have the major disadvantage that they contain high proportions of chlorine. This is a disadvantage, as chlorine contamination in the films has a detrimental effect on the electrical properties of coatings, by causing scattering of the carriers. Problems with solid precursors for CVD and the problems of chlorine contamination are well documented. Whilst many new methods for the development of a stabilised vapour flow from solid precursors are under investigation, both of these problems need to be solved if an industrially viable CVD precursor is to be developed.^{10,11}

9.3.3 Study of Addition Reactions:

The reaction of TiCl₄ with one equivalent of the amines, N,N,N, trimethylethylenediamine, t-butyl-amine and cyclohexylamine has been investigated. The

products produced by the addition reaction to produce the products (1) $\text{TiCl}_4(\text{NHMeCH}_2\text{CH}_2\text{NMe}_2)$, (2) $[\text{TiCl}_4(\text{NH}^t\text{Bu})]_n$, (3) $[\text{TiCl}_4(\text{NHC}_6\text{H}_{11})]_n$, have been studied by a range of spectroscopic techniques.

9.3.3.1 Structures Of (1) - (3):

Previous literature reports suggest that the addition reactions of TiCl_4 with oxygen and nitrogen containing ligands results in an increase in the co-ordination number of the titanium metal centre. Due to the preference of titanium for 4 or 6 co-ordination, addition compounds often results in the formation of two adducted bonds to the titanium centre resulting in a six co-ordinate octahedral titanium centre, as in $\text{TiCl}_4(\text{thf})_2$. The amine $\text{HNMeCH}_2\text{CH}_2\text{NMe}_2$ can act as a chelate and thus satisfy the co-ordination sphere of the titanium with six bonds, four Ti-Cl and two Ti-N adducted bonds. The single crystal X-ray structure of compound (1) is in agreement with this showing the complex to be an adduct of TiCl_4 with one N,N,N-trimethylethylenediamine ligand acting as a chelate and producing a six co-ordinate distorted octahedral titanium centre.¹² The chelate bridge can be seen to have a delta-gauche conformation.

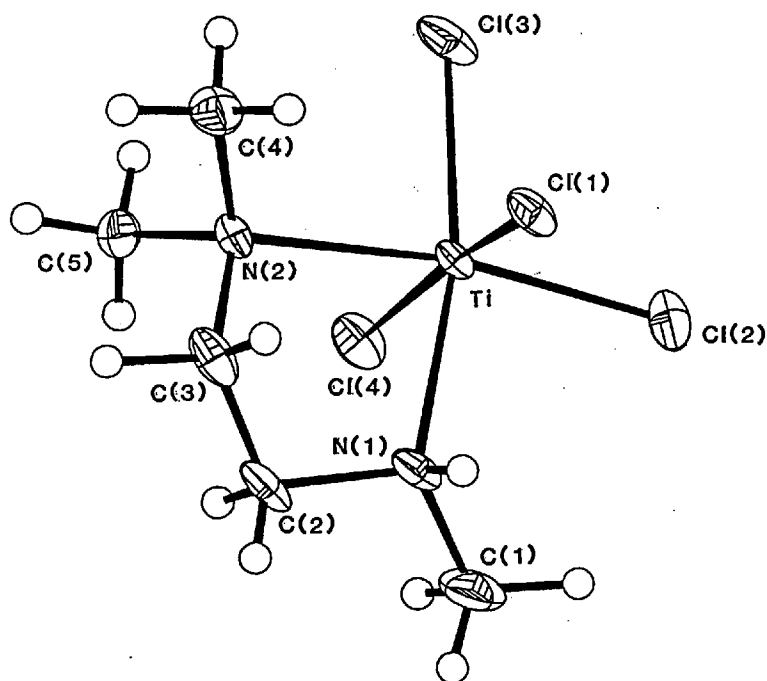


Figure 9-1 Single Crystal X-Ray Structure Of $\text{TiCl}_4(\text{HNMeCH}_2\text{CH}_2\text{NMe}_2)$

The Cl-Ti-Cl angles vary from Cl(2)-Ti-Cl(1) 91.5(1)^o to Cl(4)-Ti-Cl(1) 169.6(1)^o. The chelate is also exerting a *trans* effect on the chlorine directly opposite it (Cl(3)), shortening the Ti-Cl(3) bond length from around 2.281(3) Å to 2.245(3) Å. The two Ti-N bond lengths also vary in the complex. This difference is as one might expect with the less sterically hindered N(1) being able to get closer in to the titanium centre than the more sterically hindered N(2). This is illustrated by the bond lengths with Ti-N(1) 2.227(4) Å whilst the Ti-N(2) 2.316(4) Å.

Table 9-3 Selected Bond Angles(°) and Bond Lengths(Å) for compound (1)

Cl(1)-Ti	2.291(3)	Cl(2)-Ti	2.281(3)
Cl(3)-Ti	2.245(3)	Cl(4)-Ti	2.279(3)
N(1)-Ti	2.227(4)	N(2)-Ti	2.316(4)
C(1)-N(1)	1.489(5)	C(2)-N(1)	1.485(5)
C(3)-N(2)	1.491(5)	C(4)-N(2)	1.488(5)
C(5)-N(2)	1.490(5)	C(3)-C(2)	1.508(6)
Cl(2)-Ti-Cl(1)	91.5(1)	Cl(3)-Ti-Cl(1)	94.8(1)
Cl(3)-Ti-Cl(2)	101.1(1)	Cl(4)-Ti-Cl(1)	169.6(1)
Cl(4)-Ti-Cl(2)	91.7(1)	Cl(4)-Ti-Cl(3)	94.3(1)
N(1)-Ti-Cl(1)	84.4(2)	N(1)-Ti-Cl(2)	91.3(2)
N(1)-Ti-Cl(3)	167.5(1)	N(1)-Ti-Cl(4)	85.6(2)
N(2)-Ti-Cl(1)	85.3(2)	N(2)-Ti-Cl(2)	169.3(1)
N(2)-Ti-Cl(3)	89.3(2)	N(2)-Ti-Cl(4)	89.7(2)
N(2)-Ti-N(1)	78.2(2)	C(1)-N(1)-Ti	119.1(3)
C(2)-N(1)-Ti	109.8(3)	C(2)-N(1)-C(1)	111.2(3)
C(3)-N(2)-Ti	105.7(3)	C(4)-N(2)-Ti	114.0(3)
C(4)-N(2)-C(3)	108.0(4)	C(5)-N(2)-Ti	114.5(3)
C(5)-N(2)-C(3)	108.6(3)	C(5)-N(2)-C(4)	105.8(3)
C(3)-C(2)-N(1)	108.5(3)	C(2)-C(3)-N(2)	110.6(4)
H(1N)-N(1)	0.851(41)		

Unlike compound (1), the amines used for the production of compounds (2) and (3) are monodentate ligands, donating through the nitrogen. The addition of one equivalent of the amine, would result in a five co-ordinate titanium metal centre. A five co-ordinate titanium compound is not a preferred co-ordination number for titanium, although some indirect evidence of five co-ordinate monomeric species does exist for compounds of the type $\text{Ti}(\text{OR})_3(\text{MeNCH}_2\text{CH}_2\text{NMe}_2)$. As a result the compounds are likely to be dimeric, with chloride bridges linking the two titanium metal centres.¹³ Dimerisation of titanium compounds by the formation of chloride bridges has previously been reported for titanium compounds such as $\text{TiCl}_3(\text{acac})$ where chloride bridging result in each metal atom having a octahedral co-ordination.¹⁴

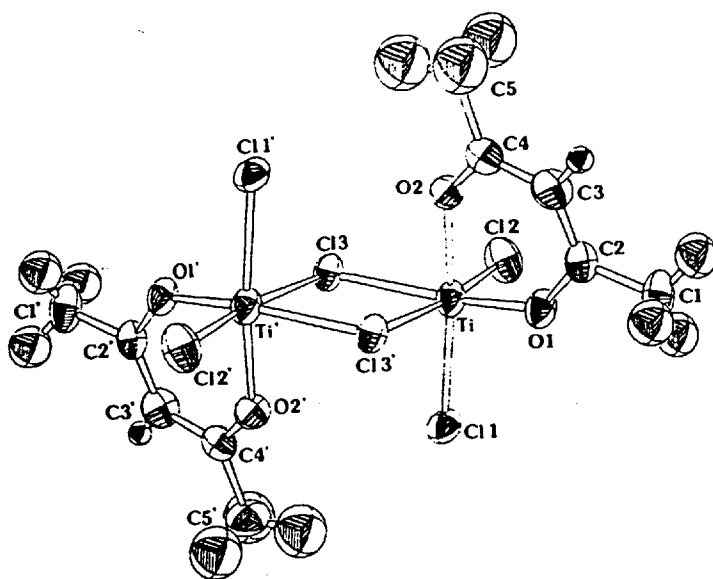


Figure 9-2 Crystal Structure Of $\text{TiCl}_3(\text{acac})$

9.3.3.2 Infra Red Data For (1) - (3)

The addition compounds (1)-(3) have been studied by infrared spectroscopy as nujol and hexachlorobutadiene mulls between KBr plates. To ensure no oxygen ingress, the samples were made up in a glove box and a press-lock holder was used to hold the plates in an air tight seal.

The main features of the infrared spectrum of these compounds are listed in Table 9-4.

Table 9-4 Main Features Of IR-Spectra Of (1)-(3)

Compound	ν N-H	ν Ti-Cl
(1)	3446 cm^{-1}	501 (br.) cm^{-1}
(2)	3414 cm^{-1}	481 (br.) cm^{-1}
(3)	3400 cm^{-1}	500 cm^{-1}

The stretches seen are in general agreement with previous literature on adducted compounds of TiCl_4 , with the broad Ti-Cl stretch that is seen in the compounds only being shifted very slightly from its position in neat TiCl_4 at 500 cm^{-1} ,¹⁵ due to slight changes in the Ti-Cl bonds resulting from the change in the co-ordination sphere of the titanium. These compounds also show the expected C-H stretches and deformations due to the ligands at approximately 2950 and 1400 cm^{-1} respectively in the hexachlorobutadiene mull.¹⁸

Determination of bridging and terminal Ti-Cl bonds has not been possible for compounds (2) and (3) due to the broad nature of the Ti-Cl band and its relative low intensity.

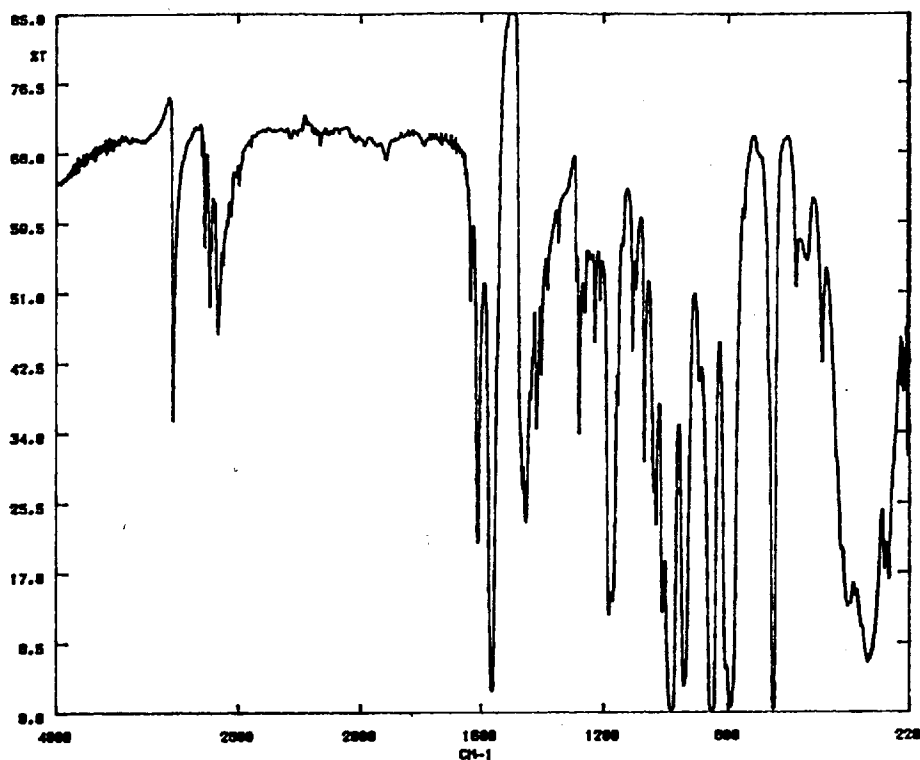


Figure 9-3 Infrared Spectrum Of $\text{TiCl}_4(\text{NHCH}_2\text{CH}_2\text{NMe}_2)$ (Nujol Mull)

9.3.3.3 NMR Studies Of (1) - (3)

The ^1H NMR of compound (1) shows the presence of three non-equivalent methyl groups, although two of these appear to overlap slightly at δ 2.65. The spectrum also shows the presence of two inequivalent CH_2 groups and of the NH proton. The NH proton peak is very broad due to its fast relaxation on the NMR timescale and appears at δ 10.97. The ^{13}C NMR spectrum of this compound is also as expected, showing the inequivalent methyl and CH_2 groups on the ligand. The inequivalence of the methyl groups in both NMR spectra is consistent with the position of the groups within the structure resulting in their non-equivalence. The dative bound NMe_2 group, results in the two Me groups being in non-equivalent electronic environments, and thus

explains their non-equivalence in the ^{13}C NMR spectrum. The third methyl group is also inequivalent due to its different electronic environment in the ligand.

Due to the poor solubility of compounds (2) and (3) in a range of deuterated solvents, analysis of these materials by NMR spectroscopy was not possible.

9.3.3.4 Mass Spectrometry Of (1) -(3):

The mass spectral analysis of compounds (1)-(3) was carried by electron impact spectroscopy (EI^+). The mass spectrum of compound (1) showed clear evidence of the mother ion ($\text{TiCl}_4(\text{NMeHCH}_2\text{CH}_2\text{NMe}_2)$) at 321 a.m.u. Below this several species were observed in the mass spectrum due to the fragmentation of the amine ligand on the molecule. Some evidence was also observed for the presence of gas phase produced species, with species with m/z above the parent ion being attributable to fragmentation products reacting, to produce new species.

Compound (2) also shows the presence of a TiCl_4L (where $\text{L}=\text{amine}$) species in the mass spectrum, with fragmentation products due to the breakdown of the amine being observed at lower a.m.u, although unlike compound (3) no evidence of dimeric titanium species is observed. The presence of what are believed to be fragmentation products of the dimeric compound (3) $\text{Ti}_2\text{Cl}_8\text{L}_2$ (where $\text{L}=\text{amine}$) is observed, but no peak due to the mother ion is observed.

9.3.3.5 Micronalyses:

Microanalyses to determine the percentage of carbon, hydrogen and nitrogen in the compounds (1)-(3) have been carried out. The results are in general agreement with the suggested formula although no determination of the oligomeric nature of the compounds (2) and (3) could be derived from this data. Determination of the degree of oligomerisation of the species was attempted by depression of freezing point measurements, however, the poor solubility of these materials in suitable solvents prevented accurate determination.

9.3.3.6 Solvolysis Reaction Products:

An investigation of the solvolysis reaction of TiCl_4 with the amines N,N,N ,trimethylethylenediamine, *t*-butylamine and cyclohexylamine in an attempt to further modify the reactivity of the TiCl_4 has been carried out. Unlike the reaction of one equivalent of the amine with TiCl_4 , liberation of HCl was observed during the reactions, and microanalyses of the products is consistent with this, suggesting the formation of compounds of the general formula $[\text{TiCl}_2(\text{L})_2]_n$.

9.3.3.7 Structures Of Compounds (4)- (6):

Unfortunately it has not been possible to obtain single crystals of any of the products (4) - (6), preventing definitive identification of the structures of the compounds.

The solvolysis of two Ti-Cl bonds by the addition of amine is believed to have occurred during these reactions, resulting in the formation of TiCl_2L_2 species (where $\text{L}=\text{amine}$). The existence of these compounds as solids, with high melting/decomposition points, implies that the compounds are not four co-ordinate species, but are likely exist as six co-ordinate materials.

In the case of compound (4), the amine $\text{HNMeCH}_2\text{CH}_2\text{NMe}_2$ is likely to act in a bidentate mode via the two nitrogen atoms, one directly bonded to the titanium centre and the second bending round to form a dative bond to the metal centre, thus completing the six co-ordination number for the titanium resulting in a distorted octahedral structure.

In the case of compounds (5) and (6), however, where monodentate amines have been used, the metal centre cannot achieve a co-ordination number of six by this method. Instead it is probable that the compounds are polymeric species, with the formation of chloride bridges. The formation of polymeric materials by the formation of halide bridging has previously been observed for a range of titanium compounds. The compound $\{\text{TiF}_2(\text{NMe}_2)_2\}_4$, consists of TiF_3N_3 distorted octahedra which are linked by bridging fluorine and NMe_2 groups.¹⁶ Halide bridging between titanium centres has also been observed in the compound $[\text{TiCl}_2\text{NSiMe}_3]_x$, which is a polymeric material, formed by bridging NSiMe_3 groups linking pairs of titanium centres, these are then linked into infinite chains by chloride bridges.¹⁷

9.3.3.8 Infrared Of (4) - (6):

Compounds (4) to (6) exhibit similar features to those of their equivalent adducted compounds (1) -(3), with C-H stretches and deformations due to the carbon containing ligands being observed at approximately 2900 and 1400 cm^{-1} respectively. The C-H stretches and deformations are displaced slightly from those seen in the adducted compounds and the free ligand, suggesting that co-ordination of the amine to the titanium centre has occurred.

Compounds (5) and (6) exhibit N-H stretches and deformations at approximately 3400 and 1700 cm^{-1} respectively. The presence of N-H stretches in these compounds is consistent with solvolysis reactions occurring, as only one of the two N-H protons of the primary amines are lost during solvolysis reactions (i.e. base catalysis reaction with the liberation of HCl). Compound (4), however, does not show the presence of any N-H stretches or deformations, due to the amine being a secondary amine and solvolysis resulting in the reaction of the N-H to form a Ti-N bond and HCl.

A broad Ti-Cl stretch is observed for each of these compounds at approximately 500 cm^{-1} , but in addition a Ti-N stretches at approximately 580 cm^{-1} is observed, although this region is still difficult to interpret due to it being partly obscured by the solvents used for sample preparation.

As with the adducted compounds (2) and (3), no determination of the presence of dimeric species has been possible with this technique, as no band due to the presence of bridging Ti-Cl bonds has been observed.

9.3.3.9 NMR Of Compounds (4) - (6)

The ^1H NMR of compound (4) on first examination appears similar to that of compound (1), although there is no N-H resonance seen in the spectrum, as a result of the N-H bond having been lost in the formation of the Ti-N bond with the liberation of HCl during the solvolysis reaction.

Differences in the splitting in the spectrum between the adducted compound and the solvolysis reaction product is observed, however, with the 1-2.5 ppm region of the spectra significantly more complicated. In the adducted material, the spectra is as

expected, with splitting due to adjacent hydrocarbon groups being observed. In the solvolysis reaction product, whilst this simple splitting is observed, extra bands are seen in the spectra. The extra complication in the spectrum is believed to be due to the presence of a second non-equivalent amine group around the metal centre. Whilst this second amine ligand, shows similar splitting to the first, its slightly non-equivalent position in the compound, has resulted in a displacement of the resonances, causing overlap in the spectrum.

The ^{13}C NMR spectrum of compound (4), could not be run, due to insufficient solubility of the material in a variety of NMR solvents. The micro analyses of the material suggests the loss of two Ti-Cl bonds has occurred. The complex nature of the spectrum in the 1-2.5 ppm region is compatible with this, and suggests that these amines are non-equivalent.

The ^1H NMR spectra of compounds (5) and (6) are similar to that of compound (4) in that they are also more complicated than those of the simple adducted compounds which exhibit splitting due to adjacent groups in the material. The extra complication in the spectra is believed to be due to the amines occupying non-equivalent electronic positions in the compound and thus are inequivalent in the NMR spectra. Unlike compound (4) these two compounds also exhibit an N-H resonance, and in compound (5) this is particularly clear with two non-equivalent N-H peaks being seen. The ^{13}C NMR of compound (5) also supports the fact that there are two non equivalent amines in the compound, with twelve CH_2 resonance's being seen due to the non-equivalent CH_2 groups present in the molecule. The poor solubility of compound (6), prevented ^{13}C NMR of this compound, but it would be expected to be similar to that of compound (5) with two non-equivalent amine groups are surrounding the titanium metal centre.

9.3.3.10 Mass Spectrometry Of Compounds (4) - (6):

Mass spectral analysis of the compounds was carried out using electron impact spectroscopy, with this yielding better results than attempts at analysis using other techniques such as fast atom bombardment.

Mass spectral analysis of compound (4) showed the presence of TiCl_2L_2 in the spectrum and also showed fragmentation of the ligand occurring in the gas phase. Some evidence of oligomerisation of the compound in the gas phase was observed with higher molecular weight species observed.

The mass spectral analysis of compounds (5) and (6) also exhibited evidence of the species TiCl_2L_2 although in both cases evidence of fragments of dimeric species were also observed. The fragmentation of the molecule appeared to result from fragmentation of the ligand used.

9.3.3.11 Investigation of Compound Volatility:

Whilst the melting points of these materials gives a rough idea of their thermal stability, it does not give an accurate idea of the volatility of the material. Therefore, thermal gravimetric analysis of the compounds produced has been carried out, to determine the thermal behaviour of the materials.

9.3.3.12 TGA Studies:

TGA studies have been carried out on compounds (1), (4) and (5).

Table 9-5 The major features of the TGA / DSC studies.

Compound	Weight Loss	Temp. Range	Residue
(1)	71%	330 - 500°C	TiO_xC_y
(4)	92.8%	255 - 315°C	C_x
(5)	77%	180 - 380°C	TiO_xC_y

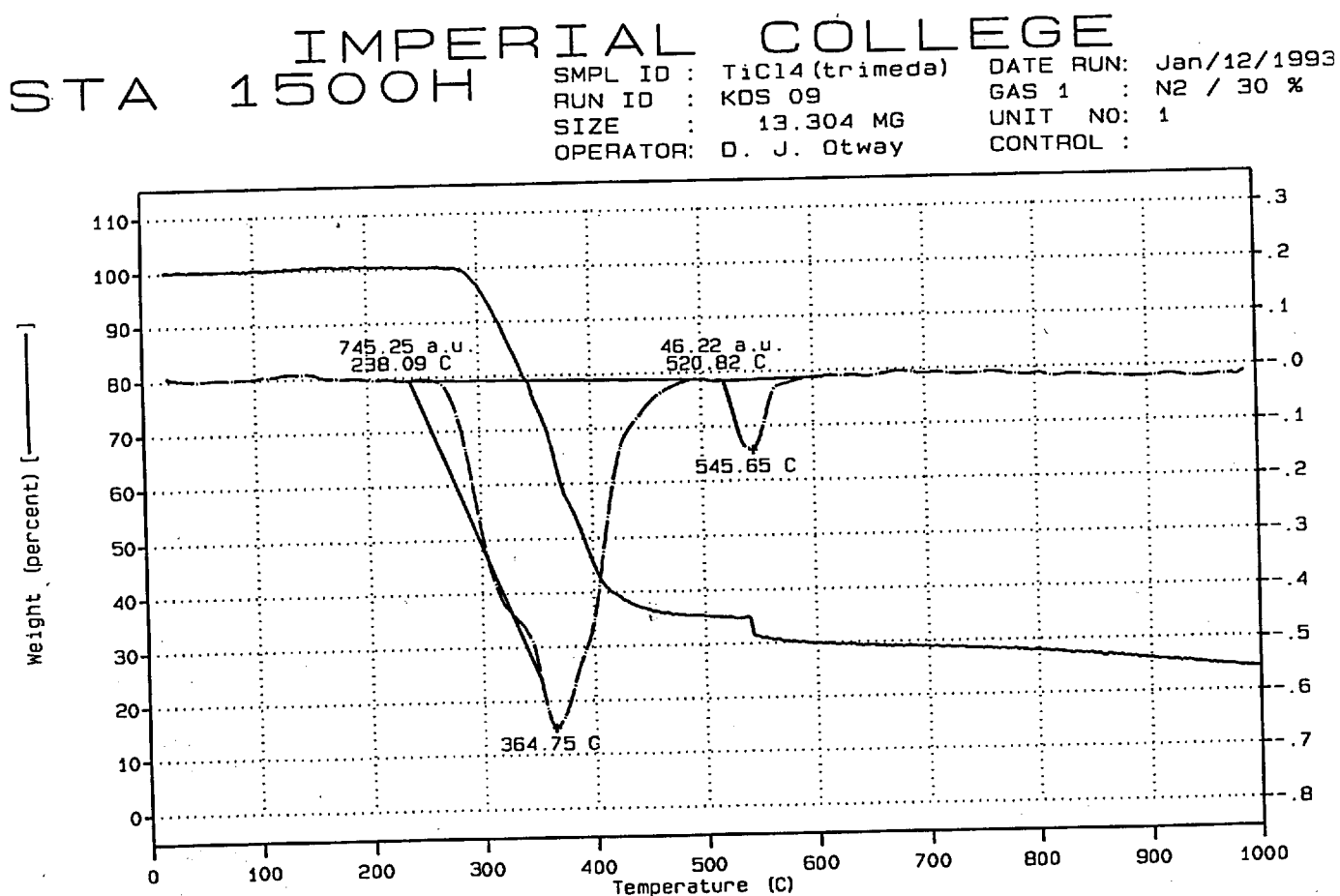
Compound (1) clearly shows a one stage breakdown of the adduct, with a 71% weight loss being seen, commencing at 330°C and being complete by 555°C. This suggests the compound is relatively stable and is not useful as a CVD precursor. The residue that remains is a white / black mixture, which is likely to have a composition of TiO_xC_y .

The TGA traces of compounds (4) and (5) also show single stage weight losses of 92.8% and 77% respectively. The residue of compound (5) appears to be similar to that of compound (1) and is again likely to be TiO_xC_y , although this weight loss occurs

at a lower temperature range of 180 - 380°C. This lower temperature breakdown, is consistent with this species not being a TiCl_4 adduct, with the trace indicating that it is a less stable compound. The compound is still too stable for CVD studies however.

Compound (4) is different to (1) and (5) in that its residue is a black colour, and is likely to be carbonaceous. The weight loss of 93% occurs in the range 255 - 315°C. This weight loss is likely to be due to the material subliming or distilling off from the crucible, leaving the small amount of carbonaceous residue.

All these compounds show that the compounds breakdown, on slow heating to result in TiO_xC_y species or carbonaceous residues.



VERSION: V5.31

Figure 9-4 TGA of $\text{TiCl}_4(\text{NHCH}_2\text{CH}_2\text{NMe}_2)$

9.3.3.13 Investigation of the use of Excess Amines:

The effect of using a large excess of the amine was also investigated during this study. The products obtained from these reactions, however, did not appear to result in the solvolysis of more Ti-Cl bonds. The products appeared to be analogous to products (4)-(6), although the products purity was diminished as a result of the presence of excess amine in the final product, which prevented facile purification of the product.

9.4 Conclusions:

The reaction of titanium tetrachloride with a cooled solution of an amine in an organic solvent has resulted in two distinct types of reaction occurring dependant upon the stoichiometry of the reaction.

Addition Reactions

The compounds produced by such reactions appear to result in six co-ordinate titanium metal centres, either by the amines completing the co-ordination sphere [as in compound (1) where the amine chelates], or alternatively by dimerisation occurring involving chloride bridges.

Solvolysis Reactions

If more than one equivalent of amine is used, there is a sufficient driving force for one or more Ti-Cl bond to be solvolysed. This solvolysis is likely to involve an initial addition reaction, which then enables the solvolysis of the bond to occur.

Both reaction types produce air and moisture sensitive solid compounds, although isolation of these solids as crystalline solids proved very difficult.

Unfortunately due to their solid nature, and stability (melting points $> 120^{\circ}\text{C}$), these materials are not suitable for investigation as precursors for the APCVD of TiN. The materials would be of little use as precursors as mass transport of the materials in the vapour phase without decomposition or condensation would require prohibitively high temperatures.

As a result of the lack of volatility of these compounds, studies of the deposition of TiN from these precursors has not been attempted. The low volatility of the addition compounds produced in this section, is believed to be related to the titanium metal centre attaining a co-ordination number of six, either by saturation of its co-ordination sphere by the formation of dative bonds with the ligand as in (1), or by the formation of chlorine bridges in the case of compounds (2) and (3). The reason for the low volatilities of the solvolysis compounds is less clear, as no exact determination of their structure has been possible, but is believed to be a result of oligomerisation occurring during reaction. In an attempt to improve the volatilities of the compounds, attempts at the production of monomeric titanium compounds with a co-ordination number of four were attempted.

9.5 References

1. W. Schauerle, H. U. Shusle, N. Knof and R. Muller, *Z. Anorg. Allg. Chem.*, 1992, 616, 186
2. S. R. Drake, M. B. Hursthouse, K. M. Malik and D. J. Otway, *Dalton Trans. In Press*
3. M. Antler and A. W. Laubengayer, *J. Am. Chem. Soc.*, 1955, 77, 5250
4. *Handbook Of Chemistry and Physics 57th Ed.*, 1976, CRC Press
5. G. W. Fowles and R. A. Hoodless, *J. Chem. Soc.*, 1963, 33
6. R. T Cowdell and G. W. A. Fowles, *J. Chem. Soc.*, 1960, 2522
7. R. T Cowdell, G. W. A. Fowles and R. A. Walton, *J. Less Common Metals*, 1963, . Muetterties, *J. Am. Chem. Soc.*, 1960, 82, 6429 and 1082
8. C. H. Winter, T. S. Lewkebandara, P. H. Sheridan and J. W. Proscia, *Mat. Res. Soc. Symp., Materials Research Society*, 1993, 282, 293
9. L. E. Manzer, *Inorg. Synth.*, 21, 135
10. F. Weiss, K. Frohlich, R. Hasse, M. Labeau, J. P. Senateur and D. Selbmann, *J. de Physique IV*, 1993, 3, 321. R. Hiskes, S. A. Di Carolis, R. D. Jacowitz and Z. Lu, *J. Cryst. Growth*, 1993, 128, 781 and F. Felten, J. P. Senateur, F. Weiss, R. Madar and A. Abrutis, *J. de Physique IV*, 1995, 5, C5-1079 and for Example Direct Liquid Injection Systems supplied by MKS Instruments and Advanced Technology Materials

11. G. Gordillo, L. C. Moreno, W. de la Cruz and P. Teheran, *Thin Solid Films*, **1994**, 252, 61
12. S. R. Drake, K. Sanderson, M. Hursthouse and A. Malik, *Polyhedron*, **1994**, 13(2), 181
13. E. C. Alyea and D. H. Merrel, *Inorg. Nuclear Chem. Lett.*, **1973**, 9, 69
14. N. Serpore, *Inorg. Chem.* , **1977**, 16, 12381
15. *The Aldrich Library of FT-IR Spectra*, C. J. Pouchert, Aldrich Chemicals Milwaukee, **1985**
16. W. S. Sheldrick, *J. Fluorine Chem.*, **1974**, 4, 415
17. N. W. Alcock, M. Pierce-Butler and G. Willey, *J. C. S. Dalton Trans.*, **1976**, 707

10. Reaction of Titanium Tetrachloride With Secondary Amines

10.1 Introduction.

In Chapter 9 the reactions of titanium tetrachloride with pure amines for the production of adducted and solvolysis reaction products of the type TiCl_4L and $[\text{TiCl}_2\text{L}_2]_n$ ($\text{L}=\text{diamine}$), were investigated. The failure of this method to replace more than two Ti-Cl bonds even when an excess of amine was used suggested that the pure amine was not sufficiently reactive to replace more Ti-Cl bonds. This is hardly surprising because, as each Ti-Cl bond is replaced, the remainder become less reactive.

Oligomerisation to produce dimeric and polymeric compounds by the formation of chloride bridges, resulted in the formation of low volatility compounds. The low volatility of oligomeric compounds, compared with their monomeric equivalent has previously been observed for Group IIA metals, where by the use of multidentate glymes, oligomerisation has been prevented resulting in monomeric species with increased volatility. This is clearly shown below from the TGA of the three compounds, $[\text{Ba}(\text{thd})_2]_4$ tetramer, $[\text{Ba}(\text{thd})_2(3\text{g})]$ monomer, $[\text{Ba}(\text{thd})_2(4\text{g})]$.^{1,2,3} (Where 3g and 4g are glymes (polyethers))

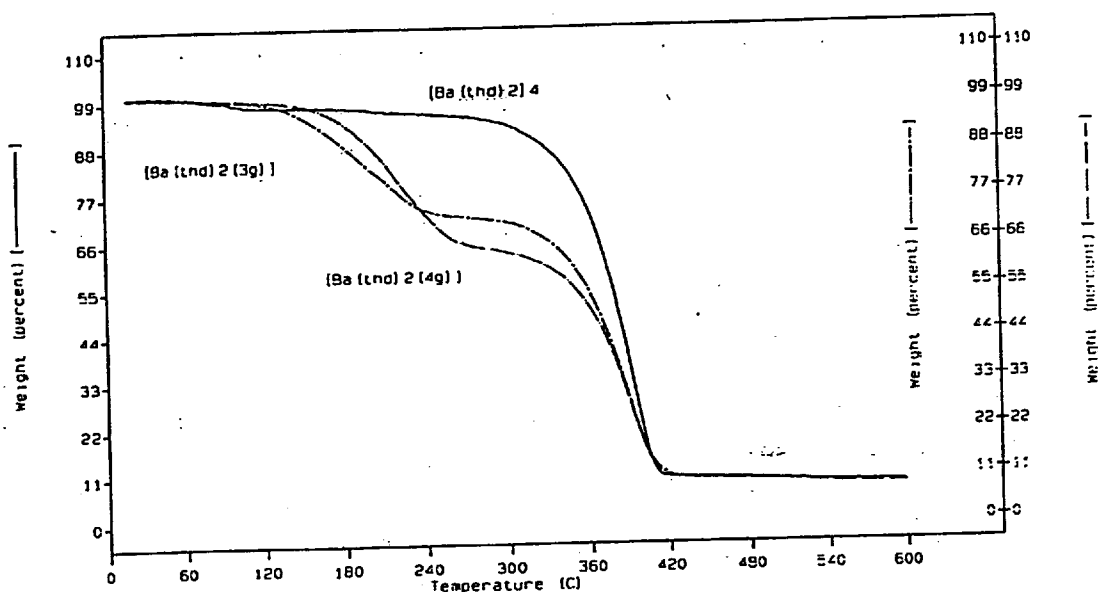


Figure 10-1 TGA Of $\text{Ba}_2(\text{thd})_8$, $[\text{Ba}(\text{thd})_3(3\text{g})]$ and $[\text{Ba}(\text{thd})_2(4\text{g})]$.^{1,2,3}

In order to increase the volatility the prevention of chloride bridge formation either by the replacement of more Ti-Cl bonds or the prevention of oligomerisation by the use of sterically demanding ligands is required. An investigation aimed at enhancing the reactivity of a range of amines has therefore been carried out, to achieve the replacement of more of the Ti-Cl bonds. Various methods for increasing the reactivity of ligands (in particular amines) are documented in the literature, including replacing one of the NH protons by a good leaving group such as TMS or by lithiation the amine.

The use of TMS as a good leaving group to increase the reactivity of the amine has previously been used by Fayos. *et. al.* who carried out the reaction:⁴

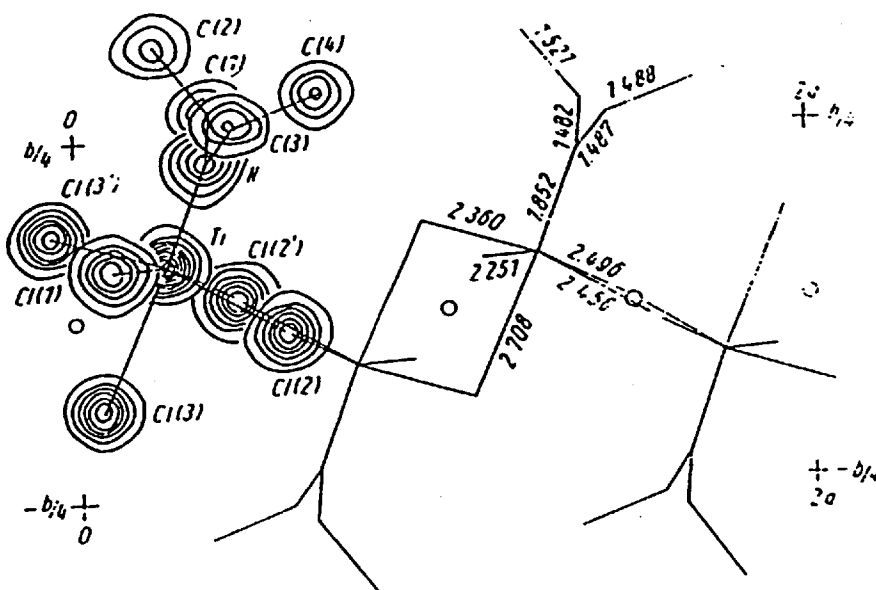
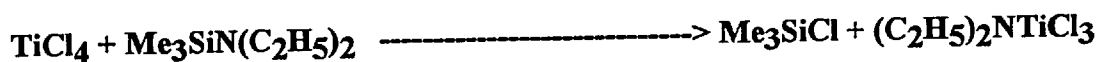
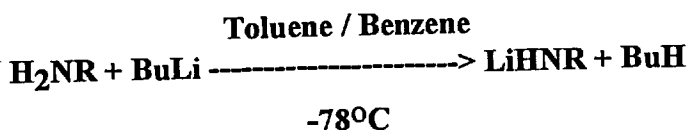


Figure 10-2 Single Crsytal X-ray Structure of $(\text{C}_2\text{H}_5)_2\text{NTiCl}_3$.⁴

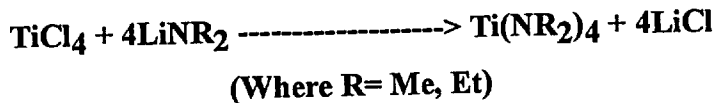
This method is not as widely used as the use of butyl-lithium. Lithiation of the amine with butyl-lithium is a standard synthetic method, with the acidic N-H proton being replaced by lithium and releasing BuH.



This synthetic route also has the advantage that the subsequent reaction with titanium tetrachloride liberates LiCl, which can then be separated from the reaction mixture by filtration due to its insolubility in a variety of organic solvents.

The reaction to form the lithiated amine can be carried out *in-situ* and then reacted with titanium tetrachloride. This method has previously been reported for use in producing a wide range of metal compounds such as $\text{Ti}(\text{NR}_2)_4$ and $\text{W}_2(\text{NMe}_2)_6$.^{5,6}

This method is still used today by industry to make various titanium amides such as $\text{Ti}(\text{NMe}_2)_4$.⁷



Other methods by which dialkylamido derivatives of titanium have been made include the utilisation of transamination reactions of titanium dialkylamino derivatives with the synthesis of compounds such as $\text{Ti}(\text{NR}_2)_2(\text{NR}'_2)_2$.⁸ Although this method is very useful for the production of mixed and tetrakis amine complexes, it has the disadvantage that a tetrakis dialkylamine complex is used as a starting material. Due to the higher cost of these compared to the widely available TiCl_4 , it was decided that this method was not worth initial study.

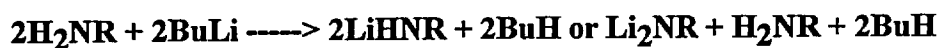
The following section describes the reactions of titanium tetrachloride with some lithiated amines.

10.2 Reaction of Lithiated Primary Amines.

Initially an investigation of the reaction of titanium tetrachloride with lithiated primary amines was undertaken. Unfortunately this synthetic strategy had two major disadvantages:

1. The LiCl by-product proved to have some solubility in the solvents used. This resulted in contamination of the product with LiCl, and therefore a complete solvent system change was required to prevent this.
2. Exact lithiation of the primary amine proved to be impossible for more than one equivalent of the amine. Instead dilithiation appeared to occur and thus prevented any prediction of the product from being possible:

i.e.



Dilithiation has previously been reported by Armstrong *et. al.* with a naphthalene complex showing dilithiation.⁹

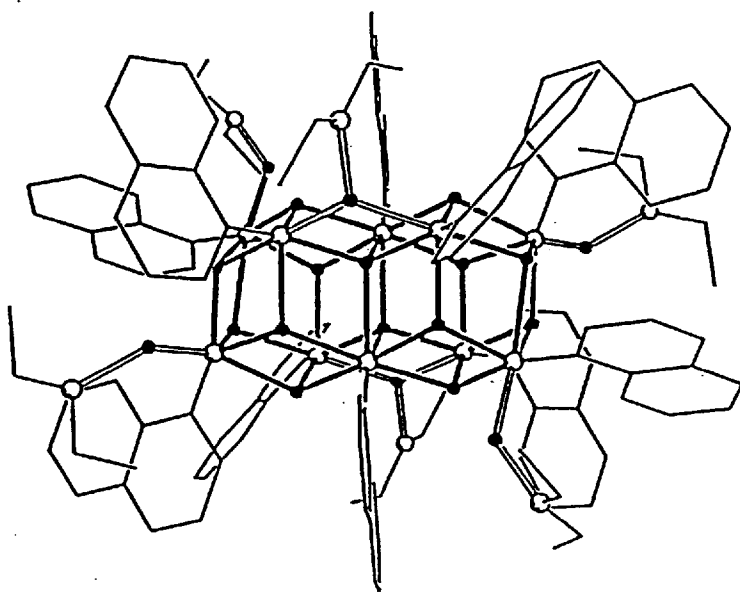


Figure 10-3 Structure of $[(\alpha\text{-Naphthyl-NLi}_2)_{10}(\text{Et}_2\text{O})_6] \cdot \text{Et}_2\text{O}$.⁹

As a result of these problems, the prediction of the final product was very difficult and a large excess of the amine and butyl-lithium was required to ensure sufficient LiHNR was present for the reaction. This would require further purification of the product being required to remove the excess pure and lithiated amine.

The compounds produced using this reaction method were impure, and low product yields of the isolated species were obtained, due to a range of by-products being produced.

The low yields of the desired product and problems in predicting the product due to dilithiation of the primary amines meant no pure material was isolated.

To overcome the problems associated with lithiation of primary amines an investigation of the reactions of lithiated secondary amines with titanium tetrachloride was undertaken.

10.3 Reaction of Lithiated Secondary Amines

The synthesis of a range of compounds utilising secondary amines are described in the literature. Some of the compounds and their properties of these compounds are shown in Table 10-1.

Table 10-1 Physical Properties of Precursors Used For Deposition of TiN By APCVD.^{10,11,12,13}

Compound	Properties
Ti(NMe ₂) ₄	Yellow Liquid B.pt. 50°C at 0.05 mmHg
Ti(NEt ₂) ₄	Orange Liquid B.Pt. 112°C at 0.1 mmHg
Ti(NMe ₂) ₃ ^t Bu	Orange Oil B.pt. 80°C at 0.1 mmHg
Ti(NC ₄ H ₈) ₄	Orange-Yellow Oil B.pt. 160°C at 0.05 mmHg
Ti(NC ₅ H ₁₀) ₄	Red Solid M.pt. 70°C, B.pt. 180°C at 0.05 mmHg
[Ti(N ^t Bu)(NMe ₂) ₂] ₂	Red Solid Sublimes at 140°C at 0.1 mmHg

The production of a range of tetrakis(dialkylamido) compounds by this method has been reported, but the use of this synthetic method for the production of the compounds of the general formula $\text{TiCl}(\text{NR}_2)_3$ has not been reported. An investigation of $\text{TiCl}(\text{NR}_2)_3$ compounds has therefore been initiated, with the use of bulky alkyl chains in an attempt to reduce the pre-reaction of the precursor with ammonia by transamination reactions, which is a major disadvantage of the current $\text{Ti}(\text{NMe}_2)_4$ precursor. Whilst such transamination reactions are a disadvantage in the gas phase the use of transamination reactions as a synthesis method have previously been reported to allow the production of mixed amine species such as the dimeric material $\text{Ti}_2(\text{NBu}^t)_2(\text{NMe}_2)_4$, which has the proposed structure shown below in Figure 10-4.¹⁴

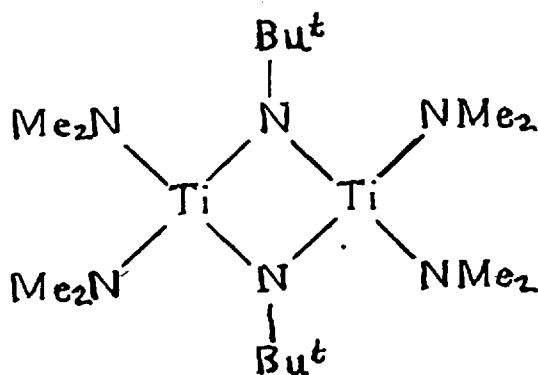


Figure 10-4 Proposed Structure Of $\text{Ti}_2(\text{NBu}^t)_2(\text{NMe}_2)_4$.¹⁴

The following section describes the synthesis of a range of precursors for the deposition of titanium nitride, formed from the reaction of titanium tetrachloride with lithiated secondary amines.

10.4 Experimental

10.4.1 Synthesis of $[\text{TiCl}(\text{N}^{\text{n}}\text{Pr}_2)_3]$ (1)

A flame dried Schlenk was charged with 20ml of dried benzene and 5.1 ml (36.3 mmol) of di-n-propylamine. This solution was then cooled to -78°C and 23.5 ml (36.3 mmol) of 1.55 M BuLi was added slowly to the solution. The solution was then slowly allowed to warm to room temperature. On reaching room temperature, the solution was recooled to -78°C , and 1ml (9.1 mmol) of TiCl_4 was added to the solution and the solution was slowly allowed to warm to room temperature. The solution was then refluxed for 2 hours. The solution was then filtered through a cellite pad and the filtrate stripped to dryness under vacuum. The resulting dark oil, 2.8g was then collected in a glove box.

Yield 2.8g, 70%; Infra Red (Neat Oil): 2955(s), 2932(s), 2872(s), 2829(s), 2730(w), 1623(w), 1465(s), 1377(s), 1360(s), 1298(m), 1261(s), 1160(s), 118(s), 1087(s), 1033(s), 971(s), 867(s), 846(m), 802(s), 745(m), 674(s), 508(w), 402(m), 371(m), 304(w), 299(w), 289(w), 278(w), 271(w), 266(w), 266(w), 256(w), 250(w), 244(w); ^1H NMR(d_6 -benzene): 0.91(CH_3 , multiplet, integration 3H), 1.55 (CH_2 , multiplet, integration 2H), 3.55 ppm (NCH_2 , multiplet, integration 2H); ^{13}C NMR(d_6 -benzene): 12.1(CH_3 , singlet), 23.3 (CH_2 , multiplet), 54.5 (NCH_2 , multiplet); Mass Spectrometry(EI^+): 383 TiClL_3 , where $\text{L}=(\text{N}^{\text{n}}\text{Pr}_2)$

10.4.2 Synthesis of $[\text{TiCl}(\text{NPr}^i_2)_3]$ (2)

In a flame dried Schlenk containing 20 ml of benzene, 5.1 ml (36.3 mmol) of diisopropylamine was added producing a colourless solution. The solution was then cooled to -78°C and 23.44 ml (36.3 mmol) of 1.55 M butyl-lithium was added. On slowly warming to room temperature the frozen solution dissolved to produce a colourless solution. This was gently heated to ensure the lithiation step had gone to completion. The solution was then recooled to -78°C and 1 ml (9.1 mmol) of titanium tetrachloride was added slowly. Initially a green precipitate was seen in a small amount of a black solution. As the solution was slowly warmed to room temperature, initially more of the green precipitate was observed in a black solution, but then on reaching near room temperature the green precipitate disappeared. This exothermic reaction coincided

with white fumes being seen. The black solution was the refluxed for 2 hours, after which time the solution was filtered to remove the LiCl by-product. The black filtrate was then stripped to dryness at 50°C to remove all the benzene, which resulted in a viscous black oil, which was collected.

Yield: 2.4g, 68.9%; **Infra Red:** (Nujol mull cm^{-1}) 1733(w), 1667(w), 1360(m), 1261(m), 1185(m), 1160(m), 1102(m), 1019(w), 924(m), 851(w), 810(m), 723(w), 635(w), 537(w), 500(w), 456(w), 393(w), 328(w), 240(w), 230(w); **Infra Red:** (Hexachlorobutadiene cm^{-1}) 2964(m), 2929(m), 2724(m), 1463(w), 1378(w), 1361(w), 1261(m), 1100(m), 1029(m); **^1H NMR:** (C_6D_6 at 23°C 270MHz ppm) 1.28 (m, CH_3), 4.28 (m, CH); **^{13}C NMR:** (C_6D_6 at 23°C 23MHz ppm) 25.6 (s, CH_3), 51.4 (s, CH); **Mass Spectrometry:** 383 [$\text{Ti}(\text{N}(\text{CHMe}_2)_2)_3$] 18%, 368 [$\text{Ti}(\text{N}(\text{CHMe}_2)_2)_2(\text{N}(\text{CHMe}_2)(\text{CHMe}))$] 25%, 282 [$\text{Ti}(\text{N}(\text{CHMe}_2)_2)_2$] 35%, 265 [$\text{Ti}(\text{N}(\text{CHMe}_2)_2)(\text{NCHMe}_2)$], 239 [$\text{Ti}(\text{N}(\text{CHMe}_2)_2)(\text{NCHMe}_2)$], 182 [$\text{Ti}(\text{N}(\text{CHMe}_2)_2)$]; **Micro Analyses:** Calc. [$\text{TiCl}(\text{N}(\text{CHMe}_2)_2)_3$] C: 56.32%, H: 10.95%, N: 11.97%. Found C: 58.76%, H: 11.21%, N: 11.97%.

10.4.3 Synthesis of $[\text{TiCl}\{\text{N}((\text{CH}_2)_3\text{Me})_2\}_3]$ (3)

In a flame dried Schlenk containing 20 ml of benzene, 6.125 ml (36.3 mmol) of dibutylamine was added producing a colourless solution. This solution was then cooled to -78° and 23.45 ml (36.3 mmol) of 1.55 M butyl-lithium was added. On slowly warming to room temperature and then heating, this produced a whitish solution, with a white precipitate in the solution. This did not change in colour despite heating the solution strongly. The solution was then recooled and 1 ml (9.1 mmol) of TiCl_4 was added. This produced an immediate exothermic reaction and a green precipitate was produced. As the solution was slowly allowed to reach room temperature, and the solution darkened to a deep green colour. The solution was then refluxed for 3 hours. After cooling the black / green solution was filtered and the dark filtrate was stripped to dryness at 80°C. This yielded 1.8g of a dark green / black oil.

Yield: 1.8g, 66%; **Infra Red:**(Neat Oil) 2961(s), 2856(s), 2731(m), 1619(m), 1457(s), 1377(s), 1361(s), 1311(m), 1262(s), 1237(m), 1220(m), 1170(s), 1146(s), 1088(s), 1016(s), 964(s), 898(s), 878(m), 852(s), 779(s), 743(m), 731(m), 666(s), 513(m), 439(m), 397(m), 352(w), 277(w), 254(w); **^1H NMR:**(C_6D_6 at 23°C 270MHz) 0.9ppm (m, CH_3), 1.2ppm (m, CH_2), 1.6ppm (m, CH_2), 3.6ppm (m, CH_2); **^{13}C NMR:**(C_6D_6 at 23°C 69.51MHz) 15.6ppm (s, CH_3), 26.3 (d, CH_2), 34.0 (d, CH_2), 53.6 (d,

CH₂); **Mass Spectrometry**: 560 TiL₄ 10%, 518 TiL₃(N((CH₂)₃Me)(CH₂)) 15%, 430 TiL₃ 100%, 372 TiL₂(N((CH₂)₃Me)) 20%, 300 TiL₂ 25% where L=N((CH₂)₃Me)₂; **TGA / DSC**: 1 step weight loss of 80%, commencing at 25°C and ending at 250°C

10.4.4 Synthesis of [TiCl(NBuⁱ)₂]₃ (4)

In a flame dried Schlenk containing 20 ml of benzene, 4.7 ml (36.3 mmol) of diisobutylamine was added producing a colourless solution. The solution was then cooled to -78°C and 23.44 ml (36.3 mmol) of 1.55 M butyl-lithium was added. On slowly warming to room temperature the frozen solution dissolved to produce a colourless solution. This was gently heated to ensure the lithiation step had gone to completion. The solution was then recooled to -78°C and 1 ml (9.1 mmol) of titanium tetrachloride was added slowly. Initially a green precipitate was seen in a small amount of a purple / black solution. As the solution was slowly warmed to room temperature, initially more of the green precipitate was seen in a purple / black solution, and some tan precipitate was seen. But on reaching room temperature both the tan and the green precipitate disappeared. The solution was then refluxed for 2 hours, after which time a black / brown solution resulted and was filtered to remove the LiCl by-product. This was then stripped to dryness at 80°C for 2.5 hours to remove all the benzene. This resulted in a very viscous orange oil which on cooling to room temperature crystallised to give orange crystals.

Yield: 2.1g, 50%; **Infra Red**: (Nujol mull cm⁻¹) 1367(s) , 1343(m), 1311(m), 1261(s), 1146(s), 1090(s), 1018(s), 955(m), 934(w), 874(s), 805(s), 716(s), 675(m), 519(w), 442(w), 411(m), 348(w), 315(w), 234(w); **Infra Red**: (Hexachlorobutadiene cm⁻¹) 2957(s), 2869(s), 1464(m), 1385(m), 1367(m), 1261(m), 1147(m), 1099(s), 1018(m), 875(m), 716(w), 519(w), 411(m); **¹H NMR**: (C₆D₆ at 23°C 90MHz ppm) 0.96 (d, CH₃, 18H), 1.85 (m, CH, 3H), 3.67 (d, CH₂, 6H); **¹³C NMR**: (C₆D₆ at 23°C 23MHz ppm) 18.99 (s, CH₃), 24.9 (s, CH), 55.9 (s, CH₂); **TGA / DSC**: The TGA shows a one step breakdown of the compound, with a 80.88% weight loss occurring between 100 and 320°C. The DSC shows a very broad exotherm at 176°C, and a further small broad exotherm at 525°C; **Mass Spectrometry**: 803 [Ti₃Cl₄(NBuⁱ)₂]₄] 8%, 551 [Ti₂Cl₂(NBuⁱ)₂]₃] 8%, 423 [Ti₂Cl₂(NBuⁱ)₂]₂] 100%, 373 [TiCl₂(NBuⁱ)₂]₂] 8%; **Micro Analyses**: Calc. [TiCl(N(CH₂CHMe₂)₂)₃] C: 61.6%, H: 11.55%, N: 8.98%. Found C: 60.15%, H: 11.75%, N: 7.88%

10.4.5 Synthesis of $[\text{TiCl}(\text{N}((\text{CH}_2)_4\text{Me})_2)_3]$ (5)

A flame dried Schlenk was charged with 20 ml of dried benzene and 7.36ml (36.3 mmol) of dipentylamine. This solution was cooled to -78°C in a card-ice bath and to the cooled solution 23.5 ml (36.3 mmol) of 1.55 M butyl-lithium was added. This solution was slowly allowed to warm to room temperature and stirred. After reaching room temperature the solution was stirred for 30 minutes. This resulted in a white precipitate in a clear solution.

The solution was then re-cooled to -78°C and 1ml (9.1 mmol) of TiCl_4 was added slowly. This solution was then allowed to slowly warm to room temperature and stirred vigorously. The dark solution with a dark precipitate in was then diluted with a further 20 ml of dried benzene and the solution was refluxed under nitrogen for 2 hours.

The resulting mixture was then filtered through a cellite pad and the dark green filtrate was collected. The filtrate was reduced to dryness by removal of the solvent in vacuum. This resulted in 3.3g of a viscous dark green oil which was collected in a glove box.

Yield: 3.3g, 55%; **Infra Red:**(Neat Oil cm^{-1}) 2957(s), 2858(s), 1733(w), 1616(w), 1466(s), 1370(m), 1363(s), 1288(m), 1261(m), 1221(m), 1205(m), 1146(s), 1094(s), 1030(s), 970(m), 937(s), 888(m), 801(m), 728(m), 669(m), 539(w), 471(w), 395(m), 303(w), 281(w), 265(w), 250(w), 236(w), 233(w), 227(s); **^1H NMR**(d_6 -benzene): 0.89 ppm(CH_3 , multiplet, integration 3H), 1.30 ppm($2\times\text{CH}_2$, multiplet, integration 4H), 1.58 ppm (CH_2 , multiplet, integration 2H), 3.66 ppm (NCH_2 , multiplet, integration 2H); **^{13}C NMR**(d_6 -benzene): 14.3 ppm (CH_3 , doublet), 23.2 ppm (CH_2 , multiplet), 29.6 ppm (CH_2 , singlet), 30.2 ppm (CH_2 , multiplet), 52.0 ppm (NCH_2 , multiplet); **Mass Spectrometry**(EI^+): 551 $[\text{TiCl}(\text{N}((\text{CH}_2)_4\text{Me})_3)]$, 494 Loss $(\text{CH}_2)_3\text{Me}$, 395 Loss Npent_2 ; **Micro Analyses:** Expected C: 65.34, H: 11.98, N: 7.62, Found C: 65.30, H: 13.41, N: 7.39; **TGA:**

1 Step weight loss of 83.72% commencing at 160.33°C and ending at circa 250°C . Residue 16.07%

10.4.6 Synthesis of $[\text{TiCl}(\text{N}(\text{CH}_2)_5\text{Me})_2]_3$ (6)

A flame dried Schlenk was charged with 30 ml of toluene and 8.47 ml (36.3 mmol) of dihexylamine. This solution was then cooled in an ice-bath and to the stirred solution 23.45 ml of (36.3 mmol) 1.55 M butyl-lithium was added. The solution was then allowed to slowly warm to room temperature, and the solution was then stirred at room temperature for 1 hour. This resulted in a white precipitate in the solution. The solution was then recooled and to the cool solution 1ml (9.1 mmol) of TiCl_4 was added slowly. The solution was then allowed to slowly warm to room temperature. This resulted in a dark solution with a green precipitate in it. The solution was then diluted with a further 40ml of toluene and then the solution was refluxed under nitrogen for 3 hours. This resulted in a dark solution, which was filtered through a celite pad. The dark green filtrate was then stripped to dryness under vacuum to yield 2.55g of a dark green viscous oil.

Yield: 2.55g; **Infra Red(Neat Oil):** 2958(s), 2927(s), 2857(s), 1466(s), 1378 (m), 1364(m), 1261(m), 1193(w), 1146(m), 1097(m), 1037(m), 941(m), 882(m), 801(m), 726(m), 671(m), 544(w), 404(w), 353(m), 348(w), 343(w), 314(w), 309(w), 304(w), 298(w), 293(w), 287(w); **^1H NMR(d_6 -benzene):** 0.89 ppm (CH_3 , multiplet, integration 3H), 1.32 ($3\times\text{CH}_2$, multiplet, integration 4H), 1.62 (CH_2 , multiplet, integration 2H), 3.71 (NCH_2 , multiplet, integration 2H); **^{13}C NMR(d_6 -benzene):** 14.3 ppm (CH_3), 23.1 ppm (CH_2), 27.7 ppm (CH_2), 29.9 ppm (CH_2), 32.6 ppm (CH_2), 52.1 ppm (NCH_2); **Micro Analyses:** Expected, C:67.97, H: 12.28, N: 6.61; Found C: 66.89, H: 12.28, N: 6.23; **Mass Spectrometry(EI^+):** 635 $[\text{TiCl}(\text{N}(\text{CH}_2)_5\text{Me})_2]_3$, 564 Loss $(\text{CH}_2)_4\text{Me}$,

10.4.7 Synthesis of $[\text{TiCl}(\text{NEtBu})_3]$ (7)

A flame dried Schlenk, was charged with 20ml of dried benzene, and 4.97 ml (36.3 mmol) of HNEtBu . This solution was then cooled to -78°C using an acetone and dry ice bath. To the cooled solution, 23.5 ml (36.3 mmol) of 1.55 M BuLi was added. The solution was stirred as it was slowly warmed to room temperature over a 30-60 minute period. This produced a white crystalline material in the benzene solvent. The

solution was then recooled to -78°C, and 1ml (9.1 mmol) of TiCl₄ was slowly added to the mixture. The mixture was allowed to slowly warm to room temperature over a 30 minute period. The dark brown/black solution with a greenish precipitate was then refluxed under a nitrogen atmosphere for 2 hours.

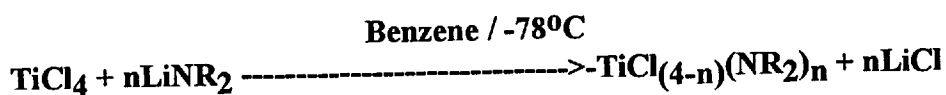
The resulting dark solution and precipitate was then filtered through a cellite pad, to produce an orange/red solution.

The solvent was then removed in vacuum, and the resulting orange / red oil, 1.71g was collected in a glove box.

Yield: 1.71g; **Infra Red(Neat Oil):** 2960(s), 2931(s), 2872(s), 1615(m), 1464(s), 1365(s), 1311(w), 1284(w), 1261(s), 1233(w), 1180(s), 1150(s), 1093(s), 1054(m), 1012(s), 975(m), 875(s), 798(s), 744(w), 642(m), 515(w), 399(w), 360(w), 290(w), 283(w), 272(w); **¹H NMR(in d₆-benzene):** 0.89 ppm(CH₃ of either Bu or Et Group, multiplet, integration 3H), 1.07 (CH₃ of either Et or Bu Group, multiplet, integration 3H), 1.29 ppm (CH₂ of Bu multiplet, integration 2H), 1.44 ppm (CH₂ of Bu Group, multiplet, integration 2H), 3.59 ppm (2xNCH₂ of Et and Bu groups, integration 4H); **¹³C NMR(in d₆-benzene):** 14.5 (CH₃ multiplet), 21.2 (CH₃ multiplet), 32.1 (2xCH₂ multiplet), 45.5 (NCH₂ multiplet), 51.7 (NCH₂ multiplet); **Mass Spectrometry (EI⁺):** 383; **Thermal Gravimetric Analyses:** 1 step weight loss of 85.33 %, starting at 180°C and ending at circa 500-500°C
Micro Analyses: Expected C:56.32, H:10.95: N:9.25: Found C:57.74 H:10.23: N:10.79

10.5 Synthesis Discussion:

The synthesis route utilised herein is similar to that previously reported for the synthesis of [Ti(NMe₂)₄] by Bradley *et. al.*¹⁰



The use of secondary amines rather than the primary has two major advantages. Firstly exact lithiation of the amines acidic NH proton can be achieved by the use of butyl-lithium. This allows exact knowledge of the reaction stoichiometry. Secondly,

literature reports have documented that tetrakis compounds using secondary amines have sufficient volatility for use as APCVD precursors, for the deposition of various metal nitrides such as AlN and HfN.^{15,16}

The first stage of the synthesis is the production of the lithiated amine. This is carried out in a benzene solution, at -78°C to slow the exothermic reaction. Once the lithiated amine had been produced, the solution is recooled to -78°C and TiCl₄ added slowly. This produces a very exothermic reaction, and the solution must be kept cool and only slowly allowed to return to room temperature. In certain cases if the reaction mixture is allowed to warm up too quickly the exothermic nature of the reaction results in the benzene boiling.

Once the initial reaction is complete, the mixture is refluxed for 2-3 hours, after which time it is allowed to cool to room temperature. In order to prevent any LiCl contamination of the final product, the mixture is then filtered through a cellite pad. Simple filtration using an anaerobic filter is not sufficient to remove the LiCl impurity.

The cellite pad technique appears more successful and also solves the problem of LiCl clogging the filter device and causing further problems.

The filtered solution, is then stripped to yield the product of the reaction. The use of benzene as a solvent appears to prevent the incorporation of LiCl impurities in the final product as LiCl is insoluble in benzene.

The more reactive lithiated secondary amines appear to be able to replace more than two Ti-Cl bonds. This solvolysis of the bonds with the production of LiCl, shows that the more reactive lithiated secondary amine is able to overcome the increasing ionic nature of the remaining Ti-Cl bonds. Rather than forming the tetrakis compounds, the compounds TiCl(NR₂)₃ are formed with more sterically hindered ligands.

The increased amount of carbon in the materials should in theory not be a significant disadvantage, provided the material is sufficiently volatile, as literature suggests that the deposition of TiN when ammonia is used occurs by reactions of the type:



10.5.1 Reaction Of TiCl_4 With Two Equivalents of Lithiated Amine

An investigation of the reaction of two equivalents of the lithiated amine with titanium tetrachloride was initially carried out. These reactions, however, produced involatile solid materials, such as $\{\text{TiCl}_2(\text{NCHMe}_2)_2\}_n$.

Initially a four co-ordinate species is likely to be formed, this then undergoes oligomerisation, to produce a more stable six-co-ordinate metal centre, as in catenatrichloro(diethylamido)titanium(IV) which is a polymeric material formed by octahedra sharing edges.⁴ The formation of a polymeric material by these reaction is consistent with the low volatility observed in these materials.

10.5.2 Discussion of Compounds (1)-(7)

Investigation of the production of $\text{TiCl}(\text{NR}_2)_3$ species by the reaction of three equivalents of the lithiated secondary amine with titanium tetrachloride has been conducted. Investigation of the materials by a range of spectroscopic techniques has been carried out.

10.5.2.1 *Infra Red of Compounds (1) - (7):*

Compounds (1) and (7) show the presence of a Ti-Cl stretch at ca. 500cm^{-1} , implying that as expected not all four of the Ti-Cl bonds of titanium tetrachloride have been replaced, and that the species are likely to be of the general formula $\text{TiCl}(\text{NR}_2)_3$.

Table 10-2 Main Features of Infra-Red Spectra(cm⁻¹):

Compound	ν C-H	ν Ti-N	ν Ti-Cl
(1)	2955, 2932,2872,2730	674	508
(2)	2964, 2724	635	500 or 537
(3)	2961, 2856, 2731	666	513
(4)	2957, 2869	675	519
(5)	2957, 2858	669	539
(6)	2958, 2927, 2857	671	544
(7)	2960, 2931, 2872	642	515

Although the compounds (1)-(7) show no N-H stretches it has been observed that if the compounds are exposed to air, all the compounds begin to show the presence of a broad band at circa 3400 cm⁻¹. This has also been observed to if the solvent used for the mull preparation (nujol or hexachlorobutadiene) are not sufficiently dry. The broad band at circa 3400cm⁻¹ is believed to be due to an OH group resulting from water vapour attacking the metal centre and the resulting displacement of an amine.

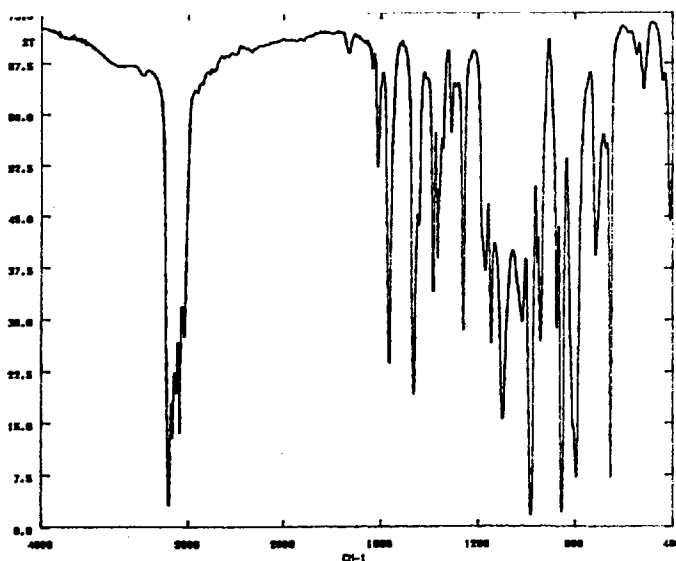
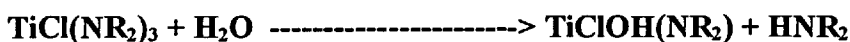
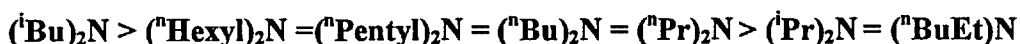


Figure 10-5 Infra-red Spectrum Of TiCl(NⁱBu₂)₃ (Neat Oil)

The Ti-N stretching frequency in compounds (1)-(7) varies depending upon the steric nature and length of the alkyl chain present on the amine. A similar effect has previously been observed for the tetrakis dialkylamine compounds of titanium, hafnium and zirconium, where the stretching frequency seen for the tetrakis compound varies with:¹⁷



This is similar to this work which has observed the Ti-N frequency varies with:



The observed change in the frequency of the Ti-N stretch cannot be due to a mass effect as increasing the alkyl chain (and thus the mass of the amine), would result in an opposite effect with the M-N stretching frequency decreasing. The observed change cannot be due to steric effect either, as increasing the steric interactions would result in a weakening in the M-N bond strength and thus move the M-N stretching frequency to a lower wavelength.

The observed change in the stretching frequency of the M-N bond is therefore likely to be due to electronic factors. The inductive effect of the alkyl chain (I^+), resulting in a change in the $p\pi-d\pi$ bonding in the $(^-\text{M})=\text{NR}_2(^+)$ bond.

The M-N bond therefore increases in strength upon increasing the alkyl chain length. The increased M-N bond strength is advantageous in pre-mixed CVD of titanium nitride as the stronger bond is likely to result in a reduction in the rate of transamination reaction between ammonia and the precursor in the gas phase, thus allowing a more controllable deposition.

10.5.2.2 NMR of Compounds (1) - (7):

The major features of the ^1H NMR of these compounds are shown in the table 10-3.

Table 10-3 Main Features Of ^1H NMR:

Compound	CH_3	CH_2	CH
(1)	0.91(m)	1.55(m), 3.55(m)	-
(2)	1.28(m)	-	4.28(m)
(3)	0.90(m)	1.2(m), 1.6(m), 3.6(m)	-
(4)	0.96(m)	3.67(m)	1.85(m)
(5)	0.89(m)	1.30{2x CH_2 (m)}, 1.58(m), 3.66(m)	-
(6)	0.89(m)	1.32{3x CH_2 (m)}, 1.62(m), 3.71(m)	-
(7)	0.89 and 1.07 (CH_3 of Et and Bu)	1.29(Bu(m)), 1.44(Bu(m)), 3.59 {2x CH_2 (m)}	-

Table 10-4 Main Features Of ^{13}C NMR:

Compound	CH_3	CH_2	CH
(1)	12.1	23.3, 54.5	-
(2)	25.6	-	51.4
(3)	15.6	26.3, 34.0, 53.6	-
(4)	18.99	55.9	24.9
(5)	14.3	23.2, 29.6, 30.2, 52.0	-
(6)	14.3	23.1, 27.7, 29.9, 32.6, 52.1	-
(7)	15.5, 21.2	32.1(x2), 45.5, 51.7	-

These spectra show that each of the compounds are free of impurities, apart from a small amount of hexane which is a result of the use of n-butyl-lithium. The spectra are all in general agreement with the suggested formula for each of these compounds. Careful examination of the spectra indicates that the coupling is not simple. In all the

spectra the alkyl-groups display some non-equivalence resulting in complex splitting of the NMR resonances.

The non-equivalent nature of the alkyl chains is clearly seen in the ^1H NMR and ^{13}C NMR of compound (1). In the ^1H NMR, the methyl group of the n-propyl chain would be expected to be a 1:2:1 triplet, due to coupling with the CH_2 next to it. However, in the spectra the methyl group peak consists of a multiplet with approximately 15 components. This is not consistent with simple coupling. Instead it indicates inequivalent methyl-groups are present in the compound. This results in a very complex multiplet being observed. Similar complication of the spectra is also seen for the CH_2 peaks in this compound. The ^{13}C NMR also shows the presence of non-equivalent alkyl chains.

The non-equivalence observed of the alkyl chains in compounds (1)-(7) is a result of the amines having different electronic environments around the metal centre. In the tetrakis compounds $\text{Ti}(\text{NR}_2)_4$, only simple splitting is observed, and $\text{Ti}(\text{NMe}_2)_4$ only displays a singlet due to the CH_3 groups, which are all equivalent. The inequivalence in the compounds (1)-(7) is likely to be a result of the chlorine in the material changing the electronic environment of at least one of the dialkylamine groups. The resulting change in the electronic environment shifts the resonance due to this group and complicates the observed spectrum.

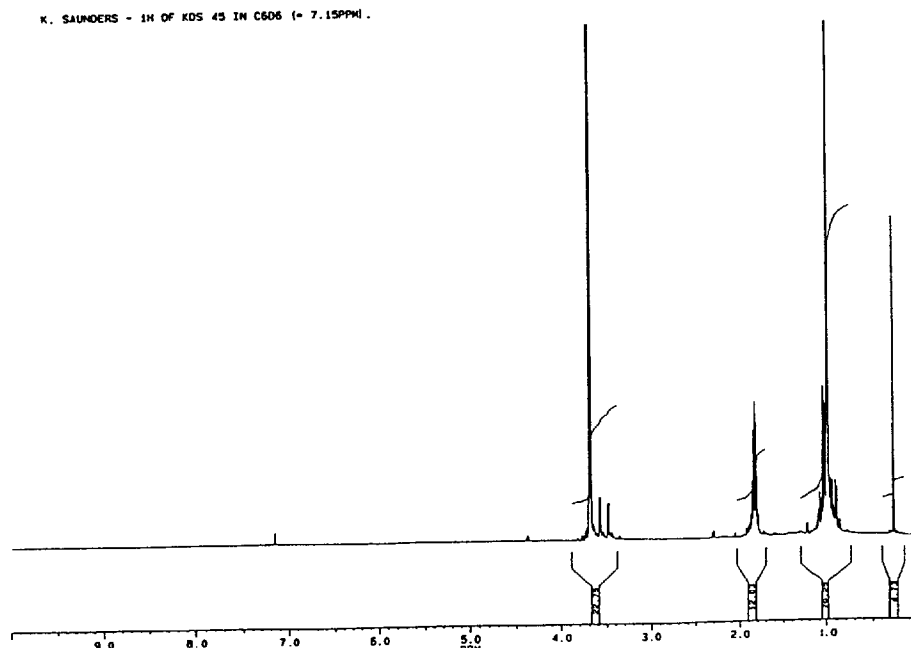


Figure 10-6 ^1H NMR of $\text{TiCl}(\text{N}^i\text{Bu})_3$

10.5.2.3 Mass Spectrometry Of Compounds (1) - (7):

The mass spectra of compounds (1) - (7) are consistent with the general formulae of $\text{TiCl}(\text{NR}_2)_3$. The spectra show the presence of the parent ion. The fragmentation of the compounds all show initial breakdown of the alkyl chains in the compound, prior to loss of the remainder of the dialkylamido ligand, including the nitrogen atom.

The spectra also indicate the presence of dimeric species and the tetrakis compound in small amounts in the gas phase, which are likely to be due to gas phase interaction between fragments.

10.5.2.4 TGA Studies:

TGA studies of the materials were carried out under a nitrogen atmosphere.

Table 10-5 Main Features Of TGA Studies:

Compound:	Weight Loss	Temp. Range	Residue
(2)	72.29	148-420	26.54
(4)	80.88	130-320°C	18.46
(5)	83.72	160-350°C	16.03
(7)	85.33%	180-500°C	13.03

The compounds produced in this section are clearly less volatile than the tetrakis compounds currently used for the deposition of TiN. However the TGA data indicates that whilst having lower volatilities, they may have sufficient volatilities at higher temperature for transport of the precursor for APCVD.

Compound (7), appears to have sufficient thermal stability to be held at $>100^\circ\text{C}$. Use of this precursor as a precursor for TiN has therefore been attempted by APCVD.

10.5.2.5 Structure of Compounds (1)-(7):

The use of dialkylamido ligands with longer alkyl chains has been investigated in an attempt to prevent oligomerisation of the species by the formation of halide bridges. The compounds produced using the n-propyl and iso-propyl dialkylamines were both liquid compounds and therefore at room temperature no structural determination for these materials was possible. The di-iso-butylamine product $\text{TiCl}(\text{N}(\text{iBu})_2)_3$, however, is

a solid material that has been structurally characterised by single crystal X-ray diffraction. This shows the compound to be monomeric, with the structure shown in Figure 10-7.

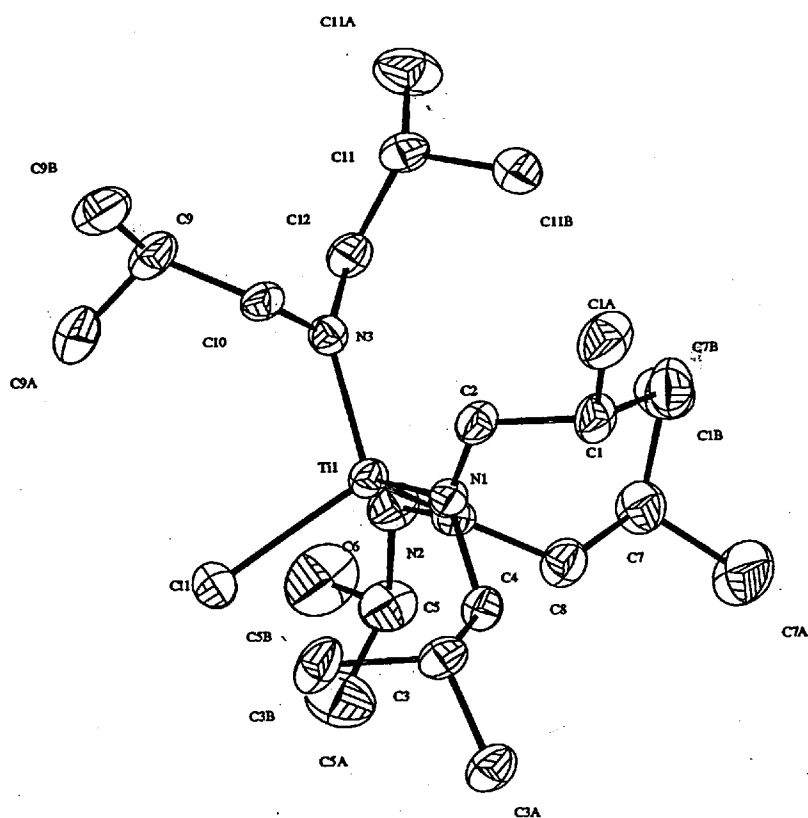


Figure 10-7 Single Crystal X-Ray Structure Of $\text{TiCl}(\text{N}^i\text{Bu})_2_3$

Table 10-6 Selected Bond Lengths(Å) and Bond Angles(°) For TiCl(N(ⁱBu)₂)₃

Ti(1)-N(2)	1.878(3)	Ti(1)-N(1)	1.881(3)
Ti(1)-N(3)	1.885(3)	Ti(1)-Cl(1)	2.313(2)
N(1)-C(4)	1.473(5)	N(1)-C(2)	1.476(4)
C(1)-C(1B)	1.521(6)	C(1)-C(1A)	1.524(5)
C(1)-C(2)	1.532(4)	C(3)-C(3B)	1.524(5)
C(3)-C(4)	1.529(5)	C(3)-C(3A)	1.542(5)
N(2)-C(6)	1.472(5)	N(2)-C(8)	1.485(4)
C(5)-C(5A)	1.503(7)	C(5)-C(6)	1.522(6)
C(5)-C(5B)	1.500(6)	C(7)-C(7B)	1.513(6)
C(7)-C(7A)	1.517(6)	C(7)-C(8)	1.526(6)
N(3)-C(12)	1.455(5)	N(3)-C(10)	1.478(5)
C(9)-C(9A)	1.514(6)	C(9)-C(9B)	1.522(6)
C(9)-C(1)	1.529(5)	C(11)-C(11A)	1.517(6)
C(11)-C(11B)	1.518(5)	C(11)-C(12)	1.536(5)
N(2)-Ti(1)-N(1)	110.05(14)	N(2)-Ti(1)-N(3)	110.3(2)
N(1)-Ti(1)-N(3)	108.84(13)	N(2)-Ti(1)-Cl(1)	108.63(10)
N(1)-Ti(1)-Cl(1)	109.27(12)	N(3)-Ti(1)-Cl(1)	109.75(10)
C(4)-N(1)-C(2)	114.7(3)	C(4)-N(1)-Ti(1)	114.4(2)
C(2)-N(1)-Ti(1)	130.8(3)	C(1B)-C(1)-C(1A)	111.3(4)
C(1B)-C(1)-C(2)	112.4(3)	C(1A)-C(1)-C(2)	107.8(3)
N(1)-C(2)-C(1)	116.8(3)	C(3B)-C(3)-C(4)	112.4(3)
C(3B)-C(3)-C(3A)	109.2(3)	C(4)-C(3)-C(3A)	110.4(3)
N(1)-C(4)-C(3)	116.1(3)	C(6)-N(2)-C(8)	115.1(3)
C(6)-N(2)-Ti(1)	112.2(2)	C(8)-N(2)-Ti(1)	132.6(2)
C(5A)-C(5)-C(6)	113.3(4)	C(5A)-C(5)-C(5B)	110.9(4)
C(6)-C(5)-C(5B)	108.4(4)	N(2)-C(6)-C(5)	115.9(3)
C(7B)-C(7)-C(7A)	112.9(4)	C(7B)-C(7)-C(8)	112.3(4)
C(7A)-C(7)-C(8)	109.1(4)	N(2)-C(8)-C(7)	116.5(4)
C(12)-N(3)-C(10)	115.1(3)	C(12)-N(3)-Ti(1)	132.5(2)
C(10)-N(3)-Ti(1)	112.4(2)	C(9A)-C(9)-C(9B)	110.3(3)
C(9A)-C(9)-C(10)	112.7(3)	C(9B)-C(9)-C(10)	109.5(3)
N(3)-C(10)-C(9)	115.7(3)	C(11A)-C(11)-C(11B)	111.1(4)
C(11A)-C(11)-C(12)	109.9(3)	C(11B)-C(11)-C(12)	112.1(3)
N(3)-C(12)-C(11)	117.0(3)		

This implies that by increasing the steric bulk of the dialkylamine used, prevention of halide bridge formation has been achieved and as such the volatility of the material is likely to have been improved. The structure of $\text{TiCl}(\text{N}^i\text{Bu})_3$ is a distorted tetrahedron with the bond angles around the titanium metal centre varying from $108.63(10)^\circ$ to $110.3(2)^\circ$. This structure is similar to that observed for the compound $\text{TiCl}(\text{N}(\text{SiMe}_3)_2)_3$, which is also monomeric.¹⁸

The structures obtained for TiClL_3 type compounds when amine ligands are used, are very different to those observed with alternative ligands; for example the compound $\text{TiCl}(\text{S}_2\text{CNR}_2)_3$ is a pentagonal bipyramidal structure with a seven co-ordinate titanium centre, with the ligand acting in a bidentate fashion.¹⁹

The other compounds studied are also likely to be monomeric species, with similar structures, with the steric bulk of the alkyl-chains preventing the formation of Ti-Cl bridges between metal centres and thus preventing the formation of oligomeric materials.

10.6 Conclusions:

The secondary amine reactions, described in this Chapter appear to be far cleaner than any of the reactions described previously. This is the type of reaction that is required for industry as it achieves:

1. Economical use of materials
2. Products that require minimal purification

These secondary amine compounds also clearly show greater volatilities than the primary amine compounds. The $\text{TiCl}(\text{NR}_2)_3$ compounds are particularly promising, with the larger dialkylamines having been used to provide steric bulk and thereby make the compound more volatile. The monomeric compound $\text{TiCl}(\text{N}^i\text{Bu})_3$ has been synthesised and structurally characterised. The prevention of Ti-Cl-Ti bridging has been possible by increasing the steric bulk of the ligand to an extent whereby a monomeric species is preferred.



For a particular amine.

The use of some of these compounds as precursors for the APCVD of TiN has also been carried out and will be described in later chapters.

10.7 References

1. S. R. Drake, S. A. S. Miller, M. B. Hursthouse and K. M. A. Malik, *Polyhedron*, **1993**, 12(13), 1621
2. S. R. Drake, S. A. S. Miller, M. B. Hursthouse, K. M. A. Malik and D. J. Otway, *J. Chem. Soc. Dalton Trans.*, In Press
3. S. R. Drake, S. A. S. Miller, M. B. Hursthouse, K. M. A. Malik and D. J. Otway, *Inorg. Chem.*, **1993**, (32), 3227
4. J. Fayos, *Z. Aorg. Allg. Chem.*, **1971**, 380, 196
5. M. H. Chisholm, *Trans. Met. Chem.*, **1978**, 3, 321
6. G. W. A. Fowles and R. A. Hoodless, *J. Chem. Soc.*, **1963**, 33
7. Private Communication Inorgtech, Mildenhall, Cambridge, England
8. R. T. Cowdell and G. W. A. Fowles, *J. Chem. Soc.*, **1960**, 2522
9. D. Armstrong, D. Barr, W. Clegg, S. Drake, R. Singer, R. Snaith, D. Stalke and D. Wright, *Angew. Chem. Int. Ed.*, **1991**, 12(30), 1707
10. D. C. Bradley, I. M. Thomas, *J. Chem. Soc.*, **1960**, 3857
11. R. M. Fix, R. G. Gordon and D. M. Hoffman, *Chem. Mater.*, (2), 235,
12. W. A. Nugent and R. L. Harlow, *Inorg. Chem.*, **1979**, 2030
13. C. Spee, J. Linden, V. Assink, K. Timmer, F. Verbeek, H. Meinema, D. Frigo and V. Ven, *J. de Pysique*, **1993**, 3, 289
14. D. C. Bradley and E. G. Torrible, *Canadian J. Chem.*, **1963**, 41, 136
15. R. Fix, R. Gordon and M. Hoffman, *Chem. Mater.*, **1991**, 3, 1138
16. M. Matloubian and M. Gershenson, *J. Electron. Mater.*, **1985**, 14, 633
17. D. C. Bradley and M. H. Glitz, *J. Chem. Soc.(A)*, **1969**, 980
18. C. Airoidi, D. C. Bradley, H. Chadzynska, M. B. Hursthouse, K. M. A. Malik and P. R. Raithby, *J. Chem. Soc. Dalton Trans.*, **1980**, 2010
19. A. H. Bhat, *Inorg. Chem.*, **1974**, 13, 886

11. An Investigation of the Use of Sterically Demanding Amines

11.1 Introduction

The previous chapter described the production of compounds of the general formula $\text{TiCl}(\text{NR}_2)_3$ where R=alkyl group. It has been shown as part of this investigation that using larger alkyl groups, volatile monomeric species that can be transported by conventional bubbler techniques can be synthesised. Unfortunately, the increased size of the alkyl chain required to prevent oligomerisation of the precursor has resulted in a larger carbon content in the precursor.

Whilst in theory the increased carbon content of the precursor should not result in an increase in carbon impurity in the grown film, due to the transamination reaction between the precursor and ammonia in the gas stream, resulting in the amine being liberated, higher carbon higher impurity levels are observed. The increased carbon impurity is believed to occur by one or both of two mechanisms. Firstly decomposition of liberated amine results in contamination of the coating. Secondly, the intermediates formed during the transamination reactions, still have a significant carbon content and thermal decomposition of these intermediates on the substrate can result in carbon contamination.

The use of ligands such as $\text{HN}(\text{SiMe}_3)_2$ would appear to provide the ideal solution. The ligand is sterically demanding and as such provides a similar level of protection for the metal centre to that of the dialkylamines. The breakdown product of the ligand is HSiMe_3 which is a volatile gas and as such should be carried out of the reactor without radical contamination of the coating being observed.

The reaction of $\text{LiN}(\text{SiMe}_3)_2$ and TiCl_4 has been reported by various workers to give the tris rather than the tetrakis derivative:^{1,2}



The single crystal X-ray structure of the zirconium derivative of this material is shown in Figure 11-1.

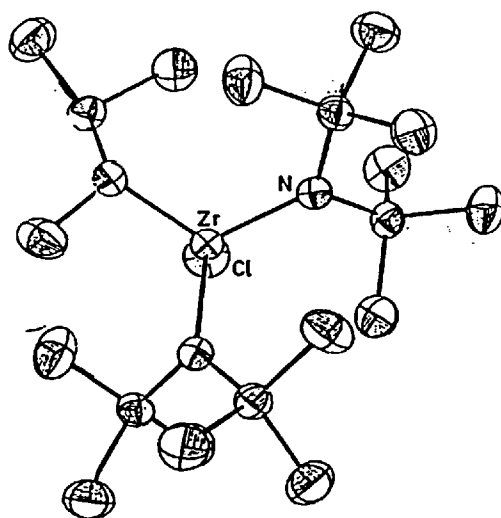
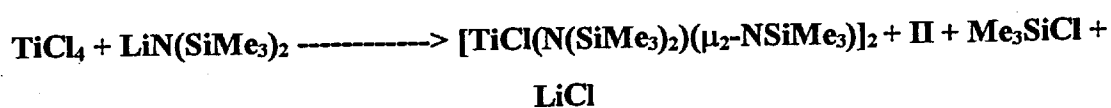


Figure 11-1 Single Crystal X-Ray Structure Of $\text{ZrCl}(\text{N}(\text{SiMe}_3)_2)_3$.¹

Other work using this ligand by Yu.Ovchinnikov *et. al.* however, has shown that the reaction of TiCl_4 with the lithiated amine $\text{LiN}(\text{SiMe}_3)_2$ can result in the formation of two titanasilazanes.²



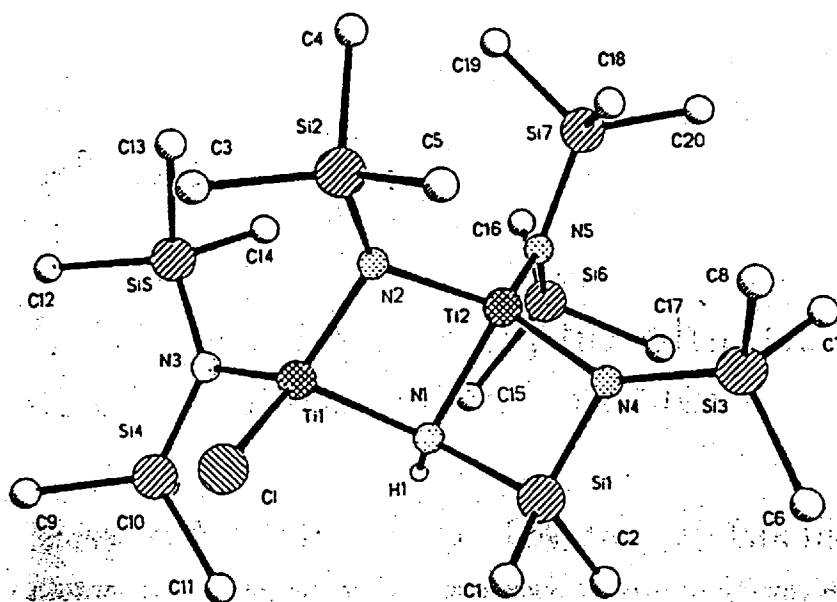
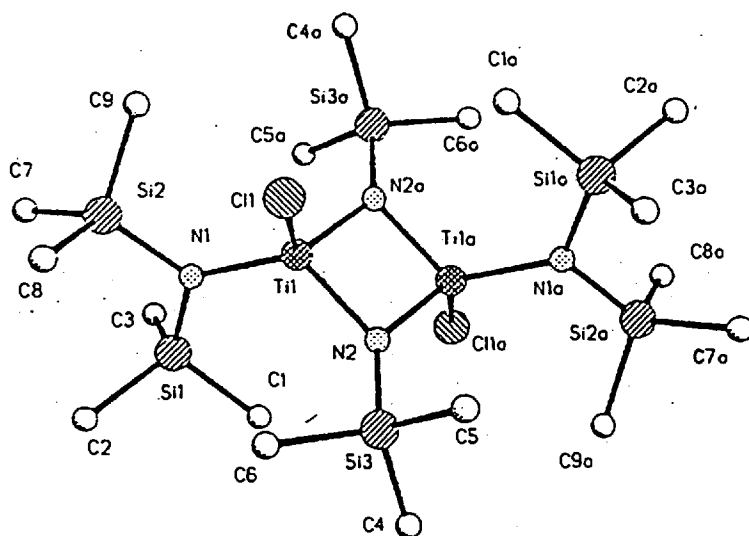


Figure 11-2 Single Crystal X-Ray Structures Of The Titanasilazanes.²

Whilst these compounds are not tetrakis compounds, the materials particularly the monomeric $\text{TiCl}(\text{N}(\text{SiMe}_3)_2)_3$ would still be of use for deposition of TiN. Unfortunately the materials have very low volatilities, and mass transport of the precursor in a CVD system would not be achievable under atmospheric pressure conditions. As with the dialkylamines, however, the use of this sterically demanding ligand, does prevent the production of Ti-Cl-Ti bridge formation and monomeric species are formed, unless bridging occurs via fragmented ligand species such as NSiMe_3 .

Investigation of derivatives of the $\text{HN}(\text{SiMe}_3)_2$ ligand such as $\text{HN}(\text{SiMe}_3)\text{R}$ where R=alkyl group have not been reported for titanium.

The ligands $\text{HN}(\text{SiMe}_3)\text{R}$ where R=alkyl group are not commercially available, apart from the ligand $\text{HN}(\text{SiMe}_3)(^t\text{Bu})$. The synthesis of these ligands has been carried out via the following route:



Where R= n-propyl, iso-propyl, n-butyl, iso-butyl

The reactions of TiCl_4 and $\text{Ti}(\text{NMe}_2)_4$ with these ligands have also been investigated.

11.2 Ligand Synthesis:

A 1 litre three necked round bottom flask was fitted with an overhead stirrer and a nitrogen gas inlet, to keep the material under an inert atmosphere. The flask was charged with 700 ml of dried diethyl-ether, and 75 ml of n-propylamine. The mixture was then cooled in an ice bath and stirred vigorously. Then 58 ml of ClSiMe_3 was added dropwise over a period of 4 hours, with vigorous stirring. After the addition was complete the mixture was stirred overnight at room temperature under an inert atmosphere.

The resulting solution and white precipitate was filtered through a sinter funnel under an inert atmosphere. The solvent was then removed under vacuum, to yield the crude ligand.

Distillation of the ligand under an inert atmosphere was then carried out and the ligand was stored under nitrogen in a glovebox.

This preparation was used for the preparation of the amines:

1. $\text{HN}(\text{SiMe}_3)(\text{C}_6\text{H}_{11})$
2. $\text{HN}(\text{SiMe}_3)((\text{CH}_2)_3\text{CH}_3)$
3. $\text{HN}(\text{SiMe}_3)((\text{CH}_2)_2\text{CH}_3)$
4. $\text{HN}(\text{SiMe}_3)(\text{CHMe}_2)$

An investigation of the reactions of TiCl_4 and $\text{Ti}(\text{NMe}_2)_4$ with the ligands and the commercially available $\text{HN}(\text{SiMe}_3)_2(\text{tBu})$ was conducted.

11.3 Synthesis:

11.3.1 The Reaction TiCl_4 and $\text{HN}(\text{SiMe}_3)(\text{tBu})$

A flame dried Schlenk was charged with 20 ml of dried benzene and 2ml (10 mmol) of the amine $\text{HN}(\text{SiMe}_3)(\text{tBu})$. This solution was then cooled to -78°C in a card-ice bath and to the cooled solution 6.78ml (10mmol) of 1.55 M BuLi was added. This solution was stirred as it was allowed to warm to room temperature, and then was stirred for a further 30 minutes. This solution was then re-cooled and 0.38 ml (3.5 mmol) of TiCl_4 was added slowly. This solution was then allowed to slowly warm to room temperature, and the resulting brown solution was refluxed under nitrogen for 3 hours. The resulting solution was filtered through a celite pad and the brown filtrate was stripped to dryness. The resulting brown solid was taken up in 10ml of toluene and allowed to stand at room temperature. Small brown crystals appeared in the solution after a period of 2-3 weeks. These were collected and stored under nitrogen with a small amount of solvent (approximately 0.5ml), and sent for X-ray analysis.

X-ray analysis of this material resulted in a compound of the formula $[\text{TiCl}(\text{N}^{\text{tBu}})(\text{N}(\text{SiMe}_3)(\text{tBu}))]_2$.

11.3.2 The Reaction of $\text{Ti}(\text{NMe}_2)_4$ and $\text{Li}(\text{N}(\text{SiMe}_3)\text{R})$

In a flame dried 1 litre three necked round bottomed flask, fitted with a nitrogen flow and two input septums, 500 ml of dried benzene was added. To this cooled solution, 18 ml (0.028 mol) of 1.55 M BuLi was added. To the cooled solution, 3.66g (0.028 mol) of amine was added. This was stirred and allowed to warm to room temperature, where it was stirred for a further 10-15 minutes. This produced a clear solution. The solution was then re-cooled and 25g (0.11 mol) of $\text{Ti}(\text{NMe}_2)_4$ was added to the cooled solution. The solution was then stirred and allowed to warm to room temperature. The solution was then stirred for a further 5 hours, with a white precipitate of LiNMe_2 being produced in the solution.

The solution was then filtered under an inert N_2 atmosphere and the resulting filtrate collected. The filtrate was stripped to remove the solvent under vacuum, and the resulting yellow oil taken back up in 50 ml of benzene. The solution was then re-filtered to remove any excess LiNMe_2 and the filtrate was again reduced to dryness under vacuum. The resulting yellow oil 32g (94 % yield) was collected and stored in the glove box.

The yellow oil produced was characterised as $\text{Ti}(\text{NMe}_2)_3\{(\text{N}(\text{SiMe}_3)(^n\text{propyl})\}$.

Infra Red(Neat Oil): 2961(s), 2766 (s), 2713(m), 2505(m), 1840(w), 1541(m), 1467(s), 1453(s), 1418(s), 1375(m), 1355(m), 1290(m), 1247(s), 1150(s), 1120(s), 1092(m), 1056(s), 1017(s), 944(s), 898(s), 839(s), 299(s), 737(s), 678(s), 634(m), 591(s), 570(s), 404(m), 282(m), 313 (m), 291(w), 279(w), 247(w), 230(w); **^1H NMR(d_6 -benzene):** 0.1 ppm (SiMe_3 , integration 9H), 0.89 (CH_3 , triplet, integration 3H), 1.53 (CH_2 , multiplet, integration 2H), 3.08 ppm (NMe , integration 18H), 3.38 ppm (NCH_2 , integration 2H); **^{13}C NMR(d_6 -benzene):** 1.8 ppm (SiMe_3 , singlet), 11.9 ppm (CH_3 , singlet), 30.3 ppm (CH_2 singlet), 44.7 ppm (NMe , triplet), 51.6 ppm (NCH_2 , singlet)
Mass Spectrum(EI^+): 310 [$\text{Ti}(\text{NMe}_2)_3\text{N}(\text{SiMe}_3)(n\text{-propyl})$], 265 Loss propyl or tBu, 237 Loss SiMe_3

11.4 Discussion:

11.4.1 The Reaction of TiCl_4 and $\text{LiN}(\text{SiMe}_3)\text{R}$

An investigation of the reaction of TiCl_4 with the lithiated amines $\text{LiN}(\text{SiMe}_3)\text{R}$, was conducted in an attempt to produce the equivalent reaction products to those obtained using the dialkylamine ligands described previously i.e. $\text{TiCl}_2(\text{NR}_2)_2$ and $\text{TiCl}(\text{NR}_2)_3$.

The lithiated ligands $\text{LiN}(\text{SiMe}_3)\text{R}$, did not react in an analogous fashion, however. The products produced appear to be mixtures of two or more materials with separation of the two products being difficult. This has lead to impure materials being obtained and resulted in low yields of the isolated material. Brown crystals of one of the products produced during the reaction of TiCl_4 with the lithiated amine $\text{HN}(\text{SiMe}_3)(^t\text{Bu})$ have been isolated. The X-ray structure of the isolated material is shown below:

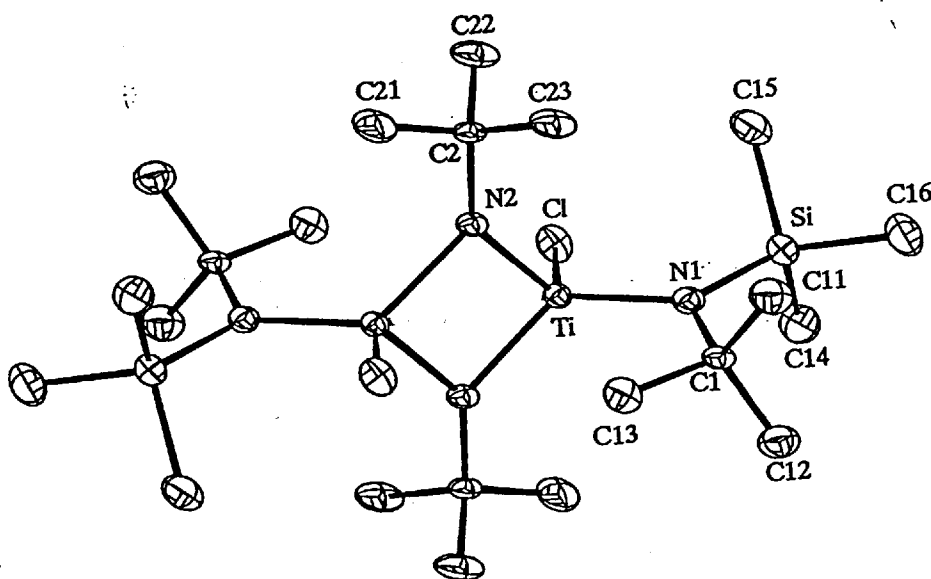
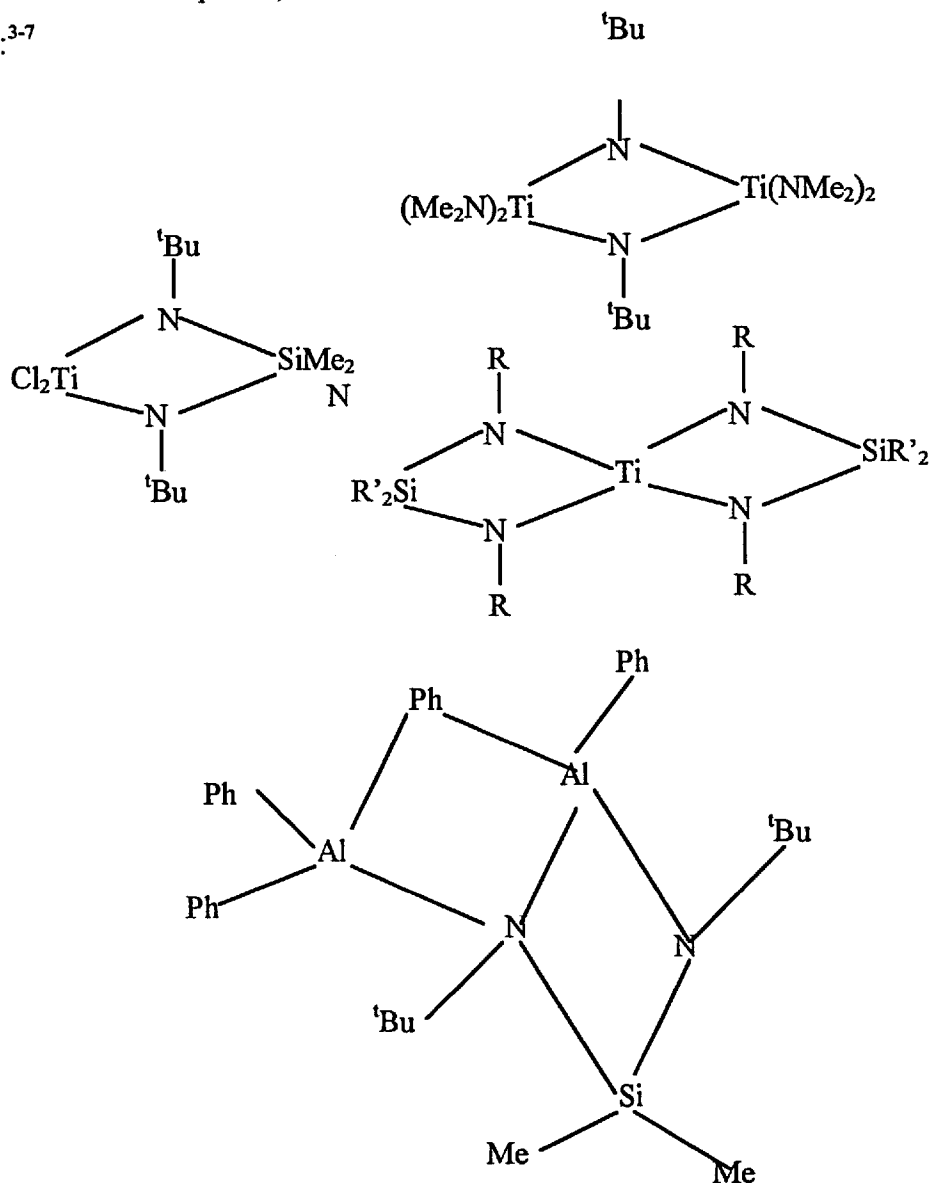


Figure 11-3 Single Crystal X-Ray Structure Of $[\text{TiCl}(\text{NSiMe}_3^t\text{Bu})(\mu_2\text{N}^t\text{Bu})]_2$

Table 11-1 Selected Bond Angles(Å) and angles(°) for [TiCl(NSiMe₃^tBu)(μ₂N^tBu)]₂

Ti-N(2)	1.880(2)	Ti-N(1)	1.935(2)
Ti-N(2)#1	1.944(2)	Ti-Cl	2.2743(7)
N(1)-Si(1)	1.779(2)	N(1)-C(1)	1.529(3)
C(1)-C(11)	1.525(4)	C(1)-C(12)	1.525(3)
Si(1)-C(14)	1.858(3)	C(1)-C(13)	1.558(3)
Si(1)-C(16)	1.862(3)	Si(1)-C(15)	1.858(3)
N(2)-Ti#1	1.944(2)	N(2)-C(2)	1.498(3)
C(2)-C(21)	1.531(3)	C(2)-C(23)	1.512(3)
N(2)-Ti-N(1)	115.93(8)	C(2)-C(22)	1.535(3)
N(1)-Ti-N(2)#1	125.49(8)	N(2)-Ti-N(2)#1	85.68(8)
N(1)-Ti-Cl	112.17(6)	N(2)-Ti-Cl	107.62(6)
N(2)-Ti-Ti#1	43.73(6)	N(2)#1-Ti-Cl	106.43(6)
N(2)#1-Ti-Ti#1	41.95(5)	N(1)-Ti-Ti#1	134.08(6)
C(1)-N(1)-Si(1)	118.21(14)	Cl-Ti-Ti#1	113.51(3)
Si(1)-N(1)-Ti	116.49(10)	C(1)-N(1)-Ti	124.57(14)
C(12)-C(1)-N(1)	111.45(2)	C(12)-C(1)-C(11)	111.8(2)
C(12)-C(1)-C(13)	107.7(2)	C(11)-C(1)-N(1)	111.9(2)
N(1)-C(1)-C(13)	107.6(2)	C(11)-C(1)-C(13)	106.1(2)
N(1)-Si(1)-C(15)	109.76(11)	N(1)-Si(1)-C(14)	108.98(11)
N(1)-Si(1)-C(16)	117.48(11)	C(14)-Si(1)-C(15)	111.83(13)
C(15)-Si(1)-C(16)	102.84(13)	C(14)-Si(1)-C(16)	105.84(13)
C(2)-N(2)-Ti#1	125.93(14)	C(2)-N(2)-Ti	139.0(2)
N(2)-C(2)-C(23)	109.8(2)	Ti-N(2)-Ti#1	94.32(8)
C(23)-C(2)-C(21)	110.0(2)	N(2)-C(2)-C(21)	109.3(2)
C(23)-C(2)-C(22)	109.7(2)	N(2)-C(2)-C(22)	107.8(2)
C(21)-C(2)-C(22)	110.1(2)		

The product produced during this reaction is similar to the titanasilazane $[\text{TiCl}(\text{N}(\text{SiMe}_3)_2)(\mu_2\text{NSiMe}_3)]_2$ reported by Ovchinnikov *et. al.*,² from the reaction of TiCl_4 with the lithiated amine $\text{HN}(\text{SiMe}_3)_2$, although a second titanasilazane was also isolated by these workers. The production of a second compound in the reaction between the lithiated amine $\text{Li}(\text{NSiMe}_3)(^t\text{Bu})$ with TiCl_4 would explain the low yield of the isolated product. Unlike the titanasilazanes previously isolated with the amine $\text{HN}(\text{SiMe}_3)_2$, however, the bridging between the titanium atoms in the product isolated in this study is achieved by bridging N^tBu groups rather than NSiMe_3 . Several other tetra-co-ordinated Ti^{IV} complexes, with similar structural characteristics are known. These include:³⁻⁷



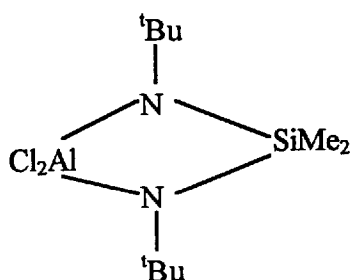


Figure 11-4 Other Similar X-Ray Structure.³⁻⁷

As in $[\text{TiCl}(\text{NSiMe}_3^t\text{Bu})(\text{N}^t\text{Bu})]_2$ the TiN_2Ti and TiN_2Si cycles in these structures are all close to planar with a nearly square form. The $\text{Ti}-\text{N}(\text{sp}^2)$ bond lengths are all in the range 1.88-1.92 Å, except for in $[\text{Cl}_2\text{Ti}(\mu_2\text{N}^t\text{Bu})_2(\text{SiMe}_2)]$ where the bond length is shorter at 1.829(5) Å due to the influence of the two electronegative chlorine atoms on the titanium.

Other metals such as aluminium have also been shown to exhibit similar structural motifs for example in the compound $\text{Cl}_2\text{Al}(\mu_2\text{N}^t\text{Bu})(\mu_2\text{N}^t\text{BuH})\text{SiMe}_2$.⁹

Whilst isolation and determination of the structure of the titanasilazane product has only been achieved for the reaction of TiCl_4 with the lithiated amine $\text{LiN}(\text{SiMe}_3)(^t\text{Bu})$, it is believed that the other amines have undergone analogous reactions, with dimeric species being formed by $\mu_2\text{-NR}$ fragments. The formation of this bridging is likely to occur by the initial formation of a $\text{TiCl}_2(\text{N}(\text{SiMe}_3)\text{R})_2$ species. Dimerisation of this material would then occur by the further rearrangement of this material.



Due to the dimeric nature and resulting low volatility of these products, the utilisation of the materials as precursors for the atmospheric chemical vapour deposition of titanium nitride has not been possible.

11.4.2 The Reaction of $\text{Ti}(\text{NMe}_2)_4$ and $\text{LiN}(\text{SiMe}_3)\text{R}$

The reaction of the titanium tetrakis dialkylamido, $\text{Ti}(\text{NMe}_2)_4$ with the neat amine was initially investigated, but no reaction was observed with any of the amines. Therefore an investigation of the reaction of the lithiated amines was conducted. Whilst the reaction of one equivalent of the lithiated amine with the tetrakis dimethylamido was

attempted for the range of amines, a reaction was only observed with the lithiated amine $\text{HN}(\text{SiMe}_3)(^n\text{Pr})$. The other amines failed to produce a product.

The failure of the other lithiated amines to react with the $\text{Ti}(\text{NMe}_2)_4$ may be due to two reasons. Firstly the driving force for the reaction may be insufficient. However attempts at heating the reaction mixture still resulted in a failure to obtain reaction and therefore may suggest that this is not the problem. Secondly the formation of an intermediate that can result in ligand exchange may not be possible with the other amines, with the increased steric bulk associated with increasing the chain length of the alkyl grouping resulting in an overcrowding of the metal centre.

The product produced from the reaction of the $\text{Ti}(\text{NMe}_2)_4$ with $\text{Li}(\text{N}(\text{SiMe}_3)(^n\text{Pr}))$ has been investigated by a range of spectroscopic techniques and identified as $\text{Ti}(\text{NMe}_2)_3(\text{N}(\text{SiMe}_3)(^n\text{Pr}))$

11.4.2.1 NMR Analysis:

Analysis of the material by ^1H and ^{13}C NMR was carried out in d_6 -benzene. The ^1H NMR of the compound is shown in figure 11-5. The spectra clearly shows the presence of the SiMe_3 protons at approximately 0.1 ppm and the n-propyl alkyl chain protons. The splitting of the resonance's of these groups is as expected with each group being split by the neighbouring protons, therefore the CH_3 of the propyl chain is a 1:2:1 triplet, being split by the CH_2 of the propyl chain, whilst the CH_2 is a multiplet, due to splitting by both the CH_3 and NCH_2 protons of the propyl chain.

A singlet due to the NMe protons is observed at approximately 3ppm. Integration of the spectra is in agreement with the formulation $\text{Ti}(\text{NMe}_2)_3(\text{N}(\text{SiMe}_3)(^n\text{Pr}))$.

The ^{13}C NMR of this material is shown below and is also consistent with the formulation of the material, showing resonances due to both the ligands present in the molecule.

Both spectra show slight impurity peaks in the spectrum due to the formation of a small amount of $\text{Li}(\text{NMe}_2)$ as a by-product. Further purification of the material to remove this by-product was attempted, but a small amount of impurity was always obtained.

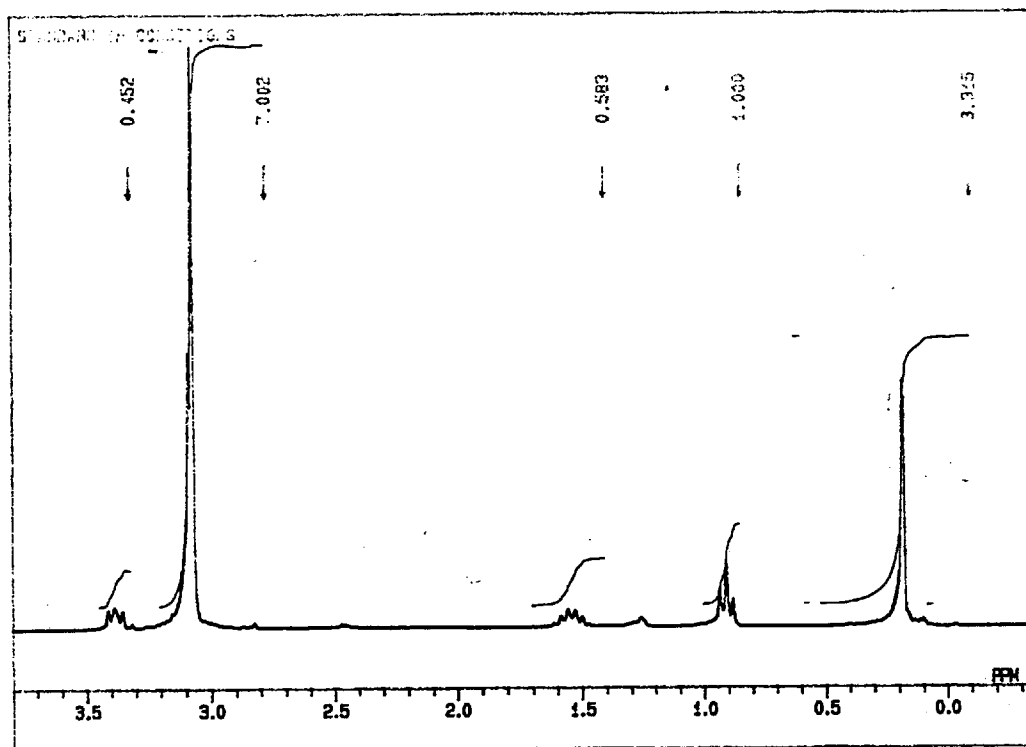


Figure 11-5 ^1H NMR Of $\text{Ti}(\text{NMe}_2)_3(\{\text{NSiMe}_3\}\{\text{nPr}\})$

11.4.2.2 Mass Spectrometry:

Mass spectral analysis of the material shows the presence of the intact parent ion $\text{Ti}(\text{NMe}_2)_3(\text{N}(\text{SiMe}_3)\text{R})$ at 310 a.m.u. Initial fragmentation of the molecule then appears to be due to the breakdown of the ligands with the loss of the n-propyl and SiMe_3 groups from the mother ion clearly visible.

11.5 Conclusion:

The investigation of the reactions of the amines $\text{HN}(\text{SiMe}_3)\text{R}$ with both titanium tetrachloride and the tetrakis(dialkylamido) compound $\text{Ti}(\text{NMe}_2)_4$ have been conducted.

Investigation of the reaction of these amines with titanium tetrachloride has shown that they do not result in analogous reaction products to the products produced from the reaction of titanium tetrachloride and dialkylamines. Whilst the initial reaction giving the materials TiCl_2L_2 may be similar the amines HNSiMe_3R , then undergo a further rearrangement, resulting in the formation of $\mu_2\text{NR}$ bridging between the titanium atoms. The resulting novel dimerised products have low volatilities and as such are not suitable as precursors for the atmospheric pressure chemical vapour deposition of titanium nitride.

Investigation of the reaction of the amines $\text{HN}(\text{SiMe}_3)\text{R}$ with titanium tetrakis(dimethylamido) compounds has also resulted in the formation of the novel compound $\text{Ti}(\text{NMe}_2)_3(\text{N}(\text{SiMe}_3)(^i\text{Pr}))$. Production of equivalent compounds with longer alkyl-chains has not been possible because the increased steric bulk of the alkyl-chain is believed to be preventing ligand exchange.

Attempts at further ligand exchange have also failed, with the material $\text{Ti}(\text{NMe}_2)_3(\text{NSiMe}_3)(^i\text{Pr})$ again being isolated along with the unreacted lithiated amine. The failure to produce ligand exchange, with larger alkyl chain materials is believed to be due to steric crowding around the metal centre.

Unlike the reaction of titanium tetrachloride with the amines, however, the novel material $\text{Ti}(\text{NMe}_2)_3(\text{N}(\text{SiMe}_3)(^i\text{Pr}))$ is a volatile liquid material similar to the tetrakis starting material. Therefore further investigation of this material as an improved precursor for the deposition of titanium nitride has been attempted.

11.6 References

1. C. Airoidi, D. C. Bradley, H. Chudzynska, M. B. Hursthouse, K. M. A. Malik and P. R. Raithby, *J. Chem. Soc. Dalton Trans.*, **1980**, 2010
2. Y. E. Ovchinnikov, M. V. Ustinov, V. A. Igonin, Y. T. Stuchkov, I. D. Kalikhman and M. G. Voroukov, *J. Organometallic Chem.*, **1993**, 461, 75
3. D. C. Bradley, H. Chudzynska, J. D. J. Backer-Dirks, M. B. Hursthouse, A. A. Ibrahim and M. Motevalli, *Polyhedron*, **1990**, 9, 1423
4. W. D. Beiersdorf, D. J. Brauer and H. Burger, *Z. Anorg. Allg. Chem.*, **1981**, 475, 56
5. D. J. Thorn, W. A. Nugent and R. L. Harlow, *J. Am. Chem. Soc.*, **1981**, 103, 357
6. R. A. Jones., M. H. Seeberger, J. L. Atwood and W. E. Hunter, *J. Organomet. Chem.*, **1983**, 247, 1
7. D. J. Brauer, H. Burger, E. Essig and W. Geschwandter, *J. Organomet. Chem.*, **1980**, 190, 343
8. C. C. Cummins, C. P. Schaller, G. D. Van-Duyne, P. T. Wolczunski, A. W. E. Chan and R. Hoffmann, *J. Am. Chem. Soc.*, **1991**, 113, 2985
9. M. Veith, H. Lange, O. Recktenwald and W. Frank, *J. Organomet. Chem.*, **1985**, 294, 273

12. Titanium Nitride Deposition Using Novel Precursors

12.1 Introduction:

During the synthetic investigation, into new molecular precursors for the atmospheric chemical vapour deposition of titanium nitride a range of novel materials have been synthesised. Many of the materials produced are of limited use as precursors due to their low thermal stability and low volatility, which prevent mass transport of the precursor. Two novel precursors which do appear to have sufficient volatility and thermal stability for mass transport have been identified.

1. $\text{TiCl}(\text{NEtBu})_3$
2. $\text{Ti}(\text{NMe}_2)_3(\text{N}(\text{SiMe}_3)(\text{iPr}))$

The steric bulk of the ligands around the titanium metal centre has been increased compared with the traditional precursors used for titanium nitride deposition such as $\text{Ti}(\text{NMe}_2)_4$ in an attempt to increase the protection of the metal centre, which is crucial in preventing pre-reaction of the precursor in the gas phase with additives such as ammonia. The investigation of deposition of titanium nitride from these novel precursors is described.

12.2 APCVD Of Titanium Nitride From $\text{TiCl}(\text{NEt}^i\text{Bu})_3$:

This precursor is a liquid material at room temperature and was prepared as described in Chapter 10. The material was loaded into a bubbler in a glove box and attached to the apparatus. Growth of TiN from these materials was then attempted using both the thermal decomposition of the precursor and using ammonia as a co-reactant.

12.2.1 Thermal Decomposition of $\text{TiCl}(\text{NEtBu})_3$:

Typical growth conditions for the deposition of TiN using this precursor were similar to those used for the tetrakis dialkylamide, $\text{Ti}(\text{NMe}_2)_4$ and are outlined in Table 12-1.

Table 12-1 Typical Growth Conditions For TiN Growth From the Thermal Decomposition of $\text{TiCl}(\text{NEtBu})_3$

Precursor Used:	$[\text{Ti}(\text{NEtBu})_3\text{Cl}]$
Substrate Used:	Glass
Gas Used:	Nitrogen.
Regulator Pressure:	0.5 bar
Substrate Temperature:	ca. 400°C
Inlet Gas Temperature:	ca. 23-25°C
Bubbler Temperature:	ca. 80-170°C
Main Gas Flow Rate:	ca. 4.5 l / min
Bubbler Gas Flow Rate:	ca. 500-600 cc / min
Heater Tape Setting:	Maximum (circa 100-130°C)
Number Of Bakeout Cycles Used:	3
Time Of Coating Run:	15 Minutes

Initial attempts at film growth using this precursor were poor with little carry over of the precursor, until the bubbler was heated to approximately 170°C. Holding the precursor at this temperature resulted in slight decomposition of the precursor, with a small amount of decomposed precursor being seen in the base of the bubbler after a period of 3-4 hours at a temperature of 170°C. Investigation of the partially decomposed material by NMR spectroscopy was not successful due to the reduced solubility of the precursor. This may be a result of partial thermal decomposition of the precursor resulting in some form of polymeric material. Transport of the bulk of the material did not initially appear to be affected by this degree of decomposition, however, although after approximately 5-6 hours at a temperature of 170°C the carryover of precursor decreased further until after 8 hours no carryover was possible.

Film growth from the decomposition of the precursor at substrate temperatures above 400°C was achieved, but as with the thermal decomposition of the precursor $\text{Ti}(\text{NMe}_2)_4$, the resulting films were dark, and appeared carbonaceous in places. This is likely to be due to incorporation of carbon impurities from the decomposition of the precursor.

The growth rate achieved for this precursor was lower than for $\text{Ti}(\text{NMe}_2)_4$. This is likely to be due to the lower volatility of this precursor resulting in less mass transport. Due to the carbonaceous nature of the coatings attempts at improving the film properties by the addition of ammonia in the gas stream were also investigated.

12.2.2 Reaction of $\text{Ti}(\text{NEtBu})_3\text{Cl}$ with NH_3 :

Typical growth conditions for the growth of titanium nitride from $\text{TiCl}(\text{NEtBu})_3$ and ammonia are outlined in Table 12-2.

Table 12-2 Typical Growth Conditions for the Growth of TiN From $\text{TiCl}(\text{NEtBu})_3$ and ammonia

Precursor Used:	$[\text{TiCl}(\text{NEtBu})_3]$
Substrate Used:	Glass
Gas Used:	Nitrogen
Regulator Pressure:	0.5 bar
Substrate Temperature:	150-400°C
Inlet Gas Temperature:	ca. 23-25°C
Bubbler Temperature:	ca. 80-85°C
Main Gas Flow Rate:	ca. 4.5 l / min
Bubbler Gas Flow Rate:	ca. 250 cc / min
Ammonia Gas Flow Rate:	ca. 10-20 cc/ min
Heater Tape Setting:	Maximum (100-120°C)
Number Of Bakeout Cycles Used:	Overnight Bakeout
Time Of Coating Run:	30 Minutes and 60 Minutes

The addition of ammonia to the gas stream resulted in similar results to the growth of TiN from the precursors $\text{Ti}(\text{NMe}_2)_4$ and NH_3 . The temperature at which film growth occurred was lowered from that required to achieve thermal decomposition of the precursor. This resulted in films of a golden colour being produced, but as with the titanium tetrakis dimethylamido several problems were encountered:

1. Film growth was very temperature dependant, with coverage of the glass plate deteriorating as the temperature of deposition was increased.
2. Some pre-reaction of the precursor with ammonia was observed, with an involatile intermediate species collecting in the gas distribution baffle.
3. Films obtained still showed significant oxygen incorporation in the coatings.

The increased steric bulk of the ligands used in this precursor were designed to reduce pre-reaction of the precursor with the ammonia in the carrier gas stream. Whilst the precursor did result in film growth under these conditions, pre-reaction of the precursor was still evident with some solids collecting in the gas distribution baffle. Involatile intermediates produced due to the pre-reaction of the precursor with the ammonia carrier gas appeared to be similar to those obtained during film deposition from the $\text{Ti}(\text{NMe}_2)_4$ and ammonia.

The amount of material collected during deposition experiments was dependent upon the ammonia concentration in the gas stream. As the ammonia concentration was increased more material was collected in the baffle. This is consistent with pre-reaction between the ammonia and the precursor resulting in a series of transamination reactions with the formation of involatile intermediates which then collect in the baffle.

The films produced using this precursor were again heavily oxygen contaminated, and typical AFM / Auger results are shown in Figures 12-1 and 12-2:

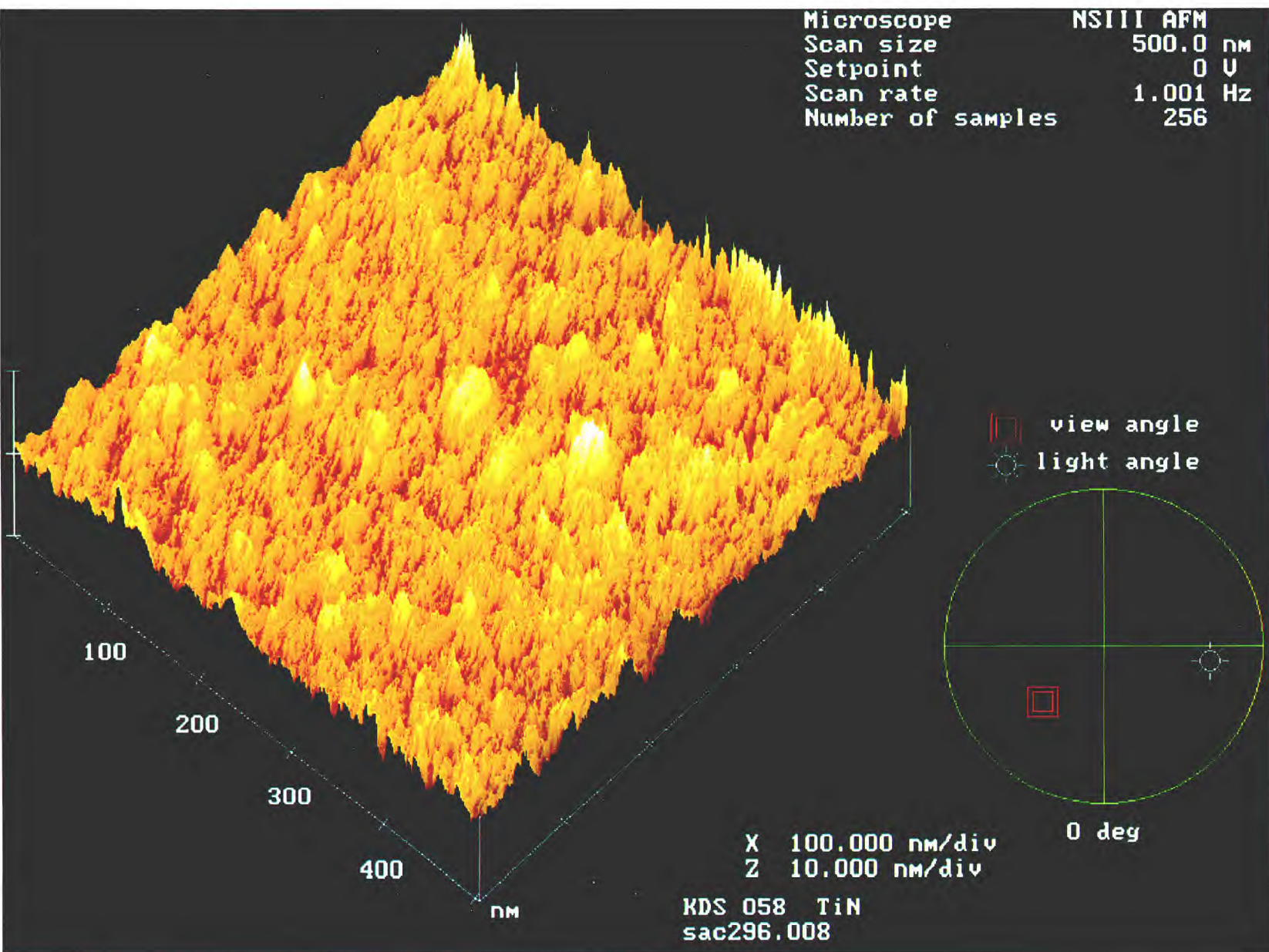
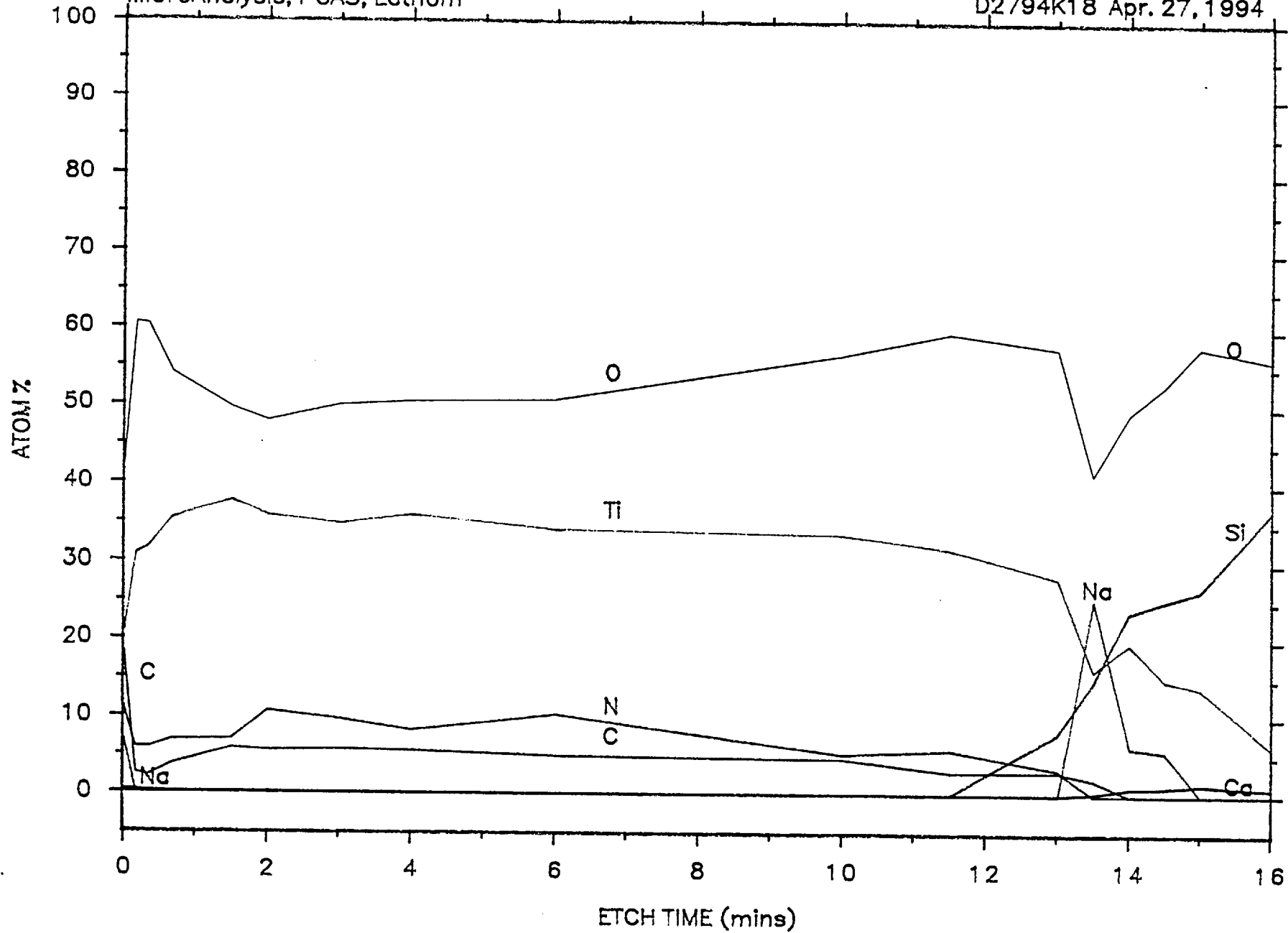


Figure 12-1 AFM Micrograph of TiN Grown From $\text{TiCl}(\text{NEtBu})_3$



Confidential

Whilst the films grown from this precursor were highly contaminated with oxygen, this is believed to be due to contamination in the reactor

12.3 APCVD of Titanium Nitride From $\text{Ti}(\text{NMe}_2)_3(\text{N}(\text{SiMe}_3)(^n\text{Pr}))$:

Film growth using this precursor has been achieved using typical growth conditions with film growth being achieved by both the thermal decomposition of the precursor and the reaction of the precursor with ammonia.

12.3.1 Thermal Decomposition of $\text{Ti}(\text{NMe}_2)_3(\text{N}(\text{SiMe}_3)(\text{Pr}))$

The deposition of titanium nitride by the thermal decomposition of the precursor was achieved using identical conditions to those initially developed for $\text{Ti}(\text{NMe}_2)_4$. Film growth was achieved, but the films were very highly contaminated with carbon and oxygen. Analysis of the films, however, showed no silicon contamination in the coatings. This suggests that thermal decomposition of the precursor resulted in the loss of SiMe_3 which was not incorporated into the film as a contaminant. Whilst the preparation of other materials containing both the NSiMe_3R and $\text{N}(\text{SiMe}_3)_2$ groups was attempted during the synthetic part of this work, no material with sufficient volatility for APCVD was isolated. Use of some of these materials by LPCVD and UHVCVD may well allow sufficient mass transport to be achieved, and may reduce the level of contamination in the films.

12.3.2 Deposition From $\text{Ti}(\text{NMe}_2)_3(\text{N}(\text{SiMe}_3)(\text{Pr}))$ and Ammonia

Addition of ammonia to the reaction stream, resulted in a similar reduction in the deposition temperature and the carbon contamination levels in the coatings. Unfortunately, however, no reproducible film growth was achieved with this precursor. Mass transport of the material appeared to be variable, with a rapid decrease in the carryover of precursor occurring on holding the precursor at a temperature of $> 50^\circ\text{C}$ for 1-2 hours. Use of the precursor by LPCVD would reduce these problems, however, by lowering the temperature the material is held at in order to achieve sufficient mass

transport.

12.4 Conclusions:

The use of sterically hindered ligands around the titanium metal centre has been investigated for its potential to:

1. Reduce pre-reaction of the precursor with ammonia.
2. Reduce the oxygen contamination in the coating.

Two novel precursors were investigated, $\text{TiCl}(\text{NEtBu})_3$ and $\text{Ti}(\text{NMe}_2)_3(\text{N}(\text{SiMe}_3)(^n\text{Pr}))$. Film growth has been achieved using both of these precursors, using two routes; firstly the thermal decomposition of the precursor and secondly pre-reaction of the precursors with ammonia.

Thermal decomposition reactions of these precursors produced coatings with heavy carbon contamination, similar to those from the titanium tetrakis(dimethylamido) precursor. As such these precursors cannot be considered to show any advantages over the tetrakis compound. Oxygen contamination of the final coating was also seen to be a significant problem throughout the film growth.

The addition of ammonia to the precursors, again allowed film growth to be achieved, with the growth temperature being reduced significantly from approximately 400°C down to approximately $150\text{-}250^\circ\text{C}$.

Whilst both of these precursors resulted in film growth, the significant problem of oxygen incorporation that was observed for the system $\text{Ti}(\text{NMe}_2)_4$ and NH_3 was not solved, with large levels of oxygen impurities still being observed in the final coating. This suggests that these more highly hindered ligands did not have the desired effect of preventing oxygen incorporation in the coating. This is believed to be a result of the

reactor chamber design, resulting in a significant water vapour level. This is then believed to have reacted with the precursor forming oxide contamination.

The growth rate of these precursors was also significantly lower than those seen for $\text{Ti}(\text{NMe}_2)_4$ and this may be due to the lower volatility of these precursors. The higher temperature required to volatilise these precursors is also likely to be a problem, with decomposition of the precursor occurring at higher temperatures after the precursor has stood at temperature for a period of time.

The films grown using both the commercially available precursors and the synthesised precursors appeared to result in heavily oxygen contaminated films. This is believed to be due to the reactor set-up used for the experiments. The atmospheric pressure at which the rig is operated and the fact that the reactor chamber is made of glass, result in a large background level oxygen sources. Due to the oxyphilic nature of the titanium metal centre, the coatings produced had a large degree of oxygen impurity, which reduced the films electrical and optical properties.

A further significant problem associated with the deposition of TiN that has been identified is the problem of pre-mixing the chemicals prior to entry into the reactor. Films grown have shown that both the oxygen impurity level in the coating and the properties of the final film appear to be related to the ammonia concentration in the gas stream. The addition of even a low level of ammonia results in a significant reduction in both the level of carbon in the final coating and also the temperature at which film growth can be achieved, and at higher ammonia concentrations a significant reduction in the oxygen contamination level is also observed.

However, the addition of ammonia also results in a large degree of pre-reaction of the precursor to produce an involatile air sensitive intermediate believed to be a transamination product. This species results in line blockage if the ammonia concentration is too high. Clearly this is not desirable and can be a safety hazard due to a risk of pressurisation.

The investigation suggests that the pre-mixing of these chemicals is important,

but the degree of pre-mixing and the ammonia concentration both appear to require close control in order to achieve good coatings.

13. Overall Conclusions and Recommendations.

This thesis has investigated the applicability of atmospheric chemical vapour deposition as a technique for the growth of thin films on glass substrates. Two types of coating have been investigated, firstly transparent conducting oxides (In_2O_3 and tin doped indium oxide-ITO) and secondly the metal nitride, titanium nitride. The effect of these coatings on the electrical and optical properties of the glass substrate have been studied. The deposition experiments have been carried on an undercoated glass substrate material that has not previously been reported in the literature for chemical vapour deposition. This layer has acted as a blocking layer to protect the coating from attack from impurities leeching out of the glass and as a colour suppressant. The apparatus used for the deposition experiments was a cold wall atmospheric pressure chemical vapour deposition apparatus in which all precursors were mixed prior to entry into the reactor chamber. This apparatus is significantly different from that used in previous literature reports for the APCVD of these materials. The size of the reactor is much larger and the chemical delivery system is different. The use of this apparatus has lead to an indication of the thermal stability and transport characteristics of a range of both commercially available and novel precursors, which has previously not been reported, and gives a direct comparison between a wide range of precursors.

13.1 *Transparent Conducting Oxides (In_2O_3 and ITO)*

The work in this thesis has shown that both In_2O_3 and ITO can be successfully deposited on glass substrates using atmospheric chemical vapour deposition. A range of chemical precursors have been investigated and the advantages and disadvantages of these precursors has been identified. The study has identified the best precursors and the optimum film growth conditions to obtain the best electrical and optical properties from the films. The conditions identified are significantly different from those previously reported by other techniques.

The study has identified that careful consideration of the deposition precursors is required if optimum properties are to be achieved. The use of gas phase chemical

reaction in a pre-mixed system to synthesise new intermediate species in the gas phase has also been shown to be a valuable technique, with utilisation of this method allowing control over the structural properties of the grown film to be achieved.

The properties of the resulting films using this system have exceeded those of previous literature reports of CVD ITO and are comparable with the best obtained from other physical deposition techniques with resistivities of $1.2\text{--}1.5 \times 10^{-4} \Omega \text{ cm}$ being achieved. The properties fulfil the requirements for the coating to be used as low emissivity coatings on glass and are close to those required for solar control products, two of the potentially largest areas for industrial application of such coatings. Future work using this system may be able to further improve the properties of the resulting films by:

1. Utilisation of gas phase chemistry to incorporate a second dopant into the film. For example the formation of a fluorine containing dopant into the gas phase intermediate species may result in the fluorine acting as a substitutional dopant for the fluorine, improving the properties of the coating further.
2. Utilisation of gas phase chemistry to reduce impurity incorporation. This has only currently been reported for the deposition of TiO_2 , and may be developed further in chemical vapour deposition systems.

The work has also identified a method for obtaining preferred orientation growth coatings by APCVD, which has previously not been reported for CVD systems. Such control over the preferred orientation growth of ITO has been identified as a crucial parameter in obtaining optimum electrical and optical properties from the coatings. Extension of this principle to other systems may further improve the properties of CVD films, and aid the future development of coatings for meeting the ever expanding requirements of industry.

13.2 Metal Nitride (Titanium Nitride)

The investigation of titanium nitride deposition in this work has highlighted some of the considerable technical challenges which must be overcome if deposition of titanium nitride by atmospheric chemical vapour deposition is to become an industrial process.

The study has identified that the currently used commercial precursor $\text{Ti}(\text{NMe}_2)_4$ is not a viable precursor for use in a pre-mixed atmospheric chemical vapour deposition process, due to the pre-reaction of the precursor with any co-reactant.

Two new precursors for the deposition of titanium nitride thin films have been identified and the control of the pre-reaction between ammonia and the titanium precursor in the gas phase has been identified as the crucial parameter for successful deposition on a pre-mixed system.

Whilst the present study has not solved the problems associated with APCVD titanium nitride, the work program has identified several new routes for the continued improvement of the process:

1. The use of gas phase reactions as a method of *insitu* precursor preparation utilising simple commercially available precursors.
2. The use of sterically demanding ligands, in conjunction with *insitu* preparation, to provide control over the rate of reaction of the precursors in the gas phase.

The results show that APCVD as a method of film preparation is a powerful technique, which gives equivalent properties to films deposited on far more expensive and widely studied coating technology. The future development of such systems, in conjunction with the chemists' ability to develop new precursors, will allow the formation of new materials and new industrial applications for thin films.

14. Appendix.

Extra crystallographic data:

Compound	[TiCl ₄ (Me ₂ NCH ₂ CH ₂ NHMe)]
Crystal Group	Monoclinic
Temperature	150 K
Wavelength	0.71069 Å
Space Group	P2 ₁ (No.4)
Unit Cell Dimensions:	
a=	7.138(1) Å
b=	10.747(1) Å
c=	8.148(1) Å
alpha=	90°
beta=	111.56(1)°
gamma=	90°
Z	2
Density (Calculated)	1.667 g cm ⁻³
F(000)	296
Theta Range For Data Collection	2.6-29.7 °
Index Ranges	-9<=h<=8, -10<=k<=14, -8<=l<=10
Reflections Collected	3842
Independent Reflections	2059 [R(int)=0.0175]
Refinement Method	Full matrix least squares on F ²
Data / Parameters	2059 / 164
R	0.0207
wR	0.0240

$R=\Sigma(\Delta F)/\Sigma(F_o) ; wR=[\Sigma\{w(\Delta F)^2/\Sigma(w(F_o)^2)\}]^{0.5}$

R and wR for the inverse enantiomorph are 0.0249 and 0.0291 respectively.

Compound	[TiCl(N ^t Bu ₂) ₃]
Crystal Group	Triclinic
Temperature	150 K
Wavelength	0.71069 Å
Space Group	P1bar
Unit Cell Dimensions:	
a=	11.095(5) Å
b=	15.75(2) Å
c=	16.977(6) Å
alpha=	88.99(4)°
beta=	87.08(3)°
gamma=	86.10(3)°
Z	2
Density (Calculated)	1.059 mg m ⁻³
F(000)	1044
Theta Range For Data Collection	1.75-25.04 °
Index Ranges	-12<=h<=12, -18<=k<=16, -19<=l<=15
Reflections Collected	9229
Independent Reflections	7489 [R(int)=0.0337]
Refinement Method	Full matrix least squares on F ²
Data / Parameters	7489 / 547
Goodness of fit on F ₂	0.533
Final R indices [I>2sigma(I)]	R1=0.0469, wR2=0.1158
R indices (all data)	R1=0.0685, wR2=0.1433

Compound	$[\text{TiCl}(\mu_2\text{N}^t\text{Bu})\{\text{N}(\text{SiMe}_3)(^t\text{Bu})\}]_2$
Crystal Group	Monoclinic
Temperature	150 K
Wavelength	0.71069 Å
Space Group	$\text{P2}_1/\text{c}$
Unit Cell Dimensions:	
a=	11.477(2) Å
b=	9.3497(8) Å
c=	15.693(1) Å
alpha=	90°
beta=	107.36(2)°
gamma=	90°
Z	4
Density (Calculated)	1.235 mg m ⁻³
F(000)	640
Theta Range For Data Collection	2.72-25.04 °
Index Ranges	-12<= <i>h</i> <=12, -10<= <i>k</i> <=10, -16<= <i>l</i> <=16
Reflections Collected	6530
Independent Reflections	2395 [R(int)=0.0578]
Refinement Method	Full matrix least squares on F ²
Data / Parameters	2395 / 154
Goodness of fit on F ₂	1.008
Final R indices [<i>I</i> >2sigma(<i>I</i>)]	R1=0.0345, wR2=0.0874
R indices (all data)	R1=0.0405, wR2=0.0886

Vapour Pressure Data:

Compound	Temperature	Estimated Vapour Pressure (Torr)
In(thd) ₃	205°C	11.49
DMT	30°C	0.15
DMTDA	30°C	0.08
SnCl ₄	30°C	30.55