THE STRUCTURE AND RESIDUAL STRESS OF THIN METAL FILMS CONDENSED IN VACUUM

by

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ABSTRACT

An investigation has been made into the factors determining the structure of tin films condensed in vacuum onto amorphous substrates at room temperature. The variation in orientation of the films with the deposition parameters, (i) residual gas pressure, (ii) rate of deposition, (iii) thickness of the film, has been studied using the electron diffraction technique. Supplementary experiments in a high partial pressure of oxygen and/or onto polymer-coated substrates were also carried out.

Several orientations were obtained depending upon the deposition conditions - these were with (110), (001), (100) or (301) planes parallel to the substrate surface.

A (110) orientation of the film was preferred for high residual gas pressures, i.e. $> 3 \times 10^{-5}$torr. Reduced mobility of the metal atoms on the substrate surface gives an initial random orientation and a (110) orientation develops with increasing thickness.

A (100) orientation was always obtained for residual gas pressures below 5×10^{-7}torr. The origin of this (100) orientation is attributed to the melting and resolidification of the small crystallites, in high-purity conditions, during the initial stages of deposition.

A mixed (100) and (001) orientation occurred for non-continuous films in the pressure range 5×10^{-7} to 1×10^{-5}

torr. A (001) orientation was found when the film became continuous and this structure was maintained up to 5000Å thickness. It is suggested that a recrystallisation takes place during the coalescence stage of film growth which gives rise to the orientation changes. It is also suggested that gas molecules adsorbed on growing crystallite surfaces create a difference in the value of surface energy between crystallites in different orientation. This is sufficient to cause preferential growth of one orientation rather than another by diffusion or coalescence of neighbouring crystallites. The possibility of controlling the structure of thin films is discussed.

The deposition of films in a high partial pressure of oxygen or onto polymer substrates showed orientation changes consistent with the previous results. The detection of SnO in films deposited in a high partial pressure of oxygen and at high rates of deposition gives an estimate of of the temperature of the surface of the film, and this is in contradiction to the values calculated by other workers. The theories of stress in thin films are therefore discussed.

1. INTRODUCTION

1. General Introduction

Thin films are now being used for numerous commercial applications especially in the electronics field and for space applications. Also, because one dimension is greatly reduced and surface effects should be significant in causing slip on a larger fraction of the slip planes, the study of the mechanical properties of some films is reaching the stage where it may yield information relevant to the theory of work hardening of crystals and the mechanism of fatigue. However, before these possibilities are realised, a more thorough understanding of the intrinsic properties of thin films themselves is required.

Frequently, the properties of the available film materials are not satisfactory for the requirements of a device and these have to be changed in a predetermined manner. This requires a detailed knowledge of the factors which determine film properties. One of the oldest approaches for changing properties in the case of metals, is that of alloying, but the use of oxides or nitrides in place of pure materials can also be used in thin films to obtain specific properties. Another possible method of changing the properties, especially in the case of films for superconductive or magnetic devices, is to alter the film structure, especially the lattice

orientation. Many films are structure sensitive; e.g. magnetic, superconductive, electrical, optical; but this approach has not been utilized so far because of the difficulties encountered in structural control; and in several cases, undesired structural variations in films have hampered industrial production.

Most of the research on the structure of thin films so far has either predominantly investigated nucleation and growth phenomena without relation to deposition parameters, or dealt with the connection between deposition parameters and film properties. Despite much progress in experimental techniques in recent years, a unifying quantitative theory of film growth and the inter-relationship between deposition parameters, film structure, and physical properties, has still to be achieved. The present experiments described below throw further light on the relation of the film structure to the conditions of deposition, especially in the case of films of tin. These results on film growth help furthermore to clarify the position concerning the origin of residual stress in thin films.

2. Nucleation and Growth of Thin Films

(i) Condensation Theory

Most of the detailed nucleation and growth studies on thin metal films have been made by examining vacuum-deposited films because of the relatively simple environmental conditions encountered with this technique. Wood (1916) concluded that when the vapour density was below what was assumed to be a critical value for a given substrate temperature, condensed films would not be obtained. Conversely, there appeared to be a critical surface temperature, for a given vapour stream density and substrate, above which no deposit formed. The critical density of the vapour stream was, in fact, a function of substrate temperature.

Volmer (1921) realised that no velocity of growth could exceed a definite maximum which is reached when every incident atom is condensed. He was then able to show, by using mercury condensing as crystals on a cooled surface, that film growth in one direction was about one thousand times greater in some directions than in others. He postulated that if an atom or molecule strikes a face of a crystal, the molecule is bound with less energy than that equivalent to the molecular heat of evaporation. He also concluded that the atom is only adsorbed onto the surface and can migrate by virtue of its thermal motion, but it cannot re-evaporate again

because it is bound by the energy given off in the form of heat of adsorption. Esterman (1923) tested this theory by condensing silver onto polished quartz at room temperature and he found that when the average thickness of the deposit was less than that corresponding to a monomolecular layer the film was not homogeneous but consisted of scattered crystallites. This can only be explained by the fact that the silver atoms, incident uniformly over the quartz surface, migrate along it before forming a less mobile aggregate by collision with another silver atom.

According to the theory developed by Frenkel (1924) to account for the existence of a critical temperature above which condensation does not occur, atoms arriving on the substrate move over the surface during their life-time at the end of which they re-evaporate. The activation energy for surface migration is much less than the evaporation energy. If the average life-time of an atom on the substrate surface is sufficiently long for another to collide with it, then an atom-pair can be formed and the average life-time of the doublet is increased. Also, the energy required to re-evaporate the pair is considerably increased.

According to Levinstein (1949), the kinetic energy of the vapour particles has no influence upon the condensation process because of the random nature of the collisions, and it is permissible to assume that the vapour atoms collide with the substrate inelastically, with a transfer of some kinetic

energy to the substrate lattice. He found with antimony films that, for slow evaporation rates, the vapour condensed to form aggregates on the substrate surface which were larger in size than those formed by fast evaporations. The explanation given for the dependence of particle size on the evaporation rate required two additions to Frenkel's theory; (i) that the number of atoms in motion on the substrate surface is proportional to the number of atoms arriving at the substrate surface/unit time; (ii) atoms or molecules will move over the surface until they suffer a collision with other deposit atoms or molecules and thereby lose their mobility. He was then able to show that the mean mobility time of antimony atoms on collodion was less than 2×10^{-5} secs.

However, when an atom approaches the substrate to within atomic distances, forces will arise between the respective atoms, and these are usually of the Van der Waals type, i.e. they are electrostatic in nature. Only in those cases where a chemical bond is formed between the film and substrate will ionic forces predominate - Mayer (1955). Therefore, although 'surface mobility' depends on the one hand upon the energy of condensation and the thermal energy corresponding to the substrate temperature, it also depends on the forces between the deposited atom and the substrate, and these will restrict mobility. For instance, Campbell (1962) has shown how the mobility of gold varied by a factor of 10 when evaporated onto different substrates, and the occurrence of

epitaxy in deposits on single crystal substrates proves that nucleation may be affected by the periodic field of the substrate. Also, seeding experiments conducted by Zehender (1950), show that heteronucleation can be predominant in certain circumstances. Even on clean amorphous substrates, nucleation centres might be provided by deep potential minima and by impurities. In fact, the more recent work on the nucleation of thin films has shown that preferential nucleation tends to take place at etch pits or steps in the surface.

Frenkel's model of the statistical formation of atomic doublets is obviously a gross simplification, but it is now generally accepted that, provided the mean free path of the residual gas molecules is much longer than the distance between the source and the substrate, the metal atoms approach the substrate to within atomic distances without collision. Forces of Van der Waals type then arise and the metal atoms can display 'surface mobility' which depends upon the thermal and condensation energies. The ratio of condensed to the total impinging atoms is called the accomodation coefficient of condensation, and for most solids approaches unity for a substrate temperature sufficiently below the melting temperature of the evaporant, (i.e. $\simeq$ 0.25 x melting temp.).

Depending upon the mobility of the condensed surface atoms, Palatnik and Komnik (1959) distinguished between two-dimensional crystalline, liquid, and gaseous condensation phases. Electron micrograph evidence, in the case of Zn,

showed that the separate particles have well-defined crystallographic shape, while for Sn the vapour to liquid transformation occurs and the particles are spherical in shape. In this case they suggest that the vapour condenses in the form of liquid drops which crystallise after supercooling without losing their spherical shape. Experiments with bismuth condensed onto a glass substrate, with a temperature gradient across it, showed where the condensation mechanism changes from vapour-solid into vapour-liquid condensation when the substrate temperature is high enough.

It can be concluded therefore, that the freshly condensed atoms on a substrate surface form a two-dimensional surface layer of relatively high mobility, resembling in many ways a liquid phase where the condensation process has a minor influence on the structure formation, and more essential are the migration and nucleation phenomena in the mobile surface-layer.

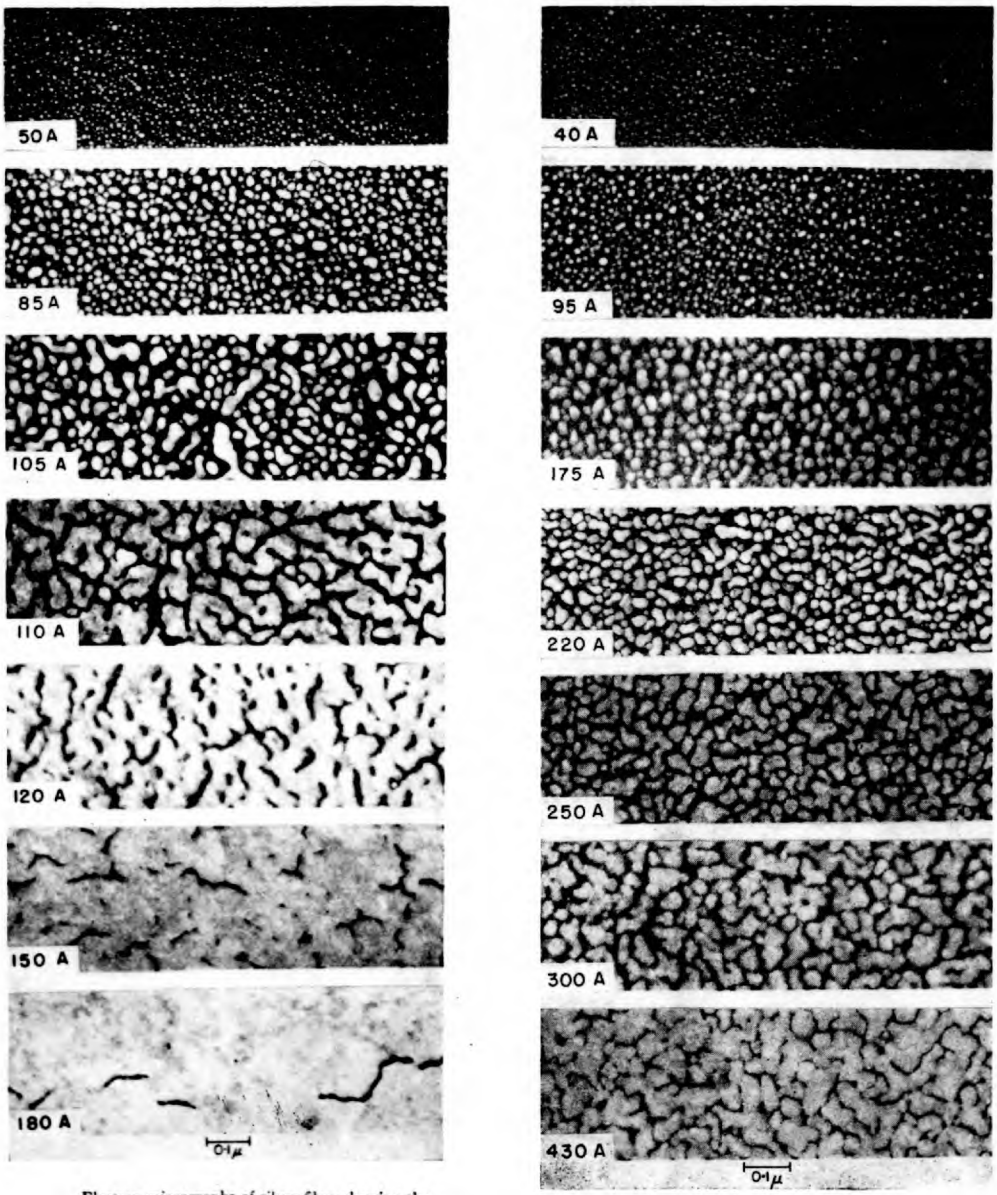
(ii) Initial Growth Processes

Since the 'pairs' or 'triplets' of atoms formed in the initial stages of deposition can serve as nucleation centres, these initial stages of film formation should be influenced by the deposition rate. This was confirmed for silver films condensed upon silica or formvar substrates by Sennett and Scott (1950) in a series of electron micrographs

shown in Fig (1). It can be seen that the 180Å film deposited at a high rate of deposition (90Å/sec) is almost continuous, while a 175Å film deposited at 0.15Å/sec consists of isolated islands. These results agree with the work of Levinstein (1949) and Picard and Duffendack (1943) for cadmium and zinc films, in that slowly evaporated films are more aggregated for thicknesses over 100Å. It can be deduced from this work that the higher deposition rate has resulted in a larger number of nucleation centres which grew together at an early stage, thus forming a continuous film. The slow rate of deposition, on the other hand, resulted in island formation. Pashley (1964) and his co-workers have also observed this phenomenon for gold films deposited onto molybdenum disulphide at 400°C, and confirm that the initial stages of growth involve the formation of three-dimensional nuclei, even when the average thickness of the deposit is less than one atomic diameter.

According to Pashley (1956), when the amount of deposit atoms on the substrate is increased to a certain value, crystallisation occurs and nuclei are spontaneously formed. The nucleus, it is assumed, can be oriented. This process might form large numbers of nuclei of almost the same size, so that for a certain period in the growth process the number of nuclei would increase, but their sizes would not increase appreciably.

Campbell (1962) has shown for lithium fluoride deposited upon carbon films that, for a constant rate of



Electron micrographs of silver films showing the structure at the seven indicated thicknesses.

Electron micrographs of silver films deposited in 20 minutes.

Fig.1. Variation of Structure of Silver Films deposited onto formvar at different Deposition Rates.

(After Sennett and Scott, 1950).

deposition, the size of the islands in the initial stages of growth increases with thickness up to a certain point above which the size decreases. This effect was most pronounced at slow rates of deposition, but the phenomena could not be observed when he tried to repeat the experiment for gold films deposited onto carbon substrates. When the deposition rate was varied, he was able to show for films of equal thickness, that the fastest deposition rate gave smaller island formation. He deduced from values obtained for the fractional area covered at different expected thicknesses and rates, that cubic nuclei of a finite size - between 50 and 100Å side - suddenly appear. The sudden appearance of nuclei of a finite size had previously been observed by Newman and Pashley (1955) for copper films deposited onto single crystal substrates, and also by Newman (1957) for the growth of tin on a silver (111) face at room temperature when the nucleation occurred at an average thickness of about 10Å to give a partially oriented layer. However, Campbell concludes that, before the nucleation point is reached, the material appears to be adsorbed on the substrate surface.

It has also been found that the solidification temperature for very small droplets of metal is lower than that of the bulk material. Turnbull (1950) found pronounced supercooling effects for 50μ diameter droplets of various metals. Takagi (1954) has observed similar effects for thin films of lead and bismuth, while Blackman and Curzon (1959)

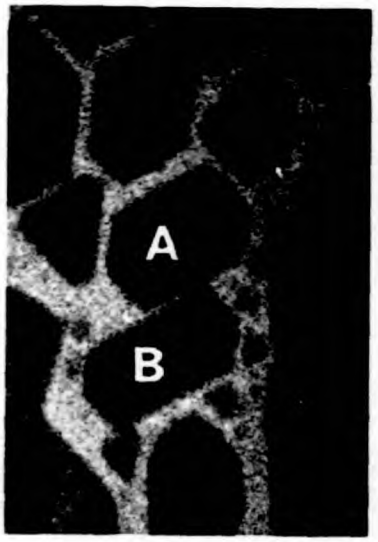
and Saikia (1961) observed the same thing for tin films. For thin films, the solidification temperature decreases as the average thickness of the deposit decreases. With this behaviour, a layer condensed onto a substrate at a given temperature could be in a liquid or an amorphous state until the thickness reaches a point at which the solidification temperature of the layer equals the temperature of the substrate. Nucleation would then occur. Contrary to this, Jones and Wood (1964) have found no reduction in the melting point of aluminium films, at least down to thicknesses of 100Å.

Direct observation of the growth process was achieved by Bassett (1961) who examined the growth of silver deposits onto molybdenum disulphide cleavage faces. Nuclei, approximately 100Å in diameter were initially observed and growth then occurred laterally. As the islands grew, the nuclei joined together with sufficient relative rotation not to introduce detectable imperfections at the joining interfaces. At a later stage, dislocations were created but it is significant that they disappeared later in the deposition process. This seems to indicate considerable mobility and rearrangement at this stage of growth. According to Bassett, the lowest energy configuration of the original interface between nuclei and the substrate corresponds to a minimum energy distribution of interfacial dislocations. The indications are that the nuclei possess considerable rotational and, in some cases, transitional mobility on the surface, especially in the early

stages of deposition.

Pashley et al (1964) examined in detail the behaviour of gold films, deposited onto molybdenum disulphide at 400°C, during the initial stages of deposition inside an electron microscope. When adjacent nuclei touched, they joined together very rapidly in a liquid-like manner, the process taking less than about 0.1 sec. Also nuclei having well-defined crystallographic shapes before coalescence became rounded during the event, and the composite island took up the crystallographic shape again, provided a long enough period elapsed before interacting with further nuclei (See Fig. 2). This effect was more pronounced with gold than with silver deposits. They conclude that the main transport mechanism responsible for the liquid-like coalescence is that of surface diffusion.

Also, since the state of aggregation of the deposit is closely related to the mode of nucleation and growth characteristics in the initial stages, the condition and nature of the substrate surface critically affects the structure during these initial stages. Watt (1960) found that a thin layer of bismuth oxide, (which has a strong affinity for gold), on glass inhibited the surface diffusion of the gold and gave rise to a more uniform deposit which became continuous at a lower thickness than films deposited onto glass substrates. Thus, the principal contribution of the initial substrate surface to the condensation process occurs when the condensed



(*a*)





(*b*) (*c*)

A set of frames from a ciné film of gold grown on MoS_2 at 400°C, showing the change in shape of islands during and after coalescence. (*a*) arbitrary zero ; (*b*) 1·2 sec ; (*c*) 60 sec. Magnification × 190 000.

Fig.2. (After Pashley et al 1964).

layer is not more than a few atom layers thickness. Subsequent condensation is then determined primarily by the state of the deposit itself.

It is now widely recognised that the initial stages of growth of vacuum-deposited metal films usually lead to the formation of discrete three-dimensional nuclei, and that continuous films are formed at a later stage of growth. The general conclusion by which growth proceeds, in f.c.c. metals, is that the nuclei increase in size as the deposition proceeds without any further nuclei being formed. After the nuclei reach a certain average size, the number of nuclei decreases continuously, with a corresponding increase in the average size. Pashley (1964) has recently shown that the deposit atoms migrating over the existing nuclei lead to important additional effects during deposition. These effects, now classed as, 'liquid-like behaviour', are associated with structural changes including recrystallisation, which occurs when the film becomes continuous.

3. The Structure of Thin Metal Films

(i) Development of Film Orientation during Deposition

(a) Growth on Amorphous Substrates

Having arrived at the substrate surface, the deposited atoms arrange themselves in a manner which usually depends upon three parameters; (i) the surface structure of the substrate (amorphous, polycrystalline, or single crystalline); (ii) the substrate temperature - which affects the mobility of the condensing atoms; and (iii) the rate of deposition, which influences the nucleation process. It will also be shown in the present experiments that the residual gas pressure influences the growth process, and the growth phenomena associated with variations in these parameters are discussed more fully in the following sections.

Under certain evaporation conditions and with low melting point metals, crystallites of polycrystalline thin films show preferred orientation even on amorphous substrates. In these films, a certain crystallographic plane is arranged parallel to the substrate surface, but the orientation is random in the other two directions; i.e. the crystals are rotated randomly about the direction normal to the substrate surface. In conditions where there is a larger binding energy between the condensing atoms than between film atoms and the

the substrate surface; or there is a high surface mobility, the first atomic layers of the film will be in a two-dimensional crystalline order corresponding to the natural atomic arrangement of the condensing material: i.e. a close-packed structure for most metals. A regular lattice plane is thus grown parallel to the substrate surface and acts as a base for crystallisation of subsequently condensing layers.

The orientations of crystalline metals on amorphous substrates at room temperature have been investigated, using electron diffraction techniques, by many workers. - Kirchner (1932), (1934); Finch and Quarrell (1933); Prins (1933); Beeching (1936); Hass (1938), (1942); Was (1939); Evans and Wilman (1952); Murbach and Wilman (1953) - and in most cases, it was observed that the deposit tended to grow with a preferential orientation. Evans and Wilman (1952) and Wilman (1952) were the first to make an extensive and detailed study of the nature of the orientations developed and their relation to the deposition conditions. They found that materials having high atomic mobility, (Zn: Cd: Sb: Bi), develop initially a densely populated plane parallel to the mean substrate surface even when the vapour stream is oblique. It was found that, as the deposits become thicker, a preferred growth of those crystals whose main faces are most nearly normal to the vapour stream developed at the expense of others. Materials with low atomic mobility, (Fe: Al), have little or no orientation in thin layers, but at oblique vapour incidence, the upper

regions of thicker deposits develop one-degree orientation with an oblique axis. It was concluded that the orientation originates from the fine scale roughness of the deposit surface followed by a progressive increase in atomic mobility during growth due to the progressive increase in temperature.

These observations on the surface mobility can only mean, as pointed out by Evans and Wilman (1952) and Wilman (1955), that the temperature of the deposit surface has risen substantially during the deposition process. They concluded that, in many cases when the deposition conditions lead to oriented deposits at the film surface, the temperature may rise to several hundred degrees centigrade in deposits formed at 15-300 Å/sec. The surface temperatures reached during deposition were in fact concluded to be higher than the normal recrystallisation temperature of the deposited metal because this is where surface mobility first becomes appreciable (see Section 3 (ii) a. on deposition at high substrate temperatures) i.e. 200-300°C for Cu; 200°C for Ag and Au; 530-600°C for Ni; and 350-450°C for Fe.

In support of these observations, it is interesting to note that Umanskii and Krylov (1936) showed that a thick layer of Fe on glass showed an orientation with a $\langle 111 \rangle$ axis normal to the plane of the glass, and suggested that the heating during the evaporation process was an essential factor in the orientation effect. Also, Schulz (1949) found that thin films of MgF_2 below 1000Å thick were amorphous but thicker

films were polycrystalline. More recently, Thun (1963) has stated that materials such as Bi and Sb which tend to condense in an amorphous state show orientation only after a certain film thickness has been reached. Recrystallisation then occurs fast and spontaneously, and he states, is probably aided by the release of thermal energy.

In recent years, orientation of films has been obtained at room temperature by employing high vacuum and low deposition rate techniques. Vook (1961) has obtained polycrystalline tin films which were (100) oriented at a substrate temperature of $0^{o}C$ in a residual gas pressure of less than 1×10^{-6} torr. However, the numerous experimental observations on film structure are still contrasted with the only limited development of a quantitative atomistic or thermodynamical theory which will enable predictions of the orientations, obtainable under the various deposition conditions, to be made.

(b) Growth on Crystalline Substrates

In the previous section, it was shown that preferentially oriented growth of film crystallites can be caused by the initial nucleation process on a plane substrate surface. However the influence of a potential field of a crystalline substrate can also have an effect on the film orientation, and when this occurs it gives rise to the phenomenon known as 'epitaxy'. Several reviews have been written on this subject especially by Royer (1928); Van der Merwe (1949); Seifert (1953);

and Pashley (1956); so only a brief discussion will be presented here.

The epitaxial type of orientated overgrowth occurs on single-crystalline substrates where the strong periodicity of the substrate surface characterises the 'force field' influencing film formation. The simplest case, not usually included as true epitaxy, is that of identical substrate and evaporant materials, where the deposited atoms continue the structure of the substrate beneath. Considerably more complex conditions are encountered if the deposit and the substrate are composed of different materials. In the case of metals on metals, the theories of Finch and Quarrell (1933); Frank and Van der Merwe (1949a); (1949b); Rhodin (1949); and Blackman and Smollett (1951), postulate that the atoms of the deposit are regularly arranged in potential wells of the substrate surface, and thus form a two-dimensional 'pseudomorphic' lattice. This arrangement can often only be fulfilled with a low misfit between the surface lattice of the substrate and a particular low-index crystal plane of the film material. Subsequent condensing layers would fill the potential minima of the next atomic plane, but the stresses in the film are reduced by a gradual approach to bulk structure as the film thickness increases. According to this model, no epitaxial growth should occur above a lattice misfit of about 15%.

However, Newman (1957) has shown that lead deposited onto (111) silver surfaces forms nuclei closely approximate to monolayers, although the misfit is about 19%. Also

Bassett (1958) and Trillatt and Conjeaud (1958) have shown that when a very thin layer of gold is deposited onto rock-salt cleavage faces at room temperature there is preferential nucleation at the step edges on the substrate surface even when they are only monoatomic in height. The preferential growth at the step edges occurred for both oriented and non-oriented deposits. However, there is no evidence to suggest that the orientation of the nuclei at the step edges is different from those which form on the smooth sections of the substrate.

Thus Bassett, Menter, and Pashley (1959) have stated that the experimental evidence disagrees with the essential aspects of the above theory. Misfits of up to 90% have been observed, and no evidence of pseudomorphism exists because the stationary nuclei on the substrate surface always show lattice spacings which correspond to the bulk material. Their theory of epitaxy therefore postulates that, (i) discrete nuclei form an atomic arrangement corresponding to the order of the bulk lattice and, (ii) further film growth proceeds by deposition onto nuclei, and the growing together of nuclei of identical orientation.

It is now clear that epitaxy is due to short range forces effective only over 2-3 atom diameters. If the temperature and other conditions allow the deposit atoms to have appreciable mobility, these tend to be held in the deepest potential troughs determined by the positions and forces on the substrate surface. Elleman and Wilman (1949) emphasized that the local atomic fitting is the primary factor initiating

the deposit orientation; but as the crystals grow laterally, the degree of lattice misfit must affect the stress and stability of the deposit crystal. Although epitaxial misfits may be expected to tend to distort the deposit crystal lattice towards the form and dimensions of the substrate lattice, ('basal-plane pseudomorphism'), there appear to be no certain examples of abnormal lattice spacings. Evans and Wilman (1952) however, showed that there is often a disorientation of the deposit crystals, consisting of a range of rotation about a main lattice row, which is probably due to the epitaxial misfit causing dislocations, stresses and slip.

Thus while Bassett's model describes the experimental evidence, it does not really account for the phenomenon of epitaxy. It seems that the regular grid of potential wells on the substrate at least determines the regular orientation of individual nuclei which form initially. From this point of view, the earlier theories describe the arrangement of the first few atoms into a nucleus, and the observations of Bassett et al. hold for further growth of the nuclei into a homogeneous film.

(c) The Mechanism of Formation of Oriented Deposits

It has been shown above that the orientation of thin films depends upon the initial mechanism of orientation in the nucleus and on the factors which influence the subsequent

growth of the film; and several theories have been put forward to explain the various types of orientation which occur under different deposition conditions.

Volmer et al (1921) attributed the predominant growth of Zn crystals with (0001) faces perpendicular to the vapour-stream direction to the higher rate of lateral extension of such crystals, due to the atoms striking the (0001) plane migrating to the edges. This assumes that supersaturation is sufficiently high to prevent two-dimensional nucleation in the initial stages being a growth rate determining factor, and also that the rate of lateral extension of a crystal face is determined by the number of atoms which strike it.

Dixit (1933) considered that the atoms in the initial stage of condensation form a two-dimensional gas. With increasing condensation, this becomes supersaturated and two-dimensional crystallites are formed. Those with the least 'two-dimensional vapour pressure' are preferentially formed and these are concluded to be the crystals with the densest atomic packing, i.e. $\{111\}$; $\{100\}$; and $\{110\}$ faces in the f.c.c. lattice.

Sachtler et al (1954) demonstrated that Ni films in the early stages of deposition are usually randomly oriented when deposited at room temperature, while they are oriented on heated substrates. They suggested that in the initial stages of deposition, the films are made up of unoriented crystals bounded by a number of crystallographic planes.

Those that grow fastest have a direction of most rapid growth perpendicular to the substrate surface. For f.c.c. metals, the $\langle 110 \rangle$ direction was derived to be the fastest growth direction, while for b.c.c. crystals, the $\langle 111 \rangle$ direction was given, without derivation and this is the most densely populated row. However this model is inconsistent, for although the growth rate in the $\langle 110 \rangle$ direction for f.c.c. crystals is higher than that in the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions, it is, according to Bauer (1961), even higher in other directions. One would therefore expect a random orientation.

Evans and Wilman (1952), as previously stated, distinguished between two kinds of orientation; (i) growth where initially a densely populated plane is preferentially developed parallel to the mean substrate surface, and (ii) thin layers having little or no orientation, and as the deposit thickness increases, one degree orientation develops. (Further clarification of this theory is given above in section 3 (i) a). However, they also describe the effects of development of facets during the growth of Zn films. These films tend to grow on an amorphous surface with (112) orientation yet with (001) habit in films about 2000Å thick. The initial spread of orientation about the mean was attributed to small variations in the inclination of parts of the substrate surface which gives an initial spread of (112) orientation. Further deposition onto the initial crystallites gave rise to preferential growth of those crystals having their (001) faces normal to the vapour

stream, or nearly so, and the orientation moves away from the initial (112) orientation. A (135) orientation was observed in the upper regions of some Zn films prepared at normal incidence of the vapour, and this was attributed to this modification of the initial orientation due to the development of facets other than (112), evidently (101).

Bauer (1961) proposed a theory which depends upon the high supersaturation of the system; i.e. where two-dimensional nucleation is not a true growth rate determining factor; and on the assumption that very small crystallites are bounded by only a few crystallographic planes. Orientations are classified according to stage of development, i.e. initial; transitional; final; and depending upon the conditions of formation, one, two, or three of these orientations may be observed. For example, very thin films may only show the initial orientation, while films grown at very high supersaturations may only develop a different final orientation. "Growth orientations" develop in a supersaturation region in which nucleation of randomly oriented crystals is sufficiently infrequent to allow growth competition between differently oriented crystals. Therefore, if a film is thin enough, only the initial orientation is observed. However in very thin films transition textures can develop; e.g. by twinning or by other oriented overgrowths on the crystals in the initial orientation. These transition orientations are growth-nucleation textures which at high enough supersaturations are soon

obscured by the final growth orientation. While this final orientation can develop from the transitional orientation, in general it usually develops from a randomly oriented deposit which is formed in the initial stages.

While Bauer's theory accounts, very generally, for the growth trends under certain conditions, it does not give an adequate quantitative explanation for the growth of one preferred orientation in preference to another. It also has two limitations, (i) orientations can be formed at lower supersaturations due to orientation of two-dimensional nuclei, and (ii) the interaction of the residual gas with the vapour at the film surface is neglected.

By considering the nucleation rate in typical vapour condensation experiments, an estimate can be made of the size of the critical nucleus. Yang et al (1954) calculated a rate equation based on a nucleation theory which assumed that a cap-shaped nucleus is formed by statistical fluctuations among atoms which are adsorbed on the substrate surface, and diffuse over it. The results obtained for Na vapour condensing, at high supersaturation ratios - $\sim 10^{19}$ at 159°K and 10^{11} at 213°K, - onto various metal substrates at a residual gas pressure of 5×10^{-5} torr, suggested that the size of the critical nucleus is about one unit cell, (i.e. 9 Na atoms). As these experiments were concerned with the critical deposition conditions, their estimate represents an upper limit of the critical nucleus size. Thus if the supersaturation is more than critical, the nucleus can be expected to be even smaller.

Walton (1962) has also considered the effect of supersaturation on the orientation of thin metal films. At the limit of high supersaturation, the critical nucleus should be a single atom, and when an atom pair is formed, it will grow rather than decay into single atoms. He therefore suggests that as the supersaturation is decreased, either by increasing the substrate temperature or by decreasing the rate of deposition, the point is reached where a pair of atoms becomes the critical nucleus. When the pair becomes unstable, the next smallest stable cluster will be the one which has a minimum of two bonds per atom, etc. (Fig. 3 shows the critical nuclei for stable clusters containing two bonds per atom). The three-atom cluster leads to an orientation such that (111) planes will be parallel to the substrate, and the four-atom cluster will give rise to a (100) orientation.

Where orientation occurs in metal films in the initial stages, it is usually such that a close-packed plane is parallel to the substrate and, as predicted by Walton's theory, the critical nuclei which give the most close packed orientations contain fewer atoms. The number of clusters per unit area of substrate decreases very rapidly with increase in size, therefore the critical nuclei which give close packed orientations will occur in greater numbers and are preferentially favoured.

However, in actual practice the situation is not quite so simple. The substrate has a considerable effect on the deposition process but it is likely that, on an amorphous

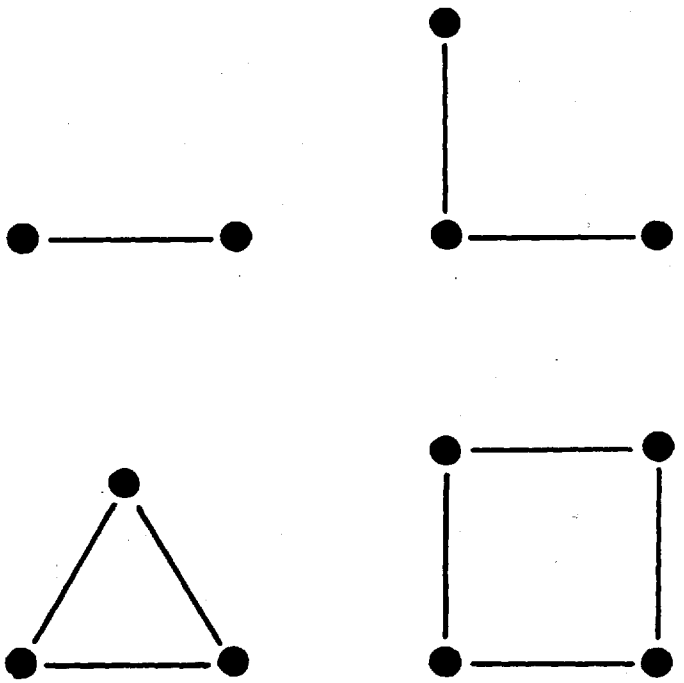


Fig.3. Schematic diagram of Critical Nuclei and Clusters.

(After Walton 1961)

substrate, considerations of the above nature prevail. Further discussion of the factors which influence film orientation is presented in the next section.

(ii) Dependence of Film Structure on the Deposition Parameters.

(a) Influence of Substrate Temperature

As stated in the previous section, the orientation of deposits grown at room temperature on inert substrates is weak or absent altogether when the deposit atoms have low mobility, as in high melting point metals. However, if deposition is carried out at elevated temperatures, the crystals grow in a strongly preferred orientation. This phenomenon is explained by the increase in surface mobility of the condensing atoms, whereby the atoms can move into positions of low potential energy, and at the same time aggregate together. This tends to give rise to growth with the most densely-populated plane parallel to the substrate.

Finch (1937) observed that films with one plane of a crystal parallel to the substrate could be obtained on glass if it was heated during deposition, and many other experimental results have shown one-degree orientation at high substrate temperatures. Dixit (1933) concluded, on the basis of theoretical calculations, that film orientation should be obtained in which planes with low atomic density are parallel to the substrate. Lassen (1934) and Rudiger (1937) found that

metals deposited onto rocksalt at temperatures below 150°C were random, while above a certain critical temperature, they were completely oriented. Herbstein (1957) showed that silver deposits prepared or annealed above about 550°C had one-degree orientation while below this temperature, no orientation was observed; (111) orientation was predominant in deposits prepared at 600°C, while (100) orientation was obtained in deposits prepared at room temperature and annealed to 600°C. Thun and Hass (1958) have shown, for aluminium films deposited onto rocksalt at various temperatures, that the film is polycrystalline at 100°C, while progressive ordering occurs at about 200°C, and at 300°C the film is highly oriented (see Fig.4). Scow and Thun (1961) obtained no orientation of chromium films deposited onto SiO over the temperature range 25-350°C, while for films deposited on glass substrates, a (110) orientation was observed between 25 and 200°C with no pronounced orientation between 200 and 350°C, while (100) orientation began to appear at about 350°C. This shows the greater binding energy between the SiO surface and the chromium atoms than for the chromium atoms on glass.

Since the probabilities for the nucleation of various lattice planes do not differ by large amounts, the formation of mixed orientations is frequently observed. Via and Thun (1961) have reported mixed (110) and (100) orientations for germanium films deposited onto borosilicate glass substrates at temperatures between 400 and 450°C. At higher temperatures the content of (100) orientation decreased and at 600°C the

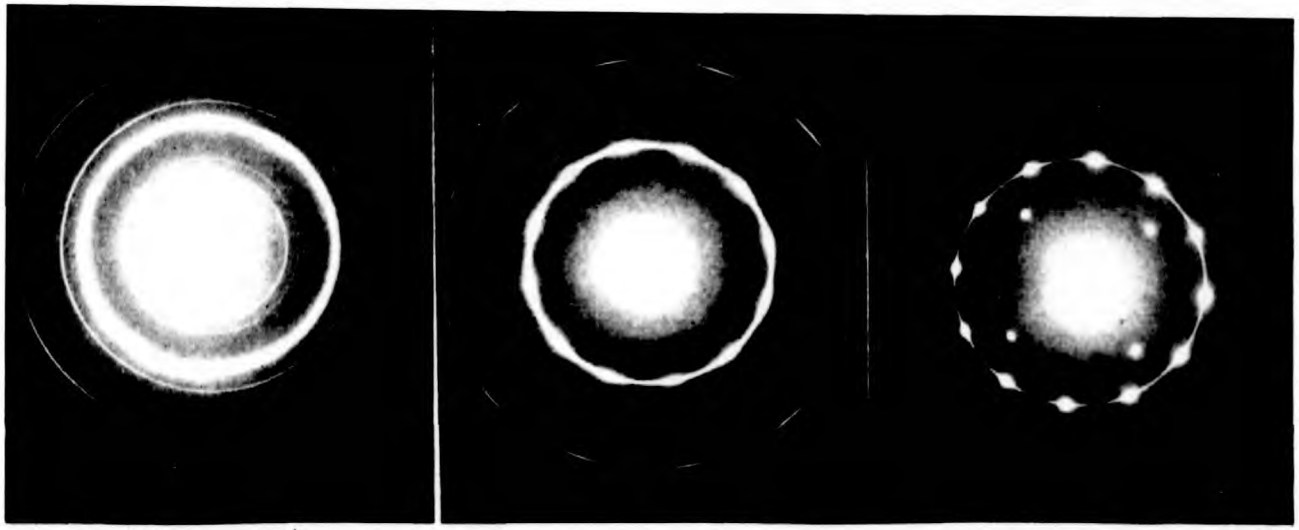


Fig. 4. Structure of Al Films at Different Temperatures on NaCl Substrates. (After Thun and Hass 1959).

(110) orientation was predominant. However, Davey (1961) found that he obtained (110) orientation at 175°C, while between 350 and 575°C, the orientation was a mixture of (110) and (111), and above 575°C, (111) orientation becomes predominant. The discrepancy between these results is probably due to variations in other deposition parameters.

Conversely, condensation of the metal at very low temperatures corresponds to a rapid quenching of the material, and the atoms lose their energy very quickly on impact with the surface. Was (1939) showed by transmission electron diffraction that gold films condensed at liquid air temperatures, and warmed to room temperature, were amorphous for thicknesses under 100Å, but thicker films developed crystalline form at room temperature. This was probably the result of aggregation of the film. Wilkinson and Birks (1949) showed that a (111) orientation was preferred for thicker gold films deposited at 78°K at various deposition rates and 1 x 10^{-6} torr.

Buckel (1954) found that at low enough substrate temperatures, metal films will grow in amorphous form; i.e. practically completely disordered atomic aggregates; but the temperature in some cases, e.g. bismuth, has to be reduced to a few degrees K. Buckel (1959) has also shown that some metals form crystalline layers at these temperatures, i.e. Cu, Al, Pb. This crystallisation is however aided by the fact that close-packed structures of these metals are not very different from a close-packed random assembly of the atoms.

Thus, at high substrate temperatures, metal films are usually expected to have a polycrystalline and oriented structure on amorphous and polycrystalline substrates; i.e. the film atoms have formed crystallites but the azimuthal axes of these crystallites are randomly distributed in the film. Alignment of these crystallographic axes can occur through epitaxial growth on single crystal substrates. However, this would not be sufficient to create a highly ordered film, as high surface mobility is also required (See section 3 (i) b.).

(b) Effect of Variation in Residual Gas Pressure

The residual gas pressure present during the evaporation process can have an important effect on film structure. Gas molecules from the residual gas atmosphere may be trapped in the film during the deposition process. Gas occlusion depends primarily on (i) the adhesion to the substrate of the residual gas molecules and their desorption probability which increases with temperature, and (ii) the '$\frac{p}{r}$' ratio, (which has been used by Behrndt (1962) to characterise the amount of trapped gas in nickel films), which is the ratio of the number of gas molecules arriving at the substrate surface per unit area and time against the corresponding number of film atoms for a given film material and substrate temperature.

Gawehn (1962) has calculated the upper limit for

trapped gas in the film. He found that for deposition rates below 300Å/sec, the phenomena occurring at the substrate surface are predominant, while at higher rates of deposition, collisions between metal atoms and residual gas atoms during transfer from the source to substrate became predominant.

Also during the deposition process, initial outgassing from the source and the fact that the evaporating metal has a gettering action on the system, can increase the amount of gas taken up in the film. This could lead to an oxide layer during the initial stages of deposition for reactive metals, and considerably increased adhesion of the film to the substrate. On this basis, Holland (1956) concluded that as a general rule evaporated metal films will be purer at higher rates of deposition.

Levinstein (1949) states that a high residual gas pressure (10^{-3} - 10^{-6} torr.) will cause collision between individual atoms before they reach the substrate, so that aggregates will be deposited. These will have a much greater lifetime on the substrate surface, possess less mobility, and lack any preferred orientation. In the case of a reactive atmosphere, he was able to show that the reaction will take place at the substrate surface. By evaporating zinc slowly at the point where no zinc film could be formed because the zinc atoms immediately re-evaporated, he found that an intermetallic compound was formed with gold when the two were evaporated simultaneously. The same effect was observed with

mercury. Since the residual gas pressure was very low, no reaction would have occurred while the atoms were moving from the source to the substrate.

Caswell (1961) has shown that indium films deposited in a high residual vacuum have (010) orientation, while films heavily doped in a high partial pressure of oxygen ($1x10^{-4}$torr) are completely randomly oriented. Pure tin films have (100) orientation but the doped films are also more randomly oriented. He states that the presence of oxygen decreases the mobility of these two metals on the substrate surface. However it is possible that the reaction of these metals with the oxygen may produce an initial oxide layer which affects the binding energy between the film atoms and the substrate.

(iii) Grain Size

The substrate temperature and the rate of deposition are the two most important parameters for controlling the grain size of a thin film. Hass and Scott (1949) showed by electron microscopy, for Al films approximately 500Å thick, that the grain size increases with substrate temperature. They attributed this result to the change in surface mobility. However, at a given substrate temperature and rate of deposition, the grain size will depend upon the material of the film. Those metals which have low melting points, i.e. Pb and Sn, have large grain sizes while the high melting point metals - e.g. Au and Ag - usually have smaller grain sizes. Also as

the work of Sennett and Scott (1950) showed (see section 2 (ii).), the rate of deposition influences the grain size. The relatively long mean free lifetime of the mobile surface atoms at low deposition rates permits the preferential growth of the crystalline surfaces which represent the lowest free energy. The resulting film exhibits large grain size and surface roughness. With increasing rates, the smoothness improves up to a point where atoms are increasingly buried in random sites by successively arriving atoms. Since re-ordering of the buried atoms requires a considerably higher activation energy, the result is a decrease in the average crystal size and an increase in the number of lattice faults.

Evans and Wilman (1952) showed that in films of high melting point metals such as Cu, Ag, Au, Ni, the crystals first formed on a substrate at room temperature are small ($\leq$ 50Å dia.), but the crystal size at the surface increases as deposition proceeds, and preferred orientation develops. Scow and Thun (1961) have shown the influence of rate of deposition upon the grain size of chromium films 1000Å thick condensed at different substrate temperatures. (see Fig.5). Up to 200Å/sec., the grain size is constant, but decreases rapidly beyond this point as the mean free path of the atoms at the substrate surface becomes the determining parameter for crystal size.

However, Sharif and Scott Clark (1964) have shown that the grain size of Al films deposited onto silicon at 580°C is dependent upon the residual gas pressure and the thickness

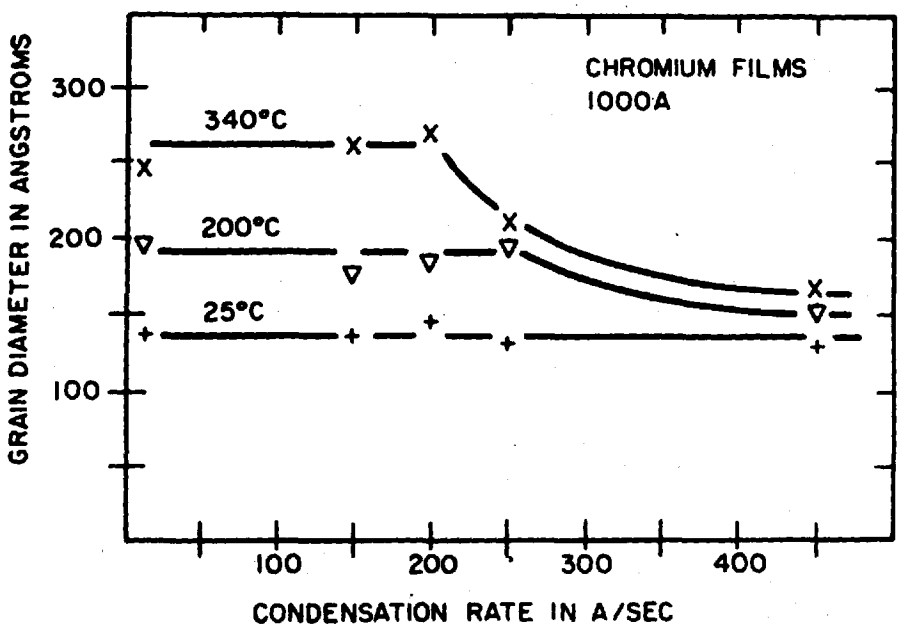


Fig.5. Variation of Grain Diameter with Rate of Evaporation and Deposition Temperature for Chromium Films.

(After Scow and Thun 1961)

of the film. With other parameters constant, the grain size increases from 2500Å at 1×10^{-4} torr residual gas pressure to 5000Å at 5×10^{-6} torr. It is concluded that the presence of the high residual gas pressure in the system, by reducing the mobility of the Al atoms on the substrate surface, results in the formation of a film with smaller grain size.

Traub (1949) and Zehander (1950) have used less than a monoatomic layer of silver to provide artificial nucleation centres on a substrate surface. This has the effect of increasing the number of nuclei formed in the initial stages of deposition, and the reduction of grain size for Cd films for increasing amounts of silver was quite marked. This technique is not limited to the Ag-Cd system: it is only necessary to provide nucleation centres, and metals with high melting points are well suited for this purpose. Jeppesen and Caswell (1963) have prenucleated Pb films with Cu, Au, and Ag, and observed the same effect. The films prenucleated with Au became continuous much earlier than those prenucleated with Cu and Ag, but they were also the only ones to form an intermetallic compound with the lead.

Caswell (1961) has shown that the presence of a high partial pressure of oxygen in the residual vacuum has a considerable effect on the grain size. For tin films the crystallites are reduced in size, and for indium films the surface also becomes very 'pebbly'. He states that heavy oxygen doping does not contribute to smaller-grained films but rather inhibits the coalescence of various grains into a

smooth film. (See Fig.6).

Recently, Pashley (1964) has examined the structure of gold films prepared under the same deposition conditions (onto thin carbon films at room temperature), but for varying thicknesses. The deposition for all the specimens was started at the same time but a shutter was used to vary the time of deposition. He found that there was considerable recrystallisation during deposition with some 100 or more initial nuclei contributing to each grain. It was concluded that the grain size of the completed film is controlled by the recrystallisation which occurs during the coalescence of nuclei or islands, rather than the density of the nuclei. (See Fig.7).

(iv) Other Factors influencing the Structure

(a) Aggregation and Annealing Phenomena

It has been shown in the preceding sections that the mobility of the deposit atoms is increased by raising the substrate temperature during deposition, and hence producing a more highly ordered film. However, it is also possible to alter the film structure by annealing after deposition.

Andrade and Martindale (1936) investigated the structure of sputtered Au and Ag films about 30 to 100 atoms thick prepared on various substrates by optical microscopy. Films of Ag held at about 250°C for 3 hrs. showed that the first stage of crystallisation is the formation of small aggregates.



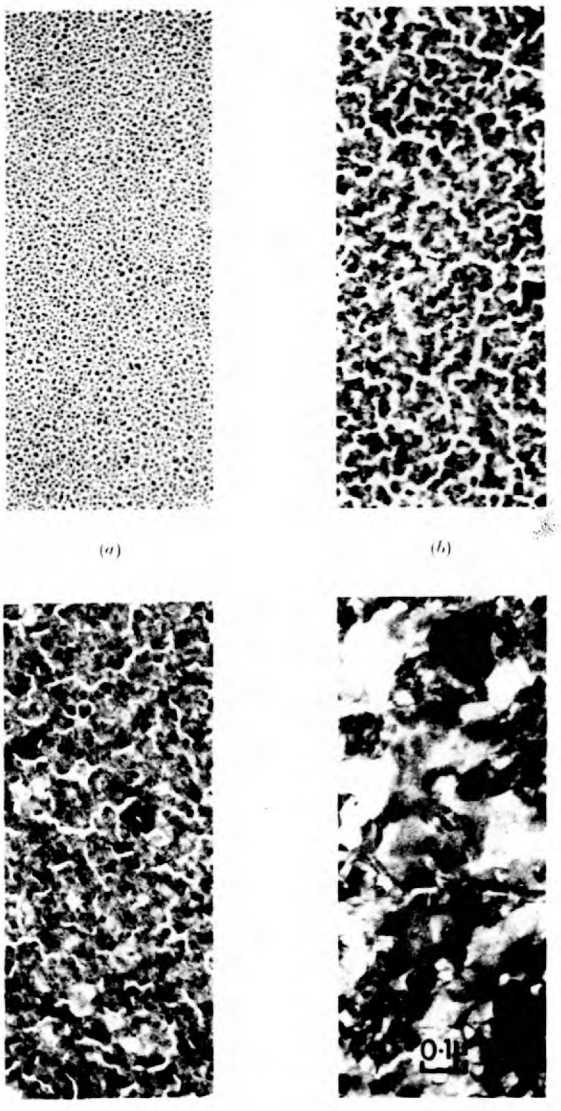
(a) Replica electron micrograph of high purity Tin Film Surface.



(b) Replica electron micrograph of oxygen doped Tin Film Surface.

Fig.8. Influence of Oxygen on the Surface Structure of Tin Films.

(After Caswell et al. 1961)



(a) (b)

(c) (d)

The sequence of growth of gold on an evaporated carbon film at 20°c.

Fig.7. (After Pashley et al 1964)

The same effect was observed for Au films annealed to about 400°C. The crystallites formed were bounded by octohedral faces and were oriented with a (111) plane parallel to the substrate. The areas between these crystallites were considered to be very thin films of metal because, upon further annealing, new crystallites appeared in the seemingly transparent areas. It also took a higher annealing temperature to initiate visible crystallisation for films only a few atoms thick than in those several hundred atoms thick. It was therefore concluded that the aggregates were formed by the increased mobility of the upper layers of the film only which evidently move freely at some 700°C below the melting point of the film material. Their explanation was that atoms aggregate in small numbers on the film surface and surface tension forces predominate to produce roughly semi-spherical aggregates.

Picard and Duffendack (1943) also considered the effect of surface tension on thin films. They stated that any imperfections in the substrate surface may cause cracking, and the surface tension forces thus released would cause the film to aggregate into the form of droplets. Thus breaking up of the film could be caused by the difference in thermal coefficients of expansion of the metal and substrate during any annealing process.

Keith (1956) observed by X-ray diffraction that copper films, 2000Å thick deposited onto glass substrates at -183°C and at a residual gas pressure of 1×10^{-7} torr, when warmed

to room temperature in vacuum, show a large increase in particle size with aggregation from 40Å to approximately 400Å. Chemisorption with a monolayer of oxygen at -183°C almost completely prevented recrystallisation and the particle size only increased to 60Å. Copper films deposited at room temperature in high vacuum had a crystal size of 400Å. These results also indicate that the aggregation of a thin film is initiated in the surface layers of atoms.

Caswell (1964) has used the same technique to prevent aggregation in tin films, 150Å thick, deposited at 78°K. The oxide layer appeared to be very effective in limiting the surface diffusion of the tin films, but this is not necessarily true for other metals.

Saikia (1961) found that tin films deposited at room temperature were initially in (110) orientation, but when annealed to near the melting point, they developed a strong (100) orientation. Also the films aggregated to form minute globules approximately 10 μ diameter.

(b) Substrate Cleanliness

It has been shown how the growth and structure of thin films are dependent upon the predominant deposition parameters, substrate temperature, residual gas pressure, and rate of deposition, but this discussion must include a further very important parameter, i.e. substrate cleanliness and the presence of contaminants.

Impurities can be present in many forms. The initial cleaning process of the substrate may still leave residues on the surface, or contamination from hydrocarbons from the pumping system may occur. The presence of hydrocarbons in the system can be adequately reduced with efficient liquid nitrogen trapping. However, both of these effects, if allowed to occur, would be sufficient to produce differences in the Van der Waals forces, as they are only operative over atomic distances, and these differences would give rise to variations in film characteristics. If the contamination is present in the form of isolated islands; i.e. dust particles etc; the film material may nucleate preferentially at these impurities. Chemical cleaning may also leave etch pits on glass surfaces and these will also act as preferential nucleation sites. It is therefore extremely important to ensure a reproducible standard of substrate cleanliness especially when investigating the variation of film structure with deposition parameters.

Many varied attempts have been made to obtain a reproducible standard of cleanliness especially in the case of glass substrates. Hunt (1961) made use of the wetting angle of water on glass as a criterion for measuring cleanliness, but for thin film work, where local nucleation of particles is important, the method is totally inapplicable. The wetting angle is only affected by organic materials and colloidal particles make a negligible effect.

Weaver (1960) has used the detergent 'Teepol' to remove dirt and grease from glass surfaces followed by a rinse in distilled water and final polishing with lens tissue. It is also possible to use a mixture of chromic sulphuric acid but while cleaning the substrate excellently, it also etches the surface. The method used in this laboratory which has proved satisfactory, as shown by reproducibility in electron diffraction experiments, is immersion of the glass substrate in a mixture of nitric acid and alcohol, followed by rinsing in distilled water. If required, a mild baking will remove adsorbed surface moisture.

It has become evident in the case of glass that perfectly clean surfaces are difficult to obtain and it is only possible to use a reproducible standard of substrate cleanliness. The method of using ion bombardment inside the deposition chamber causes pitting and therefore also causes erraneous nucleation sites. The method of ultra sonic vibration probably produces the cleanest surface for external cleaning processes, while it is possible to deposit a layer of silicon monoxide onto the substrate just prior to the metal deposition to obtain a perfectly clean surface.

4. Residual Stresses in Thin Films

(i) The Origin of Stress in Thin Metal Films

Stresses have been known to exist in thin films for some years but it is only recently that they have developed a practical significance. Work by Lock (1951) showed that the stress which may be developed in a thin film deposited onto a supporting substrate and then cooled to liquid helium temperature gives rise to a shift in the critical temperature of the superconducting state. This would tend to degrade the operating characteristics of practical devices. Behrndt (1961) has also found that the magnetic properties of thin films are influenced by residual stresses, while Budo and Priest (1963) have shown how the stresses present in multi-layer devices can cause buckling and eventual separation of the film from the substrate. Although these stresses can be reduced by annealing, this is not always a practical proposition during preparation, especially in the case of multi-layer films. A basic understanding of the stresses and the mechanism of their formation in thin films is, therefore, essential.

Stresses in thin films are the result of two phenomena. Firstly, the substrate temperature at which the film is deposited usually differs from the ambient, and a planar stress system arises upon cooling by virtue of the differences in the co-efficients of expansion of the material of the film and that of the substrate. Secondly, intrinsic stresses are induced

by the mode of growth of the film.

Work on these stresses began comparatively recently. Maltman (1952) studied the line broadening in electron diffraction patterns from condensed nickel deposits on silicon dioxide substrates. He deduced that the line broadening was a result of large microstresses rather than a small particle size in the film. He also suggested that distortion caused by stacking faults might be the explanation of these strains in the crystallites. From the work that followed, two theories have been advanced to explain the high residual stresses obtained by virtue of the growth processes of the film.

Hoffman et al (1950), (1953), (1954) studied the tensile stresses in evaporated nickel films approximately 1500Å thick deposited at a rate of deposition of 60Å/sec. by measuring the change in curvature of thin mica strips. They examined particularly the effect of depositing films on substrates at raised temperatures and the effects of annealing the film after deposition. They found a gradual reduction in stress up to about 250°C while further annealing resulted in a small increase in the minimum stress value. The residual stress in films deposited at a higher substrate temperature was less than that in films deposited at room temperature. (Fig.9).

To account for these results, they have suggested that lattice defects and dislocations are formed during deposition of the film and undergo a change shortly after being

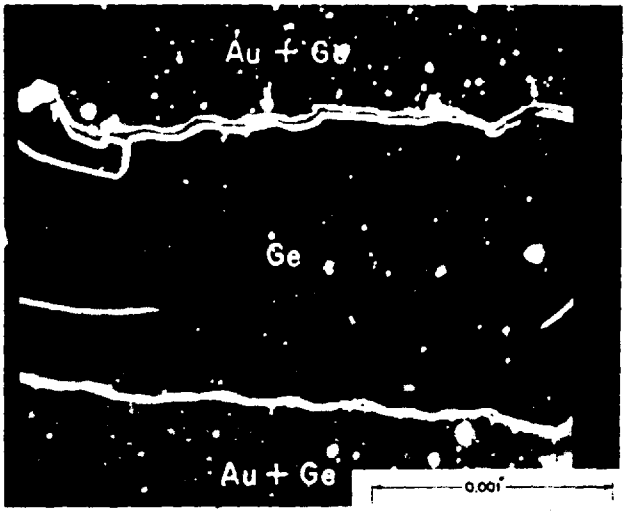


Fig.8. Cracking of Thin Germanium Film.

(After Budo and Priest 1963)

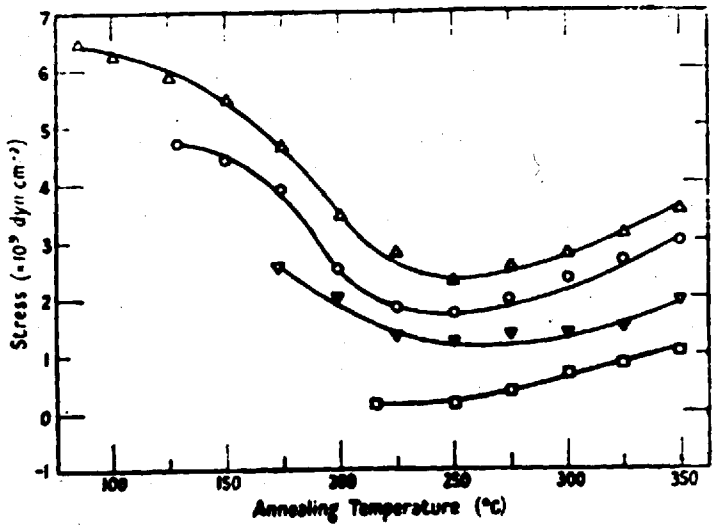


Fig.9. Variation in Stress of Thin Nickel Films.

(After Hoffman and Crittenden 1954)

trapped by successive metal layers. This process takes place at the substrate temperature. The irregular regions on the growing surface which become crystal boundaries, are rearranged and give rise to stresses through a reduction in volume. They considered that at higher substrate temperatures the arriving deposit atoms would have more mobility and would be less likely to attach themselves at abnormal surface sites, with a corresponding reduction in the observed stress. The increase in stress observed at high annealing temperatures is attributed to the migration of lattice imperfections at a rate dependent upon the temperature. At the lower temperatures, vacancies in the lattice are filled; the neighbouring atoms relax outwards and this results in a crystal expansion whence the stress is relieved. Further increase in the temperature causes the vacancies to coalesce into larger aggregates and finally results in the collapsing of the surrounding crystal into a dislocation ring. This process would bring about a contraction in the crystal and a resultant increase in the stress.

Murbach and Wilman (1953), and Wilman (1955), however, have explained these stresses in terms of the temperature of the surface of the growing deposit and in the recrystallisation temperature of the material of the film.

They measured the stress in a series of eleven metals, - Ni, Fe, Pd, Au, Cu, Ag, Sb, Al, Bi, Mg and Zn, - condensed in a vacuum of approximately 1×10^{-5} torr on copper strips used

as substrates. These copper strips were rigidly clamped at one end and the stresses in the films, which were about 2000Å thick and deposited onto one side of the strip, could be calculated by observing the deflection of the free end. All the stresses observed were tensile and the amount of stress varied for different metals. However, it was noticed that the residual stress was in proportion to the recrystallisation temperature of the material of the film. The metals with the highest residual stress - Ni, Fe, Pd, Cu, Au, Ag, and Al - were randomly or weakly oriented, whereas films with low stress - Sb, Mg, Bi, Zn - were highly oriented with a net plane parallel to the substrate.

The previous evidence of Evans and Wilman (1952) had shown that these two types of orientation were associated respectively with low and high atomic mobility of the deposit atoms on the growing surface, and the melting point of the metal was shown to be a rough inverse measure of the degree of mobility (see section 3 (i) a). Thus the films possessing high residual stress were those of metals having low mobility during the formation of the deposit. They therefore concluded that the stress was related to the temperature of the upper regions of the growing deposit. The observed tensile stress was then the direct result of cooling of the deposit below the recrystallisation temperature, after its formation at a surface temperature which must have been several hundred degrees centigrade for high-melting-point materials. Three features of

the observations agreed well with this explanation: (i) the stresses were tensile in every case, (ii) the magnitude of the stresses agreed with the calculated values which were based on the thermal expansion coefficients and recrystallisation temperature; (iii) the residual stresses were decreased by about the expected value when the metals were deposited on substrates at raised temperatures. They also showed that the effect of increasing the residual pressure for the deposition of Al was to reduce and then reverse the stress, and this was attributed to oxide formation which occupied more volume than the metal from which it was formed.

Thomas (1959) found that copper films deposited in 0.2 mm Hg oxygen pressure were in compression when traces of cuprous oxide could be detected in the electron diffraction patterns whereas silver films were under tensile stress in all conditions. This agreed with the above suggestion by Murbach and Wilman (1953) that the growth of oxide results in a 'wedging' action in the grain boundaries.

Recent work on the residual stress in thin metal films has been mainly concerned with superconducting films where a device must operate at low temperatures. Caswell et al (1963) measured the stresses in In, Pb and Sn films at 78°K and 4.2°K after deposition at room temperature and 100-200Å/sec. Comparison was made between pure films (residual gas pressure 1×10^{-6} torr) and oxygen-doped films (Po_2 between 5×10^{-5} and 1×10^{-4} torr). The stress in lead films was found to be

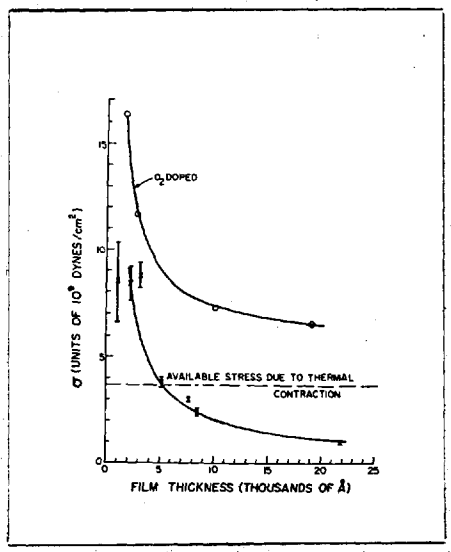


Fig.10. Residual Stress in Lead Films at 4.2°K as a Function of Film Thickness and Film Purity.

(After Caswell et al. 1963)

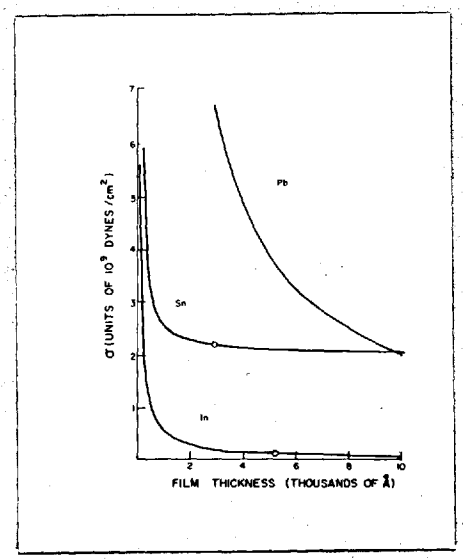


Fig.11. Residual Stress in Indium, Lead, and Tin Films at 4.2°K as a Function of Film Thickness.

(After Caswell et al. 1963)

higher in oxygen-doped films (see Fig. 10.) but although a similar effect was observed for tin, it was only for films less than 150Å thick. The stress in lead films was also a function of thickness (see Fig. 11.) whereas the stress in In and Sn was independent of thickness above 500Å. They did not find it possible to explain the high stresses in the lead films, but it was pointed out that the films were supporting stresses of the order of $5 \times 10^{+9}$ dyn/cm^2 while plastically deforming and this is as high as the U.T.S. of gold and silver films deposited at room temperature.

However it must be concluded that the residual gas pressure and the type of gas present in the system will have an effect on the observed value of residual stress in thin films.

(ii) Film Temperature during the Deposition Process

As stated in the previous section, Murbach and Wilman (1953) concluded for their theory of stress, in metal and other deposits, that the immediate surface region of the growing film attains a high temperature. This conclusion is based on the electron diffraction evidence of Evans and Wilman (1952) and Murbach and Wilman (1953) on the structure of growing deposits and the influence of the mobility of the metal atoms on the nature of the deposit orientation.

Hoffman, Crittenden and Daniels (1954) stated that the first and second neighbours of an incident atom will

undergo an instantaneous temperature rise of about 700°C when an incident atom shares its sublimation energy with them. As the relaxation time for such a thermal pulse is about 10^{-12} sec., they concluded that it is incapable of producing any bulk rise in temperature or recrystallisation. This argument is valid for an isolated incident atom but the conclusion is controversial when the film is heated by the continuous deposition of material.

Gafner (1960) has attempted to calculate the rise in temperature of films deposited onto both thick and thin substrates, with upper limits on film thickness and rate of deposition of 10,000Å and 1,000Å/sec. respectively. He assumes that the upper limit to the temperature in a film growing on a semi-infinite substrate will follow from the calculation of the surface temperature of the substrate during deposition. He then uses the relevant special case solution given by Carslaw and Jaeger (1948) to obtain the maximum film temperature, i.e. when the heat associated with deposition is generated on a semi-infinite substrate, in which case $v = \frac{2Q}{K}\left(\frac{\alpha t}{\pi}\right)^{\frac{1}{2}}$ where v is the temperature increase, Q the rate of heat input in cals/cm^{2}sec., t the time of deposition and K and α are the thermal conductivity and diffusivity of the solid respectively. This leads to the result that any film growing on a thick substrate to a thickness of 10,000Å at 1,000Å/sec. rises as a whole to a maximum temperature of 17°C above the initial substrate temperature.

In the case of a thin substrate when a small temperature difference across the substrate occurs, the solution is given by the rate of change of temperature with time at any instant, i.e.

$$\frac{dv}{dt} = \frac{Q - C(v^4 - v_o^4)}{A + Bt}$$

where the heat losses are considered to be solely by radiation and can be represented in the form $C(v^4 - v_o^4)$ where v is the varying temperature of the system and v_o is the initial substrate temperature. It is then shown that temperature rises of 100°C or more will be attained during the deposition of a film of thickness 10,000Å only if the substrate has a thickness of 0.03" or less. He thus concludes that a temperature increase of hundreds of °C will not occur unless the deposition is onto very thin substrates.

For the above argument, the basic assumption is that the temperature of the film is that of the substrate beneath and this is open to question on the following counts; (i) the heat transfer coefficient between the metal and the substrate surface will not be unity and, (ii) the initial stages of growth are by means of three-dimensional aggregates.

However Gafner (1960) states that the actual method of growth of an island in thin films can be approximated to a continuous growing disc source of heat on the substrate surface. In this case, he states that the temperature v at a point r in an infinite solid upon the surface of which heat

is generated at a rate of Q cal/sec., is given by;

$$v = \frac{Q}{4\pi kr} \quad \text{erf. c} \quad \frac{r}{(4\alpha t)^{\frac{1}{2}}}$$

Calculations of v at various values of t, show that the mean temperature of the aggregate falls to 86°C above that of the substrate after 10^{-6} sec. and to 9°C above that of the substrate after 1 sec. It is concluded that a three-dimensional aggregation process leads to high temperatures of the aggregates only in the early stages of growth when both rate of deposition and surface migration rates are high.

This solution does not take into account the continuous deposition of material onto the substrate and no examination of the film temperature has been undertaken beyond the point where the film becomes continuous.

Blackburn and Campbell (1963), in their investigations into the stress in lithium fluoride deposits, have stated that the heating effect is due to the latent heat of the depositing lithium fluoride vapour, while the heat derived from the molecular velocity and radiation from the source were negligible. Calculations of the substrate temperature with time (derivations not given), showed that the final temperature would have been 47°C above the surroundings with a temperature difference of 0.054°C across the substrate, if heating was continued indefinitely. They therefore stated that there is no high temperature surface to the substrate and that any heat pulse arriving at the surface is rapidly dissipated. But here again

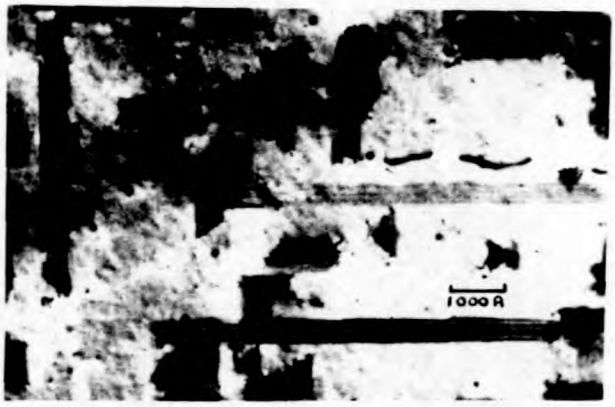
the temperature of the substrate has been derived and not the temperature at the surface of the growing film.

It would therefore appear that the above conclusions do not throw further light onto the theory made by Evans and Wilman (1952) on the extent of the progressive increase in the surface temperature of the deposit as the thickness of the film increases. It is not a valid conclusion to assume that the surface temperature of the film during deposition will be that of the substrate onto which it is being deposited.

(iii) Microstructure and Defects in Thin Films

The application of the diffraction contrast technique in transmission electron microscopy led Hirsch, Horne and Whelan (1956) to show that a dislocation appears as a projected line on the image. When a dislocation splits into two partial dislocations, the stacking fault between the two partials is made visible and appears as a set of parallel fringes (see Fig. 12.).

The occurrence of twins in metal films formed by condensation onto rocksalt and other alkali halides has been known from electron diffraction evidence since the work of Kirchener and Lassen (1935), and Ogawa et al (1955) observed stacking faults or twins in electron micrographs from films of silver, gold, copper and nickel deposited on rocksalt. According to Brame and Evans (1958) no twinning occured in gold deposits formed on silver single crystal substrates.



Stacking faults in a (100) gold film, 800A in thickness, prepared by deposition on to rocksalt at 270°C.

Fig.12. (After Pashley et al 1959)



Fig.13. Dislocations and Grain Boundaries in Tin Films.

(After Vook 1964)

Bassett et al (1958) examined the microstructure of gold films deposited onto (111) silver surfaces and stated that no obvious sub-grain structure due to small misorientations occurred. However, dislocations extended from one surface to the other through the film and an estimation of the dislocation density was 10^{10} - 10^{11} per cm^2. Gold films in (100) orientation prepared on rocksalt had the same microstructure as those prepared on silver except that they contained a high density of narrow twin bands. The dislocation density was again 10^{10} - 10^{11} per cm^2.

The presence of the dislocation loop in single crystal gold films was reported by Pashley (1959), and Silcox and Hirsch (1959) showed that the collapse of vacancy aggregates in gold films gives rise to tetrahedra of stacking faults and not single loops. The movement of dislocations in a (111) gold film during examination in the electron microscope was observed by Pashley et al (1959) and was presumably due to stresses set up by the localised heating of the electron beam. The fact that dislocation movement can occur in evaporated films is important in relation to microstructure because it shows that the structure is sufficiently similar to that of bulk materials for crystalline slip to occur, and because it shows that normal glissile dislocations are produced in evaporated films during growth.

Several suggestions have been made to account for the origin of dislocations in thin metal films. Phillips (1960) suggested that stresses which develop when the film

becomes continuous generate dislocations at the edges of holes, while Bassett (1960) found that large silver nuclei, whose lattices were slightly rotated relative to one another about the (111) direction, coalesced to form a single grain containing a boundary composed of widely spaced dislocations. Matthews (1959) suggested that nuclei coalesce in such a way that holes in the deposit are formed and these contain dislocations. However, these nuclei will contain stacking faults that end on their surfaces and dislocations must therefore be produced when the nuclei grow together to form a continuous film.

Matthews (1962) showed that silver deposits, prepared on mica at 280°C and at a rate of deposition of about 20Å/sec., contained dislocations, stacking faults, and twins whose twinning plane was parallel to (111). It is suggested that initial ($1\bar{1}1$) and ($\bar{1}11$) orientations of the silver can be explained by assuming that the mica controls the positions of atoms in the first (111) layer, but cannot completely control the sites occupied by the second layer of atoms. Lateral twin boundaries are then formed when nuclei of different orientation coalesce.

Vook (1964) has observed dislocations in evaporated tin films with (001) orientation. These films were formed by evaporating onto rocksalt at liquid nitrogen temperature and at about 50Å/sec. in a residual gas pressure of 1×10^{-7} torr. The dislocations lay in planes approximately normal to

the surface of the film and their density was about 10^{10} per cm^2. It was also shown that the film possessed small angle grain boundaries (see Fig. 13.) and no stacking faults were observed in either single crystal or polycrystalline films.

2. EXPERIMENTAL

1. Vacuum Apparatus

(i) System to Investigate Variations in Orientation of Tin Films.

In order to investigate the variations in the structure of tin films with the deposition parameters, it was essential to use an apparatus in which the deposition conditions were easily reproducible during the span of approximately one hundred separate evaporations, and in which the various parameters to be investigated could be conveniently measured. The parameters to be measured were (i) rate of deposition, (ii) residual gas pressure, (iii) thickness of the film. The methods used to obtain the value of these parameters are given in section (2.2).

The system consisted of a Metrovac D.R.1. rotary backing pump, an Edwards F203 diffusion pump using Apiezon 'C' oil, a cold baffle, and liquid nitrogen trap. This system produced an ultimate residual gas pressure of approximately 1×10^{-6} torr in a cylindrical pyrex vessel 3½" dia. x 6" long. Diagrams are given in Figs. (14) and (15). The pressure was measured using an Edwards IG2M ionisation gauge head brazed to a brass end piece which was in turn sealed to the pyrex tube using piccin wax. The seals between the metal/metal surfaces were made by using neoprene 'O' rings. Tungsten

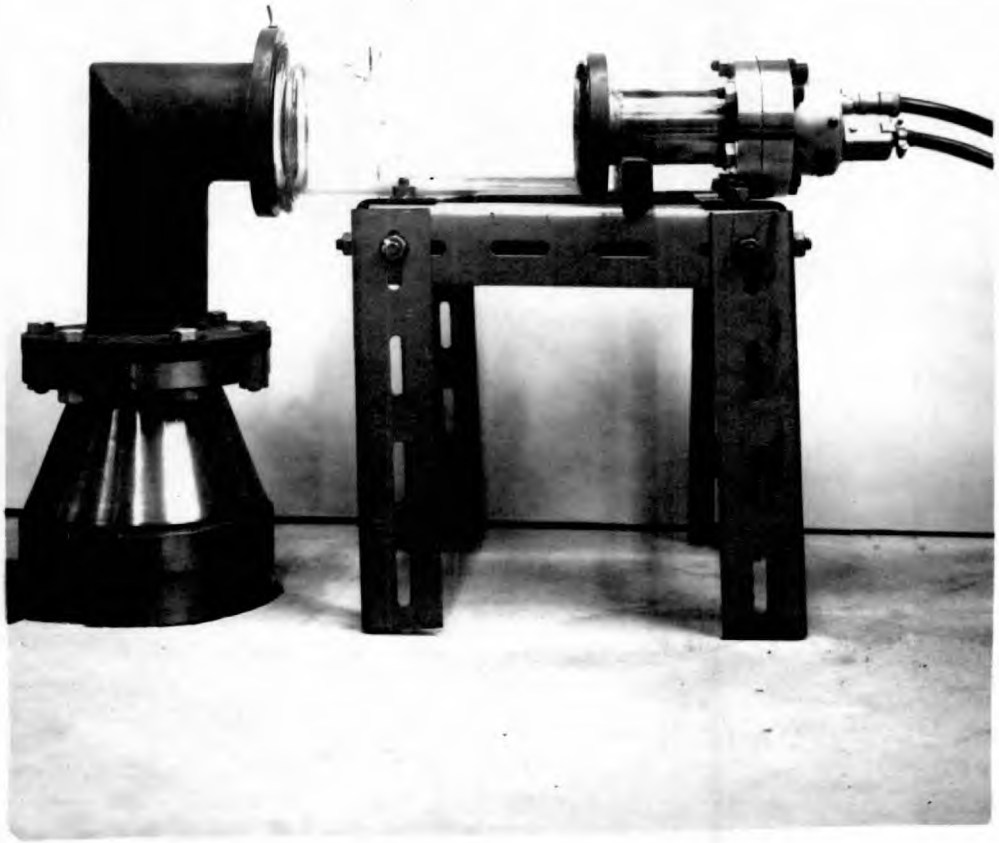


Fig.14. Vacuum system for obtaining residual gas pressures to 1 x 10^{-6} torr.

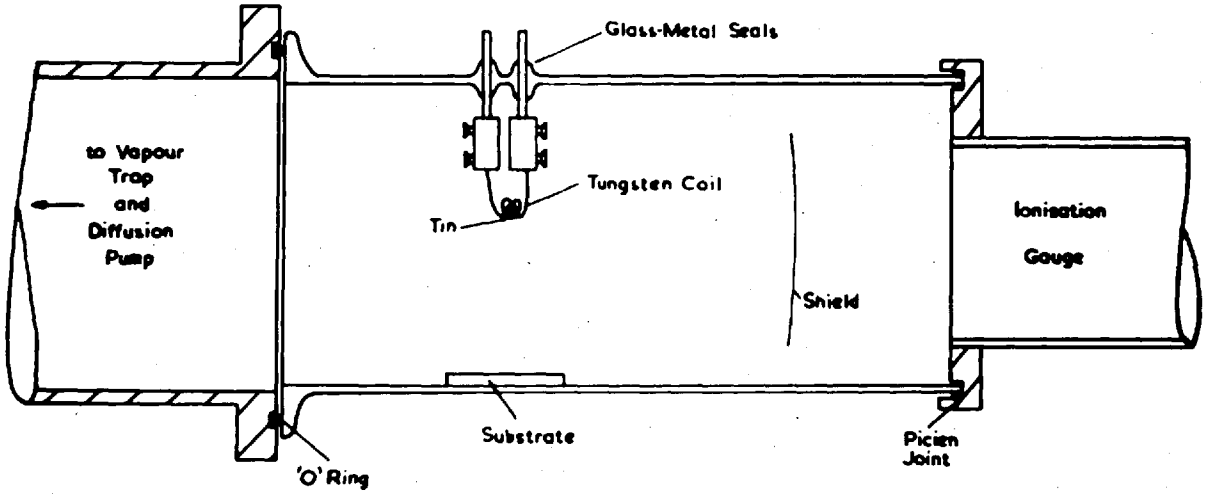


Fig.15. Schematic diagram of Vacuum System shown in Fig.14.

glass-metal seals 1 mm. dia. provided electrical connections through the walls of the tube to a heater filament of three turns of 0.012" dia. tungsten wire in a coil approximately 2 mm. wide by 3 mm. long. A pyrex shield prevented metal vapour from entering the ionisation gauge head during the deposition process and the deposition distance between the source and substrate was 3.5 cms. The tin used in all experiments was 99.999% purity provided by the Consolidated Mining and Smelting Co. of Canada Ltd. and the approximate combined weight of tungsten filament and tin before deposition was about 0.1 grms.

(ii) Ultra-High Vacuum System

Before high-purity films can be deposited, it is necessary to reduce the ratio of the number of residual gas atoms to the number of metal atoms striking the substrate surface to a negligible percentage. At normal rates of deposition, ($>10\text{Å}/\text{sec.}$) this means that the residual gas pressure must be about 1×10^{-8} torr. It was therefore necessary to design and construct a bakeable ultra-high vacuum system.

This system (see Figs. 16 & 17.) consisted of a cylindrical stainless steel vessel (Grade EN58B) with six flanged ports for connecting hemispherical glass windows (supplied by A.E.I. Research Labs. Ltd. Rugby), electrical connections, and an ionisation gauge. All the flange seals in the system were

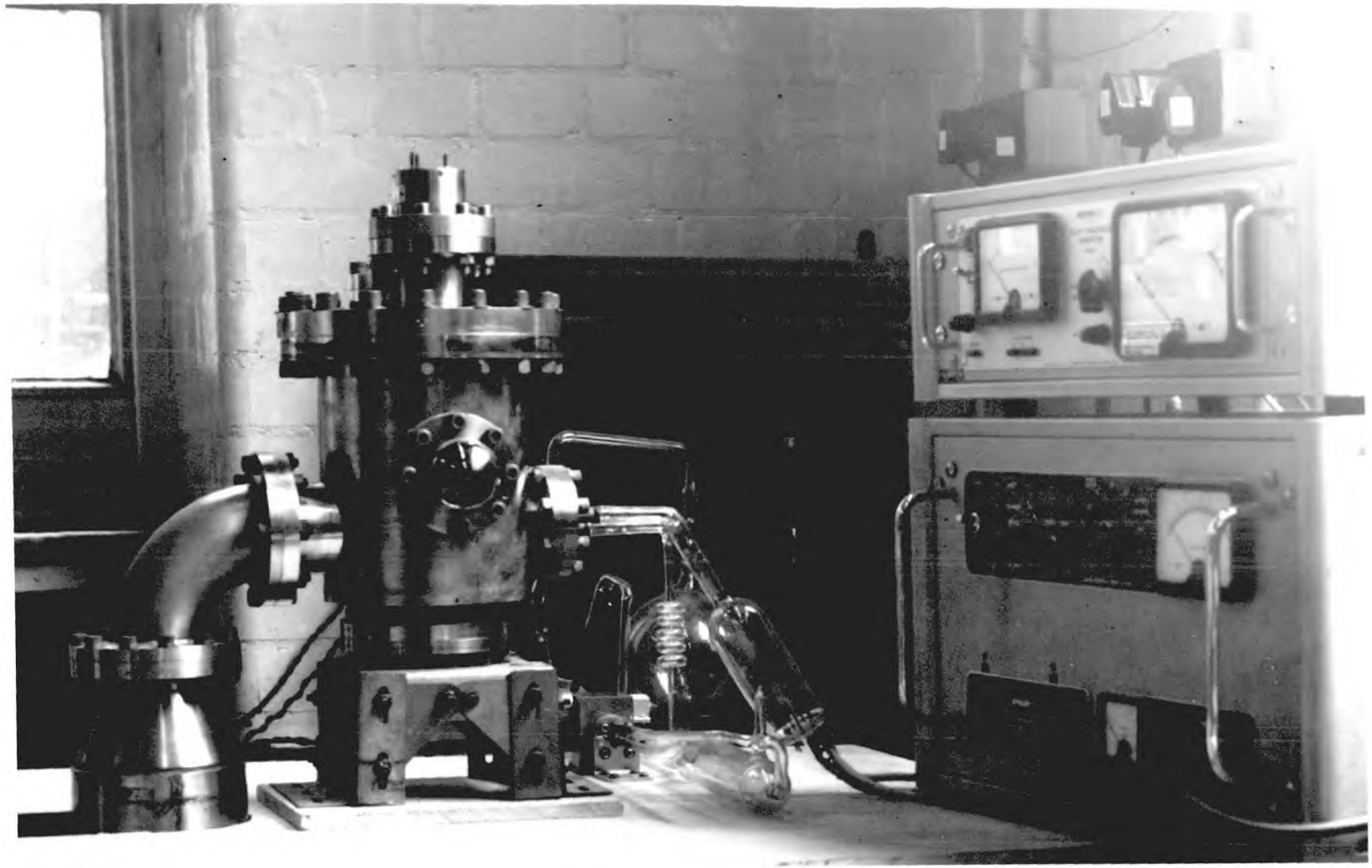


Fig. 16. Photograph of Ultra-High Vacuum System.

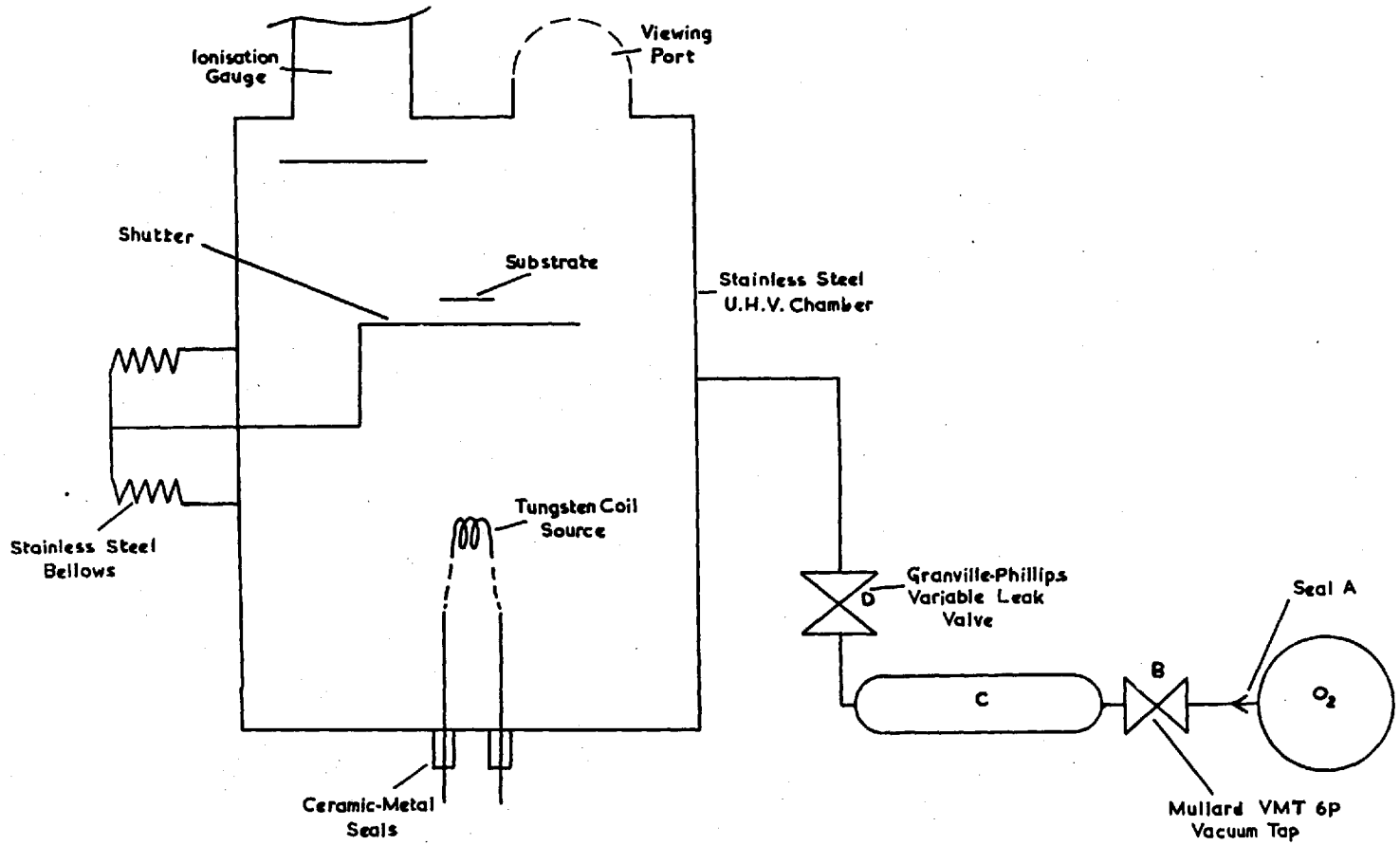


Fig. 17. Schematic Diagram of U.H.V. Apparatus.

made by compressing 20 thou. industrial grade gold wire, (supplied by Johnson Matthey & Co. Ltd.), between the two fine-machined mating surfaces of the flanges by using high tensile bolts. The thickness of the 'gasket' after use was approximately 7 thou.

The system was pumped by a Metrovac D.R.1. pump and an Edwards E02 diffusion pump connected through a liquid nitrogen trap and a cold water baffle. 'Convalex 10' diffusion pump oil was used and the system could be baked to 250°C which reduced the pressure to 4×10^{-8} torr after 12 hours baking.

The substrate holder was a stainless-steel box connected to the top closing flange by two tubes through which a temperature-controlling fluid could be passed, and a central tube allows a heater to be inserted into the system for work on substrates at elevated temperatures. The substrates were attached to the substrate holder by means of stainless steel clips. All joints in the system were argon-arc welded.

A stainless-steel bellows system constructed from 20 pairs of cantilever bellows 2" dia. (supplied by the Welded Components Divn., Elliott Automation Ltd.) was used to move a stainless steel shutter to control deposition from outside the vacuum chamber. Electrical connections were made through the base of the system to a tungsten coil source.

Oxygen doping experiments were carried out by bleeding into the system a high partial pressure of oxygen. A Granville-Phillips Inc. variable-leak valve was used to regulate the partial pressure of oxygen in the system from a

reservoir of spectroscopically pure oxygen, (supplied by the British Oxygen Co. Ltd.), the supply of which was controlled by a Mullard VMT6P bakeable vacuum tap. (Schematic diagram, Fig. 17).

2. Measurement of Rate of Deposition and Thickness of Films

Except for experiments carried out in the U.H.V. system, the thickness of the specimen was calculated by assuming evaporation from a point source onto a plane surface and radial distribution of the vapour from the source.

If it is assumed that evaporation takes place from a point source onto a surface of a sphere of radius r, a uniform thickness of deposit T_o would be obtained where,

$$T_o = \frac{m}{4\pi d r^2}$$

where m = mass of metal evaporated

d = density of the metal

r = source-substrate distance

The rate of deposition, $\frac{dT}{dt}$, is given by,

$$\frac{dT}{dt} = \frac{m}{4\pi d r^2 t}$$

$$= \frac{T_o}{t}$$

where t = time of deposition.

In the U.H.V. system it was not practicable to use

this method of measuring the rate of deposition and it had also become apparent that the rate of deposition is a critical factor in film evaporation, and required stringent control. An Edwards FTM1 quartz-crystal film-thickness monitor was used to measure the rate of deposition. This consists of a 6 Mc/s quartz crystal contained in a small stainless-steel can approximately $\frac{1}{2}$" x $\frac{3}{4}$" x $\frac{1}{4}$" which is placed next to the film substrate inside the vacuum system. A 1/16" dia. hole through one side of the can allowed the metal vapour to reach the crystal. It was essential to ensure that the flat surface of the crystal formed a tangent to its radius from the evaporation source - this ensures normal incidence.

An oscillator unit contains a 6.5 Mc/s reference crystal andthe control panel enables the selection of any convenient frequency above 100 c/s to be made. The film deposited on the crystal surface during the deposition process, increases the effective mass of the crystal and it will oscillate at a gradually reducing frequency. It is possible to read directly the rate of change of frequency on a moving coil micro-ammeter. The working principle assumed is,

$$\frac{\Delta F}{F} = \frac{\Delta M}{M} = \frac{\Delta T}{T}$$

where F is the frequency; M, the mass deposited; and T, the thickness of the film.

Since $T = \frac{1}{F}$

$$\Delta T = - \frac{\Delta F}{F^2 + F\Delta F}$$

and $\frac{\Delta F}{F^2}$. $F\Delta F$ becomes negligible.

However, it is necessary to calibrate the instrument for each material to be deposited, but as the frequency characteristic is normally considered linear, this only requires three or four depositions. At low mass levels, however, the effective density of the material deposited may be many times lower than its bulk density, and the characteristics may be non-linear at these low mass levels. The thickness of the film used to calibrate the instrument were measured by using a stylus method of an 'improved' Talysurf machine made by Taylor - Hobson Ltd. This involved depositing films with a sharp step edge and this was achieved by masking the substrate with a section of a No. 1 Chance micro-coverslip. As the talysurf probe tended to scratch the surface of the tin instead of following the step contour, a thin layer of SiO was deposited over the tin. This material has very low mobility when deposited onto substrates at room temperature and the resulting film gives a hard uniform amorphous surface which follows almost exactly the contour of the film beneath it.

A sample of the calibration is given below,

Prior to evaporation $F = 100$ c/s

Evaporation terminated $F = 5$ Kc/s

Say, Ratemeter during evaporation $\frac{\Delta F}{\Delta t} = \frac{1}{4}$ div/sec.

Hence $\Delta F = 5$ Kc/s - 100 c/s = 4.9 Kc/s.

Say, Measured $\Delta T = 2{,}450$ Å

Then $\frac{\Delta F}{\Delta t} = 5$ Kc/s $\times \frac{1}{4} \times \frac{1}{100}$

$= 12.5$ c/s/sec.

$\therefore \frac{\Delta T}{\Delta t} = 6.25$ Å/sec/sec.

The calibration curve for tin is shown in Fig.18.

3. Preparation of the Substrates

The validity of results obtained from experiments concerned with the variation of structure of thin films with deposition parameters, depends on the reproducibility of the substrate surface cleanliness. The substrates used for the first series of experiments were pieces cut from microscope slides (soda glass) approximately 2.5 cms x 1 cm x 0.2 cms. These were thoroughly degreased in propyl alcohol and then chemically cleaned in a mixture of concentrated nitric acid and propyl alcohol. They were then rinsed in running tap water for 20 mins. and given a final rinse in distilled water before being vacuum dried with one edge touching a clean filter paper. As previously stated (see section 3 (iv) b), it is evident that, in the case of glass, it is only possible to obtain a reproducible standard of substrate cleanliness prior to the evaporation of the film, and the method used was considered to fulfil these requirements.

The above method was also used to clean pyrex substrates for experiments in the U.H.V. system. Pyrex slides were used because they would have a greater resistance to etching by the nitric acid. However, pyrex substrates coated

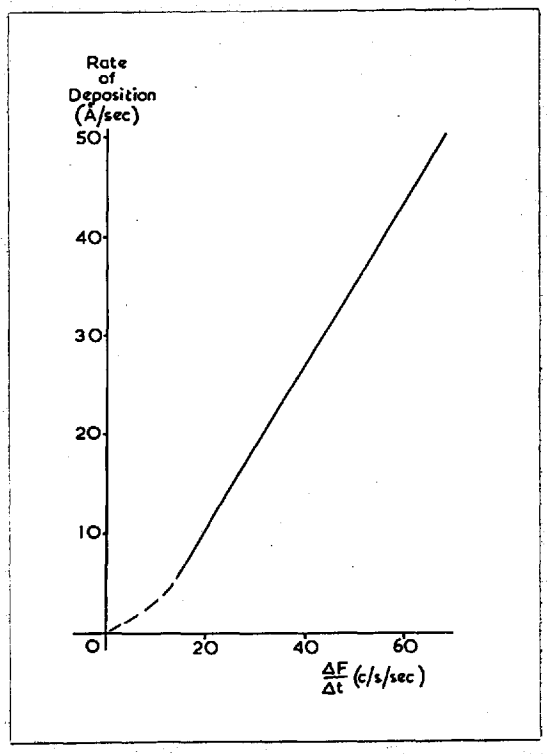


Fig.19. Calibration Curve for Rate of Deposition of Tin using an Edwards FTM1 Quartz Crystal Ratemeter.

with a polymeric compound (supplied by Dr. Allam of the Autonomics Divn. of the National Physical Laboratory) were also used to give a greater reproducibility of substrate surface. These substrates were smooth and amorphous and eliminated any effects from an unclean glass surface on the growth process. The polymer was formed by polymerising a siloxane vapour, in a vacuum system at a partial pressure of 1×10^{-4} torr, by means of an electron beam. The substrates were degreased in isopropyl alcohol before being inserted in the U.H.V. system.

4. Experimental Procedure

(i) Variation of Orientation with Deposition Parameters

The system was pumped to the residual gas pressure required - pressures in the 10^{-6} range required liquid nitrogen trapping in the system - and the source outgassed by heating the tin just to its melting point until the residual gas pressure reduced to its previous value. No shutter was used for this set of experiments but it is reasonable to assume that no contamination of the substrate took place from small amounts of evaporating tin during this procedure, (vapour pressure of Sn is 1×10^{-6} torr at 1100°C - Honig (1962).). The maximum pressure rise during the deposition process was approximately by a factor of two and this is the direct result of using a small source. With larger

sources, the rise in gas pressure would have been considerably higher. To obtain the approximate deposition rate required, the power input could be predetermined from the experience gained from several initial depositions. The source was weighed before and after the deposition process and a stop-watch was used to time the deposition.

(ii) Ultra-High Vacuum Techniques

The system was baked and liquid nitrogen trapped (residual gas pressure is approximately inversely proportional to baking time between 10^{-7} and 10^{-8} torr.) and the system allowed to cool. Outgassing was carried out in the previously described manner. The power input to the source was then increased until the required deposition rate was indicated by the rate-meter (the quartz crystal was not obscured from the vapour stream by the shutter). Deposition onto the substrates was then controlled by moving the shutter predetermined distances after specific intervals of time to give various thicknesses of film as required.

For oxygen doping experiments, the system was pumped as far as seal A in the oxygen supply vessel (see Fig.17). The vacuum tap B was then closed and the seal A broken. A small quantity of oxygen (a few mm. Hg) was then allowed into the reservoir C and the graduated variable leak valve D used to control the flow and partial pressure of oxygen into the system. Repetition of experiments using the same oxygen

supply was achieved by pumping the system as far as tap B to a residual gas pressure of approx. 5×10^{-8} torr. and the above procedure repeated.

5. Electron Diffraction Technique

Electron diffraction techniques were used throughout this work to determine the film structure. The diffraction of electrons by both metallic and non-metallic crystals and surfaces, and the interpretation of electron diffraction patterns, has been fully described in various standard texts and papers, i.e. Finch and Wilman (1937); Finch, Quarrell and Wilman (1935); Thomson and Cochrane (1939); Pinsker (1953); Beeching (1936); and Wilman (1948 a,b), (1951) and (1952). Consequently only a brief resume of the interpretation of electron diffraction patterns encountered during this work will be given here.

The electron diffraction cameras used were those described by Finch and Wilman (1937) but incorporating oil diffusion pumps in place of mercury pumps. The accelerating potential for the electrons was between 55 and 60 kV and the camera length, (the distance between the specimen and the photographic plate), was 49-50 cms. (see Fig.19).

Electron diffraction patterns are produced by mutual interference of secondary wavelets scattered by the atoms of the crystal lattice. The penetration of the surface

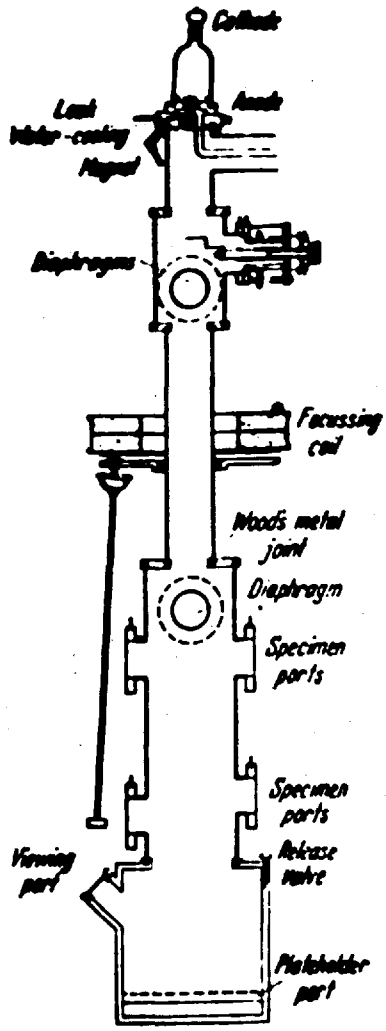


Fig.19. The Electron Diffraction Camera

is of the order of 100Å depending upon the material being examined. The main types of pattern encountered with thin films are: single crystal spot patterns and twinned crystals or other groupings; arc patterns from one-degree oriented polycrystalline specimens; and ring patterns from random polycrystalline specimens. Several types of preferred orientation can occur simultaneously in a polycrystalline specimen.

It is possible to obtain an expression for the scattering of a parallel beam of electrons by a single atom as a function of the distance from the scattering centre and for different angles of deviation. Using this function, the intensity of the diffracted waves from a three dimensional lattice can be calculated. The factor resulting from the repetition of the atoms in a lattice is called the Laue interference function, and shows that the main interference maxima fulfil the 'Laue conditions'. These maxima lie on the cones, for which the Laue indices h, k, l are integers, and intersect the photographic plate in 'Laue zones'. The Laue conditions are,

$$a(\cos\varepsilon - \cos\varepsilon_0) = h\lambda$$
$$b(\cos\eta - \cos\eta_0) = k\lambda$$
$$c(\cos\zeta - \cos\zeta_0) = l\lambda$$

where a,b,c are the distances between adjacent atoms in three non-coplanar axial directions, and ε, η, ζ and ε_0, η_0, ζ_0; the angles between the h, k, l diffraction direction and the diffracted and primary beams, respectively.

A single crystal spot pattern may be considered to be the result of the intersection of the cones associated with three non-coplanar rows of atoms in the crystal lattice. A parallel electron beam is scattered by a two-dimensional lattice in such a way as to produce a regular two-dimensional network of diffraction spots. The third row produces a concentric set of circular Laue zones with their common axis normal to the lattice row. The two-dimensional network of spots appear as strong diffractions only if they lie on the circular zones.

In the Bragg reflection method of interpretation, the spot patterns are interpreted in terms of the reflection of the primary beam of electrons by the crystal lattice planes. The condition for the reinforcement of the specularly reflected beams from a parallel set of consecutive planes is given by,

$$n\lambda = 2d\sin\theta$$

where n is the order of the reflection, λ the wave-length of the electrons, d the distance between the lattice planes and θ is the glancing angle of the electron beam. A 'reciprocal lattice' can be defined which bears a reciprocal relationship to the crystal lattice. A simple construction of this lattice gives rise to the Ewald sphere of reflection.

In the case of single-crystal spot patterns, the diffraction spots can be considered to correspond to the intersection of points (and surrounding 'intensity regions') of a hypothetical lattice λL times the dimensions of the

reciprocal lattice, with the Ewald 'sphere of reflection' whose radius is L. It is therefore possible to work back from the arrangement of spots on the photographic plate to the arrangement of points in the reciprocal lattice, and finally to the arrangement of atoms in the crystal lattice.

The interpretation of arc patterns from one-degree oriented specimens can be made in a similar manner, when the pattern is considered equivalent to the pattern produced by the rotation of a single crystal about the orientation axis. The arc pattern is then considered to be the λL times magnified intersection of the reciprocal lattice with the Ewald sphere.

However, the diffraction positions must also be at points which are simultaneously on the ring positions which would correspond to random orientations. They are also on certain of the horizontal Laue zones of reinforcement of spherical wavelets which expand out from successive lattice points along the lattice rows parallel to the orientation axis, which is common to all the crystals. These horizontal Laue zones of reinforcement are $\lambda L/T$ apart where T is the lattice period along the lattice row concerned, i.e. the common axis of orientation. A diffraction having indices hkl must lie on the hkl ring position, and also on the h'th order Laue zone which corresponds to the lattice row along the orientation axis, and

$$h' = hu + kv + lw$$

where $[uvw]$ are the indices defining the lattice row

direction relative to the crystallographic axes. Further details of the methods of interpretation of patterns from 'one-degree oriented' polycrystalline specimens are described by Wilman (1952).

It is more convenient to consider ring patterns from random polycrystalline materials as being produced by Bragg reflections from the atomic planes of the crystals which are randomly disposed to each other. Thus, whereas reflection of the primary beam by a set of atomic planes of a single crystal produces a single spot; if the crystals are randomly arranged, the locus of such spots forms a ring. The radius R of a ring on the photographic plate is related to the distance d between the atomic planes by the expression,

$$R = \frac{\lambda L}{d}\left[1 + \frac{3}{8}\left(\frac{R}{L}\right)^2 \cdots\cdots\right]$$

$$\simeq \frac{\lambda L}{d}$$

The relative intensities I of the diffractions in a ring pattern are normally roughly similar to those of an X-ray diffraction 'powder' pattern of the same material. The A.S.T.M. file of X-ray powder pattern data thus provides the most extensive direct comparison of d and I values for many thousands of crystalline materials without requiring the determination of the lattice form.

3. RESULTS

1. Variation in Structure of Tin Films with the Deposition Parameters

(i) General Introduction

Tin films are used in the thin film version of the cryotron - a device which exploits the unusual properties of superconductors and may be commercially attractive as a high-speed circuit switching and memory element for computers. One of the outstanding problems delaying the availability of superconductive stores is the lack of reliability and low yields in the fabrication process. This may be due to several causes but Blumberg and Seraphim (1962) have shown that the crystalline orientation of tin films is significant in determining the magnitude of the stress in the film when it is cooled to liquid helium temperature. They have also shown that the critical temperature depends upon the stress in the film, and thus the performance of any superconducting device using tin films can be expected to vary to some extent with the film orientation. This would be particularly so when the orientation is not uniform across the area of the film. The work presented here is part of that carried out under an extra-mural contract between Imperial College and the Autonomics Division of the National Physical Laboratory for studies on the structure of thin films, especially tin.

Evaporated tin films deposited onto an amorphous substrate are usually highly polycrystalline, and when deposited in high vacuum are frequently selectively oriented. According to Vook (1961) single-crystal tin films can be obtained under very special conditions, - short successive evaporations at 50Å/sec., onto (001) faces of NaCl at liquid nitrogen temperature in a vacuum of about 1×10^{-8} torr. Recently several different orientations of vacuum-deposited tin films have been observed including, (110) - Saikia (1961); (100) - Vook (1961); and Caswell (1961); and (001) - Kahan (1960) and Stuart (1961 - private communication). Fig. (20) shows the tin unit cell and the various orientation planes. Saikia (1961) and Stuart (1961) both used conventional vacuum systems while Vook and Caswell (1961) deposited their films in ultra-high vacuum. However these orientations were observed during other investigations and no systematic study has been made. It has therefore not been possible, to date, to predetermine preferred orientations according to the deposition parameters in any given system, and to state whether film orientation is uniform. Also no growth mechanism consistent with the known phenomena has been suggested and it was considered that this could not be done until a detailed study of the factors influencing the growth of tin films had been carried out.

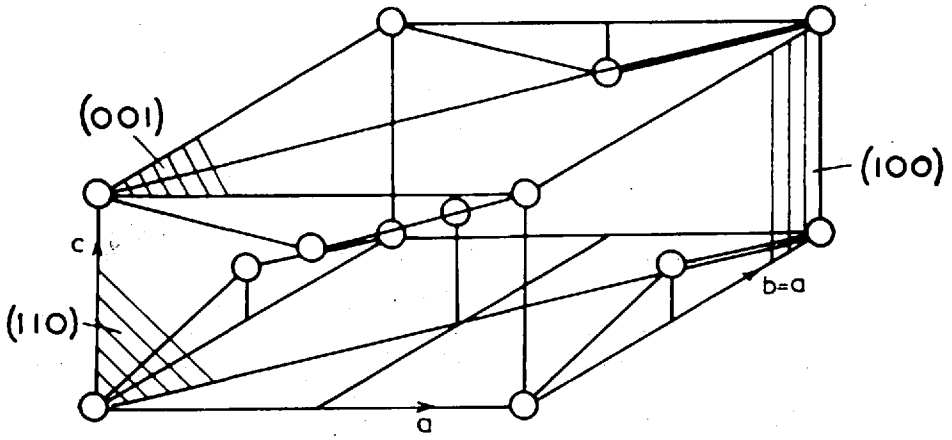


Fig.20. White tin unit cell

Body centred tetragonal lattice, a = 5.831Å, c = 3.182Å Atoms at (000), $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$, $(\frac{1}{2}\ 0\ \frac{1}{4})$, and $(0\ \frac{1}{2}\ \frac{3}{4})$.

(ii) Variation in Structure of Tin Films with Rate of Deposition and Residual Gas Pressure.

In this series of experiments, it has been attempted to investigate the structure of many tin films deposited under reproducible conditions to show how the deposition parameters of residual gas pressure, rate of deposition, and thickness of the film, influence the structure.

Approximately fifty specimens were deposited onto glass substrates at room temperature. Some auxiliary experiments were carried out by depositing tin onto polymer-coated glass substrates because these polymer films are likely to be used as the insulating layers in cryotrons.

(a) Tin Condensed in Vacuum between 1×10^{-4} and 1×10^{-6} torr onto Glass Substrates at Room Temperature

The system described in section 2.1 (i) was used for experiments in this pressure range. All the films deposited, at rates of deposition between 5 and 150Å/sec. and in residual gas pressures between 1×10^{-4} torr and 1×10^{-6} torr, were polycrystalline, and when the films were oriented, they were one-degree oriented with a certain plane parallel to the substrate surface and with a random orientation about an axis normal to the substrate surface.

The initial stages of formation of the deposit, by the growth and development of the structure of the nuclei, determine the final orientation of the film, and therefore a

study of the structure of very thin films was made, i.e. of approximately 500 Å thickness. Fig. (21) shows the observed variation of orientation for tin films with rate of deposition and residual gas pressure between 5×10^{-5} torr and 1×10^{-6} torr. The thickness of the films ranged from 450 - 600 Å.

Four different orientations of the film were obtained for this range of deposition conditions; random polycrystalline; (110) orientation; (001) orientation; and a mixed (100) and (001) orientation. Above a rate of deposition of approximately 70Å/sec., all the films were randomly oriented for all values of residual gas pressure. Below this value of rate of deposition, the films were one-degree oriented, and at high values of residual gas pressure - from 2×10^{-5} torr to 1×10^{-4} torr - had a weak (110) orientation. (See also Fig. 41). At lower gas pressures - approximately 1×10^{-5} torr at 5Å/sec. and 1.5×10^{-5} torr at 75Å/sec. - a mixture of (100) and (001) orientations was obtained. A (001) orientation on its own occurred for depositions in the range 1×10^{-5} torr to 3×10^{-5} torr residual gas pressure only.

Fig.(22) shows the electron diffraction patterns obtained from a selection of films giving the results shown in Fig.(21). The interpretation of these diffraction patterns is given in section 3.1 (iv).

The electron micrographs in Fig.(23) show that the films are not continuous in the early stages of growth. Fig.(23)a shows the island structure of a film approximately

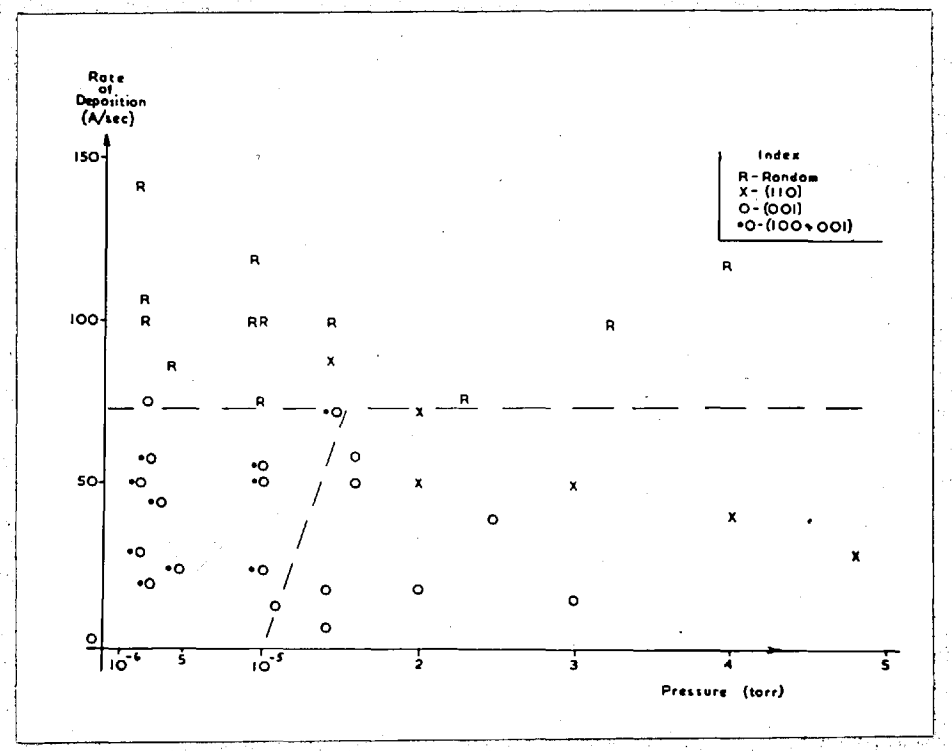
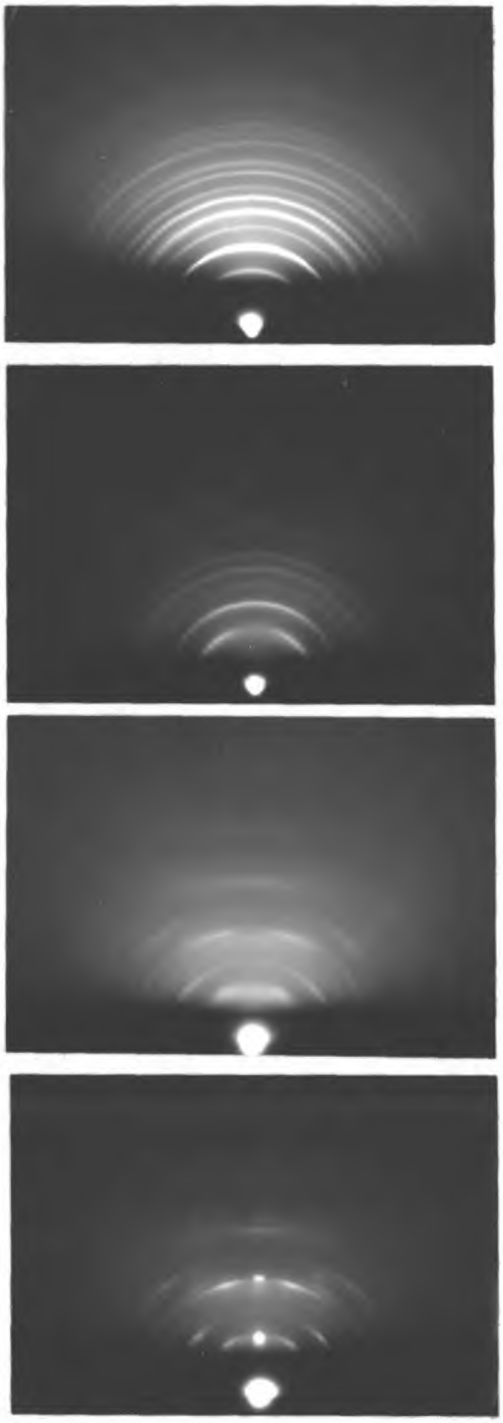


Fig.21. Variation of Surface Orientation of Tin Films, approx. 500A thick, with Residual Gas Pressure and Rate of Deposition.



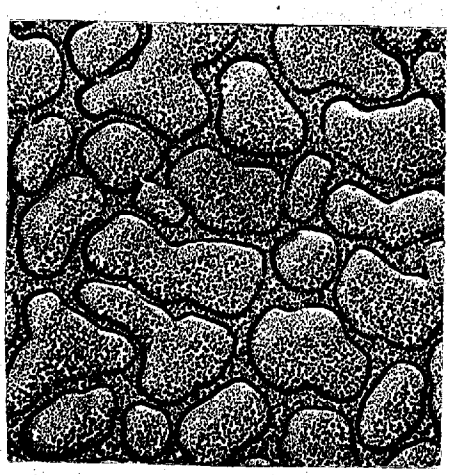
(a) Random Orientation.
Pressure - 1.0×10^{-5} torr.
Rate of Dep. - 100Å/sec.
Thickness - 500Å.

(b) (110) Orientation.
Pressure - 1.3×10^{-5} torr.
Rate of Dep. - 85Å/sec.
Thickness - 550Å.

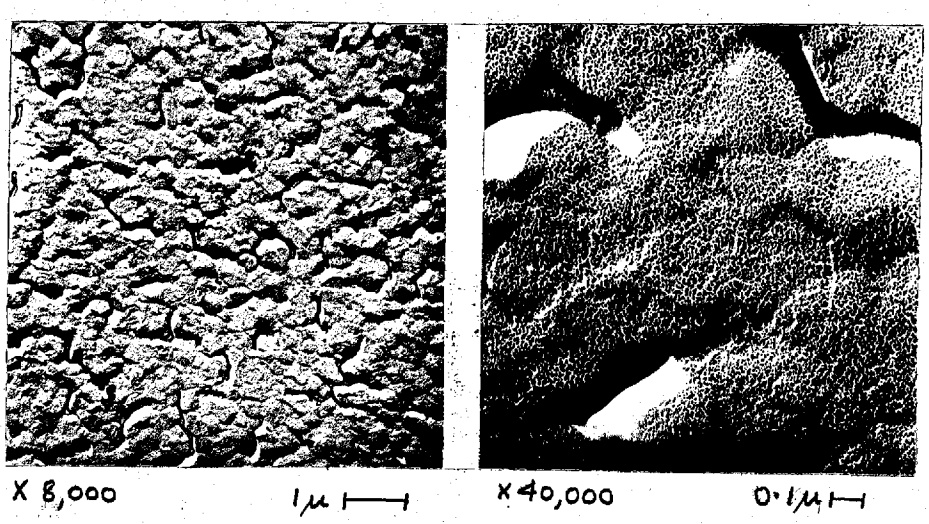
(c) (001) Orientation.
Pressure - 2.0×10^{-5} torr.
Rate of Dep. - 20Å/sec.
Thickness - 500Å.

(d) (100) and (001) Orientation.
Pressure - 1.0×10^{-5} torr.
Rate of Dep. - 50Å/sec.
Thickness - 550Å.

Fig. 22. Examples of Electron Diffraction Patterns Obtained from Tin Films giving the Results shown in Fig. 21.



(a) 500Å thick Tin Film



(b) 1500Å thick Tin Film

Fig. 23. Carbon Replica Electron Micrographs of Tin Films Condensed on to Glass Substrates at Room Temperature.

500Å thick deposited onto a glass substrate while Fig.(23)b shows that the film is almost continuous at 1500Å thickness. However from the shadowing data it is possible to estimate the depth of the channels (45° gold shadowing: magnification 40,000x) and these are almost 1500Å deep. These channels therefore go down almost to the glass substrate beneath. The above results, (Fig.21), thus correspond to the island stage of growth before the islands coalesce into a continuous film. Fig.(24) shows results obtained for tin films 1500Å thick deposited at various residual gas pressures. The results are similar to those of the 500Å thick films except for the occurrence of the (100) orientation. At 1×10^{-4}torr, (110) orientation is predominant (Fig.24a) while (001) orientation only is obtained at 1×10^{-5}torr residual gas pressure. At 2×10^{-6}torr, two orientations of the film can be obtained for the same rate of deposition (i) a (001) orientation on its own and (ii) a mixed (001) and (100) orientation where the (100) orientation is very weak.

An overall view of the orientation of tin films which can be obtained at various residual gas pressures is given in Table 1 at the end of this section.

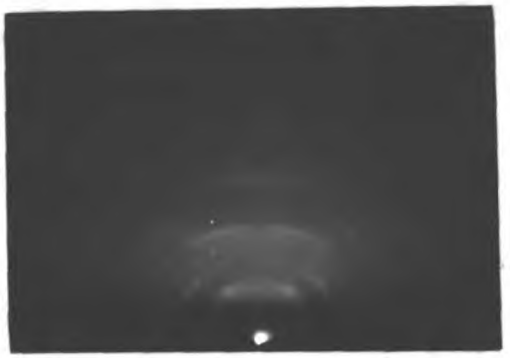
(b) <u>Tin Condensed in Vacuum between 1×10^{-6} and 4×10^{-8} torr onto Glass Substrates at Room Temperature.</u>

When the films were deposited in the U.H.V. system at room temperature, the pressure rose during the deposition



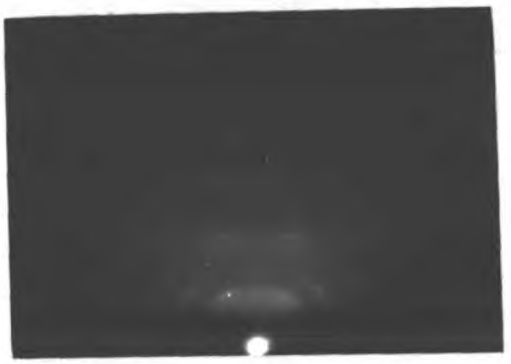
(a) (110) Orientation.

Pressure - 1×10^{-4} torr.
Rate of Dep. - 75 Å/sec.
Thickness - 1550 Å.



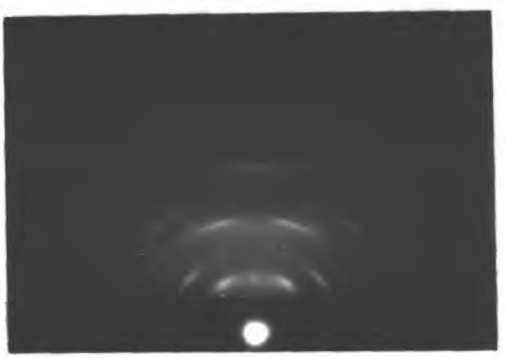
(b) (001) Orientation.

Pressure - 1×10^{-5} torr.
Rate of Dep. - 55 Å/sec.
Thickness - 1500 Å.



(c) (001) Orientation.

Pressure - 2×10^{-6} torr.
Rate of Dep. - 75 Å/sec.
Thickness - 1600 Å.



(d) (001) and Weak (100) Orientation.

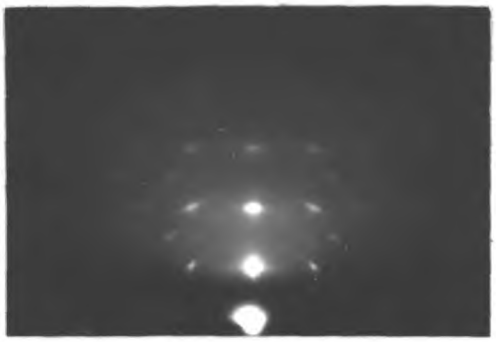
Pressure - 2×10^{-6} torr.
Rate of Dep. 60 Å/sec.
Thickness - 1450 Å/sec.

Fig. 24. Variation of Surface Orientation of Tin Films, 1500Å thick and deposited on to glass substrates at room temperature, with Residual Gas Pressure.

process into the 10^{-7}torr range even for low rates of deposition (< 10Å/sec.). This was due to the outgassing of the source during deposition even after the prior outgassing treatment as described in section 2.4 (ii). Rates of deposition had therefore to be kept as low as possible to obtain films in a vacuum of less than 1×10^{-6}torr. Also, as will be pointed out in the discussion, the orientation phenomenon occurring in the nucleus influence the final structure of the film only at low rates of deposition.

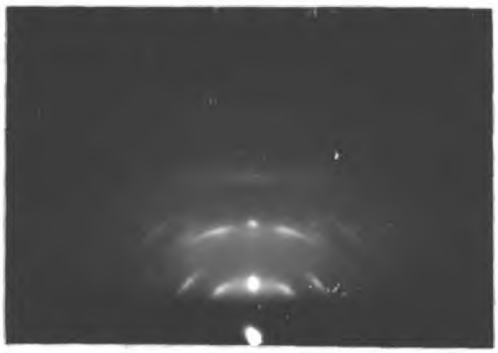
Fig.(25) shows the electron diffraction patterns and the deposition conditions for films 500 and 1500Å thick deposited in this pressure range onto glass substrates. (See also Table 1 for further clarification). When the gas pressure was maintained at 1×10^{-7}torr during the deposition process, only (100) orientation was obtained for both thicknesses of film. When the maximum pressure during the deposition was allowed to rise into the high 10^{-7} range, some (001) orientation of the tin was also produced and a mixed (100) and (001) orientation occurred (see Fig. 25b). However at 1500Å, the orientation in the surface region was predominantly (100), (see Fig.25d).

The overall results in Table 1 show that the orientation of tin films on glass substrates is dependent upon the residual gas pressure. A (110) orientation predominates in the 10^{-4}torr range and this changes through (001) orientation until a (100) orientation predominates in ultra-high vacuum



(a) (100) Orientation.

Res. gas press. - 4×10^{-8} torr.
Max. gas press. - 1×10^{-7} torr.
Rate of dep. - 15 Å/sec.
Thickness - 500 Å.



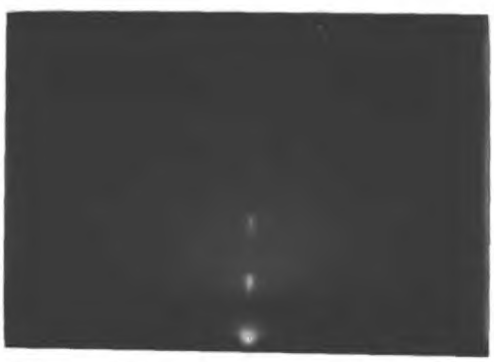
(b) (100) and (001) Orientation.

Res. gas press. - 1×10^{-7} torr.
Max. gas press. - 15×10^{-7} torr
Rate of dep. - 5 Å/sec.
Thickness - 500 Å.



(c) (100) Orientation.

Res. gas press. - 4×10^{-8} torr.
Max. gas press. - 1×10^{-7} torr.
Rate of dep. - 15 Å/sec.
Thickness - 1500 Å.



(d) (100) and weak (001) Orientation

Res. gas press. - 1×10^{-7} torr.
Max. gas press. - 5×10^{-7} torr.
Rate of dep. - 15 Å/sec.
Thickness - 1500 Å.

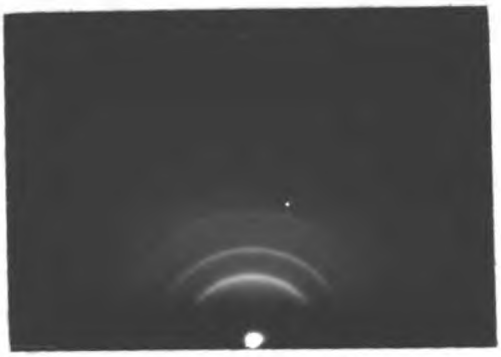
Fig. 25. Variation of Surface Orientation of Tin Films, deposited on to glass substrates at room temperature, with Thickness for residual gas pressures about 1×10^{-7} torr.

regions ($< 5 \times 10^{-7}$ torr). However, it can also be seen from the different orientations obtained at two thicknesses, 500Å and 1500Å, in the same residual gas pressure conditions that there is also a change in orientation with thickness as the film changes from the island stage of growth into a continuous film.

(c) Effect of Substrate

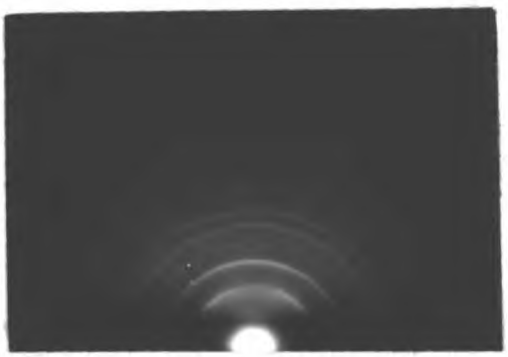
It has been previously stated (section 3.1 ii) that the tin film in the cryotron will probably be deposited onto a polymer insulating film. This ensures that the metal film will be deposited onto a clean surface and also that all the layers of the device can then be put down without breaking the vacuum in a multi-layer deposition unit. It was therefore necessary to investigate the variation of structure of tin films deposited onto polymer substrates in the light of the above results. This also helps to show the additional effects introduced into the growth mechanism by changing the nature of the substrate surface.

Fig.(26) is a series of electron diffraction patterns showing the variation in orientation of tin films 500Å thick, deposited onto polymer coated substrates, with residual gas pressure. Low rates of deposition were used (< 50Å/sec) where, according to the previous results, (Fig.21), the effects of changing the rate of deposition are non-influential on the structure. It can be seen that the orientations observed are similar to those produced by depositing tin films onto glass



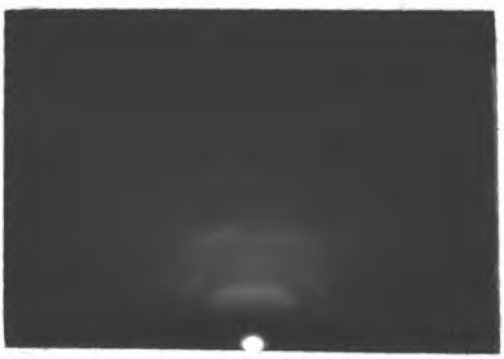
(a) Random Orientation.

Pressure - 1 x 10^{-5} torr.
Rate of Dep. - 25 Å/sec.
Thickness - 500 Å.



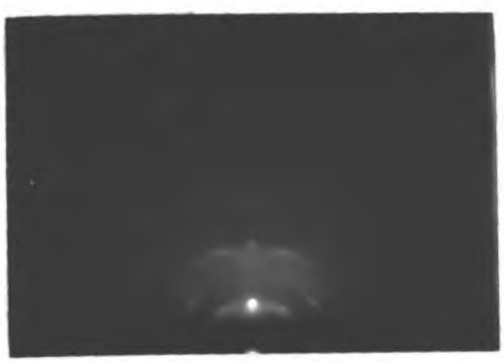
(b) (110) Orientation.

Pressure - 2 x 10^{-6} torr.
Rate of Dep. - 50 Å/sec.
Thickness - 500 Å.



(c) (001) Orientation.

Pressure - 1 x 10^{-7} torr.
Rate of Dep. - 15 Å/sec.
Thickness - 500 Å.



(d) (001) and (100) Orientation.

Pressure - 4 x 10^{-8} torr.
Rate of Dep. - 15 Å/sec.
Thickness - 500 Å.

Fig. 26. Variation of Surface Orientation of Tin Films, 500 Å thick and deposited on to polymer substrates at room temperature, with Residual Gas Pressure.

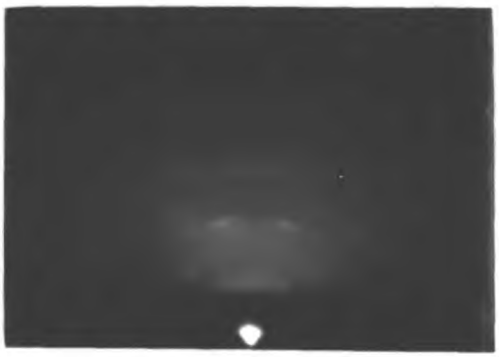
substrates except that a lower residual gas pressure is required, i.e. a 500Å thick film deposited on to glass substrates at 4×10^{-8} torr has a (100) orientation, but a mixed (001) and (100) orientation on a polymer coated substrate. This is the orientation obtained on glass substrates at a residual gas pressure of 2×10^{-6} torr. (See also Table 1). A similar effect occurs for thicker deposits. The electron diffraction patterns for 1500Å thick films are shown in Fig. (27). For a film 1500Å thick deposited on to a polymer substrate, at 5×10^{-8} torr residual gas pressure a mixed (001) and (100) orientation is obtained, but for identical conditions on glass substrates, a (100) orientation is predominant. (Compare Figs. (25)c and (27)c). The same thing occurs for other values of residual gas pressure as shown by comparison of the results in Figs. (24) and (25) with Fig. (27).

The orientations obtained for films deposited on to polymer substrates with various deposition conditions are incorporated into Table 1.



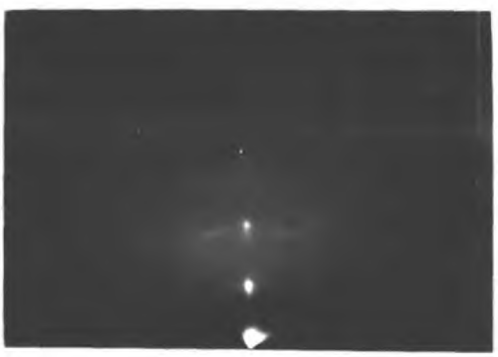
(a) (110) Orientation.

Pressure - 2×10^{-6} torr.
Rate of Dep. - 20Å/sec.
Thickness - 1500 Å.



(b) (001) Orientation.

Pressure - 1×10^{-7} torr.
Rate of Dep. - 15Å/sec.
Thickness - 1500 Å.



(c) (001) and (100) Orientation.

Pressure - 5×10^{-8} torr.
Rate of Dep. - 5.Å/sec.
Thickness - 1500 Å.

Fig. 27. Variation of Surface Orientation of Tin Films, 1500 Å thick and deposited on to polymer substrates at room temperature, with Residual Gas Pressure.

(iii) Variation in Structure of Tin Films with Rate of Deposition and Thickness of the Film.

(a) Residual Gas Pressure - 1×10^{-5} torr.

The results from section (i) were combined with those from other deposits, condensed onto glass substrates at various thicknesses, to investigate the variation of structure with thickness of the film.

Fig.(28) shows the variation in orientation of tin films with rate of deposition and film thickness for depositions carried out in a residual gas pressure of 1×10^{-5} torr. A random orientation of the crystallites in the film was predominant for thin films (< 500Å thick) deposited at high rates of deposition. Some of these developed (110) orientation as the thickness increased but others developed a (001) orientation instead, up to about 1500Å. For thicknesses above 1500Å at high rates of deposition, a (301) orientation of the tin film was also found and this became increasingly predominant with increasing thickness. A 4000Å thick film deposited at 80Å/sec. showed (301) orientation only (see Fig.32a).

With deposition rates below approximately 60Å/sec., a (100) orientation is found to be present in thinner films. This appears to be mainly confined to the thinner films, i.e. thicknesses < 1000Å. In this region some of the films have a (100) orientation only, a (001) orientation only, or a

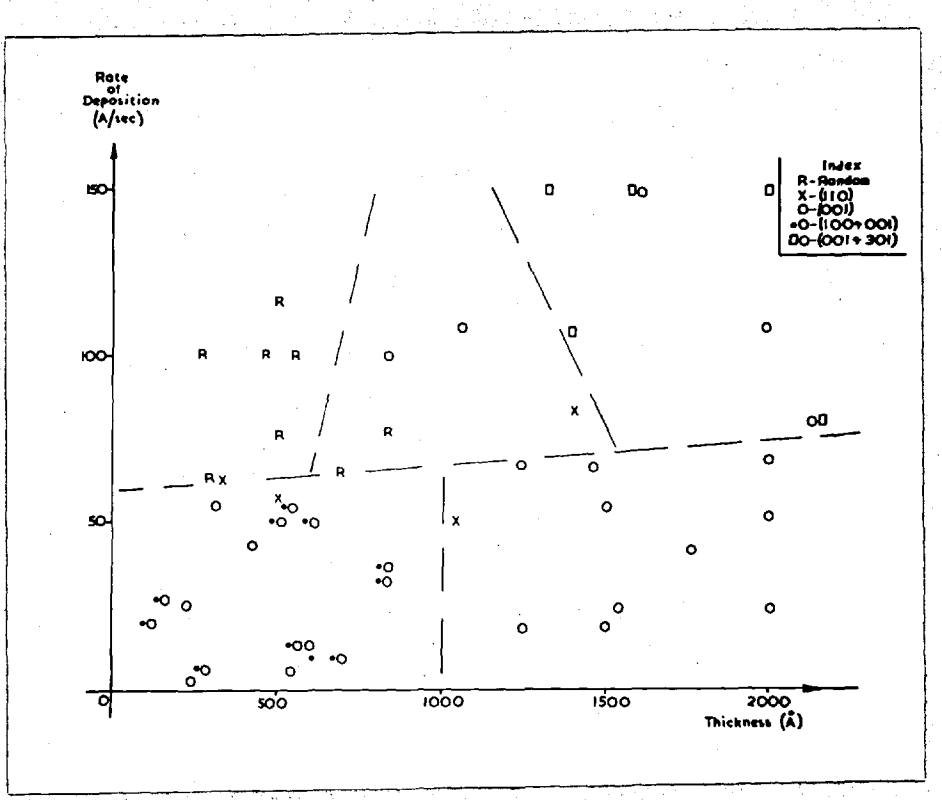
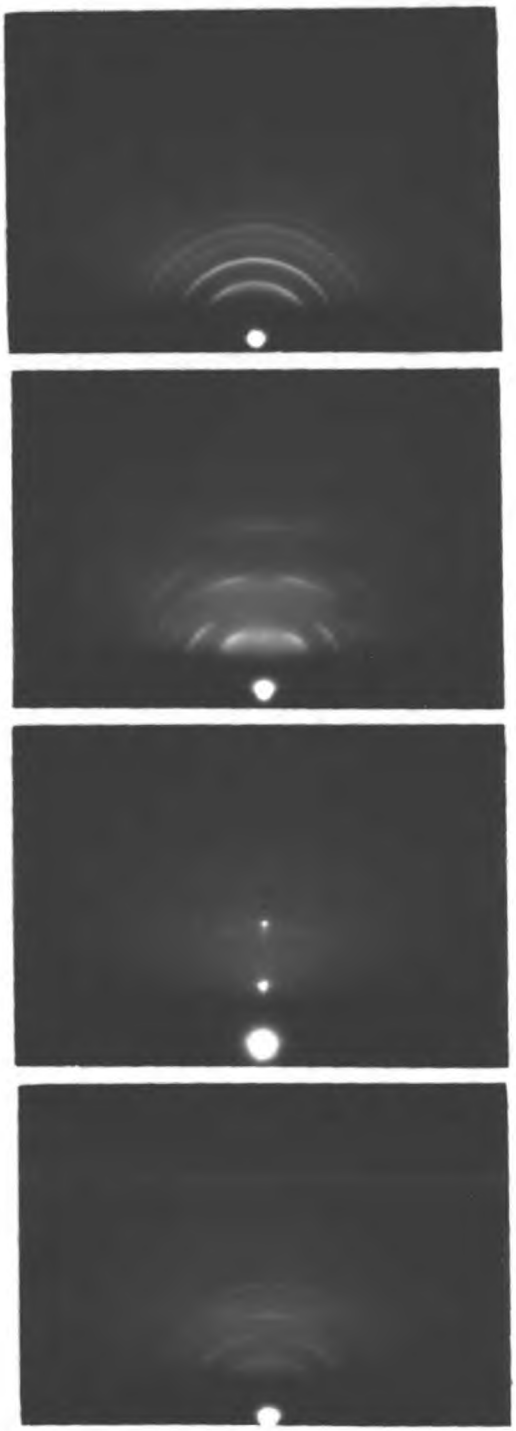


Fig.28. Variation of Surface Orientation of Tin Films, Deposited onto Glass Substrates at Room Temperature, with Rate of Deposition and Film Thickness for a Residual Gas Pressure of 1 x 10^{-5} torr.



(a) Random Orientation.
Pressure - 1 x 10^{-5} torr.
Rate of Dep. - 100Å/sec.
Thickness - 250Å.

(b) (001) Orientation.
Pressure - 1 x 10^{-5} torr.
Rate of Dep. - 20Å/sec.
Thickness - 1500Å.

(c) (001) and (100) Orientation.
Pressure - 1 x 10^{-5} torr.
Rate of Dep. - 50Å/sec.
Thickness - 500Å.

(d) (301) Orientation.
Pressure - 1 x 10^{-5} torr.
Rate of Dep. - 150Å/sec.
Thickness - 2000Å.

Fig. 29. Examples of Electron Diffraction Patterns Obtained from Tin Films giving the Results shown in Fig. 28.

mixed (100) and (001) orientation. A (001) orientation is obtained for films with increasing thickness up to 2500Å. A 4000Å thick film deposited at 15Å/sec. had (001) orientation. (See Fig.32b). Sample electron diffraction patterns from which the results shown in Fig.(28) were obtained are given in Fig.(29).

(b) Residual Gas Pressure - 2×10^{-6} torr.

Fig.(30) shows the variation in orientation of tin films with rate of deposition and thickness for films condensed onto glass substrates at room temperature in a residual gas pressure of 2×10^{-6} torr. The results are similar to those obtained at 1×10^{-5} torr. A random orientation was again predominant for deposition rates above 70Å/sec. and thicknesses below 500Å. However, no (110) orientation was observed in any of the specimens deposited at high rates of deposition when the thickness was increased above 500Å. A (001) orientation only was observed up to about 1500Å thickness. This is a different result from those presented in Fig.(28) where a (110) orientation was also obtained. For deposition rates above 80Å/sec. and thicknesses above 1500Å a (301) orientation again becomes predominant.

At rates of deposition below approximately 75Å/sec. the films had either a (100) or a mixed (001) and (100) orientation for thicknesses below approximately 1200Å. Above 1200Å thickness however, a (001) orientation becomes increasing-

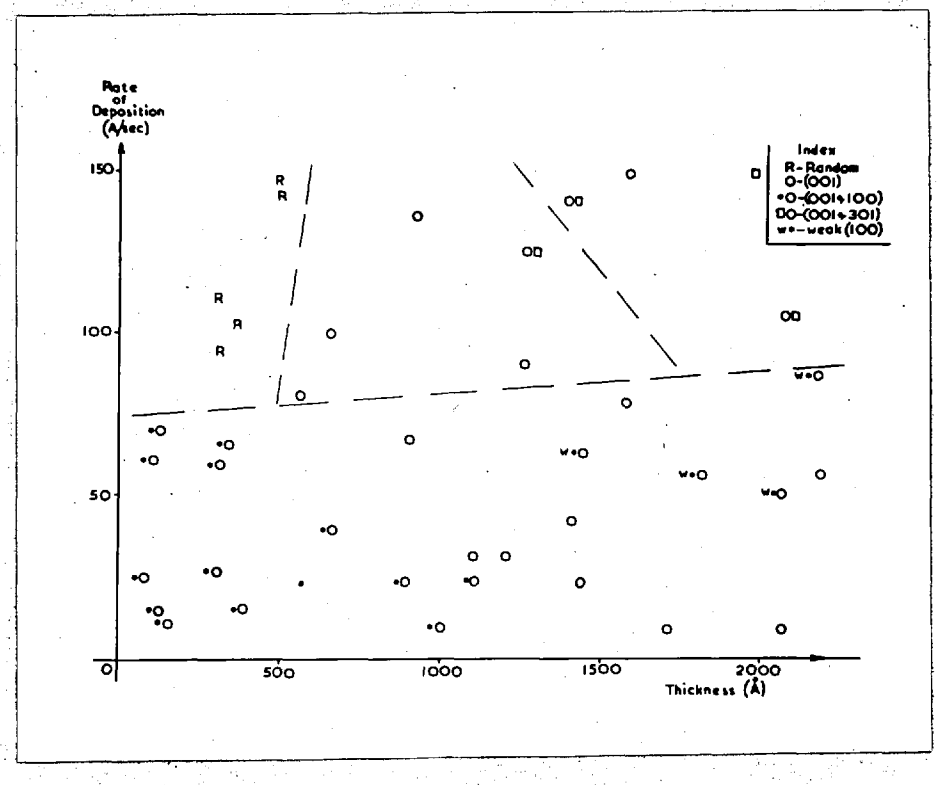
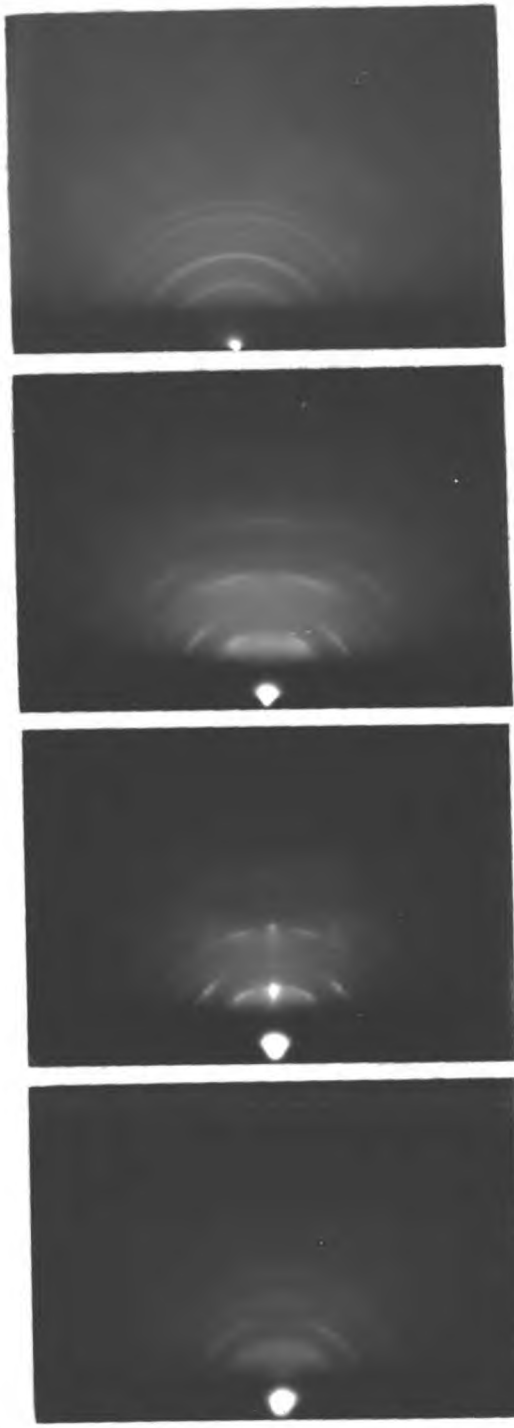


Fig.30. Variation of Surface Orientation of Tin Films, Deposited onto Glass Substrates at Room Temperature, with Rate of Deposition and Film Thickness for a Residual Gas Pressure of 2 x 10^{-6} torr.



(a) Random Orientation.
Pressure - 2×10^{-6} torr.
Rate of Dep. - 105Å/sec.
Thickness - 315Å.

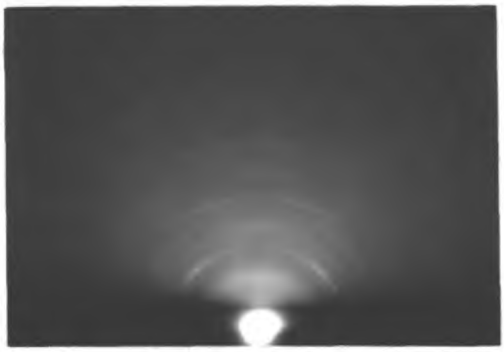
(b) (001) Orientation.
Pressure - 2×10^{-6} torr.
Rate of Dep. - 30Å/sec.
Thickness - 1200Å.

(c) (001) and (100) Orientation.
Pressure - 2×10^{-6} torr.
Rate of Dep. - 40Å/sec.
Thickness - 650Å.

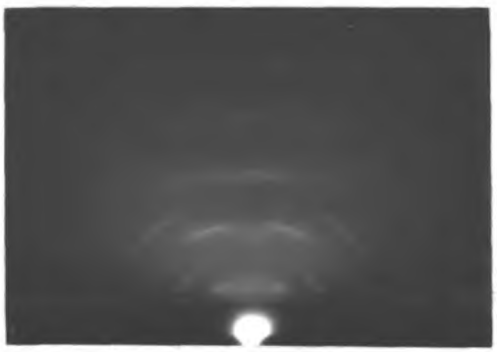
(d) (301) Orientation.
Pressure - 2×10^{-6} torr.
Rate of Dep. - 150Å/sec.
Thickness - 2000Å.

Fig. 31. Examples of Electron Diffraction Patterns Obtained from Tin Films giving the Results shown in Fig. 30.

ly predominant but a co-existing (100) orientation of the film is still obtained for thicknesses up to 2000 Å . This is contrary to the results obtained at 1 x 10^{-5} torr where a (001) surface orientation only was obtained for thicknesses greater than approximately 1000 Å. Electron diffraction patterns from which the above results were obtained are shown in Fig. (31). Fig. (33) shows the surface orientation of 5000 Å thick tin films deposited at 2 x 10^{-6}torr. Fig. (33)a shows the orientation of a film deposited at 100 Å/sec. and is (301) orientation. This is similar to a film deposited at 1 x 10^{-5}torr (see Fig. 32a). Fig. 33b shows that a (001) orientation is obtained for films 5000 Å thick deposited at 2 x 10^{-6} torr and at low rates of deposition. The (001) orientation is therefore preferred for thicknesses above 2000 Å.

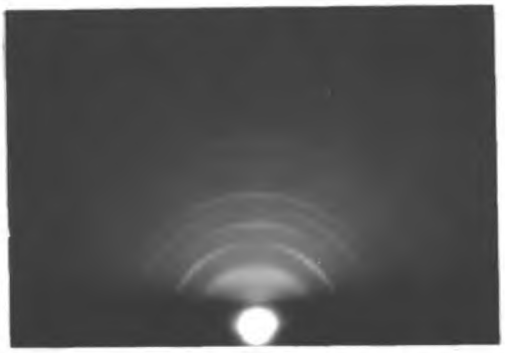


(a) (301) Orientation of Tin Film. Thickness 4000A. Rate of Deposition 80A/sec. Residual Gas Pressure 1 x 10^{-5}torr.

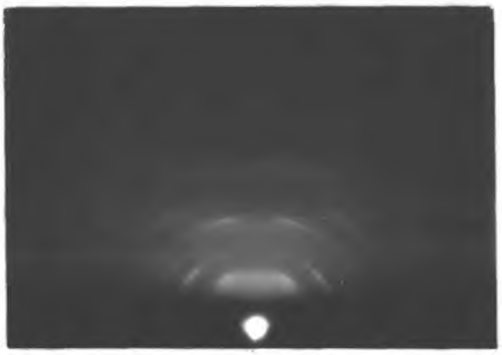


(b) (001) Orientation of Tin Film. Thickness 4000A. Rate of Deposition 15A/sec. Residual Gas Pressure 1 x 10^{-5}torr.

Fig.32. The Surface Orientation of Tin Films, 4000A thick, deposited onto Glass Substrates at Room Temperature and Residual Gas Pressure 1 x 10^{-5}torr.



(a) (301) Orientation of Tin Film. Thickness 5000A. Rate of Deposition 100A/sec. Residual Gas Pressure 2 x 10^{-6}torr.



(b) (001) Orientation of Tin Film. Thickness 5000A. Rate of Deposition 20A/sec. Residual Gas Pressure 2 x 10^{-6}torr.

Fig.33. The Surface Orientation of Tin Films, 5000A thick, deposited onto Glass Substrates at Room Temperature and Residual Gas Pressure 2 x 10^{-6}torr.

Table 1.(a). The Variation of Surface Orientation of Tin Films with Residual Gas Pressure and Substrate for Films (a) 500Å thick (b) 1500Å thick, and for Low Rates of Deposition, i.e. < 75Å/sec.

Residual Gas Pressure	Thickness (Å)	Orientation	
		Glass Substrate	Polymer Substrate
1×10^{-4}	500	(110)	-
1×10^{-5}	500	(001)	Random
2×10^{-6}	500	(100)(001)W	(110)W
1×10^{-7}*	500	(100)(001)W	(001)
4×10^{-8}*	500	(100)	(100)(001)
1×10^{-4}	1500	(110)	-
1×10^{-5}	1500	(001)	-
2×10^{-6}	1500	(001)(100)W	(110)
1×10^{-7}*	1500	(100)	(001)
1×10^{-8}*	1500	(100)	(001)(100)

* This is the value of the residual gas pressure. The actual pressure during the deposition process rose to the values quoted in Fig. 25.

W - Weak orientation.

Table 1.(b). The Variation of Surface Orientation of Tin Films with Residual Gas Pressure and Thickness for High Rates of Deposition, i.e. $> 75\text{Å}/\text{sec}$.

Thickness (Å)	Orientation	
	Pressure 1×10^{-5} torr	Pressure 2×10^{-6} torr
500	Random	Random
1000	(001) (110)	(001)
1500	(001)	(001)
2000	(301)	(301)
5000	(301)	(301)

(iv) Electron Diffraction Interpretation

The experimental net plane spacings of the film material were calculated from the ring radii of the electron diffraction patterns in the manner described in Section 2.5. An example of the interpretation is given below. The values obtained from the diffraction pattern shown in Fig.22(b) are compared with the A.S.T.M. X-ray diffraction data from card no. 4-0673 in Table 2, and this shows that the film corresponds to tetragonal β -tin. The orientation of the film is determined from the arc positions of the pattern.

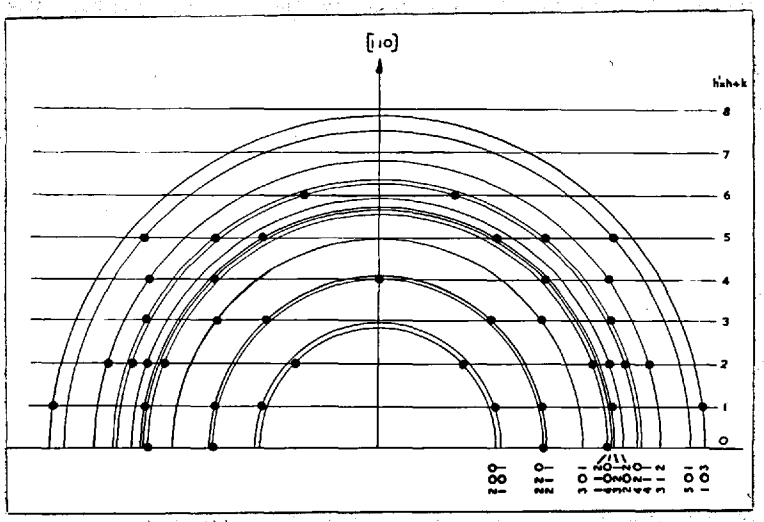
In Fig.22(b), the second ring (combined 220 and 211 rings) is arced in the plane of incidence and the film has an orientation with one of these planes parallel to the substrate surface. Fig.(34) shows the theoretical diffraction pattern for (110) and (211) - oriented tin films. As the first ring in Fig.(22)b is broken in the plane of incidence, and lateral arcing is shown in the theoretical pattern for (110) orientation, it was concluded that the film was in (110) orientation.

The (100) orientation of the film shown in the electron diffraction pattern of Fig.(25)a can be obtained in a similar manner. This film gives a spot pattern and the spots in the plane of incidence correspond to the positions of the 200 ring and the 400 ring - i.e. second order. By comparing the experimental pattern with the theoretical patterns for (100) and (101) - oriented tin films - Fig.(35) -

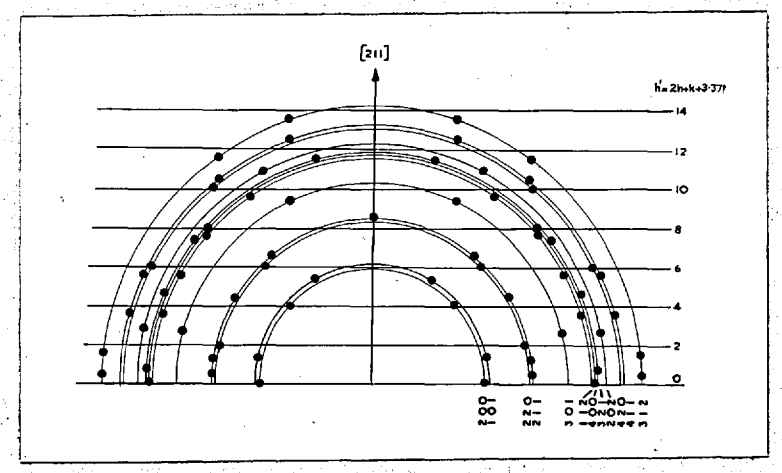
Table 2. Comparison of Experimental Lattice Spacings for Tin Films with A.S.T.M. X-Ray Diffraction Data.

Electron Diffraction Data Fig. 22(b).			Data Obtained from ASTM Card 4 - 0673[3]		
Ring Radius (mm)	Calculated Lattice Spacing d (A) (1)	Intensity[2]	Laue Indices hkl	Lattice Spacing d (A)	Intensity $\frac{I}{I_1}$
7.80	2.92	S	200	2.915	100
8.15	2.80		101	2.793	90
10.98	2.07	S	220	2.062	34
11.24	2.02		211	2.017	74
13.70	1.66	W	301	1.659	17
15.55	1.47	M	112	1.484	23
			400	1.458	13
15.80	1.44	M	321	1.442	20
			202[4]	-	-
17.38	1.31	M	420	1.304	15
17.57	1.29		411	1.292	15
18.90	1.21	W	312	1.205	20

1. Data calculated with ref. to $d_{301} = 1.659\text{Å}$
2. S - Strong; M - Medium; W - Weak
3. Sn : Tetragonal $a_o = 3.182\text{Å}$: $c = 5.831\text{Å}$
4. No data given on ASTM card.

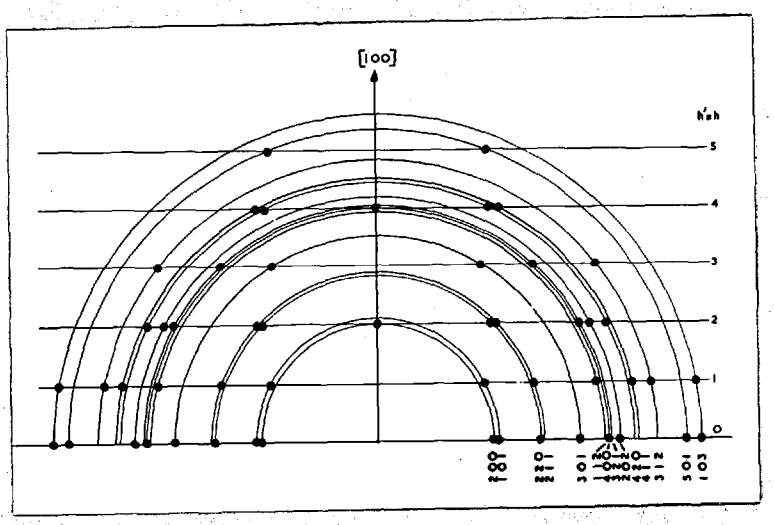


(a) Theoretical (110) Electron Diffraction Pattern.

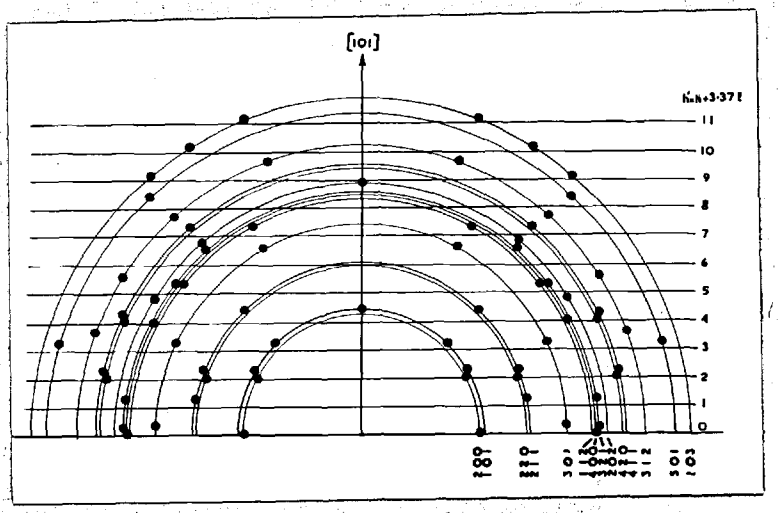


(b) Theoretical (211) Electron Diffraction Pattern.

Fig.34. Theoretical one-degree orientation Electron Diffraction Patterns from Tin Specimens. (Radii of rings calculated from ASTM data card 4-0673).



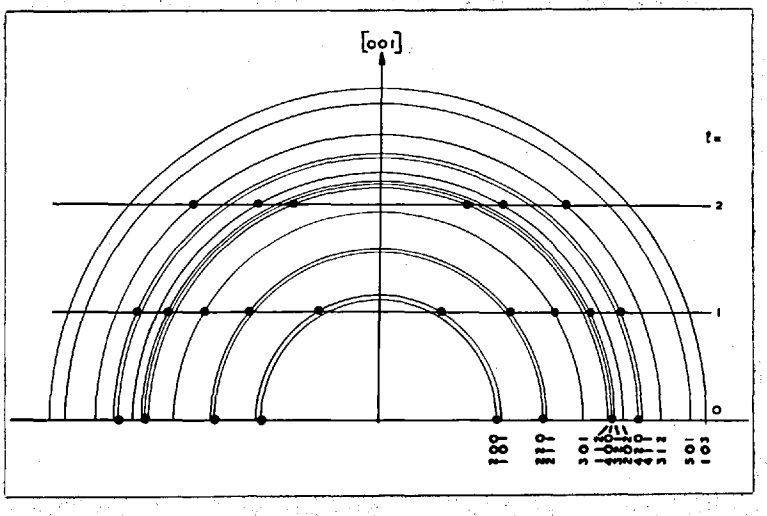
(a) Theoretical (100) Electron Diffraction Pattern.



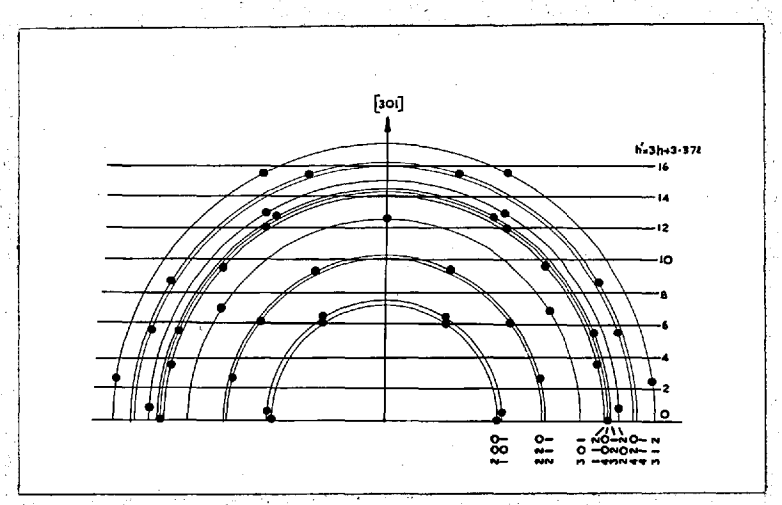
(b) Theoretical (101) Electron Diffraction Pattern.

Fig.35. Theoretical one-degree orientation Electron Diffraction Patterns from Tin Specimens.

it can be seen that the lateral arcs of the 'square' spot pattern correspond to the arcing on the (220) and (211) rings and the (420) and (411) rings respectively on the theoretical (100) pattern. Therefore the film shown in Fig.(22)c has a (100) orientation. The films in other orientations were determined in a similar manner. Fig.(36) shows the theoretical patterns corresponding to tin films possessing (001) and (301) orientations respectively. These should be compared with the experimental patterns as shown in Figs.(22)d, (32)a, etc.



(a) Theoretical (001) Electron Diffraction Pattern.



(b) Theoretical (301) Electron Diffraction Pattern.

Fig.36. Theoretical one-degree orientation Electron Diffraction Patterns for Tin Specimens.

2. Influence of a High Partial Pressure of Oxygen during Tin Deposition.

(i) General Introduction

In his work on copper films deposited at liquid oxygen temperature at 10^{-9}torr, Keith (1956) found that the grain size of films 2000Å thick was approximately 40Å, but upon warming to room temperature, this increased to at least 400Å. However, if the film was raised to room temperature in a partial pressure of oxygen, the final grain size was only 60Å. This led him to propose that oxygen could be used as a 'brake' to stop kinetic processes so that the films could be examined at room temperature. Caswell (1961) has also used this technique to prevent agglomeration effects and impede annealing in very thin tin films (approximately 150Å thick and deposited at 80°K) and has also shown how the structure of these films can be 'frozen' by injecting a high partial pressure of oxygen into the system. The oxygen thus significantly reduces the surface mobility during the annealing process. It is therefore permissible to assume that the presence of a high partial pressure of oxygen in the vacuum system during the deposition process would also reduce the surface mobility of the tin during deposition.

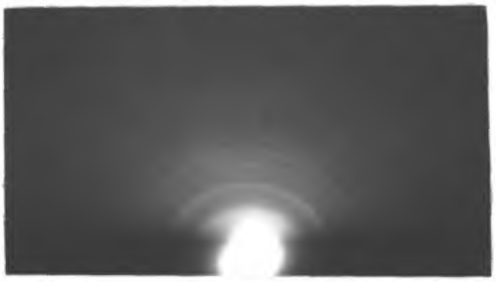
The previous results have shown that the orientation of tin films varies with the rate of deposition - at high rates of deposition an initial randomly oriented stage modifies the growth process and also no (100) orientation is obtained.

These 'doping' experiments were therefore carried out at two different rates of deposition, (i) at 100Å/sec.; (ii) at 5Å/sec. The results obtained in these experiments are given below.

(ii) Structure of Tin Films Deposited at High Rates of Deposition (100Å/sec) in High Partial Pressure of Oxygen

The U.H.V. System was pumped to a pressure of 1×10^{-8} torr. Assuming the metal film has the bulk density, the ratio of gas/metal atoms striking the substrate is reduced to less than 0.1% at this pressure for rates of deposition of tin above 5Å/sec. The system was then arranged so that pure oxygen flowed through the system, the partial pressure being maintained at 1×10^{-5} torr. All the specimens were deposited in one evaporation with a shutter being used to control the thickness of the films. This ensured identical deposition conditions for all the specimens. The deposit thicknesses ranged from 200Å to 1800Å. Because of the limitations of the vacuum system described in section 2.1(ii) for obtaining a high rate of deposition at large enough deposition distances for the correct use of the ratemeter, this set of specimens was kindly provided by Dr. C.C. Stoddart of the Autonomics Divn. of N.P.L. They were deposited in a similar system to that described in Section 2.1(ii). The thicknesses were measured after the electron diffraction examination by using an optical interferometer. The diffraction patterns giving the structure of the films with varying thickness are shown in sequence in Fig.(37). The results are also incorporated into Table 4.

Fig. (37)a shows the surface structure of the film 100 - 200Å thick which has a predominantly random orientation



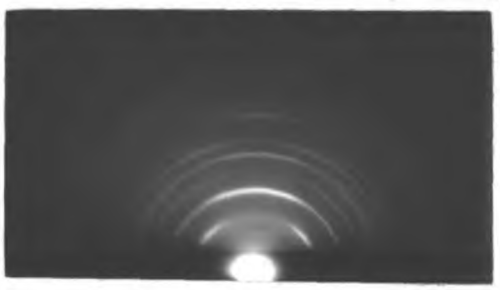
(a) Random Orientation.
Thickness - 100-200 Å.



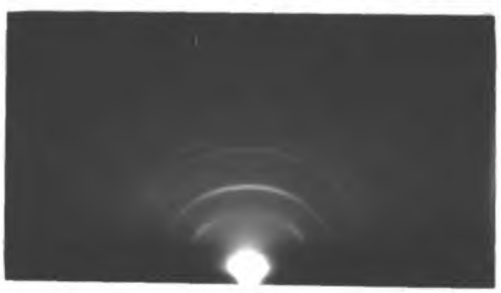
(b) Weak (110) and (301) Orientation
Thickness - 250 Å.



(c) (110) Orientation.
Thickness - 600-1000 Å.



(d) (110) Orientation.
(001) Orientation. SnO.
Thickness - 1200 Å.



(e) (110) Orientation.
(001) Orientation. SnO.
Thickness - 1800 Å.

Fig. 37. Variation of Surface Oxidation of Tin Films with Thickness, when deposited on to glass substrates at room temperature in a partial pressure of O_2 - 1 x 10^{-5} torr. at 100 Å/sec.

of the crystallites parallel to the substrate surface. There is a slight arcing on the (301) ring in the plane of incidence showing an initial (301) orientation.

Fig.(37)b is the diffraction pattern obtained from the film 250Å thick and shows that the tin at the surface is already in (110) orientation. The 200 and 101 rings are just broken in the plane of incidence. For only (110) orientation present, the 301 ring should be broken in the plane of incidence (see theoretical (301) orientation pattern: Fig. 36b). Some of the tin is therefore in (301) orientation. For only (301) orientation present, the (110) ring should be arced laterally, but it is in fact continuous in the plane of incidence, showing that (110) orientation is present. It is concluded therefore that there is a mixture of (301) and (110) orientations in the specimen.

Fig.(37)c shows the arced pattern for (110) orientation of tin parallel to the substrate: the degree of orientation is $\pm 30^{\circ}$ about the mean. This specimen was 600-1000Å thick.

Fig. (37)d for a specimen 1200Å thick is also the diffraction pattern for (110) orientation and only (110) orientation is present (cf. theoretical (110) orientation pattern Fig.34c). However there is a faint but moderately sharp diffraction arc in the plane of incidence about 0.50cm. from the central spot. This corresponds to crystalline stannous oxide in (001) orientation within the surface region of the deposit. As can be seen from Table 3, the other tin

oxide diffractions are nearly coincident with the tin diffractions and are therefore difficult to detect. The intensity of the outer rings will also be considerably reduced and will therefore not be apparent.

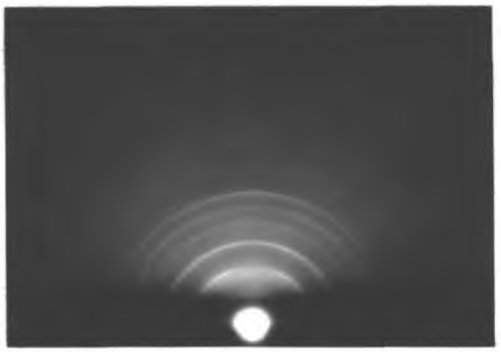
Fig.(37)e obtained from the film 1800Å thick also shows the film in (110) orientation and with (001) oriented tin oxide still present. Fig.(38) shows a (110) orientation for films,(i) 650Å thick (ii) 1400Å thick, deposited under identical conditions but not in a partial pressure of oxygen. However it can be seen that tin oxide is obtained for the film 1400Å thick whilst no oxide is detectable in the thinner film.

The results obtained at high rates of deposition are incorporated into Table 4.

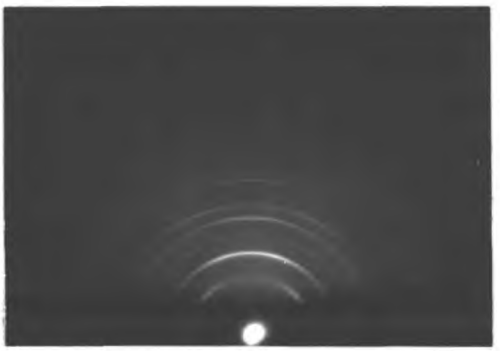
Table 3. Comparison of Experimental Lattice Spacings for Tin Films deposited in a High Partial Pressure of Oxygen with A.S.T.M. X-Ray Diffraction Data for Sn and SnO.

Electron Diffraction Data. Fig.37(d).		Data for SnO from ASTM Card 6-0395[1]		Data for Sn from ASTM Card 4-0673[2]	
Ring Radius (mm)	Calculated Lattice Spacing $\overset{o}{d}(\overset{o}{A})$[3]	Laue Indices hkl	Lattice Spacing $\overset{o}{d}(\overset{o}{A})$	Laue Indices hkl	Lattice Spacing $\overset{o}{d}(\overset{o}{A})$
5.01	4.80	001	4.850	-	-
8.19	2.92	101	2.989	200	2.915
8.58	2.80	110	2.688	101	2.793
-	-	002	2.418	-	-
11.66	2.06	102	2.039	220	2.062
11.93	2.01	200	1.901	211	2.017
13.10	1.83	112	1.797	-	-
14.5	1.66	211	1.604	301	1.659
16.2	1.48	202	1.494	112	1.484

1. SnO Tetragonal $a_o = 3.802$; $c_o = 4.836$
2. See Table 2 for complete data on ASTM Card 4-0673
3. Data calculated with ref. to $d_{301} = 1.659\overset{o}{A}$



(a) (110) Orientation of Tin Film. Thickness 650A. Rate of Deposition 93A/sec. Residual Gas Pressure 1 x 10^{-5}torr.



(b) (110) Orientation of Tin Film. Thickness 1400A. Rate of Deposition 95A/sec. Residual Gas Pressure 1 x 10^{-5}torr.

Fig.38. Electron Diffraction Patterns showing variation in (110) orientation of Tin Films with increasing Thickness of the Film.

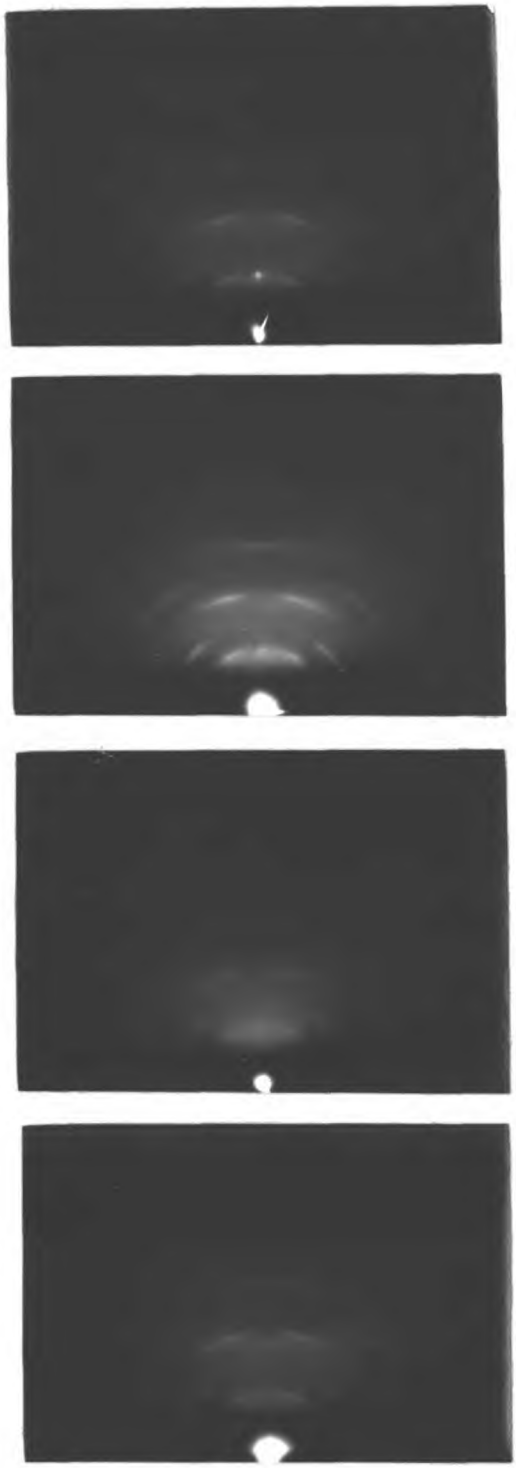
(iii) Structure of Tin Films Deposited at Low Rates of Deposition (5Å/sec) in High Partial Pressure of Oxygen.

All the films deposited at low rates of deposition were obtained in the U.H.V. system described in the section entitled experimental, and were deposited in a similar manner to those in the previous section at high rates of deposition. Films were deposited onto both glass and polymer substrates simultaneously so that direct comparison of the relative orientations can be made.

Fig.(39) shows the variation of the tin surface orientation with thickness for films deposited onto glass substrates up to 1500Å thick. Figs.(39)a and (39)b, obtained from films 200Å and 600Å thick respectively, are similar and show a mixed (001) and (100) orientation in which the (100) orientation is quite weak. As the thickness increases, the (100) orientation becomes even weaker - Fig.(39)c shows the orientation for a film 1000Å thick - and at 1500Å thickness, a (001) orientation predominates. The orientation for a 1500Å thick film is shown in Fig.(39)d.

Fig.(40) shows the variation of orientation with thickness for films deposited onto polymer substrates up to 1500Å thick. For the thinner films, 200Å and 600Å shown in Fig.(40)a and (40)b, the tin surface orientation is random. However at about 1000Å, a (110) orientation is also obtained - see Fig.(40)b&c.

There was no trace of SnO in any of the films



(a) (001) and Weak (100) Orientation.
Thickness - 200 Å.

(b) (001) and Weak (100) Orientation.
Thickness - 600 Å.

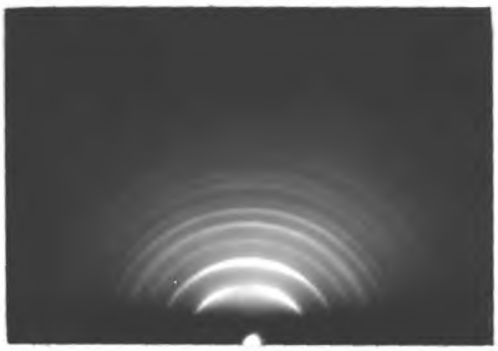
(c) (001) and Weak (100) Orientation.
Thickness - 1000 Å.

(d) (001) Orientation.
Thickness - 1500 Å.

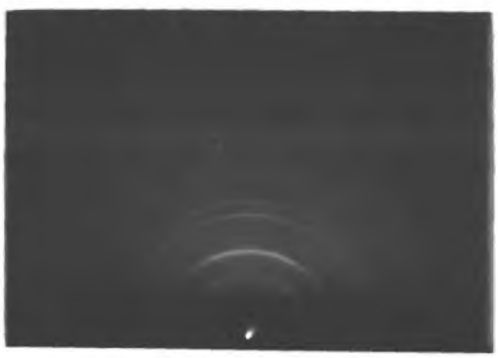
Fig. 39. Variation of Surface Orientation of Tin Films with Thickness, when deposited on to glass substrates at room temperature in a partial pressure of O_2 - 1 x 10^{-5} torr. at 5 Å/sec.



(a) Random Orientation.
Thickness - 200 and 600 Å.



(b) (110) Orientation.
Thickness - 1000 Å.



(c) (110) Orientation.
Thickness - 1500 Å.

Fig. 40. Variation of Surface Orientation of Tin Films with Thickness, when deposited on to polymer substrates at room temperature in a partial pressure of O_2 - 1 x 10^{-5} torr. at 5 Å/sec.

deposited at low rates of deposition.

The variation of orientation of tin films with increasing thickness, when deposited in a partial pressure of oxygen of 1×10^{-5} torr, is shown in Table 4.

It is interesting to compare the results shown in Fig. (39) for films deposited in a pressure of oxygen of 1×10^{-5} torr with those of Fig. (31) obtained for films deposited in a residual gas pressure of 1×10^{-6} torr. The predominance of the (001) orientation for thicknesses above 1000 Å, when oxygen is present during the deposition process - see Fig. (39)d and Fig. (31)b - suggests that this gas is primarily responsible for the orientation changes which occur.

Table 4. The Variation of Orientation of Tin Films with Thickness and Substrate when Deposited at Room Temperature in a Partial Pressure of Oxygen of 1×10^{-5} torr.

Thickness of Film (Å)	Rate of Deposition (Å/sec)	Tin Surface Orientation	
		Glass Substrates	Polymer Substrates
100-250	100	Random (301)	-
250	100	(301) (110)	-
600-1000	100	(110)	-
1200	100	(110) SnO	-
1800	100	(110) SnO	-
200	5	(001) (100) W	Random
600	5	(001) (100) W	Random
1000	5	(001) (100) W	(110)
1500	5	(001)	(110)

4. DISCUSSION

1. General Considerations of the Structure of Tin Films Condensed in Vacuum.

Attempts to interpret the various orientations obtained in thin metal films have been chiefly concerned with deposits prepared by vacuum evaporation rather than electro-deposited or sputtered films. This is because relatively simple environmental conditions are encountered and the control of the various deposition parameters is easier.

The crystal orientation obtained in evaporated tin films appeared to be a complicated function of such parameters as rate of evaporation, thickness of the deposit, substrate temperature, etc. Curzon (1961-62) also found that the orientation of tin films on single-crystal substrates, even when epitaxial orientations were developed, was highly susceptible to the deposition conditions mentioned above. In fact, it has already been stated - see section 3.1(i) - that Vook (1961) has obtained 'single-crystal' tin films only under very special conditions. Observations that the presence of substrate contaminants can also affect the growth process of thin films probably explains the limited success achieved so far in formulating a single theory to account for the various orientations obtained.

However, it has been possible in the present

experiments, by depositing tin films under highly reproducible conditions, to obtain systemmatic results on the structure of films deposited onto amorphous substrates at room temperature in relation to rate of deposition, film thickness, and residual gas pressure. The effects of a high partial pressure of pure oxygen during the deposition process has also been investigated.

Although it has been previously admitted that the residual gas pressure influences the growth process in thin films (Caswell 1961, Pashley 1964, Murr 1965) little evidence has been put forward to account for the various orientations obtained. In the absence of adsorbed gas atoms, the value of the activation energy for the migration of the metal atoms on the substrate surface is related to the heat of sublimation. However, the mobility is drastically reduced by the presence of active gases such as oxygen or carbon monoxide which can react with them, or be adsorbed with them. This may be so, but it is concluded below that the residual gas pressure has a decisive influence on the orientation of tin films by its effect, during the deposition process, on the surface energy of crystallites. It will also be shown below that the results obtained are in agreement with those already published by other workers, and the possibility of controlling the orientation in thin films will be discussed.

Saikia (1961) found that, for normal incidence

of the vapour stream, tin films were polycrystalline when deposited onto glass substrates at room temperature and were (110) oriented for all rates of deposition at a pressure of 1×10^{-4} torr. In thicker deposits, preferential growth of some crystals whose faces were nearly normal to the vapour stream occurred. A (321) orientation was attributed to a slight deviation from the usual (110) orientation of the initial stages of growth.

This effect was first observed by Evans and Wilman (1952) in Zn, Sb, and NaCl deposited onto glass substrates and it was pointed out that this was evidence of high mobility of the metal atoms on the growing crystallites. The atoms move over the crystal face on their arrival and reach low potential energy sites at the edge of the face and give rise to lateral growth. Saikia (1961) also found that tin films deposited onto glass substrates at elevated temperatures ($100^{\circ}C$, $164^{\circ}C$, $200^{\circ}C$) were oriented with (100) planes parallel to the substrate surface and it was suggested that a (100) orientation was characteristic of film growth at a raised temperature.

All the films deposited in this series of experiments were polycrystalline and were one-degree-oriented with a random azimuthal orientation about an axis normal to the substrate surface, except for films less than approximately 500Å thick deposited at rates of deposition above 75Å/sec. These films were randomly oriented in these

initial stages. Similar crystallite orientations to those already found by other workers were obtained (see section 3.1(i).), i.e. with either (110), (001), or (100) planes parallel to the substrate according to the residual gas pressure in the system and the thickness of the film. Two new orientations not previously reported for tin films were also observed, i.e. a mixed (001) and (100) orientation for non-continuous films and (301) orientation for films thicker than 1500Å deposited at a rate greater than 75Å/sec.

Metal films usually grow in preferred orientations such that a densely populated plane is parallel to the substrate. The orientation is induced by two factors: a larger binding energy between the condensing atoms than between condensed atoms and the substrate surface, and a sufficient surface mobility. On inert, amorphous substrates the most favourable orientation which the metal atoms can take in terms of energy is therefore that of closest packing in the first atomic layer. A particular lattice plane is thus grown parallel to the substrate surface as the base for crystallisation of subsequently condensing layers. After nucleation, the nuclei grow at first mainly laterally and maintain their crystallographic shape until coalescence with neighbouring nuclei commences. This has been shown in the case of tin by Blackman and Curzon (1959) and Matthews and Wronski (1962) from electron microscopy evidence. The initial tin nuclei are therefore lens shaped in the early stages of growth.

The orientations observed in the present experiments for tin films under conditions of high mobility of the tin atoms on the substrate are characteristic of lateral growth. The order of density of atomic population of the crystal net-planes is : (100) - 0.11 atms/$\mathring{A}^2$: (110) - 0.076 atms/$\mathring{A}^2$: (101) - 0.0518 atms/$\mathring{A}^2$: and (001) - 0.029 atms/$\mathring{A}^2$. Although the (101) plane is one of the more densely populated planes, no (101)-oriented films have been deposited during this work and none have been reported elsewhere. At present, no explanation can be offered for this fact.

The electron micrographs in Fig.(23) show that the film is aggregated into separate islands during the initial stages of growth and does not become completely continuous until about 1500$\mathring{A}$ thickness.

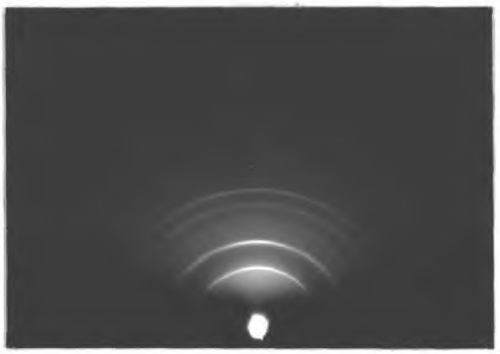
Caswell (1961) states that continuous films less than 2000$\mathring{A}$ thick are extremely difficult to obtain on room temperature substrates in ultra-high vacuum. It has not been possible to obtain a complete sequence of micrographs because of difficulties with replication techniques. However, it is reasonable to assume that the thickness at which the film becomes continuous varies with the residual gas pressure - the reduction caused in the surface mobility will give rise to a larger number of initial nuclei and the film will become continuous at an earlier stage of growth.

2. <u>The Variation in Orientation of Tin Films with Residual Gas Pressure and Thickness of the Film.</u>

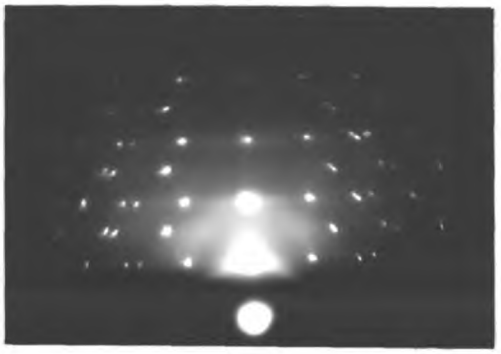
The variation in orientation of tin films 500Å thick with residual gas pressure is shown in Fig.(21), and Fig.(25) shows that where the influence of the gas molecules in the system was negligible, i.e. $< 5 \times 10^{-7}$ torr, the films were all (100) oriented.

A (100) orientation has been observed previously. Caswell (1961), depositing in a vacuum below 10^{-9} torr and at deposition rates of several hundred Å/sec. to obtain very pure films, reported a (100) orientation in films between 4000Å and 8000Å thick, and Vook (1961) also obtained (100) orientation for 1500Å thick polycrystalline tin films deposited onto NaCl substrates. It is concluded therefore from the present work that (100) orientation of tin films is consistently obtained under sufficiently pure conditions.

Acharya (1948) found by electron diffraction that large tin globules (½" - 1" dia.) solidified onto glass substrates as single crystals with (100) orientation. Saikia (1961) then found that tin films prepared at room temperature, and having initially a (110) orientation, when annealed above the melting point developed a very strong (100) orientation, see Fig.(41). These films had aggregated to form globules about 10μ dia. Vook and Baltz (1964) have also obtained (100) - oriented single-crystal tin films by quickly cooling a melted film of high purity tin between two glass



(a) Tin Film with (110) Orientation



(b) Tin Film with (100) Orientation after annealing to 235°C.

Fig.41. Change in Orientation of Tin Film after annealing above the Melting Point.

(After Saikia 1961)

microscope slides.

Annealing experiments have been carried out in the present work and it was found that specimens with initially (001) orientation or a mixed (100) and (001) orientation also developed a very strong (100) orientation when annealed in a vacuum of 1 x 10^{-4} torr to just above the melting point, i.e. 235°C. As annealing phenomena represent an irreversible change from a state of low structural order to a structure of high perfection and as the (100) plane in the tin lattice is the most densely packed, it is concluded that a (100) orientation in tin films is an indication that the crystallites have obtained a state of minimum surface energy i.e. in high purity conditions $\gamma_{100} < \gamma_{hkl}$ where γ is the free surface energy.

Synonymous with this conclusion, Vook (1961) has pointed out that defects which appear in the form of dislocations in (001) - oriented films never occur in (100) oriented films. This also indicates a state of high structural perfection in (100) - oriented films.

It can be concluded that when the diffraction pattern is predominantly spots instead of arcs this indicates a high mobility of the atoms over the substrate surface. The very strong (100) orientation in tin films is therefore evidence of the occurrence of melting and recrystallisation of the film at some stage during film growth. This view is enhanced by the conclusions of Plaskett and Winegard (1959-60) and Winegard (1961) who showed that the solid-

liquid interface in solidifying tin grows by the edgewise extension of the most densely populated plane, i.e. the (100) plane.

It is now necessary to take into account the reduction in melting point with particle size which has been reported by several workers. This phenomenon was first investigated by Turnbull (1950) for 50 μ dia. droplets of many metals including tin. Takagi (1954) then found that droplets of liquid tin about 50 Å in radius solidified at 40°C which is 192°C below the melting temperature. Blackman and Curzon (1959) subsequently showed that the solidification temperature for 50 Å radius droplets was 90°C. (The discrepancy between the two values was probably associated with a difference in the substrate material). Fig.(42) shows the variation of the solidification temperature with particle size for tin films reported by Blackman and Curzon (1959). Takagi (1954) also showed theoretically that the decrease in the melting point of the solid depends upon γ, the free energy/unit area of the interface dividing solid from liquid tin and also on R, the ratio of the surface area to the volume of the solid. Thus lens shaped nuclei would give lower solidification temperatures than spheres. For a given γ, the decrease in the melting point increases with increasing R.

It is conceivable that the lowest energy orientation of a very small island, consisting of only a few atoms in the initial stages of deposition, is different from the

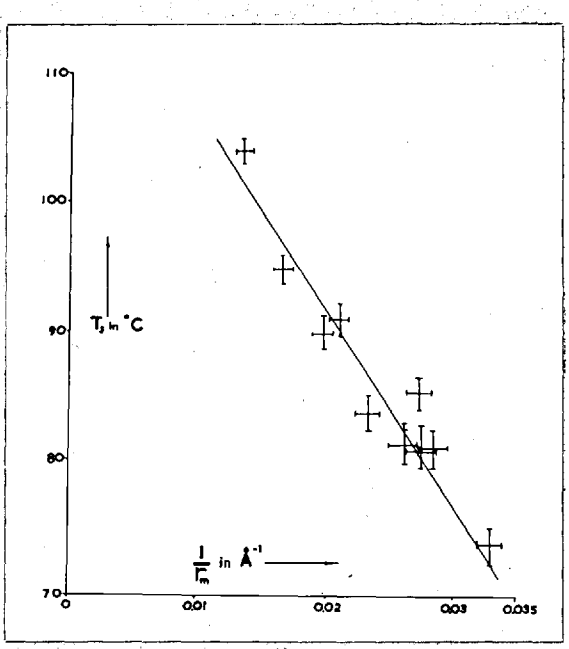


Fig.42. Graph showing the variation in the solidification temperature, T_s and the crystallite radius of tin, r_m.

(After Blackman and Curzon 1959)

lowest energy after it has grown to contain many atoms. Levinstein (1949) has already suggested that the atoms of a condensing vapour collide with the substrate inelastically with a transfer of the kinetic energy to the substrate lattice, and that the heat of sublimation may be a significant contribution to the thermal energy at the substrate surface. Thus if the substrate temperature becomes high enough, such an island will be able to re-orient itself to a more stable condition. This probably occurs during the initial stages of growth of tin films with (100) orientation. The rise in temperature required for recrystallisation is small because of the supercooling phenomenon and the heat of sublimation is sufficient to cause this process provided the interaction of the metal atoms with the residual gas molecules is negligible.

For films less than 500Å thick and prepared at pressures between 5×10^{-7} torr and 1×10^{-5} torr at rates of deposition below 75Å/sec., a mixed (100) and (001) orientation was obtained, see Fig.(21). The film at this stage of growth was non-continuous and it can be deduced that some of the aggregates were (100) oriented while others were (001) oriented. The effect of the gas impurities in the system was either to reduce the occurrence of melting and resolidification of the initial nuclei or adsorbed gas on the crystallite surfaces caused further recrystallisation from (100) to (001) orientation in some aggregates. Further clarification of this point will be given later.

In pressures greater than approximately 5×10^{-5} torr, a (110) orientation of the film was obtained. This agrees with the work of Saikia (1961) who obtained (110) oriented films for all rates of deposition and thicknesses up to 100Å/sec. and 7000Å respectively for a pressure of 1×10^{-4}torr. It can be seen from Fig.(38) that the strength of the orientation increases with increasing film thickness. Levinstein (1949) has suggested that aggregates may be deposited instead of individual atoms at high residual gas pressures because of collisions before reaching the substrate. These aggregates will possess less mobility and will lack any preferred orientation. However, it seems certain that in high residual gas pressures an initially random layer is formed and (110) orientation develops as one of the most densely packed planes.

At high rates of deposition (> 75Å/sec) in the pressure range 1×10^{-6} to 1×10^{-5}torr, the growth of the film is influenced by the formation of an initially randomly oriented layer about 500Å thick. The random orientation in this layer is probably the result of the outgassing of the source during the early stages of deposition. The gas emitted from the source will temporarily increase the pressure in the system which will reduce the mobility of the tin atoms on the substrate surface and give rise to a random orientation.

It is interesting to note here that the theory

proposed by Walton (1962), and discussed in section 1.3(i)c, predicts that at high rates of deposition and high mobility of the depositing atoms, only large clusters will be stable and this gives rise to randomly oriented deposits. However the rate of deposition consistent with this view will be in excess of 75Å/sec. in the case of tin because oriented deposits have been obtained by Caswell (1961) for rates of deposition up to 200Å/sec.

However, for high rates of deposition, it is essential to use a shutter between the source and the substrate and to allow deposition to commence after the outgassing of the source has been considerably reduced. Then, in the case of tin, the nucleation and growth phenomena shown to exist for rates of deposition below 75Å/sec. in this work should apply at higher rates of deposition.

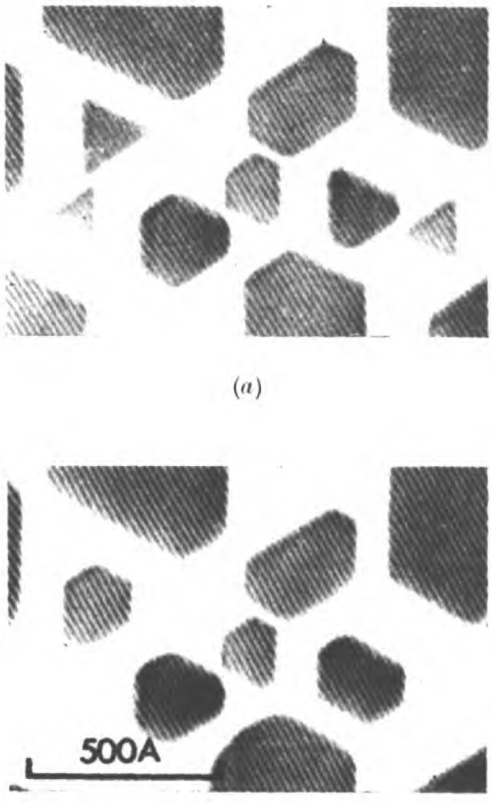
The results obtained for various thicknesses of film and shown in Figs.(28); (30) and Table 1, clarify the orientation changes occurring during deposition. For a residual gas pressure of 1×10^{-5} torr at a rate of deposition below 75Å/sec., a mixed (100) and (001) orientation is confined to, thicknesses below 1000Å and a (001) orientation predominates for thicker deposits up to 4000Å (see Fig.32). For a pressure of 1×10^{-6} torr, a mixed (100) and (001) orientation is obtained up to about 1500Å thickness but a (001) orientation is obtained for thicker deposits - a weak (100) orientation was observed in some films for thicknesses between 1500Å and 2000Å. It therefore appears

that some type of recrystallisation occurs during the coalescence stage of film growth.

Mixed orientations in germanium films have been found by Via and Thun (1961), see section 3(ii)a, but different orientations of initial nuclei have been observed by Bassett (1961) and Pashley et al (1964) for gold deposited onto MoS_2 at 400°C and onto thin carbon films at room temperature. Also Matthews (1962) has found two orientations in the initial stages of deposition of silver onto mica.

In the case of gold films, it appeared that two orientations of the nuclei are randomly formed on the substrate, they grow laterally and maintain their crystallographic shape until coalescence with neighbouring nuclei commences. Although the nuclei are only slightly misoriented, when they coalesce the compound island is entirely of one of the two orientations, see Fig.(43). It appears that recrystallisation occurs during coalescence. It is thought that the effect is not caused by the rotation of the nucleus as a unit but by the boundary forming the interface between the two touching nuclei sweeping across one of the nuclei while 'liquid-like' coalescence is in progress.

It has not been possible to deposit tin inside the electron diffraction camera to examine the film during deposition, because the residual gas pressure in the camera is not low enough for direct comparison with the results obtained by deposition in the conventional vacuum systems.



(*a*)

(*b*)

The coalescence of doubly positioned nuclei of gold on MoS_2 at 400°c. Magnification $\times 500\,000$.

Fig.43. (After Pashley et al 1964)

However, it is now suggested that a similar mechanism to the one discussed above occurs during coalescence of the tin aggregates, and the resulting continuous film possesses crystallites with similar orientation. The mobility of tin at room temperature is considerably higher than gold and the recrystallisation can involve larger misorientations than those reported by Bassett (1961). (The mechanism involved in this process is discussed in a later section). It is concluded that the orientation of the film does not vary with thickness, i.e. the initial layers are a mixed (100) and (001) orientation while the surface layers have only (001) orientation because of preferential growth of (001) faces because of some form of facet development.

The same recrystallisation can occur at high rates of deposition ($> 75\text{Å}$/sec.). The randomly oriented crystallites re-orient themselves on coalescence with (001) planes parallel to the substrate at a pressure of 2×10^{-6} torr, or with either (001) or (110) planes parallel to the substrate at a pressure of 1×10^{-5} torr. (See Figs. 28 & 30).

For thicknesses above 1500Å, a (301) orientation developed at these high rates of deposition and this orientation was maintained up to a thickness of 5000Å, see Figs. (32) and (33). Little is known about the final orientations in films from tetragonal metals but Bauer (1963) has stated that thick films of MgF_2 prepared at room temperature have (301) and (302) orientations for thicknesses between 2000A and 10000A. On the other hand, a (001) orientation was

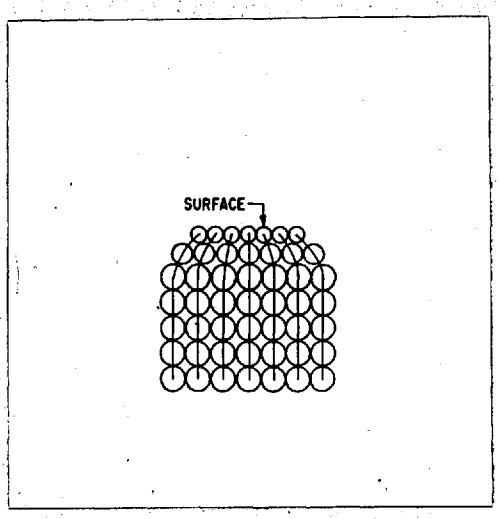
formed in films up to 500Å thick. The occurrence of a mixed (001) and (301) orientation in some films about 1500Å thick infers that (301) facets develop with increasing thickness at high rates of deposition. Figs.(32) and (33) show that this orientation is maintained at least up to 5000Å thickness.

The mechanism whereby the gaseous impurities in the vacuum system give rise to orientation changes during the deposition process will be discussed in the next section.

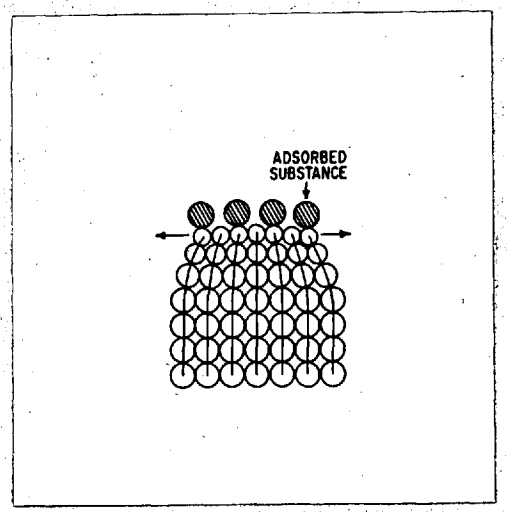
3. The Development of Preferred Orientations during the Growth of Metal Films.

At a metal surface, the surface atoms of the lattice have less than the usual number of neighbouring atoms. According to Uhlig (1952), the surface atoms will have twice the number of bonds and a higher bond strength per bond than the average for the lattice if it is assumed that an electron-shared bond distributes itself among all the available positions. With a higher bond strength, it follows that the characteristic atomic radius of the surface atoms will be less than the average for the lattice and the surface will be under tension. Herring (1953) maintains that the surface tension represents an excess energy per unit area as the result of the presence of the surface and it is therefore reasonable to assume that the different crystal faces, having different interatomic spacing, will have different values of surface energy.

However, any substance in the environment which forms bonds with the metal surface atoms will weaken the bonds of the surface atoms with each other and with their neighbours and consequently reduce the surface tension. This is shown schematically in Fig.(44). The surface energy of densely packed crystal surfaces will be less affected by foreign atoms than will less densely packed crystal surfaces. Thus the adsorption of foreign atoms at a gas-metal interface increases the difference in surface energy between different



(a) Metal surface



(b) Effect of adsorbed gases

Fig.44. Schematic view of a metal surface.
(After Uhlig 1952).

crystal planes exposed at the surface. The difference, although small, may be sufficient to cause grain boundary migration as the lower energy surfaces enlarge at the expense of the higher energy surfaces.

Chalmers (1948) thought that the change in surface energy of heated silver specimens depended upon the manner in which oxygen is adsorbed on different crystal planes. However, the possibility that differences in surface energy may lead to the migration of metal atoms from one crystal to a neighbouring one, and thus to the growth of grains with specific orientation was put forward by Mullins (1958) and later by Detert (1959). This hypothesis was suggested to explain spontaneous growth, after primary recrystallisation, of a few grains in copper sheet into large grains while the average size increased only slightly.

Further evidence of the effect of oxygen on the surface orientation has been given by Walter and Dunn (1959) and Walter (1965) for thin silicon-iron specimens (0.3 mm. thick, annealed to 1200°C). In a vacuum anneal, (110)-oriented grains grew into (i.e. the grain boundary advanced into) (100) oriented grains, while in the presence of oxygen atoms, the (100) oriented grains grew into the (110) grains. The driving force for the grain boundary migration was obtained from the difference in surface energies of the differently oriented grains; i.e. in vacuum $\gamma_{110} < \gamma_{100}$ and the (110)-oriented grains grew at the expense of the (100)-oriented grains;

while in oxygen $\gamma_{100} < \gamma_{110}$ and the (100)-oriented grains grew in preference. An estimation given of the difference in surface energy was as low as 70erg/cm^2. The fact that $\gamma_{100} < \gamma_{110}$ in the presence of oxygen indicates that the effect of oxygen atoms adsorbed on the least densely populated plane is greater than those adsorbed on densely packed planes.

Thus if the temperature of a metal is sufficiently high, the transfer of atoms may occur across a grain boundary by volume or surface diffusion. The transfer is always in such a direction as to decrease the over-all free energy of the system. As the difference in the values of the surface energies are small, there must be a minimum of restraint to grain boundary migration, i.e. the material must be relatively pure.

A direct analogy cannot be made but it is suggested that similar reorientation considerations occur in the case of thin films, especially tin. Tin films deposited in high-purity conditions have initial nuclei with (100) orientation through melting and solidification of the small particles. When these coalesce (during further deposition) the film remains in that orientation by the extension of the existing lattice.

In the pressure region where the residual gases start to interfere appreciably with the deposition process (5×10^{-7} to 1×10^{-5}torr), a reduction in mobility on the

substrate surface, possibly caused by gas adsorbed on the substrate surface, gives rise to (001)-oriented nuclei. Some melting and resolidification still occurs and gives a mixed (100) and (001) orientation. (Above 1 x 10^{-5}torr, only (001)-oriented crystallites are formed - see Fig.21).

When the mixed orientation occurs, gas atoms adsorbed on the less densely populated (001) plane will reduce the surface energy of these crystallites more than those on (100)-oriented planes (Sufficient gas is present in the system for this process to occur - at 1 x 10^{-5}torr, about five monolayers of gas hit the substrate surface/second while a film deposited at 50Å/sec. takes more than 10 secs. to become continuous). When coalescence occurs, the system will try to attain a state of minimum free energy and a (001) orientation will predominate.

An interesting unexplained example of a similar mechanism in thin tin films has been reported by Vook (1961). He has shown that rapid grain growth of oriented polycrystalline tin films can be made to occur by electron-beam bombardment in an electron microscope but not in a diffraction camera. (The latter has a much lower intensity of the beam). An initially (100)-oriented polycrystalline film developed into a (001) single crystal film: the transformation occurring rapidly by the addition of small amounts of energy. The electron-beam bombardment resulted in local heating of the film and the formation of a contaminated layer on the surface of the film - see Pashley and Presland (1961) - which

affected the surface energy of the system, i.e. the (001)-oriented grains grew because they had a lower surface energy than (100)-oriented grains in the presence of the contaminants.

At high rates of deposition, the effect of the adsorbed gas is seen best for results with increasing thickness at a pressure of 2×10^{-6} torr - Fig.(30). The initial layers of the film were randomly oriented but the 'built-in' annealing in the deposition process gives rise to grain growth and re-orientation. However, crystals having the most densely-packed plane, i.e. (100), parallel to the substrate are not preferred because the gases adsorbed on the (001) oriented grains reduce their surface energy sufficiently for them to be preferred.

For an orientation change to occur during coalescence the common boundary must move across one of the islands and this will be by a diffusion mechanism. This process, which is still imperfectly known even in bulk specimens, probably occurs by atoms at the sides of the boundary jumping, individually or in small groups, from a configuration which is part of one crystal to a configuration which is part of another.

The driving force on a grain boundary in a bulk specimen resulting from the difference in surface energy will be F where,

$$F \propto \left(\frac{1}{r_c} + \frac{1}{r_s} \right)$$

and r_c and r_s are the curvatures of the boundary on the

surface and in the cross-section respectively. The actual force is the product of the net boundary curvature and the difference in surface energy, i.e.

$$F = \left(\frac{1}{r_c} + \frac{1}{r_s} \right) \gamma$$

In thin films when nuclei in unlike orientation coalesce, the value of $\left(\frac{1}{r_c} + \frac{1}{r_s} \right)$ will be larger than for bulk specimens and a larger driving force for recrystallisation will exist. In bulk specimens the speed of this process v, depends upon the activation energy U where,

$$v = CF \exp \left(- \frac{U}{kT} \right)$$

C is a constant, Fb is the free energy gained per atom when the boundary moves an amount b, F is the force acting on the boundary. In thin films the time taken for recrystallisation can be very much quicker because of the relative increase in F and the decrease in U because of the high mobility and sublimation energy of the condensing atoms, and the fact that re-orientation changes occur during the deposition process itself is therefore not unreasonable.

Thus the process of controlled adsorption of a gas during deposition may offer new opportunities for controlling the structure of thin films during the deposition process by influencing the surface energies of initial nuclei. Although Chalmers (1948) found that the effect of argon on the surface energy was undetectable in bulk samples of silver, this may not be the case in thin films and it may

be possible to alter the structure with non-oxidising atmospheres. Pre-nucleation with a monolayer of gold will reduce the mobility in the initial stages of growth and will probably reduce the occurrence of the (100) orientation by preventing melting and recrystallisation of the initial nuclei in high purity conditions. Electron-beam bombardment of the film after deposition will also be a valuable technique. The temperature rise caused by the electron beam may be sufficient for growth of grains of specific orientation to be possible by using gaseous annealing atmospheres to create surface energy differences between grains of differing orientation. Further work to investigate the possibility of orientation control in tin films is to be carried out.

4. The Effect of a High Partial Pressure of Oxygen during the Deposition of Tin Films.

Caswell (1961a) has shown that the presence of oxygen during the deposition of indium films affects adversely the electrical and structural properties of the films. He found that in high purity films, the surface is considerably rougher and he states that the oxygen is evidently contained interstitially in the lattice since there is no indication of indium oxide in the films. Also, the pure films were polycrystalline but highly oriented with (101) planes parallel to the substrate surface but films deposited in oxygen at 1×10^{-4}torr were completely randomly oriented.

In the case of tin, Caswell (1961b) compared the superconducting characteristics of films prepared in residual gas pressures less than 1×10^{-9}torr with those prepared in high partial pressures of a large number of gases. He gives the critical values of partial pressures of certain gases for obtaining high purity tin films showing an absence of impurities produced by residual gases as observed in electron micrographs of the specimen surface. These are $P_{O_2} < 5 \times 10^{-8}$ torr; $P_{H_2O} < 4 \times 10^{-7}$torr; $P_{CO_2} < 8 \times 10^{-7}$torr; for a rate of deposition of 50Å/sec. The value quoted for oxygen agrees well with the results presented in the present experiments, showing the variation of structure with residual gas pressure, (Table 1) where films are highly ordered and (100)-oriented

provided the pressure during deposition is kept below 5×10^{-7}torr. Because of preferential pumping of different gases by the diffusion pump, water vapour, nitrogen, hydrogen and oxygen respectively are the main residual constituents of conventional vacuum systems - Caswell (1963) - and it is probable that the partial pressure of oxygen in the present system is in the region of 5×10^{-8}torr. The deterioration in the superconducting critical temperature reported by Caswell (1961), although attributed to presence of oxygen, may thus be the result of structural changes consistent with variations in the deposition parameters.

It has been shown above (Table 4) that the orientation of tin films, prepared at low rates of deposition (5Å/sec.) in a partial pressure of oxygen of 1×10^{-5}torr, is similar to that obtained in the conventional system with a residual gas pressure of 1×10^{-5}torr., i.e. a mixed (100) and (001) orientation is obtained for thicknesses less than 1000Å and a (001) orientation predominates above this thickness. There is no evidence of SnO in the diffraction patterns obtained from these films - see Fig.(39).

From these results it can be concluded that the orientation variations with residual gas pressure, presented in Fig.(21), are predominantly due to corresponding increases in the partial pressure of oxygen. This infers that surface energy variations discussed in the preceeding section are mainly caused by adsorbed oxygen in the case of tin films.

At high rates of deposition (100Å/sec.), the structure of films prepared in a high partial pressure of oxygen is consistent with the results obtained in a conventional vacuum of 1×10^{-5}torr. - a (110) orientation was obtained as the thickness increased. However, from the results shown in Fig.(37) and Table 3, it is concluded that tin oxide was formed during the growth process of these films. This is in contradiction to the work of Caswell (1961) who concluded that oxygen is contained interstitially in the lattice. This may be the case for films deposited at low rates of deposition, but Caswell used X-ray diffraction analysis and it is probable that this method was not sensitive enough to detect small amounts of oxide in the film.

At 1×10^{-5}torr, about five monolayers of gas atoms hit the surface of the film each second, and it is not known what percentage of these atoms is trapped. Alessandrini (1964), in electron diffraction observations on nickel films deposited at 1×10^{-5}torr, has pointed out that the oxygen is probably trapped in pockets with a semblance of NiO structure. Annealing of the films to 400°C causes the oxygen to penetrate into the nickel where it tends to form an ordered structure in the nickel lattice and he concludes that the resulting structure is dependent upon the substrate temperature and other deposition parameters.

However, Hart (1952) has shown that when tin foil is annealed in air, an amorphous oxide layer is formed at

temperatures up to 130°C. Above 130°C, only crystalline SnO and SnO_2 are formed. Further Steiner (1953) has shown that practically no oxide is formed when tin is exposed to dry oxygen at room temperature for intervals of time up to 1 hour, but when heated above 150°C, stannous oxide is formed. It is therefore reasonable to conclude that when SnO was observed in the above experiments for tin films deposited in oxygen, the film surface temperature during deposition was in excess of 150°C, and according to Fig.(37) this occurs at about 1000Å thickness, i.e. presumably when the film becomes continuous. This result is further confirmed by the results obtained for films deposited at a residual gas pressure of 1×10^{-5} torr. - see Fig.(38). The electron diffraction pattern from the 650Å thick film shows no trace of oxide whereas the continuous film at 1400Å thick has crystalline stannous oxide present. This result is in contradiction to the estimates of film temperature made by other workers and discussed in Section 1.4(ii). This work shows experimentally that the film surface temperature in the case of tin films when it becomes a continuous film is in excess of 150°C

5. The Effect of the Substrate.

On inert amorphous substrates, the binding energy between the metal atoms is high and the forces between the substrate and the film negligible, so that the substrate should have no effect on the ordering process of the film. However it is clear from the results presented in Table I(a) that the orientation of tin films deposited onto polymer-coated substrates is different from those deposited under identical conditions but onto glass substrates. It can also be seen that the variations in orientation occurring with the deposition parameters are similar to those prepared on glass substrates but for correspondingly lower values of residual gas pressure, i.e. a 500Å thick film deposited at 4×10^{-8} torr on glass substrates has a (100) orientation, but there is a mixed (100) and (001) orientation in tin deposited on the polymer substrate.

This presents an interesting case of the effect of the substrate surface. Work on the properties of these polymer films has been reported by Hill (1965) and they are formed by recombination of organic free radicals on the substrate surface by electron bombardment. In this case the films were formed from polymerized siloxane molecules and the resulting films are heavily cross-linked which would leave free bonds available at the substrate surface. A probable explanation for the structural variation of the tin films on polymer as opposed to glass substrates is that the

mobility of the tin atoms on the substrate surface is reduced by a higher binding energy of the substrate surface.

However, the similarity of the variations in orientation with the deposition conditions provides evidence that the main factors determining the structure of tin films are the mobility of the atoms on the substrate surface during the deposition process and the degree of vacuum in the system. The substrate will influence the initial orientation of the film but further growth depends upon the deposition conditions.

6. The Stress in Thin Films.

It has been pointed out in Section 4.4 that the available evidence indicates that the temperature of the surface of a continuous tin film is of the order of 150°C, and this fact has a significant bearing on the origin of stress in thin films.

Recently Freedman (1965) has investigated the effect of oxygen adsorbed during the evaporation process on the magnetic anisotropy as a stress-sensitive property of nickel films grown at room temperature onto glass substrates. A change of oxygen partial pressure from 1×10^{-10} to 1×10^{-7} torr caused an increase in stress from 5×10^{9} dyn/cm^2 to 2×10^{10} dyn/cm^2. Reflection electron diffraction did not reveal any nickel oxides but the extremely small grain size in room temperature nickel films caused sufficient broadening of the reflections so that it could not be stated with certainty that there was a complete absence of oxide. He maintains that the fact that water vapour had a similar effect, whereas nitrogen did not, inferred that the increase in stress was related to an oxidation effect. In this case the changes must occur by a metal-gas interaction rather than by adsorption on the substrate and reaction at the film-substrate interface. The results for tin films presented above would lead one to infer that adsorption of gas occurs on the film surface and oxidation of the tin followed through an increase in temperature during the film growth. It is

possible that the heat of crystallisation changes the temperature at which the crystals are growing but the above results imply a high surface temperature of the film as postulated by Murbach and Wilman (1952) at least when the film becomes continuous.

However the high density of grown-in dislocations in thin films (10^{10} - 10^{11}/cm^2 - Bassett 1961: 10^{10}/cm^2 - Vook 1964) must mean that the films are under stress from this source. But a discrepancy occurs here for some tin films have a high dislocation density but low residual stress.

It therefore appears that neither theory of residual stress in thin films - see Section 1.4 - is fully in agreement with experimental and calculated values of stress and film temperature respectively. Further work is required to clarify the problem, preferably using ultra-high vacuum techniques where the effects of gaseous impurities can be eliminated.

CONCLUSION

An investigation of the variation in structure of thin tin films, condensed onto amorphous substrates at room temperature, has shown that hitherto unexplained structural variations of tin films deposited in different systems can now be accounted for in terms of the respective deposition parameters.

The growth of (100) oriented films in pure conditions is preferred because the initial nuclei orient themselves with the most densely packed plane parallel to the substrate surface. This occurs through high mobility of the metal atoms on the substrate surface and the melting and recrystallisation of the initial nuclei.

An examination of the film orientation before and after a continuous film was formed, by the coalescence of the island structure developed in the initial stages of deposition, helped to clarify the effect of the residual gas on the growth process of tin films. It is considered that the adsorbed gases on the surface of the crystallites was responsible for recrystallisation phenomena occurring during the coalescence by its effect on the surface energy of nuclei in differing orientation. Experiments carried out in a high partial pressure of oxygen showed that oxygen is mainly responsible for the orientation changes, but further clarification could be achieved by depositing films in high partial pressures of other gases.

The identification of stannous oxide in some films gives an estimate of the surface temperature of the film during growth and this is in the region of 150°C.

Deposition of tin films onto polymer substrates verifies that the orientation is determined by the deposition parameters, but mainly the residual gas pressure. The polymer films influence the initial stages of growth by reducing the mobility of the tin atoms on the substrate surface.

The results presented here provide a sound basis for further study on the structure of tin films especially using pre-nucleation techniques, depositing onto substrates at various temperatures, or using adsorption of gases either during deposition or in annealing experiments afterwards to investigate methods of controlling the structure of the films.

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