

STRESS IN THIN FILMS

by

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ABSTRACT

2.

A survey of electrodeposited, chemically deposited, thermally grown, anodic, vapour phase, sputtered and evaporated thin films shows that internal stress is a common problem, particularly in industrial applications of such films. Severe stress may cause the films to buckle or crack.

Evaporated films in the initial stages of growth have been studied. The eleven models current for the stress in evaporated films have been reviewed in detail. A table summarising the assumptions and predictions of the models has been drawn up.

An apparatus of bakeable construction, based on the bending beam method, has been developed for the stress measurement. This apparatus is more sensitive than any apparatus described in the literature. The relationship between the stress in a film and the resulting beam deflection has been re-derived, and the conditions for its validity considered.

The total internal stress has been measured in polycrystalline silver and gold films, extending published work to better vacua and to lower film thickness regions. The thermal stress has been calculated and subtracted from the total stress to give the intrinsic stress. This has been correlated with the film structure.

The results from silver and gold films are similar. Intrinsic stress, tensile in nature, has been observed in

island structure films. The magnitude of the intrinsic force per unit width increased with film thickness in discontinuous films, and was constant after the last hole in the film structure had been filled.

From the results obtained it was concluded that an imperfection-type model, based on the actual structure of silver films as observed by scanning electron diffraction, was the most probable of the models considered.

The stress in oriented and polycrystalline lead telluride films has also been measured, but the origin of the intrinsic stress could not be determined unambiguously.

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C H A P T E R I

INTRODUCTION

1.1. INTRODUCTION

This year, 1967, is the ninetieth anniversary of the first quantitative measurement of stress in a thin film. During the intervening years many stress determinations have been made in thin films produced by various means, but as yet no single quantitative theory has been offered which explains all the results obtained.

The research on the magnitude of the stress in thin films was intensified with the industrial applications of electroplated films. More recently industrial applications of evaporated films have caused interest in the stress in such films. At the same time a certain amount of more fundamental research on the origins of the stress has been continuing. Four reviews of this work have recently appeared^(1,2,3,4). The present work is concerned with the origins of stress in evaporated films.

In this chapter the intrinsic stress in a film will be defined. Then a brief introduction to the common methods of measuring the stress in thin films will be given. Finally the effects of stress on some industrial applications of thin films, the measurements of the stress in such films and the theories that have been proposed for its origin will be considered.

Electrodeposited, chemically deposited, thermally grown oxide, anodically grown oxide, vapour phase, sputtered and evaporated

films will be considered. Evaporated films are treated in more detail than the other types of film because they are the subject of investigation in the present work. The choice of techniques and materials for the study of stress in evaporated films is discussed in the final section.

1.2. DEFINITION OF INTRINSIC STRESS

A system of forces applied to a body produces a change in its dimensions. This change in dimensions is called the strain in the body. The force per unit area required to produce the strain is called the stress. Stresses in real materials may be external or internal. When a metal bar is extended by a force the applied stress is external. When the same metal bar is cold worked it becomes stressed internally.

Nearly all thin films, by whatever means they are produced, are found to be in a state of internal stress. In some cases the stress may be very high, as high as the elastic limit of the material. In other cases, the type of stress may depend on the preparation conditions, so that films of zero stress may be prepared by slightly altering these conditions. Two technologically important types of film in which the stress may be adjusted are electroplated nickel, and vacuum evaporated silicon monoxide.

When the coefficients of thermal expansion of a film and its substrate are not the same then heating or cooling will

produce a stress, which will tend to deform the film substrate combination. For example, if a film is deposited at an elevated temperature on to a substrate of smaller expansion coefficient, a stress will be produced in the film on cooling to room temperature, and the direction of this stress is said to be tensile (contractile). If the film substrate combination is thin enough it will be bent into the surface of a sphere. A tensile stress will bend it so that the film surface is concave, and a compressive (expansive) stress will bend it so that the film surface is convex.

The stress arising from the different thermal coefficients of expansion of film and substrate is called the thermal stress. Even after accounting for this stress many films are, however, found to have a high residual internal stress, and this residual stress has been named the intrinsic stress in the film.

Thus the total stress in a deposited film, S_{Total} is equal to the sum of the externally applied stress, S_{external} and the internal stress, S_{internal} and this latter is composed of the thermal stress, S_{thermal} and the intrinsic stress, $S_{\text{intrinsic}}$. Thus one can write:-

$$S_{\text{Total}} = S_{\text{external}} + S_{\text{internal}} = S_{\text{external}} + S_{\text{thermal}} + S_{\text{intrinsic}}$$

In technological applications the total stress must be

kept small. However the intrinsic stress is the predominant component in many systems, so the intrinsic stress in deposits of many materials has been the subject of much scientific enquiry over the past ninety years. The subject of investigation in the present work is the intrinsic stress in vacuum evaporated metal films.

1.3. STRESS MEASURING TECHNIQUES

In section 1.2 it was mentioned that depositing a film on to a substrate caused a deformation of the substrate. The most common methods "mechanical methods" for measuring the stress in a thin film are based on this principle. The deformation of the substrate due to the stress is measured by using a thin cantilevered beam as a substrate, and calculating the radius of curvature of the beam from the deflection of the free end. This method, which is called the bending beam method, was devised by Stoney⁽⁵⁾ (see section 1.4.2) and the formula connecting the stress and the beam deflection is often called the Stoney formula.

The stress may also be measured by X-ray or electron diffraction methods. The position of the diffracted line gives the interplanar spacing of the set of lattice planes corresponding to the line, and the strain in the crystallites forming the film may be deduced from this. Alternatively the stress may be deduced from the shape of the diffracted

beam, by analysing the line broadening into components from particle size broadening and strain broadening.

These methods for measuring the stress in thin films are the ones generally used. However other methods, which have been applied particularly to the measurement of stress in evaporated thin films will be discussed in section 1.11.1.

1.4. ELECTRODEPOSITED FILMS

1.4.1. Industrial Applications

The first observations of the effects of stress in thin films were made in the early days of electrodeposition when it was observed that thick electrodeposits tended to crack or to peel from the cathode. (Gore, 1858, quoted by Stoney⁽⁵⁾). With the extensive development of the electroplating industry the effects of internal stresses in the coating assumed great importance.

Three examples of the effects of stress will be considered. Perhaps the most important is the effect of stress on the fatigue range (resistance to repeated vibrational stresses, which may be either compressive or tensile) of coated metal parts. When a metal part is built up by plating the fatigue range is much reduced^(6,7,8). Although the externally applied stress may be within the safe range, the total stress in the coating, being the sum of the external stress and the internal

stress from the deposition process, can exceed the safe limit. This leads to cracking in the coating and these cracks become propagated through the metal part, which then fails.

Another example is that the stress in nickel films can be such that there is appreciable contraction in the film when it is removed from the cathode. This can become very important in electroforming, particularly in colour printing where nickel electrotypes are used⁽⁹⁾.

Finally, with the advent of plated wire computer memory systems, the stress in the deposited alloy assumes importance because of its possible effects on the magnetic anisotropy of the films⁽¹⁰⁾. However, later work⁽¹¹⁾ has suggested that the stress anisotropy is not the sole cause of magnetic anisotropy, as changing the sign of the stress in plated nickel films from tensile to compressive by the use of organic additives did not, within the experimental error, change the magnetic anisotropy.

1.4.2 Measurements of the Stress

Mills⁽¹²⁾ made the first quantitative measurement of stress in a thin film in 1877. He coated the bulb of a mercury in glass thermometer with silver by a chemical technique, and used it as a cathode in an electroplating bath. He found that deposited nickel films caused the bulb

of the thermometer to contract, thus forcing the mercury higher up the tube than it would have been due to temperature alone. The stress he found in nickel was thus tensile. He also found tensile stress in iron, copper and silver but compressive stress in cadmium and zinc films. He calibrated the thermometer by noting the effect of a hydrostatic pressure, and thus found the magnitude of the stress. Using the same method, Bouty⁽¹³⁾ confirmed Mills' work. Thirty years later, in 1909, Stoney⁽⁵⁾ used as a cathode a long thin rectangular steel rule, which was clamped at one end. Using this apparatus, the first use of the bending beam method to be reported, he found that the stress in nickel film deposited at a plating bath temperature of 10-15°C was of the order of 3×10^9 dyne cm.⁻²

1.4.3. Parameters Found to Affect the Stress.

Much work has been carried out on the stress in electrodeposited films since the time of Stoney, and the work has been reviewed by Soderburg and Graham⁽⁷⁾ and more thoroughly by Murbach⁽¹⁴⁾. More recent reviews have been given by Evans⁽¹⁵⁾ and Popereka⁽¹⁶⁾. Although there have been many stress measurements, most of these are inadequate as the many variables which alter the stress have not been recorded. Some of these variables are listed below in order of discovery.

Stoney⁽⁵⁾ referred to the fact that increasing the

bath temperature reduced the stress in the film, and this fact has been reconfirmed more recently^(6,17-21). The stress varies with the pH of the plating solution⁽²²⁾, the current density, and small amounts of inorganic additives⁽²²⁾. Stager⁽²³⁾ discovered that superimposing an alternating current on the direct plating current reduced the stress. This effect was later confirmed^(24,25). Vuilleumier⁽²⁶⁾ discovered that the smaller the crystallite size in the deposit the larger the stress recorded. Kohlschutter et al⁽²⁷⁾ also noted this effect, but explained it as a fault of their apparatus. MacNaughton and Hothersall⁽¹⁷⁾ however discovered just the opposite effect, but they were plating from different solutions.

Marie and Thon⁽²⁸⁾ found that the stress in copper films could be compressive or tensile depending on whether the cathode was made of bright or dull platinum. Jaquet^(29,30) found that organic additives had strong and varied effects on the stress. Phillips and Clifton⁽¹⁹⁾ found that the stress also depended on the concentration of the plating solution.

Notwithstanding all these variables, Kohlschutter and Jacober⁽²⁷⁾ drew up a list of metals in descending order of stress, starting with chromium in tensile stress, through palladium, nickel, cobalt, iron, silver (which could be tensile or compressive, depending on the deposition conditions) to lead and zinc, which are always compressive.

1.4.4. Theories for the Origin of the Stress

A theory for the origin of the stress was proposed by Wyllie⁽³¹⁾. The stress was considered as due to co-deposited hydrogen diffusing out of the film immediately after its deposition, thus allowing it to contract and producing a tensile stress. This was in accord both with the large amounts of hydrogen released at the cathode during chromium deposition, and with the effects of a superimposed alternating current, which oxidised the hydrogen at the cathode and thus reduced the stress. It was also in accord with annealing experiments⁽³²⁾ in which gas was evolved from the deposit, and the tensile stress increased at the same time. However the formation of compressive stress and the fact that the ratio of metal deposited to hydrogen released at the cathode does not in any case accord with the stress measured were much harder to explain on this theory.

The most recent theory⁽¹⁶⁾ for the origin of stress in electrodeposited films, due to Popereka, considers the final stress to be the sum of a tensile component, arising from effects within the crystallites, and a compressive component arising from effects at grain boundaries. According to this theory, as the crystallites grow any dislocations which may be formed due to the growth process will have like signs, and will thus repel each other and be attracted to the

crystallite boundary. Thus a contraction in volume of the crystallite will take place, and a tensile stress will result. The compressive component arises from adsorption of impurity particles at grain boundaries. Popereka⁽¹⁶⁾ showed that sufficient energy was available from this model to give the stresses recorded in typical electrodeposits.

1.4.5. Stress and Preferred Orientation

The relationship between stress and preferred orientation has also been considered, both practically and theoretically. Bozorth⁽³³⁾ measured the preferred orientations in deposits using X-ray diffraction methods, and he decided that these were due to plastic deformation of the metals where the local stresses exceeded the plastic limit. Wyllie⁽³¹⁾ cited the work of Hume-Rothery and Wyllie^(34,35) in support of this theory. The whole problem was thoroughly investigated by Yang⁽³⁶⁾, who measured the stresses and orientations in electrodeposits of a wide range of metals. Yang showed that the Bozorth-Wyllie theory did not hold for electrodeposits. Later the Bozorth-Wyllie theory was shown to be inapplicable to vacuum evaporated films by Murbach⁽¹⁴⁾.

1.5. CHEMICALLY DEPOSITED FILMS

Stress in films produced by chemical reduction from

solution has not yet been examined in the detail devoted to stress in electrodeposited films. However the subject has recently become important in connection with the properties of magnetic films grown by this technique. Henry, Richards and Simpson⁽³⁷⁾ have found that Ni-Co-P alloys deposited on to glass substrates tended to crack or peel from the substrate if they were allowed to reach thicknesses in excess of 3,000Å. A value of 1.4×10^9 dyne cm⁻² measured by the bending beam method in a Co-P deposit⁽³⁸⁾ is of the same order as the stress found in electrodeposited nickel by Stoney⁽⁵⁾. The stress may be minimised by choosing suitable preparation conditions⁽³⁹⁾.

1.6. THERMAL OXIDE FILMS

1.6.1. Introduction

It has long been known that oxide films on metals are in a state of stress. Pilling and Bedworth⁽⁴⁰⁾ in 1923 divided metals into two groups, those in which the oxide film protected the metal from further oxidation, and those in which it assisted the oxidation process. They defined a ratio, the Pilling-Bedworth ratio, which is the ratio of the volume of the oxide to the volume of the metal from which it was formed. This ratio is greater than unity for metals such as silicon (2.04) and aluminium (1.28) in which the oxide is protecting, and it is less than unity for metals such as

calcium (0.78) in which the oxide is not protecting. Thus it appears that the oxide film on the former metals is in compressive stress, and on the latter is in tensile stress. It is now agreed that the ratio will not apply if the metal ions diffuse through the lattice, and new oxide is formed at the oxide-atmosphere interface.

Mechanisms for oxidation have been reviewed by Vermilea⁽⁴¹⁾, Evans⁽⁴²⁾ and Tomashov⁽⁴³⁾.

1.6.2. Measurements of the Stress

Jaccodine and Schlegel⁽⁴⁴⁾ have recently drawn attention to the possible detrimental effects of stress in thermally grown oxide films on silicon on the processing of silicon integrated circuits. These authors used a bending beam method to measure the stress in films of silicon dioxide produced by the thermal oxidation of chemically and mechanically polished silicon slices at temperatures from 900-1, 200°C, and they found a fair agreement between the stresses they measured and the stresses to be expected from the difference in expansion coefficient of silicon and silica on cooling from the deposition temperature. The stresses were of the order of 3×10^9 dyne cm.⁻² Thus, although the type of stress is that predicted by the Pilling-Bedworth ratio, the origin of the stress is thermal. Stresses in such silica films have also been observed by X-ray extinction topography⁽⁴⁵⁾.

In order to reduce the thermal stress in silicon oxide films the temperature at which the films are grown must be reduced. Techniques such as plasma oxidation⁽⁴⁶⁾, which reduces the substrate temperature from 1,100 to 300°C, and anodisation, which reduces the substrate temperature to room temperature, have been applied to the oxidation of silicon.

However, not all stress in oxide films is thermal in origin. Borie et al^(47,48) have used X-ray line broadening techniques to measure the stress in single crystal films of copper oxide grown at 250°C. Their conclusion is that the stress is due to the lattice mismatch at the copper-copper oxide interface.

1.7. ANODIC OXIDE FILMS

The stress in anodic films assumes importance in the field of electronic engineering with the application of such films, grown on materials such as tantalum and aluminium, as dielectrics.

Stress in anodic films of aluminium has been measured by Bradshaw and Clarke⁽⁴⁹⁾ and more recently by Bradhurst and Leach⁽⁵⁰⁾. Anodising from ammonium borate solution the latter authors found that the stress was not constant with film thickness, but passed through a maximum at 200Å film thickness. The stress was of the order of 5×10^8 dyne cm⁻² and was tensile in direction, thus not agreeing with the Pilling-Bedworth ratio. This raises once again the problem of whether it is the metal ions or the oxygen ions which move during anodisation. The problem has been mentioned by

Holland⁽⁵¹⁾ and Young⁽⁵²⁾, who point out that, in principle, the direction of the stress in the films could be used to determine this. If the metal ions moved the film would be in tensile stress, and vice versa. However any stress from this cause is masked by the occurrence of stress "due to misfit between the oxide and metal lattice"⁽⁵³⁾.

Holland⁽⁵¹⁾ offered no explanation for the effects commonly observed in anodic films, such as the rupture of the film at the electrolyte surface, which may be due to stress. Croft⁽⁵⁴⁾ has ascribed the discontinuities in the anodising current to the relief of mechanical stresses in the film by cracking. Young⁽⁵²⁾ suggests that the anomalous behaviour of the anodising voltage when a rough surface is anodised at constant current^(55,56) arises from the stresses set up in the film due to roughness. Asperities in the substrate are flattened out, and, where the asperity has been, the surface of the oxide occupies a smaller area, and the film becomes in a state of very high compressive stress.

1.8. VAPOUR PHASE FILMS

A common practice in the production of silicon integrated circuits is to grow an epitaxial film of high resistivity silicon on to a substrate of low resistivity silicon. Because of the different doping levels in the film and the substrate, and the difference in atomic radii of the silicon and the dopant, the average distance between silicon atoms may differ by as much as 40 ppm. If this difference is taken

up as strain the substrate may be deformed into the surface of a sphere, as in the usual bending beam experiment. If the epitaxial film is 10 microns thick and the silicon substrate is 200 microns thick, the radius of curvature from a 40 ppm strain will be 16 metres, and the stress will be about 1×10^8 dyne cm^{-2} . The stress may even be high enough to produce misfit (interfacial) dislocations (see section 2.8), which are often observed after diffusion of dopants into high resistivity silicon⁽⁵⁷⁻⁶²⁾ and which have a considerable influence on the characteristics of any semiconductor device formed subsequently⁽⁶³⁾.

The stress in vapour phase grown films of silicon on to sapphire substrates has been strong enough to crack the sapphire substrate⁽⁶⁴⁾. The stress in such films has been measured^(65,66) by the bending beam method. The stress found, 9×10^9 dyne cm^{-2} , could be entirely attributed to thermal stress on cooling from the deposition temperature, $1,150^\circ\text{C}$.

1.9. SPUTTERED FILMS

No detailed reports of stress measurements in sputtered films have been found in the literature to date. However, it would be expected that such stresses are of importance in the production of sputtered magnetic and dielectric films. Jackson et al⁽⁶⁷⁾ have found that films of zirconia wrinkled when the bond between the film and substrate was relieved

by etching, suggesting that these films are in compressive stress.

Stress has also been observed in the preparation of single crystal films by sputtering⁽⁶⁸⁾. In the case of GaAs films sputtered on to NaCl substrates at a substrate temperature of 300°C, the thermal stress on cooling to room temperature has been high enough to crack the films⁽⁶⁹⁾.

1.10. EVAPORATED FILMS

The internal stress in evaporated thin films raises problems in almost every industrial application. The earliest stress determinations were in optical coatings, where too thick a coating tended to crack, cloud or even peel from the substrate. By measuring the stress in films of various materials, and by using alternately layers with compressive and tensile stress, Turner⁽⁷⁰⁾ was able to increase the total thickness of coating which could be deposited, from 6 to 40 microns. Stresses in a range of optical coatings have recently been measured^(71,72). Ennos⁽⁷²⁾ has pointed out that, although in principle the stress in the film is large enough to distort the optical component being coated, in practice this might be important for only the highest precision optics.

Other measurements of stress in dielectric films have been made because of their application in thin film circuits as capacitor dielectrics. A small compressive stress is

preferred in a dielectric⁽⁷³⁾, and the direction of stress in a wide range of materials has been studied⁽⁷⁴⁾. The stress in evaporated organic dielectrics has also been measured⁽⁷⁵⁾.

Stress in evaporated metal films has been studied principally with regard to the applications of the films to computer memory systems, both magnetic and cryogenic. One of the possible origins of the uniaxial anisotropy parallel to the plane of the substrate in evaporated magnetic films⁽¹⁰⁾ is an anisotropy in the stress, although in the case of single crystal films an isotropic stress combined with anisotropic magnetostriction would give anisotropy of magnetic properties⁽⁷⁶⁾. The stress anisotropy in permalloy films is less than 10% of the isotropic stress (10^9 dyne cm^{-2}). Nevertheless a stress anisotropy of this magnitude (10^8 dyne cm^{-2}) could account for a large part of the magnetic anisotropy observed in nickel and iron films. Permalloy is chosen for a magnetic material partly because its composition is near that for zero magnetostriction (81:19 Ni:Fe).

Stress in cryogenic films is known to affect the critical temperature for superconduction in indium⁽⁷⁷⁾, tin⁽⁷⁸⁾, aluminium⁽⁷⁹⁾ and lead⁽⁸⁰⁾ films. However the intrinsic stress from the film deposition is relatively unimportant in this case as cooling to the low temperatures needed for cryogenic operation leads to thermal stress in excess of the elastic

limit, and plastic flow in the film takes place⁽⁸¹⁾. Some of these stress measurements have been reproduced by Hoffman^(2,3).

Because of the emphasis on the industrial applications of evaporated films, relatively few measurements have been made solely with a view to finding the origin of the stress, although a large body of results has accumulated on the industrially important materials, nickel, iron, permalloy and silicon monoxide. (In nickel and iron films see references 76 and 82-93; in permalloy references 94-98; and in silicon monoxide references 74 and 99-108).

1.11. PRESENT WORK

1.11.1. Introduction

At the present time there are current eight models for the origin of stress in evaporated metal films. These are discussed and considered in chapter two. Some of these models are similar to those already mentioned in connection with other types of film. However it will be shown that none of them is universally applicable to all types of film of all materials. Nor do all the models predict quantitative values for stress.

In order to single out the best model for the origin of stress in evaporated films, measurements must be made on the simplest possible system (see also section 2.1.2 "Requirements for a Model"). A polycrystalline film with its grain boundaries

and other defects is more complex in structure than an epitaxial film. However, although the need for measurements of intrinsic stress in epitaxial films has long been recognised⁽¹⁰⁹⁾ this had not yet been achieved because of experimental difficulties.

The primary object of this work, then, was to measure the stress in the simplest possible system, with a view to finding the origin of the stress. At the same time an attempt was made on the measurement of stress in an epitaxial film.

1.11.2. Choice of Apparatus

The first simplification was to choose to study the stress in island structure films, where interaction of the crystallites at grain boundaries is at a minimum. The only study of stress in island structure films has been made by Campbell^(110,111,112) who has studied the stress in island structure alkali halide films. The reason for the lack of study of the stress in island structure films is the great sensitivity of the apparatus needed, for the sensitivity of the apparatus required to measure a given stress is inversely proportional to film thickness. Blackburn and Campbell had devised an extremely sensitive apparatus based on the bending beam method (see section 3.4).

Unfortunately this apparatus is rather expensive, can only be used with one substrate at a time, and, due to the materials used in its construction is limited to vacua of the

of the order of 10^{-5} torr. Therefore, in the present work before stress measurements could be started, an apparatus had to be devised to measure stress to the required sensitivity.

The stress in a film may be deduced from its effects on the properties of the film. For instance an order of magnitude value of the stress may be deduced from the optical band gap⁽¹¹³⁾, or from the critical temperature for superconductivity for a cryogenic film, or from Hall effect measurements⁽⁹⁸⁾ or ferromagnetic resonance^(114,115,116) in a ferromagnetic film. However a direct measurement is preferable for a fundamental study. X-ray diffraction on gold⁽¹¹⁷⁻¹²¹⁾, copper⁽¹²²⁾, nickel^(76,89,123) and silver⁽¹²⁴⁾ films; electron diffraction and the bending beam method have been used for measuring stress in evaporated thin films. X-ray diffraction is limited in application to thicker films, or to well oriented films due to broadening effects⁽⁸⁹⁾ associated with the very small crystallite sizes in films. These broadening effects hinder the interpretation of the exact position of the line, and hence the exact lattice spacing of the film. Electron diffraction measurements are suitable for much smaller crystallite sizes. It was interesting to discover that one of the first determinations of stress in an evaporated metal film was made by analysing the line broadening of electron diffraction patterns⁽¹²⁵⁾. There are, however, difficulties in interpreting

the electron diffraction patterns in terms of stress; some of these problems are discussed in sections 2.3 and 2.7.3.3.

The most suitable method for the highest sensitivity measurements of stress is the bending beam method. This method and the development of the apparatus used in subsequent stress determinations is described in Chapter 3. During the development of the apparatus, difficulties were experienced with thermal problems, and the problems of stress relief. Sections are devoted to these problems, and to the interpretation of the raw data to give the stress in the film.

1.11.3. Choice of Materials

Campbell's measurements of stress in island structure films were on the dielectric, LiF. Metal films were therefore chosen for these measurements on island structures. In metal films stoichiometry problems do not arise. Also electron microscopic observation of the film structure is much easier in metal than in dielectric films. The first stress determinations were made on silver films deposited on to glass substrates. This system was chosen because previous stress measurements using the same substrates but in thicker silver films were available to check the results obtained. At the same time the structure and properties of thin polycrystalline silver films have been studied. An extension of the stress results to lower

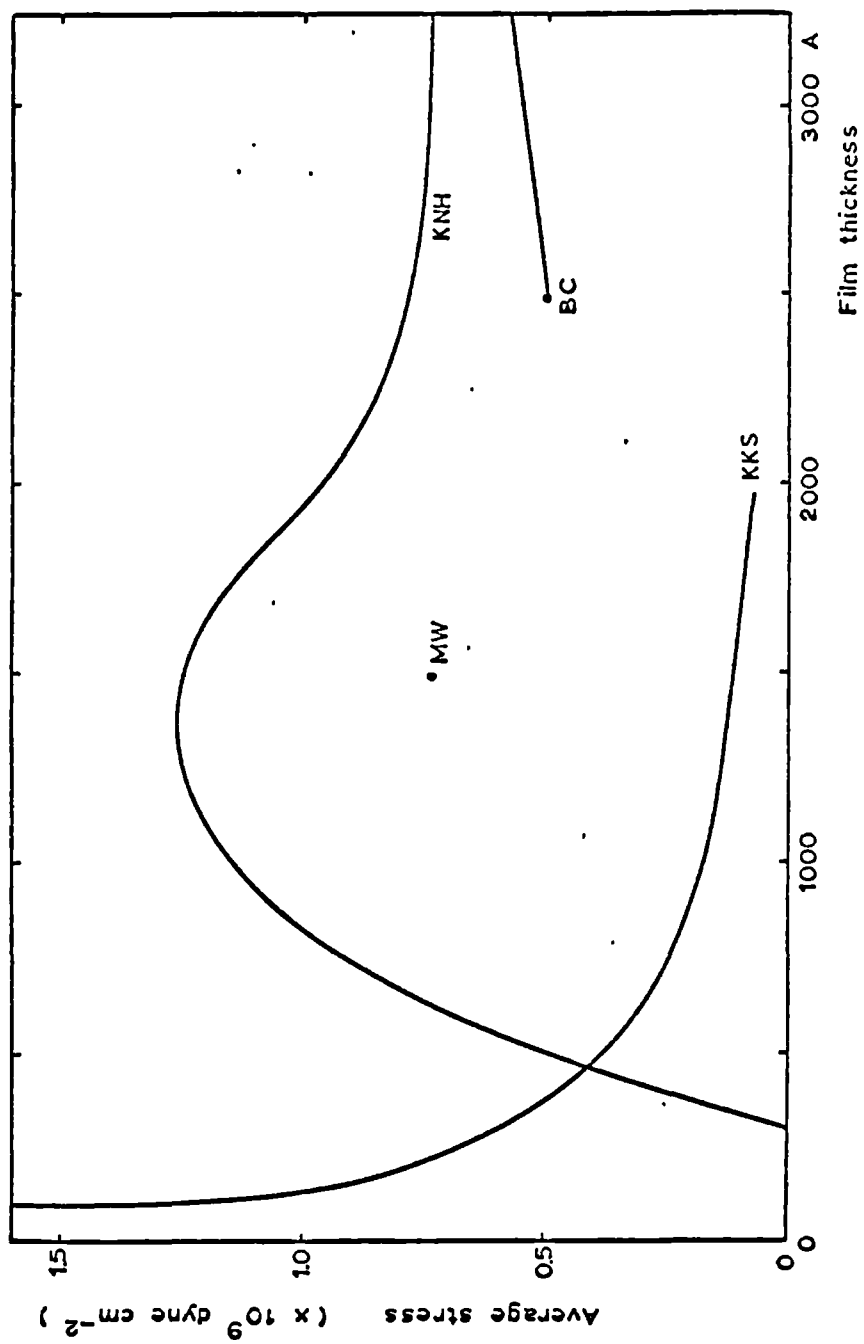


Figure 1.1.1 Stress in silver film

film thicknesses was also worthwhile, as examination of all previous stress results on silver films will show. These results are plotted in Figure 1.1. BC signifies the results of Blackburn and Campbell⁽⁷⁴⁾; MW those of Murbach and Wilman⁽⁸²⁾; KNH those of Kato, Nagashima and Hasunuma⁽¹²⁶⁾; KKS those of Kinoshita, Kondo and Sawamura⁽¹²⁷⁾ and Kinoshita, Kondo^(128a,128b). Kato's results indicate that the stress in films thinner than $200\text{\AA}$ is very small, while Kinoshita's results indicate that it is infinite. While Kato was evaporating on to copper substrates, Kinoshita was using mica. When the stress was measured in silver it was found to be neither zero nor infinite, but to follow more closely to the results of Kinoshita than to those of Kato.

1.11.4. Outline of Project

One interesting observation was that the stress passed through a maximum value at a film thickness of the order of $150\text{\AA}$. A part of the project, then, was set aside to see if this maximum occurred in systems other than silver on to glass. The stress in silver films on mica substrates, and that in gold films on glass substrates was investigated.

As an attempt on the measurement of stress in epitaxial films, mica was chosen as the substrate, and lead telluride as the evaporant. This is because oriented films of lead

telluride may be obtained on room temperature mica substrates.
The reasons for the choice of lead telluride are discussed in
section 6.4.1.

C H A P T E R I I

MODELS FOR THE ORIGIN OF INTRINSIC STRESS

2.1. INTRODUCTION

2.1.1. Models for Stress in Films Other Than Evaporated

We have already considered, in chapter one, some models which have been proposed for the origin of stress in films other than evaporated films. These models will be summarised in this section and their applicability to evaporated films examined.

Stress in electrodeposited films has been considered as due to co-deposited hydrogen diffusing out of the lattice, thus allowing it to contract and producing a tensile stress. This model is not applicable to evaporated films as the hydrogen is not present. However this model bears similarities to the "imperfection" model as considered by Story and Hoffman (section 2.3) where the stress is considered to arise from "co-deposited" vacancies diffusing out of the lattice.

Another theory for the stress in electrodeposited films is the thermal model, proposed by Wilman⁽¹²⁹⁾ to predict the stress in both evaporated and electrodeposited films. This model is considered in section 2.2.

Finally, the most recent model for stress in electrodeposited films⁽¹⁶⁾, explains the stress in terms of two components, a tensile component arising from the mutual

repulsion of dislocations formed during the growth of the film, and a compressive component arising from the adsorption of impurities at grain boundaries. Impurities are not as significant in evaporated as in electrodeposited films, but dislocations may indeed be present. The existence of dislocations in evaporated films is considered in section 2.3 on the "imperfection" model.

In oxide films an important contribution to the total stress comes from the thermal stress on cooling from the high formation temperatures. However the results cited in section 1.6.2 show that a contribution from the difference in lattice parameters of oxide and metal is present. This contribution may be treated by the methods of Van der Merwe, as described in section 2.8 on "interfacial phenomena".

Thus there are basic similarities between models which have been proposed for stress in evaporated films, and those which have been proposed for the stress in other types of film.

2.1.2. Requirements for a Model

Any model must predict the stress in terms of the film structure, which in turn is determined by such factors as the substrate material, the substrate temperature, the evaporant and the rate of deposition. The structure of polycrystalline

films is more complicated than that of epitaxial films, so most structural studies have been on the latter. However, most of the reported measurements of stress have been carried out on polycrystalline films because of the difficulties of measuring the stress in epitaxial films (see section 6.4), and because the stress in polycrystalline films affects their properties in industrial applications. In addition, it is often found that measurements of stress on identical materials by different workers give entirely different results, and the results that are obtained are often very complex. The complexity of the results indicates that more than one mechanism may be operative, while the differences between various workers' results shows the difficulties of framing a general model.

2.1.3. Contents of this Chapter

Eight models have been considered in this chapter. They are 1. the thermal model; 2. the imperfection model; 3. the density model; 4. the grain boundary model; 5. the grain gap model; 6. the electrostatic model; 7. the surface stress model; 8. the interfacial phenomena model. The last three of these models have been treated in slightly greater detail than the others. Values have been computed for the stress predicted by the electrostatic and surface stress models. An atomistic treatment of the problem of a crystalline interface

has been introduced in order to demonstrate the concepts involved in this model, as applied to stress in thin films, while avoiding the complex mathematics usually involved in a discussion of this model.

2.2. THERMAL MODEL

The stress predicted by the thermal model must not be confused with the thermal stress. Throughout the present work "thermal stress" means the thermal stress as defined in section 1.2.

2.2.1. The Thermal Model

The thermal model was proposed by Murbach and Wilman^(14,82) to explain the results of their stress measurements on a variety of evaporated metal films. This model was later criticised by Hoffman et al⁽⁸³⁾ whose experimental approach was to measure the stress in one metal, nickel, in greater detail, and who had proposed the imperfection model (to be discussed in the next section) for the origin of the stress. The publication of these papers led to a comparative discussion of these models in the literature^(129,130,131).

Murbach evaporated a range of eleven metals on to copper substrates, and compared the electron diffraction patterns from the deposits with the stress and the deposition temperature.

Metals with higher melting points, Ni, Fe, Pd, Cu, Au, Ag, Al, had smaller crystallite sizes and higher stresses, whilst lower melting point metals, Sb, Mg, Bi, and Zn had larger crystallite sizes and small or negligible stress. Thus it was concluded that the larger the mobility of the metal atoms on the growing surface the smaller the stress. This conclusion was substantiated when measurements were made at substrate temperatures higher than room temperature, when the magnitude of the stress in the films was found to be lower.

Wilman considered that, due to heat, both latent and radiant, arriving at the growing surface, the upper layers of the film are at a temperature which may be several hundred degrees above room temperature. Thus in the upper layers recrystallization processes (i.e. elimination of grain boundaries) may take place, but, as these layers reach the average substrate temperature they will pass through a temperature, T_c below which no recrystallization will be able to occur. At this temperature the crystal lattice will be in an expanded state, and thus on cooling to the average substrate temperature a tensile stress will be developed, given by⁽³²⁾

$$S = E.\alpha.(T_c - T_m) \quad (2.1)$$

where T_m is the average substrate temperature.* As the substrate temperature increased during the evaporation, T_m was taken to be the substrate temperature at the end of the evaporation. The critical temperature, T_c was assumed to be $T_m + \Delta T_c$, where ΔT_c is the critical temperature above T_m . α is the thermal coefficient of expansion of the evaporant and E its Young's modulus.

be related to the recrystallization temperature of bulk material grown from the melt. By measuring the stress in a nickel film grown on to a substrate at 125°C , and plotting stress against substrate temperature the critical temperature for nickel was found from Equation 2.1 to be of the order of 600°C in agreement with the theory.

Hence metals with a higher melting point will have higher recrystallization temperatures and higher stresses. Assuming that such a high temperature can exist on the surface of the substrate this model predicts the magnitude, direction, sign, variation with metal and variation with substrate temperature of the stresses found in most metal evaporated films.

2.2.2. Objections to the Thermal Model

Three grounds for objection to this model will be considered. Hoffman⁽⁸³⁾ was the first to consider the temperature rise which would be expected at the surface of the film, given values for the latent heat contribution, the radiant heat contribution and the thermal conductivity. He concluded that a 'temperature' pulse of roughly 700°C would disappear with a relaxation time of the order of 10^{-12} seconds. Blackburn and Campbell⁽¹¹¹⁾ have also considered the temperature rise in the film surface, and Gafner⁽¹³³⁾ has calculated the substrate and island temperatures and concluded that the temperature drops to less than 100°C above the substrate temperature after 10^{-6} seconds, and to only 9°C

after 1 second. Although these thermal calculations are order of magnitude only they err on the side of too low a temperature. Hence, the temperature rise at the film surface is much smaller than the value (600°C for Ni and 400°C for Fe) required to explain the observed stresses on the thermal model. On the other hand it must be remembered that the thermal model requires a surface temperature only 30°C higher than the average substrate temperature to explain the stresses observed in Al and Mg films.

A second very valid objection raised by Hoffman⁽⁸³⁾ is that annealing nickel films at a temperature below the recrystallization temperature causes a decrease in stress, whereas on the thermal model the stress should not start annealing out until the recrystallization temperature is reached. Stress is also reduced by annealing copper^(130,131) and iron⁽¹³⁴⁾ films. However it is interesting to note that on annealing an iron film the stress passes through a minimum value at about 400°C , the recrystallization temperature given by Wilman, although for nickel films the minimum is at 250°C , rather lower than Wilman's recrystallization temperature for nickel.

A third objection to the existence of the high surface temperature layer arises from the work of Buckel^(135,136). Films of materials such as Bi, Ga and Sb have been evaporated on to substrates held at liquid helium temperatures. At these

temperatures the films condense in a highly disordered amorphous state, which can be annealed out by a temperature rise of 10° or 15°C . As these amorphous films have been observed, it was concluded that any temperature rise in the film during the evaporation was less than 10°C , and so that a high temperature surface layer did not exist.

It must also be noted that this model predicts tensile stress only, decreasing to zero as the substrate temperature approaches the recrystallization temperature of the evaporant. However, compressive stresses have been observed in films of permalloy^(96,97) and copper⁽¹³⁷⁾ at substrate temperatures above approximately 100°C . The compressive component of the stress has been attributed to surface tension effects⁽⁹⁶⁾, but the reason for the subsequent return to tensile stresses at even higher substrate temperatures is not clear. Unpublished work⁽¹³⁸⁾ however suggests that the stress in permalloy films does not become compressive at all at higher substrate temperature, but decreases to zero. As there is a large measure of disagreement between these measurements of stress in permalloy films, no definite conclusion can be drawn from these observations as to the validity of the thermal model.

2.2.3. The Thermal Model Applied to Continuous Films

In conclusion the weight of evidence cited above shows

that the thermal model is not generally applicable to the growth of continuous metal films.

2.2.4. The Thermal Model Applied to Island Films

Blackburn and Campbell⁽¹¹¹⁾ have found the cross sectional area of the islands in an island structure lithium fluoride film by applying a growth model⁽¹³⁹⁾ to give the cross section in terms of the island area as observed by transmission electron microscopy. From this data they found the stress in a crystallite as a function of crystallite size. They found that the stress in a crystallite was not independent of the crystallite size, as would be predicted by this model. Thus the model is inapplicable to island structure lithium fluoride films.

2.3. IMPERFECTION MODEL

2.3.1. The Imperfection Model

As a result of annealing experiments on nickel films^(83,84,140), Hoffman⁽⁸³⁾ proposed that the observed stress in the films was due to "imperfections" formed during the growth of the film, and the reduction of the stress during annealing was due to the "imperfections" being annealed out. At the time of these experiments the particular "imperfection" could not be identified 'with certainty'. The stress is formed immediately after deposition of a layer as the "imperfections" migrate to the free

surface of the film, with a consequent reduction in volume and the production of a tensile stress.

2.3.2. Evidence for Imperfections in Evaporated Films

Direct evidence for the existence of imperfections in epitaxial films may be obtained from transmission electron microscopy⁽¹⁴¹⁾. Electron diffraction studies have also given direct evidence on the defect content of polycrystalline metal films. High precision electron diffraction patterns from evaporated metal films show that the diffraction rings do not have the exact diameters expected; some are shifted towards the centre of the pattern, and some away. Thus the crystallites in the film are in anisotropic strain. An isotropic strain would cause a proportional shift to all the diffraction rings, which could only be detected by an absolute measurement, or by comparison with a reference diffraction pattern. The reason for these anomalous ring ratios varies from material to material. Where it has been attributed to defects in the film, it has usually been attributed to dislocations⁽¹⁴²⁾ or stacking faults^(125,143,144). In particular it has been attributed to the presence of stacking faults in evaporated silver films⁽¹⁴⁵⁾ where the fault probability was found to be 0.19. (that is 19 stacking faults in every 100 atomic planes).

Other independent evidence for the existence of high

defect concentrations in evaporated metal films is the reduction in electrical resistance with time of thick films⁽¹⁴⁶⁻¹⁵⁰⁾. This has been attributed to both vacancy annealing⁽¹⁵⁰⁾ and to recrystallization phenomena⁽¹⁴⁸⁾.

Later work on the annealing of copper films⁽¹³¹⁾ (see also reference 130 by Story and Hoffman) showed that an earlier suggestion that vacancies were the particular imperfection causing the stress was probably correct. Copper films were deposited at substrate temperatures of -50 to -150°C , and on annealing the stress and the electrical resistivity of the films decreased together. The agreement between the electrical and the mechanical measurements was particularly good at annealing temperatures between -25°C and $+50^{\circ}\text{C}$. Story and Hoffman found that the annealing behaviour in this range corresponded to that found in cold work experiments, suggesting a vacancy mechanism. The resistivity and the stress variations were attributed to vacancies migrating to the free surface of the film. In this temperature range, they suggested that 3 micro-ohm cm of resistivity ($\approx 2\%$ of vacancies) and 2.10^9 dyne cm^{-2} of stress ($\approx 1\%$ of vacancies) had annealed out, suggesting that the stress was due to between one and two atomic per cent vacancies.

However, as later pointed out⁽⁸⁸⁾, the stress observed would increase, not decrease, during annealing if the vacancies migrated to a grain boundary rather than to the film surface.

2.3.3. Objections to the Imperfection Model

The idea of the stress being due to vacancies has been criticised⁽⁸⁸⁾ on the grounds that the vacancy concentration implied in these experiments is very much larger than the vacancy concentration expected in bulk copper in thermodynamic equilibrium at the temperature of 75°C, a temperature rather higher than the deposition temperature. In order to decide the question of vacancy concentration in evaporated films Fujiki⁽¹⁵¹⁾ measured the electrical resistivity and thickness of evaporated gold films, during annealing, and concluded that the vacancy concentration was 5%, a figure in order of magnitude agreement with Story's work.

Vacancy concentrations of the magnitude of 1 or 2% are very much higher than the thermodynamically possible values. However void content of this order is expected because of the small crystallite size found in evaporated films. For instance a film which consists of square islands, 100Å along the side, separated by tilt boundaries so that the average island separation is 1.5Å, has a void content of 3%. If this situation obtained, annealing such a film would cause recrystallization, due to sintering of the islands, and thus the electrical resistivity of the film would decrease, as found in practice. The stress would also decrease if it were inversely dependent on the crystallite size. Hoffman⁽²⁾ has

recently indicated that it is not unlikely that Story and Hoffman's results can be attributed to recrystallization phenomena.

Thus although earlier work suggested that the stress in evaporated films could be due to vacancies, more recently it has been shown that vacancies are not the sole cause of the observed stresses.

2.3.4. Imperfection Model in Island Structure Films

Recent scanning electron diffraction (section 2.7.3.5) studies of island structure silver films evaporated on to carbon substrates⁽¹⁵²⁾ showed that imperfections of the type which could cause stress on the imperfection model exist in such films.

Comparison of the diffraction pattern from the specimen with that calculated from diffraction theory showed that the film growth proceeded through three stages. The transition from one stage to the next was a gradual process. An initial amorphous structure transformed in to a crystalline structure at a film thickness corresponding to about two thirds of a monolayer coverage. This crystalline structure had an average lattice parameter slightly smaller than bulk silver, and transformed in to a crystalline structure with bulk lattice parameter. However, although the island diameter, as observed by transmission electron microscopy, was, e.g. $100\text{\AA}$, the

scanning electron diffraction pattern corresponded most closely to a theoretically calculated pattern from groups of only 250 atoms. Thus the structure of a $100\text{\AA}$ island of silver is polycrystalline.

The amorphous-crystalline transition might cause a stress on the density model (see section 2.4.4). The change in lattice parameter in the transition from the second to the third stage could cause stress by the surface stress mechanism (see section 2.7). Finally, a tensile stress contribution could arise on the imperfection model after the third stage had been reached. A contraction in volume of an island would occur as the grain boundaries between the 250 atom groups annealed out, and the size of the groups approached the size of the islands, as observed by electron microscopy.

A calculation of the stress predicted by this model is given in Chapter 7. The model has been named the imperfection (grain boundary in islands) model to distinguish it from the imperfection (vacancy) model.

2.4. DENSITY MODEL

2.4.1. Introduction

Oswald's rule⁽¹⁵³⁾ predicts that when a system changes from one phase to another of more stable configuration it will pass through all the intermediate phases. This implies that in the growth of a thin film the evaporant will pass through

a liquid phase and any high temperature solid phases in between the vapour phase and the equilibrium solid phase.

2.4.2. Applicability to Stress in Thin Films

Buckel^(135,154) has considered the applicability of this rule to evaporated thin films. Continuous films of materials with metallic bonding (i.e. the usual metals) give ring diffraction patterns even when condensed on to substrates at temperatures as low as liquid helium temperatures, whereas films of elements with pure covalent bonding (e.g. Ge) grown in an amorphous state when deposited on to room temperature substrates. Intermediate elements, such as bismuth, gallium and antimony, with a large amount of covalent bonding, can be grown in a crystalline state or an amorphous state, depending on the substrate temperature used. These amorphous phases may be considered as intermediate liquid phases as required by Oswald's rule, and can be transformed in to a normal crystalline phase by an increase of temperature.

Covalent elements crystallize from the melt with a decrease in density, whereas metallic elements crystallize with an increase in density, due to the nature of the interatomic bonding^(155,156). Hence, if, during film growth, the film structure at the surface of the film passes through a liquid phase, and if the intrinsic stress in the film is due to the change in density of the film during the transition from the liquid to the crystalline phase,

then the stress in metal films will be tensile, and that in covalent films compressive. The stress in metal films is normally tensile, as predicted by this reasoning. Buckel and Gunther^(157,158) measured the stress in gallium films which should be compressive on the basis of the above model.

Although they were unable to explain all their results they were able to draw conclusions concerning the applicability of Oswald's rule. Gallium films below 2,500Å in thickness, deposited at a substrate temperature of 80°K developed compressive stress (note, above this thickness the stress was tensile), suggesting that the growth was by a V→L→C mechanism, and that the stress was due to a density change during the L→C transition. Films deposited at a base substrate temperature of 4°K exhibited tensile stress, which was annealed out on heating the film to 80°K. Earlier work⁽¹³⁵⁾ had shown that films of gallium deposited at this temperature had a metastable amorphous structure, so it was suggested that there was an increase in density on going from the liquid phase to the metastable phase, and a decrease in the transition from the metastable phase to the crystalline phase. A theoretical value of stress was calculated from the strain $\frac{\Delta L}{L}$ expected during the volume change

$$\frac{\Delta L}{L} = \frac{1}{3} \frac{\Delta V}{V} = \frac{1}{3} \frac{V_L - V_c}{V_L} = 9 \times 10^{-3} \text{ for gallium} \quad (2.2)$$

2.4.3. Objections to the Density Model

Horikoshi⁽¹⁵⁹⁾, however, has measured the stress in antimony films evaporated on to copper substrates at room and higher temperatures. The transition from an amorphous structure into a crystalline structure⁽¹⁶⁰⁾ takes place when the film reaches a certain critical thickness, usually about 1,000Å. Below this thickness the stress is very small, and during the transition it increases very rapidly in magnitude, being tensile in direction. The stress was attributed to the reduction in volume in going from the amorphous state to the crystalline state. Wilman⁽⁸²⁾ also measured the stress in 2,200Å thick⁽¹⁴⁾ antimony films evaporated on to copper substrates, and found that the stress was tensile in direction. He also observed the structure of the films by electron diffraction, and found that the crystallite size was large, i.e. it was not in the amorphous state.

Thus there is a disagreement between these results on antimony and the direction of the stress predicted by the density model. However, antimony differs from bismuth⁽¹³⁵⁾ in that a large amount of covalent bonding is present even when the film structure is amorphous. This is because antimony evaporates as a molecule, Sb_4 whereas bismuth and gallium evaporate monatomically⁽¹⁶¹⁾.

When the density model, as stated by Buckel and Günther,

is applied to films grown on to substrates at room temperature and above, it is similar to the imperfection model. The mechanism for the origin of the stress in the transition amorphous phase $\rightarrow$ crystalline phase is another description of the imperfection model, as originally proposed by Hoffman, since a crystalline structure with a high enough imperfection content may be considered as essentially amorphous. Thus the arguments⁽⁸⁸⁾ leading to the rejection of the concept of such a disturbed layer at the growing surface, and thereby the imperfection model, may be applied also to the rejection of this model.

2.4.4. Density Model Applied to Island Structure Films

As mentioned in section 2.3.4 an amorphous layer may be formed in the initial stages of growth of an fcc metal on to a carbon substrate. This amorphous layer crystallizes in to small nuclei, (which then grow in the normal manner) at a thickness corresponding to two thirds of a monolayer coverage. Once the layer had recrystallized no stress could arise from this recrystallization mechanism. However it might be argued that a stress could arise on the density model from such an amorphous-crystalline transition. A tensile stress would result, but no stress would be added to a film thicker than, say, 5 or 6Å.

2.5. GRAIN BOUNDARY MODELS

2.5.1.1. Introduction

Two models in which the stress in evaporated thin films is considered to arise from interactions between the crystallites forming the film have been proposed. (See also section 1.4.4.). Turner⁽⁷⁰⁾ based his proposals on the results of his stress measurements in dielectric films, whereas a later model, due to Finegan and Hoffman⁽⁸⁸⁾ was based on stress measurements in iron films. After examining these models in turn, the predictions of a general grain boundary model, in which no assumptions are made concerning the nature of the interactions at the boundary, will be considered.

2.5.1.2. Dielectric Films

One of the first models for the origin of stress in evaporated films, and the first model to explain the stress in terms of the interaction between crystallites at their boundaries, was proposed by Turner⁽⁷⁰⁾ to explain his comparative measurements of stress on a range of eleven dielectric materials. In materials such as zinc sulphide, the anion is very much larger than the cation, so that a crystallite surface will present a net negatively charged layer. Hence an electrostatic repulsion will exist between adjacent crystallites, and a compressive stress will be observed in a bending beam experiment. On the other hand, materials of low polarisability will present a surface

with no net charge, so that the stress from this cause will be zero. When the electrostatic contribution is smaller than the interatomic forces of attraction between atoms in adjacent grains, the net stress may be tensile.

2.5.1.3. Metal Films

Finegan and Hoffman^(86,88,3) found that the stress in iron films was tensile, and that the stress-film thickness product* increased linearly with film thickness and made a small positive intercept with the film thickness axis. They proposed a model based on the relaxation of the atoms at the edges of the grain boundary into the voids at the boundary to explain the linear part of the curve, and the grain gap model (next section) to explain the intercept.

In order to calculate the stress in the film from the grain boundary relaxation, Finegan and Hoffman considered the ideal case of a one dimensional low angle, symmetrical, pure tilt boundary, which was represented by a gap between the adjacent crystallites varying in thickness between 0 and a where a is the diameter of an atom. Due to the forces of attraction between opposite atoms in the two crystallites a net relaxation into the gap takes place, and a tensile stress is observed in the film. The strain in a crystallite is taken

*The stress film thickness product (or force per unit width) is defined in section 3.4.

to be $\bar{D}/\bar{L}$ where $\bar{D}$ is the average distance over which an atom relaxes into the boundary, and $\bar{L}$ is the average crystallite diameter. $\bar{D}$ was found by deriving a force-distance relationship between iron atoms, and $\bar{L}$ was found from published electron microscopy studies of iron films. After correcting $\bar{D}$ for surface tension effects, the model gave very good agreement with the experimental results.

2.5.2. General Grain Boundary Model

Predictions about the relationship between stress and film thickness may be made on the basis of a grain boundary model, assuming only that there is a given force per unit area of the grain boundary acting on a crystallite. This force will arise from interatomic attraction between atoms in the surface of adjacent crystallites.

In any grain boundary model the strain in a crystallite will be inversely proportional to the crystallite size. This is because the strain energy in a crystallite is proportional to $\frac{1}{2} \mu \cdot \epsilon^2 \cdot A \cdot h$ where μ is an elastic modulus, ϵ is the strain, and Ah is the volume of the crystallite. When the strain in the crystallite is evaluated by associating a certain energy E per unit area of grain boundary and minimising the total energy of the system, ϵ becomes inversely proportional to the crystallite thickness, h . This assumes that ϵ is so small that quadratic and higher terms in ϵ can be neglected in E .

The incremental stress will be constant with increasing film thickness if the crystallites in the film grow in columnar form. If recrystallization occurs, the incremental stress will decrease with increasing film thickness.

The magnitude of the stress will depend on the nature of the adjacent crystallographic faces at the boundary. Thus it will depend on the orientation of the exposed faces, and the nature of bonding in the material.

The forces between crystallites at boundaries have been calculated by Van der Merwe for particular cases. These calculations are considered in the next section with application to the stresses associated with the boundary between a film and a substrate, but they are equally applicable to the boundary between two crystallites. The general problem of a grain boundary has not yet been solved: however order of magnitude figures can be deduced from Van der Merwe's calculations.

2.5.3. Discussion

A grain boundary model sets out to predict the stress in metal and dielectric films, the relationship between stress and film thickness and the relationship between stress and substrate temperature. However in the absence of extremely detailed knowledge of the structure of the grain boundaries in polycrystalline films, and in the absence of a generalised theory of the stress from a grain boundary no precise calculations can be made on this theory.

2.5.4. Grain Gap Model

As a film becomes continuous small voids may be left at the substrate between the crystallites if the contact angle is greater than 90° . These voids have recently been demonstrated by Waterbeemd⁽¹⁶²⁾ who grew tin films on to formvar substrates. He observed just-continuous films in the electron microscope and found that the crystallites could be separated by stretching the formvar substrate. In between the crystallites, small isolated nuclei were observed, showing that voids existed at the grain boundaries near the substrate.

Finegan and Hoffman⁽⁸⁸⁾ made an estimate of the force per unit width due to such voids, and it agreed reasonably well with the intercept found experimentally.

Later work, however, has shown that the existence of the intercept in the stress results is in doubt. Nevertheless we may consider the shape the force per unit width versus film thickness curve would take for such a model. (Figure 2.1). In a film much thicker than the thickness for continuity, f_c , no stress will be added to the film, and the graph will have zero slope. Below f_c the slope of the graph will increase as the number of grain boundaries increases.

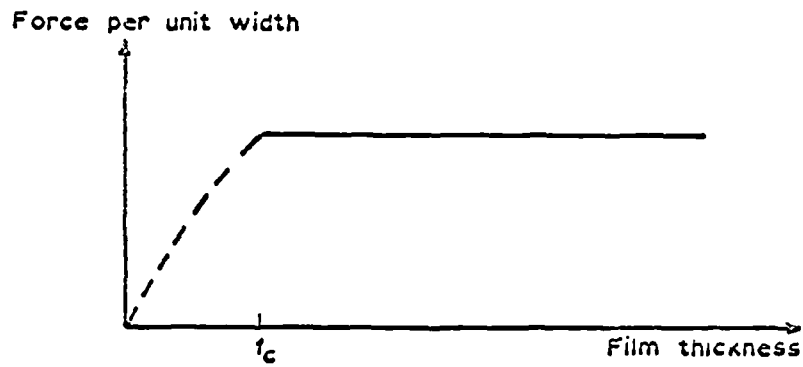


Figure 2.1. Force per unit width versus film thickness
 curve predicted by the grain gap model.

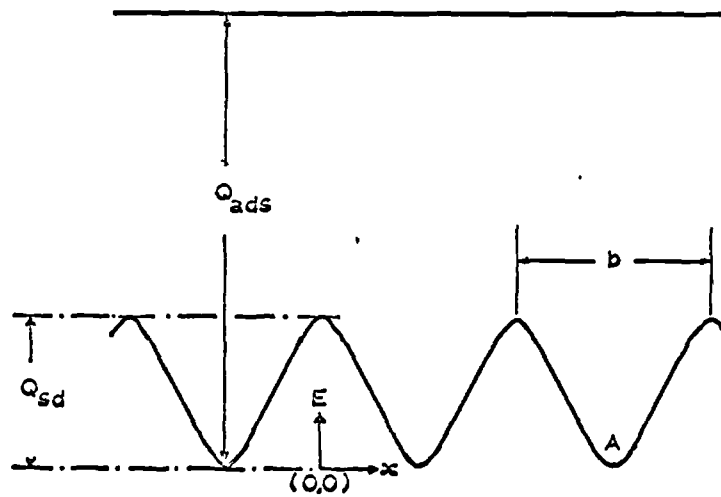


Figure 2.2 Potential energy of an atom on a substrate
 surface with lattice spacing b .

2.6. ELECTROSTATIC MODEL

2.6.1. Introduction

Dove⁽¹⁶³⁾ has considered the possibility that the liquid-like behaviour observed during film growth in the electron microscope is due to electrostatic forces of attraction between islands overcoming the forces of adhesion of an island to the substrate. A force of attraction can be produced even when the islands have the same sign charge, providing they are relatively close to each other. A force of attraction always occurs between a charged island and an uncharged island. Such forces are more likely in a film grown under observation in an electron microscope (where about 10^7 electrons per second may pass through a $20\text{\AA}$ diameter island) than in a normal film growth.

However, the observations of Hill⁽¹⁶⁴⁾ on the effect of an electric field perpendicular to the plane of the substrate, and the observations of Chopra⁽¹⁶⁵⁾ on the effects of an electric field in the plane of a film show that the growth of a film can be altered by an electric field. This shows that charge is present in a film. Electron bombardment of the substrate affects the epitaxial growth of gold films on to rock salt substrates⁽¹⁶⁶⁾. Even smaller concentrations of electrons, produced by the operation of an ionisation gauge during evaporation, have been shown to affect the growth of tin⁽¹⁶⁷⁾ and other⁽¹⁶⁸⁾ films.

2.6.2. Calculation

It was therefore decided to calculate the stress that would be observed in an island structure film if the islands were charged. Calculations, based on the derivation of the electrostatic forces between two spheres given by Jeans⁽¹⁶⁹⁾ (see appendix) gave the stress to be expected for various film thicknesses, island diameters and number of electrons on each island. Jeans⁽¹⁶⁹⁾ has reproduced a table of the coefficients required to give the inter-island forces, but this table only contains values for spheres of equal radius. This table was extended to cover more values of island separation and to cover spheres of different radius using the computer programme reproduced in the appendix. The computation was carried out on the Imperial College IBM 7090 computer.

Some of the values of force per unit width, in units of dyne cm^{-1} as a function of the radii of the islands, the island separation, and the number of electron charges on the islands are given in table 2.1. It is seen that the magnitude of the effect decreases rapidly with increasing film thickness, especially above a thickness of $10\text{\AA}$. However the force per unit width which would be produced by the charge distributions given is very much larger than that observed experimentally when the film thickness is below $4\text{\AA}$. Thus the presence of charge might be expected to affect the nucleation stages of film growth considerably.

Radius of island A in Å	Radius of island B in Å	Island separation in Å	Film thickness in Å	Charge on island A. Units of electronic charge	Charge on island B	Force per unit width dyne cm^{-1}	Type of Stress
10	10	30	4.6	-7	+1	101	tensile
10	10	30	4.6	-7	-1	23	compressive
10	10	30	4.6	-1	+1	7	tensile
10	10	30	4.6	-1	-1	10	compressive
40	40	120	18.	-7	+1	8	tensile
100*	20	200	25.	-7	0	1.2	tensile
100	20	200	25	-7	0	0.0045	tensile
100	20	200	25	0	-7	0.6	tensile

*The value for the force per unit width given here is based on the inter-island force given by Dove. It is much higher than the value given by the computer calculation for the same geometry, which is given in the next line for comparison. The discrepancy is, however, much smaller if the seven electrons are on the smaller island, and not the larger.

Table 2.1. Force per unit width which would be observed in a bending beam experiment if the origin of the stress was electrostatic force between islands.

2.7. SURFACE STRESS MODEL

2.7.1. Introduction

Intuitively one can imagine that the equilibrium spacing between an isolated pair of atoms is not, in general, going to equal the spacing between the same pair of atoms in the bulk material. This effect, if it existed, would be more important for ionic and co-valent materials than for metals, due to the shorter range of the interatomic forces in the metallic lattice. Thermodynamically the effect may be considered as due to the action of surface stresses associated with the crystal surface. Whether such an effect leads to a contraction or an expansion, or even whether it exists at all has been a problem of considerable interest for both the theoretician and the experimentalist^(170,171,172). If it does exist it might cause stress in a thin film through the mechanism discussed in section 2.7.4.

Let us first consider the thermodynamical definition of surface stress and its relation to surface energy, and then the experimental evidence for the existence of surface stress. Finally, on the basis of the experimental evidence, we can predict the order of magnitude of the stress expected in the island stages of the growth of silver films.

2.7.2. Surface Stress and Surface Tension

The surface tension of a solid, usually denoted by the

quantity γ is the measure of the work required to create unit area of new surface^(173,174,175). The name 'surface tension' was chosen by Herring⁽¹⁷⁴⁾ in place of the longer title 'surface free energy per unit area' as γ and the Helmholtz free energy of the surface are not, in general, equal. Some authors (Shuttleworth, Benson) refer to γ as the 'surface energy'.

A second parameter, the 'surface stress' is used in conjunction with solid surfaces. Gibbs⁽¹⁷⁶⁾ has pointed out the distinction between surface tension and surface stress. Whereas the surface tension is the work required to create a surface, the surface stress is a measure of the work to deform a surface. In a liquid the surface stress and the surface tension are numerically identical. In solids, however, a deformation of the surface will alter the distribution of the atoms on the surface, and hence the surface tension. Thus the surface tension and the surface stress are not necessarily identical in a solid.

The nature of the surface tension and the surface stress also differs. The surface tension is a scalar which is constant for a given crystallographic face, but which varies from face to face. The surface stress is vectorial in character, and varies with direction over a given face.

The relationship between the surface tension and the surface stress, σ , has been derived in a scalar form by

Shuttleworth⁽¹⁷⁷⁾

$$\sigma = \gamma + A \frac{\partial \gamma}{\partial A} \quad (2.3)$$

and in a more general tensor form by Herring^(174,175) (see also reference⁽¹⁷⁸⁾). A recent clear exposition of the derivation of this relationship has been given by Mullins⁽¹⁷³⁾.

For liquids $\frac{\partial \gamma}{\partial A} = 0$ and σ is equal to γ .

For solids the quantities γ and $A \frac{\partial \gamma}{\partial A}$ are of the same order of magnitude; but whereas γ is always a positive quantity, $A \frac{\partial \gamma}{\partial A}$ may be positive or negative. Thus the theoretical calculation of σ may involve the subtraction of two large terms, neither of which can be precisely evaluated. This has led considerable difficulties in deriving theoretical values of σ . Benson and Yun⁽¹⁷⁹⁾ have recently calculated the surface stresses in the (100) faces of the alkali halides, and they have compared their positive values with the negative values found by Shuttleworth⁽¹⁷⁷⁾ and the positive values calculated by Nicolson⁽¹⁸⁰⁾ and Lennard-Jones and Dent⁽¹⁸¹⁾.

2.7.3. Experimental Observations on Surface Stress

2.7.3.1. Introduction

No clear indication as to the sign and the magnitude of the surface stress is obtained from experimental observations.

The spontaneous bending of a (111) aluminium nitride platelet (182) indicates that there is a difference in surface stress between the (111) and the ($\bar{1}\bar{1}\bar{1}$) surface of 3.6×10^3 dyne cm^{-1} .

Absolute measurements usually depend on searching for a change in the interplanar spacing at the surface of a material, or a deviation from bulk lattice spacing in small crystals. Techniques used have been X-ray diffraction, high energy electron, low energy electron diffraction and scanning electron diffraction. The most significant results of these techniques will be discussed in the following paragraphs.

2.7.3.2. X-ray Diffraction

Nicolson⁽¹⁸⁰⁾ calculated the surface stress of the alkali halides, and also made measurements of the contraction of the lattice parameter in MgO and NaCl by X-ray diffraction techniques. The contraction he measured agreed with the calculated values, although the effect was very small in crystallites large enough to give sharp diffraction rings. Morita and Inoue⁽¹⁸³⁾ found that the lattice spacing of nickel decreased with decreasing crystallite size, but it is not certain whether this effect is due solely to surface stress, or whether other factors such as oxidation affected the result. Suhrman et al⁽¹⁸⁴⁾ have also found a contraction of the lattice of nickel films, and have found a similar contraction in copper films. Piuze and Ghez⁽¹⁸⁵⁾ have found a lattice contraction in silver crystallites.

2.7.3.3. High Energy Electron Diffraction

Small crystallites exhibit a larger percentage change of lattice parameter than large crystallites. Because the particle size broadening is less in electron diffraction than in X-ray diffraction smaller crystallites may be used, and the measurements of surface stress effects become more precise. The usual technique, which is to measure the lattice spacing of the crystallite from the position of the strongest diffraction ring^(186,187) (or the average of a number of rings, reference 188), has been criticised by Rymer⁽¹⁸⁹⁾ in his review of electron diffraction measurements of surface stress. In order to obtain a large percentage shift in ring diameter very small crystallites must be used. On the other hand, the smaller the crystallites the broader the diffraction ring, and the harder it becomes to define its position. Furthermore, as Berry⁽¹⁸⁶⁾ and later Rymer⁽¹⁸⁹⁾ have pointed out, the ordinary diffraction theory breaks down for very small crystallites, and the theory of scattering from the individual cells must be used^(190,191,192). Rymer⁽¹⁸⁹⁾ concluded that the only reliable electron diffraction surface stress value for an alkali halide was that of Halliday, Rymer and Wright⁽¹⁹³⁾ because the value was deduced from the deviations of the rings from their normal position rather than from an absolute measurement of ring diameter. After eliminating other interpretations of the deviations of the ring diameters, such

as those discussed in section 2.3, it was concluded that the surface stress of LiF was $-750 \text{ dyne cm}^{-1}$.

2.7.3.4. Low Energy Electron Diffraction

Although, with the small penetrating power of the electron beam, low energy electron diffraction might be considered the ideal way of measuring deviations of lattice spacing at the surface from bulk values, the evidence so far is very contradictory. For instance, while Germer and McRae⁽¹⁹⁴⁾ found a 5% distortion normal to the surface in nickel, Park and Farnsworth^(195,196) concluded that any distortion was less than 2%. McRae and Caldwell⁽¹⁹⁷⁾ found that the atoms in a (100) LiF surface relax to the positions predicted by Benson, Freeman and Dempsey⁽¹⁹⁸⁾, but that the average interplanar spacing normal to the surface increases from 4.02 to 4.10 Å, at the surface. This implies that LiF exhibits a negative surface stress, which is contrary to the positive value predicted by Benson and Yun⁽¹⁷⁹⁾. Agreement between experimental observations and the theory of Benson, Freeman and Dempsey⁽¹⁹⁸⁾ was also found in the case of (100) faces of NaCl by Markland and Andersson⁽¹⁹⁹⁾. However the surface stress was again found to be negative, as the interplanar spacing at the surface was expanded by 2.5% normal to the surface.

2.7.3.5. Scanning Electron Diffraction

Scanning electron diffraction⁽²⁰⁰⁾ has several important advantages over the techniques just mentioned. It enables the position of the diffracted rings to be accurately defined, by eliminating inelastically scattered electrons from the diffraction pattern. The diffraction pattern can also be measured more accurately. As mentioned in section 2.3.4 measurements on silver films grown in the diffraction camera showed that the radius of the (111) ring decreased as the crystallite size increased, implying a contraction of the lattice with decreasing crystallite size. This shift in ring diameter cannot be accounted for by the use of the correct diffraction theory which predicts a variation of ring diameter with crystallite size opposite in direction to that observed in silver films. Hence, if this shift is due to surface stress effects, silver has a positive surface stress.

2.7.3.6. Discussion of these Results

Because Halliday, Rymer and Wright⁽¹⁹³⁾ have eliminated causes of the observed ring shift other than surface stress, it is concluded that their measurement on LiF is the most reliable measurement of surface stress in an alkali halide.

The application of the correct theory of diffraction shows that the lattice contraction in silver films found by Berry⁽¹⁸⁶⁾, de Planta, Ghez and Pluz⁽¹⁸⁷⁾ and Grigson⁽²⁰¹⁾

is not due to incorrect theory, but is due to other effects. Hence it is very likely that the surface stress in silver is positive in sign.

2.7.4. SURFACE STRESS AS A CAUSE OF STRESS IN FILMS

2.7.4.1. Introduction

Weiss and Smith^(96,202) have shown that the strain energy in a typical film is less than the surface energy which would be released if two neighbouring spherical islands coalesced. However they do not suggest a specific mechanism for the production of stress from this available energy.

A specific model will therefore be considered in the following section, based on the hydrostatic pressure in a crystallite due to an isotropic surface stress.

2.7.4.2. A Surface Stress Model

As we have seen the weight of evidence suggests that silver has a positive surface stress. The planes of atoms near a free surface are closer together than the planes in a bulk crystal. This means that the interior of the crystal is subject to a compressive stress, and that the average lattice parameter of a small enough island is less than that of bulk material. If this island were tightly bound to a substrate, adding a layer of new atoms would cause the lattice

spacing to attempt to expand towards that of bulk silver. Due to the interaction of the island with the substrate this cannot happen, and instead a stress is transmitted to the substrate. The stress will be compressive when the surface stress is positive.

The relationship between the strain in a hemispherical island radius r , and the surface stress σ is: ^(179,187,185)

$$\frac{\Delta r}{r} = \frac{2 \sigma \chi}{3 r} \quad (2.4)$$

where χ is the compressibility of the island material. Hence the linear contraction (or expansion) in an island is

$$\Delta r = \frac{2 \sigma \chi}{3} \quad (2.5)$$

If there are N islands per square cm. of substrate, the mean distance between islands will be $N^{-\frac{1}{2}}$ cm. Hence the strain, ϵ , in the substrate surface is

$$\epsilon = \frac{2\Delta r}{N^{-\frac{1}{2}}} = \frac{4 \sigma \chi N^{\frac{1}{2}}}{3} \quad (2.6)$$

A stress S in a film with Young's modulus E would produce a strain ϵ in the substrate surface given by

$$\epsilon = S / E \quad (2.7)$$

Hence, from Equations (2.6) and (2.7) the stress film thickness product (force per unit width) in a bending beam experiment would be

$$S f = (4 \sigma \times E N^{\frac{1}{2}} f) / 3 \quad (2.8)$$

where f is the film thickness.

2.7.4.3. A Surface Tension Model

In the previous section we have assumed that the island was solid, and that the stress arose from the surface stress. If the island were liquid-like, the tendency for the surface area to decrease, to diminish the total free energy of the island substrate system, would be opposed by a force parallel to the substrate surface. This would always produce a tensile stress in a bending beam experiment. The derivation of the magnitude of the effect is the same as that given in the previous section, only "surface tension" must be used in place of "surface stress", where "surface tension" is the quantity defined in section 2.7.2.

2.7.4.4. Calculation of Values of Stress

The surface stress in silver is positive (section 2.7.3.6). The value found by de Planta, Ghez, Piuze⁽¹⁸⁷⁾ was 6,000 dyne cm⁻¹. The 2.7% contraction in lattice parameter

found by Berry⁽¹⁸⁵⁾ in a $30\text{\AA}$ diameter island corresponds to a surface stress of $6,600 \text{ dyne cm}^{-1}$. Thus on the surface stress model the force per unit width in silver films is $3.1 \times 10^3 N^{\frac{1}{2}} f \text{ dyne cm}^{-2}$ and is compressive in direction.

The surface tension of silver⁽²⁰³⁾ is $1140 \text{ dyne cm}^{-1}$. Thus if the islands are liquid, the force per unit width is $5.3 \times 10^2 N^{\frac{1}{2}} f \text{ dyne cm}^{-2}$ and is tensile in direction.

In order to find a typical value of the force per unit width we must know $N^{\frac{1}{2}} f$. It will be shown that $N^{\frac{1}{2}} f = 0.2$ for a silver film $20\text{\AA}$ thick. Thus the force per unit width in a $20\text{\AA}$ film of silver is 600 dyne cm^{-1} compressive, if the surface stress model applies, and 100 dyne cm^{-1} tensile if the surface tension model applies.

2.8. INTERFACIAL PHENOMENA

2.8.1. Introduction

Van der Merwe⁽²⁰⁴⁾ has considered the energies and stresses associated with various types of interface between infinitely thick crystal having similar elastic properties. The cases treated are (i) a boundary due to a difference in atomic spacing between the crystallites; (ii) a twist boundary and (iii) a symmetrical tilt boundary. In a later paper⁽²⁰⁵⁾ he extended the method to cover the case of an infinitely long one dimensional interface in which the crystals could take different elastic properties, and in which one crystal could

take any thickness from a monolayer to an infinite thickness. This latter treatment is of direct relevance to the subject of the overgrowth of an epitaxial film on a single crystal substrate, where it predicts various internal stresses due to the interface. It may also be applicable to the stress in films evaporated on to a substrate such as glass, which, although not single crystal, has a periodicity of surface structure⁽¹¹²⁾.

The mathematics involved in these calculations is rather complex, but the essential conclusions may be reached by considering a simple model in which the size of the overgrowth crystallite is built up atom by atom. The assumptions made in the simple model about the elastic properties of the overgrowth film are only justified in the light of Van der Merwe's calculations^(204,206) which show that the misfit between an overgrowth crystallite and the base crystallite is taken up by localised regions called interfacial dislocations, and in between these regions there is relatively good fit between the atomic planes in the crystallites. The existence of these interfacial dislocations is not self evident.

2.8.2. Atomistic Model

Let the one dimensional substrate lattice be infinitely hard. Let the potential energy of a single adatom on the substrate surface have a sinusoidal form, periodic in the

lattice spacing of the substrate surface. A sinusoidal form is chosen as being the first term of a more general fourier representation of the potential. This potential is represented in Figure 2.2.

The amplitude of the potential is of the order of $Q_{\text{surf diff.}}/2$ where $Q_{\text{surf diff.}}$ is the activation energy for surface diffusion of an adatom. For a close packed structure, using the nearest neighbour approximation, $Q_{\text{sd}} \approx 1/3 Q_{\text{ads}}$ where Q_{ads} is the adsorption energy of a single atom on the surface^(207,208). The adsorption energy of a material on to itself is the latent heat of condensation per bond.

A single adatom adsorbed on to the surface of such a substrate lattice will choose a position of minimum potential energy, at A in the diagram. It must be noted that the lowest energy state for atoms on the surface corresponds to the strongest binding to the substrate.

Taking the zero of energy as marked on the diagram, the energy of a single atom at distance x from the origin is given⁽²⁰⁶⁾ by

$$E = \frac{Q_{\text{sd}}}{2} (1 + \cos(kx)) \quad (2.9)$$

here k is related to the distance between the potential maxima on the substrate, b , by $k = 2\pi/b$. b is the lattice parameter of the substrate lattice. For simplicity in later computation we may write E in the units of $Q_{sd}/2$ and we can write

$$E = 1 + \int (e^{ikx}) \quad (2.10)$$

If we now add another atom to the surface, and let its separation from the first atom be a the total energy of the two atoms is

$$E = \int \left[(1 + e^{ikx}) + (1 + e^{ik(x+a)}) \right] \quad (2.11)$$

Similarly, the total potential energy of a rigid chain of n atoms is given by

$$E = \int \left[n + e^{ikx}(1 + e^{ika} + \dots + e^{ik(n-1)a}) \right] \quad (2.12)$$

If this chain is allowed to move to its equilibrium position, it will choose a value of x to minimise E . Equating $\frac{dE}{dx}$ to zero we find that the equilibrium potential

energy of a chain of n atoms, $E_s(n)$, is given by

$$(E_s(n) - n)^2 = \frac{1 - \cos(2 \pi n \delta)}{1 - \cos(2 \pi \delta)} \quad (2.13)$$

and the equilibrium position of the first atom of the chain is given by

$$\frac{x_n}{a} = \frac{m_n}{1 + \delta} - \frac{n - 1}{2} \quad (2.14)$$

where δ is the mismatch between the atomic lattices given by

$$a = b(1 + \delta) = 2\pi(1 + \delta) / k \quad (2.15)$$

and m_n is an integer. Hence

$$E_s(n) = n - \left(\frac{1 - \cos(2 \pi n \delta)}{\cos(2 \pi \delta)} \right)^{\frac{1}{2}} \quad (2.16)$$

taking the negative sign to minimise the energy. This function has been computed on the Imperial College IBM 7090 computer. It is reproduced in Figure 2.3. The programme is given in Appendix 2.2.

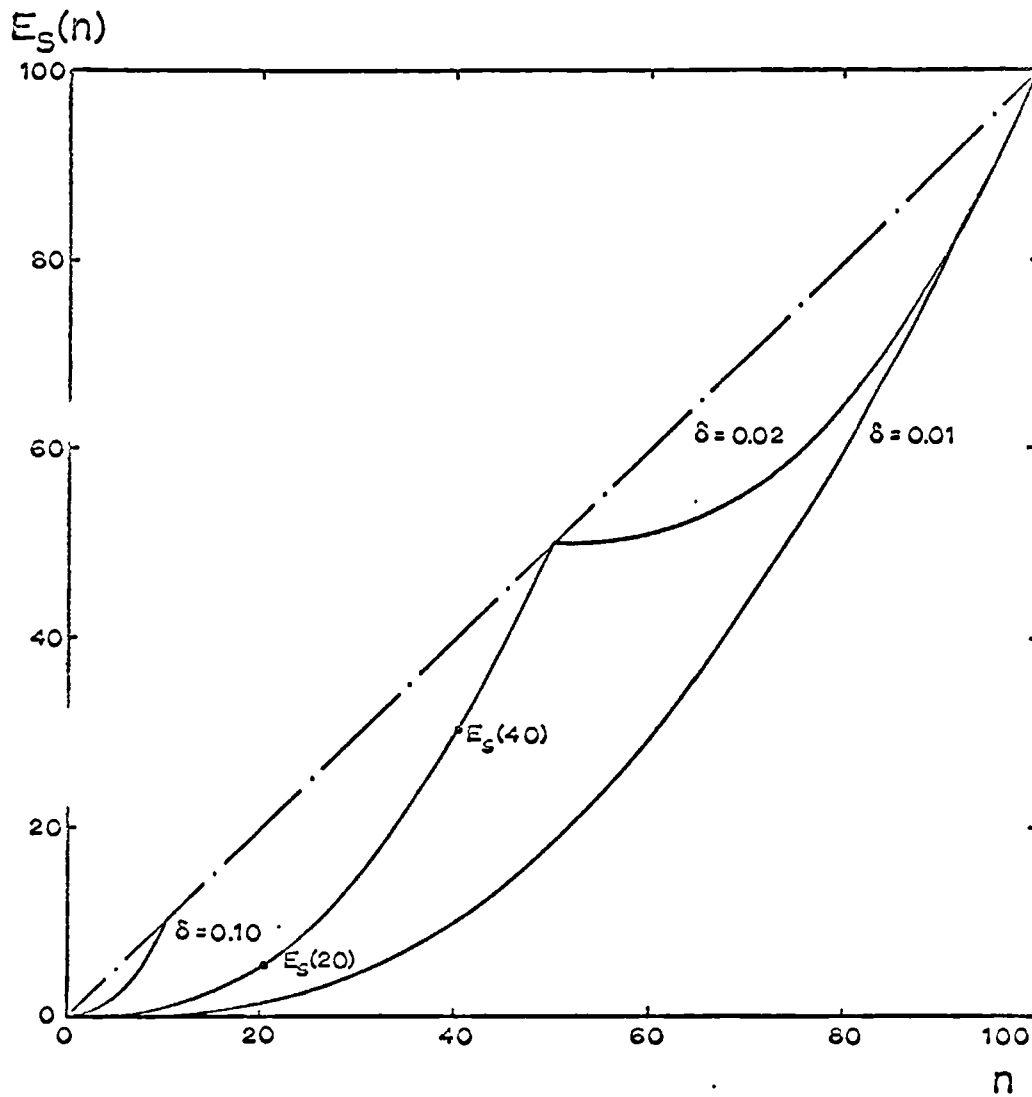


Figure 2.3 Minimum potential energy, $E_s(n)$, of a chain of n atoms as a function of n for three values of the mismatch, δ .

Consider now, for example, a chain of 40 atoms of a film with a 2% mismatch, i.e. $\delta = 0.02$. The potential energy of this chain, marked $E_s(40)$ on the graph, is 30 units. But the potential energy of two chains each of 20 atoms (marked $E_s(20)$) is only 2×5 units. Hence such a 40 atom chain is in unstable equilibrium, and can reduce its potential energy by splitting in to two smaller chains. Elastic energy is stored at the gap between the new chains, which then becomes an interfacial dislocation.

The production of such an interfacial dislocation will be favourable if the potential energy available is greater than the strain energy stored at the gap. Let us consider these energies separately.

The potential energy available when a chain splits is given by

$$E_{Av} = E_s(n) - 2E_s(n/2) \quad (2.17)$$

for even values of n , and by

$$E_{Av} = E_s(n) - E_s((n+1)/2) - E_s((n-1)/2) \quad (2.18)$$

for odd values of n . The expression $E_s(n)$ is given in Equation (2.16). Values of E_{Av} have been computed on the Imperial College IBM 7090 computer, and these values

are plotted in Figure (2.4). The programme is given in Appendix 2.2.. The available energy will increase with the increasing Q_{sd} and hence with increasing Q_{ads} . It is also seen that there is a maximum amount of energy available for a given mismatch, and this maximum is reached as the number of atoms in the chain approaches $1/6$.

The strain which occurs at the gap may be found from Equation (2.14). Consider even values of n . The distance, d , between the first atom of a chain of length n and the first atom of a chain of length $n/2$ is $(x_n - x_{n/2})$. From Equation (2.14) this is

$$d = a \left[\frac{m'}{1 + \delta} - \frac{n}{4} \right] \quad (2.19)$$

where m' is an integer, chosen so that $-b/2 < d < +b/2$. There will in general be only one such value of m' . The strain at the gap, ϵ , may then be found from

$$\epsilon = \frac{2d}{a} = \left[\frac{2m'}{1 + \delta} - \frac{n}{2} \right] \quad (2.20)$$

where m' is now chosen so that $-1 < \epsilon < +1$. If this derivation is carried out for odd values of n it is found

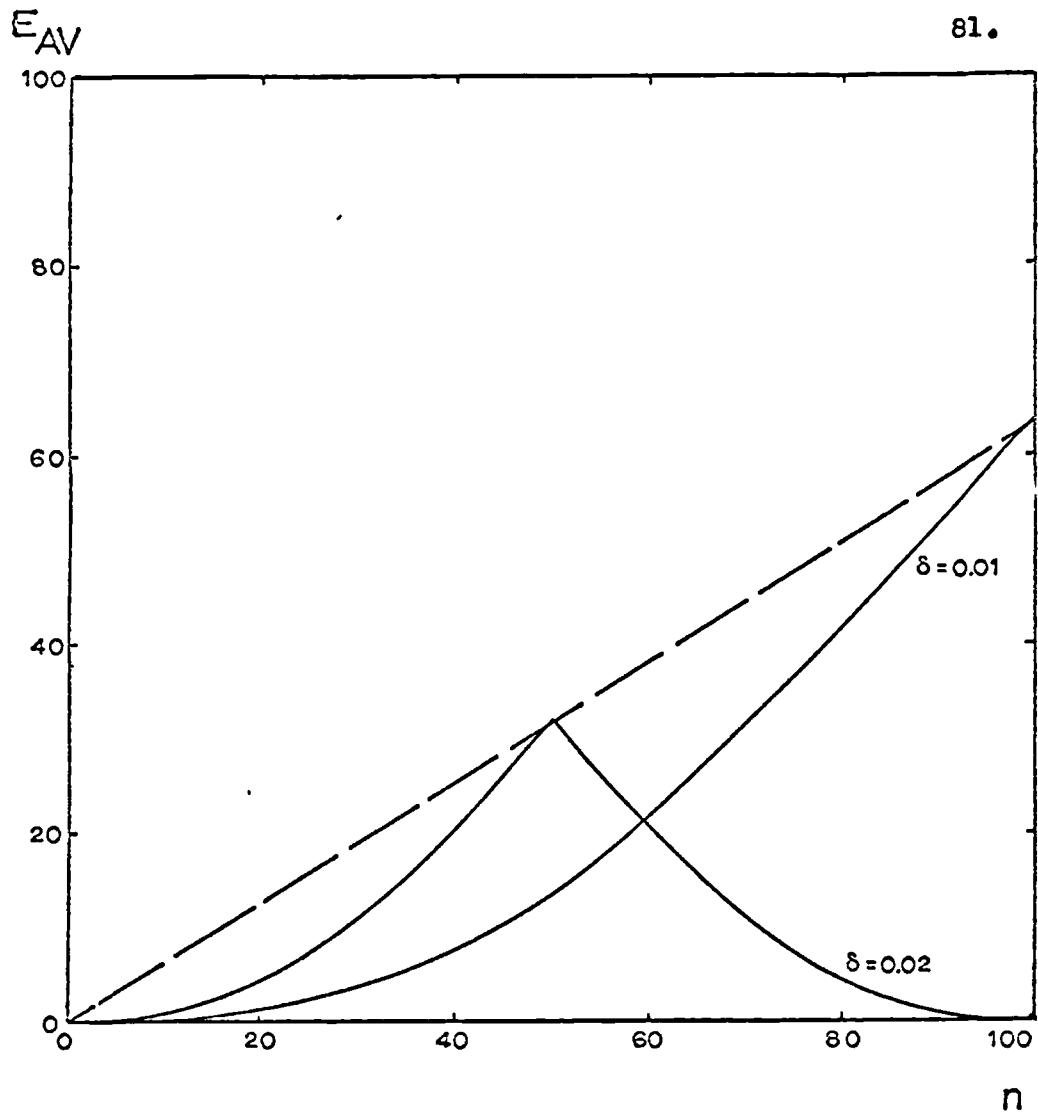


Figure 2.4 Potential energy, E_{AV} , available when a chain of n atoms splits into two smaller chains as a function of n for three values of the mismatch, δ .

to give the same result. The Imperial College IBM 7090 computer has been used to choose m' and to give the values of strain. The strain has been plotted as a function of n for three values of mismatch in Figure 2.5. The strain has been considered positive when the chains of atoms move apart to minimise their potential energy, and negative when they move together. The lines are the loci of the discrete points corresponding to whole number values of n , the number of atoms in the chain before it splits. Some of the discrete points have been marked in Figure 2.5.

The strain energy at the gap is equal to $\frac{1}{2} \mu m \alpha^3 \epsilon^2$ where μ is the shear modulus for the island, and m is the number of atomic layers of thickness. Thus the strain energy is small for 'soft' (i.e. μ small) platelet (i.e. m small) islands, and for n approaching $1/\delta$ (strain small).

This model predicts that interfacial dislocations will be formed when the adsorption energy is high, when the misfit is small, and when the overgrowth film is 'soft' and thin. Interfacial dislocations have indeed been observed under such conditions.

The strain we have considered is inhomogeneous, being localised in the region of the interfacial dislocation. Van der Merwe has pointed out that the total energy of the system may be reduced by the presence of a homogeneous strain, in such a direction as to minimise the mismatch between film and substrate.

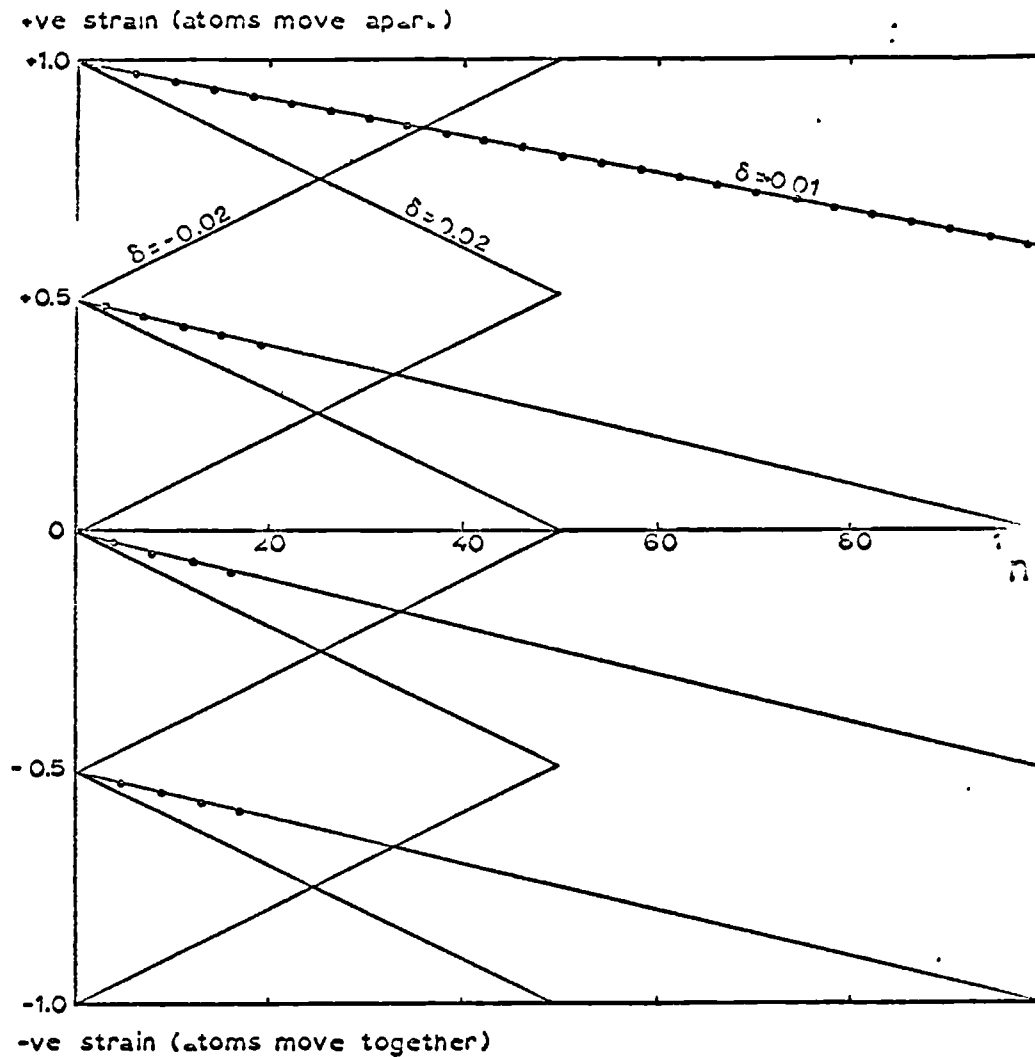


Figure 2.5 When a chain of, n atoms breaks into two smaller chains to reduce its potential energy, there will be a certain strain at the gap. This strain, considered positive when the chains of atoms move apart and negative when they move together, is plotted as a function of n for three values of the mismatch δ .

If the homogeneous strain is ϵ then the strain energy per chain per unit width is given by

$$\frac{1}{2} \epsilon^2 E h (n-1) a \quad (2.21)$$

where h is the thickness of the island.

The new potential energy, E_g , of the chain is found from Equation (2.16), with the new value of $\delta, (\delta_n)$, given by

$$a = b_0 (1 + \delta_n) \quad (2.22)$$

where b_0 is the lattice parameter of the substrate, and a is the new value of the lattice parameter of the film, given by

$$a = a_0 (1 + \epsilon) \quad (2.23)$$

Total elimination of dislocations

If no interfacial dislocations are formed the total energy of the chain will be the sum of the potential energy and the homogeneous strain energy. The relationship between strain and thickness can then be found from the strain to minimise the total energy. The resulting expression is

$$\epsilon E h (n-1) a = \pi (1 + \delta) \left[\frac{n \tan(2\pi \delta_n) - \tan(2\pi \delta)}{(1 - \cos(2\pi \delta_n))^{\frac{1}{2}} - (1 - \cos(2\pi \delta))^{\frac{1}{2}}} \right] \quad (2.24)$$

where δ and δ_n are as already defined.

Partial elimination of dislocations

It may also be possible to find the number of interfacial dislocations and the strain in the film by minimising the total energy, being the sum of the potential energy, the inhomogeneous strain energy and the homogeneous strain energy. In order to do this assumptions must be made about the magnitude of the strain and the mismatch. Van der Merwe has treated this problem, and the result will be discussed in section 2.8.3.

It is not advisable to extend this model beyond this point because of the invalid assumptions made about the elastic properties of film and substrate. Van der Merwe has considered the model from a more rigorous mathematical point of view, and his results will be presented in the next section.

2.8.3. Van der Merwe's Analysis

Van der Merwe⁽²⁰⁵⁾ has given a more rigorous analysis to a similar model. He allowed the overgrowth lattice and the substrate lattice to have different elastic properties, and he evaluated the sum of the potential energy of the lattices, and the elastic strain energy stored due to the interfacial dislocations. He assumed that the potential energy was periodic in c where c is a reference lattice defined by $p = Pa = (P+1)b = (P+\frac{1}{2})c$ where P is an integer. He found that the equilibrium bonding energy was given by

$${}_aE_b = \left[\frac{\mu}{4\pi^2} \right] \times \left[\begin{array}{c} 1 - \beta - (1 + \beta^2)^{\frac{1}{2}} \\ -\beta \ln(2\beta(1 + \beta^2)^{\frac{1}{2}} - 2\beta^2) \end{array} \right] \quad (2.25)$$

$$\text{where } \beta = 2\pi(c/p) (\lambda_+ / \mu) \quad (2.26)$$

$$1/\lambda_+ = (1 - \sigma_a) / \mu_a + (1 - \sigma_b) / \mu_b \quad (2.27)$$

The binding energy E is measured in units of $\frac{\mu}{4\pi^2} \frac{c}{\lambda_+}$ where μ is a shear modulus associated with the interface, and β is a parameter proportional to the lattice mismatch. The bonding energy which is the total specific energy to split the interface is related to the interfacial energy by

$${}_aE_b = E_a + E_b - E_{ab} \quad (2.28)$$

where E_a and E_b are the specific surface energies of crystals A and B. Thus the lower the interfacial energy, the stronger the bonding, and the higher the activation energy for surface diffusion. Hence the lower the interfacial energy the lower the mobility of an adsorbed atom on the surface.

The first term in expression (2.25) is the potential energy term, and the second term is the strain energy term. As the misfit increases the strain energy term decreases.

This is because fewer interfacial dislocations are formed, and the mismatch between the lattices is taken up by a uniform relative displacement of the atoms.

The inhomogeneous strain energy term would cause a stress to be observed in thin films in a bending beam experiment, but this stress would be important only for small misfits between film and substrate. Of more importance is the possibility of a homogeneous strain, as discussed earlier. Van der Merwe finds that below a certain critical misfit the mismatch will be taken up entirely by homogeneous strain. In analogy to our Equation (2.24) he finds that the critical misfit f_c is related to the film thickness by

$$\ln \left[\frac{4\pi f_c (\mu_b/\mu_o)}{(1-\sigma)(1+\mu_b/\mu_o)} \right] + \frac{2\pi(1-\sigma)^2 (1+\mu_a/\mu_b) h f_c}{(1-2\sigma) a} = 0 \quad (2.29)$$

and, by minimising the total energy, including inhomogeneous strain he find that the homogeneous strain in a film containing interfacial dislocations is given by

$$\varepsilon = \frac{(1-2\sigma)(2-f)(1+f)\mu_o a}{8\pi^2(1-\sigma)(2+f)f\mu_o h} \beta \ln(2\beta(1+\beta^2)^{\frac{1}{2}} - 2\beta^2) \quad (2.30)$$

$$f = (b - a_o) / a_o$$

$$\beta = 8\pi\mu_a f / (1-\sigma)(1+\mu_a/\mu_b)(2+f)^2 \mu_o$$

2.8.4. Applicability to Stress in Thin Films

There are three ways in which interactions between crystal interfaces, as treated by Van der Merwe could cause the observed stresses in evaporated films. The stresses could be due to:

1. the equilibrium inhomogeneous strain due to the presence of interfacial dislocations between film and substrate;
2. the equilibrium homogeneous strain which reduces the mismatch between film and substrates;
3. non-equilibrium conditions giving rise to more strain than predicted by the theory.

2.8.4.1. Inhomogeneous Strain

The tangential stresses in the film due to the interfacial dislocations may be deduced from the stress function given by Van der Merwe⁽²⁰⁵⁾. It is found that the stresses decrease exponentially with distance from the interface. The stress at a distance z from the interface is proportional to $m^2 B z \exp(-mz)$ where B is a constant and $m = 2(a-b)/ab$. We may find the form of the force per unit width versus film thickness curve by integrating this with respect to z . This gives the form of curve shown in Figure 2.6 which is of the type found in experimental work on stress in thin films, and is similar to the form for silver and gold found in the present work. Klokholm⁽²⁰⁹⁾ has considered this curve. On the basis

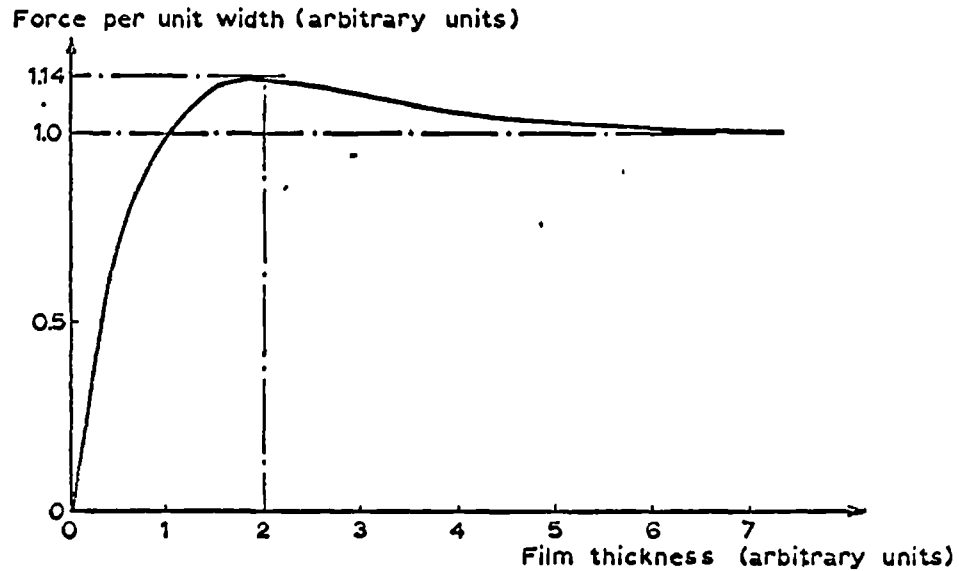


Figure 2.6 Force per unit width versus film thickness curve predicted by the interfacial (inhomogeneous strain) model.

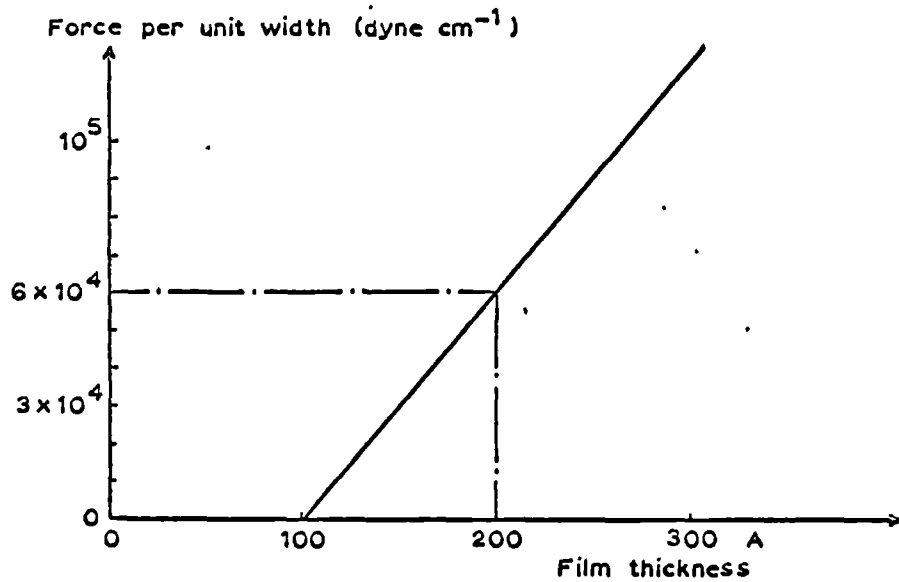


Figure 2.7 Force per unit width versus film thickness curve predicted by the interfacial (non equilibrium strain) model.

of his experimental work he divides metals into two classes, those in which $F \ll 1/m$ and those in which $F \gg 1/m$ and he explains his results on this model.

However, unless m is very small the curve flattens off at a very low film thickness. For instance this model predicts that the curve flattens off at $15\text{\AA}$ film thickness when the mismatch is only 1%. But published results on stress in nickel and iron films, at least, show no sign of flattening off at this film thickness, even though the mismatch is larger. Clearly this model does not explain the shape of the experimental curves obtained. Furthermore, as the type of stress on this model depends on the mismatch, it does not account for the fact that the stress in most metal films is tensile.

2.8.4.2. Homogeneous Strain

Homogeneous strains in a film to minimise the misfit between film and substrate have been observed between PbS-PbSe⁽²¹⁰⁾ and between Au-Pd and Pt-Au⁽²¹¹⁾. For instance in the case of the system PbS-PbSe the spacing between the interfacial dislocations, as observed by transmission electron microscopy, was about 4% larger than that expected from the known difference in lattice parameters of the layers. This implied a strain of 0.06%

in each lattice in the direction to reduce the mismatch. The strain agrees with that calculated from Equation 2.30. However, in the case of the experiments on the noble metals it

was found that the percentage of the misfit accommodated by strain was larger than predicted by the theory. For instance the experimental value for the system Au-Pd was 13% while Equation 2.30 predicts only 1.4% to be accommodated by strain. This, it was suggested, was probably due to non equilibrium conditions obtaining during the growth of the film.

2.8.4.3. Non Equilibrium Strain

Cabrera^(212,213,214) has suggested a mechanism which might explain the observations of Matthews^(210,211) and which he has proposed as the origin of the observed stresses in thin films.

According to Cabrera, as an island becomes thicker the amount of misfit accommodated by elastic strain decreases. This follows from Equation 2.30. As the amount accommodated by strain decreases the amount accommodated by interfacial dislocations must increase. This implies that the number of dislocations per unit area of island must increase as the island grows. Cabrera suggests that these dislocations are nucleated at the edges of the islands, and move towards the centre. However, once a film has become continuous no new interfacial dislocations can be nucleated. Hence more strain energy will be stored in the film than predicted by Van der Merwe's model.

Cabrera^(213,214) has derived a formula for the contribution to the observed stress in a film from this cause. Assuming

that the misfit is rather less than 10%, and that the lattice parameter of the film is greater than that of the substrate, a compressive stress given by

$$S = \frac{\lambda\beta}{H_0} \left(1 - \frac{H_0}{H} \right)$$

is produced. λ is an elastic modulus (as defined in Equation 2.27); β is of the order of the lattice parameter, H_0 is the film thickness for continuity and H is the actual film thickness. Substituting $\beta = 2.8\text{\AA}$; $\lambda = 3 \cdot 10^{11}$ dyne cm^{-2} ; $H_0 = 100\text{\AA}$ we find the compressive stress in a silver film to be as plotted in Figure 2.7.

2.9. SUMMARY

Table 2.2 shows the magnitude and the type of stress predicted by these models for three common metals, copper, silver and iron. Column one shows the model; column two the parameters required to predict stress values; column three the film thickness to which the calculated value of stress relates; column four the type of stress, compressive or tensile, predicted by the model; and column five the values of stress in units of 10^9 dyne cm^{-2} . Where the properties of the substrate are required to predict the stress it has been assumed that the substrate is made of the same glass as that used in the present experiments. Thus the thermal stress, for instance, which is tensile for copper silver and iron films deposited

on to glass substrates would be compressive if rock salt substrates were used.

The models are discussed in the light of the present experimental evidence in chapter seven.

Table 2.2 Summary of Stress Predicted by Various Models.

Model	Data needed to predict stress	film thickness $\text{\AA}$	type of stress	Stress in units of $10^9 \text{ dyne cm}^{-2}$		
				Cu	Ag	Fe
	Tensile strength of wire			4.0	0.9	4.0
Thermal stress	Thermal expansion coefficient film; thermal expansion coeff. substrate; Young's mod. film; Temperature rise.	any	T	0.24	0.16	0.07
Thermal model	Thermal expansion coefficient film; Young's mod. film; recrystallization temperature film.	any	T	1.0	1.2	2.8
Imperfection (vacancy)	Atomic % vacancies in film; (say $\frac{1}{2}\%$); stress per vacancy	any	T	1.2	---	---
Imperfection (grain boundary)	Island radius; film thickness; number of crystallites per island; Young's mod. film.	200	T	---	0.45	---
Density	Density change on solidification; Young's mod. film.	any	T	19.	8.7	---

Model	Data needed to predict stress	film thickness $\text{\AA}$	type of stress	Stress in units of $10^9 \text{ dyne cm}^{-2}$		
				Cu	Ag	Fe
Grain boundary	Atomic radius; surface tension; surface stress; crystallite size; Young's mod. film.	any	T	----	----	9.0
Grain gap	same as grain boundary	200	T	----	----	5.0
Electrostatic	Island radius; film thickness; available charge (say 7 electrons per island).	5	T	2.0	2.0	2.0
		20	T	0.05	0.05	0.05
Surface stress	Island radius; film thickness; surface stress; elastic constants film.	20	C	----	3.0	---
Surface tension	same as surface stress, but with surface tension	20	T	----	0.5	---
Interfacial	Mismatch; elastic constants film and substrate; thickness of film and substrate.		Ag-Au 1.6 Ag-Pd 52.			
Inhomogeneous	Mismatch; atomic radius; shear mod. film; thick-	1000	-	----	54.	---
	ness for continuity film thickness.	200	-	----	30.	---

CHAPTER III

MECHANICAL METHODS FOR MEASURING STRESS IN THIN FILMS

3.1. INTRODUCTION

The bending beam method (see section 1.3) was chosen for the measurement of stress in evaporated films for the reasons discussed in section 1.11.2.

In this chapter the differences between a disc method and a beam method are discussed. Then the relationship between beam end deflection and stress in a film are derived. The derivation is extended to give the stress which would be in a film if (a) it were deposited on to an infinitely hard substrate, (b) the Young's modulus of the film and the substrate differed, and, (c) if the film thickness was not negligible in comparison with the substrate thickness. The derivation leads to comments on the interpretation of results from a bending beam experiment.

Apparatus for the measurement of stress by the bending beam method is then considered, and reasons for the choice of the capacitance system given. Finally, the apparatus used for stress measurement in the present work is described.

The design of the jig, methods for measuring small changes in capacity, the relationship between the beam end deflection and the observed capacity change, and the precautions and limitations of a capacitance system are treated.

3.2. BEAM AND DISC

Mechanical methods for measuring stress in thin films may be divided into two classes, the disc method and the beam method, depending on the shape of the substrate. In the disc method (used in References 85-88, 91, 92, 94, 95, 97, 117-119 and 218) a circular substrate is used. The curvature due to the stress in the film is normally observed by a Newton's rings interferometric technique. In the beam method the substrate is usually between 2.5 and 50 times longer than it is broad. The beam curvature is found by measuring the deflection of one end of the beam when the other end is clamped. The beam and disc methods are compared in Table 3.1.

The disc method is ideal for measuring stress anisotropy. However, the advantage of the beam method is that the sensitivity of the apparatus may be increased at will by increasing the length of the substrate. In the disc method the only way to increase sensitivity is by reducing the substrate thickness, and the thickness reduction is limited both by the problems of electrostatic attraction⁽⁸⁶⁾ and the inapplicability of the usual relationships between stress and beam deflection for very thin substrates (see section 3.3.2). Thus for highest sensitivity the beam method must be used, and it was, therefore, the method developed in this project. Before entering into discussion of the beam method as such it is necessary to consider the relationship between the stress in a film and the beam end deflection.

Disc Method

No clamping involved.

Measurements may be made a long way from the free edge of the substrate.

The substrate must be horizontal and the evaporation downwards for continuous observation of stress during film growth.

Electrostatic problems arise if the substrate is made thin for increased sensitivity. Thickness reduction is also limited by invalidation of the assumptions in the derivation of the Stoney formula.

Young's modulus of substrate extremely hard to measure.

Sensitivity is about 100 dyne cm.

Beam Method

Clamping introduces possible errors in the relationship between stress and end deflection.

As the substrate is long and narrow the edge is always involved.

The substrate may be in any plane for continuous observation.

Substrate may be made as long as desired, to increase sensitivity.

Young's modulus measurement is relatively easy.

Sensitivity may be as low as 1.5 dyne cm.

Table 3.1. A comparison of the disc and beam methods for measuring stress in thin films assuming that the substrate deformation is measured by a Newton's rings technique in the disc method and a capacitance technique in the beam method.

3.3. RELATIONSHIP BETWEEN STRESS AND BEAM END DEFLECTION

3.3.1. Introduction

Until recently the formula used by all thin film workers to relate an isotropic film stress to the resulting substrate curvature was that originally derived by Stoney⁽⁵⁾:-

$$S = \frac{E h^2}{6 r f} \quad (3.1)$$

which is applicable providing that the film thickness f is very much smaller than the substrate thickness h . E is the substrate Young's modulus and r is the radius of curvature of the substrate. However in electrodeposition work the film thicknesses were often comparable to the substrate thicknesses: under these conditions any difference in Young's modulus of film and substrate must be taken into account, as must the particular experimental techniques used. For instance Soderburg⁽⁷⁾ clamped the cathode into position during the deposition because the movement of the free end of the beam - which was a significant fraction of the separation of the electrodes - caused uneven film growth.

Also the meaning of "deflection of the substrate" was ambiguous. It had been defined as both the end deflection when the substrate was cantilevered, and as the camber of the substrate.

Eventually Brenner and Senderoff⁽²¹⁹⁾ reviewed the derivations and derived definitive formulae to cover all the

common experimental techniques.

However, as has recently been pointed out^(1,220), all these derivations neglect the effect of stress in the plane of the substrate and at right angles to the beam length on the beam curvature. The correct formula is

$$S = \frac{E h^2}{6(1-\nu) r f} \quad (\text{for } f \ll h) \quad (3.2)$$

where E , h , r and f are as defined previously, and ν is the Poisson's ratio for the substrate. Hence most of the published values of stress are about 25% too low.

Confusion still exists, however, as to the conditions under which this formula is valid.^(221,3) The formula has therefore been derived in the following section, and the assumptions are stated as they are made.

3.3.2. Derivation of the Relationship Between Stress in a film and Beam End Deflection

The first derivation gives the stress in the film as it is after the substrate has bent (ATSHB). A more absolute figure would be the stress in the film were it deposited on to an infinitely hard substrate (IHS). The derivation has been extended to cover this case.

Four cases will now be considered:-

1. $E_{\text{film}} = E_{\text{substrate}}$ $f \ll h$ ATSHB
2. $E_{\text{film}} = E_{\text{substrate}}$ $f \nless h$ ATSHB
3. $E_{\text{film}} = E_{\text{substrate}}$ $f \nless h$ IHS
4. $E_{\text{film}} \neq E_{\text{substrate}}$ $f \nless h$ IHS

The fourth case has been considered by Davidenkov⁽²²⁰⁾, who derived an expression which could only be integrated numerically. The same expression has been derived by a different method, and has been evaluated analytically by making the assumption that $(f/h)^4 \ll 1$.

3.3.2.1. Case 1

Assume that $E_{\text{film}} = E_{\text{substrate}}$ and that $f \ll h$.

Assume that the neutral axis lies in the middle of the beam.

(This assumption is justified in the derivation of case 4, section 3.3.2.4). Assume that when the beam is deformed the radius of curvature of the upper surface of the beam is the same as that of the lower surface. (i.e. $r \gg h$).

Consider a section through the beam thickness h and area dx by dy (Figure 3.2). The x and y co-ordinates are taken as in Figure 3.1.

Consider the element of thickness dz at a distance z from the neutral axis. The elongations ϵ_x, ϵ_y in the x

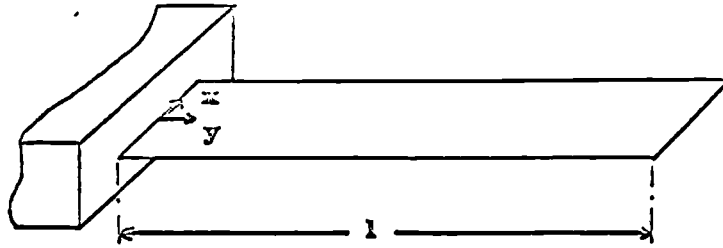


Figure 3.1 The definition of the x and y co-ordinates

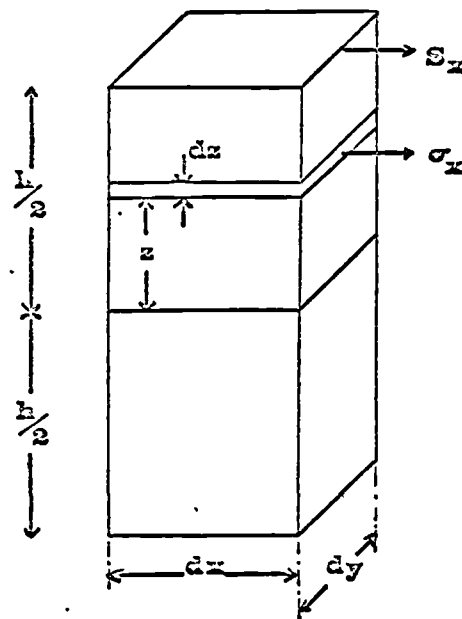


Figure 3.2 An element of cross section of the beam,
thickness h and area dx by dy .

and y directions are given by

$$\epsilon_x = z / r_x \quad (3.3)$$

$$\epsilon_y = z / r_y \quad (3.4)$$

where r_x , r_y are the radii of curvature of the beam in the x and y directions.

Hooke's law gives

$$\epsilon_x = (\sigma_x - \sigma_y) / E \quad (3.5)$$

$$\epsilon_y = (\sigma_y - \sigma_x) / E \quad (3.6)$$

where σ_x , σ_y are the stress components in the lamina.

Solving Equations 3.3, 3.4, 3.5 and 3.6 for σ_x we obtain:-

$$\sigma_x = \left[\frac{E z}{1 - \nu^2} \right] \times \left[\frac{\nu}{r_y} + \frac{1}{r_x} \right] \quad (3.7)$$

Taking moments about the neutral axis:-

$$\begin{aligned} \frac{h}{2} + f \quad \frac{h}{2} \cdot S_x \cdot dy \cdot dz &= \int_{-h/2}^{h/2} \sigma_x z \, dy \cdot dz \\ &= \int_{-h/2}^{h/2} \frac{E z^2}{(1 - \nu^2)} \cdot \left[\frac{\nu}{r_y} + \frac{1}{r_x} \right] dy \cdot dz \end{aligned}$$

from Equation 3.7.

$$\begin{aligned} \text{Hence} \quad \frac{S_x f h}{z} &= \int_{-h/2}^{h/2} \frac{E z^2}{(1 - \nu^2)} \cdot \left[\frac{1}{r_x} + \frac{\nu}{r_y} \right] dz \\ &= \frac{E}{(1 - \nu^2)} \left[\frac{1}{r_x} + \frac{\nu}{r_y} \right] \frac{2}{3} \left(\frac{h}{2} \right)^3 \end{aligned}$$

Hence

$$S_x f = \frac{E h^2}{6(1-\nu^2)} \left[\frac{1}{r_x} + \frac{\nu}{r_y} \right] \quad S_y f = \frac{E h^2}{6(1-\nu^2)} \left[\frac{1}{r_y} + \frac{\nu}{r_x} \right] \quad (3.8)$$

If there is stress anisotropy $S_x \neq S_y$ and these equations are the same as those given by Finegan and Hoffman.⁸⁶⁻⁸⁸ If the stress is isotropic $S_x = S_y$ and $r_x = r_y$. The equations become

$$Sf = \frac{E h^2}{6(1-\nu).r.} \quad (3.9)$$

If θ is the angle subtended by the length of the substrate at its centre of curvature, then $\tan \frac{\theta}{2} = d/l$ and $\sin(\theta/2) = l/2r$. If $\theta/2$ is so small that $\tan(\theta/2) = \sin(\theta/2) = \theta/2$, then $d/l = l/2r$ and we can express the relationship in terms of the end deflection d of a beam of length l .

$$Sf = \frac{E h^2 d}{3(1-\nu)l^2} \quad (3.10)$$

3.3.2.2 Case 2.

Assume that $E_{\text{film}} = E_{\text{substrate}}$ and that $f \ll h$.

The neutral axis will now be at a distance $(f + h)/2$ from the bottom of the substrate. Considering isotropic stress, and taking moments as in Case 1:-

$$\int_{-(\frac{h+f}{2})}^{+(\frac{h+f}{2})} \sigma z dz = \int_{(\frac{h-f}{2})}^{(\frac{h+f}{2})} S. z. dz \quad (3.11)$$

Using $\sigma = E z / (1 - \nu) r$

and integrating Equation 3.11 we finally obtain

$$S_f = \frac{E (h+f)^3}{6 r h (1 - \nu)} \quad (3.12)$$

This equation is identical to Brenner and Senderoff's²¹⁹ Equation (9), but differs from Davidenkov's²²⁰ Equation (2), which is

$$S_f = \frac{E (h+f)^2}{6r}$$

Equation 3.12 reduces to Equation 3.9 when $f \ll h$.

3.3.2.3 Case 3

Assume that $E_{\text{film}} = E_{\text{substrate}}$ and that $f \ll h$.

In order to allow for the fact that the stress in the first layers deposited is relieved by the substrate curvature due to the deposition of further layers, we must find the change in substrate curvature due to a small increment in film thickness. This may be done by putting $d(1/r)$ for $(1/r)$ in Equation 3.11

$$d\left(\frac{1}{r}\right) \int_{-(\frac{h+f}{2})}^{(\frac{h+f}{2})} \frac{E}{1-\nu} \cdot z^2 \cdot dz = S \cdot z \cdot dz \quad (3.13)$$

We may put $d(1/r)$ outside the integration in Equation 3.13 because we have assumed that r is constant for all values of z .

Integrating Equation 3.13 we obtain:-

$$\bar{r} = \int_0^f \frac{6 \cdot (1 - \nu) \cdot S \cdot df}{E (h+f)^2} \quad (3.14)$$

Integrating Equation 3.14 we obtain:-

$$Sf = \frac{E h (h+f)}{6r(1-\nu)} \quad (3.15)$$

This equation is identical (apart from the $(1-\nu)$ term) to Brenner and Senderoff's²¹⁹ Equation (27) and to Davidenkov's²²⁰ Equation (4). It reduces to Equation 3.9 when $f \ll h$.

3.3.2.4 Case 4

Assume that $E_{\text{film}} \neq E_{\text{substrate}}$ and that $f \ll h$.

The method is essentially the same as that used for Case 3. However, the position of the neutral axis must be found by resolving forces. Let the neutral axis be a distance x from the bottom of the substrate. Then resolving forces

$$\int_0^x E_1 z \, dz - \int_0^{h-x} E_1 z \, dz - \int_{h-x}^{h-x+f} E_2 z \, dz = 0 \quad (3.16)$$

where

$$E_1 = E_{\text{substrate}} (1 / (1 - \nu_s))$$

$$E_2 = E_{\text{film}} (1 / (1 - \nu_f))$$

ν_s and ν_f are the substrate and film Poisson's ratios.

Eventually:-

$$x = \frac{h}{2} \left[\frac{1 + 2\alpha w + \alpha w^2}{1 + \alpha w} \right] \quad (3.17)$$

where $E_2 = \alpha E_1$ and $f = hw$

The assumption about the position of the neutral axis made for Case 1 and Case 2 may now be verified by putting $\alpha = 1$ in Equation 3.17.

Taking moments as before

$$\int_0^x E_1 z^2 dz + \int_0^{h-x} E_1 z^2 dz + \int_{h-x}^{h-x+f} E_2 z^2 dz = S(f) (h-x+f) \frac{df}{d(\eta/r)} \quad \dots (3.18)$$

After integrating the left hand side of this equation, and substituting the value of x from Equation 3.17 we may integrate the whole equation, obtaining:-

$$\frac{E h^3}{2r} = \int_0^f \frac{S h (1 + 2w + \alpha w^2) df}{2(\alpha^2 w^4 + 4\alpha w^3 + 6\alpha w^2 + 4\alpha w + 1)} \quad (3.19)$$

This is identical to Davidenkov's²²⁰ Equation (12). Although it may not be integrated as it stands, if fourth power terms in w are neglected in comparison with unity, it may be integrated by expanding the denominator binomially. The result of this integration is:-

$$\frac{E h^2}{6r} = S.f. \left(1 + (1 - 2\alpha)w + \frac{\alpha}{3} (16\alpha - 13)w^2 - (16\alpha^3 - 19\alpha^2 + 4\alpha)w^3 \right) \quad (3.20)$$

This formula reduces to Equation 3.9 when $f \ll h$. It also reduces to Equation 3.15 when $w^4 \ll 1$ and $E_1 = E_2$.

In the present work E_{film} does not differ greatly from $E_{\text{substrate}}$ and $f \ll h$. Typical values for Young's modulus are given in Table 5.2. Equation 3.9 has therefore been used in evaluating the stress in the film from the beam end deflection.

3.4. INTERPRETATION OF STRESS MEASUREMENTS IN THIN FILMS

There are two points which should be considered when interpreting the results of stress measurements in thin films.

1. The stress is the force per unit cross section of the film. Thus if the film is not in the form of a flat slab, but has an island structure, either the stress must be defined by the Stoney equation or the cross sectional area of the island must be found, to give the stress in an island.
2. The stress does not necessarily tend to zero as the film thickness tends to zero, because the film thickness, f , appears in the denominator of the Stoney equation. However the end deflection of the beam does tend to zero as the film thickness tends to zero, so it is often more convenient to plot end deflection versus film thickness. As different substrates have slightly different dimensions, the same stress would cause different end deflection. Hence it is preferable to plot the force per unit width, which is proportional to the end deflection, and which equals the stress film thickness product. It is measured in units of dyne cm^{-1} . This quantity is in some respects more fundamental than the average stress as it is proportional to the force exerted by the film at the film substrate interface. The average stress is the gradient of a line from the origin to any point on the curve of force per unit width versus film thickness, and the incremental stress is the gradient of the curve at any point. As an illustration of the misinterpretation

which may arise, consider the graph of force per unit width versus film thickness (Figure 3.3). This graph indicates that the stress in the film tends to zero as the film thickness tends to zero, and, that after thickness f_0 no further stress is added to the film. However the average stress versus film thickness curve (Figure 3.3) deduced from this seems to indicate that the stress passes through a maximum, and that stress relief is taking place in thicker films. In fact no stress relief is taking place at all. This illustrates the type of misinterpretation possible if the average stress rather than the force per unit width is plotted against film thickness.

3.5. APPARATUS FOR THE MEASUREMENT OF THE STRESS IN THIN FILMS

Blackburn and Campbell⁽¹¹¹⁾ have given a review of the sensitivities of various apparatus used to measure stress in evaporated films, and this table has been extended by Hoffman⁽³⁾. However all the figures given in Hoffman's table appear to be a factor of ten too small. As mentioned in section 3.2, the sensitivity of a bending beam apparatus may be increased by choosing longer substrates, so that the sensitivities reported in the literature for a particular apparatus may be lower than the ultimate obtainable.

The simplest method for measuring the change in substrate end deflection has been to observe it directly through a

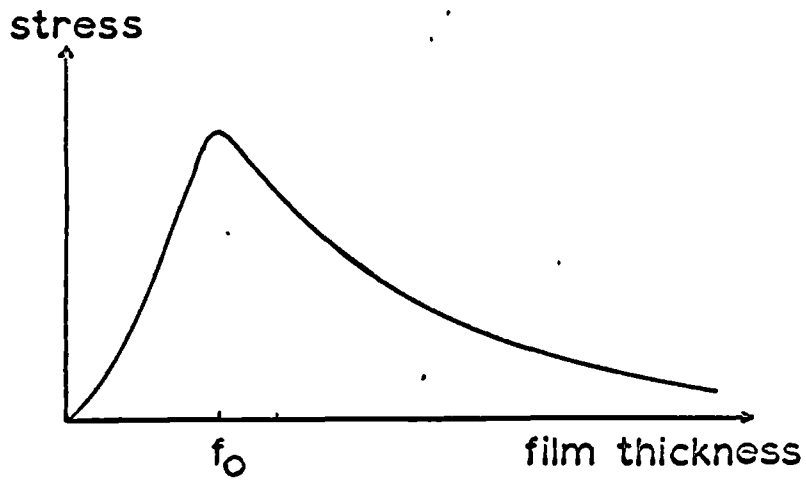
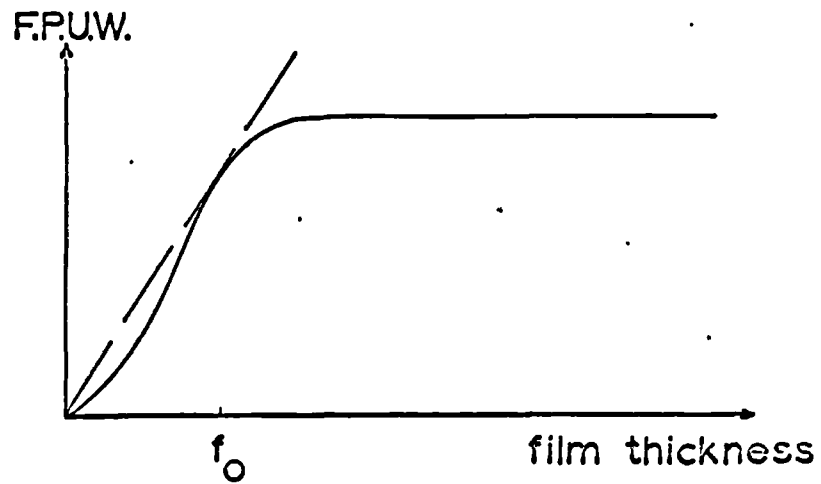


Figure 3.3 Equivalent graphs of force per unit width (F.P.U.W.) versus film thickness and average stress versus film thickness. The average stress is the gradient of the line joining the origin to any point on the F.P.U.W. versus film thickness graph.

microscope⁽²²¹⁾. (References 70,82-84,96,101,127,157,158). Since the experiments of Murbach and Wilman⁽⁸²⁾ the sensitivity of the apparatus has been increased by eight times, so that Novice^(101,102) could detect a minimum force per unit width change of 500 dyne cm^{-1} . However, the minimum end deflection change was 10 microns in each case; only the substrate material and dimensions have been changed.

Three methods have been developed in which the beam is restored to its undeflected position by applying a force to the end of the beam⁽²²²⁾. In general these devices have insufficient sensitivity and are unsuitable for elevated substrate temperatures due to the materials used in their construction.

Interferometry has also been used to measure the end deflection in a conventional bending beam method, although one disadvantage of this method is the broadening of the fringes by substrate vibrations⁽⁷²⁾. The substrate may be mounted on knife edges at both ends to reduce vibration, and, if the area illuminated by the interferometer is in the middle of the beam it remains flat and parallel to its position before the evaporation whatever the beam curvature. A Michelson's interferometer is sometimes used^(72,225,226). The sensitivity of the Michelson's interferometer apparatus used by Ennos⁽⁷²⁾ was 57 dyne cm^{-1} .

Methods, in which the change in electrical capacitance

between the back of a conducting substrate and a fixed reference electrode are measured, have also been used⁽²²⁷⁾. The minimum detectable beam deflections obtained by such apparatus lie between 12.5 and 0.5 microns.

Finally the most sensitive method is that due to Blackburn and Campbell⁽¹¹⁰⁾ in which they used the probe from the "Talysurf", a surface profile measuring instrument, to measure the end deflection. A change in deflection of only $25\text{\AA}$ can be detected, although, for practical purposes, noise and other effects limit the working sensitivity to a minimum end deflection change of $500\text{\AA}$.

3.6. PRESENT APPARATUS

3.6.1. Introduction

Of the methods mentioned the capacitance system was chosen as the best for three reasons. It could be used with a recorder to chart the changes in deflection of the substrate as they occurred during the evaporation: it could be constructed of suitable materials for high vacuum: and it was a system potentially suitable for development to high sensitivity. The apparatus which was finally developed was 1,000 times more sensitive than the capacitance apparatus used by Blackburn and Campbell. For instance the full width of the graph of results presented in Figure 6.15 is six times smaller than the minimum

detectable stress difference obtainable by the capacitance method of Blackburn and Campbell. The smallest force per unit width detectable above noise and drift was 1.5 dyne cm^{-1} which is smaller than that of any apparatus described in the literature.

After considering the jig which carries the substrates and which is within the vacuum system, devices for measuring small changes in electrical capacity will be considered. Finally the relationship between capacitance change and beam deflection will be derived, and a list of experimental precautions and limitations of the device as a stress measuring apparatus will be given.

3.6.2. The Jig

In capacitance transducers for applications such as this the moving surface may be made part of the electrical circuit, or it may be isolated. Although the latter technique has been used in a stress measuring apparatus for thin films⁽¹⁶⁷⁾, the former method has been used more extensively⁽²²⁸⁾, as the total electrical capacity to be measured is four times greater, and thus the effect of a given stray capacitance is four times smaller. The former method has been used in the present work.

Figure 3.4 illustrates the principle of operation of the jig, Model I. The glass or mica substrate, S, which has a conducting film evaporated on to its reverse is clamped in the

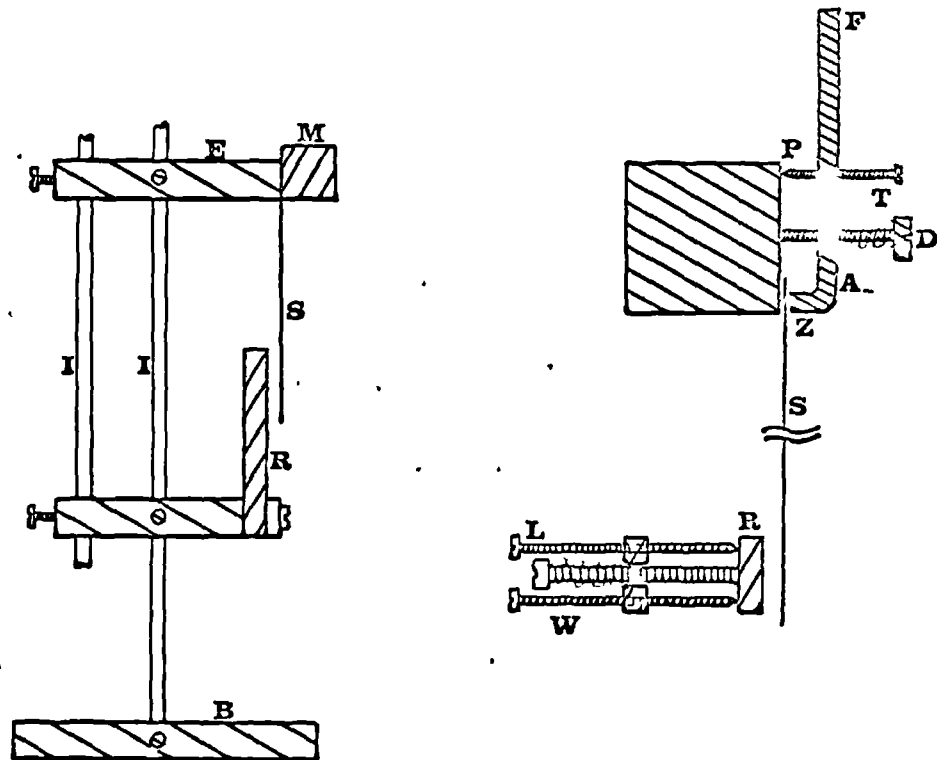


Figure 3.4 The model i jig illustrating the principle of operation. S is the substrate and R the reference electrode. The substrate is clamped to electrode E by means of magnet M. The electrodes are separated by insulating glass rods, I. The whole jig is supported on base B.

Figure 3.5 The clamp and levelling screw arrangement for the model iii jig. The clamp arm A is pivoted about point P and clamps the substrate between ground surfaces Z. The clamp pressure, provided by spring T may be varied by screw D. The levelling screw arrangement for the reference electrode R consists of three screws L. The tension is provided by spring W.

vertical plane with its short side horizontal. It is clamped to one metal electrode, E, at the upper end, and the lower third of the substrate overlaps the reference electrode, R, and is separated from it by a gap of $\frac{1}{2}$ - $1\frac{1}{2}$ mm. In a later model, Model ii, (Plates 3.1, 3.2) the lower electrode was mounted on levelling screws, so that it could be set accurately parallel to the substrate. Care was taken to prevent the evaporant landing on the glass insulators, I, by placing a shield between the source and the substrate. The whole jig could be removed from the evaporator to facilitate the mounting of the substrate. The substrate was normally clamped to the top electrode, E, which was of mild steel, by a bar magnet, M, $\frac{1}{4}$ " by $\frac{1}{4}$ " by $1\frac{1}{2}$ " (Mullard type M2727). This ensured evenly distributed and reproducible clamping pressure. Substrates of any shape were suitable.

The photographs of the Model ii jig (Plates 3.1 and 3.2) show the electron microscope grid holder, G, which held three grids.

The Model iii jig, which was designed for making measurements on three substrates at a time, is shown in Plates 3.3 and 3.4. This jig was restricted to substrates $\frac{7}{16}$ inch (11mm) wide. The levelling screws, L, for the reference electrode, R, the crystal film thickness monitor, X, and holders, G, for electron microscope grids on either side of the crystal can be seen.

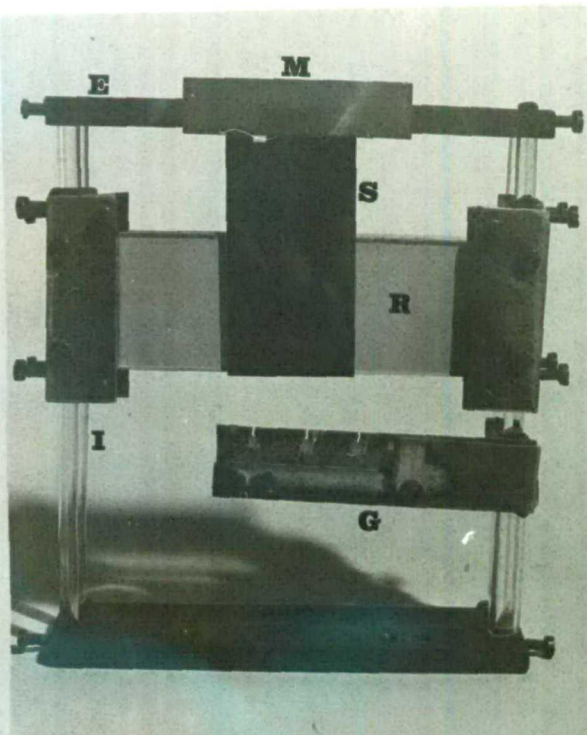


Plate 3.1

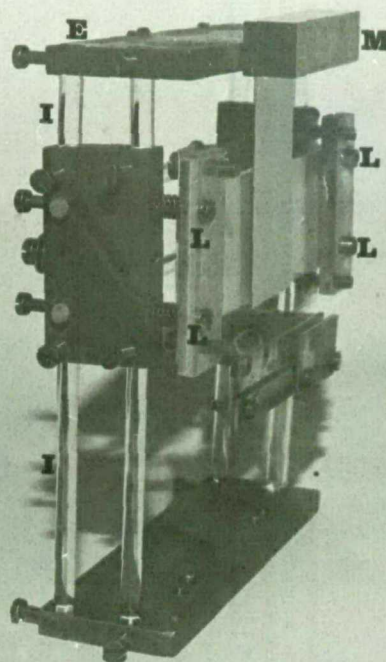


Plate 3.2

Front and side view of the model ii jig. The substrate is $\frac{7}{8}$ " wide, and the insulator separation is $3\frac{1}{4}$ inches. S is the substrate; R the reference electrode. The substrate is clamped to electrode E by magnet M. The electrodes are separated by insulating glass rods, I. G is the grid holder, and L is a levelling screw.

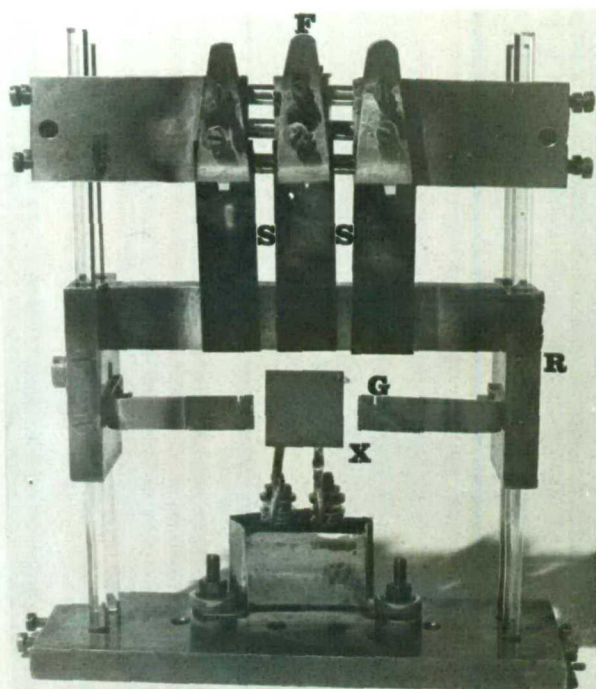


Plate 3.3

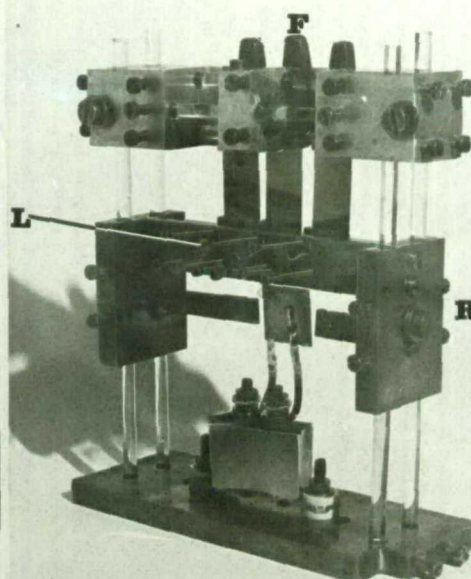


Plate 3.4

Front and side view of the model iii jig. The substrates are $7/16$ inch wide. The insulator separation is $3\frac{1}{4}$ inches. S is a substrate; F is a substrate clamp; R is the reference electrode; L is a levelling screw; G is a grid holder; and X is the crystal film thickness monitor.

The substrate clamps ensured that the clamping pressure remained uniform over the width of each substrate, and constant from evaporation to evaporation. Figure 3.5 shows a side view of the clamp: the substrate, S, and the reference electrode, R, are also shown. The clamp arm A is pivoted about a single point P, and clamps the substrate between ground surfaces Z. The clamping pressure is provided by spring T and can be varied by increasing the tension in T by means of screw D. If screw D is left unaltered, the clamping pressure remains unaltered from substrate to substrate. When a substrate is to be inserted the pressure is released by applying a small force, F with the thumb. The reference electrode is set on three levelling screws as shown in the Figure 3.5. The substrate overhangs the edges of the electrode by about $\frac{1}{2}$ mm on each side in order to eliminate non linearity due to distortion of the edges of the substrate, which always occurred on the mica substrates⁽²²⁹⁾.

3.6.3. Measurement of Small Changes in Electrical Capacity

Small changes in electrical capacity may be measured by techniques such as a feedback circuit⁽²³⁰⁾; an off-resonance oscillator⁽⁷⁴⁾; beat frequency methods; phase detector⁽¹⁰⁸⁾; non linear twin-tee⁽²³¹⁾; or bridge circuits. The method chosen for the present work was the transformer ratio arm bridge⁽²³²⁾.

A Wayne Kerr universal bridge type B 221 was used in conjunction with an autobalance adaptor type AA221. Measurements

were made using a three terminal method; the stray capacity was 2pf (0.5pf)^{*}, and the total capacity was 8pf (5pf)^{*}. The autobalance adaptor produced a signal proportional to the change in capacity, and this signal was fed to an AEI 10 inch potentiometric recorder, type 10S via an attenuating and smoothing circuit. A block diagram of the electrical apparatus is in Figure 3.6.

The bridge reads capacity to four figures, with a nominal accuracy of 0.1%. The discrimination is better than 1 part in 10^4 . The first two significant figures of the capacitance value are set up on switches on the bridge, and the last two figures are read on the meters, or in this case the recorder. In a typical experiment the zero deflection on the chart corresponded to a total capacity of 7.900 pf (5.400pf)^{*}, and the full scale deflection on the chart corresponded to a capacity of 8.000 pf (5.500pf). The chart may be read easily to 1/200 fsd, or change in capacity of 0.0005pf. Thus it is possible to detect fractional changes of capacity to 1 part in 20,000.

^{*} The first figure refers to the Model ii jig, and the figure in brackets to the Model iii jig.

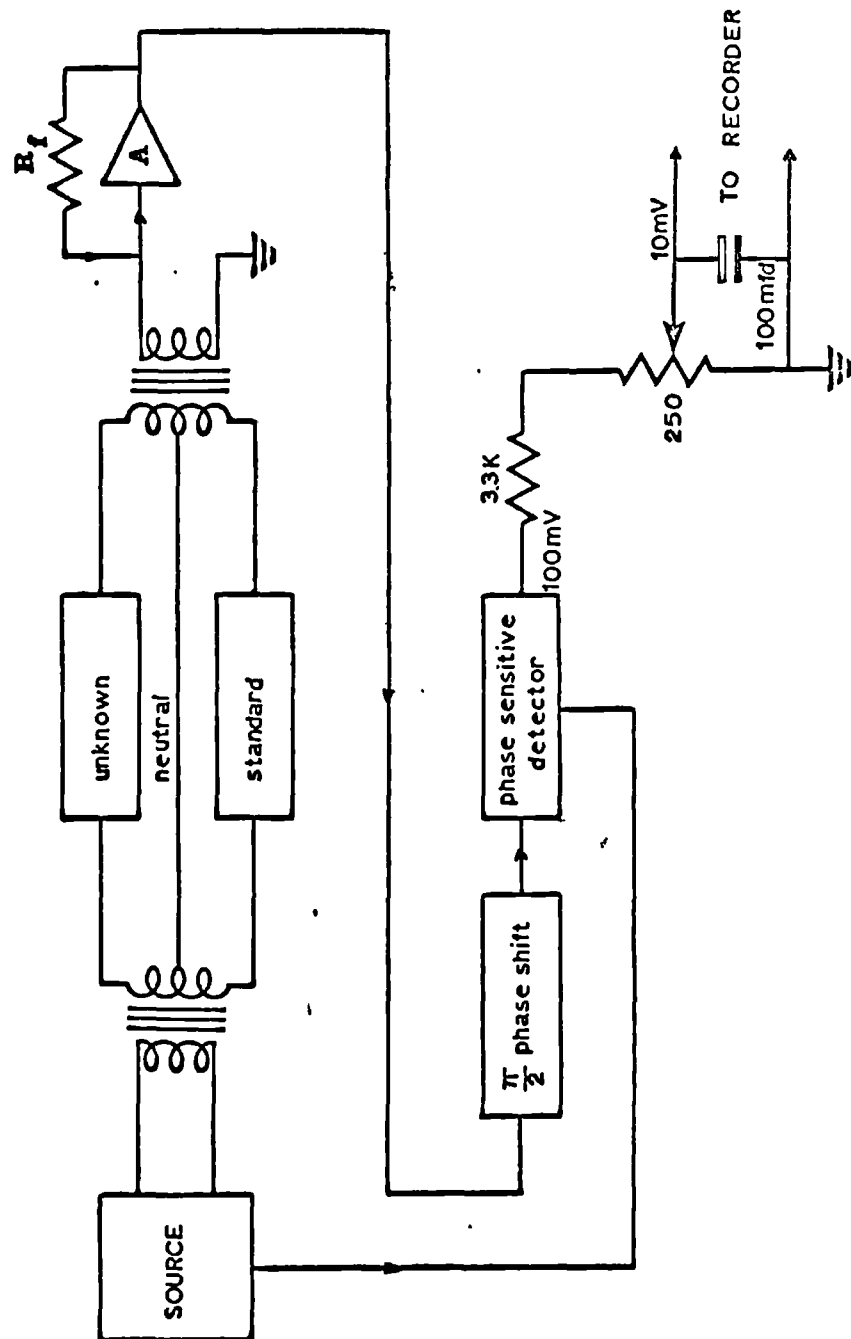


Figure 3.6 Block d'gram of capacitance bridge showing the connection to the recorder.

3.6.4 Relationship between beam end deflection and the capacity change

Let the substrate length be l , the overlap with the reference plate $(1-b)$, the initial separation d_0 , the substrate width l_0 , and the deflection due to the stress d . These, together with the x and y co-ordinates are illustrated in Figures 3.7 and 3.8 for the earlier and the later models of the jig.

The initial capacity, C , in esu, is given by:-

$$C = \frac{K (1-b) l_0}{4 d_0} \quad (3.21)$$

where K is the dielectric constant of the medium.

The curvature of the substrate may be represented by a parabola. (Equation 3.10). Thus the curvature is represented by

$$x^2/l^2 = y/d \quad (3.22)$$

Consider an element of substrate, width dx and length l_0 .

The capacity between this element and the reference electrode is

$$C = \frac{K l_0 dx}{4\pi(y+d_0)} \quad (3.23)$$

Hence the total capacity between the substrate and the reference electrode is

$$\int_b^1 \frac{K l_0 dx}{4\pi(y+d_0)} \quad (3.24)$$

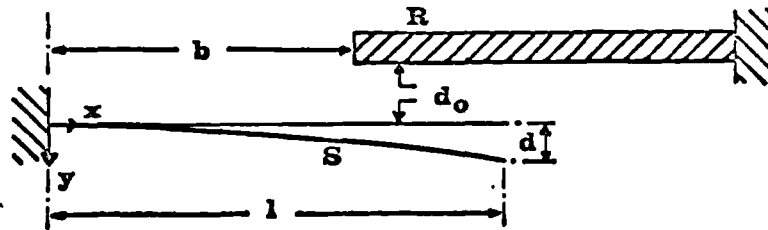


Figure 3.7. Definition of symbols and co-ordinates for the theory in section 3.6.4. The initial separation between the substrate S and the reference electrode R is d_0 . The deflection due to the stress is d .

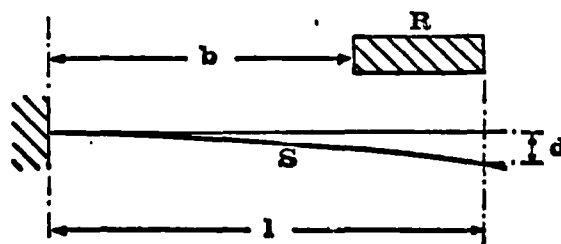


Figure 3.8 When the substrate was longer than the jig, as for the model ii and the model iii jigs, l and d were taken as in this diagram.

If we assume that $y \ll d_0$ we can integrate this by expanding the denominator binomially and using Equation 3.22 obtaining:-

$$\begin{aligned}
 C_{\text{TOTAL}} &= \frac{K l_0}{4\pi d_0} \int_b^1 \left(1 - \frac{d}{d_0} \cdot \frac{x^2}{l^2} + \frac{d^2 x^4}{d_0^2 l^4} \dots \right) dx \\
 &= \frac{K l_0}{4\pi d_0} \left[(1-b) - \frac{d}{3d_0 l^2} (1^3 - b^3) + \frac{d^2}{5d_0^2 l^4} (1^5 - b^5) \dots \right] \\
 &= C - \frac{K l_0}{4\pi d_0} \cdot \frac{d}{3d_0 l^2} \cdot (1^3 - b^3) + \text{higher term.}
 \end{aligned} \tag{3.25}$$

from Equation 3.21.

The error in neglecting the higher terms is only 1% for $d/d_0 = .02$ and is .05% in the usual case, when $d/d_0 = .005$. The change in capacity due to the beam deflection is therefore

$$\Delta C = \frac{K d l_0 (1-b)(1^2 + bl + b^2)}{12 l^2 d_0^2 \pi} \tag{3.26}$$

We may eliminate d_0 from this equation by substituting from Equation 3.2.1

$$d = \frac{3 l_0 K (1-b)(1^2)}{4\pi C^2 (1^2 + bl + b^2)} \Delta C \tag{3.27}$$

If l_0 , l and b are measured in cm, if the capacitance C is in pf; and if $k = 1$ then the chart full scale deflection ($\Delta C = 0.1\text{pf}$) in microns is given by

$$\text{f.s.d.} = \frac{263 l_0 (1-b) l^2}{(1^2 + bl + b^2) C^2} \tag{3.28}$$

which is the formula used in computation of the results.

A list of the assumptions made in deriving the relationship between the change in electrical capacity and the stress is now given.

1. $r \gg h \gg f$ from the relationship between radius of curvature of the beam and stress.
2. $r \gg l \gg d$ from the relationship between radius of curvature and end deflection.
3. $d_0 \gg d$ from the relationship between end deflection and capacity.
(i.e. $C \gg \Delta C$)

Representative values of these quantities are:-

$$\begin{aligned}
 r &= 10^4 \text{ cm.} \\
 h &= 1.5 \times 10^{-2} \text{ cm.} \\
 f &= 5 \times 10^{-6} \text{ cm.} \\
 l &= 3 \text{ or } 4 \text{ cm.} \\
 d &= 5 \times 10^{-4} \text{ cm.} \\
 d_0 &= \frac{1}{2} \text{ to } 1 \times 10^{-1} \text{ cm.}
 \end{aligned}$$

Thus these assumptions are valid for the substrate geometries used in the present work.

3.6.5 Precautions and limitations in the use of a capacitance method

The following precautions concerning the measurement of small capacity changes were found to be necessary:-

1. The jig and connecting leads were electrostatically screened by earthing a conducting coating which had been evaporated over the inside of the bell jar.
2. Precautions were taken to prevent any stray capacity from being altered by conducting evaporant landing on an insulating surface.
3. The shutter was placed as far away as possible from the jig, as, in earlier experiments, opening it caused a significant change in capacity (0.005 pf). In the final system the change in capacity on opening the shutter was less than 0.0002 pf.
4. The chromium coating on the reverse of the substrate had to be electrically continuous or the deposition of a conducting film caused a sudden increase in capacity, and hence an apparently compressive stress.
5. The time response of the system was limited by the inertia of the pen movement of the recorder. However this very conveniently filtered out part of the noise caused by vibrations of the substrate.
6. Thermionic emission from the substrate heater affected the electrical stability of the bridge readings, but this was eliminated by a suitable biasing arrangement (Section 4.4).

3.6.6 Conclusions

1. A potentially bakeable, ultrahigh vacuum, very sensitive stress measuring apparatus has been designed and built. The

maximum stress resolution obtained was 1.5 dyne cm^{-1} above noise and drift, which is higher than that of any apparatus described in the literature. The normal resolution was $5\text{-}15 \text{ dyne cm}^{-1}$

2. This system has three very attractive features, in that

- a) it can be used for making measurements on more than one substrate at a time at no extra cost; b) it is ideal for measuring the substrate Young's modulus (see Section 5.4)
- c) the substrate may be in any plane.

3. The principle limitations on the sensitivity are due to factors such as the poor elastic properties of the substrates, and drift of the deflection with time after the evaporation. These factors, and those affecting the reproducibility of results are considered in the chapter five.

CHAPTER IV

APPARATUS

4.1. INTRODUCTION

In this chapter apparatus other than the stress measuring apparatus is described. Special attention is given to the substrate heater, and the crystal film thickness monitor. Plate 4.1 is an overall view of the apparatus.

4.2. APPARATUS OUTSIDE THE BELL JAR

The evaporations were performed in a NGN semi-automatic pumping unit type CU100 fitted with a mild steel baseplate and a twelve inch bell jar. The three inch diffusion pump was charged with silicon fluid type DC704. Greased seals were used throughout. With liquid nitrogen in the cold trap, the pressure which could be attained without baking after an overnight pump was $1-2 \times 10^{-7}$ torr. The pressure was measured on an ionisation gauge type IG3-H.

4.3. APPARATUS INSIDE THE BELL JAR

The apparatus inside the bell jar, as set up for horizontal evaporation is shown in Plates 4.2 and 4.3. The evaporation sources are drawn in Figure 4.1. Open, dimpled, 2 mil, molybdenum boats were used for silver and gold evaporation. A

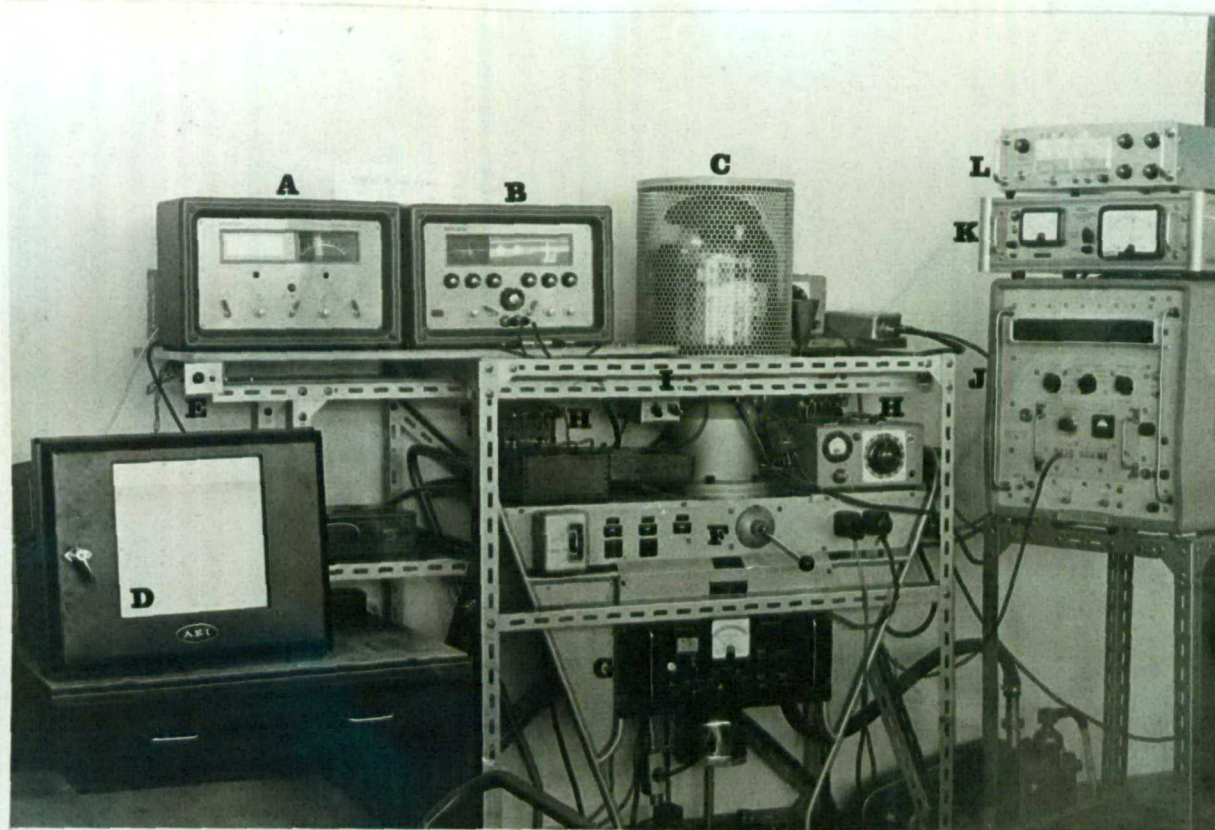


Plate 4.1

An overall view of the apparatus. In the upper third of the picture, from left to right, can be seen the autobalance adaptor, A; the bridge, B; and the bell jar, C. In the lower third of the picture, from left to right, is the recorder, D, and above it the switch, E, for the bias voltage; the pumping unit, F; the pirani gauge, G; and the transformers, H, for the high current supplies. The local oscillator, I, for the film thickness monitor is mounted just below and to the left of the bell jar. On the right of the picture are the digital counter, J, for the film thickness monitor; the ratemeter, K; and the ionisation gauge control unit, L.

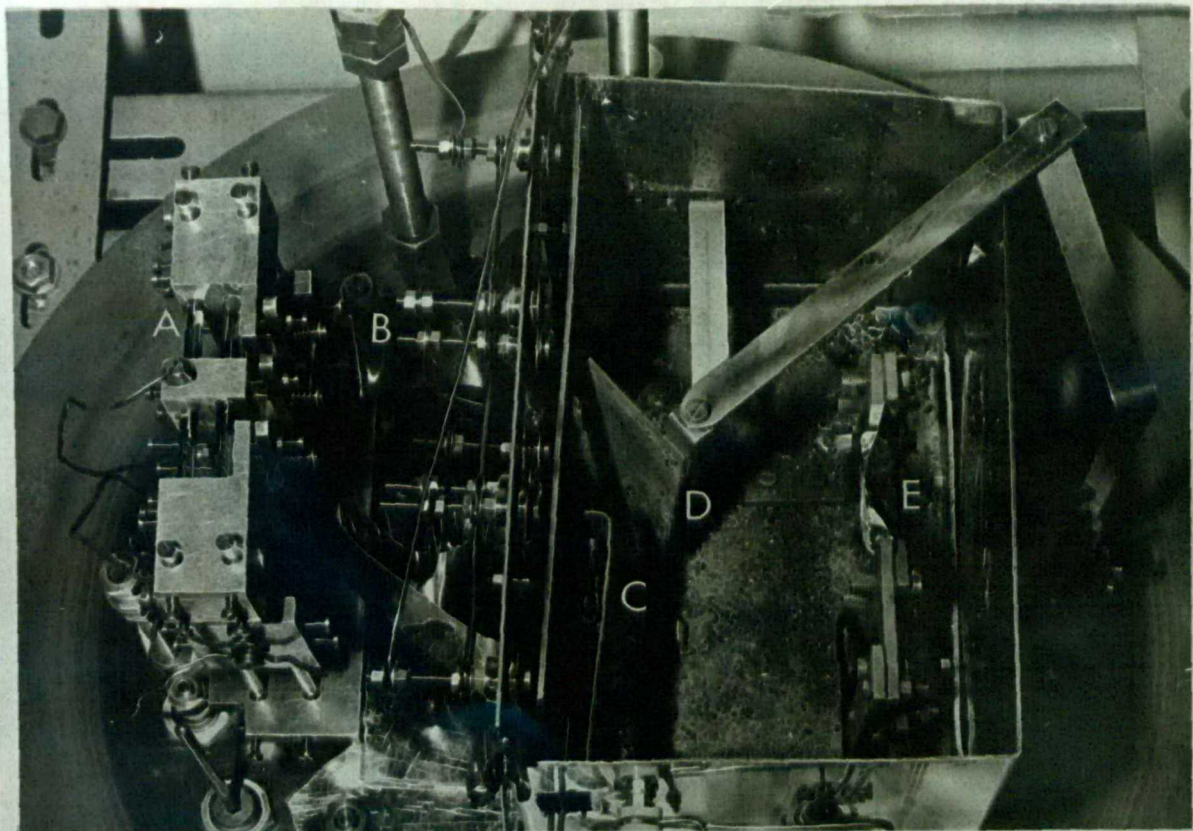


Plate 4.2

Plate 4.2 illustrates the apparatus inside the bell jar with the heat shield removed. A is the model iii jig; B the substrate heater; C the crystal rate monitor; D the shutter; and E the sources.

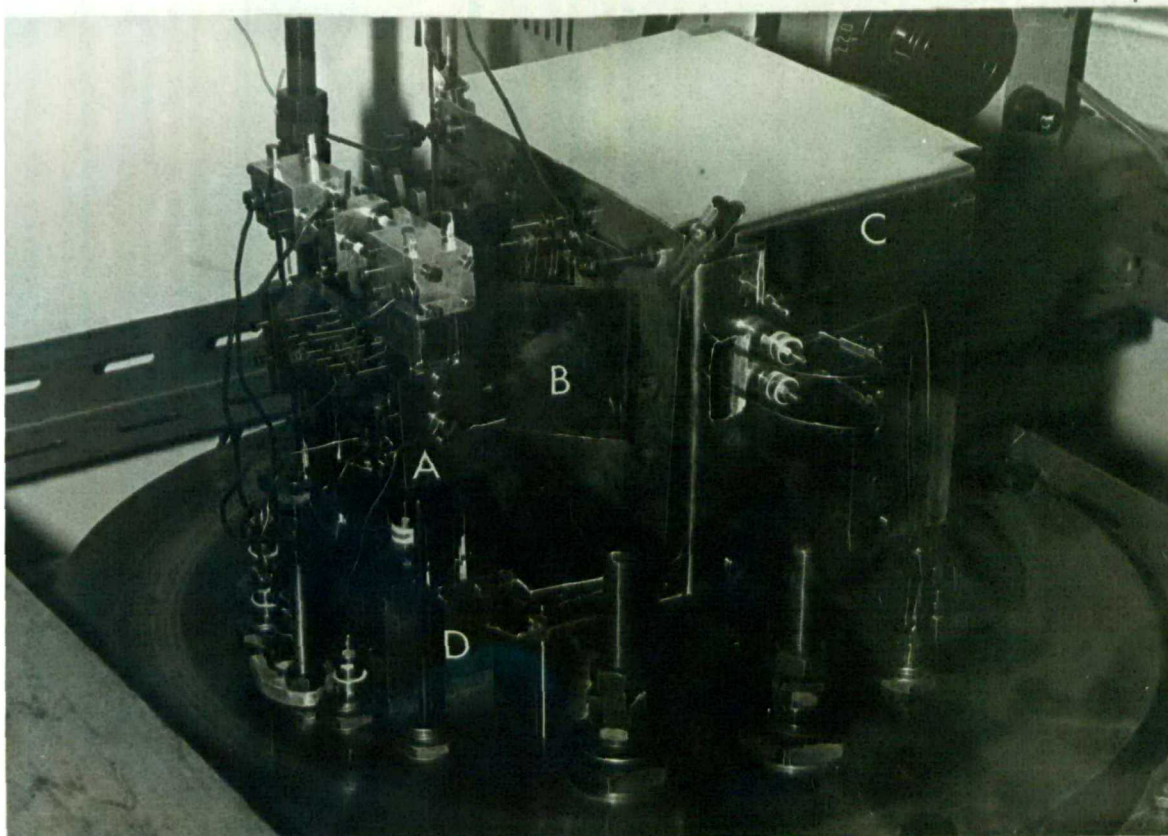


Plate 4.3

Plate 4.3 illustrates the apparatus inside the bell jar. A is the model iii jig; B the substrate heater; C the heat shield. The jig is mounted on stand D which is rigidly attached to the base plate.

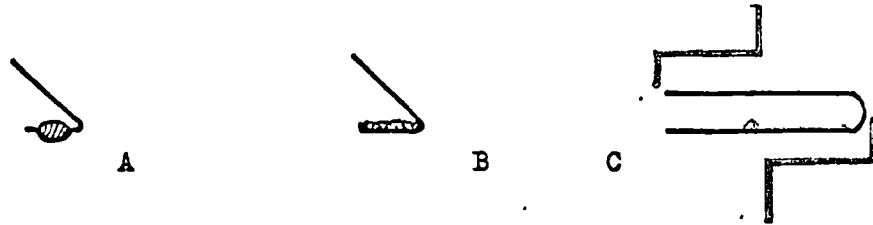


Figure 4.1 Evaporation sources, drawn life sized.
 A is a side view of the source used for the evaporation of silver or gold.
 B is the source used for silicon monoxide evaporation.
 C is the quartz tube source used for evaporating PbTe and SnTe. The spiral heater wire is a close fit around the quartz tube.

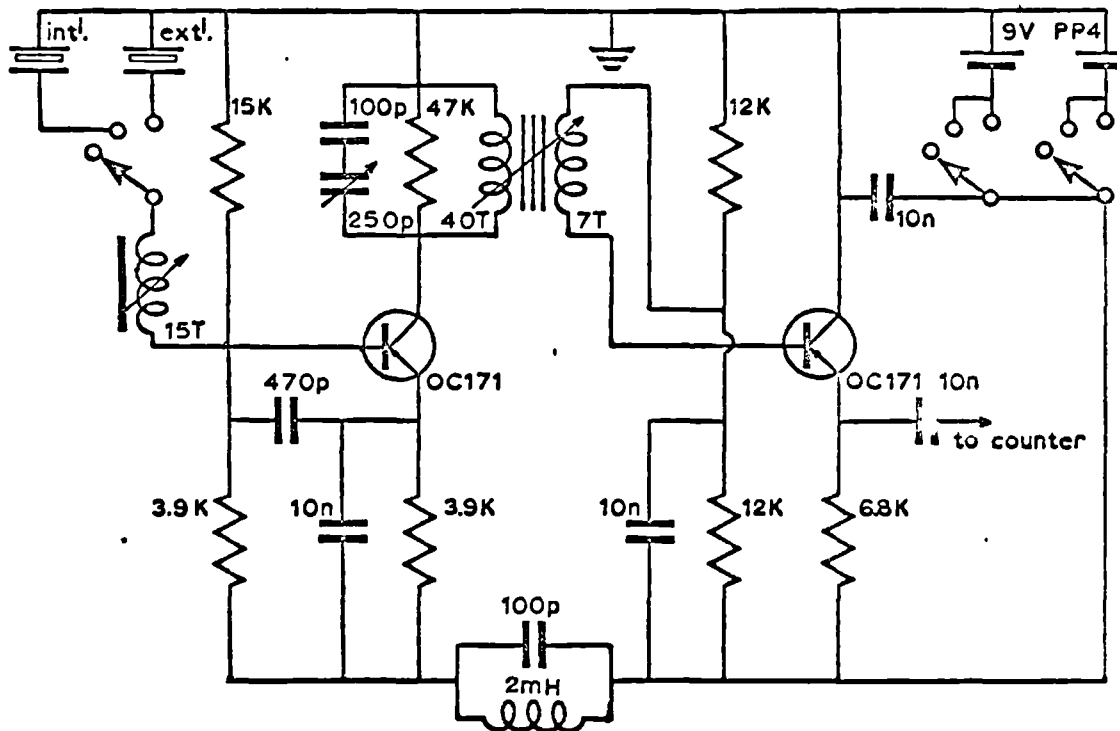


Figure 4.2 Circuit diagram of the quartz crystal film thickness monitor.

lip was added to the boats used for silicon monoxide evaporation to hold the powder and to prevent any line of sight path between the charge in the boat and the substrate. The evaporant is re-evaporated from the back of the source. The technique of re-evaporating from a hot strip was originally devised⁽²³³⁾ to reduce the incidence of pinholes in silicon monoxide films. PbTe and SnTe were evaporated from a quartz tube⁽²³⁴⁾ 0.2" in diameter by 1" long. It was enclosed in a tightly wound tantalum spiral heater wire. The source-substrate distance was 15 cm. The evaporation characteristics of the quartz tube source when used for lead telluride evaporations are illustrated in Figure 4.3. The source temperature and the evaporation rate, in units of Å/sec at the substrate, are given as a function of the heater current. The source did not give very uniform films. The variation in film thickness across the short edge of a 2" by 1" substrate was $\pm 7\%$ and across the long edge $\pm 15\%$. For silver and gold films the thickness variation was $\pm 5\%$ across the short edge and $\pm 10\%$ across the long edge.

The shutter was hinged, and rotated about a vertical axis. The sources were completely enclosed in an aluminium box when the shutter was closed (see Plate 4.3) to prevent unwanted radiation during the setting up of the evaporation rate.

4.4. RATE AND THICKNESS MEASURING APPARATUS

In the work reported on silver films deposited on to glass

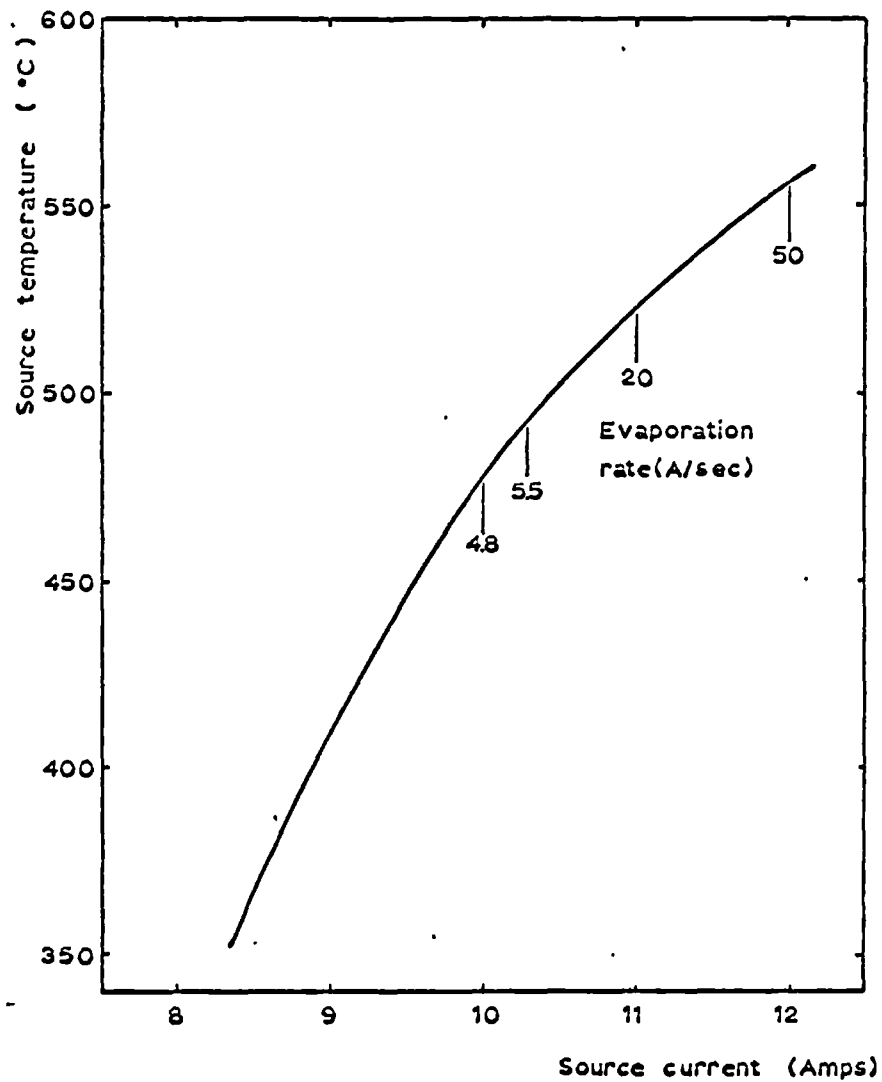


Figure 4.3 Source temperature and evaporation rate at the substrate as a function of the heater current for the quartz tube source.

substrates the rate of evaporation was indicated by a cylinder ratemeter⁽³²⁵⁾. This was constructed from an aluminium alloy 35 mm film can, etched to a weight of 2 gm and suspended from 9 inches of $\frac{1}{2}$ mil tungsten wire. The sensitivity of this apparatus was of the order of $10\text{-}20^\circ$ rotation per $\text{\AA}/\text{sec}$ at the substrate.

Table 4.1 is a comparison of the advantages and disadvantages of cylinder and crystal ratemeters. (Note. After the present work on silver films had been completed, Beavitt⁽²³⁶⁾ described a disc ratemeter, which retained the advantages of a cylinder ratemeter, while eliminating many of the disadvantages.)

In later work the evaporation rate was measured on an Edwards Crystal Film Thickness Monitor. The crystal, which was placed on the source side of the shutter, is visible in Plate 4.2.

The film thickness was measured on another crystal mounted on the jig adjacent to the substrate, and visible in Plates 3.3 and 3.4. The crystals for monitoring film thickness were AT cut government surplus types, unsoldered from their cans. The frequencies were from 5.5 to 6.5 MHz. The local oscillator circuit, which was a modification of an RCA circuit with an emitter follower added, because of the long lead to the counter, is given in Figure 4.2. The frequency was measured on a Hewlett Packard counter type 524C. The crystal was nude,

TABLE 4.1

A Comparison of Cylinder and Crystal Ratemeters.

The cylinder rate meter has the advantage that it is

1. Simple in design.
2. Cheap.
3. Bakeable.
4. No inlet electrodes required.
5. Measures rate of incidence of atoms.

It has the disadvantage that it has

1. Long time constant.
2. A starting inertia.
3. Does not return to starting deflection after an evaporation: 10% offset.
4. Mass of material landing on cylinder upsets balance, especially when cylinder is very light weight.
5. Assumes constant sources geometry, i.e. that it is so close to the source that a small change in position of the evaporant causes a large change in rate.
6. Rotation depends on source temperature.
7. Must use a light source to see position of cylinder, i.e. a table lamp.
8. Needs a large amount of chamber space, almost 12" by 3" by 3".

In comparison a crystal ratemeter has

1. Practically instant response.
2. 3% accuracy (manufacturers figure).
3. Easy to change crystal.
4. More sensitive than cylinder ratemeter, so can be further from source, and less dependent on source geometry.
5. Enables same rate to be set up in successive evaporations.
6. No table lamp, and less chamber space, so that evaporation source may be completely boxed in, thus reducing thermal problems.
- y. Very easy to read rate from meters, rather than from peering into bell jar.

but the frequency was stable to .4Hz in 5.9 MHz over half an hour. This stability is similar to that obtained by Haller and White⁽²³⁷⁾ who used a special water cooled enclosure to keep the crystal temperature constant.

4.5. SUBSTRATE HEATER

The substrate heater consisted of two pairs of vertical 10 mil tantalum or tungsten wires mounted in a nickel heat reflector, so as to heat the substrate by radiation from the front. A mask was arranged so as to shield the wires from the evaporant, while allowing the evaporant to land on the substrate (Plate 4.3). The maximum substrate temperature reached was about 250°C for a heater current of the order of 0.8 amp. When the substrate heater was first brought into operation it was found to affect the stability of the readings on the capacitance bridge. This trouble was finally traced to thermionic emission from the heater wires (Reference 238 pp 224-225). It was cured by biasing the whole bridge-recorder system 120 volts negatively with respect to earth. Biasing the heater positively was found to have little effect.

The radiant heat caused a deflection of the substrate for the reasons discussed in section 5.2.1. The substrate heater did not have a constant heat output, and the substrate deflection drifted considerably. A typical drift after a four hour stabilisation period was one full scale deflection of the recorder

pen in 20 minutes. The maximum tolerable drift during a measurement was of the order of $1/20$ full scale deflection per minute.

Attempts were therefore made to control the substrate temperature, with the dual objective of minimising drift when the substrate heater was used, and of keeping the temperature constant during an evaporation (see section 5.3.3.4.). A 40 swg chromel-alumel thermocouple was attached to the back of a substrate with a dab of colloidal graphite, and the output from this was used to control the heater current by means of

1. an Ether type 991 0-300°C on-off controller, and
2. an Ether type 992 proportional controller, 0-1,600°C

with a pilot amplifier type 570/3 and a 3 Kw saturable reactor with a 12:1 step up transformer. Typical charts are shown in Figure 4.4.

Under optimum conditions the proportional controller almost gave a small enough drift for high sensitivity stress experiments. However these optimum conditions were hard to achieve. It was not possible to control the temperature quickly enough to compensate for the radiant heat and latent heat pulse during an evaporation.

Reasonable control could possibly be achieved if the time response of the system was fast enough. Replacing the saturable reactor by a silicon control rectifier set, and decreasing the heating time of the substrate heater would both reduce the response time.

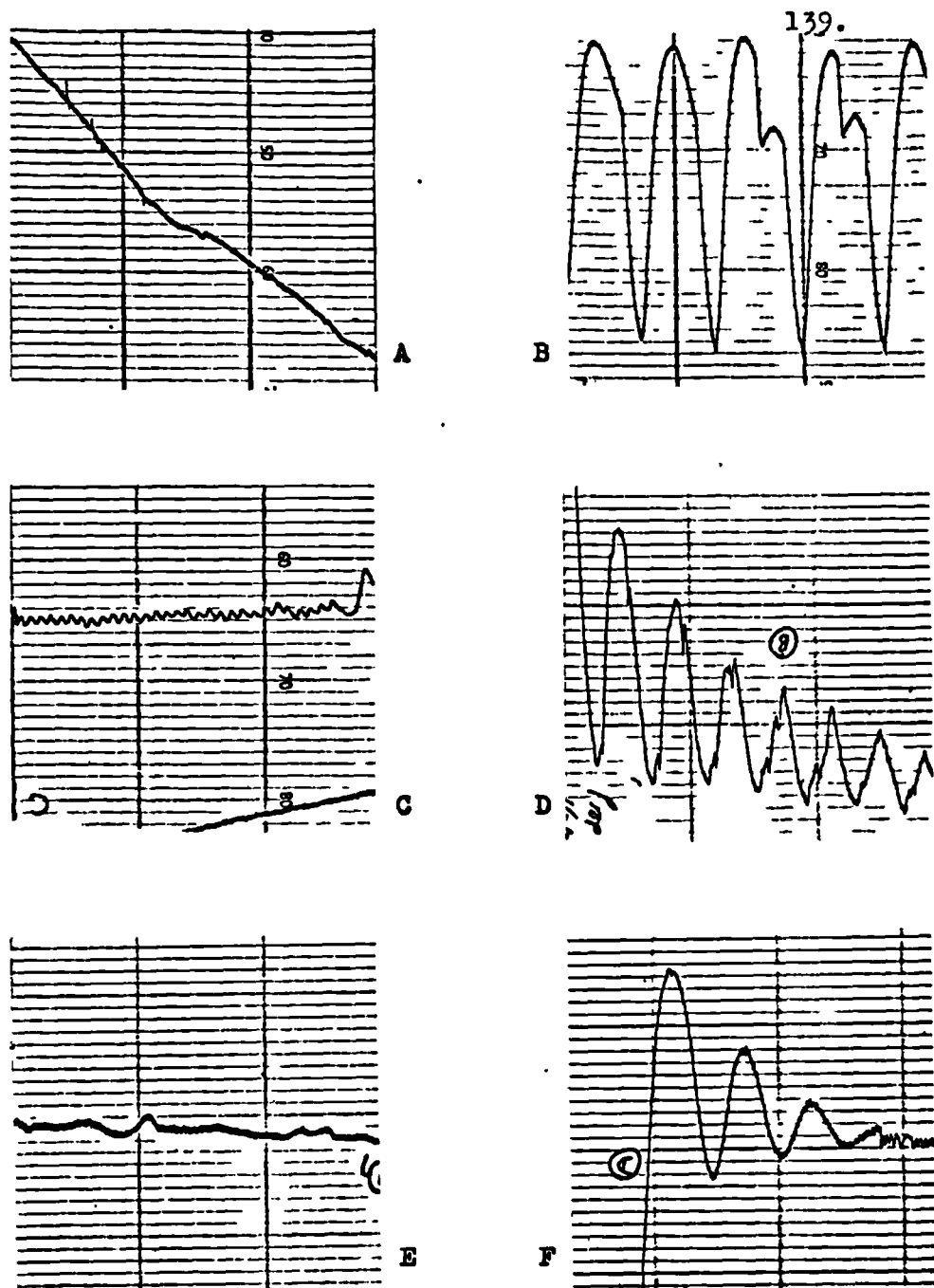


Figure 4.4 Typical charts obtained during the experiments on substrate temperature control.

- A** no control.
- B** on - off control.
- C** on - half off control.
- D** proportional control, typical setting.
- E** proportional control, best setting obtained.
- F** effect of exposing substrate to radiant heat from an empty boat when using proportional control.

C H A P T E R V

EXPERIMENTAL PROCEDURE

5.1. SUBSTRATE PREPARATION

5.1.1. Glass Substrates

The glass substrates were microscope cover slips, size 2" by 1" by 0.005" ($1\frac{1}{2}$ " by $\frac{7}{16}$ " by 0.0035)* made from Chance CMD soda-lime-silica glass. The manufacturer's analysis of this glass is given in Appendix 5.1. As supplied the thickness was uniform to $\pm 15\%$. They were selected for thickness uniformity to $\pm 2\%$ by thickness measurements, and by examination of the interference fringes formed between the front and back surfaces. Typical interferograms for 2" by 1" substrates are reproduced in Plate 5.1.

After ultrasonic cleaning in a dilute detergent solution, batches of six substrates were thoroughly rinsed in running distilled water, and then refluxed for 24 hours in a Soxhlet extractor charged with isopropyl alcohol. Immediately after cleaning the substrates passed the "water break test".⁽²³⁹⁾ That is, the glass surface dried uniformly after being held in running distilled water. This test is sensitive to about a monolayer of organic contamination. However the substrates were contaminated after two or three minutes exposure to the

*The first figures refer to the Model ii jig, and the figures in brackets to the Model iii jig.

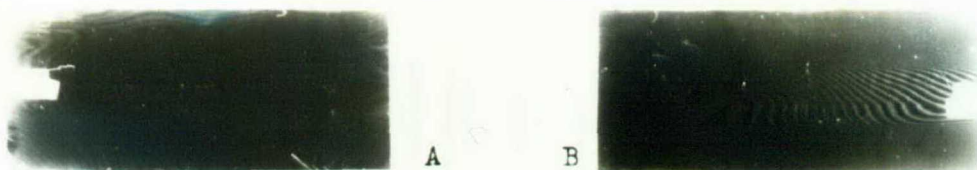


Plate 5.1 Interferograms formed in sodium light between the surfaces of 2" by $\frac{7}{8}$ " glass substrates, showing contours of constant thickness. Substrate A is uniform in thickness; substrate B is not.
x 1 magnification.

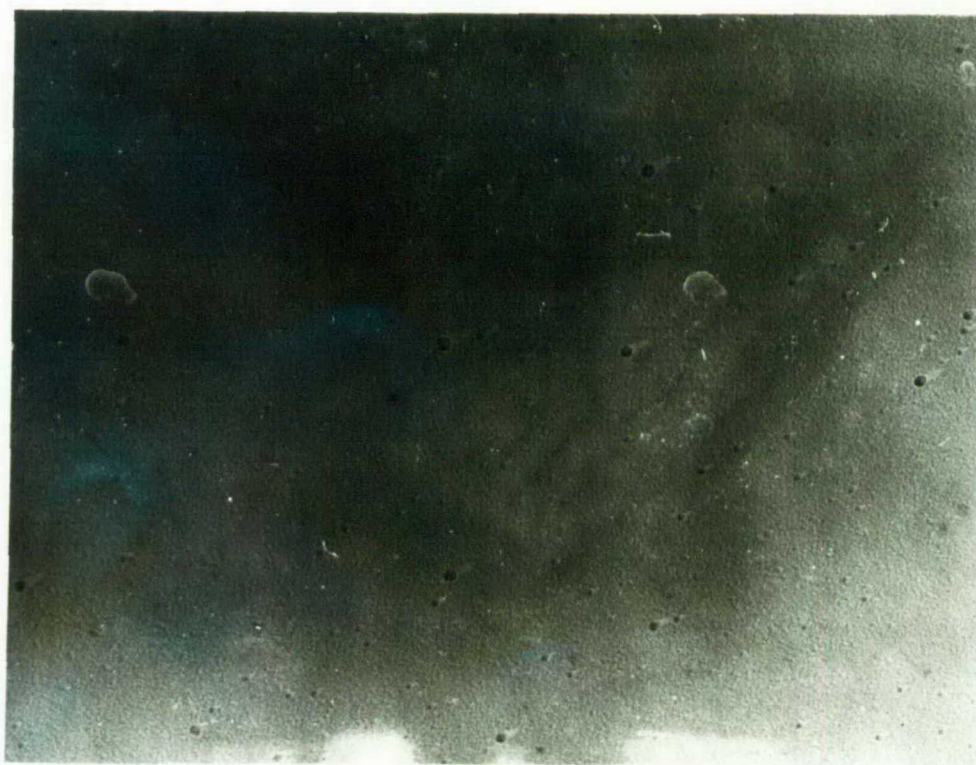


Plate 5.2 Platinum carbon replica of the surface of a glass substrate. x 48,000 magnification.

laboratory atmosphere. A platinum-carbon replica of a substrate surface is shown in Plate 5.2. The fine structure in the background is due to the replication process. The small particles are probably dust. The glass substrates, therefore, have a relatively smooth surface.

After cleaning the substrates were coated with the chromium conducting coating, which was evaporated as a powder from a tungsten strip in a vacuum of 2×10^{-5} torr, at a substrate temperature of about 130°C until the film became opaque to light (about $600\text{\AA}$). The substrates were then returned to the extractor until use.

5.1.2. Mica Substrates

Mica substrates were scratch free, best quality, die cut, ruby, muscovite mica, size 2" by 1" by 0.005" ($2\frac{1}{4}$ " by $\frac{7}{16}$ " by 0.007") from Mica and Micanite Ltd. They were coated with chromium in batches of ten, and were then cut to size and cleaved (to 0.005") with a Sharps No. 10 needle just before use. The crystallographic b-axis was found by viewing the mica between crossed polaroids, to find two angles for extinction. The mica was then pricked with a sharp needle to give the direction of the three fold symmetrical arrangement of atoms (Plate 5.3). The direction of cleavage which is parallel to one of the extinction axes is the b-axis.

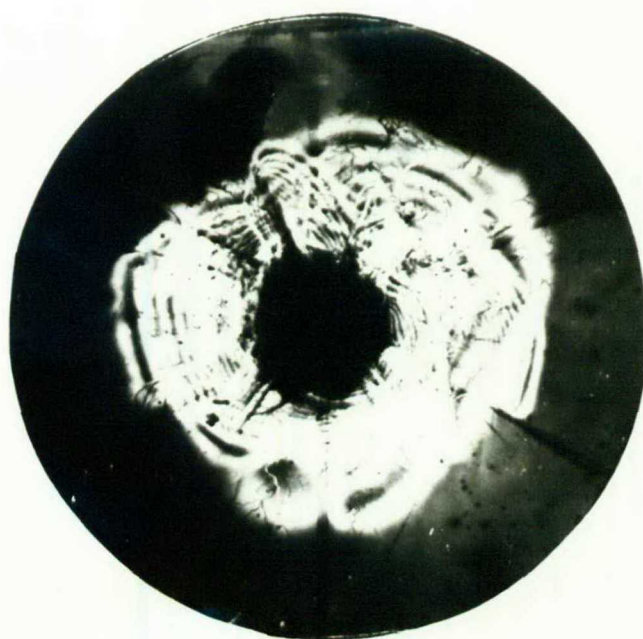


Plate 5.3 The effect of pricking a mica sample. The cleavages run parallel to the rows of potassium atoms in the mica surface. x 20 magnification.

5.1.3. The Evaporants

The silver used for evaporation was Johnson Matthey "spec-pure" silver. It was spectroscopically analysed by the Imperial College Analytical Services Laboratory where it was found to contain of the order of 5 ppm of Mg and Si and less than about 1 ppm of Cu and Fe.

The gold was also supplied by Johnson Matthey. Spectroscopic analysis by the above laboratory showed that it contained of the order of 5 ppm of Mg, Si and Fe and less than about 1 ppm of Cu.

5.2. EXPERIMENTAL PROCEDURE

5.2.1. Thermal cycling

Before making the stress determination the effect of thermal cycling was found for each substrate. The substrates were exposed to radiant heat from an empty boat which had previously been outgassed. They were then allowed to cool to room temperature. The effect of this was to cause a deflection of the substrate. The substrate deflection was monitored on the recorder, and the direction of deflection on heating, the magnitude of the deflection and the difference between the position of the end of the substrate before and after cycling was noted. This difference was significant in comparison with the deflection expected in a stress measuring experiment. The deflection due to heating and cooling is illustrated in Figure 5.2.

The deflection was due mainly to the difference in thermal expansion coefficient of the conducting film and the substrate although a contribution to the deflection could also arise from any temperature gradient across the substrate, and from any inhomogeneity in the composition of the glass. Chromium, with an expansion coefficient (6.8×10^{-6}), near to that of the glass substrates (7.3×10^{-6}), was chosen for the coating so as to reduce the total excursion of the substrate during heating.

The problem was overcome by clamping the substrate with a magnet, by hanging it vertically and by using chromium as the conducting coating. A small number of carefully annealed substrates, kindly lent by Mr. Carpenter, of the Plessey Co. Ltd., were coated with chromium in the usual way. They showed no significant improvement in reliability over unannealed slides. The glass substrates used in these stress determinations were, therefore, not annealed.

5.2.2. Evaporation Procedure

The maximum residual gas pressure during an evaporation was about $2 \cdot 10^{-6}$ torr for silver; $3 \cdot 10^{-6}$ torr for gold and $3 \cdot 10^{-7}$ torr for lead telluride.

All substrates were at room temperature at the start of the evaporations.

The chart speed was set to one inch per minute before and after an evaporation, but was increased to three inches per

minute during the evaporation.

The evaporation rate was set up on the rate monitor, and when it had become stable at the required value the shutter was opened and the substrate deflection was recorded continuously.

When the Model iii jig was used only one substrate at a time was connected to the bridge. The leads from the other two substrates were earthed. The initial capacity from each substrate was recorded in turn. Then the deflection during evaporation was followed in the middle substrate of the three. After the deflection had reached a stable value the other substrates were connected, and their capacity measured in turn.

A typical chart of deflection versus time during an evaporation is shown in Figure 5.1, and is discussed in section 5.3. After closing the shutter the deflection took between three and ten minutes to reach a stable value.

5.2.3. 'Pulsed' Experiments

In earlier ('pulsed') experiments only 20-200 $\text{\AA}$ thickness of film were deposited. After the substrate deflection had come to equilibrium the deflection on the chart was noted, and the process was repeated with another evaporation. Thus half a dozen to one dozen points of the force per unit width versus film thickness curve were obtained for each substrate. Because the points were from measurements on the same substrate they all lay on a relatively smooth curve. However this technique was

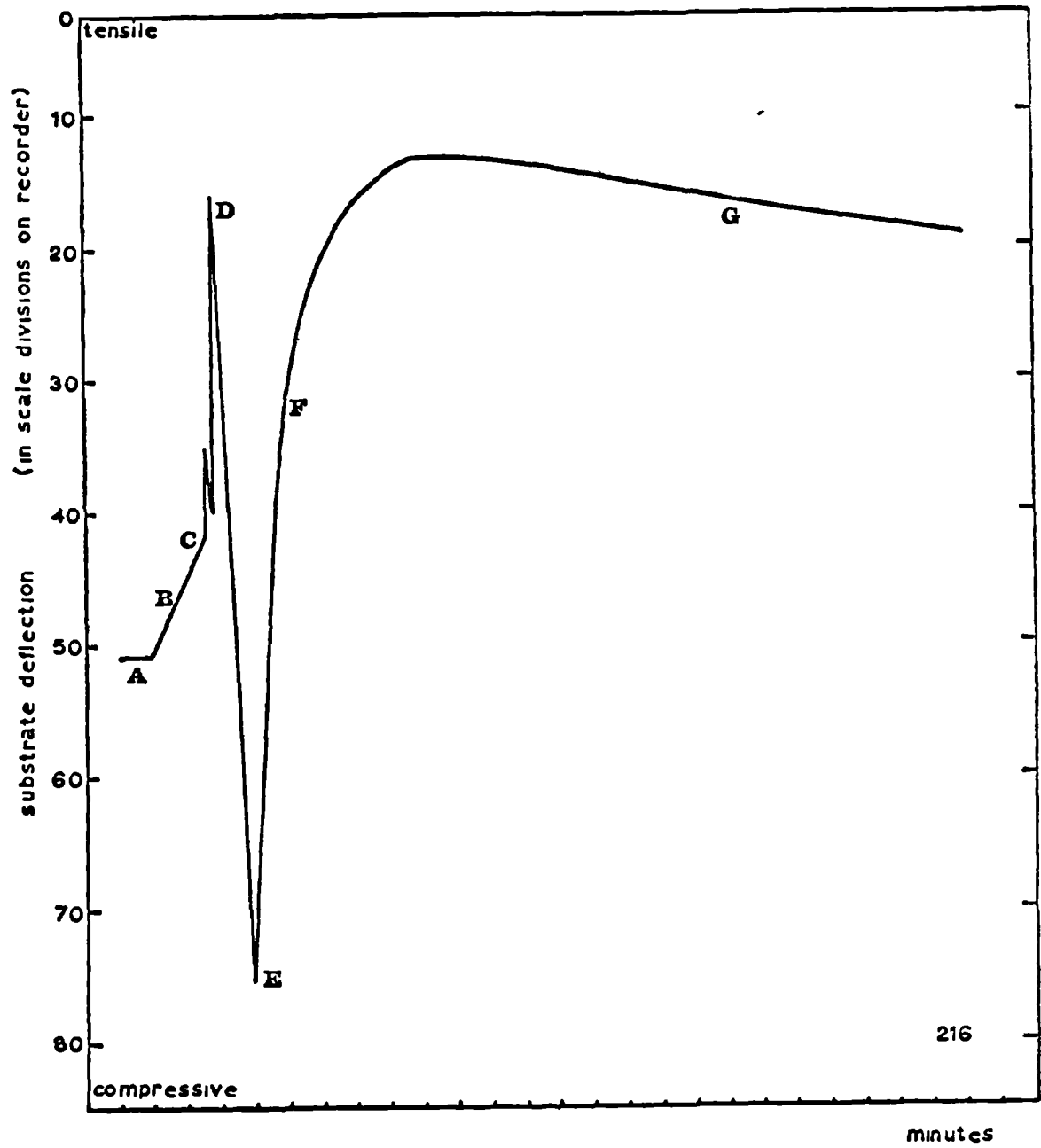
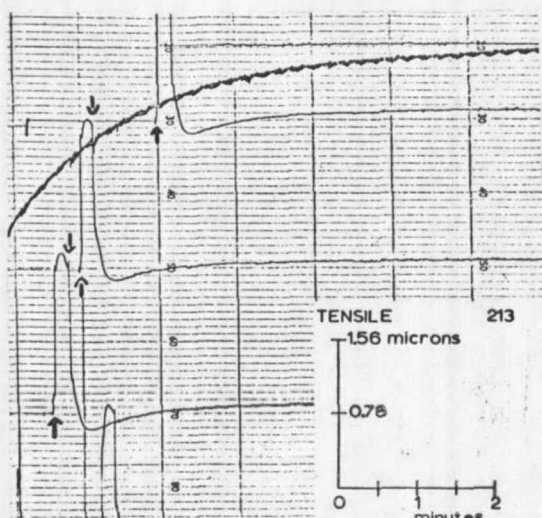
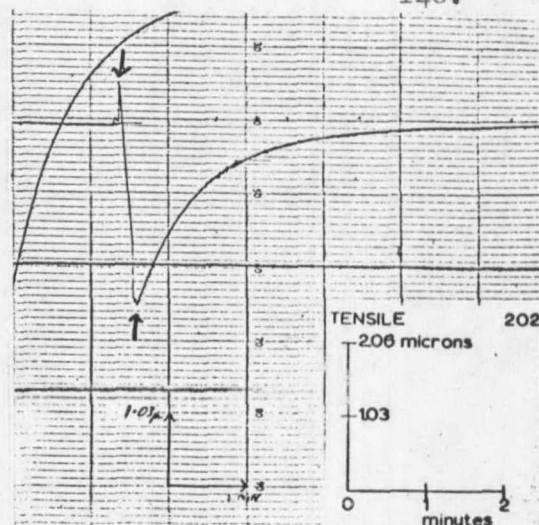


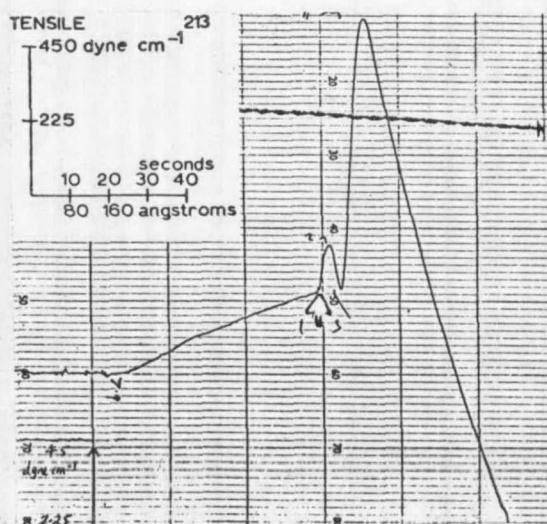
Figure 5.1 A typical chart, drawn to scale.



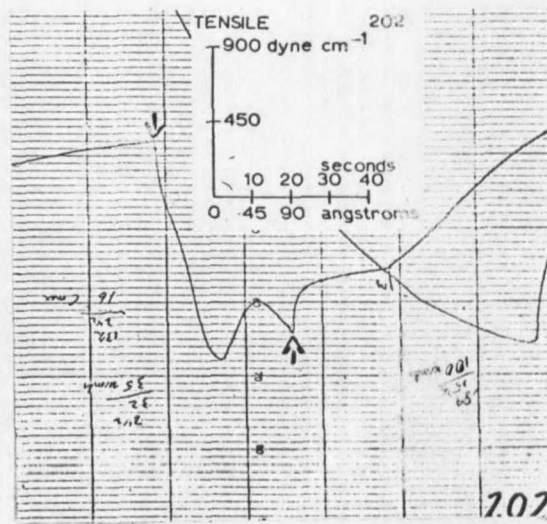
A



B



C



D

Figure 5.2. A,B:- Thermal cycling test. The arrows mark the point where the empty boat was brought up to the evaporation temperature, and the point where the current was turned off.

C,D:- Shape of the curve obtained during a typical deposition. Curves C and D obtained during deposition correspond respectively to curves A and B obtained during thermal cycling. The arrows mark the commencement of deposition.

rejected because of inherent inaccuracies.

The results obtained by this method are open to errors in both film thickness and stress values. The film thickness values, being determined by timing the duration of the pulse of evaporation, and by assuming constant rate over the series of experiments, is very dependant on small errors in rate during the evaporation. The values of rate were not reproducible from one pulse to the next because of limitations of the cylinder ratemeter, so that errors in the film thickness accumulated.

The stress values would not correspond to the values in a continuously evaporated film if stress relief occurred during the period the system took to come to equilibrium. However stress relief almost certainly occurred after the end of deposition (section 5.3.2). Contamination problems could also occur. If the deflection takes ten minutes to come to equilibrium, and if there are ten increments of thickness, then the film surface will have been exposed for almost two hours, in which time the surface would probably be contaminated.

5.2.4. Film Thickness Measurement

The frequency of the crystal thickness crystal took between three and ten minutes to become constant, and the value of frequency shift was taken as the difference between the initial value and the final constant value. The frequency shifts on the rate and thickness monitors were converted in to rate and

thickness measurements by independent calibration. A thick (2,500Å) film was evaporated and its thickness measured on the Talysurf⁽²⁴⁰⁻²⁴²⁾ in the usual way, after coating the step edge with a hard layer of silicon monoxide. Typical crystal r calibrations were 4 Hz per Å for Ag; 9 Hz per Å for Au; 4 Hz per Å for PbTe; and 1 Hz per Å for SiO. All thickness values were taken from the frequency shift of the thickness crystal, which was measured to the nearest Hz. As a check, some thicker experimental films were also measured on the Talysurf, and the values given by the crystal lay within the scatter on the Talysurf measurements.

At the time of the experiments on silver films the crystal thickness monitor had not been installed. After the stress measurement had been completed the lower half of the substrate was covered by a sliding shutter, and silver was condensed on the uncovered half at the same rate as that used during the evaporation, in order to give a sufficient thickness (>250Å) for the film to be measured on the Talysurf. Then the covered half of the substrate was exposed, and the rest covered, and a thin support film of silicon monoxide was evaporated for the electron microscopy specimens (section 5.2.5, (1)).

5.2.5. Structural Examination

The structure of the films was examined by transmission electron microscopy and selected area electron diffraction

on a JEM7 electron microscope. Various techniques were examined for preparing specimens. No technique was entirely satisfactory.

(i) Some specimens for examination were prepared by stripping the film which had been used for the stress determination from its substrate. After cutting up the glass substrate into conveniently sized pieces, a piece was exposed to HF fumes for $\frac{1}{2}$ -1 minute. The silver films, together with the support film was then floated off the glass substrate in distilled water, and picked up on an electron microscope grid in the usual way. It was examined in the electron microscope with as short a delay as possible, to minimise oxidation. However, structural damage (see section 6.1.5) was visible in these films.

(ii) Other specimens were prepared by using a film, already mounted on a grid, as a substrate, so that no damage to the film structure due to the stripping process would occur. Soda-glass was blown from a tube, and found to be almost electron transparent. After etching⁽²⁴³⁾ in a polishing etch, it became electron transparent, but was not thin enough for high resolution electron microscopy.

(iii) Silicon monoxide coated carbon was also tried. Carbon films, prepared by evaporating carbon on to mica substrates, were mounted on microscope grids. The grids were then mounted in a coating unit so that they could be shuttered off from the vapour stream in turn. Silicon monoxide was then evaporated on to the set of grids. The silver was evaporated without

breaking the vacuum, and the grids were shuttered off from the vapour stream one by one during the evaporation. Examination of these specimens showed some signs of structural damage.

(iv) Techniques (i), (ii) and (iii) may be criticised on the grounds that silver films become oxidised very rapidly when exposed to air. This oxidation affects the adhesion⁽²⁴⁴⁾ and the optical properties⁽²⁴⁵⁾ of silver films, and could affect the structure.

Therefore sets of films were grown in which a further layer of silicon monoxide was evaporated on top of the silver film to form a carbon-SiO-Ag-SiO sandwich. The resolution of the micrographs of such a sandwich was not as good as it might have been due to the thickness of the film. Little structural damage was observed.

When interpreting the micrographs produced by method (iv) it must be remembered that the structure of films grown on to silicon monoxide is not necessarily the same as the structure of such films grown on to glass substrates.

The micrographs to be presented in Chapter 6 were obtained by techniques (i) or (iv).

5.3. INTERPRETATION OF A TYPICAL CHART

5.3.1. Description of a Representative Chart

Figure 5.1 shows a typical chart plotted on a constant time scale. At point A before evaporation has begun, the

deflection on the chart is constant. During the setting up of the rate a deflection due to stray radiant heat was observed (B). This deflection was only large in earlier experiments such as this one when the cylinder ratemeter was being used, because then the source was not entirely shielded from the substrate. The shutter is opened at point C and the deflection passes through a number of turning points (e.g. D) until the shutter is closed at point E. The deflection at point E is on the compressive side of the origin, as discussed in the section 5.3.3.1. As the substrate cools to equilibrium the deflection becomes tensile (F), and it has become constant five minutes after closing the shutter. It was found, however, that if the recorder was left running the deflection started to drift towards minimising stress (at G) and that this drift was constant with time, with no sign of decreasing in rate even after half an hour. This drift was always found to be towards minimising stress except in one or two island structure films. The value of the end deflection used in the calculation of the stress was found by extrapolating the part of the chart G to give the end deflection that would have been present at the end of the evaporation.

5.3.2. Interpretation of the Drift

The drift is opposite in direction to the deflection during cooling, and it has an extremely long time constant. It is

therefore unlikely to be a cooling effect. Further evidence that it is not a cooling effect comes from specimens such as 523 which had a drift rate of 34 dyne cm^{-1} per minute, which had not altered appreciably after fifty minutes. For this specimen a change of temperature of 1°C would have caused a change in stress of 7 dyne cm^{-1} . Thus if the drift had been due to temperature, the temperature had fallen by 250°C without showing signs of coming to equilibrium.

Another possibility is that the drift is due to electrical or other drifts in the measuring apparatus. However the substrate deflection had been recorded for periods longer than 24 hours on more than one occasion, and the maximum drift rate found was 1.6 dyne cm^{-1} per minute.

A third possibility is that the drift is due to stress relief. It is known from electrical measurements that the structure of gold and silver films changes with time immediately after deposition. For instance, the electrical resistance of silver films has been found to decrease⁽²⁴⁶⁻²⁵¹⁾ or increase⁽²⁵²⁻²⁶⁰⁾ after deposition. Films of other metals (see for instance Ref. 261) also show similar effects.

The increase of resistance with time is usually found in discontinuous films, and is interpreted as agglomeration, whereas the decrease in resistance occurs in thicker films, and is interpreted as self annealing of defects (see section 2.3). Any change in film structure, such as these changes which affect

the electrical resistivity of the films, may be expected to cause, or to be caused by, a change in stress in the film. Thus it is not unlikely that stress relief is occurring in our films, and that the part of the chart marked G can be interpreted as showing stress relief.

In evaluating the chart it was assumed that the drift was due to stress relief. In order to obtain the stress that was in the film at the end of the evaporation, the part of the graph G, was extrapolated to give the substrate deflection at the instant the shutter was closed. It was not possible to ascertain if the drift was linear during the cooling period, F. Thus the masking of any stress change, during the first five minutes after an evaporation, by the larger cooling effect is a possible source of random error in stress measuring experiments.

5.3.3.1. Interpretation of Turning Points

Although the subsequent results on the stress in thin films do not depend on the interpretation of the turning points, such as D, in a typical chart, the thesis would be incomplete without some comment on their origin.

No two charts produced in these experiments were identical. However, when the deflection was tensile during thermal cycling tests (Figure 5.2 A) the substrate deflection at the start of the evaporation was also tensile, and charts such as Figure 5.2 C were produced. When the deflection was compressive during thermal cycling (Figure 5.2. B) charts such as D were produced

during the evaporation. Thus a significant contribution to the substrate deflection during evaporation arises from thermal effects.

A compressive stress was always indicated after a long enough evaporation. The compressive deflection arises from the difference in expansion coefficients of the evaporant and the substrate as the substrate heats up. The contribution from this cause will be discussed in section 5.5.

The last common feature of the charts was a minimum followed by a maximum (Figure 5.2 C,D). In the following sections it will be shown that the most likely origin of the maximum is the temperature gradient across the substrate, and the most likely origin for the minimum is the sum of the contributions from the stress in the film and the difference in expansion coefficient of the substrate and the chromium coating.

5.3.3.2. The Origin of the Maximum

A simple calculation⁽⁹²⁾ shows that, for the particular substrate geometry used in these experiments, a force per unit width of 9×10^3 dyne cm^{-1} would be recorded per degree centigrade temperature gradient across the substrate. Thus even a temperature gradient as small as 0.1°C would cause a deflection comparable to that due to the maximum stress observed.

The major contribution to the heat input raising the substrate temperature during an evaporation comes from radiation,

for the temperature rise of a substrate with a reflecting coating on the front is smaller than that of a fresh substrate, when deposition at a given rate is carried out.

Now, during a thermal cycling test a turning point was often observed in the deflection on heating, with a corresponding turning point on cooling, (Figures 5.2 A). This implies that the contribution to the deflection comes from two sources, which act in opposite directions. If the contribution with the longer time constant arises from the difference in thermal expansion coefficient of glass and chromium it agrees in sign with the direction of deflection expected from the published expansion coefficient values. If the shorter time constant contribution arises from a temperature gradient across the substrate, it implies that the back of the substrate is hotter than the front. This is likely as the chromium film absorbs, and the glass substrate transmits, the radiant heat.

At the end of an evaporation, when a continuous film has been deposited, any heat absorption will occur at the front of the substrate, so that the front will be at a higher temperature than the back.

Thus the temperature gradient across the substrate may reverse during an evaporation. If it does, the deflection produced is of the correct sign to explain the maximum found in typical charts.

5.3.3.3. Origin of the Minimum

The contribution to the substrate deflection from the intrinsic stress, and the contribution to the substrate deflection from the difference in thermal expansion coefficient of the chromium coating and the substrate tend to deflect the substrate in the opposite direction. Taken together, their magnitudes could explain the minimum always observed in the chart recordings.

5.3.3.4. Summary

The explanations put forward for the turning points are the most satisfactory found so far. In order to eliminate the contributions to the deflection from thermal sources, the substrate temperature must be kept constant during an evaporation. The only way to do this is to use refined temperature control methods, such as those described in section 4.5.

5.4. YOUNG'S MODULUS DETERMINATION

5.4.1. Introduction

In a bending beam experiment a knowledge of the elastic constants of the substrate is necessary to relate the stress in the film to the deflection of the beam. For a beam of material with isotropic elastic properties it is necessary to know both the Poisson's ratio and the Young's modulus of the beam material.

Poisson's ratio has been neglected in stress experiments

until recently, but where the Poisson's ratio correction has been applied a value for ν of 0.2 or 0.25 has usually been taken. As it appears in a $(1-\nu)$ or a $(1-\nu^2)$ form, the error due to a 25% difference in ν is less than 10%. In the present work ν has been taken to be 0.25 for both glass and mica. This figure is reasonable for the high soda content glass used for substrates, as Poisson's ratio increases with soda content and is 0.19 for silica⁽²⁶²⁾. The same figure is also reasonable for mica substrates, where its measured value⁽⁸⁷⁾ was 0.23 ± 0.02 .

The Young's modulus of the beams was determined either by applying a known force to the end of the beam and noting the resultant end deflection, or by measuring the natural resonant frequency of flexural vibrations of the substrate.

In the former method the force was one of electrostatic attraction, and was obtained by applying a potential difference of the order of 100 volts across the jig. For the normal substrate geometry this caused a force of about 5 mg on the end of the beam, which for a 150 micron thick substrate yielded a 7 micron end deflection. This was easily detectable on the capacitance bridge. The circuit was such that the applied potential difference did not affect the bridge reading. A typical graph of change in capacity due to the electrostatic field versus the square of the charge on the plates showed the straight line relationship expected.

However, this result was obtained on the 2" by $\frac{7}{16}$ " substrates; on the 2" by 1" substrates the results obtained were not reproducible, so, even though this method had several advantages over the vibrating reed method, the latter was developed and used for Young's modulus determination.

5.4.2. The Vibrating Reed Method

5.4.2.1. Apparatus

The block diagram of the apparatus designed and built to make the measurements appears in Figure 5.3. The substrate was excited into vibrations by an alternating electrostatic field, applied as above across the jig. The exciting potential was produced by a low frequency sine wave oscillator capable of delivering 150 volts. The amplitude of the vibrations of the substrate was measured by an off-resonance oscillator technique. The circuit is drawn in Figure 5.4. The output of the oscillator consisted of a high frequency (4.5 MHz) signal amplitude modulated by a signal of depth and frequency corresponding to the amplitude and frequency of vibration of the substrate. After rectification the amplitude of the modulation signal was read on a valve voltmeter. The choice of frequency (4.5 MHz) was determined by the only radio crystal available at the time. The high and low frequency signals were separated by a filter network. Plate 5.4 is a general photograph of the apparatus.

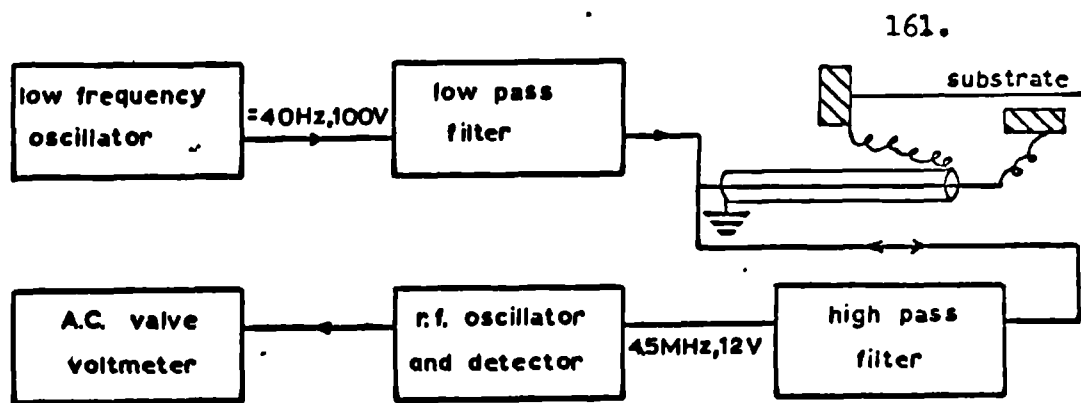


Figure 5.3 Block diagram of the apparatus used to measure the substrate Young's modulus.

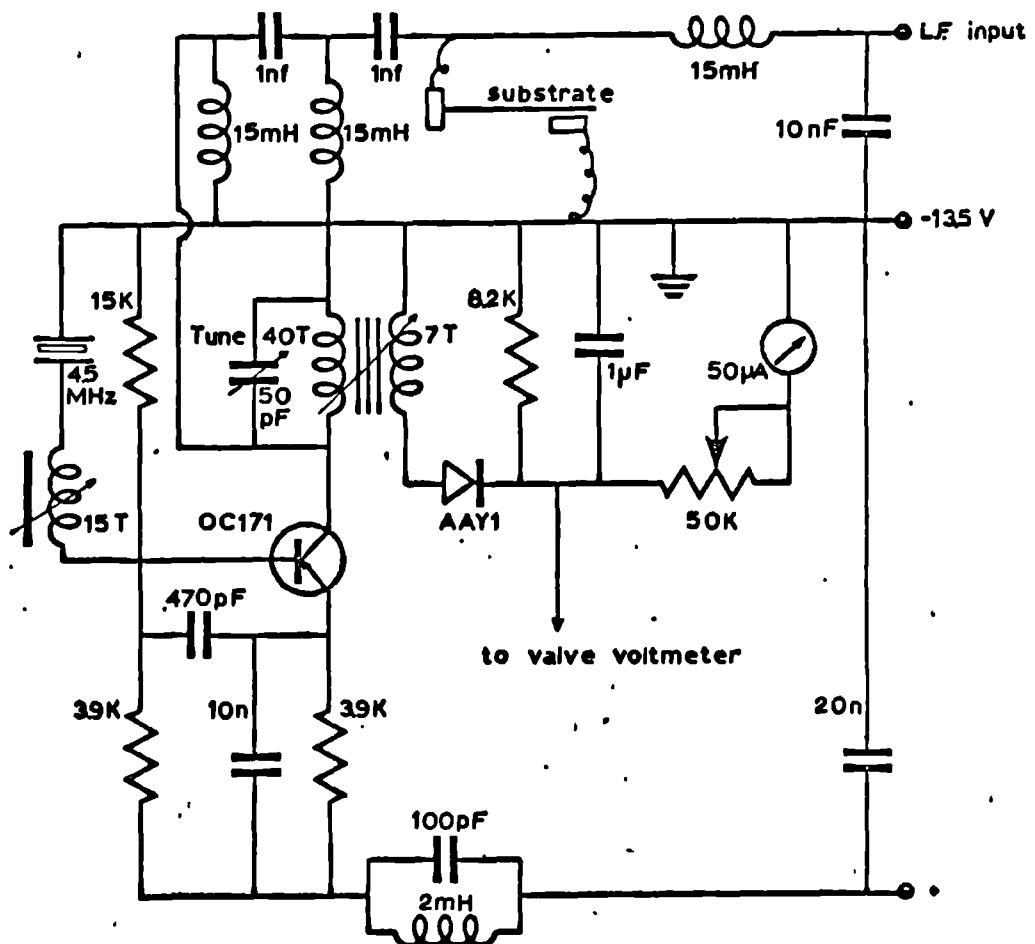


Figure 5.4 Circuit diagram of the apparatus used to measure the substrate Young's modulus.

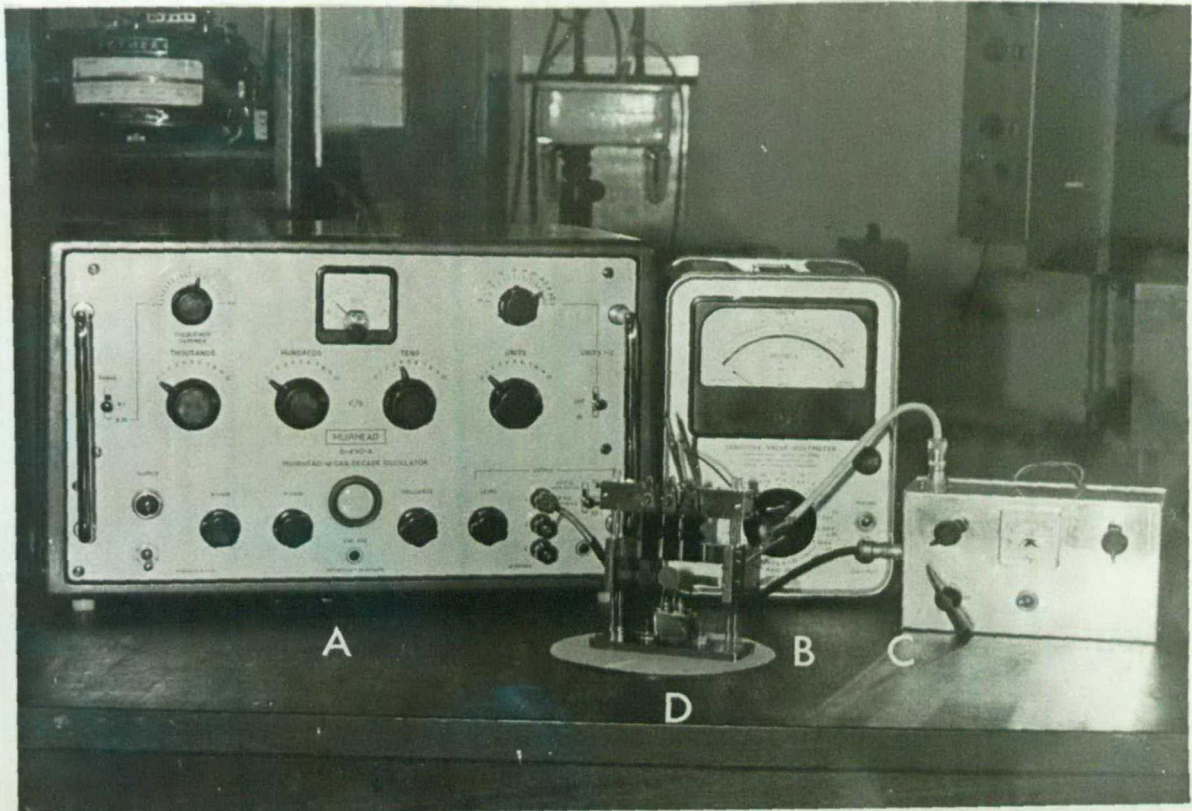


Plate 5.4

Apparatus for the measurement of the substrate Young's modulus by the vibrating reed method. A is the low frequency oscillator; B is the valve voltmeter; C is the crystal oscillator and detector circuit; and D is the model iii jig.

5.4.2.2. Experimental

The low frequency oscillator was calibrated against its internal crystal frequency standard at $33\frac{1}{3}$, 40 and 50 Hz. The usual frequency range was 40-60 Hz. The tank circuit was tuned off resonance until the r.f. output, as indicated on the meter, was about 60% of its maximum value. The exciting signal was then increased, and the resonance found at the point where the reading on the valve voltmeter, V , passed through the maximum. The exciting amplitude was adjusted so that V was of the order of 10 mV. A plot of V against the exciting frequency showed a sharp maximum at a frequency w_s where $2w_s$ is the natural vibrational frequency of the substrate. The factor of 2 is necessary because the substrate is attracted towards the reference electrode in both the positive and the negative half cycles of the signal.

5.4.2.3. Theory

The derivation of the relationship between natural vibrational frequency and Young's modulus of a beam has been given by Lamb⁽²⁶³⁾ and by Wood⁽²⁶⁴⁾. By considering the forces acting on an element of the beam the equation of motion,

$$\frac{d^2y}{dt^2} + \frac{h^2 E \cdot d^4y}{12 \rho dx^4} - \frac{h^2 \cdot d^4y}{12 dt^2 dx^2} = 0 \quad (5.1)$$

is found. The co-ordinates are defined in Figure 3.7; h and E are defined in Section 3.3.1; ρ is the density of the substrate; and t is time. It can be shown that the third term may be neglected for small amplitude vibrations. After separating the variables the equation may be solved graphically. Wood⁽²⁶⁴⁾ has pointed out that a more accurate solution than that found from the graph is

$$f = (1.19372)^2 \cdot \frac{\pi^2}{8} \cdot \frac{h}{l^2 \sqrt{12}} \sqrt{\frac{E}{\rho}} \quad (5.2)$$

If f now refers to the frequency as measured on the oscillator, and if h is in microns, then

$$E = 1.533 \cdot 10^{10} \cdot \frac{f l^2}{h} \quad (5.3)$$

5.4.2.4. Results

The plot of V versus w_s for specimen number 359 is reproduced in Figure 5.5. Although the frequency could usually be measured to 0.1 Hz the maximum was not always as sharp as the one shown, particularly at frequencies below about 30 Hz, where accurate measurements were impossible. It was not easy to deduce the amplitude of the vibrations of the substrate during the measurements. However, dropping a 20 mg weight on the end of the beam suggested that it was about

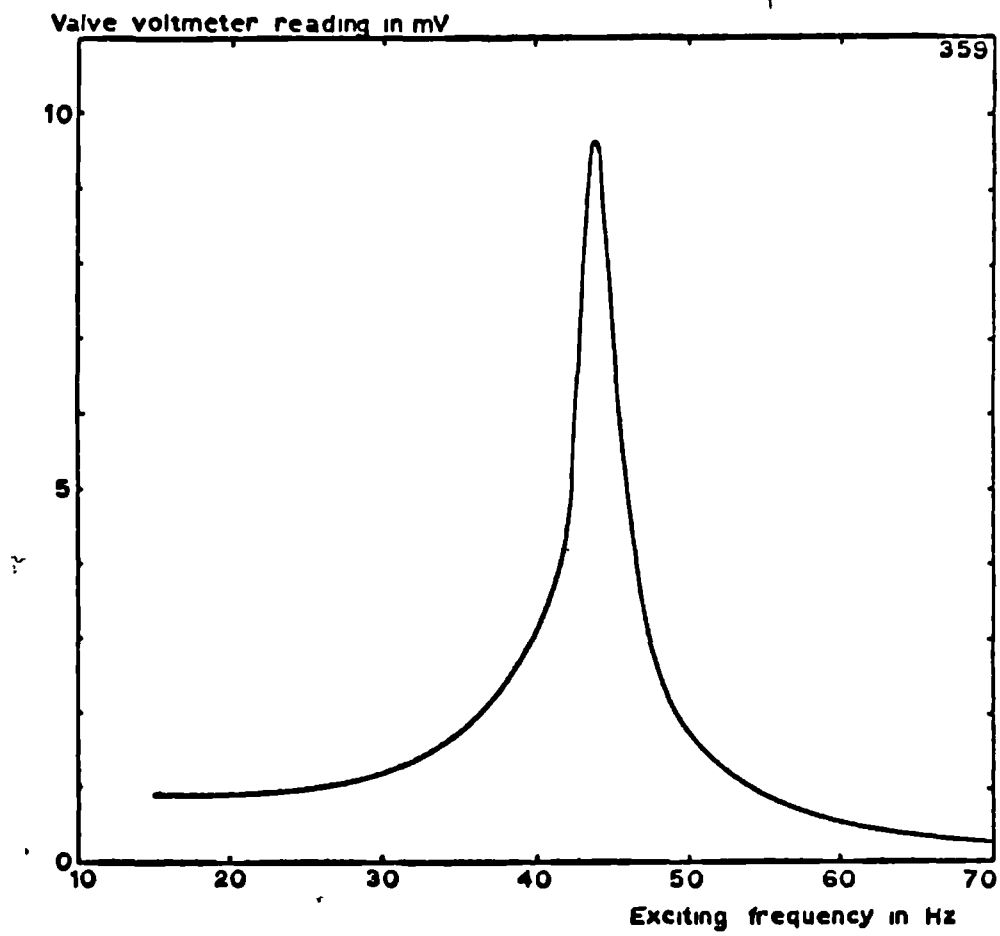


Figure 5.5 Resonance curve for specimen 359

10 microns, which is well within the amplitude for the theory to apply.

The effect of the amplitude of the exciting signal on w_g is illustrated in Figure 5.6. Increasing the amplitude of the signal decreases w_g . However, the effect is small, and it is clear from these curves that the frequency should be accurate to within 0.5 Hz in 50 Hz, or 1%.

An attempt was made to find the effect of the substrate clamping pressure on the Young's modulus of mica substrates, but no significant effect was found.

5.4.3. Conclusions

The value of Young's modulus obtained for glass and mica substrates are given in the Table 5.1. A value of 5.0×10^{11} was used in the computation of the results of stress measurements on glass substrates, and a value of 12.3×10^{11} dyne cm^{-2} for stress measurements on mica substrates.

	<u>Density</u>	<u>Number of Substrates</u>	<u>E dyne cm^{-2}</u>	<u>Standard Deviation</u>
Glass	2.48 ⁽²⁶⁵⁾	12	5.19×10^{11}	0.17×10^{11}
Mica	2.75 ⁽²⁶⁶⁾	70	12.31×10^{11}	1.11×10^{11}

Table 5.1 Experimental values of Young's modulus for
glass and mica substrates.

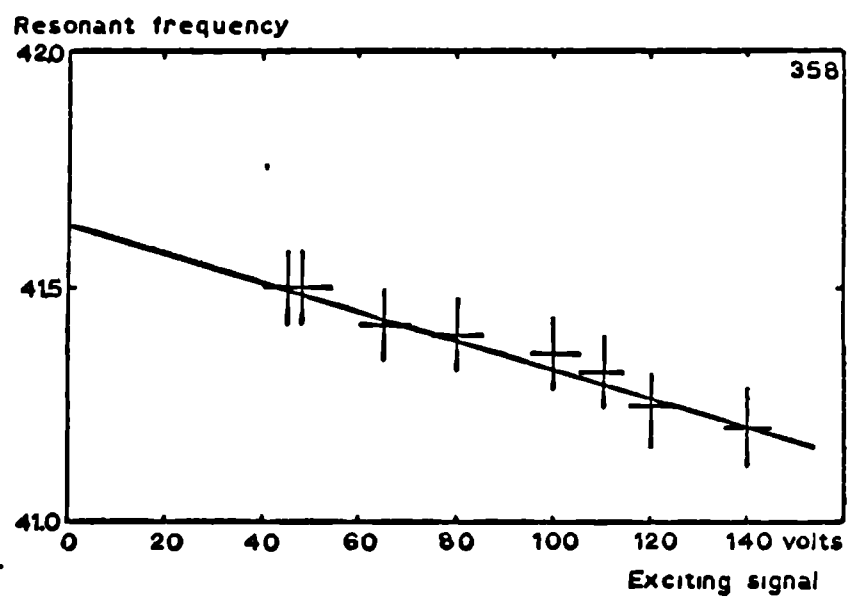
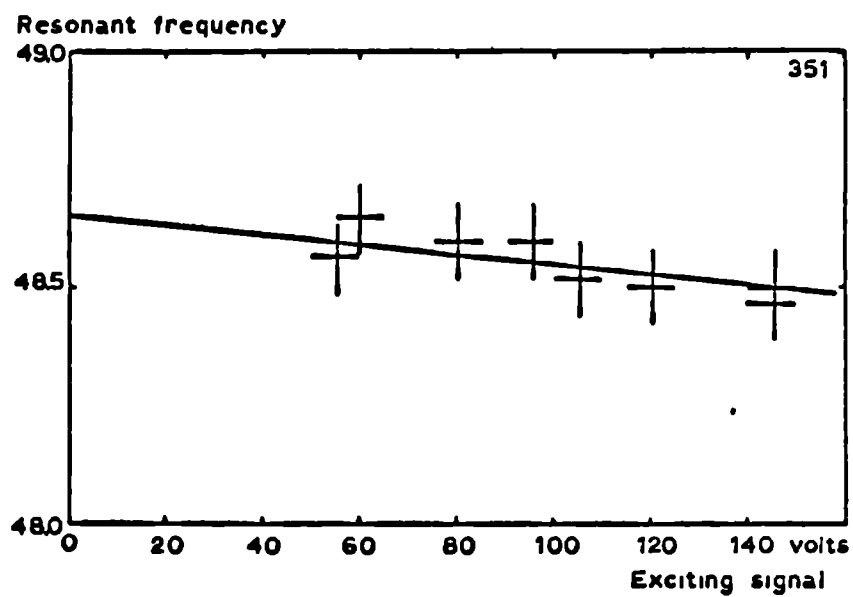


Figure 5.6 The effect of the amplitude of the exciting signal on the resonant frequency.

5.5. THERMAL STRESS CORRECTION

The substrate temperature increase during an evaporation was due to radiant and latent heat inputs. This caused a thermal stress to be present in the film, in addition to the intrinsic stress. As mentioned in section 1.2 this thermal stress must be calculated and subtracted from the total stress to give the intrinsic stress.

Assume that at any instant during an evaporation the substrate and the film are at the same temperature. This temperature will increase during evaporation, so that the temperature of a given layer of film will increase with time as further layers are deposited on top of it. If, as in the present case, the thermal coefficient of expansion of the film material is greater than that of the substrate, the temperature rise will cause a compressive deflection. This compressive deflection was observed in all the experiments performed.

Consider, then, the deflection versus time curve for a film with no intrinsic stress (Figure 5.7). There will be a compressive deflection S_{end} at the end of the evaporation, and a final thermal stress, S_{th} which is the quantity to be calculated.

Let the ambient temperature be T_0 and the substrate temperature at the end of the evaporation T_f . Let the substrate temperature at time t be T . Let the final film thickness be f and let the film thickness at time t be z .

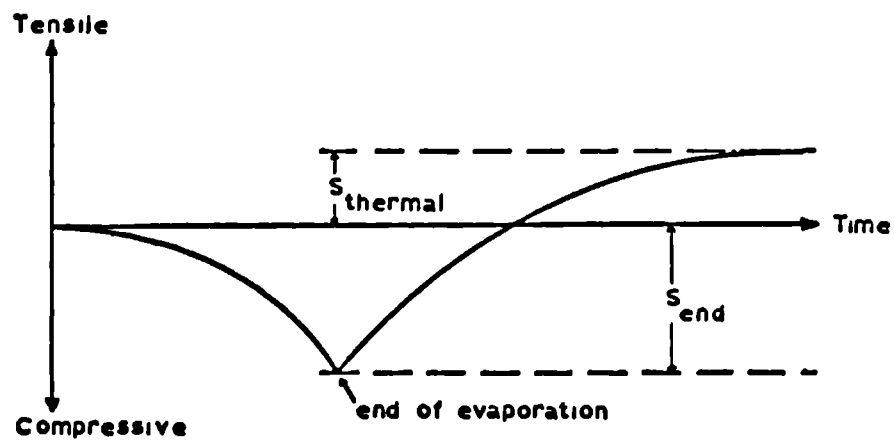


Figure 5.7 End deflection versus time curve for a substrate during the evaporation of a film with no intrinsic stress. The only contribution to the substrate deflection arises from thermal stress.

Let the Young's modulus of the film be E , and the difference in thermal expansion coefficients of the film and the substrate be $\Delta\alpha$ and the rate of evaporation, (constant) R .

Case 1 Assume that the temperature rises linearly with time. Then:-

$$\frac{T - T_o}{z} = \frac{T_f - T_o}{f} \quad (5.4)$$

The force per unit width in a lamina of film thickness dz on cooling from T to T_o is⁽¹³²⁾:

$$E\Delta\alpha(T - T_o) dz \quad (5.5)$$

The total force per unit width in a film thickness f is given by:

$$S_{th} = \int_0^f E\Delta\alpha(T - T_o) dz \quad (5.6)$$

$$= \frac{1}{2} E\Delta\alpha(T_f - T_o) f \quad (5.7)$$

Case 2 Assume that the temperature rises exponentially with time, as found in practice.

Then:-

$$T - T_o = T_{\infty} (1 - \exp(-t/\tau)) \quad (5.8)$$

$$T_f - T_o = T_{\infty} (1 - \exp(-t'/\tau)) \quad (5.9)$$

where t' is the time of evaporation, and τ is the time constant.

From Equation 5.6:-

$$S_{th} = \int_0^f E\Delta\alpha(T - T_o) dz \quad (5.10)$$

$$= \int_0^f E\Delta\alpha.T_{\infty} (1 - \exp(-z/Rt)) dz \quad (5.11)$$

$$= E\Delta\alpha T_{\infty} f (1 + \tau(\exp(-t'/\tau) - 1) / t') \quad (5.12)$$

By a similar method it may be shown that:-

$$S_{end} = E\Delta\alpha T_{\infty} (\tau(1 - \exp(-t'/\tau)) / t' - \exp(-t'/\tau)) f \quad (5.13)$$

where S_{end} is the contribution to the deflection during the evaporation (section 5.3.3.1).

5.5.2. Computation

Values of temperature rises observed for silver and gold and lead telluride films are given in Table 5.3. Using these values, and those in Table 5.2 the thermal stress correction for silver and gold films evaporated on to glass substrates has been plotted in Figure 5.8 and the thermal stress correction for lead telluride films evaporated on to mica substrates has been plotted in Figure 5.9

	Young's Modulus	Ref.	Coefficient of expansion	Ref.
Silver	7.9×10^{11}	267	18.1×10^{-6}	270
Gold	8.0×10^{11}	267	13.9×10^{-6}	270
PbTe	6.75×10^{11}	268	17×10^{-6}	271
Glass	5.19×10^{11}	269	7.3×10^{-6}	265
Mica	12.3×10^{11}	269	8.5×10^{-6}	272
Chromium			6.8×10^{-6}	267

Table 5.2: Data required for the thermal stress calculation.

Material	Rate	T	τ
Ag	3Å/sec	28°C	26.5 seconds
Ag	6Å/sec	23°C	16 seconds
Ag	30Å/sec	17°C	10 seconds
Au	5Å/sec	38°C	10.5 seconds
PbTe	5Å/sec	7 or 8°C	29 or 30 seconds
PbTe	15Å/sec	7 or 8°C	29 or 30 seconds

Table 5.3: Observed temperature rise in films evaporated on to glass (Au, Ag) and mica (PbTe) substrates.

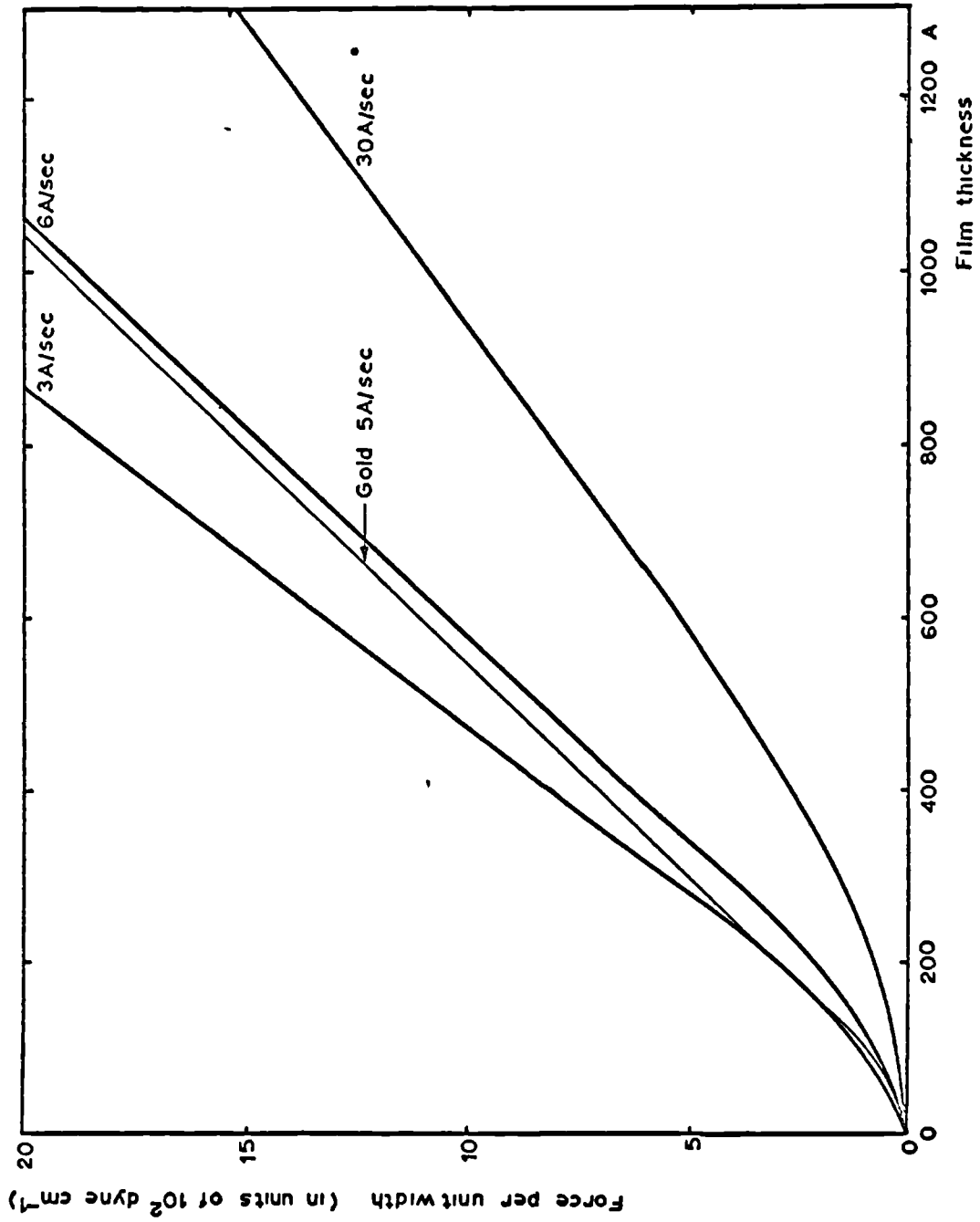


Figure 58 Thermal stress correction for silver films Force per unit width versus film thickness

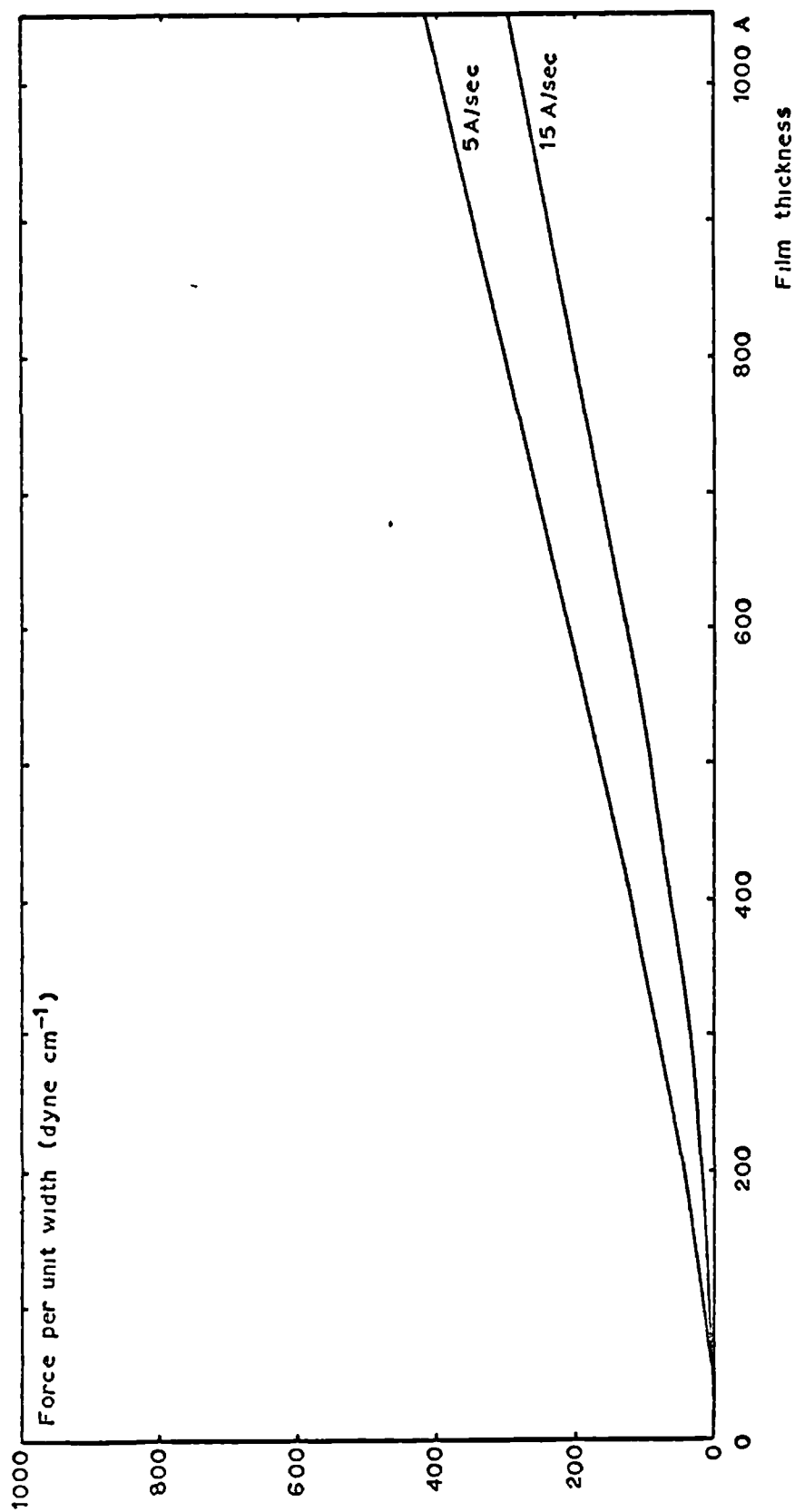


Figure 5.9 Thermal stress correction for lead telluride films.

CHAPTER VI

RESULTS

6.1. STRESS IN SILVER FILMS DEPOSITED ON TO GLASS SUBSTRATES

6.1.1. Introduction

The object of the work on stress in polycrystalline silver films was to confirm previous results on stress in silver films, and then to extend these results by measuring the stress in discontinuous and island structure films. Seventy five glass substrates were used in conjunction with the Model iii jig.

Section 6.1 is divided into two parts. The first deals with 'pulsed' experiments. The second deals with the results of the continuous deposition experiments.

6.1.2. 'Pulsed' Experiments

The overall results of the 'pulsed' experiments are reproduced in Figure 6.1. Although there is a fair measure of agreement in the film thickness range below about $100\text{\AA}$ above this film thickness the results diverge. This is illustrated in Figure 6.2 in which two results under similar preparation conditions are compared. The only difference between the results was the pulse length, which was in $50\text{\AA}$ increments for Specimen 193 and in $150\text{\AA}$ increments for Specimen 194. The stress in the film with the shorter pulse

Force per unit width (in units of $10^2 \text{ dyne cm}^{-1}$)

177.

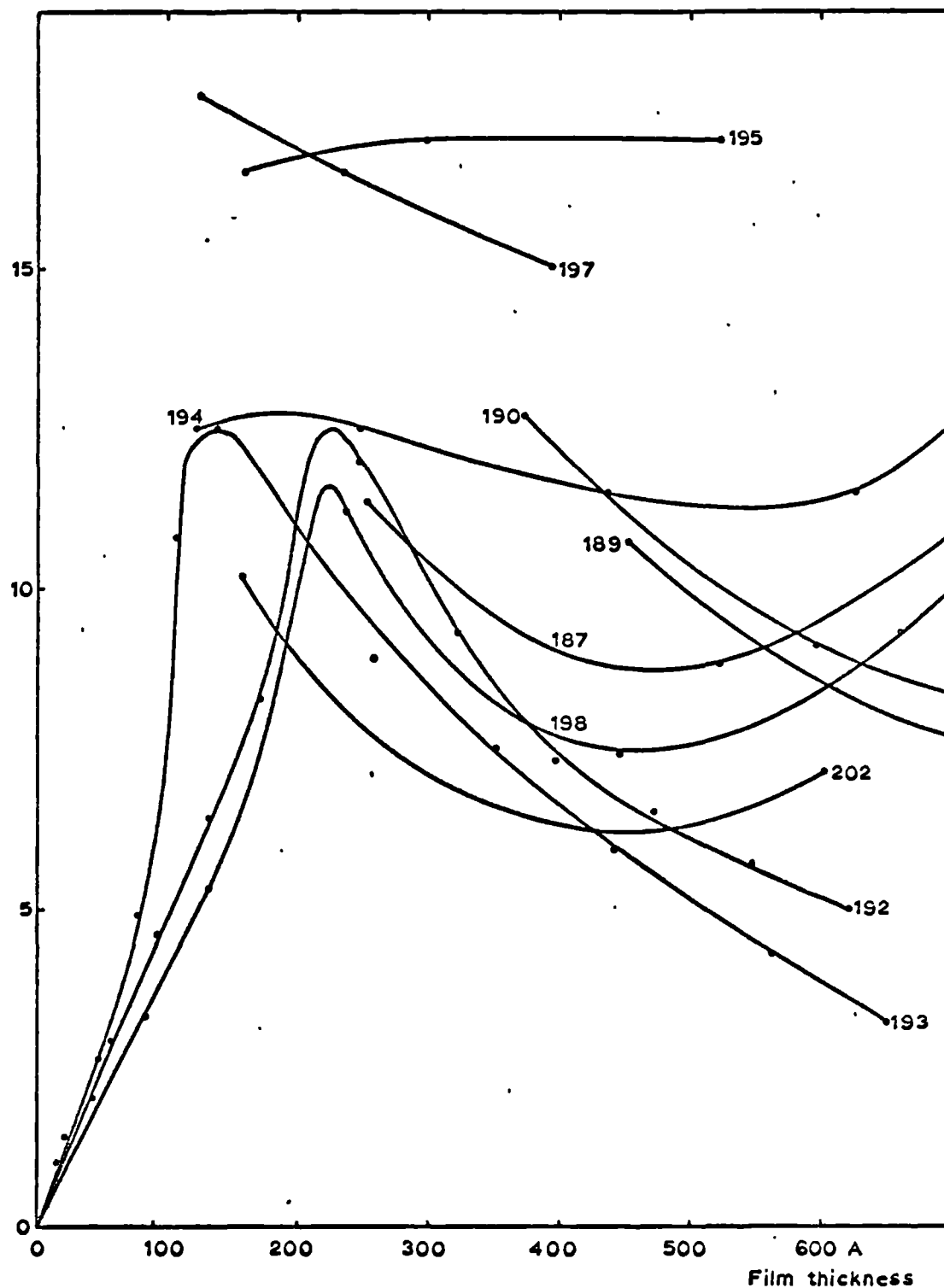


Figure 6.1 Results of all the pulsed evaporations. Force per unit width versus film thickness for silver films evaporated on to glass substrates.

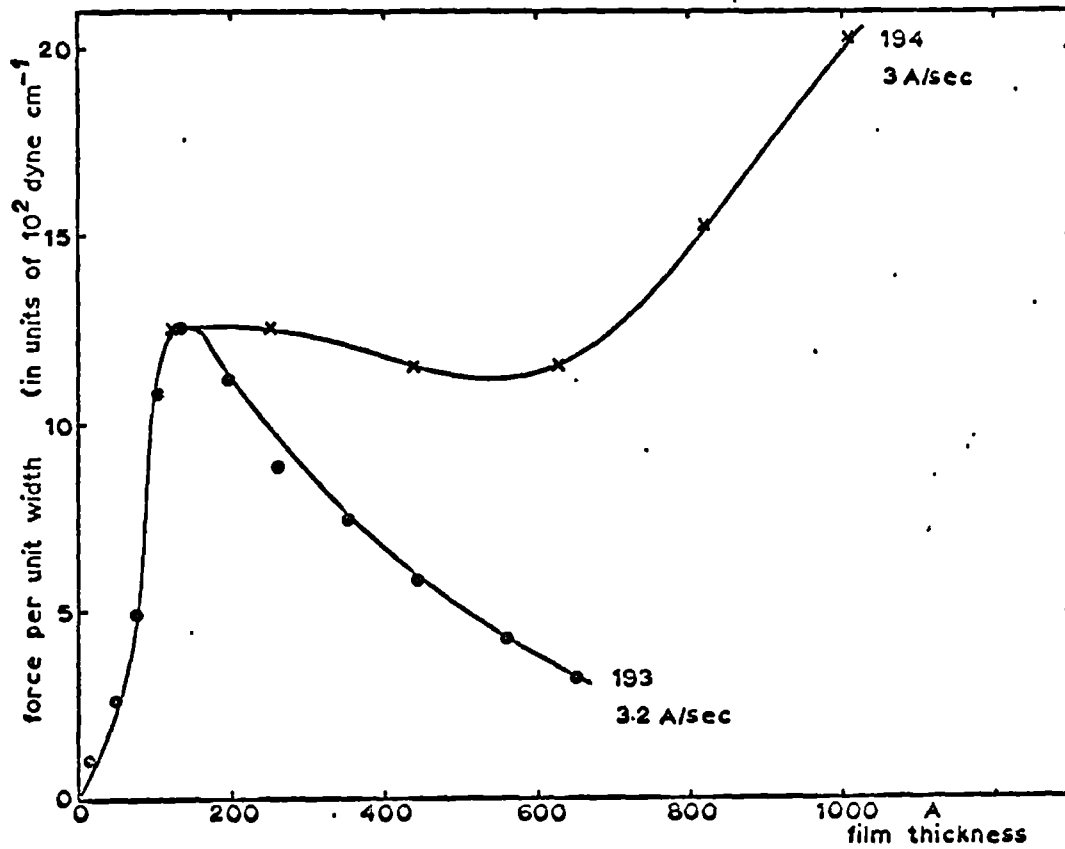


Figure 6.2 The effect of different thickness increments on the force per unit width versus film thickness curve for silver evaporated on to glass substrates. The thickness increments were 50 A for specimen 193 and 150 A for specimen 194.

length was lower, indicating that contamination or stress relief during the cooling period (section 5.2.3) at the end of the evaporation reduces the stress.

The results from Specimen 184 are reproduced in Figure 6.3. Both the stress and the force per unit width have been plotted, and these curves are exactly equivalent.

Taken together these results⁽²⁸⁶⁾ indicate that the force per unit width passes through a maximum value at a film thickness of 100-250 Å.

6.1.3. 'Pulsed' Experiments, Conclusions.

1. Pulsed experiments will not give accurate quantitative information on the shape of the force per unit width versus film thickness curve, because of stress relief and contamination effect between pulses.

2. The results indicate qualitatively that the force per unit width passes through a maximum value at a film thickness between 100 and 250 Å, and that the stress tends to zero as the film thickness tends to zero.

6.1.4. Continuous Deposition Results, Stress Results

The results obtained over the whole film thickness range are plotted in Figure 6.4. The rates of evaporation lie between 3 and 8 Å/sec. The numbers adjacent to the points on the graphs refer to the specimen numbers. The specimen numbers are listed in Appendix 6.1 where the results are tabulated.

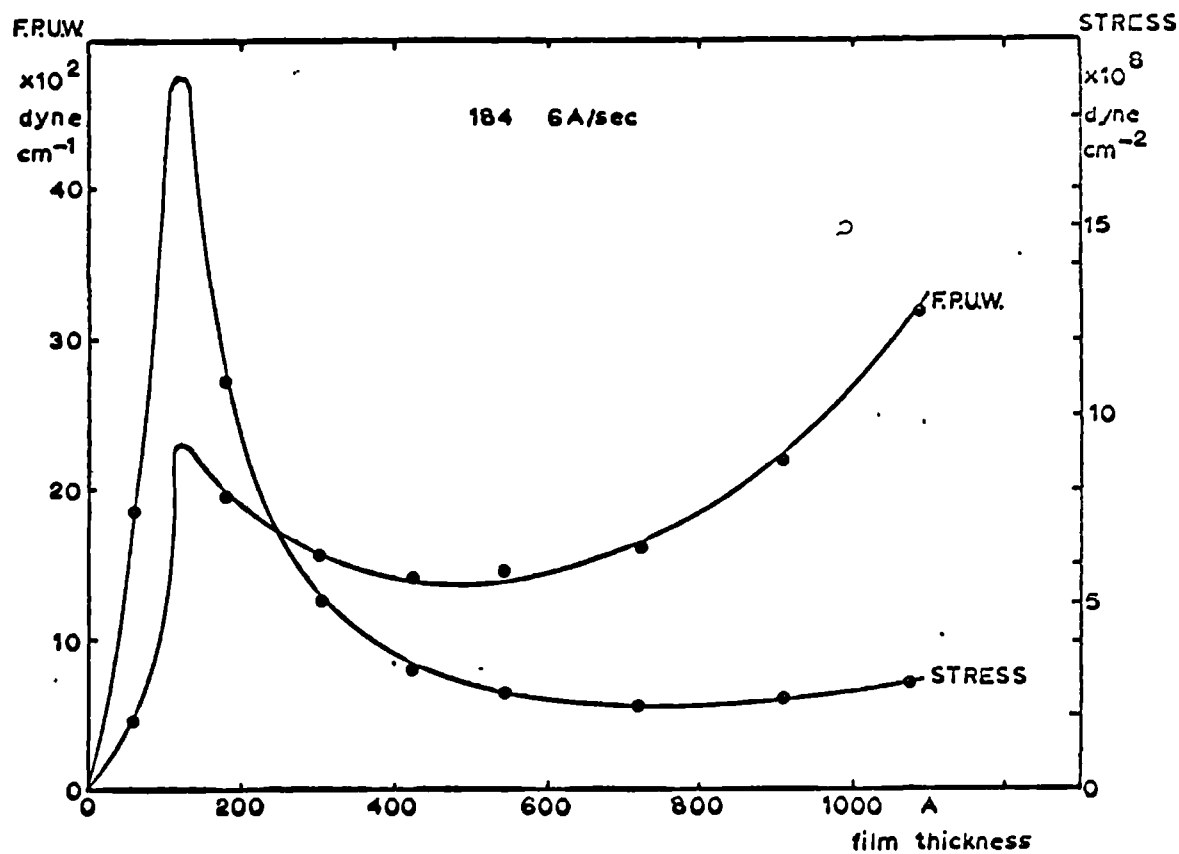


Figure 6.3 Comparison of the average stress versus film thickness curve and the force per unit width versus film thickness curve plotted from the same data. Silver evaporated on to a glass substrate.

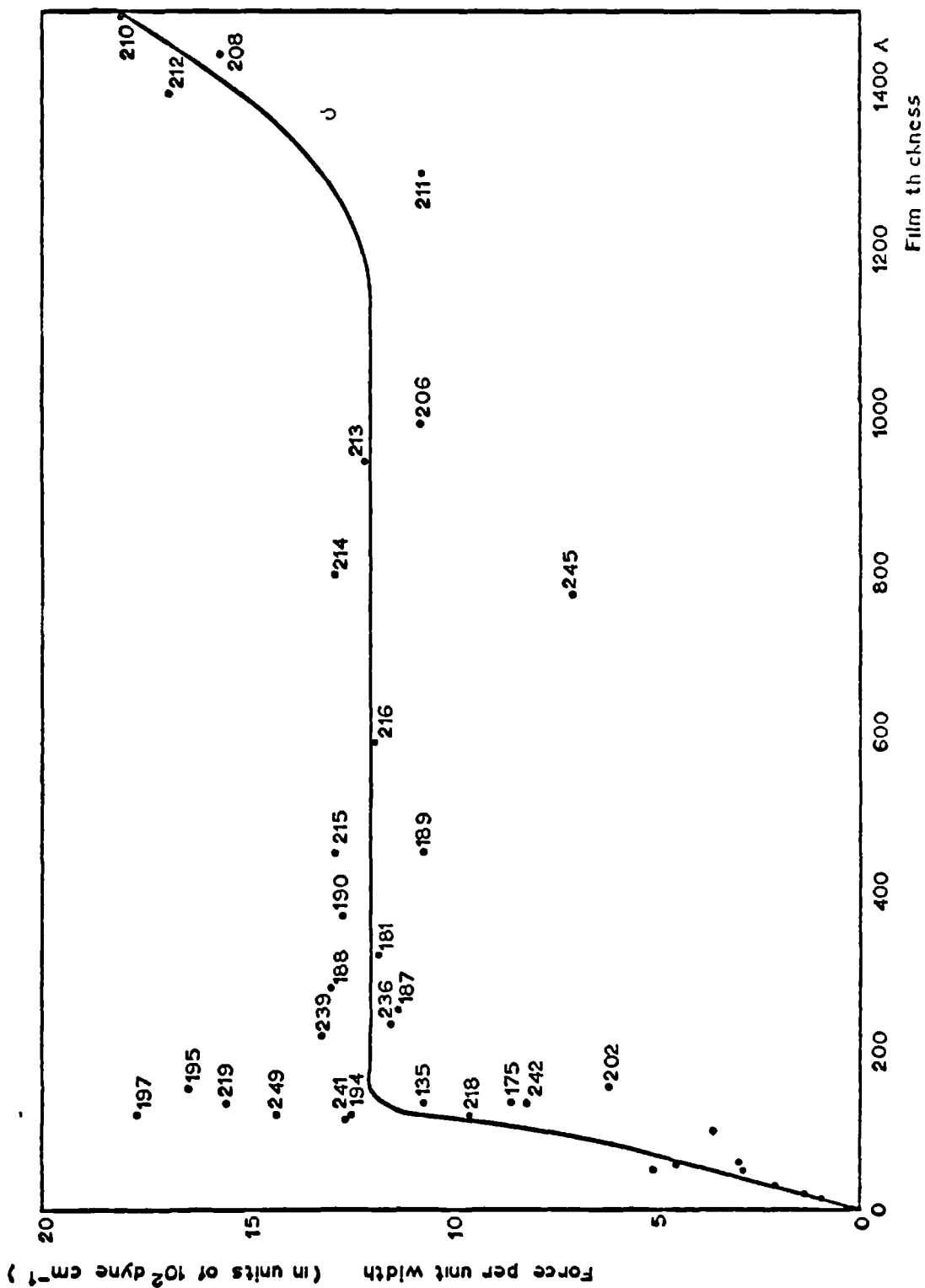


Figure 6.4 Force per unit width versus film thickness for silver films deposited on glass substrates

The measurements of force per unit width in the low thickness range are plotted in Figure 6.5. The thermal stress correction has not been applied to these results. The jig was biased 120 volts negatively with respect to the evaporation source in all these experiments (Section 4.4). It may therefore be assumed that no thermionic electrons from the evaporation sources are reaching the substrate. In order to see whether the bias affected the stress results, the measurements in the initial stages of growth were repeated with the substrate at earth potential. These results (Figure 6.6) are very similar to those with the bias in operation (Figure 6.5), but show a slightly greater scatter. The same curve has been drawn through both sets of results.

The force per unit width rises with increasing film thickness to a constant value of about $1,200 \text{ dyne cm}^{-1}$ at a film thickness of about $120\text{\AA}$. It starts to rise again at a film thickness of about $1,100\text{\AA}$, but at this point the thermal stress (Figure 5.8) is comparable to the total stress. The thermal stress has been plotted on the same scales as Figure 6.4 for easy comparison.

The shape of the curve in Figure 6.4 is the same as that in Figure 3.3. That is the stress in silver films passes through a maximum value.

Because the total force per unit width is constant between 150 and $1,000\text{\AA}$ film thickness, and because the thermal stress contribution is increasing in this thickness range it is

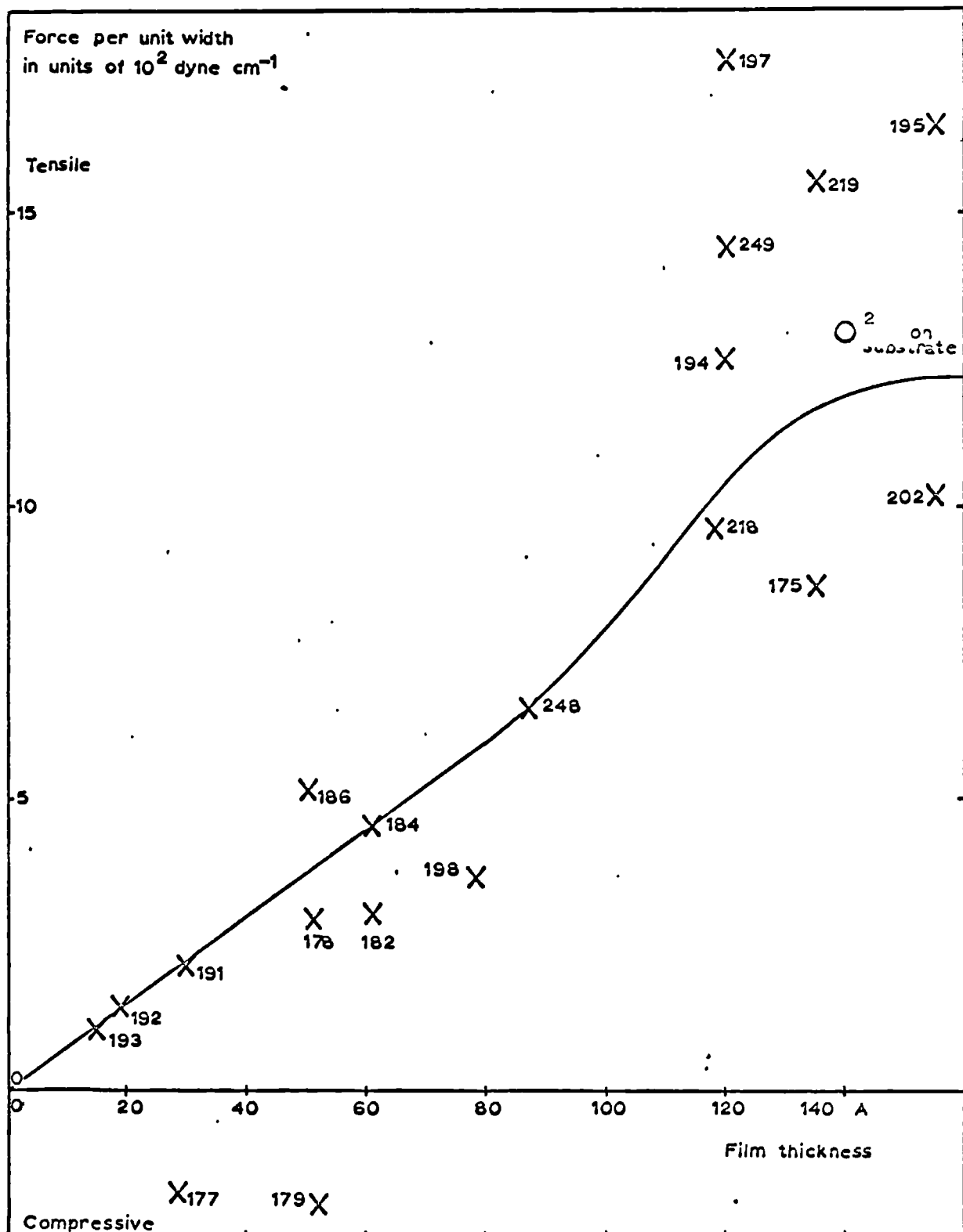


Figure 6.5 Force per unit width versus film thickness in the case of growth of silver films with the jig bias was on. (Compare to Figure 6.0).

Figure 6.6 Force per unit width versus film thickness in the initial stages of growth of silver films evaporated on to glass substrates. The jig bias was off. (Compare to Figure 6.5).

likely that the intrinsic force per unit width also passes through a maximum value. This implies that stress relief is taking place in films thicker than $150\text{\AA}$.

6.1.5. Structure Results

Two sequences of micrographs are shown (Plates 6.1 - 6.6). The micrographs in sequence A are from films deposited on to silicon monoxide support films already mounted on electron microscope grids while those in sequence B are from films stripped from the glass substrates used for stress determinations. The rates of evaporation in the micrographs of sequence B varied from specimen to specimen, and were from 3 to $8\text{\AA}/\text{sec}$. The micrographs of sequence A were deposited at about $5\text{\AA}/\text{sec}$.

Structural damage may be observed in the micrographs of set B. This takes the form of rounding or coalescence of the islands. This could have been due to

1. the attack of the hydrofluoric acid fumes used in stripping on (a) the glass substrate or
(b) the silicon monoxide support film;
2. mechanical forces exerted on the film during the stripping of the films from the substrates;
3. chemical attack of the film by exposure to air or to the distilled water.

Because of the distortion of the film structure the micrographs in sequence B were not used to give quantitative structural data.

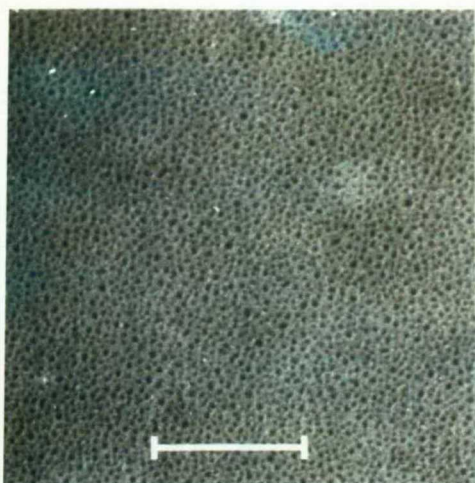


Plate 6.1 A

10A: 5A/sec

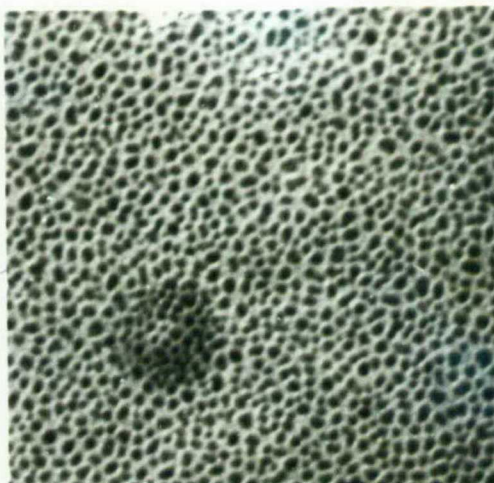


Plate 6.2 A

20A: 5A/sec

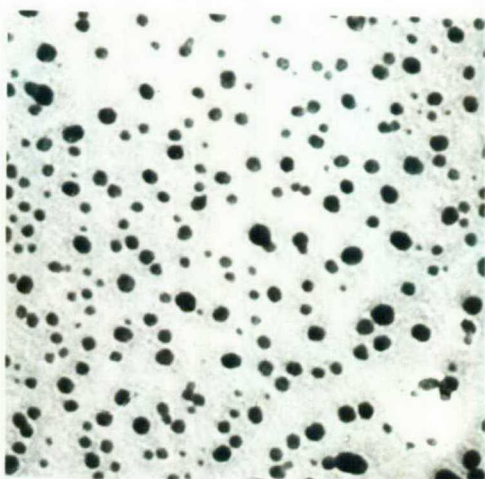


Plate 6.1 B

12A: 6A/sec: specimen 231

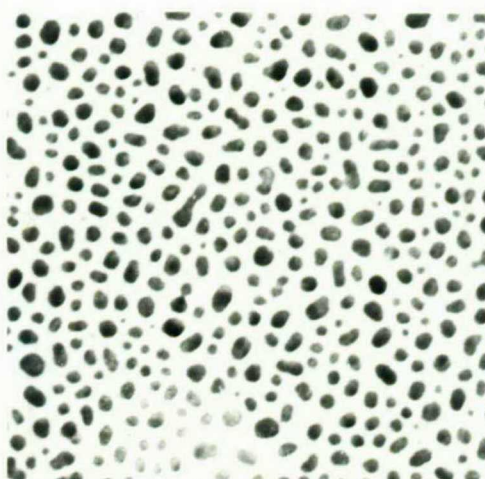


Plate 6.2 B

20A: 5A/sec: specimen 232

Growth of silver films. Set A were evaporated on to silicon monoxide substrates, and set B on to glass substrates. The mark in plate 6.1 A represents 1,000A. x 200,000 magnification.

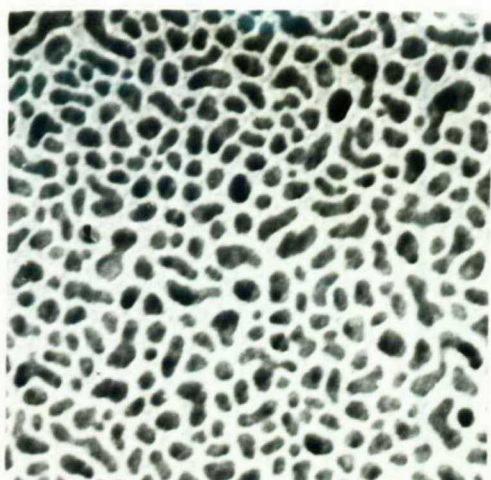


Plate 6.3 A

40A: 5A/sec

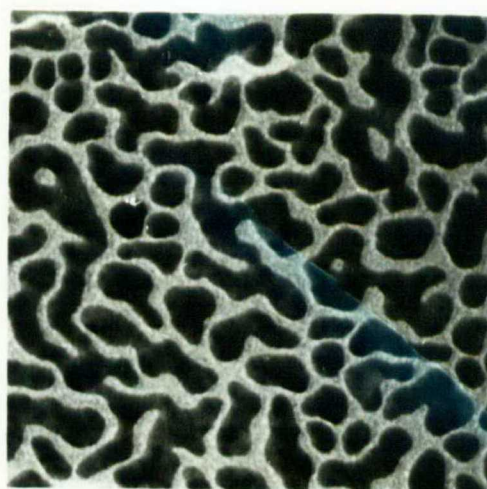


Plate 6.4 A

60A: 5A/sec

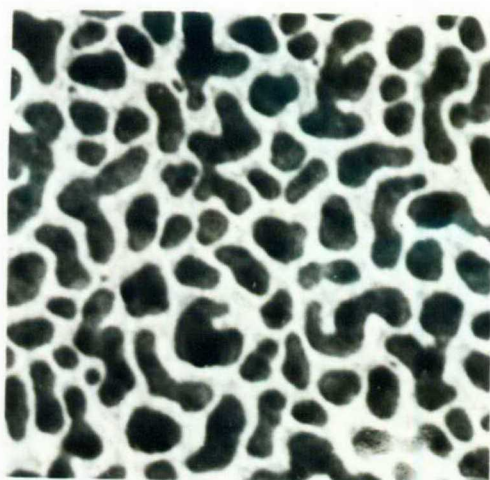


Plate 6.3 B

43A: 7A/sec: specimen 235

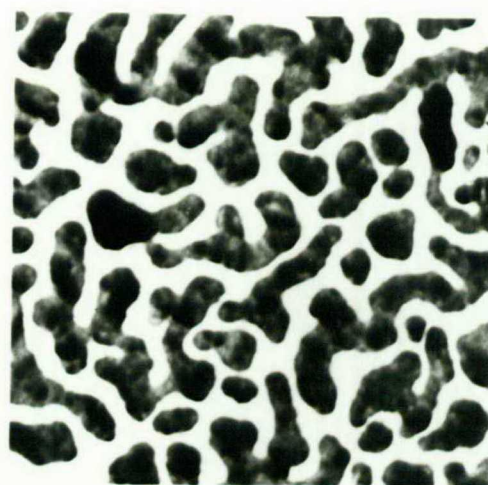


Plate 6.4 B

60A: 3A/sec: specimen 239

Growth of silver films. x 200,000 magnification.

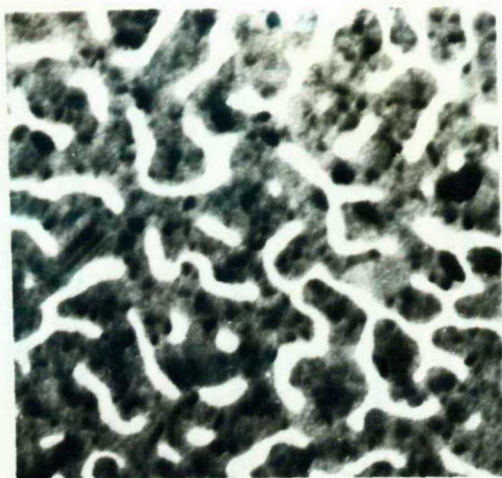


Plate 6.5 A

80A: 5A/sec



Plate 6.6 A

130A: 5A/sec

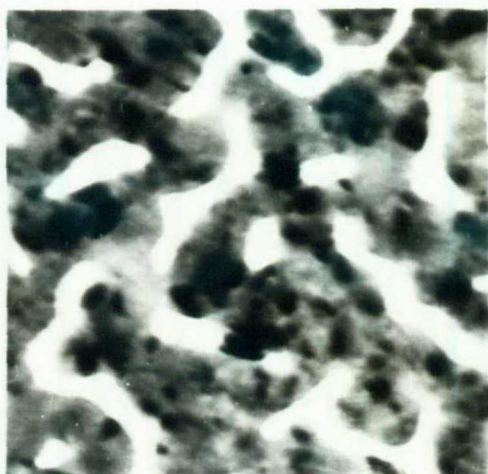


Plate 6.5 B

80A: 3A/sec: specimen 228

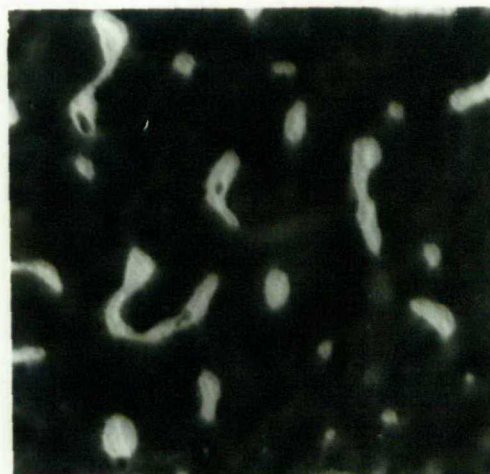


Plate 6.6 B

115A: 2.5A/sec: specimen 229

Growth of silver films. x200,000 magnification.

However, as the micrographs of sequence A are of films deposited on to silicon monoxide substrates the structure does not necessarily represent the structure of the films used for stress experiments, which were deposited on to glass substrates.

Bearing in mind the reservations made above about quantitative conclusions from the electron microscopy, the number of islands per unit area of substrate (N of section 2.7.4.2) has been plotted versus film thickness in Figure 6.16. The graph shows that N decreases with increasing film thickness, indicating that island coalescence has taken place, even in the thinnest films examined. From this graph $N^{\frac{1}{2}}f$ versus f has been plotted in Figure 6.17. Figure 6.17 shows that the quantity $N^{\frac{1}{2}}f$ decreases with increasing film thickness.

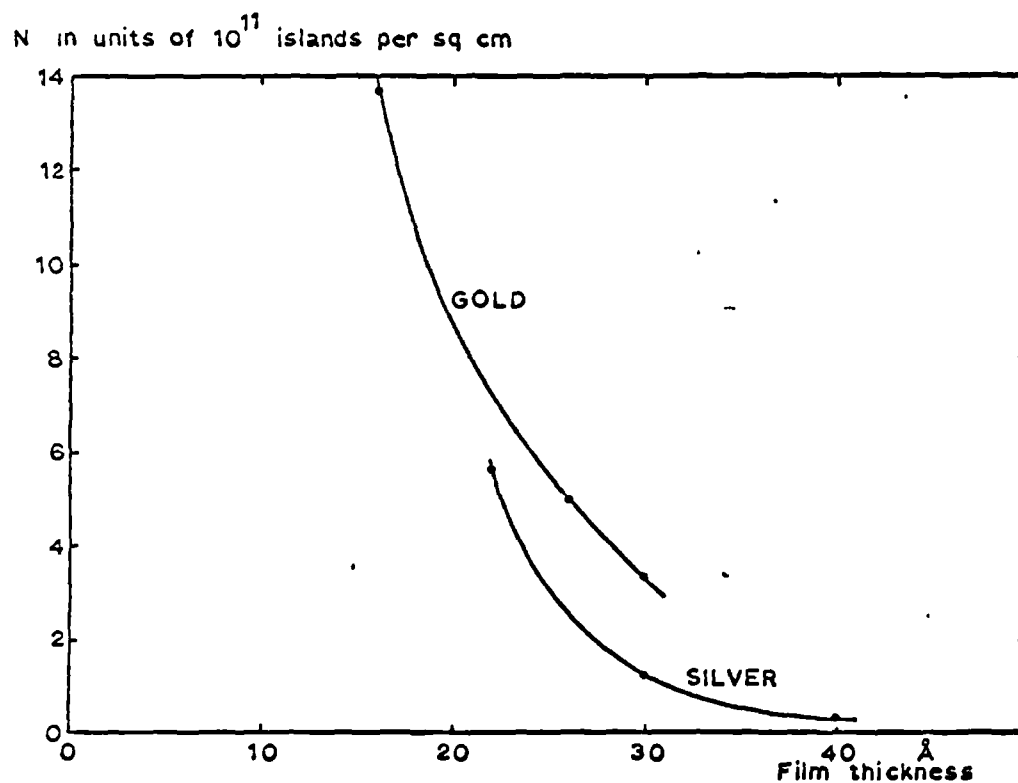


Figure 6.16. The number of islands per unit area of substrate, N , as a function of the film thickness, f .

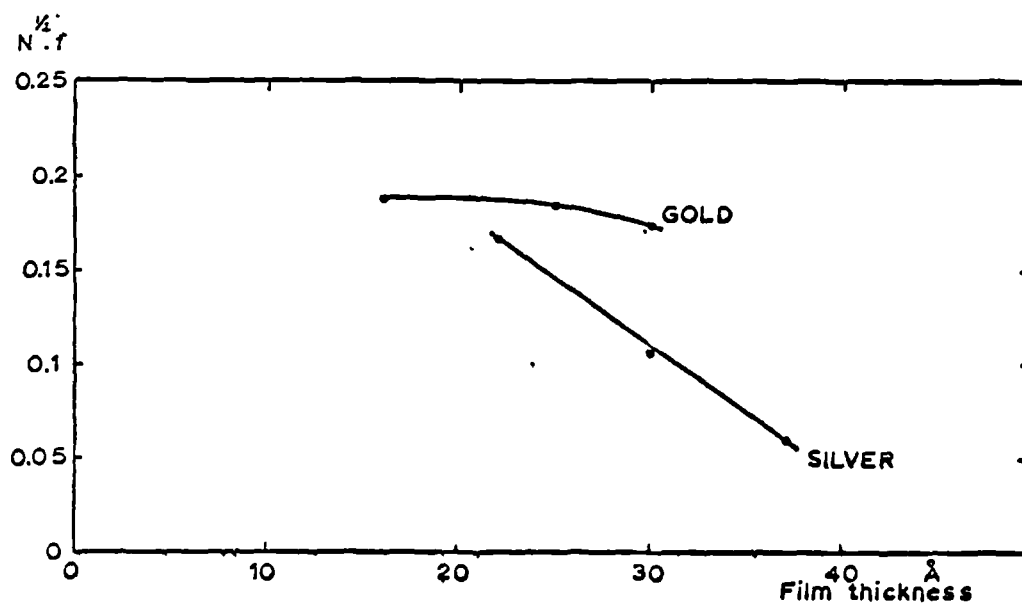


Figure 6.17. The quantity $N \cdot f^{\frac{1}{2}}$ plotted as a function of f from the same data.

The qualitative results of the electron microscopy are presented in Table 6.1.

Structure	Film Thickness ($\text{\AA}$)
Single islands, irreg. shapes	30
Starting to coalesce	25.....50
Chains, discontinuous	45.....70
Continuous, channels	65.....115
Continuous, holes	110.....125
Complete	120.....

Table 6.1 Qualitative Results of Electron microscopy
on Silver Films.

The micrographs indicated that the films became electrically continuous at a thickness of about $70\text{\AA}$. This has been confirmed by some recent electrical measurements on silver films⁽¹⁶⁵⁾.

The crystallite size was observed to increase with increasing film thickness after the film has become continuous. This confirms work on crystallite sizes in silver films by Moss et al⁽²⁷³⁾.

6.1.6. Conclusions

From our measurements on the stress and the structure of silver films we draw the following conclusions.

1. The stress in silver films, deposited under the conditions specified on to glass substrates is tensile.
2. Stress exists in island structure films.
3. The stress in island structure films is tensile.
4. The stress in films below $400\text{\AA}$ in thickness is mainly intrinsic.
5. The stress (defined by the Stoney formula) tends to zero or becomes constant as the film thickness tends to zero. The stress does not tend to infinity.
6. No intrinsic stress is added to a film after it reaches a thickness of about $120\text{\AA}$. The point in the film structure at which the last hole becomes filled occurs at a thickness of about $120\text{\AA}$.
7. The total stress and the intrinsic stress pass through a maximum value at a film thickness of about $120\text{\AA}$.
8. The intrinsic force per unit width passes through a maximum value at a film thickness of about $120\text{\AA}$.
9. Stress relief occurs with time immediately after film deposition.

6.2. STRESS IN SILVER FILMS DEPOSITED ON TO MICA SUBSTRATES.

6.2.1. Introduction.

The primary object was to compare the stress and the structure of silver films deposited on to freshly cleaved mica substrates with the stress and structure of silver films deposited on to glass substrates. The secondary object was to discover whether the scatter on the stress results was due to variations of Young's modulus between substrates.

Thirty three mica substrates were used in conjunction with the Model iii jig. The 120 volt bias was on throughout. The substrate clamp pressure on the central substrate was decreased slightly for Specimens 382-400 inclusively. Otherwise the clamp pressures were unaltered. The specimens to be used for electron microscopy were coated with a support film of silicon monoxide without breaking the vacuum after deposition.

6.2.2. Results

In these and subsequent results the sets of three points on the graphs correspond to the results from the three substrates used in a particular evaporation.

The results are tabulated in Appendix 6.2 and plotted in Figures 6.7 and 6.8. The rates of evaporation lie between 3.5 and 5 Å/sec. Figure 6.7 shows the results assuming a value of 12.3×10^{11} dyne cm⁻¹ for the Young's modulus of mica, and Figure 6.8 shows the results with the values of Young's

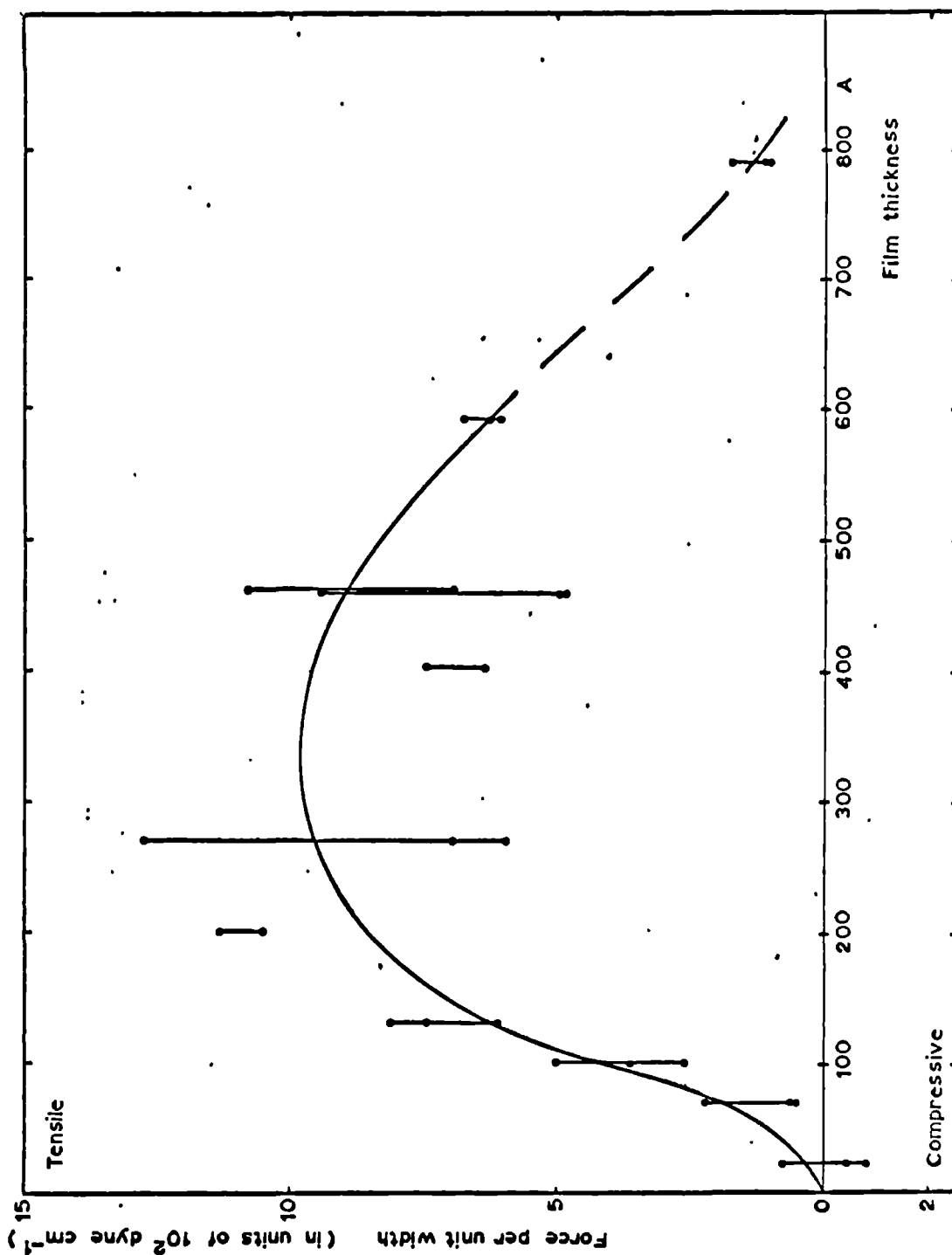


Figure 6.7 Force per unit width versus film thickness for silver films evaporated on to mica substrates. An average value was taken for Young's modulus. (Compare to Figure 6.8).

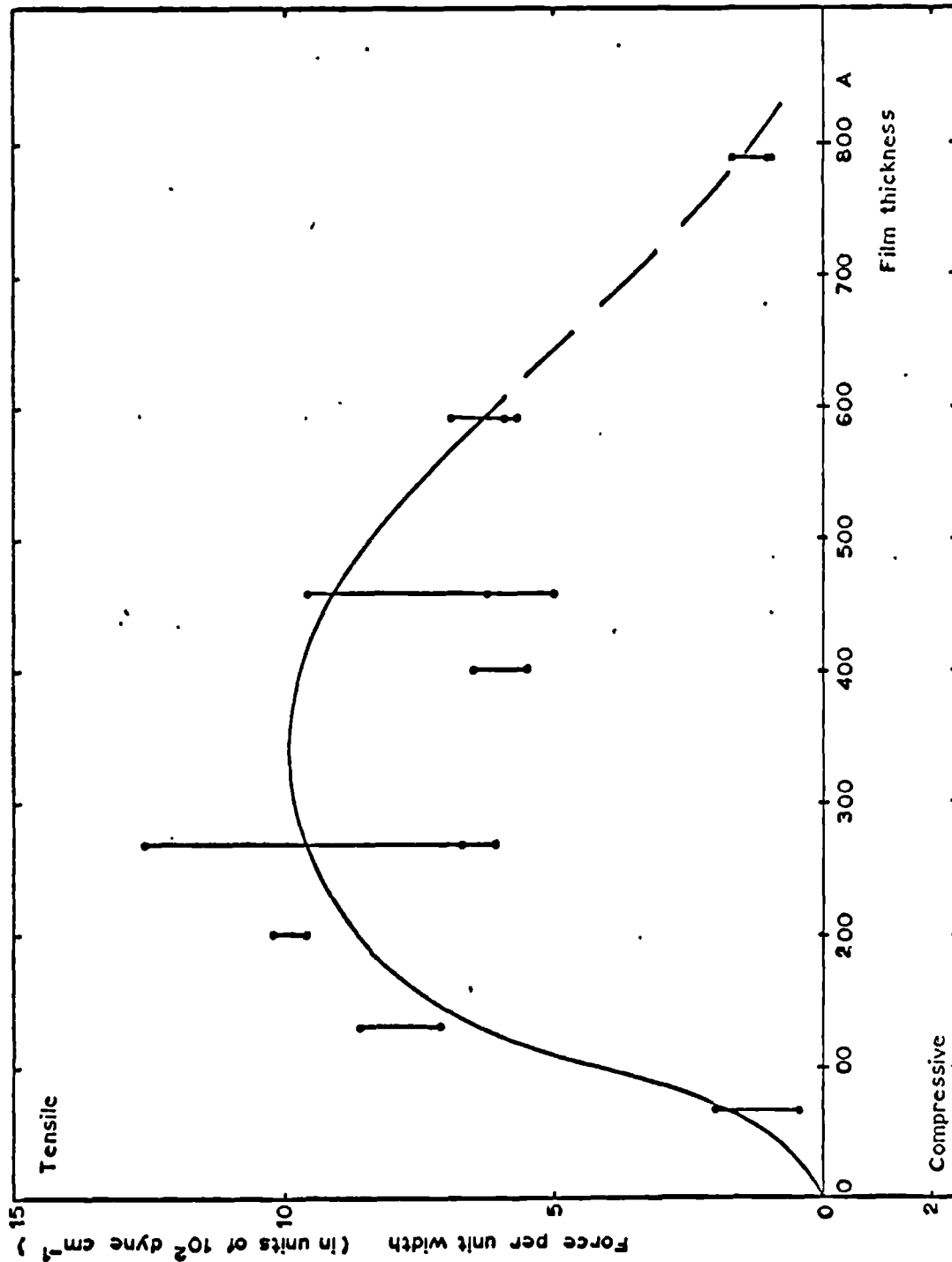


Figure 6.8 Force per unit width versus film thickness for silver films evaporated on to mica substrates. Young's modulus values were taken from measurements on individual substrates. (Compare to Figure 6.7).

modulus taken from measurements on the individual substrates. There is no significant reduction in scatter when the Young's modulus measurements are taken on individual substrates.

It is seen from these graphs that the stress tends to zero as the film thickness tends to zero, and that the force per unit width reaches a maximum value between 200 and 400 Å film thickness and decreases at higher film thicknesses. The stress is of the same order of magnitude as the stress in silver films deposited on to glass substrates.

Electron microscopy showed island structure films at a thickness of 23Å, continuous films with channel or hole structure at 100Å film thickness, and continuous and complete films at 200Å and above. Some crystallites in Specimen 379 were 700-800Å across. A very slight degree of (111) orientation was observed in Specimen 391, but not in any other film.

6.2.3. Conclusions

1. The stress in silver films deposited on to mica substrates is tensile, and is of the same order of magnitude as that in silver films deposited on to glass substrates.
2. The scatter on the results in stress measuring experiments on mica substrates is not due solely to variations in Young's modulus between substrates.

3. The force per unit width versus film thickness curve passes through a maximum value at a film thickness of 200 - 400Å. The last channel in the film structure becomes filled at a film thickness of about 200Å.

6.3. STRESS IN GOLD FILMS DEPOSITED ON TO GLASS SUBSTRATES

6.3.1. Introduction

The object of this work was to verify the existence of a maximum in the graph of force per unit width versus film thickness. This maximum had been found in the work on silver films at the thickness at which the last holes in the film structure were being filled.

One hundred and sixteen glass substrates $1\frac{1}{2}$ " by $7/16$ " by 0.0035" were used in the Model iii jig. The substrates and the experimental procedure have already been described.

The 120 volt bias was on during these experiments. The substrate clamping pressures were unaltered.

6.3.2. Stress Results

Unfortunately the gold wetted the material of the evaporation source and ran to the corners of the boat which were cooler than the central part. When this happened the calibration of the ratemeter and the thickness uniformity of the films across the three substrates were considerably affected.

For this reason the stress value given by the outer of the three substrates was sometimes different from that given by the other two. In these cases it has not been plotted on the graphs of results. It has still, however, been tabulated together with the other results in Appendix 6.3.

Compressive stresses were indicated in a tenth of the measurements made. The chart was used to follow the behaviour of the deflection of the middle substrate of the three during an evaporation and it can be seen from the tabulated results that the middle substrate stress, which was therefore the most accurate, was never compressive. Also in any evaporation the stress in two of the three films was tensile. Hence the type of stress in gold films deposited on to glass substrates was taken to be tensile.

The rates of evaporation are marked adjacent to the points in the graphs of results.

The results for films evaporated at a rate of $3 \text{ \AA/sec}$, Figure 6.9, show a linear rise of force per unit width versus film thickness. A maximum is not indicated. The stress is considerably higher in magnitude in these films than in films evaporated at higher rates. The stress in these films tends to zero as the film thickness tends to zero.

The results for films evaporated at rates between 4 and $6 \text{ \AA/sec}$, Figure 6.10, show the same initial rise of force per unit width with film thickness, but after a film thickness of

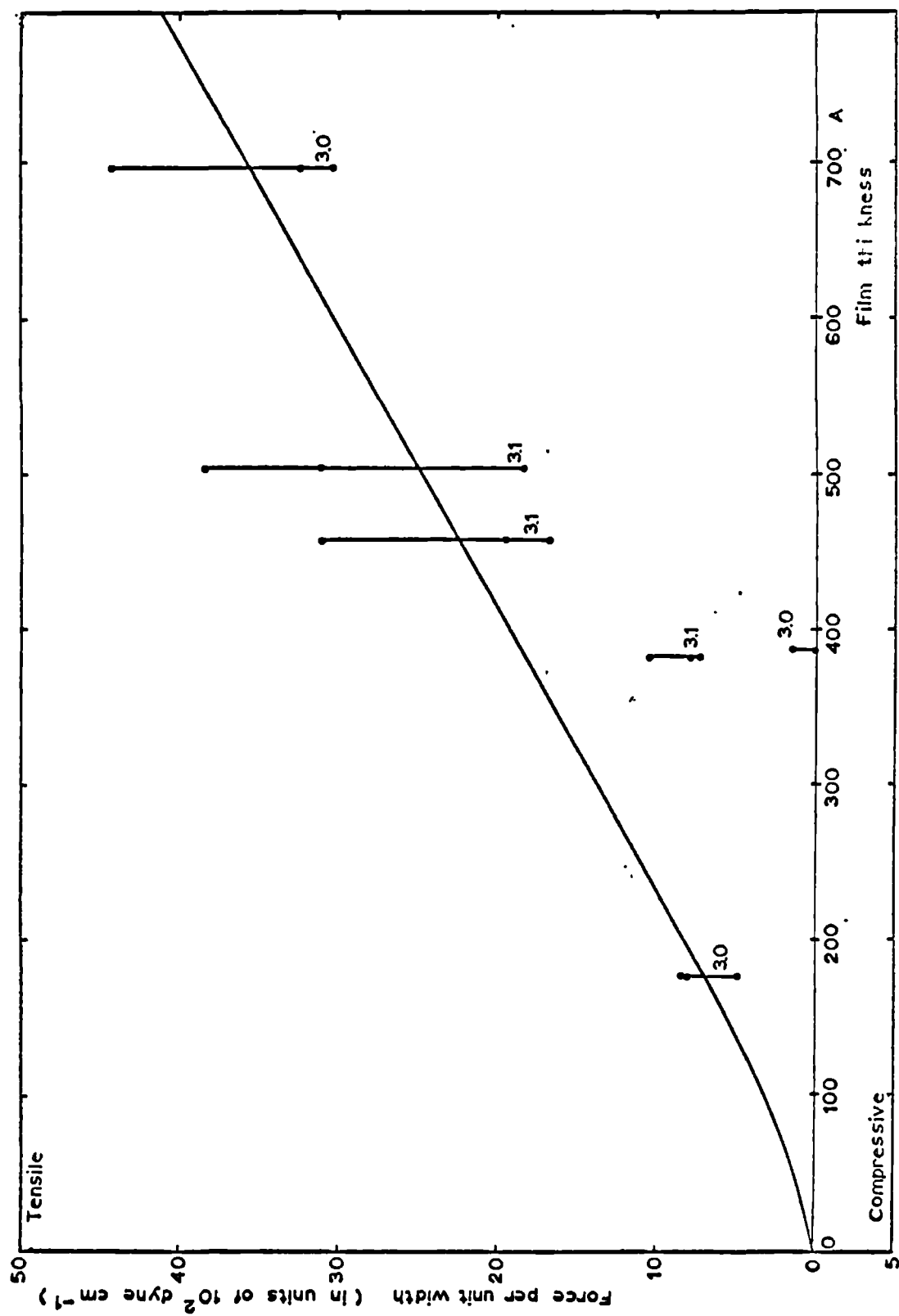


Figure 6.9 Force per unit width v film thickness for gold films evaluated on glass substrates at about 3 A/

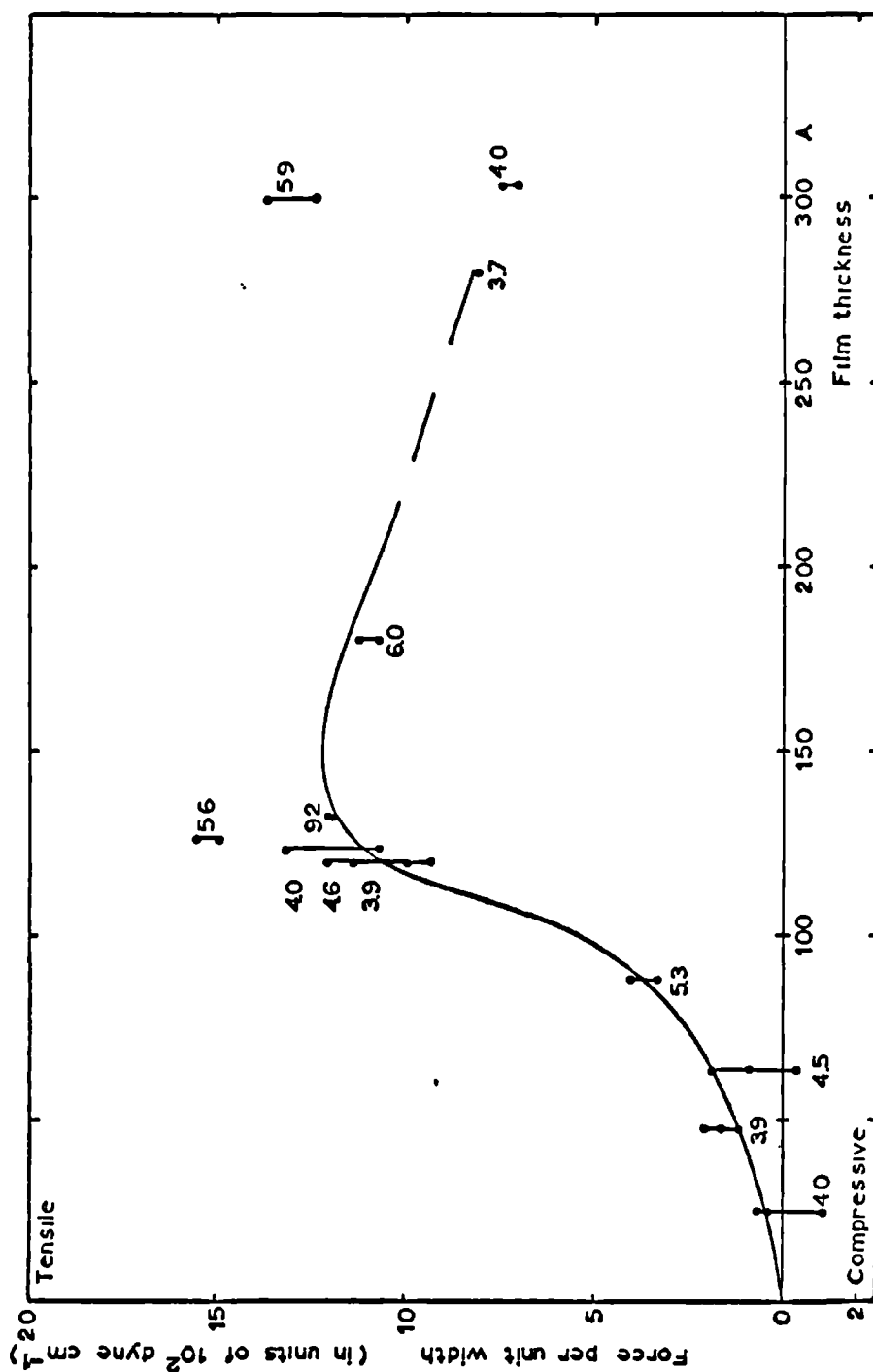
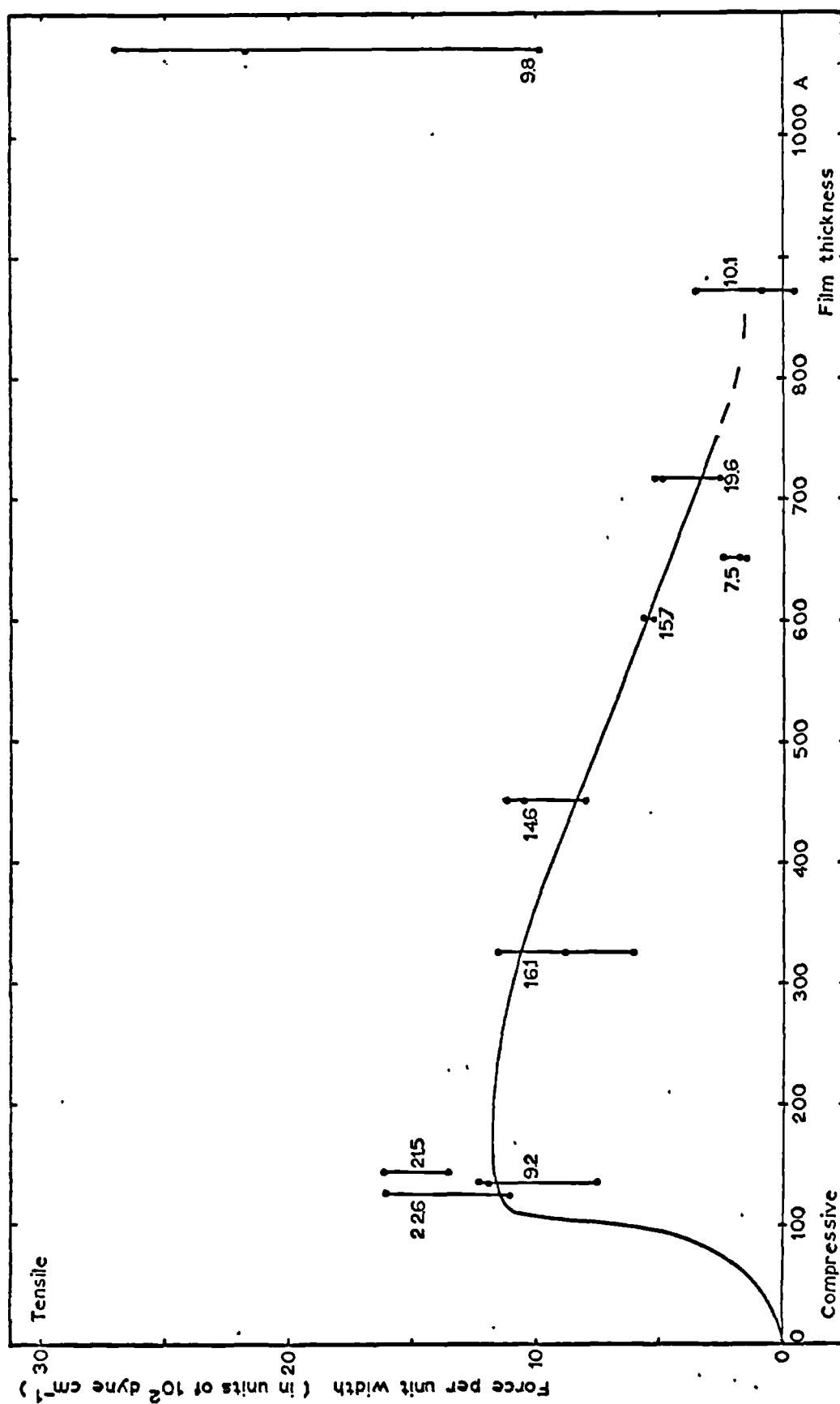


Figure 6.10 Force per unit width versus film thickness for gold films evaporated on to glass substrate at rates of evaporation between 4 and 6 A/s c.



201.

Figure 6.11 Force p r unit width versus film thickness for gold films evaporated on to glass substrates at rates above 9 A/sec.

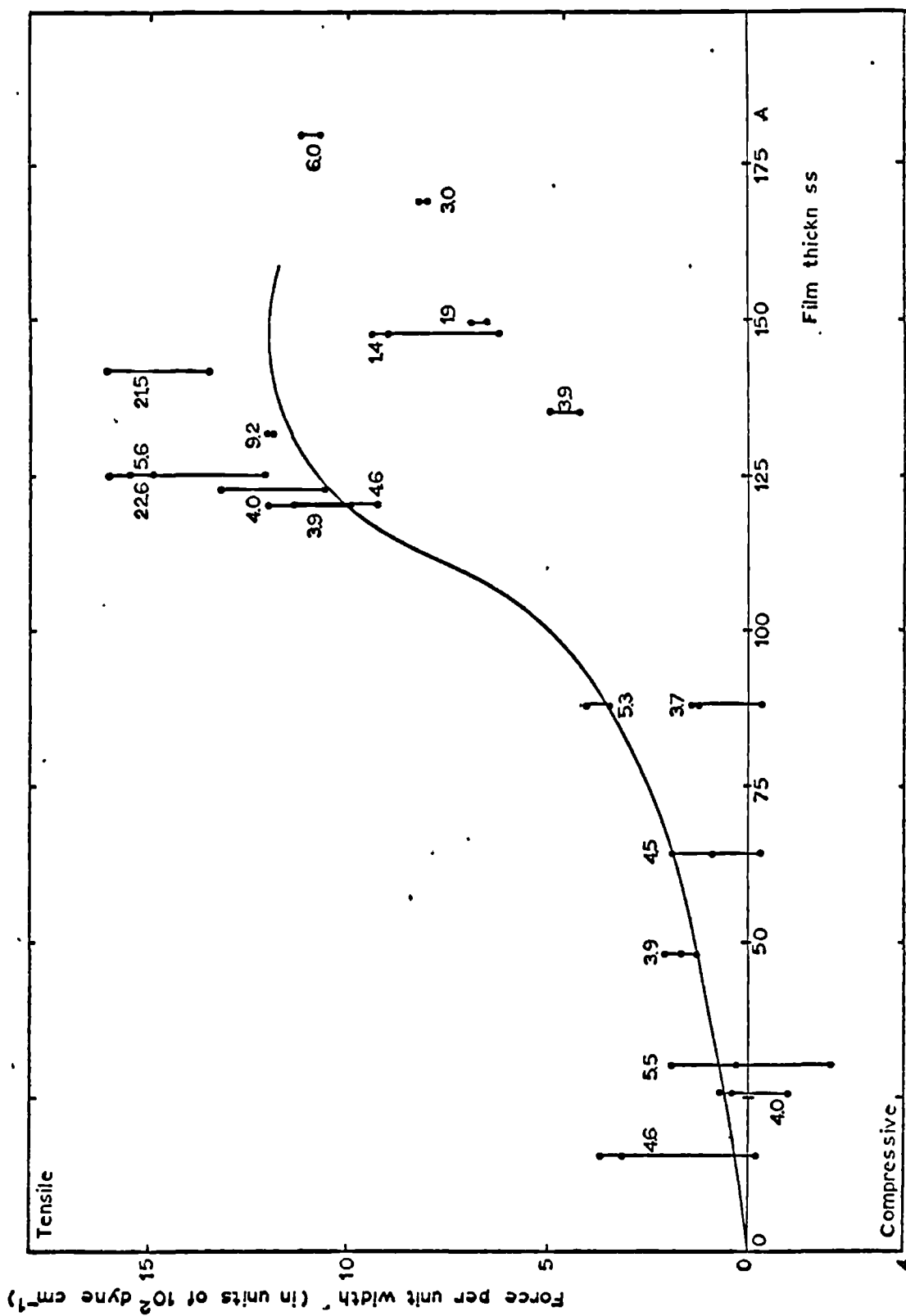


Figure 6.12 Force per unit width versus film thickness in the initial stage of growth of glass films evaporated on to glass substrate.

125 Å the curve tends to flatten, or even decrease. This curve is very similar to that obtained for silver films, although the magnitude of the force per unit width is very slightly higher.

The force per unit width in films evaporated at rates over 9 Å/sec, Figure 6.11, shows a definite decrease as the film thickness exceeds 500 Å. The subsequent increase after 1,000 Å may be due to thermal stress. The thermal stress correction is plotted in Figure 5.8.

The results in the initial stages of film growth have been plotted in Figure 6.12. These results show that the stress tends to zero as the film thickness tends to zero, and that the stress in the initial stages of film growth is tensile, in agreement with the work on silver films.

6.3.3. Structure Results

Plates 6.7 - 6.14 are micrographs of films which had been used for stress determinations. At 5 Å/sec the thickness for continuity was 40 Å, and the last hole became filled at a thickness of about 130 Å. The crystallite size in continuous films increased with increasing film thickness. The small channels in the micrographs of Specimens 553, 550, 559 and 556 are probably not due to damage of the film on stripping, but are part of the normal growth sequence. The difference in structure of films of the same thickness deposited at different rates is very small. The films deposited at

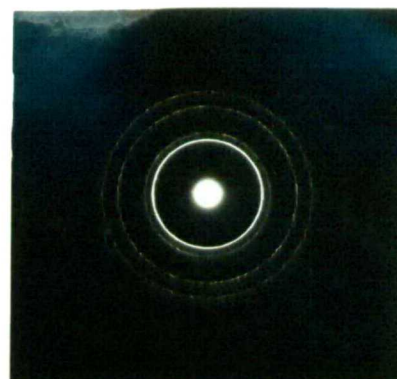
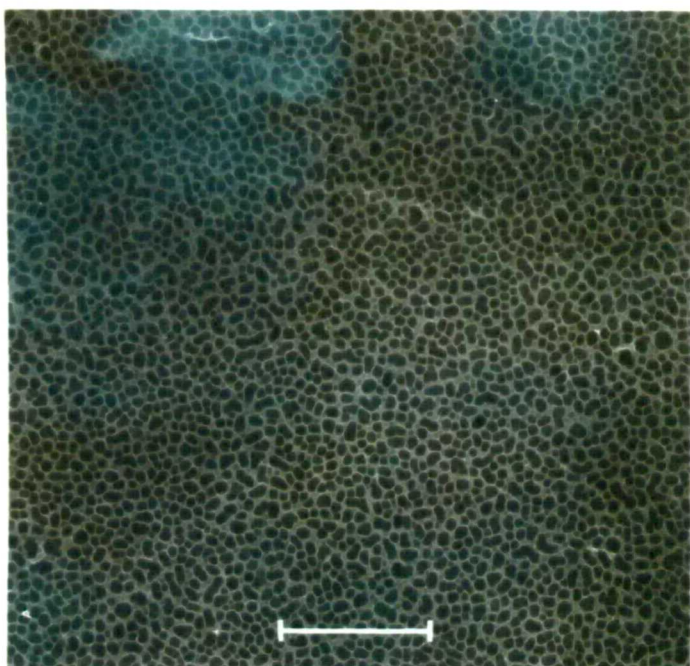


Plate 6.7
Specimen 532
16A: 4.5A/sec
360 dyne cm⁻¹

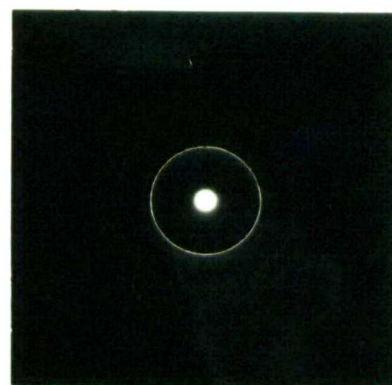
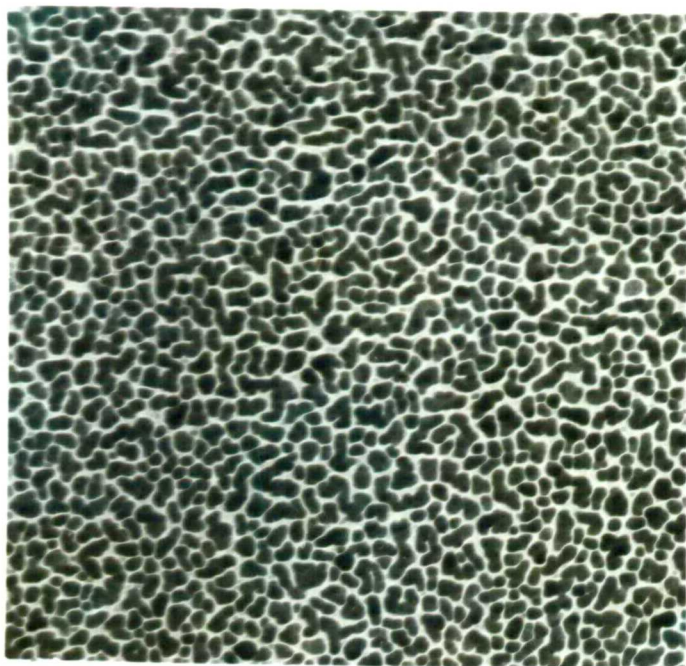


Plate 6.8
Specimen 520
26A: 4A/sec
60 dyne cm⁻¹

Growth of gold films on to glass substrates. The mark in plate 6.7 represents 1,000A. x 200,000 magnification.

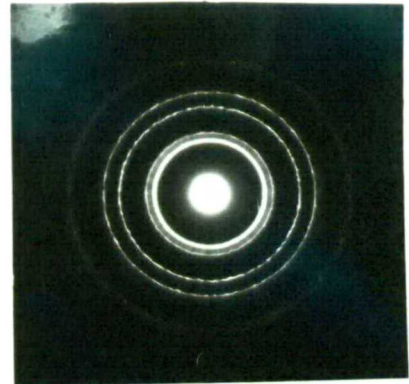
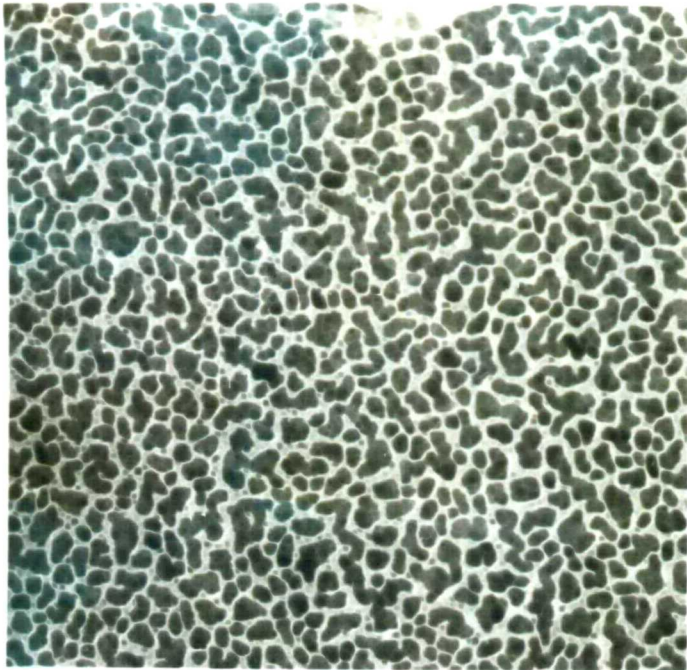


Plate 6.9
Specimen 529
30A: 5.5A/sec
180 dyne cm⁻¹

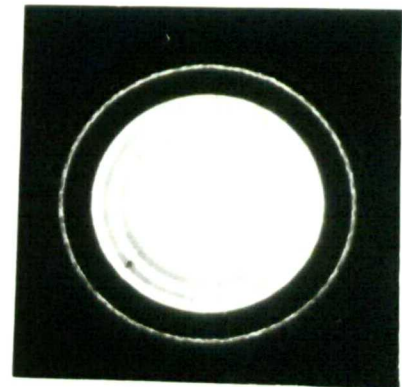
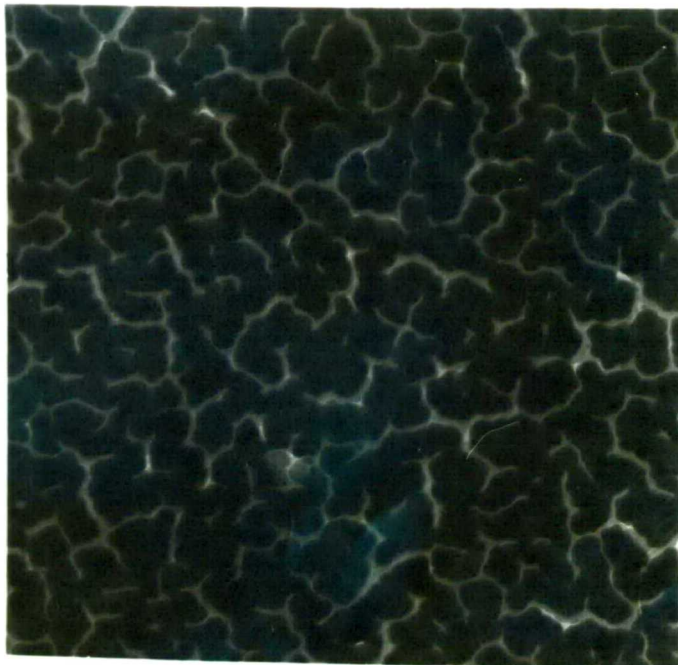


Plate 6.10
Specimen 514
48A: 3.9A/sec
200 dyne cm⁻¹

Growth of gold films on to glass substrates. x 200,000 magnification

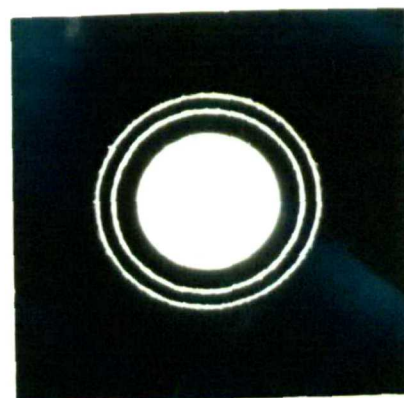
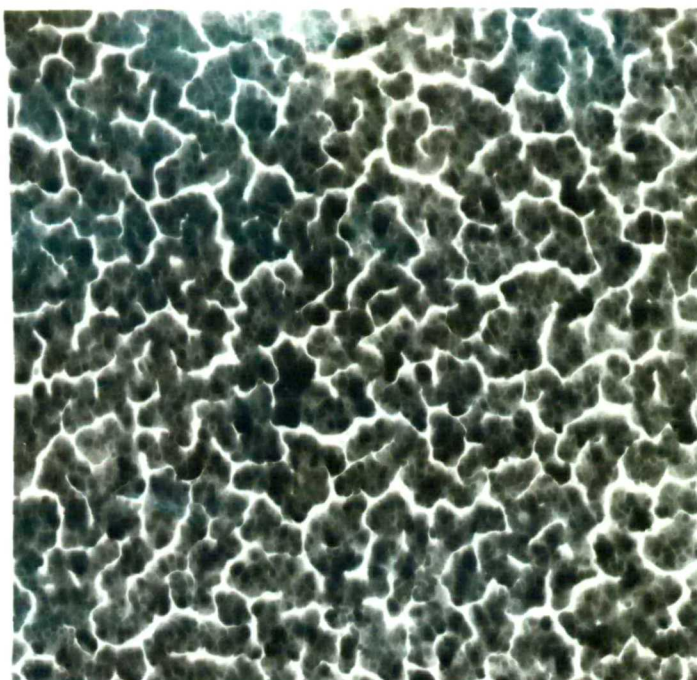


Plate 6.11
Specimen 499
88A: 3.7A/sec
130 dyne cm⁻¹

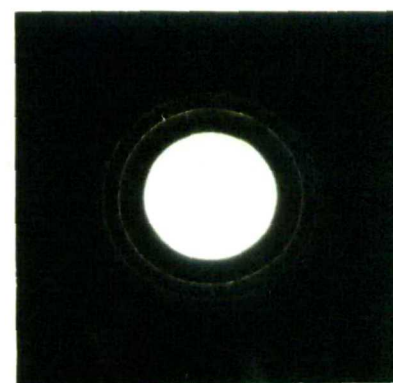
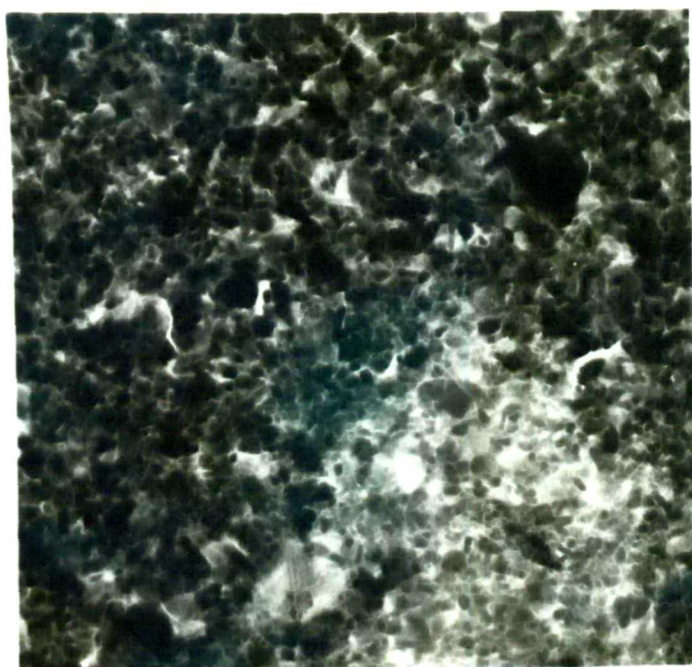


Plate 6.12
Specimen 550
126A: 5.6A/sec
1550 dyne cm⁻¹

Growth of gold films on to glass substrates. x 200,000 magnification.

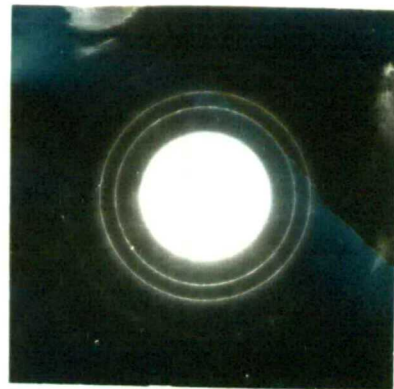
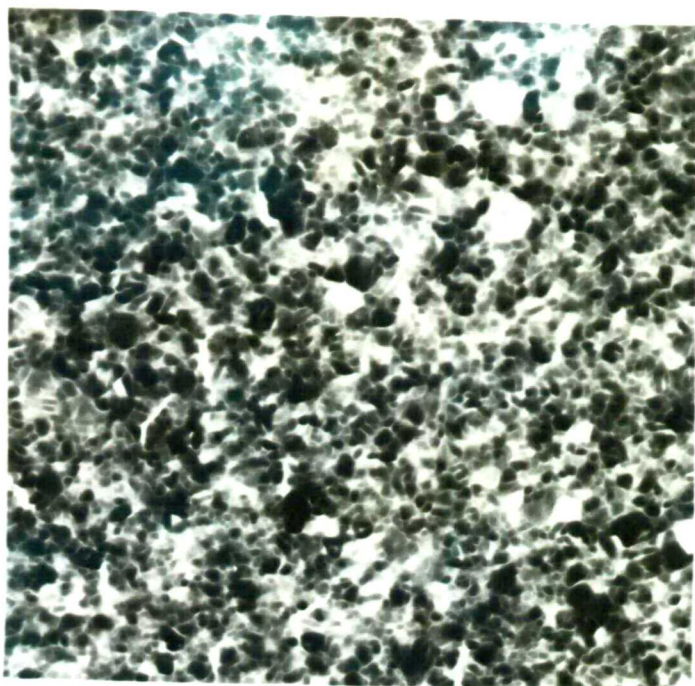


Plate 6.13

Specimen 559

126A: 22.6A/sec

1600 dyne cm⁻¹

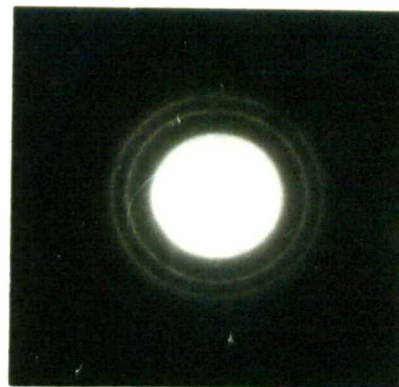
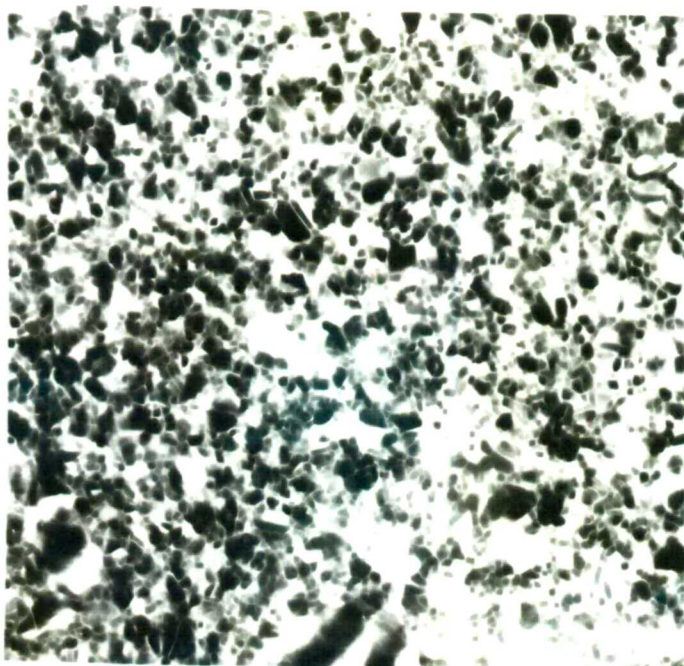


Plate 6.14

Specimen 556

142A: 21.5A/sec

1610 dyne cm⁻¹

Growth of gold films on to glass substrates. x 200,000 magnification.

higher rates have smaller crystallite sizes.

The structure of these gold films is similar to that found by Pashley et al⁽²⁷⁴⁾ in polycrystalline gold films grown on carbon substrates.

6.3.4. Conclusions

1. The stress in gold films, deposited under the conditions specified on to glass substrates is tensile.
2. Stress exists in island structure films.
3. The stress in island structure films is tensile.
4. The stress in films below $400\text{\AA}$ in thickness is mainly intrinsic.
5. The stress (defined by the Stoney formula) tends to zero as the film thickness tends to zero.
6. The total stress passes through a maximum value at some film thickness between 100 and $200\text{\AA}$.
7. The point in the film structure at which the last hole becomes filled occurs at a thickness of about $130\text{\AA}$.
8. The intrinsic force per unit width passes through a maximum value.
9. The magnitude of the force per unit width is not strongly rate dependent.
10. Stress relief occurs with time immediately after film deposition.

6.4. LEAD TELLURIDE RESULTS

6.4.1. Introduction

The thermal problems (sections 4.4. and 5.2) encountered in the preliminary experiments with the stress measuring apparatus necessitated the choice of a material with the lowest possible epitaxial temperature for the study of stress in epitaxial thin films. One such material was lead telluride, which was observed to form oriented films on room temperature substrates. An additional advantage of this material was the low evaporation temperature which reduced the thermal contribution to the substrate deflection.

Another possible material was tin telluride, but although a large degree of orientation existed in sample films, no films gave a perfect spot diffraction pattern. Plate 6.23F is a typical tin telluride diffraction pattern.

Lead telluride was therefore used for these experiments.

Stoichiometry problems arise with any evaporation of a compound. However mass spectroscopic studies have shown that lead telluride evaporates as a molecule⁽²⁷⁵⁾, and good stoichiometry of PbTe films has been reported⁽²⁷⁶⁾. Zemel⁽²⁷⁷⁾ found bulk properties in thick PbTe films evaporated from silica crucibles, although Mountvala⁽²⁷⁸⁾ found a deficiency of tellurium using electron bombardment evaporation.

No bending beam stress measurements on lead telluride films have been reported, although the effects of thermal stress

on the optical properties of similar films have been observed⁽²⁷⁹⁾. The thermal stress in epitaxial PbS films grown on to rock salt at a temperature of 300°C and cooled to room temperature was 5×10^9 dyne cm⁻¹, in agreement with stress calculated from optical band gap measurements.

The intrinsic stresses measured in the present experiments were two orders of magnitude lower, being in the range 5×10^7 to 5×10^8 dyne cm⁻¹.

6.4.2. Stress Results

The chart records produced did not show the turning points always associated with the evaporations of silver and gold, but they did show the compressive deflection due to the heating up of the substrates as the films were deposited.

'Pulsed' evaporations were tried initially. Figure 6.13 shows some of the results obtained. It can be seen that the slope of the force per unit width versus film thickness graphs is the same whether the thickness increments are 50Å or 500Å. Therefore, 'pulsed' experiments were used throughout the work on lead telluride.

Figure 6.14 shows the effect of the rate of deposition on the stress. It is observed that the stress increases with increasing rate. On this graph Specimen 324 was evaporated with the bias off. The absence of the bias produced no significant difference in the stress behaviour.

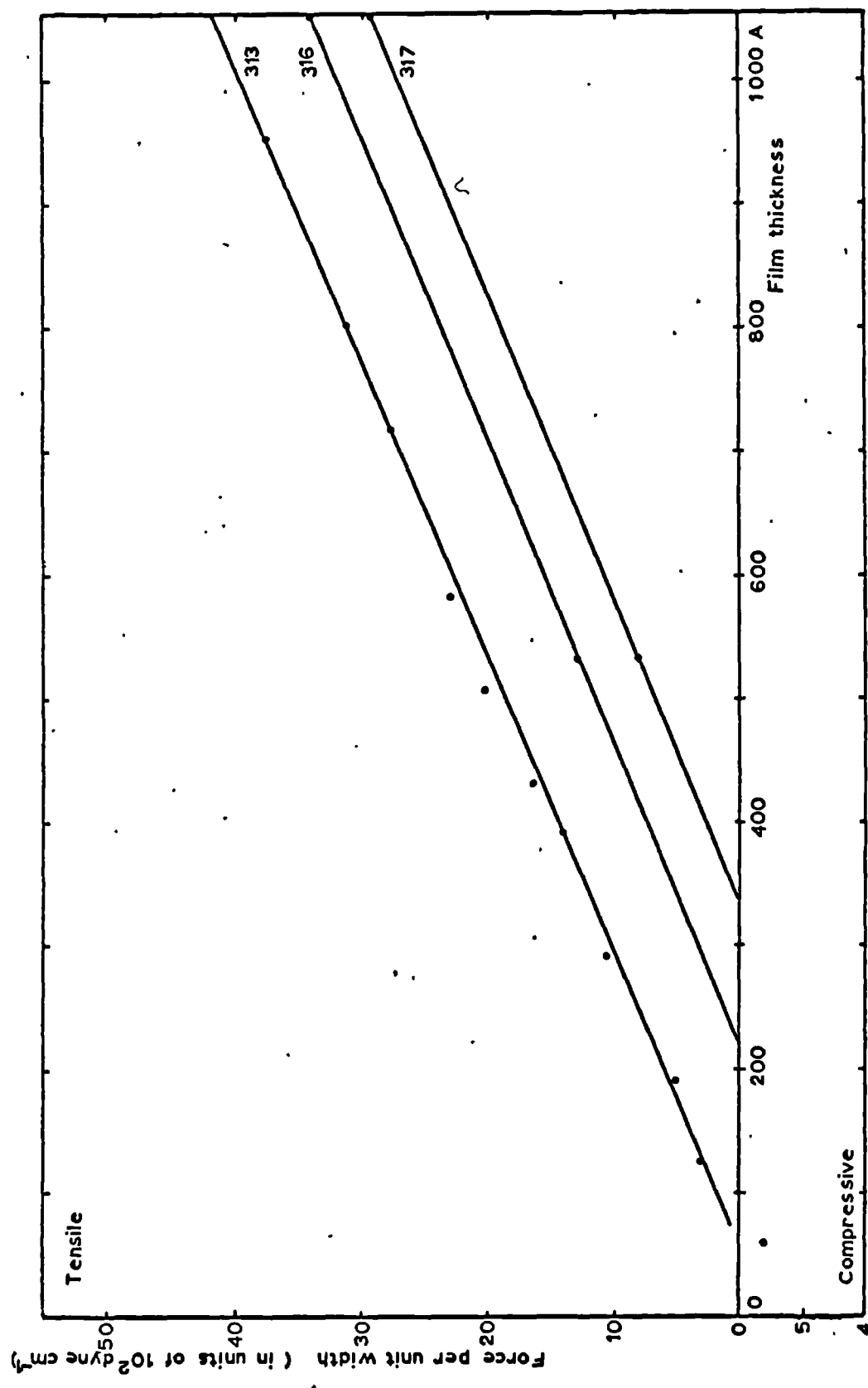


Figure 6.13 The effect of different thickness increments on the force per unit width versus film thickness curve for lead telluride evaporated on to mica substrates.

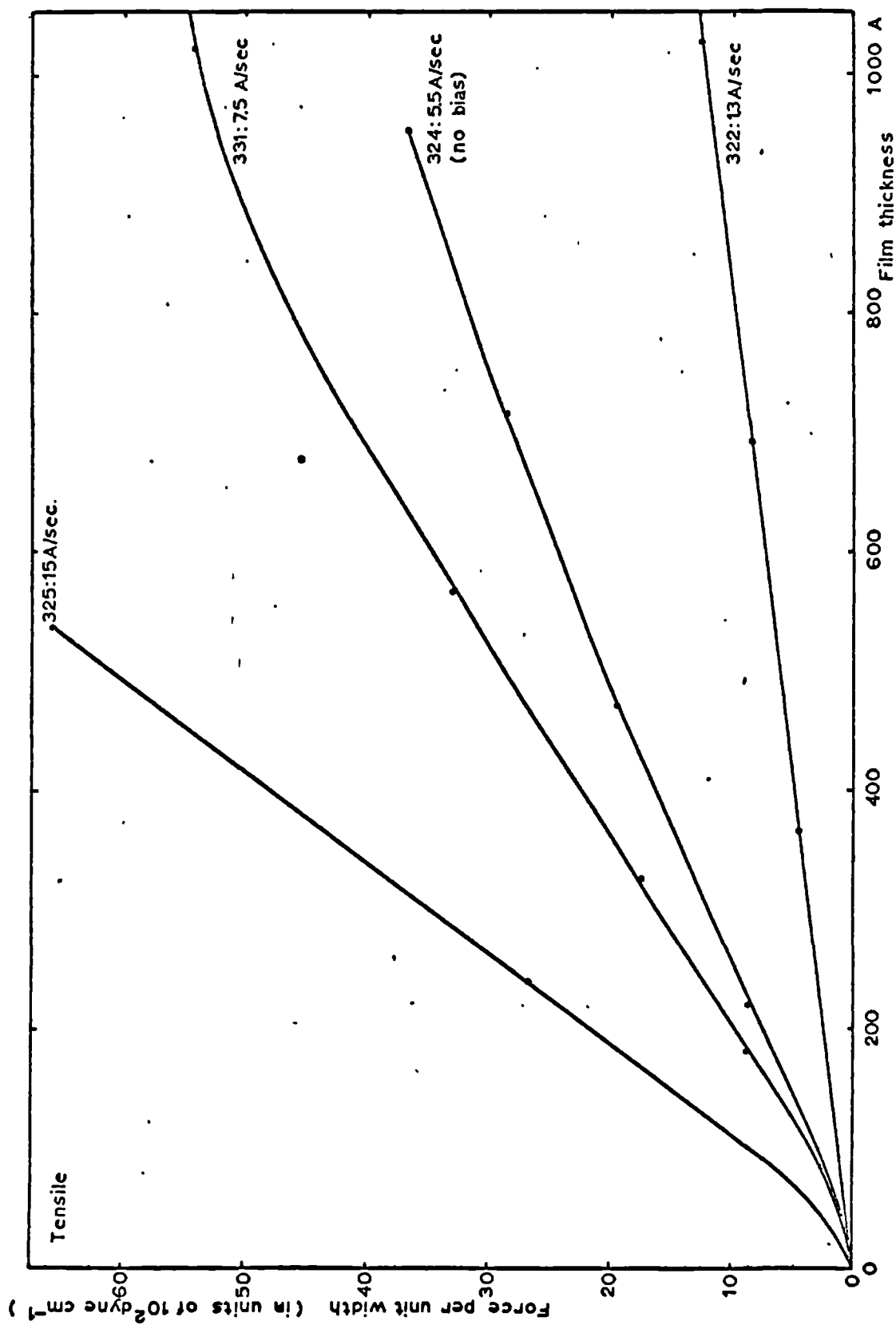


Figure 6.14 The effect of the rate of evaporation on the force per unit width versus film thickness curve for lead telluride evaporated on to mica substrates.

Most of the results were the straight line graphs shown here. However when these straight lines were extrapolated about 60% of the results obtained would cross the force per unit width axis below the origin in the compressive region. The results in Figure 6.13 are examples of those which cross in the compressive region, while those of Figure 6.14 pass through the origin.

In order to find out whether the stress was compressive at any point during an evaporation measurements were made of the stress in the initial stages of growth. There was a large scatter on the results so that Figure 6.15 shows some representative values for evaporation rates of 1, 3 and 4Å/sec. This graph has been drawn on a five times enlarged scale, so that a given slope corresponds to the same stress as it would in Figures 6.13 and 6.14. The indication is that the stress is always tensile. The compressive trend implied by the results in Figure 6.13 could have arisen from incomplete coating on the substrate reverse (section 3.6.5, item 4).

The thermal stress correction has been plotted in Figure 5.9. The magnitude of the thermal stress is very much less than that of the total stress. Even if possible errors in the measurement of the substrate temperature are taken into account the thermal stress remains much smaller than the total stress. Thus intrinsic stress exists in lead telluride films.

The results of all the stress measurements on lead telluride films are tabulated in Appendix 6.4 and are

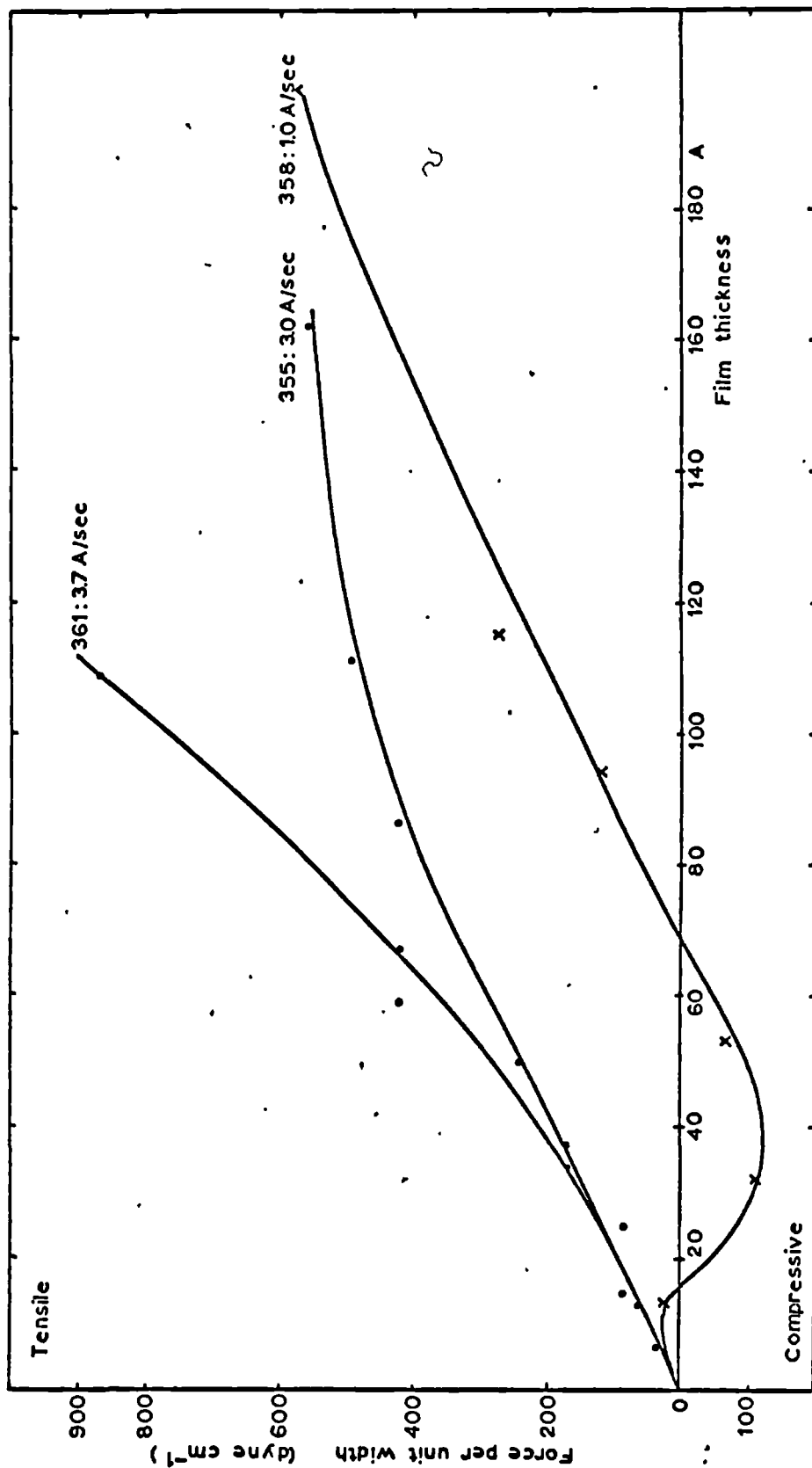


Figure 6.15 Force per unit width versus film thickness in the initial stages of growth of lead telluride films evaporated on to mica substrates.

summarised in Table 6.2. Included in this table are the results of a number of measurements of stress in films deposited on to glass substrates. In order to compare the stress in films deposited on to glass and mica substrates the results have been isolated in Table 6.3. From this table it is apparent that the stress in lead telluride films deposited on to glass substrates is less dependent on the evaporation rate than the stress in such films deposited on to mica substrates.

6.4.3. Structure Results

Thermoelectric probe measurements indicated that none of the films were semiconducting. The sheet resistivity was of the order of $50 \text{ K} / \square$ in the final films which were $1,000 \text{ \AA}$ thick.

The film structure was observed by transmission electron microscopy and selected area electron diffraction. Specimens were grown specifically for structure examination, and at the same time some of the films which had had their stress measured were examined. Great difficulty was experienced in stripping the carbon backed lead telluride films from the mica substrates. For instance out of eight sets of specimens grown specially for structure examination only one set stripped enough to enable a complete growth sequence to be observed, and of seven attempts to strip films from the substrates used for stress determination only two were successful. The specimens which

1	2	3	4	5	6
2	S	off	10^{-5}	medium	8.0
3	S	on	10^{-7}	medium	4.2
1	C	off	10^{-7}	medium	3.9
8	C	on	10^{-7}	low	4.0
9	C	on	10^{-7}	medium	4.0
8	C	on	10^{-7}	high	11.2
6	glass	on	10^{-7}	medium	7.2
6	glass	on	10^{-7}	high	7.4

Table 6.2. Summary of results on lead telluride films. Column 1 is the number of different substrates used; Column 2 is whether cleaved mica (C), mica as supplied (S) or glass substrates; Column 3 is whether the bias was on or off; Column 4 is the residual gas pressure during evaporation in torr; Column 5 is the rate of evaporation - low = $1\text{\AA}/\text{sec.}$, medium = $3 - 7\text{\AA}/\text{sec.}$, and high = $10 - 20\text{\AA}/\text{sec.}$; Column 6 is the average stress at a film thickness of $500\text{\AA}$ in units of $10^8 \text{ dyne cm}^{-2}$.

did strip required long exposures to hydrofluoric acid fumes, and showed evidence of structural damage. Exposure to concentrated hydrofluoric acid liquid, and to hydrofluoric acid fumes for more than twelve hours did not enable the films to be stripped. Hence the structures which were observed did not necessarily represent the structures which were present in the stress films. It is also clear that very tight bonding exists between PbTe and mica. All these experiments were with room temperature mica substrates.

Plates 6.15 - 6.20 show the growth sequence. The film thickness are approximate. The evaporation rate was about $10\text{\AA}/\text{sec}$. The films were deposited on to uncleaved mica substrates at room temperature. The film became continuous at a very early stage of growth. The (111) spot diffraction patterns indicated epitaxial growth, although the micrographs showed that the crystallite size was only of the order of $200\text{\AA}$.

No difficulty was experienced in stripping PbTe films from glass substrates. Two micrographs, Plates 6.21 and 6.22 corresponding to 5 and $10\text{\AA}/\text{sec}$ evaporation rates showed very similar structure, and the characteristic simple cubic diffraction ring pattern.

Diffraction patterns from specimen films (Plates 6.23) showed a ring pattern or a spot pattern, and one film showed a partially oriented film.

Of all the specimens examined only one small area contained

218.



Plate 6.15
20A: 10A/sec

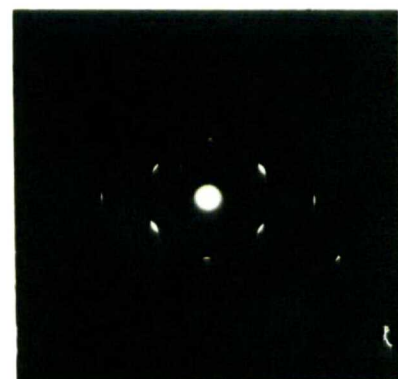
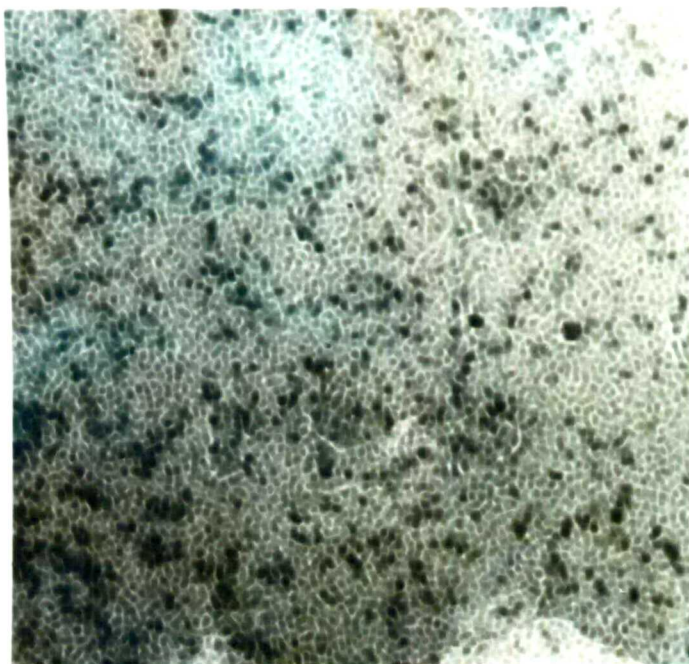


Plate 6.16
40A: 10A/sec

Growth of lead telluride films on to mica substrates. The mark in plate 6.15 represents 1,000A. x 200,000 magnification.

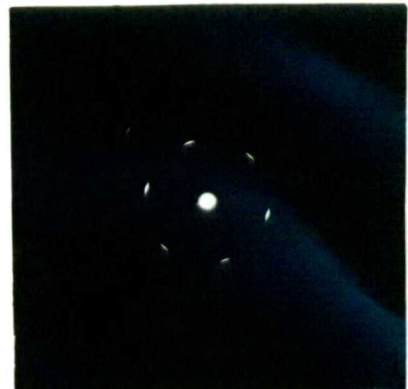
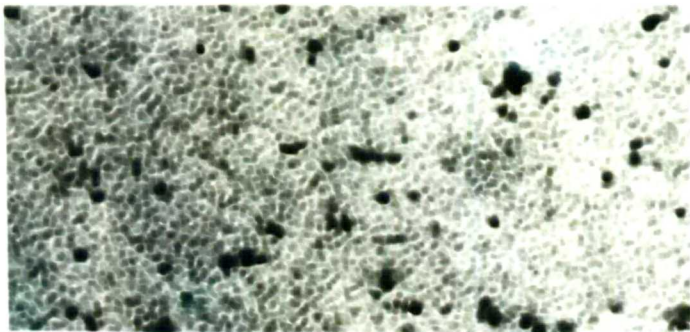
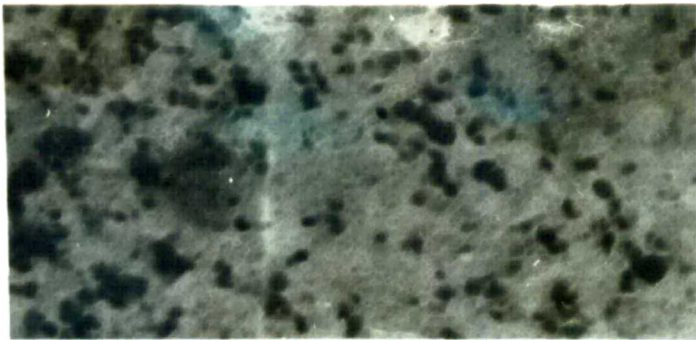


Plate 6.17
80A: 10A/sec

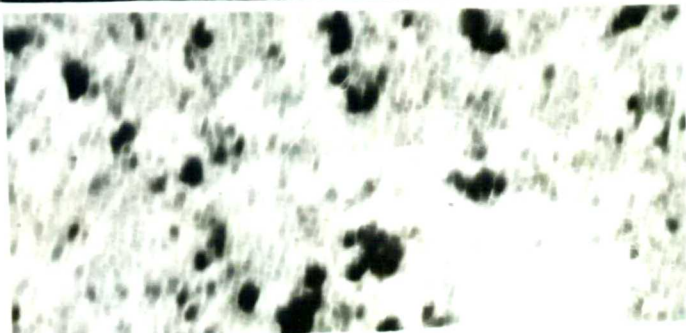


Plate 6.18
160A: 10A/sec

Growth of lead telluride films on to mica substrates. The pairs of micrographs are from different areas of the same grid square. x 200,000 magnification.

220.

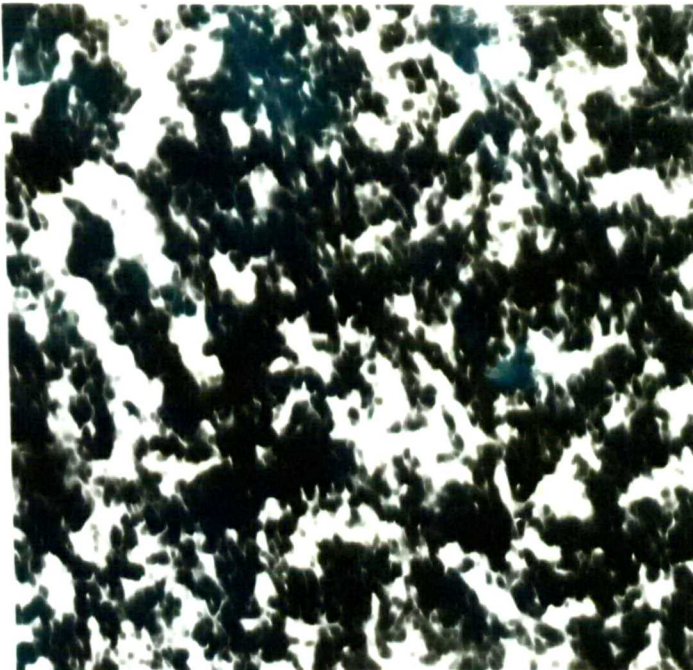


Plate 6.19
320A: 10A/sec

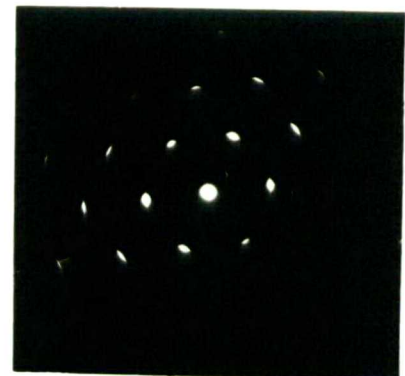
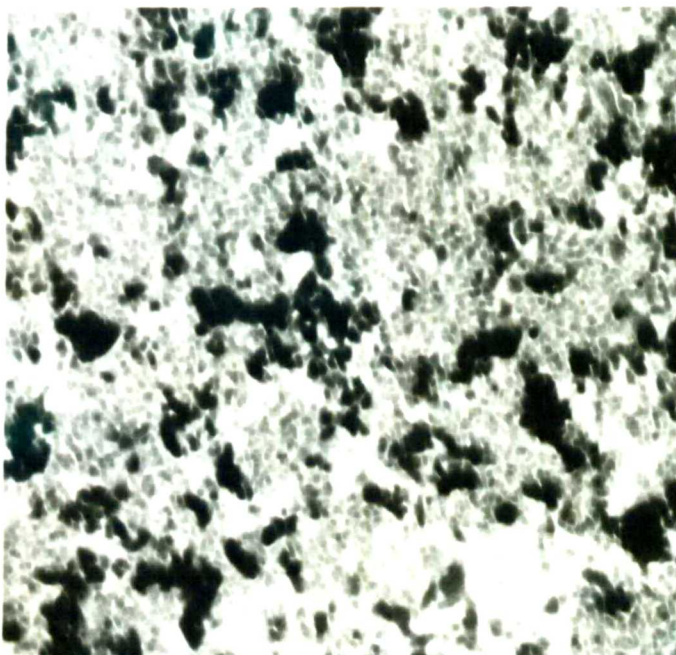


Plate 6.20
640A: 10A/sec

Growth of lead telluride films on to mica substrates.
x 200,000 magnification.

221.

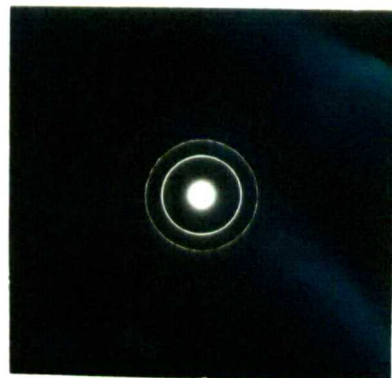
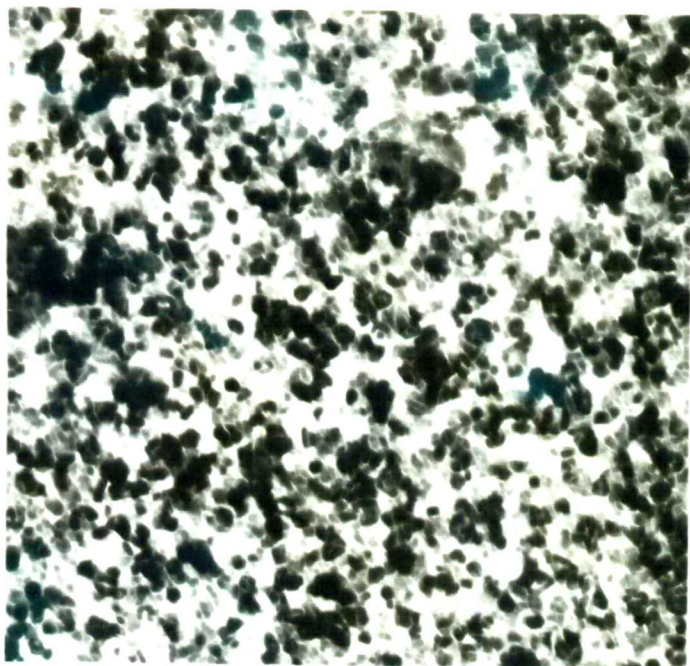


Plate 6.21
Specimen 538
580A: 5.3A/sec
3,500 dyne cm⁻¹

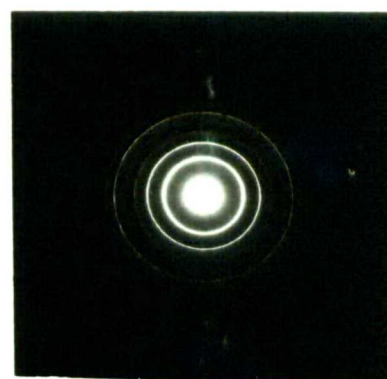
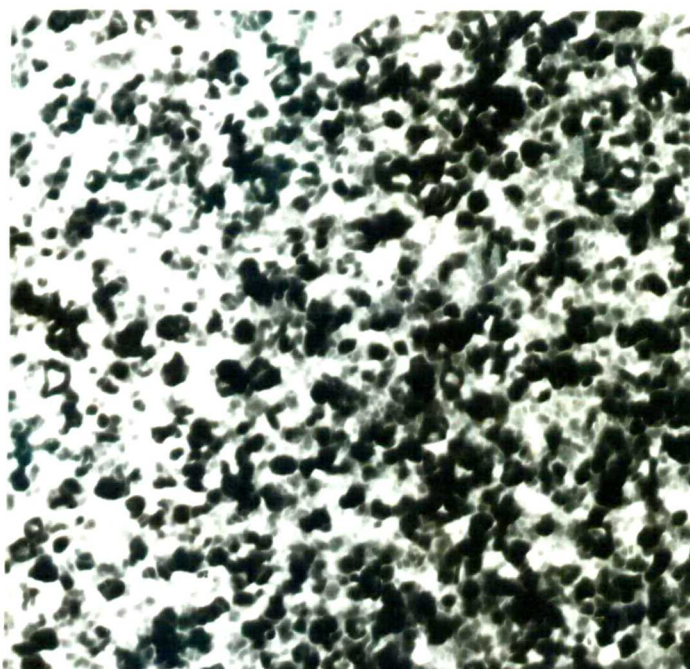


Plate 6.22
Specimen 541
565A: 11A/sec
4,300 dyne cm⁻¹

Growth of lead telluride films on to glass substrates.
x 200,000 magnification.

a thick enough layer of PbTe on a thin enough layer of mica to enable a superimposed diffraction pattern to be obtained. This diffraction pattern (Plate 6.23E) indicated that the orientation relationship was (111) PbTe // (111) mica, [321] PbTe // [633] mica: that is an angle of 12° between the (100) direction of film and substrate. This result, which was not confirmed in any other experiment was contrary to Makino's⁽²⁷⁶⁾ work. Makino found that the orientation relationship was (111) PbTe // (001) mica, [110] PbTe // [100] mica.

An attempt was made to find a dependence of stress on the orientation of the substrate. No dependence was found. However an orientation dependence might have been masked by the scatter ($\pm 30\%$) in the experimental results.

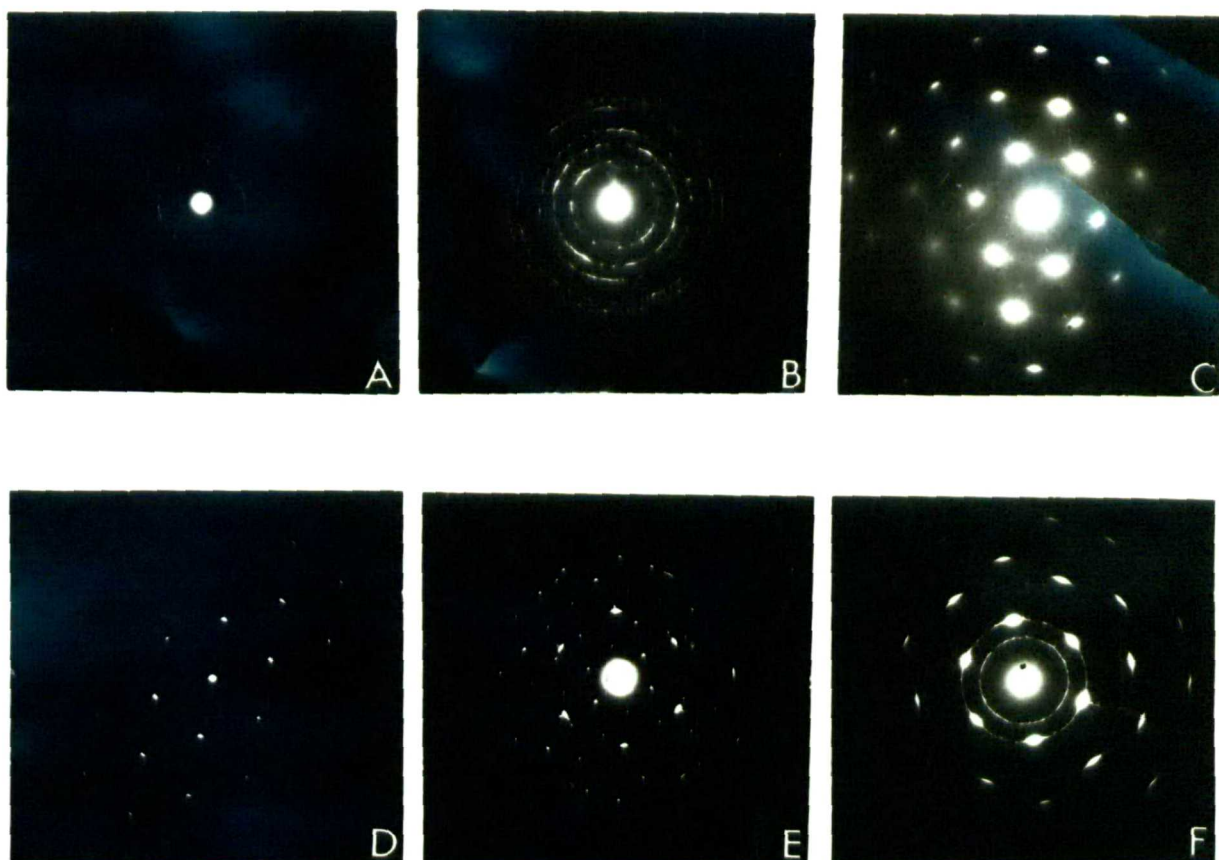


Plate 6.23

A, B, C and D are four diffraction patterns from lead telluride evaporated on to mica substrates. A is specimen 316; B is specimen 318; C is specimen 324; D is specimen 325.

E is the only diffraction pattern obtained illustrating the orientation relationship between a lead telluride film and its mica substrate.

F is a typical diffraction pattern from a tin telluride film.

Evaporation Rate	Glass Substrates	Mica Substrates
5.5Å/sec	7.1	4.0
11Å/sec	7.4	11.2

Table 6.3. A comparison of the effect of evaporation rate on the stress in lead telluride films deposited on to glass and mica substrates. The stress is in units of 10^8 dyne cm^{-2} .

6.4.4. Conclusions

1. The total stress in lead telluride films deposited on to mica or glass substrates is tensile.
2. The total stress in the earliest stages of film growth (10-30Å) is tensile.
3. The force per unit width in lead telluride films deposited on to mica substrates rises linearly with increasing film thickness. That is the stress is constant.
4. The stress in lead telluride films deposited on to mica substrates is mainly intrinsic.
5. It is probably that the structure of lead telluride films deposited on to room temperature freshly cleaved mica substrates consists of well oriented films with crystallite size about 200Å.

6. Lead telluride films deposited on to glass substrates have randomly oriented crystallites with a crystallite size of the order of $100\text{\AA}$.
7. The stress is less rate dependent in films deposited on to glass than in films deposited on to mica substrates.

CHAPTER VII

7.1. INTRODUCTION

In this chapter the models discussed in chapter two will be considered in the light of the experimental results presented in chapter six. The discussion will be divided into two parts, on silver and gold films and on lead telluride films. The discussion of the lead telluride results is necessarily incomplete as the structure of the films could not be precisely determined.

Lead telluride films will be considered in section 7.2 in the light of the available evidence on stress and film structure. The remainder of the chapter will be devoted to the silver and gold films, where there is sufficient data to enable a satisfactory conclusion to be drawn.

7.2. LEAD TELLURIDE FILMS

The results showed that the intrinsic stress in lead telluride films deposited on to mica substrates was independent of film thickness. Five of the models (thermal, imperfection (vacancy), density, grain boundary and interfacial) introduced in chapter two predicted such a type of stress.

The stress in the films was also dependent on the deposition rate. However the stresses predicted by the thermal model and the density model depend only on the physical properties of the evaporant, such as its recrystallization temperature. Hence these models predict a stress independent

of the deposition rate. Thus the stress found in lead telluride films was probably due to the imperfection (vacancy) model, the grain boundary model or the interfacial phenomena models.

Unfortunately the lack of data on the structure of the lead telluride films and the lack of data on the physical properties of bulk lead telluride prevent any firmer conclusions being drawn.

7.3. SILVER AND GOLD FILMS

7.3.1. Introduction

The discussion in the remainder of the chapter will be confined to silver and gold films deposited on to amorphous substrates.

The results in chapter six fall into two categories, stress and structure results. On the basis of the structure results it is convenient to divide the discussion into two parts, island structure films, to be discussed in section 7.4, and continuous films, to be discussed in section 7.5.

The results on gold and silver films in the present work are very similar to each other. This similarity has not been previously observed. Published results on silver and gold films have been reproduced in Figures 7.1 and 7.2. The relevant evaporation conditions have been given in Table 7.1.

The salient points of the results of chapter six which will be utilised in this chapter are:-

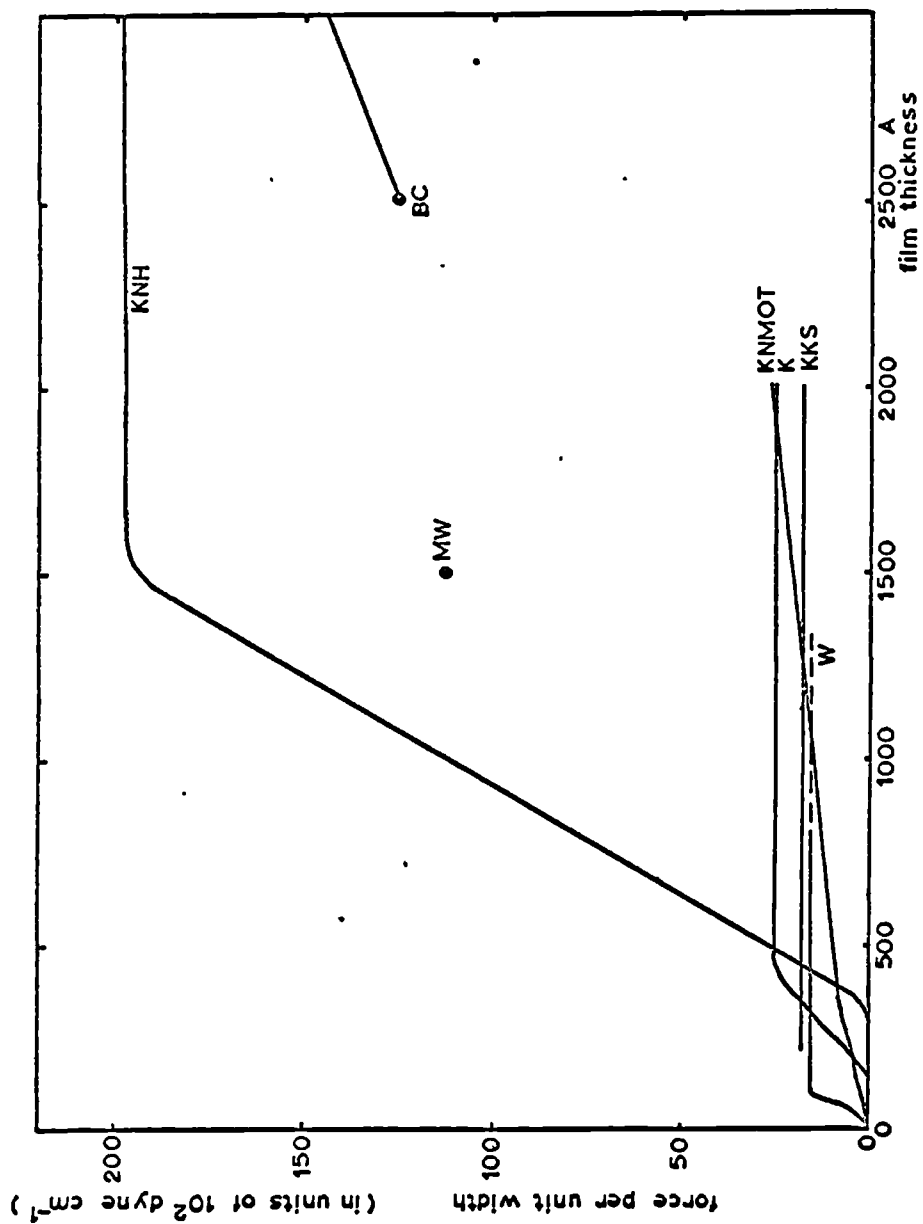


Figure 7.1 Force per unit width versus film thickness for silver films. Results from literature.

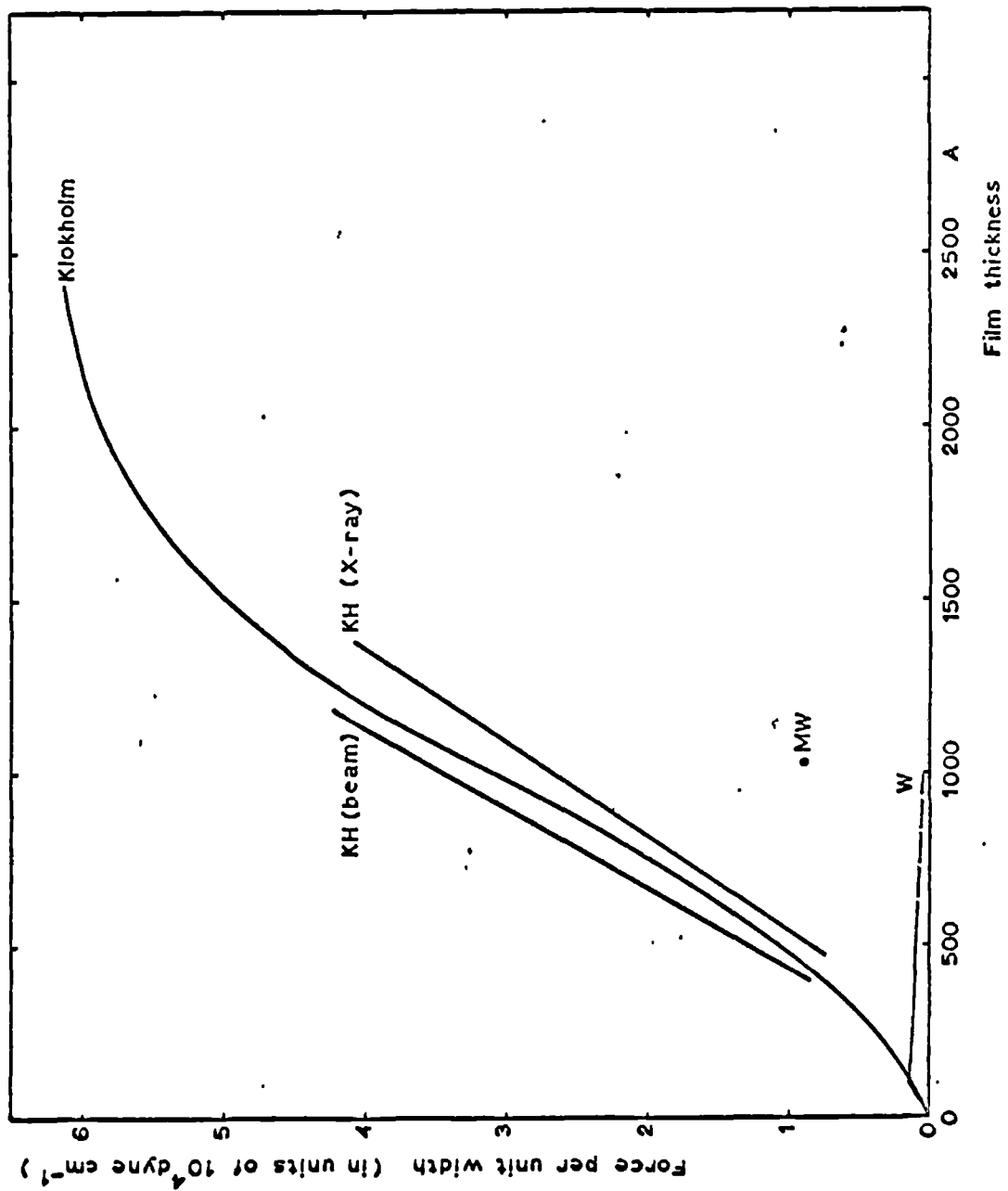


Figure 7.2 Force per unit width versus film thickness for gold films. Results from literature.

Substrate material	rate Å/sec	Pressure torr	Authors initials	Ref.	Authors names
silver films					
copper	30-60	10^{-4} - 10^{-5}	MW	82	Murbach, Wilman
copper	?	$5 \cdot 10^{-5*}$	KNH	126	Kato, Nagashima, Hasunuma
mica	20-40	$2 \cdot 10^{-5}$	KKS	127	Kinosita, Kondo, Sawamura
mica	20-40	$\approx 10^{-5}$	KNMOT	280	Kinosita et al.
soda glass	15	10^{-4} - 10^{-5}	BC	74	Blackburn, Campbell
soda glass*	5-15*	$\approx 10^{-6*}$	K	281	Klokholm
soda glass	3-10	$2 \cdot 10^{-6}$	W		Wilcock
gold films					
copper	30-60	10^{-4} - 10^{-5}	MW	82	Murbach, Wilman
quartz	15-20	$\approx 10^{-5}$	KH	119	Kinbara, Haraki
soda glass*	5-15*	$\approx 10^{-6*}$	K	281	Klokholm
soda glass	1-20	$3 \cdot 10^{-6}$	W		Wilcock

Table 7.1. Evaporation conditions and key for Figures 7.1 and 7.2. The values marked thus* are not stated explicitly, but are well informed guesses based on similar work by the same authors.

1. The stress is tensile throughout the whole film thickness range studied.
2. During the island and coalescence stages the intrinsic force per unit width increases with increasing film thickness.
3. After the film has become continuous in structure the intrinsic force per unit width decreases with increasing film thickness.

These statements are true for silver and gold films deposited on to glass substrates, and for silver films deposited on to mica substrates.

Statements 2 and 3 state that, after the coalescence stages, once the last hole in the film structure is filled, no further intrinsic stress is generated. This result is important in the discussion of the models.

Other information about the structure of silver films not obtainable by conventional electron microscopy or diffraction was cited in chapter two. This was the scanning electron diffraction (SCED) evidence. A discussion of the validity of the structural evidence obtained in the present experiments has been given in section 6.15. A discussion of the validity of the SCED evidence will now be given

7.3.2. Structural considerations

In the earliest stages of film growth the number of islands per unit area of substrate increases as the islands are

nucleated⁽²⁸²⁾. At some later time coalescence takes place and the number of islands per unit area of the substrate decreases. Thus the number of islands per unit area of substrate passes through a maximum value. Different nucleation conditions cause this maximum to occur at different film thicknesses, and thus lead to a different film structure at a given thickness.

A comparison of the micrographs obtained in the SCED studies with those from the present studies showed that the present films were much less agglomerated. This difference in structure was attributed to a difference in nucleation conditions. The nucleation theory of Lewis and Campbell²⁸² showed that under conditions similar to those used in the present work, for a given film-substrate combination, the film thickness, $f_{\max}$, at which the number of islands per unit area of substrate passed through a maximum was inversely proportional to the evaporation rate. As the rates of evaporation in the SCED work were about two orders of magnitude smaller than those in the present experiments $f_{\max}$ would have occurred at a much greater film thickness.

The film thickness, $f_{\max}$, depends very critically on the choice of values of adsorption and surface diffusion energies. If the surface diffusion energy is assumed to be one tenth of the adsorption energy the two different published values for the adsorption energy of silver on to glass (5.2 Kcal/mole²⁸³ or 3.4 Kcal/mole²⁸⁴) gives values of 1.5 seconds or 3×10^3 seconds for the time taken to reach $f_{\max}$ when the

evaporation rate is $10\text{\AA}/\text{sec}$. These times become longer if the surface diffusion energy is assumed to be one third of the adsorption energy.

The times to reach f_{max} in the SCED work is then 3×10^4 seconds or 6×10^7 seconds depending on the choice of adsorption energy values.

The fact that f_{max} occurs at a low film thickness in the present work is confirmed by the graph of island density versus film thickness, Figure 6.16.

Thus the film structure found at a given film thickness in the SCED work is not comparable with that at the same thickness in the present work. The experimental conditions during deposition also differed in certain other respects. The SCED depositions were carried out on to carbon substrates, not on to glass. Furthermore the residual gas pressure in the SCED work was the same as that used in the present work, so that the ratio of residual gas atoms to evaporant atoms landing on the substrate was two orders of magnitude higher.

7.4. MODELS FOR STRESS IN THE INITIAL STAGES OF GROWTH

7.4.1. Introduction

Models for stress in films thinner than about $100\text{\AA}$ will be considered in this section. The models to be discussed have been listed in Table 7.2, and they have been numbered for ease of reference.

MODEL		Type of stress, tensile or compressive.	Does the model predict the quantitative stress behaviour in island structure films.	Does the model predict the quantitative stress behaviour in continuous films.
1	Thermal	T		No
2	Imperfection (vacancy)	T		No
3	Imperfection (grain boundary in islands)	T	Possibly	
4	Density	T		No
5	Grain Boundary	T		No
6	Grain Gap	T	Possibly	Yes
7	Electrostatic	T or C	No	No
8	Surface stress	C	No	
9	Surface tension	T	No	
10	Interfacial	C or T		
11	Inhomogeneous strain modification of interfacial	C or T	No	

Table 7.2 Models for intrinsic stress in silver and gold films deposited on to glass substrates.

The thermal model, the imperfection (vacancy) model, the density model, the grain boundary model and the interfacial models (models 1,2,4,5,10 and 11 of Table 7.2) were originally proposed in connection with continuous films. The discussion of these models will therefore be deferred until section 7.5. It will be shown that these models are not applicable to the present continuous films. Hence it is probable that they are not applicable to island structure films either.

Of the remaining models the grain gap and the imperfection (grain boundary in islands) model are singled out for further discussion in sections 7.4.3. and 7.4.4.

7.4.2. General discussion of models

7.4.2.1. The electrostatic model (model 7 of Table 7.2)

The calculations made in chapter two on the electrostatic model apply to any system of conducting islands on an insulating substrate. The silver and gold films used in the present investigation form such a system. The calculations showed that the force per unit width fell very rapidly with increasing film thickness. The predicted values of stress were of the same order of magnitude as observed stresses only in films thinner than $10 \text{ \AA}$.

In thicker films they were negligible. Thus this mechanism is not the sole cause of stress in the present films. In added proof, the model predicts no stress in an electrically

continuous film, whereas stress in such a film was certainly observed.

In Table 7.2. it has been noted that this model does not apply quantitatively to either thick or island structure films.

7.4.2.2 The surface stress model (model 8 of Table 7.2)

On the basis of the electron diffraction data presented in section 2.7.3 it was concluded that the lattice spacing of small crystallites of silver was smaller than that of bulk silver. This implies that silver has a positive surface stress. It was shown that a positive surface stress would lead to a compressive stress being observed in a bending beam experiment. Taken in conjunction with the structural evidence presented in section 6.1.5 the theoretical derivation given in section 2.7.4 shows that, on the surface stress model, the force per unit width decreases with increasing film thickness in island structure films. However the experimental stress results show an increasing force per unit width in this thickness range. Thus in the light of available evidence the surface stress model does not seem applicable to the present films.

In Table 7.2 it has been noted that this model predicts compressive stress, and that it predicts an incorrect film thickness dependence of stress.

7.4.2.3 The surface tension model (model 9 of Table 7.2)

The surface tension model requires the islands in an island

structure film to exhibit liquid-like properties. Liquid-like behaviour of islands in growing films has been observed by transmission electron microscopy: however electron diffraction patterns from films of silver and gold growing on to substrates at temperatures well below their melting points show crystalline structures. But even if the islands in the film behaved as perfect liquids, the quantitative calculation (section 2.7.4) shows that the model predicts the same film thickness dependence of force per unit width as the surface stress model, and thus, by the arguments in section 7.4.2.2, does not account for the experimental results.

In Table 7.2. it has been noted that this model predicts an incorrect film thickness dependence of stress.

7.4.3 The grain gap model (model 6 of Table 7.2)

As mentioned in section 2.5.4 the quantitative calculation of the stress due to gaps between islands at the substrate is an extremely difficult mathematical problem. Finegan and Hoffman ⁽⁸⁸⁾ have attempted a crude calculation. They showed that the contribution expected in an iron film was $8 \times 10^3 \text{ dyne cm}^{-1}$.

The model predicts a stress contribution as the island coalesce, but no further stress once the last holes in the film structures are filled. This is the type of stress behaviour found in the present experiments.

As in the general grain boundary model, this model predicts that the stress in a film will be higher as the crystallite size is smaller.

The origin of the stress, on this model, is the interatomic forces of attraction between adjacent crystallites. These same forces would lead to a stress contribution on the grain boundary model if they were significant. But we will show that the grain boundary model does not apply to the present films. Therefore it is likely that the interatomic forces of attraction are not significant in the present films. Thus the grain gap model is probably inapplicable.

7.4.4 The imperfection (grain boundary in islands) model. (model 3 of Table 7.2)

The quantitative evidence for the existence of, and the subsequent annealing of, grain boundaries in the islands of island structure silver films comes from SCED experiments as described in sections 2.3.4 and 7.3.2.

An island, as observed by transmission electron microscopy, consists of a large number of randomly oriented crystallites or grains. Each crystallite or grain consists of a number of atoms. The crystallites or grains are separated by grain boundaries, with the average gap between grains being half the diameter of an atom.

Let the number of atoms in a crystallite be m . Then the volume, V , of a crystallite is given by:-

$$V = m c_1 d^3 \quad (7.1)$$

where either $c_1 = 1$ and d is the cube edge, for cubic atoms

or $c_1 = \frac{1}{2} \sqrt{2}$ and d is the diameter of an atom, where

the atoms are close packed spheres.

The surface area of a crystallite, S , is given by:-

$$\begin{aligned} S &= V^{2/3} c_2 \\ &= (m c_1 d^3)^{2/3} c_2 \end{aligned} \quad (7.2)$$

where either $c_2 = 6$ if the crystallites are cubic in shape

or $c_2 = 4 \pi (3/4\pi)^{2/3}$ if the crystallites are spherical.

Rhombohedral crystallites were assumed by Grigson ⁽²⁸⁵⁾ in the theoretical diffraction pattern calculations.

Let the radius of an island be r . Then the volume of an island will be $c_3 r^3$ (7.3)

where either $c_3 = \frac{2}{3} \pi$ for hemispherical islands

or $c_3 = 4/3 \pi$ for spherical islands.

The number of crystallites per island is equal to the volume of an island divided by the volume of a crystallite. Hence the number of crystallites per island is

$$c_3 r^3 / m c_1 d^3 \quad (7.4)$$

The void content (in cc) per island, due to the grain boundaries, is equal to the total area of grain boundaries in an island multiplied by the average gap between grains. That is

$$(m c_1 d^3) c_2 \times c_3 r^3 / m c_1 d^3 \times \frac{1}{2} \times \frac{1}{2} d \quad (7.5)$$

The void content per unit volume of island is hence:-

$$c_2 / (4 m^{1/3} c_1^{1/3}) \quad (7.6)$$

If the grain boundaries are eliminated as the film grows the void content will decrease and the islands will shrink in volume. Let us consider the strain that would be produced if the void content decreased to zero. If the void content decreases to zero the volume strain will be given by -

$$c_2 / (4 m^{\frac{1}{3}} c_1^{\frac{1}{3}}) \quad (7.7)$$

Hence the linear contraction per island will be:-

$$r c_2 / (6 m^{\frac{1}{3}} c_3^{\frac{1}{3}}) \quad (7.8)$$

If N is the number of islands per unit area of the substrate the distance between adjacent islands will be $N^{-\frac{1}{2}}$ cm.

If the Young's modulus of the film is E , and the film thickness f the force per unit width from this linear contraction per island is:-

$$(r c_2 N^{\frac{1}{2}} m^{-\frac{1}{2}}, c_1^{-\frac{1}{2}} E f) / 6 \quad (7.9)$$

Remembering that $f = N c_3 r^3$ we can eliminate either r or N .

Assuming that the crystallites are cubic, the atoms spherical, the islands hemispherical and the material silver we obtain:-

$$f.p.u.w. = r^{\frac{1}{2}} f^{3/2} m^{-1/2} (7.0 \times 10^3) \text{ dyne cm}^{-1}$$

where r and f are in $\text{\AA}$. This, it must be remembered, is not the actual force per unit width in a film at thickness f , but it is the change in force per unit width that would occur if all the grain boundaries were eliminated.

Heritage has analysed his SCED data on silver films deposited on to carbon substrates to give values of f , N , $\bar{r}$ and m .

This data is reproduced in Table 7.3. The force per unit width that would be present in a film if all the grain boundaries were eliminated has been calculated from this data. The data is sufficient for three points to be plotted on a force per unit width versus film thickness curve. These points indicate that the force per unit width is tensile and decreasing in magnitude below a film thickness of $30\text{-}40\text{\AA}$, increasing in magnitude with increasing film thickness in thicker films.

These results cannot be compared directly with the present results for the reasons discussed in section 7.3.2. However it is possible that SCED structural data taken under suitable evaporation conditions, and used in conjunction with Equation 7.9 may provide a possible origin for the stress.

It is interesting to observe that the difference between the last two SCED results suggests that the stress is becoming more tensile as the film thickness increases.

7.5 MODELS FOR STRESS IN CONTINUOUS FILMS

7.5.1 General discussion of models

7.5.1.1 Constant stress models (models 1, 2 and 4 of Table 7.2)

The thermal model (model 1 of Table 7.2) predicts constant stress, independent of film thickness, in continuous films. A constant stress in such films is also predicted by the density model (model 4 of Table 7.2) and by the imperfection

f	N	$\bar{r}$	m	f.p.u.w.
10	7.8	26	4	11×10^3
18	7.4	36	5 or 6	$14.5 \text{ or } 17.5 \times 10^3$
29	4.9	48	6 or 7	$21.5 \text{ or } 25 \times 10^3$
45	1.9	86	10	21×10^3

Table 7.3 Data for the stress calculation on the imperfections (grain boundary in islands) model. The film thickness f is in Å; N is in units of 10^{11} islands per sq. cm.; $\bar{r}$ is in Å and the force per unit width is in dyne cm^{-1} .

(vacancy) model (model 2 of Table 7.2) insofar as the imperfection (vacancy) model predicts any quantitative variation of stress with film thickness. The results obtained in the present experiments show that no stress is built in to the growing film once it has become complete in structure. These three models, therefore, cannot be applied to explain the present stress results in continuous films.

7.5.1.2 The interfacial phenomena models (models 10 and 11 of Table 7.2)

It is not certain that models 10 or 11, based on the theory of crystal interfaces, may be applied to the stress in random polycrystalline films grown on amorphous substrates. However (section 7.8.1) they have been successfully applied to alkali halide films grown on to glass substrates. In order to find the type of stress predicted by these models the lattice mismatch must be estimated.

The lattice constants of silver and gold are $4.086\text{\AA}$ and $4.078\text{\AA}$ respectively. Thus the nearest neighbour distance is about $2.89\text{\AA}$ in both cases.

The average separation of adjacent oxygen atoms in the glass substrates used in the present experiments was calculated from the data in Appendix 5.1. It was $2.86\text{\AA}$. A similar calculation for the oxygen atoms in a silica structure gave $2.65\text{\AA}$. The average distances between sodium, calcium and magnesium atoms was also calculated. They were $5.50\text{\AA}$, $7.75\text{\AA}$ and $9.15\text{\AA}$ respectively.

Thus, depending on which atoms in the substrate surface the silver or gold atoms have an affinity for, the mismatch may be such as to produce a tensile or a compressive stress. If the film structure is such that a close packed plane lies adjacent to the substrate, and if the film atoms interact more strongly with the oxygen atoms in the substrate surface than with, say the sodium atoms, then the atomic spacing in the film will be greater than that of the substrate, and a compressive stress would result on this model. Similarly if the film forms with a (100) surface parallel to the substrate and if it interacts with the silicon atoms in the substrate surface, a tensile stress would be produced.

Thus either tensile or compressive stresses may be predicted by this model depending on the choice of interacting atoms.

The experimental results showed similar stresses in films evaporated on to mica or glass substrates. Thus it appears that the structure of the substrate surface has little effect on the stress. As the prediction of this model depends strongly on the film-substrate interface this result appears to invalidate the model. The inhomogeneous strain modification (model 11 of Table 7.2) predicts no stress in island structure films, and a stress in continuous films. This is the opposite situation to that found in the present experiments, and thus model 11 is inapplicable.

7.5.2 The grain boundary model (model 5 of Table 7.2)

In the grain boundary model the stress arises from the

interatomic force of attraction between adjacent atoms in neighboring crystallites. Thus the stress depends on the same forces of attraction that might lead to stress on the grain gap model. As discussed in section 2.5.2 the model predicts constant stress with increasing film thickness when the crystallite dimensions on the plane of the substrate remain constant. If the crystallite size increases as the film grows then the incremental stress decreases. Any crystallite boundaries would lead to some stress contribution on this mechanism. But the results summary shows that no incremental stress occurs in films thicker than about $150\text{\AA}$. Therefore either film growth in films thicker than this is in the form of single crystal growth, or no stress contribution occurs on this model. Structural evidence shows that thick films are polycrystalline in nature and do not grow as single crystals. Hence there is no stress contribution on the grain boundary models in the present films.

7.6 CONCLUSIONS

The internal stress was measured in thin films of silver and gold deposited on to glass and mica substrates and also in lead telluride films.

A full discussion could not be given to the lead telluride results, but three of the models introduced in chapter two were considered more likely than the remaining models.

The results obtained on silver and gold films were similar to each other. The thermal stress contribution was calculated from the substrate temperature rise during the evaporation, and was subtracted from the total stress to give the intrinsic stress. The stress in films thicker than $400\text{\AA}$ was predominantly thermal. Below this thickness the majority of the stress was intrinsic. The intrinsic stress was found to pass through a maximum value at the film thickness at which the last hole in the film structure became filled ($100\text{-}200\text{\AA}$). The intrinsic force per unit width also passed through a maximum at this film thickness.

In the region where the intrinsic force per unit width was increasing with increasing film thickness the imperfection (grain boundary in islands) model was considered to be the most likely of the models discussed. A quantitative theory was derived for this model. Unfortunately the SCED data needed to apply this theory to the present system was insufficient for the reasons discussed in section 7.3.2. However the evidence from the thickest films examined by SCED showed some agreement with the present experiments.

The surface stress model cannot be categorically rejected as the two experimental results on which the discussion was based may, in the light of future experiments, both prove to be in error. The results were (i) positive surface stress and (ii) $N^{\frac{1}{2}}f$ decreases with increasing f . As

it is unlikely that both these experimental results will prove to be false the surface stress model was not considered as likely as the grain gap or imperfection (grain boundary in islands) model.

It is concluded that the most likely model for the stress in island structure films of silver and gold is the imperfection (grain boundary in islands) model.

No intrinsic stress was observed in continuous films. However many of the models we have considered have, naturally, set out to predict stress in such films. Therefore we can reject such models in connection with our films.

The models we have considered for island structure films are both valid for continuous films, and neither predicts stress. Furthermore mechanisms for stress relief can be found for both these models, to account for the decreases in force per unit width after the stress maximum.

Table 7.2 summarises the discussion. After eliminating those models which predict compressive stress, and those which predict an incorrect film thickness dependence of stress we are left with the grain gap or the imperfection (grain boundary in islands) models. Of these the imperfection (grain boundary in islands) model was favoured.

ADDENDUM

A paper (Ref. 128b) on stress in evaporated silver and gold films has recently (January 1967) been published. The publication occurred after the present experimental work had been completed and after the bulk of the thesis had been written.

Silver was deposited on to mica, collodion and silica substrates in a vacuum of $1-2 \times 10^{-5}$ torr. By using thin (12μ) mica substrates the minimum end deflection detectable (6μ) corresponded to a sensitivity of 30 dyne cm^{-1} . The end deflection due to a typical stress was much larger (250x) than the substrate thickness.

The stress found in silver films deposited on to silica substrates was similar in form to the total stress in the present experiments. The results on mica and collodion substrates were also similar in form to the present results but were higher in magnitude.

The deflection versus time curve during evaporation (Figure 9 of this paper) corresponded well to the type of curve discussed in section 5.3. However no discussion of the shape of the curve was given.

It was not stated whether the thermal stress contribution had been subtracted from the results, but a comparison of Figure 9 of this paper with the force per unit width versus film thickness curve suggested that it had not.

Thus the results presented in this paper confirmed many of the present results.

APPENDIX 2.1CALCULATION OF THE ELECTROSTATIC FORCE BETWEEN TWO SPHERES

The theory for the electrostatic forces between two spheres which follows is taken from Jeans⁽¹⁶⁹⁾.

The energy of a system of two conductors may be written in terms of the coefficients of potential, p_{11} , p_{22} , p_{12} and the charges E_1 , E_2^2 on the bodies thus:-

$$W = \frac{1}{2} p_{11} E_1^2 + p_{12} E_1 E_2 + \frac{1}{2} p_{22} E_2^2$$

The force between the bodies is obtained by differentiating with respect to the separation of the bodies, c .

$$F = \frac{\partial W}{\partial c} = -\frac{1}{2} \frac{\partial p_{11}}{\partial c} E_1^2 - \frac{\partial p_{12}}{\partial c} E_1 E_2 - \frac{1}{2} \frac{\partial p_{22}}{\partial c} E_2^2$$

If U^2 , V^2 , W^2 are positive quantities the force may be rewritten:-

$$F = -U^2 E_1^2 + V^2 E_1 E_2 - W^2 E_2^2$$

If the charges on the bodies are of opposite signs then F will be negative and there will always be attraction. If the charges are the same sign there will be a repulsion at large separations, because the middle term predominates. However, as the bodies are brought together the sum of the other terms increases more rapidly than the middle term, and eventually there will be

attraction between the bodies. The larger the ratio of the charges the greater the separation at which attraction sets in. If one body is uncharged there will always be attraction.

Lord Kelvin⁽²¹⁵⁾ quotes experimental work on the force between two charged spheres, which was carried out by Harris⁽²¹⁶⁾. His results were summarised thus:

1. If the distance between the bodies is large, the force is proportional to the charge and the inverse square of the distance.

2. If the distance is small and the bodies are equally charged the force is less than if it followed the inverse square law.

3. If the charges are unequal, repulsion ceases at a certain distance and at a smaller distance there is attraction between the bodies.

Jeans⁽¹⁶⁹⁾ has reproduced a table, originally given by Lord Kelvin, of values $\frac{\partial p_{11}}{\partial C}$; $\frac{\partial p_{12}}{\partial C}$; $\frac{\partial p_{22}}{\partial C}$

for the case of two spheres of equal radius. This table was confirmed, and extended to the case of islands with different radii, by the following calculation.

Following Jeans⁽¹⁶⁹⁾ the coefficients of capacity and inductance are found by putting a charge E on one sphere, and finding the resultant image charge on the other sphere. The image charge of the image charge is then found. Eventually

(for example) the charge on sphere A due to unit potential on island A, which is the coefficient of capacity q_{11} , is found as a series. The other coefficients of capacity are found by similar means. The series may be put in a more convergent form by suitable manipulation. The form used in the computation was that due to Russell⁽²¹⁷⁾. His series are:

$$q_{11} = a (1 - \xi^2) \left[\sum_{s=0}^{n-1} \frac{\alpha^s}{1 - \xi^2 \alpha^{2s}} + \alpha^n \sum_{p=0}^{\infty} \frac{(\xi \alpha^n)^{2p}}{1 - \alpha^{2p+1}} \right]$$

$$q_{12} = -\frac{a b}{c} (1 - \xi^2) \left[\sum_{s=0}^{n-1} \frac{\alpha^s}{1 - \alpha^{2s+2}} + \alpha^n \sum_{p=0}^{\infty} \frac{(\alpha^{n+1})^{2p}}{1 - \alpha^{2p+1}} \right]$$

$$\text{where } \alpha = \frac{c^2 - a^2 - b^2 - \sqrt{(c^2 - a^2 - b^2)^2 - 4 a^2 b^2}}{2 a b}$$

$$\text{and } \xi = \frac{a + b}{c}$$

and a is the radius of sphere A

b is the radius of sphere B

c is the distance between the centres of the spheres.

The coefficients of potential may be found from the usual

formula:

$$p_{11} = \frac{q_{22}}{q_{11}q_{22} - q_{12}^2} \quad p_{22} = \frac{q_{11}}{q_{11}q_{12} - q_{12}^2} \quad p_{12} = \frac{-q_{12}}{q_{11}q_{12} - q_{12}^2}$$

In the computer program the coefficients were calculated in a subroutine called COEFFS. Other computer variables corresponded to variables in the equations as follows:

$a \equiv A$	$q_{11} = \text{SUM (1)}$	$\frac{\partial q_{11}}{\partial C}$	$=$	DPDC (1)
$b \equiv B$	$q_{12} = \text{SUM (2)}$	$\frac{\partial q_{11}}{\partial C}$	$=$	DPDC (2)
$c \equiv C$	$q_{22} = \text{SUM (3)}$	$\frac{\partial q_{22}}{\partial C}$	$=$	DPDC (3)
$\alpha = \text{ALPHA}$	$p_{11} = \text{SUM (4)}$	$\frac{\partial p_{11}}{\partial C}$	$=$	DPDC (4)
$\gamma \equiv \text{-SQUIC}$	$\bar{p}_{12} \equiv \text{SUM (5)}$	$\frac{\partial p_{12}}{\partial C}$	$=$	DPDC (5)
$\text{DELTAC} = C$	$p_{22} = \text{SUM (6)}$	$\frac{\partial p_{22}}{\partial C}$	$=$	DPDC (6)
$= \text{a small increment in } C$		∂C		

ANGSTR = film thickness (in Å)

FORCE = force between islands (in dyne)

TENUW = force per unit width (in dyne cm⁻¹)

STRESS = stress in the film (dyne cm⁻²)

In Russell's series n was taken as 2 and p was taken as 6. The differentiation was carried out by an iterative procedure, and checks for convergence were made after each iteration. The flow diagram for this procedure is reproduced in Figure 2.8 and the whole programme on Page 255.

The values for the force between the island was found by putting the charges, E_1, E_2 in terms of the charge of an electron, $4.8 \cdot 10^{-10}$ esu, and by putting b and c in Å. The force per unit width was found by dividing the force between the islands by the island separation, and the stress was the force per unit width divided by the film thickness.

The force between the islands is:-

$$\frac{e^2}{r_A^2} \left[\frac{1}{2} \frac{\partial p_{11}}{\partial C} n_A^2 + \frac{\partial p_{12}}{\partial C} n_A n_B + \frac{1}{2} \frac{\partial p_{22}}{\partial C} n_B^2 \right]$$

where C is charge on the electron and n_A, n_B is the number of electrons on island A and island B. r_A is the radius of island A.

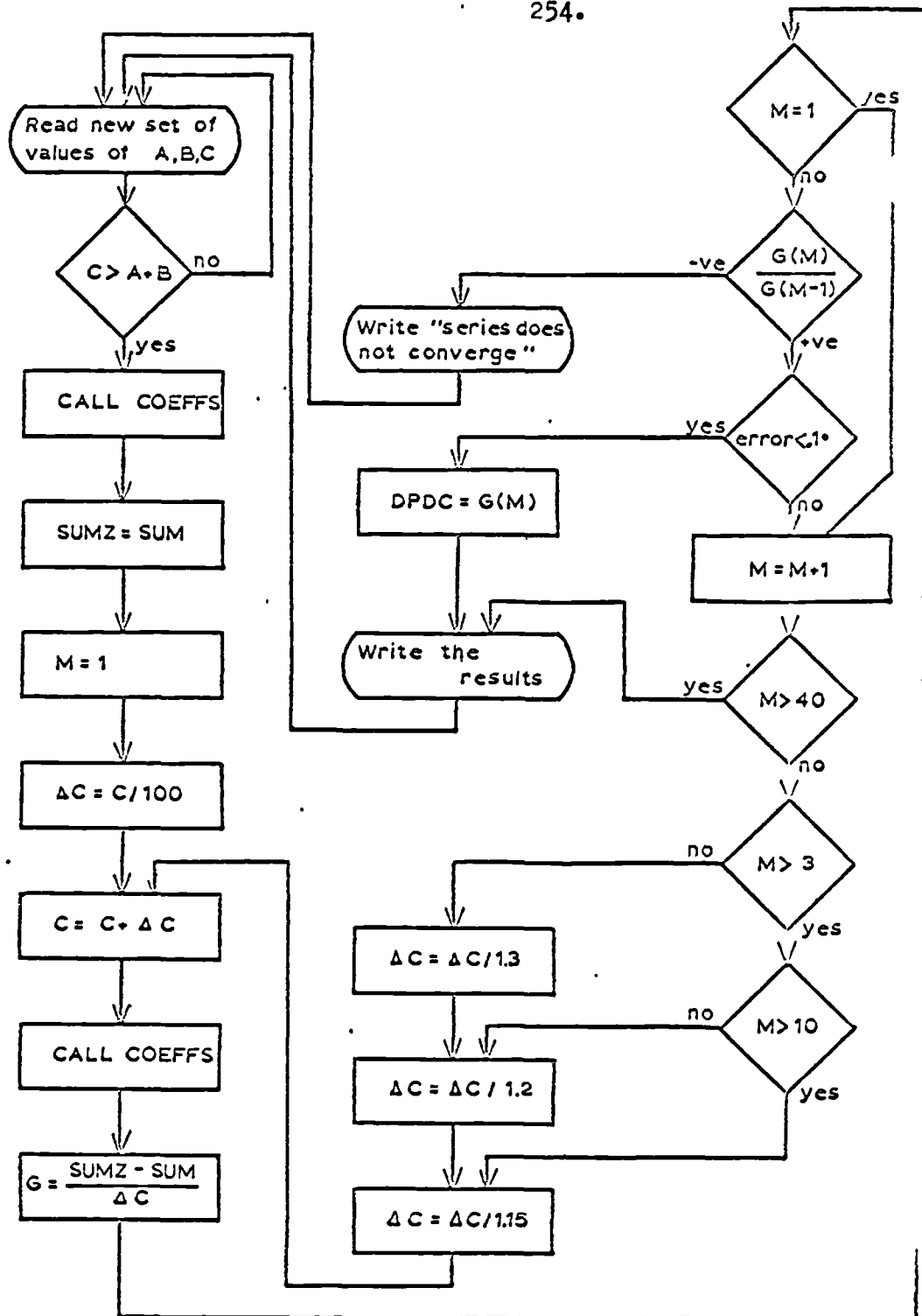


Figure 2.8 Flow diagram for the part of the programme which differentiated the coefficients of potential.

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C          COEFFICIENTS OF POTENTIAL AND CAPACITY
C          FOR ISLANDS OF UNEQUAL DIAMETER
C          SUBROUTINE COEFFS ( I,J,K,L)
C          COMMON/BLK / A(3), B(5), D(16), SUM(6)
C          EVALUATE COEFFICIENTS QAA
11 BRACK = D(K)**2 - A(I)**2 - B(J)**2
  ALPFA = (BRACK - (BRACK**2 - (2.0*A(I)*B(J))**2)**0.5) /
  & (2.0*A(I)*B(J))
  SQUIG = (A(I)*B(J)*ALPFA) / D(K)
  SUMAA = 0.0
  DO 1C N=1,2
10G SUMAA = SUMAA + 1.0/(2.0*(1.0-SQUIG**2)) + ALPHA**N /
  & (1.0 - (SQUIG*ALPHA**N)**2)
  SUMAB = 0.0
  DO 2C N=1,6
20G SUMAB = SUMAB + 1.0/(6.0*(1.0-ALPHA)) + ((SQUIG*ALPHA**3)**(2*N)
  & 1/(1.0 - ALPHA**(2*N + 1)))
  SUM(1) = A(I) * (1.0 - SQUIG**2) * (SUMAA+SUMAB*ALPHA**3)
C          EVALUATE COEFFICIENT QBB
  SQUIG = (B(J) + A(I)*ALPHA) / D(K)
  SUMAA = 0.0
  DO 3C N=1,2
30G SUMAA = SUMAA + 1.0/(2.0*(1.0-SQUIG**2)) + ALPHA**N /
  & (1.0 - (SQUIG*ALPHA**N)**2)
  SUMAB = 0.0
  DO 4C N=1,6
40G SUMAB = SUMAB + 1.0/(6.0*(1.0-ALPHA)) + ((SQUIG*ALPHA**3)**(2*N)
  & 1/(1.0 - ALPHA**(2*N + 1)))
  SUM(3) = B(J) * (1.0 - SQUIG**2) * (SUMAA+SUMAB*ALPHA**3)
C          EVALUATE COEFFICIENT QAB
  SQUIG = ALPFA
  SUMAA = 0.0
  DO 5C N=1,2
50G SUMAA = SUMAA + 1.0/(2.0*(1.0-SQUIG**2)) + ALPHA**N /
  & (1.0 - (SQUIG*ALPHA**N)**2)
  SUMAB = 0.0
  DO 6C N=1,6
60G SUMAB = SUMAB + 1.0/(6.0*(1.0-ALPHA)) + ((SQUIG*ALPHA**3)**(2*N)
  & 1/(1.0 - ALPHA**(2*N + 1)))
  USUM(2) = A(I)*B(J)*(1.0 - ALPHA**2)*(SUMAA + SUMAB*ALPHA**3)
  & / D(K)
  DENOM = SUM(1) + SUM(3) - SUM(2)**2
  SUM(4) = SUM(1) / DENOM
  SUM(5) = SUM(2) / DENOM
  SUM(6) = SUM(3) / DENOM
  RETURN
  END

```

Fortran IV program for the computation of the stress from electrostatic forces between islands. The subroutine is on this page. the main program is overleaf.

```

CCPMON/BLK / A(3), B(5), D(16), SUM(6)
DIMENSION SUMZ (6), G(100,6), OPDC (3,5,16,6), C(16)
REAC (5,107) (A(1), 1=1,1)
REAC (5,107) (B(1), 1=1,5)
REAC (5,107) (C(1), 1=1,6)
REAC (5,107) (C(1), 1=9,16)
107 FCRPAT ( 8F5,1)
I=1
CC 222 J=1,5
WRITE (6,2C0)
200 FCRPAT ( 4D+1 VALUES OF DIFFERENTIAL CCEFFICIENTS )
WRITE (6,2C1)
2G10FCRPAT ( 72+0 A B C M L P OR Q
10P/DC OR DC/DC )
DC 222 K=1,16
WRITE (6,2C2)
2G2 FCRPAT ( 3+ )
DC 222 L=1,6
IF ( C(K) - A(I) - B(J) ) 223,223,11
11 C(K) = C(K)
CALL CCEFFS ( 1,J,K,L)
SLMZ(L) = SLM (L)
M=1
DELTAC = C(K) / 100.
C(K) = C(K) + DELTAC
CALL CCEFFS ( 1,J,K,L)
G(M,L) = ( SUM(L) - SUMZ(L) ) / DELTAC
IF (M-1) 32,32,31
31 IF ( G(M,L) / G(M-1,L) ) 33,33,34
33 WRITE (6,203) A(I),B(J),C(K), M, L, SUMZ(L),G(M-2,L),G(M-1,L),
1 G(M,L)
203 FCRPAT ( 3(F5,1,2X), 2(I6,2X), 4E15,5 , 26M SERIES DOES NOT COM
AVERAGE )
OPDC (1,J,K,L) = 0.
GC TO 54
34 IF ( ABS (G(M,L)-G(M-1,L)) - ABS (G(M-1,L)/1000.0 ) ) 52,32,32
32 M=M+1
IF (M- 40 ) 53,52,52
53 IF (M- 3 ) 55,56,56
56 IF (M- 10 ) 57,58,58
55 DELTAC = DELTAC / 1.3
57 DELTAC = DELTAC / 1.2
58 DELTAC = DELTAC / 1.15
GC TO 41
52 CPCC(1,J,K,L) = G(M,L)
WRITE (6,204) A(I),B(J),C(K), M, L, SUM(L) , OPDC(1,J,K,L)
204 FCRPAT ( 3(F5,1,2X),2(I6,2X), 2E15,5 )
GC TO 54
223 WRITE (6,91C3) A(I),B(J),C(K)
9103 FCRPAT (3(F5,1,2X), 37M REJECTED BECAUSE C IS LESS THAN A+B )
CPCC (1,J,K,L) = 0.
54 CCNTINUE
222 CCNTINUE
C END OF PART TWO AND START OF PART THREE
DIMENSION EA(7), EB(7)
REAC (5,1C08) (EA(1), 1=1,7 )
REAC (5,1C08) (EB(1), 1=1,7 )
1008 FCRPAT (7F5,1)
I=1
DC 20C1 J=1,2
DC 20C1 K=1,16
IF ( C(K) - A(I) - B(J) ) 2001,2001,1004
1004 IF ( CPCC ( 1,J,K,6 ) ) 4001,2001,4001
4001 WRITE (6,10C5)
1005 FCRPAT (107+1 A B C OA OB FORCE
1 FILM THICKNESS TENSION UW STRESS )
WRITE (6,10C9)
1009 FCRPAT (107+ A,B ARE ISLAND RADII CA,OB ARE CHARGES DYNE
1 ANGSTROM DYNE/CM DYNE/CM**2 )
DC 10C1 M=1,7
DC 10C1 N=1,7
WRITE (6,10C6)
1006 FCRPAT ( 2+ )
ANGSTR = 2.5
1003 R = (3.0*ANGSTR+C(K))*21 / (4.0*3.1416)
OPRCE = 0.0C2306 * ( (ABS(EA(M)))**2*OPDC(1,J,K,4)
1 + EA(M)*EB(N)*OPDC(1,J,K,5)
2 + (ABS(EB(N)))**2*OPDC(1,J,K,6) ) / R **2
TENUW = FORCE*FLOAT(10**8) / (C(K)*R)
STRESS = PLCAT(10**8)*TENUW / ANGSTR
IF ( ABS(TENUW) - 2570. ) 1000,1101,1101
1000 IF ( ABS(TENUW) - 5. ) 1101,1002,1002
1002 WRITE (6,10C7) A(I),B(J),C(K),EA(M),EB(N),OPRCE,ANGSTR,TENUW,
1 STRESS
1007 FCRPAT ( 3(F5,1,3X), 4E17,4 )
1101 ANGSTR = ANGSTR * 2.5
1102 IF (ANGSTR - 102.5 ) 1003,1001,1001
1001 CCNTINUE
2001 CCNTINUE
STOP
END

```

17.

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```

C       STRESS CALCULATION - ADSORPTION ENERGY
       DIMENSION DELTA(10) , ES(100)
       READ (5,100) (DELTA(I) , I=1,10 )
100  FORMAT (10F5.3)
       DO 101 I=1,10
       WRITE (6,102)
102  CFORMAT ( 65H1       DELTA       N       ES       AVEVEN
       1       AVCCD       )
       DO 101 N=1,100
       A = 3.1416 * 2.0 * DELTA(I)
       B = A * FLOAT (N)
       ES(N) = FLOAT(N) - ( ABS((1.-COS(B))/(1.-COS(A))))** 0.5
       J = N/2
       L = (N+1)/2
       K = (N-1)/2
       AVEVEN = ES(N) - 2.0* ES(J)
       AVCCD = ES(N) - ES(L) - ES(K)
101  WRITE (6,106) DELTA(I), N, ES(N),AVEVEN,AVCCD
106  FORMAT ( 5X, F5.3, 5X, I4,3E16.6 )
       STOP
       END

```

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```

C       STRAIN ENERGY TO SPLIT CHAINS
       DIMENSION DELTA(10) , ES(100)
       READ (5,100) (DELTA(I) , I=1,10 )
100  FORMAT (10F5.3)
       DO 111 I=1,10
       J = 1. / DELTA(I)
       DO 111 N=1,J
       DO 112 M=1,30
       STRAIN = -FLOAT(N)/2. + 2.0*FLOAT(M-1) / (1.0 + DELTA(I))
       IF (ABS(STRAIN)-1.) 111,112,112
112  CONTINUE
111  WRITE (6,113) DELTA(I), N, M, STRAIN
113  FORMAT ( 5X, F5.3, 2(5X,I4) , E16.6 )
       STOP
       END

```

Fortran IV programs for the computation of $E_g(n)$ as defined
by equation 2.16; E_{av} as defined by equations 2.17 and 2.18;
and S as defined by equation 2.20.

APPENDIX 5.1

Chance CMD soda-lime glass (from manufacturer's data sheet G3, Issue 1, 1963).

Composition:-

SiO_2	71.5%
Na_2O	12.5%
CaO	8.1%
MgO	3.5%
Al_2O_3	1.3%
TiO_2	1.8%
Sb_2O_3	1.0%

Specific gravity 2.48 at 20°C .

Thermal expansion coefficient. 7.3×10^{-6} per $^\circ\text{C}$.

From the above data it can be shown that the average separation of two oxygen atoms in the glass is $2.86\text{\AA}$, the average separation of two silicon atoms is $3.8\text{\AA}$ and that of sodium, calcium and magnesium atoms is $5.50\text{\AA}$, $7.75\text{\AA}$ and $9.15\text{\AA}$ respectively.

1	2	3	4	1	2	3	4
175	13	135	8.6	212	8.3	1400	16.9
177	4.7	29	1.75	213	7.9	940	12.1
178	5.1	51	2.9	214	6.7	800	12.9
179	5.2	53	2.0	215	4.5	450	12.9
180	11.5	236	11.5	216	6.5	590	11.9
181	16	320	11.8	217	3.4	?	12.3
182	6.1	61	3.0	218	3.8	118	9.6
184	6.0	61	4.5	219	9.7	135	15.5
186	5.2	50	5.1	225	7.1	134	10.7
187	4.5	252	11.4	227	2.7	75	6.2
188	2.8	281	13.0	228	2.9	75	10.9
189	4.5	450	10.7	230	1.0	30	6.8
190	3.8	370	12.7	231	4.8	19	0.6
191	6.5	30	2.1	232	5.9	12	1.3
192	3.8	19	1.4	233	4.0	16	2.6
193	3.0	15	1.0	234	28.0	11	2.6
194	3.2	120	12.5	235	6.7	43	1.0
195	5.6	156	16.5	239	3.2	220	13.2
197	5.4	120	17.7	240	3.0	15	0.3
198	7.5	78	3.6	241	2.0	115	12.6
202	4.5	155	10.2	242	4.9	135	8.15
204	3.2	1120	3--6	244	5.0	60	2.9
206	5.5	985	10.8	245	15.2	775	7.1
208	21.6	1450	15.7	246	3.5	78	1.7
210	7.6	1500	18.0	248	6.5	87	2.2
211	6.9	1300	10.8	249	3.1	120	14.3

Appendix 6.1 Silver films deposited on to glass substrates: tabulated results.

Column 1 is the substrate index number; column 2 the evaporation rate in Å/sec; column 3 the film thickness in Å; column 4 the force per unit width in units of 10^2 dyne cm^{-1} .

1	2	3	4	5	6
369-371	3.5	460	10.8	---	6.9
372-374	3.2	458	4.9	9.4	4.8
375-377	4.9	590	6.0	6.2	6.7
378-380	4.2	268	5.9	12.7	6.9
381-383	4.5	129	8.1	7.4	6.1
384-386	3.5	23	.43	.86	.74
387-389	4.9	98	5.0	3.6	2.6
390-392	4.2	202	11.3	10.5	---
393-395	4.4	68	2.2	.57	.49
396-398	4.2	399	6.3	7.4	---
399-401	4.8	788	1.7	1.1	1.1

7	8	9	10	11	12
---	---	---	---	---	---
15.5	12.6	12.8	6.2	9.6	5.0
11.7	11.8	12.5	5.7	5.9	6.9
.217	12.2	12.0	6.1	12.6	6.7
12.2	11.8	---	8.6	7.1	---
---	---	---	---	---	---
---	---	---	---	---	---
11.1	11.2	11.1	10.2	9.6	---
11.4	---	10.6	2.0	---	.12
10.8	10.9	11.1	5.5	6.5	---
12.2	11.7	11.7	1.7	1.05	1.05

Appendix 6.2 Silver films deposited on to mic substrates: tabulated results.

Column 1 is the substrate index number; column 2 is the evaporation rate in Å/sec; column 3 is the film thickness in Å; columns 4, 5 and 6 give the force per unit width in units of 10^2 dyne cm^{-1} assuming a value of 12.3×10^{11} dyne cm^{-2} for Young's modulus; columns 7, 8 and 9 give the measured values of Young's modulus in units of 10^{11} dyne cm^{-2} ; and columns 10, 11 and 12 give the force per unit width using the measured values.

1	2	3	4	5	6
432-434	3.1	460	31.	19.3	16.7
435-437	2.8	366	10.6	1.2	1.9
438-440	4.0	450	0.0	4.9	2.0
441-443	1.4	148	6.15	9.4	9.0
444-446	3.7	280	9.4	8.1	10.0
447-449	1.9	150	6.5	6.9	8.1
450-452	3.5	255	5.3	5.0	6.0
453-455	3.0	169	8.0	8.2	4.9
456-458	4.0	304	7.4	7.0	6.7
459-461		320	1.3	6.4	0.4
462-464	3.1	508	31.1	38.2	18.3
465-467	3.0	389	1.3	0.0	9.1
468-470	7.5	650	1.6	1.7	2.4
471-473	3.1	386	10.4	7.2	7.7
474-476	3.0	700	44.2	30.3	32.3
477-479	9.8	1070	27.0	21.8	9.8
480-482	10.1	870	3.4	0.8	0.5
486-488	15.7	598	5.2	5.6	1.2
489-491	5.9	299	12.3	13.7	7.8
492-494	6.0	180	11.2	10.7	13.2
495-497	16.1	322	6.0	11.6	8.8
498-500	3.7	88	0.4	1.3	1.3
501-503	19.6	716	4.9	2.6	5.1
504-506	14.6	450	8.0	10.4	11.1
510-512	5.3	88	4.0	3.33	1.75
513-515	3.9	48	1.2	1.95	1.6
516-518	4.6	121	9.9	12.0	7.5
519-521	4.0	26	1.1	0.6	0.3
522-524	9.2	132	12.0	11.9	7.6
525-527	4.0	123	10.6	13.2	5.0
528-530	5.5	30	2.2	1.8	0.2
531-533	4.5	16	3.1	3.6	0.3
534-536	4.5	64	0.4	1.8	0.8
549-551	5.6	126	14.9	15.5	---
552-554	3.9	121	9.3	11.4	---
555-557	21.5	142	13.5	16.1	13.0
558-560	22.6	126	12.1	16.0	7.1

Appendix 6.3 Gold film deposited on to glass substrates:
tabulated results.

Column 1 is the substrate index number; column 2 the evaporation rate ($\text{\AA}/\text{sec}$); column 3 the film thickness ($\text{\AA}$); columns 4, 5 and 6 the force per unit width (in units of $10^2 \text{ dyne cm}^{-1}$).

1	2	3	4	5
311	$\begin{smallmatrix} +58 \\ -34 \end{smallmatrix}$ $\begin{smallmatrix} +90 \\ +90 \end{smallmatrix}$	6.3	11.1	
312	$\begin{smallmatrix} +34 \\ -17 \end{smallmatrix}$ $\begin{smallmatrix} +90 \\ +90 \end{smallmatrix}$	4.5	4.9	
313	$\begin{smallmatrix} +17 \\ -60 \end{smallmatrix}$ $\begin{smallmatrix} +90 \\ +90 \end{smallmatrix}$	4.8	4.43	
316	$\begin{smallmatrix} +60 \\ -60 \end{smallmatrix}$ $\begin{smallmatrix} +90 \\ +90 \end{smallmatrix}$	4.1	4.18	ring diffn. pattern
317	63	4.4	3.94	
315	130	5.4	2.46	
318	45	6.5	4.43	
319	28	1.27		ring diffn. pattern
320	155	1.07		
321	9	1.05		
322	25	1.25	1.13	
323	115	1.10	1.08	
324	105	5.6	3.94	spot pattern
325	62	15.0	11.1	spot pattern
348	0	.98	7.88	
349	0	1.0	7.14	
350	90	.96	5.16	
351	90	1.0	4.8	
352	0	1.0	6.4	
353	90	1.0	3.44	
357	90	1.05		Initial stages
358	0	1.05		Initial stages
359	90	1.05		Initial stages
354	0	3.0		Initial stages
355	0	3.0		Initial stages
356	0	3.0		Initial stages
360	0	3.7		Initial stages
361	0	3.7		Initial stages
362	0	3.7		Initial stages
345	90	5.2	6.15	
346	90	5.3	---	
347	90	5.1	---	
333	0	5.4	2.95	
334	0	5.5	2.46	
335	90	5.0	2.70	
330	90	7.3	4.8	
331	0	7.5	5.9	
332	0	6.9	4.18	
339	90	10.1	13.8	
340	90	10.3	11.5	
341	0	9.9	9.35	
336	0	12.5	12.0	
337	0	12.7	10.6	
338	0	12.2		

1	2	3	4	5
342	90	16.5	11.3	
343	90	16.8	12.8	
344	90	16.2	8.4	
363	0	4.1	4.92	
364	0	4.1	7.63	
365	0	4.1	4.18	
537		5.3	6.15	average
538		5.3		
539		5.3		
543		5.5	8.03	average
544		5.5		
545		5.5		
546		10.8	7.46	average
547		10.8		
548		10.8		
540		11.1	7.35	average
541		11.1		
542		11.1		

Appendix 6.4 Lead telluride films: tabulated stress results.

All substrates were freshly cleaved mica, except for substrates numbers 311-317 inclusive, which were air exposed, and 537-542 which were glass substrates. The 120 volt bias was applied in every case, except 311, 312 and 324.

Column 1 is the substrate number; column 2 the angle between the mica b-axis and the long side of the substrate; column 3 the evaporation rate in Å/sec; column 4 the stress in units of 10^8 dyne cm^{-2} ; and some comments on particular evaporations are given in column 5.

Bibliography

1. R. W. Hoffman; in "Thin Films", ASM, 1963 page 99.
2. R. W. Hoffman; in "The Use of Thin Film in Physical Investigations (Ed. J. C. Anderson), Academic Press, 1966 page 261.
3. R. W. Hoffman; in "Physics of Thin Films", Vol.111, Academic Press, page 211.
4. D. S. Campbell; in "Basic Problems in Thin Film Physics", Ed. Niedermayer, Mayer; Vandenhoeck and Ruprecht, 1965, page 223.
5. G. G. Stoney; Proc. Roy. Soc. A32, 172, 1909.
6. R. H. Barklie, J. J. Davies; Proc. Inst. Mech. Eng., I, 731, 1930.
7. K. G. Soderberg, A. K. Graham; Proc. Am. Electroplaters Soc., 74, 1947.
8. J. O. Almen; Product. Engineering, 22, 109, 1951.
9. A. Brenner, C. W. Jennings; Am. Electroplaters Soc., 34th Tech. Session, 25, 1947.
10. M. Frutton; 'Thin Ferromagnetic Films'; Butterworths 1964 Chapter 7 .
11. I. W. Wolff; J. Appl. Phys., 33, 1152, 1962.
12. E. J. Mills; Proc. Roy. Soc., 26, 504, 1877.
13. M. Bouty; C. R. Acad. Sci., 88, 714, 1879.
14. H. P. Murbach; "A Study of Stress and Orientation in Crystalline Deposits" D.I.C. Thesis, Imperial College, London. 1953.
15. U. R. Evans; "The Corrosion and Oxidation of Metals", Arnold. 1960.
16. M. Ya. Popereka; Phys. Met. Metallography, 5, 20, 1966.
17. D. J. Ma naughton, A. W. Hothersall; Trans. Faraday Soc., 24, 387, 1928.
18. N. M. Mahla; Trans. Am. Electrochem. Soc., 77, 145, 1940.
19. W. M. Phillips, F. L. Clifton; Am. Electroplaters Soc., 34th Tech. Session, 97, 1947.
20. C. E. Heussner, A. R. Balden, L. M. Morse; Plating, 35, 719, 1948.
21. A. W. Hothersall; "Symposium on Internal Stresses in Metals and Alloys", Inst. Metals, London, 1948, page 107.

22. V. Kohlschutter, E. M. Vuilleumier; *Zeits.f.Elektrochemie*, 24, 300, 1918.
23. H. Stager; *Helvetica Chimica Acta*, 4, 584, 1920.
24. V. Kohlschutter, Schodl; *Helvetica Chimica Acta*, 5, 490, 1922.
Also *ibid* 5, 593, 1922.
25. P. M. Walker, N. E. Bentley, L. E. Hall; *Trans. Inst. Metal Finishing*, 32, 349, 1954-55.
26. E. A. Vuilleumier; *Trans. Am. Electrochem. Soc.*, 42, 99, 1922.
27. V. Kohlschutter, F. Jacober; *Zeits.f.Elektrochemie*, 33, 290, 1927.
28. C. Marie, N. Thon; *C. R. Acad. Sci.*, 193, 31, 1931.
29. P. A. Jaquet; *C. R. Acad. Sci.*, 194, 456, 1932.
30. P. A. Jaquet; *Trans. Am. Electrochem. Soc.*, 66, 393, 1932.
31. M. R. J. Wyllie; *J. Chem. Phys.*, 16, 52, 1948.
32. D. J. Macnaughton, A. W. Hotherhall; *Trans. Faraday Soc.*, 31, 1168, 1935.
33. R. M. Bozorth; *Phys. Rev.*, 26, 390, 1925.
34. W. Hume-Rothery, M. R. J. Wyllie; *Proc. Roy. Soc.*, A181, 331, 1943.
35. W. Hume-Rothery, M. R. J. Wyllie; *Proc. Roy. Soc.*, A182, 415, 1943.
36. L. Yang; "Electrodeposition of Metals" DIC Thesis, Imperial College, University of London, 1948.
37. J. C. Hendy, H. D. Richards, A. W. Simpson; *J. Mats. Sci.*, 1, 127, 1966.
38. J. S. Judge, J. R. Morrison, D. E. Spelotis, G. Bate; *J. Electrochem. Soc.*, 112, 681, 1965.
39. A. H. Graham, R. W. Lindsay, H. J. Read; *J. Electrochem. Soc.*, 112, 401, 1965.
40. N. B. Pilling, R. E. Bedworth; *J. Inst. Metals.*, 29, 529, 1923.
41. D. A. Vermilea; *Acta. Met.*, 5, 492, 1957.
42. U. R. Evans; "The Corrosion and Oxidation of Metals", Arnold, London, 1960.
43. N. D. Tomashov; "Theory of Corrosion and Protection of Metals" Macmillan, 1966.

44. R. J. Jaccodine, W. A. Schlegel; J. Appl. Phys., 37, 6,2429, 1966.
45. E. S. Meieran, I. A. Blech; J. Appl. Phys., 36, 10,3162, 1965.
46. J. R. Ligenza; J. Appl. Phys., 36, 2703, 1965.
47. B. Borie, C. J. Sparks; "Thin Films", ASM, 1963, page 45.
48. B. Borie, C. J. Sparks, J. V. Cathcart; Acta. Met., 10, 691, 1962.
49. W. N. Bradshaw, S. Clarke; J. Electrodepositors Tech. Soc., 24, 147, 1949.
50. D. H. Bradhurst, J. S. L. Leach; Trans. Brit. Ceram. Soc., 62, 9, 793, 1963.
51. L. Holland; "Vacuum Deposition of Thin Films" Chapman and Hall, 1956. See page 348.
52. L. Young; "Anodic Oxide Films" Academic Press, 1961. See pp.123ff.
53. Reference 52 page 71.
54. G. T. Croft; J. Electrochem. Soc., 106, 278, 1959.
55. D. A. Vermilea; Acta. Met., 2, 476, 1954.
56. L. Young; Acta. Met., 5, 711, 1957.
57. D. B. Holt; J. Phys. Chem. Solids, 27, 1053, 1966.
58. W. Czaja; J. Appl. Phys., 37, 9, 3441, 1966.
59. G. H. Schwuttke, H. Rupprecht; J. Appl. Phys., 37, 167, 1966.
60. H. J. Queisser; Disc. Faraday Soc., 38, 305, 1964.
61. G. H. Schwuttke, H. J. Queisser; J. Appl. Phys., 33, 1540, 1962.
62. S. Prussin; J. Appl. Phys., 32, 10, 1876, 1961.
63. W. Bardsley; Progress in Semiconductors, (Ed. A. F. Gibson) 4, 155, 1960.
64. A. Miller, H. M. Manasevit; J. Vac. Sci. Tech., 3, 2, 68, 1966.
65. C. Y. Ang, H. M. Manasevit; Solid State Electronics, 8, 994, 1965.
66. D. J. Dumin; J. Appl. Phys., 36, 9, 1965.
67. N. F. Jackson, E. J. Hollands, D. S. Campbell; in "Applications of Thin Films in Electronic Engineering" (IERE), 1966. Paper 13.
68. C. K. Layton, D. S. Campbell; J. Mats. Sci., 1, 367, 1966.

69. C. K. Layton; Private communication, 1966.
70. A. F. Turner, F. K. Truby; "Thick Thin Films" Bausch and Lomb Tech. Report, 1951.
71. O. S. Heavens, S. D. Smith; J. Opt. Soc. Am., 47, 469, 1957.
72. A. E. Ennos; Applied Optics, 5, 1, 51, 1966.
73. D. S. Campbell; Electronics, Reliability and Microminiaturization, 2, 3, 207, 1963.
74. H. Blackburn, D. S. Campbell; Trans. 8th Nat. Vac. Symp., 943, 1961.
75. M. White; Vacuum, 15, 9, 499, 1965.
76. J. F. Freedman; IBM J. Res. Dev., 6, 449, 1962. and J. Appl. Phys., 30, 597, 1959.
77. A. M. Toxen; Phys. Rev., 123, 442, 1961.
78. R. H. Blumberg, D. P. Seraphim; J. Appl. Phys., 33, 163, 1962.
79. H. A. Notarys; Appl. Phys. Letters, 4, 79, 1964.
80. H. L. Caswell, J. R. Priest, Y. Budo; J. Appl. Phys., 34, 11, 3261, 1963.
81. R. E. Joynson; in "Applications of Thin Films in Electronic Engineering" (IERE), 1966. Paper 10.
82. H. P. Murbach, H. Wilman; Proc. Phys. Soc., B66, 905, 1953.
83. R. W. Hoffman, R. D. Daniels, E. C. Crittenden; Proc. Phys. Soc., B67, 497, 1954.
84. R. W. Hoffman, F. J. Anders, E. C. Crittenden; J. Appl. Phys., 24, 231, 1953.
85. J. D. Finegan, R. W. Hoffman; J. Appl. Phys., 30, 597, 1959.
86. J. D. Finegan, R. W. Hoffman; Trans. 8th Nat. Vac. Symp., 935, 1961.
87. J. D. Finegan, R. W. Hoffman; AEC Tech. Report No. 15, 1961.
88. J. D. Finegan, R. W. Hoffman; AEC Tech. Report No. 18, 1961.
89. A. Segmuller; IBM J. Res. Dev., 6, 464, 1962.
90. E. Klokholm; IBM Research Report No. RC-1508, Dec. 1965.
91. J. Riesenfeld; AEC Tech. Report No. 32, 1964.
92. J. Riesenfeld; AEC Tech. Report No. 39, 1965.

93. R. Gontarz, H. Ratajczak, P. Suda; *Phys. Stat. Solidi.*, 15, 1, 137, 1966.
94. M. S. Cohen, E. E. Huber, G. P. Weiss, D. O. Smith; *J. Appl. Phys.*, 31, 291S, 1960.
95. E. E. Huber, D. O. Smith; *J. Appl. Phys.*, 30, 267S, 1959.
96. G. P. Weiss, D. O. Smith; *J. Appl. Phys.*, 33, 1166S, 1962.
97. M. Prutton; *Nature*, 193, 565, 1962.
98. R. L. Coren; *J. Appl. Phys.*, 33, 1168S, 1962.
99. L. Holland, T. Putner, R. Ball; *Brit. J. Appl. Phys.*, 11, 167, 1960.
101. M.A. Novice; *Brit. J. Appl. Phys.*, 13, 561, 1962.
102. M.A. Novice; *Vacuum*, 14, 10, 385, 1964.
103. J. Priest, H. L. Caswell; *Trans. 8th Nat. Vac. Symp.*, 947, 1961.
104. J. Priest, H. L. Caswell, Y. Budo; *Trans. 9th Nat. Vac. Symp.*, 121, 1962.
105. J. Priest, H. L. Caswell, Y. Budo; *Vacuum*, 12, 301, 1962.
106. J. Priest, H. L. Caswell, Y. Budo; *J. Appl. Phys.*, 34, 347, 1963.
107. Y. Budo, J. Priest; *Solid State Electronics* 6, 159, 1963.
108. A.E. Hill, G. R. Hoffman; *Brit. J. Appl. Phys.*, 18, 13, 1967.
109. M. Blackman, in "Single Crystal Films" Ed. Francombe, Sato; Pergamon, 1964, page 7.
110. D. S. Campbell; *Trans. 9th Nat. Vac. Symp.*, 29, 1962.
111. H. Blackburn, D. S. Campbell; *Phil. Mag.* 8, 89, 823, 1963.
112. R. Carpenter, D. S. Campbell; *J. Mats. Sci.*, 2, 173, 1967.
113. J. N. Zemel, J. D. Jensen, R. B. Schoolar; *Phys. Rev.*, 140, 1A, A330, 1965.
114. J. R. MacDonald; *Phys. Rev.*, 106, 890, 1957 (see also *Proc. Phys. Soc.*, A64, 968, 1951).
115. M. Kuriyama, H. Yamanouchi, S. Hosoya; *J. Phys. Soc. Japan*, 16, 4, 701, 1961.
116. M. Pomerantz, J. F. Freedman, J. C. Suits; *J. Appl. Phys.*, 33, 3, 1164S, 1962.
117. A. Kinbara; *Jap. J. Appl. Phys.*, 30, 441, 1961 (In Japanese).

118. A. Kinbara; Jap. J. Appl. Phys., 30, 647, 1961. (In Japanese).
119. A. Kinbara, H. Haraki; Jap. J. Appl. Phys., 4, 4, 243, 1965.
120. R. W. Vook, F. Witt; J. Appl. Phys., 36, 7, 2169, 1965.
121. R. W. Vook, F. Witt; J. Vac. Sci. Tech., 2, 5, 243, 1965.
122. R. W. Vook, F. Witt; J. Vac. Sci. Tech., 2, 1, 49, 1965.
123. A. Segmuller; Z. Metallk, 54, 248, 1963.
124. T. B. Light, C. N. J. Wagner; J. Vac. Sci. Tech., 3, 1, 1, 1966.
125. E. K. Halteman; J. Appl. Phys., 23, 150, 1952.
126. H. Kato, K. Nagashima, H. Hasunuma; Jap. J. Appl. Phys., 30, 700, 1961. (In Japanese).
127. K. Kinoshita, H. Kondo, I. Sawamura; J. Phys. Soc. Japan, 15, 5, 942, 1960.
- 128a. K. Kinoshita, H. Kondo; J. Phys. Soc. Japan, 15, 7, 1339, 1960.
- 128b. K. Kinoshita, K. Maki, K. Nakamizo, K. Takeuchi; Jap. J. Appl. Phys., 6, 1, 42, 1967.
129. H. Wilman; Proc. Phys. Soc., B68, 474, 1955.
130. R. W. Hoffman, H. S. Story; J. Appl. Phys., 27, 193, 1956.
131. H. S. Story, R. W. Hoffman; Proc. Phys. Soc., B70, 950, 1957.
132. S. Timoshenko; J. Opt. Soc. Am., and Rev. Sci. Instr., 11, 233, 1925.
133. G. Gafner; Phil. Mag., 5, 1041, 1960.
134. Reference 1, Figure 14.
135. W. Buckel; Liege Conference Proceedings. p.264, 1960.
136. W. Buckel; Z. Phys., 138, 136, 1954.
137. H. Horikoshi, Y. Ozawa, H. Hasunuma; Jap. J. Appl. Phys., 1, 304, 1962.
138. H. Hoffman, Roll; Private communication, 1965.
139. D. S. Campbell, D. J. Stirland, H. Blackburn; Phil. Mag., 7, 1099, 1962.
140. E. C. Crittenden, R. W. Hoffman; Phys. Rev., 78, 349, 1950.
141. D. W. Pashley; Advances in Physics, 14, 55, 327, 1965.
142. E. C. Williams; Research, 5, 392, 1952.

143. R. I. Garrod; Proc. Phys. Soc., B69, 260, 1956.
144. T. B. Rymer; Proc. Roy. Soc., A235, 274, 1956.
145. T. B. Rymer, F. J. Fayers, S. J. Hewitt; Proc. Phys. Soc., B69, 1059, 1959.
146. V. Vand; Proc. Phys. Soc., 55, 222, 1943.
147. F. W. Reynolds, G. R. Stilwell; Phys. Rev., 88, 418, 1952.
148. R. A. Aziz, G. D. Scott; Canadian J. Phys., 35, 7, 785, 1957.
149. A. W. Smith; J. Phys. Chem., 68, 6, 1465, 1964.
150. V. V. Shah, Y. G. Naik; Indian J. Appl. Phys., 3, 1, 20, 1965.
151. Y. Fujiki; J. Phys. Soc. Japan, 14, 1308, 1959.
152. C. W. B. Grigson, M. Heritage; Private communication.
153. W. Oswald; Z. Phys. Chem., 22, 289, 1879.
154. W. Buckel; in "Structure and Properties of Thin Films" (Ed. C. A. Neugebauer, J. B. Newkirk and D. A. Vermilyea.) Wiley, 1959. Page 53.
155. J. C. Brice; "The Growth of Crystals from the Melt", North Holland, 1965.
156. A. R. Ubbelohde; "Melting and Crystal Structure" Clarendon, Oxford, 1965.
157. G. Gunther, W. Buckel; in "Basic Problems in Thin Film Physics" Ed. Niedermayer, Mayer; Vandenhoeck and Ruprecht, 1965. page 231.
158. G. Gunther; Private communication.
159. H. Horikoshi, N. Tamura; Jap. J. Appl. Phys., 2, 328, 1963.
160. R. Suganuma, Y. Tanaka; Jap. J. Appl. Phys., 4, 3, 232, 1965.
161. J. Drowart; in "Condensation and Evaporation of Solids" Ed. Rutner, Goldfinger and Hirth; Gordon and Breach, 1964. page 255.
162. J. Van der Waterbeemd; Phillips Research Reports, 21, 1, 27, 1966.
163. D. B. Dove; J. Appl. Phys., 35, 9, 2785, 1964.
164. R. M. Hill; Nature, 204, 35, 1964.
165. K. L. Chopra; J. Appl. Phys., 37, 6, 2249, 1966.
166. D. J. Stirland; Appl. Phys. Letters, 8, 12, 326, 1966.
167. P. R. Stuart; (Abstract only) Vacuum, 16, 5, 254, 1966.
168. R. Carpenter; Private communication.

169. Sir James Jeans; "The Mathematical Theory of Electricity and Magnetism" 5th Edition, CUP, 1943. Chapter VIII.
170. J.J. Bikerman; Phys. Stat. Solidi., 10, 1, 3, 1965.
171. A. S. Argon; Phys. Stat. Solidi., 12, 2, K121, 1965.
172. J. J. Bikerman; Phys. Stat. Solidi., 12, 2, K127, 1965.
173. W.W.Mullins; in "Metal Surfaces" ASM, 1963. Page 17.
174. C. Herring; in "Structure and Properties of Solid Surfaces" (Ed. Gomer and Smith). Univ. of Chicago Press, 1952.
175. C. Herring; in "The Physics of Powder Metallurgy" (Ed. Kingston). McGraw Hill, 1950.
176. J. W. Gibbs; "Collected Works" Longmans Green and Co. 1928. Vol. 1, page 219.
177. R. Shuttleworth; Proc. Phys. Soc., A63, 444, 1950.
178. R. Ghez, F. Piuz; C. R. Acad. Sci., 257, 19, 2795, 1963.
179. G. C. Benson, K. S. Yun; J. Chem. Phys., 42, 9, 3085, 1965.
180. M. M. Nicolson; Proc. Roy. Soc., A228, 490, 1955.
181. J. E. Lennard-Jones, B. M. Dent; Proc. Roy. Soc., A121, 247, 1928.
182. C. M. Drum; Phil. Mag., 13, 126, 1239, 1966.
183. N. Morita, N. Inoue; J. Phys. Soc. Japan, 20, 5, 1965.
184. R. Suhrmann, G. Wedler, H.G.Wilke, G.Reusmann; Z. Physik. Chem. Frankfurt., 26, 85, 1960.
185. F. Piuz, R. Ghez; Helv. Phys. Acta., 35, 7-8, 507, 1962.
186. C.R. Berry; Phys. Rev., 88, 596, 1952.
187. T. de Planta, R. Ghez, F. Piuz; Helv. Phys. Acta., 37, 74, 1964.
188. F. W. C. Boswell; Proc. Phys. Soc., A64, 465, 1951.
189. T. B. Rymer; Nuovo Cimento, 6, series x, 1, 294, 1957.
190. L. H. Germer, A. H. White; Phys. Rev., 60, 447, 1941.
191. C. W. B. Grigson, E. Barton; Brit. J. Appl. Phys., 17, 1019, 1966.
192. C. W. B. Grigson, E. Barton; Brit. J. Appl. Phys., 18, 175, 1967.
193. J. S. Halliday, T. B. Rymer, K. H. R. Wright; Proc. Roy. Soc., A225, 548, 1954.
194. L. H. Germer, A. U. McRae; Annals New York Acad. Sci., 101, 605, 1963.

195. R. L. Park, H. E. Farnsworth; in "Solid Surfaces" (Ed. Gatos) North Holland, 1964. Page 527.
196. R. L. Park, H. E. Farnsworth; J. Chem. Phys., 40, 2354, 1964.
197. E. G. McRae, C. W. Caldwell; in "Solid Surfaces" (Ed. Gatos) North Holland, 1964. Page 509.
198. G. C. Benson, P. I. Freedman, E. Dempsey; J. Chem. Phys., 39, 2, 302, 1963.
199. I. Markland, S. Andersson; Surface Science, 5, 197, 1966.
200. C. W. Grigson, D. B. Dove; J. Vac. Sci. Tech., 3, 3, 120, 1966.
201. C. W. B. Grigson; Private Communication.
202. D. O. Smith, M. S. Cohen, G. P. Weiss; J. Appl. Phys., 31, 1755, 1960.
203. E. R. Funk, H. Udin, J. Wulff; J. Metals, 3, 1206, 1952.
204. J. H. Van der Merwe; Proc. Phys. Soc., A63, 616, 1950.
205. J. H. Van der Merwe; J. Appl. Phys., 34, 1, 117, 1963, and also page 123.
206. F. C. Frank, J. H. Van der Merwe; Proc. Roy. Soc., A198, 206, 1949.
207. J. H. Van der Merwe; in "Single Crystal Films" (Ed. Francombe, Sato). Pergamon, 1964. Page 139.
208. J. H. Van der Merwe; in "Basic Problems in Thin Film Physics" (Ed. Niedermayer, Mayer). Vandenhoeck and Ruprecht, 1965. Page 122.
209. E. Klokholm; Private Communication. (A paper presented at the 12th National Vacuum Symposium, but not published).
210. J. W. Mathews; Phil. Mag., 6, 1347, 1961.
211. J. W. Mathews; Phil. Mag., 13, 126, 1207, 1966.
212. N. Cabrera; Short note in reference 154 page 529.
213. N. Cabrera; in "Solid Surfaces" (Ed. Gatos). North Holland 1964. Page 320.
214. N. Cabrera; Memoires Sci. Rev. Metallurg., 62, 205, 1965.
215. Lord Kelvin; "Papers on Electricity and Magnetism" Macmillan, 1872.
216. S. Harris; Phil. Trans., 1824 page 213 and 1836 page 417.

217. A. Russell; Proc. Phys. Soc., 23, 352, 1911.
218. R. Glang, R. A. Holmwood, R. L. Rosenfeld; Rev. Sci. Instr., 36, 1, 7, 1965.
219. A. Brenner, S. Senderoff; J. Res. Nat. Bur. Stand., 42, 105, 1949.
220. N. N. Davidenkov; Soviet Phys. Solid State, 2, 11, 2595, 1961.
221. References 70,82,83,84,96,101,127,157 and 158.
222. References 131,223 and 224.
223. E. Klokholm; IBM Research Report RC1352, Feb. 1965.
224. J. Priest; Rev. Sci. Instr., 32, 12, 1349, 1961
225. Reference 138.
226. P. Croce, G. Devant, J. Reynaud, M. F. Verhaeghe; J. Phys. France, 25, 138, 1964.
227. References 74,108,126,159 and 167.
228. References 74,108,126 and 159.
229. A. I. Bailey; J. Appl. Phys., 32, 8, 1407, 1961.
230. For example the Wayne Kerr Distance Meter Type DM100.
231. K. S. Lion; Rev. Sci. Instr., 35, 3, 353, 1964.
232. J. F. Golding; Wireless World, 6, 329, 1961.
233. W. C. Vergara, H. M. Greenhouse, N. C. Nicholas; Rev. Sci. Instr., 34, 5, 520, 1963.
234. R. B. Schoolar, J. N. Zemel; J. Appl. Phys., 35, 1848, 1964.
235. C. A. Neugebauer; J. Appl. Phys., 35, 3599, 1964.
236. A. R. Beavitt; J. Sci. Instr., 43, 182, 1966.
237. I. Haller, P. White; Rev. Sci. Instr., 34, 677, 1963.
238. L. Holland; "Thin Film Microelectronics". Chapman and Hall, 1965.
239. J. F. Pudvin; Proc. IEE paper No. 3094E, Suppl. 17, 106B, 1125 and 1153, 1959.
240. D. S. Campbell, H. Blackburn; Trans. 7th Nat. Vac. Symp., 313, 1960.
241. M. D. Silver, E. T. Chow; J. Vac. Sci. Tech., 2, 4, 203, 1965.
242. N. Schwartz, R. Brown; Trans. 8th Nat. Vac. Symp., 836, 1961.
243. R. H. A. Crawley; Chemistry and Industry, 1205, 1953.
244. P. Benjamin, C. Weaver; Proc. Roy. Soc., A261, 516, 1961

245. W. F. Koehler; J. Opt. Soc. Am., 43, 738, 1953.
246. A. Blanc-Lapierre, M. Perrot; C. R. Acad. Sci., 230, 1641, 1950.
247. J. P. Borel; Helv. Phys. Acta., 24, 389, 1951.
248. F. W. Reynolds, G. R. Stilwell; Phys. Rev., 88, 418, 1952.
249. C. Boulesteix; C. R. Acad. Sci., 257, 10, 1695, 1963.
250. R. A. Aziz, G. D. Scott; Canad. J. Phys., 35, 7, 785, 1957.
251. A. Kinbara, Y. Sawatari; J. Appl. Phys. Japan, 4, 3, 161, 1965.
(gold films).
252. C. Uny, N. Nifontoff; C. R. Acad. Sci., 246, 6, 906, 1958.
253. J. Savornin, A. Donnadieu, F. Savornin; C. R. Acad. Sci.,
252, 15, 2195, 1961.
254. F. Savornin, J. Savornin, A. Donnadieu; C. R. Acad. Sci.,
254, 19, 3348, 1962.
255. R. Grigorovici, N. Croitoru, A. Devenyi; Z. Phys., 160, 277, 1960.
256. N. Nifontoff; Bull. Acad. Sci. USSR., 25, 5, 665, 1961.
257. Reference 249.
258. A. W. Smith; J. Phys. Chem., 68, 6, 1465, 1964.
259. Reference 250.
260. G. N. Srivastava, G. D. Scott; Brit. J. Appl. Phys.,
12, 255, 1961.
261. R. B. Belser; J. Appl. Phys., 28, 109, 1957.
262. "Properties of Selected Glasses", The Corning Glass Co., Jan 1965.
263. H. Lamb; "The Dynamical Theory of Sound" Dover, 1960 Pp 122 ff.
264. A. B. Wood; "A Textbook of Sound" Bell and Sons, 1957
Pp 111 ff and 117.
265. In Appendix 5.1.
266. Measured on some of the present substrates.
267. T. M. Yarwood, F. Castle; "Physical and Mathematical Tables"
Macmillan 1957.
268. A. A. Chudinov; Soviet Phys. Solid State, 4, 553, 1962.
269. See Table 5.1.
270. "Handbook of Chemistry and Physics", 36th Edition, page 2096.
271. W. Lugschieder, H. Ebel, G. Langer; Z. Metallkde, 56, 12, 851,
1965.

272. P. Hidnert, G. Dickson; J. Res. Nat. Bur. Stand., 35, 309, 1945.
273. R. L. Moss, M. J. Duell, D. H. Thomas; Trans. Faraday Soc., 59, 216, 1963. Also Brit. J. Appl. Phys., 15, 673, 1964.
274. D. W. Pashley, M. J. Stowell, M. H. Jacobs, T. J. Law; Phil. Mag., 10, 127, 1964.
275. R. F. Porter; J. Chem. Phys., 34, 583, 1961.
276. Y. Makino; J. Phys. Soc. Japan, 19, 580, 1964. (Also *ibid*, 19, 1242, 1964).
277. J. N. Zemel, J. D. Jensen, R. B. Schoolar; Phys. Rev., 140, 1A, A330, 1965.
278. A. J. Mountvala, G. Abowitz; J. Am. Ceram. Soc., 48, 12, 651, 1965.
279. D. L. Mitchell; in "The Use of Thin Films in Physical Investigations" (Ed. J.C. Anderson) Academic Press, 1966. Page 363.
280. K. Kinoshita, K. Nakamizo, K. Maki, K. Onuki, K. Takeuchi; Jap. J. Appl. Phys., 4, Suppl., 1, 340, 1965.
281. E. Klokholm; Private Communication, 1965.
282. B. Lewis, D. S. Campbell; J. Vac. Sci. Tech., to be pub.
283. J. A. Bennett, M. A. Novice, I. M. Watt; in "Condensation and Evaporation of Solids" (Ed. Rutner, Goldfinger and Hirth), Gordon and Breach, 1964. Page 255.
284. P. Benjamin, C. Weaver; Proc. Roy. Soc., A252, 418, 1959.
285. C. W. B. Grigson; in "Advances in Electronics and Electron Physics" Academic Press, 1967.
286. J. D. Wilcock; Vacuum, 15, 6, 317, 1965. (Abstract Only).