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STRUCTURE AND INTRINSIC STRESS OF PLATINUM THIN FILMS

ROBERT E. ROTTMAYER

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Abstract

A detailed analysis of the cantilevered beam technique for measuring stress in thin films has been performed. The limits of applicability of the derived equations have been defined with respect to large deflections, shear distributions at the edge of the substrate and boundary conditions at the clamp.

The stress in platinum thin films has been measured on glass and single crystal silicon substrates as a function of thickness with substrate temperatures ranging from 100°C to 600°C. The stress was found to have a high tensile value at low temperatures, to decrease sharply at 300°C and to be very small at 500°C and 600°C.

At 1 MeV microscope enabled very thick (1300Å) films to be examined. Their growth was found to be columnar at 100°C and 300°C with grains of average lateral extent, 100Å. At 600°C the small 100Å grains grew together and formed large grains, 1000Å in lateral extent.

A comprehensive theory based on the structural observations was proposed. The high tension at 100°C was explained by the interaction at the grain boundaries. The decrease in stress at

300°C was ascribed to diffusion in the growing film. The small stress at 500°C and 600°C was the result of a larger grain size.

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Introduction

In the early 1950's the first quantitative measurement of the intrinsic stress in evaporated metal films appeared in the literature even though the effects of stress must have been observed before. Since the 1950's many workers have measured the stress in metal and dielectric films. This report will not consider any of the work on dielectric films, but will consider only metal films. With the many investigations of metal films there has yet to emerge a generally accepted, quantitative theory of intrinsic stress in thin metal films.

Part of the problem of understanding the stress in thin metal films has been the variety of sometimes contradictory data obtained by various workers. Another problem has been that workers have not in general characterized both the structure and the stress in thin films simultaneously. Most of the structural work has been done on epitaxial films deposited at high temperatures while most of the stress work has been done on polycrystalline films grown at low temperatures.

It has long been believed by the Case Laboratory that the key to understanding the stress has been in knowing the detailed structure of the films. It was known that changing the deposition temperature could cause large changes in both the structure and stress of thin films. It had also been observed by many workers

that single crystal substrates could, under proper conditions, lead to epitaxial or oriented crystal growth. Thus stress measurements were made over a wide range of temperatures (100°C to 600°C) on both amorphous and crystalline substrates with the goal of obtaining changes in both the stress and structure which would lead to a quantitative theory of the intrinsic stress based on the detailed structure of platinum thin films.

Theory of Stress Measurement with a Cantilevered Beam

The cantilevered beam has long been a favorite method of stress measurement for vacuum deposited thin films. More measurements have been made by this method than any other; however, there still exist some misconceptions about the proper way of analysing the cantilevered beam. A general theory of the cantilevered beam will be developed and certain errors in the literature will be pointed out. Also, a method which has not been previously published for measuring the stress with a cantilevered beam will be demonstrated. This method permits greater accuracy under practical conditions.

Finegan⁽¹⁾ treats the problems of the strain introduced in a substrate due to a thin film with simple plate theory. He finds explicitly the stress distribution in the substrate. For instance, his results show that the neutral plane lies a distance of $\frac{2}{3}h$ from the film side of the substrate, where h is the substrate thickness. Even though the neutral plane is shifted, Finegan's result is the same as for a plate with constant bending moment of magnitude $Th/2$ where T is the tension in the film (having dimensions of force/unit width) applied in two perpendicular directions. For a rectangular beam of length, l , width, b , and thickness, h , following Finegan's treatment, the deflection, δ_1 , is given by

$$\delta_1 = -\frac{3T(1-\nu)l^2}{Eh^2} \quad (1)$$

where E is the elastic modulus of the substrate and ν its Poisson's ratio. Figures 1 and 2 show the geometry.

The problem is treated as though the force were uniformly distributed through the thickness of the film. In practice, it is commonly found that there is a small gradient. Clearly the treatment could be expanded to treat the stress distribution in thicker films where it might be important.

Davidenkov⁽²⁾ quotes the same result as Finegan and then extends it to the case where the film is not negligible in thickness. He shows that if $t \ll h$ where t is the film thickness then Finegan's result is valid. For the case where the film is thick enough to require correction, a form which may be numerically integrated is given in Davidenkov. In our experiment where $h = 10^3 t$ these corrections are negligible.

Shown in Figure 3 is a shear and moment diagram for a substrate with a stressed film on it. The assumption that the thin film applies a constant bending moment everywhere on the substrate as was assumed in deriving Equation (1) cannot be strictly true since this implies an infinite shear at the edge. (The shear, V , is given by $V = \partial M / \partial x$ where M is the bending moment.) It is clear that this shear has to relax over a finite distance, but if this distance is short then the approximation of a constant bending moment will be valid.

Figure 1--Substrate and Film

Figure 2--Geometry for Stress Measurement Using a Cantilevered Beam

Figure 3--Shear and Bending Moment Diagram across a Typical Substrate with Film Attached

An exact calculation is difficult in this case but direct x-ray measurement has been made by Haruta and Spencer⁽³⁾ on a single crystal quartz substrate. It shows the bending moment having reached a constant value a distance less than h from the edge of the film. If a worst case analysis is used, and it is assumed that there is uniaxial tension for a distance h in from the side of the beam, then the bending moment in this region will be decreased by a factor $1-\nu$, resulting in a maximum error of $2h\nu/b = 1\frac{1}{2}\%$ when Equation (1) is used. Since the beam is much longer than it is wide the shear distribution at each end can be safely neglected. This error of less than 2% has been neglected in our work, and in most thin film stress measurements there is only a small error in neglecting the effect of the shear distribution at the edge of the substrate.

The factor $(1-\nu)$ in Equation (1) had not been used before the work of Pinegan. It can be seen from the arguments just presented that Equation (1) is valid in the case where $h \ll b$. Only in the case where $h \gg b$ would the factor $1-\nu$ in Equation (1) be omitted; however, the use of a beam which is thick compared to its width seems impractical for thin film due to a lack of sensitivity. Equation (1) is a good approximation for the typical thin film geometry.

If a force, F , is applied to the end of the beam, then the deflection is

$$\delta_2 = \frac{4Fl^3}{Eh^3b} \quad (2)$$

Equation (2) is obtained from the elementary, orthodox theory. Ashwell⁽⁴⁾ has done an exact calculation of the bending of a cantilevered beam and finds that the orthodox theory is valid for $(b^2/Rh \leq 1)$ where R is the radius of curvature of the beam. He finds that the inextensional theory in which the strains of bending cause the cross section of the beam to flatten is not valid until $(b^2/Rh > 100)$. The equation in which the plate is flattened has been used by Klokholm⁽⁵⁾ to measure the stiffness of his substrates and it reduces the deflection in Equation (2) by a factor $(1-\nu^2)$. Klokholm uses beams of about the same dimensions as in this work with values of (b^2/Rh) which are less than 1. Thus, Equation (2) should have been used. The deflections and beam geometries used in thin film measurements generally satisfy the condition $(b^2/Rh \leq 1)$.

Equation (2) presumes that the deflection and the slope of the beam are exactly zero at the clamp. A rather small relaxation of this boundary condition can lead to rather large errors in using Equation (2). Most workers in thin films appear to have used friction clamps in their experiments. It was found during the course of this investigation (see Appendix I) that friction clamps do not define the boundary conditions sufficiently well for Equation (2) to be used, and determinations of E may be in error by 20% to 30%. Campbell and Wilcock⁽⁶⁾ found values of E low by at least 20% for cover glass and mica using a magnetic friction clamp.

By solving the problem of a rectangular cantilevered plate

of arbitrary length and width with a load on the extremity of the plate, it is seen that Equation (2) is valid if $l \geq 3b$.

If it is assumed that a cantilevered beam has a force applied at the end as well as film on it, then the deflection is given by

$$\delta = \delta_1 - \delta_2 = \frac{3T(1-\nu)l^2}{Eh^2} - \frac{4Fl^2}{Eh^3b} \quad (3)$$

After rearranging,

$$T = \frac{Eh^2\delta}{3(1-\nu)l^2} + \frac{4Fl}{3bh(1-\nu)} \quad (4)$$

The stress, σ , is given by $\sigma = T/t$. It should be noted that σ is the average stress in the film.

If δ is zero then we have the equation for a force restoring technique and if F is zero we have the equation for a deflection measurement. Experiments have previously been done with either F or δ zero, but as will be shown in the next section there are advantages to having both of them appreciable.

The question for what range of deflections Equations (1) and (2) are valid has been discussed by several authors. Ashwell has given the answer for Equation (2) and one has only to examine the magnitude of (b^2/Rh) for a particular experiment. With substrates such as were used in this investigation deflections of at least $25h$ can be treated with negligible error.

The justification for the use of Equation (1) for large deflections has generally followed the argument first proposed by

Finegan which states that if the problem of a plate with only a bending moment applied to its two opposite edges is solved one gets the same result as simple plate theory. This is true since the plate with bending moments applied at only two edges is essentially bent to a developable surface (i.e. one with no strain in the middle plane). Timoshenko⁽⁷⁾ has treated the problem of a circular plate with uniformly distributed bending moments around its edge and found that for maximum deflections of $\frac{1}{2}h$ there is a 9% error compared to simple plate theory. This magnitude of error is not negligible in many experiments.

As stated by Timoshenko the main limitation of the simple theory of the bending of plates is the magnitude of the strain in the middle surface of the plate. In the case where the deflection of a plate from a true developable surface is small the strain in the middle plane will be small, and simple plate theory can be applied. In this case the bending of the plate perpendicular to its length by the film results in a non-developable surface. However, for a tension of 10^5 dynes/cm. the deflection at the edge of the beam with respect to the middle will be about $10^{-4}h$ even though the deflection at the end will be over 100 times greater. Thus, the beam is still very close to a developable surface and Equation (1) is valid. In fact, with our geometry it is not unreasonable to use Equation (1) even with end deflections of $10h$ since the deflection at the edge will still be much less than h . Again the strain in the middle plane will not be important, and the errors

from using Equation (1) will be within 2%.

The problem of a plate with bending moments applied at its edge is not exactly the same as that of a plate with a thin film on it. A detailed analysis of the thin film problem is extremely difficult since two coupled fourth order differential equations must be solved, but in the case of a free plate or cantilevered beam the strain in the middle surface may play an insignificant role in resisting bending and thus small deflection theory may be valid for geometries other than the long beam.

The justification for using Equation (4) is that the stress system from end loading the beam superposes with the strain from the thin film. An examination of the shape of the cross section of the beam which is end loaded and also has a highly stressed thin film shows that the deflections at the edges with respect to the center are still small. With these small deflection superposition will hold and Equation (4) will be valid to deflections of at least $10h$ at the end of the beam. This is not particularly restrictive since the deflections are larger than should be encountered in any thin film stress measurement. The deflections in this experiment were all within $3h$.

In summary, Equation (4) is the correct equation for either a force restoring or a deflection measurement of the stress. It is correct within the restrictions outlined above, which are less restrictive than had been previously stated in the literature. Equation (4) can be used to analyze an experiment where a deflec-

tion is measured and a force applied simultaneously permitting an increase in accuracy.

Apparatus

Both single crystal silicon and glass substrates were used in this investigation. At temperatures of 300°C and lower, microscope cover glass was used; at temperatures of 300°C and higher, fused quartz was used. Single crystal silicon was also used at temperatures of 300°C and lower.

The substrates were about 4.5 cm. from clamp to hook, 0.4 cm. wide and .015 cm. thick. The length and width were measured on a traveling microscope; the thickness was determined with a dial indicator accurate to .00015 cm.

The cover glass substrates were selected from commercially available Gold Seal⁽⁸⁾ cover glass, 22mm. x 60 mm., thinness #1. They were uniform in thickness to $\pm 1\%$. A precision diamond scribe was used to cut accurate rectangular beams from the cover glass. The silicon substrates were cut by the diamond scribe from Westinghouse web silicon, which has its [111] direction perpendicular to the surface of the beam. The silicon was selected uniform in thickness to $\pm 2\%$.

The glass substrates were ultrasonically washed in warm (50-60°C) distilled water with a small amount of Alconox detergent added. They were then rinsed in boiling distilled water and dried in air. After drying, the beam was cemented into a stainless steel clamp and a small quartz hook (about .020 in. dia.)

was attached to the end of the beam. The cement used was Autostic.⁽⁹⁾ The substrates were then put in the vacuum system after the cement had dried (about 2 hours).

The silicon substrates were cleaned by immersion in chemically pure hydrofluoric acid and then rinsed in distilled water. A hook was cemented to the end of the beam, and it was placed in the vacuum system. The silicon was held in a weighted friction clamp for stress measurement and thus could be immediately inserted in the vacuum system.

A modified Cahn RG microbalance⁽¹⁰⁾ was used for the stress measurement. The microbalance was modified for vacuum use by the replacement of insulated, stranded wire, fiber washers, and a plastic bulb holder and connector with more vacuum compatible material such as solid wire, ceramic, and teflon. Vacuum relief was provided by slotting screws and milling away part of the aluminum case. A special meter movement was obtained from Hickok⁽¹¹⁾ to replace the one supplied with the Cahn. This meter had its coil fastened with high temperature epoxy since the original movement could not stand outgassing at 100°C. A few minor electrical modifications were also made.

The microbalance operates by feeding back an amplified signal from a phototube to give a current through the meter movement. The beam of the microbalance is attached to the moving coil of the meter and has a flag at one end which covers part of the phototube thus providing a position sensor, since a shielded

bulb is on the other side of the flag. The current through the meter is directly proportional to the voltage from the phototube amplifier. The voltage from the amplifier is directly proportional to the deflection of the beam over most of the range of the microbalance. Thus, over a wide range the voltage output of the microbalance is directly proportional to a certain deflection and force at the end of the beam.

To measure the stress, Equation (4) is rewritten as

$$T = \left[\frac{Eh^2y}{3(1-\nu)l^2} + \frac{4fl}{3bh(1-\nu)} \right] \times [\text{Cahn output (mv.)}] \quad (5)$$

where f is the force/mv. and y is the deflection/mv. at the hook on the Cahn beam. If Equation (5) is rewritten

$$T = [C] [\text{Cahn output (mv.)}] \quad (6)$$

where

$$C = \frac{Eh^2y}{3(1-\nu)l^2} + \frac{4fl}{3bh(1-\nu)} \quad (7)$$

Then, if $\frac{Eh^3by}{4l^3f} = \frac{1}{2}$ the constant, C , does not change for small changes in the parameter (l/h) .

Since the ratio (y/f) is electrically adjustable (within limits) it was a simple matter to pick the value of (y/f) so that C was insensitive to the parameter (l/h) . This was done in the case of the glass substrates. In the case of the silicon (with its much higher value of E) it would have affected the temperature compensation and stability of the balance too much.

It is desirable for C to be insensitive to small changes in l or h because in any practical case it is impossible to obtain highly accurate values for l or h . The limit of commercial grinding and polishing techniques is ± 0.0001 in. giving an error in h of about 2% for a 0.006 in. beam although cover glass can be selected slightly flatter as mentioned before. In this type of experiment a hook about .020 in. thick is cemented on the end of the beam; thus the actual point of application of the force and the point at which deflection is measured is not precisely defined. This again gives rise to another uncertainty of 1-2%. The above method which has not been used before in thin film stress measurement permits quite high accuracy under practical conditions.

The Cahn microbalance is a very stable instrument and drifted less than 1 mv. in several hours when connected to a substrate in the vacuum system. This corresponds to a sensitivity limit during a typical run time of 15 minutes of better than 200 dynes/cm.

The constant, y , was determined by measuring the deflection of the microbalance beam with a traveling microscope. This served to determine the region of proportionality between the voltage and deflection and to determine the value of y in this region. The constant, f , was determined by hanging calibration weights on the balance. Both constants could be determined to better than $\pm 1\%$. As will be seen, the sensitivity of the balance or the ac-

curacy of determining these constants were not limiting factors in this experiment.

As shown in Figure 4, the Cahn microbalance was mounted on an adjustable table over the substrate. The table consisted of two plates of aluminum, the bottom plate providing shielding from thermal radiation. The top plate was supported by four adjustable legs and could be moved up and down to exactly position the microbalance. The table and substrate were attached to Invar supports. The quartz fiber and Invar supports minimized thermal expansion between the substrate and table. The microbalance was about 6 in. above the substrate.

The substrate was mounted in its clamp which was inside an enclosed oven as shown in Figure 4. Next to the substrate was an identical beam with a .001 in. Chromel-Alumel thermocouple cemented in its middle. Along either side were heating coils of .010 in. tungsten wire wound on four alumina tubes, giving a capability of at least 300 watts. Under the oven were two shutters used to expose the substrate to the vapor beam after a certain rate had been established and to terminate deposition on the substrate at the appropriate thickness. The shutters were spring loaded and released by blowing fuse wires of 0.010 in. Nichrome wire. The fuse wires were shielded from line of sight of the substrate. The oven was surrounded by a double radiation shield of OFHC copper and stainless steel with aperture for the substrate holder and quartz fiber. The substrate in the oven reached a temperature of well

Figure 4--Apparatus for Stress Measurement

over 600°C.

A specially designed temperature controller amplified the signal from the thermocouple (referenced to an ice water bath) and compared it to a predetermined reference voltage. The error signal drove the light bulb of a coupled photocell light bulb modulator, and the resistance of the photocell controlled the power via an SCR. The isolation between the sensing circuit and the power circuit was found necessary because of leakage resistance in the feed-throughs. The controller could control to $\pm \frac{1}{4}^{\circ}\text{C}$.

A Denton Minigun Electron Beam Gun, with a DEG-744 power supply,⁽¹³⁾ was positioned with its hearth about $6\frac{3}{8}$ " below the substrate. About 15 grams of very pure, zone refined platinum were placed in its water cooled copper hearth. The platinum is "Marz" grade,⁽¹²⁾ nominal purity of 99.99+% and contains less than 30 ppm of any particular impurity element. The gun was capable of about $2\frac{1}{2}$ KW maximum power. It bent the electrons 180° focusing them in a line on the hearth. An SCR controller could be used to control the power to the filament and thus the current impinging on the sample. The gun was operated at 300 ma. and 5KV during evaporation.

The vacuum chamber consists of an 18" pyrex bell jar, a stainless steel collar, and a steel base plate. A hood may be placed over the bell jar to heat for outgassing. The base plate is heated by circulating hot water through it. Outgassing was done at 75°C. The pump is an MCF-300 four inch diffusion pump.

A trap filled with aluminum wool is constructed so that it may be outgassed and, at the time of a run, cooled with liquid nitrogen to pump condensible vapors. After outgassing and filling the trap, the system reaches a base pressure of 5×10^{-8} Torr. During an evaporation the pressure, however, rises to $1-2 \times 10^{-5}$ Torr, due presumably to the heat produced by the gun.

The thickness is measured by a Sloan Omni II⁽¹⁴⁾ quartz crystal monitor. The Omni II acts as an electrical control center for the system. It blows the shutters, controls the rate, turns off the beam gun at the end of run, marks the strip chart recorder with a blip, and records the opening and closing of the shutters. It also, of course, provides a signal proportional to the thickness deposited.

The crystal itself was mounted in a Sloan UHV remote head. The crystal was mounted by means of a spring clip against a flat part of the head. The head, made of gold plated copper, was cooled by circulating tap water through it. Although the quartz crystals are cut so as to be insensitive to changes in temperature some change in crystal frequency was observed when the beam gun was turned on. These are believed primarily due to the "bowing" of the crystal as a result of thermal gradients induced when exposed to a hot source. These frequency shifts ceased after the crystal had come into equilibrium (about 2 minutes). Since the shutters were not opened until the crystal had stabilized these jumps did not influence the thickness measurement.

Although the crystal monitor was placed about the same distance from the substrate, it was calibrated to correct for any geometrical effects or errors in the manufacturer's suggested values of sensitivity. Every crystal used was individually calibrated.

The thickness calibration was done in the vacuum system using the Cahn microbalance to weigh the amount of material deposited on a round glass cover slip suspended at the exact position of the substrate. Care was taken to make the cover slip exactly perpendicular to the impinging beam of metal. About a thousand angstroms of metal was deposited on a 22 mm. coverslip and the frequency change of the crystal monitor noted. From this a calibration constant was calculated and used with that crystal. The Cahn microbalance could weigh the film to better than 1%, the frequency could be read to great precision, and the area of the coverslip accurately determined. The main source of error in this determination was the drift in the VFO of the Sloan. The values of thickness quoted in this work are better than $\pm 2\%$.

The procedure for a typical run was as follows. The shutters were loaded, and the substrate inserted and attached to the Cahn via the quartz fiber. The table was adjusted and the system pumped down. It was outgassed overnight and then allowed to cool until everything inside had reached room temperature. The substrate was brought to the desired temperature and the system allowed to come into thermal equilibrium. The trap was filled

with liquid nitrogen and allowed to cool. Then the beam gun, controlled by the Sloan, rose to about half of deposition power in about 5 minutes. It remained at this power for about 2 minutes and then started evaporating. After about 200 Å had been deposited the shutters were opened automatically and a rate of about 120Å/min. established. The temperature of the dummy was recorded on a strip chart recorder which also recorded thickness increments by the event marker. The thickness and Cahn output were recorded on an x-y recorder. The Cahn output was also monitored on a strip chart recorder. Blips were placed on the x-y recorder so that it was known exactly when the shutters had opened and closed. After a predetermined thickness had been reached, the shutter was closed and the electron gun turned off automatically.

Analysis and Results

Equation (5) was used to evaluate the data for cover glass and fused quartz. Shown in Table I are the values of E and ν used at the various temperatures. The fused quartz data is taken directly from Spinner.^(15,16) The room temperature value for E of the cover glass was determined by the author as described in Appendix I. The room temperature value for E for cover glass was extrapolated to higher temperatures using Spinner's data for light crown glass #512. Its composition is similar to that of cover glass; common composition glasses show about the same temperature dependence for E. The Poisson's ratio is also from Spinner. The clamp using Autostic cement was found to provide satisfactory boundary conditions for end loaded beams of cover glass and quartz.

In the case of the single crystal silicon, a friction clamp was used. It was thus necessary to add a correction factor to Equation (5). The resulting equation is

$$T = \left[\frac{Eh^2y}{3(1-\nu)l^2} + \frac{4fl(1.19)}{3bh(1-\nu)} \right] \times [\text{Cahn output (mv.)}], \quad (8)$$

where the multiplication by 1.19 represents the correction for the effective increase in l as shown in Appendix I. The E and ν for silicon were determined from the single crystal elastic constants⁽¹⁷⁾ since silicon in the [111] direction orientation is

Table I

Elastic Modulus and Poisson's Ratio
as a Function of Temperature

SUBSTRATE	TEMPERATURE	ELASTIC MODULUS (dynes/cm ²)	POISSON'S RATIO
Fused Quartz	300°C	7.58×10^{11}	.18
" "	400°C	7.70 "	.185
" "	500°C	7.75 "	.19
" "	600°C	7.80 "	.19
Cover Glass	Room Temp.	6.96×10^{11}	.21
" "	100°C	6.92 "	.21
" "	200°C	6.86 "	.21
" "	300°C	6.62 "	.21
Silicon	100°C to 300°C	16.91×10^{11}	.262

isotropic in the plane perpendicular to [111]. The formulae are⁽¹⁸⁾

$$E^{-1} = \frac{1}{2}S_{11} + \frac{1}{2}S_{12} + \frac{1}{2}S_{44} \quad (9a)$$

and

$$\nu/E = -\frac{5}{6}S_{12} - \frac{1}{6}S_{11} + \frac{1}{12}S_{44} \quad (9b)$$

The change in E and ν was less than 1% when the elastic constants were extended to temperatures as high as 300°C using accepted values of their temperature derivatives. A temperature correction was thus unnecessary.

The values of E and ν used for all the substrates in analyzing the data are shown in Table I.

The weight of the film deposited on the substrate gives a compressive contribution of

$$T = \frac{-\rho g t l^2}{6h(1-\nu)} \quad (10)$$

where ρ is the density of the film. This correction was added whenever it would make a 1% or greater difference in the data; however, the correction is very small and was only needed in the higher temperature runs where T was close to zero.

The thermal stress introduced into a layer of film whose temperature has changed from T_i to T_f is given by

$$\sigma_f = \frac{E(\alpha_f - \alpha_s)(T_i - T_f)}{(1-\nu)} \quad (11)$$

where the α 's are the coefficients of thermal expansion for the

film and substrate respectively. Thus, if there is a temperature rise or fall during deposition, the stress measured must be corrected by Equation (11) in order to give the intrinsic stress. The temperature controller described previously eliminated the effect of differential thermal expansion by keeping the substrate at the same temperature throughout deposition. There is a possibility that the dummy was at a different temperature than the substrate but due to the exactly symmetric positioning the two, this difference should be very small. The 0.001 in. thermocouple conducted a negligible amount of heat from the substrate. In addition the coefficients of thermal expansion of the platinum and cover glass were the same thus making $\alpha_F - \alpha_S = 0$ in Equation (11) for the runs on cover glass. There is a thermal spike at the opening of the shutter when the substrate first sees the hot source. It is typically about 5°C, but it is of too short a duration to contribute to the stress.

The main source of uncertainty in temperature measurement will be a difference in temperature between the thermocouple and the substrate. The thermocouple is held against the substrate by a very small amount of Autostic cement. A worst case estimate shows that the thermocouple should be within 5°C of the substrate. The temperature controller in this experiment is a significant improvement over most previous work and allowed meaningful data to be taken as high as 600°C, higher than any previously reported work.

Another effect which can give apparent contributions to the

stress is a change in thermal gradient during a run. The effect of the thermal gradients are rather hard to calculate or measure, although attempts have been made. The effective tension from a thermal gradient is given by

$$T = \frac{E\alpha_s \Delta T}{6(1-\nu)} \quad (12)$$

where ΔT is the temperature difference through the substrate. From Equation (12) it can be seen that if substrates with either low coefficients of thermal expansion or high values of thermal conductivity are chosen they will tend to minimize the contributions of the thermal gradient. The fused quartz had a low coefficient of thermal expansion and the silicon had a high thermal conductivity.

If it is assumed that ΔT is inversely proportional to the thermal conductivity of the substrate, κ , then the tension due to a thermal gradient will be proportional to $\left(\frac{\alpha_s E}{\kappa(1-\nu)}\right)$ since all substrates have about the same value of h . Comparing values of the parameter $\left(\frac{\alpha_s E}{\kappa(1-\nu)}\right)$, silicon should reduce the effect of the thermal gradient by a factor of 37 and quartz by a factor of 22 compared to cover glass. Therefore, if there is a significant contribution at 300°C to the observed stress it should be evident from intercomparing the results from the three substrates.

The data obtained is shown in Figures 5 through 14. On the

Figure 5--Force/Unit Width Versus Thickness for Platinum Deposited on Cover Glass at Various Substrate Temperatures

Figure 6--Stress Versus Thickness for Platinum Deposited on Cover Glass at Various Temperatures

Figure 7--Force/Unit Width Versus Thickness for Platinum on Silicon at Various Temperatures

Figure B--Stress Versus Thickness for Platinum Deposited on Silicon at Various Temperatures

Figure 9--Force/Unit Width Versus Thickness for Platinum Deposited on Fused Quartz at Various Temperatures

Figure 10--Stress Versus Thickness for Platinum Deposited on Fused Quartz at Various Temperatures

Figure 11--Force/Unit Width Versus Thickness for Platinum on Cover Glass and Silicon at Various Temperatures

Figure 12--Stress Versus Thickness for Platinum Deposited on Cover Glass and Silicon at Various Temperatures

Figure 13--Stress Versus Reduced Temperature for 1000Å of Platinum on Glass. T_m is the Melting Temperature of Platinum and T_s the Deposition Temperature

Figure 14--Instantaneous Stress Versus Reduced Temperature for 1000 Å Platinum Films on Various Substrates

figures the biaxial tension, T , is labelled "Force/Unit Width". On both cover glass and silicon a tensile stress is observed at 100°C and 200°C. This stress is large and relatively independent of thickness. At 300°C compression is observed in the smaller thicknesses and tension in the higher. On quartz a small compression is observed for all the thicknesses at 400°C. At 500°C and 600°C a negligibly small stress is observed. The run at 600°C showing very small stress was only made to 500A.

At least two runs were made on the cover glass at 100°C, 200°C and 300°C. The runs at 100°C and 200°C were quite reproducible. With this reproducibility as well as the sources of error discussed previously a $\pm 10\%$ uncertainty is ascribed to the data on silicon and cover glass at 100°C and 200°C. Comparing the data at 100°C, it is seen that the stress on silicon is higher by about 25% than on the cover glass.

The runs at 300°C are not as quantitatively reproducible as the runs at lower temperatures; however, they are qualitatively the same on cover glass, silicon, and fused quartz. They all show a compression at lower thicknesses and a tension at higher thicknesses. The magnitude of the tension is much reduced from the lower temperature data. Of course, the lower values of stress at 300°C make percentage errors larger.

Figures 11 and 12 show the results of runs made to only a thickness of 300A. These runs were needed for electron microscopy. A comparison with the data in Figures 5 through 10 shows that there

is not quantitative agreement, but that all curves have qualitatively the same behavior.

It can be seen that the magnitude of the compression in the 300°C runs is greater for quartz and silicon than for cover glass. As discussed before the magnitude of the thermal gradient should be less on the silicon and quartz. Therefore, it is concluded that if there is an appreciable effect of the thermal gradient it is tensile and cannot account for the compression observed.

After closing the shutter, a significant stress relaxation took place on the 300°C run. This relaxation was fairly large and was always such that the stress became more tensile, i.e. compression at 300A decreased and tension at 1300A increased. This relaxation was not significant at the 100°C temperatures where it accounted for less than 5% of the total stress value and was tensile.

The data for 500°C and 600°C showed a very small value of stress. This small stress tends to show that the errors from thermal gradients, differential thermal expansion, and apparatus expansion are quite small.

Shown in Figure 13 is the average stress at 1000A versus reduced temperature for the glass substrates. Figure 14 shows the instantaneous stress at 1000A versus the reduced temperature for all substrates. The instantaneous stress is the slope of the force/unit width curve versus thickness at a particular thickness. Both the average and instantaneous stress show a sharp decrease

from a high tensile value at $T_m/T_s = 4$. The agreement among the various substrates is very good for the instantaneous stress as a function of temperature, and so it can be concluded that the instantaneous stress at 1000A is independent of substrate.

In summary, there is a high tensile stress at the lower temperatures on both silicon and glass. At 300°C some compression is observed at the lower thicknesses changing to tension at the higher. At temperatures of 500°C and above the stress is essentially zero.

Electron Microscopy

The primary tool used for the structural investigation of the films was the electron microscope. X-rays were used, but they were only used as a preliminary, non-destructive tool or to confirm what was seen in the microscope. Two microscopes were used in the investigation, the JEM 6A at Case and the 1 MeV RCA machine at U.S. Steel Research Laboratory in Monroeville, Pa. The results reported on the platinum films represents some of the first work on thicker polycrystalline films which cannot be studied on the 100 KeV machines because the beam penetration is insufficient.

The resolution of both the 100 KeV and 1 MeV microscopes is about the same (approximately 20A) for our samples, but the 1 MeV microscope has two advantages. The higher voltage and smaller Bragg angles allow a much smaller area to be examined by selected area diffraction (SAD), and as mentioned before greater thicknesses can be penetrated. Although in crystalline samples there are channelling and other enhancement effects, the relatively short range crystalline order of our films means that any increase in penetration achieved is primarily "brute force". Thus, even at 1 MeV, 1300A was very close to the limit of penetration.

Two methods were used to prepare the platinum evaporated on silicon for microscopy. The first consisted of placing a sample in

a bowl of CP-4 etch and letting the film float free of the substrate. The film was then rinsed in distilled water and mounted on a microscope grid.

In the second method, a disk about $1/10''$ in diameter was cut from the beam with an abrasive machine. The disk was fastened in a teflon holder and placed in the CP-4 etch until the appearance of a red transparent area under strong light indicated that the substrate was thin enough to be transparent to electrons in that region. It was placed in a special microscope sample holder and held in with a lead gasket.

Both of these methods yielded good microscope samples, although the etched disk was difficult to handle since it could be easily broken when inserting and removing from the sample holder. The samples were virtually identical when examined indicating that the stripping process left the films relatively undamaged. All the micrographs reproduced in this report are from the stripped films.

The 1300A Pt films evaporated on cover glass at 100°C could be stripped by immersing them slowly in distilled water. They could then be mounted on a microscope grid. The adsorption of water vapor on the substrate is believed to account for the poorer adhesion which leads to this "water stripping" phenomenon in the highly stressed thicker films.

All the other films on glass were stripped by immersion in diluted hydrofluoric acid. When the film detached from the sub-

strate it was rinsed in distilled water and mounted on a microscope grid.

At 100°C the films made on silicon are polycrystalline, randomly oriented as shown in Figure 18. The grains range in size from 50-100A with an average size of 100A and the same lateral grain size is observed for both the 300A and 1300A film. The diffraction pattern consisted of uniform rings. Neither tilting in the microscope nor x-raying in a deep Debye-Schener camera indicated any preferred orientation.

At 300°C the 300A film on silicon gave a spotted diffraction pattern indicating preferred orientation on the substrate. The observable grains were still the same lateral size, but the grains had definite and limited number of orientations with respect to the substrate and each other. The values of the lattice spacings determined from the diffraction patterns indicated the formation of Pt-Si compounds such as PtSi and Pt₂Si along with Pt. The 1300A film gave a pattern with intense rings corresponding to the d values of Pt. There were spots of lesser intensity indicating that at 300°C the thicker film probably has an oriented underlayer of Pt-Si compounds with polycrystalline Pt on top.

At 600°C an interesting phenomenon was noticed on the silicon substrate; the smaller grains tended in certain areas to grow together into large grains about 1000A in lateral extent. This is shown clearly in Figure 21.

The results for glass at 100°C in both the 300A and 1300A

films are about the same as silicon. As shown in Figures 15 and 16 the grains are 50-200A with an average size of 100A. The orientation is random and polycrystalline with no evidence for a preferred orientation.

As can be seen by comparing Figures 19 and 20 with Figures 15 and 16 the structure of both the 300A and 1300A films grown on cover glass at 300°C are about the same. The grains have the same average lateral size of about 100A. A comparison of Figure 20 with Figure 16 shows that there are more clumps of grains having the same diffracted intensity in the film deposited at 300°C. The same diffracted intensity suggests that the grains comprising a clump all have about the same crystallographic orientation.

Shown in Figure 17 is a selected area diffraction pattern from the 1300A film (300°C) using a 5 micron aperture. A calculation using kinematical theory shows that for a film of thickness, t , composed of square columnar grains of side, d ,

$$N = \frac{m\pi R^2}{2gtd^2M^2} \quad (13)$$

where N is the number of spots in a ring, R is the radius of the aperture, g is the reciprocal lattice vector, M is the magnification, and m is the multiplicity. For the (111) ring of platinum with $d = 100A$, N is equal to about 2. Counting the number of distinct spots in the first ring of Figure 17 yields about 10 spots. The smaller number of spots calculated than observed may be due to the fact that the selected area defined by the 5 micron aperture is

larger than 5 microns. This could be the result of spherical observation or a derivation from exact focus of the objective lens.

The small selected area available on the high voltage microscope may be of use in determining grain size and orientation in thin films with small grains. There are three problems in this type of analysis. One is that plates are consistently underexposed. There is a limit to how long a plate may be exposed without fogging the other plates in the microscope. Another problem is the validity of the kinematical calculation; it is felt that the calculation just presented gives the right order of magnitude. The third problem is knowing the exact area defined by the selecting aperture. Our results with the 5 micron selected area aperture are subject to these limitations.

From the microscopy data presented the following conclusions can be drawn. 1) The average lateral grain size is the same for Pt films deposited on both silicon and glass substrates at 100°C and 300°C. The grains have an average lateral extent of 100A for all thicknesses, suggesting columnar growth. 2) There is no gross change in the structure of platinum films on cover glass when the deposition temperature is changed from 100°C to 300°C. The only change appears to be that adjacent grains take on the same crystallographic orientation. 3) There is some orientation with respect to the silicon substrate in the films grown on silicon at 300°C as well as formation of Pt-Si compounds. 4) At higher temperatures (600°C) the small grains grow together to form large single crystal grains about 1000A in lateral extent.

FIGURE 15 - PLATINUM DEPOSITED ON COVER GLASS AT 100°C,
300A THICK, BRIGHT FIELD, 100 KV

FIGURE 16 - PLATINUM DEPOSITED ON COVER GLASS AT 100°C,
1300 Å THICK, BRIGHT FIELD, 1000 KV

FIGURE 17 - PLATINUM DEPOSITED ON COVER GLASS AT 300°C, 1300A
THICK, SELECTED AREA DIFFRACTION USING A 5 MICRON
APERTURE, 800 KV

FIGURE 18 - PLATINUM DEPOSITED ON SILICON AT 100°C, 300Å THICK,
DARK FIELD USING (111) AND (200) RINGS, 100 KV

FIGURE 19 - PLATINUM DEPOSITED ON COVER GLASS AT 300°C, 300A
THICK, DARK FIELD USING (111) AND (200) RINGS, 100 KV

FIGURE 20 - PLATINUM DEPOSITED ON COVER GLASS AT 300°C,
1300Å THICK, BRIGHT FIELD, 800 KV

FIGURE 21 - PLATINUM DEPOSITED ON SILICON AT 600°C, 300A
THICK, BRIGHT FIELD, 100 KV

Review of Other Temperature Data

The problem of the temperature dependance of the stress in evaporated metal films has been studied for the last 15 years. A satisfactory explanation of the temperature dependance will, undoubtedly, contribute much to our understanding of the origin of the stress. The solution to this problem has been complicated by the lack of quantitative models to test and the variety of experimental data which sometimes seem to disagree. The Case Laboratory has long believed that the key to understanding the stress has been in knowing the detailed structure of the thin films. It is unfortunate that workers have not in general characterized both the structure and the stress in thin films simultaneously. Most of the structural work has been done on epitaxial films grown at elevated temperatures while much of the stress work has been done on polycrystalline films at room temperatures.

In this work the stress has been determined as a function of temperature at a variety of thicknesses, and the structure of the films on which the stress measurement was made determined. This approach is believed necessary for a comprehensive theory of stress in thin films.

A review of the work available at this time seems to show that the metals divide themselves into two families when characterized by the temperature dependance of the stress. Nickel, iron,

and permalloy are members of one family which is characterized by an approximately linear decrease in stress with temperature. Copper, aluminum and platinum form another family which is characterized by a sharp decrease in stress when the ratio of the melting temperature to the deposition temperature, T_m/T_s , is less than 4. It is believed that there are structural differences in these two families which account for these two stress behaviors.

The stress in nickel films as a function of temperature has been measured by Hoffman, Daniels and Crittenden,⁽¹⁹⁾ Klokholm and Freedman,⁽²⁰⁾ and Klokholm.⁽²¹⁾ The measurement by Hoffman, et al. was of 1500A nickel films on mica and showed roughly a linear decrease in stress from 75°C to 225°C. Klokholm and Freedman obtain a curve for 1000A nickel on glass substrates which show a more rapid decrease in tensile stress with increasing deposition temperature. The stress changes to compressive at about 100°C, reaches a maximum compression about 150°C and then shows a decrease in the magnitude of the compression until 200°C. Klokholm⁽²¹⁾ in his latter work finds a stress for 1000A nickel on nickel substrates which decreases roughly linearly with substrate temperature going to zero about 400°C. The temperature dependance found by Klokholm and Freedman⁽²⁰⁾ is very different than that found by Klokholm⁽²¹⁾ in his earlier work and that found by Hoffman et al.⁽¹⁹⁾ It is hard to understand why the stress should vary so much unless there were structural differences in the films that are not well understood at present. This could be due to the different substrates

used.

Pruett⁽²²⁾ finds a linear decrease in stress with temperature for 1000A permalloy films evaporated on cover glass. The stress goes to zero around 300°C and is compressive at still higher temperatures. Weiss and Smith,⁽²³⁾ on the other hand, observe a rapid decrease in stress from room temperature for permalloy films evaporated on glass and mica. The stress is zero about 100°C, stays compressive from about 100°C to 200°C and then becomes tensile again.

Riesenfeld⁽²⁴⁾ has measured the stress in 1000A iron films on fused quartz substrates. The stress decreases linearly from a high value at room temperature to zero around 300°C. Some of the runs show compression at temperatures higher than 300°C.

A comprehensive picture of the temperature dependence of the stress in iron, nickel and permalloy is hard to form due to the different results obtained by various workers. Part of the problem may be experimental (such as poor thermal control) and part may be due to different structures in the various films. However, the data seem to be weighted in favor of a temperature dependence where the stress decreases linearly from room temperature going to zero about 300°C to 400°C with a small compression at higher temperatures.

The structure of polycrystalline nickel films has been determined by Fleet⁽²⁵⁾ who finds that the crystallite size increases rapidly in the region from room temperature to 500°C. Doljack⁽²⁶⁾

finds an increase in grain size in nickel films when the substrate temperature is raised from room temperature to 100°C. Klokholm and Freedman⁽²⁰⁾ find grain sizes of 50A, 100A and 1000A for deposition temperatures of 25°C, 100°C and 200°C respectively. Thus, in the case of nickel there is much evidence for a rapid change with temperature of the structure, particularly the formation of large grains.

An explanation of the stress in nickel, and probably also in iron and permalloy, will have to take into account these structural changes.

Shown in Figures 22 and 23 are the stress versus reduced temperature for copper and aluminum respectively. Although only Klokholm⁽²¹⁾ has measured the stress in aluminum, Klokholm,⁽²¹⁾ Horikoshi, Ozawa and Hasunuma,⁽²⁷⁾ and Story and Hoffman⁽²⁸⁾ have measured the stress in copper. Horikoshi, et al. and Klokholm use copper substrates, but Story and Hoffman use mica with a thin coat of nickel. Copper shows a higher value of stress at low temperatures in Klokholm's work than in the work of Story and Hoffman. This may be due partially to the fact that Klokholm measures the instantaneous stress whereas Story and Hoffman measure the average stress. Also the data of Story and Hoffman does not fall off quite so sharply as a function of temperature when compared to the data of Klokholm. As regards the present work, there is a similarity between the author's data in Figure 14 and the data shown in Figures 22 and 23.

Figure 22--Stress Versus Reduced Temperature for Copper Films at 1000 Å by Various Workers

Figure 23--Instantaneous Stress Versus Reduced Temperature for Al Deposited on Al Substrates
(data from Klokholm)

Unfortunately, there exists no detailed structural work on the copper and aluminum films at the lower temperatures. It would be interesting to compare the structure of copper and aluminum with that of platinum at 100°C.

Annealing data has been taken by Story and Hoffman on copper and by Hoffman et al. on nickel. The copper films show a decrease in stress when annealed to temperatures above the deposition temperature for deposition temperatures less than 50°C. They show an increase in stress with annealing temperatures higher than deposition temperatures of 50°C. Nickel films also show a decrease in stress when annealed to temperatures higher than the deposition temperature.

A model which explains the stress in platinum thin films should apply also to copper and aluminum. The ideas in the model, it is hoped, will apply also to nickel, iron and other metals although differences in structure in these other metals will probably require some detailed modifications of the model.

A theory of the stress in platinum thin films should explain the fact that the stress is relatively independent of thickness at the lower temperatures and the fact that the stress drops very rapidly to a small value at a temperature, $T_m/T_s = 4$, remaining small at still higher temperatures. The explanation of these facts should be consistent with the structural observations on the films.

The magnitude of the compression in platinum is not known due to experimental uncertainty. Thus, while there exists a com-

pression at the higher temperatures it would be impossible to compare any theory quantitatively with experiment. Because of the experimental uncertainty and the difficulty in explaining both the tension and compression with one model it is not considered essential that the theory explain the compressive stress.

Presumably platinum would show a decrease in stress similar to copper when annealed from a 100°C to higher temperatures. This fact has not been verified experimentally, and consequently, an explanation of the annealing behavior is also not essential to a model for the stress.

A Model for the Stress

Although many stress measurements have been performed on evaporated films in the last 20 years, there has yet to emerge a generally accepted, quantitative theory of the intrinsic stress in evaporated metal films. In fact, there are almost as many theories as there are measurements.

However, there are certain observations on which most workers agree. One is that the stress for many metals deposited at room temperature is high, tensile and relatively independent of thicknesses. The agreement between the present data on platinum and Klokholm's data on copper and aluminum with respect to the temperature dependence of the stress also seems to be experimentally sound. The decrease in tension when metal films are made at room temperature and annealed to higher temperatures also does not seem to be in dispute.

An important feature of models which attempt to explain the large intrinsic stress in thin films is a volume shrinkage which generates the stress when this volume shrinkage is allowed to proceed with the substrate constraining the film. Some important models proposed to explain the stress will now be considered.

It has long been known that evaporated films have an extremely high imperfection density. The stress in thin films has been ex-

plained by Story and Hoffman,⁽²⁸⁾ Hoffman, Crittenden and Daniels,⁽¹⁹⁾ and Hoffman, Anders and Crittenden⁽³⁰⁾ as resulting from a volume shrinkage when a high vacancy concentration is lost. The vacancy model has the drawback that the number of vacancies assumed (about 1%) is far in excess of the equilibrium concentration of vacancies. The vacancies were presumed to be quenched in during the deposition process. Annealing leads to the migration of the vacancies to a free surface (at the top of the film) and thus to a reduction in stress. However, if an appreciable number of vacancies migrate to grain boundaries without mass transfer down the boundaries the stress will be increased rather than reduced. The resistivity data obtained from annealing the films once used as evidence for the vacancy model, can be re-interpreted as a change at the grain boundaries rather than as the migration of vacancies to a free surface.

Klokholm and Berry⁽³¹⁾ explain the large intrinsic stress in metals deposited at low temperatures as arising from the annealing and shrinkage of disordered material buried behind the advancing surface of a growing film. The material is envisaged to have a structure and density lying between the two extremes represented by a perfect crystal and a highly defective supercooled liquid. The fact that the stress in many metals falls off sharply at $T_m/T_s \approx 4.5$ is thought to be due to the removing of the disorder in the surface of a growing film by a process having an activation energy of about 0.4 that of self diffusion.

The Klokholm and Berry model of the stress can be criticized on three points: 1) For pure metals Klokholm and Berry estimate that the volume shrinkage will be inhibited below 4.2°K. Copper, for instance, has $T_m/T_s = 4$ at a temperature of $T_s = 340^\circ\text{K}$. Therefore, Klokholm and Berry have postulated a process where the volume shrinkage has an activation energy about 75 times lower than that of the surface relaxation. This seems unreasonable in the light of what is known about activation energies for diffusion. (In many metals surface diffusion activation energies are about one half the bulk self diffusion energies.) 2) The detailed structure of the film after the shrinkage is not specified nor is the mechanism for stress generation during the amorphous to crystalline transition. 3) Still another mechanism is needed to explain the volume rearrangement which reduces the stress during annealing.

Wilcox, Campbell and Anderson⁽³²⁾ explain the tensile stress that they measure in silver and gold as arising from the shrinkage of the film due to the elimination of grain boundaries as the thickness increases. This model does not apply to the present data since the platinum films exhibit columnar growth with no elimination of grain boundaries after the initial growth at thicknesses less than 100Å. By the model of Wilcox, Campbell and Anderson no stress would be generated in platinum greater than 100Å thick; this is clearly not the case.

Models have also been proposed which limit the stress which

may exist in thin films but which do not explain the origin of the intrinsic stress. In many metals deposited at lower temperatures the stresses are very high (up to 1% of E), and thus some stress limiting mechanism is reasonable. Blumberg and Seraphim⁽³³⁾ and Caswell, Priest, and Budo⁽³⁴⁾ explain their data on tin, lead and indium in terms of dislocation pinning at the surface. The pinning limits the value of stress which can be realized from the differential thermal expansion between the substrate and film. This leads to a stress which increases as thickness decreases.

Chaudhari⁽³⁵⁾ suggests that grain boundary sliding or diffusional creep can lead to stress relief in small grained films. Chaudhari, Mader, and Freedman⁽³⁶⁾ have calculated the stress required to form a dislocation loop the size of a grain where the loop forms within a grain, at a grain boundary and in grains adjacent to grains where a loop is already present. The stress is about the same value as the stress observed in fine grain, polycrystalline films suggesting the intrinsic stress may be flow stress limited.

The calculation of Chaudhari, Mader, and Freedman show that for a thick film with 100A grains $\sigma/\mu = 2 \times 10^{-2}$ where μ is the shear modulus. This value represents a lower bound on values of the stress required for dislocation activity. This implies a σ is about the same value as observed at 100°C in this experiment. Thus, the small grained films of platinum in this work are perhaps flow stress limited as suggested by Chaudhari, Mader and Freedman, but this is not important to the mechanism for stress generation.

Finegan and Hoffman⁽³⁷⁾ proposed a crystallite boundary relaxation model to explain the stress in iron films. It is proposed that this model with some modification will explain our data. The model originally proposed that the high tensile stress observed in metal films was generated by the forces arising when the small grains grew together.

The model considered that small clumps (essentially perfect crystallites) were formed on the substrate surface. The effect of surface tension and constrained growth of the isolated islands resulted in a small compression. This effect is not important to our results since it gives only an offset from zero intercept on the force/unit width versus thickness curve. As the grains grew together they would experience a strong attraction for each other, but the crystallites would be prevented from moving due to a strong bond to the substrate. The crystallite would then be strained as it relaxed into the gaps between grains.

In order to evaluate this model, Finegan and Hoffman constructed a model for the force between crystallites which had a linear force versus displacement curve for small distances and an exponential tail as the distance between crystallites increased. Using force model and an average boundary, a stress of 9×10^9 dynes/cm² was obtained for iron. This was in good agreement with their measured values.

It is believed that the model of Finegan and Hoffman is essentially correct in its explanation of the origin of the large value

of intrinsic stress in metal films. In bulk metals, grain boundaries consist of channels of bad fit which surround islands of good fit (see Grifkins,⁽³⁸⁾ for instance). In the regions of good fit the misorientation allow atoms to belong to lattices of both grains, forming a kind of "super-lattice" common to the two grains. These regions of good fit are lower in energy than the regions of bad fit and thus a boundary would tend to maximize the regions of good fit subject to the minimization of the total energy. For the constrained film case, increasing the area of regions of good fit would at the same time introduce a strain in the sample. Thus the strain energy and even the crystallite size should be related to the properties of the grain boundaries.

Chaudhari and Mader⁽³⁹⁾ are attempting to extend the concept of coherent boundaries to microscopic samples not subject to substrate constraint. For instance, they find that free MgO crystallites deposited from vapor tend to be oriented with a coincident-lattice boundary (CLB) most of the time. Their calculations show that the local energy minima associated with the orientation of a CLB dip about 200 ergs/cm^2 below the high angle boundary represented by orientations a bit different from the CLB. The energy at angles near a CLB can be treated as the superposition of the CLB energy at its exact orientation and the energy of a low angle grain boundary.

It is proposed that the small crystallites in a growing thin film tend to orient themselves with CLB's when they grow together.

However, since the crystallites started out as randomly oriented nuclei they cannot completely accomplish the growth into the minimum energy configuration. As in the model of Finegan and Hoffman the crystallites then have areas of low density between them. The boundaries of the grains strain into this low density area and attempt to form CLB's but are prevented because they are anchored to the substrate and because of the interactions of their neighbors. (If a crystallite tries to orient itself in a minimum energy position with respect to one neighbor it may increase its energy with respect of another.) This straining to fill in the boundary leads to the observed high tensile stress in the manner explained by Finegan and Hoffman.

It might be argued that the crystallites would, on the average, be on either side of the energy dip and thus the stress would be compressive as much as tensile and average to zero. However, the straining of the boundary into the low density areas between grains makes the stress tensile. This, in effect, negates the interaction on the other side of the dip.

Energy considerations show that this relaxation can account for the high stress. If the relaxation of the boundary converts a 100 ergs/cm^2 into strain energy, then the energy density, U , for a four sided square column of side length, d , will be

$$U = \frac{1}{2}(100)d/d.$$

Thus $U = 2 \times 10^8 \text{ ergs/cm}^3$ for $d = 100\text{\AA}$. The energy density of a

thin film with uniform stress, σ , is given by the equation

$$U = \frac{1}{2} \sigma^2 / E .$$

For $U = 2 \times 10^8$ ergs, $\sigma = 2.4 \times 10^{10}$ dynes/cm² which is in excess of the highest value of stress measured in our experiment.

Straining of the crystallite boundaries is believed . . . to be the correct physical picture for the origin of the intrinsic stress in platinum thin films. The reason for the small value of stress when $T_m/T_s \leq 4$ will now be discussed. The high tensile stress observed in platinum will be inhibited if the grain boundaries are prevented from relaxing toward each other. It is proposed that diffusion will allow these regions of low density to be filled with platinum during deposition thus preventing the stress generation.

Melmed⁽⁴⁰⁾ has studied the surface diffusion in platinum by field emission microscopy and found an activation energy of 29.5 ± 3.0 Kcal/mole. Jackson⁽⁴¹⁾ and Schumacher, Seeger and Harlen⁽⁴²⁾ have studied the recovery of platinum quenched from its melting point. They find a complex recovery in the electrical resistivity involving two second order processes with activation energies of 1.00 ev and 1.34 ev respectively corresponding to the migration of vacancy pairs and single vacancies.

The activation energies mentioned above are the right value to give diffusion coefficients on the order of 10^{-13} cm²/sec which are appropriate for diffusion in a few seconds across 100A grains.

On this basis, it is reasonable to suppose that a thermally activated process such as surface or vacancy diffusion fills in the low density areas between the grains during the film's growth. This results in a lower value of the stress. The diffusion is too slow at the lower temperatures and the stress is developed as explained above.

The diffusion mechanism just proposed explains the decrease in stress at 300°C where the grain size remains constant as the temperature is increased. At still higher temperatures it was observed (see Figure 21) that smaller grains grew together to form larger grains about 1000Å in extent. This different structure, with its bigger grains, should result in a very small stress since the grain boundaries have a much smaller area per unit area of film. Also since this "recrystallization" takes place as the film is growing the grains can change their orientations to minimize the strain energy at the interface (i.e. they can form CLBs).

In summary, the large stress at low temperatures is explained by the interaction at the grain boundaries, the stress is reduced at a temperature of about 300°C by diffusion in the growing film. At still higher temperatures the very small stress is a result of a different structure with much larger grains.

Conclusion

In the course of this work a general equation for the cantilevered beam was developed. The limits of applicability of this equation was defined with respect to large deflections, shear distributions at the edge of the substrate and boundary conditions at the clamp. Some errors by various workers were pointed out.

The stress in platinum thin films was measured over a wide range of temperatures on amorphous and crystalline substrates. Neither the stress in platinum nor any stress measurements to such a high temperature has been previously reported. A comprehensive structural investigation was made of the films using, in particular, a 1 MeV electron microscope for thick films.

The results of the stress measurements were explained in a comprehensive theory based on the structural observations.

Appendix I

During the course of this investigation, it was found necessary to measure the elastic modulus for the cover glass substrates. The first measurements were made in a weighted friction clamp. Friction clamps are commonly used in thin film stress measurements. The equations used to determine E , presume a clamp in which the slope and deflection of the beam are zero at the clamp jaws. The friction clamp was found to allow enough relaxation of this boundary condition to cause significant error in the usual equations, since a small relaxation in this boundary condition at the clamp can result in a large error in the measured stiffness.

The elastic modulus, E , of a beam was measured by two techniques, vibrating reed (VR) and static loading (SL). In the VR technique a beam was coated with a thin conducting film and placed in the clamp. The beam was then plucked and the displacement was measured by a capacitive probe. The probe was connected to an amplifier and the output of the amplifier went to both an oscilloscope and a frequency meter. The oscillations were observed on the oscilloscope and the frequency meter was triggered when their amplitude was the correct value. The frequency meter was used to measure the period of oscillation. The following equation applies

$$E = [\ell^2(6.19051)/Th]^2 \rho \quad (1)$$

where ℓ is the length from the end of the beam to the clamp, h , the thickness of the beam, T , the period of oscillation, and ρ , the density of the beam.

A correction for the effect of air on the density of the beam was calculated by assuming that

$$\rho_{\text{eff}} = \rho_{\text{glass}} + \beta \rho_{\text{air}} .$$

β was then determined by measuring the period of oscillation in both freon (with a high density) and air. β ranged in value between 10 and 20 for the beams tested. This resulted in a correction to the density in Equation (1) of 1% to 2%.

Since the period of oscillation could be measured very accurately ($\pm .1\%$), the main error in using Equation (1) was in measuring ℓ and h . Thus, values of E could be determined to $\pm 3\%$.

In the SL technique a weight was hung from a quartz hook cemented on the end of the beam. The deflections were measured with a traveling microscope. The appropriate equation is

$$E = 4mg\ell^3/\delta h^3b \quad (2)$$

where m is the mass hung on the end of the beam, ℓ , the distance from hook to clamp, δ , the deflection at the end and b , the width of the beam. The theoretical limitations of Equation (2) have been discussed in the body of this report. The experimental limitations

on the determination of E were in measuring distances. E could be determined to $\pm 5\%$.

The friction clamp used in this investigation consisted of a stainless steel base with a top jaw of the same material. Both jaws were ground flat. A beam was placed in the jaws and shims were added to make the faces of the jaws parallel. Weights were then placed on top to hold the beam firmly.

It was noticed that the values of E determined in this friction clamp were outside the handbook range for similar glasses. They were low by at least 20%. A silicon beam also gave a value of E which was low when compared to the value given by the single crystal elastic constants. As mentioned before this is due to a relaxation of the boundary conditions at the friction clamp.

Using the same clamp and weight with which the stress measurements on silicon had been made results in an E which was too small by 19%, using Equation (2). For Equation (2) to yield the correct value of E , it must be multiplied by a factor of 1.19. This factor is also used to correct the stress data for the runs made on silicon. Although slightly better results could be obtained by increasing the weight on the clamp, it was found that no matter how much weight was used the friction clamp was still unsatisfactory.

A clamp was then constructed by cementing the beam between two flat steel jaws with epoxy. This was felt to give a good approximation to the correct boundary conditions. The clamps actually used in measuring the stress (which were cemented with Auto-

stic) were also evaluated.

The clamps using epoxy and Autostic were found to give the same value of E for cover glass. The value determined was $6.96 \pm .20 \times 10^{11}$ dynes/cm. In addition quartz beams were also tested in the Autostic clamp. Values of E determined were equal to the handbook value for fused quartz within the experimental error.

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