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GROWTH EFFECTS THIN NICKEL FILMS

R. W. SPRINGER

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ROBERT WILLIAM SPRINGER

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Department of Physics

CASE WESTERN RESERVE UNIVERSITY

January 1973

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Abstract

by

ROBERT WILLIAM SPRINGER

The intrinsic stress of vacuum deposited 2000 Å nickel films was examined and correlation between the microstructure and the measured stress was found.

The cantilever plate technique for measuring the stress using a microbalance was analyzed in detail. The bending equations were slightly revised from the former closed form approximations used in the past. Linear bending theory was shown to be adequate for the bending arising from the stressed film. The temperature problems associated with this technique were examined and adverse effects were minimized. No bending due to thermal gradients was observed. Stress from early stages of film growth was recorded accurately for the first time.

A new technique for determining the average grain diameter was developed. High voltage electron diffraction of a small selected area produced spotty diffraction rings. A calculation relating the spots observed and the number of grains in a diffracting volume yields an average grain diameter. Agreement

between grain sizes deduced from this technique and the grains observed in bright field micrograph graphs is good. This tends to confirm columnar growth in the nickel films.

The intrinsic stress is 0.8×10^9 dynes/cm² at 35 C and decreases to zero at a temperature of about 250 C. Substrate preparation and material was found to affect the initial mechanical properties of a growing film but does not appear to alter behavior above 1000 A. A linear stress thickness product was observed for both films deposited on nickel as well as NiO.

A growth process is postulated, and a quantitative calculation based on this growth model was made for the stress using the bulk parameter of nickel and the measured grain size. Agreement with the measured values is good for both the nickel and NiO coated nickel substrates. The nature of the substrate material does not appear to affect the stress after 1000 A, as no memory of the nucleation differences are apparent.

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I. INTRODUCTION

Stress in growing thin films formed by electrochemical or vacuum deposition has been observed for many years. Stoney¹ was among the first to actively investigate this property quantitatively. The interest waned and was reviewed again in the early 1950's. This laboratory has actively engaged in the measurement of stress in vacuum deposited thin films since that time. The stress developed in the film during its growth is normally observed by a deformation of the thin substrate. This stress can be compressive or tensile or both depending upon the conditions during growth. Sputtered films may exhibit compressive stress due to impurities in the film as a result of electrical bias during deposition. Impurity diffusion into the film during growth can also alter the mechanical behavior. However, if films are evaporated at low pressures, on clean substrates and at constant temperature, a stress in the growing film is still observed. This intrinsic stress is still not well understood. A number of models do exist, but are unable to explain the observed stress behavior in any detail.

Wilcock, Campbell and Anderson² propose a model based on constrained grain growth in the early stages of film growth. It has been observed by Grigson and Heritage³ that in the early

growth of Ni, Ag, Au, and NiFe films small isolated islands are formed. In 20 Å thick films these islands, ~ 40 Å in diameter, contain three or four crystals. As the film grows thicker, the islands increase in size until they merge. As the film approaches ~ 60 Å in thickness, these merged islands have become single crystal and random in orientation. Evidently a recrystallization has occurred in this time. The Wilcock, Campbell, Anderson model proposes that this recrystallization produces the observed stress. A void content in each island is computed due to the presence of grain boundaries and dislocations. As these voids are annealed out during the film growth, a shrinkage in the film is envisioned to occur. Because the film is rigidly attached to the substrate a tensile stress is developed. Once this void annealing is completed, no further stress is predicted. This will not explain the constant stress curves observed in many experiments with thicker films.

Klokholm and Berry⁴ propose a model based upon a constrained self diffusion process. A steady state process occurs in the growing film. As atoms arrive at the surface of the film, they migrate around and attempt to move to crystal positions. Before these atoms can become fixed in these positions, more atoms arrive causing them to become buried. This buried layer of disordered atoms is imagined to continue its rearrangement through a self diffusion process. As order is established, a constrained volume

shrinkage occurs in the film and a stress is produced. Thus, the amount of disorder buried behind advancing layers determines the intrinsic stress. In order to obtain a decrease in stress at increasing temperatures that is in agreement with existing data, an activation energy about half the bulk value is postulated for the migration of atoms on the film surface. This model can explain a constant intrinsic stress as a function of thickness. A difficulty does arise in understanding the temperature dependence however, if the disorder buried is proportional to the jump frequency, then estimates of the decrease in stress as a function of temperature can be made. The exponential temperature behavior of the jump frequency predicts a very rapid decrease in the stress with increasing temperature. However, the actual connection of this self-diffusion process and the disorder in buried layers is only loosely made. Thus, this model remains too vague for quantitative prediction of the stress magnitude.

A very recent model by Chaudhari⁵ attempts to explain the origin of the stress by a continuous nucleation and lateral recrystallization as the film grows. He indicates that small crystalites $\sim 13 \text{ \AA}$ are constantly nucleating and recrystallizing to $\sim 50 \text{ \AA}$ diameters, and proposes that a balance between the grain boundary energy and an increase in strain energy determine the final grain diameter. As the grains grow, the vacancies at the grain boundaries are eliminated and create strains in the

crystals. As the boundaries are eliminated, the free energy of the system decreases. The minimum in the energy correspond to $\sim 50 \text{ \AA}$ diameter grains. The stress generated in this process is $\sim 6 \times 10^{10}$ dynes/cm². This indicates strains of $\sim 1.7\%$ if usual elasticity relations are applied. Chandhari agrees that this stress prediction is too high and postulates that plastic flow occurs to relieve the stress. The measured stress value is then determined by "the critical stress required for dislocation propagation in films." This plastic flow will also allow lateral grain growth to continue without constraint to the substrate as before. It is difficult to understand why the stress produced by constrained grain growth continues past the flow stress limit until the energy is minimized. Only then is the increased grain growth due to plastic flow introduced. Also, the grain diameter predicted at this equilibrium decreases with temperature, as grain boundary free energies decrease with increasing temperature.⁶ Unless a plastic flow mechanism is invoked to allow further grain growth, both the order of magnitude and temperature dependence of the grain diameter disagrees with experimental evidence. Although the order of magnitude stress is incorrect, the model would predict a constant intrinsic stress as a function of thickness.

Another model based upon contractions occurring at grain boundaries was proposed by Finegan and Hoffman⁷, and revised by Doljack.⁸ This model attempts to explain qualitatively the

entire region of the stress vs thickness curve and allows a numerical prediction to be made for the constant intrinsic stress. Atoms are envisioned to arrive at the substrate, nucleate into small islands and finally adhere. These islands are isolated at first, but increase in size as more atoms arrive. The growth of these isolated islands is expected to produce a compressive stress because the outer layer of atoms deviate from the bulk lattice positions. As a new layer of atoms condenses on the island, this former outer layer attempts to relax toward a bulk position. Since the island is anchored to the substrate, this attempted relaxation is constrained, producing a compressive stress. As the islands fill the substrate area such that the spaces between adjacent islands approaches a lattice constant, interatomic forces attract them. Thus, the stress changes to tensile from compressive. This high tensile stress is envisioned to drive a recrystallization to a final stable grain diameter. The details of the grain diameter stabilization are not understood at this time. However, the grains do stabilize and columnar growth is postulated beyond this point. The recrystallization process does not completely relieve the initial stress and a tensile force exerted by the boundaries on the grains is propagated as the film grows. Thus, this model will also predict a constant intrinsic stress as a function of film thickness. It will also allow a quantitative prediction of this temperature dependent

stress with the use of a few bulk material constants and the observed grain diameter.

II. EXPERIMENTAL CONSIDERATIONS

The intrinsic stress developed in the vacuum deposited films is measured by monitoring the deformation of the substrate. This experiment uses nickel substrates cut to a rectangular shape. One end is mounted in a rigid clamp (Fig. 1), and the deflection of the other end is observed to determine the deflection. The deflection is determined by coupling the free end of the substrate to a modified microbalance. A hook attached to the free end of the substrate is coupled to the microbalance beam with a quartz fiber. Thus, any deflection of the substrate is transmitted to the microbalance. The deflection of the microbalance and substrate may be calibrated directly in terms of an applied force eliminating the need for explicit knowledge of the elastic constants of either substrate or microbalance.

The voltage reading from the microbalance represents the force/unit width of the film and is recorded as a function of time during the experiment. Almost all of the stress data obtained from a deflecting plate suffers from experimental difficulties inherent in the technique. In particular, it is very hard to maintain constant temperature in the changing thermal environment while leaving the plate free to deflect. In some extreme cases, thermal problems mask the intrinsic stress.

Figure 1. Substrate and Clamp

For the present experiment, a substantial effort was made to minimize these effects.

As the experimental conditions cannot be made ideal, the deviation from assumptions made in calculations must be examined. It will be shown that corrections to the working equations as derived in Appendix II are not needed.

A. Substrate Material and Thermal Performance

The choice of nickel for the substrate material was made to minimize unwanted thermal effects. A long standing problem in the measurement of intrinsic stress is the temperature rise of the substrate during deposition. If the film and the substrate have different coefficients of thermal expansion, then a bending due to a bi-metallic strip effect is expected for any temperature change. An expression for the stress developed in a bi-metallic strip, allowing one side to be much thinner than the other, is given by Shanely.⁹

$$\sigma_F = \Delta T (\alpha_s - \alpha_F) E_F \quad (1)$$

σ_F is the stress developed in the film for a temperature change of ΔT . α_s , and α_F are the thermal coefficient of expansion for the substrate, and the film. E_F is the Young's modulus of the film. In this study, nickel was chosen as the substrate material

because the coefficient of thermal expansion is the same as the film. For this geometry, a temperature rise from room temperature evaporations through 150 C cannot be avoided.

The temperature rise in the substrate is due to the radiated power incident from the source of molten nickel as well as the heat of condensation from the nickel vapor. At room temperature, the reradiated power is negligible compared to the incident power. The clamp is thermally massive relative to the substrate and acts as a heat sink. At room temperature, the power incident must be conducted away from the substrate which produces a temperature gradient along the length. With an estimate of the incident power, and the assumptions of steady state conditions, the temperature rise at the free end may be computed from the heat flow equation.¹⁰

$$\frac{dQ}{dt} = -KAVT \quad (2)$$

$\frac{dQ}{dt}$ is the heat conducted through a given area A, K is the thermal conductivity and VT is the temperature gradient across the face of the area. At any point along the length of the substrate, the heat conducted through that area must be equal to the total power incident from that point to the free end. Then $\frac{dQ}{dt}(x)$ is equal to Pbx where P is the power/unit area incident on the substrate, b is the substrate width and x is the distance

from the conducting cross-section to the free end. Integrating the heat equation and evaluating the result for the length l , equation (3) results, where h is the thickness.

$$\Delta T = \frac{Pl^2}{2Kh} \quad (3)$$

For our geometry, the estimate for P is roughly 20 milliwatts/cm². Using the thermal conductivity of nickel at room temperature as .5944 watts/cm/°C⁻¹, 5 cm for the length and .0127 cm for the thickness, a ΔT of 33 C is predicted. This estimate is a bit high when compared to experimental evidence, presumably due to the fact that the experiment is terminated before steady state conditions are reached.

A temperature gradient through the thickness of the substrate may also occur. A worst case estimate of this gradient can be computed assuming that the power incident must be conducted from one side to the other. Appealing to equation (2) and solving for the gradient to produce a heat flow of P through a thickness of h gives equation (4).

$$\Delta T = \frac{Ph}{K} \quad (4)$$

Evaluating with the same values as before, a temperature difference of 0.5 millidegree C is found. This temperature

gradient causes a thermal expansion to occur through the substrate. This, in effect, will cause a deflection that could be interpreted as a bending moment due to the film. The magnitude of this equivalent bending moment is computed as follows.

The strains ϵ_x and ϵ_y are zero in the neutral plane and vary linearly to the top and bottom of the substrate.

$$\epsilon_x = \epsilon_y = \Delta T \propto (z/h) \quad (5)$$

where z is the distance from the neutral plane to a point in the substrate. Then,

$$\sigma = \frac{E}{1-\nu} \Delta T \propto (z/h) \quad (6)$$

and the total equivalent moment is

$$\int_{-h/2}^{h/2} \sigma z dz = \frac{E}{1-\nu} \frac{\Delta T \propto h^2}{12} \quad (7)$$

The moment applied by a surface traction is

$$M = \frac{2hT}{3} \quad (8)$$

Solving for T , the implied force/unit width becomes

$$\frac{E}{1-\nu} \frac{\Delta T \alpha h}{8} \quad (9)$$

with ν as Poisson's ratio.

The temperature gradient of 0.5 millidegree gives a value of 20 dynes/cm for the force/unit width. Since the force/unit width values measured are $\sim 10^4$ dynes/cm this effect may be neglected.

B. Working Equations

In other bending beam experiments, the standard beam equation has been used to describe the bending of a cantilever beam with a force applied at the free end. This equation does not really apply to the substrates used because the effect of the clamp on the cantilever plate is not correctly described by this equation. Numerical calculations were done for this geometry and a new expression to describe the bending due to a force applied to a hook located at the free end was obtained. Equation (10) represents the deflection δ at the hook due to an applied force F .

$$\delta = \frac{F}{A} \frac{(1-\nu^2)24f(x,y)}{Eh^3} \quad (10)$$

where $f(x,y)$ is a function determined from the calculation. This

equation deviates from the usual equation because there is flattening at the clamp. This tends to reduce the Poisson effect and hence reduces the deflection by about 3% for the same applied force.

The equation describing the bending of a free rectangular plate due to uniform surface tractions was solved by Finegan.¹² It represents the bending of a free plate into a synclastic shape. However, because one end of the substrate is placed in a rigid clamp, the substrate is not allowed to have curvature parallel to the edge of the clamp at the clamp. This tends to reduce the stiffness of the plate and accounts for about 7% difference in the resulting equation for the same applied surface traction. The deflection of the free end W due to a uniform surface traction T is given in Equation (11).

$$W = \frac{12T(1-\nu^2)}{h^2E} g(x,y) \quad (11)$$

The surface traction cannot be considered uniform out to the edges of the substrate. A shear is developed in the film as required by elasticity theory. However, Doljack¹³ has calculated the stress distribution in the film and finds that the length characteristic of this change from a uniform surface traction to a shear is less than a film thickness. Since these films are a maximum thickness of 2000 Å, the error in assuming a uniform stress to the edges of the substrate is negligible. A detailed derivation of equations (10)

and (11) appears in Appendix II.

The microbalance and substrate are connected with a quartz fiber. As the substrate deflects from stresses in the growing film, the microbalance tends to restore it to the original position. Since the substrate and the microbalance can be represented as ideal springs, a two spring model is formulated. The analysis of this model appears in Appendix I. Using the ideas presented there and the equations of deflection presented in this chapter, the working equation coupling the bending moment T and the microbalance deflection is deduced.

Decouple the substrate and microbalance, but picture the end of the quartz fiber just at the hook position. Evaporate the film and observe the deflection W . Pull down the quartz fiber, connect it to the hook and allow the substrate to relax back by an amount δ . $W - \delta$ represents the net deflection of the microbalance, Δn . Thus, an equation in deflections is found.

$$W - \delta = \Delta n \quad (12)$$

Upon substitution of the equations representing these deflections and solving for T , the force/unit width, is shown in equation (13).

$$T = F \left[\frac{h^2 E}{K 24(1-\nu^2)} + \frac{2}{hA} \frac{f(x,y)}{g(x,y)} \right] \quad (13)$$

F is the voltage recorded from the microbalance, and E/K is the ratio of the Young's modulus to the spring constant of the microbalance.

E/K is determined at the beginning of each experiment. The technique for this calibration is outlined in Appendix I. The stress in the film is related to T by the integral of the stress through the film. Thus T is defined as

$$T = \int_0^t \sigma_i(t') dt' \quad (14)$$

The value σ_i deduced from T can be in error if the following assumptions are not true. The substrate must be plane and free of scratches, and the stress in the film must be isotropic.

If the stress in the film is not isotropic, the bending equation will be in error. An anisotropic stress distribution can be introduced during the computation of equation (12). Experiments designed to measure stress anisotropy¹⁴ find none for normal incidence evaporation. Thus an isotropic stress is expected here.

The remaining scratches may have several effects. Nucleation occurs along scratches during early stages of film growth

as observed in the electron microscope.¹⁵ Magnetic anisotropy may be introduced when an array of scratches is present.¹⁶ It is difficult to know the characterization of the scratches on the intrinsic stress. But assuming that the intrinsic stress is only changed by the angle of incidence, a reduction in the stress measured can be predicted for an array of scratches. Suppose there is one scratch on the surface. The normal to the side of the scratch makes an angle θ with the direction of evaporation. (See Fig. 2). The stress must lie in the plane of the film, which roughly follows the contour of the substrate. The force/unit width is reduced as the thickness of the film normal to the section of the scratch is reduced by $\cos\theta$. Only the force/unit width parallel to the neutral plane contributes to the bending. Thus, the applied force/unit width is reduced again by $\cos\theta$. Angle of incidence experiments show that the intrinsic stress is further lowered by $\sim \cos^2\theta$. Hence, the intrinsic stress in the region of the scratch is $\cos^4\theta$ lower than on the flat surface. Thus a smooth and scratch free surface is required.

C. Initial Deformation

The substrates used in this study are metal. It is very difficult to obtain initially flat substrates 0.005 inches thick after polishing both sides. The two most pronounced deviations produced by handling during the polishing are an initial curva-

SCRATCH EFFECT

Figure 2. Scratch Effect on Stress Measurement

ture and end twist.

The initial curvature may be examined from the point of view that the neutral axis is shifted. As the curved beam is bent, the plane cross-section rotates about some new shifted axis. The problem then becomes that of finding the new location of the neutral axis and correcting the bending equations. This analysis is known as the Winkler-Bach method.¹⁷ The shift of the neutral axis from the centroid is given by equation (15).

$$y_0 = \frac{-zR}{z+1} \quad (15) \quad z = -1 + R/h \ln \frac{R+h/2}{R-h/2} \quad (16)$$

where R is the initial curvature. Assuming that any beam with an initial end deflection greater than .5 cm was discarded, R is ~ 25 cm for a substrate 5 cm in length. Using .0127 cm for the thickness, z becomes $\sim 10^{-7}$. Thus, y_0 is small enough to be neglected and the deflection of the slightly curved beam behaves as an initially flat beam.

The beam may also be slightly twisted at the end. Goodier and Griffin¹⁸ have examined the effect of the twist on the moment expression for the curvature. Their result is that the expression for the curvature in the flexible direction is unaltered, and the expression for the stiff direction is altered by second order in the rate of pretwist. Assuming a 5° twist for a 5 cm substrate only a 2% change in stiffness occurs in the stiff direc-

tion. Thus, no significant change in the bending of either direction is expected and any twist effects may be neglected.

D. Total Deformation Limit

In the derivation of the bending equation in Appendix II, it was assumed that transverse shear deformation and stretching were small compared with any bending due to an applied moment.

The transverse shear contribution can be determined by calculating the effect in the center of the beam and assume it to be uniform throughout the thickness. This will give a worst case estimate as the transverse shear varies parabolically through the thickness, having a maximum at the center of the beam.

The total contribution of transverse shear deflection of a uniformly loaded beam is proportional to¹⁹

$$\beta = 1 + \frac{48K}{5} \frac{r^2}{l^2} \frac{E}{G} \quad (17)$$

If β is ≈ 1 , then any transverse shear effects can be considered negligible. Taking $K = 3/2$, $r = .0127$, $l = 5$, $E = 2 \times 10^{12}$, $G = 7 \times 10^{11}$ for a rectangular beam this term is found to be ≈ 1.0005 . While uniform loading does not represent the actual physical case, it gives an order of magnitude estimate of any transverse shear effect neglected.

The effect of stretching manifests itself in a nonlinear

behavior in the beam as the shape of the bending changes from anticlastic²⁰ to cylindrical bending. Timoshenko²¹ has given a calculation as to how this transformation takes place and gives an expression for the corrected beam equation. This is needed to justify the use of a theory that can only guarantee proper bending description if the maximum plate deflection is less than 1/2 the plate thickness. However, the serious errors usually enter in the case where there are no free edges. Such is the case of a drum head under uniform loading. Here it is perfectly clear that not much deformation can occur without sizeable stretching effects. However, in the case of the cantilever, only one edge is built in and the others are free. Hence, if the shape taken is developable, i.e., no strain in the neutral plane, then the theory is valid for large deflections. Because of the dimensions of the substrate, any stretching effects in taking the synclastic²² shape are assumed to be small. This is also the case for bending of the beam due to a vertical load. Both assumptions may be justified by examining the Timoshenko calculation. In this calculation, Timoshenko corrects the usual beam equation for small deflections to the large deflection cylindrical bending. The modified equation is

$$M = \frac{EI}{R} \frac{v^2 - C}{v^2 - 1} \quad (18)$$

C varies from 0 to 1 depending on the quantity

$$1.286 \frac{b}{Rh} \quad (19)$$

where b is the width and h is the thickness. Choosing C such that the quantity $\frac{v^2 - C}{v^2 - 1}$ changes from 1 by 1%, a maximum deflection may be determined such that non-linear behavior is avoided. This deflection, for the dimensions of substrate used, is 0.3840 cm, or roughly 30 times the thickness of the substrate.

Since any of the expected bending gives rise to a maximum deflection of less than $5h$, it is felt that the bending theory adequately describes the experiment.

Thus, all the effects neglected in the derivation of the bending theory have been examined and the validity of the original assumption is demonstrated.

III. EXPERIMENTAL APPARATUS

A brief description of all the experiment components is given. The schematic representation of the apparatus appears in Fig. 3.

A. Vacuum System

The vacuum system consists of a 3/4 inch thick base plate, stainless steel collar and an 18 inch diameter belljar. The total internal volume is a nominal 130 liters. The system was pumped by a new Mini Imp. 4 inch diffusion pump. Dow 705 pump oil was used to minimize backstreaming and contamination. The pump also has a liquid nitrogen trap and a butterfly valve so that it can be isolated from the system during venting operation. The rated speed of this pump is 400 liters/sec. The nominal base vacuum achieved after an overnight bake out was 5×10^{-7} Torr.

The collar had 8 available flats for various feed throughs. The base plate was also constructed to contain 16 specially designed high current aluminum feed throughs. These feedthroughs used o-rings for the vacuum seals and have a leakage resistance in excess of 0.5 meg ohms.

Figure 3. Apparatus Layout

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Figure 3. Apparatus Layout

The ionization pressure gauge was a Bayard-Alpert type.

This gauge was mounted inside the vacuum in a nude head configuration.

B. Beam Gun

The beam gun used was a Denton Vacuum Mini Gun. A supplementary SCR controller was connected and allowed deposition rate control from the thickness monitor. The basic design of the gun is such that 5 kV electrons are bent through 180° by two pole pieces to the Ni boule in a water cooled copper hearth. The magnet is located at the bottom of the pole pieces. This form of evaporation produces little or no contamination of the source during evaporation as with tungsten filament operation.

C. Nickel

The nickel used for the evaporation was Marz grade, i.e., 99.997% pure, and obtained from MRC.²³ It came in pellets 1/4 inch diameter by 1/2 inch long. A button nominally 1 cm in diameter by .5 cm thick was always maintained as the charge in the beam gun hearth.

D. Temperature Control

The temperature was measured at two places: just before the substrate entered the clamp; and at the free end. The

thermocouple used at the clamp end was 0.005" chromel-alumel²⁴ bonded to the substrate by a drop of Autostick cement.²⁵ The free end thermocouple was 0.001" chromel-alumel and was likewise bonded by Autostick. Both thermocouples were of the beaded type and were formed in a carbon arc. The use of the small diameter wire at the free end was to minimize the conduction of heat away from the substrate and hence affect the measurement. The Autostick appeared to have a reasonable thermal conductivity as the thermocouple responded readily to air temperature fluctuation.

Since any external wires mechanically coupled to the substrate would necessarily affect the bending, a dummy substrate was placed next to the measured substrate. A check of the temperature performance of both positions was made under the same deposition parameters. The results appeared identical to within a few degrees.

Two sets of heaters and controllers were used in the experiment. Heaters placed along the length of the substrate and dummy were used to maintain the free end temperature.

The second set of heaters was used at the clamp end. This was found necessary in that the free end could come to temperature much quicker in that less thermal mass is involved. Hence, to eliminate any initial thermal gradients along the length of the substrate, the additional heater was employed. Since the thermal mass of the clamps are large compared to the substrate,

a sensitive control is not needed. Small [5-10 C] temperature oscillations are permitted in that the period of these oscillations was about 30 min. Thus over the 1-2 minutes during a run, the temperature was essentially "constant."

The main controller could maintain a substrate to within a fraction of a degree centigrade while idling. The other controller has coarser limits, but since oscillations are long compared to experimental times, the temperature remains constant during a run.

E. Thickness Monitor

The thickness of the films and rate of evaporation was controlled by Sloan Omni II A film thickness monitor. The technique used to measure the film thickness is to correlate the mass change on a crystal with the frequency change.

The limits of linearity for a mass change is about 100 khz. In practice they were only used to about 60 khz.

The controller was used to open the shutter at a prescribed frequency and to close another at a second frequency. This was accomplished by the blowing of 0.005 inch diameter nichrome fuse wires holding the spring loaded shutters in position.

The frequency from the controller was internally converted to a proportional D.C. voltage, differentiated, and compared with a pre-set voltage, (the rate control). The resultant error, if

any, was fed to the SCR power controller for the beam gun. Thus, constant rates to a few percent were established during all runs.

Upon the completion of a run, a two second delay prevented the beam gun from being shut off simultaneously with the closing of the shutter. This kept the rate of evaporation constant during the closing.

The frequency was monitored with an Eldorado frequency meter. This circuit had been modified to allow a pulse to be produced each time the kilocycle digit changed. This pulse was fed to an event marker on a Baush and Lomb V07 chart recorder. Thus a record of rate and thickness could be established during a run.

Another event marker was used on the main trace to indicate the opening and closing of the shutters. Thus these critical events were also recorded.

The geometric placement of the crystal was calibrated by using the microbalance. A thin slide of known area was placed on the quartz fiber of the microbalance at the same location of a substrate and exactly normal to the source. Then a trial evaporation was taken and the change in mass of the slide was compared to the change in frequency of the quartz monitor. This calibration was performed 50 runs apart and the variation in the constant used was $\sim 5\%$.

F. Microbalance

The microbalance was a modified Cahn RG. The basic operation of the device is described in Appendix I. The arms of the main beam were replaced with austenitic stainless steel capillary tubing. The new beams were strussed with capillary tubing and soldered with cadmium free Eutectic 157. This was done as the old beams would flex and account for 30% of the associated spring constant. The new beams reduced this effect by a factor of 6, to a more acceptable limit. This also helps to improve the sensitivity of the instrument.

A circuit was added to the microbalance so that it could not distinguish between an electronic signal or force. The circuit potentiometer could be calibrated in milligrams. This was done and accuracy of the circuit proved to be better than 1%. Also, weights measured with the circuit in and out of the microbalance agreed in value to better than 1%.

One last check was to observe that the deflection of the beam by a weight is cancelled by an equivalent negative setting of the mass dial. The null position was good to the limits of the eye with an optical microscope, $\sim .001$ inch, further proving that the microbalance could not distinguish between a change of the potentiometer setting and a weight applied.

The overall sensitivity of the stress measurement was governed by circuit noise levels and the dimensions of the substrate. For this experiment, the lower level was nominally 200

dynes/cm. If this occurred in a 2000 Å film, the lower limit of an average intrinsic stress detectable would be $\sim 10^7$ dynes/cm².

The microbalance was located on an adjustable table supported by invar posts. The substrate support was anchored to these posts about half way between the base plate and the microbalance. Since invar has a near zero coefficient of thermal expansion, the spacing between the substrate and microbalance should not be affected by any heating effects in these posts.

The table was adjustable so that a pre-load could be established in the beam to eliminate any slack effects due to the various hooks. The pre-load used was nominally 70 milligrams.

G. Substrate Preparation

There were two types of nickel used for the substrates. All the stress measurements made directly on the nickel were made with 1/4 hard nickel. All the measurements made on the NiO coated substrates were made with dead soft nickel. The main difference between these two types was the nature of the surface. The 1/4 hard material had a stipple surface while the dead soft nickel was polish rolled.

The substrates were cut from rolls of the nickel in a sharp shear. The shear left the edges very clean and without curl. The substrate was held for polishing by glueing in a .004 inch deep

slot milled in a faced aluminum block using a varnish stick dissolved in ethanol as the adhesive. A polishing wheel was constructed that had a rate of revolution of about 2 times per second. Gamal billiard cloth was glued to flat interchangeable aluminum plates that were charged with different sized gamal alumina.

The first step of the polish used particles of 10μ . After the initial surface artifacts were removed, $.3\mu$ dust was used. When all of the scratches from the 10μ dust were removed, the process was stopped. The final polish using $.1\mu$ dust was performed by hand using about 100 figure eight passes over the cloth until no artifacts were observed by eye. Under the optical microscope, only occasional scratches were observed at a power of 350. Both sides were polished so as to insure no surface anisotropy.

Sections were subsequently cleaned and examined in a scanning electron microscope located on the Case campus. Using magnification of 10000, no array or network of scratches was visible. In fact, the surface was free enough of artifact that focusing could be accomplished at the edges, since no measureable variation in the electron signal was detected on the surface. Thus, while it cannot be concluded that the substrates are atomically smooth, there was no apparent gross structure as from scratches or hill and valley undulation apparent.

IV. PROCEDURE AND DATA RESULTS

A. Measuring, Cleaning and Mounting

After the polishing process of the substrates was completed, the substrates were profiled for dimensions. The width was determined at both ends with a micrometer accurate to 0.0001 inches. The thickness was determined by a dial indicator gauge modified by using two 3/16 inch diameter stainless steel balls for the anvils. Thus, spot checks on the sample thickness were taken as opposed to a gross average as with flat anvils. A total of fifteen thickness determinations were taken for each substrate with an accuracy to 0.00005 inch or about 1% of the total thickness. Most variations in thickness occurred near the ends and edges. Since a reasonable portion of the substrate went into the clamp, the thickness uniformity at the clamp was good. The free end was chosen to have the least taper. The allowed fluctuation at a distance of one width from the free end was 10%. Since a thickness profile is taken, in principle, the moment of inertia of the plates could be determined as a function of position. If the profiles of thickness were used in determining the bending equations, each substrate could be calibrated individually. However, the average

thickness was good to a few percent and is considered acceptable, in light of the tedious preparation. The dead soft substrate required little mechanical polishing and, as a result; the thickness uniformity was better than 1/2% in every case.

A number of cleaning techniques were tried and evaluated. Early attempts at cleaning included wiping the substrate with a soft cloth saturated with acetone or ethanol. Then, before the remaining solvent could dry, the substrate would be wiped dry. This, however, could still leave a residue in that there is no guarantee that any cloth used is not a source of new contamination. The solvent being wiped could dissolve impurities in the cloth, and they become more evenly distributed over the surface. There is no soft cloth either. They all leave scratches in the finish of the metal substrates.

A vapor degreasing technique was attempted. Both ethanol and trichloroethylene were used. Here, the solvent is boiled and condenses out on the substrate supported over the liquid by a magnet. The hot vapor would loosen and dissolve any grease present. The theory is that since the liquid is being constantly distilled in the boiling process, only solvent reaches the substrate. However, examination of the substrate after this process always revealed a residue of some type on the surface. The initial shape of the stress curve was greatly altered when this technique was used rather than the following one.

The substrate was first "abraded" clean with .1 μ gamal alumina, distilled water and lens tissue. The substrate was then flushed with distilled water and immediately put into a vial of absolute ethanol. This vial was subsequently placed in a Bransonic Ultrasonic cleaner capable of 100 watts of cleaning power. The cleaning cycle was limited to 30 seconds, as it was found that severe surface dislocations and pit damage were induced with cleaning times above 15 minutes. The vial was then emptied, refilled, and the 30 seconds cleaning was repeated. This process was cycled three times for each substrate.

Next, a glass vial was cleaned using Alconox. Four to five rinses with deionized water were followed by three to four rinses with distilled water. The vial was then subsequently filled with distilled water.

The substrate was drawn from the ethanol with a magnet and placed in the water. Thus any impurity held in suspension by the alcohol presumably went into solution with the alcohol as it was placed in the water. Since distilled water does not wet a clean metal surface, it was possible to draw the substrate from the water at a constant rate absolutely dry. If any oil coatings or spot impurities remained on the substrate, that section remained covered with a thin layer of water. No wiping of the substrate was necessary to remove solvents.

The cleanliness could still be questioned on the fact that

if a layer of contamination remained on the surface of the water, this could conceivably be re-distributed on the surface as the substrate was pulled out. However, the black breath test revealed no structure except where the substrate may have made a slight retrograde due to vibration as it was drawn out. If the angle of receding water was changed rapidly, a layer of droplets is envisioned to break off. As these dry, a line of residue would remain and provide nucleation points for the water vapor in breath and hence show up as lines. But aside from this feature, no gross wiping marks were evident as with the use of any cloth, regardless of the care taken.

This cleaning procedure, however, does nothing to reduce the gasses such as CO and CO₂ absorbed on nickel surfaces. However it is expected that these would remain regardless of the cleaning procedure used external to the vacuum system.

The substrate, now handled only by gloves, was mounted in a stainless steel clamp and bonded with Autostick cement. Rottmayer²⁶ pointed out that any slipping from the clamp would relax the rigid boundary conditions and hence produce errors in bending. The substrate was cemented to a clamp that was screwed together.

Next a hook of 0.003 inches tungsten wire was bonded to the top side of the substrate at the free end. Great care was taken to insure that the hook was normal to the top surface of the clamp. This was done because any initial curvature would mean that the

force applied was not normal to the substrate. It is deduced that if the hook were placed in line with the vertical axis, rather than normal to the substrate this error is minimized. This can be seen as the force is only reduced by the cosine of the angle (as seen in Fig. 4) and is second order. But if the hook is perpendicular to the substrate the cosine effect remains, but also a moment is applied to the substrate with the length of the hook as a lever arm. This could cause serious error in measurement as this force varies as the sine of the angle and hence is linearly proportional to the angle, for small angles.

The substrate clamp assembly was placed on a traveling microscope and the distance from the clamp to the hook and the end of the beam was recorded. After a check list was completed, the clamp assembly was mounted on its platform next to the dummy. Both were secured by 6-32 stainless steel screws.

The system was then pumped down and a thermal hood was placed over the belljar and heating tapes. A timer was set for a 12 hour bake out. During the bake out, the tapes could achieve better than 100 C. The air nominally around them was 60 C. Although higher temperatures would be preferred, care was taken not to heat the microbalance too much. The pressure four hours after bake out was usually 5×10^{-7} Torr, and LN_2 was introduced in the cold trap.

After the trap was filled the temperature controller was

HOOKS ON BENT SUBSTRATES

Figure 4. Angle of Hook Relative to Bent Substrate

turned on and all substrates were heated to 250 C for 1 - 2 hours. Then the substrate was brought to the final evaporation temperature. The vacuum at this point was usually $1-2 \times 10^{-7}$ Torr.

All the recording equipment had been sufficiently warmed up at this point to ensure faithful readings. The beam gun was next turned on and allowed to idle during the measurement of the system response. The water temperature for the Sloan UHV head was adjusted. Stability of the frequency was achieved within a few seconds.

The system response was determined by dialing in forces from the electronics and the microbalance force read from a digital voltmeter. After this was accomplished, the experiment was begun. The Sloan Omni brought the boule to melting temperature in about 1 minute. It was then held at this temperature for another minute. The pressure at this point had risen to the low 10^{-6} Torr region.

As the evaporation began, the pressure usually rose to about 3×10^{-5} Torr. However, it rapidly fell to about 1×10^{-5} Torr and remained constant during the measurement.

After about 500 Å thickness was evaporated and the rate well established, the opening shutter fuse was blown. One to two minutes later the closing shutter fuse was blown, and two seconds following the closing the beam gun was shut off. The pressure returned to 2×10^{-7} Torr almost immediately. The position of the substrate was monitored at least until temperature stability had been re-attained. No relaxation effects comparable to this time constant

for temperature stabilization were observed.

The small change in position of the beam after the closing pulse seen in the raw data trace of Fig. 5 is nothing more than a time constant effect from the microbalance.

B. NiO Film Preparation

The NiO films were electrodeposited on the cleaned substrate according to the procedure given by Hersch.²⁷ The oxide films were grown to a thickness of a few thousand angstroms. Both sides of the substrate were coated. If only one side were coated, a possible bi-metallic strip effect could occur during a run due to a temperature rise. If both sides are identical, only a uniform tension or compression would occur. The measured temperature performance of the NiO coated substrate was nominally the same as the nickel. Since the emissivity of NiO and polished Ni differs by a factor of ten, some difference was expected. However, since the coating was less than one optical wavelength thick, it is not difficult to see that long wavelengths may not be heavily attenuated and the substrate would behave thermally as if the film was not present.

The procedure for mounting and running was identical to the uncoated substrates except that the substrates were not heated prior to the run, except to bring them to the temperature of the run.

Figure 5. Raw Data Trace Indicating No Bending After Shutter Closing

C. Stress Data Results

Evaporations were made on the nickel substrates dried by pulling from the water at 32 C, 43 C, 75 C, 81 C, 107 C, 122 C, 125 C, 150 C, 183 C, 225 C, 287 C, and 410 C. The force/unit width curves are plotted in Figs. 6 - 10. The character of the bending is the same for all these measurements except the 32 C run in which an anomalous shift occurred after the shutter opened and the early stages of measurement are subject to question.

Note the initial compression apparent in all but the 32C run. The intrinsic stress in this region is $\sim 0.5 \times 10^{10}$ dynes/cm². As a thickness of $\sim 75 \text{ \AA}$ is approached, the intrinsic stress passes through zero and becomes tensile. This tensile stress is high, $\sim 10^{10}$ dynes/cm². It does not remain constant but decreases as 500-700 $\text{\AA}$ of film has been deposited. At this point, the stress lowers in value, becomes constant to the highest thickness studied. The linear region of the force/unit width curve is used to determine the intrinsic stress of the film. These values are plotted in Fig. 15 as circles. The pertinent data for the run and the numerical values of the intrinsic stress are given in Table 1.

Conventionally cleaned substrates were used in runs made at 31 C, 34 C, 98 C, and 410 C. The force/unit width curves are plotted in Fig. 11. The important difference occurs in the initial stress of these runs. The initial compression present before

TABLE I

Temperature	Temperature Rise	Measured Stress $\times 10^{-9}$ dynes/cm ²	Measured Grain Diameter in Angstroms	Calculated Stress $\times 10^{-9}$ dynes/cm ²
Ni on Ni				
32 C	+23 C	.77	470	.59
43 C	+21 C	.77	---	---
75 C	+14 C	.55	555	.48
81 C	+14 C	.77	---	---
107 C	+11 C	.46	585	.44
122 C	+ 3 C	.59	505	.53
125 C	---	.67	---	---
150 C	+ 4 C	.48	575	.43
183 C	---	.53	530	.45
225 C	---	.26	1058	.23
287 C	---	.06	---	---
410 C	---	0	---	---
Ni on Wiped Ni				
31 C	+25 C	.96	430	.6
34 C	+22 C	.95	---	---
98 C	+10 C	.92	---	---

Figure 6. Anomalous force/unit Width Curve for Ni on Ni at 32 C

Figure 7. Force/unit Width Curve for Ni on Ni at 43 C and 75 C

Figure 8. Force/unit Width Curve for Ni on Ni at 81 C, 107 C, and 122 C

Figure 9. Force/width Curve for Ni on Ni at 125 C, 150 C, and 183 C

Figure 10. Force/unit Width Curve for Ni on Ni at 225 C, 287 C, and 410 C

Figure 11. Force/unit Width Curves for Ni on Wiped Ni at 31 C, 34 C, and 98 C

is now absent. A tensile stress is built up at the beginning of the run. However, the intrinsic stress increases in value to about 500 $\frac{\text{O}}{\text{A}}$ where it becomes constant to the highest thickness studied. The intrinsic stress from these runs is represented as dark circles in Fig. 15. The 410 C data for the nickel cleaned by both techniques is the same.

The nickel was evaporated on the NiO coated substrate held at 35 C, 80 C, 140 C, 167 C, and 225 C. The force/unit width curves are plotted in Figs. 12-13. Note that these curves, as the curves in Fig. 11, exhibit no initial compression. A tensile stress is developed at the beginning of the deposition and increases in value through $\sim 500 \frac{\text{O}}{\text{A}}$ of thickness. Again, above this thickness, the intrinsic stress approaches a constant to the highest thickness studied. Table 2 contains the pertinent data from these runs. The intrinsic stress is plotted as triangles in Fig. 15.

Thermal expansion effects were not a problem during the experiment as predicted earlier. They would be manifest in a changed deflection after the evaporation was terminated. No such continued bending was observed.

The nature of the substrate seems only to affect the stress and growth of the films in early stages. The force/unit width curves all show the linear behavior above $1000 \frac{\text{O}}{\text{A}}$. The intrinsic stress of the different substrate surfaces is not apparent in Fig.

TABLE II

Temperature	Temperature Rise	Measured Stress $\times 10^{-9}$ dynes/ cm^2	Measured Grain Diameter in Angstroms	Calculated Stress $\times 10^{-9}$ dynes/ cm^2
35 C	+25 C	.93	480	.57
80 C	+10 C	.45	575	.44
140 C	+ 4 C	.32	600	.40
167 C	+ 2 C	.46	570	.42
225 C	--	.22	730	.32

Figure 12. Force/unit Width Curves for Ni on NiO at 35 C, 80 C, and 140 C

Figure 13. Force/unit Width Curves for Ni on NiO at 167 C, and 225 C

Figure 14. Expanded Force/unit Width Curves Showing the Basic Differences of the Initial Mechanical Behavior of the three Different Substrate Surfaces

Figure 15. Intrinsic Stress Plotted as a Function of Temperature with the Experimental Curve of Klokholm Superposed

15 . The scatter of the points for all the runs appears to indicate that the initial growth of the film is not too important at higher thicknesses.

Large compression for the films grown on NiO was not observed. It was thought that a diffusion process might occur from this surface as was suspected to occur with nickel evaporated on silicon.

The high temperature data taken at 410 C may be in question. Bulk nickel begins a primary recrystallization at this temperature. As a result the substrate tended to deflect plastically during the run, and the stress curve had to be corrected. Because the magnitude of the deflection from the film above 500 Å and the plastic sagging were on the same order of magnitude, it cannot be stated that the film was in compression. This was the only run where the elasticity of the substrate was in question and the substrate position was not stable before and after the evaporation.

The largest single errors occur in the film thickness determination and the substrate thickness measurements. The RMS resultant error from all considerations in the stress measurement is 7%.

V. MICROSCOPY

All the microscopy was performed on the Hitachi 650 kV transmission electron microscope located on the Case Western Reserve University campus. The higher voltage is necessary to penetrate 2000 Å thick foils. A good rule for maximum thickness that can be penetrated is 10 times the extinction distance at that voltage. Thus, for a typical extinction distance of 230 Å at 100 kV, examination is not practical. However, as the voltage applied increases, the extinction distance also increases, thus allowing the examination of thicker foils.

There are certain stability problems with this new machine. The problem has its origin in the local power company. The company can not maintain the incoming line voltage to tolerances necessary for 650 kV stabilization. Thus, all the microscopy performed in this paper was done at 500 kV. At these lower voltages, stability was no problem. If the high voltage is not stable, then the wavelength of the electrons is not well defined and the beam is no longer monochromatic. This has the effect of washing out direct images and broadening diffraction patterns.

A. Sample Preparation

During the sample preparation, for the nickel on nickel case, a 1 mm drop of 1% Alconox solution was placed at the very free end. Since the area contaminated was past the hook, it would not affect the bending should the stress be different. This was necessary so that microscopy samples could be obtained. When stripping was attempted, samples could only be obtained where the end had been soiled.

The stripping attempts consisted of variation of all the following techniques: scratching, bending, glueing, and stripping with tape. The first three schemes yielded nothing.

The usual Scotch Brand cello tape along with the newer magic tape were both tried. The adhesive seemed insufficient to peel the film. As a last resort, the Scotch filament tape was used. Only after repeated stripping attempts were samples removed. Also, no samples were obtainable from specimens elevated to temperatures such that the stress was zero.

The sections of tape containing any film specimens were cut from the tape and immersed in a solution of trichloroethylene. The films were left in the solution for at least one hour before any attempt to retrieve them was made. This was to insure that all adhesive had thoroughly been dissolved. A pair of needle nose tweezers with a lock, to hold a microscope grid, was used to scoop up a piece of film. It was carefully withdrawn and

touched to an absorbent towel. Many of the films had a tendency to curl into a tight scroll in the solution. Clearly, if the scroll remained as such on the grid, not much useful area could be examined. However, upon blotting the scrolls would unwind and lie perfectly flat.

The grid was then placed in a gelatin capsule, which was placed in a small marked vial.

The same stripping procedure was applied to the NiO coated substrates. In this case the entire Ni film and NiO coating was easily stripped as contrasted with the previous statements.

B. Procedure

The films were examined for artifacts. If none could be found, two representative selected areas of bright field images were taken at 20000 magnification. The selected area was superimposed on an exposure of the entire area. Thus the selected area may be seen as part of the surrounding area. Three selected area diffraction patterns were taken. Therefore, a minimum of five plates were taken yielding in excess of 60 plates.

Extreme care was taken in the development process to insure good contrast, yet minimum grain such that good photographic enlargements could be made. The temperature of the development solution, its age and use were recorded. Also Kodak anti-fog was added to reduce fogging effects.

C. Analysis

It is evident that these films are in a high degree of disorder. The only interesting film is the large grained one shown in Fig. 19. Here fringes can be seen in the larger grain. These are probably characteristic of stacking faults. The rest of the films exhibit a structure of random orientations and relatively uniform sized grains.

Attempts at measuring the grain size from the direct image often fail. There are areas of great contrast which appear as separate grains. This more than likely is true. However, the spaces between high contrast may have little contrast. Thus, if a measurement of the number of grains per unit length is attempted, the efforts are thwarted by this lack of contrast for small grained films $\sim 100 \text{ \AA}$. Hence any measurements of this type are expected to be inaccurate.

A different approach was taken by Palatnick.²⁸ He looked at the diffraction patterns from a large area. Hence rings appear due to the fact that all orientations are present. This is in effect taking the single crystal pattern and forming rings by rotating it through 2π . The width of these rings can be shown to be dependent upon the size of the crystallites. However, the analysis shows that all the shape effects occur in the wings of the intensity profile of the rings. A small shift in the background due to improper processing or inelastic scattering can

change these results drastically. While corrections for this scheme have been tried the technique is still not palatable.

Another technique has been presented recently by Boiko.²⁹ Diffraction patterns are taken from a small selected area of the film. The area of film is small enough such that the diffraction rings become spotty. The rings are scanned and the average number of spots is recorded. By plotting the number of spots as a function of film thickness, information about the relative number of crystallites in a diffracting volume may be obtained. In this manner, a polyblock structure may be distinguished from a columnar growth. The number of spots is proportional to the number of crystallites in the exposed volume. However, much care must be taken to insure that the main beam is always of the same intensity and that the exposure times for the photographic plates is standardized. Also, because the intensity of the diffracted spots depends on the crystal thickness, some changes will occur in the patterns as the films increase in thickness although they are columnar. Rottmayer and Hoffman proposed that if a small enough selected area is taken for the diffraction, the rings become spotty, rather than continuous. They attempted a calculation correlating the average grain size with the number of spots in a ring using a simple kinematic calculation. While the order of magnitude was correct, it was still a long way from an accurate prediction.

Certain annoying difficulties appear. Since the intensity of diffraction from a crystallite is dependent upon its size and deviation from the exact Bragg condition, the exposure time and development times change the number of apparent spots.

A new calculation has been made and appears in Appendix III.

The average grain size as determined from Appendix III is given as

$$d = \left[\frac{16mR^2S_{\max}}{3\sqrt{3}M^2N_s g} \right]^{1/2} \quad (20)$$

where m is the multiplicity

R radius of selected area on plates in cm,

M is the magnification,

n_s is the number of spots,

$S_{\max}$ is the maximum deviation from Bragg,

g is the reciprocal lattice vector.

The only undetermined parameters are the number of spots and $S_{\max}$ for each ring of any plate. If the total number of spots is known, and the number of spots as a function of intensity is known, the problem is solved. The intensity of reflection falls off as $1/s^2$. But the number of spots increase as s increases. Thus, there should be many more spots of lower intensity than high

intensity which is observed. The curve $1/s^2$ is modulated by a $\sin^2(\delta_{eff})$. Thus, if the total number of spots above an intensity is plotted as a function of intensity, the resulting curve will not be smoothly varying, but will have definite changes in slope as new peaks from the $\sin^2$ function are encountered. By knowing the number of changes in the shape of this curve, the smallest peak can be determined and hence the location of s_{max} is fixed.

In the calculation of equation 20, columnar growth was assumed. Thus it is necessary to compare the measured size to the direct image. In this manner, the validity of columnar growth may be established. The calculation may be changed to allow for a polyblock type structure. If the diffracting volume is considered to be two crystallites thick, then the number of grains in that volume becomes doubled for the same grain size. However, suppose that the total number of grains in the diffracting volume remains the same as for the columnar case, the two cases can be distinguished in that the thickness of each crystallite will be diminished. Since the S_{max} is inversely proportional to the film thickness, it will become larger. Hence, for the same number of spots, the second case would predict a larger grain diameter. For the case of 2000 Å thick films, this size is different by a factor of 1.7 for the ratio of the columnar size to the polyblock size. When direct comparison is made with the bright field micrographs,

the cases can be distinguished.

D. Apparatus

In order to determine the intensity of the spots, and their number a modified Hilger microphotometer was employed. An extremely stable light supply was built to insure light reference stability. A rotating disk was attached to the bed of the photometer. A large hole in the center permitted the plates to be placed on the rotating plate, but allowed the reference light to pass through. A clock motor was used in a rim drive configuration to turn the plate. Typical revolution times were ~ 15 minutes/ring.

The plates were centered on the rotating disk so that the ring of spots always passed over a well defined slit area. The rate of revolution was chosen to be fast enough so that electron noise on the plates would be high enough in frequency so as to be filtered, yet gross density changes due to spots would be accurately determined.

Since the spots didn't cover the slit completely on rotation a background error results. However, from the following argument it can be seen to produce only a constant shift in the result. Assume that I_0 is the background intensity and I_1 is the signal. The equation relating the density of the film and hence the intensity is

$$t \propto 10^{-K(I_0 + I_1)} \quad (21)$$

where t is the percent transmission. Taking the $\log_{10}$ of both sides, it is readily seen that the error of the constant intensity results only in a constant shift of the reduced data.

E. Data and Results

Twenty-seven diffraction patterns were analyzed for those film that could be stripped. The temperatures represented for nickel on nickel are 31 C, 32 C, 75 C, 107 C, 127 C, 150 C, 183 C, and 225 C. The bright field micrographs of these specimens are shown in figures 16 to 19. The temperatures for the nickel evaporated on NiO are 35 C, 80 C, 140 C, 167 C, and 225 C. The bright field images of these films appear in figures 20 to 22.

If the polyblock structure were evident, the grains would not appear as uniform as seen. Boiko²⁹ points out that the observed grain sizes would be extremely varied in that masking of lower and upper grains occurs due to mis-registry. This causes parts of diffracting grains to cover other grains of different orientation. It is thus possible to have contrast changes due to this masking effect and not due to a change in grains. The uniformity of the grains is good.

Figure 16. Bright Field Micrographs of Ni deposited on Ni
at 31 C and 75 C

31 C

75 C

Figure 17. Bright Field Micrographs of Ni Deposited on Ni
at 32 C and 107 C

32 C

107 C

Figure 18. Bright Field Micrographs of Ni Deposited on Ni
at 122 C and 150 C

122 C

150 C

Figure 19. Bright Field Micrographs of Ni Deposited on Ni
at 183 C and 225 C

183 C

225 C

Figure 20. Bright Field Micrographs of Ni Deposited on NiO
at 35 C and 80 C

35 C

80 C

Figure 21. Bright Field Micrographs of Ni Deposited on NiO
at 140 C and 167 C

140 C

167 C

Figure 22. Bright Field Micrograph of Ni Deposited on NiO
at 225 C

225 C

Figure 23. Average Grain Diameter Deduced from Diffraction Patterns of Ni Deposited on Ni

Figure 24. Average Grain Diameter Deduced from Diffraction Patterns of Ni Deposited on NiO

There is some apparent fluxuation in size; however, this is not surprising. The grain size can fluxuate around a mean in a gaussian nature. Also, because of the random mixture of the orientation, adjacent grains may be almost identically aligned. This gives the appearance of occasional larger grains.

The grain diameter was determined using the diffraction technique with the assumption of columnar growth. These diameters are plotted in figure 23 for the nickel on nickel and in figure 24 for the nickel on NiO. If these sizes are compared with the micrographs, the agreement is good. Thus, the assumption of columnar growth is consistent with direct observation.

VI. THEORETICAL STRESS CALCULATION

Several stress models were presented in the Introduction. In order to produce a stress in the film, all models use a constrained volume change during the growth of the film. The disagreement arises in determining both what causes this volume change and where the volume change is allowed to occur. The Wilcock and Campbell² model envisions the volume change to occur as voids and dislocations are eliminated. The shrinkage occurs only in the early growth stages and does not predict a linear stress thickness product. The Klokholm - Berry⁴ model theorizes a buried, disordered layer to crystallize. Because the layer is buried in the film, the volume shrinkage is constrained during this process. This model will predict a linear stress thickness product but will not allow a quantitative calculation. The Chaudhari⁵ model proposes a constant nucleation and recrystallization process. The voids in between the crystals are eliminated by lateral recrystallization only. It will predict a linear stress thickness product. The numerical results predict a stress value above experimental values by a factor of ten. It is postulated that this process does not produce a stress that exceeds the flow stress limit, thus, the temperature dependence of the flow stress value for the film would predict the observed stress. As long as this plastic process

was continuous during the film growth, a linear stress thickness product is still predicted.

The grain boundary model can be broken into three regions. The first region covers the stress developed in the early stages of film growth. The second region covers the stress from the time the film becomes continuous through the completion of any lateral recrystallization process. The third region is the steady state production of the stress as the film thickness increases and the grains grow only in the vertical direction.

Atoms arrive at the substrate, condense, migrate around and form small clusters. These clusters must exceed a certain minimum radius in order to achieve stability against re-evaporation. As these clusters grow somewhat larger, they may still remain mobile on the surface. The motion is governed basically by a surface diffusion process. The surface layer of atoms compared to interior atoms differ in relative spacing between their neighbors. They are envisioned to be closer than they would be in bulk.³⁰ However, as they become interior atoms, due to more condensation, they move closer to the bulk position. If these atoms are not allowed to expand, a compressive stress is produced in the clump. If the clump is small, this constraint will produce a stress in excess of the ideal shear of the material. Thus, the atoms slip unconstrained with respect to the substrate until the stress produced by this process falls below the ideal shear. At

0
this point, ~ 10 Å diameter, the clumps are considered to adhere to the substrate. As more material is deposited, strains are produced as the clumps are fixed relative to the substrate. These transmitted strains cause the substrate to bend from which the stress is calculated. This process continues until the clumps become large enough that they almost fill the substrate area. At this point the second stage begins.

As the clumps become large enough that the space between them is reduced to about a lattice constant the interatomic forces become apparent. The crystals attract each other across this gap and become strained in the tensile direction because they adhere to the substrate. The initial stress produced in these clumps is very high because the amount they must be stretched relative to their diameter is so large. This high state of stress drives a lateral recrystallization process in which the stress is relieved. The process does finally stop and the grain diameter becomes stable. The actual details of this process are not well understood. A thermodynamic minima of the Gibbs free energy does not produce the proper results. Possibly a mixture of a dynamic process and a Gibbs free energy are needed to explain this final grain size and its stability. The grain size is temperature dependent. However, this process does lower the intrinsic stress as it occurs. As the grain diameter is stabilized the third region of growth is entered.

Figure 25. Calculated and Measured Values of the Intrinsic Stress for Ni Deposited on Ni

Figure 26. Calculated and Measured Values of the Intrinsic Stress for Ni Deposited on NiO

Now that grains have stabilized, the atoms fill up lattice positions on the grains they condense. As the grain top becomes filled with atoms and the boundary is approached, the atoms from an adjoining grain attract the atom close to the boundary. Atoms may also move into positions causing local compression. However, due to the asymmetry of the potential, an average contraction produces a tensile stress.

Appendix IV is a modified from a calculation of Doljack and Hoffman³¹ for the average contraction occurring at a grain boundary in the growing films. This expression is given by eq. 22.

$$\langle \Delta \rangle = \frac{ra - r^2/2}{2a - r} \quad (22)$$

where a is the nearest neighbor distance and r is the closest approach two atoms may take. Using 2.48 Å for a and 1.9 Å for r , a $\langle \Delta \rangle$ of .9 is found. This value is relatively insensitive to temperature since lattice constants vary ~ 1 part in $10^5/^{\circ}\text{C}$.

Using this average contraction and the grain size, the average stress is given by eq. 23.

$$\sigma = \frac{E}{1-\nu} \frac{\langle \Delta \rangle}{d} \quad (23)$$

Using the values of the grain size, computed earlier, the calculated stress may be seen in Figs. 25,26. The measured values

are also plotted. The agreement for Ni on Ni and Ni on NiO is very good. It is seen that the stress scales as the grain size.

The Young's modulus used was the unsaturated value of E measured by Quimby and Siegel.³² Nickel has the elinvar property, such that the state of magnetization of the nickel affects the Young's modulus. The effect is temperature dependent and vanishes at the Curie point. E decreases in value about 18% from room temperature to 150 C. From 150 C, the value of E rises about 16% to the Curie point and then follows a temperature curve explained by normal thermal effects on lattices.

The value of Poisson's ratio used for all calculations was .31.³³

A calculation for the effect of impurities can also be made. After the grain boundary is formed, the average spacing of atoms is $\bar{r}$ of the nearest neighbor distance. A new potential for the impurity versus host material is constructed. If impurity atoms are placed in the boundary, they are all close to the lower limit of separations between the host and themselves. This is because there is basically a small distribution of positions for the host atom separation. The expansion due to the impurity then becomes a difference between the equilibrium distance of the new potential and the spacing as the atoms are put in.

$$\langle \Delta_i \rangle = r' - a' \quad (24)$$

If the concentration of impurity atoms is known, then an estimate for the value of $\langle \Delta_i \rangle$ can be made. The net contraction is given in equation 25.

$$\langle \Delta_n \rangle = \langle \Delta \rangle + \langle \Delta_i \rangle \quad (25)$$

The net intrinsic stress is then calculated using equation 23 only replacing the $\langle \Delta \rangle$ with $\langle \Delta_n \rangle$. A negative value for $\langle \Delta_n \rangle$ can be easily achieved with only a monolayer of atoms in the boundary. This may explain the compressive regions of stress observed by Doljack.³⁴

In summary, a model has been presented which will allow a computation of intrinsic stress and a stress due to impurity concentration. It is based upon the assumptions that the material remains elastic. The average grain diameter, along with the boundary contraction then determine the observed stress. The agreement of the intrinsic stress measured and calculated stress confirms the applicability of the model to nickel films.

APPENDIX I

Measurement Technique

The Cahn microbalance is an electromechanical device that is used in measuring small quantities of mass. Two lever arms are attached to a taut band meter with hooks placed at each end. The choice of the taut band meter over the usual pivot meter is to eliminate frictional effects and hence any hysteresis in weighing. An aluminum foil is attached to act as a flag on one beam of the microbalance. On one side of this flag is a light source, and on the other is a photodiode. The light source is zener diode stabilized for constant light output. The photodiode is placed in a light tight box with a slit to shield it from ambient room light. As the flag moves between the light and the photodiode the amount of light allowed to pass through the slit to the photodiode is metered by the flag's position relative to the slit. Hence, the angle of the beam relative to a horizontal is proportional to the signal from the photodiode as seen in Fig. 27. This signal is subsequently differentially amplified with respect to a reference voltage and the result fed to the meter movement. As the beam is displaced from the equilibrium by a force, the photodiode generates a larger or smaller signal which results in an error signal which is applied to the meter movement. A torque is produced by the meter

Figure 27. Basic Design of a Microbalance

movement to finally cancel the applied torque and the system is in a new force equilibrium. The signal applied to the meter movement to achieve this balance is directly proportional to the force applied.

The meter windings have some resistance along with other external resistors added in the circuit. Assume that the total resistance in the meter circuit including temperature compensation resistance is a constant R_{es} . If an error voltage V is applied to the circuit, current flows through the circuit. The windings inside the movement, then produce a torque $T = rN\bar{I}XB$. The windings are placed in the movement such that for all small deflections, $IXB = IB\sin\theta = IB$, or that $\theta = 90^\circ$. The r represents the distance of the wires in the winding relative to the pivot point. This also remains the same during any movement. The torque applied at one end of the beam then is equal to $T = \bar{R}x\bar{F}$. But here again, the beam remains nominally perpendicular to the force, in this case gravity, and hence $|\bar{R}x\bar{F}| = RF\sin\theta = RF$.

Thus, in equilibrium, $T_{\text{meter}} = T_{\text{applied}}$ and

$$RF = rNIB = \frac{rNB}{R_{es}} V \quad (26)$$

Any applied force is then directly proportional to the voltage across the microbalance and can be calibrated to give a true reading of mass in volts (e.g., $1\text{MV} \equiv 1\text{ Mg}$). But this analysis must be carried yet one step further.

It has been stated that as the voltage from the photodiode is proportional to the angle of deflection, θ . The change in position of one end of the microbalance beam in the vertical direction is $\Delta y + R \sin \theta$. For small changes in $\theta = 10^\circ$, $y = R\theta$ to an excellent approximation. But in practice, the actual deflection is 50 times less than 10° , and hence, contributes no significant error.

The voltage from the photodiode is differentially amplified and fed to the meter movement circuitry. Thus, $(V_p - V_r)A = V$, where V_p , V_r , and A are the photodiode voltage, the reference voltage, and the gain of the amplifier respectively. But $(\theta - \theta_r) = V_p$, where θ is the angle due to some applied force, and θ_r is the angle of reference with no force applied. Then, $\theta_r = V_r$ and $\theta A = V$ which results in the following equation:

$$RF = \frac{rNB}{Res} A\theta = \frac{rNB}{Res} \frac{Ay}{R} \quad (27)$$

$$F = \frac{rNB}{Res} \frac{A}{R^2} y \quad (28)$$

The most important aspect of this relation is that all the elements multiplied times y are constant. This means that the Cahn can be represented as an ideal spring,

$$F = Ky, \text{ with } K = \frac{rNB}{Res} \frac{A}{R^2} \quad (29)$$

In a previous experiment it was found necessary to determine the value of K in dynes/cm, but this experiment has found it unnecessary to know the absolute value of this quantity, or for that matter, the absolute value of the elastic constant of the substrate. Moreover, the ratio of the two is what is required to find the value of the stress. This ratio is rather easy to determine and can be done so prior to each measurement. The justification for these two crucial statements follows.

Any of the bending of the cantilever, i.e., the end deflection, due to a normal pressure exerted at the end is linearly proportional to the force applied. Also, if a uniform traction is applied to one surface of the cantilever beam, the bending, hence the end deflection, is also linearly proportional to the applied surface traction. Although the bent shape of the beam is different for the two types of bending, the deflections are still linear in applied forces.

A two spring model for the stress measurement can be formulated. Observe the two springs in Fig. 28. They are both at equilibrium length (neglecting gravity and any other forces for the moment), ends just touching but not coupled, and opposite ends fixed to rigid walls. Let spring 1 represent the microbalance and spring 2 represent the substrate, or cantilever beam. Allow some "internal" force to act upon spring 2 compressing it to a new distance $y_2 - \Delta$, as in the figure. Next pull spring 1 down

Figure 28. Two Spring Model for Measuring the Stress

to spring 2, couple the two springs and allow them to relax back to some new equilibrium position $y_2 - \Delta + \delta$, as shown.

Since the compression in spring 2 was done by an "internal" force, the new true equilibrium value for the length is properly set to $y'_2 = y_2 - \Delta$.

Since the two springs are now in equilibrium, $F_1 = F_2$.

But, $F_1 = K_1(y_1 + \Delta - \delta - y_1) = K_1(\Delta - \delta)$ and

$F_2 = K_2(y'_2 + \delta - y'_2) = K_2\delta$.

Solving for the deflection of each spring and adding the two

$$\frac{F_1}{K_1} = \Delta - \delta ; \quad \frac{F_2}{K_2} = \delta \quad (30)$$

$\frac{F_1}{K_1} + \frac{F_2}{K_2} = \Delta - \delta + \delta = \Delta$. Making use of the force equilibrium, the expression becomes

$$F_1 \left[\frac{1}{K_1} + \frac{1}{K_2} \right] = \Delta \quad (31)$$

F_1 represents the force in spring 1 and hence the weight read out on the microbalance. The Δ corresponds to the initial deflection of spring 2 by some "internal" force. That force is now identified as that due to a stress in a film acting on the cantilever beam. An expression relating this bending to the applied surface traction can be derived and cast into a form

$$T = K'_2 \Delta \quad (32)$$

K'_2 is related to K_2 by some dimensional constants and the fundamental elastic constants of the material used for the substrate. Thus a ratio K'_2/K_2 is determined.

Replacing Δ in the last equation by T/K'_2 , the following result is obtained,

$$F_1 \left[\frac{K'_2}{K_1} + \frac{K'_2}{K_2} \right] = T \quad (33)$$

As was stated above, $K'_2 = \beta K_2$, where β depends only upon the physical dimensions of the cantilever. Thus the final result is obtained

$$T = F_1 \left[\frac{\beta K_2}{K_1} + \beta \right] = F_1 \beta \left[\frac{K_2}{K_1} + 1 \right] \quad (34)$$

The principal quantities are the applied force/unit width, T ; the force in the microbalance, F_1 ; the shape factors from the two types of bending, β ; and the ratio of the spring constants of the cantilever to the microbalance, K_2/K_1 .

If K_2 and K_1 are known by calibrating the microbalance and using the accepted values of the elastic constants, then the

resulting stress value may be obtained.

However, during the course of this experiment, it was found that the constants in the microbalance were not necessarily independent of temperature and aging. The elastic constant of nickel was also found to vary by 20% over the temperature range used to investigate the stress. This variation is due to the large magnetostriction term present in nickel.³² Hence a method was sought to vindicate both the value of the elastic modulus of the nickel and the precalibrated value of k , for the microbalance. This test would be performed just preceding any measurement taken.

Referring again to the two spring model, consider the situation where both springs are connected together and opposite ends attached to rigid walls. The spacing of the walls is such that the two springs are at their natural unstrained lengths, shown in Fig. 29. A known force is applied at the junction of the two springs. The two springs must deflect the same amount since they are rigidly coupled. Also, because the system comes to equilibrium, the sum of the forces must vanish.

Then, the following expressions may be written.

$$F_{app} = F_1 + F_2 \quad F_1 = K_1 \delta \quad F_2 = K_2 \delta \quad (35)$$

$$\text{or } \frac{F_1}{K_1} = \frac{F_2}{K_2} \quad (36)$$

They may be combined to give the following result

Figure 29. Two Spring Model in Determining the ratio E/K

$$F_{app} = F_1 + \frac{K_2}{K_1} F_1 \quad (37)$$

Whence the ratio of the elastic parameters can be determined,

$$\frac{K_2}{K_1} = \frac{F_{app}}{F_1} - 1 \quad (38)$$

The force applied at the junction is a known quantity as is F_1 since it is simply the force read from the microbalance.

A circuit was developed to solve this problem. The basic function is to determine the system response to a prescribed force.

It can apply a known force to the junction of the microbalance and substrate by the application of a voltage to the meter movement. Knowing this force and the force read from the microbalance, the ratio K_2/K_1 can be determined experimentally.

APPENDIX II

Derivation of the Bending Equation

The equations used to describe this experiment in the past were the standard beam equation and the result found by Finegan for surface tractions on a free plate. Certain doubts were raised as to the validity of the form of these equations based upon the fact that these equations were approximations not exactly meeting the necessary boundary conditions.

The simple beam equation from elementary beam theory is given by³⁵

$$\delta_{\max} = \frac{F l^3}{3EI} \quad (39)$$

where l = length of beam, E = Young's modulus, and I is the moment of inertia of a plane area around the neutral axis. The neutral axis or plane is defined as a section in the material that suffers no strains during deformation. Thus, all bending and strain are referred to this location during any calculations for simple bending.

This equation yields a shape for the bending beam that is called anticlastic bending. This behavior is due to the Poisson

contraction. If the beam is deflected to certain limits, stretching in the neutral plane occurs and the Poisson effect eventually becomes cancelled and the beam flattens. This then is known as cylindrical bending, and the δ max becomes smaller by a factor of $(1-\nu^2)$ where ν is Poisson's ratio. This equation for cylindrical bending was used incorrectly by another worker as pointed out by Rottmayer.³⁷ The region of validity for equation ³⁹ was shown earlier.

The bending due to the stress of the film on the substrate was calculated assuming that the beam was simply supported. This gives the following result: ³⁶

$$\Delta = \frac{3T(1-\nu)l^2}{Eh^2} \quad (40)$$

where Δ = max deflection, T = total force/unit width; l = length; b = width; and h = thickness of the substrate. This expression cannot be strictly correct in that it is the result of a parabolic shape in x and y . The true boundary conditions of the experiment require that at the edge of the clamp there be no variation in shape along the edge of the clamp. While the error is not expected to be large, it nevertheless exists and heretofore has not been pointed out.

A better estimate of the experimental arrangement has been

calculated from the linear bending theory of plates. The basic assumption of this theory is that all the strains are small compared with 1. Three basic statements of this hypothesis are:

1. $\epsilon_z = 0$. i.e., the strain in the z direction is zero.
2. Plane sections remain plane upon bending, which implies no serious non-uniform stretching during bending.
3. Normal sections remain normal. This essentially implies that the transverse shear deformations are small.

With these assumptions, linear bending theory can be established from expressions for the strain in terms of the coordinates, and the stress strain relationships. The method is straightforward and is outlined as follows:

A function for the shape of the plate is assumed,

The stress distribution is given, and

The total work done in deforming the plate to a given shape is calculated and set equal to the strain energy stored in the plate for this configuration.

The variational principle is applied to the equality and a differential equation for the deflection in terms of the applied load is found with necessary boundary conditions. The equation is³⁹

$$\frac{EI}{1-\nu^2} \nabla^4 W = P \quad (41)$$

where P represents the normal pressure, I is the moment of inertia about the neutral plane, E is Young's modulus and ν is Poisson's ratio. The quantity $\frac{EI}{1-\nu^2} = D$ is referred to as the flexural rigidity of a plate. This equation has accompanying boundary conditions which will not be listed here.

The experimental boundary conditions require that three edges be free while the fourth be clamped. The clamped condition requires that

$$W[x,y] \Big|_{x=0, \text{ all } y} = 0 \quad (42)$$

and

$$\frac{\partial W[x,y]}{\partial x} \Big|_{x=0, \text{ all } y} = 0 \quad (43)$$

Thus the deflection and slope of the plate emerging from the clamp are rigidly fixed. In practice, an edge shear doesn't represent the experiment since the hook is bonded to the top side of the plate. The situation is described by two patch loads symmetrically placed about the X axis and at the free end. With the aid of a computer, the resultant shape may be numerically computed. As was stated earlier, the differential equation and boundary conditions were derived by taking the variation of the shape to equalize the strain energy and the work done by external forces.

At this point a calculation is made known as assumed modes. A shape, with variable coefficients, is assumed for the deflection that satisfies all the boundary conditions. In this case, a solution must meet only the criteria stated above.

Assume a solution for W of the following form

$$W[x,y] = \sum_{i,j=0}^{\infty} A_{ij} x^{i+2} y^j \quad (44)$$

Clearly, this equation must be truncated some place in order to achieve a finite number of linear equations. Where to cut off this series is decided with the aid of the differential equation

$$\nabla^4 W = \frac{P(1-\nu^2)}{IE} \quad (45)$$

Suppose that P is constant everywhere over the plate, thus:

$$\nabla^4 W = \text{CONSTANT} \quad (46)$$

Try evaluating with the assumed series.

$$\nabla^4 W = \left[\frac{\partial^4}{\partial x^4} + 2 \frac{\partial^4}{\partial x^2 \partial y^2} + \frac{\partial^4}{\partial y^4} \right] W = \sum_{i,j=0}^{\infty} \left[A_{ij} (i+2)(i+1)(i)(i-1) x^{i-2} + \dots \right]$$

$$2 \left[(i+2)(i+1)(j)(j-1) X^{i-2} Y^{j-2} + (j)(j-1)(j-2)(j-3) X^{i+2} Y^{j-4} \right] = \text{CONST.} \quad (47)$$

It is now necessary to find some i and j minimum such that equations of the coefficients can satisfy the equation and retain y variation.

After some examination, it is seen that the following polynomial just satisfies these conditions

$$\begin{aligned} & X^2 \quad X^3 \quad X^4 \quad X^5 \quad X^6 \quad X^7 \\ & X^2 Y^2 \quad X^3 Y^2 \quad X^4 Y^2 \quad X^5 Y^2 \\ & X^2 Y^4 \quad X^3 Y^4 \end{aligned} \quad (48)$$

It is interesting to note the way in which the terms drop off in higher power of y . If a longer solution were felt necessary, terms could be added on using the general form of this scheme to make a "consistent" solution.

The equation used to vary the coefficients of this solution is:

$$\int W P dA = \frac{1}{2} \frac{EI}{1-\nu^2} \int \left[|\nabla^2 W| - 2(1-\nu) \left\{ \frac{\partial^2 W}{\partial x^2} \frac{\partial W}{\partial y^2} - \left(\frac{\partial^2 W}{\partial x \partial y} \right)^2 \right\} \right] dA \quad (49)$$

where the integrals are over the area of the plate.

The left hand side represents the work done in deforming the plate, while the right hand side is the stored strain energy. The right hand side can be simplified by expanding the terms and recombining to get:

$$= \frac{1}{2} \frac{EI}{1-\nu^2} \int \left[\left(\frac{\partial^2 W}{\partial x^2} \right)^2 + \left(\frac{\partial^2 W}{\partial y^2} \right)^2 + 2\nu \frac{\partial^2 W}{\partial x^2} \frac{\partial^2 W}{\partial y^2} + 2(1-\nu) \left(\frac{\partial^2 W}{\partial x \partial y} \right)^2 \right] dA \quad (50)$$

Now, if the assumed solution is differentiated and inserted into this expressions, the following result is obtained.

$$W = \sum_{i=2, j=1} A_{ij} x^i y^{2j-2} \quad (51)$$

$$\frac{\partial^2 W}{\partial x^2} = \sum_{i=2, j=1} A_{ij} i(i-1) x^{i-2} y^{2j-2} \quad (52)$$

$$\frac{\partial^2 W}{\partial y^2} = \sum_{i=2, j=1} A_{ij} |2j-2| |2j-3| x^i y^{2j-4} \quad (53)$$

$$\frac{\partial^2 W}{\partial x \partial y} = \sum_{i=2, j=1} A_{ij} i |2j-2| x^{i-1} y^{2j-3} \quad (54)$$

hence,

$$\begin{aligned}
 &= \frac{1}{2} \frac{EI}{1-\nu^2} \int \left[\sum_{ij,kl} |A_{ij} A_{kl}| |i||i-1||k||k-1| x^{i+k-4} y^{2j+2l-4} \right. \\
 &\quad + A_{ij} A_{kl} |2j-2||2j-3||2l-2||2l-3| x^{i+k} y^{2j+2l-8} \\
 &\quad + 2\nu A_{ij} A_{kl} |i||i-1||2l-2||2l-3| x^{i+k-2} y^{2j+2l-6} \\
 &\quad \left. + 2(1-\nu) |A_{ij} A_{kl}| |i||k||2l-2||2j-2| x^{i+k-2} y^{2j+2l-6} \right] dA \quad (55)
 \end{aligned}$$

Now, the limits of integration are

$$0 \leq x \leq b/2 = Y$$

Performing the integrations and evaluating the following is obtained.

$$\begin{aligned}
 &= \frac{EI}{1-\nu^2} \left[\sum_{ij,kl} |A_{ij} A_{kl}| \left| \frac{i!|i-1||k||k-1|}{(i+k-3)(2j+2l-5)} \right| \left(\frac{b}{2} \right)^{i+k-3} \left(\frac{b}{2} \right)^{2j+2l-3} \right. \\
 &\quad + \frac{(2j-2)(2j-3)(2l-2)(2l-3)}{(i+k+1)(2j+2l-7)} x^{i+k+1} \left(\frac{b}{2} \right)^{2j+2l-7} \\
 &\quad + 2\nu \frac{(i)(i-1)(2l-2)(2l-3)}{(i+k-1)(2j+2l-5)} \left(\frac{b}{2} \right)^{i+k-1} \left(\frac{b}{2} \right)^{2j+2l-5} \\
 &\quad \left. + 2(1-\nu) \frac{(i)(2j-2)(k)(2l-2)}{(i+k-1)(2j+2l-5)} \left(\frac{b}{2} \right)^{i+k-1} \left(\frac{b}{2} \right)^{2j+2l-5} \right] \quad (56)
 \end{aligned}$$

Before the work is calculated for the deformation, the variation of the coefficients of the strain energy can be taken. The results of this variation are used for both the normal force and the applied moment.

Because the sums over ij and kl are identical, taking the partial $\partial / \partial A_{\alpha\beta}$ will eliminate one sum, fix the value of two indicies, and bring a factor of two out in

front.

$$\begin{aligned} \frac{\partial}{\partial A_{\alpha\beta}} \left(\frac{\text{STRAIN}}{\text{ENERGY}} \right) &= \frac{2EI}{1-\nu^2} \sum_{ij} |A_{ij}| \left(\frac{(i)(i-1)(\alpha)(\alpha-1)}{(i+\alpha-3)(2j+2\beta-3)} \right) \left(\frac{b}{2} \right)^{(i+\alpha-3)(2j+2\beta-3)} \\ &+ \frac{(2j-2)(2j-3)(2\beta-2)(2\beta-3)}{(i+\alpha+1)(2j+2\beta-7)} \left(\frac{b}{2} \right)^{(i+\alpha+1)(2j+2\beta-7)} + 2\nu \frac{(i)(i-1)(2\beta-2)(2\beta-3)}{(i+\alpha-1)(2j+2\beta-5)} \left(\frac{b}{2} \right)^{(i+\alpha-1)(2j+2\beta-5)} \\ &+ 2(1-\nu) \frac{(i)(2j-2)(\alpha)(2\beta-2)}{(i+\alpha-1)(2j+2\beta-5)} \left(\frac{b}{2} \right)^{(i+\alpha-1)(2j+2\beta-5)} \end{aligned} \quad (57)$$

It is thus seen that a system of $(i_{\min} + j_{\min}) \times (i_{\min} + j_{\min})$ linear equations is generated by substituting in different values for the α and β . The remainder of the calculation involves finding expression for the work done by a normal force and by the surface tractions. Since the theory is linear, the two resultant shapes may be calculated and added to give the final result. This will allow comparisons with the equations listed that were used in the past.

The experimental location of the hook is at the end of the substrate. The hook is cemented to the substrate over two small areas. These areas, then, are patch loads over which pressure is applied.

$P = F/A$, where P , F , and A are the pressure, force, and area respectively.

The work to obtain the deformation is given by

$$\text{WORK} = \int P W dA \quad (58)$$

Since the pressure is applied only over patch loads at the very ends, the integral is taken only over these areas.

$$\text{WORK} = \int P \left(\sum_{ij} A_{ij} x^i y^{2j-2} \right) dA \quad (59)$$

The integral results in the following:

$$\text{WORK} = 2P \sum_{ij} \frac{A_{ij}}{(i+1)(2j-1)} x^{i+1} y^{2j-1} \Big|_0^{l-a} \Big|_{b/2}^{b/2-a} \quad (60)$$

The two out in front results from the fact that there is a symmetrical load on each side of the X axis.

Taking the partial derivative of the work with respect to will give just one term for each of the equations generated from the strain energy.

Hence, for applied forces on the patch loads at the end of the beam, the resultant system of equations becomes

$$\text{EQ. (1)} = 2P \frac{x^{\alpha+1} y^{2\beta-1}}{(\alpha+1)(2\beta-1)} \Big|_0^{l-a} \Big|_{b/2}^{b/2-a} \quad (61)$$

By placing this system of simultaneous equations in a computer program, values for the coefficients A_{ij} may be determined.

Next, the resulting expression for the effect of the stress must be determined. Since the stress in the film is biaxial and uniform for film grown at normal incidence, the surface traction is uniform. For the moment, the compression contribution of the stress will be ignored, but later treated. The moment applied to the plate by the surface stress is

$$\frac{h}{2} \int_0^t \sigma_i dt = M \quad (62)$$

σ_i is the instantaneous stress, t is the film thickness, and h is the plate thickness. Since $\sigma_{ix} = \sigma_{iy}$, $M_x = M_y = M$, The expression for the work done by moments to deform a plate is given by

$$\text{WORK} = \int (M) \left(\frac{\partial^2 W}{\partial x^2} + \frac{\partial^2 W}{\partial y^2} \right) dA \quad (63)$$

This results in the expression for the work done by moments as follows.

$$\text{WORK} = M \int \sum_{ij} A_{ij} \left[(i)(i-1)X^{i-2}Y^{2j-2} + (2j-2)(2j-3)X^iY^{2j-4} \right] dA \quad (64)$$

Taking two integrals followed by the partial derivative with respect to $A_{\alpha\beta}$ the following result is obtained.

$$M \left[\frac{\alpha}{2\beta-1} X^{\alpha-1} Y^{2\beta-1} + \frac{2\beta-2}{\alpha+1} X^{\alpha+1} Y^{2\beta-3} \right] \Bigg|_{x=0}^a \Bigg|_{y=-b/2}^{b/2} \quad (65)$$

This then gives another set of linear equations which will determine the values of the coefficients of the solution.

Both of these calculations were performed and the resulting solutions can be put together to obtain the following working equations.

In the computer program, certain constants were left out to facilitate the computation and must be replaced.

$$f(x,y) = \sum_{ij} A_{ij} X^i Y^{2j-2} \quad \frac{1}{2} \frac{EI}{P(1-\nu^2)} A'_{ij} = A_{ij} \quad (66)$$

$$\delta = \frac{2F}{A} \frac{(1-\nu^2)}{Eh^3} \int f(x,y) \quad (67)$$

The moment of inertia was computed using the center of the plate as the reference.

The same may be done for the stress expressions, yielding,

$$\Delta = \frac{12T(1-\nu^2)}{h^2 E} g(x, y) \quad (68)$$

Since the shape and hence the deflections are additive, the net resultant deflection is

$$W_{\text{net}} = \Delta - \delta \quad (69)$$

The net deflection is the amount the microbalance is moved from its initial position. Hence W_{net} may be replaced by F/K as shown in Appendix I.

Hence,

$$\frac{F}{K} = \frac{12T(1-\nu^2)}{h^2 E} g(x, y) - \frac{2F(1-\nu^2)12}{A h^3 E} F(x, y) \quad (70)$$

from which T may be deduced.

$$T = \frac{h^2 E F}{24 K(1-\nu^2)} g(x, y) + \frac{F F(x, y)}{2 A h g(x, y)} \quad (71)$$

The above equation is the working equation for the reduction of the data. For the purposes of calculation, A was assumed to be .01 cm² for the patch.

This gives a final working equation for the assumptions used as follows

$$\int_0^t \sigma_i dt = \frac{h^2 E F}{K 24 (1-\nu^2)} g(x, y) + \frac{50 F f(x, y)}{h g(x, y)} \quad (72)$$

The ratio E/K is determined as shown in Appendix I.

One last point is that the surface traction is applied only at one surface. This means that the moment applied is accompanied by a uniform compression. This means that the neutral plane is shifted as can be seen in Fig. 30. It is then necessary to perform all calculations referenced to this new neutral place. However Finegan⁴⁰ solved for the value of this shift and found it to be $2/3 h$. Hence, the neutral surface lies $2/3 h$ below the top surface of the plate. Thus, the correct moment is

$$M = \frac{2Th}{3} \quad (73)$$

Now, compute the moment of inertia.

$$I = \int_{-\frac{h}{3}}^{\frac{2h}{3}} x^2 dx = \frac{h^3}{9} \quad (74)$$

The ratio $\frac{M}{I}$ then $\frac{6T}{h^2}$.

Figure 30. Location of Neutral Axis in the Plate for Applied Surface Traction

SHIFT IN NEUTRAL AXIS DUE TO FILM

If the moment of inertia is computed using the center of the plate, the following is found.

$$I = \int_{-\frac{h}{2}}^{\frac{h}{2}} x^2 dx = \frac{h^3}{12} \quad (75)$$

$$M = \frac{Th}{2} \quad (76)$$

and the ratio $\frac{M}{I}$

$$= \frac{6T}{h^2} \quad (77)$$

It is thus shown that the attendant compression does not alter the bending equation.

At this point, it is useful to compare the terms from the calculation to the closed expressions given at the beginning of this appendix.

The expression for the standard beam equation is

$$\delta = \frac{4Fl^3}{Eh^3b} \quad (78)$$

It is useful to assume the same applied force and compare the deflections.

$$\frac{\delta - \delta_{\text{calc.}}}{\delta_{\text{calc.}}} \cong 3.5\% \quad (79)$$

This difference is small and is probably attributed to the fact that the anticlastic behavior doesn't become apparent until about one width away from the clamp. This makes the substrate stiffen and the moment calculation shows a larger discrepancy as follows.

$$\frac{\Delta - \Delta_{\text{calc.}}}{\Delta_{\text{calc.}}} = -7\% \quad (80)$$

This 7% error is due to the fact that the beam is not allowed to have any y variation in the solution at the clamp edge. This reduces the force necessary to bend the beam at the clamp and thus causes a greater deflection to appear at the end.

Of course, these errors are not very large, and the use of the new equations in light of other possible errors in many experiments is probably not worthwhile. However, since many of these

factors have been minimized in this experiment, the use of the new calculations was felt justified as these errors could be among the largest contributed.

APPENDIX III

Microscopy Calculation

It is desired to correlate the number of spots in a diffraction ring with the number of grains within a certain selected volume. Thus, with the knowledge of a few parameters, the number of spots and their relative intensity distribution, an average grain diameter in a film may be deduced.

The first thing that must be known is the intensity of a diffracted spot from a perfect crystal as a function of deviation from exact Bragg condition. Since the energy of the electrons used is comparable to its rest mass, standard Schoedinger theory is inadequate. So, relativistic effects must first be evaluated.

Fujiwara⁴¹ begins with the relativistic Dirac equation and computes the scattering intensity from perfect crystals. He finds, after a series of approximations, that the form of the scattering result is cast the same as the Schroedinger result with two differences; the wavelength used must be the relativistic wavelength; and the mass of the electron must be the relativistic mass. Since these are the two most serious differences, intensity profiles may be determined much easier from the modified Schroe-dinger result.

A. Two Beams vs. Many Beams

When a solution is attempted, the number of terms retained depends on two things: how close to the Bragg condition the crystal is oriented; and the energy of the incoming beam. This may be visualized by the standard construction in reciprocal space. The Ewald sphere represents the k vector of the incoming electrons. The points in reciprocal space represent calculated scattering amplitudes for the crystal. Thus, if the Ewald sphere intersects two points squarely in reciprocal space, the crystal is said to be exactly at Bragg condition. Because the points have size, due to the construction from the solution and the sphere is oriented slightly to one side or the other, the amount of the reciprocal point intersected changes and hence the scattered intensity.

As the energy of the electrons is increased, the k vector increases as it is proportional to the momentum. This makes the Ewald sphere flatten out. Thus as the crystal is oriented in reciprocal space and a Bragg condition is approached between two reciprocal points, points of higher order also become intersected. This indicates that more terms in the former solution must be taken or that higher multiples of the reciprocal lattice vector must be included in the solution. However, if the region studied is far from the exact Bragg condition two beams may be used safely.

The intensity of the two beam equation appears in many

m

references and is not repeated here. However, the result is:

$$\frac{I}{I_0} = \left(\frac{\pi}{\xi_g}\right)^2 \frac{\sin^2(\pi t S_{eff})}{(\pi t S_{eff})} \quad S_{eff} = \sqrt{S^2 + 1/\xi_g^2} \quad (81)$$

where t is the crystal thickness, ξ_g is the extinction distance for the particular reflection and S is the deviation vector connecting the incident k vector, the reciprocal lattice vector and the elastically scattered vector.

This expression indicates the relative intensity of the perfect crystal as a function of orientation but nothing about the size of crystal for which it is valid.

The column approximation solves the question about the range of validity of the perfect crystal intensity to the small crystal. Takagi⁴² has published a very simple explanation. Suppose a point at the bottom of the foil is examined to see the origin of all the electrons passing through it. If we look at two extreme cases, a maximum area at the top surface will contribute. First, suppose the crystal is at Exact Bragg condition. An electron entering the top of the foil at one point may pass completely through the foil without being diffracted emerging at the reference point on the bottom. Another may be immediately diffracted upon entry and emerges at the reference point. Thus, the separation of these two entry points at the top surface gives the minimum lateral

dimension necessary for perfect crystal intensity calculations.

The angular divergence between the two points and the reference point must necessarily be the Bragg angle θ . Thus, if the film has thickness t , the dimensions at the top of the foil can be expressed as:

$$x = t\theta = t \frac{\sqrt{h^2 + k^2 + l^2}}{2dk} \quad (82)$$

But $K = \frac{2\pi}{\lambda}$, or the wave vector, and hkl are the indices of the reflection. Taking the lowest order reflection and using $2000\text{\AA}$ for the thickness, the maximum value for x is $5\text{\AA}$. Thus, a small crystallite about $100\text{\AA}$ diameter may be treated as a single crystal with very little error.

B. Averaging Process

Consider that all the crystallites are randomly oriented with no preferred direction. If the reciprocal space is examined under this assumption, then the reciprocal lattice is rotated over all angles about one point of the lattice. Thus, if the Ewald sphere intersects the center point, it will also intersect the sphere just described at approximately a hemisphere. If the Ewald sphere intersects a point in this uniform distribution of reciprocal points, as it is most likely, a reflection is generated by that crystallite. Thus, if the total number of reciprocal points

is known and the amount the point can be deviated from the Ewald sphere intersection to produce a visible reflection, a number of reflected spots may be predicted.

Thus, the number of crystallites available times the multiplicity of a reflection divided by 4π gives the density of points on the reciprocal sphere.

If the maximum deviation from Bragg is known that can produce a visible spot on the plate, a number of spots may be predicted.

Thus, if S_{max} is known,

$$\phi_{max} \approx \frac{S_{max}}{g} \quad \rho = \frac{NM}{4\pi} \quad (83)$$

$$N_s = \frac{8\phi_{max}}{g} \rho = \frac{2MN}{\pi} \frac{S_{max}}{g} \quad (84)$$

N is the number of crystallites and may be deduced as follows. If the selected area of diffraction is known on the bright field plate, the corresponding area on the film becomes

$$\frac{\pi R^2}{M^2} \quad (85)$$

where R is the radius on the plate, and M is the overall magnification.

If hexagonal grains are assumed, the area per grain becomes

$$\frac{3\sqrt{3}}{8} d^2 \quad (86)$$

where d is the diameter.

Then, the number of grains in the selected area becomes

$$\frac{\pi R^2 8}{M^2 3\sqrt{3} d^2} = N \quad (87)$$

and the number of spots

$$N_s = \frac{2m}{\pi} \frac{S_{max}}{9} \left(\frac{\pi R^2 8}{M^2 3\sqrt{3} d^2} \right) \quad (88)$$

The average grain diameter $\bar{d}$ is then

$$\bar{d} = \left[\frac{16 m R^2 S_{max}}{9 M^2 3\sqrt{3} N_s} \right]^{1/2} \quad (89)$$

C. Accuracy

The scheme depends upon knowing a number of parameters well, however, the largest error is in the number of spots expected. Since the points in the reciprocal space are randomly distributed, there are bound to be fluctuations. Thus, if the number of spots N is the average predicted from a probability, the fluctuation can be on the order of $\sqrt{N}$.

Hence the uncertainty in the grain size is $\frac{1}{2} \frac{\sqrt{N}}{N}$ just from the assumption made for the calculation. If $n \approx 100$, then the error is $\sim 5\%$. Thus, if other parameters are known well, such as $S_{\max}$, and the magnification, etc., the method is very powerful in predicting an average grain size representative of the film.

APPENDIX IV

Boundary Contraction

To compute the net contraction for the intrinsic stress, the concept of the interaction potential between two atoms is useful. If two free surfaces are brought together to form a grain boundary, the change in energy is $2\gamma_{sv} - \gamma_{gb}$, where γ_{sv} is the surface vacuum free energy and γ_{gb} is the grain boundary energy. An average grain boundary energy is $\sim 1/3\gamma_{sv}$.⁴³ Thus, the depth of the potential becomes $5/3\gamma_{sv}$. In the region of small strains, $< 2\%$, the potential may be described by the elastic constant of the material. As two atoms are brought close together, a repulsion is encountered. An estimate for the limit of nearest approach is twice the ionic radii for the material. The minimum of the potential is at the nearest neighbor distance of the material. The potential is also made to vanish at twice the nearest neighbor spacing. Then, the potential appears as in Fig. 31, with values for the nearest neighbor distance and minimum separation shown for Ni. When atoms condense from the vapor, they have $\sim .1$ ev of kinetic energy. Thus these atoms may approach any spaces where the energy required on the potential is zero or less. Hence the closest approach is defined as r and the farthest of interest is $2a$. If an atom moves between two other atoms defining the boundary at the surface,

Figure 31. Constructed Interatomic Potential for Ni Used to Determine the Limits of Integration for $\langle \Delta \rangle$

the separation must be between r and $2a$. If it lies between r and a , then that layer must relax out to allow the energy of that layer of the grain to be minimized. If it lies between a and $2a$, they will contract in order to minimize the energy. In either way, strain energy is produced. The minimum produced between the strain energy and the potential energy defines the contraction or expansion. If all initial separations between r and $2a$ are present with equal probability, the average value for the contraction may be calculated. This entire calculation follows.

Since the separation of the atoms in the boundaries is only a few percent from their unstrained positions, then a calculation for the contraction can be performed numerically. The base of the potential can be constructed from the relation

$$\phi = -\int F \, dx \quad (90)$$

where F is the force/unit area, or

$$\sigma = \frac{E}{1-\nu} \epsilon \quad (91)$$

where ϵ is the strain and σ is the force/unit area.

$$\epsilon = \frac{x-a}{a} \quad (92)$$

x is the parameter of separation.

$$\phi = \int \sigma dx = \frac{E}{1-\nu} \int \frac{x-a}{a} dx \quad (93)$$

$$\phi = \frac{E}{1-\nu} \left\{ \frac{x^2}{2a} - x \right\} + C \quad (94)$$

but,

$$\phi(a) = -5/3\gamma_{sv} \quad (95)$$

and

$$C = \frac{E}{1-\nu} \left(\frac{a}{2} \right) - 5/3\gamma_{sv} \quad (96)$$

$$\phi(x) = \frac{E}{1-\nu} \left(\frac{x^2}{2a} - x + \frac{a}{2} \right) - 5/3\gamma_{sv}. \quad (97)$$

The total strain energy can be found by integrating the force, using the stress strain relations, and multiplying by the volume of the top layer.

$$E_s = Ad \int_0^{\epsilon} \sigma d\epsilon = Ad \frac{E}{2(1-\nu)} \epsilon^2 \quad (98)$$

Since the potential is expressed in energy/unit area, let the strain energy be written the same way.

$$E_s = \frac{E}{2(1-\nu)} \cdot \frac{(y-x)^2}{d} \quad (99)$$

The total energy is then the sum of E_s and ϕ .

$$E_t = \frac{E}{2(1-\nu)} \frac{(y-x)^2}{d} + \frac{E}{1-\nu} \left(\frac{x^2}{2a} - x + \frac{a}{2} \right) - 5/3 \gamma_{sv} \quad (100)$$

The new minimum in the energy is found by minimizing E_t with respect to x .

$$\frac{\partial E}{\partial x} = 0 = \frac{-E}{1-\nu} \frac{(y-x)}{d} + \frac{E}{1-\nu} \left(\frac{x}{a} - 1 \right) \quad (101)$$

The solution for x becomes

$$x = \left(\frac{y}{d} + 1 \right) \frac{ad}{a+d} \quad (102)$$

The strain in the boundary can be evaluated. Since $d \gg a$, then,

$$\frac{x-a}{a} = \epsilon \approx \frac{y}{d} \quad (103)$$

The maximum value for y is $2a$. $d \sim 500 \text{ \AA}$ and $2a$ is $\sim 5 \text{ \AA}$. Hence, the maximum strain in the boundary is 1%. It is seen that using elasticity relations to describe the potential is justified.

The value for Δ is then given by equation 104.

$$\Delta = y' - x = y\left(1 - \frac{a}{a+d}\right) - \frac{ad}{a+d} \quad (104)$$

The average value of Δ is given by equation 105.

$$\langle \Delta \rangle = \frac{\int_r^{2a} \left(y\left(1 - \frac{a}{a+d}\right) - \frac{ad}{a+d}\right) dy}{\int_r^{2a} dy} \quad (105)$$

$$\langle \Delta \rangle = \frac{y^2}{2} \left(1 - \frac{a}{a+d}\right) - y \frac{ad}{a+d} \Bigg|_r^{2a} \quad (106)$$

Given that $\frac{a}{a+d} \approx 0$, and $\frac{d}{a+d} \approx 1$, $\langle \Delta \rangle$ becomes

$$\langle \Delta \rangle \approx \frac{ra - \frac{r^2}{2}}{2a - r} \quad (107)$$

Then, the average value of the stress becomes equation 108.

$$\langle \sigma \rangle = \frac{E}{1-\nu} \frac{\langle \Delta \rangle}{d} \quad (108)$$

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