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THE ORIGINS OF STRESS IN THIN NICKEL FILMS

FRANK ANTHONY DOLJACK

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THE ORIGINS OF STRESS IN
THIN NICKEL FILMS

by

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Submitted in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

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Abstract

by

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The intrinsic stress in thin, polycrystalline nickel films vapor deposited onto polished silicon substrates was measured by viewing the substrate deflection using an optical interference method. The method measured the force per unit width as a function of film thickness during film growth in high vacuum. The derivative of the force per unit width curve gave the instantaneous stress as a function of film thickness. Runs were made at controlled substrate temperatures between -42°C and 225°C by using a clamped substrate geometry which provided good thermal contact to a temperature controlled body. Films were deposited at normal incidence and at 20° , 30° , and 40° incidence. Samples were stripped from their substrates, and since they were all approximately $2000\text{ \AA}$ thick, a 650 KV electron microscope was used to directly observe the microstructure.

The instantaneous stress in the films was found to be

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constant except for the development of compressive stresses in the first 500-1000 Å of growth at the higher substrate temperatures. The stresses were calculated using a grain boundary model for stress and the measured average grain sizes, which were observed to increase from about 300 Å to greater than 1000 Å over the range of substrate temperatures. The fall off of stress with increasing substrate temperature was matched well by the calculated values, and the calculated stress values agreed within roughly 30% of the measured values. It was concluded that the constant stress was produced by a constrained grain boundary relaxation.

The compressive stresses were the result of grain boundary diffusion of silicon into the nickel film. At 200° C sufficient silicon diffuses along grain boundaries to form Ni_3Si in times less than the time of a deposition. The estimated amount of silicon that diffused was shown to be capable of producing observable compressive stresses.

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I. INTRODUCTION

A. Models for Stress

The origin of the intrinsic stress in metal films has been actively investigated now for twenty years. The results of numerous investigations have shown that there exists causes that produce changes in the observed intrinsic stress: inclusion of foreign atoms in the condensed film, chemical reactions, and phase transformations. Barring the occurrence of these effects, one still finds remaining in most cases a large value of intrinsic stress which has its origin in the structure of the condensed film and in the detailed process by which the film is formed.

Wilcock, Campbell, and Anderson proposed that a grain boundary annealing mechanism is responsible for the intrinsic stress observed in polycrystalline gold and silver films.¹ They based their model on the result of Grigson and Heritage that the discontinuous island structure of Ag, Au, Ni, and NiFe films observed during their early stages of growth possesses many microcrystals per island, and that the number of these crystallites per unit volume decreases as each film grows into a continuous structure.² The intrinsic stress is produced as the microcrystals anneal into larger crystallites and the elimination of microscopic voids at the former grain boundaries produces crystallite lattice

strains. This model is consistent only with a force per unit width versus thickness curve that stops increasing at continuous film thicknesses and consequently cannot explain the data for numerous high melting point metals that exhibit linearly increasing force per unit width to large thicknesses.

A model more consistent with the bulk of the data has been one proposed by Klokholm and Berry.³ A very similar model has also been proposed by Buckel.⁴ The stress is produced in each incremental layer of film when it transforms from a nearly amorphous, frozen liquid-like state to a crystalline state. The magnitude of the stress is determined by the density increase of the transition that would result if the layer were unconstrained. Therefore at a given substrate temperature the value of stress depends upon the initial density of a layer. The initial density is determined by the amount of order achieved by thermally activated movements of the atoms before they become buried. The model predicts a constant value of stress per incremental layer, a maximum value of stress that roughly equals 1% of Young's modulus because density increases of freezing metals are 1%, and no intrinsic stress in amorphous films. Experiments support these predictions.^{3,5} On the other hand, the earlier grain boundary model proposed by Finegan and Hoffman, which shall be expanded in this paper, predicts about the same results.⁶

Since the magnitude of the intrinsic stress is determined by the number of thermally activated surface movements of the

atoms before the layer anneals, the Klokholm and Berry model does not appear to permit any correlation of the stress with the microstructure of the completed film. It is usually the case, however, that the decrease of stress at higher substrate temperatures is usually accompanied by a higher degree of crystallinity. The stress as predicted by the grain boundary model proposed by Finegan and Hoffman depends directly upon the gap at the grain boundary and inversely upon the grain diameter of the final structure. Consequently, this model is subject to the test of precise electron microscope measurements.

The models for stress so far discussed do not explain the compressive stresses that are sometimes observed. Buckel predicts that metals that increase in density upon melting should exhibit compression during condensation.⁴ It is likely, however, that most, if not all, compressive stresses are the result of chemical reactions or the inclusion of foreign atoms in the film structure, which can originate from residual gases or diffusion processes.

B. Angle of Incidence Effects

Anisotropic magnetic effects produced by evaporation at large incident angles have been studied extensively since they have been first observed.⁷ Angle of incidence induced stress anisotropy, first reported in 1959,⁸ has received little emphasis.

If the y axis is taken to lie in the plane of the film and the plane of incidence, then the stress ratio, σ_y/σ_x , has been reported to decrease with increasing incident angle as $\cos \theta_i$, where θ_i is the incident angle.⁹ Further, the values of both σ_x and σ_y have been reported to decrease with increasing θ_i .^{10,11} One reason proposed for the lowering of both the stress and stress ratio is that self-shadowing produces an increased, but anisotropic, porosity in the films and consequently increased oxidation down the grain boundaries.¹⁰ In light of the grain boundary model mentioned earlier,⁶ an anisotropic nucleation and growth of grains has been proposed to explain the approximate $\cos \theta_i$ behavior of the stress ratio.¹² This model postulates nuclei during the early stages of growth when the film is discontinuous to be elongated in the direction perpendicular to the plane of incidence. This elongation has been confirmed and an explanation given for its existence.¹³ However, elongation in the plane of incidence must result when the film becomes continuous according to this model and such elongated grains have not been seen except for very large angles of incidence.¹⁴

C. Goal of This Experiment

In this experiment we sought to explain the intrinsic stress in nickel films by (1) measuring the manner in which the stress was distributed throughout the thickness of the film for

different substrate temperatures and for deposition angles of incidence which ranged from 0° to 40° , and (2) by observing directly the microstructure of such films with an electron microscope. The force per unit width versus thickness curve was measured directly and the intrinsic stress distribution was given by the derivative of this curve.

Further, the previously mentioned grain boundary model⁶ was stated in more precise terms (Appendix III) because it was desired to test its validity by using the microstructure observations to give stress values with which one could compare measured values.

II. EXPERIMENTAL

A. Description of the Bending Force Measurement

The determination of bending force per unit width versus thickness curves was made by recording the bending of a substrate in the form of a thin plate as the film grows at a constant rate. The measurement used an optical interference technique to record on photographic film the substrate elevation profiles at known times during the vapor deposition of nickel. In such a measurement the change in elevation of points on the substrate from their initial elevation is directly proportional to the bending force per unit width in the film.

Poor substrate temperature control has long been a problem in dynamic bending force measurements, particularly at temperatures around room temperature. This bending experiment was so designed such that all substrate temperatures were effectively controlled. The details of the design follow.

B. Substrate Design

1. Bending Plate Geometry

The bending plate arrangement consisted of a circular thin plate rigidly clamped over a central, concentric circular area.

The plate deflection equation for this configuration is solved in Appendix I. Other in situ bending plate stress measurements have used either freely supported circular plates or long, narrow plates supported as cantilever beams. Either of these arrangements do not possess the capability of maintaining the substrate temperature sufficiently constant for depositions made under 100°C and for deposition rates of tens of Angstroms per second. Since it was the desire in this experiment to measure the stress and stress anisotropy in a single measurement on a single substrate, it was necessary to use a circular plate geometry. For reasons of substrate temperature control the substrate was thermally in contact with a OFHC copper block whose temperature could be regulated. Thus both thermal and mechanical clamping was accomplished by the substrate holder. For best deflection sensitivity (see Appendix I) the substrate was clamped over a central, concentric circular area, leaving an annular portion free to bend.

Silicon was chosen as the substrate material over such other possible choices as fused quartz and sapphire because of the following reasons: (1) silicon has a thermal conductivity much higher than the other choices, $1.40\text{ watts/cm/}^{\circ}\text{K}$ at 300°K dropping to $.74\text{ watts/cm/}^{\circ}\text{K}$ at 500°K ,¹⁵ (2) single crystal wafers with a $\langle 111 \rangle$ orientation are readily available with diameters up to and exceeding 30 mm, (3) optically polished silicon surfaces have high reflectivity in the visible region and consequently do not need the addition of a reflecting coating to enhance interference

fringes, (4) the elastic properties exhibit no peculiarities and the elastic constants are known. The high thermal conductivity of silicon was a major consideration and this consideration is discussed in one of the following subsections.

The $\langle 111 \rangle$ orientation was chosen because Young's modulus, E , and Poisson's ratio, ν , are isotropic in the plane perpendicular to $\langle 111 \rangle$ for the cubic system.¹⁶ An approximate calculation showed that E varied less than 1% in the plane of the substrate if $\langle 111 \rangle$ were less than $1/2^\circ$ off the normal to the plane. Consequently, $1/2^\circ$ was the tolerance set for the substrates in this experiment.

From the elastic stiffnesses¹⁷ the elastic constants were calculated to be $E = 1.69 \times 10^{12}$ dynes per cm^2 and $\nu = .26$.

Since the deflection of bending plates is proportional to the inverse of the quantity Eh^2 where h is the plate thickness, the substrates all were chosen to have nominally 0.015 cm thickness. This choice enabled changes in the force per unit width of approximately 0.2×10^4 dynes per cm to be observed. Further, lapping and polishing silicon wafers down to this thickness was feasible.

2. Substrate and Clamp Assembly

The substrates had diameters that varied approximately from 22 to 24 mm and were cemented to a two piece, washer-shaped

clamp fashioned from 9.54 mm diameter molybdenum rod. A cross-sectional view of this assembly is shown in Figure 1. The inner and outer diameters were chosen to optimize the viewing area available to observe interference fringes and to minimize the temperature difference between points on the substrate at the outer radius and at the clamp. For each run the input power to the evaporation filament was typically 900 watts. If one assumed all of this power was isotropically radiated and all incident power on the substrate was absorbed and conducted to the clamp, a heat flow calculation showed that the above mentioned temperature difference acquired during an evaporation would be around 7°C . This value proved to be large, as will be shown in the section regarding substrate temperature performance. Since this temperature difference is inversely proportional to the thermal conductivity of the substrate, a material with a high thermal conductivity such as silicon was an absolute requirement. A worst case estimate of $1/4^{\circ}\text{C}$ for the temperature difference between top and bottom substrate surfaces was made by assuming all power incident on the top surface flows through to and out the bottom surface.

The use of molybdenum for the clamp material instead of copper was necessitated by the need to match the thermal expansion coefficient of the clamp with that of silicon. The use of copper for the clamp invariably lead to the fracturing of the silicon when the substrate-clamp assembly was elevated in tempera-

Figure 1. Substrate Clamp Assembly

ture. At room temperature the linear expansion of molybdenum is twice that of silicon whereas the linear expansion of copper is nearly 7 times that of silicon.¹⁸ The use of molybdenum enabled successful temperature elevations to at least 225° C. Furthermore, the thermal conductivity of molybdenum is only 3 times smaller than that of copper,¹⁸ which made it an acceptable heat sink material.

The substrate-clamp assembly in Figure 1 was mounted onto the copper heat sink and held by a screw as shown in Figure 2. The thermal contact across the molybdenum-copper interface was guaranteed by insertion of a soft, gold washer fashioned from 0.005 inch sheet which was crushed by the tightening of the screw. A Chromel-Alumel thermocouple junction was clamped in the interior of the copper heat sink with a screw in the approximate position shown in Figure 2. Four stainless steel support members brazed to the copper rigidly held the assembly. The location of the copper tubing which carried coolant was made necessary by the location of the fused quartz optical flat (shown later in Figure 3).

C. General Description of Apparatus

The stress measurement was made in a conventional, liquid nitrogen cold-trapped high vacuum system pumped by a CVC PMCS-4C four inch diffusion pump which used Dow Corning 705 silicone fluid.

Figure 2. Details of Substrate Support

The system was equipped with a stainless steel collar with viewing ports and with an eighteen inch Pyrex bell jar which could be out-gassed at approximately 75° C.

The evaporation filament was made by fashioning 0.040 in. dia. tungsten wire into a square "pancake", which consisted of seven parallel legs each about 30 mm long and spaced so that the overall width was about 30 mm. About 50 cm of 0.005 in. dia. tungsten wire was wound onto the seven legs with extra turns at the corners. This technique helped keep the nickel spread uniformly along the legs during deposition. The extra tungsten at the corners added bulk to a region where the nickel tended to flow. The nickel charge consisted of about 100 cm of No. 28 B & S gauge pure nickel wire (about 99.999%) wound tightly and uniformly onto the filament. This filament was capable of depositing roughly 3000 Å of nickel at the substrate distance of 15 cm while maintaining a rate at the substrate of approximately 30 Å per second.

The principal experimental arrangement is shown schematically in Figure 3. The circular silicon substrate, clamped at its center to a copper heat sink, was positioned over a fused quartz optical flat so that interference fringes were produced by the top surface of the flat and the bottom surface of the substrate. The flat floated on three adjusting screws and consequently could be positioned parallel to the substrate to produce observable fringes. The top surface of the flat was coated with, very

Figure 3. General Experimental Arrangement

approximately, 50 Å of aluminum. The purpose of this coating was to enhance the sharpness and visibility of the interference fringes and to produce two perpendicular lines by shadowing. One line was perpendicular to the plane of incidence of deposition and the other, of course, lay in the plane of incidence. It was along these directions that the stress was inferred from the substrate profile. The y direction was defined to be along the line that lay in the plane of incidence.

The interference fringes required in this experiment were Fizeau fringes. These are localized fringes, their plane of localization being in or near the substrate-flat gap. An interference system with non-localized fringes was unacceptable because, in general, other interfering components in the optical system produced fringes in the final image that obscured the fringes of interest. Consequently the beam from the light source, a one-tenth milliwatt helium-neon laser, was appropriately diffused to meet the requirements for Fizeau fringes.¹⁹

As a deposition proceeded, the fringe pattern, and therefore the substrate profile, was recorded on 35 mm film about every five seconds by an electric motor driven Nikon F camera equipped with focussing bellows. The flash synchronization output on the camera provided a signal marking when each frame was made. This signal drove a circuit which pulsed the recording pen on a strip chart recorder which was recording the frequency output from a Sloan quartz crystal thickness monitor as the deposition proceeded.

The blowing of Nichrome fuse wires to open and close the shutters provided signals to another circuit which also pulsed the chart recorder. This circuit also marked another strip chart recorder that monitored the pressure during the run. Consequently, the history of each run was automatically recorded.

The Sloan quartz crystal monitor provided signals which were used to blow the shutter fuse wires at pre-set times and to maintain the evaporation rate constant at a pre-set value. The quartz crystal was located the same distance from the evaporation filament as the substrate, and it was mounted on the same assembly that the evaporation filament was affixed; hence, the quartz crystal rotated with the filament when the angle of incidence was changed. However, the exact position of the quartz crystal was not important in knowing the sample thickness because each sample thickness was measured individually by the method described later.

The angle of incidence was variable in steps of 5° up to 40° . Given the filament-to-substrate distance in each case as 15 cm and given the approximate filament dimensions, one sees that the angle subtended by the filament was about 10° . Therefore the angle of incidence, θ_i , was defined by the angle off normal of a line passing through the center of the substrate and the center of the filament.

The substrate was temperature controlled either by a small, tungsten lamp filament heater in the copper heat sink or by running tap water or dry ice chilled ethanol through 1/8 inch copper

tubing brazed to the heat sink with BT solder. When the heater was used, the temperature was regulated by a closed-loop circuit that used a Chromel-Alumel thermocouple that was clamped to the heat sink. A small ring heater concentric with the substrate assisted the clamp heater for runs made at 200° C or higher by radiantly supplying power.

D. Procedure

1. Substrate Preparation

In order to prepare the substrate-clamp assembly that is shown in Figure 1 it was necessary to cut a center hole in the silicon wafers. The hole in each case was made with an air abrasive machine.

Prior to being cemented to the molybdenum clamp, each substrate was cleaned in the following manner. A pea-sized volume of Alconox detergent powder was added to 150 ml of water and this solution with substrate in it was heated until warm. This beaker of solution with substrate was then placed in an ultrasonic cleaner for approximately 5 minutes. Two rinses with deionized water were followed with a final rinse which consisted of placing the substrate in distilled water and heating the water. The substrate was then blotted dry on bibulous paper.

The cement used to bond the substrate to the clamp was Autostic.²⁰ In order to avoid thermally insulating the silicon

from the molybdenum the bonding layer was made thin by diluting the Autostic cement with an equal part of water and by squeezing together lightly the substrate-clamp assembly.

2. Run Procedure

Prior to each run the shutter fuse wires were degassed by running current through them for approximately twenty minutes. Also the substrate temperature was elevated to the neighborhood of 200° C before liquid nitrogen was added to the cold trap. Only after condensable vapors began being trapped as shown by a drop in pressure read by a Bayard-Albert type ionization gauge was the substrate cooled to the run deposition temperature. During this time the filament with nickel charge was outgassed for 10 minutes at a temperature just below the melting point of nickel. Previously, the bare tungsten filament had been flashed briefly in high vacuum to a temperature at or above the average temperature attained during deposition. For a few minutes immediately before the actual deposition the filament was again outgassed to below the nickel melting point. The camera was started before the evaporation in order to guarantee recording the initial substrate profile. The open shutter was in every case set to operate after about 500 Å had been evaporated. This procedure served two purposes: (1) the deposition controller had the opportunity to establish a constant, controlled rate, (2) the pressure had the opportunity to recover to nearly its base after a brief, initial

burst. In every case a frame was recorded at five minutes and at ten minutes after the closing shutter. This information was used to observe any relaxation effects.

The initial curvature of the substrate at the appropriate locations had been determined previously by lightly pushing down on the substrate and observing the motion of the fringes. Consequently, the change in spacing of the fringes during a run unambiguously determined the direction of the deflection and hence the sign of the intrinsic stress.

E. Sample and Deposition Parameters

1. Run Data

The pertinent deposition parameters for each run are listed in Table 1. The angles of incidence listed are at best only average values. Since the evaporation filament subtended about 10° , points on the substrate received incident vapor from directions approximately 5° higher and 5° lower than the average incident angle.

The Sloan thickness monitor held the deposition rates constant to within a few per cent of the values listed in Table 1.

The pressure values listed represent the average pressure during the time each film was made. In no case were the shutters opened when the pressure was above 8×10^{-7} Torr. The pressure-to-rate ratios achieved in this experiment were comparable to

TABLE 1. Run Deposition Data

Run Number	Substrate Temperature (°C)	Final Thickness (Å)	Angle of Incidence (degrees)	Deposition Rate (Å/sec)	Average Pressure (x10 ⁻⁷ Torr)	Pressure/Rate (x10 ⁻⁸ Torr-sec/Å)
21	-42	2210 ^a	0	32 ^a	3.0	0.9
16	15	2220	0	33	2.0	0.6
09	50	2170	0	30	2.5	0.8
05	99	2110	0	30	4.0	1.3
07	150	2130	0	29	4.0	1.4
08	195	2080	0	30	4.0	1.3
14	192	1360	0	33	4.0	1.2
11	225	2310	0	33	4.5	1.4
Dummy	197	--	0	--	~100.	--
18	17	2180(x) ^b 2320(y)	20	33	2.5	0.8
13	10	1900(x) ^b 2100(y)	30	28	3.5	1.3
15	16	1660(x) ^b 1930(y)	40	27	2.0	0.8
19	95	1880(x) ^b 2040(y)	30	29	2.5	0.9
20	195	1670(x) ^b 1940(y)	30	27	4.0	1.5

^aBecause film material loss caused by the adhesion failure precluded X-ray fluorescence, these numbers were estimated by using an average quartz crystal calibration constant determined from the other normal incidence runs.

^bThese are the average film thicknesses along the x and y directions. See Part II, Section F, Subsection 2 for further description.

those ratios that have been characteristic in ultra-high vacuum experiments.²¹

Except for run number 05 all substrates were supplied by Material Research Corporation (MRC). These substrates consisted of two batches, designated I and II, which were made and delivered each at a different time. The substrates were single crystal silicon wafers with $\langle 111 \rangle$ within $1/2^\circ$ of the normal of the plane of the wafer. Both sides of the substrates were polished to an optical finish by a standard semiconductor polishing technique. Because these substrates were not subjected to high enough temperatures in high vacuum prior to each run, the substrate surfaces consisted of roughly tens of monolayers of SiO_2 .^{22,23}

From each batch substrates were selected for best thickness uniformity. For each run the substrate thickness at the x axis location and at the y axis location was each individually measured because in most cases the difference in the values obtained was not negligible. The values in Table 2 show that this difference did not exceed 0.0005 cm except for the dummy run, where this difference was 0.0007 cm. The substrate used in run 05 was prepared in this laboratory and exhibited thickness non-uniformity less than 0.0001 cm, but its surface contained micro-scratches left by the final mechanical polish.

The dummy run consisted of a simulated evaporation where the tungsten evaporation filament was operated with a current typical of real runs, but it held no nickel charge. The shutters

TABLE 2. Substrate Data

Run Number	Substrate Diameter (cm)	Substrate Thickness		Substrate Supplier
		x direction ($\times 10^{-2}$ cm)	y direction ($\times 10^{-2}$ cm)	
21	2.399	1.549	1.549	MRC II
16	2.174	1.499	1.524	MRC II
09	2.383	1.549	1.549	MRC I
05	2.193	1.549	1.549	Author
07	2.359	1.321	1.372	MRC I
08	2.360	1.473	1.524	MRC I
14	2.379	1.422	1.422	MRC I
11	2.361	1.473	1.524	MRC I
Dummy	2.300	1.422	1.499	MRC I
18	2.216	1.270	1.270	MRC II
13	2.360	1.549	1.524	MRC I
15	2.201	1.422	1.397	MRC II
19	2.388	1.320	1.270	MRC II
20	2.364	1.524	1.473	MRC I

were opened for a typical length of time (about 70 seconds), and the camera took pictures at its usual rate. The purpose of this run was to measure any thermally produced bending. The substrate temperature was held at 197°C for the dummy run because the compressive behavior of the intrinsic stress in this temperature region created suspicion of thermal effects in this region.

2. Substrate Temperature Performance

The substrate temperature behavior was measured during simulated evaporations and in one case during an actual evaporation in order to check the validity of the simulated tests, which were verified. The three temperatures monitored were those of the clamp thermocouple, a 0.001 inch Chromel-Alumel junction cemented on the substrate near the clamp, and a similar junction cemented to the substrate at the outer edge. The results are summarized in Table 3. In each case the substrate temperatures quickly rose from the initial values and reached the final values approximately by the time half the evaporation was over. In no case did the clamp thermocouple change temperature by more than $1/2^{\circ}\text{C}$ during a test. At the higher clamp temperatures the table shows that the initial temperatures of the substrate thermocouples lagged behind the clamp thermocouple in a way which showed heat flow from the clamp radially outward. The final temperatures in every case were such that heat flow radially inward toward the clamp resulted.

TABLE 3. Substrate Temperature Performance

Clamp Thermocouple (°C)	Outer Thermocouple (°C)		Inner Thermocouple (°C)		Conditions
	initial	final	initial	final	
9	8	12	8	11	Tap water
10	10	15	10	13	Tap water
9	9	12	9	11	Tap water. Actual Evaporation
75	75	81	75	77	Clamp heater
127	126	134	127	132	Clamp heater
179	174	184	176	183	Clamp heater
227	216	229	217	228	Clamp & ring heater.

The largest temperature rise observed was 13° C and the biggest difference in temperature between the two substrate positions was 4° C.

It was important in this experiment to understand the effect a 13° C temperature rise would have upon the observed bending force. A reasonably accurate but simple calculation was made by assuming that the whole substrate uniformly rose in temperature linearly with time and reached its final temperature by the time half the film had been deposited. Consequently, during the first half of an evaporation the force per unit width caused by differential thermal expansion would be expected to drop linearly with thickness to a compressive value given by

$$F_{DTE}(\text{compressive}) = \frac{E_F}{1 - \nu_F} (\alpha_S - \alpha_F) t \frac{\Delta T}{2} ,$$

where E_F and ν_F are the elastic constants of the nickel, α_F is the thermal expansion of nickel, α_S is the thermal expansion of silicon, and t is the thickness of the nickel when ΔT would reach 13° C (therefore about 1000 Å). This value of bending force, which is -0.25×10^4 dynes per cm, would remain constant until the evaporation terminated, at which time the substrate would cool to its initial temperature. The DTE bending force would then relax toward tensile values by changing by an amount given by

$$F_{DTE}(\text{relaxation}) = \frac{E_F}{1 - \nu_F} (\alpha_S - \alpha_F) t \Delta T ,$$

where t would now be about $2000 \text{ \AA}$ and ΔT would be -13° C . Consequently, this relaxation was expected to be 1.0×10^4 dynes per cm in the worst case and the initial compression to be four times smaller.

The other possible temperature effect that could be a factor in this experiment would be the force per unit width produced in the film due to the difference in temperature between top and bottom substrate surfaces. Using the worst case estimate of $1/4^\circ \text{ C}$, a compressive force of 0.3×10^4 dynes per cm is found. The dummy run showed no discernible bending and it was concluded that the $1/4^\circ \text{ C}$ estimate was much too high. The sensitivity of the bending plate measurement in the dummy experiment was 0.1×10^4 dynes per cm; consequently, the dummy run showed that the temperature difference between top and bottom substrate surfaces could be no larger than about 0.1° C .

F. Film Thickness Determination

1. Method

The nickel film thicknesses listed in Table 1 were determined by a standard X-ray fluorescence technique which compared the amount of nickel K_α radiation from the samples with that

from four calibration samples. The calibration samples, 505 Å, 925 Å, 1150 Å, and 1975 Å had previously been made on glass substrates by weighing with a sensitive vacuum microbalance. The radiation from a platinum target excited with 50 kilovolt electrons illuminated a 4.77 mm diameter sample area, and the subsequent nickel K_{α} radiation was measured with a Xenon filled Geiger tube counter, chosen for its particular sensitivity to nickel K_{α} radiation.

The resulting film thicknesses were determined to about 4% accuracy. This figure included statistical error, X-ray tube voltage drift, and a 1.3% uncertainty in the 1975 Å calibration sample.

2. Off Normal Incidence Samples

Table 1 shows that for each off normal incidence sample the thickness measured by irradiating the area located along the x axis was significantly lower than the thickness measured in the area located along the y axis. The plane of incidence contained the y axis and in every case the area located along the y axis was one that came nearest to the filament when the filament was rotated to an off normal incidence position. Thus the percent thickness difference was expected to increase with increasing incidence angle, a trend which the numbers in Table 1 verify.

Measurement of a normal incidence sample showed that

different irradiated areas yielded thicknesses that varied less than 3%, a variation which was within the 4% accuracy of the measurement.

G. Electron Microscope Sample Preparation

Microscopy samples were prepared from run samples by a simple peeling technique using cellulose-backed adhesive tape. The main and important feature of the technique involved scratching the nickel film with sharp-pointed forceps prior to applying the tape. The scratches loosened the adhesion by creating edge forces as described in Appendix II and in every case large areas of film were successfully removed. The higher temperature run samples exhibited significantly better adhesion and stripped off only after repeated attempts. In one case the film stripped only at the broken edge of a substrate.

Stripped samples were loosened from the adhesive by washing in chloroform and transferred to electron microscope grids. The remaining adhesive was removed by repeatedly washing each grid in chloroform followed by blotting the backside of the grid on bibulous paper. The samples were dried and stored in capsules until they were examined by a 650 KV electron microscope.

III. DATA RESULTS

A. Stress Measurement

1. Data Analysis

For each run the deflection profiles of the substrate were determined as a function of film thickness by subtracting from the profile in each 35 mm film frame the profile of the substrate just prior to the beginning of deposition. The substrate profiles along two orthogonal directions were determined by measuring the positions of the interference fringes. The orthogonal directions were the x and y substrate axes where the y axis lay in the plane of incidence. The substrate elevation change between adjacent fringe positions was $\lambda/2$, where $\lambda = 6340 \text{ \AA}$.

The bending forces per unit width, F_x along the x direction and F_y along the y direction, were found by fitting the corresponding deflection profiles, w_x and w_y , to equation 11 in Appendix I. Since the substrate thickness sometimes varied slightly as shown in Table 2, the corrected deflection profiles, $Eh_x^2 w_x$ and $Eh_y^2 w_y$ were fitted, where E is the Young's modulus of the substrate and h_x and h_y are the substrate thicknesses along the x and y directions, respectively.

Examination of equation 11 in Appendix I shows that the sum of $Eh_x^2 w_x$ and $Eh_y^2 w_y$ is proportional to $F_x + F_y$, and

the difference is proportional to $F_x - F_y$. Consequently, the sum and difference of the corrected deflection profiles were least squares fitted with respect to equation 11 to find the bending force values.

The runs made at off-normal incidence had significant anisotropy in film thickness between x and y directions, as listed in Table 1. Because for all of these runs the results showed that the bending forces were very nearly linear with thickness, corrected force values were obtained by increasing or decreasing the appropriate deflection profile by the percent difference of the corresponding thickness from the average thickness.

Figures 4, 5, 6, 7, and 9 are the force per unit width versus film thickness curves obtained in this experiment. In every case the open symbol represents the values for F_x . The data points define relatively smooth curves. Departures from smoothness were usually traced to the inaccuracy caused by deflection profiles being defined by only a few fringe positions, which occurred at times when the changing substrate profiles became nearly flat. For some of the normal incidence runs the values of F_x and F_y do not match well. The above mentioned inaccuracy can produce this effect, but in addition, it is felt that the somewhat less-than-desired substrate thickness uniformity which prompted the first order correction to the analysis is also responsible for this mismatch.

2. Description of Results

The force per unit width versus thickness curves for normal incidence and substrate temperatures ranging from -42°C to 225°C are presented in Figures 4 through 6. A short normal incidence run at 192°C is plotted at the top of Figure 7. The -42°C film in Figure 4 experienced adhesion failure around $1400\text{ \AA}$. The -42°C and 15°C curves are obviously increasing linearly with thickness. Scanning the other curves, one sees that they start out with a "droop" that increases with increasing substrate temperature and that the curves become linear at higher thicknesses. At 150°C and above the force per unit width curves actually start out with negative slope. Over the linear portion of the curves the instantaneous stress in the layers of film at these thicknesses was found by the slope of the least squares fit of a straight line to these linear portions. These values of instantaneous stress are plotted as a function of substrate temperature in Figure 8.

The results of the normal incidence runs then are: (1) the instantaneous stress always becomes a constant value during latter film growth and falls off with increasing substrate temperature as shown in Figure 8, and (2) with increasing substrate temperature a compressive component to the instantaneous stress becomes significant and operates only up to thicknesses of roughly $500\text{ to }1000\text{ \AA}$.

Figure 4. Force Per Unit Width Versus Thickness at Normal Incidence for -42° C

Figure 5. Force Per Unit Width Versus Thickness at Normal Incidence for 15°C, 50°C, and 99°C

Figure 6. Force Per Unit Width Versus Thickness at Normal Incidence for 150° C, 195° C, and 225° C

Figure 7. Force Per Unit Width Versus Thickness at Normal Incidence for 192° C, for a Dummy Run, and at 30° Incidence Angle for 90° C and 195° C

Figure 8. Instantaneous Stress Versus Substrate Temperature for Measured Values and Calculated Values

The possibility that the compressive stress is produced by a temperature gradient through the thickness of the substrate is eliminated by the results of the dummy run made at 197° C and shown in Figure 7. An uncoated substrate was used and the filament power to an unloaded filament approximated the power delivered during an evaporation.

Since the average substrate temperature did increase during deposition to a small extent with increasing substrate temperature (see Table 3), one is forced to suspect a possible differential thermal expansion effect. As discussed earlier in this paper (Part II., Section E, Subsection 2) a DTE bending force would decrease initially to some compressive value before becoming constant at this value when the substrate temperature quit rising. Upon terminating the deposition the force would rise toward tensile values as the substrate temperature cooled to its original temperature, and the increase would always be about four times the amount of initial compression. For this experiment this increase was calculated to be about 1.0×10^4 dynes/cm at 200° C depositions. Figure 9 shows the force as a function of time after deposition termination for the higher temperature runs. The lower temperature runs showed no trend. For higher temperatures examination shows that shortly after shutter closing there appears to be a relaxation of about $1-2 \times 10^4$ dynes/cm toward increasing tensile values, which is the above calculated DTE relaxation. This re-

Figure 9. Relaxation of Force Per Unit Width after Shutter Closing

laxation is particularly noticeable for the short run at 192° C in Figure 7, since most of the compressive force relaxes. If the initial compression is due to DTE, then its magnitude should be four times smaller or between 0.25×10^4 dynes/cm and 0.5×10^4 dynes/cm. However, the net compression goes to about -2×10^4 dynes/cm for the runs near 200° C. The conclusion is that DTE cannot be responsible for the observed compression because the observed compression is always larger than the observed relaxation. Consequently the compression must be explained by the details of the film formation.

Figure 10 shows the force per unit width versus thickness curves for runs made at about the same substrate temperature but for angles of incidence of 20°, 30°, and 40°. The y stress to x stress ratio was determined from the slopes of least squares fits for each case. The values are .71, .64, and .70 for 20°, 30°, and 40°, respectively. No conclusions could be made from these data other than that there exists a significant stress anisotropy over this range of low incidence angles.

The average values of the slopes of least squares straight lines fitted to the curves in Figure 10 yield average values of stress of 10.0×10^9 , 9.2×10^9 , and 7.1×10^9 dynes/cm² for 20°, 30°, 40°, respectively. Consequently, the magnitude of the stress falls off strongly with increasing incidence angle.

Two 30° incidence runs are shown in Figure 7, one made at

Figure 10. Force Per Unit Width Versus Thickness
 20° , 30° , and 40° Incidence Angle

95° C and the other at 195° C. The "droop" and fall off with temperature increase is evident in these runs, however, the "droop" for the 195° C run is not nearly so large as the comparable normal incidence 195° C run. These two runs show that the stress anisotropy may have inverted. Because of the inaccuracies present in this experiment stress anisotropy inversion cannot be concluded from these two runs. However, these data suggest at least a possible decrease or elimination of the anisotropy that was so evident in the runs at 10° C to 17° C.

B. Electron Microscopy Results

The normal incidence samples were viewed in bright field and dark field, and selected area diffraction patterns were recorded. The structure of the nickel films evaporated in this experiment was fine grained polycrystalline with random orientation.

The dramatic increase observed in average grain size for increasing substrate temperature between - 42° C to 225° C is represented by the four micrographs in Figures 11 through 14. The samples at 195° C and 225° C contained large, well developed crystals (about 3000 Å across) in a field of more numerous, smaller crystals (about 500 Å average diameter). Figure 15 presents the average grain diameters as a function of substrate temperature. These grain sizes were measured by measuring grain images in both bright field micrographs and dark field micrographs.

Figure 11. Bright Field Micrograph of 15° C, Normal
Incidence Film of 2220 Å Thickness

Figure 12. Bright Field Micrograph of 99° C, Normal
Incidence Film of 2110 Å Thickness

Figure 13. Bright Field Micrograph of 150° C, Normal
Incidence Film of 2130 Å Thickness

Figure 14. Bright Field Micrograph of 225° C, Normal
Incidence Film of 2310 Å Thickness

Figure 15. Average Grain Size Versus Substrate Temperature for Normal Incidence

A representative selected area diffraction pattern is shown in Figure 16 from a 20,000 Å diameter circular area on the 150° C sample. 10° specimen tilt revealed no fiber texture and otherwise no preferred orientations were evident among the small polycrystals.

Figure 17 shows a bright field micrograph of the 16° C sample deposited at 40° angle of incidence. Examination shows no obvious elongation of grains or any other anisotropy in the contrast of the micrograph image. Fine grained polycrystalline films, however, do not yield high resolution images in conventional transmission electron microscopes and therefore one might expect only very large directional structure differences to be apparent. The average grain size measures to be approximately 300 Å, very nearly the same as for the 15° C normal incidence sample.

The microstructure of the 30° angle of incidence sample made at 195° C is shown in Figure 18. The significant feature regarding this micrograph is that the size of the large crystals is not nearly so big as the ones that the normal incidence 195° C and 225° C samples possess. Consequently the average grain size for 30° incidence at 195° C is somewhat smaller than the average grain size for normal incidence at the same temperature.

In summary the average grain size of evaporated nickel films has been observed to increase significantly with increased substrate temperature. Further, no anisotropies could be observed in the microstructure of films deposited at incidence angles up to 40°.

Figure 16. Selected Area Diffraction Pattern from a
20000 Å Diameter Circular Area

Figure 17. Bright Field Micrograph of 16°C , 40°
Incidence Film of 1750 Å Thickness

Figure 18. Bright Field Micrograph of 195°C , 30°
Incidence Film of 1750 Å Thickness

IV. CONCLUSIONS

The results of Part III show in every case except one that the value of instantaneous stress found from the linear portion of each force per unit width versus thickness curve corresponds in a one to one fashion with the average grain size for the respective sample. The correspondence is that larger grain sizes are associated with smaller values of stress. The exception is that the 40° angle of incidence 16° C run, which exhibits stress with about one half the magnitude of the comparable normal incidence run, does not exhibit any larger grain size. In the case of the 30° angle of incidence 195° C run, where the grain size is smaller than the corresponding normal incidence run, the linear portion of the force per unit width versus thickness has slope which does not appear very different from its normal incidence counterpart; yet one sees that the grain size correspondence is maintained in the sense that the entire force per unit width behavior matches more closely to that of the 150° C normal incidence run, whose grain size is more nearly equal to the one in question. On the basis of these results it is believed that a grain boundary relaxation is responsible for the constant intrinsic stress that is observed. A separate phenomenon dominant during the first part of film growth at high substrate temperatures is believed to be

responsible for the compressive stresses observed and this will be discussed later. The dependence of stress upon the deposition angle will also be discussed.

In the grain boundary relaxation model the crystallites in a growing film are envisioned to grow together from a stage where they are isolated, randomly oriented clumps. The average clump diameter at which the growing together occurs is estimated to be less than $50 \text{ \AA}$ for the nickel films in this experiment. Up to this point of growth the bending force per unit width observed is governed by the changing surface tension of growing clumps that are constrained from expansion by their adhesion to the substrate. The linear force per unit width versus thickness for the normal incidence -42° C run (Figure 4) very nearly intersects the origin and indicates that the initial surface tension forces were not large enough to be observed, particularly at the thicknesses over which the bending force was measured.

At the point the clumps grow together the interatomic forces exerted across the gap between two clump boundaries produce an elastic relaxation of the boundaries toward each other. This relaxation is constrained by the adhesion of the clumps to the substrate. Consequently, the change in energy of the free surface of a clump becoming a grain boundary goes into volume strain energy in the clump because of the constraint of the substrate. Vertical growth of the film proceeds with the addition

of layers of atoms to the tops of growing grains, and each layer suffers elastic strain in its plane by the relaxation produced at the grain boundary wall. In this way the stress in each layer is constant.

Since the final grain sizes observed in this experiment are considerably bigger than the probable size of the clumps when they grow together, apparently an annealing or recrystallization takes place among clumps to produce much larger grains. The atomic rearrangement during this process is three-dimensional and eliminates the strains produced by the former clump boundaries. The total energy that goes into volume strain energy in the clump equals the grain boundary surface area times the change in energy per unit area that a free surface experiences by becoming a grain boundary. This latter energy does not depend upon the clump volume. Since the surface to volume ratio increases with decreasing particle size, the volume strain energy density will become very high in small clumps when grain boundary relaxation occurs. This high strain energy density drives the recrystallization of clumps into larger grains because the strain energy is reduced through the elimination of grain boundaries and their associated strains by the net shrinkage of the dimension normal to the plane of the film. The latter can occur during recrystallization because the growing surface of the film is unconstrained. Since adhesion to the substrate is maintained during the develop-

ment of the final grain sizes, the elastic strain left in the grain will be determined by the forces at the grain boundary wall of the final grain. At higher substrate temperatures the recrystallization is more complete, resulting in larger final grain sizes.

In all, the intrinsic stress is determined only by the final grain size, the surface free energy of nickel, γ_{sv} , the average grain boundary energy, $\bar{\gamma}_{gb}$, and Young's modulus. It does not matter whether the initial clumps contain many small crystallites as observed by Grigson and Heritage, or whether clumps recrystallize into larger grains upon growing together to form a continuous film. The process by which the final grains are formed will always reduce the strain by allowing shrinkage of the grain dimension normal to the film plane. Since the forces at the grain boundary of the final grain still operate and adhesion to the substrate is always maintained, the strain in the final grain will be that which is calculated from the relaxation due to the grain boundary forces at boundary of the final grain. The details of the derivation of the calculation of the intrinsic stress are given in Appendix III.

The resulting stress values are calculated by using the measured grain sizes in Figure 15 and constructing the grain separation potential $U(r)$ for nickel. Figure 19 shows the potential used and Figure 20 is the interboundary force associated

Figure 19. Energy Per Unit Area Versus Separation Distance for a Grain Boundary Wall Made From a Perfect Crystal

Figure 20. Force Per Unit Area Versus Separation Distance
Exerted on a Grain Boundary Wall in a Perfect Crystal.

with this potential. Room temperature values for γ_{sv} and $\bar{\gamma}_{gb}$ were found by extrapolating the data from Hayward and Greenough using the value $0.6 \text{ ergs/cm}^2/^{\circ}\text{C}$ for the temperature variation of γ_{sv} .^{24,25} Young's modulus for nickel is $2.1 \times 10^{12} \text{ dynes/cm}^2$ and the value for ν was calculated to be 0.44 from the values of Young's modulus and the shear modulus, $7.3 \times 10^{11} \text{ dynes/cm}^2$. The lattice constant of nickel is $3.5 \text{ \AA}$. These numbers were used together with the average grain diameter, d , for each substrate temperature to find the corresponding value of grain boundary relaxation distance, Δ . The procedure for finding Δ is graphically depicted in Figure 19. For the normal incidence runs between -42°C and 225°C the values of Δ were found to lie between $0.85 \text{ \AA}$ and $0.90 \text{ \AA}$. The variation of Δ is not expected to be large because $U(r)$ in Figure 19 is always steeply rising. The values of intrinsic stress for each grain size were calculated by using the value of Δ in equation 3 of Appendix III. The values calculated for the normal incidence runs are superposed onto the measured results plotted in Figure 8. If one includes the approximately 10% decrease in Young's modulus over the temperature range involved, one would find that the calculated stresses would fall off slightly faster with increasing temperature. The calculated stresses reproduce well the form of the measured stress versus substrate temperature curve, and numerical agreement is within roughly 30%. Development of a more precise

technique for measuring grain sizes will permit a more precise quantitative comparison of calculated grain boundary stresses with measured stresses.

As pointed out in Appendix III, the formation of low energy grain boundaries during film growth will lower the value of $\bar{\gamma}_{gb}$, the average grain boundary energy, but the effect upon lowering $U(0)$, which is -4200 ergs/cm² for nickel, will not be pronounced because changes in $\bar{\gamma}_{gb}$ are on the order of a few hundred ergs per cm². Even less pronounced will be the change in the value of relaxation distance, Δ , because of the steeply rising nature of $U(r)$ in the vicinity where Δ is determined. It is important to note, however, that the formation during film growth of low energy grain boundaries such as coincident lattice boundaries would produce a slight increase in intrinsic stress, assuming the grain size remains constant, because Δ increases. This result is physically reasonable since two growing, merging crystals, which begin to exert forces upon each other across their boundary when the last layer of atoms for each arrives from the vapor, will relax toward each other the greatest amount when the lattices in both crystals are in perfect registry and orientation. From an energy point of view the preceding statement says that the energy change in boundary relaxation becomes elastic strain energy in the grains when they grow together, and the greatest change occurs when the boundary gets eliminated after relaxation.

The grain boundary model that has been presented here is highly successful in calculating the intrinsic stress from basic principles. The models proposed by Klokholm and Berry³ and by Wilcock, et al.,¹ although consistent with the data observed in each respective case, have been unable to quantitatively predict the intrinsic stress that was measured.

The grain boundary model first proposed by Finegan and Hoffman⁶ has been criticized on the basis that it claims that the existence of grain boundaries cause stress.¹ This criticism is inaccurate because the grain boundary model clearly requires a constrained relaxation during growth to produce the stress. On the other hand, the crystallite annealing and grain boundary elimination model proposed by Wilcock, et al. fails to explain why atoms do not fill the former grain boundary gaps when the crystallites anneal into larger grains. In other words, the model does not permit a dimension change normal to the film plane. Further, this model proposes that annealing leads to an increase of volume strain energy, but does not account for the sources of energy. The grain boundary model detailed in this paper explains that the energy of free surface elimination at the grain boundary produces volume strain energy which in turn can drive recrystallization processes. The recrystallization will evolve heat.

The Klokholm and Berry model,³ which proposes a constrained relaxation of film layers when they anneal from an amorphous to crystalline state, also ignores the rearrangement of atoms in the

direction normal to the plane of the layers. The model, in addition, does not consider the microstructure in the final film and does not easily lend itself to quantitative treatment based upon the physical process that it proposes.

Since in each case the force per unit width versus thickness curves eventually increase linearly with increasing thickness, the instantaneous compressive stresses in each sample during the first part of film growth can be characterized by the maximum compressive force per unit width they would produce in the absence of the grain boundary relaxation tensile bending force. This maximum compressive force can be found by the value of force per unit width at zero thickness given by a straight line extrapolation of the linear portion of each force per unit width versus thickness curve. For the normal incidence runs at -42°C , 15°C , 50°C , 99°C , 150°C , 195°C , and 225°C these compressive forces are -0.9 , -1.5 , -5.8 , -3.7 , -4.0 , -6.0 , and -6.3 (in units of 10^4 dynes/cm), respectively. These data indicate a rough, but definite, increase of compression with substrate temperature. Since the possibility that a thermal expansion bending produced these compressive forces was eliminated in this experiment, it was concluded that a thermally activated process was occurring during roughly the first half of film thickness growth.

The measurement of diffusion induced strains in thin films are absent from the literature except for one case, where the bending of a glass substrate measured a diffusion induced film

stress of about 2×10^9 dynes/cm² in a deposited gold-aluminum couple.²⁶ An Arrhenius plot of the rate of stress development yielded an activation energy in agreement with other measurements for the formation of Au₂Al. The significant result of the experiment just mentioned was that the volume changes produced in a composite film by diffusion are large enough to cause stresses comparable with the yield stress of the bulk material.

The possibility that diffusion of nickel into the silicon substrates was responsible for the observed compression in this experiment was ruled out on the following basis. Although nickel rapidly diffuses interstitially in silicon,^{27,28} diffusion will take place up to the solubility limit and stop, where at 200° C the solubility limit is about 10^{10} atoms/cm³.²⁸ Crudely speaking, one needs a concentration of the order of 10^{21} atoms/cm³ to produce 1% strains. Consequently, the diffusion of nickel into silicon at 200° C cannot produce significant volume changes.

If the film-substrate were a true SiO₂ layer, the diffusion constant for nickel into SiO₂ is so low that any volume change from this sort of diffusion is negligible.²⁹

However, low temperature diffusion of Co, Cu,³⁰ and Au³¹ into nickel films has been observed and the mechanism responsible was shown to be grain boundary diffusion.³⁰ In the case of Au into nickel the diffusion was observed to be markedly dependent upon grain size.³¹ The possibility that significant amounts of silicon diffused into the growing nickel films at the

higher substrate temperatures in this experiment was examined.

Metal solute atoms diffuse into nickel with activation energies very close to the self-diffusion activation energy. Mg, Si, Mo, Al, Ti, Mn, and W diffuse through the nickel lattice with activation energies ranging from 56 to 77 kcal/mole.³² The lattice self-diffusion energy for nickel is 66.8 kcal/mole.³³ The grain boundary diffusion of Cu into nickel has an activation energy of 23.5 kcal/mole³⁰ while the grain boundary self-diffusion activation energy is 27.4 kcal/mole.³³ On the basis of this evidence it is reasonable to approximate the grain boundary diffusion constant of silicon into nickel, since no data for it exists, by

$$D \approx 0.01 e^{-\left(\frac{23000 \text{ kcal/mole}}{RT}\right)} \text{ cm}^2/\text{sec} ,$$

where 0.01 cm²/sec is D_0 for grain boundary self-diffusion.³³ At 200° C one obtains $D = 10^{-12}$ cm²/sec. Assuming Ficke's law, one can make a simple calculation of the concentration of silicon that diffuses into a nickel film from a boundary of constant concentration (the film-substrate interface).³⁴ If one takes the number densities of pure silicon and pure nickel to be equal, an approximate expression for the atomic percent concentration of silicon in nickel at the free surface of a film of thickness t after an elapsed time t' is, for t' greater than 10 seconds,

$$1 - \frac{4}{\pi} e^{-\frac{\pi^2 D t'}{4 t^2}}$$

For a 1000 Å thick film at 200° C the concentration of silicon in the grain boundaries would be roughly 40% at the end of 30 seconds. This calculation shows that at 200° C silicon can diffuse along nickel grain boundaries up to the solubility limit in times short compared to the length of a deposition. At 10 atomic percent of silicon the formation of Ni_3Si begins to occur.³⁵ Any lattice diffusion of silicon into the nickel grains is negligible because the volume diffusion activation energy is nearly triple³² the approximate grain boundary diffusion activation energy, resulting in a very small diffusion constant of the order of 10^{-30} cm²/sec.

On the basis of the evidence cited it is concluded that the film compressive stresses observed at higher substrate temperatures are produced by the volume changes in the film due to the grain boundary diffusion of silicon. It is supposed that the diffusion is limited to the initial film thicknesses by the formation of Ni_3Si along the grain boundaries. This, of course, assumes a concentration dependent diffusion constant.

The volume changes in the film and substrate will occur as follows. Assuming that the diffusion of silicon takes place until the local grain boundary concentration is 25% (the atomic percent of silicon in Ni_3Si), then for square-sided grains which are 1000 Å on a side and are 1000 Å thick roughly a monolayer of

silicon from the substrate will be required. Since the substrate is a uniform source of silicon, the average result will be a decrease of the substrate dimension normal to the interface by about one monolayer thickness. For the nickel film, however, the location of silicon in grain boundaries which are normal to the interface will try to produce an increase in the dimensions parallel to the plane of the film. In this way a net compression will result since film adhesion to the substrate constrains this expansion. The 25 atomic percent local grain boundary concentration of silicon in a film with the previously mentioned grain dimensions produces an average silicon concentration of about 0.3 atomic percent. The addition of each silicon atom to the nickel film will produce a volume change, very crudely, of a few tenths of an atomic volume. A few tenths times 0.3% gives strains on the order of 0.01%, which is roughly 10 times lower than the compressive strains observed. However, this calculation is only a very rough approximation which shows that the diffusion induced strain can be significant. The details of grain boundary diffusion of silicon into fine grained polycrystalline nickel films need to be known before a proper estimation of strains can be made.

Increasing initial compressive stresses with increasing substrate temperatures has been reported for platinum films deposited on fused quartz, glass, and silicon.³⁶ The size of the

compression was greatest for silicon. The force per unit width for nickel deposited on nickel substrates at 400° C has been reported and no compression was seen.⁴³ Further measurement of stress in nickel on nickel substrates at elevated substrate temperatures will cast light upon the accuracy of the conclusion that has been stated here.

No firm conclusions regarding the angle of incidence stress can be made based upon the results in this experiment, although the high substrate temperature runs suggest that the accompanying higher mobility leads to stress isotropy. The conclusions of grain boundary relaxation and diffusion hold for the angle of incidence results. The stress decrease with incidence angle increase, however, remains to be explained. The proposal by Gontarz¹⁰ concerning an increased porosity leading to increased grain boundary oxidation is a possible explanation.

In summary, the mechanism for intrinsic stress in vapor deposited nickel films has been shown to be constrained relaxation produced by the forces across grain boundaries. A model based upon the physics of the film growth processes involved has been formulated and stress values calculated from measured grain sizes agreed very well with the measured value. At elevated substrate temperatures it was shown that grain boundary diffusion of silicon into the growing nickel film during initial growth was responsible for observed compressive stresses.

APPENDIX I

Deflection Equation For a Circular Plate Clamped Along an Inner Circumference

One can easily see that a uniformly stressed coating adhering to a plate applies a uniform surface traction to the plate. The applied surface traction is statically equivalent to both a uniform compression (tension) applied to the ends and in the plane of the plate and to a bending moment also applied to the ends of the plate. By Saint Venant's principle the strain of the plate away from the ends will be identical in both instances. Generally the compression is not measured, but rather the bending is observed in order to measure the applied surface traction. In what proceeds, the surface traction will be considered to be biaxial, that is, F_x and F_y will represent the force per unit width applied to the surface of the plate in the x and y directions, respectively. Figure 21 defines the coordinate system with respect to the plate. Note that the coordinate axes are chosen to be the principle axes, that is, the applied forces produce only bending moments and no twisting moments. In the case where the surface tractions are produced by the anisotropic intrinsic stress in a thin film, one has

Figure 21. Coordinate System Affixed to the
Undeflected Thin Plate

$$F_x = \int_0^t \sigma_x dt',$$

$$F_y = \int_0^t \sigma_y dt',$$

where t is the thickness of the film and σ_x and σ_y are the net stress distributions in the film. The net stress is the intrinsic stress minus the elastic relaxation stress which depends upon the mechanical constraints on the plate during formation of the film. For thin films, that is, $t \ll h$, the elastic part of the stress may be neglected independent of substrate constraints.³⁷ The intrinsic stress is called tensile if the surface traction compresses the plate. This definition comes about because the plate applies a tensile stress to the thin film to prevent it from elastically relaxing by shrinking.

The equations for bending are

$$\frac{\partial^2 w}{\partial x^2} = \frac{12}{Eh^3} (M_x - \nu M_y), \quad \dots(1a)$$

$$\frac{\partial^2 w}{\partial y^2} = \frac{12}{Eh^3} (M_y - \nu M_x), \quad \dots(1b)$$

$$\frac{\partial^2 w}{\partial x \partial y} = 0. \quad 38 \quad \dots(1c)$$

E and ν are Young's modulus and Poisson's ratio of the substrate, respectively. M_x and M_y are the moments applied to an

infinitesimally small element of the substrate at (x,y) with volume $h \, dx \, dy$. These moments are simply

$$M_x = F_x \frac{h}{2}, \quad \dots(2a)$$

$$M_y = F_y \frac{h}{2}, \quad \dots(2b)$$

where $h/2$ is just the distance from the point of application of the surface tractions to the neutral plane of the plate. In this case, the neutral plane is defined as the plane for which the bending stress (or strain) is zero. The superpositioning of the attendant uniform compressive stress shifts the plane for which the total stress is zero to a distance $(2/3)h$ away from the surface with the applied tractions. Writing all moments with respect to this zero stress plane, one arrives at slightly different expressions for equations 1 and 2, but the same following expressions:

$$\frac{\partial^2 w}{\partial x^2} = \frac{6}{Eh^2} (F_x - \nu F_y), \quad \dots(3a)$$

$$\frac{\partial^2 w}{\partial y^2} = \frac{6}{Eh^2} (F_y - \nu F_x), \quad \dots(3b)$$

$$\frac{\partial^2 w}{\partial x \partial y} = 0. \quad \dots(3c)$$

This result comes about by virtue of the fact that the attendant uniform compression does not apply any bending moments.

In polar coordinates the bending equations corresponding to equations 1 are

$$\frac{\partial^2 w}{\partial r^2} + v \left(\frac{1}{r} \frac{\partial w}{\partial r} + \frac{1}{r^2} \frac{\partial^2 w}{\partial \theta^2} \right) = \frac{12(1-v^2)}{Eh^3} M_r, \quad \dots (4a)$$

$$\frac{1}{r} \frac{\partial w}{\partial r} + \frac{1}{r^2} \frac{\partial^2 w}{\partial \theta^2} + v \frac{\partial^2 w}{\partial r^2} = \frac{12(1-v^2)}{Eh^3} M_\theta, \quad \dots (4b)$$

$$\frac{1}{r^2} \frac{\partial w}{\partial \theta} - \frac{1}{r} \frac{\partial^2 w}{\partial r \partial \theta} = \frac{12(1+v)}{Eh^3} M_{r\theta} \quad .39 \quad \dots (4c)$$

M_r and M_θ are the moments produced by forces applied in the r and θ directions, respectively, to a plate element of volume $h r d\theta dr$. $M_{r\theta}$ is the applied twisting moment. These moments relate to those referred to the principal axes as follows:

$$M_r = M_x \cos^2 \theta + M_y \sin^2 \theta, \quad \dots (5a)$$

$$M_\theta = M_x \sin^2 \theta + M_y \cos^2 \theta, \quad \dots (5b)$$

$$M_{r\theta} = \frac{1}{2} (M_x - M_y) \sin 2\theta. \quad \dots (5c)$$

If there are any shears on the plate element produced by forces normal to the plane of the plate, then the deflection $w(r, \theta)$

must also satisfy

$$Q_r = \frac{12(1 - \nu^2)}{Eh^3} \frac{\partial}{\partial r} (\Delta w) , \quad \dots(6a)$$

$$Q_\theta = \frac{12(1 - \nu^2)}{Eh^3} \frac{1}{r} \frac{\partial}{\partial \theta} (\Delta w) , \quad \dots(6b)$$

where

$$\Delta = \frac{\partial^2}{\partial r^2} = \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} .$$

Q_r is the shear applied to the face of the plate element that is perpendicular to the r direction and Q_θ is the shear applied to the face that is perpendicular to the θ direction.

If the only applied forces on the plate are the biaxial surface tractions mentioned previously and the plate is otherwise free, that is, there are no other applied shears or moments, then the solution to equations 4 is

$$w_f = \alpha r^2 \cos 2\theta + \beta r^2 , \quad \dots(7a)$$

where

$$\alpha = \frac{3(1 + \nu)}{2 Eh^2} (F_x - F_y) , \quad \dots(7b)$$

$$\beta = \frac{3(1 + \nu)}{2 E h^2} (F_x + F_y) . \quad \dots(7c)$$

Consequently, the plate bends to a familiar elliptic paraboloid. If the outer radius of the plate is a and if one clamps the plate along inner radius b , then the clamp applies those moments and shears to the plate that are necessary to change the deflection and the slope of the deflection to zero at $r = b$. Therefore, the final deflection of the clamped plate with thin film on it is

$$w = w_f + w_c , \quad \dots(8)$$

where w_c is the deflection of the plate due to the forces applied by the clamp alone. w satisfies the following boundary conditions:

$$w_{r=b} = 0 , \quad \dots(9a)$$

$$\left(\frac{\partial w}{\partial r}\right)_{r=b} = 0 , \quad \dots(9b)$$

The solution w_c alone must satisfy the condition for a free edge at $r = a$.

$$M_r(w_c)_{r=a} = 0 ,$$

$$(Q_r(w_c) - \frac{1}{r} \frac{\partial}{\partial \theta} M_{r\theta}(w_c))_{r=a} = 0 \quad ^{40}$$

When both shears and moments are present, the general solution to equations 4 and 6 also satisfies a fourth order differential equation.⁴⁰ Since w_f varies azimuthally as $\cos 2\theta$, w_c will vary only as $\cos 2\theta$; hence, in the general solution⁴⁰ only the $\cos 2\theta$ term is kept and terms that are a function of r alone are kept.

$$w_c = A_0 + B_0 r^2 + C_0 \log r + D_0 r^2 \log r + (A_2 r^2 + B_2 r^{-2} + C_2 r^4 + D_2) \cos 2\theta \quad \dots(10)$$

Enforcing the boundary conditions results in solving two sets of four simultaneous equations for four unknowns in each set. The resulting solution is

$$w = \beta [(1 - A)(r^2 - b^2) - B b^2 \log(\frac{r}{b})] + \alpha [(1 + C) r^2 + D b^2 (\frac{b}{r})^2 + F b^2 (\frac{r}{b})^4 + G b^2] \cos 2\theta \quad \dots(11)$$

where

$$A = \frac{U}{U + V\rho^2} \quad ,$$

$$B = \frac{2 V^2}{U + V^2} ,$$

$$C = \frac{-4 Q + 3 P \rho^{-2} - R \rho^{-6}}{H} ,$$

$$D = \frac{R \rho^2 + P \rho^{-2}}{H} ,$$

$$F = \frac{2 P \rho^{-2} - 2 P \rho^{-4}}{H} ,$$

$$G = \frac{2 P \rho^{-2} - 2 P \rho^{-4}}{H} ,$$

$$H = 4 Q + R \rho^2 - 6 P \rho^{-2} + 4 P \rho^{-4} + R \rho^{-6} ,$$

$$P = (1 - v)^2 ,$$

$$Q = 3 + v^2 ,$$

$$R = (3 + v)(1 - v) ,$$

$$U = 1 - v ,$$

$$V = 1 + v ,$$

$$\rho = \frac{a}{b} .$$

Note that the solution is of the form

$$\alpha g(r) \cos 2\theta + \beta f(r),$$

which is similar to the form of the free plate deflection. Figure 22 shows the anisotropic bending of the same substrate both for the free plate and centrally clamped configurations.

It is also interesting to note the solution to the problem where the plate is instead clamped around its outer circumference at $r = b$. It is easy to show that w_c is just $-w_f$, and there is no deflection of the plate at all. In this case the clamp applies opposite bending moments that precisely cancel those applied by the surface tractions. Furthermore, one can see that the clamp will prevent any compressive or tensile strain in the plane of the plate. If this circular plate now has a concentric hole cut out with radius $r = a$, the plate will deflect and the solution will be that given by equation 11, except the roles of a and b are interchanged. For this configuration the overall bending produced by the same surface tractions is, as one would expect, smaller than the bending one obtains with the center-clamped configuration.

A last configuration that is worth mentioning is the case of a free circular plate with a thin film deposited over the central circular area of the plate. The solution to this problem shows that as the outer diameter of the plate becomes very large

Figure 22. Bending of the Same Plate for Both the Free Centrally Clamped Geometries

the bending of the plate in the region of the film does not decrease significantly.

APPENDIX II

The Interfacial Stresses between Film and Substrate

In order to understand both quantitatively and qualitatively the manner in which a stressed thin film transmits forces to its substrate a continuum elasticity approach is taken. If a thin film of thickness t is deposited on a square substrate with side length L , and a very narrow cross-sectional slab of length L is sliced from the coated substrate, the side view of the slab is one of a rectangular plate of length L and height t attached along its long edge to what shall be assumed as a semi-infinite, rigid medium. This last assumption is very reasonable since the substrate thickness is usually at least 1000 times thicker than the film.

Bending plate experiments show that the condensed thin film possesses a large intrinsic stress, σ_i , that lies in the plane of the film, is isotropic, is nearly uniform throughout the thickness, and is uniform over most of the area of the film. Consequently, a slab of thin film attached to its substrate, depicted in Figure 23, is under a state of stress nearly identical to that of a rectangular plate that is clamped along an edge and that has undergone thermal expansion. The latter situation has been treated

Figure 23. Cross-sectional View of a Thin Film Attached
to a Rigid Substrate

approximately by Aleck.⁴¹ According to Aleck the problem is first converted to one of boundary tractions. The film is detached from the substrate and allowed to relax. To bring it back into a uniform state of intrinsic stress one imagines applying a uniform normal stress of magnitude σ_i to the ends of the film as shown at the top of Figure 24. Next one imagines attaching the film back to the substrate and applying to the ends a uniform compressive stress σ_r , which in this case is equal in magnitude to σ_i because at the edge of the film there are no net applied normal boundary tractions. Consequently, one arrives back at the original situation which is depicted at the bottom of Figure 24 with $\sigma_i - \sigma_r = 0$. The problem is therefore one of finding the state of stress for the situation depicted at the middle of Figure 24 and adding to it the state of stress depicted at the top of Figure 24.

Aleck solved the case for the stresses along the film-substrate interface for $L \gg t$. The curves plotted in Figure 25 are based on Aleck's result. The origin is at the edge of the film. The pertinent features are (1) σ_x is just equal to σ_i until one gets within a distance t of the edge, (2) a large shear ($>2\sigma_i$) lies within a distance t of the edge, (3) a concentrated stress normal to the interface of magnitude of about $10\sigma_i$ lies at the edge, and (4) there exists no nonzero shear stresses or stresses normal to the interface once one gets a distance slightly greater than t from the edge. Since in films

Figure 24. The Problem of a Thin Film Under Uniform
Intrinsic Stress Constrained to a Rigid
Substrate

Figure 25. The Interfacial Stresses Near the Free Edge of a Thin Film Whose Length is Very Much Greater Than its Thickness

that possess high intrinsic stress σ_i is about 10^{10} dynes per cm^2 , one concludes that film adhesion failure can occur at sharp edges of the film or sharp edges that are produced by scratching the film. This phenomenon is indeed one that is observed. Additionally, no such failure is expected at locations interior to the film that are more than a film thickness away from any edge.

If one wishes to push the assumption of continuum elasticity and the merits of the problem just considered down to further microscopic limits, then one can imagine that the object shown in Figure 23 is a grain in a fine-grained polycrystalline film and a boundary stress σ_i is produced by the interatomic forces across a grain boundary when grains grow together. The boundary stress σ_r shown at the middle of Figure 24 is equal to $-\sigma_i$ and the top of Figure 24 is absent from the problem.

The curves plotted in Figure 26 are the interfacial stresses calculated by extending Aleck's results. The origin is placed at the center of the grain and $L = t$. Again one can count on large forces near the edge of the grain if σ_i is appreciable. Since σ_r is $-\sigma_i$, the interfacial normal stress σ_y acts in a direction opposing film-substrate cleavage. It is therefore supposed that the grain boundary forces lead to large local shear deformations that can possibly cause adhesion failure at the film-substrate interface. The variation of the elastic stress σ_x with the distance from the substrate is shown in Figure 27. As

Figure 26. The Interfacial Stresses for a Grain Whose Length Equals its Thickness and Has a Uniform Stress Applied to its Boundaries Normal to the Substrate Plane

Figure 27. The Distribution of Stress Parallel to the Substrate Plane Through the Film Thickness in a Grain Whose Length Equals its Thickness

one moves from the boundary toward the center of the grain the σ_x distribution changes continuously from $\sigma_x = \sigma_i$ to the one shown for the center. One may then conclude that the elastic stress within a grain differs significantly from the boundary stress only near the substrate, and the assumption that the applied boundary stress σ_i produces a uniform stress within the grain is a reasonable one. The grain boundary stress σ_i can therefore produce a uniform intrinsic stress in the film.

APPENDIX III

The Grain Boundary Model for Intrinsic Stress

The following is basically the model as first proposed by Finegan and Hoffman.⁶ This treatment considers the model in slightly more detail and corrects the expression for finding the grain boundary relaxation distance.

The crystallites in a growing film are envisioned to grow as isolated, randomly oriented clumps until they grow together at some particular average thickness. It might be true that each clump consists of more than one crystallite, but in any event attention is focussed upon the boundary of the merging clumps. The growing together process is thought of in two steps. First, the arriving atoms from the vapor beam enlarge the clumps until between two adjacent clumps there exists a gap, the spacing between atoms across the gap having equally probable values between a and $2a$, where a is the bulk lattice spacing. Second, the interatomic forces acting across the gap cause a constrained relaxation such that the values of gap spacings decrease by an amount Δ . Now the interatomic distances in the gap range uniformly from $a - \Delta$ to $2a - \Delta$. The relaxation is constrained because the clumps adhere to the substrate and the average force

per unit area of boundary after relaxation must just equal the average elastic stress produced throughout the volume of the clump, $\frac{E}{1-\nu} \frac{\Delta}{d}$, where d is the average clump or grain diameter, E is Young's modulus, and ν is Poisson's ratio.

It is probable, depending upon substrate temperature, that clumps may anneal upon growing together and form larger final grain sizes. It is envisioned that during annealing there is sufficient three-dimensional atomic rearrangement to eliminate any strains due to the former gaps. Consequently, one is left considering the relaxation at the final grain boundary.

The curve of the interatomic force per unit area of grain boundary versus the difference in atomic spacing from the bulk lattice spacing is shown in Figure 20. This force is taken to be elastic up to 10% strains from the bulk spacing. The slope of the curve from $-0.1a$ to $0.1a$ is E/a . Above $0.1a$ the force peaks and rapidly decreases until it is zero at $r = a$. For compressive values of $r \leq -0.1a$ the force is nonlinear and goes at least as r^2 .

The curve shown in Figure 19 is the energy per unit area of grain boundary and is related to the force in Figure 20 by

$$U(r) = \int_{\infty}^r F(r') dr' .$$

The energy is essentially zero at $r = a$, is parabolic for

- $.1a \leq r \leq .1a$, and rises as r^3 for $r \leq -0.1a$.

The energy minimum $U(0)$ is determined as follows. If one cleaves a perfect crystal in a vacuum and thereby creates two new surfaces each of area A , then the energy of the crystal has been increased by

$$2 \Delta G_{sv} = 2 \gamma_{sv} A,$$

where ΔG_{sv} is the Gibb's free energy of the solid-vacuum interface and γ_{sv} is the surface tension of the same interface. If on the other hand, one starts with a crystal having a grain boundary of area A and the atoms on each side of the boundary are rearranged to eliminate the boundary and achieve a perfect crystal, then the energy of the crystal is lowered by an amount

$$\Delta G_{gb} = \gamma_{gb} A.$$

Consequently, when two isolated crystals are brought together to form a grain boundary, their energy per unit area of boundary is lowered an amount

$$2 \gamma_{sv} - \gamma_{gb}$$

γ_{gb} is determined by the misorientation and disregistry of the interface. If all possible types of grain boundaries occur equally among the merging clumps, then

$$U(0) = -2 \gamma_{sv} + \overline{\gamma_{gb}} ,$$

where $\overline{\gamma_{gb}}$ is the average grain boundary energy. In principle $\overline{\gamma_{gb}}$ could be found by the grain boundary energy averaged over all possible grain orientations. The persistence of certain types of boundaries over others can be accounted for by proper weighting in the averaging. The frequent occurrence of low angle and coherent grain boundaries can only lower the value of $\overline{\gamma_{gb}}$ from its value for random orientations. Since

$$\gamma_{gb} \text{ (high angles)} \sim \frac{1}{3} \gamma_{sv} \quad 42$$

for most metals, the more than random occurrence of low energy grain boundaries will not have a pronounced effect on lowering the value of $U(0)$.

Given both curves $F(r)$ and $U(r)$, there are two ways of looking at the problem of solving for Δ . The first approach involves equating forces. Before relaxation is allowed to occur, the total force per unit area acting on the grain boundary is

$$\overline{F} = \frac{1}{a} \int_0^a F(r) dr = \frac{1}{a} [U(a) - U(0)] = -\frac{1}{a} U(0) ,$$

because $U(a) = 0$. One writes this expression because the total force is just the sum of the force acting at each separation r

times the frequency of occurrence of r , which is dr/a . If one now allows constrained relaxation, the net force per unit area of grain boundary becomes

$$\bar{F}' = \frac{1}{a} \int_{-\Delta}^{a-\Delta} F(r) dr = \frac{1}{a} [U(a-\Delta) - U(-\Delta)] .$$

This force is in equilibrium with the elastic stress in the volume of the grain.

$$\frac{1}{a} [U(a-\Delta) - U(-\Delta)] = \frac{E}{1-\nu} \frac{\Delta}{d} . \quad \dots(1)$$

Knowing the form of $U(r)$ permits solution of equation 1 for Δ .

From an energy point of view one may write the total energy per unit area of grain boundary after the boundary has relaxed an amount Δ .

$$U(\Delta) = \frac{1}{a} \int_{-\Delta}^{a-\Delta} U(r) dr + \frac{E\Delta^2}{2(1-\nu)d} .$$

Again each value of $U(r)$ occurs equally over the range $-\Delta$ to $a - \Delta$. The second term on the right-hand side of the above equation is the elastic energy produced in the volume of the grain. The equilibrium energy will occur when the proper choice of the value of Δ makes $U(\Delta)$ minimum. If $\frac{d}{d\Delta} U(\Delta) = 0$, then equation 1 results.

Since the growing clumps are small particles, the effect of surface tension is significant and must be considered. The strain in a new shell of atoms at radius r in a growing hemispherical clump is

$$\epsilon_r = \frac{\gamma \pi r}{2} = \frac{2 \gamma}{E r} \cdot \frac{\pi r}{2}$$

γ is the surface tension for the film-vacuum interface. A more nearly correct expression would include the film-substrate interface surface tension. When this shell of atoms has become buried by additional layers of atoms out to radius r' , the change in the strain in the shell at radius r is

$$\Delta \epsilon(r) = \frac{2 \gamma}{E r} - \frac{2 \gamma}{E r'}$$

This change, of course, is constrained by the compressive stress that the rigid substrate applies if the clump is adherent. For shells at radii less than some radius r_0 , the compressive stress will exceed the ideal shear strength, $G/30$, when the clump grows. Consequently, the radius r_0 for which the atoms within begin to adhere to the substrate is given by

$$\frac{2 \gamma}{r_0} = \frac{G}{30} = \frac{1}{30} \frac{E}{2(1 + \nu)}$$

The clumps merge at radius $d'/2$ and the distribution of strains will be

$$\Delta\epsilon(r) = \begin{cases} \frac{2\gamma}{E r_0} - \frac{4\gamma}{E d'}, & r \leq r_0 \\ \frac{2\gamma}{E r} - \frac{4\gamma}{E d'}, & r_0 \leq r \leq d'/2 \end{cases}$$

The average compressive strain in the constrained clumps is

$$\bar{\epsilon} = \frac{2}{d'} \int_0^{d'/2} \Delta\epsilon(r) dr = \frac{4\gamma}{E d'} \ln \left(\frac{d'}{2 r_0} \right).$$

The net stress in the clumps at merger should then be

$$\sigma_i = \frac{E}{1-\nu} \left[\frac{\Delta}{d'} - \frac{4\gamma}{E d'} \ln \left(\frac{d'}{2 r_0} \right) \right]. \quad \dots(2)$$

Finegan and Hoffman accounted for the surface tension effect in an equivalent fashion. They reasoned that the relaxation distance is really $\Delta - 2u$, where u is the displacement of the last shell of atoms if it were free to expand from its position in the constrained clump. Thus

$$u = \int_0^{d'/2} \frac{du}{dr} dr = \int_0^{d'/2} \Delta\epsilon(r) dr,$$

and equation 2 results.

The average diameter of clumps when they grow together depends upon deposition rate and substrate temperature. For the nickel films deposited in this experiment it is probable that this diameter is less than $50 \text{ \AA}$. The evidence is, however, that final grain sizes in such films are greater than $100 \text{ \AA}$. One must then conclude that the initial clumps anneal into final larger crystallites as suggested by Grigson, et al.² It would be reasonable to suppose that the annealing relieves the initial surface tension stress just calculated. The exact details of the growing together process will determine how the value of stress given by equation 2 changes.

In any event, once the final grain size is established (at about $100 \text{ \AA}$ thickness for nickel) the grains are envisioned to grow in a columnar fashion. In the simple picture presented here, the vertical growth of each grain occurs by the addition of shells of atoms with lateral dimension d in the plane of the film, where d is the final grain size. Since d does not increase with the addition of more shells, the strain in the shell does not change in the plane of the film except for the grain boundary relaxation. Consequently, the instantaneous stress in each additional layer of atoms for thicknesses greater than $100 \text{ \AA}$ is

$$\sigma_i = \frac{E}{1 - \nu} \frac{\Delta}{d} \quad \dots(3)$$

The bending force per unit width is

$$F(t) = \int_0^t \sigma_i dt = \frac{E}{1-\nu} \frac{\Delta}{d} (t - 100 \overset{\circ}{\text{A}}) + F(100 \overset{\circ}{\text{A}}) + \gamma + \gamma' \quad \dots(4)$$

As discussed previously, the value of $F(100\overset{\circ}{\text{A}})$ will depend upon the details of the initial growth. γ is the film-vacuum surface tension. The $\gamma + \gamma'$ term comes from the fact that these surface tensions are surface stresses that exist at the interfaces. In fact the bending force per unit width that is measured in a bending plate measurement will be equal to the first two terms in equation 4 plus the constant $\gamma + \gamma' - \gamma''$, where γ'' is the surface tension of the substrate surface opposite the film side. In the case of nickel deposited on silicon, γ is 2600 dynes/cm and one can approximately take γ' equal to γ'' . The magnitude of surface tension produced force per unit width is approximately 0.3×10^4 dynes/cm and will contribute along with the term $F(100\overset{\circ}{\text{A}})$ a small offset of the force per width versus thickness curves from the origin.

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