MECHANICAL PROPERTIES OF THIN FILMS OF GOLD AND SILVER*

J. W. Beams
University of Virginia
Charlottesville, Virginia

In 1933 Orowan (1933) reported that very thin sheets of mica exhibited abnormally high tensile strengths. A few years ago we (Beams et al., 1952, 1955; Beams, 1956) observed a marked increase in the tensile strength of polycrystalline films of silver and gold when their thicknesses were reduced below about 2×10^{-5} cm. Also D. W. Pashley (1959) has found very thin single crystal gold films to have relatively large tensile strengths. In our first experiments the thin silver films were electrodeposited uniformly on the complete cylindrical surfaces of small steel rotors in such a way as to reduce the adhesion to a small value. The rotors were then spun in a vacuum until the films were ruptured. From the size and speed of the rotor, both the tensile strengths and adhesions of the films were determined. With this centrifugal method a simple stress pattern is applied and stress concentrations with resultant tearing is avoided. On the other hand, when the film thicknesses were reduced below 3×10^{-6} cm the adhesion became erratic and the measurements in this range were not reliable. Consequently it was desirable to carry out the tensile strength measurements by an independent method. Because metal films of 10^{-5} cm thickness and less are fragile and difficult to stress by ordinary pulling methods, a so-called "bulge" method was used to apply the stress. Preliminary results with this method (Ford et al., 1956; Kraft et al., 1958) gave essentially the same phenomena both for gold and for silver films as was observed for silver with the centrifugal method. The purpose of this paper is to describe more recent measurements of tensile strengths of thin polycrystalline films of silver and gold and of single crystal gold films. The major part of the work to be described was carried out by my collaborators and I am acting primarily as a reporter.

Most of the polycrystalline films of silver and of gold were deposited upon plastic film substrates by evaporation. The plastic films were made by dropping a small amount of Zapon on a clean water surface. This spreads immediately into a very thin film which hardens after a minute or two. The film is removed from the water in such a way that it is folded into two films in intimate contact. This double film is practically free of minute holes since the probability of a hole in one film falling on top of a hole in the other is very small. These films are then carefully cemented over the polished ends of a copper tube with a very thin coating of cement (Evanol) which is insoluble in amyl acetate. They are then placed in a standard evaporating unit and covered with the metal film to the desired thickness. In all cases the air pressure in the evaporator was less than 10^{-5} mm of Hg at the beginning of the evaporation process. After removal from the evaporating unit each Zapon plastic substrate was dissolved by amyl acetate leaving the metallic film covering the end of the copper tube. Air pressure was then applied to one side of the film and the height and shape of the "bulge" was measured by a microscope or by light interference methods. The thickness of the films was determined by a weighing technique which was calibrated by optical interference. If a is the inside radius of the copper tube, D the height of the center of the bulged film above the end of the

---

*Supported by the Office of Ordnance Research, U.S. Army.

Offprints From
Neugebauer, Newkirk and Vermilyea
STRUCTURE AND PROPERTIES OF THIN FILMS
Published by
John Wiley & Sons, Inc., 1959

copper tube, h the thickness of the film, p the difference in air pressure on the two sides of the film, then the tension T at the top of the bulge is given approximately by the relation $T = pa^2/4hD$ and the strain ϵ is given roughly as $\epsilon = 2/3\, D^2/a^2$. This approximate theory assumes that the bulged film is a hemispherical cap and that the film initially was in a plane across the end of the tube when the tension T was zero. Professor Cabrera has shown that if the tension is T_0 when D = 0, then the approximate theory gives

$$T = T_0 + \frac{2}{3}\,\frac{E}{1-v}\,\frac{D^2}{a^2} \tag{1}$$

and

$$p = 4\,\frac{h}{a}\,\frac{D}{a}\left(T_0 + \frac{2}{3}\,\frac{E}{1-v}\,\frac{D^2}{a^2}\right) \tag{2}$$

where E is Young's Modulus and v is Poisson's ratio. A more exact theory, also worked out by Professor N. Cabrera, gives

$$p = 4\,\frac{h}{a}\,\frac{D}{a}\left[T_0 + \frac{1}{4}\,\frac{(5-v)E}{1-v}\,\frac{D^2}{a^2} + \frac{(13-7v)E^2}{288(1-v)T_0}\,\frac{D^4}{a^4}\right] \tag{3}$$

Figure 1 shows a typical plot of the pressure p applied to the film versus the observed height D of the bulged hemispherical cap for a typical film of gold. The

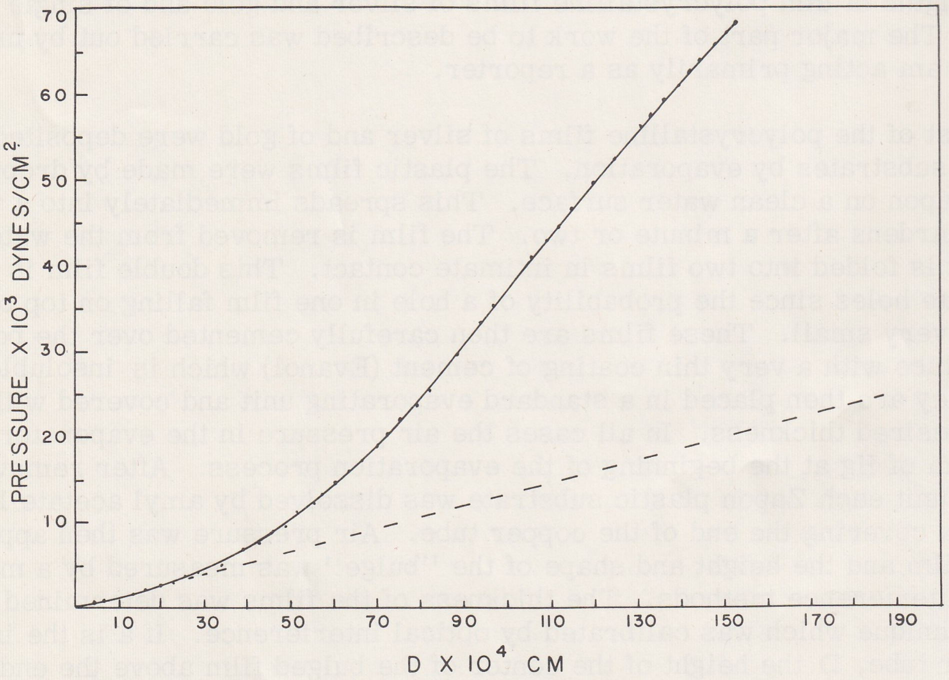

Fig. 1 Air pressure versus observed height D of the bulged hemispherical cap for typical gold films.

thickness h of this particular film was 0.66×10^{-5} cm. The same kind of curves were found for silver. These data were obtained by D.E. Kraft, H.H. Pattillo and T.P. Strider. It will be observed that the curve starts from zero and follows almost a straight line for a number of points before starting upward. This approximately straight line region may be accounted for if it is assumed that the film is under an initial tension T_0 and that the film deforms elastically in this region since D^3/a^3 is small in comparison to D/a. From the slope of this dotted line T_0 can be estimated. In most of the polycrystalline films evaporated on Zapon substrates the initial tension varied from a few tenths to a few times 10^9 dynes/cm^2. Figure 2 gives a plot of the difference in pressure between the solid curve and the dotted line in Fig. 1, versus D^3/a^3. It will be noted that this curve also initially follows a straight (dotted) line before bending downward. Since the approximate theory, Eq. (2), which is probably as accurate as the data, contains only two terms and since the higher terms in Eq. (3) are small and positive, the region where the curve of Fig. 2 deviates from the straight line indicates that plastic flow is taking place. It also indicates that the material essentially deforms elastically up to this region. From the slope of the dotted line in Fig. 2, Young's Modulus E for the film may be computed. Figure 3 shows the stress versus the strain in the film calculated from the data of Fig. 1 and Fig. 2. It is interesting to note that the initial tension in the film was approximately 10^9 dynes/cm^2 and that plastic flow did not become appreciable at least until the stress reached almost 3×10^9 dynes/cm^2. The film ruptured at about 3.8×10^9 dynes/cm^2, so considerable plastic flow and strain hardening occurred. In order to determine the possible influence of the stress pattern, a number of gold and silver films were bulged through a rectangular hole 3 mm wide and 15 mm long instead of the circular holes used in Figs. 1, 2, and 3. The data were very similar to those obtained with the circular hole. Figure 4 gives the tensile or breaking strength of silver films versus thickness of the films and Fig. 5 gives the same data for the gold films.

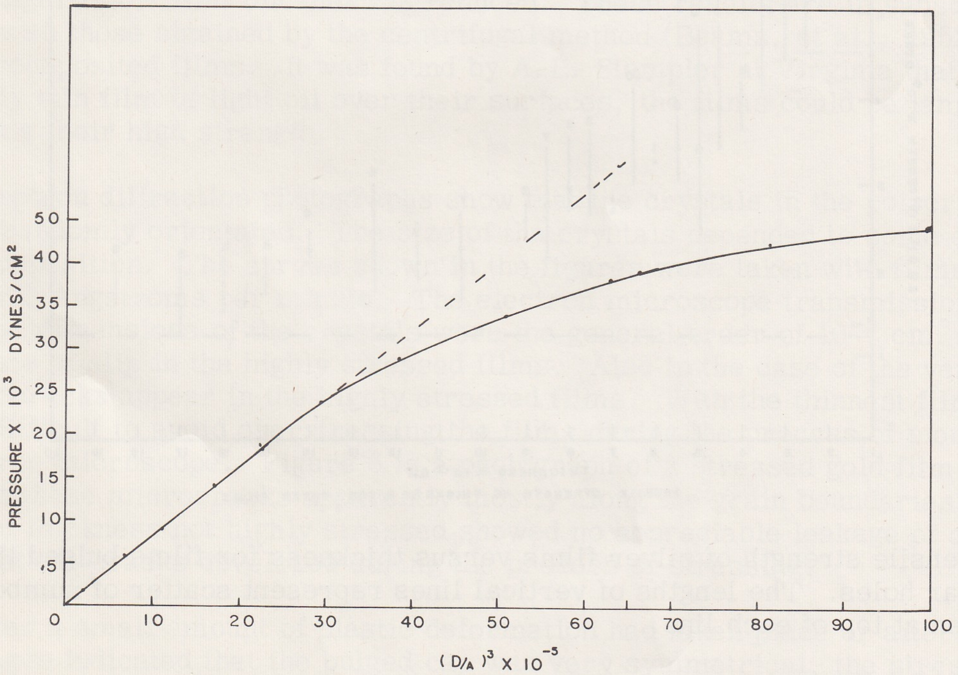

Fig. 2 Difference in pressure between straight line and curve of Fig. 1 versus D^3/a^3.

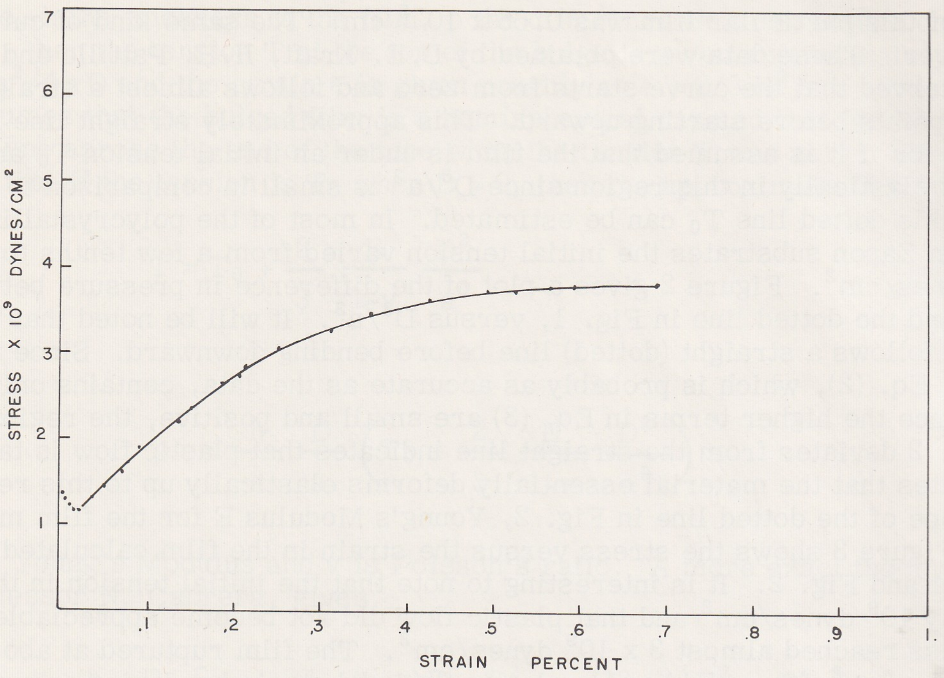

Fig. 3 Stress versus strain curve calculated from data of Fig. 1. The film thickness was 660 A.

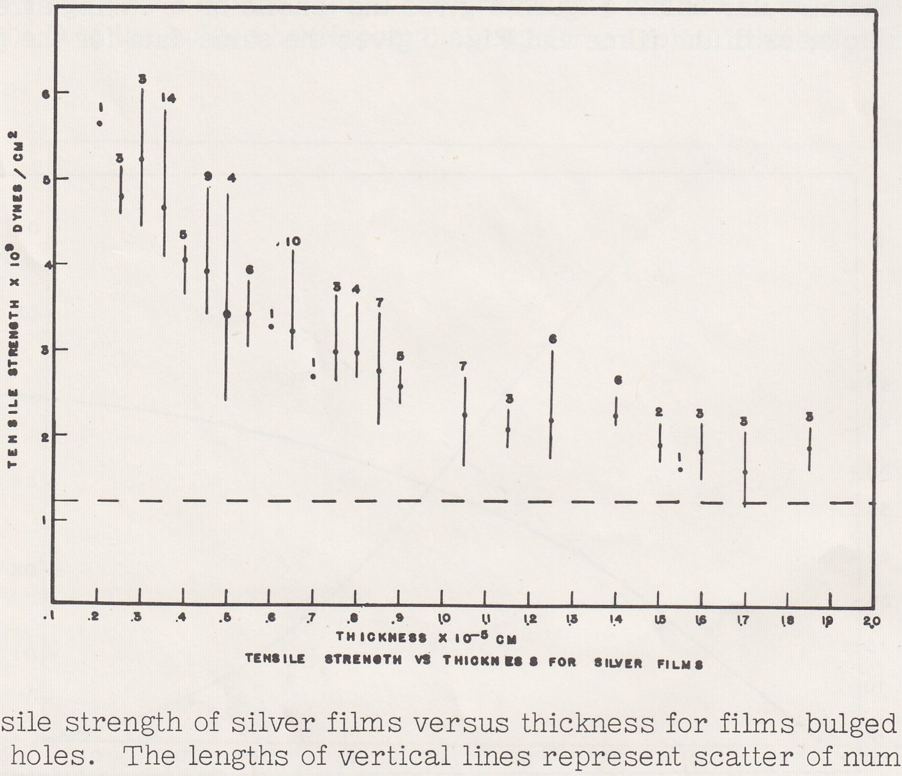

Fig. 4 Tensile strength of silver films versus thickness for films bulged through rectangular holes. The lengths of vertical lines represent scatter of number of films given at top of each line.

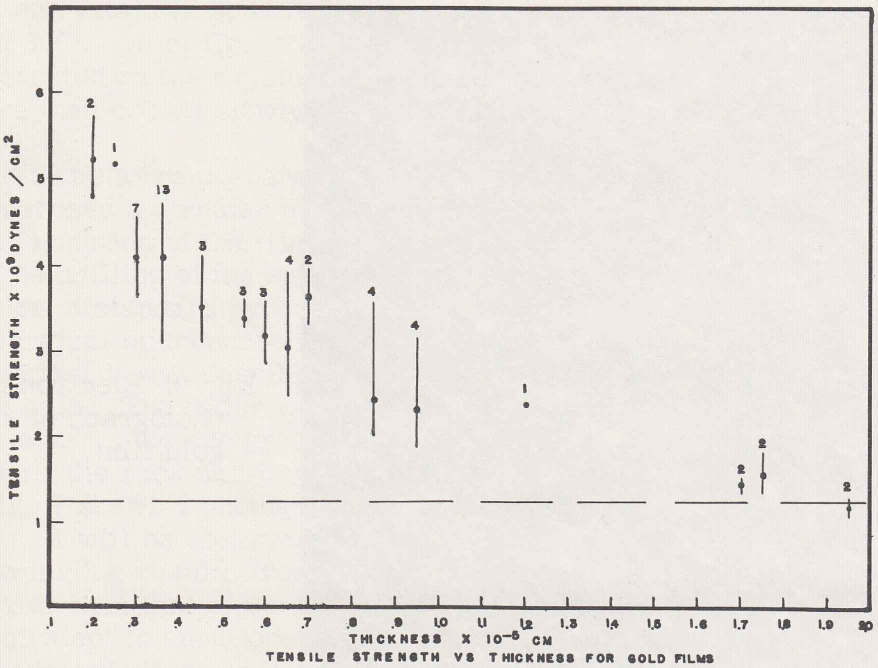

Fig. 5 Tensile strength versus thickness for gold films bulged through rectangular holes. The lengths of vertical lines represent scatter of the number of films given at top of each line.

These films were bulged through the rectangular holes but the same kind of results were obtained with the circular holes. It will be observed that there is a marked increase of tensile strength as the film thickness is reduced. These results are in substantial agreement with those obtained by the centrifugal method (Beams, et al., 1952, 1955) using electrodeposited films. It was found by A. L. Stampler at Virginia that by spreading an extremely thin film of light oil over their surfaces, the films could be laminated without losing their high strength.

Electron diffraction photographs show that the crystals in the polycrystalline films were randomly orientated. The size of the crystals depended to some extent upon the rate of deposition. The curves shown in the figures were taken with films deposited at roughly 100 Angstroms per minute. The electron microscope transmission pictures show that the dimensions of the crystals were the general order of 10^{-5} cm. The crystals show evidence of slip in the highly stressed films. Also in the case of the very thin films small microcracks appear in the highly stressed films. With the thinnest films, it is extremely difficult to avoid overstressing the films during the process of mounting them in the electron microscope. Figure 6 is a photograph of a stressed gold film 260 A thick which shows these microcracks apparently mostly along the grain boundaries. Films of this order of thickness not highly stressed showed no appreciable leakage of air which indicated that the cracks developed during the process of stressing.

After a small amount of plastic deformation had taken place or after the interference fringes indicated that the bulged cap was very symmetrical, the stress was reduced by a small amount and the resulting change in strain measured. This gave the

Fig. 6 Electron microscope photograph of stressed 260 A gold film. 63,000X

Young's Modulus. The data indicate that Young's Modulus is increased in the very thin films. However, the reliability of this conclusion possibly may be in question because of the uncertainties in the strain determinations. It is believed that the stress values are much more reliable than the values of the strain.

Single Crystal Gold Films

The observed increase in the tensile strength of polycrystalline films of gold and silver when the thickness was reduced to the order of 10^{-5} cm raises the question as to whether or not the same phenomenon occurs in the case of single crystal films. Pashley (1959) has found an increased strength of very thin gold crystals grown on a silver substrate which in turn was grown on mica. His crystals were comparatively small and deformed elastically until just before rupture. A. Catlin and W.P. Walker at Virginia have been measuring the tensile strengths of thin single crystal gold films grown on a heated rock salt crystal substrate. They have found an increase of the tensile strength by a factor of at least two by decreasing the thickness from 3000 A to 1000 A. The rock salt crystals were obtained commercially in one centimeter square bars sawed from an oriented ingot along the principal crystallographic axes. These bars were then cleaved with a sharp razor blade until a crystal blank one centimeter square by approximately two millimeters thick was obtained. This freshly cleaved crystal was placed in an evaporator and gold was evaporated from a molybdenum strip heater on to the (001) plane of the crystal. The salt crystals were radiantly heated by a special induction furnace installed inside the evaporator which maintained the temperature at an accurately known value. The crystals first were heated for an hour at 420°C with the surrounding pressure at least 10^{-5} mm of Hg. The temperature was then slowly reduced to 375°C and the gold evaporated on the crystal at the rate of approximately 2000 A per minute. The crystals were then cooled slowly for at least an hour.

The gold films were prepared for testing by drilling a hole through the salt substrate which exposed a circular disk of the film. The films were then stressed by measuring the deformation of the film produced by a differential pressure across the circular disk. The drilling of the substrate was performed with a low pressure jet of water obtained from a standard hypodermic needle. The needle was mounted under the stage of a metallurgical microscope in the position normally occupied by the condenser lens in such a way that it was possible to determine when the water had dissolved the desired diameter hole. The water was then removed by two baths each in ethyl alcohol and in anhydrous ether. We are greatly indebted to Dr. J. W. Mitchell who suggested the method of preparing the rock salt crystals as well as the method of drilling the holes in the crystals. Fig. 7 shows a photograph of a 1 mm disk gold film covering the hole in the rock salt crystal. It will be observed that it is remarkably circular and that it is badly wrinkled. The wrinkling results from the fact that the coefficient of expansion of rock salt is much greater than that of the gold so the gold film was initially under high compression (equivalent to about one per cent strain). The deformation of the film was measured by light interference contour fringes (Newton rings), Fig. 8. These were observed with monochromatic light under 100X magnification by placing a flat cover glass (coated with 300 A of gold on the lower side) over the test area. The glass slide was

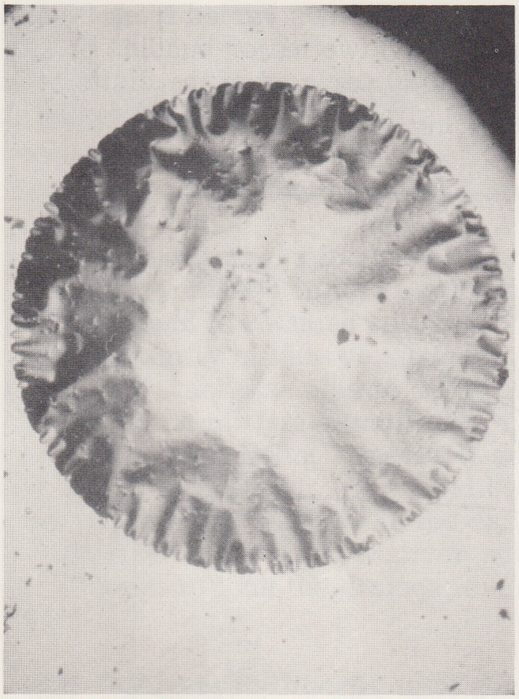

Fig. 7 Photograph of gold film covering 1 mm hole in rock salt crystal.

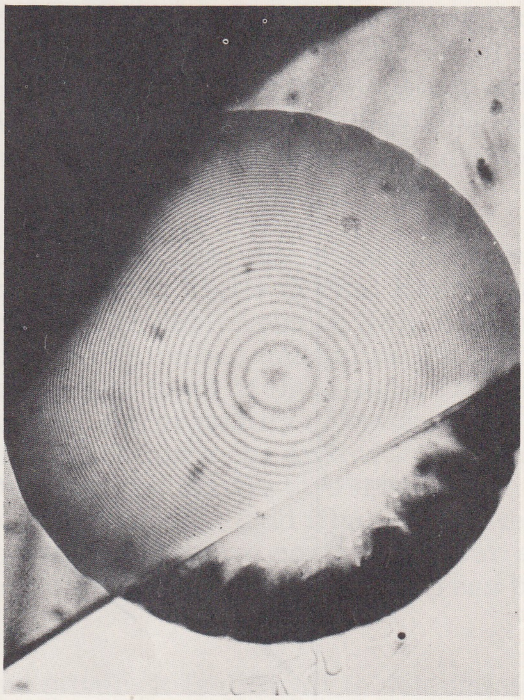

Fig. 8 Photograph of interference fringes formed when single crystal gold film of Fig. 8 is bulged through 1 mm hole in rock salt crystal.

placed only partially over the test surface to assure that atmospheric pressure remained on top of the film as the pressure below was reduced. The strain could be determined both from the number of fringes and by the contour of the fringes near the top of the bulge.

Figure 9 shows curves of stress versus strain for two typical single crystal gold films. It will be observed that the 1050 A film had about double the strength of the 2790 A film and that both films exhibited elastic deformation followed by plastic deformation and strain hardening. There also seems to be an increase of the Young's Modulus for the thinner film. Both films exhibit a small amount of short term creep. The stress was applied at the rate of about 5×10^8 dynes/cm^2 per minute and upon stopping the creep was of the order of 5×10^{-3} per cent in 15 sec. No further slip was observable after an hour. Figure 10 shows an electron microscope photograph of a typical film used in the tests. Electron diffraction patterns taken of this film showed it to be continuous and completely oriented with the plane of the gold film being the (001) plane of the gold crystal which is identical with the orientation of the substrate. It has not yet been possible to produce hole free films with thicknesses of less than 1000 A. It is important that the film temperature be near 375°C to avoid holes. When properly prepared the films adhere very strongly to the rock salt. Below 250°C the films are usually polycrystalline. It will be observed that the film contains a large number of stacking faults and perhaps twin lines. The stacking faults lie along the (111) planes which are inclined at an angle of approximately 55° with respect to the plane of the film. Measurement of the width of these faults gave a check on the determination of the thickness of the films by the weighing technique.

Further proof of plastic deformation was obtained by observing the formation of slip lines during the stressing process. Short slip lines parallel to the (110) direction were observed in all of the films. The length of the slip lines varied from 20 to 100 microns in the 1500 A films. In the thick films (2790 A) two major bundles of slip lines parallel to the (110) direction occurred and extended 80 per cent of the distance across the film. Diffraction studies showed that the small slip lines were of pure slip since the

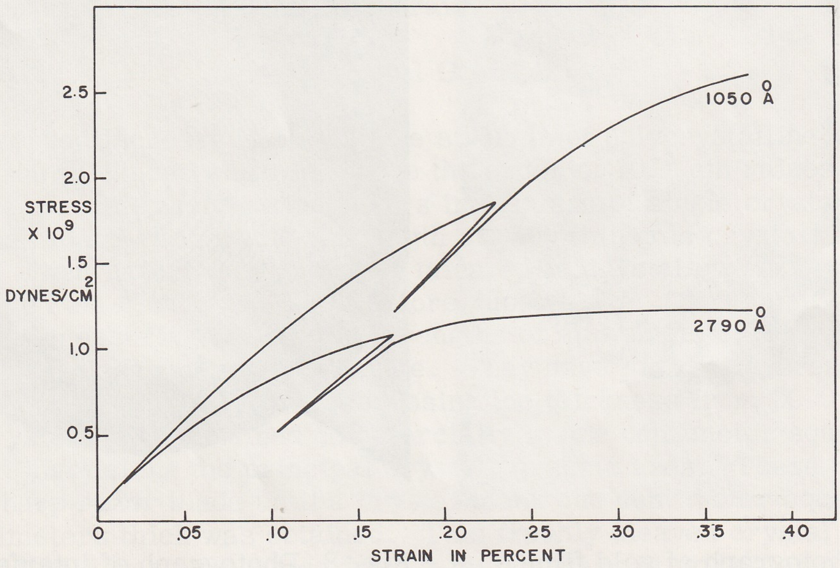

Fig. 9 Stress versus strain curves of single crystal films of gold.

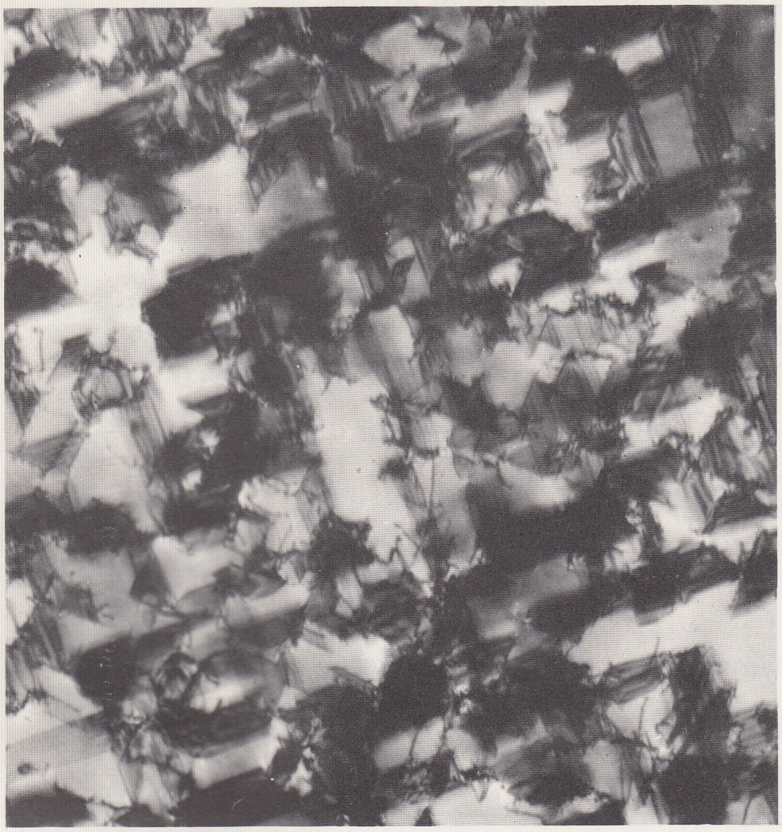

Fig. 10 Electron microscope photograph of typical single crystal gold film. 90,000X

films did not rupture and no microreorientation of the film could be observed. On the other hand the major slip lines caused a sudden large and unsymmetrical deformation of the film which however did not rupture. We are indebted to Dr. K.R. Lawless for taking the electron microscope photographs of the films.

The observed large increase in tensile strength over that of the bulk metal of the evaporated polycrystalline films of gold and silver and of single crystal films of gold when their thickness is reduced below 10^{-5} cm very probably results from the general effect of the proximity of the two surfaces upon the motion and multiplication of the dislocations. The fact that plastic deformation occurs in all of the films indicates that the dislocations both move and multiply. However, the proximity of the surfaces may shorten the dislocation lines, especially as the dislocation loops expand. This should increase the tensile strength. It should be noted that the plastic strain here observed is larger than observed by Pashley in the case of single crystal gold films. However, Pashley's films were grown on a silver substrate and may have contained silver atoms in sufficient numbers to lock the dislocations and thus prevent slip until the stress became very large.

In the polycrystalline films of gold and silver it is difficult to determine with certainty the stresses originally required to produce plastic flow because the films were found to be under initial stress which was probably not uniform. However, the experiments indicate that the thinner films require higher stresses to start the plastic flow.

It will be noted that even in the case of the thickest films of silver, for example, the observed strength of 1.2×10^9 dynes/cm^2 is the order of 200 times the yield strength of an annealed single crystal of silver.

REFERENCES

Beams, J. W., Walker, W. E., and Morton, H. S., Jr., Phys. Rev. 87, 524 (1952); Beams, J. W., Breazeale, J. B. and Bart, W. L., Phys. Rev. 100, 1657 (1955).

Beams, J. W., Tech. Proc. Am. Electroplaters Soc. 43, (1956).

Pashley, D. W., Phil. Mag. 4, 316 (1959).

Ford, W. K., Jr., Stampler, A. L., and Beams, J. W., Bull. Am. Phys. Soc. II, 1, 333 (1956).

Kraft, D. B., Strider, T. P., and Beams, J. W., Bull. Am. Phys. Soc. II, 3, 299 (1958).

Orowan, E., A. Physik, 82, 235 (1933).

DISCUSSION

Wilson: From the picture of your films grown at low temperatures, one would get the impression that they might be somewhat porous. Are they?

Beams: The films show no measurable leakage of gas and we believe that they are free of holes. The thinnest films which were about 250 angstroms thick were apparently overstressed in transferring them to the electron microscope and consequently showed cracks.

Wachtel: I would like to mention that we have done some stress-strain measurements on self-supported aluminum films 1 inch in diameter and about 500 A thick. We used a modified bulge method similar to yours. The stress-strain curves we obtained look very much like yours also.