JOURNAL OF CATALYSIS 3, 528–538 (1964)

The Surface Structure of Films of Silver on Glass

J. G. ALLPRESS AND J. V. SANDERS

From the Commonwealth Scientific and Industrial Research Organization, Division of Tribophysics, University of Melbourne, Australia

Received March 31, 1964

Films of silver were prepared by condensation in vacuum onto glass substrates in the temperature range −160° to 300°C and examined by electron microscopy. Their surface structure, revealed by decorating the films with gold, depends on the conditions of preparation, and can be understood in terms of the processes occurring during the growth and annealing of the films. These results are significant in relation to the interpretation of the surface chemistry of evaporated metal films.

INTRODUCTION

Large areas of clean metal surfaces can be prepared most easily by evaporation in vacuum, and although such metal films are widely used in surface chemical experiments, their surface topology has rarely been studied. In some cases (*1–3*), the surfaces of these films have been assumed to consist predominantly of close-packed planes, and the interpretation of results is based on some correlation of the geometry of these planes with the shape of interacting gas molecules. The aim of the present work was to obtain information on the real structure of polycrystalline films, using electron microscopic methods. Thin (1000 Å) silver films were prepared by vacuum deposition onto glass substrates, and three different methods were used to examine their structure:

(*i*) The films were stripped from their substrates, and could then be examined by transmission microscopy which gave the grain size and the nature and concentration of defects within the films.

(*ii*) Shadowed replicas indicated the over-all surface features with moderate resolution.

(*iii*) Decorated replicas were prepared in order to detect variations in the concentration of kink sites on the surface, and the presence of atomically flat areas free of kink atoms. This method depends on the preferential nucleation of gold at kink sites and steps on surfaces. It was first applied successfully to cleavage faces of rock salt (*4, 5*), where steps of monatomic height were revealed. More recently, faceted surfaces of silver have been studied by the same method (*6*).

Silver was chosen for this work, because under our vacuum conditions (10^{-4}–10^{-5} Torr), films of other more reactive metals (such as Cu and Ni) would be seriously contaminated by gases chemisorbed during and following film preparation.

2. EXPERIMENTAL

2.1 Preparation of Films

The silver films were prepared in a standard Edwards Model 12E6 vacuum bell jar, at pressures of 10^{-5}–5×10^{-5} Torr. Spectrographically pure silver (Johnson-Matthey and Co. Ltd.) in the form of short cylinders (150 mg, 0.06-inch diam.) was cleaned in nitric acid and evaporated from a helical, stranded, tantalum filament. The distance between the filament and the substrate was 10 cm, giving a calculated film thickness of 1000 Å. Unless otherwise stated, the rate of condensation was approximately 30 Å sec^{-1}. The substrates were small pieces of soda glass from microscope slides, and were cleaned by heating them to their softening point in a gas flame immediately before use. Following the deposition of silver, gold wire (2 mg, 0.008-inch diam.) was evaporated rapidly (<1 sec) from a tungsten filament 12 cm from the substrate to give a mean thickness of about 5 Å on the silver surface. Immediately before the evaporation of gold, a 200-mesh grid of nickel was dropped into position about 1 mm above the silver surface. By this means, square areas of gilding were obtained in which the surface density of the gold decreased gradually to zero at the edges, thus providing a section where the changes in decoration with density could be observed.

In order to prepare and anneal films above room temperature, the substrate was placed in a tantalum tray and heated by radiation from a molybdenum spiral mounted between it and a tantalum radiation shield. Because of the low heat capacity of this arrangement, rapid heating and cooling rates were obtained. Temperatures were measured with a chromel-alumel thermocouple spot-welded to the underside of the tray. This assembly was outgassed at about 800°C before each experiment.

For the preparation of films at subzero temperatures, a block of brass containing a copper-constantan thermocouple close to its upper face was cooled in liquid air, and placed on a silica platform in the bell jar, immediately before evacuation. When the pressure had fallen to 10^{-4} Torr, the substrate was dropped onto the cold block. The silver was evaporated after a standard time of 2 min had been allowed for the substrate to reach thermal equilibrium.

In some experiments, the resistance of the film was measured as it was warmed from -160°C to room temperature. A Philips Universal A.C. Bridge (GM4144) was used, and contact was made with the film by means of platinum leads sealed into the substrate surface.

2.2 Examination of Films

Each specimen was broken into several portions and the pieces were treated as follows:

(a) **The films.** The film was stripped from the substrate by floating the glass on the surface of a 10% solution of hydrofluoric acid in water; it was then washed and mounted on grids.

(b) **Decorated replicas.** A thin layer of carbon was evaporated onto the gilded surface of the film, and the "sandwich" of carbon, gold, and silver was stripped from the substrate as above. The silver was carefully dissolved by floating the sandwich on warm dilute nitric acid for a short period, and the gilded carbon replica was washed and collected on grids. Attempts to separate these replicas by simply floating the sandwich on nitric acid in order to strip it from its substrate failed, because in this case the nitric acid attacked mainly from the edges of the film, and it was found that many of the gold particles embedded in the carbon were dislodged.

(c) **Shadowed replicas.** The film was shadowed with carbon-platinum evaporated at 5–10° to the surface (*7*), followed by carbon at normal incidence to ensure that the replica was continuous.

The film itself and the shadowed and decorated replicas were examined in a Siemens Elmiskop I electron microscope operated at 100 kv.

3. RESULTS

3.1 Bulk Structure of Films

Features found by transmission electron microscopy of the films can be identified as grain boundaries, twin boundaries, and defects such as stacking faults and dislocations (*8–11*). Selected electron micrographs (Fig. 1) show these features, and Table 1 summarizes the details of grain size and relative strain for films prepared under various conditions.

(a) **Influence of substrate temperature during evaporation.** There is some uncertainty in the substrate temperature and

FIG. 1a

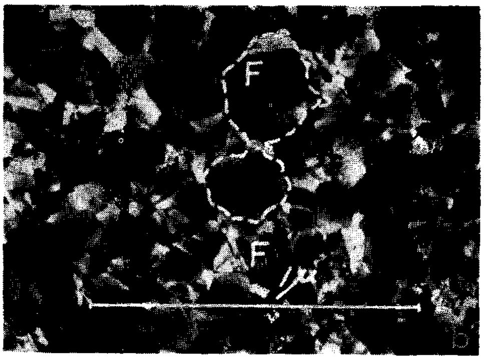

FIG. 1b

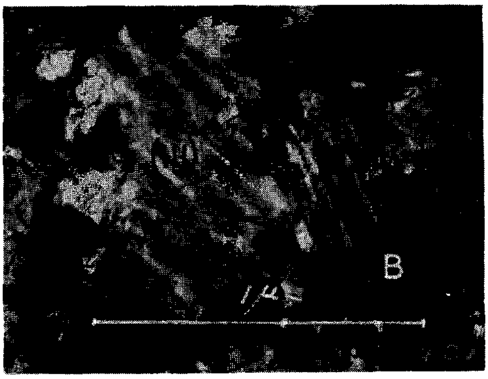

FIG. 1c

FIG. 1d

FIG. 1. Transmission micrographs showing the grain structure of silver films condensed onto glass under various conditions (43,000×). A, isolated large grains; B, many small grains; F, fringes from stacking faults or twins; (111), large grain with {111} planes approximately parallel to the surface. (a) Substrate at room temperature. (b) Substrate at 220–260°C. (c) Deposited on substrate at −160°C, then annealed to room temperature. (d) Deposited on substrate at room temperature, then annealed at 250°C.

the values quoted are those given by the thermocouple attached to the substrate holder. In addition to this, a lack of reproducibility was introduced by the absorption of radiation from the filament, which produced temperature rises of up to 50°C in some experiments.

Films thrown at about room temperature and at about 30 Å $\sec^{-1}$ [Fig. 1(a)] consist of large crystals up to 10,000 Å wide, containing some stacking faults and twins, surrounded by masses of very small, highly strained crystals about 500 Å across. Above 200°C, the small crystals are larger and less strained, and finally a polycrystal of more uniform grain size is produced [Fig. 1(b)]. In general, there are some exceptionally large grains in all the films, and these grains have their {111} planes nearly parallel to the substrate. This gives rise to some preferred orientation.

(b) Influence of annealing on films thrown at room temperature. Very extensive grain growth occurs when films are annealed for 10 min [Fig. 1(d)], and for any particular annealing temperature the grain size is greater than in films thrown at that temperature at our standard rate

TABLE 1

BULK STRUCTURE OF FILMS OF SILVER ON GLASS

Substrate temperature °C		Structure					
		Large grains			Small grains		
Evaporation	Annealing[a]	Proportion of total area (%)	Size (μ)	Strain[b]	Proportion of total area (%)	Size (μ)	Strain
20–60[c]	—	70	0.5–1.0	High	30	0.05	High
20–60[d]	—	90	0.5–1.0	Medium	10	0.05	High
20–60[e]	—	20	0.2–0.5	High	80	0.05	High
100–180	—	70	0.3–0.5	Low	30	0.05	High
220–280	—	90	0.2–0.5	Low	10	0.1–0.2	Low
−160	20	70	0.7–1.0	High	30	0.05	High
−60	20	60	0.5–1.0	High	40	0.05	High
20	100	100	0.5–1.0	High	0	—	—
20	170	100	0.5–1.0	Medium	0	—	—
20	340	100	0.5–1.0	Medium	0	—	—

[a] Annealing times were all 10 min.

[b] Strain is estimated from the appearance of the grains in transmission. In most cases, individual dislocations cannot be resolved.

[c] Evaporation rate, 30 Å sec^{-1} (standard rate).

[d] Evaporation rate, 100 Å sec^{-1}.

[e] Evaporation rate, 8 Å sec^{-1}.

and cooled quickly. Again there is a slight {111} preferred orientation. The large {111} grains have a much lower concentration of twins and stacking faults than the small grains.

(c) Influence of rate of evaporation. Trapping of gases in the films during their preparation has been suggested as a likely cause of variations in their structure (*12, 13*). Since the amount of trapped gas should depend upon the rate of condensation, films were condensed at rates different within an order of magnitude from the standard rate (Table 1). As the rate was increased, the large grains took up an increasing proportion of the area because they increased in number and size.

(d) Films prepared at very low temperatures. The films thrown on substrates maintained at —160°C could not be examined until they had been warmed to room temperature. After this annealing, they consisted of very large and heavily faulted grains, surrounded by small grains [Fig. 1(c)]. The distribution of sizes of the grains was very similar to that in films condensed at room temperature [Fig. 1(a)]. As the films were warmed in vacuum, a distinct drop in resistance was observed at about —60°C.

3.2 Surface Structure of Films, Revealed by Shadowing

The platinum-carbon shadowing technique was adequate to reveal the more prominent surface details, but we found that the resolution was hindered by a certain amount of structure inherent in the method, which was particularly obvious at the low shadowing angles used.

The surfaces of films cast on substrates at room temperature consisted of roughly circular bumps about 500 Å across, corresponding in size to the small grains in the films [Fig. 2(a)]. The larger grains are not distinguishable until the substrate temperature is raised to above about 150°C during condensation, when they appear as flatter areas in an otherwise bumpy surface [Fig. 2(b)].

When films thrown at room temperature were annealed at temperatures above about 150°C, the 500 Å bumps disappeared, and grain boundary grooves were formed. Large

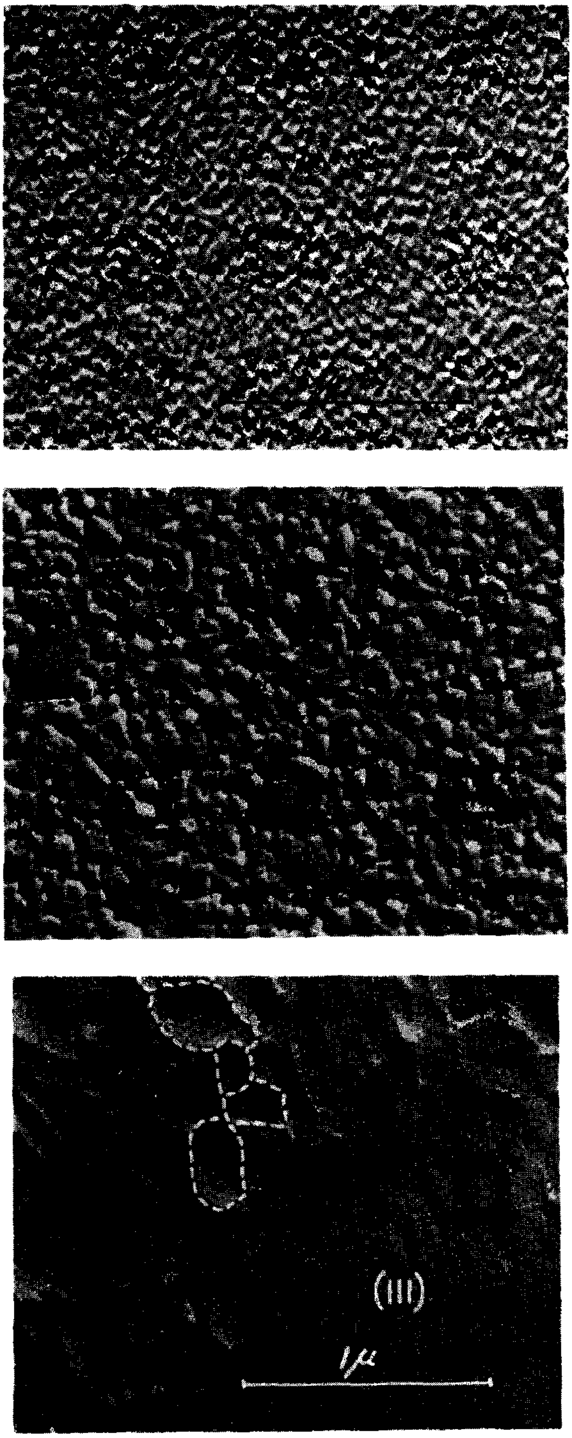

FIG. 2. Shadowed replicas of the surfaces of silver films (Pt-C shadow 10°, 32,000×). (a) Substrate at room temperature. (b) Substrate at 170–190°C. (c) Deposited on substrate at room temperature, then annealed at 260°C. Some grooves at grain boundaries have been outlined. Curved terraces are just visible on the large (111) grain.

grains were thus clearly visible, and after annealing about 200°C, terracelike features were just resolved on these areas [Fig. 2(c)].

3.3 Surface Structure, Revealed by Decorating

Contrary to the experiences of Bassett *et al.* (*14*), we had little difficulty in separating the very thin gold films from the silver using our method of first stripping the silver from its substrate. The gold took up distinctive structures which we have classified broadly into three forms—sheets, filaments, or dots.

(a) **Decoration of films as condensed.** Decoration of films prepared at room temperature was in the form of dots and filaments whose shape and concentration vary sufficiently from grain to grain for the large grains to be just distinguishable (Fig. 3). At temperatures above about 100°C,

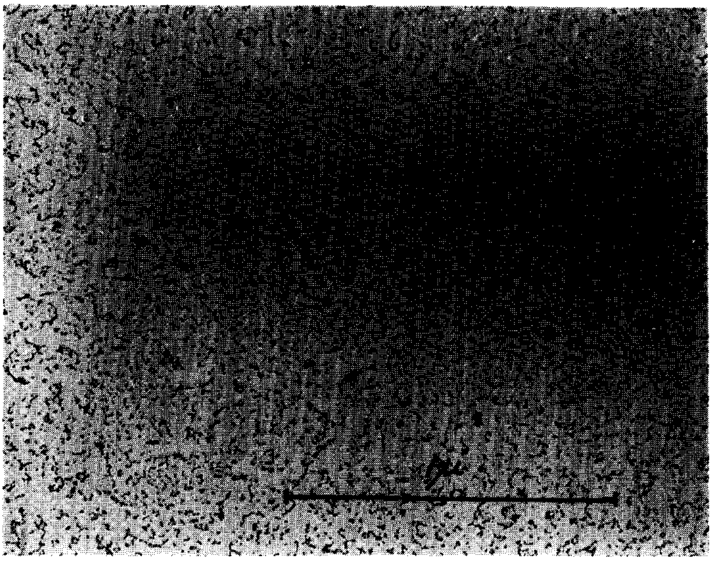

FIG. 3. Decorated replica of film of silver deposited on glass at room temperature. 44,000×.

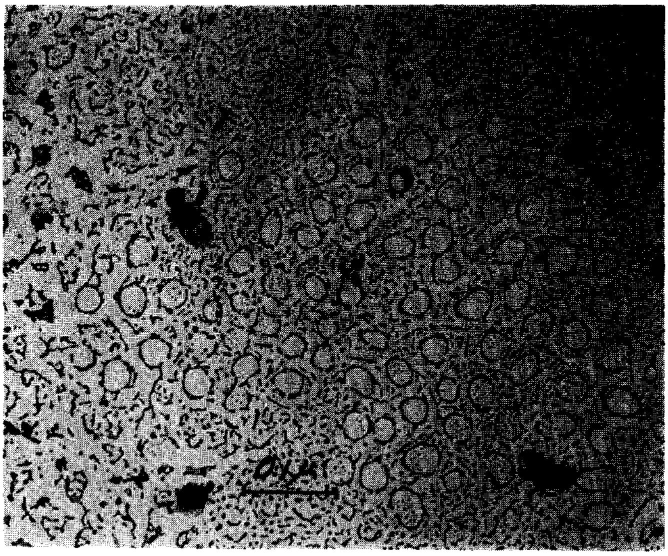

FIG. 4. Decoration of a large grain in a film deposited on glass at 160°C. 120,000×.

distinctive circular filaments about 300 Å in diameter appeared on the large grains. With increasing temperature, these circles increased in size, changed shape, and dots appeared inside them (Figs. 4, 5).

On smaller grains, there were irregular, twisted filaments of gold (Fig. 3) and no details of surface structure could be distinguished except at the highest temperatures where some lines of dots and straight filaments appeared (Fig. 5). There was no gold in the grain boundaries.

The decoration on films prepared and gilded at −160°C and annealed at room temperature took the form of loops of about 300 Å diameter. Slight differences in the shapes of the loops enabled the large grains to be distinguished. In an attempt

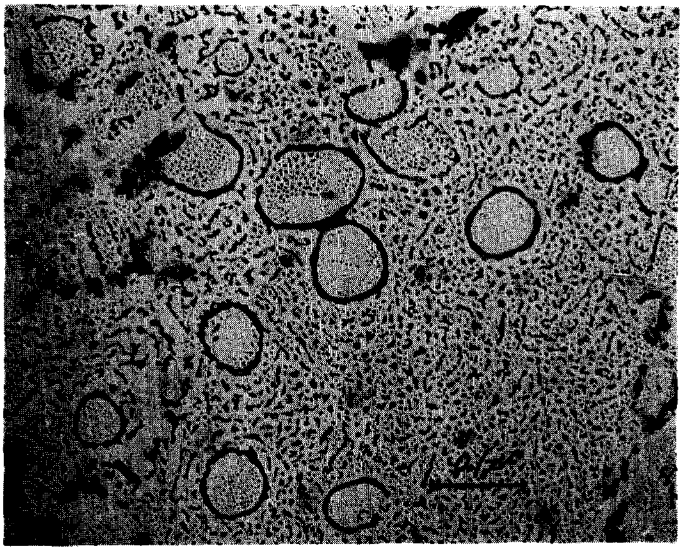

Fig. 5. Decoration of a large grain in a film deposited on glass at 250°C. 120,000×.

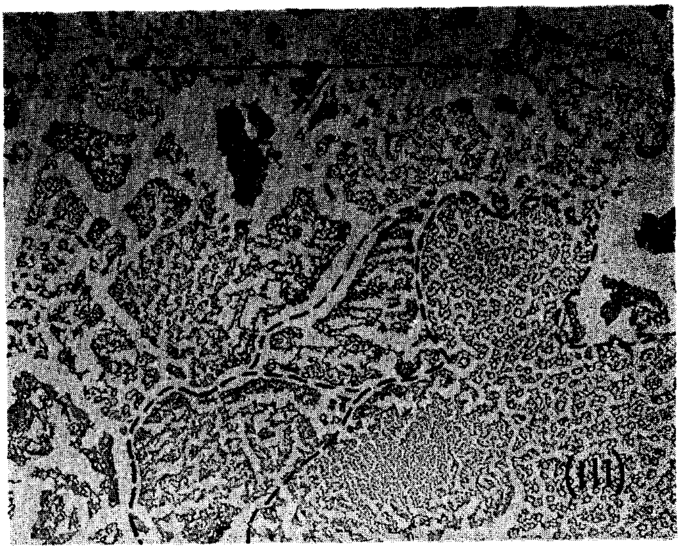

Fig. 6. Decorated replica of a film deposited at room temperature and then annealed at 90°C (48,000×). Some grains have been outlined, and a (111) grain marked.

to inhibit changes occurring while the film warmed to room temperature, carbon was condensed on to a specimen immediately after the gold at —160°C. The decoration in this case was very similar to that on the previous film.

(b) Decoration of films after annealing. *Large grains.* Loops of gold, about 300 Å in diameter were visible in the decoration of the large grains in films cast at room temperature and annealed at up to about 200°C (Fig. 6). At higher annealing temperatures (Figs. 7, 8), the fine details of surface structure produced very complex patterns in the gold; the most noticeable features were curved filaments about 50 Å wide, with finely cusped edges. There was usually a blank area adjacent to the con-

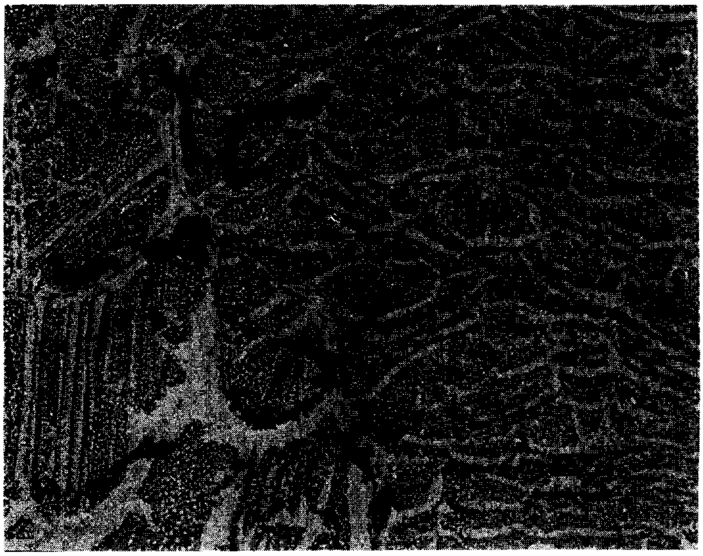

FIG. 7. Decorated replica of a film deposited at room temperature and then annealed at 260°C (90,000×). Some grain boundaries and a large (111) grain are marked.

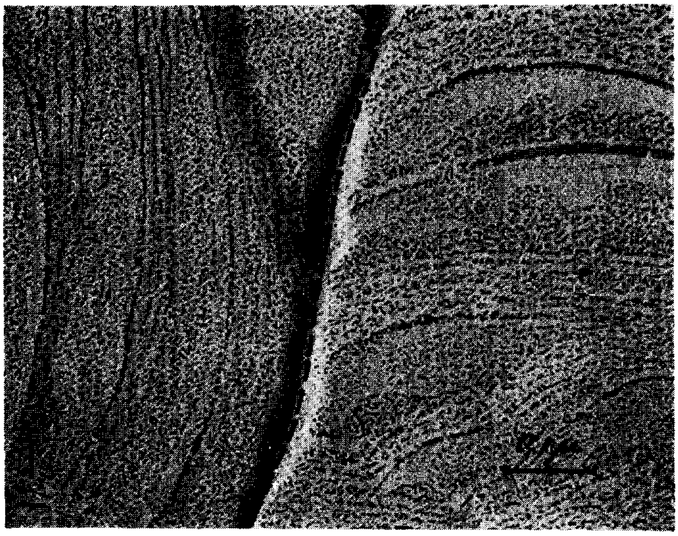

FIG. 8. Detail of decoration on two large grains in a film deposited at room temperature and then annealed at 320°C (120,000×). The grain boundary is marked.

vex side of the filament, and commonly a row of dots running parallel to the filament within this area. The features in Fig. 8 are typical of most large grains in the films.

Small grains. With annealing below 200°C, the small grains were covered by sheet, sometimes continuous, but mostly containing holes. Grain boundaries were empty (Fig. 6). After annealing above 250°C, linear bands of gold separated by blank gaps developed. We suppose that these are related to some surface structure associated with stacking faults or twins cutting the surface. Because of the high fault concentration in small grains, these features generally dominate the decoration on them.

(c) **Epitaxy.** The epitaxy of the gold on the largest grains in the silver film was studied by means of selected area electron diffraction. In all cases the epitaxy was improved by annealing the film before the gold was condensed on it. The gold on films annealed at 300°C was perfectly oriented.

(d) **Thickness of gold.** A gradation in thickness of the gold was obtained by evaporating it through a grid as described earlier. The decoration in the fringe areas showed no significant difference from that in the areas of normal gold thickness, other than that sheets tended to become filaments, and filaments dots, as we scanned away from the center across the margin of a gilded area.

4. DISCUSSION

We are primarily concerned with the structure of the surface of evaporated metal films, as revealed by decorated replicas. However, in order to understand some of the features of the decoration, it is necessary to propose a mechanism for the growth of the films and the way they achieve their final structure, as observed by transmission microscopy.

4.1 Growth of Films

From our experiments, and those of Sennett and Scott (*15*) and Moss, Duell, and Thomas (*16*), we have developed the following model in which a number of stages of film growth can be distinguished.

(*i*) Nucleation. The initial clusters of atoms will grow either at preferred sites on the surface, or they will be produced spontaneously when the supersaturation of mobile atoms on the surface reaches its critical value. The latter process is more likely on flame-polished glass, and has recently been considered in detail by Walton (*17, 18*).

(*ii*) Growth of nuclei. Once the nuclei are formed, they will grow because arriving atoms will prefer to be adsorbed at kink sites on their surfaces, rather than on the glass on which they are highly mobile. No more nuclei should be produced at this stage. The shape of the growing crystals will depend on the substrate temperature because at temperatures where surface diffusion of silver is sufficiently rapid to allow minimization of surface energy, the crystals will become smoother and rounded. Because of this, gaps may still be present in films several hundred Å thick on substrates at high temperatures.

(*iii*) The growing crystals contact one another, the geometry of the contacts depending on the shape of the crystals. At this stage, nearly all the arriving atoms condense directly on the silver, and not on the glass, so that the structure depends upon the substrate temperature, which now controls diffusion rates.

(*iv*) The crystals will continue to grow in height, and surface diffusion of silver atoms will modify their shape. We believe that at −160°C, this diffusion is so slow that narrow gaps between the crystals are maintained, and give rise to the observed high electrical resistance (*19*) and surface area (*20*) of films condensed at low temperatures. It appears that the sudden drop in resistance of these films as they are warmed through −60°C marks the onset of surface diffusion and the filling of these gaps.

(*v*) When the film is continuous, recrystallization can occur to produce the large grains of preferred orientation in the film. The final distribution of grain size is determined by the temperature. At low temperatures, the gaps between the crystals prevent recrystallization, and the grain size remains very small (*21*).

These processes should be similar for any metal condensed onto a substrate which is free from preferred sites, but the temperature dependence of the various processes will vary from one metal to another. In particular, the rate of surface diffusion of metal atoms is a controlling factor. The presence of adsorbed gases, by modifying this rate, may affect the surface structure and the rate of sintering (*21, 22*).

4.2 Surface Topography

(a) **Pt–C replicas.** The shadowed replicas of films condensed at room temperature indicate a uniform "orange peel" surface structure [Fig. 2(a)]. The individual bumps correspond in size (300 Å) to the small grains in the film. Thus, although narrow gaps between crystals can be filled by surface diffusion, the rate of this process at room temperature is not sufficient to obliterate the average surface contours which correspond to the grain size at step (*iii*) rather than that at step (*v*). Thus the large recrystallized grains are not revealed in the shadowed replicas until the substrate temperature is above about 150°C, when surface diffusion produces grooves at grain boundaries and a more uniform flatness elsewhere during the time of condensation (Fig. 2b).

(b) **Interpretation of gilded replicas.** Previous work on decoration of faceted surfaces has shown that gold condenses in the form of a thin sheet on a flat surface which has a high concentration of kinks, and as separate rounded crystals on a surface which has no kink atoms (*6*). Twisted, irregular filaments on replicas probably decorate surfaces which are atomically rough, so that the gold sheet is of varying thickness and collapses.

When films are decorated immediately after condensation of the silver, the gold atoms should go to positions similar to those taken up previously by silver atoms. These decorated replicas should therefore show how the surface structure is related to the growth process. The decoration of films condensed at room temperature suggests that the surface is uniformly rough, but as the temperature during condensation is increased, small crystals become smooth with a high concentration of kink sites (decorated by sheet), and the large {111} crystals develop an interesting structure. The closed loops of gold which increase in diameter from about 200 Å at 100°C to up to 800 Å at 300°C (Figs. 4, 5), confirm that the orange peel structure is becoming progressively smoother by surface diffusion. The tops of the bumps become flat and the gold has diffused to the edge of these areas into the region of high kink atom concentration. At 300°C, the terrace structure typical of films annealed at high temperatures begins to appear, and the flat areas become more extensive and change their shape (Fig. 5).

Decoration of films after they have been annealed for 10 minutes reveals that the surface becomes increasingly inhomogeneous as the annealing temperature is raised. The curved bands of gold which appear on the large grains (Figs. 7, 8) no doubt correspond to inclined areas between the terraces just visible on shadowed replicas [Fig. 2(c)], which are regions at which kink sites are concentrated. Since these large grains have {111} planes almost parallel to the substrate, the terraces might be almost atomically flat. This is probably true of the areas adjacent to the curved bands in Figs. 7 and 8, where very little or no gold is visible. This kind of terraced surface which develops on the large grains during annealing could be a consequence of some chemisorption of residual gases in the vacuum. Sundquist (*23*) has recently observed effects of this kind.

It is difficult to draw conclusions about the development of a similar fine structure on the surfaces of the small grains of random orientation because of their limited area and the interference produced by twins or stacking faults. The parallel strips of gold and blank bands suggest that some facets and adjacent kinky areas are associated with the places where the faults cut the surface.

4.3 Interpretation of the Decoration in Terms of Chemical Reactivity

We believe that the patterns of decoration are a fair representation of the distribution of kink sites on the surface. It is at these sites that adsorbing species would be expected to be most strongly bound. In addition, where adsorption is followed by the growth of a second phase, as in tarnishing reactions, we expect the reaction product to grow in regions which correspond to those which are decorated by gold.

Catalytic reactions are frequently carried out at temperatures where considerable surface diffusion of metal atoms is possible, and structures may develop which are similar to those obtained here when silver films are annealed. There are many instances in which considerable changes in rate of reaction have been observed during the first few runs on a freshly prepared catalyst surface, and it seems likely that these changes may often be caused by changes in surface structure (*24*). This decoration technique reveals that the surface structure varies with the conditions of preparation of the films. It indicates that films prepared at low temperatures contain a very high concentration of kink atoms. When time and an increase of temperature allow sufficient surface diffusion, some facets, which may be atomically smooth, appear under our vacuum conditions. It seems clear that in all cases, the concentration of kink sites is sufficiently high to render them an important feature of the surface, particularly in view of the fact that they should be the most important sites for adsorption. Thus we believe that it is most important to consider the influence of these sites on chemical reactions, rather than treating the surface simply as an array of small flat facets.

REFERENCES

1. BALANDIN, A. A., *Advan. Catalysis* **10, 96** (1958).

2. PRITCHARD, J., *Trans. Faraday Soc.* **59,** 437 (1963).

3. BOND, G. C., "Catalysis by Metals," p. 30. Academic Press, London and New York, 1962.

4. BASSETT, G. A., *Phil. Mag.* **3,** 1042 (1958).

5. SELLA, C., CONJEAUD, P., AND TRILLAT, J. J., *Proc. Intern. Conf. Electron Microscopy, 4th, Berlin, 1958,* p. 1508 (Springer, Berlin, 1959).

6. ALLPRESS, J. G., AND SANDERS, J. V., *Phil. Mag.* **9,** 645 (1964).

7. BRADLEY, D. E., *Brit. J. Appl. Phys.* **10,** 198 (1959).

8. WHELAN, M. J., HIRSCH, P. B., HORNE, R. W., AND BOLLMAN, W., *Proc. Roy. Soc. (London)* **A240,** 524 (1957).

9. BASSETT, G. A., AND PASHLEY, D. W., *J. Inst. Metals* **87,** 449 (1958–1959).

10. MATTHEWS, J. W., *Phil. Mag.* **4,** 1017 (1959).

11. PHILLIPS, V. A., *Phil. Mag.* **5, 571** (1960).

12. BASSETT, G. A., MENTER, J. W., AND PASHLEY, D. W., *Discussions Faraday Soc.* **28, 7** (1959).

13. CASWELL, H. L., *J. Appl. Phys.* **32,** 105 (1961).

14. BASSETT, G. A., MENTER, J. W., AND PASHLEY, D. W., "Structure and Properties of Thin Films" (C. A. Neugebauer, J. B. Newkirk, and D. A. Vermilyea, eds.), p. 11. Wiley, New York, 1959.

15. SENNETT, R. S., AND SCOTT, G. D., *J. Opt. Soc. Am.* **40,** 203 (1950).

16. MOSS, R. L., DUELL, M. J., AND THOMAS, D. H., *Trans. Faraday Soc.* **59,** 216 (1963).

17. WALTON, D., *J. Chem. Phys.* **37,** 2182 (1962).

18. RHODIN, T. N., AND WALTON, D., "Metal Surfaces," p. 259. American Society for Metals, Ohio, 1963.

19. ALLEN, J. A., EVANS, C. C., AND MITCHELL, J. W., "Structure and Properties of Thin Films" (C. A. Neugebauer, J. B. Newkirk, and D. A. Vermilyea, eds.), p. 46. Wiley, New York, 1959.

20. Evans, C. C., and Mitchell, J. W., "Structure and Properties of Thin Films" (C. A. Neugebauer, J. B. Newkirk, and D. A. Vermilyea, eds.), p. 263. Wiley, New York, 1959.

21. KEITH, H. D., *Proc. Phys. Soc. (London)* **69,** 180 (1956).

22. ANDERSON, J. R., BAKER, B. G., AND SANDERS, J. V., *J. Catalysis* **1,** 443 (1962).

23. SUNDQUIST, B. E., *Acta Met.* **12,** 67 (1964).

24. BAGG, J., JAEGER, H., AND SANDERS, J. V., *J. Catalysis* **2,** 449 (1963).