Recrystallization of Vacuum-Deposited Silver
and Copper Films

By Mitsuhiko Yoshida*, Saburo Nakamura* and Hajime Suto**

Silver and copper were vacuum-deposited onto an electro-polished aluminium substrate cooled by running water to a thickness of about 2 μm, and the films were investigated by means of transmission electron microscopy, electrical resistivity measurement, differential thermal analysis and X-ray diffraction. The results obtained are as follows.

In as-deposited silver films, the {111} preferential orientation was observed, but it disappeared after recrystallization. Continuous heating caused rapid recrystallization in the temperature range from 30 to 50 °C accompanied by the change in resistivity and the heat evolution. The activation energy for recrystallization was estimated at 84 kJ/mol.

For copper, the recrystallization gave rise to such a complete reorientation that the {100} plane was parallel to the substrate.

The contribution of the strain energy to the heat released during recrystallization was negligibly small. The grain boundary energies for silver and copper were estimated from the heat evolution to be approximately $3.2 \times 10^{-1}$ and $8.1 \times 10^{-1}$ J/m², respectively.

(Received August 8, 1977)

I. Introduction

Several investigators have reported on the recrystallization of vacuum-deposited films of Fe(1), Au(2), ZnS(3) and Sn(4). It has been found that the film thicknesses are less than several thousand Å, and that the effect of surfaces and/or surface contamination is very important for the recrystallization of films(2)(4). In a previous paper(5), the present authors reported that the vacuum-deposited Cu and Cu-C films were recrystallized at 50~110°C. In this work, the texture of vacuum-deposited silver and copper films greater than 1.0 μm in thickness and the heat evolution during their recrystallization have been investigated by means of transmission electron microscopy, electrical resistivity measurement, differential thermal analysis and X-ray diffraction.

II. Experimental Procedures

Pure silver (99.999 %) and copper (99.998 %) were used as source materials, and these were vacuum-deposited from molybdenum boats on an electro-polished aluminium substrate placed on a copper plaque cooled with running water under a vacuum of $5.3 \times 10^{-4}$ Pa. The distance between source and substrate was 190 mm, and the deposition rate being about 500 nm/min for silver and 300 nm/min for copper. The thickness of the films was determined from the surface area and weight of the deposited films. For X-ray diffraction, CuKα radiation was used with nickel filter. Electrical resistivity was measured in liquid nitrogen by means of the four-terminal method. The change in resistivity was measured continuously on heating up to 250°C and on cooling in a vacuum furnace of $6.65 \times 10^{-3}$ Pa. The heating rate was about 5°C/min and the cooling rate was 10~15°C/min.

In the differential thermal analysis (D.T.A.), Al₂O₃ powder was used as an inert reference and the temperature difference ($ΔT$) between the specimen and the inert reference was recorded automatically as a function of heating time.

In order to prepare the specimens for transmission electron microscopy, the films were electro-polished with the following solutions:
For Ag: 5 g KCN + 5 g gelatine
+ 5.6 mol H₂O
For Cu: 2.3 mol CH₃COOH
+ 25 g Cr₂O₃ + 2.5 mol H₂O

III. Results and Discussion

A typical structure of as-deposited silver films is shown in Photo. 1. The average grain diameter is about 100 nm. Figure 1 shows the change in X-ray line profile with elapsed time at room temperature. It can be seen that the peak height increases with the elapsed time. Corresponding to this, the recrystallization can be observed in Photo. 2, which was taken for the film kept for 11 h at room temperature. The recrystallization at room temperature has been observed in sputtered copper films of 1 mm thickness. In contrast to this, the thinned foils for the use of transmission electron microscopy did not recrystallize even after preservation in a desiccator for 30 d. This structural stabilization by thinning has also been observed by Bailey, who investigated the recrystallization in cold-worked silver by the use of a hot stage installed in an electron microscope. On the other hand, the ratio of 200 and 111 diffracted intensities from the powder specimen is known to be 0.42, but the observed ratio was about 0.2 for the as-deposited films. This indicates that the {111} planes are parallel to the surface preferentially. This preferred orientation disappeared after recrystallization.

A typical resistivity-temperature curve is shown in Fig. 2. The changes observed at

![Photo. 1 Transmission electron micrograph of a silver film deposited on an aluminium substrate placed on a copper plaque cooled with water.](image1)

![Photo. 2 Transmission electron micrograph of a recrystallized silver film kept at room temperature for 11 h.](image2)

![Fig. 1 Change in the 111 and 200 X-ray line profiles of an as-deposited silver film as a function of the time after deposition. CuKα radiation.](image3)
temperatures between 30 and 50°C in the heating curve are due to the recrystallization. Electron microscopic observations confirmed the recrystallization as seen in Photo. 3.

Figure 3 represents the fractional changes in resistivity $R=(r_0-r_t)/(r_0-r_\infty)$ at 40, 50 and 60°C as a function of annealing time, where $r_0$, $r_\infty$ and $r_t$ are the electrical resistivities before and after annealing and at the time $t$, respectively. According to our previous paper(5), the fractional change corresponds to the fraction of recrystallization. The temperature dependence of recrystallization can usually be expressed by the equation

$$t_X = C \cdot \exp \left( \frac{\Delta H}{kT} \right),$$

where $t_X$ is the time at which the fraction $X$ has recrystallized at $TK$, $k$ is the Boltzmann constant and $C$ a constant. Figure 4 shows the time for 50% recrystallization (at $R=0.5$) against the inverse of the absolute temperature. The obtained activation energy for recrystallization $\Delta H$ is 84 kJ/mol. This is about a half of the activation energy for the volume diffusion in silver(11).

Figure 5 represents the results obtained by D.T.A. The heat evolution in the temperature range from 40 to 80°C is 100.8 J/mol. The heat evolution is considered to be due to the release of strain energy and decrease of the grain boundary energy accompanied with recrystallization. In order to estimate the respective contributions to the heat evolution, the internal
Equation (1) gives 90 nm and eq. (2) $\varepsilon = 1.6 \times 10^{-3}$. The heat evolution caused by releasing the strain energy is 1.0 J/mol, and this is only 1% of the observed value. Accordingly, we can say that the greater part of the heat evolution comes from the decrease in the grain boundary energy due to the decrease of grain boundary area by recrystallization. The grain size before and after the recrystallization is about 90 nm and 1.5 $\mu$m respectively, and this gives the specific grain boundary energy $(3.2 \pm 0.6) \times 10^{-1} \text{ J/m}^2$ for silver. This value is nearly equal to $2.7 \times 10^{-1} \text{ J/m}^2$ obtained by other investigators. Similar results were obtained in the case of copper films. Figure 6 represents a D.T.A. curve for a copper film. The heat evolution in the temperature range from 50 to 90°C is $240 \pm 50$ J/mol. Since the internal strain was estimated at $5.6 \times 10^{-4}$ from X-ray line broadening, its contribution to the heat evolution is negligibly small. The grain size was estimated as 70 nm. Photographs 4 and 5 show transmission electron micrographs of as-deposited and recrystallized copper films, respectively. The grain size of the latter is about 1.3 $\mu$m. On the assumption that the heat evolution came only from the decrease in grain boundary area, the specific grain boundary energy for copper is estimated at $(8.1 \pm 1.7) \times 10^{-1} \text{ J/m}^2$. This value is a little larger than $6.7 \times 10^{-1} \text{ J/m}^2$ obtained by McLean (16).

The ratio of diffracted intensity ($I_{200}/I_{111}$) for the as-deposited copper film is 0.15 and that for the recrystallized film is 1.08. As the ratio for powdered sample is 0.46 (10), the as-deposited
IV. Conclusion

The recrystallization of vacuum-deposited silver and copper films was investigated metallographically. The results can be summarized as follows.

The as-deposited silver film takes \{111\} preferred orientation to the substrate, but this preferred orientation disappears after recrystallization. The recrystallization was observed in the temperature range from 30 to 50°C and the activation energy was estimated at 84 kJ/mol. For copper, the recrystallization produced such a complete reorientation that \{100\} planes were parallel to the substrate.

The contribution of the strain energy to the heat released during recrystallization was negligibly small. The grain boundary energies for silver and copper were estimated from the amount of the heat evolution to be about $3.2 \times 10^{-1}$ and $8.1 \times 10^{-1}$ J/m², respectively.

REFERENCES

(9) J. E. Bailey: Phil. Mag., 5 (1960), 833.