

Grain-boundary scattering in aluminium films deposited on to calcite substrate

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Electrical resistivity and temperature coefficient of resistivity of polycrystalline aluminium films deposited onto calcite substrates have been measured *in situ*. It was observed that films deposited at 130° C substrate temperature show reversible and reproducible behaviour with thermal cycling. The grain-boundary scattering theory of Mayadas and Shatzkes reproduces the experimental observations quite faithfully with the coefficient of specular reflection $p = 0$ and grain-boundary reflection coefficient $R = 0.38$ indicating that the grain-boundary scattering plays a significant role in electron transport in aluminium film deposited on to calcite substrate.

1. Introduction

The size-dependence of electrical resistivity of polyvalent metal films has been the subject of many investigations in the past. In general, polycrystalline films have much higher resistivities than the bulk values. Data analysis is usually made using the Fuchs relation [1] with the usual conclusion that $p \approx 0$ for polycrystalline films, while $p \approx 0.5$ for epitaxial single crystal films [2] where p is the coefficient of specular reflection and could be taken to be the ratio of electrons reflected at an angle θ to the surface normal to those incident at an angle θ . Mayadas *et al.* have shown that for evaporated polycrystalline aluminium films, the assumption that the intrinsic resistivity (ρ_i) and intrinsic mean free path are constant with thickness is incorrect and that in fact ρ_i decreases with increasing thickness [3, 4]. It is commonly believed that the grain boundaries have little effect on the resistivity of metals which can be true only when the grain size is much larger than the mean free path due to other scatterers (l_0). However, in the case of thin films, the distance between grain boundaries, D , is generally smaller than l_0 , and hence the grain-boundary contribution can no longer be regarded as negligible. In practice, crystal structure is often of the columnar type in which the individual crystals grow roughly vertically from the substrate to the upper surface of the

film. Consequently, the only boundaries which need to be considered are those lying parallel or perpendicular to the applied field. Mayadas and Shatzkes [5] evaluated the problem in a simplified way (henceforth M–S theory) to allow a qualitative description of grain-boundary scattering in polycrystalline films. In this laboratory various physical properties of polycrystalline aluminium films are being studied. As a part of this work, the resistivity–thickness dependence of the films was studied and the results, analysed in the light of the M–S theory, are presented here.

2. Experimental methods

Pure aluminium (99.999%, Johnson & Matthey, UK) was deposited from a tungsten helix on to a freshly air-cleaved calcite crystal ($a'_0 = 6.412 \text{ \AA}$, $\alpha = 101^\circ 55'$). The calcite crystal was cleaned by conventional methods and was baked at 130° C for 2 h at a system pressure of $\sim 10^{-6}$ Torr before deposition. Resistance measurements were carried out *in situ* using the standard four-probe technique of Van der Pauw [6]. The rate of deposition was 5 to 10 \AA sec^{-1} . The thicknesses of the films were measured by a multiple beam interferometer with an accuracy of 30 \AA . The temperature of the substrate was controlled by an electronic on/off controller ($\pm 0.5^\circ \text{C}$) and the actual temperature was measured using a copper–constantan thermo-

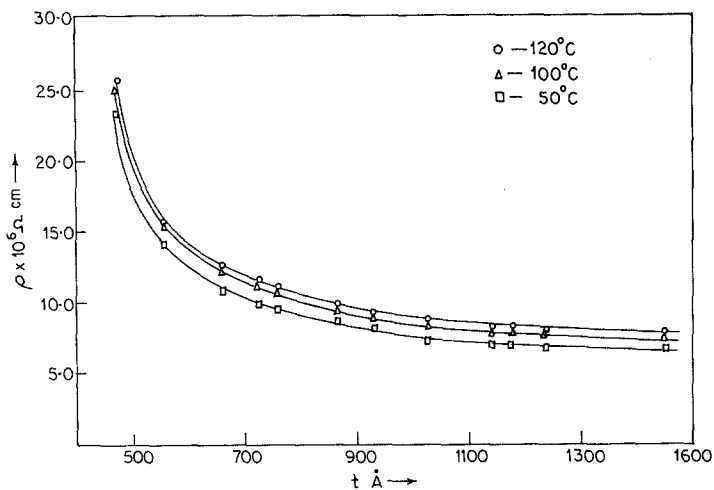


Figure 1 Resistivities of aluminium films as a function of thickness at temperatures of 50, 100 and 120° C.

Figure 2 Dependence of temperature coefficient of resistivity on reciprocal thickness.

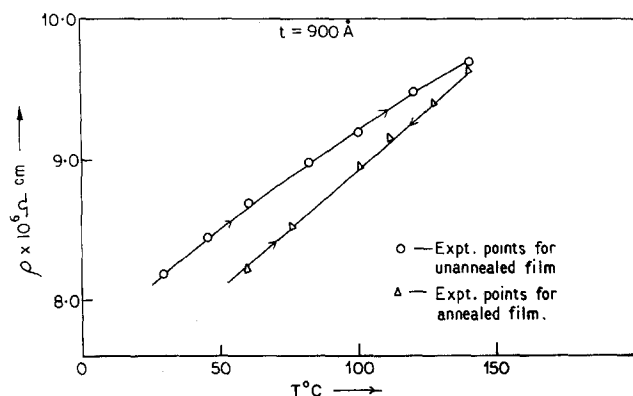
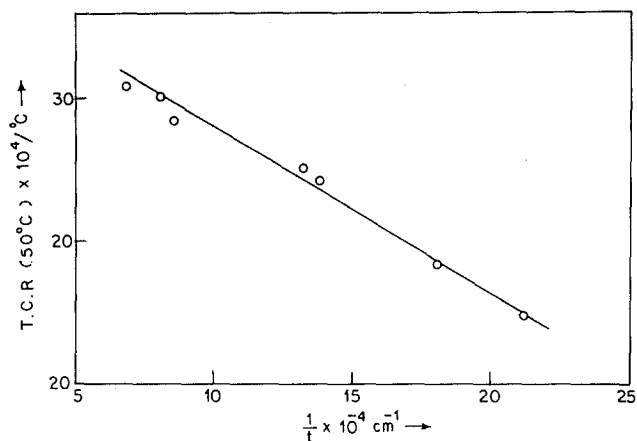


Figure 3 Effects of thermal cycling and annealing of room temperature deposited film (900 Å).

couple placed on a dummy sample. Transmission electron micrographs were taken using a Philips EM 200 electron microscope. Films for electron microscope study were taken off the calcite substrate by chemical means.

3. Results and discussion

The resistivities of aluminium films deposited onto a heated (130° C) calcite substrate are shown in 1322

Fig. 1. The curves show a gradual decrease in resistivity with increasing thickness. Variation of the temperature coefficient of resistivity (TCR) of the films with thickness is shown in Fig. 2 which indicates that the TCR is always positive within our experimental range. The bulk value of TCR at 50° C obtained from the intercept of TCR versus $1/t$ plot (Fig. 2) is $3.8 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$. The room-temperature deposited films show an irreversible

behaviour when subjected to thermal cycling (Fig. 3). Annealing at 140° C for several hours makes the film follow a reversible path so far as the resistivity–temperature variations are concerned. It has been shown by Palatnik and Komnik [7, 8] that depositions should be made at substrate temperature T_s ($\frac{1}{3} T_m < T_s < \frac{2}{3} T_m$, T_m being the bulk melting point) to facilitate vapour → solid condensation. The $\frac{1}{3} T_m$ limit is essentially that below which adatoms do not have sufficient mobility to produce ordered structure. The crystallite size of a vapour-deposited polycrystalline film increases with the increasing surface mobility of the adatoms which cluster during deposition. Therefore, the crystallite size is expected to increase with increasing substrate temperature. Annealing at a temperature higher

than the deposition temperature also increases the crystallite size, but the growth effect is significantly different from that obtained by using the same temperature during deposition. The difference arises from the high activation energy process of thermal diffusion of the surface atoms of a condensate in the former case (annealing) as compared with the orderly process of condensation of mobile adatoms in the latter case.

We have critically examined the structure of the films studied here using an electron microscope. Figs. 4 and 5 show the electron micrographs and diffraction pattern of aluminium films deposited at room temperature and at 130° C, respectively. The micrographs clearly reveal an entirely different texture of the two films. The room-temperature deposited films (Fig. 4) have a fine-grained texture

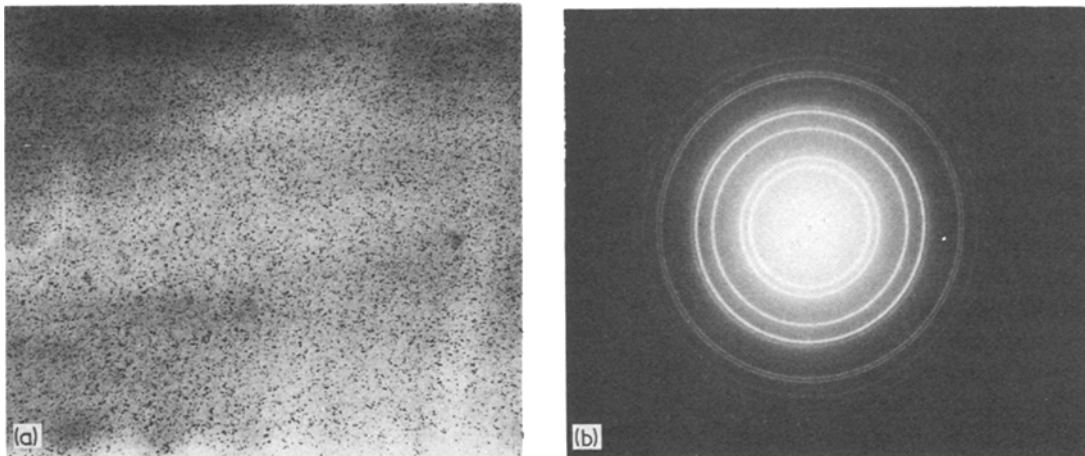


Figure 4 Electron micrograph and diffraction pattern (same area) of room-temperature deposited Al film (600 Å), × 29 700.

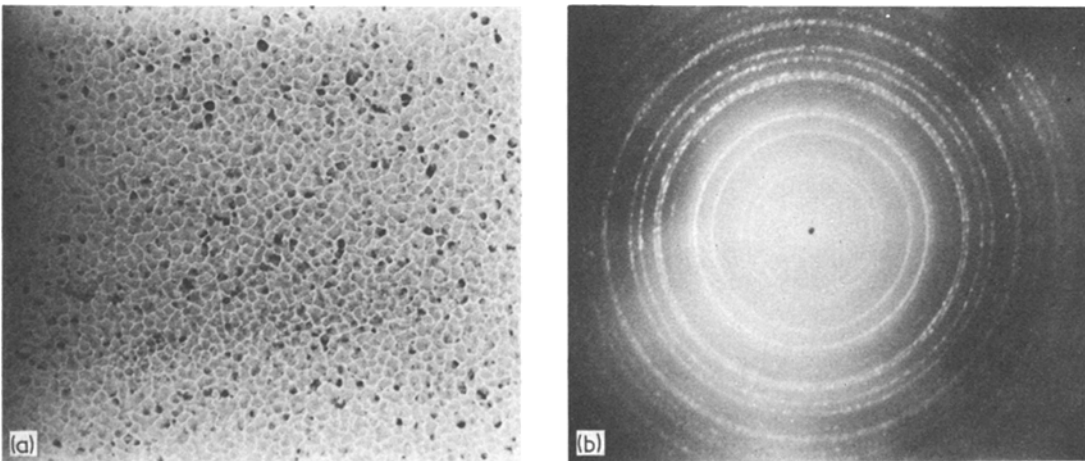


Figure 5 Electron micrograph and diffraction pattern (same area) of Al film deposited at 130° C (800 Å), × 22 300.

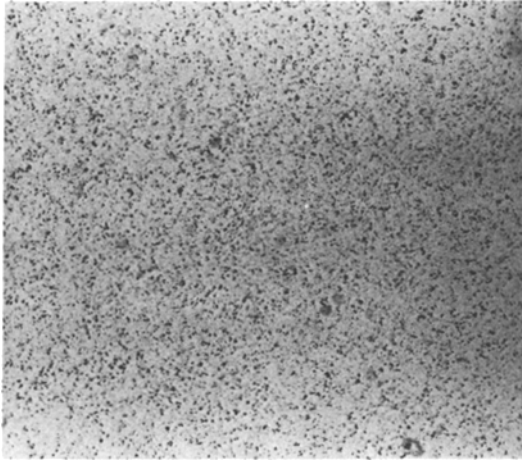


Figure 6 Electron micrograph of an annealed Al-film (600 Å), $\times 22\,300$.

with no orientation what-so-ever, whereas the high-temperature deposited films show large-grained texture with a tendency to orientation (Fig. 5). The grain sizes were observed to increase with thicknesses in our experimental range being nearly equal to the thicknesses of the films. The effect of annealing could be observed from the electron micrograph (Fig. 6) for a film of 600 Å where the texture of the films remains the same as that of room-temperature deposited film (Fig. 4) but the size of the grain has increased slightly.

The electrical conductivity of thin, continuous metal films is given by

$$\frac{\rho}{\rho_i} = \left[1 - \frac{3(1-p)}{2\gamma} \int_1^\alpha \frac{(a^{-3} - a^{-5})(1 - e^{-\gamma a})}{1 - pe^{-\gamma a}} da \right]^{-1} = \phi(p, \gamma), \quad (1)$$

where ρ_i is the resistivity of bulk material, ρ is the resistivity of the thin films, γ is the ratio of the

film thickness, t , to the electron mean free path l_i in bulk, and p is the specularity parameter. a equals $1/\cos\theta$, where θ is the angle which the electron mean free path makes with the normal to the film.

Analysis is generally carried out by selecting a value of p for which Equation 1 closely resembles experimental observation, assuming ρ_i and l_i to be thickness independent. Mayadas and Shatzkes evaluated the problem by considering the resistivity caused by the scattering of the conduction electrons at the grain boundaries together with the normal background scattering by defects and phonons superimposed on the surface scattering effect in films. The M-S expression for the film resistivity can be written as

$$\frac{\rho}{\rho_0} = \frac{\phi(p_i, \gamma_i)}{f(\alpha)} \quad (2)$$

where ρ_0 is the single crystal resistivity and

$$f(\alpha) = 3 \left[\frac{1}{3} - \frac{\alpha}{2} + \alpha^2 - \alpha^3 \ln \left(1 + \frac{1}{\alpha} \right) \right]$$

α being equal to $lR/D(1-R)$, $\phi(p_i, \gamma_i)$ is given by Equation 1 in which γ is replaced by $\gamma_i = \gamma/f(\alpha)$. D is the grain size and R is the coefficient of reflection at the grain boundary.

The experimental plot of ρ/ρ_0 versus γ along with the theoretical one (Equation 2) is shown in Fig. 7. It is clear from the figure that the M-S curve with $p=0$ and $R=0.38$ reproduces the experimental observations quite faithfully. The value of $R=0.38$ implies that the contribution due to grain-boundary scattering in aluminium films deposited on to heated calcite substrate is quite appreciable. In computing the theoretical

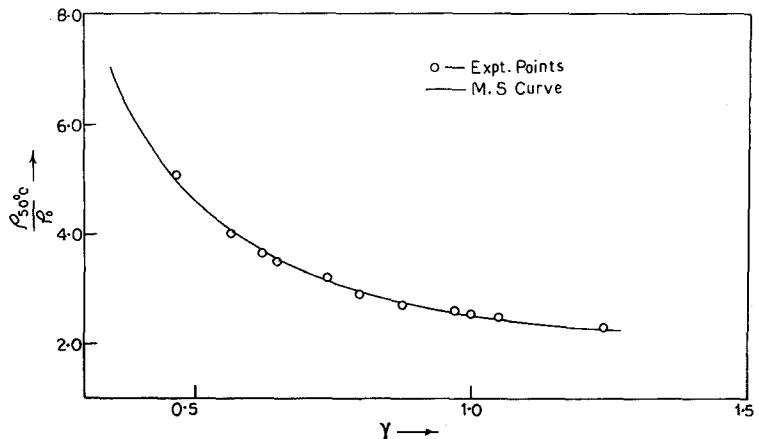


Figure 7 Plot of ρ/ρ_0 versus γ . For the M-S curve, $p=0$, $R=0.38$.

curve, the grain size was taken to be equal to the thickness of the film, which was in accordance with our electron microscope study. It is to be noted that Mayadas *et al.* obtained $R = 0.15$ for aluminium films deposited on to a heated (200°C) SiO_2 substrate, whereas Andrews *et al.* [19] reported $R = 0.17$ for bulk samples. However, the thickness range of Mayadas *et al.* was in the high-thickness range (1 000 to 10 000 Å) and, as such, they obtained a mean value of $R = 0.15$ to obtain a satisfactory fit in the entire range of measurement. They also observed that there appears to be a systematic trend for data points at small thicknesses to fall above the calculated curve while those at large thicknesses fall below.

The initial growth pattern and hence the final texture of a film is generally governed by the initial nucleation of two-dimensional lattice on the substrate surface plane. This growth is determined by the binding forces between the condensed atoms, whereas the influence of the potential field of the substrate could be neglected in the case of an amorphous substrate. But in the case of a single-crystal substrate, the strong periodicity of the substrate surface is often found to be the predominant force influencing the film formation. Thus the growth mechanism and hence the texture of aluminium films deposited on to calcite is very likely to be different from that deposited on glass or SiO_2 substrates and as such no comparison

should be made to justify the R values obtained in the above two cases.

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