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1993 J. Phys.: Condens. Matter 5 559

(http://iopscience.iop.org/0953-8984/5/5/007)

J. Phys.: Condens. Matter 5 (1993) 559–566. Printed in the UK

Influence of grain-boundary and surface scattering on the electrical resistivity of single-layered thin copper films

N Artunç[†] and Z Z Öztürk[‡]

[†] Department of Physics, Faculty of Science, Ege University, 35100 Bornova, İzmir Turkey

[‡] Tübitak, Marmara Research Centre, PO Box 21, 41470 Gebze, Kocaeli, Turkey

Received 4 August 1992, in final form 11 November 1992

Abstract. The resistivity of single-layered thin copper films with thicknesses of 17–124 nm, is studied as a function of the temperature and grain diameter. The resistivity of both as-deposited and 500 K annealed films is found to increase with decreasing film thickness. Our analysis has shown that the grain-boundary scattering is the dominant contribution and the surface scattering cannot be the cause of the excess resistivity of both as-deposited and 500 K annealed films. The average reflection coefficient R of the electrons scattered by the grain boundaries is found to be 0.38 for both as-deposited and 500 K annealed films over the whole temperature and thickness range studied.

1. Introduction

It is a well known fact that the electrical resistivity of single-layered thin metallic films increases with decreasing film thickness and is greater than that of the bulk material. This observed resistivity increase $\Delta\rho \equiv \rho_f - \rho_\infty \propto 1/d$ is known as the size-dependent deviation from the Mathiessen's rule, where ρ_∞ is the bulk resistivity, ρ_f is the measured total resistivity and d is the film thickness. Quite often this increase is explained in terms of the Fuchs–Sondheimer (FS) theory (Fuchs 1938, Sondheimer 1952), which describes the scattering of electrons at the surfaces of thin films. With the use of electron microscopy, it has been seen that the polycrystalline films are built up of small grains where the electrons can be scattered at the grain boundaries. In addition, many experimental results have also been analysed in terms of the grain-boundary scattering model of Mayadas and Shatzkes (1970) (MS). Both the FS surface scattering theory and the MS grain-boundary scattering theory lead to a resistivity increase $\Delta\rho \propto 1/d$. Sambles (1983) and van Attekum *et al* (1984) have pointed out that, if grain-boundary scattering is the dominating contribution to the excess resistivity of single-layered thin films, then the temperature-dependent part of the resistivity is almost identical to that of the bulk material and independent of the film thickness. On the other hand, the temperature-dependent resistivity curves of the films with different thinknesses are almost parallel to each other and to that of the bulk material, whereas this is not the case with surface scattering. Therefore, temperature-dependent resistivity measurements are necessary in order to distinguish between the two models.

Recently, there has been extensive interest in the properties of multilayered thin films as a new class of materials with novel electronic, magnetic and mechanical

0953-8984/93/050559+08$07.50

properties (Carcia and Suna 1983, Schuller 1980, Shiroishi *et al* 1987). It is well known that the grain diameter and the transport properties of multilayered thin films depend strongly on the properties of the uncovered base layer (Carcia and Suna 1983, Kozono *et al* 1987, de Vries and den Broeder 1988). For this reason, the single-layered thin films are still of great interest for research in this field.

Several authors (van Attekum *et al* 1984, Tochitskii and Belyavskii 1980, de Vries 1987a, b, 1988, Wedler and Alshorachi 1980) have found that the total film resistivity is inversely proportional to the film thickness. They have analysed their resistivity data of single-layered metallic films by taking into account the grain-boundary scattering model alone, assuming the Fuchs specularity p to be unity.

In the earlier studies (Pal *et al* 1975, Schlemminger and Stark 1987) on single-layered copper films, the resistivity data have been analysed using only FS theory. Few published results appear for single-layered thin copper films on a (001)-cleaved NaCl single crystal, in which the resistivity data are explained in terms of the MS theory (Tochitskii and Belyavskii 1980). Therefore the aim of this work is to study the temperature-dependent resistivity measurements in order to show which scattering mechanism is the more dominating effect in the single-layered thin copper films.

In this paper we present an analysis of the resistivity data of as-deposited and 500 K annealed single-layered copper films, using the grain-boundary scattering model of Mayadas and Shatzkes (1970) and the combined model of Sambles *et al* (1982).

2. Experimental details

The samples were prepared as follows, using 99.99% pure copper wire. Copper films with thicknesses of 17–124 nm were deposited at room-temperature onto the well cleaned glass substrates in a vacuum of about 1×10^{-6} Torr by the thermal evaporation technique in a Varian 3119 R&D Coater System. The substrates were covered with a mask such that a Hall bar pattern was obtained suitable for resistivity measurements. Both as-deposited and annealed samples were studied for each thickness. The annealing was carried out in high vacuum (10^{-6} Torr) at a temperature of 500 K for 30 min. In order to determine the bulk resistivity $\rho_\infty(T)$ of copper, a thick copper film of 301 nm thickness was also made at room temperature.

For the thickness measurements, both Taly Step (Tencor Instruments Alpha Step) and atomic absorption techniques were used. The average grain diameter was determined for each sample directly from TEM micrographs obtained using a Jeol 100C microscope.

The resistivity measurements were carried out using a standard four-probe DC technique.

3. Results and Discussion

3.1. Grain dimater

The average grain diameter was determined for each sample directly from TEM micrographs with a relative error of 22%. The relative error for gold films was found to be as large as 30% (de Vries 1987a). Some TEM micrographs are shown in figure 1. We have found from the TEM micrographs that these films have a polycrystalline structure and that in the thickness range of 17–81 nm the grain diameter increases

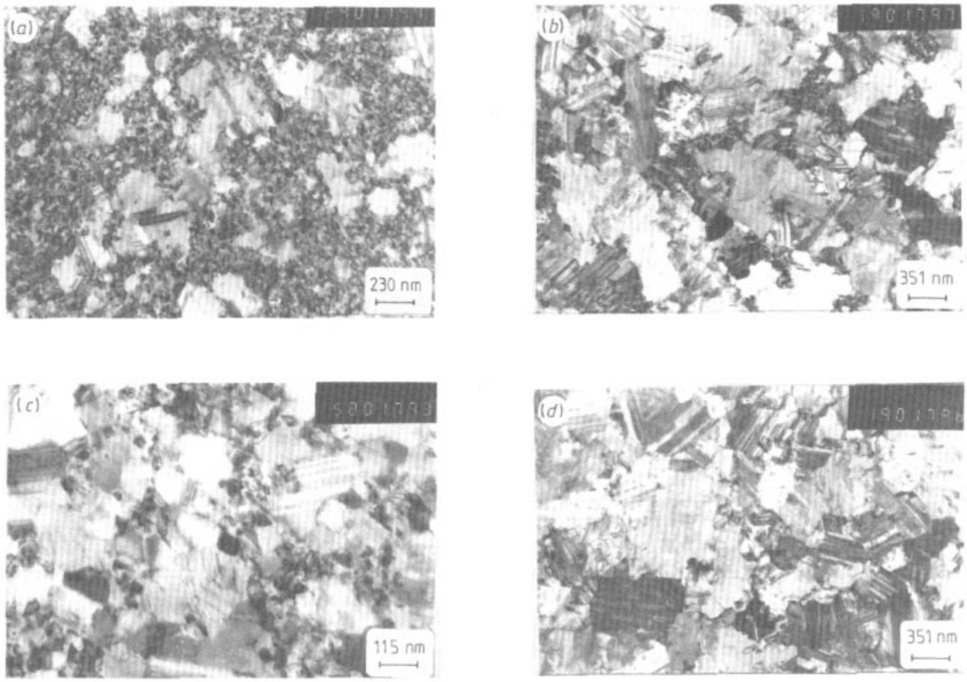

Figure 1. Transmission electron micrographs of as-deposited copper films of thickness (*a*) 57 nm, (*b*) 81 nm and of 500 K annealed films of thickness (*c*) 57 nm, (*d*) 81 nm.

almost linearly with thickness. The obtained D/d ratios were 1.12 (as-deposited films) and 1.50 (500 K annealed films).

3.2. *Temperature-dependent resistivity measurements*

The temperature-dependent resistivity measurements of as-deposited and annealed single-layered copper films of different thicknesses are given in figures 2 and 3. They show the decrease of the resistivity with increasing thickness and with heat treatment. In figures 2 and 3, the observed decrease of resistivity with increasing thickness is caused by the increase in grain diameter. The observed decrease of resistivity for a constant thickness should be due to both the increase in the grain diameter and the decrease of the defect density in the film with annealing (Chopra 1969, Maissel and Glang 1970).

It is seen from figures 2 and 3 that the temperature-dependent resistivity curves of as-deposited and 500 K annealed copper films of different thicknesses are parallel to each other. This indicates that the grain boundary scattering should be the dominating contributions to the excess resistivity of the single-layered copper films (Sambles 1983, van Attekum *et al* 1984, de Vries 1987b).

3.3. *Analysis of the resistivity measurements*

In the MS grain-boundary scattering model the grain boundary enhanced resistivity is given by

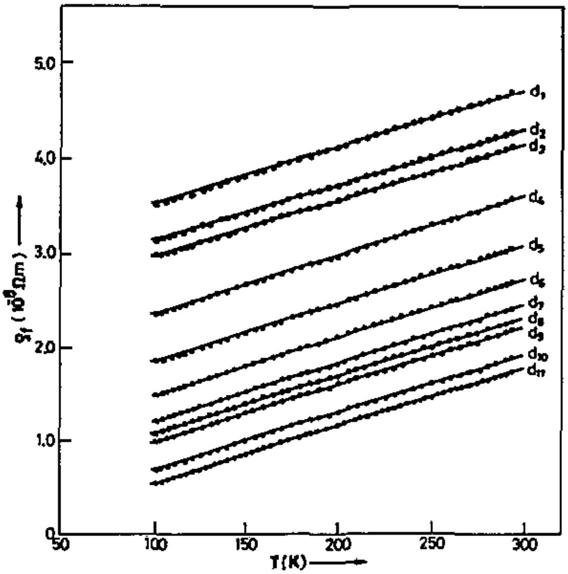

Figure 2. Resistivity ρ_f against temperature T for deposited copper films of different thickness (thickness: $d_1 = 17$ nm; $d_2 = 19.5$ nm; $d_3 = 21$ nm; $d_4 = 27.5$ nm; $d_5 = 38$ nm; $d_6 = 51$ nm; $d_7 = 62$ nm; $d_8 = 73$ nm; $d_9 = 81$ nm; $d_{10} = 124$ nm; $d_{11} = 301$ nm). Solid curves fitted according to equations (1)–(3) with $R = 0.38$. Some of the experimental data are not shown for clarity.

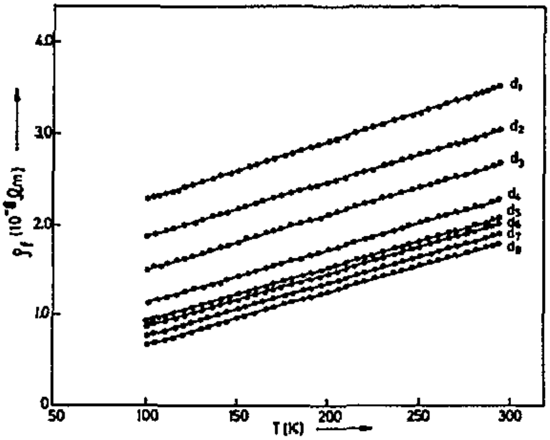

Figure 3. Resistivity ρ_f versus temperature T for 500 K annealed copper films of different thickness (thickness: $d_1 = 19.5$ nm; $d_2 = 29$ nm; $d_3 = 38$ nm; $d_4 = 51$ nm; $d_5 = 63$ nm; $d_6 = 73$ nm; $d_7 = 81$ nm; $d_8 = 124$ nm). Solid curves fitted according to equations (1)–(3) with $R = 0.38$.

$$\rho_{gr}(T) = \rho_\infty(T)/f(\alpha) \tag{1}$$

$$f(\alpha) = 1 - \tfrac{3}{2}\alpha + 3\alpha^2 - 3\alpha^3 \ln(1 + 1/\alpha) \tag{2}$$

$$\alpha = [\lambda_\infty(T)/D]R/(1 - R). \tag{3}$$

In these equation, $\rho_\infty(T)$ is the total resistivity of the bulk material at temperature T, D is the average grain diameter in the film and R is the reflection coefficient of the electrons striking the grain boundaries ($0 \leqslant R \leqslant 1$), $\lambda_\infty(T)$ is the mean free path of the bulk material at temperature T without grain boundaries. The bulk mean free path λ_∞ as a function of temperature is calculated from the production $(\rho\lambda)_\infty$ and $\rho_\infty(T)$. We assume that the product $(\rho\lambda)_\infty$ has a constant value (Mayadas and Shatzkes 1970) of 0.66×10^{-15} Ω M^2 for copper.

Using equation (1) and the limiting form of equation (2) for $\alpha \ll 1$ we obtain

$$\rho_{gr} D = \rho_\infty D + \tfrac{3}{2}(\rho\lambda)_\infty R/(1-R) \tag{4}$$

or, assuming a constant D/d ratio

$$\rho_f d = \rho_\infty D + \tfrac{3}{2}(\rho\lambda)_\infty [R/(1-R)]/n \tag{5}$$

$$C = \tfrac{3}{2}(\rho\lambda)_\infty [R/(1-R)/n \tag{6}$$

where C is the size-effect-induced grain-boundary scattering (n is the ratio D/d).

The theory for the total film resistivity, including both surface and grain-boundary scattering, was given by Sambles *et al* (1982). They combined the angle-dependent surface scattering of Soffer (1967) with MS grain-boundary scattering theory to give

$$\frac{\rho_\infty}{\rho_f} = f(\alpha) - \frac{4}{\pi}\int_0^{\pi/2} \mathrm{d}\phi \int_0^1 \mathrm{d}u \frac{\cos^2\phi}{H(u,\phi)} S\{\kappa H(u,\phi), p(u), u\} \tag{7}$$

$$H(u,\phi) = 1 + \alpha/[(1-u^2)^{1/2}\cos\phi] \tag{8}$$

$$S\{\kappa H(u,\phi), p(u), u\} = \frac{3(u-u^3)(1-p)[1-\exp(-\kappa H/u)]}{2\kappa H[1-p\exp(-\kappa H/u)]} \tag{9}$$

$$p(u) = \exp[-(4\pi r)^2 u^2]. \tag{10}$$

Here $\kappa = d/\lambda_\infty$ is the reduced film thickness, $r = h/\lambda_e$ is the surface roughness parameter (h is the RMS surface roughness and λ_e is the Fermi wavelength) and $u = \cos\theta$ (θ is the angle of incidence of the electron relative to the surface normal).

Equations (1)–(3) of the MS model can be used for the analysis of the data by considering the influence of only the grain-boundary scattering on the excess resistivity, assuming the Fuchs specularity parameter $p = 1$. We have fitted equations (1)–(3) to the data as a function of temperature at a given film thickness by using the known values of $\rho_\infty(T)$ (from our experiment), $(\rho\lambda)_\infty = 0.66 \times 10^{15}$ Ω m^2 (Mayadas and Shatzkes 1970) and D (from the TEM micrographs). In carrying out this fit, we have derived a reflection coefficient $R = 0.38$ by averaging over all thicknesses. Tochitskii and Belyavskii (1980) found $R = 0.29$ in copper films onto a (001)-cleaved NaCl single crystal.

We have also fitted equations (1)–(3) to the data of the 500 K annealed films in the same manner as for the as-deposited films. We have obtained the same value of the reflection coefficient $R = 0.38$ by averaging over all thicknesses. de Vries (1987a) also found the reflection coefficient $R = 0.35$ for both as-deposited and annealed gold films onto Si substrate.

The size effect C in equation (5) of the MS model can be obtained from the plot of $\rho_f d$ against d and thus a reflection coefficient R can be found. As seen in figure 4, the $1/d$ dependence of the total film resistivity ρ_f also strongly indicates the dominance of grain-boundary scattering in both as-deposited and 500-K annealed single-layered copper films. From the intercept of the straight lines with the vertical axis we have obtained the value of the size effect $C = 0.55 \times 10^{-15}\ \Omega\ \mathrm{m}^2$ for as-deposited and $C = 0.41 \times 10^{-15}\ \Omega\ \mathrm{m}^2$ for 500 K annealed films. Since we know the ratios $n = D/d$ to be 1.12 (as-deposited films) and 1.500 (500 K annealed films), we have derived a reflection coefficient $R = 0.38$ for both as-deposited films and 500 K annealed films, using equation (6). Very clearly the agreement between values of R obtained from theoretical fit and from figure 4, as described above, is good.

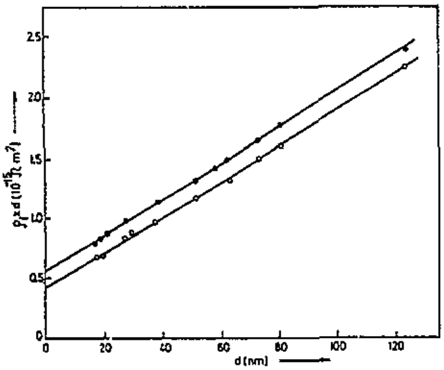

Figure 4. The product of room-temperature resistivity and thickness ($\rho_f d$) versus thickness d for as-deposited (●) and 500 K annealed (○) copper films.

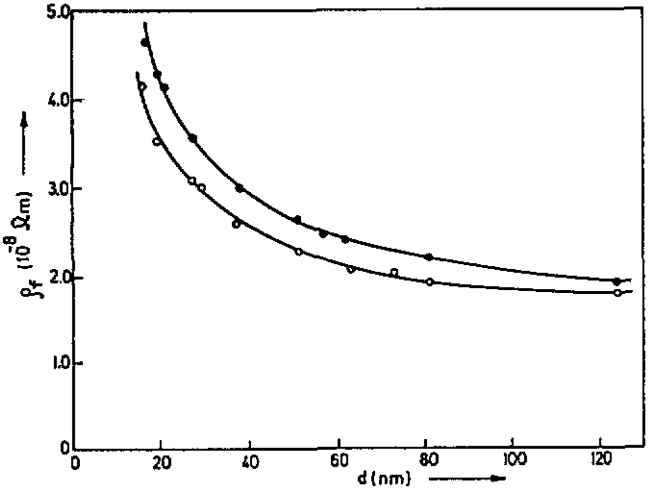

Figure 5. Experimental room-temperature resistivity ρ_f versus d for as-deposited (●) and 500 K annealed (○) copper films and the corresponding calculated curves.

In figure 5 we have plotted the experimental room-temperature resistivity data as a function of the film thickness together with the resistivity calculated from MS theory, using the average values of $R = 0.38$ for both as-deposited and 500 K annealed films. It is clearly seen that there is good agreement between MS theory and experiment.

Finally, equation (7) of the combined model of Sambles *et al* (1982) can be fitted to the data of both as-deposited and 500 K annealed films by considering the influence of both grain-boundary and surface scattering on the excess resistivity. We have fitted equation (7) to the data at 293 K to derive the values of surface roughness parameters r ($r = 0$ means no surface scattering and $r = 1$ means maximum surface scattering) using the known values of D, $\rho_\infty(293\ \mathrm{K})$, $(\rho\lambda)_\infty$ and $R = 0.38$. From this fitting procedure, we have found the same values of $r = 0.0$ for all the as-deposited and 500 K annealed films except for the thinnest samples of 16.6 nm thickness where we found $r = 0.025$ and $r = 0.035$ respectively.

If we transform the obtained values of r into the well known Fuchs specularity parameter p, in the high-temperature limit, at 293 K (Sambles and Elsom 1980), we then find the specularity parameters $p = 1$ for $r = 0$ in all the films, both as-deposited and 500 K annealed, except for the thinnest samples of 16.6 nm thickness. In the as-deposited and 500 K films of 16.6 nm, $p \approx 0.98$–0.99 for $r = 0.025$ and $p \approx 0.93$–0.94 for $r = 0.035$ respectively. The surface roughness parameters derived for the as-deposited and 500 K annealed films of 16.6 nm are too small. The obtained values of r or p indicate that the scattering of conduction electrons at the surfaces of both as-deposited and 500 K annealed films can be considered almost specular in all the films studied. Consequently, our analysis demonstrates that the resistivity of as-deposited and 500 K annealed films is almost dominated by grain-boundary scattering and thus the data can be interpreted solely in terms of grain-boundary scattering, taking $p = 1$.

4. Conclusion

We have shown that the resistivity data of both as-deposited and 500 K annealed and single-layered copper films could also be analysed very well in terms of the grain-boundary scattering model of Mayadas and Shatzkes (1970) over the whole temperature and thickness range studied.

According to our analysis, grain-boundary scattering is the dominant contribution over the whole temperature and thickness range and surface scattering cannot be responsible for the excess resistivity of both as-deposited and 500 K annealed films.

Acknowledgments

This work is a part of project No TI-91/05 supported by TÜBİTAK Marmara Research Centre. We thank A Altındal for preparing the single-layered copper films and S Selvi for carrying out the fitting for the analysis of the resistivity data.

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