Influence of grain boundaries and surface Debye temperature on the electrical resistance of thin gold films

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(Received 21 June 1983)

The electrical resistivity of thin gold films deposited on amorphous substrates is found to increase with decreasing film thickness. The temperature-dependent part of the resistivity, however, is independent of the film thickness. This observation cannot be reconciled with existing theories that deal with surface scattering effects. We show that electron scattering at grain boundaries explains our measurements. Moreover, the main effect of the surface appears to be a change in the effective Debye temperature.

INTRODUCTION

It is a well-known fact that the electrical resistivity of thin metallic films increases with decreasing film thickness.[1] This increase is usually explained as being due to increased electron scattering at the film surface.[1] It is also well known that annealing of the films can reduce the resistivity (see Fig. 1). For a quantitative description of the experimental data the Fuchs-Sondheimer (FS)[2,3] theory is widely applied.[1] In the limit that the film thickness d is very much smaller than the bulk mean free path of the electrons λ_∞, the FS theory predicts

$$\rho_{f\,\mathrm{FS}}=\rho_\infty+\frac{3}{8}\frac{\rho_\infty\lambda_\infty}{d}(1-p_{\mathrm{FS}})\,, \tag{1}$$

where ρ_{FS} and ρ_∞ are the resistivities of the thin film and the bulk material, respectively. The so-called specularity coefficient p_{FS} is a phenomenological parameter which characterizes the fraction of carriers that are not diffusely scattered at the surface. Since $0\leq p_{\mathrm{FS}}\leq 1$, the resistivity of a thin film increases with decreasing film thickness. In the spirit of the FS theory, annealing of thin films is believed to have the effect of smoothing the surface and enhancing the specularity coefficient.

The FS theory assumes that the thin films are homogeneous in the sense that scattering of electrons at grain boundaries can be neglected. It is just this assumption that does not hold for many experiments, since often films are polycrystalline with grains that are comparable in dimension with the film thickness. In this paper we will show that in thin gold films deposited on various amorphous substrates electron scattering at grain boundaries is the mechanism that dominates the electrical resistivity. To this end we have studied the temperature and thickness dependence of the electrical resistivity.

EXPERIMENTAL

Sample characterization

The gold used in this study was 99.95% pure. It was in the form of small pellets. Two different types of samples were prepared. For the first type, gold was evaporated in a vacuum of 10^{-4} Pa using an electron-beam evaporator system. Between the gold source and the polished Pyrex substrate a specially designed shutter was rotating, which allowed several samples to be prepared in one run with a constant difference in thickness determined only by geometrical factors. The shape of these samples was rectangular and the electrical contacts were made on the film itself. The second type of samples were prepared by evaporation (~ 1 Å/sec) from a tungsten crucible. The substrate was either polished Pyrex, or silicon dioxide or silicon nitride grown on a silicon wafer. A molybdenum mask was placed on top of the substrate. The sample configuration was again rectangular with separate electrical contact pads to allow an accurate four-probe measurement. In one run three samples of different width but the same thickness could be prepared. In all cases electrical leads were made to the samples using indium. In all evaporations the substrate was kept at room temperature; just before evaporation a short glow discharge was applied.

The thickness of the sample during evaporation was monitored with a quartz-crystal oscillator. After the preparation the thickness was measured with a talystep (Rank-Taylor-Hobson type). The uncertainty in the thickness was $\sim 3\%$. Combined with the uncertainty in the ratio of the length and width of the film, this leads to an overall error range of less than 10% for the samples of the second type. In the first type the ratio of length to width was less accurately known. For this reason, we tried to use the temperature-dependent part of the resistance to obtain the thickness. Since in gold the surface contribution to the resistivity is very small, the thickness can be calculated by comparing the experimental difference in resistance at 295 and 125 K with the corresponding bulk value.[4,5] The agreement was within 5% where both thickness determinations could be used. In the following we will give the thickness as determined from the resistance.

Part of the samples were heat-treated in an attempt to lower the resistivity. The heating was done in air and it was found that the best results were obtained at a temperature of 350 °C. The heating step at a given temperature lasted 15—30 min. Above 350 °C the resistance in-

creased again due to the forming of droplets and islands. Transmission-electron-microscopy (TEM) measurements to study the morphology of the samples were done with a Philips EM400 microscope.

Measurement of the resistance

Resistances were measured using a standard dc four-probe technique. To avoid heating of the samples the total power dissipated by the measuring current was 1—10 μW. The effect of spurious thermal voltages was eliminated by taking two voltage readings at each temperature, one with reverse current. The samples were mounted in a vacuum can immersed in liquid helium. The temperature could be varied from 1.1 to 300 K.

EXPERIMENTAL RESULTS AND DISCUSSION

Plots of the resistivity versus thickness at 295 K for both as-deposited and heat-treated films are shown in Fig. 1. As-deposited films on Pyrex and silicon-oxide substrates follow the same curve. The heat-treated samples all have a lower resistivity; this decrease is more pronounced for some of the films on silicon oxide. A similar dependence of the resistivity versus thickness is found at all temperatures. On the other hand it is also observed (see Fig. 2) that the temperature-dependent contribution to the total resistivity $\rho^*(T)$, i.e., the total resistivity minus the temperature-independent part for which we choose $\rho(T)$ at 8 K, varies very little ($<5\%$) between the different as-deposited films and is a little larger than in bulk material.[4] For the heat-treated samples the same observation was made.

This experimental fact, namely that the temperature-dependent part of the resistivity is almost independent of the film thickness while the total resistivity as a function of film thickness changes quite strongly, gives the decisive indication for the mechanism dominating the resistivity in thin gold films. In Fig. 3(a), $\rho^*(T)$ according to the complete FS theory is plotted versus temperature for three representative values of the film thickness. Clearly, a dependence on thickness is predicted. A more extended theory for surface scattering developed by Soffer[6] introduces a specularity parameter which depends on the angle of incidence of the electrons scattered at the surface. His theory also takes into account the influence of the surface roughness on the resistivity. In Fig. 3(b) we have plotted $\rho^*(T)$ according to the Soffer theory. Again a variation with thickness is predicted. Thus neither the FS nor the Soffer theory explains our experimental observation that the temperature-dependent contribution to the resistivity is almost independent of the film thickness.

We turn now to grain-boundary scattering. A one-dimensional theory was proposed by Mayadas and Shatzkes (MS).[7] In the MS theory the grain-boundary-enhanced resistivity ρ_{gr} is

$$\rho_\infty/\rho_{gr}=1-\tfrac{3}{2}\alpha+3\alpha^2-3\alpha^3\ln(1+\alpha^{-1}) , \tag{2a}$$

where

$$a=(\lambda_\infty/D_{gr})(R_{gr}/1-R_{gr}) , \tag{2b}$$

D_{gr} being identified with the mean-grain diameter and R_{gr} being the reflection coefficient for carriers striking the grain boundary. In this description the temperature dependence of the resistivity is contained in λ_∞. Note that it is implicitly assumed that the interior of the grains

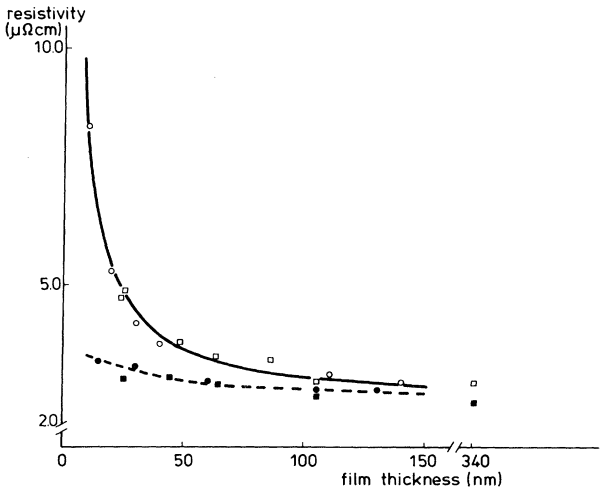

FIG. 1. Resistivity of gold films vs thickness at 295 K. ○, as-deposited on Pyrex; □, as-deposited on silicon oxide; ●, heat-treated on Pyrex; ■, heat-treated on silicon oxide. Solid line is a theoretical fit to the data using Eq. (2) (see text). Dashed line is to guide the eye.

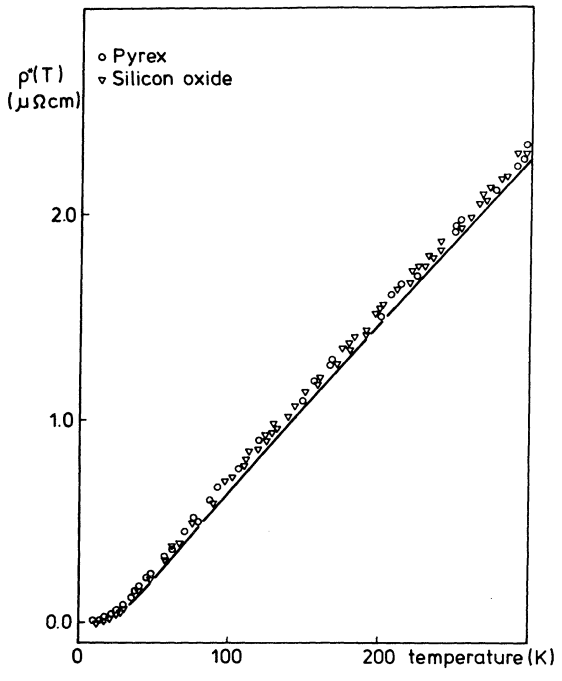

FIG. 2. Temperature-dependent contribution to resistivity vs temperature for as-deposited films. Symbols are for films deposited on Pyrex and silicon oxide, respectively. For both substrates, values for films of different thickness, ranging between 10 and 350 nm, are included. Solid line is temperature-dependent resistivity in bulk gold (Ref. 4).

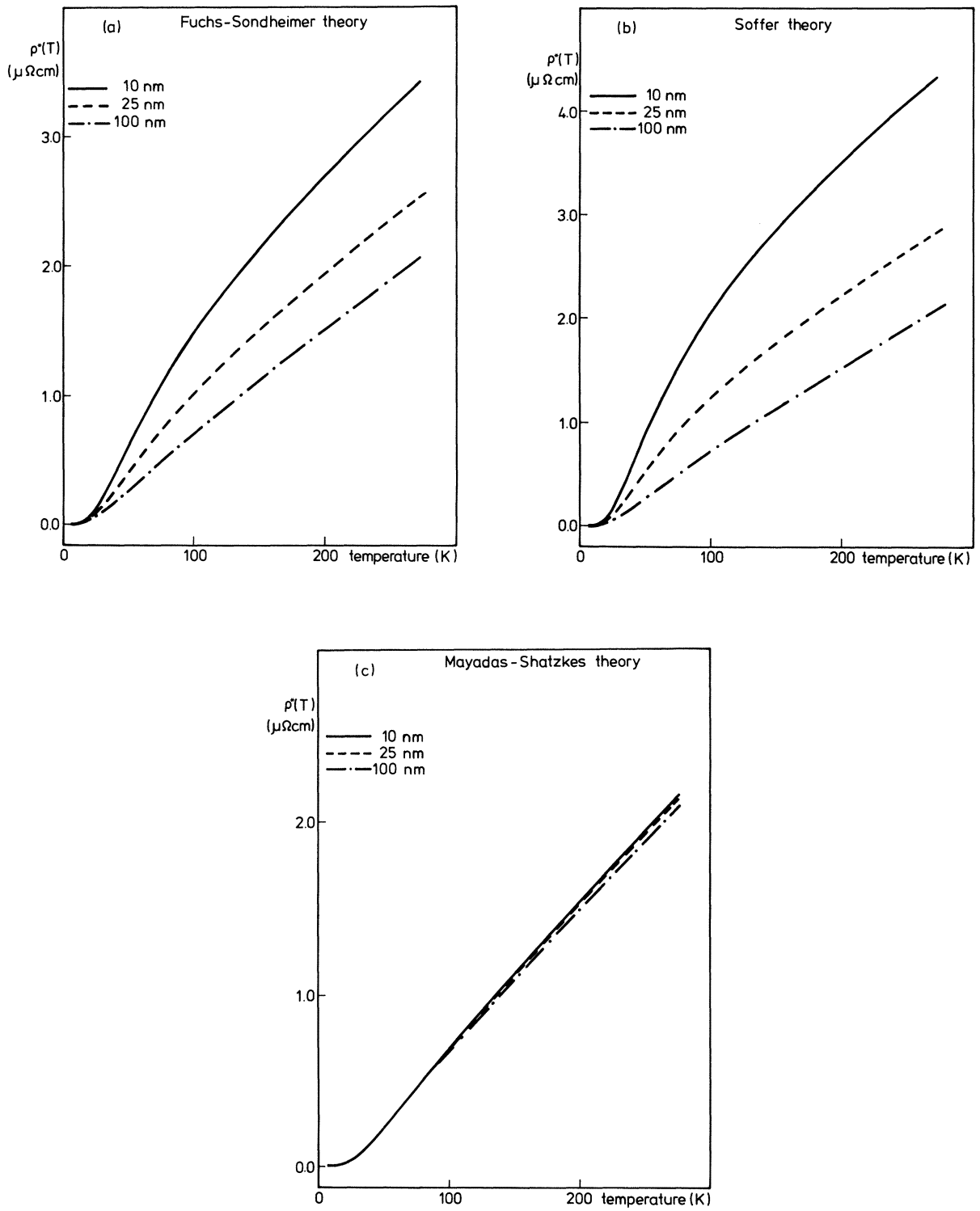

FIG. 3. Temperature-dependent contribution to resistivity vs temperature according to (a) FS theory with $p_{FS}=0$, (b) Soffer theory with surface roughness equal to 1.0 (see Ref. 6 for details), and (c) MS theory with average grain size equal to film thickness.

behaves in the same way as the corresponding bulk material. So the temperature dependence is derived as follows: Using $\rho_\infty \lambda_\infty = 9.6\ 10^{-12}\ \Omega\,\mathrm{cm}^2$ (Ref. 8) for gold at all temperatures, which is equivalent to stating that the number of carriers involved in the electrical conduction is constant, and applying Matthiesen's rule that

$$\rho_\infty = \rho_p + \rho_i \ , \tag{3}$$

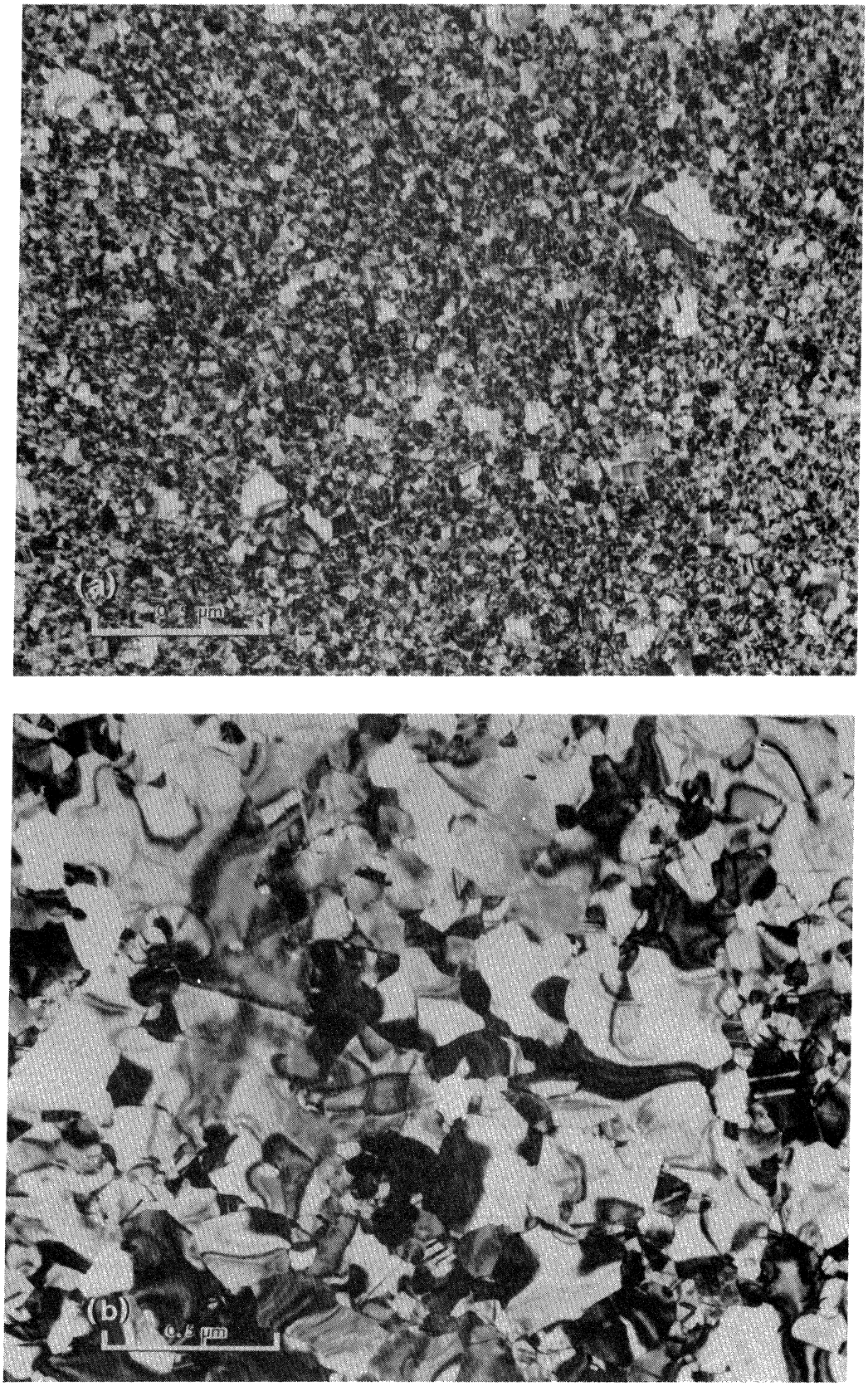

FIG. 4. TEM Photographs of a 30-nm-thick gold film deposited on Si_3N_4: (a) as-deposited and (b) after heat treatment.

where ρ_p is the phonon contribution to the resistivity and ρ_i is the residual resistivity, the bulk mean free path can be calculated from the Bloch-Grüneisen formula for ρ_p with the Debye temperature Θ_D as the only parameter. The value of the residual resistivity can be derived from two different experimental pieces of information. First, from the resistivity ratio of the thickest sample (340 nm) after heat treatment, i.e., $\rho(T=295\ \text{K})/\rho(T=8\ \text{K})$, and secondly from the slope in plots of ρ_f^d vs d at both 295 and 8 K.[9] In this way we found that the residual resistivity of the bulk material amounts to $0.18\pm0.01\ \mu\Omega\,\text{cm}$. Plots of $\rho^*(T)$ versus temperature according to the MS theory with the assumption that the average grain size equals the film thickness are shown in Fig. 3(c). Only a very small dependence on thickness is predicted, in agreement with the experimental results of Fig. 2.

We fitted the experimental resistivity as function of temperature at a given film thickness using Eq. (2) with Θ_D and α/λ_∞ as free parameters and keeping ρ_i constant. We focus first on the as-deposited films. The fits show quite good agreement both for the films on Pyrex and on silicon oxide. For the parameters it was found that $\Theta_D=172\pm1$ K at all thicknesses, i.e., equal to the bulk value.[4] Furthermore, it was observed that the values of α/λ_∞ [i.e., $(1/D_{\text{gr}})R_{\text{gr}}/(1-R_{\text{gr}})$] are inversely porportional to the film thickness. From a separate TEM measurement on a 30-nm-thick gold film deposited on a specially prepared Si_3N_4 substrate[10] [see Fig. 4(a)] we conclude that the average grain diameter equals the film thickness, although some grains are as large as 0.5 μm. This was also observed in other studies.[9,11] However, for the film of 340 nm it was found that the grain size was only about half the film thickness. From the fact that the average grain size equals the film thickness it is calculated that the reflection coefficient R_{gr} is 0.295 ± 0.02, which is in good agreement with results on sputtered films[12] and somewhat smaller than in gold films evaporated on mica and KBr.[8] The solid line in Fig. 1 is the theoretical curve calculated from Eq. (2) with the assumption that the grain size equals the film thickness and with $R_{\text{gr}}=0.295$ and $\rho_i=0.18\mu\Omega\,\text{cm}$. The agreement with the experimental data is remarkably good. Concluding this section it can be said that the electrical resistivity of thin gold films deposited at room temperature on Pyrex and silicon-oxide substrates give very similar results, which can be only explained by grain-boundary scattering. Note that the MS theory is essentially a one-dimensional theory. Thus, the exact numbers may be slightly idealized, although the observed trends are probably correct.

We turn now to the morphology of the heat-treated films. Figure 4(b) shows a TEM photograph of a film of the same thickness as in Fig. 4(a) after heat treatment. As can be seen, the grain size has *increased drastically.* Thus, an important contribution to the reduction in resistivity of the heat-treated samples, which was shown in Fig. 1, is identified with the larger average grain size, implying more bulklike behavior. Computer fits using again only grain-boundary scattering gave satisfactory agreement with the experimental data (see Fig. 5). Setting $R_{\text{gr}}=0.295$, the average grain diameter can be calculated. It is found for the films on glass that at $d=15$ nm the grain size becomes about 65 nm, while for $d=100$ nm the grains grow only by a factor of 2. This explains why the decrease in resistivity for films of thicknesses less than 50 nm is more pronounced than for thicker films. Two of the films on silicon are in line with the results on Pyrex, while the other three films give a larger increase in the grain size. For the 340-nm-thick film we obtained *a grain size of 2* μm. The reason for this different behavior on silicon oxide is not understood at present.

Another remarkable observation in the computer fits on the heat-treated films is that the effective Debye temperature turns out to be lower than the bulk value. Although the effect is small, only a few degrees, we believe it to be significant, especially as it increases with decreasing film thickness. It might be thought that the decrease of the fitted Debye temperature is an artifact of the fitting procedure. Since in the thinnest films the bulk mean free path is larger than the film thickness and in the heat-treated samples is no longer limited by the grain size, surface scattering is expected to be more important. However, fits incorporating grain-boundary scattering and surface scattering[8] using the Soffer theory with the Debye temperature fixed at the bulk value result in systematic deviations between the calculated and experimental curves (see Fig. 5). It is necessary to reduce the Debye temperature to obtain a reasonable fit. A lower Debye temperature for the surface layer seems physically reasonable in view of the missing bonds at the vacuum interface, leading to different vibration amplitudes; furthermore, a lowering of the Debye temperature for the surface layer has also been deduced from other experiments.[13,14]

In conclusion, we have shown that grain-boundary scattering is very important both in as-deposited and

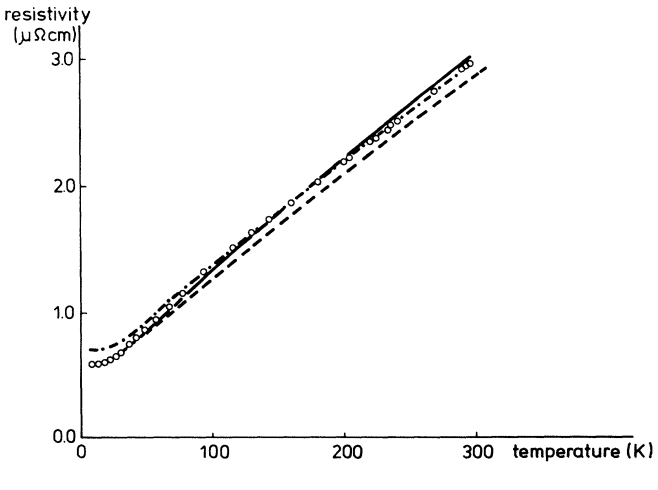

FIG. 5. Effect of surface scattering on the resistivity in heat-treated films: Open circles—experimental data of a film with a thickness of 25 nm on silicon oxide; solid line—fit using only grain-boundary scattering ($\Theta_D=165.1$ K); dashed line—fit using grain-boundary scattering and Soffer theory (optimal fit at low temperature; $\Theta_D=172.1$ K); and dashed-dotted line—fit using grain-boundary scattering and Soffer theory (optimal fit at room temperature; $\Theta_D=172.1$ K).

heat-treated films of gold. The surface manifests itself primarily by a lowering of the effective Debye temperature. Consequently, to observe surface scattering effects in pure form, it is necessary to use single crystals.

ACKNOWLEDGMENTS

We thank J.C.N. Rijpers for the preparation of several films in the early stage of this study.

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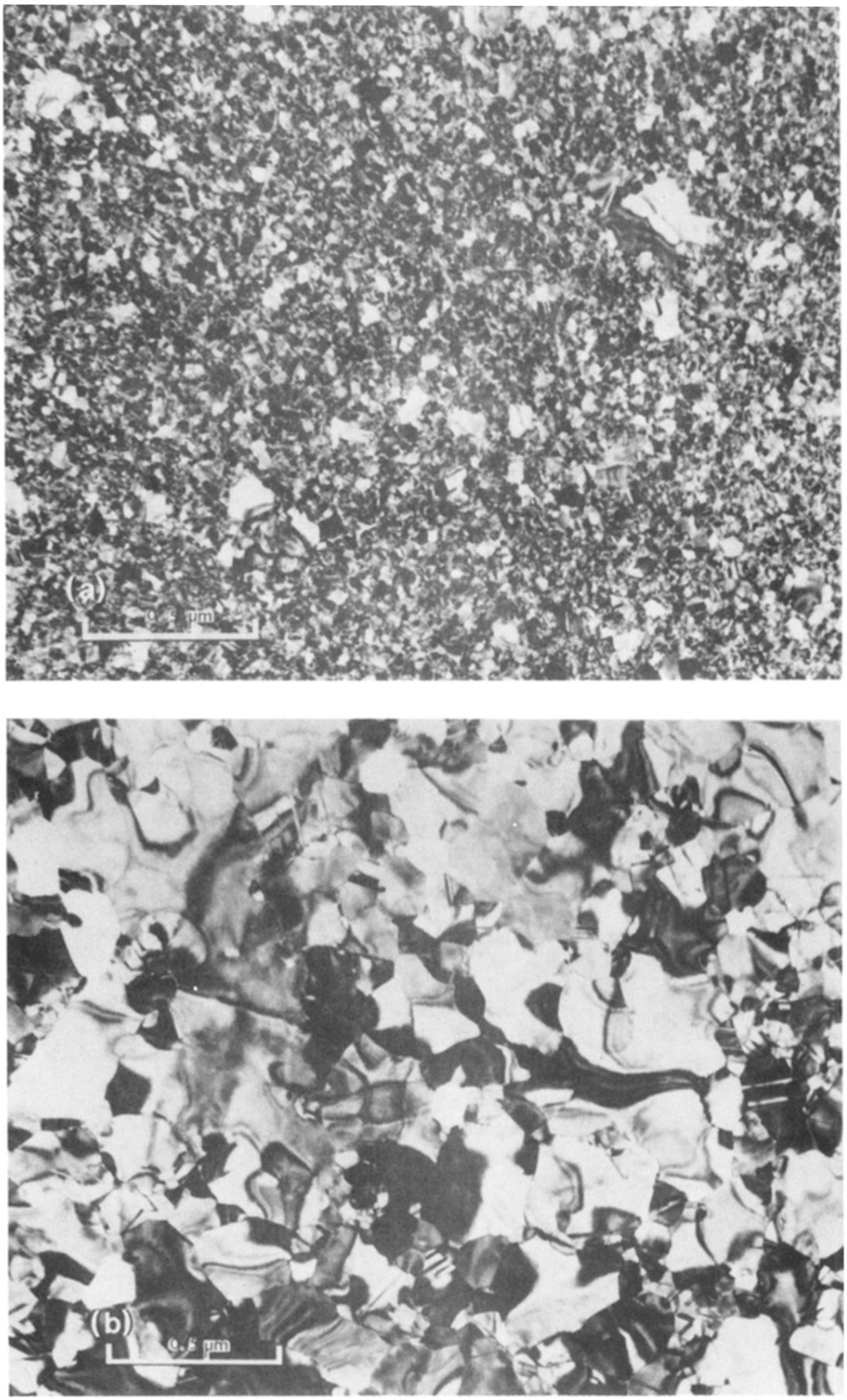

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