in Eq. (2) by δ function, since[18]

$$\mathrm{Im}\left(\frac{1}{\epsilon(q,\omega)}\right)=\left|\frac{\partial\epsilon_1(q,\omega)}{\partial q}\right|^{-1}_{\omega=\omega_p(q)}\delta(q-q_p(\omega)). \quad (8)$$

The quantity $|\partial\epsilon_1(q,\omega)/\partial q|_{\omega=\omega_p(q)}{}^{-1}$ is the plasmon strength and is plotted in Fig. 3. One notices that it is a monotonically decreasing function of q and vanishes as $q>q_c$. Then the plasmon-contributed absorption can be easily evaluated by substituting the relation (8) into Eq. (2), and we obtain

$$\epsilon_2(\omega)=\tfrac{1}{2}Z\left(\frac{\omega_p}{\omega}\right)^4 \times\left[\left(\frac{\sin qR}{R}\right)^2 \mathcal{A}(q)\left|\frac{\partial\epsilon_1(q,\omega)}{\partial q}\right|^{-1}_{\omega=\omega_p(q)}\right]_{q=q_p(\omega)}. \quad (9)$$

The result is shown in Fig. 4 as a dashed line. The sum of Drude absorption and the plasmon-contributed absorption is the solid line in Fig. 4. Our result shows a well-defined plasmon resonance peak in the optical absorption with threshold at $\hbar\omega_p=(5.83\text{ eV})$, maximum at 6.23 eV, and upper bound at 8.5 eV. The magnitudes of the plasmon-contributed absorption and the Drude absorption are of the same order. Therefore, the plasmon resonance effect should be observable.

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Resistivity Studies of Single-Crystal and Polycrystal Films of Aluminum*

A. VON BASSEWITZ AND E. N. MITCHELL
University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514
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The resistivities of condensed polycrystal and single-crystal aluminum films have been measured as a function of thickness (1600–36000 Å) and temperature (4.2–300°K). Both the temperature-independent residual resistivity and the temperature-dependent resistivity increase with decreasing film thickness. The residual resistivity agrees very well with the Fuchs-Sondheimer theory. Both groups of films have the same bulk electron mean free path but different reflection parameters. The increase in the temperature-dependent part of the resistivity is larger but similar to the deviations predicted by the Fuchs-Sondheimer theory.

INTRODUCTION

THE electrical resistivity of a thin film or wire is known to depend on the specimen dimensions whenever one dimension is comparable with the mean free path of the conduction electrons. Both the residual and the temperature-dependent part of the resistivity increase with decreasing dimensions because of the scattering of the electrons at the specimen boundaries. The increase of the residual resistivity is well understood in the form of the Fuchs-Sondheimer (FS) theory.[1,2] Using this theory, one can determine the mean free path of the conduction electrons and the reflection parameter p which gives the probability of specular reflection of the electrons at the boundaries of the specimen. In a specimen whose surfaces are so smooth that the electrons are specularly reflected, the increase of the resistivity in thin films is reduced.

The dependence on size of the variations of the resistivity with temperature is much less understood. In pure bulk material, no deviations from Matthiessen's rule are observed, meaning that all scattering processes are independent. This is not valid any more in alloys and thin films. According to the FS theory, one should observe an inverse variation with thickness of the temperature-dependent part of the resistivity in thin films because of anisotropy of the relaxation time for scattering near surfaces.[1–3] However, there seems to be an excess increase with decreasing thickness which cannot be explained by the FS theory. Such deviations were first observed by Andrew[4] in Hg wires and Sn foils and by Olsen[5] in In wires. These measurements were observed at temperatures between 1 and 4.2°K. Olsen suggested the following explanation: At low

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temperatures the normal electron-phonon process is a small-angle event. That means it takes a large number of collisions to remove the momentum from the electron. In bulk material this would not contribute very much to the resistivity but in a thin specimen it requires only a few collisions to deflect the electron to the surface where diffuse scattering contributes to the resistivity. This mechanism has been treated theoretically by Blatt and Satz[6] for thin wires and by Azbel and Gurzhi[7] for films. The measurements by Olsen agreed very well with this theory. But other measurements on indium samples by Wyder[8] and by Aleksandrov[9] did not show any deviations from Matthiessen's rule. The temperature dependence for films was investigated by Holwech and Jeppesen[10] in Al films, and by Chopra[11] and by Tanner and Larson[12] in condensed Ag films. Only Chopra found a dependence as predicted by Azbel and Gurzhi. Holwech and Jeppesen found deviations only slightly larger than the ones predicted by the FS theory. Tanner and Larson found large deviations in the residual and temperature-dependent resistivity, although, as stated in an earlier paper,[13] for films grown under similar conditions the residual resistivity agreed very well and with this theory.

Because of the importance of Al technically, in printed and condensed circuits, and theoretically, for solving many conduction phenomena, many size-effect measurements have been carried out on this material. But all these measurements were done with samples which were either cut from bulk material or grown out of a melt. There is only one very recent and limited investigation which has been done on condensed Al films.[14] Because of our interest in superconducting phenomena in aluminum films, it was decided to look further into the conduction phenomena of Al films in general. As the evidence for specular reflection is generally greater in single-crystal films and because of our stated interest, we have measured size effects in single-crystal Al films, which had not been done until now. We have compared the size effect in single crystal to the size effect in polycrystal films. Both groups of films were grown on the same kind of substrate in order to determine the size effects due to the single-crystal nature of the film and not to different substrates. In the first part of the experiment we measured the residual resistivity to see whether polycrystal and single-crystal Al films have a different bulk mean free path and a different reflection parameter. Because of the great uncertainty concerning deviations from Matthiessen's rule, we investigated also the temperature dependence of four single-crystal films with differing thicknesses as well as a bulk sample.

EXPERIMENTAL TECHNIQUES

The single-crystal Al films were prepared by evaporation of commercial 99.999% Al and 99.9999% Al from an outgased tungsten wire filament condensed onto a KBr substrate, heated to 380°C. The substrates were air-cleaved and polished parallel to the (100) surface in order to avoid cleavage steps.[15] Previous to the evaporation the substrates were baked for 2 h at 400°C in a vacuum better than 5×10^{-7} Torr. The evaporation rate was about 300 Å/sec. During the evaporation, the pressure in the vacuum system rose to 2×10^{-6} Torr. A gas analyzer indicated that this rise was due to water. The polycrystal films were prepared under the same conditions, except that the evaporation took place at room temperature followed by an annealing to 380°C in the vacuum system. After removal from the vacuum system, all films were examined in an Hitachi HU-11A electron microscope. The film resistance was measured by a four-terminal technique while the temperature was varied from 4.2 to 300°K. The thickness t of the films was determined from the temperature-dependent part of the film resistance.[1] Bassewitz and Minnigerode[3] have established the validity of this method for lead and copper films deposited at room temperature. One finds that

$$t=(\Delta\rho_\infty/\Delta R)L/W.$$

Here $\Delta\rho_\infty$ is the change in the resistivity of an infinitely thick sample between the temperatures 120 and 300°K. This value was taken from resistance-ratio measurements by Grüneisen[16] and by Aleksandrov and D'Yakov[17] and from resistivity measurements by Revel,[18] by Reich and Montariol,[19] and by Førsvoll and Holwech[20] ($\rho_{273°\mathrm{K}}=2.65\times10^{-6}\ \Omega$ cm). ΔR is the change in the film resistance between the same temperatures. In this temperature range, size effects are assumed independent of temperature. L and W are the length and the width of the film.

The resistivity $\rho(\tau)$ of the film is given by

$$\rho(\tau)=R(\tau)\Delta\rho_\infty/\Delta R,$$

where $R(\tau)$ is the film resistance. Using this method, one can determine the film resistivity without knowing the specimen dimensions.

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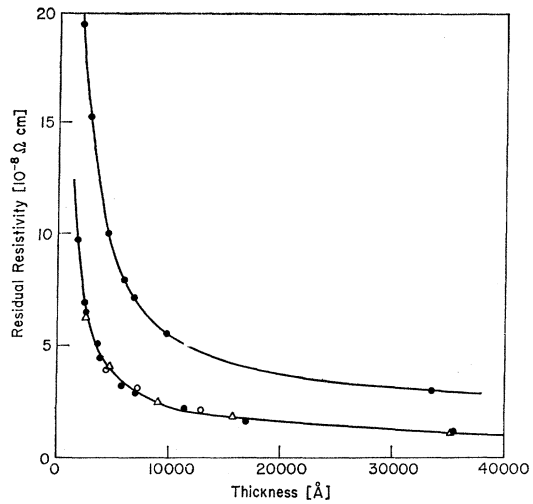

FIG. 1. Residual resistivity of condensed polycrystal and single-crystal aluminum films as a function of thickness. (Upper curve: polycrystal films; lower curve: single-crystal films; ●: 99.999% Al on polished KBr; ○: 99.999% Al on cleaved KBr; △: 99.9999% Al on polished KBr.)

EXPERIMENTAL RESULTS

All Al films evaporated at 380°C in the above-mentioned way were perfectly (100) oriented: (100) film‖(100) substrate and [100] film‖[100] substrate. Grain boundaries were hard to find since the grain size was at least 30 μ. There were no structure differences visible in films evaporated from 99.999% Al or 99.9999% Al nor any differences between films grown on an air-cleaved or polished substrate. Films condensed at room temperature and then annealed to 380°C were polycrystalline with a grain size of about 2500 Å. These films had a [111] texture axis. Films in the thickness range 1600–36 000 Å were investigated. Single-crystal films, thinner than 1600 Å, were not continuous because of the high substrate temperature during evaporation. In these films the electron mean free path is not determined by the film thickness but by channels and holes in the film. This lower thickness limit for useful size-effect measurements can be much higher for slower evaporation rates.

In Fig. 1 the film resistivities at 4.2°K are plotted as a function of film thickness. The resistivity measured at 4.2°K is equal to the residual resistivity: Lowering the temperature from 4.2 to 2.0°K did not change the film resistivity. In the thickness range investigated the resistivity of single-crystal films is smaller than the resistivity of polycrystal films; in single-crystal films the residual resistivity varies from 8.5×10^{-8} to 1.1×10^{-8} Ω cm for the polycrystal films from 18×10^{-8} to 2.0×10^{-8} Ω cm for thicknesses between 2000 and 36 000 Å. The room-temperature resistivity varied from 2.66 to 2.85×10^{-6} Ω cm for single-crystal and polycrystal films. This is only slightly above the bulk value of 2.65×10^{-6} Ω cm. The resistivity ratio $r=\rho_{293°K}/\rho_{4.2°K}$ varies for single-crystal films from 30 to 230 and for polycrystal films from 14 to 90.

No difference in resistivity was observed for 99.999% or 99.9999% Al, nor for air-cleaved or polished substrates, which was expected, since no differences in film structure were observed. For the study of the temperature dependence of the resistivity four typical single-crystal films with thicknesses of 1600, 4750, 9000, and 17 000 Å have been chosen. In order to see deviations from bulk behavior the resistivity of a bulk sample made from 99.999% Al (the same material used for the evaporation) has been studied. The resistivity ratio was about 800 and rose to 2000 after annealing under vacuum at 300°C for 4 h. This change in residual resistivity was accompanied by only an insignificant change in the temperature-dependent part of the resistivity for temperatures below 25°K. Figure 2 shows the result of these measurements. The resistivity is plotted versus temperature from 4.2 to 80°K. There are differences in the temperature dependence of the resistivity of the films and of the bulk sample, and this will be discussed later.

DISCUSSION

Residual Resistivity

The low temperature resistivity of these films (single crystal as well as polycrystal) indicates that the impurity-determined electron mean free path is much larger than the film thickness, even for the thickest films. In this range the film resistivity ρ as a function of thickness t is given by a simple approximation of the

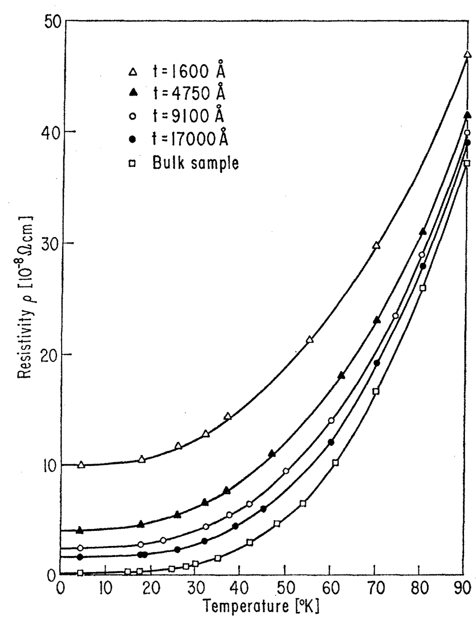

FIG. 2. Total resistivity of four aluminum films with different thicknesses and of a bulk sample as a function of temperature from 4.2 to 90°K.

FS equation

$$\frac{\rho_\infty}{\rho}=\frac{3}{4}\frac{t}{l_\infty}\frac{1+p}{1-p}\ln\frac{l_\infty}{t}.$$

Here ρ_∞ and l_∞ are the values of resistivity and electron mean free path for an infinitely thick film. p is the reflection parameter. This equation can be written

$$\frac{r}{t}=\frac{3}{4}\frac{r_\infty}{l_\infty}\frac{1+p}{1-p}\ln\frac{l_\infty}{t},$$

where r and r_∞ are, respectively, the resistivity ratios of a given film and an infinitely thick film.

In Fig. 3, r/t is plotted as a function of $\ln t$. All of our films satisfy this approximation very well, indicating that the impurity-determined electron mean free path and the reflection parameter do not vary with film thickness. Both the curves, for single-crystal and for polycrystal films, intersect the x axis at the same thickness. This point determines the mean free path of an infinitely thick film. The same intersection for single-crystal and polycrystal films means that they have the same bulk mean free path of 17.5 μ. This result is very remarkable because the grain size in single-crystal and polycrystal films is different by a factor greater than 100. We have to assume that the electrons are scattered primarily by impurities and defects within the grains and not at the grain boundaries. The polycrystal and single-crystal films give different slopes for the two curves, however. The slope is determined by the reflection parameter and bulk resistivity ratio. Because it is unlikely that the bulk resistivity ratio is different in these films when both single-crystal and polycrystal films have the same bulk mean free path, the reflection parameter has to be larger in single-crystal films. If it is assumed that in polycrystal films the electrons are diffusely scattered at the film surfaces, then a probability of 42% for

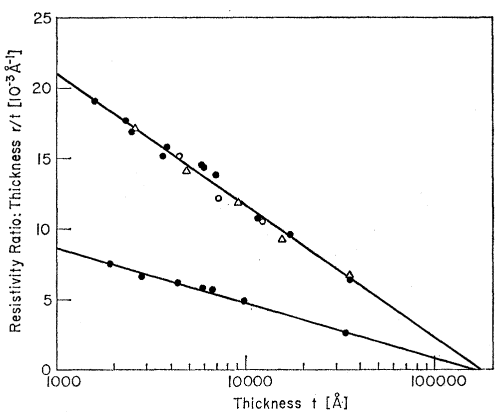

FIG. 3. Resistivity ratio divided by thickness as a function of thickness. (Upper curve: single-crystal films; lower curve: polycrystal films; ●: 99.999% Al on polished KBr; ○: 99.999% Al on cleaved KBr; △: 99.9999% Al on polished KBr.)

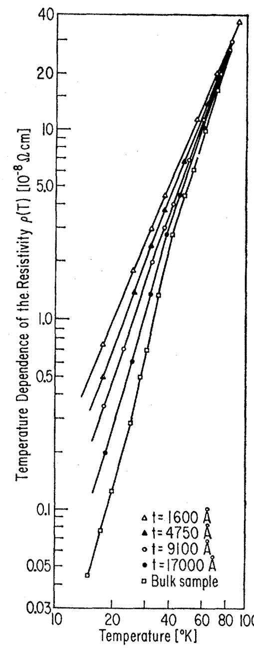

FIG. 4. Temperature-dependent part of the resistivity of four films with different thicknesses and of a bulk sample as a function of temperature from 15 to 90°K.

specular reflection is obtained in single-crystal films, indicating that one observed partly diffuse and partly specular surface reflection in this case.

Because one finds no difference in the reflection parameter for films grown on cleaved substrates and on polished substrates, although the surface of the latter is much rougher, one is inclined to assume that most of the specular reflection occurs on the upper surface of the film. With a total reflection parameter of 42%, assuming the above, the reflection for the upper surface has to be nearly specular.

A possible explanation for the smoothness of the upper surface in single-crystal films may lie in the large grains. The grain size in these films is larger than the impurity-determined mean free path, whereas in polycrystal films the grain size is 1/50 of the mean free path. Thus the surface is much more disturbed, and this suppresses the specular reflection in polycrystal films.

If one assumes diffuse scattering for polycrystal films, this determines the value of ρl for these films. According to the free-electron model this product should be constant. Instead, it has been shown that the value in Al increases with increasing impurity content. For high-purity Al this value is between 7 and 8×10^{-12} Ω cm^2.[19–23] From our measurements we determine a value of $\rho l=11.5\times10^{-12}$ Ω cm^2, which is consistent with the measurements of Montariol and Reich[19] and of Førsvoll and Holwech[20] since the resistivity ratio for an infinitely thick film is only 400. The value of ρl should be larger

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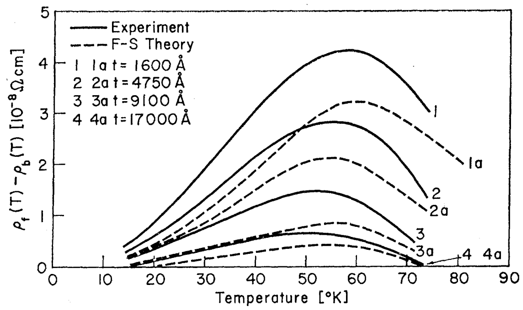

FIG. 5. Difference between the temperature-dependent part of the film resistivity and the bulk-sample resistivity as a function of temperature.

for films than the value for the high-purity Al with much higher resistivity ratios.

Temperature Dependence of the Resistivity

The effect of the film thickness on the temperature dependence of the resistivity can be seen in Fig. 2. There is a marked difference in the resistivity between the different films and the bulk sample. In Fig. 4, the temperature-dependent part of the resistivity, i.e., the total resistivity less the residual resistivity, is plotted versus temperature. If Matthiessen's rule is valid in this case, all curves would be coincident at all temperatures. Indeed, the resistivity increase with temperature of the film is less than in the bulk sample and becomes even less as the films are made thinner. For the bulk sample one finds a $R \sim T^{4.6}$ dependence between 25 and 45°K. At higher temperatures the power becomes smaller and approaches a linear dependence for $T > 100$°K. For temperatures below 25°K one finds a smaller change with temperature, indicating that one does not have a simple electron-phonon process. Instead, umklapp scattering and electron-electron scattering contribute to the resistivity. The power of the temperature dependence in the four measured films decreases from 3.4 to 2.4 with decreasing thickness. No one of these films showed the temperature dependence predicted by Azbel and Gurzhi[7] for small-angle scattering.

In Fig. 5 is plotted the difference between the temperature-dependent part of the film resistivity and of the bulk sample. This difference vanishes at high and low temperatures and reaches a maximum at temperatures between 50 and 60°K. Although the maximum deviations are small compared to the total resistivity, they are for the thinnest film almost 50% of the temperature-dependent part at this temperature. These results are in good agreement with the measurements of Holwech and Jeppesen.[10] Because they used very much thicker films (their thinnest film was 100× thicker than ours), their deviations from Matthiessen's rule are much smaller, and the maximum has shifted to lower temperatures. In Fig. 5 are also plotted the deviations between film and bulk behavior according to the FS theory. For this calculation the values obtained from Fig. 3 were used as was the temperature dependence of the measured bulk sample. These deviations from Matthiessen's rule are quite similar to the experimental results, although the calculated deviations are smaller, especially on the low-temperature side. Since the temperature dependence of the resistivity predicted by Azbel and Gurzhi was not found, and since the measured deviations are similar to the deviations calculated with the FS theory, it is tempting to speculate that our measured deviations have the same origin as the FS theory, although the explanation of a similar result offered by Holwech and Jeppesen[10] in terms of variation of phonon-electron scattering probability over the Fermi surface cannot be ruled out. One recalls that the FS temperature dependence is due to anisotropy of the relaxation time for scattering processes near the film boundaries.

CONCLUSIONS

The resistivities of condensed polycrystal and single-crystal Al films have been measured. The residual resistivity agrees very well with the FS theory. Both groups of films, single-crystal and polycrystal, have the same bulk electron mean free path (17.5 μ at 4.2°K) but different reflection parameters. Assuming diffuse scattering for the polycrystal films, we find a probability for specular reflection of 42% for the single-crystal film and a value for $\rho l = 11.5 \times 10^{-12}$ Ω cm^2. A size-dependent increase in the temperature-dependent part of the resistivity has been observed. This increase is similar to the increase predicted by the FS theory, and it is postulated to be due to anisotropy of the relaxation time for the different scattering processes near the boundaries of the film.

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