Mean-free-path concept in polycrystalline metals

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A crude analysis of the observed thickness dependence of the conductivity in fine-grained metals shows a very weak connection with the resistivity caused by grain-boundary scattering. An "effective intrinsic mean free path" for the whole polycrystal, as introduced in the well-known theory of Mayadas and Shatzkes, cannot explain the observed size effect. It is impossible to define a mean free path for the whole polycrystal, especially if the resistivity is governed by grain-boundary scattering.

INTRODUCTION

The resistivity of a thin film will be strongly thickness dependent as soon as the thickness is comparable to the mean free path (MFP). This effect is therefore a direct manifestation of the MFP of the conduction electrons (CE's). The basic theory for metal films containing statistically distributed scattering centers was given in 1938 by Fuchs.[1] A simple approximation (Sondheimer approximation[2]) of Fuchs's equations has often been used in the literature:

$$\frac{\sigma_0}{\sigma_f}=1+\frac{3}{8}\frac{l_0}{d}(1-p)\ , \quad d>l_0\ , \tag{1}$$

with σ_f the conductivity of the film with thickness d, σ_0 the conductivity of the infinite thick film, l_0 the background scattering length, and p the specularity.

From the point of view of first-order perturbational theory, any additional scattering mechanism should reduce the MFP of the CE's. Therefore, the validity of the Fuchs theory for polycrystalline metal films was questioned in 1970 by Mayadas and Shatzkes (MS).[3] Considering multiple reflections of CE's at potential walls with average separation D (mean grain size) and quantum-mechanical reflection probability R, they adopted an effective intrinsic MFP, l_g, for the whole polycrystal, given roughly by[1,4,5]

$$l_g\simeq\left[\frac{\sigma_g}{\sigma_0}\right]l_0\simeq f\left[\frac{l_0}{D},R\right]l_0\ , \quad l_g<l_0\ , \tag{2}$$

with σ_g the conductivity of the polycrystal in the presence of grain-boundary scattering. Consequently, the thickness dependence of conductivity will be suppressed by grain-boundary scattering because

$$\frac{\sigma_f}{\sigma_g}=f\left[\frac{l_g}{d},p\right]\ , \tag{3}$$

i.e., for films with strong grain-boundary scattering no size effect will be observed, except when the crystallite size permanently equals the film thickness.[3]

According to the idea of Mayadas and Shatzkes, the analysis of the experimental thickness dependence only by the Fuchs theory leads to wrong values for the MFP; instead of the background MFP, l_0, in fact the effective intrinsic MFP, l_g, will be determined. This result, however, requires the definition of a characteristic MFP for both background and grain-boundary scattering using the Mathiessen rule. However, as far back as 1957, Landauer mentioned that there is no single relaxation time for the whole conduction process in the presence of reflecting potential walls. For simultaneous background scattering and reflection at potential walls the Matthiessen rule will not be satisfied (see Ref. 6).

In this Brief Report we show that even a simple (qualitative) check of the experimental thickness dependence of the conductivity of fine-grained metals disagrees with the application of the first-order perturbational theory to the conductivity of polycrystalline metals. Otherwise, the values of the MFP evaluated from Eq. (1) or (2) should be approximately the same.

RESULTS AND DISCUSSION

Figure 1 shows the thickness dependence of the conductivity of copper measured during deposition at 2×10^{-10} mbar and a substrate temperature of 80 K (the experimental method is described in Ref. 7). Even at $d=45$ nm, an important size effect can be observed, although the grain size (measured by transmission electron microscopy) for the final thickness shows a value of 7.5 nm. The resistivity, however, amounts to 40 $\mu\Omega$ cm, i.e., a factor 25 larger than the bulk value at 300 K.[8,9]

The shortest possible MFP which could produce this size effect can be estimated from Eq. (1) for $p=0$ (in the thickness range where the ρd vs d plot shows a linear dependence):

$$(l_g)_{\text{size}}\simeq\frac{8}{3}\left[\frac{\Delta\sigma}{\sigma}\right]_f\frac{d_2d_1}{d_2-d_1}\ , \tag{4}$$

with

$$\left[\frac{\Delta\sigma}{\sigma}\right]_f=\frac{\sigma_f(d_2)-\sigma_f(d_1)}{\sigma_f(d_1)}\ .$$

The measured relative increase of the conductivity of 4%

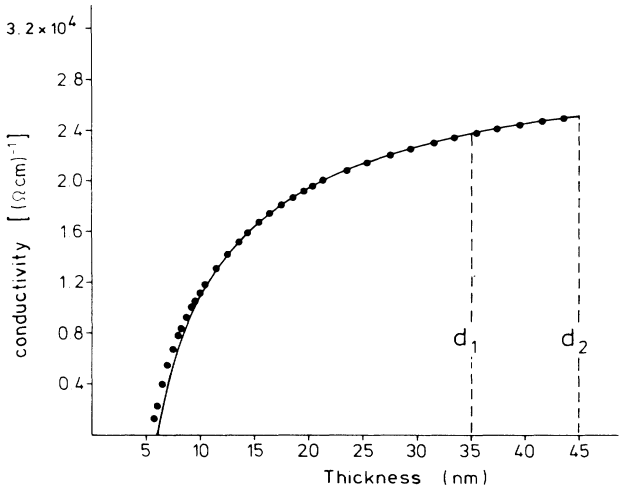

FIG. 1. Measured thickness dependence of the conductivity for copper (2×10^{-10} mbar, $T_{\text{substrate}}=80$ K). The mean crystallite size amounts to 7.5 nm at 45-nm film thickness.

between 35 and 45 nm results consequently in a minimum value of

$$(l_g)_{\text{size}}\simeq 17 \text{ nm} .$$

Alternatively, the effective intrinsic MFP (l_g) can be evaluated from Eq. (2) leading to

$$l_g\simeq 2.6 \text{ nm} .$$

The uncertainty is less than 10%, mainly as a result of using σ_f (at $d=45$ nm) for the calculation instead of σ_g; here the product $\rho_0 l_0=6.6\times10^{-12}$ $\Omega\,\text{cm}^2$ was used as a material constant for copper. Consequently, although the resulting scattering lengths evaluated by the two methods should be the same, a discrepancy by a factor 6 is found, far outside of any possible experimental error.

As another example, Fig. 2 shows the thickness dependence of the conductivity for an $Al_{83}Si_{17}$ film deposited at 10^{-7} mbar and a substrate temperature of 300 K. The silicon atoms segregate mainly to the grain boundary and reduce the grain size, in this case, to 4 nm.[10] The resistivity increases to 82 $\mu\Omega$ cm at 30 nm film thickness and is purely metallic [the percolation threshold lies at 45% Si (Ref. 10)]. From the observed relative increase of 3.4% between 20 and 30 nm,

$$(l_g)_{\text{size}}\simeq 6 \text{ nm}$$

can be calculated. On the other hand, from Eq. (2) it follows that

$$l_g\simeq 0.5 \text{ nm} ,$$

using $\rho_0 l_0=4.5\times10^{-12}$ $\Omega\,\text{cm}^2$ for Al. The reduction of the grain size is accompanied by a strong increase in the resistivity; this enhances the above-discussed inconsistency by a factor 12. According to the MS theory, no size effect is to be expected for 30-nm $Al_{83}Si_{17}$ films; the experiment (as also in the example of Cu), contradicts this prediction.

A last example is given by the experimentally observed size effect for a $Ag_{40}Cu_{60}$ substitutional alloy deposited at 10^{-9} mbar and a substrate temperature of 300 K (Fig. 3). Although the film is "quasiamorphous" (grain size less than or equal to 2 nm at 40 nm film thickness), the corresponding resistivity is only 11 $\mu\Omega$ cm. The relative increase of the conductivity between thicknesses of 30 and 40 nm is 3.8%; the corresponding minimal value of the MFP responsible for this size effect is

$$(l_g)_{\text{size}}\simeq 12 \text{ nm} .$$

The effective MFP [calculated from Eq. (2) with $\rho_0 l_0=7.3\times10^{-12}$ $\Omega\,\text{cm}^2$] in this case is closer to the value determined from the size effects:

$$l_g\simeq 7 \text{ nm} .$$

As a matter of fact, the reduction of the grain size to an extremely small value now is accompanied by a poor increase of the resistivity compared to the foregoing examples; this relatively low grain-boundary resistivity reduces the above discussed inconsistency to a factor 2. A columnar structure can be excluded for the analyzed films. Structural arguments which should explain the observed size effect fail in this case.

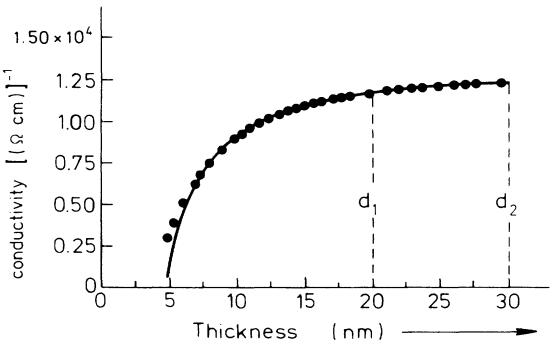

FIG. 2 Thickness dependence of the conductivity for an $Al_{83}Si_{17}$-mixed film (10^{-7} mbar, $T_{\text{substrate}}=300$ K). The mean crystallite size at 30-nm film thickness amounts to 4 nm.

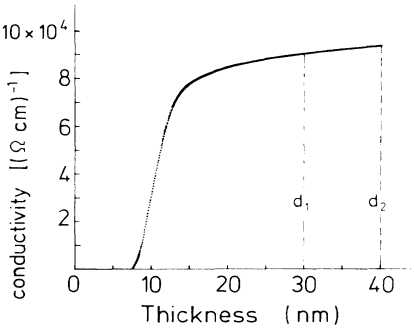

FIG. 3. Measured thickness dependence of the conductivity for a $Ag_{40}Cu_{60}$ substitution alloy (10^{-9} mbar, $T_{\text{substrate}}=300$ K). The mean "grain size" amounts to 2 nm at 40-nm film thickness.

The inconsistency of the MS theory can, however, be directly correlated with the absolute value of resistivity. The observed size effect shows a very weak connection with this value. The reason for this dilemma is to be seen in the conduction mechanism proposed by Mayadas and Shatzkes. The evaluation of the MFP from the measured size effect is done independent of the absolute value of the resistivity, whereas the determination of the effective intrinsic MFP requires

$$\rho_g l_g = \rho_0 l_0 \ . \tag{5}$$

This requirement represents the crucial point of the dilemma. It seems really impossible to define an effective intrinsic MFP for the entire polycrystal. Equation (5) represents, in fact, the Matthiessen rule, with the exception that the background and grain-boundary scattering times are not independent of each other. Therefore, deviations from the Matthiessen rule are to be expected, and depend on the "coupling strength" of the two scattering times. Equation (5) is approximately valid only for very transparent barriers. In the case of enhanced grain-boundary scattering, the adoption of an effective intrinsic MFP for the whole polycrystal by means of the Matthiessen rule is no longer justified.

An attempt to escape this situation has been made by the present authors (see Ref. 11). The product $\rho_g l_0$ should be responsible for the electrical conduction in a polycrystal, i.e., the conductance of the grain boundary is given by the number of CE's which pass through the potential wall by remaining in the same k state. Therefore, only the background scattering MFP can be defined in a polycrystal and is responsible for the observed size effect.

In summary, the main result of our work should be kept in mind: Grain-boundary scattering cannot be described by a relaxation-time approach. More theoretical work is needed to understand this problem in detail. Furthermore, some limiting MFP criteria for disordered (commonly fine-grained) metals, as for example Ioffe-Regel[12] and Mooij[13] criteria, have to be considered as open to question from an experimental point of view.

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