Grain-Boundary Resistance in Polycrystalline Metals

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Grain boundaries are known to reduce significantly the electrical dc conductivity of polycrystalline metallic materials. In this paper, we give a quantum mechanical calculation of the grain-boundary resistance based on the transfer-matrix approach. The results show an exponential decrease of the conductivity with respect to the number of grain boundaries per mean free path in acccord with an empirical model proposed recently.

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The conductivity of thin polycrystalline films strongly deviates from the conductivity of the corresponding bulk single-crystalline material: The conductivity is reduced, which commonly is explained by a reduction of the mean free path (mfp). The negative temperature coefficient of the resistivity (TCR) shown by such films in some cases usually is assumed to be a nonmetallic behavior.

Negative values of the TCR, however, often cannot be explained by a weak localization of a two-dimensional electron system[1] or by the hopping mechanism of a heavily distorted material.[2] There exist numerous experimental data fitting neither to the one nor to the other model. See, for example, the problem of the Mooij criterion and incipient localization[2-5] and the problem of the metallic regime of granular films.[2,6-9] Furthermore, the influence of the grain boundaries on the Hall effect, magnetoresistance, and so on is not yet clear. On the basis of a great number of experiments, Hoffmann and coworkers[10-16] stated that the reduction of the conductivity depends exponentially on the number of grain boundaries per mfp l_∞/D (D is the mean grain diameter). At sufficiently high temperatures, the length scale approximately equals the elastic mfp. This suggests that the reduction of the conductivity equals the mean probability for electron transmission through the l_∞/D grain boundaries along one mfp. The dc conductivity of polycrystalline metallic films is given by[3-6,17,18]

$$\sigma_\infty = (ne^2 l_\infty / m v_F)\,\mathrm{grain}(l_\infty, D, T), \tag{1}$$

where l_∞ is the innercrystalline mfp describing the volume scattering of the electrons and T is the probability for an electron to pass a single grain boundary. The function designated as grain (l_∞, D, T) in Eq. (1) is introduced in order to take into account the influence of the grain boundaries on the conductivity.

Following the experimental results, we propose a calculation of grain (l_∞, D, T) based on the following assumptions:

(a) The function grain (l_∞, D, T) introduced in Eq. (1), which reduces the Drude conductivity, is given by the total probability for electron transmission through the l_∞/D grain boundaries along one mfp. This means that grain (l_∞, D, T) is the mean value of all transmission probabilities $T^i (i = 1, \ldots, J)$ for all possible arrays of grain boundaries along one mfp. These arrays are given by the statistical distribution of the grain sizes.

(b) The electron transmission through grain boundaries being a percolation free problem, T^i can be calculated by means of the one-dimensional transfer-matrix approach described by Azbel and Soven[19] and by Azbel and Rubinstein.[20]

In order to calculate $T^i(l_\infty, D, T)$ the Schrödinger equation for the situation illustrated in Fig. 1 has to be considered:

$$(\psi^i)'' + \left[k_F - \frac{2m}{\hbar^2} S \sum_{n=1}^{N^i} \delta(x - x_n^i)\right]\psi^i = 0. \tag{2}$$

Here, k_F is the wave vector of the electron and S is the strength of the potential given by the product of the height of the potential times its width. S is related to T by

$$S = [(1 - T)/T]^{1/2} (k_F \hbar^2 / m). \tag{3}$$

The wave function of the electron in the special array x_n^i $(n = 1, \ldots, N^i)$ of grain-boundary potentials is

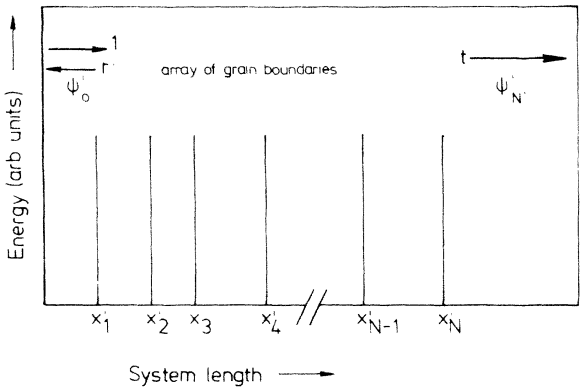

FIG. 1. Model of the grain-boundary potential introduced in the Schrödinger equation for a special array x_n^i $(n = 1, \ldots, N^i)$ of grain boundaries. The total length is one mean free path l_∞.

given by (compare Fig. 1)

$$\psi_0^i = e^{ik_F x} + r^i e^{-ik_F x}, \quad x < x_1^i,$$

$$\psi_n^i = A_n^i e^{ik_F x} + B_n^i e^{-ik_F x}, \quad x_n^i < x_{n+1}^i \quad (n = 1, \ldots, N^i - 1), \tag{4}$$

$$\psi_{N^i}^i = t^i e^{ik_F x}, \quad x > x_{N^i}.$$

Here, r^i and t^i are the amplitudes of the reflected and transmitted waves, respectively; t', r', A_n^i, and B_n^i are complex ($n = 1, \ldots, N^i - 1$).

The values of t^i, r^i, A_n^i, and B_n^i can be calculated by use of the matrix $\theta_n^i (n = 1, \ldots, N^i - 2)$, which transfers the solutions of Eq. (2) for the electron from the nth grain ($x_n^i < x < x_{n+1}^i$) to grain number $n+1$:

$$\begin{pmatrix} A_{n+1}^i \\ B_{n+1}^i \end{pmatrix} = \theta_n^i \begin{pmatrix} A_n^i \\ B_n^i \end{pmatrix}, \tag{5}$$

with the transfer matrix

$$\theta_n^i = \begin{bmatrix} \left(1 - \frac{imS}{h^2 k_F}\right) e^{ik_F \Delta x_n^i} & -i \frac{mS}{h^2 k_F} e^{-ik_F \Delta x_n^i} \\ i \frac{mS}{h^2 k_F} e^{ik_F \Delta x_n^i} & \left(1 + \frac{imS}{h^2 k_F}\right) e^{-ik_F \Delta x_n^i} \end{bmatrix}. \tag{6}$$

The grain sizes Δx_n^i are given by

$$\Delta x_n^i = x_{n+1}^i - x_n^i. \tag{7}$$

The total transmission coefficient $T^i(l_\infty, D, T)$ for the special array x_n^i ($n = 1, \ldots, N^i$) of grain boundaries then is given by

$$T^i(l_\infty, D, T) = |t^i|^2. \tag{8}$$

Considering the statistics of the probability distribution of the grain sizes Δx_n^i, the calculation described above has to be repeated for various arrays x_n^i ($n = 1, \ldots, N^i$) of δ potentials.

With J being the number of different arrays of δ potentials [the superscript i in Eqs. (2)–(8) runs from 1 to J], the mean value of the transmission probabilities $T^i(l_\infty, D, T)$ of Eq. (8) is given by

$$\bar{T}^J(l_\infty, D, T) = \frac{1}{J} \sum_{i=1}^{J} T^i(l_\infty, D, T). \tag{9}$$

If we repeat a great number of cycles (typically $J > 1000$), the mean value given in Eq. (9) converges towards the desired mean probability for electron transmission through l_∞/D grain boundaries:

$$\text{grain}(l_\infty, D, T) = \lim_{J \to \infty} \bar{T}^J(l_\infty, D, T). \tag{10}$$

First, we focus on the influence of the mean grain size D on the results of the calculations. According to the experimental data of transmission electron microscopic observations of polycrystalline metallic thin films, the grain sizes are log-normal distributed with the most probable value D^* being $D^* = 0.8D$. If we restrict the calculations to physically meaningful grain sizes ($D > 3$ nm), the results depend only on the ratio of l_∞/D equal to the number of grain boundaries per mfp. Such behavior of grain (l_∞, D, T) can be expected as long as $D - D^*$ is greater than the wavelength of the electron.

Therefore, the correction introduced in Eq. (1) and given in Eq. (10) can be rewritten as

$$\text{grain}(l_\infty, D, T) = \text{grain}(l_\infty/D, T). \tag{11}$$

In Fig. 2, the results of the grain-boundary correction according to Eqs. (10) and (11) are given by plotting the logarithm of grain$(l_\infty/D, T)$ given in Eq. (10) as a function of l_∞/D for various values of the transmission factor T (lines). As can be seen from this plot, $\ln[\text{grain}(l_\infty/D, T)]$ becomes an almost linear function of l_∞/D for values of $l_\infty/D > 1$.

As mentioned at the beginning, such behavior has been experimentally observed by Hoffmann and coworkers.[10–13, 16, 21, 22] These authors investigated the conductivity of thin polycrystalline metal films, as a function of the film thickness (using the model of Fuchs[23] and Namba[24]) and evaluated the influence of the grain boundaries on the conductivity (see Refs. 10–13).

In Fig. 2, some of their experimental results for different metal films are given. As can be seen from this plot, the experimentally evaluated grain-boundary

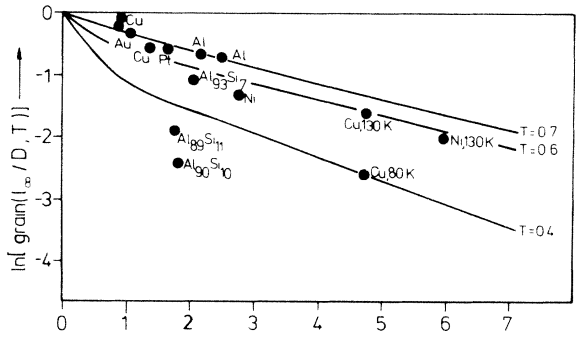

FIG. 2. The logarithm of the grain-boundary correction grain $(l_\infty/D, T)$ as a function of l_∞/D for different values of T. The lines are the result of the present calculations. The points are experimental results taken from Refs. 4, 11, and 12. Where no temperature is noted, the samples had been prepared at 300 K.

correction of the conductivity is fairly well described by the model proposed above, with $T=0.7\pm0.1$ for polycrystalline pure metal films prepared at room temperature under UHV conditions. The films composed of a metal and a semiconductor are polycrystalline too, showing purely Ohmic behavior (see Refs. 21 and 22). For such granular metallic films, T decreases because the nonmetallic material segregates into the grain boundaries (for example, $T\simeq 0.3$ for $Al_{90}Si_{10}$).

Based on this experimentally observed dependence, Hoffmann and co-workers[10–13] proposed that all electrons reflected by the grain boundaries along one mfp do not contribute to the resulting current. Therefore, he obtained

$$\mathrm{grain}(l_\infty/D,T)=T^{l_\infty/D}. \tag{12}$$

This model predicts a linear behavior of $\ln[\mathrm{grain}(l_\infty/D,T)]$ as a function of l_∞/D in agreement with our results [compare Fig. 2 (lines)].

A striking effect predicted by this model is a change of sign of the TCR from positive to negative values when l_∞ and T fullfil the condition

$$(l_\infty/D)\ln(1/T)>1, \tag{13}$$

very often characterized as "nonmetallic" behavior. In order to test whether our calculations agree with this prediction, we simply have to look for a maximum of the function $l_\infty\,\mathrm{grain}(l_\infty/D,T)$ with respect to l_∞/D (note that D is fixed). Here we take into account that the conductivity σ_∞ is proportional to $l_\infty\,\mathrm{grain}(l_\infty/D,T)$, and assume that the mfp increases with decreasing temperature. Note that none of the existing models[17,18] can explain negative values of the TCR connected with this maximum.

Using the present results for $\mathrm{grain}(l_\infty/D,T)$, in fact, we find this maximum value of σ_∞; the values of T and l_∞/D at the maximum, however, deviate from Eq. (13) only by a factor of 2, i.e., our calculations predict a negative TCR, when l_∞/D and T fulfill the condition

$$(l_\infty/D)\ln(1/T)>2. \tag{14}$$

For comparison with experiment, in Fig. 3 the published values of the TCR (normalized to the values of single-crystalline material) from Refs. 10–13 and 22 are plotted as a function of the numerical value of the grain-boundary correlation evaluated from the experiments. The region where the TCR is expected to change its sign [see Eq. (14)] is marked by a square.

As can be seen from this plot, our model correctly explains the striking effect of a negative value of the TCR in the metallic regime of the conductivity.

In the present paper, we gave a quantum mechanical calculation of the dc grain-boundary resistance of polycrystalline metallic materials. The results show a maximum of the calculated conductivity with respect to the number of grain boundaries per mfp, leading to a change of sign of the calculated TCR from positive to negative values, although the conductivity shows Ohmic behavior. Therefore, our calculations are in agreement with the empirical model proposed by Hoffmann and co-workers,[10–13] which is based on the experimental investigation of the conductivity of polycrystalline metallic films.

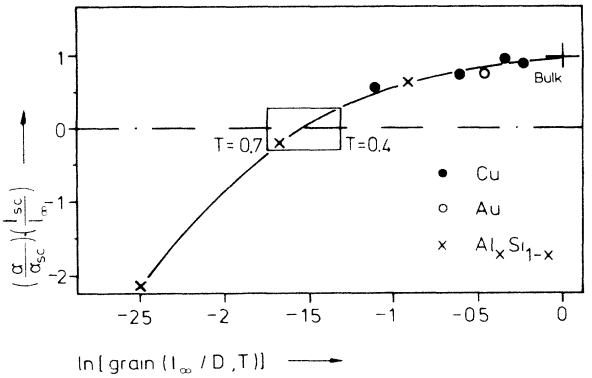

FIG. 3. The TCR α of metallic materials at 100 K as a function of the logarithm of the grain-boundary correction of the conductivity. α_{sc} and l_{sc} are the values of the corresponding single-crystalline material taken from literature. The square marks the region where the change of sign of the TCR is expected following the calculations of this paper.

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