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The electrical conductivity of polycrystalline metallic films

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ABSTRACT

We calculate the electrical conductivity of polycrystalline metallic films by means of a semi-numerical procedure that provides solutions of the Boltzmann transport equation, that are essentially exact, by summing over classical trajectories according to Chambers' method. Following Mayadas and Shatzkes (MS), grain boundaries are modeled as an array of parallel plane barriers situated perpendicularly to the direction of the current. Alternatively, according to Szczyrbowski and Schmalzbauer (SS), the model consists in a triple array of these barriers in mutual perpendicular directions. The effects of surface roughness are described by means of Fuchs' specularity parameters. Following SS, the scattering properties of grain boundaries are taken into account by means of another specularity parameter and a probability of coherent passage. The difference between the sum of these and one is the probability of diffuse scattering. When this formalism is compared with the approximate formula of Mayadas and Shatzkes (Phys. Rev. B 1, 103 (1986)) it is shown that the latter greatly overestimates the film resistivity over most values of the reflectivity of the grain boundaries. The dependence of the conductivity of thin films on the probability of coherent passage and grain diameters is examined. In accordance with MS we find that the effects of disorder in the distribution of grain diameters is quite small. Moreover, we find that it is not safe to neglect the effects of the scattering by the additional interfaces created by stacked grains. However, when compared with recent resitivity-thickness data, it is shown that all three formalisms can provide accurate fits to experiment. In addition, it is shown that, depending on the respective reflectivities and distance from a surface, some of these interfaces may increase or diminish considerably the conductivity of the sample. As an illustration of this effect, we show a tentative fit of resistivity data of gold films measured by Chen et al. (Appl. Phys. 60, 659 (2005)). Finally, we present a new version of Matthiessen's rule that describe, with high accuracy, the way in which the contributions from surface scattering and grain boundary combine to form the total resistivity of the sample.

1. Introduction

The fact that the transport coefficients of small samples are not independent of size or shape was first observed in measurements of the electrical conductivity of thin silver films [1]. It was noted that this phenomenon occurs when one or more of the dimensions of the sample is comparable in length with the mean free path of the carriers.

The earliest theoretical treatment of the electrical conductivity of thin films was given by Thomson, who assumed that—in accordance with Drude's theory—the conductivity in metals was proportional to the mean free path and that the scattering at the external surfaces was completely diffuse [2]. The theory was considerably advanced by Fuchs, who proceeded from a solution of Boltzmann transport equation (instead of using the restricted tools of kinetic theory) and introduced appropriate boundary conditions [3,4].

If the conduction electrons are perturbed only by an electric field $\mathbf{E}$, and we assume further the validity of Ohm's law and the existence of a time of relaxation τ, the Boltzmann equation is [5]

$$\mathbf{v}\cdot\frac{\partial f_1}{\partial \mathbf{r}} + \frac{f_1}{\tau} = -e(\mathbf{E}\cdot\mathbf{v})\left(-\frac{\partial f_0}{\partial \mathcal{E}}\right). \tag{1}$$

This equation is solved for the function $f_1(\mathbf{r}, \mathbf{v})$ that describes the distribution of carriers that are out of thermodynamical equilibrium. The equilibrium population is given by the Fermi-Dirac distribution $f_0 = \{\exp[(\mathcal{E}-\mu)/k_BT] + 1\}^{-1}$. As boundary conditions

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Fuchs assumed that, at each external surface, a fraction p of the incoming electrons are specularly reflected (that is, the tangential component of the velocity is conserved but the normal component changes sign), while the remaining fraction $q = 1 - p$ is randomly scattered and thereafter lost from the conduction process. Fuch's boundary conditions have been generalized by Lucas who allowed for the fact that different surfaces may have different specularity parameters [6]. A number of authors have additionally generalized this schema by assuming that these parameters are in fact functions of the angle of incidence [7].

Fuch's theory accounts only for the scattering of the conduction electrons by the external surfaces and, thus, strictly applies only to single-crystal films. Mayadas and Shatzkes proposed a formula that explains the additional resistivity often found in practice as arising from the scattering from grain boundaries—a mechanism that becomes especially important when grain diameters are comparable in size to the electronic mean free path [8]. In this formalism grain boundaries are represented by a parallel array of plane barriers, in the form of repulsive Dirac delta potentials, and oriented perpendicularly to the direction of the electric field $\mathbf{E}$ (which we take to be the x-axis)

$$V(x) = \sum_n S\delta(x - x_n), \tag{2}$$

where the strength of the potential S is an adjustable parameter. The set of inter-planar distances $D_n = x_{n+1} - x_n$ is a random process with mean D and standard deviation s. Alternatively, the effects of scattering by grain boundaries are often parameterized in terms of the reflectivity R of an individual barrier, since this quantity is more accessible to measurement than the strength S. In the present model, these are related as follows:

$$R = \frac{2(S/\hbar v_F)^2}{1 + 2(S/\hbar v_F)^2}. \tag{3}$$

The scattering properties of each barrier is taken into account by first-order perturbation theory and is incorporated into Fuchs' formula as an angle-dependent contribution to the time of relaxation. In this way, the formula of Mayadas and Shatzkes for the electrical conductivity σ of a film of thickness d is [8]

$$\frac{\sigma}{\sigma_0} = \frac{\sigma_{GB}}{\sigma_0} - \frac{3\lambda}{\pi d}\int_0^{\pi/2} d\theta \int_0^{\pi/2} G\sin^3\theta\cos\theta\cos^2\phi d\phi; \tag{4}$$

where

$$G = \frac{(1 - E_d)}{H^2}\frac{q_0 + q_d + (p_0 q_d + q_0 p_d)E_d}{1 - p_0 p_d E_d^2}; \tag{5}$$

and

$$H = 1 + \frac{\alpha}{|\sin\theta\cos\phi|}; \quad \text{with } \alpha = \frac{\lambda}{D}\frac{R}{1 - R}; \tag{6}$$

where D is the mean grain diameter and λ is the mean free path of the conduction electrons. Also

$$E_d = \exp\left(-\frac{dH}{\lambda|\cos\theta|}\right). \tag{7}$$

We note that Mayadas and Shatzkes considered further the effect on the resistivity of disorder in the distribution of grain diameters, characterized by a standard deviation s. They found that the disorder contributed with terms of the order $\exp(-k_F^2 s^2)$; i.e. a negligible quantity for ordinary metals.

Finally, let σ_{GB} and σ_0 denote the conductivity of a bulk sample made of identical material than the film; respectively in presence and absence of grain boundaries. It is found that [8]

$$\frac{\sigma_{GB}}{\sigma_0} = 1 - \frac{3}{2}\alpha + 3\alpha^2 - 3\alpha^3\ln\left(1 + \frac{1}{\alpha}\right). \tag{8}$$

In the formalism of the Boltzmann equation, the scattering of carriers by the perturbations of the perfect lattice can be accounted for in two different ways. First, the scattering probability of the electrons by the lattice imperfections may be inserted into the collision operator—or, in a well-known approximation—added as a contribution to the time of relaxation τ. The second procedure consists in taking them into account by means of adequate boundary conditions. Usually, the first procedure is reserved for distributed impurities or phonons, while the second is used in order to account for external surfaces [9]. Unfortunately, the strength of the impurity scattering can be incorporated into the collision operator at best only in the form of a self-consistent Born approximation [10].

Szczyrbowski and Schmalzbauer have criticized the treatment of Mayadas and Shatzkes—where the effects of the grain boundaries enter only via a modification of the time of relaxation—by pointing out that, for typical values of the Fermi wavelength, the scattering strength from the barriers is so hight that the use of Born's approximation may result in serious errors [11]. They proposed that instead, for a more adequate treatment, these should be taken into account by imposing adequate boundary conditions at the added interfaces. Furthermore, reasoning that the exact shape of the grains is not as important as their size or relative distribution, they proposed an alternative theory in which grain boundaries are represented by a triple array of parallel barriers oriented in three perpendicular directions, one of which is the direction of the current. The scattering at each barrier is described by a specularity parameter p_{GB} and a transmittance, or probability of coherent passage, T_{GB}. The remaining probability $q_{GB} = 1 - p_{GB} - T_{GB}$ measures the fraction of electrons that are diffusely scattered at the barriers. These quantities q_{GB}, p_{GB} and T_{GB} are numbers between zero and one [11].

Unfortunately, Szczyrbowski and Schmalzbauer were unable to present a complete prescription for calculating electrical conductivities based on these premises. To do so is the objective of the present work. In this paper we solve the Boltzmann transport Eq. (1), for the case of a polycrystalline metallic film, by means of Chambers' method [12]. Following Lucas, for a thin film of thickness d, the boundary conditions are described by p_0 and p_d, as the respective specularity parameters characterizing the surfaces at $z=0$ and $z=d$; and we further define the quantities $q_0 = 1 - p_0$ and $q_d = 1 - p_d$. Grain boundaries are modeled as single array of parallel barriers (MS model) or, alternatively, as a triple, mutually perpendicular, array of such barriers (SS model).

It is well known that the method of Chambers prescribes that the out-of-equilibrium distribution function $f_1(\mathbf{r}, \mathbf{v})$ can be calculated by summing a certain characteristic function over all classical trajectories that end at a given point $\mathbf{r}$ inside the sample with a given terminal velocity $\mathbf{v}$. (The fact that Chambers' method provides an exact solution of Boltzmann transport equation has been proved in multiple occasions [13].) Since the summation over all classical trajectories cannot be exactly performed (except in a very restricted number of cases) in this paper we proceed by summing over a finite random sample of these paths, which is numerous enough to result in a conductivity calculated within a prescribed accuracy. We note that, recently, a similar method was applied to the calculation of the conductivity of thin polycrystalline wires [14].

There has been some recent work using Monte Carlo simulations to calculate the electrical conductivity in polycrystalline metallic films, in which the authors examine the impact of surface roughness and microstructure on the conductivity and make