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Quantum theory of the effect of grain boundaries on the electrical conductivity of thin films and wires

Luis Moraga [a,b,*], Ricardo Henriquez [c], Basilio Solis [a]

[a] Departamento de Ciencias Básicas, Facultad de Ingeniería, Universidad Central de Chile, Santa Isabel 1186, Santiago 8330601, Chile
[b] Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Blanco Encalada 2008, Casilla 487-3, Santiago 8370449, Chile
[c] Departamento de Física, Universidad Técnica Federico Santa María, Avenida España 1680, Valparaíso, Chile

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ABSTRACT

We calculate the electrical conductivity of a metallic sample under the effects of distributed impurities and a random distribution of grain boundaries by means of a quantum mechanical procedure based on Kubo formula. Grain boundaries are represented either by a one-dimensional regular array of Dirac delta potentials (Mayadas and Shatzkes model) or by its three-dimensional extension (Szczyrbowski and Schmalzbauer model). We give formulas expressing the conductivity of bulk samples, thin films and thin wires of rectangular cross-sections in the case when the samples are bounded by perfectly flat surfaces. We find that, even in the absence of surface roughness, the conductivity in thin samples is reduced from its bulk value. If there are too many grain boundaries per unit length, or their scattering strength is high enough, there is a critical value R_c of the reflectivity R of an individual boundary such that the electrical conductivity vanishes for $R > R_c$. Also, the conductivity of thin wires shows a stepwise dependence on R. The effect of weak random variations in the strength or separation of the grain boundaries is computed by means of the method of correlation length. Finally, the resistivity of nanometric polycrystalline tungsten films reported in Choi et al. J. Appl. Phys. (2014) 115 104308 is tentatively analyzed by means of the present formalism.

1. Introduction

The continuous progress of modern semiconductor industry has resulted in a progressive shrinkage of the linear dimensions of the electronic components. The dimensions of the thin films and wires that constitute the building materials of the devices now reach nanoscale sizes, which are not only smaller than the electronic mean free path λ of the carriers but are such that quantum size effects begin to become important [1].

The electrical resistivity of large samples has been found to be independent of size and shape. But, when one of its linear dimensions becomes comparable with the mean free path of the conducting electrons, the resistivity increases over its bulk value. This effect has been explained by Fuchs [2] and Sondheimer [3] (FS) in terms of diffuse scattering occurring at the boundaries of the film. The theory is based on an appropriate solution of the Boltzmann transport equation and is, thus, semiclassical in nature. When data is interpreted in terms of this formalism, the only unknown parameter is p — the fraction of electrons that are specularly scattered at the film surfaces. The FS formula for the conductivity σ_{FS} is

$$\frac{\sigma_{FS}}{\sigma_0} = 1 - \left(\frac{3\lambda}{2t}\right)(1-p)\int_1^\infty \left(\frac{1}{s^3} - \frac{1}{s^5}\right)\frac{1-\exp(-ts/\lambda)}{1-p\exp(-ts/\lambda)}\,ds, \tag{1}$$

where t is the thickness of the film and σ_0 is the conductivity of a bulk sample of identical composition.

Similar explanations have been found for the increase in the electric resistivities of thin wires of circular cross-section [4] and of square cross-section in case of completely diffuse surface scattering [5]. (For many years it was believed that the formalism of Chambers [6] — which is known to be equivalent to solving the Boltzmann transport equation — could be used for obtaining formulas expressing the resistivity of wires of arbitrary shapes and surface reflectivities. But this conjecture is now known to be erroneous [7].)

Further measurements on thin films and wires of increased purity did show that the electrical resistivity increases beyond the predictions of the FS theory. Mayadas and Shatzkes (MS) attributed this additional resistivity to scattering of electrons by grain boundaries [8]. According to this theory, the electrical conductivity σ_{MS} of a bulk sample with average grain diameter d and mean free

* Corresponding author at: Departamento de Ciencias Básicas, Facultad de Ingeniería, Universidad Central de Chile, Santa Isabel 1186, Santiago 8330601, Chile. Fax: +56 2 25826927.
E-mail address: luismoragajaramillo@gmail.com (L. Moraga).

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path λ is (in units of σ_0, the conductivity of an identical sample having no grain boundaries)

$$\frac{\sigma_{MS}}{\sigma_0} = 3\left[\frac{1}{3} - \frac{1}{2}\alpha + \alpha^2 - \alpha^3 \ \ln(1+\alpha^{-1})\right]; \tag{2}$$

where

$$\alpha = \frac{\lambda}{d}\frac{R}{1-R} \tag{3}$$

and where the parameter R denotes the reflection coefficient of a single grain boundary.

Furthermore, Mayadas and Shatzkes obtained a second formula describing the electrical conductivity of a polycrystalline thin film. This expression is similar in the form to FS formula, except that the unperturbed mean free path is incremented by an angle-dependent quantity that describes the additional scattering taking place at the grain boundaries. Again, the relevant parameter is the reflectivity R [8].

The conductivity σ_{MSS} predicted by this formula is

$$\sigma_{MSS} = \sigma_{MS} - \left(\frac{6\lambda\sigma_0}{\pi t}\right)(1-p)\int_0^{\pi/2} d\phi \int_1^{\infty} ds \frac{\cos^2\phi}{H^2} \times \left(\frac{1}{s^3} - \frac{1}{s^5}\right)\frac{1-\exp(-tsH/\lambda)}{1-p\exp(-tsH/\lambda)}, \tag{4}$$

where

$$H(s,\phi) = 1 + \frac{\alpha}{\sqrt{1-s^{-2}}\cos\phi}. \tag{5}$$

For a long time, these formulas were the only tools possessing firm theoretical foundations that the experimenters could use in order to interpret their results. For lack of anything better, a number of semi-empirical formulas were also proposed and used [9–11]. Thus, the electrical conductivity of thin films of copper [12], gold [13] and tungsten [14] was measured, together with their respective thicknesses and grain diameters. It was found that the measurements of Cu films could be adequately interpreted by a combination of Eqs. (1) and (2), according to Matthiessens' rule [12]. On the other hand, it was determined that the dependence of the resistivity of Au films [13] on thickness and grain diameters was better explained by means of MS formula (4). Finally, Choi et al. tried to interpret the resistivities of thin W films by means of these methods, concluding that they were essentially equivalent in this case and that both resulted in systematic deviations from the experimental values [14].

The electrical conductivity of thin polycrystalline wires of gold [15], copper [10,11,16], and silver [7] was also measured for a number of thicknesses and grain diameters. Here, the lack of any formalism corresponding to (2) and (4) was most sorely felt. Josell et al. [7] noted that the many formulas employed in this connection were not equivalent. Furthermore, their purported justification in terms of Chambers' method [6] was shown to be erroneous [7].

Recently, a semi-numerical procedure for calculating the combined effects of surface roughness and grain boundaries on the conductivity of polycrystalline metallic films has been published [17]. The method is essentially equivalent to using an exact solution of the Boltzmann transport equation. By means of this formulation, it was possible to obtain tentative fits of the measurements of Steinhögl et al. of thin Cu films [16] and Josell et al. of thin Ag wires [7].

When solving the Boltzmann transport equation, the effects of the scattering by distributed impurities may be taken into account by fixing the time of relaxation, whilst those of diffuse surface scattering may be accounted by choosing appropriate boundary conditions. However, the contribution of grain boundaries cannot be adequately described by either of these procedures. In the formalism of MS, grain boundary scattering is represented by the transition probability of scattering between two momentum states, calculated by first-order perturbation theory [8]. Thus, it appears that the theory can adequately describe the facts only for small enough values of R, the reflection coefficient of an individual grain boundary. Indeed, the analysis of thin film data made by Henriquez et al. [13] suggests that the corresponding MS formula is reasonably accurate only for values of R that do not exceed $\simeq 0.3$.

Fortunately, the combined effects of distributed impurities and a regular array of grain boundaries can be accounted for at all orders of perturbation theory by means of a procedure that is quantum throughout. The purpose of the present work is to extend the ideas developed in Ref. [18]. In this paper we compute the effects of grain boundaries on the electrical conductivity of bulk samples and thin films and wires by means of the Kubo formula.

In the formalism of Kubo [19], the electrical conductivity σ is given by

$$\sigma = -\frac{2e^2\hbar^3}{\pi m^2 V}\int d^3\mathbf{r}\int d^3\mathbf{r}'\left[\Im\frac{\partial G(\mathbf{r},\mathbf{r}')}{\partial x}\right]\left[\Im\frac{\partial G(\mathbf{r}',\mathbf{r})}{\partial x'}\right], \tag{6}$$

where $-e$ and m are the charge and mass of the carriers, respectively, V is the volume of the sample and $G(\mathbf{r},\mathbf{r}')$ is Green's function appropriate for each case. For instance, it is customary to account for the effects of distributed impurities by adding an imaginary part to the Fermi energy — or to the Fermi wave vector k_F — as the quantum analogue of the mean free path λ [20]. By inserting into (6) Green's function for an infinite system

$$G_0(\mathbf{r},\mathbf{r}') = -\frac{2m}{4\pi\hbar^2}\frac{e^{ik_F|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}; \tag{7}$$

one obtains, for the conductivity of a bulk sample,

$$\sigma_0 = \frac{e^2}{6\pi^2\hbar}\frac{(\Re k_F)^2}{\Im k_F}. \tag{8}$$

This coincides in the form with the well known Sommerfeld–Drude prescription [21]

$$\sigma_0 = \frac{e^2\bar{k}_F^2}{3\pi^2\hbar}\lambda \tag{9}$$

if we identify the real part of k_F with the observed value of the Fermi wave vector $\bar{k}_F$ and its imaginary part as $\Im k_F = 1/2\lambda$ [22].

2. Grain boundaries and bulk conductivity

Excluding many-body effects, Green's function is the solution of the inhomogeneous Schrödinger equation

$$\left(\frac{\hbar^2}{2m}\nabla_{\mathbf{r}} + \mathcal{E}_F - V(\mathbf{r})\right)G(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r},\mathbf{r}'), \tag{10}$$

that is symmetrical in its arguments $G(\mathbf{r},\mathbf{r}') = G(\mathbf{r}',\mathbf{r})$ and satisfies appropriate conditions at the boundaries of the sample. Here $\mathcal{E}_F = \hbar^2 k_F^2/(2m)$ is the Fermi energy (k_F is the Fermi wave vector) and $V(\mathbf{r})$ is an effective potential to be chosen in order to adequately model the effects of grain boundaries.

As a first approximation, Mayadas and Shatzkes noted that grain boundaries may be roughly classified as being oriented parallel or perpendicular to the applied electric field **E**. Therefore, since the parallel barriers are encountered mainly at grazing incidences and, thus, do not contribute much to the scattering of the