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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

detailed comparison with the Fuchs–Sondheimer [3,4] and Mayadas et al. [8] theories [15,16]. These authors also employ a description of the grain morphologies that is somewhat more realistic than that of the SS model [16].

2. Chambers' method

The *method of characteristics*, known in this context as Chambers' method, is a powerful procedure for integrating partial differential equations [12,17]. The characteristics are curves along which the partial differential equation is equivalent to an ordinary one; and also along which information is transmitted from the boundary conditions to the point of interest. A particular property of the Boltzmann transport equation is that these characteristics are the classical trajectories; obtained by integrating $\mathbf{F}/m = d\mathbf{v}/dt$ and $\mathbf{v} = d\mathbf{r}/dt$. In the case of Eq. (1) these trajectories are straight lines. (However, the situation is complicated in practice, because the number of characteristics connecting the point of interest with the boundaries is often countable infinite.) Integrating the Boltzmann equation in this way, it is seen that

$$f_1(\mathbf{r}, \mathbf{v}) = -e\tau(\mathbf{E}\cdot\mathbf{v})\left(-\frac{\partial f_0}{\partial \mathcal{E}}\right)\left(1 - \sum_i F_i e^{t_i/\tau}\right), \tag{9}$$

where the sum is taken over all classical trajectories that end at the point $\mathbf{r}$, with final velocity $\mathbf{v}$, and start at some boundary—the external surfaces of the sample or any grain boundary. Here t_i is the time spent by the classical particle when moving from the given boundary to the point of interest along a given trajectory.

In a limited number of cases the sum $\sum_i F_i e^{t_i/\tau}$ may be evaluated exactly. It is further known that, in most occasions, the sum cannot be described by an ordinary function [14]. In this paper we apply a procedure that works even in these cases. The method is only approximate, but its accuracy can be maintained at a pre-determined level. Instead of considering the complete set of denumerable trajectories, we envision only a finite random sample of them. Given a point $\mathbf{r}$ inside the sample and a possible velocity $\mathbf{v}$, we compute a number of trajectories that start at $\mathbf{r}$ in the direction of $\mathbf{v}$. Each time that the trajectory encounters a surface or interface, a random number is generated and the subsequent fate of the particle is decided according to the assumed set of probabilities. If the trajectory reach an external surface then, following Lucas [6], a fraction p_a of the trials the particle is specularly reflected—meaning that the normal component of velocity is reversed—while the remaining fraction of the trials $q_a = 1 - p_a$ the particle is removed and the trajectory is ended. ($a=0$ or $a=d$ for the surfaces at $z=0$ or $z=d$ in a film of thickness d.) If the trajectory encounters a grain boundary then, following Szczyrbowski and Schmalzbauer [11], a fraction p_{GB} of the trials the particle is specularly reflected, another fraction T_{GB} of the trials the particle traverses unmodified the boundary, while in the remaining fraction of cases $q_{GB} = 1 - p_{GB} - T_{GB}$ the particle is again removed and the trajectory terminated. The net time of flight t_i from start to finish of each trajectory is accumulated, and the sum in (9) is performed, with each trajectory having equal weight.

This is a procedure that is essentially exact within the framework of Boltzmann semiclassical theory. In this paper, we apply it to two different models that purport to mathematically represent grain boundaries. The first (MS model) is an infinite array of plane barriers, distributed at random distances D_n in the direction of perpendicular to the electric field $\mathbf{E}$; as in Eq. (2). The second (SS model) assumes a triple array of similar barriers, situated in three mutually perpendicular directions.

In order to compare the results of these procedures with those of the Mayadas and Shatzkes (Eqs. (4)–(8)) we assume that we can approximately identify $R = 1 - T_{GB}$ in the case $p_{GB} = 0$. In Fig. 1 we plot the resistivity of a film with thickness $d=22$ nm, having grains with diameters $D=12.3$ nm, in case that the mean free path is $\lambda = 42$ nm. It is assumed that the scattering from the film's surfaces is completely diffuse. It is seen that the Mayadas and Shatzkes theory overestimates the effect of grain boundary scattering on the resistivity of thin films. This is especially evident in cases when the reflectivity coefficient R is comparable with one. Instead, our treatment predict a nearly lineal dependence of the resistivity on R. The slight increment of the resistivity in the SS model, in comparison with that of the MS, is due to the small contribution due to grain boundaries that run parallel to the direction of the electric field.

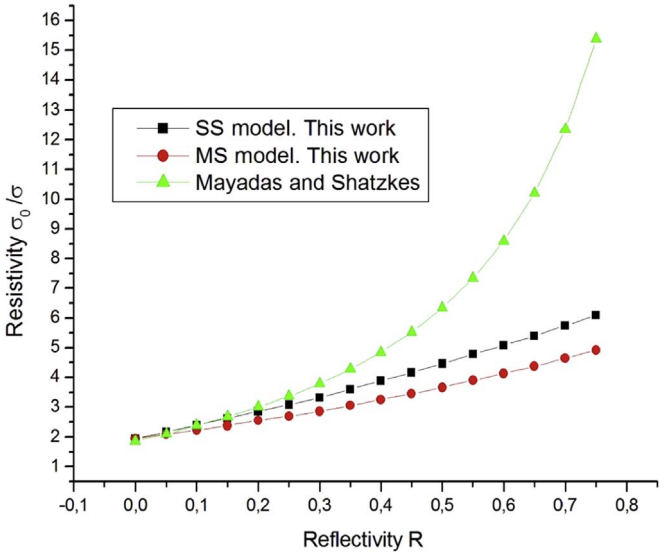

Fig. 1. Electrical resistivity (in units of bulk resistivity) of a polycrystalline film as a function of the reflectance R of an individual grain boundary, according to the theory of Mayadas and Shatzkes and the MS and SS models of the present paper. The film thickness is $d=22$ nm, with columnar grains with diameter $D=12.3$ nm and absence of disorder. Mean free path $\lambda = 42$ nm and $p_0 = p_d = p_{GB} = 0$. $T_{GB} = 1 - R$.

It is interesting to consider the dependence of the resistivity of thin films on the transmissivity of grain boundaries T_{GB}. Typical curves, calculated according to the SS model, are shown in Fig. 2. We assume that the surfaces are totally diffuse with $p_0 = p_d = p_{GB} = 0$ and where $d=49$ nm and $D=11.1$ nm. It is observed that the resistivity monotonically increases as the transmissivity diminishes; and that this dependence may result in an important effect.

The effects of changing the diameter of grain boundaries may also be considerable. This is shown in Fig. 3, were we plot the film's resistivity versus mean free path, according with the SS model, for of film of thickness $d=49$ nm and also in the extreme diffuse case $p_0 = p_d = p_{GB} = 0$; with the transmissivity set to $T_{GB} = 0.7$.

In these calculations we have assumed that all grains have the same diameter. We consider now the effects on the resistivity of the film caused by disorder in the distribution of diameters. As a typical example, we assume (in the SS model) a lognormal distribution of grain diameters, with mean $D=49$ nm and standard deviation $s = 0.3$ D. In Fig. 4 we plot the fractional change in resistivity as a function of the mean free path for a film in the case $p_0 = p_d = p_{GB} = 0$ for $d=49$ nm. It is seen that, in accordance with the calculation of Mayadas and Shatzkes, the effect of disorder in the distribution of grain diameters on the film's resistivity is quite small [8].

We conclude this section by investigating the degree of accord

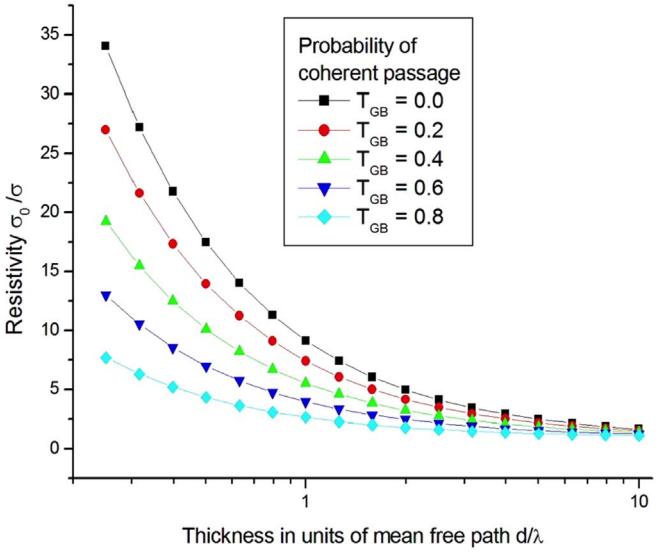

Fig. 2. Electrical resistivity (in units of bulk resistivity) of a polycrystalline film as a function of the mean fee path λ for different values of the probability of coherent passage T_{GB}, according to the SS model of the present paper. The film thickness is $d=49$ nm, with columnar grains with diameter $D=11.1$ nm and absence of disorder. The rough limit $p_0 = p_d = p_{GB} = 0$ is assumed.

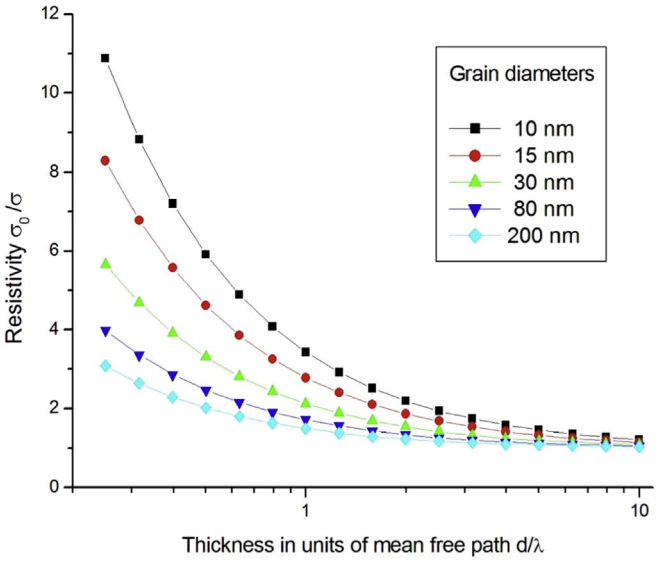

Fig. 3. Electrical resistivity (in units of bulk resistivity) of a polycrystalline film as a function of the mean fee path λ for different values of the grain diameters, according to the SS model of the present paper. The film thickness is $d=49$ nm, with columnar grains and absence of disorder Extreme rough limit is assumed $p_0 = p_d = p_{GB} = 0$. The probability of coherent passage $T_{GB} = 0.7$.

of the present formalism with experimental results. We examine the data of two recent determinations of the dependence on thickness of the resistivity of thin polycrystalline gold films, where the authors have also measured the mean grain diameter D. In Fig. 5a we plot the values of the resistivities measured by Zhang et al. [18]. It is seen that the values can be fitted to the present MS model by assuming that $p_0=0.7$, $p_d=0.6$, $R=0.65$ and mean free path $\lambda = 2600$ nm; and also to the SS model with around the same values of p_0 and p_d, but with $R=0.50$ and $\lambda = 3200$ nm. On the other hand, we found that the data can also be accurately fitted to the original Mayadas and Shatzkes theory, with $p_0=0.5$, $p_d=0.5$, $R=0.37$ and a mean free path $\lambda = 4480$ nm [8]. We note that the latter quantity accords in an average sense with the values of R inferred by Zhang et al. from the residual resistivities [18]. The

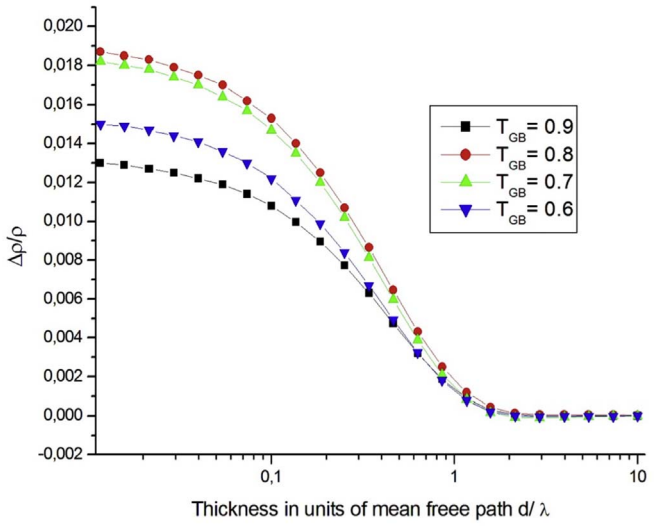

Fig. 4. Fractional resistivity change $\Delta\rho/\rho = (\rho_D - \rho)/\rho$ (where ρ_D, ρ are the resistivities with and without disorder) of a polycrystalline film as a function of the mean free path λ for different values of the probability of coherent passage T_{GB}, according to the SS model of the present paper. The film thickness is $d=49$ nm, with columnar grains with mean diameter $D=49$ nm. Grain diameters are distributed with lognormal probability with standard deviation $s = 0.3D$. Extreme rough limit is assumed with $p_0 = p_d = p_{GB} = 0$.

procedure advanced by these authors indicates that the value of R depends on thickness, varying from around 0.40 for thin films to 0.23 for thick ones.

The second set of measurements, reported by Bahamondes et al., are plotted in Fig. 5b [19].

3. Stacked grains

There is a notable phenomenon, related to the fabrication of thin metallic films, whose importance appears to have not been adequately appreciated in the past. If a metallic film is thin enough, the grains (which are present in greater or smaller sizes in most fabrication processes) extend from one of the external surfaces to the other, in the shape of a column. When the thickness is greater than a certain threshold, this columnar structure is replaced by another where the grains are stacked, forming two or more layers (Fig. 6). The surface created in this way—formed by the set of grain boundaries with the approximate shape of a plane parallel to the external boundaries of the film—scatters additional electrons and contribute to the resistivity of the film.

The fact that the resistivity of a film increases when a fresh interface parallel to the plane of the film is created was first found experimentally in 1964 [20]. The earliest theoretical treatment of this phenomenon assumed that no additional scattering occurs at this interface [21]. This approximation soon proved to be inadequate. Carcia and Suna proposed a new treatment based on the introduction of a probability of coherent passage across the interface [22]. This formalism was extended by Dimmich [23], who added the effects of grain boundaries localized perpendicularly to the plane of the film, in a way that parallels the theory of Mayadas and Shatzkes [8]. However, a detailed examination of the scattering process at the interface shows that there coexist specular and diffuse processes that should be modeled by parameters of two different kinds. One describes the probability that a conduction electron is reflected in a nondiffuse way by the interface. The other measures the probability of traversing the interface in a coherent way. The sum of these probabilities is less than one. The difference describes the probability that the carrier leaves the out-of-

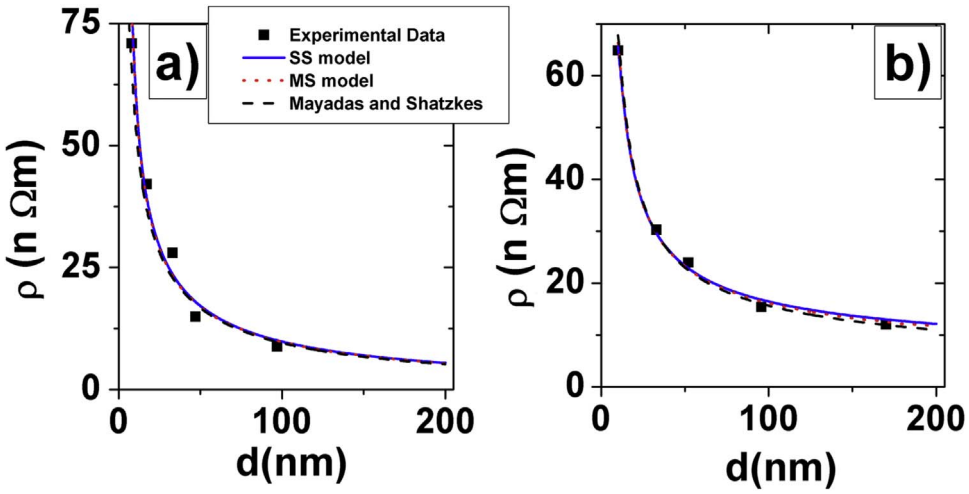

Fig. 5. (a) Experimental data (Ref. [18]). (R, p_0, p_d, λ) parameters: SS model (0.50, 0.6, 0.7, 3.2 μm); MS model (0.65, 0.7, 0.6, 2.6 μm) and Mayadas and Shatzkes theory (0.37, 0.5, 0.5, 4.48 μm). (b) Experimental data (Ref. [19]). (R, p_0, p_d, λ) parameters: SS model (0.16, 0.0, 0.0, 3.9 μm); MS model (0.23, 0.0, 0.0, 3.9 μm) and Mayadas and Shatzkes theory (0.18, 0.0, 0.0, 18 μm).

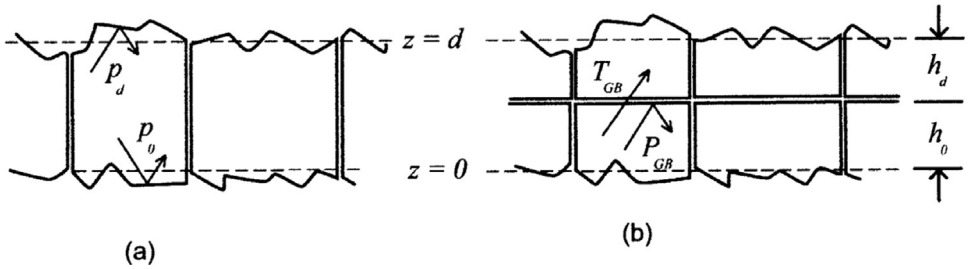

Fig. 6. (a) If a metallic film is thin enough, grains tend to grow in the form of a columnar structure. (b) When the thickness is increased beyond a threshold, grains are stacked. The scattering properties of the grain boundaries are described by a specularity parameter p_{GB} and a probability of coherent passage T_{GB}. The fraction $q_{GB} = 1 - p_{GB} - T_{GB}$ is the probability of being diffusely scattered at the interface.

equilibrium distribution and do not contribute further to the conduction process [24,25]. This prescription coincides with the boundary conditions independently advanced by Szczyrbowski and Schmalzbauer [11]. We note that, nowadays, all theoretical descriptions of the scattering of carriers at magnetic multilayers are made in terms of these two kinds of parameters [25,26].

In this section we calculate the effect of stacked grain by the same semi-numerical version of Chambers' method already described. This differs with previous treatments that proceed by matching distribution functions along the interfaces [27]. An example of the effects of the creation of new interfaces is shown in Fig. 7. We consider a film with thickness $d=99$ nm and with $p_0 = p_d = 0$. In order to illustrate the case with two stacked grains, we assume that these have equal height $h=49.5$ nm. Similarly, in the case of three stacked grains, we assume that all heights are equal with $h=33$ nm, etc. In all the cases shown, we assume that $p_{GB} = T_{GB} = 0.01$. It is clear that the effect of the stacking of grains may be considerable. Furthermore, it is seen that the added fractional resistivity is nearly proportional to the number of stacked grains.

It is interesting to note that the creation of a new interface inside a film does not always result in an increment of its resistivity. In order to see how this effect works, we envision a polycrystalline thin film with thickness $d=49$ nm, with $\lambda = 98$ nm, $p_0=1.0$ and $p_d=0.1$ (Fig. 8). Inside the film, we create an interface characterized by $T_{GB} = 0$ and different values of the reflectivity p_{GB}. By examining the values of the electrical conductivity of this film as a function of the distance between the interface and an external surface we conclude that—if the interface is near enough to the surface and its reflectivity p_{GB} is sufficiently high—the presence of this interface may enhance the film conductivity, instead of diminishing it.

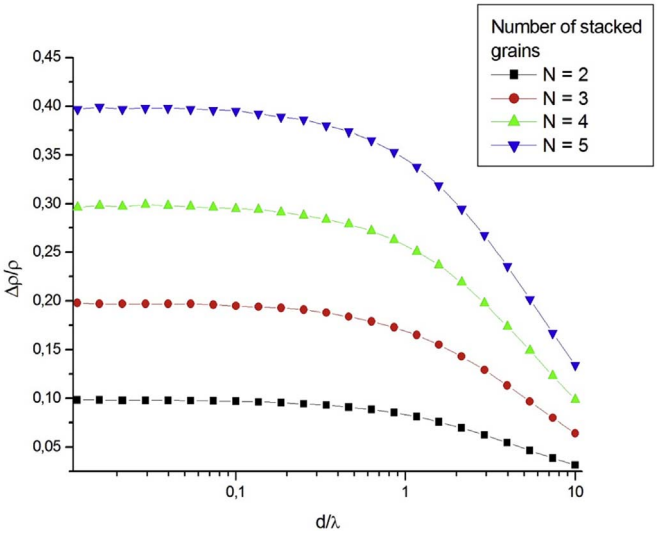

Fig. 7. Fractional resistivity change $\Delta\rho/\rho = (\rho_S - \rho)/\rho$ (where ρ_S, ρ are the resistivities with and without stacked grains) of a polycrystalline film as a function of the mean free path λ for different numbers of stacked grains, according to the SS model of the present paper. The film thickness is $d=99$ nm, with columnar grains with mean diameter $D=41$ nm and absence of disorder. Extreme rough limit is assumed $p_0 = p_d = 0.00$; with $p_{GB} = T_{GB} = 0.01$.

As an example of how this circumstance may appear in practice, let us consider the measurements of the electrical

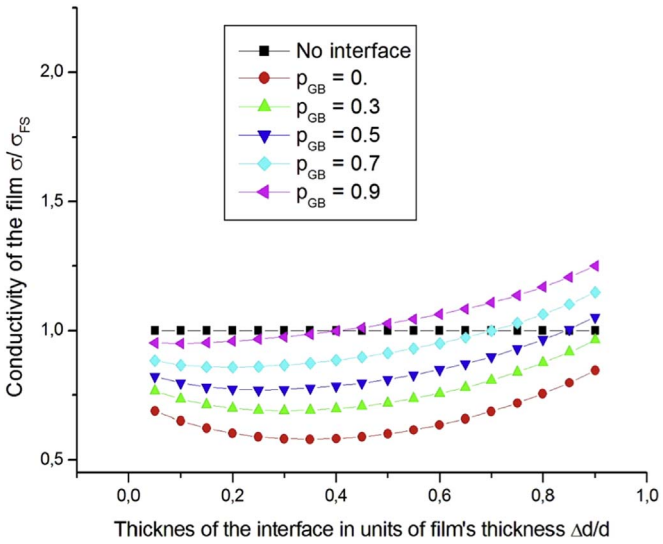

Fig. 8. Electrical conductivity with an interface created between two stacked grains (in units of the conductivity without interface) of a polycrystalline film as a function of the distance Δd between the interface and a film surface $z=d$ for different values of the p_{GB} parameter. The film thickness is $d=49$ nm. Mean free path $\lambda = 98$ nm and $p_0 = 1.0$, $p_d=0.1$. $T_{GB} = 0.0$.

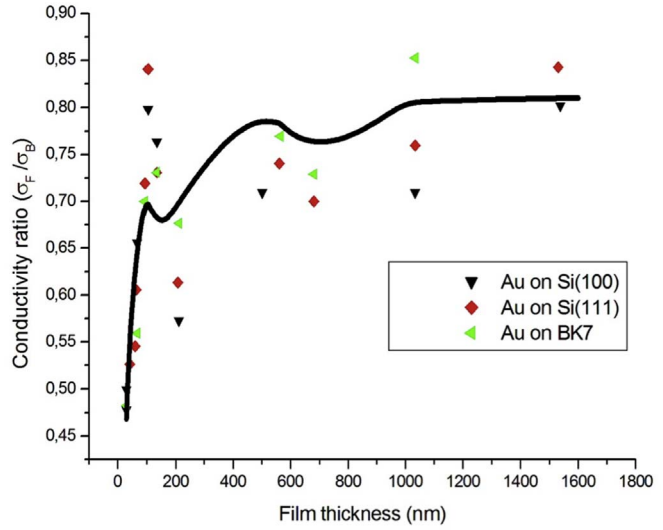

Fig. 9. Tentative fit of conductivity data σ_F of gold films (in units of bulk conductivity σ_B) from Chen et al. [28]. Continuous line is the present theory with assumed interfaces at $d_1 = 105$ nm and $d_2 = 560$ nm. Following Chen et al. we take $\lambda = 41$ nm and the relation between grain diameter and film thickness follows from Table 2 of this reference. In this fit, we uniformly assume that $T_{GB} = p_{GB} = 0.01$, and $p_0 = p_d = 0.2$.

conductivity of polycrystalline Au films reported by Chen et al. [28] (Fig. 9). These authors measured the surface roughness of the films and conclude that it results in completely diffuse scattering. They also measured the diameters of the grains as a function of the film's thickness d, and observed that the crystallite size increased roughly linearly with increasing d for $d \leq 100$ nm; and was constant thereafter. Also, they found that the conductivity had a pronounced non-monotonous dependence on thickness; a fact that they interpreted as a conductivity drop occurring at a thickness of around 200 nm that was caused, in turn, by a redistribution of crystallites inside the film.

As an exercise, we offer an alternative interpretation in which these unusual measurements are explained in terms of a conductivity enhancement (instead of a conductivity drop) caused by the mechanism just illustrated in Fig. 8. We note that the careful measurements of the samples' microstructure reported by the authors are consistent with the stacking of grains, giving rise to a new interface at $d \simeq 100$ nm. Indeed, they wrote that "small {111} crystallites began their growth in 125 nm $<d<$ 200 nm and they grew on top of previously {220} crystallites." [28] We conjecture that a second similar interface occurs at $d \simeq 600$ nm. The fact that this interpretation is reasonable is shown by the continuous line in Fig. 9; which is a fit of our SS model obtained by the simple prescription of a mean free path $\lambda = 41$ nm, $p_{GB} = T_{GB} = 0.01$, $p_0 = p_d = 0.2$ and added interfaces appearing at $d=105$ nm and $d=560$ nm.

4. Matthiessen's rule

As is well known, Matthiessen's rule is an empirical prescription which states that the resistivities due to different scattering processes approximately combine additivity to give the total resistivity of the sample. The rule has been related to the additivity of the transition probabilities in the collision operator, and to the maximization of the production of entropy [29]. In the present formalism, we have found a different form of Matthiessen's rule that has proved to be valid with high accuracy.

As previously explained, the resistivity ρ of a given sample is a function of the reflectivities p_0 and p_d, which describes the scattering by the external surfaces, and the probabilities p_{GB}, T_{GB} which characterize the effect of the scattering by grain boundaries. We define the resistivity ρ_{GB} as the component of the total resistivity ρ that is produced by the exclusive influence of grain boundaries—with the exclusion of the effects of surface scattering—by calculating the resistivity for the given values of p_{GB} and T_{GB}; but by putting $p_0=p_d=1$. In the same way, the resistivity ρ_S—accounting for the effects of surface scattering only—is calculated by retaining the given values of p_0, p_d, but by setting $p_{GB} = 0$ and $T_{GB} = 1$. (Thus, ρ_S coincide with the resistivity calculated according to the Fuchs–Sondheimer prescription [3,4]). The sum of ρ_{GB} and ρ_S cannot be equal to ρ, because both contain the resistivity of the bulk ρ_0. Thus, we should subtract ρ_0 once. In this way, the proposed form of Matthiessen's rule appears in the form

$$\rho = \rho_{GB} + \rho_S - \rho_0. \tag{10}$$

In Fig. 10 we show a typical example of the validity of this expression. It is seen that, even if the values of both components ρ_{GB} and ρ_S vary widely, Matthiessen's rule, in its version of Eq. (10), is accurately obeyed within the precision of the present numerical calculation.

5. Conclusions

In this paper we report calculations of the electrical conductivity of thin polycrystalline metallic films, resulting from an application of the method of Chambers—a procedure that is known to provide accurate solutions of the Boltzmann transport equation [12]. These results are contrasted with the well-known theory of Mayadas and Shatzkes, which proceeds from an approximation valid only for small values of the reflectivity R of an individual grain boundary [8]. Also, in contrast with the latter formalism, we characterize grain boundaries by means of two independent parameters: a probability p_{GB} of specular reflection and a probability T_{GB} of coherent passage; with the balance $q_{GB} = 1 - p_{GB} - T_{GB}$ measuring the probability of diffuse scattering that demotes the carriers from the out-of-equilibrium distribution and, thus, contributes directly to the resistivity.

We note that the present procedure can be extended in ways

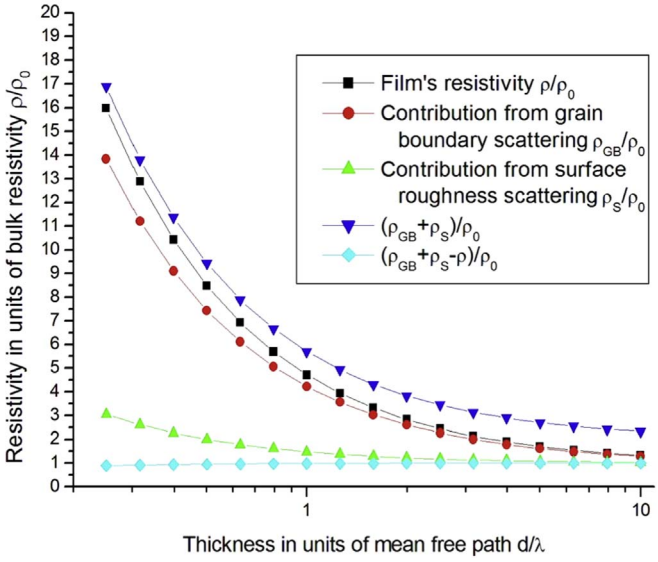

Fig. 10. Illustration of the validity of Matthiessen's rule Eq. (10) expressing the film resistivity as a combination of contributions from grain boundaries (ρ_{GB}), surface scattering (ρ_S) and bulk (ρ_0). In this case, the film thickness is $d=49$ nm, grain diameter $D=11.1$ nm with no disorder; and $p_0 = p_d = 0.0$; $p_{GB} = 0.3$, $T_{GB} = 0.2$.

quite beyond the reach of the theory of Mayadas and Shatzkes. In this paper we have considered the effects of stacked grains. Also, recently, the method has been applied to the calculation of the resistivity of polycrystalline thin wires where there is no analogue to Mayadas and Shatzkes treatment [14]. Of course, the basics assumption of these models—that grain boundaries are parallel planes—are convenient from the theoretical point of view; but perhaps no very accurate in practice. We note that the present Montecarlo procedure can cope with grain boundaries provided with more realistic morphologies [16] or having precise scattering properties obtained from microscopic calculations [30,31].

On the other hand, we have found that it is possible to obtain accurate fits of measurements of the resistivity versus thickness of thin films to any one of the three theories examined here—resulting, of course, in different values of the fitting parameters. Although this obviously means that neither MS nor SS models contradict reality, it does not result in a clear-cut criterium that rejects one in comparison with the other. Furthermore, the present comparison with experience indicates that the experimental evidence may not, at present, be capable of discriminating between these approximate and the more realistic formulations.

Finally, we note that even preposterous theories result in somewhat accurate fits to resistivity-thickness data [32]. Thus, we must conclude that a decisive confirmation of the superiority of the present—or an alternative—formalism must be a consequence of independent measurements of some of these fitting parameters or, alternatively, the determination of physically different quantities depending on common parameters—as, for instance, the resistivity and Hall voltage of Ref. [19]. Thus, the resolution of this important issue must be reserved for future research.

A copy of the program (in FORTRAN) used here for calculating the conductivity of thin polycrystalline films may be obtained from the corresponding author.

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References

[1] I. Stone, Phys. Rev. 6 (1898) 1.
[2] J.J. Thomson, Proc. Camb. Philos. Soc. 11 (1901) 119.
[3] K. Fuchs, Proc. Camb. Philos. Soc. 34 (1938) 100.
[4] E.H. Sondheimer, Proc. R. Soc. A 193 (1948) 484;
E.H. Sondheimer, Adv. Phys. 1 (1952) 1.
[5] J.M. Ziman, Principles of the Theory of Solids, Cambridge University Press, London 1972, p. 213. Instead of the wave vector **k** we use the velocity **v**, according to $m\mathbf{v} = \hbar\mathbf{k}$.
[6] M.S.P. Lucas, J. Appl. Phys. 36 (1955) 1632.
[7] J.E. Parrot, J. Proc. Phys. Soc. 85 (1965) 1143;
J.M. Ziman, Electrons and Phonons, Claredon Press, London, 1962;
S.B. Soffer, J. Appl. Phys. 38 (1967) 1710.
[8] A.F. Mayadas, M. Shatzkes, J.F. Janak, Appl. Phys. Lett. 14 (1964) 345;
A.F. Mayadas, M. Shatzkes, Phys. Rev. B 1 (1970) 1382.
[9] A.H. Wilson, The Theory of Metals, Cambridge University Press, London, 1954.
[10] J. Rammer, Rev. Mod. Phys. 58 (1966) 323.
[11] J. Szczyrbowsky, K. Schmalzbauer, J. Phys. F 16 (1986) 2079.
[12] R.G. Chambers, Proc. Phys. Soc. 65 (1952) 458.
[13] H. Budd, Phys. Rev. 127 (1962) 4;
C. MacCallum, Phys. Rev. 132 (1963) 930;
A. Lodder, Physica 29 (1970) 137;
F.E. Richards, Phys. Rev. B 8 (1974) 3126.
[14] L. Moraga, C. Arenas, R. Henriquez, B. Solis, Phys. Status Solidi B 252 (2015) 219.
[15] J.M. Rickman, K. Barmak, J. Appl. Phys. 112 (2012) 013704.
[16] J.M. Rickman, K. Barmak, J. Appl. Phys. 114 (2013) 133703.
[17] R. Courant, D. Hilbert, Methods of Mathematical Physics, vol. 2, Wiley, New York, 1962.
[18] X. Zhang, X. Song, X.-G. Zhang, D. Zhang, Europhys. Lett. 96 (2011) 17010.
[19] S. Bahamondes, S. Donoso, A. Ibanez-Landeta, M. Flores, R. Henriquez, Appl. Surf. Sci. 332 (2015) 694.
[20] M.S.P. Lucas, Appl. Phys. Lett. 4 (February) (1964) 15.
[21] M.S.P. Lucas, Thin Solid Films 2 (1968) 337;
M.S.P. Lucas, Thin Solid Films 7 (1971) 435.
[22] P.F. Carcia, A. Suna, J. Appl. Phys. 54 (1983) 2000.
[23] R. Dimmich, J. Phys. F: Metal Phys. 15 (1985) 2477.
[24] M.I. Kaganov, V.B. Fiks, Zh. Eksp. Teor. Fiz. 73 (1977) 753;
M.I. Kaganov, V.B. Fiks, Sov. Phys. JETP 42 (1977) 393;
V.V. Ustinov, Fiz. Met. Metalloved. 49 (1980) 31.
[25] S. Zhang, P.M. Levy, Phys. Rev. B 57 (1998) 5336.
[26] J. Barnaś, A. Fuss, R.E. Camley, P. Grünberg, W. Zinn, Phys. Rev. B 42 (1990) 8110;
V.V. Ustinovand, E.A. Ktavtsov, J. Phys. Condens. Matter 7 (115) (1995) 3471;
V.V. Ustinovand, E.A. Ktavtsov, J. Magn. Magn. Mater. 48 (1995) 307.
[27] E. Dimmich, F. Warkuz, Thin Solid Films 109 (1983) 103;
C.-X. Chen, Appl. Phys. A 40 (1986) 37;
A.M. Chornus, I.O. Shpetnyi, Ukr. J. Phys. 49 (2004) 587.
[28] G. Chen, P. Hui, K. Pita, P. Hing, L. Kong, Appl. Phys. A 80 (2005) 659.
[29] J.M. Ziman, Electrons and Phonons, Claredon Press, London 1962, p. 285.
[30] B.-h. Zhou, Y. Xu, S. Wang, G. Zhou, K. Xia, Solid State Commun. 150 (2010) 1422.
[31] B. Feldman, S. Park, M. Havery, S. Shankar, S.T. Dunham, Phys. Status Solidi B 247 (2010) 1791.
[32] F. Lacy, Nanoscale Res. Lett. 6 (636) (2011) 1.