Electrical-Resistivity Model for Polycrystalline Films: the Case of Arbitrary Reflection at External Surfaces

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(Received 31 July 1969)

In this paper, the total resistivity of a thin metal film is calculated from a model in which three types of electron scattering mechanisms are simultaneously operative: an isotropic background scattering (due to the combined effects of phonons and point defects), scattering due to a distribution of planar potentials (grain boundaries), and scattering due to the external surfaces. The intrinsic or bulk resistivity is obtained by solving a Boltzmann equation in which both grain-boundary and background scattering are accounted for. The total resistivity is obtained by imposing boundary conditions due to the external surfaces (as in the Fuchs theory) on this Boltzmann equation. Interpretation of published data on grain-boundary scattering in bulk materials in terms of the calculated intrinsic resistivity, and of thin-film data in terms of the calculated total resistivity suggests that (i) the grain-boundary reflection coefficient in Al is ≈ 0.15, while it is somewhat higher in Cu; (ii) the observed thickness dependence of the resistivity in thin films is due to grain-boundary scattering as well as to the Fuchs size effect; and (iii) the common observation that single-crystal films possess lower resistivities than polycrystalline films may be accounted for by grain-boundary effects rather than by differences in the nature of surface scattering.

I. INTRODUCTION

ELECTRICAL conduction measurements in size-effect samples, i.e., samples having some physical dimension comparable to the electron mean free path, have been of interest for many years. Data analysis for such measurements is generally carried out by applying the well-known Fuchs size-effect theory.[1]

The theory was developed by Fuchs to explain the fact that in thin films of alkali metals, the resistivity is always higher than in the original bulk, and increases rapidly as the thickness decreases. He postulated that ordinary scattering mechanisms in the bulk material (described by a relaxation time τ) carry over to the film; in addition, external surfaces impose a boundary condition on the electron-distribution function, which enhances the thickness-independent bulk, or intrinsic resistivity ρ_i, to a thickness-dependent total resistivity ρ. The result of the Fuchs theory for thin foils is

$$\rho = \rho_i \left[1 - (3/2\kappa)(1-p) \int_1^\infty \left(\frac{1}{t^3} - \frac{1}{t^5} \right) \frac{1 - e^{-\kappa t}}{1 - p e^{-\kappa t}} dt \right]^{-1}, \quad (1)$$

where κ $(\equiv a/l_i)$ is the ratio between film thickness a and intrinsic electron mean free path, l_i; p (a completely phenomenological parameter) is the probability that an electron will be specularly reflected upon scattering from a film surface and takes on values from 0 to 1. Since ρ and a are measurable quantities, Eq. (1) contains three unknown parameters: ρ_i, l_i, and p. However, only two of these are independent since

$$\rho_i l_i = \frac{12\pi^3 \hbar}{e^2 S_F}, \quad (2)$$

in which e is the electron charge and S_F is the free area of the Fermi surface.

In recent years there has been much interest in metal films grown on dielectric substrates by vacuum evaporation or sputtering, and various attempts have been made to fit resistivity data for these films to Eq. (1).[2] The interest has focused mainly on the parameter p. The fitting procedure generally has consisted of assuming that ρ_i and l_i are constant with thickness so that Eq. (1) reduces to a family of ρ versus a curves with p as an adjustible parameter. Values for p are then determined by noting which of these curves the data most resemble.

In nearly all instances, it has been observed that single-crystal films show a lower resistivity than the corresponding polycrystalline films and the normal analysis has led to the conclusion that $p \approx 0$ for polycrystalline films, while for epitaxial single crystal films, $p \approx 0.5$.[2] Recently, Mayadas et al. have shown that for evaporated polycrystalline Al films the assumption that ρ_i and l_i are constant with thickness, is incorrect and that in fact ρ_i decreases with increasing thickness, a.[3,4] For the particular case when these films are deposited on noncrystalline SiO_2 substrates held at $200°C$,[4] it is found that average grain diameter D is about equal to a (at least within the thickness range investigated, 1000 Å $\lesssim a$ $\lesssim$ 10 000 Å). Transmission electron microscopy showed the grains to be free of dislocations or other resolvable defect structure; since there is no compelling reason to believe that chemical purity is a function of thickness,

[1] See, e.g., E. H. Sondheimer, Advan. Phys. 1, 1 (1952).

[2] See, e.g., D. S. Campbell, in *The Use of Thin Films in Physical Investigations* (Academic Press Inc., New York, 1966), p. 315.

[3] A. F. Mayadas, J. Appl. Phys. 39, 4241 (1968).

[4] A. F. Mayadas, R. Feder, and R. Rosenberg, J. Vac. Sci. Technol., 6, 690 (1969).

it was concluded that the decrease in ρ_i (or increase in l_i) with thickness was due to the increasing grain size. The total, or measured resistivity at any temperature T, ρ_T, must therefore depend on thickness, not only through the ordinary Fuchs size-effect, but also because of the dependence of ρ_i on D.

It is commonly believed that grain boundaries have little effect on the resistivity of metals. Usually this is the case, for although the scattering of electrons by grain boundaries may be substantial, the grain size is usually much larger than the mean free path due to other scatterers (l_0), so that the grain-boundary contribution to the resistivity is small.[5] However, in the case of a thin film, the distance between grain boundaries, D, is generally smaller than l_0, and here the grain-boundary contribution can no longer be regarded as negligible.

In a recent publication, we have proposed a model for estimating electrical and galvanomagnetic effects due to electron scattering at grain boundaries, occurring simultaneously with isotropic background scattering (e.g., phonon plus point defect).[6] It was shown that even when scattering from external surfaces was completely specular (or could be neglected), a strong thickness-dependent resistivity, comparable in magnitude to the Fuchs effect could exist if $D \approx a$.

In this paper, the effect of film surfaces is superimposed on the earlier grain-boundary model and the overall film resistivity is computed (Sec. II). Numerical results based on this model are compared with available experimental data (Sec. III). The over-all validity of the model, its usefulness in helping to determine new physical information and various predicted phenomena are also discussed (Sec. IV).

II. FILM MODEL AND MODEL CALCULATION

Obviously, the problem of computing the electron-velocity distribution for scattering by grain boundaries of arbitrary shape, size, and orientation, simultaneously occurring with isotropic background scattering, presents enormous difficulties. However, with certain simplifications, some based on physical observation, others assumed, the problem can be made more tractable.

The first simplification comes from noting that in thin films deposited (e.g., by evaporation or sputtering) on substrates, the grains are not isotropic in form but tend to grow in a "columnar" fashion with the column axis normal to the film plane.[7] Since such grains generally extend from the substrate to the top surface of the film, the only grain boundaries which must be considered are those whose normals lie in the film plane. To simplify
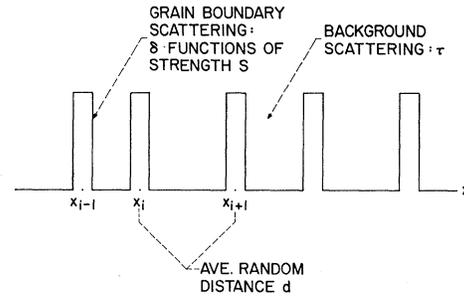

FIG. 1. Model for computing ρ_g, the resistivity due to both grain-boundary scattering and isotropic background scattering.

the problem further, it is assumed that the grain boundaries can be represented by two types of randomly spaced planes: those parallel to the electric field **E** and those perpendicular, and that the grain-boundary potential is short-ranged and smooth, so that the parallel boundaries produce only specular reflection.[8,9] The problem therefore reduces to finding the resistivity, ρ_g, caused by electron scattering from a series of partially reflecting, randomly spaced planar grain boundaries, occurring simultaneously with isotropic background scattering (caused by point defects and phonons).

In this section, the Boltzmann equation for this problem is solved to find ρ_g. It is assumed that a grain boundary can be represented by the simplest type of smooth, short-ranged potential, namely a δ-function potential, and that the electron states of the pure single crystal can be described sufficiently well by free-electron states. The standard perturbation-theory formula is used to compute the electron-transition rate for assembly of parallel δ-function potentials. This is then used in the linearized Boltzmann equation, where the additional assumption is made that the transition rate due to all other scattering mechanisms (except for the film surfaces) can be expressed in terms of a relaxation time. Scattering at the external surfaces is taken into account by imposing the standard Fuchs boundary conditions on the electron-distribution function.]

A. Grain-Boundary Resistivity

The proposed model of a polycrystalline film is shown in Fig. 1. In this model, the grain boundaries are represented by N parallel planes, oriented perpendicular to the direction of the constant electric field **E**, with an average separation d (Fig. 1).[9] There is a potential $S\delta(x-x_n)$ at the position x_n of the nth plane, S being the "strength" of the potential. (Physically, S is approxi-

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[5] See, e.g., J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1962), p. 352.

[6] A. F. Mayadas, M. Shatzkes, and J. F. Janak, Appl. Phys. Letters, **14**, 345, 1969.

[7] See, e.g., J. M. Nieuwenhuizen and H. B. Haanstra, Phillips Tech. Rev. **27**, 87 (1966).

[8] See, e.g., Ref. 5, p. 353.

[9] In our model of a polycrystal, the grains are bounded by perpendicular planes, the δ-function potentials, which are continuous throughout the polycrystal. These planes are distributed in the same way for any orientation in the film plane, and are uncorrelated. It is easy to verify for a spherical Fermi surface, that the conductivity derived on this model is a scalar. (As indicated in the text, there are no planes parallel to the film surface.) The choice of the direction of the electric field is irrelevant and our choice was made to simplify the presentation.
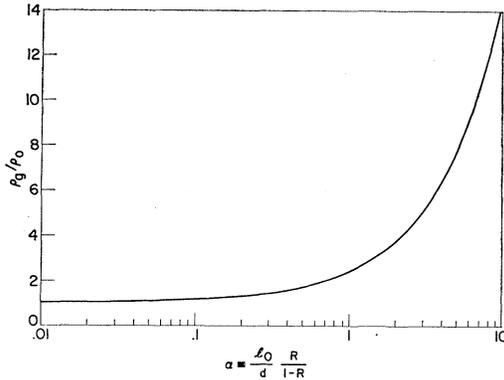
FIG. 2. Plot of Eq. (10).

mately equal to the height of the potential multiplied by its width). The positions x_n are distributed according to the Gaussian

$$g(x_1,\cdots,x_N) = \frac{\exp\left[-\sum_{i=1}^{N-1}(x_{i+1}-x_i-d)^2/2s^2\right]}{L_x(2\pi s^2)^{(N-1)/2}}, \quad (3)$$

where L_x is the length of the film and s is the standard deviation.

With the assumption that the scattering from other sources (point defects and phonons) can be described by a relaxation time τ, the Boltzmann equation for the geometry of Fig. 1 is

$$eEv_x\frac{\partial f_0(\mathbf{k})}{\partial\epsilon} = \int P(\mathbf{k},\mathbf{k}')[\Phi(\mathbf{k})-\Phi(\mathbf{k}')]d\mathbf{k} + \frac{\Phi(\mathbf{k})}{\tau}. \quad (4)$$

Here, $P(\mathbf{k},\mathbf{k}')$ is the transition probability for an electron in state $\mathbf{k}$ to be scattered to $\mathbf{k}'$ by the planes, $\Phi(\mathbf{k})=f(\mathbf{k})-f_0(\mathbf{k})$ is the deviation of the distribution function $f(\mathbf{k})$ from its equilibrium value $f_0(\mathbf{k})$, e is the electron charge, and ϵ and v_x are the electron energy and x component of velocity, respectively.

To find $P(\mathbf{k},\mathbf{k}')$, let

$$V(x) = S\sum_n \delta(x-x_n),$$

and consider $V(x)$ as a perturbation on the free-electron Hamiltonian. The unperturbed states are

$$\psi_{\mathbf{k}} = \Omega^{-\frac{1}{2}}e^{i\mathbf{k}\cdot\mathbf{r}},$$

where $\Omega\equiv L_xL_yL_z$ is the volume of the sample. Then the square of the matrix element, $\langle\mathbf{k}|V|\mathbf{k}'\rangle$, is found to be

$$|\langle\mathbf{k}|V|\mathbf{k}'\rangle|^2 = (S/L_x)\Delta(k_t-k_t')$$

$$\times\sum_{n,n'} e^{i(k_x-k_x')(x_n-x_{n'})}, \quad (5)$$

where k_t is the component of k in the y, z plane and $\Delta(k_t-k_t')$ is a Kronecker δ.

Averaging Eq. (5) over the distribution $g(x_1,\ldots,x_n)$, we obtain in the limit of continuous $\mathbf{k}$,

$$P(\mathbf{k},\mathbf{k}') = F(|k_x|)\delta(k_t-k_t')\delta(k_x+k_x'), \quad (6a)$$

$$F(|k_x|) = \frac{\alpha}{2\tau}\frac{k_F}{|k_x|}\frac{1-e^{-4k_x^2s^2}}{1+e^{-4k_x^2s^2}-2e^{-k_x^2s^2}\cos 2k_xd}, \quad (6b)$$

$$\alpha = \frac{m}{\hbar^3d}\frac{S^2}{k_F}2\tau = \frac{l_0}{d}\frac{R}{1-R}. \quad (6c)$$

In the second equality of Eq. (6c), S has been expressed in terms of a reflection coefficient R, the relation being that for the reflection from a single plane. The magnitude of the Fermi wavevector has been denoted by k_F, while l_0 is the background mean free path.

The solution of the Boltzmann equation is then

$$\Phi(\mathbf{k}) = \tau^*eEv_x(\partial f_0/\partial\epsilon), \quad (7a)$$

where

$$1/\tau^* = 1/\tau + 2F(|k_x|). \quad (7b)$$

The conductivity in the presence of both grain-boundary and background scattering, σ_g, is found from

$$\sigma_g = \frac{e^2}{4\pi^3}\int\frac{\tau^*v_x^2}{|\text{grad}_{\mathbf{k}}\epsilon|}dS_F = \frac{3}{2}\frac{\sigma_0}{\tau}\int_{-1}^{1}\tau^*(q)q^2dq. \quad (8)$$

Here, the first integral is over the Fermi sphere; $q=\cos\theta$ (with θ measured from the x axis so that $k_x=k_F q$ in the integral) and σ_0 is the conductivity in the absence of grain boundaries.

In the limit $s\to 0$, $\sigma_g\to\sigma_0$, and thus a periodic array of planes provides no resistance. An important simplification occurs if the interplanar spacing d is identified with the measured average grain diameter D, for we have found experimentally that $k_F^2s^2\gg1$. In this case, $F(|k_x|)$ can be written simply as

$$F(|k_x|) = \frac{\alpha}{2\tau}\frac{k_F}{|k_x|}. \quad (9)$$

The resultant conductivity is then readily evaluated to be

$$\sigma_g/\sigma_0\equiv\rho_0/\rho_g = 3[\tfrac{1}{3}-\tfrac{1}{2}\alpha+\alpha^2-\alpha^3\ln(1+1/\alpha)]. \quad (10)$$

In this equation, the appropriate resistivities have been written as ρ's. A plot of ρ_g/ρ_0 is shown in Fig. 2. In the limits of very small and very large α, Eq. (10) goes to the simple forms

$$\rho_g/\rho_p\approx 1+\tfrac{3}{2}\alpha, \quad \alpha\ll1,$$
$$\approx\tfrac{4}{3}\alpha, \quad \alpha\gg1. \quad (11)$$

B. Total Resistivity for Film (Fuchs Theory)

To find the total conductivity in the presence of film surfaces, we follow the lines of the Fuchs calculation.

The Boltzmann equation (see Fig. 1) is now

$$v_z(\partial\Phi/\partial z)+eEv_x(\partial f_0/\partial\epsilon)=\Phi/\tau^*, \qquad (12)$$

with the external film surfaces being the planes $z=0$ and $z=a$; τ^* has been defined in Eq. (7b). If $\Phi^{\pm}(v_z,z)$ is defined to be the deviation of the distribution function for $v_z>0(+)$ and $v_z<0(-)$, then the requisite boundary conditions at the film surfaces are

$$\Phi^+(v_z,0)=p\Phi^-(-v_z,0),$$
$$\Phi^-(v_z,a)=p\Phi^+(-v_z,a), \qquad (13)$$

where p, as defined earlier, is the fraction of electrons specularly scattered at the external surfaces. Then the $\Phi^{\pm}(v_z,z)$ are given by

$$\Phi^+(\mathbf{v},z)=e\tau^*Ev_x\frac{\partial f_0}{\partial\epsilon}$$

$$\times\left\{1-\frac{(1-p)e^{(-z/\tau^*v_z)}}{1-pe^{(-a/\tau^*v_z)}}\right\}, \quad v_z>0, \quad (14a)$$

$$\Phi^-(\mathbf{v},z)=e\tau^*Ev_x\frac{\partial f_0}{\partial\epsilon}$$

$$\times\left\{1-\frac{(1-p)e^{[(a-z)/\tau^*v_z]}}{1-pe^{(a/\tau^*v_z)}}\right\}, \quad v_z<0. \quad (14b)$$

The total film conductivity σ_f is computed as usual; with

$$J(z)=-\frac{e}{4\pi^3}\left(\frac{m}{\hbar}\right)^3\int v_x\Phi(\mathbf{v})d\mathbf{v},$$

we obtain

$$\sigma_f=\sigma_g-\frac{6\sigma_0}{\pi\kappa_0}(1-p)\int_0^{\pi/2}d\phi\int_1^\infty dt\frac{\cos^2\phi}{H^2(t,\phi)}$$

$$\times\left(\frac{1}{t^3}-\frac{1}{t^5}\right)\frac{1-e^{t-\kappa_0tH(t,\phi)]}}{1-p\,e^{[-\kappa_0tH(t,\phi)]}}, \quad (15a)$$

$$\rho_f=\left\{\frac{1}{\rho_g}-\frac{6}{\pi\kappa_0\rho_0}(1-p)\int_0^{\pi/2}d\phi\int_1^\infty dt\frac{\cos^2\phi}{H^2(t,\phi)}\right.$$

$$\left.\times\left(\frac{1}{t^3}-\frac{1}{t^5}\right)\frac{1-e^{[-\kappa_0tH(t,\phi)]}}{1-p\,e^{[-\kappa_0tH(t,\phi)]}}\right\}^{-1}. \quad (15b)$$

Here,

$$H(t,\phi)=1+\alpha/\cos\phi(1-1/t^2)^{1/2},$$

$$\kappa_0=a/l_0,$$

and l_0 is the mean free path within a grain.

For a single-crystal film ρ_f defined by (15b) must be identical to ρ [derived from the Fuchs theory and defined by Eq. (1)]. The resistivity which a single-crystal film would possess if it were infinitely thick (i.e., the intrinsic resistivity) is ρ_0. Thus by making the following
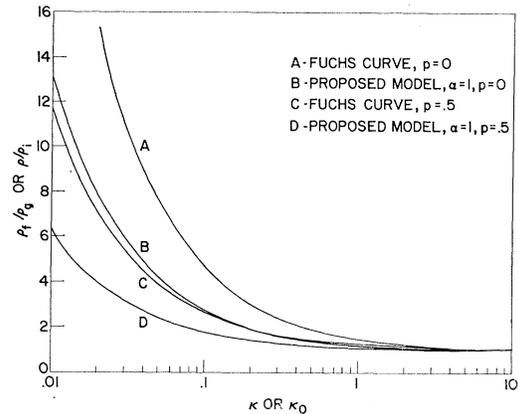

FIG. 3. Comparison between proposed model (for $\alpha=1$) and Fuchs theory.

substitutions into (15b): $\alpha=0$, $\rho_g=\rho_0$, $\rho_0=\rho_i$, $\kappa_0=\kappa$, it is easy to verify that the right hand sides of Eqs. (15b) and (1) are identical. As in Eq. (2), ρ_0 and l_0 are related by

$$\rho_0l_0=12\pi^3\hbar/e^2S_F. \qquad (16)$$

For a polycrystalline film, the parameters α and κ_0 play roles of equal importance; the intrinsic resistivity is now ρ_g but there is no parameter which can correctly be identified as the intrinsic mean free path. Equation (16) of course is always valid. Hereafter, to avoid confusion, the symbols ρ_i, l_i, and κ are only used in connection with the Fuchs theory.

Unfortunately Eqs. (15) cannot be evaluated analytically and for comparison with experiment, numerical solutions are necessary. A program written for the APL/360 time-sharing terminal system[10] has been used to obtain several solutions of Eq. (15b). In Fig. 3, plots of ρ_f/ρ_g versus κ_0 are shown for $p=0$ and $p=0.5$; for both these curves (B and D), α was held constant and equal to 1. Curves B and D of Fig. 3 can be interpreted as showing enhancement of the intrinsic resistivity ρ_g of a polycrystalline sample for which grain size is constant and independent of thickness. For comparison, the corresponding Fuchs curves (ρ/ρ_i versus κ) are also shown. The form of the grain-boundary curves is similar to the Fuchs curves. They lie below the corresponding Fuchs curves since ρ_f is determined only partially by p and l_0, while ρ depends exclusively on p and l_i.

In fact, deviations between the Fuchs theory and the proposed model are not large, in the sense that if measurements were made on films having constant values of grain size (d), l_0, ρ_0, and R, but variable thickness, then the data could be fitted to the Fuchs theory. It has already been stressed that an intrinsic mean free path cannot be correctly defined for a polycrystalline film. A corollary to this is that poly-

[10] A. D. Falkoff, K. E. Iverson, and E. H. Sussenguth, IBM Systems Tech. J. **3**, 198 (1964).
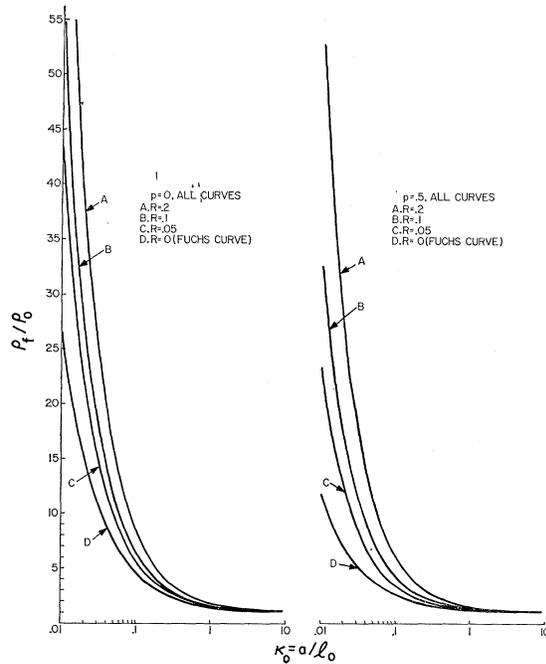
FIG. 4. Plots of Eq. (15b) for the case where average grain diameter equals film thickness.

crystalline films will, generally, exhibit a deviation from Matthiessen's Rule over and above that predicted by the ordinary Fuchs size effect: ρ_g cannot be expressed as the sum of a resistivity due solely to grain boundaries and the background resistivity ρ_0. However, it might be hoped that an "effective intrinsic mean-free path" might be definable for a polycrystal by use of the relation

$$l_g = (\rho_0/\rho_g)l_0. \tag{17}$$

In Fig. 3, α has been assumed constant and equal to 1, which corresponds to $\rho_g/\rho_0 = 2.378$ [from Eq. (10)]. For direct comparison with the Fuchs theory, ρ_f/ρ_g should be plotted against an effective kappa, $\kappa_g = a/l_g$. From the value $\alpha = 1$ and Eq. (17), it follows that $\kappa_g = 2.378k_0$; i.e., if curve B, for example, is translated horizontally by a factor of 2.378, it will be found to coincide with the Fuchs curve (curve A) to within about 5%.

In practice, it is generally found that grain-size increases with thickness; in many cases the grain size is found to be equal to thickness over a certain thickness range. Figure 4 shows plots of ρ_f/ρ_0 versus κ_0, assuming that grain size is exactly equal to thickness [or $\alpha = (1/\kappa_0)(R/(1-R))$] for various values of the grain boundary reflection coefficient R. Fuchs curves (or the case $R=0$) are also shown. A significant conclusion from these curves is that even relatively weak scattering from grain boundaries ($R=0.05$) results in a large resistivity for small κ_0; this resistivity decreases far more rapidly with increasing thickness than what would be expected from the Fuchs size effect.

III. COMPARISON WITH DATA

In spite of the very substantial number of electrical-resistivity measurements made in both single-crystal and polycrystalline films over the past few years, it is difficult to obtain a correlation between those results and the model presented here. First of all, a large fraction of the experimental work has been conducted in the vicinity of room temperature or liquid-nitrogen temperature, where structural contributions are superimposed on a large phonon-scattering component. However, at the higher temperatures, a sufficiently fine grain size (e.g., as might be found in a very thin film deposited on an unheated substrate) which varied with thickness would provide detectible effects. Unfortunately, structural examinations have seldom accompanied resistivity measurements.

The common observation that single-crystal films of a material show a lower resistivity than polycrystalline films of the same material is usually explained away by postulating, on rather unconvincing grounds, that polycrystalline films must possess lower values of p than single crystals. Furthermore, the three parameters of the Fuchs theory, p, ρ_i, and l_i have quite often been varied independently without regard to Eq. (2). Varying these parameters to fit the data is, of course, quite permissable so long as the values selected for ρ_i and l_i are such that the product $\rho_i l_i$ is in reasonable agreement with that obtained from a measurement in a bulk size-effect sample or by anomalous skin effect. The existence of a significant discrepancy implies a variation of ρ_i and l_i with thickness. This point has not always been appreciated.

As discussed earlier, grain-boundary effects in bulk materials are difficult to isolate experimentally because of the large average grain sizes encountered, even though the scattering power of a single boundary may be high. Three attempts have been reported in the literature to measure resistivity due to grain boundaries: The first was by Andrews in Cu [11] and the second by Arajs et al., in Fe [12]; recently, Andrews et al. have refined the earlier measurements in Cu and have also observed grain-boundary contributions to resistivity in pure Al.[13] In all cases it was the conclusion of the authors that grain boundaries are extremely effective in scattering electrons.

Interpretation of experimental results in terms of the proposed model is limited to two cases: the recent data of Andrews et al.[14] for bulk Cu and bulk Al and the data reported by Mayadas et al.[4] for evaporated Al films. The bulk data are analyzed in terms of Eq. (10) to yield the grain-boundary reflection coefficient R for Cu and Al. The data on Al thin films are fitted to Eq. (15b) to yield

[11] P. V. Andrews, Phys. Letters **19**, 558 (1965).
[12] S. Arajs, B. F. Oliver, and J. T. Michalak, J. Appl. Phys. **38**, 1676 (1967).
[13] See, e.g., R. G. Chambers, Proc. Roy Soc. (London) **A202**, 378 (1950).
[14] P. V. Andrews, M. B. West, and C. R. Robeson, Phil. Mag. **19**, 887 (1969).

values of p, ρ_0, l_0, and R. The data of Arajs *et al.* are not discussed because the magnetoresistance effect in Fe complicates interpretation. Other thin-film data are not discussed further because of the various reasons cited above.

A. Data of Andrews *et al.*

These measurements were made on high-purity Cu and Al. The bulk material was drawn into wires and then recrystallized by annealing. After recrystallization was complete, annealing was continued to induce grain growth, and resistivity measurements were performed on samples of various grain sizes.

The authors provide results in terms of an excess resistivity due to grain boundaries, ρ_{gb}. For the range of α's relevant to this work and neglecting the small deviation from Matthiessen's rule, the approximate expression [from Eq. (11)]

$$\rho_{gb} \approx \tfrac{3}{2}\rho_0 \cdot l_0[R/(1-R)]$$

may be used. Taking the values provided[14] for ρ_{gb}, i.e.,

$$\rho_{gb} = 3.12 \times 10^{-12} \ \Omega\text{cm}^2 \quad \text{for Cu},$$

$$\rho_{gb} = 2.45 \times 10^{-12} \ \Omega\text{cm}^2 \quad \text{for Al},$$

and the values

$$\rho_0 l_0 = 6.6 \times 10^{-12} \ \Omega\text{cm}^2 \quad \text{for Cu} \quad (\text{Ref. 13}),$$

$$\rho_0 l_0 = 8.2 \times 10^{-12} \ \Omega\text{cm}^2 \quad \text{for Al} \quad (\text{Ref. 15}),$$

we obtain

$$R = 0.24 \quad \text{for Cu},$$

$$R = 0.17 \quad \text{for Al}.$$

It is shown in the next section that the value of R for Al so obtained is in good agreement with the value deduced from our experimental observations on thin films. The value of R for Cu so obtained is in good agreement with a few preliminary observations (unpublished) made by us on Cu films.

B. Polycrystalline Al Films

As discussed above, substantially more experimental results are required for both single-crystal and polycrystalline films before the various parameters of the model can be accurately estimated.

Here we make a tentative fit of data obtained for polycrystalline Al films deposited onto heated (200°C) noncrystalline SiO$_2$ substrates.[16] Under these deposition conditions it is found that the average grain size is approximately equal to film thickness in the range $1000 \ \text{Å} \lesssim a \lesssim 10\ 000 \ \text{Å}$.

Attempts to fit the data of $\rho_{4.2K}$ (measured resistivity at liquid-helium temperature) versus a to a Fuchs curve characterized by single values of ρ_i and ρ were not
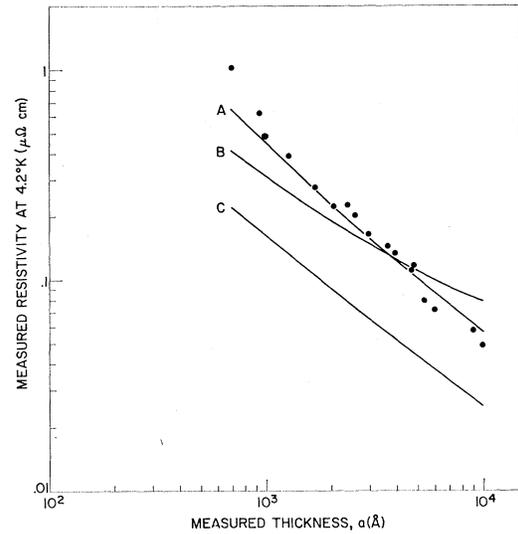
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[15] I. Holwech and J. Jeppesen, Phil. Mag. **15**, 217 (1967).

[16] For details of deposition procedure, see Ref. 4.

FIG. 5. Fit of experimental data on Al films to proposed model for a $\equiv d$ (curve A: $p = 0.2$, $R = 0.15$, $l_0 = 75\ 000$) and Fuchs theory for constant l_i (curve B: $p = 0$, $l_i = 20\ 000$ Å; curve C: $p = 0$, $l_i = 500\ 000$ Å).

successful. In Fig. 5 we show two such Fuchs curves. Curve B is a plot of Eq. (1) for the value $p = 0$, $\rho_i = 0.041 \ \mu\Omega$ cm, $l_i = 20\ 000$ Å. The values were selected to make the curve pass approximately through the midpoint of the thickness-data spread. It can be seen that curve B provides a poor fit to the data because its slope is too small. Curve C ($p = 0$, $\rho_i = 0.00164$, $l_i = 500\ 000$ Å) has the correct slope but does not pass through any data points because the theoretical resistivities are much smaller than the measured resistivities. The fact that the slope of the Fuchs curves increases as smaller values of ρ_i are selected is solely a consequence of Eq. (2). Curve C, for example, can be translated upward to fit the data but such a fit is devoid of physical meaning since the product $\rho_i l_i$ in this case will be much larger than those measured in bulk material. It is also easy to verify that selecting constant values of $p > 0$ provides a worse fit than simply using $p = 0$.

A good fit to these experimental data can be made by applying the proposed model [Eq. (15b)] for the parametric values $R = 0.15$, $l_0 = 75\ 000$ Å ($\rho_0 = 0.01093 \ \mu\Omega$ cm), $p = 0.2$, and the additional assumption that $d \equiv a$. We have estimated the values for ρ_0 and l_0 from the purity of the bulk-source material and some preliminary single-crystal data. An independent estimate of R was obtained in the following fashion: A thick Al film was deposited onto an unheated substrate. The average grain diameter was ≈ 1500 Å and the thickness was great enough so that scattering from external surfaces could be neglected. For this film, $\rho_{4.2K}$ was measured and then Eq. (10) was used to evaluate R, with $d = 1500$ Å, $l_0 = 75\ 000$ Å, $\rho_{4.2K} = \rho_g$. The resulting R, 0.15, was used to fit the data of Fig. 5. This value of R is certainly

compatible with theoretical estimates, and is in remarkably good agreement with the value estimated above from the bulk data of Andrews *et al*. The parameter p was varied arbitrarily to get a best fit. As a point of interest, it might be added that we always find a very significant difference between the $\rho_{4.2K}$ values for films deposited on unheated substrates and those deposited on heated substrates. As is well known, average grain diameter increases with increasing substrate temperature and thus measurements of resistivity versus substrate temperature (with thickness and other variables being held constant) may be of greater usefulness in studying grain-boundary scattering than the usual $\rho_{4.2K}$ versus a measurements, since in the former case observed variations in resistivity can only be due to structural changes.[17]

While this fit to the data is quite good, there appears to be a systematic trend for data points at small thicknesses to fall above the calculated curve while those at large thicknesses fall below. This is attributed not so much to deficiencies in the model but rather to the difficulty in describing films which vary in thickness by a single set of constant parameters. There are a number of systematic changes in structure, purity, and gross topography which are likely to occur as the film increases in thickness. The significant point is that these other variations seem relatively small and that the main features of the data can be described by the constant set of aforementioned parameters coupled with the assumption that $d \equiv a$.

DISCUSSION

Although many simplifying assumptions have been introduced in order to make the mathematical problem tractable, the model presented here satisfies essential qualitative physical requirements expected from a system in which grain-boundary scattering is significant, e.g.,

(1) Current flow must occur through the grain boundaries since no alternate paths are available.

(2) A consequence of (1) above is that the total resistivity ρ_f must become infinite when the grain-boundary reflection coefficient R approaches 1. This requirement is satisfied [see, e.g., Eqs. (6c), (10), and (15b)].[18]

(3) A deviation from Matthiessen's rule, over and above that due to the Fuchs size effect is expected when isotropic background scattering is occurring simultaneously with grain-boundary scattering, even though the

two processes are independent.[19] That this is so, can be verified from the equation defining ρ_g [Eq. (10)]; i.e., ρ_g cannot be written solely as the sum of a resistivity arising solely from grain boundaries and the background resistivity ρ_0. This is to be expected since the scattering from grain boundaries is not a function only of the angle between the incident and scattered electron wave vectors, but depends in addition on the orientation of the boundary. On the other hand, it is easy to verify that this deviation from Matthiessen's rule is small, generally being less than 5%. As a consequence, the Fuchs theory is approximately valid even for fine-grained films if the intrinsic mean free path is identified with l_g, defined by Eq. (17). In this sense, curve A of Fig. 5 can be regarded as a fit of the Fuchs theory to the data for an l_g that varies with thickness.

It should be noted that none of these conclusions or other significant results due to the model are qualitatively affected when boundaries other than those strictly parallel and perpendicular to $\mathbf{E}$ are considered (see Ref. 9). Due to the columnar nature of the grains in films, this model does predict that while the resistivity is isotropic in the film plane, the intrinsic resistivity measured perpendicular to the film plane must be different from that measured in the film plane.

We have not examined in detail the effect of grain boundaries on the galvanomagnetic coefficients; it can be expected, however, that internal size effects affect galvanomagnetic phenomena and cause characteristic deviations from the bulk behavior.

The assumptions of representing grain boundaries by short-ranged δ-function potentials and of representing the background scattering by an isotropic relaxation time are reasonable on physical grounds. It is interesting to note that recently Kaner and Fel'dman have independently worked out a model for electrical resistivity due to dislocation scattering and point-defect scattering occurring simultaneously,[20] which is similar in spirit to some of this work and that reported earlier[6]: These authors assume that dislocations can be represented by δ-function potentials and that the remaining scattering processes can be lumped into a relaxation time; their Boltzmann equation is similar in form to Eq. (4) and they use perturbation theory to obtain the relevant transition rate for their problem, as we have done.

We have employed a constant phenomenological parameter p as used in the original Fuchs theory[1] to describe surface scattering of electrons. Recently, surface scattering has been the subject of various studies and several theories have evolved which go beyond the simple Fuchs description.[21,22] As yet, in our point of

[17] In a recent independent study, A. von Bassewitz and E. N. Mitchell [Phys. Rev. **182**, 712 (1969)] have found that the measured resistivity of single crystal Al films is lower than that in polycrystalline films. In contrast to the interpretation presented here, however, they attribute this result to differences in the surface scattering parameter p between the two types of films.

[18] R. Landauer [IBM J. Res. Develop. **1**, 223 (1957)] obtained the same result earlier by a detailed analysis of the local electric field associated with the scatterers.

[19] See Ref. 5, p. 285.

[20] E. A. Kaner and E. P. Fel'dman, Fiz. Tverd. Tela **10**, 3046 (1968) [English transl.: Soviet Phys.—Solid State **10**, 2401 (1969)].

[21] See discussion and references, R. G. Chambers, in *Solid State Physics*, edited by J. F. Cochran and R. R. Haering (Gordon and Breach Science Publishers, Inc., New York, 1968), Vol. I, p. 321.

[22] S. B. Soffer, J. Appl. Phys. **38**, 1710 (1967).

view, the experimental evidence does not unambiguously dictate a choice from among the theories. Our choice was based for the most part on the greater simplicity of the Fuchs theory and also because experimental results are generally quoted in that framework. The recent theories have in common one qualitative prediction: that the κ dependence of the resistivity is weaker than that predicted by the Fuchs theory or that thinner films will appear to scatter more specularly than thicker ones (l_i being constant). If such an effect is sought experimentally, investigations should be limited to use of single crystals for which variations of intrinsic resistivity with thickness can probably be ruled out. By doping with a suitable impurity, κ in single crystals could be varied by varying dopant concentration. Use of polycrystals is not likely to yield fruitful conclusions since variations of grain size with thickness and attendant changes in ρ_g will swamp out other more subtle thickness-dependent effects. For example, it is easy to verify that in the data on Al films presented here and earlier,[4] the fit to the Fuchs curves (for constant ρ_i and l_i) is actually made worse if an increase in p with decreasing thickness is postulated. This does not rule out the existence of a thickness dependence in p, but merely suggests that the main features of the data can be explained by postulating a constant p and a variable ρ_g.

The two conditions necessary to observing large grain-boundary scattering effects, i.e., availability of a wide range of grain sizes and $l_0 \gg d$ can be easily obtained in films. Thus fundamental scattering parameters such as R, which are difficult to measure in bulk material can be extracted from data on clean thin films by using the present model and regarding p as a constant averaged parameter.

CONCLUSIONS

A model describing a polycrystalline metal film has been presented, which is then used to calculate the total electrical resistivity of the film in terms of unknown parameters characterizing the three mechanisms assumed to contribute to electron scattering: an isotropic contribution described by a scalar relaxation time; a contribution due to grain boundaries; and a contribution due to external surfaces.

It is our conclusion that a major portion of the total resistivity in polycrystalline films comes from electron scattering at grain boundaries. In Al films the grain-boundary-reflection coefficient for electrons is ≈ 0.15, in good agreement with the recently published bulk data of Andrews et al.

It follows that the dependence of thin-film resistivity on thickness (substrate temperature and other variables being held constant) includes variations of grain size with thickness, as well as the Fuchs (thickness) size effect. Dependence of thin-film resistivity on substrate temperature (thickness and other variables being held constant) comes about mainly due to variations of grain size with substrate temperature.

We suggest that the surface scattering-parameter p used in the Fuchs theory has about the same value for both single-crystal and polycrystalline films of a given material. The grain-boundary-reflection coefficient R can therefore be determined from measurements on polycrystalline films if the parameters p and l_0 are independently obtained from single-crystal films of the same class.

ACKNOWLEDGMENTS