JOURNAL OF MATERIALS SCIENCE 16 (1981) 2798–2802

Cumulative size effects in electrical conductivity of thin semi-metal films

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In the general framework of conduction models for monocrystalline and polycrystalline metal films, analytical expressions are derived for the electrical conductivity of semi-metal films. The existence of two cumulative size effects is thus predicted. These new equations agree with those previously derived in a special case of energy dependence of the relaxation time.

1. Introduction

General theoretical expressions for the electrical conductivity of thin metal films have been proposed by Ziman [1]; in the case of semi-metal films the Taylor expansion [2] of the energy dependence term in the integral expression of the current density gives rise to an additional term which depends on the square power of temperature [1].

The purpose of this paper is to present an analytical relationship between the usual conduction term (which does not explicitly depend on temperature) and the extra temperature dependent term.

2. General theoretical expression for thin metal electrical conductivity

In pure metal films three types of electronic scatterings can be operating simultaneously: background scattering, scattering at grain boundaries and scattering at external surfaces. Several analytical studies have been proposed [3–9], to describe completely the electronic conduction in polycrystalline or monocrystalline films. Linearized analytical expressions have also been empirically [3, 10,–16] and theoretically [7, 17, 18] proposed. The ratio of film conductivity, σ_f^m, to bulk conductivity, σ_0^m, can be expressed by a relationship of the following general form

$$\frac{\sigma_f^m}{\sigma_0^m} = F(\lambda_0, a, D, \{\mathscr{P}\}), \qquad (1)$$

where λ_0 is the electronic mean free path in the bulk material, a is the film thickness, D is the average grain diameter and $\{\mathscr{P}\}$ is the set of electrical parameters defining the effects of roughness at film surfaces and at grain boundaries; this set could contain, for instance, the usual specular reflection coefficient at film surface, p, initially introduced by Fuchs [19], but alternative representations could also be used [20]; similarly, the roughness of grain boundaries can be represented by the so-called electronic reflection at grain boundary, mathematically defined by Mayadas and Shatzkes [3]; a statistical electronic transmission coefficient could also be used [6–8, 21].

3. Electrical conductivity of thin semi-metal films

If the effects of electronic scatterings can be analytically represented by a relaxation time, τ, which is clearly the case for most of the con-

0022–2461/81/102798–05$02.50/0

duction models [3, 4, 7, 8] when the assumptions of Cottey [22] hold, the general macroscopic transport coefficients of Ziman [23] can be expressed from τ [1].

For instance, the electrical conductivity is given by [1]

$$\sigma_f = \frac{e^2}{12\pi^3\hbar} \times \left[\int v\tau \, \mathrm{d}A + \frac{(\pi BT)^2}{6}\frac{\partial^2}{\partial E^2}\int v\tau \, \mathrm{d}A\right]\Bigg|_{E=E_F}, \tag{2}$$

where $2\pi\hbar$ is Planck's constant, v is the electron velocity, B is Boltzmann's constant, T is the temperature in K, E is the electron energy, E_F is the Fermi energy, A is the area of the Fermi surface and e is the electronic charge.

In the case of semi-metals Equation 1 is even valid if the conductivity is measured at low temperature and if any electrical parameter is obtained by averaging the parameters related to electrons and holes, respectively. This theoretical assumption is sustained by recent experimental data related to antimony films [24], which have been theoretically interpreted by equations derived from the Mayadas–Shatzkes (M–S) model [3] in a special case of energy dependence for τ (see Equation 4 in [24]).

If we assume that the only energy dependence to be retained is that of λ_0, Equation 2 can be rewritten as follows

$$\frac{\sigma_f}{\sigma_0} = F(\lambda_0) + \frac{(\pi BT)^2}{6\lambda_0 E_F}\frac{\partial^2}{\partial E_F^2}[\lambda_0 E_F F(\lambda_0)]. \tag{3}$$

The bulk mean free path, λ_0, is defined [25] from

$$\lambda_0 = \tau_0(E_F)v_F, \tag{4}$$

where τ_0 is the relaxation time due to background scattering and v_F is the electron velocity at the Fermi surface. For convenience we put

$$\tau_0(E) = \tau_b E^s, \tag{5}$$

where τ_b does not depend on energy. Equation 3 consequently goes to the form

$$\frac{\sigma_f}{\sigma_0} = F(\lambda_0) + \frac{(\pi BT)^2}{6E_F^2} \times \left[(s+\tfrac{3}{2})(s+\tfrac{1}{2})F(\lambda_0) + (2s+3)E_F\frac{\partial F(\lambda_0)}{\partial E_F} + E_F^2\frac{\partial^2 F(\lambda_0)}{\partial E_F^2}\right]. \tag{6}$$

Further, taking into account Equations 4 and 5 gives

$$\frac{\partial \ln F(\lambda_0)}{\partial \ln E_F} = (s+\tfrac{1}{2})\frac{\partial \ln F(\lambda_0)}{\partial \ln \lambda_0} \tag{7}$$

and

$$\frac{\partial^2 \ln F(\lambda_0)}{\partial (\ln E_F)^2} = (s+\tfrac{1}{2})^2\frac{\partial^2 \ln F(\lambda_0)}{\partial (\ln \lambda_0)^2}. \tag{8}$$

Hence Equation 6 yields

$$\frac{\sigma_f}{\sigma_0} = F(\lambda_0)\left(1 + \frac{1}{6}\left(\frac{\pi BT}{E_F}\right)^2 \times \left\{(s+\tfrac{3}{2})(s+\tfrac{1}{2}) + 2(s+1)(s+\tfrac{1}{2})\frac{\partial \ln F(\lambda_0)}{\partial \ln \lambda_0} + (s+\tfrac{1}{2})^2\left[\frac{\partial \ln F(\lambda_0)}{\partial \ln \lambda_0}\right]^2 + (s+\tfrac{1}{2})^2\frac{\partial^2 \ln F(\lambda_0)}{\partial (\ln \lambda_0)^2}\right\}\right). \tag{9}$$

Taking the derivative of Equation 1 with respect to temperature, T gives

$$\frac{\beta^m_{f,u}}{\beta^m_0} = 1 + \frac{\partial \ln F(\lambda_0)}{\partial \ln \lambda_0}, \tag{10}$$

where $\beta^m_{f,u}$ is the temperature coefficient of resistivity, tcr, of unsupported film, at low temperature, neglecting any thermal variation but in λ_0, and β_0 is the bulk tcr at low temperature. Further differentiating Equation 10 yields

$$-\frac{1}{\beta^m_0}\frac{\partial}{\partial T}\left(\frac{\beta^m_{f,u}}{\beta^m_0}\right) = \frac{\partial^2 \ln F(\lambda_0)}{\partial (\ln \lambda_0)^2}. \tag{11}$$

An alternative form of Equation 9 is

$$\frac{\sigma_f}{\sigma_0} = F(\lambda_0)\left\{1 + \frac{1}{6}\left(\frac{\pi BT}{E_F}\right)^2 \times \left[(s+\tfrac{3}{2})(s+\tfrac{1}{2}) - 2(s+1)(s+\tfrac{1}{2})\left(1 - \frac{\beta^m_{f,u}}{\beta^m_0}\right) + (s+\tfrac{1}{2})^2\left(1 - \frac{\beta^m_{f,u}}{\beta^m_0}\right)^2 - (s+\tfrac{1}{2})^2\frac{1}{\beta^m_0}\frac{\partial}{\partial T}\left(\frac{\beta^m_{f,u}}{\beta^m_0}\right)\right]\right\}. \tag{12}$$

In the next section, comments are made on these theoretical results.

4. Discussion

4.1. The special case of the M–S conduction model

In the case of the M–S conduction model [3] it has recently been assumed [20] that the electronic reflection coefficient at grain boundary, R, depends on reciprocal Fermi energy; consequently the parameter α, defined by [3]

$$\alpha = l_0 D^{-1} R (1-R)^{-1} \tag{13}$$

(where $l_0 \equiv \lambda_0$) exhibits the following energy dependence

$$\alpha \sim E_{\mathrm{F}}^{s-1/2}. \tag{14}$$

Equation 6 must then be replaced by

$$\frac{\sigma_g}{\sigma_0} = f(\alpha) + \tfrac{1}{6}\left(\frac{\pi BT}{E_{\mathrm{F}}}\right)^2 \left[(s+\tfrac{3}{2})(s+\tfrac{1}{2})f(\alpha) + (2s+3)E_{\mathrm{F}}\frac{\partial F(\alpha)}{\partial E_{\mathrm{F}}} + E_{\mathrm{F}}^2 \frac{\partial^2 F(\alpha)}{\partial E_{\mathrm{F}}^2}\right], \tag{15}$$

where σ_g is the conductivity of an infinitely thick film. The partial derivatives are easily calculated from Equation 14,

$$\frac{\sigma_g}{\sigma_0} = f(\alpha) + \tfrac{1}{6}\left(\frac{\pi BT}{E_{\mathrm{F}}}\right)^2 \left[(s+\tfrac{3}{2})(s+\tfrac{1}{2})f(\alpha) + 3(s-\tfrac{1}{2})(s+\tfrac{1}{2})\alpha\frac{\partial f(\alpha)}{\partial \alpha} + (s-\tfrac{1}{2})^2 \alpha^2 \frac{\partial^2 f(\alpha)}{\partial \alpha^2}\right] \tag{16}$$

for $s = -1/2$. The above equation reduces to

$$\frac{\sigma_g}{\sigma_0} = f(\alpha) + \tfrac{1}{6}\left(\frac{\pi BT}{E_{\mathrm{F}}}\right)^2 \alpha^2 \frac{\partial^2 f(\alpha)}{\partial \alpha^2} \tag{17}$$

with, as shown by [3],

$$f(\alpha) = 1 - \tfrac{3}{2}\alpha + 3\alpha^2 - 3\alpha^3 \ln(1+\alpha^{-1}) \tag{18}$$

and

$$\alpha^2 \frac{\partial^2 f(\alpha)}{\partial \alpha^2} = 6\alpha^2 + \frac{12\alpha^3}{1+\alpha} + \frac{3\alpha^3}{(1+\alpha)^2} - 18\alpha^3 \ln(1+\alpha^{-1}). \tag{19}$$

This result agrees with the previously published result, derived from direct calculations, in the special case of $s = -1/2$ (see Equation 6 in [24]).

4.2. The three-dimensional conduction model [21] and the M–S conduction model [3]

In the framework of the three-dimensional conduction model [21], the grain boundary conductivity, σ_g, is given by [21]

$$\frac{\sigma_g}{\sigma_0} = G(v) = \frac{3}{2}\frac{v}{1-c}\left\{\frac{v+c^2}{1-c} - \frac{1}{2} + \left[1 - \left(\frac{v+c^2}{1-c}\right)^2\right]\ln\left(1 + \frac{1-c}{v+c^2}\right)\right\} \tag{20}$$

with

$$v = D\lambda_0^{-1}\left(\ln\frac{1}{t}\right)^{-1}, \tag{21}$$

where t is the statistical transmission coefficient at the grain boundary [21], independent of electron energy. Equation 6 then becomes

$$\frac{\sigma_g}{\sigma_0} = G(v) + \tfrac{1}{6}\left(\frac{\pi BT}{E_{\mathrm{F}}}\right)^2 \times \left[(s+\tfrac{3}{2})(s+\tfrac{1}{2})G(v) - (s+\tfrac{1}{2})(s+\tfrac{3}{2})v\frac{\partial G(v)}{\partial v} + (s+\tfrac{1}{2})^2 v^2 \frac{\partial^2 G(v)}{\partial v^2}\right]. \tag{22}$$

Since it has been shown [21] that the M–S function, $f(\alpha)$, and the three-dimensional function, $G(v)$, approximately coincide for

$$\alpha v = 1 \tag{23}$$

one could compare Equations 17 and 24 derived from Equation 22 by putting $s = -1/2$

$$\frac{\sigma_g}{\sigma_0} = G(v) \tag{24}$$

Since [21]

$$G(v) \approx f(\alpha). \tag{25}$$

An alternative form for Equation 24 is

$$\frac{\sigma_g}{\sigma_0} \approx f(\alpha) \tag{26}$$

which differs from Equation 17.

This is not surprising since Equation 17 has been obtained under the assumption of energy dependence of the reflection coefficient at grain boundary, R, whereas the transmission coefficient, t, is independent of energy. Since a non-linear variation in σ_g with temperature was observed in antimony films [24], Equation 24 is not adequate. In the framework of the three-dimensional model [21] it seems convenient to calculate the conductivity of antimony films by introducing

$$\tau(E_\mathrm{F}) \sim E_\mathrm{F}^{-3/2} \tag{27}$$

in order that Equation 27 may give the same energy dependence of the parameter, v^{-1}, as the parameter α, for $s = -1/2$ (cf. Equation 14).

For $s = -3/2$, Equation 22 becomes

$$\frac{\sigma_\mathrm{g}}{\sigma_0} = G(v) + \frac{1}{6}\left(\frac{\pi BT}{E_\mathrm{F}}\right)^2 v^2 \frac{\partial^2 G(v)}{\partial v^2} \tag{28}$$

which may be rewritten, from Equations 23 and 25, as

$$\frac{\sigma_\mathrm{g}}{\sigma_0} \approx f(\alpha) + \frac{1}{6}\left(\frac{\pi BT}{E_\mathrm{F}}\right)^2 \left[\alpha^2 \frac{\partial^2 f(\alpha)}{2} + 2\alpha \frac{\partial f(\alpha)}{\partial \alpha}\right]. \tag{29}$$

The deviation between Equations 17 and 29 is due to the term

$$\frac{1}{6}\left(\frac{\pi BT}{E_\mathrm{F}}\right)^2 2\alpha \frac{\partial f(\alpha)}{\partial \alpha}$$

with

$$2\alpha \frac{\partial f(\alpha)}{\partial \alpha} = 6\left[f(\alpha) - \frac{1}{1+\alpha}\right]. \tag{30}$$

This correcting term generally takes negative values, since an accurate approximate expression for $f(\alpha)$ is

$$f(\alpha) \approx (1 + C_1\alpha)^{-1} \qquad \text{for } 0.01 \leqslant \alpha \leqslant 10 \tag{31}$$

with $C_1 = 1.34$. However this correcting term is of low magnitude since $(\pi BT)/E_\mathrm{F} < 1$ and only qualitative conclusions can be proposed.

Deschacht *et al.* [24] observed that the reciprocal conductivity σ_g^{-1} of antimony films rarely varies with temperature according to Equation 17 for a given grain diameter D. However it could be noted that an increasing deviation from the theoretical low occurs for increasing temperature, specially for $D < 200$ nm (see Fig. 2 in [24]). Since it was assumed that the relaxation time τ is a decreasing function of temperature T ($\tau \sim T^{-3/2}$); it was also the case for α and, consequently, for the correcting term (with negative value) in Equation 29. It can then be predicted that an increase in temperature induces an increase in σ_g^{-1}, in good qualitative agreement with experimental data [24]. Nevertheless, this does not give a choice for the effect of electron energy on the parameter defining the grain boundary, but it suggests that the assumptions of energy dependence of the reflection coefficient R mathematically defined by Mayadas and Shatzkes [3] and of the bulk relaxation time according to

$$\frac{R}{1-R} \sim E_\mathrm{F}^{-1} \quad \text{and} \quad \tau \sim E_\mathrm{F}^{-1/2}, \tag{32}$$

respectively, can be replaced in the framework of the three-dimensional model only by the assumption

$$\tau \sim E_\mathrm{F}^{-3/2}. \tag{33}$$

Moreover, it may be noted that experimental [26] and theoretical evidence have been presented for sustaining the assumption of negligible thermal variation in $R(1-R)^{-1}$, that is in correlation with negligible effects of electron energy. The fact that adequate descriptions for the thermoelectric power of monocrystalline and polycrystalline films [27–31] have been derived from the M–S model [3] under the assumption that $R(1-R)^{-1}$ does not depend on energy [32, 33] could also sustain the above assumption, since the calculated values [28–31] of the energy dependence of the bulk mean free path, u, defined by

$$u = \left|\frac{\mathrm{d}\ln\lambda_0}{\mathrm{d}\ln E}\right|_{E=E_\mathrm{F}}, \tag{34}$$

are not markedly different from the theoretical one whereas in the opposite assumption of energy dependence of $R(1-R)^{-1}$ the apparent value of the energy dependence of the bulk mean free path, u', would be: $u' = (u-1)$. Hence much more marked deviations would be obtained, which does not seem to generally be the case. However some extra effects, such as impurities [25] could play a role and then the situation is not so clear [30]. Therefore it is realistic to say that the problem still remains unsolved.

4.3. Approximate expressions for $\sigma_\mathrm{f}/\sigma_0$

In the case of thin films the tcr ratio $\beta_{\mathrm{f,u}}^\mathrm{m}/\beta_0^\mathrm{m}$ takes values less than unity [25] and the thermal variations in the tcr ratio are negligible [25]. Equation 12 then reduces to

$$\frac{\sigma_\mathrm{f}}{\sigma_0} \approx F(\lambda_0)\left[1 + \tfrac{1}{6}\left(\frac{\pi BT}{E_\mathrm{F}}\right)^2 (s + \tfrac{1}{2})\frac{\beta_{\mathrm{f,u}}^\mathrm{m}}{\beta_0^\mathrm{m}}\right]. \tag{35}$$

Equation 35 shows that the size effect in the electrical conductivity of thin semi-metal films consists of two parts: the first one is the ordinary size effect and the second one is an extra size effect term which modulates the conductivity term specifically due to the semi-metal nature of the material, i.e. the conductivity term which depends on the square power of temperature.

To our knowledge experimental data related to this theoretical point has not been published up to now. Since the extra size effect term acts as a correcting term with respect to the ordinary size effect, it could be wise to perform experiments specially for this purpose, for instance at high temperature; this aspect will be considered in the future.

5. Conclusion

The general theoretical expressions derived for the electrical conductivity of polycrystalline and monocrystalline semi-metal films predict that two size effects are simultaneously operative; the ordinary size effect which effects the ordinary conductivity (i.e. conductivity at low temperature) and two cumulative size effects which affect the conductivity term typical of semi-metal films.

In the framework of the Mayadas–Shatzkes conduction model [3], these theoretical equations take forms which agree with previous theoretical calculations [24].

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Received 11 February and accepted 26 March 1981.