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Energy dependence of transport parameters derived from correlated variations in the thermoelectric power and temperature coefficient of resistivity of polycrystalline metal films

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Literal and general expressions of the thermoelectric power (TEP) of polycrystalline metal films are derived in the framework of the recently proposed three-dimensional model of conduction. Theoretical plots of the thickness dependence of film TEP are given and show that the TEP of infinitely-thick polycrystalline film markedly depends on the grain parameter. These theoretical results, as well as the general relation which expresses the film TEP in terms of the film temperature coefficient of resistivity (TCR), suggest two convenient ways for graphically determining the energy dependence of the bulk mean free path and the Fermi surface area.

1. Introduction

The transport properties of thin polycrystalline metal films with grain size constant with thickness have motivated extensive investigations [1–10] in the past few years. Pichard *et al.* [1, 11] have recently proposed a three-dimensional conduction model to describe the electrical properties of polycrystalline films in which three types of electron scattering mechanisms occur (i.e. background, grain-boundary and external surface scatterings) and have shown that their model can be satisfactorily used to fit the thickness dependence of both the resistivity ρ_{Fp} and its temperature coefficient β_{Fp} of sputtered polycrystalline metal films [1].

However, among the various transport properties the thermoelectric power (TEP) is of particular interest because of its sensitivity to distortions of the Fermi surface [12]. Thus, it is the purpose of this paper to present a theoretical expression of the thin polycrystalline film TEP in the framework of the three-dimensional model, and to propose a convenient way for determining the terms u and v which represent the energy dependence of the bulk mean free path l_0 and the Fermi surface area $\mathscr{A}$, respectively.

2. Theoretical

It has previously been shown [1, 13] that the conductivity, σ_{Fp}, of a thin metal polycrystalline film is given by:

$$\frac{\sigma_{FP}}{\sigma_0} = \frac{3}{2b}\left[\alpha - \tfrac{1}{2} + (1-\alpha^2)\ln(1+\alpha^{-1})\right], \qquad (1)$$

where σ_0 is the bulk conductivity and

$$b = \mu^{-1} + (1-C)\nu^{-1} \qquad (2)$$

$$\alpha = (1 + C^2\nu^{-1})b^{-1}, \qquad (3)$$

where μ is the thickness parameter, C is $4/\pi$ and ν is the grain parameter.

The grain parameter, ν, is related to the mean free path, l_0, the electronic transmission coefficient through grain-boundaries, t, [1, 11] and the average grain size a_g by

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$$\nu = a_g l_0^{-1} \left(\ln \frac{1}{t}\right)^{-1}, \qquad (4)$$

whereas the thickness parameter, μ, is related to l_0, the specularity parameter, p, [14] and the film thickness a by [1, 15]

$$\mu = a l_0^{-1} \left(\ln \frac{1}{t}\right)^{-1} \qquad (5)$$

From Equations 2 to 5 it can be seen that Equation 1 can be rewritten in the general form

$$\frac{\sigma_{\mathrm{Fp}}}{\sigma_0} = \mathrm{F}(l_0) \qquad (6)$$

where $\mathrm{F}(l_0)$ is a function of l_0.

The fine-graned film TEP, S_{Fp}, is defined as [6, 16]

$$S_{\mathrm{Fp}} = -\frac{\pi^2 k_0^2 T}{3e\epsilon_{\mathrm{F}}}\left[\frac{\mathrm{d}(\ln \sigma_{\mathrm{Fp}})}{\mathrm{d}(\ln \epsilon)}\right]_{\epsilon=\epsilon_{\mathrm{F}}}$$
$$= -S\left[\frac{\mathrm{d}(\ln \sigma_{\mathrm{Fp}})}{\mathrm{d}(\ln \epsilon)}\right]_{\epsilon=\epsilon_{\mathrm{F}}}, \qquad (7)$$

where k_0 is the Boltzmann constant, T is the absolute temperature and ϵ_{F} is the Fermi energy. Equation 7 may then be rewritten as

$$S_{\mathrm{Fp}} = -S\left\{\left[\frac{\mathrm{d}(\ln \sigma_0)}{\mathrm{d}(\ln \epsilon)}\right]_{\epsilon=\epsilon_{\mathrm{F}}} + \left[\frac{\mathrm{d}(\ln \mathrm{F}(l_0))}{\mathrm{d}(\ln \epsilon)}\right]_{\epsilon=\epsilon_{\mathrm{F}}}\right\}. \qquad (8)$$

Recalling that the absolute TEP of bulk metal is expressed as [16]

$$S_0 = -S\left[\frac{\mathrm{d}(\ln \sigma_0)}{\mathrm{d}(\ln \epsilon)}\right]_{\epsilon=\epsilon_{\mathrm{F}}} = -S(v+u), \qquad (9)$$

with

$$u = \left[\frac{\mathrm{d}(\ln l_0)}{\mathrm{d}(\ln \epsilon)}\right]_{\epsilon=\epsilon_{\mathrm{F}}} \qquad (10)$$

and

$$v = \left[\frac{\mathrm{d}(\ln \mathscr{A})}{\mathrm{d}(\ln \epsilon)}\right]_{\epsilon=\epsilon_{\mathrm{F}}} \qquad (11)$$

where $\mathscr{A}$ is the area of the Fermi surface, introducing Equations 9 to 11 into Equation 8 gives

$$S_{\mathrm{Fp}} = -S\left\{v + u + \frac{\mathrm{d}(\ln \mathrm{F}(l_0))}{\mathrm{d}(\ln l_0)}\left[\frac{\mathrm{d}(\ln l_0)}{\mathrm{d}(\ln \epsilon)}\right]_{\epsilon=\epsilon_{\mathrm{F}}}\right\}. \qquad (12)$$

It follows that

$$S_{\mathrm{Fp}} = -S\left\{v + u\left[1 + \frac{\mathrm{d}(\ln \mathrm{F}(l_0))}{\mathrm{d}(\ln l_0)}\right]\right\}. \qquad (13)$$

Now, assuming that the rigid band model of metals is valid, and that the number of free electrons per unit volume is temperature independent and further neglecting, as is usually the case [1, 16–18], the linear expansion coefficient of thickness, a, and grain size a_g, the temperature coefficient of the resistivity (TCR, β_{Fp}) defined by

$$\beta_{\mathrm{Fp}} = -\frac{\mathrm{d}(\ln \sigma_{\mathrm{Fp}})}{\mathrm{d}T}, \qquad (14)$$

may be written in the following form, after some mathematical manipulations,

$$\beta_{\mathrm{Fp}} = \beta_0\left\{1 + \frac{\mathrm{d}(\ln \mathrm{F}(l_0))}{\mathrm{d}(\ln l_0)}\right\} \qquad (15)$$

where β_0 is the bulk TCR.

Substitution of Equation 15 into Equation 13 gives

$$S_{\mathrm{Fp}} = -\left\{v + u\frac{\beta_{\mathrm{Fp}}}{\beta_0}\right\} \qquad (16)$$

Introducing into Equation 16 the exact expression of the TCR ratio $\beta_{\mathrm{Fp}}/\beta_0$, which has been derived in a previous paper [1], Equation 16 finally becomes

$$S_{\mathrm{F}} = -\frac{\pi^2 k_0^2 T}{3e\epsilon_{\mathrm{F}}} \times \left\{v + u\left(\frac{1}{b}\right)\frac{\alpha^{-1} - 2 + 2\alpha\ln(1+\alpha^{-1})}{\alpha - \frac{1}{2} + (1-\alpha^2)\ln(1+\alpha^{-1})}\right\} \qquad (17)$$

It should be noted that Equation 16 exhibits a form similar to that obtained on the basis of other conduction models by Leonard and Lin [19], Thompson [20] and Tellier and Tosser [6].

It is interesting to note that in the limit of infinitely-thick polycrystalline film the TCR, β_{Fp}, tends to the grain boundary TCR value, β_g, which is expressed as [1]

$$\frac{\beta_g}{\beta_0} = \frac{\nu}{1-C}\left[\frac{\gamma^{-1} - 2 + 2\gamma\ln(1-\gamma^{-1})}{\gamma - \frac{1}{2} + (1-\gamma^2)\ln(1+\gamma^{-1})}\right], \qquad (18)$$

with

$$\gamma = \lim \alpha|_{\mu\to\infty} = \frac{\nu + C^2}{1-C} \qquad (19)$$

In the same way the infinitely-thick polycrystalline film TEP becomes

$$S_g = -S\left\{v + u\frac{\beta_g}{\beta_0}\right\}, \qquad (20)$$

where β_g verifies Equation 18 above.

3. Discussion

Numerical values of the TCR ratio β_{Fp}/β_0 have been extensively tabulated [1, 21] for large ranges of the thickness parameter, μ, and grain parameter, ν; numerical evaluation of the polycrystalline film TEP is easily derived. Plots of the film TEP, S_{Fp} against μ are given in Fig. 1 for different values of the grain parameter, ν; as predicted, the TEP markedly depends on the grain parameter, ν, and tends to the grain boundary TEP, S_g, in the limit of large μ.

It is then appropriate to define the difference in thermoelectric power ΔS_g as

$$\Delta S_g = S_{Fp} - S_g \tag{21}$$

A calculation, in the way suggested by Thompson [20], gives

$$\Delta S_g = -Su \frac{\beta_g}{\beta_0}\left(\frac{\beta_{Fp}}{\beta_g} - 1\right) \tag{22}$$

Consequently a plot of ΔS_g versus β_{Fp}/β_g should yield a straight line with an abscissa intercept at unity and an ordinate intercept at $Su(\beta_g/\beta_0)$. These features are illustrated in Fig. 2 where the theoretical plots of ΔS_g against β_{Fp}/β_g are given, for different values of the grain parameter.

As the β_g value is easily deduced from data reporting the thickness dependence of the fine grained film TCR, β_{Fp} [1], the value of the energy dependence of the bulk mean free path (i.e. μ) can be graphically determined. It must be emphasized that the ordinate intercept of the difference between film TEP and infinitely-thick film TEP (which is sometimes ambiguously taken as the bulk TEP) against TCR, in the framework of the three dimensional model, markedly differs from the ordinate intercept, Su which corresponds to theoretical Fushs–Sondheimer plot of $\Delta S = S_F - S_0$ against β_F/β_0 [20]. Therefore it is necessary to obtain consistent representation of transport phenomena in order to perform careful analysis of film data.

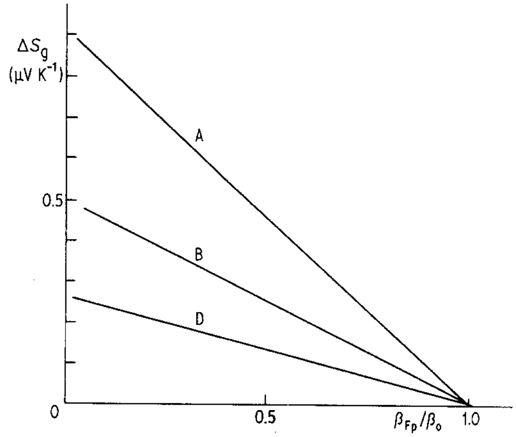

Figure 2 Theoretical plots of the difference in TEP, ΔS_g against the TCR ratio β_{Fp}/β_g, for different values of the grain parameter, ν. The calculation has been performed under the same assumptions as for Fig. 1. For curve A, $\nu = 4$; for curve B, $\nu = 1$; for curve D, $\nu = 0.4$.

It may be also useful to analyse the TCR ratio β_{Fp}/β_g dependence of the TEP ratio S_{Fp}/S_g. According to Equation 16

$$S_{Fp}/S_g = -\frac{v}{S_g} - \left(\frac{u}{S_g}\frac{\beta_g}{\beta_0}\right)\frac{\beta_{Fp}}{\beta_g}. \tag{23}$$

As S_g, β_g, u and v may be regared as "intrinsic" parameters for polycrystalline films with well-defined conditions of preparation it is concluded that a S_{Fp}/S_g against β_{Fp}/β_g plot should yield a straight line with an ordinate intercept at $-v/S_g$ and a slope of $-(u/S_g)(\beta_g/\beta_0)$. Furthermore

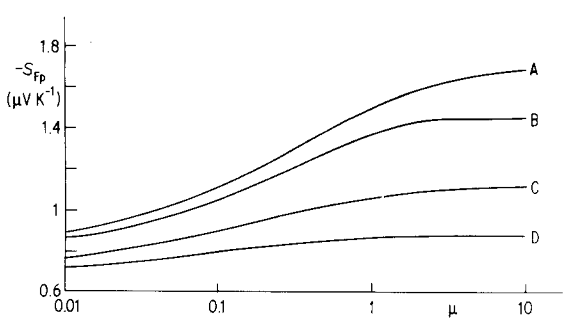

Figure 1 Theoretical plots of the thickness dependence of the polycrystalline film TEP. For the calculation it has been assumed that the Fermi energy is 11.6 eV, the temperature is 300 K and that $[d(\ln \mathscr{A})/d(\ln \epsilon)]_{\epsilon=\epsilon_F} = 1$ and $[d(\ln l_0)/d(\ln \epsilon)]_{\epsilon=\epsilon_F} = 2$. For curve A, $\nu = 10$; for curve B, $\nu = 4$; for curve C, $\nu = 1$; for curve D, $\nu = 0.4$.

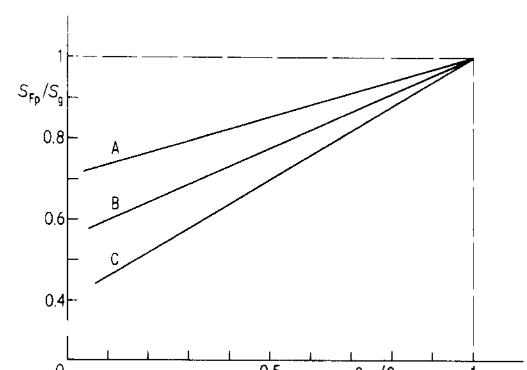

Figure 3 Theoretical plots of the TEP ratio S_{Fp}/S_g against the TCR ratio β_{Fp}/β_g, for different values of the grain parameter, ν. For curve A, $\nu = 0.4$; for curve B, $\nu = 1$; for curve C, $\nu = 4$.

this line must pass through the point $\{(S_{Fp}/S_g) = 1, (\beta_{Fp}/\beta_g) = 1\}$. (See Fig. 3).

Finally, it appears that simultaneous analyses of TEP data in the form ΔS_g and S_{Fp}/S_g against β_{Fp}/β_g plots allow the graphical determination of both u and v.

4. Conclusions

Theoretical expressions of the TEP of fine-grained metal films have been derived in the framework of the three-dimensional model. It appears that, as previously demonstrated on the basis of other conduction models, the TEP can be generally expressed in terms of the temperature coefficient of resistivity. A convenient method is then suggested to determine the terms representing the energy dependence of bulk mean free path and Fermi surface area.

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