A reinterpretation of the effects of impurities on the thermoelectric power of thin gold films

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Previously published data are re-examined in the light of a grain-boundary model for monocrystalline films. New interpretations are proposed which show that the thermo-electric power due to thickness-dependent scattering attains a constant value.

1. Introduction

Leonard and Lin [1] have previously presented a procedure for determining the effect of electronic scattering at the external surfaces of metal film. They started from the correlated variations in film resistivity and differences in thermoelectric power during annealing.

Since the effect of scattering at grain boundaries was not taken into account, we attempt in this paper to give a new interpretation of the observed phenomena.

2. Preliminary remarks

It is well known that for large thickness the monocrystalline film resistivity, ρ_{Fm}, can be expressed in the following linear form [2–4]:

$$\rho_{Fm} \approx \rho_0 + \rho_0[A(p) + B(t)]k^{-1}, \quad k > 1, (1)$$

where ρ_0 is the bulk resistivity, k the reduced thickness (equal to al_0^{-1}), a the film thickness, l_0 the electronic mean free path in the bulk material, $A(p)$ a function describing the effect of electronic scattering at external surfaces, p being the usual specular reflection coefficient defined by Sondheimer [5], and $B(t)$ a function describing the effect of electronic scattering at grain boundaries, t being a parameter related to the electrical behaviour of a grain boundary.

For Equation 1 to be valid it must be assumed

that the average grain diameter is equal to the film thickness.

Starting from a bi-dimensional model of conduction [6] it has been shown recently [7] that Equation 1 can be written as:

$$\rho_{Fm}/\rho_0 \approx 1 + k^{-1}\left[0.36 \ln\frac{1}{p} + 1.144 \ln\frac{1}{t}\right]$$

$$(2)$$

for $t > 0.3$; $p > 0.3$; $k > 0.01$, where t is the statistical electronic transmission coefficient at the grain boundary [6].

For convenience, the thickness-dependent resistivity, ρ_t, is defined by

$$\rho_{Fm} = \rho_0 + \rho_t \qquad (3)$$

where

$$\rho_t = \rho_0 k^{-1}\left[0.36 \ln\frac{1}{p} + 1.144 \ln\frac{1}{t}\right]. \quad (4)$$

According to the Wiedemann–Franz law [8], the film thermoelectric power, S_{Fm}, can then be derived from Equation 3 according to the general equation:

$$S = \left(\sum_j \rho_j\right)^{-1}\left(\sum_j \rho_j S_j\right) \qquad (5)$$

where ρ_j and S_j are the components of resistivity and thermoelectric power due to the jth scattering.

Hence:

$$S_{Fm} = \rho_{Fm}^{-1}(\rho_0 S_0 + \rho_t S_t). \qquad (6)$$

When the film contains impurities, Equations 3 and 6 are replaced by:

$$\dot{\rho}_{Fm} = \rho_0 + \rho_t + \rho_i \qquad (7)$$

$$\dot{S}_{Fm} = \dot{\rho}_{Fm}^{-1}(\rho_0 S_0 + \rho_t S_t + \rho_i S_i), \qquad (8)$$

where the subscript i indicates impurities.

The difference in thermoelectric power between a film and bulk material $\Delta\dot{S}_{Fm}$ is then:

$$\Delta\dot{S}_{Fm} = \dot{S}_{Fm} - S_0 = \dot{\rho}_{Fm}^{-1}(\rho_0 S_0 + \rho_t S_t$$
$$+ \rho_i S_i) - S_0. \qquad (9)$$

Alternative forms of Equation 9 are:

$$\Delta\dot{S}_{Fm} = (S_i - S_0) + \dot{\rho}_{Fm}^{-1}[\rho_0(S_0 - S_i)$$
$$+ \rho_t(S_t - S_i)] \qquad (10)$$

$$\Delta\dot{S}_{Fm} = (S_t - S_0) + \dot{\rho}_{Fm}^{-1}[\rho_0(S_0 - S_t)$$
$$+ \rho_i(S_i - S_t)] \qquad (11)$$

$$\Delta\dot{S}_{Fm} = \dot{\rho}_{Fm}^{-1}[\rho_t(S_t - S_0)$$
$$+ \rho_i(S_i - S_0)]. \qquad (12)$$

3. New interpretation of previous experiments [1]

When gold films have been annealed for 2 h, the reduced resistivity, ρ_{Fm}/ρ_0, is a linear function of reciprocal reduced thickness, k^{-1}, as shown in Fig. 1 derived from the experimental data of Leonard and Lin [1]. This result agrees with Equations 3 and 4, except for thinner thickness.
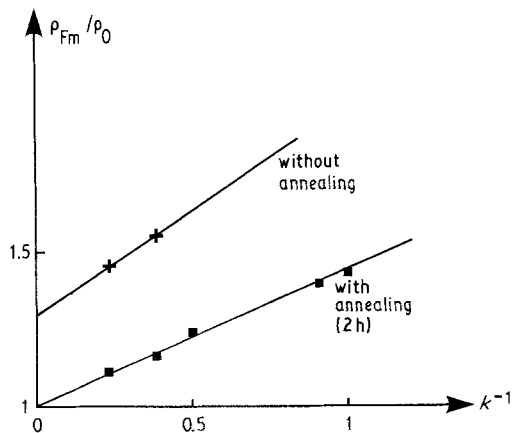

Figure 1 Variations of the reduced resistivity, ρ_{Fm}/ρ_0, with reciprocal reduced thickness, k^{-1}, for unannealed and annealed films, from [1].
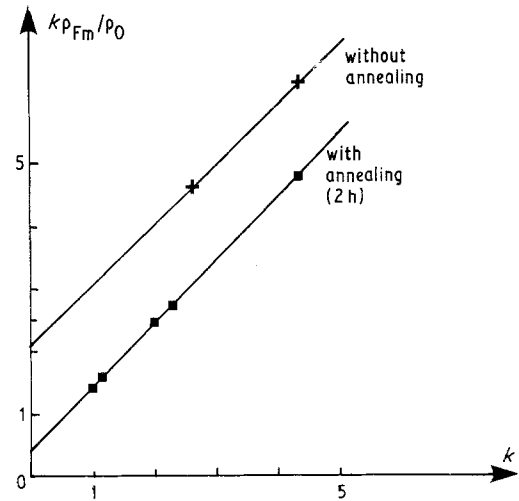

Figure 2 Plot of the product reduced thickness × reduced resistivity against reduced thickness, for unannealed and annealed films, from [1].

For infinitely thick films, i.e. $k^{-1} = 0$, it is observed [1] that $\rho_{Fm} = \rho_0$; it shows that the film has a monocrystalline structure and does not contain impurities. A plot of $k(\rho_{Fm}/\rho_0)$ against k gives a linear plot with slope of unity (Fig. 2); hence the general expression for ρ_{Fm}/ρ_0 is:

$$(\rho_{Fm}/\rho_0) \approx 1 + 0.4k^{-1}. \qquad (13)$$

In the Fuchs–Sondheimer conduction model [5, 8], the asymptotic expression is:

$$\rho_{Fm}/\rho_0 \approx 1 + 0.375(1 - p)k^{-1} \qquad (14)$$

and could be in agreement with experimental law (Equation 13) if p takes very low values.

Since the films have been firmly annealed at 480° C for 2 h, it should not be assumed that $p = 0$; consequently, we deduce that both external surface and grain-boundary scatterings are simultaneously operative in this annealed film (without impurities), and the F–S model does not hold.

The resistivity of as-deposited film is known for only two values of film thickness; the values of resistivity are much larger than for annealed films. This phenomenon cannot then be due to the effect of ageing on p and t and it must be assumed that impurities exist in unannealed films, and progressively vanish when the ageing process is operative. This conclusion has been presented in terms of a physically reasonable assumption by Leonard and Lin [1].

The experimental data of the authors [1] show that the variation in resistivity due to annealing is

thickness dependent; if it is assumed, with Leonard and Lin [1], that the variation is only due to the vanishing of impurities, we then deduce that the resistivity due to impurities markedly decreases for increasing thickness. This feature cannot be easily interpreted since the films are deposited with a technological apparatus (10^{-7} torr, ionic pump, deposition rate $10\,\mathrm{nm\,sec^{-1}}$) which would reasonably give a constant amount of impurities; we then assume that the annealing procedure induces the elimination of impurities (corresponding to a constant resistivity, ρ_i) but also modifies the thickness-dependent resistivity, ρ_t.

This last assumption is not retained by the authors [1], but their justification can now be examined. The temperature variation of resistivity was measured before and after annealing and it was found [1] that the slope of $d\rho/dT$ did not vary with successive annealing even though the magnitude of ρ decreased [1]. This result shows that, below any given annealing temperature, ρ_i and ρ_t are temperature independent; this feature is not surprising since it can be assumed that ρ_i is temperature independent [5], and it has been shown [9] that, in absence of impurities, $\rho_{Fm}\beta_{Fm} \approx \rho_0\beta_0$. It can be concluded that the thickness-dependent scattering is not temperature dependent in this temperature range but it does not allow one to deduce [1] that the parameters describing these scatterings do not vary with annealing temperature. In the same way, ρ_i varies with annealing temperature but is not temperature dependent below the annealing temperature. Consequently, the assumption presented by Leonard and Lin [1], i.e. the constant value of the size-effect resistivity, is not retained.

We then assume that ρ_i takes thickness-independent values and that the annealing procedure modifies p and t. This last assumption is consistent with the fact that excess annealing leads to discontinuous film, as observed [1]. Since the thickness dependence of the resistivity of unannealed films cannot be seriously determined from the data related to two thicknesses (a problematical dotted line can be drawn in Fig. 1) we define the extra resistivity, ρ_e, by the equation:

$$\dot{\rho}_{Fm} = \rho_{Fm} + \rho_e, \qquad (15)$$

or

$$\dot{\rho}_{Fm} = \rho_0 + \rho_t + \rho_e, \qquad (16)$$

i.e. ρ_e represents the impurity resistivity and,

eventually, that part of the thickness-dependent resistivity which vanishes during annealing.

It yields, by analogy with Equations 7, 8, 10 and 11 (Equation 12 is out of the scope of the following calculation):

$$\dot{S}_{Fm} = \dot{\rho}_{Fm}^{-1}[\rho_0 S_0 + \rho_t S_t + \rho_e S_e], \quad (17)$$

and:

$$\Delta \dot{S}_{Fm} = (S_e - S_0) + \dot{\rho}_{Fm}^{-1}[\rho_0(S_0 - S_e) + \rho_t(S_t - S_e)] \qquad (18)$$

$$= (S_t - S_0) + \dot{\rho}_{Fm}^{-1}[\rho_0(S_0 - S_t) + \rho_e(S_e - S_t)], \qquad (19)$$

and from Equations 5 and 6:

$$\Delta S_{Fm} = S_{Fm} - S_0 = \rho_{Fm}^{-1}\rho_t(S_t - S_0). \quad (20)$$

The corresponding equations proposed by Leonard and Lin were [1]:

$$\rho = \rho_0 + \rho_i + \rho_s \qquad (16a)$$

$$\Delta S = (S_i - S_0) + \frac{1}{\rho}[\rho_0(S_0 - S_i) + \rho_s(S_s - S_i)] \qquad (18a)$$

$$\Delta S|_{\rho_i \to 0} = (S_s - S_0)\rho^{-1}\rho_s. \qquad (20a)$$

Comparing the set of Equations 16, 16a, 18, 18a and 20, 20a shows that the equations can be formally identified by transforming the notations according to the rule shown in Table I. It is then valid to assume that ρ_t is unaltered by annealing. Consequently, all the calculations performed by the authors [1] can be used.

4. Discussion

Since the thermopower is an intensive property with respect to the scattering processes at external surfaces and grain boundaries, the constant value of S_t only signifies that a thickness-independent relation exists between the film thickness, a, and the average grain diameter, a_g (i.e. $a \sim a_g$ or $a_g > a$) which is commonly observed in monocrystalline films [8].

The constant value of S_e has no immediate physical signification, but it must not be omitted that ρ_e has been mathematically introduced in the equations. In fact, ρ_e represents the resistivity due to impurities and an additional resistivity, ρ_{add},

TABLE I Indexes for notations

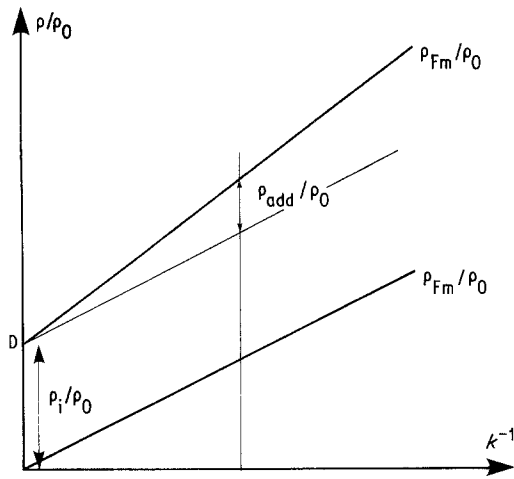| Leonard and Lin [1]	Proposed in the text
i	e
s	t

Figure 3 Definition of the additional resistivity, ρ_{add}.

which is the difference between the thickness-dependent resistivity before and after annealing. The approximate values of ρ_{add} can be roughly measured in Fig. 1, with the following assumptions (Fig. 3):

1. ρ_i is constant and its value is given by the ordinate intercept D of the plot of $\dot{\rho}_{Fm}/\rho_0$ against k^{-1};

2. ρ_{add} is the ordinate difference between the $(\dot{\rho}_{Fm}/\rho_0, k^{-1})$ plot and the linear curve parallel to $(\rho_{Fm}/\rho_0, k^{-1})$ plot passing through point D. This resistivity is a convenient tool for calculation but cannot be separately measured.

The accuracy of the $(\dot{\rho}_{Fm}/\rho_0, k^{-1})$ plot is questionable but the above procedure shows that $(\rho_{add}/\rho_i)(\rho_e/\rho_0)^{-1} < 0.21$. From the expression of ρ_e:

$$\rho_e = \rho_i + \rho_{add}, \qquad (21)$$

S_e may be derived:

$$S_e = \frac{\rho_i}{\rho_e}S_i + \frac{\rho_{add}}{\rho_e}S_{add}. \qquad (22)$$

Since S_{add} is due to thickness-dependent scattering, it can be assumed that:

$$S_{add} \approx S_t. \qquad (23)$$

Hence:

$$S_i \approx \rho_e \rho_i^{-1} S_e - \rho_{add}\rho_i^{-1} S_t. \qquad (24)$$

The values of S_i can then be calculated from the above equations, assuming that $\rho_{add} = 0$ for $k^{-1} = 0$. In agreement with the assumption of constant value for ρ_i, the associated thermopower, S_i, also takes practically constant values; the values

obtained for ρ_i (Table II) are consistent with those reported in the literature [8, 10]. There is no marked difference between these results and those reported by Leonard and Lin [1] but the physical interpretations differ, since they considered that the size effect was exclusively due to electronic scattering at external surfaces and that the influence of annealing on surface roughness was negligible. The fact [1] that agglomeration occurs in the film when annealing is maintained, even if the minimum value of resistivity has been obtained, shows that, at this step, annealing modifies the grain-boundary scattering; it must not be omitted that it is generally assumed [8] that annealing modifies the external surface scattering. Calculations (Table II) show that the resistivity, ρ_{add}, before agglomeration, is roughly proportional to the reciprocal film thickness whereas the ratio ρ_{add}/ρ_t does not take a constant value; we then conclude that annealing both modifies grain-boundary and external surface roughness. These modifications cannot be separately determined from the linear equations recently proposed [9], because the set of experimental data is too restricted (two values).

It must be pointed out that the variations in roughness of external surfaces during annealing have been neglected by Leonard and Lin [1].

The thermopower, S_t, can then be associated with the two thickness-dependent scatterings and its constant value (for the two experimented thicknesses) gives physical evidence for identical structures of the films. Since the value of ρ_{im} is constant, we assume that the films are homogeneous and that impurities vanish under the action of the ageing procedure. Since it is not physically acceptable that the action of annealing on grain boundaries is the same when the thickness varies from 100 to 160 nm, we finally assume that the annealing mainly modifies the surface scattering coefficient, p.

The validity of this assumption can be empirically estimated as follows. The variation in ρ_t with thickness is derived from Equation 3, i.e.:

$$\Delta\rho_t = \rho_0 \left[0.36 \ln \frac{1}{p} + 1.144 \ln \frac{1}{t} \right] \Delta(k^{-1}). \tag{25}$$

In annealed films, p takes values larger than 0.4 [8]. Hence:

$$\ln \frac{1}{p} \approx 1 - p. \tag{26}$$

An approximate form for the thickness variations in ρ_t due to external surface scattering is then:

$$\Delta\rho_t|_{ext} \approx \rho_0 0.36 (1 - p) \Delta(k^{-1}). \tag{27}$$

In unannealed films the electron scattering at external surfaces is probably diffuse [8], i.e. $p \approx 0$. Equation 3 consequently does not hold, since it is derived from the Cottey model [11] for specular scattering at external surfaces, i.e. for $p = 1$ (in fact, the validity range extends down to $p = 0.4$) [12].

Nevertheless Equation (27) does hold, and for unannealed films:

$$\Delta\rho_{to}|_{ext} = \rho_0 0.36 \Delta(k^{-1}). \tag{28}$$

Consequently, the variation in ρ_{add} with thickness is:

$$\Delta\rho_{add} = \Delta\rho_{to}|_{ext} - \Delta\rho_t|_{ext}, \tag{29}$$

i.e.:

$$\Delta\rho_{add} = \rho_0 0.36 \Delta(k^{-1}) p. \tag{30}$$

Hence, from Equations 27 and 30:

$$\Delta\rho_{add} \approx \frac{p}{1 - p} \Delta\rho_t|_{ext}.$$

From experimental data and assuming that the value of p is $p = 1/2$ (for easy calculation), we then deduce:

$$\Delta\rho_t|_{ext} \approx \tfrac{1}{4} \Delta\rho_t.$$

This relation qualitatively agrees with new linear equations [7] from which is derived:

$$\Delta\rho_t = \Delta k^{-1} \left\{ 0.36 \ln \frac{1}{p} + 1.144 \ln \frac{1}{t} \right\},$$

where k is the reduced thickness. Consequently, the original paper of Leonard and Lin [1] cannot be entitled as initially proposed; we suggest the substitution of "thickness-dependent scattering" for "surface scattering". The title of this paper is then justified.

5. Conclusion

Previous experiments on evaporated gold films can be reinterpreted by assuming that electronic scattering occurs both at external film surfaces and at grain boundaries.

Qualitative interpretation is suggested, assuming that the annealing eliminates impurities and mainly modifies the surface scattering.

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