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General expression for the temperature coefficient of resistivity of polycrystalline semi-metal films

D. DESCHACHT, A. BOYER
Laboratoire de Physique Appliquée, Université des Sciences et Techniques du Languedoc, Place E. Bataillon 34060 Montpellier Cedex, France

After calculating the different contributions to the resistivity of a thin film, a general expression for the temperature coefficient of resistivity in a polycrystalline semi-metal film is derived by taking into consideration the influence of internal size effects on the film resistivity in terms of the Mayadas–Shatzkes function, thermal strains and the difference in the thermal expansion coefficients between the film and its substrate. A comparison with experimental data, in the temperature range 77 to 500 K, over grain size range 30 to 200 nm, for antimony films, 200 nm thick, is made. Good agreement has been found between experiments and the theoretical equations we proposed.

1. Introduction

Polycrystalline thin films exhibit three kinds of electronic properties: bulk properties, properties that are induced by the surfaces, and properties that are connected with the crystal arrangement and the size of the aggregates.

For a polycrystalline semi-metal film, the total resistivity, ρ_f, including isotropic background scattering, grain-boundary scattering and external surfaces scattering, can be calculated from Matthiessen's rule [1]:

$$\rho_f = \rho_0 + \rho_D + \rho_s \qquad (1)$$

where ρ_0 is the bulk resistivity, ρ_D the contribution to the resistivity due to structure defects, and ρ_s the contribution to the resistivity due to surfaces.

Calculation of the specularity parameter value, with the Fuchs–Sondheimer theory [2, 3] gives the external surfaces scattering contribution to the resistivity, ρ_s. This, for the grain-boundary scattering, calculated on the assumption that $\rho_g = \rho_f - \rho_s$ is connected to ρ_0 by the relation [4]:

$$\rho_g = \rho_0 F(\alpha)^{-1}, \qquad (2)$$

with

$$F(\alpha) = f(\alpha) + \tfrac{1}{6}\left(\frac{\pi kT}{E_f}\right)^2 \times [6f(\alpha) - 6(1+\alpha)^{-1} + 3\alpha(1+\alpha)^{-2}], \qquad (3)$$

where $f(\alpha)$ is the Mayadas–Shatzkes function [5], k the Boltzmann constant, and E_F the Fermi energy.

In most experiments related to thin films, it is generally assumed that the thermal expansion coefficients of film thickness and grain diameter are negligible with respect to the bulk temperature coefficient of resistivity (TCR) β_0 [6–8]. The validity of this assumption fails when β_0 takes very low values, as happens for semi-metal films. When the film is attached to a substrate, thermal strains are operative if the expansion coefficients of the film and its substrate, χ_f and χ_s, respectively, differ. The difference between the TCR of supported and unsupported films is calculated. The general expression for the TCR, including the effects of thermal expansions of the film thickness of the grain diameter and of the electronic reflection coefficient, R at a grain-boundary, is given starting from the expression of Equation 2.

Few comparisons with experimental data have been made up to now, only for some noble metals, but without variation of the structure (dimension of crystallites). The influence of grain boundaries is all the more important, when the bulk mean free path (mfp) l_0, is comparable to the dimensions of crystallites.

A material such as antimony, which has an mfp

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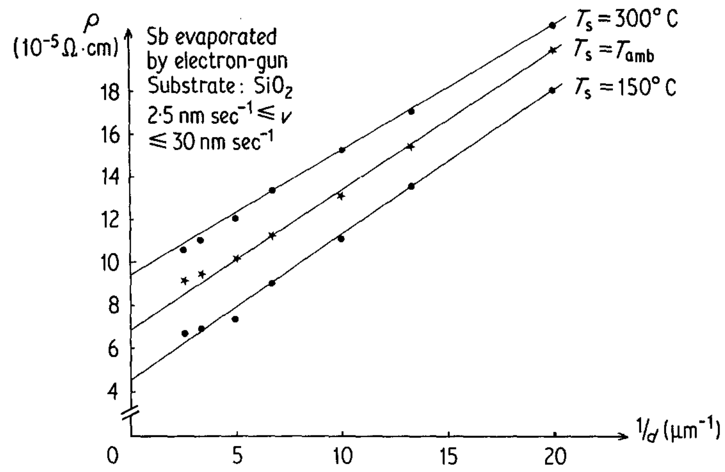

Figure 1 Thickness variation in the resistivity of antimony films deposited at different substrate temperatures.

equal to 230 nm at room temperature [9], is especially appropriate to judge the adequacy of a grain-boundary model.

2. Different contributions to the resistivity

The first analysis of electrical measurement data for thin films was carried out by Fuchs [2] and developed by Sondheimer [3], who proceeded from the solution of the Boltzmann equation.

Generally, to compare experimental data with the theoretical predictions of the Fuchs–Sondheimer model, it is usual to fit data with the limiting form of the resistivity:

$$\rho_f = \rho_\infty \left[1 + \tfrac{3}{8}(1-p)\frac{l_\infty}{d}\right], \tag{4}$$

ρ_∞ and l_∞ are, respectively, the resistivity and the mfp of bulk metal having the same structure as the film, p is the specularity parameter.

We have plotted, for different substrate temperature, the data in the form ρ_f against $1/d$ (Fig. 1) and obtain straight lines. The ordinate intercept determines the infinitely thick film resistivity, ρ_∞, and the slope, $\frac{3}{8}(1-p)\,\rho_\infty l_\infty$. We cannot deduce separately the values of l_∞ and p. We must evaluate l_∞, according to the law $\rho l =$ constant (at room temperature, $\rho_0 = 46\,\mu\Omega$ cm; $l_0 = 230$ nm [9], before calculating the specularity parameter. These results are given in Table I. p does not depend on the structure of the film. Its value shows that the surfaces appear to be largely specular for charge carriers, according to a recent paper of Pariset [10]. ρ_∞ is different and dependent on substrate temperature, T_s.

These results are not surprising, since we have shown that the dimensions of crystallites are different [11]. A general analysis including size effect and internal size effect is needed to describe the total resistivity. Estimating the contribution to the resistivity due to surfaces by:

$$\rho_s = \tfrac{3}{8}(1-p)\frac{\rho_\infty l_\infty}{d} \tag{5}$$

with the determinated value of p ($p = 0.83$) and attributing the difference to defects (grain-boundaries).

For antimony films, deposited by evaporation using an electron gun, in a vacuum of 10^{-7} torr, on a fused quartz substrate at 150° C, with a rate of deposition of $2.5\ \text{nm sec}^{-1} \leqslant v \leqslant 3\ \text{nm sec}^{-1}$, the different contributions to the resistivity at room temperature as a function of thickness are summarized in Table II.

3. Variation of grain-boundary resistivity with temperature

To confirm the validity of the extended Mayadas and Shatzkes model to describe the grain-boundary

TABLE I Results of size effects

T_s (° C)	ρ_∞ ($\mu\Omega$ cm)	l_∞ (nm)	$(1-p)\,l_\infty$ ($10^{-2}\,\mu$m)	p
150	45	235	4	0.83
Room temperature	69	153	2.6	0.83
300	95	111.4	1.6	0.86

TABLE II Different contributions to the resistivity

	d (nm)					
	50	100	150	200	300	400
ρ_f ($\mu\Omega$ cm)	180	112	87	73	69	66
ρ_D ($\mu\Omega$ cm)	120.5	59.3	36.5	23.6	20.8	18.3
ρ_s ($\mu\Omega$ cm)	13.5	6.7	4.5	3.4	2.2	1.7

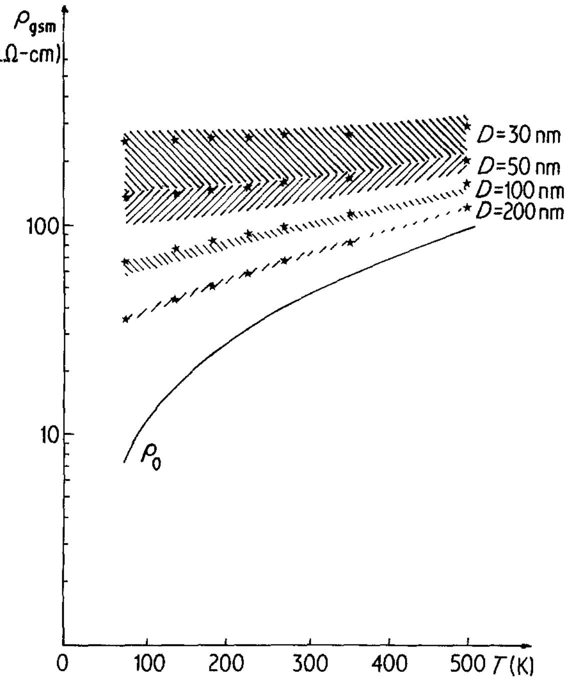

Figure 2 Variation of ρ_g with temperature.

effect, we have chosen to follow the experimental variations of ρ_g with temperature, see Fig. 2, for four samples of antimony, 200 nm thick, with different sized crystallites, whose fabrication conditions are summarized in Table III.

4. General expression for the temperature coefficient of resistivity

The film TCR β_g is defined by the usual relation:

$$\beta_g = \frac{1}{\rho_g}\frac{d\rho_g}{dT}\,. \tag{6}$$

we obtain:

$$\beta_g = \beta_0\left\{1 + \frac{\alpha}{F(\alpha)}\left[\frac{df(\alpha)}{d\alpha}\left(1 + \frac{1}{\beta_0 D}\frac{dD}{dT}\right.\right.\right.$$

$$\left.-\frac{1}{\beta_0 R(1-R)}\frac{dR}{dT}\right) + \frac{1}{6}\left(\frac{\pi kT}{E_F}\right)^2\frac{\alpha}{F(\alpha)}$$

$$\left.\left.\left.\times\frac{dh(\alpha)}{d\alpha}\left(1 + \frac{1}{\beta_0 D}\frac{dD}{dT} - \frac{1}{\beta_0 R(1-R)}\frac{dR}{dT}\right)\right]\right\}$$

$$-\frac{\pi^2 k^2 T}{3E_F^2}\frac{h(\alpha)}{F(\alpha)}\,. \tag{7}$$

We have to consider the thermal expansion coefficient of the grain diameter

$$\chi_D = \frac{1}{D}\frac{dD}{dT};$$

the average grain diameter corresponds to a dimension lying in the direction of the longitudinal electric field. If the width of the grain boundary is significantly smaller than the grain diameter, then:

$$L = nD$$

and

$$\frac{1}{L}\frac{dL}{dT} = \frac{1}{nD}\frac{d(nD)}{dT} = \frac{1}{D}\frac{dD}{dT} = \chi_f. \tag{8}$$

The parameter R is by its definition, a function of energy. It follows that a thermal variation can exist. Experimental data of resistivity gives the value of α, verifying Equation 2, for all temperatures. We can then calculate R and

$$\frac{1}{R(1-R)}\frac{dR}{dT}$$

When the film is attached to a substrate, thermal strains are operative if the expansion coefficients of the film and its substrate, χ_f and χ_s, respectively, differ. To express the total effect of thermal strains on the TCR, it is convenient to introduce the mechanical strain coefficients ϵ of the film: (L = length, w = width, d = thickness)

$$\epsilon_L = \epsilon_W = (1 - p_f)^{-1} \tag{9}$$

p_f being Poisson's ratio

$$\epsilon_d = -\;[2p_f/(1 - p_f)]\,\epsilon \tag{10}$$

TABLE III Conditions of deposition

	Sample			
	1	2	3	4
Method of deposition	Evaporation with electron gun	Evaporation with electron gun	Evaporation with electron gun	R.F. Sputtering
Substrate temperature (° C)	150	250	20	150
Rate of deposition (nm sec^{-1})	30	50	50	2
Annealing temperature (° C)	250	250	250	250
Dimension of crystallites (nm)	200	100	50	30

$$\epsilon = (\chi_s - \chi_f)\Delta T. \qquad (11)$$

The differential variation in resistivity due to thermal strains is then given by:

$$\frac{d\rho_f}{\rho_f} = \gamma_{Lu}\epsilon_L + \gamma_{wu}\epsilon_w, \qquad (12)$$

where γ_{Lu} and γ_{wu} are the longitudinal and transverse strain coefficients of resistivity of unsupported films. The partial thermal variation in $d\rho_f/\rho_f$ which is exclusively due to thermal strains gives the difference between the TCR of supported and unsupported films [12]:

$$\beta_{fs} - \beta_f = \gamma_{Lu}\frac{\partial \epsilon_L}{\partial T} + \gamma_{wu}\frac{\partial \epsilon_w}{\partial T}. \qquad (13)$$

The general expression for the TCR including the effects of thermal expansions of the film thickness, of the grain diameter for a supported semi-metal film is:

$$\beta_{fs} = \beta_0\left\{1 + \frac{\alpha}{F(\alpha)}\left[\frac{df(\alpha)}{d\alpha}\left(1 + \frac{\chi_f}{\beta_0} - \frac{1}{\beta_0 R(1-R)}\frac{dR}{dT}\right) + \frac{1}{6}\left(\frac{\pi k T}{E_f}\right)^2 \frac{dh(\alpha)}{d\alpha}\left(1 + \frac{\chi_f}{\beta_0} - \frac{1}{\beta_0 R(1-R)}\frac{dR}{dT}\right)\right]\right\} - \frac{\pi^2 k^2 T}{3E_F^2}\frac{h(\alpha)}{F(\alpha)} + (\gamma_{Lu} + \gamma_{wu})(\chi_s - \chi_f)(1 - p_f)^{-1}. \qquad (14)$$

5. Comparison with experiments

Experimental data on strain coefficients of antimony films have been reported by Thureau *et al.* [13]. They give:

$$\gamma_{Lu} = 1.2, \quad \gamma_{wu} = 2.3.$$

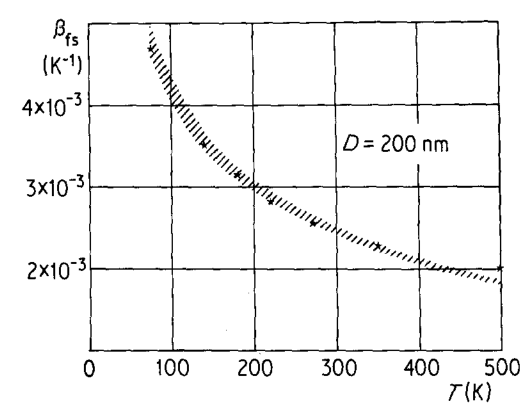

Figure 3 Temperature variation in the TCR of supported antimony films, with crystallites of 200 nm. /// Theoretical variation; ⋆ experimental points.

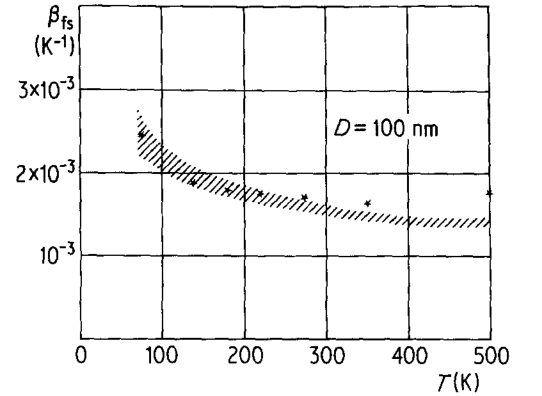

Figure 4 Temperature variation in the TCR of supported antimony films, with crystallites of 100 nm. See Fig. 3 for key.

we have also [14–16]

$$\chi_s = 4 \times 10^{-7}\ \mathrm{K}^{-1}, \quad \chi_f = 10.23 \times 10^{-6}\ \mathrm{K}^{-1},$$

$$p_f = 0.33.$$

We have then

$$\beta_{fs} - \beta_f = 5.14 \times 10^{-5}\ \mathrm{K}^{-1}.$$

To calculate the polycrystalline semi-metal film TCR, we must know β_0. We have only the experimental values of ρ_0 as a function of temperature given by Oktu and Saunders [9]. We have determined an analytical expression for ρ_0, before calculating the theoretical value of β_0.

$$\rho_0 = a + bT + cT^2$$

with $a = 4.9201$, $b = 0.1466$, and $c = 0.74 \times 10^{-4}$. We can now plot the theoretical curves of the temperature coefficient of resistivity of supported polycrystalline antimony films, taking into account the error on D ($D = D_{mean} \pm 10$ nm) and corresponding experimental points (Figs. 3 to 6).

The shape of the theoretical variation is the

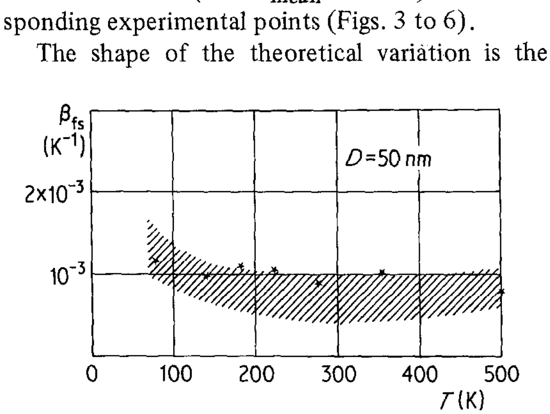

Figure 5 Temperature variation in the TCR of supported antimony films, with crystallites of 50 nm. See Fig. 3 for key.

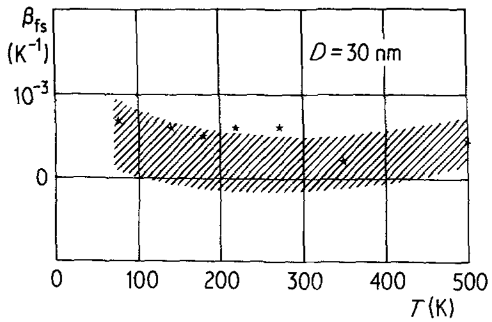

Figure 6 Temperature variation in the TCR of supported antimony films, with crystallites of 30 nm. See Fig. 3 for key.

same as the experimental one. The inaccuracy of experimental determination of β_f (15% if ρ is measured at 5%), shows that reasonable fits are obtained.

6. Conclusion

The thickness dependence of the electrical resistivity of thin antimony has shown that the surfaces appear to be largely specular for charge carriers. To solve the influence of grain boundaries on the total resistivity, a study of the temperature variation is needed. The effect of thermal strains on the TCR is not negligible, because of the very low values of β_g. A general expression for the temperature coefficient of resistivity in a polycrystalline semi-metal film was derived, and good agreement has been found between experimental data, in the temperature range 77 to 500 K over a grain size range 30 to 200 nm, for antimony 200 nm thick. These experimental results show the validity of internal size effect, and the adequacy of the Mayadas grain-boundary model.

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