JOURNAL OF MATERIALS SCIENCE 10 (1975) 1879–1882

Size-dependence of electrical resistivity of vacuum-evaporated antimony films

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Electrical resistivity and temperature coefficient of resistivity of polycrystalline antimony films (400 to 2100 Å) have been measured *in situ.* Coherent and reproducible films are obtained by evaporating antimony from a molybdenum boat onto a heated glass substrate (150° C) at a low deposition rate (2 to 4 Å $\sec^{-1}$). Both expressions for resistivity given by Lucas and Fuchs seem to reproduce the experimental observation quite faithfully indicating partial specular scattering of electrons.

1. Introduction

Size-effect study in semi-metals has drawn attention from various workers in the past, owing to the fact that two distinct types of effect could be observed, namely (1) classical, where the thickness becomes comparable with the electron mean free path, and (2) quantum, where the electron de Broglie wavelength is comparable to the film thickness. The most extensively studied semi-metal is bismuth [1–4], masked with contradictory experimental observations. Surprisingly, antimony has drawn lesser attention as a representative semi-metal in studying the size effect of electrical resistivity. Maki [5] studied the thickness dependence of electrircal resistivity of antimony films deposited in oil- and ion-pumped evaporators and observed that the resistivity was independent of thickness. The resistivity was also found to decrease and to approach a constant value after completion of deposition which is in agreement with the observation of Horikoshi and Tamura [6]. Komnik *et al.* [7, 8] studied the quantum oscillation of conductivity in antimony films, while Harris [9] and Gotzberger [10] limited their observations to the phenomenological study of growth and nucleation of antimony films. In this paper attempts have been made to study classical size effect from our experimental measurements of electrical resistivity and temperature coefficient of resistivity of antimony films (400 to 2100 Å), in the temperature range from 30 to 150° C (film temperature). Conditions to produce coherent and reproducible films have also been determined.

2. Experimental

Antimony (99.999%, Johnson and Mathey, UK) was evaporated from a molybdenum boat onto a glass substrate, which was properly cleaned and degassed [11]. Potentiometric measurements were carried out *in situ* by using the four-probe technique of van der Pauw [12]. The pressure in the evaporation chamber during the entire experiment was maintained at 10^{-6} Torr. The rates of deposition, as measured by a quartz crystal thickness monitor, were 10 to 15 and 2 to 4 Å $\sec^{-1}$. Actual thicknesses were measured by a multiple beam interferometer. The temperature of the film was controlled by an electron on–off controller and the film temperature was measured by a copper–constantan thermocouple placed on the glass substrate. The maximum rise in temperature during deposition was 4 to 6° C.

3. Results and discussion

Peculiarities in the nucleation and growth of antimony films was observed by Komnik [7], Harris [9] and Palatnik *et al.* [13, 14]. When antimony is condensed on to a substrate at room temperature, an amorphous phase is first produced and crystallization begins at thickness above 100 Å which spreads from the thicker to the thinner regions. The effect of crystallization on resistivity

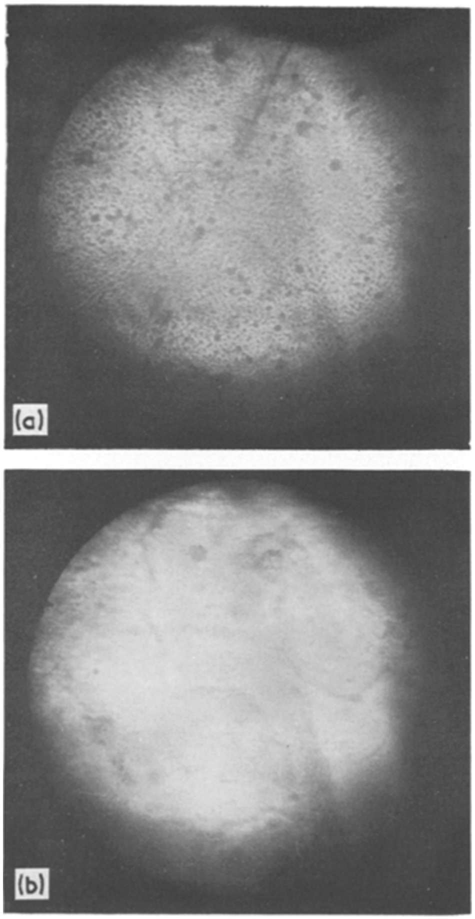

Figure 1 Photomicrographs of antimony film (1000 Å) (a) deposited at room temperature and etched down to ~ 400 Å (b) deposited at 150° C at low deposition rate (2 to 4 Å $\sec^{-1}$) and etched down to ~ 400 Å.

was studied by Harris [9] and Horikoshi and Tamura [6]. They observed that the resistance of the film decreases after deposition and approaches a certain value. This is in accordance with our observations of when the films (400 to 2600 Å) are deposited at a rate of 10 to 15 Å $\sec^{-1}$ on to the glass substrate at room temperature. The films thus produced show a negative TCR even on annealing at 150° C for 2h. Definite patterns could be observed [9] on the film surfaces even with the unaided eye. Photomicrographs (Fig. 1a) taken of an antimony film (1000 Å) etched [15] to 400 Å clearly show some sort of cracks possibly due to localized heating during nucleation. Owing to the low mobility of the atoms with respect to the substrate at room temperature, the incoming atoms just adhere to the sites of impingment, and as the film thickens the surface becomes smoother, which could be easily appreciated from the patterns observed at the two surfaces of the film (i.e. top and glass–film interface). Annealing at 150° C does not impart sufficient mobility to the adatoms to revert to a smooth polycrystalline texture and the films do not show a reversible character when subjected to thermal cycling. With the increase in temperature the pattern on the film surfaces tends to smooth out, resulting in a decrease in resistance and a negative TCR. However, if the film is deposited at a low rate (2 to 4 Å $\sec^{-1}$) on the substrate at a temperature [16] 150° C ($\sim \frac{1}{3} T_m$, with due consideration to the depression of melting point, T_m, with thickness [17, 19] no such patterns are visible as seen from Fig. 1b (1000 Å film etched down to 400 Å) and the film behaves bulk-like with positive TCR (Fig. 2). The $\frac{1}{3} T_m$ limit is essentially that below which the adatoms do not have sufficient mobility to produce an ordered structure. The films thus produced no longer show a fall in resistivity after deposition as observed by previous workers [6. 9]. Recently, Bharti [20] also observed that the antimony films deposited at a substrate temperature of 150° C or above, show a homogeneous character. The size of the spots decreases with rise in substrate temperature and completely disappear at about 150° C.

The experimental observations reported here (Fig. 2) are analysed by using the equations [21, 22],

$$\frac{\rho_0}{\rho} = 1 + \frac{3}{8\gamma}(1-p); \quad \gamma > 1 \tag{1}$$

and

$$\frac{\alpha}{\alpha_0} = 1 - \frac{3}{8\gamma}(1-p); \quad \gamma > 1 \tag{2}$$

where ρ is the resistivity of the film, ρ_0 is the bulk resistivity, γ is the ratio of the film thickness, t to the electron mean free path, l, p is the specularity parameter and α, α_0 are the TCR of the film and bulk metal respectively.

Another useful equation, assuming different specularity parameters p and q for the two surfaces of the film, was given by Lucas [23] as

$$\frac{\rho_0}{\rho} = 1 - \frac{3}{4\gamma}\int_1^\infty \left(\frac{1}{a^3} - \frac{1}{a^5}\right) \frac{1-e^{-\gamma a}}{1-pqe^{-2\gamma a}} \times [2-p-q-(p+q-2pq)e^{-\gamma a}]\, da \tag{3}$$

where $1/a$ is equal to $\cos\theta$ (the electron mean free path makes an angle θ with the normal to the film).

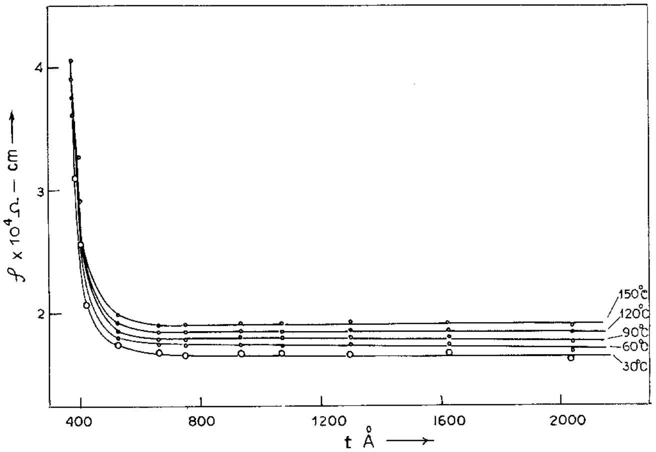

Figure 2 Plot of resistivity of antimony films (substrate temperature during deposition 150° C) versus thickness (t) at temperatures 30 60, 90 120 and 150° C.

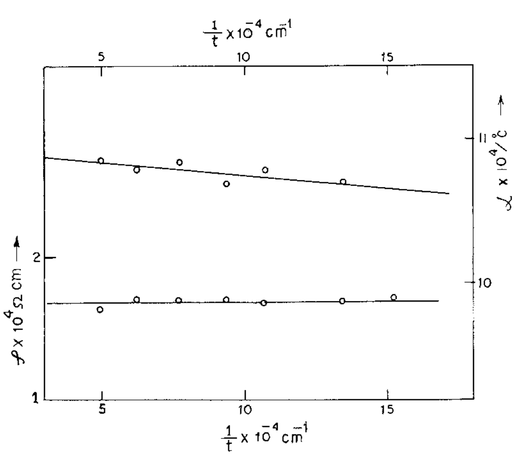

Figure 3 Dependence of resistivity and TCR on reciprocal thickness. Solid line indicates least-square fit. o – experimental points.

Equations 1 and 2 indicate the linear dependence of ρ and α on $1/t$. The values of ρ_0 and α_0 as obtained from the incepts of the plots of ρ versus $1/t$ and α versus $1/t$ (Fig. 3) are 1.64×10^{-4} Ωcm and $0.0011\,^\circ C^{-1}$, respectively. The values of $l(1-p)$ obtained from the slopes of the curves ρ versus $1/t$ and α versus $1/t$ are 64 and 53.2 Å, respectively, which are in good agreement with each other.

To show the degree of agreement between theory and experiment throughout the entire range of thicknesses, experimental ρ/ρ_α versus γ were plotted (Fig. 4) along with the equations 1 and 3. The approximate value of the mean free path as determined from the plot of ρt versus t (Fig. 5) is 79 Å. It is quite apparent from Fig. 4 that both the theories given by Lucas with $p = 0.25$, $q = 0.25$ and Fuchs with $p = 0.25$ reproduce the experimental observations quite faithfully,

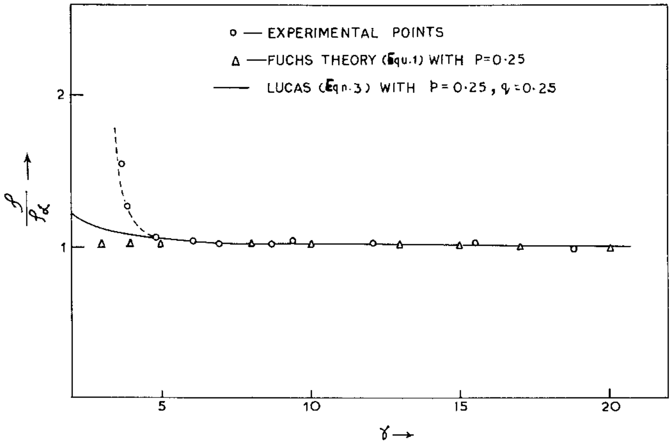

Figure 4 Theoretical and experimental variation of ρ/ρ_α with normalized thickness $\gamma (= t/l)$.

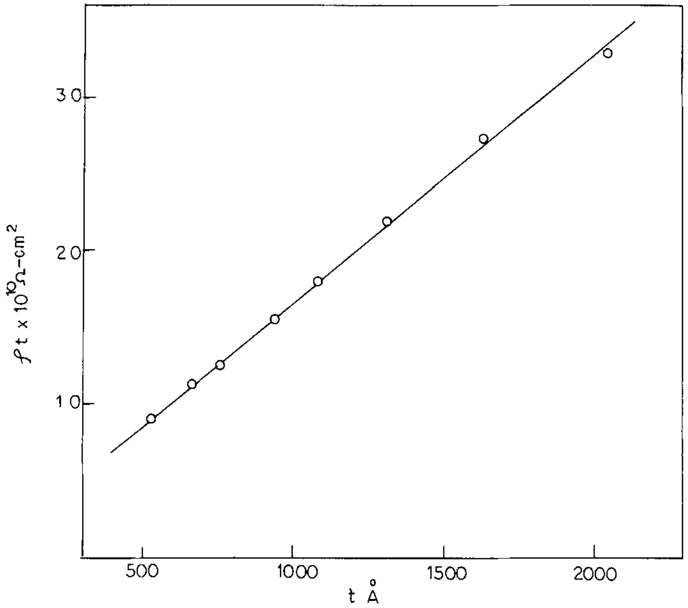

Figure 5 Plot of ρt against t. ○ – Experimental points; —— least-square fit curve.

thus indicating partial specular scattering in antimony films. For discontinuous films ($\gamma < 5$) the disagreement is quite pronounced because of dominant inter-island (gap) resistance and, as such, Fuchs and Lucas' theory cannot be applied to these films.

Acknowledgement

The authors wish to thank Professor A. K. Barua for his interest in this work.

References

1. YU. F. OGRIN, V. N. LUTSKII and M. I. ELINSON, *Zh. Eksperim. i. Teor. Fiz. Pisma V Redaktsiym* **3** (1966) 114.
2. M. INOUE and H. YAGI, *Mem. Fac. Eng. Fukui Univ.* **20** (1972) 123.
3. N. GARCIA, Y. H. KAO and M. STRONGIN, *Phys. Rev.* **B5** (1972) 2029.
4. P. SEN and ARUN K. PAL, to be published.
5. Y. MAKI, *Jap. J. Appl. Phys.* **12** (1973) 146.
6. H. HORIKOSHI and N. TAMURA, *ibid* **2** (1963) 328.
7. YU. F. KONMIK and E. I. BUKHSHTAB, *JETP Letters* **6** (1967) 58.
8. *Idem, ibid* **8** (1968) 4.
9. L. HARRIS, *J. Appl. Phys.* **17** (1946) 757.
10. A. GOTZBERGER, *Z. Phys.* **142** (1955) 739.
11. ARUN K. PAL, U. DE and P. SEN, *Phys. Stat. Sol.* (a) **27** (1975) K1.
12. L. J. VAN DER PAUW, *Phillips Res. Rept.* **13** (1958) 1.
13. L. S. PALATNIK and V. M. KOSEVICH, *Kristallografiya* **3** (1958) 709.
14. *Idem, Sov. Phys. Crystallogr.* **3** (1959) 716.
15. G. L. KEHL, "The principles of Metallographic Laboratory Practice", (McGraw Hill, New York, 1943).
16. L. S. PALATNIK and YU. F. KOMNIK, *Sov. Phys. Dokl., Eng. Trans.* **5** (1960) 1072.
17. M. TAKAGI, *J. Phys. Soc. Japan* **9** (1954) 359.
18. L. S. PALATNIK and B. T. BOIKO, *Phys. Met. Metallog.* **11** (1961) 119.
19. N. T. GLADKICH, R. NEIDERMAYER and K. SPIEGEL, *Phys. Stat. Sol.* **15** (1966) 181.
20. P. L. BHARTI, *Thin Solid Films* **23** (1974) 859.
21. E. H. SONDHEIMER, *Adv. Phys.* **1** (1952) 1.
22. R. G. CHAMBERS, *Proc. Roy. Soc. Lond. A* **202** (1950) 378.
23. M. S. P. LUCAS, *J. Appl. Phys.* **36** (1965) 1632.

Received 21 March and accepted 23 May 1975.