Resistivity and temperature coefficient of resistivity of tin films

ARUN K. PAL, PARAMITA SEN
Department of General Physics and X-rays, Indian Association for the Cultivation of Science, Calcutta 700032, India

The electrical resistivity and the temperature coefficient of resistivity of tin films (490 to 5000 Å) deposited onto glass substrates at room temperature (30° C) were measured *in situ* in the temperature range 30 to 150° C. It is concluded that Mayadas–Shatzkes' theory reproduces the experimental observations more faithfully than Fuchs–Sondheimer's theory.

1. Introduction

Variation of electrical resistivity of polyvalent metal films with thickness at different temperatures has been the subject of many investigations. Fuchs' theory has generally been applied to analyse the experimental observations resulting in contradictions among the various findings [1]. To derive a meaningful conclusion from the experimental observations one must ensure the coherency of the films studied. Anomalous data are always associated with anomalous conditions in the structure of the films which depend very much on the deposition conditions. So in order to derive an unambiguous conclusion, experiments must be carried out *in situ* under extremely controlled evaporation conditions and with precise determination of the thicknesses of the films.

In practice the structure of a thin film does not resemble a single crystal plane parallel slab but rather consists of an array of randomly oriented polycrystallites. The structure of evaporated films is often of a columnar type, in which the individual crystals grow roughly vertically from the substrate to the upper surface of the film, so the only boundaries which need to be considered are those lying parallel or perpendicular to the applied field. An additional deviation from Mattiessen's rule [2], due to scattering at the boundaries of the crystal, should be taken into account where the linear dimension of the crystallites in the plane of the film is of the same order as the electron mean free path. Mayadas and Shatzkes (M–S) [3] evaluated the problem in a simplified way to allow a quantitative description of grain-boundary scattering in polycrystalline films, which more or less faithfully reproduced the experimental observations on aluminium [3], tungsten [4], cobalt [5, 6], bismuth [7] and indium [8] films.

Earlier measurements on tin films were made by Niebuhr [9], Learn and Spriggs [10] and Andrew [11]. Niebuhr reported his measurements of the thickness dependence of the resistivity of tin films deposited on quartz at temperatures between 20 and 200 K, and concluded that the films deposited at low temperatures have $p > 0$ (p is the specularity parameter). Learn and Spriggs' measurements concern mainly with the effect of deposition condition on the electrical conduction of films. They observed that the scattering is more specular for films that are much thicker than the mean free path. Specularity is greater for lower deposition rates and higher substrate temperatures. A study on tin foils at 3.8 K by Andrew suggested satisfactory agreement with the theory of diffuse scattering.

In the present paper, we have reported *in situ* measurement of resistivity and temperature coefficient of resistivity (TCR) of tin films (490 to 5000 Å) at 30 to 150° C (Fig. 1).

2. Experimental method

The substrate was thoroughly cleaned and mounted on a holder, whose temperature could be

© 1977 Chapman and Hall Ltd. Printed in Great Britain.

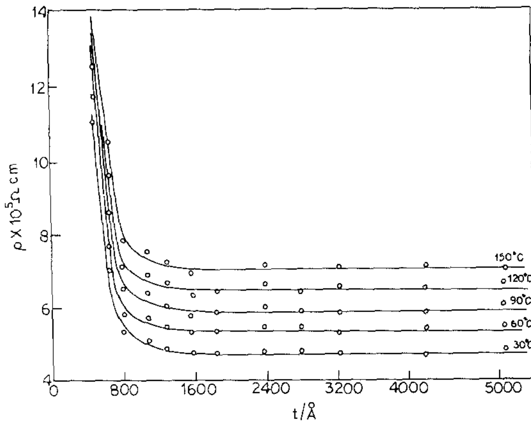


Figure 1 Thickness dependence of resistivity of tin films at temperatures 30, 60, 90, 120 and 150° C.

varied from liquid nitrogen temperature (77 K) to 200° C [12]. The electrical leads for potentiometric measurements were connected to the substrate using zinc–tin solder (15% Zn, 85% Sn). Prior to deposition, the system was ion cleaned and baked at 150° C for 2 h at a pressure of 10^{-6} Torr for complete degassing. The substrate was then cooled to room temperature and pure tin (99.999% Johnson, Matthey & Co UK) was deposited at an average rate of 7 to 8 Å sec^{-1} from a molybdenum boat onto a cleaned glass substrate kept at room temperature.

The measurements of resistance were carried out potentiometrically by the four probe technique of van der Pauw [13], and the film was removed from the evaporation chamber and the thickness determined to an accuracy of 30 Å with a multiple beam interferometer. This procedure was repeated for each of the films studied. In order to obtain coherent films the evaporation conditions (temperature, pressure, deposition rates, etc.) were rigorously controlled throughout the entire course of measurements. Sample checking of the structure of the films studied was done by transmission electron microscopy and no significant deviation from general structure behaviour was observed.

The rate of deposition and the thickness were controlled by a quartz crystal thickness monitor. The distance of the substrate from the source was 35 cm and the temperature rise of the substrate during film deposition, as measured by a copper–constantan thermocouple, was at most 2 to 4° C. The temperature was controlled electronically (to ± 0.5° C).

3. Results and discussion

Using the Boltzman transport equation and assuming a spherical Fermi surface, an isotropic electron mean free path and partial specular scattering of electrons from the surface of a film, Fuchs [14] obtained for the resistivity of bulk to that of films as

$$\frac{\rho}{\rho_0} = \left\{1 - \frac{3(1-p)}{2\gamma} \int_1^{\infty} (a^{-3} - a^{-5}) \frac{[1-\exp(-\gamma a)]}{[1-p\exp(-\gamma a)]} \cdot \mathrm{d}a\right\}^{-1} = \phi(p,\gamma) \quad (1)$$

where ρ_0 is the bulk resistivity, ρ is the resistivity of the film, γ is the ratio of the film thickness, t, to the electron mean free path l, p is the specularity parameter and a is equal to $1/\cos\theta$ (the electron mean free path makes an angle θ with the normal to the film). A convenient form of the above expression for the resistivity has been given by Chambers [15] and Sondheimer [16]. The limiting forms of resistivity and TCR are given by,

$$\frac{\rho}{\rho_0} = 1 + \frac{3}{8}\frac{(1-p)}{\gamma}; \quad \gamma > 1 \quad (2)$$

and

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

where α and α_0 are the TCR of the film and bulk respectively. Fig. 2 shows the linear dependence of the experimental values of $(\rho)_{30°\,C}$ and $(\alpha)_{30°\,C}$ on the reciprocal thickness as indicated by the

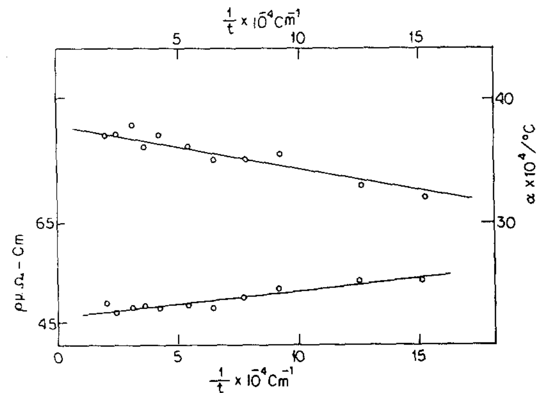


Figure 2 Dependence of resistivity and TCR on reciprocal thickness; ⊙ experimental points, — least-square fit curve.

expression given in Equations 2 and 3. The values of ρ_0 (30° C) and α_0 (30° C) obtained from the intercepts of the plots of ρ versus t^{-1} and α versus t^{-1} are 45.8 $\mu\Omega$ cm and 0.003794 $(°C)^{-1}$, respectively. The values of $l(1-p)$ obtained from the slope of the above plots are 315 and 270 Å respectively.

The value of ρ_0 obtained here is somewhat larger than those obtained by other workers and this discrepancy could be attributed to the fact that the ρ_0 obtained by the above procedure is not the same as for bulk metal, since the method of preparation will almost certainly produce a different grain size, different mechanical stresses etc. Thus the ρ_0 value will contain an additional term ρ_p representing the contribution to the resistivity caused by the method of preparation. This total value, $\rho_0 + \rho_p$, is generally obtained experimentally (from the plot of ρ versus t^{-1}) if the films are made sufficiently thick. The same argument applies to the use of Fig. 2 (the plot of α versus t^{-1}). α_0 for a thick film will be given by

$$\operatorname*{Lt}_{t \to \infty} \alpha = \frac{1}{\rho_0 + \rho_p} \cdot \frac{d\rho_0}{dT}$$

This is why the values of $l(1-p)$ obtained from the plots of ρ versus t^{-1} and α versus t^{-1} differ from each other. The high bulk resistivity value of thick films obtained experimentally may come from the fact that the films are not really planar. In order to show the agreement between the experimental observation and the theory (Equation 1) we have plotted ρ/ρ_0 (experimental values) against $\gamma(t/l)$ together with the calculated ones (Fig. 3). Clearly the expression given in Equation 1 with $p = 0.25$ reproduces the experimental observation only in the thick region (beyond 800 Å). The value of l_0 obtained from the thick films (> 800 Å) is 390 Å, which compares favourably with value of $l_0 = 550$ Å at 200 K obtained by Niebuhr [8].

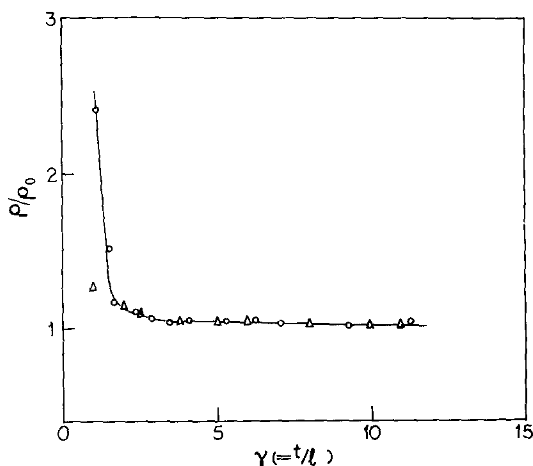


Figure 3 Plot of ρ/ρ_0 versus γ; ⊙ experimental points, △ approximate relation given by Equation 1 with $p = 0.25$.

The properties of thin films of low melting-point metals prepared by vacuum deposition are extremely sensitive to substrate conditions. In general, low-melting point films prepared by evaporation on room temperature glass substrate are likely to be highly non-uniform up to the range of appreciable thickness and the resistivity of such films is modified by the granular effects in the film. Indeed the sharp rise in the resistivity (Fig. 1) below approximately 800 Å of the tin films studied here indicate that the films are highly non-uniform in that thickness range. Fig. 4a and b are electron micrographs of tin films showing the non-uniform growth in these films. Fig. 4c represents the electron diffraction pattern of tin film which shows the polycrystalline nature of the films studied.

Mayadas and Shatzkes [2] initiated the idea of grain-boundary scattering in polycrystalline films and evaluated the problem by considering the resistivity caused by scattering of conduction electrons by grain boundaries together with the normal background scattering caused by defects and phonons. Mayadas and Shatzkes' expression for film resistivity can be expressed as,

$$\frac{\rho}{\rho_0} = \frac{\phi(p, \gamma_i)}{f(\alpha')} \tag{4}$$

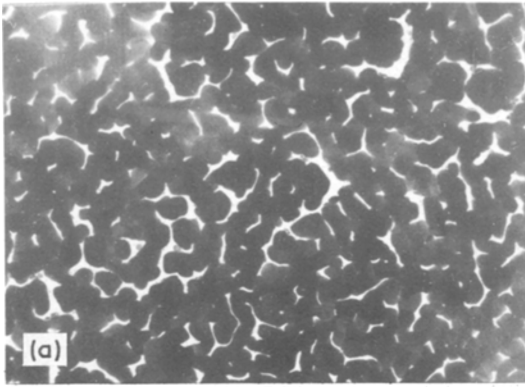
where

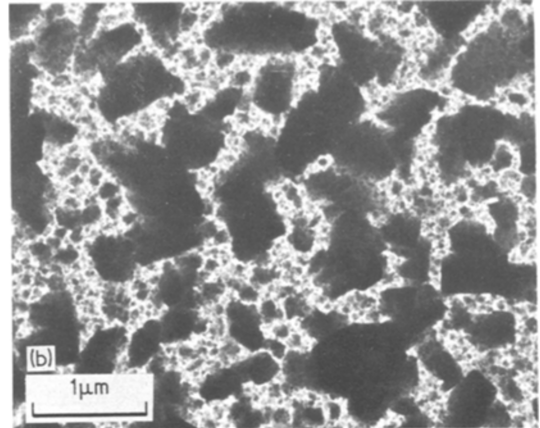
$$f(\alpha') = 3\left[\frac{1}{3} - \frac{\alpha'}{2} + \alpha'^2 - \alpha'^3 \ln\left(1 + \frac{1}{\alpha'}\right)\right]$$

$$\alpha' \text{ being equal to } \frac{l_0 R}{D(1-R)}$$

$\phi(p, \gamma_i)$ is given by Equation 1 in which γ is replaced by $\gamma_i = \gamma/[f(\alpha')]$; D is the grain size and R is the coefficient of reflection at the grain boundary.

Comparison with the M-S theory is generally done by considering the grain size to be equal to the thickness, which should be true up to a certain thickness but not indefinitely, since the grain size becomes nearly constant as the film thickens.





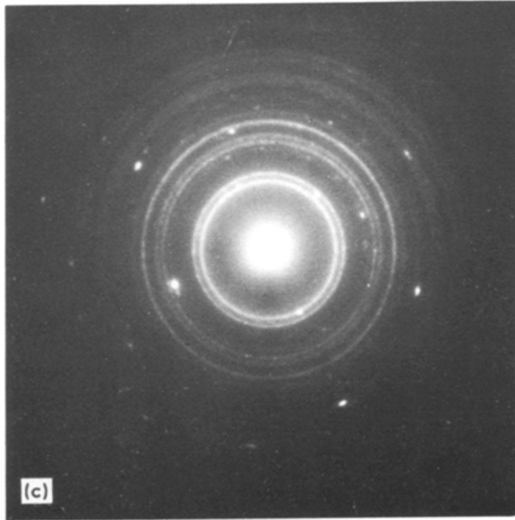


Figure 4 Electron micrographs of tin films (a) 600 Å (X 20 000), (b) 1500 Å (X 33 480), and (c) electron diffraction of tin film (1500 Å).

A curve corresponding to $p = 0$ and $R = 0.428$ using grain size equal to thickness is shown in curve 2 of Fig. 5. The agreement between the experiment and M-S theory is good up to a certain thickness (~ 860 Å) and then M-S curve substantially deviates from the experimental graph. However if we assume the grain size to be constant beyond ~ 860 Å (nearly the point at which curve 2 separates from the experimental curve), the M-S curve (curve 1, Fig. 5) reproduces the experimental data faithfully in the entire range of measurement. This clearly indicates that in the early stages of film growth, individual grains grow in a columnar fashion from the substrate to the upper surface of the film. The tin grains grow with thickness but not indefinitely, since after attaining a thickness ~ 860 Å, the grain size becomes nearly constant as the film thickens.

In order to study the effect of annealing, films were annealed at 150° C for 2 h at a system pressure of 2×10^{-6} Torr. It was observed that the films thus annealed, and consequently subjected to thermal cycling, show reversible behaviour with temperature. Also films deposited at an elevated substrate temperature (150° C) have the same

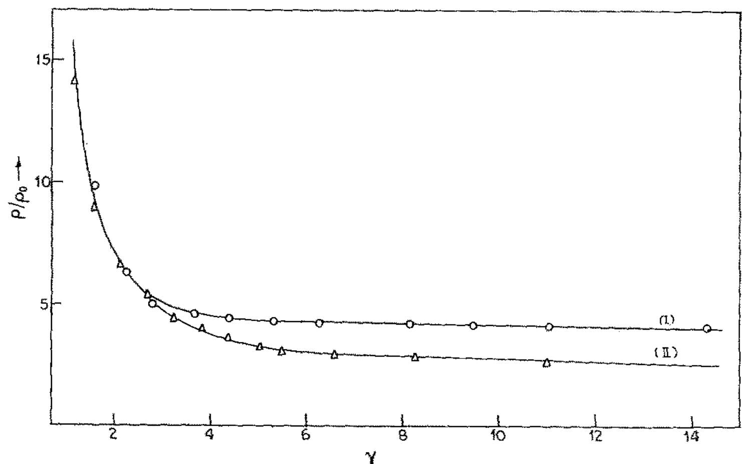


Figure 5 Comparison of experimental curve (ρ/ρ_0 versus γ) with that obtained from the M–S theory: ⊙ experimental points, — Curve I – M–S curve ($D = 860$ Å, $R = 0.428$, $p = 0$) assuming constant grain size after 860 Å thickness, △ Curve II – M–S curve ($R = 0.428$, $p = 0$) assuming grain size equal to thickness.

resistivity as those measured for films deposited at room temperature.

Acknowledgements

We wish to thank Professor A.K. Barua for his keen interest in this problem and to acknowledge the co-operation of Dr S. K. Sharma, National Physical Laboratory, New Delhi, for his kind assistance in electron microscopy work.

References

1. D. C. LARSON, "Physics of Thin Films", Vol. 6 (Academic Press, New York, 1971) p. 81.
2. D. S. CAMPBELL and A. R. MORLEY, "Reports on Progress in Physics" Vol. 34, Part I, edited by J. M. Ziman, (1971) p. 283.
3. A. F. MAYADAS and M. SHATZKES, *Phys. Rev.* **B1** (1970) 1382.
4. R. C. SUN, T. C. TISONE and P. D. CRUZEN, *J. Appl. Phys.* **44** (1973) 1009.
5. E. E. MOLA, J. B. BORRAJO and J. M. HERAS, *Surf. Sci.* **34** (1973) 561.
6. A. K. PAL, S. CHAUDHURI and A. K. BARUA, *J. Phys. D. Appl. Phys.* 9 (1976) 2261.
7. A. V. JOGLEKAR, R. N. KAREKAR and J. SATHIANANDAN, *J. Vac. Sci. Technol* **11** (1974) 528.
8. A. K. PAL and S. CHOWDHURI, *J. Mater. Sci.* **11** (1976) 872.
9. J. NIEBUHR, *Z. Physik.* **132** (1952) 468.
10. A. J. LEARN and S. SPRIGGS, *J. Appl. Phys.* **34** (1963) 3012.
11. E. R. ANDREW, *Phys. Soc. London* **A62** (1949) 77.
12. A. K. PAL, P. SEN and A. K. BARUA, *Thin Solid Films* **25** (1975) 825.
13. L. J. VAN DER PAUW, *Philips Res. Rept.* **13** (1952) 1.
14. K. FUCHS, *Proc. Cambridge Phil. Soc.* **34** (1938) 100.
15. R. G. CHAMBERS, *Proc. Roy. Soc.* **A202** (1950) 378.
16. E. H. SONDHEIMER, *Adv. in Phys.* **1** (1952) 1.

Received 21 June and accepted 5 November 1976.