Composition dependence of electrical properties of Al–Sb thin films

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Abstract. Thin films of Al–Sb of varying compositions and thickness have been formed on glass substrates employing three-temperature method. Electrical resistivity (ρ) and activation energy (ΔE) have been studied as a function of composition, thickness (d) and temperature of the film. Films of Al–Sb system with aluminium < 50 at.%, ~ 50 at.% and > 50 at.% exhibit metallic, semiconducting and metallic to semiconducting behaviours respectively. Activation energy (ΔE) of semiconducting films found to vary inversely with thickness, is attributed to combined effects of change in barrier height due to the size of grains and stoichiometry in the films.

Keywords. Three-temperature method; electrical resistivity; temperature coefficient of resistance.

1. Introduction

The semiconducting compound aluminium antimonide (Al–Sb) with energy gap of 1·62 eV, is potentially a high efficiency solar cell material (Rittner 1954). Al–Sb has rapidly growing interest in optoelectronics (Lefebvre et al 1987; Raisin et al 1987). Several workers studied electrical, thermal, optical and structural properties of stoichiometric AlSb in bulk (Yee et al 1977; Mattes 1984; Matsuo and Soma 1986, 1987) as well as in thin film states (Francombe et al 1976; Patel and Biradar 1983; Upadhyay et al 1986).

From the survey of the literature it can be seen that almost no attempt has been made to study the electrical properties of Al–Sb system over the entire range of compositions in the thin film state. Therefore, it was thought interesting to investigate electrical transport properties of Al–Sb films of varying compositions and thickness prepared by using three-temperature method (George and Palson 1985; Nikam and Pawar 1990, 1991a, b; Nikam and Aher 1996).

2. Experimental

Thin films of Al–Sb were prepared by three-temperature method. Aluminium (99·999%) was evaporated directly from preflashed conical basket of tungsten wire and antimony (99·999%) from basket of nichrome wire. The evaporation was done at room temperature in an IBPTORR-120 vacuum unit, under a vacuum of the order of 10^{-5} torr. The flux rate from each source could be easily adjusted by controlling the current through each filament. Both elements were simultaneously evaporated. After adjusting the flux rates from the two sources by varying the source current, films of varying compositions and different thicknesses were obtained. The films were annealed at 150°C for 6 h in vacuum of the order of 10^{-5} torr.

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The methods employed to determine the composition, thickness and uniformity of the film were similar to those reported earlier (Nikam and Pawar 1990; Nikam and Aher 1993, 1994). The composition of the films was determined by employing absorption spectroscopy at 550 mμ (Charlot 1964).

In the present work the thin films of aluminium antimonide are used. The concentration of antimony (Sb) was determined in Al–Sb films colorimetrically by oxidizing trivalent Sb to pentavalent Sb (Charlot 1964).

The Al–Sb films after measurements are weighed accurately, and dissolved in 5 ml concentrated H_2SO_4 and diluted to 100 ml with distilled water to make 3N solution. This acts as stock solution. This stock solution contains trivalent Sb. This trivalent antimony is oxidized to pentavalent by the procedure described by Charlot (1964). The amount of Sb(V) is then quantitatively estimated colorimetrically by using optical filter of 550 mμ wavelength.

To check the uniformity of the film as regards its composition, different portions of the film were subjected to absorption spectroscopic analysis. The analysis confirmed that the films were of uniform composition and thickness.

Film thickness (*d*) was measured using multiple beam interferometry and also by gravimetric method (Nikam and Aher 1993, 1994),

$$d = \frac{M}{g \times A} \text{cm},$$
(1)

where *A* is surface area of the film, *M*, the mass of the film and *g*, the density of the film material expressed as

$$g = x_1 g_1 + x_2 g_2,$$
(2)

where g_1, g_2 and x_1, x_2 are densities and atomic fractions of Al and Sb elements respectively. Films prepared for electrical measurements had composition ranging between $Al_{10}Sb_{90}$ and $Al_{85}Sb_{15}$ and thickness between 1400 and 10,000 Å.

Electrical resistance of the films was measured at various temperatures using two-probe technique (Pandit *et al* 1991) in a vacuum of the order of 10^{-5} torr by using pressure contacts (Uen *et al* 1988; Nikam and Pawar 1990; Nikam and Aher 1993). This avoided the contamination of films.

3. Results and discussion

Figures 1–3 show the variation of resistance with temperature for the films deposited on a glass substrate at room temperature containing Al < 50 at.%, Al ~ 50 at.% and Al > 50 at.%, respectively. The films having Al concentration less than 50 at. % show positive TCR suggesting metallic behaviour (figure 1) and the films having concentration ~ 50 at.% of Al show negative TCR indicating semiconducting behaviour (figure 2). On the contrary, those with Al concentration > 50 at.% show positive and then negative TCR, implying metallic to semiconducting transition with temperature (figure 3).

For Al–Sb deposits the room temperature resistivity is considerably higher (~ $10^5 \, \Omega$ cm) irrespective of composition of the film. Francombe *et al* (1976) also reported the same order of ρ for stoichiometric AlSb thin films. The variation of ρ with
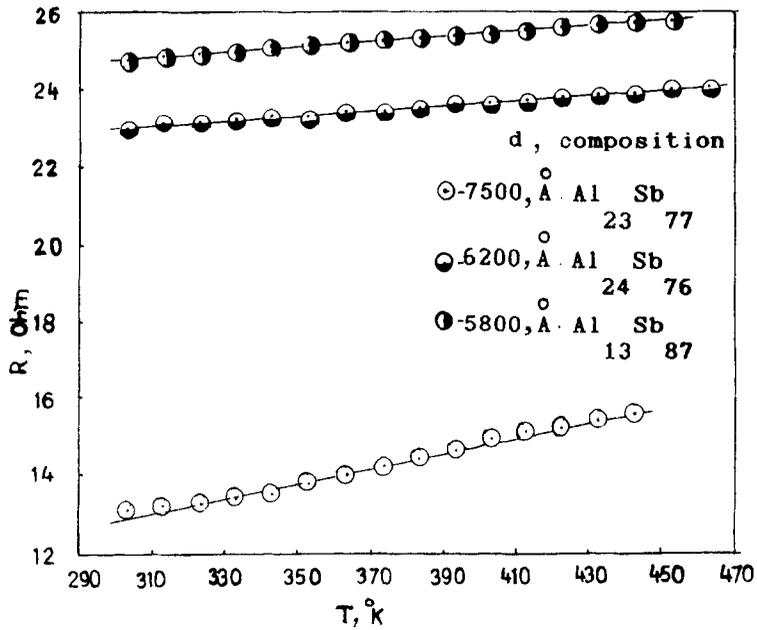
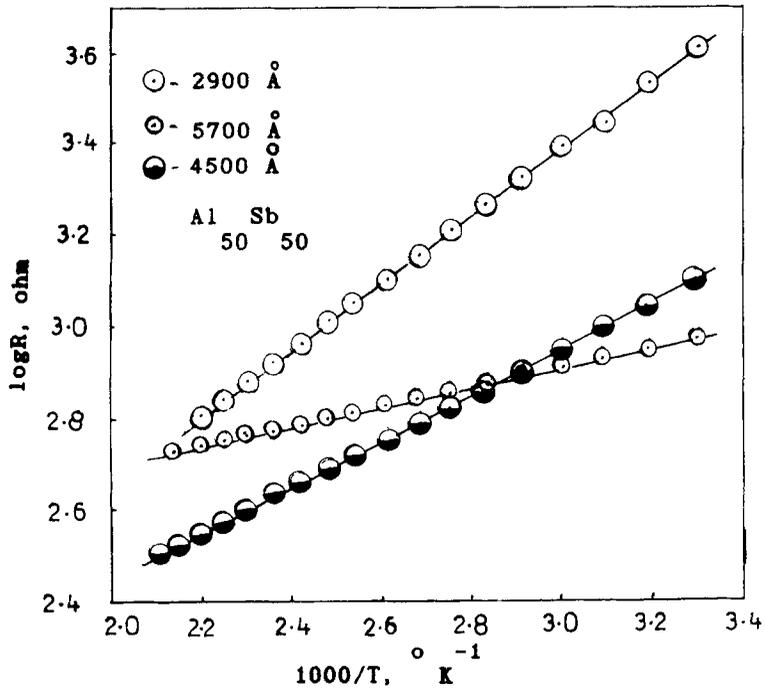**Figure 1.** Variation of resistance with temperature of Al–Sb films containing Al < 50 at.%.

Figure 2. Plot of log R vs $1/T$ of stoichiometric AlSb films.

thickness of the Al–Sb films deposited at room temperature with Al ⩽ 50 at.% and Al > 50 at.% is shown in figure 4. In all cases ρ decreases with increase of film thickness. In order to study the size effect and grain boundary scattering effect on electrical
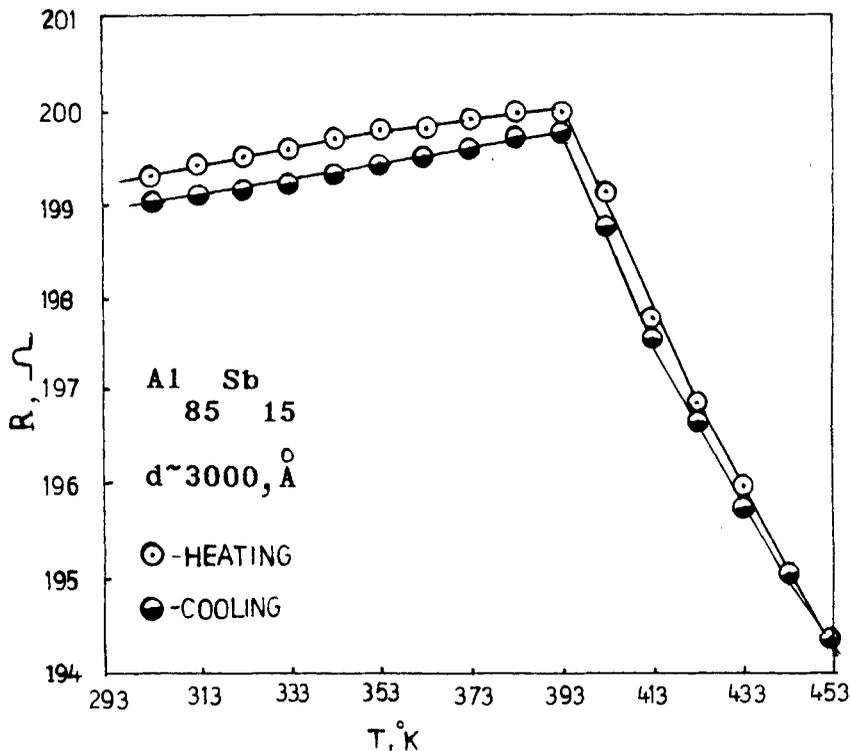
Figure 3. Variation of resistance with temperature of Al–Sb films containing Al > 50 at.%.
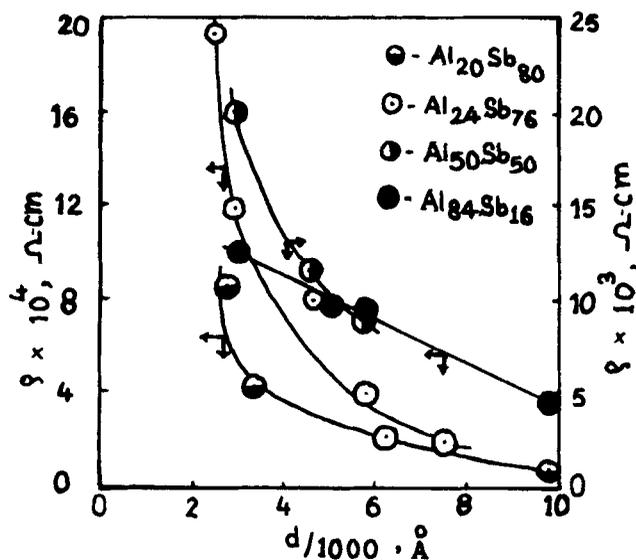

Figure 4. Variation of room temperature resistivity (ρ) with thickness (d) for Al–Sb films.

resistivity of metallic Al–Sb films, the non-linear plot of ρd vs d was obtained. Therefore ρ of metallic Al–Sb films can not be related to Fuch–Sondheimer size effect and Mayadas–Shatzkes grain boundary scattering effect. In addition to film surface and

lattice impurities, the enormous number of frozen-in-structural defects in films, will also scatter the conduction electrons. According to Matheissen rule, various electron scatterings (and hence resistivity contribution) are additive, provided that the lattice scattering predominates. We can therefore write,

$$\rho_F = \rho_B + \rho_S + \rho_I,\tag{3}$$

where the contributions ρ_B, ρ_S and ρ_I are due to the ideal lattice, surface scattering and imperfections including impurities respectively. Depending on deposition process, the contribution ρ_I can be quite significant as compared with ρ_B and ρ_S. Since frozen-in-imperfections vary with growth changes in film, ρ_I is expressed to show thickness dependence. If a film is susceptible to oxidation and contamination, further thickness dependent effect results. This situation complicates the analysis and interpretation of the film resistivity versus thickness data. It needs to be emphasized that Fuch theory is applicable only to the thickness dependence arising out of the limitation of the free path of electron by the geometrical boundaries. In the present investigation the resistivity contribution is mostly due to imperfections including impurities such as aluminium oxide (Kushida *et al* 1993).

It is observed that, ρ increases with increase of Al concentration and reaches maximum at ~ 50 at.% of Al (figure 5). The maximum in the curve ρ versus composition of the films corresponds to the formation of semiconducting stoichiometric AlSb phase. After this maxima, ρ decreases with further addition of Al. This decrease in ρ for the films containing excess of Al (Al > 50 at.%) is attributed to the metallic behaviour as can be seen from figure 3.

Variation of activation energy (ΔE) with thickness (d) for stoichiometric semiconducting AlSb films is given in table 1. It is seen from the table that ΔE decreases with increase of film thickness. Variation of activation energy with thickness of the films can be due to any one or combined effects of the following causes (Das and Karunakaran 1989). (i) The change in the barrier height due to the size of the grains in a polycrystalline film; (ii) a large density of dislocations; (iii) quantum size effect; and (iv) change in stoichiometry.
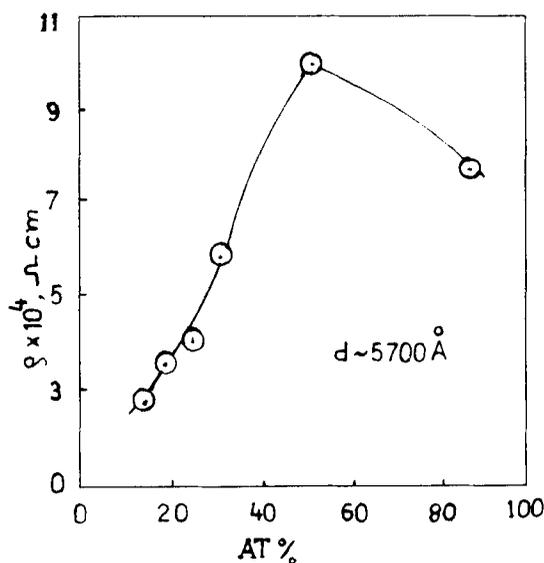
Figure 5. Variation of room temperature resistivity (ρ) with at.% of Al in Al–Sb films.

Table 1.   Variation of activation energy (ΔE) with thickness (d) for stoichiometric AlSb films.

$d(\text{Å})$	$\Delta E(\text{eV})$
2900	0·27
4500	0·10
5700	0·09

According to Slater's (1956) model energy barriers are associated with grain boundaries and their barrier heights can vary because of the charge accumulation at the boundaries. According to him, the increased barrier height is given by

$$\Delta E = \Delta E_o + C(x - fD)^2, \tag{4}$$

where ΔE_o is the original barrier height, C, a term depending on density of charge carriers, electronic charge, and dielectric constant of material, x, the barrier width of about 200 to 300 Å, D, the dimension of the grain, and f a fraction of the order of 1/15 to 1/50 depending on the charge accumulation at the grain boundaries. It is known from literature (Chopra 1969) that the grain size (D) is approximately proportional to thickness (d), and hence increases as thickness increases. Therefore ΔE should be proportional to $(x - fd)^2$. In the present observations ΔE decreases with increase of thickness and it is reasonable to regard the possibility of the effect of the barrier height due to the size of grains in the film.

It is also known that a fairly large number of dislocations are created during the formation of the films and their density increases as the thickness increase up to a particular thickness, beyond which the density is practically constant. It has been suggested (Matare 1971) that when the dislocation density is fairly high as in the case of thin films, there is an increase in the activation energy of a semiconductor material, because of the presence of dislocations, provided that the dislocations are separated by a distance greater than the interatomic distance. However, in the present observations the activation energy decreases with increase of thickness and hence the possibility of dislocation effect on activation energy can be disregarded.

In case of quantum size effect (Sandomirskii 1963, 1967), ΔE varies inversely with d^2 which is not observed in the present work.

Considering the fourth possibility, viz. stoichiometry change influencing the activation energy, it is likely that, there may be slight variation in stoichiometry during the deposition of the film.

Thus we can only say that the decrease in activation energy with increasing thickness observed in AlSb films may possibly be due to combined effects of change in barrier height and stoichiometry in the films.

From the above studies it appears that thin films of Al–Sb formed on glass substrate at room temperature employing three-temperature method exhibit metallic (Al < 50 at.%), semiconducting (Al = 50 at.%) and metallic to semiconducting (Al > 50 at.%) behaviours.

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