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Electrical conductivity, defect density and structure of obliquely vacuum-deposited tin antimonide alloy thin films

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Thin films of tin antimonide alloy have been vacuum deposited on glass substrates at room temperature at different angles of deposition. These films have been heat-treated *in situ* and their electrical resistance has been continuously monitored during the heating–cooling cycle. From the resistance against temperature data during heat-treatment, "initial lattice distortion energy spectra" of these films have been determined using Vand's theory. It has been found that for angles of deposition below 50°, the defect density increases with increasing angle of deposition. At higher angles of deposition, the resistance against temperature behaviour during heat-treatment is different. This is attributed to the columnar structure of the film. It is also found that preferential decay energies of the defects exist and these are 1.45 and 1.80 eV.

1. Introduction

The measurement of the electrical conductivity of vacuum-deposited thin films during heat-treatment can give important information regarding the defect structure and density of defects present in the as-grown thin films and can also throw light on the changes that take place during the annealing process in the thin film. The information obtained concerns mainly point defects and point defect clusters and to some extent grain boundaries at higher temperatures. It is also possible to study the influence of deposition parameters on the defect density and structure of thin films by the conductivity measurements.

Several theories have been developed connecting electrical conductivity changes during annealing and the defect density and decay energy of the defects by Vand [1], Primak [2], Meechan and Brinkman [3] and the grain boundaries by Mayadas and Shatzkes [4]. Vand's [1] theory has been extensively used for the analysis of electrical conductivity data during annealing to study the defect structure of vacuum-deposited thin films by several investigators (Narayanadas *et al.* [5–7], Olumekar and Beynon [8], Shah and Nayak [9] and Damodara Das *et al.* [10–13]). In the present paper the results of such an analysis of the electrical conductivity data during annealing of SnSb alloy thin films vacuum-deposited at different angles of deposition are presented using Vand's theory.

2. Experimental procedure

Tin antimonide alloy thin films of thickness 50 nm were vacuum deposited at different angles (angle between the vapour beam and the substrate normal) on cleaned glass substrates at a deposition rate of 1 nm sec^{-1} using a Mo boat in a vacuum of 2×10^{-5} torr. In order to ensure that the composition of the thin film formed would be the same as that of the bulk (50:50), the required quantity of the bulk alloy was placed in the boat each time and all the material in the boat was completely evaporated each time. In a single evaporation, films were formed on differently inclined substrates so that the deposition conditions for the films formed at different angles would be the same. After film formation, each of the films was individually mounted in the conductivity measurement set-up in the vacuum chamber for the annealing treatment and electrical conductivity monitoring. The conductivity was monitored during the heat-treatment in a vacuum of 2×10^{-5} torr using press-

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ure contacts on thick silver films (500 nm) (pre-deposited at the ends of the alloy films) by means of a Wheatstone bridge to an accuracy of 0.2%. Thickness was measured using a quartz crystal thickness monitor and the temperature of the film was measured using an Fe–constantan thermocouple.

3. Results and discussion

Fig. 1a, b and c show typical plots of resistance against temperature during heat-treatment for three films of SnSb alloy of the same thickness (50 nm), vacuum deposited onto glass substrates in a single deposition at angles of deposition of 0°, 25° and 50°. It can be seen from Fig. 1 that during heating the resistance remains nearly constant, or increases or decreases only very slightly with increasing temperature up to about 160° C. Thereafter it decreases at a faster rate up to about 320° C, the highest temperature to which the films were heated during the studies. This maximum temperature was chosen after trial experimentation to avoid rapid increases in resistances of the films with increasing temperature, which is due to grain growth and agglomeration in the films which causes discontinuities. It can also be seen from Fig. 1 that during cooling the film resistances decrease with decreasing temperature and these decreases are linear in all three cases. It can be concluded from this observation that during cooling, the electron scattering changes are due solely to decreasing lattice vibrations, and hence, we obtain a linear increase of resistance with temperature as in a normal metallic alloy. The resistance against temperature behaviour during heating is due to the combined effect of increasing lattice scattering

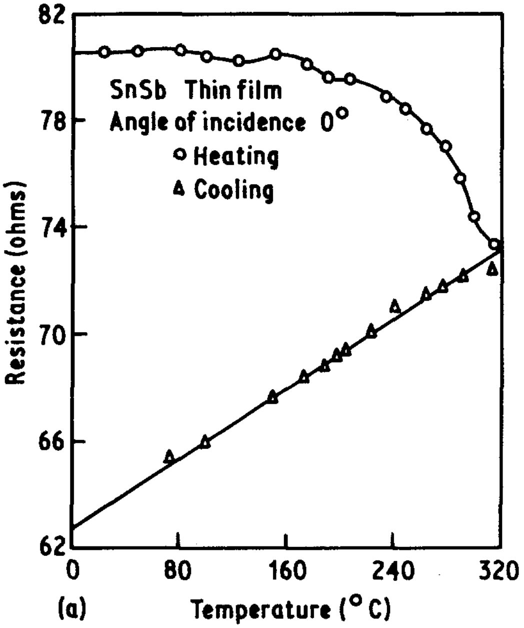
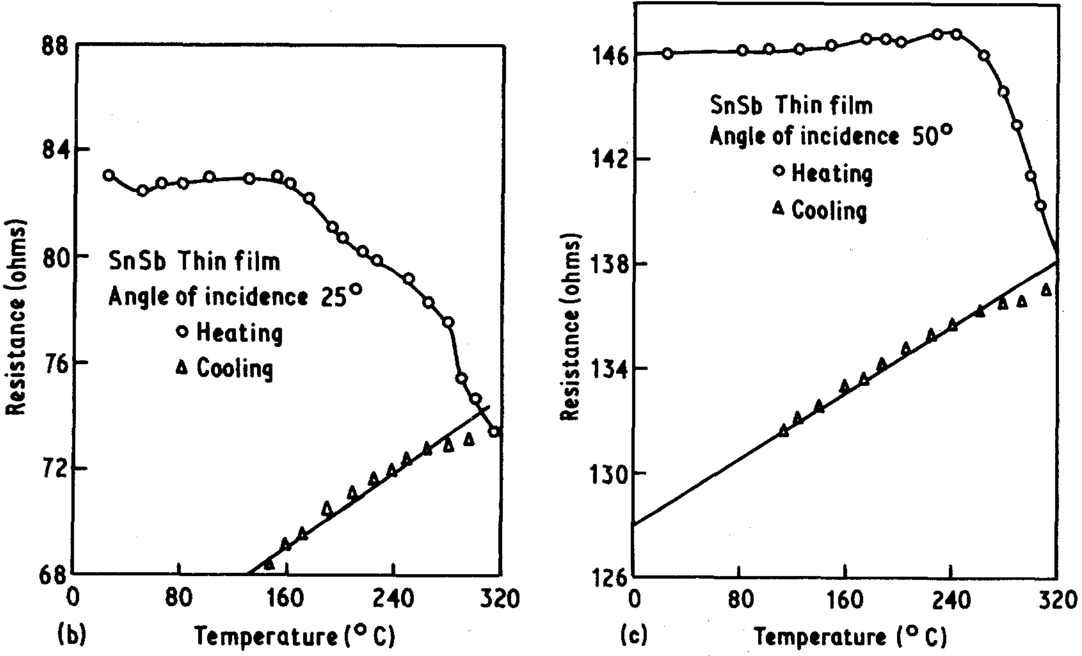


Figure 1 Resistance against temperature plots during heat treatment of SnSb alloy thin films vacuum-deposited in a single evaporation at angles of deposition of (a) 0°, (b) 25° and (c) 50°, respectively.



with increase of temperature and the decreasing defect scattering due to the removal of defects during the heating process. It can also be seen from the figures that the initial resistance of the as-grown films increases with increasing angle of deposition (80.5, 83.0 and 146.0 Ω for 0°, 25° and 50° angles of deposition, respectively). It should also be noted however, that, after heat-treatment, the films have resistances at 20° C equal to 63.5, 64.0 and 128.5 Ω, respectively. The fact that the resistance of the as-grown films increases with increasing angle of deposition indicates that the films formed at higher angles of deposition have larger densities of defects incorporated in them. Also, the increase in the defect density increases rapidly at higher angles. Similar increase of resistance of annealed films with angle of deposition indicates that not only are the defects incorporated in a larger number but also the structure of the film itself is different in the case of films formed at higher angles of deposition. Fig. 2 which shows the resistance against temperature plot for the film deposited at an angle of 75° supports this view. As is seen in Fig. 2, the initial resistance of the film is very high (837 Ω), and during annealing, its resistance increases with increase in temperature unlike the case of low-angle deposited films and also this increase is not uniform. During cooling also, the film resistance does not decrease linearly. This indicates that the film formed at this high angle of incidence has a markedly different structure, and during heat-treatment, several processes like defect removal, grain growth and agglomeration and others are taking place; hence, the resistance against temperature plot is complicated. It should be mentioned here that this kind of behaviour is certainly due to the columnar structure of the films formed at high angles of deposition [14–17]. As the angle of deposition increases, the metal atoms/molecules from the beam strike the substrate surface more and more tangentially. As the growth of individual grains which have formed proceeds, these individual grains protect the regions behind them from the metal beam thereby causing a self-shadowing effect. This leads to the growth of columnar type grains in the beam direction. This kind of growth does not occur at normal or near normal incidence as there will be no shadowing effect. As there will exist discontinuities between columnar grains due to self-shadowing effect, the film resistances will be high. During heat-treatment, this kind of film undergoes structural changes and agglomeration at comparatively low temperatures with a consequent increase in resistance.

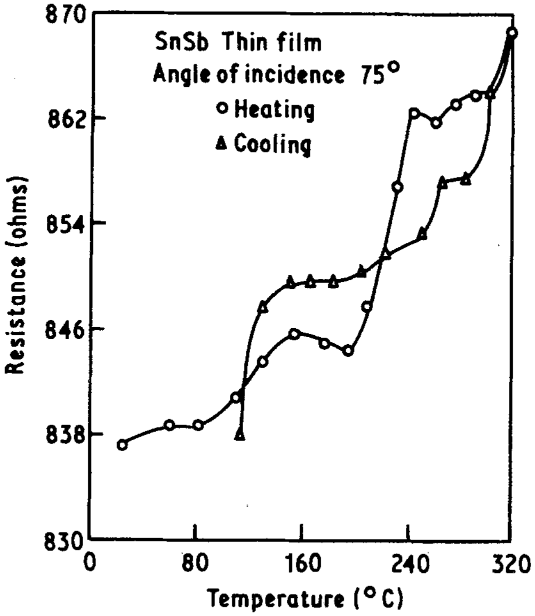


Figure 2 Resistance against temperature plot during heat-treatment of SnSb alloy thin film vacuum deposited at an angle of 75°.

By taking the differences in resistance at given temperatures during heating and cooling in the plots of resistance against temperature in Fig. 1, we get the defect resistances of the films at each of the temperatures during heating. From these data, we can calculate the variation of the rate of change of defect resistance of the films with temperature during heating. Using this information and employing Vand's theory, the defect density and the distribution in activation energy of these defects can be evaluated. According to Vand [1], the decrease in resistance with temperature during annealing of a metallic alloy is principally due to the distortions of the combined type rather than due to individual vacancies and interstitials. This is because the distortions of the combined type are point-defect clusters, consisting of collections of vacancies and interstitials in close proximity with one another and, hence, they need only very low activation energies for removal by recombination of the point defects constituting them, as the latter have to diffuse only through a distance equal to three to five interatomic distances. Individual vacancies and interstitials on the other hand have to travel over a large number of atomic distances to meet one another or to reach the surface for

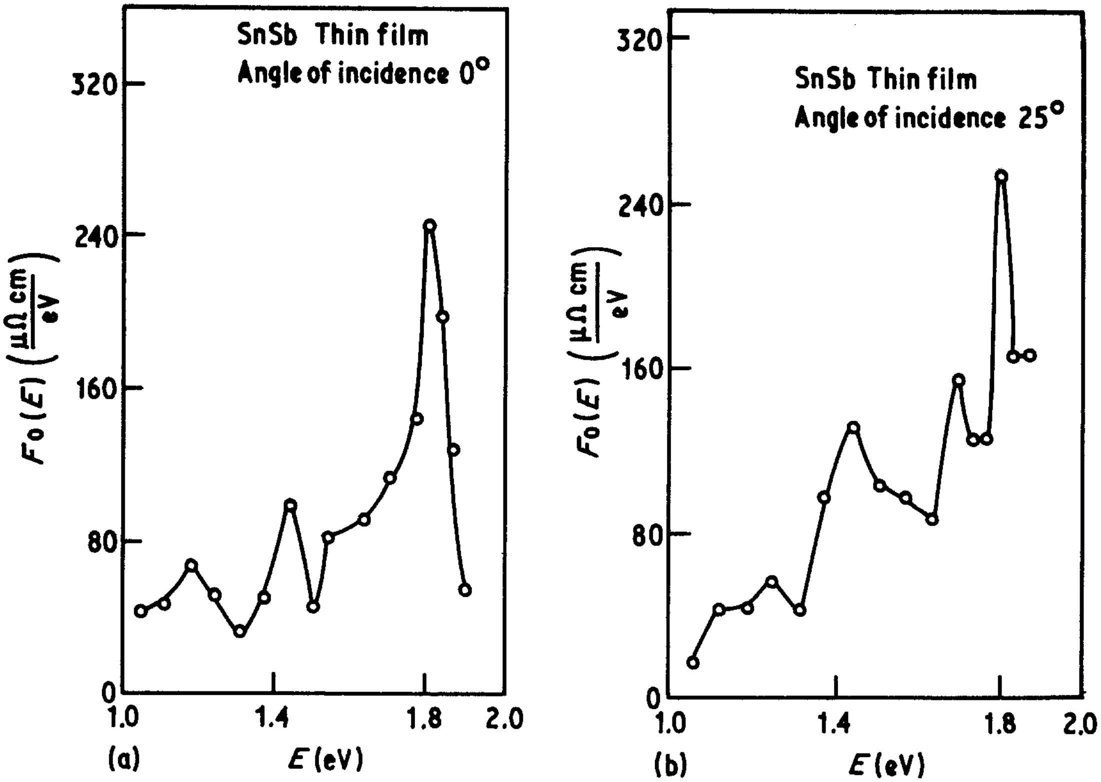


Figure 3 a, b and c: $F_0(E) = \rho(E)N_0(E)$ against E plots (initial lattice distortion energy spectra) for the films of Fig. 1.

their removal. The point-defect clusters have variations in decay energies depending on the number and configuration of vacancies and interstitials constituting a given cluster. Vand [1] has obtained expressions for the decay energy distribution of these defects in terms of the rate of change of defect resistivity with temperature during heating. According to him, the initial lattice distortion energy function $F_0(E)$ which is a product of $N_0(E)$, the initial defect density, and $\rho(E)$, the contribution to resistivity by one defect per volume, is given by

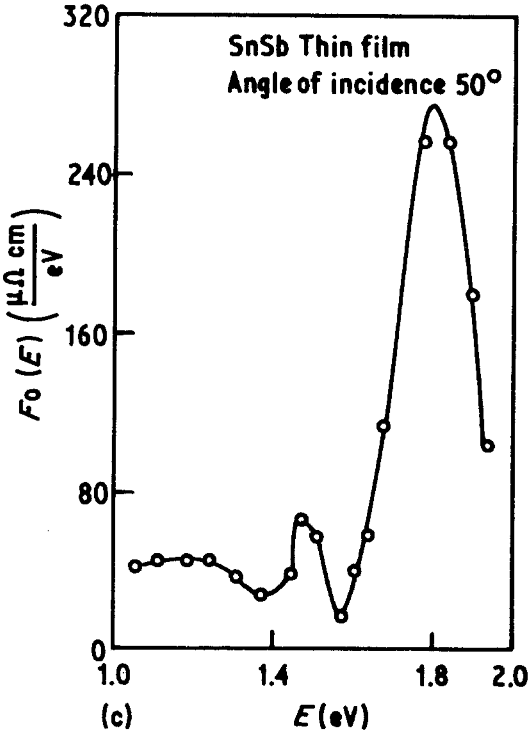
$$F_0(E) = \frac{-\mathrm{d}\rho_i}{\mathrm{d}T} \Big/ kU \qquad (1)$$

and the decay energy of the defect is given by

$$E = ukT. \qquad (2)$$

Here $\mathrm{d}\rho_i/\mathrm{d}T$ is the rate of change of defect resistivity at a temperature T, k is the Boltzmann constant and U is given by

$$U = \frac{u(u+2)}{(u+1)}. \qquad (3)$$



u can be calculated by successive approximation using the relation $u + \log_e u = \log_e Ct = \log_e 4\nu_{\max}nt$, where $\nu_{\max}$ is the Debye cut-off frequency of the lattice (10^{13} Hz), n is the number of atoms initiating the decay of a point-defect cluster and t is the time in seconds required to reach the temperature T at which $d\rho_i/dT$ is measured.

Thus, by determining $d\rho_i/dT$ at various temperatures, $F_0(E)$ and E can be calculated using Equations 1 and 2 and can be plotted against each other to give the initial lattice distortion energy spectrum of the thin film under study. Such an evaluation has been carried out for the films of Fig. 1a, b and c, and Fig. 3a, b and c shows the initial lattice distortion energy spectra of the films. It is seen from Fig. 3 that there are peaks at decay energy values of about 1.45 and 1.8 eV. There also appears to be a peak around 1.2 eV in two cases. As the decay energy of the defect will be determined by the configuration and number of vacancies and interstitials constituting the point-defect cluster, this indicates that the point-defect clusters prefer to have particular configurations. It is also seen that the $F_{0,\max}(E)$ values (heights of peaks) are 248, 254 and 275 μohm cm eV^{-1} at 1.8 eV, and 100, 132 and 65 μohm cm eV^{-1} at 1.45 eV, respectively, indicating an increasing tendency as the angle of deposition increases. If we assume that the contribution to resistivity by a defect per unit volume is independent of its energy, then $F_0(E) = \rho(E)N_0(E)$ can be considered to represent the defect density directly. Thus, the increasing tendency of $F_{0,\max}(E)$ with the angle of deposition implies increasing density of defects having preferential energy with increasing deposition angle. Further, the total areas under the curves (between 1.05 and 1.9 eV) are 74, 76 and 86 μohm cm. As the total area under the curve gives the total defect resistivity in the film $[= \int F_0(E)dE = \rho(E) \int N_0(E)dE]$, it is directly proportional to the total defect density, and hence, it can be concluded from the above that the total defect density also increases with increasing angle of deposition.

As mentioned earlier, the resistance against temperature behaviour during heat-treatment of the film formed at an angle of deposition of 75° is different from those formed at lower angles and several processes like agglomeration, grain growth and defect removal are simultaneously operating during heat-treatment. Also, the film microstructure itself will be markedly different due to the columnar growth, as evidenced by high initial resistance of the film. Hence, Vand's [1] theory, applicable only to defects, can be applied only when the defects are being removed and cannot be applied here.

The observation that the films formed at 0°, 25° and 50° behave similarly while that formed at 75° behaves differently both initially and during heat-treatment, can be explained by the fact that the self-shadowing effect and columnar growth phenomenon become increasingly prominent only at larger angles of deposition above about 40° to 50°. This is supported by the observations of Chopra and Randlett [14] who observed a rapid increase (20% per degree) in critical thickness in Ag films only above about a 40° angle of deposition while at lower angles, the critical thickness increased moderately (0.75% per degree).

4. Conclusions

It can be concluded from the above study that as the angle of deposition during oblique vacuum deposition of thin films increases, the defect density in the films also increases. It is also found that there are preferential decay energies of the defects (1.45 and 1.80 eV), indicating preference for particular configurations by the defect clusters. It is also observed that at larger angles of deposition the film structure is predominantly columnar and, hence, resistance against temperature behaviour is complex.

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