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Lattice distortion energy spectra of as-grown bismuth thin films and their thickness dependence

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Bismuth thin films of various thicknesses between 15 nm and 350 nm were vacuum deposited at room temperature on to glass substrates, immediately after which they were twice heat treated at a uniform rate. During the heat treatment, the resistance changes were monitored and, using these data, the initial lattice distortion energy spectra of as-grown bismuth thin films have been evaluated. It is found that the defects have preferential activation energy values around 1.06 eV, 1.14 eV and 1.32 eV. It is also found that $\int F_0(E)\,dE$ oscillates with thickness, which is attributed to the quantum size effect.

1. Introduction

Because, in the vacuum deposition process, metal atoms condensing on the substrate initially form isolated nuclei which grow into islands and then coalesce to form the continuous film, a large number of defects are incorporated in the thin film. The defects incorporated are far in excess of the equilibrium concentration. Therefore, during heat treatment, the majority of the defects are annealed out. The kinetics of the removal of these defects (mainly point-defect clusters) can be studied by the measurement of electrical conductivity during heat treatment. Damask and Dienes [1] have developed a general theory and method of analysis of the annealing process, while Primak [2] has reviewed the kinetics of the processes, which are distributed in activation energy. Vand [3] has developed a theory of resistivity changes during the annealing of defects applicable to thin films, and this has been widely applied in the analysis of defect density and distribution in thin films of various materials by a number of workers [4–9]. The transport properties of bismuth in the thin-film state have been studied by a number of researchers (e.g. [10]) because they exhibit anomalous behaviour due to the emergence of a quantum size effect. For example, Sandomirskii [11], Komnik and Andrievsky [12], Ogrin *et al.* [13] and Damodara Das and Jayaprakash [14, 15] have shown that bismuth films exhibit an oscillatory behaviour of resistivity, Hall effect and magneto-resistance with thickness with a period of about 35 to 40 nm and an anomalous variation of this behaviour with temperature. However, no studies have been carried out about the defect contribution to resistivity and the effect of annealing in bismuth films. The present work reports the study of defect density variation with thickness in as-grown bismuth thin films.

2. Experimental details

Bismuth thin films of various thicknesses between about 15 nm and 350 nm were vacuum deposited at a pressure of about 2×10^{-5} torr on to clean glass substrates held at room temperature. Specific film thicknesses mentioned later were chosen with the knowledge from literature [10, 13, 15] that bismuth film resistivity oscillates with thickness with a period of about 35 to 40 nm. The vacuum deposition was carried out in a conventional diffusion pump–rotary pump vacuum deposition unit with a stainless steel base plate and bell jar and tungsten–inert-gas-welded joints (Leybold–Heraues). The pressure during evaporation rose to about 4 to 5×10^{-5} torr. Spectrographically pure bismuth (purity 99.999 %), obtained from Johnson

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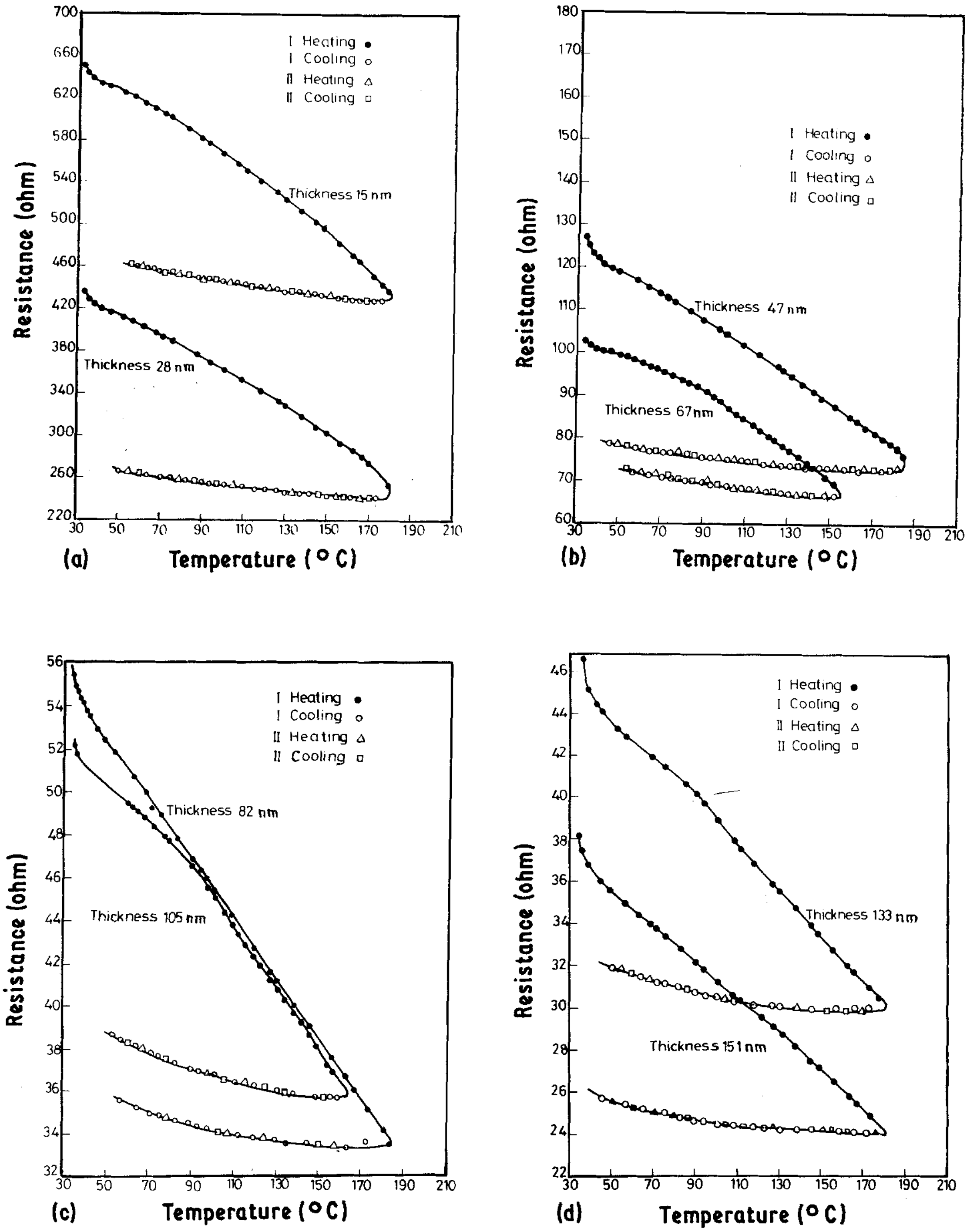


Figure 1 Resistance against temperature variation curves for films of different thicknesses during two cycles of heat treatment.

Mathey Chemicals Ltd, London, was used as the charge and the resistive heating filament was a conventional dimpled molybdenum boat of dimensions about 1 cm × 5 cm × 0.02 cm. The boat was fully filled with charge (about 700 mg) and heated in vacuum initially to degas the charge and to remove any impurities present. The films were deposited at a constant source current of

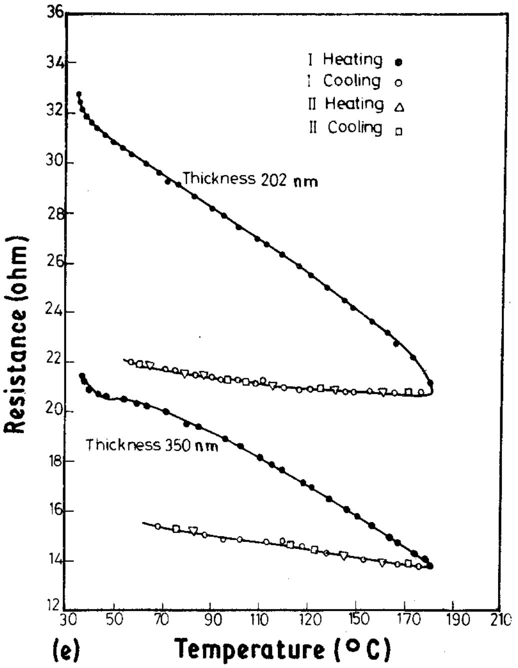


Figure 1. Continued.

60 A and the deposition rate was 0.3 nm sec^{-1}. The thickness of the films was varied by varying the deposition time. The thicknesses were measured and monitored using a quartz crystal thickness monitor. The source-to-substrate distance was 20 cm. The glass substrates used were Pyrex glass microscope slides and were cleaned before film deposition with warm dilute chromic acid, then with a detergent solution and distilled water. Finally, they were degreased with isopropyl alcohol before mounting them in the deposition chamber. In the deposition chamber they were cleaned with a glow discharge.

Immediately after formation, the films were heated *in situ* at a uniform rate of about 3° C min^{-1} up to a maximum temperature of about 190° C and then cooled to about 50° C. The films were then again heated to the same maximum temperature and cooled. During the process of heat treatment, the resistance of the films was continuously recorded as a function of temperature with the help of pre-deposited thick silver electrodes at the ends of the experimental films and a Wheatstone bridge network. Each of the films was separately prepared in individual evaporations and heat treated in the above manner. The accuracy of the resistance measurement was 0.1 %. The major error involved in the evaluation of resistivity was in the thickness measurement and was about 1.0% for a 100 nm film but much larger and smaller for lower and higher thicknesses, respectively (5 % to 0.3 %). The accuracy of temperature measurement was about 0.5 %. The maximum temperature of heating (190° C) was chosen after trials to correspond to a temperature below that at which there was a rapid increase in resistance with increasing temperature, due to the discontinuties formed in the films by agglomeration, recrystallization and evaporation, rather than a gradual decrease in resistance observed below and up to this temperature, due to defect removal. Thus, the principal changes that occur during heat treatment should be the removal of defects [6]. X-ray diffractograms of the films taken before and after the heat treatment indicated that the films were polycrystalline and did not contain additional peaks corresponding to any oxide that could have formed during film preparation and/or heat treatment.

3. Results and discussion

Fig. 1a to e shows the resistance variation with temperature for films of different thicknesses between 15 nm and 350 nm. It is seen from Fig. 1 that the resistance decreases continuously with temperature during the first cycle of heating. It should be noted that during the initial stages the resistance falls at a rapid rate in the interval of about 5° C and then at a much lower rate more or less uniformly. This behaviour is in contrast to observation on tin–antimony alloy films [5, 6] where the rate of decrease of resistance continuously increases with temperature. This behaviour is peculiar to the material bismuth because of its anomalous change in resistance with temperature [14] when the film is properly annealed. It is also seen from the figures that, during the first-cycle cooling and the second-cycle heating and cooling, the changes in resistance with temperature are reproducible. This implies that all the defects that can be removed by the maximum temperature reached are removed during the first heating and hence, during the first-cycle cooling, the defects do not contribute to resistivity. Thus, during the first-cycle cooling and second-cycle heating and cooling, the changes in resistance with temperature are due to the nature of the material. It is interesting to note that during these cycles the resistance decreases as the temperature increases. This kind of behaviour is due to the removal of overlap between the conduction and valence bands in

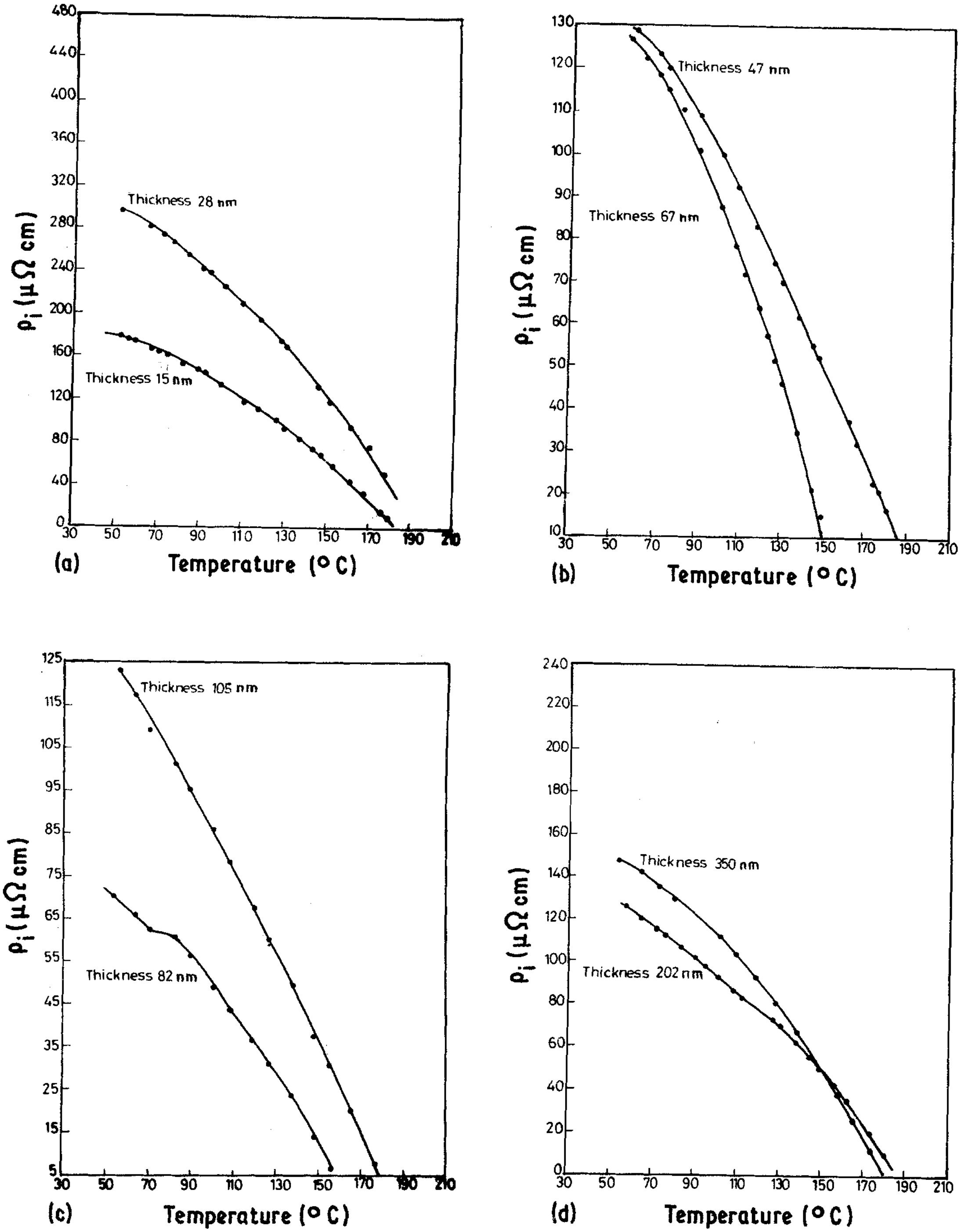
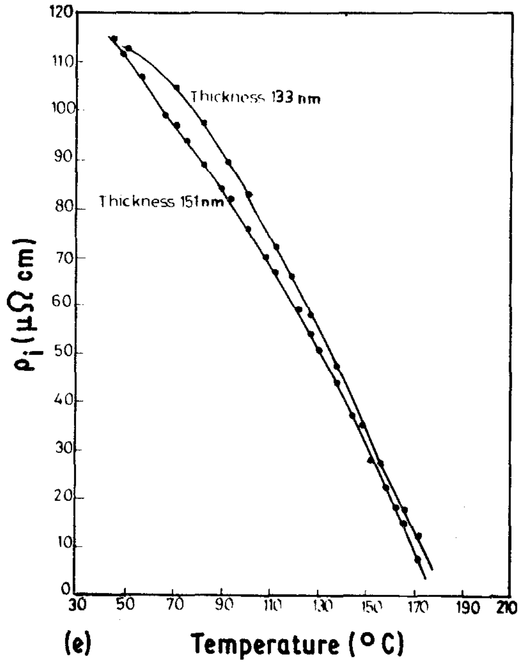


Figure 2 Defect resistivity against temperature curves for the films of Fig. 1.

thin-film bismuth and has been explained elsewhere [14]. It should be mentioned that if the maximum temperature of heating is increased beyond 190° C, even then there will be removal of point defects and point-defect clusters and a consequent decrease in resistivity. However, in addition to this, extensive grain growth and agglomeration would take place making the film electrically discontinuous. Hence, it is not experimentally possible to study the defects that would



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be annealed beyond this temperature as the extensive grain growth and agglomeration that take place cause a more drastic change, namely, electrical discontinuity in the film. This is the reason why the study is confined to heat treatment below 190° C [6, 16].

According to Mathiessen's rule, the resistivity of a material is given by $\rho = \rho_T + \rho_i$, where ρ_i is the resistivity contribution by the defects and ρ_T is the resistivity contribution due to effects other than defect scattering in the film. Thus, by taking the difference between resistances in the first-cycle heating and in any of the subsequent cycles at a given temperature, we can evaluate ρ_i, the defect resistivity at that temperature.

Even though structural defects such as dislocations, stacking faults and grain boundaries will be present in thin films in addition to the point defects and point-defect clusters, dislocations make only a very small contribution ($\sim 10^{-9}\,\Omega$ cm per disolcation) to resistivity. Further, stacking-fault density would be of the order $\sim 10^5$ cm^{-1} and hence its contribution would be very small. Point defects (especially vacancies) and point-defect clusters, on the other hand, make a large contribution (1 to 6 $\mu\Omega$ cm/at%) to resistivity. Grain boundaries contribute to resistivity due to diffuse scattering of electrons [17]. However, if there is no reorganization of the grains, no agglomeration and no recrystallization, the grain-boundary contribution will be the same before and after annealing and will be nearly independent of temperature. As mentioned earlier, the maximum temperature of heating was chosen to be much below the temperature beyond which rapid increase in resistance takes place due to crystalization and agglomeration. Hence, changes in the resistivity during annealing can be considered to be principally due to the removal of point-defect clusters and point defects and due to the increased thermal scattering [6].

Fig. 2a to e shows the variation of ρ_i with temperature for the above films, determined in the manner described earlier. Using these curves, the concentration of defects and their distribution in activation energy in the as-grown films were evaluated using Vand's [3] theory. Vand [3] considers that the changes in resistivity during annealing are due to the removal of combined type of defects which are nothing but aggregates of interstitials and vacancies in close proximity with one another. These defects can be annealed out by small amounts of energies because they can be removed by small-scale diffusion of the point defects constituting the combined defect. However, depending upon the number and configuration of point defects constituting a combined type of defect, the decay energy of the defect can have any possible decay energy value between zero and the activation energy for self-diffusion. The isolated vacancies and interstitials are not annealed out significantly, because they can only be removed by recombination or migration to the surface by long-range diffusion, which would involve a much larger amount of energy. Vand has obtained expressions for the initial lattice distortion function, $F_0(E)$, given by

$$F_0(E) = N_0(E)\rho(E), \tag{1}$$

where $N_0(E)$ is the initial defect concentration and $\rho(E)$ is the resistivity contribution by a single defect per unit volume, as

$$F_0(E) = \frac{-(\mathrm{d}\rho_i/\mathrm{d}T)}{kU}, \tag{2}$$

where $\mathrm{d}\rho_i/\mathrm{d}T$ is the rate of change of defect resistivity with temperature during the first heating, k is Boltzmann's constant and

$$U = \frac{u(u+2)}{(u+1)}, \tag{3}$$

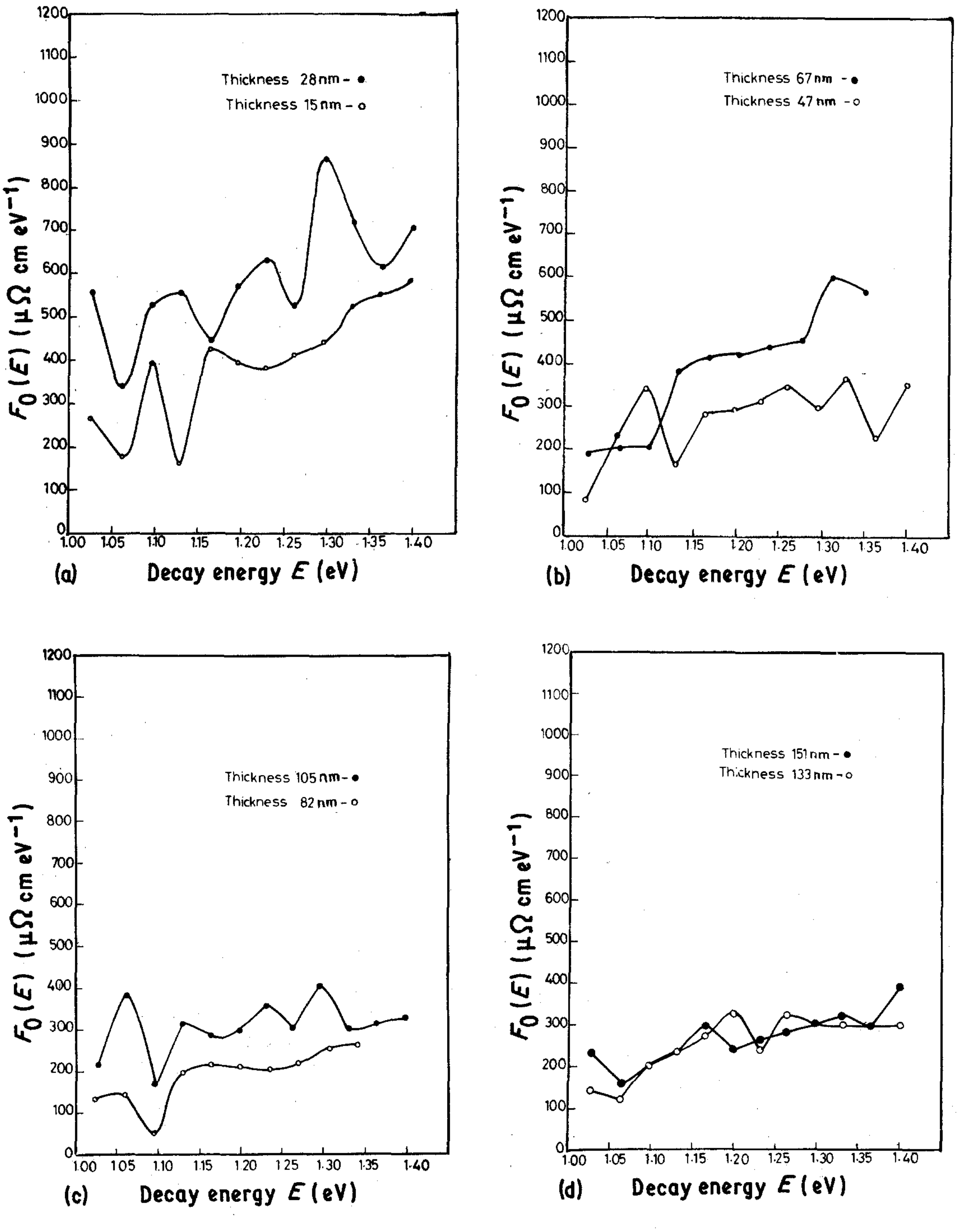

Figure 3 Initial lattice distortion energy spectra for the films of Fig. 1.

where u can be evaluated, with knowledge of the time, t, taken to reach the temperature at which $d\rho_i/dT$ is measured, using the relation $u + \log_e u = \log_e ct = \log_e 4\nu_{\max} nt$, where $\nu_{\max}$ is the Debye frequency of the lattice (for bismuth $\nu_{\max} = 2.5 \times 10^{12}$ Hz) and n is the number of atoms participating in the removal of a combined type of defect and is taken to be about 10.

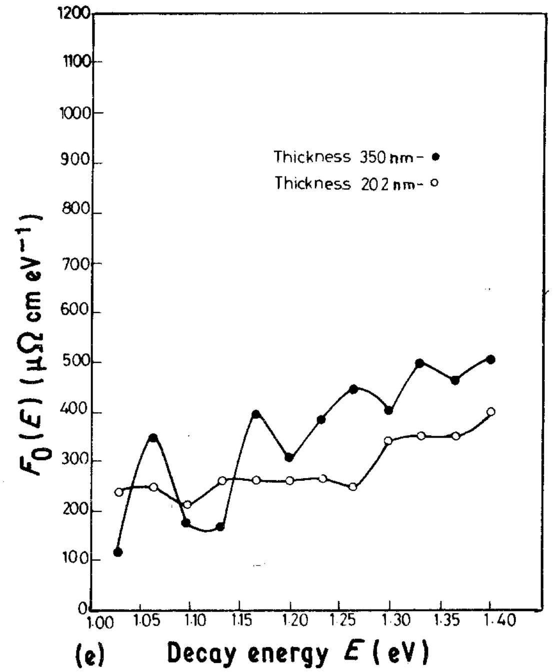

Figure 3 Continued.

The decay energy of the defects, E, is given by

$$E = ukT$$

and the total contribution to the resistivity by the defects is

$$\rho_i = \int \rho(E) N_0(E)\,\mathrm{d}E = \int F_0(E)\,\mathrm{d}E. \quad (5)$$

By knowing the rate of change of defect resistivity with temperature at various temperatures and the time taken to reach those temperatures, $F_0(E)$ and E can be evaluated using the above formulae. Such an evaluation has been carried out and Fig. 3a to e shows $F_0(E)$ against E for various thicknesses.

These are called the initial lattice distortion energy spectra. It is seen from Fig. 3 that there are maxima around energies of 1.06 eV, 1.15 eV and 1.32 eV in the case of some of the films of different thicknesses, but they are weak. This indicates that the defects have a tendency to prefer some activation energies and hence tend to have particular configurations. However, we cannot more positively assert the existence of these preferential activation energies and their values, as the maxima observed in the present case of bismuth films are very weak, unlike in the case of SnSb thin films [5, 6] and the error involved in the $F_0(E)$ against E plots would be between 2 and 5% in the light of errors involved in the experimental measurement.

If we consider $\rho(E)$ to be independent of energy as a first approximation, $F_0(E)$, which is proportional to $N_0(E)$, can itself be considered to represent the density of defects. It is interesting to note that the total contribution to the resistivity by the defects between the activation energies 1.025 eV and 1.40 eV (the total area under the the curves) oscillates with thickness as shown in Fig. 4. The amplitudes of oscillations are much larger than the error involved in the data points which as mentioned earlier was about 5%. This kind of behaviour is contrary to that observed in the case of tin–antimony alloy films [5], where the defect density was found to increase with increase in thickness. The oscillatory behaviour, with thickness, of

$$\int_{E=1.025}^{E=1.40} F_0(E)\,\mathrm{d}E$$

in the present case, however, cannot be attributed to the defect density varying in an oscillatory manner with thickness because the oscillatory behaviour arises because of restrictions to scattering by the defects imposed due to the quantum size effect in Bi films, as explained by Sandomirskii [11], Damodara Das and Jayaprakash [12] and Malone and Deering [18]. It is also noteworthy that the period of oscillations observed, 35 to 40 nm, agrees with the earlier observations by Ogrin *et al.* [13]. Thus, the oscillations of the above integral with thickness are due to the oscillation of $\rho(E)$ (the resistivity contribution by one defect/volume) with thickness because the mobility due to scattering oscillates with thickness. However, in addition to the oscillatory behaviour, the average value of the integral $\int F_0(E)\,\mathrm{d}E$ decreases with thickness up to about 140 nm and then increases uniformly. This average-value behaviour would give information about the $N(E)$ variation with thickness as

$$F_0(E) = \rho(E) N_0(E). \quad (6)$$

Thus, it can be said that the defect density first decreases with increasing thickness and then increases with it.

4. Conclusions

The initial lattice distortion energy spectra of bismuth films of different thicknesses have been evaluated. From these plots, the integral

$$\int_{E=1.025}^{E=1.14} F_0(E)\,\mathrm{d}E$$

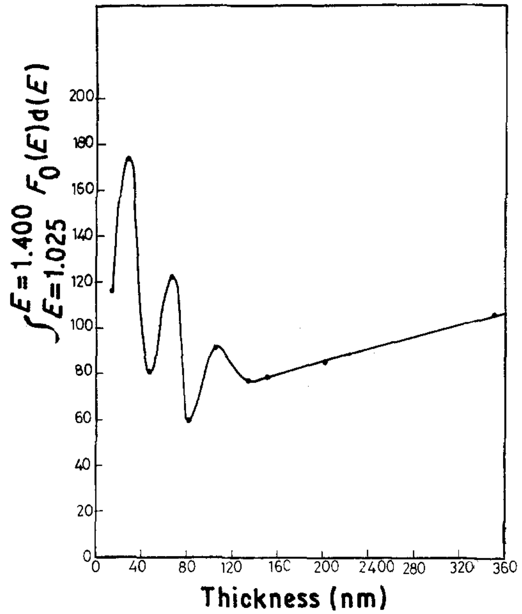

Figure 4 Plot of $\int_{E=1.025}^{E=1.4} F_0(E)\,\mathrm{d}E$ against thickness.

is found to oscillate with thickness. This is attributed to the restrictions imposed on scattering due to manifestation of the quantum size effect in Bi thin films rather than to oscillatory changes in defect density with thickness.

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