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Semiconducting behaviour of thin bismuth films vacuum-deposited at different substrate temperatures

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Thin bismuth films (thickness 25 nm) have been vacuum-deposited onto glass substrates at different substrate temperatures in a vacuum of 2×10^{-5} torr. The resistance of the films has been measured as a function of temperature *in situ* during and after annealing. It is found that the resistance of all the annealed films decreases with increasing temperature thus showing a semiconducting type of behaviour. The films do not show a resistivity minimum observed in thicker films [1]. The absence of a resistivity minimum is attributed to the thinness of the films and consequent larger energy band gap and smaller grain size.

1. Introduction

Several workers [2–7] have investigated the transport properties of bismuth both in the bulk state and in the thin film state because of its anomalous and peculiar behaviour especially in the thin film state. Bismuth is a Group V semi-metal, its semimetallic behaviour in the bulk state arising due to overlapping conduction and valence bands [8, 9]. It was shown theoretically by Sandomirskii [10, 11] that in the thin film state bismuth and other similar materials which have low Fermi energy and small electron/hole effective mass [12, 13] can show anomalous transport properties because of a quantum size effect which arises due to quantization of the normal (to film plane) component of electron momentum. The consequences of this quantization are (1) the non-zero zero point energies of the electrons and the holes which lead to a decrease in the overlap between the valence and the conduction bands, or the separation of the bands depending on film thickness, and (2) the step-wise variation of the density-of-states function with thickness [10, 11]. These lead to entirely different and anomalous properties of the material in the thin-film state as compared to those in the bulk state.

Damodara Das and Jayaprakash [1] have observed an anomalous variation of resistance with temperature in bismuth thin films of thickness ~ 70 nm. They find that the resistance of the film first decreases and then increases with temperature, thus showing a minimum. They also find that the magnitude and the position of this resistance minimum is a function of the substrate temperature during deposition. The present authors [14] have also recently reported a similar behaviour of resistance with temperature in bismuth films of thickness between 23 and 225 nm. We had observed that the film of thickness around 23 nm does not show any resistance minimum in the temperature range studied, while films of greater thicknesses showed a resistance minimum which shifted to lower temperatures as the thickness increased. Thus it was considered of interest to study the effect of substrate temperature on the anomalous behaviour of thin bismuth films of thickness about 25 nm as the grain size of the film would increase with an increase in the substrate temperature during deposition. The present paper reports and explains the results of the above study.

2. Experimental details

Bismuth thin films of thickness 25 ± 2 nm were vacuum-deposited in individual evaporations onto

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clean glass substrates held at different temperatures at a constant deposition rate in a vacuum of 2×10^{-5} torr. The glass substrates were cleaned with warm dilute chromic acid, detergent solution, distilled water and isopropyl alcohol in that order. Thick silver contact films (~ 500 nm thick) were vacuum-deposited at the ends of the glass plates beforehand for resistance monitoring, which was carried out immediately after the bismuth film deposition *in situ* using a Wheatstone network with an accuracy of 0.1%. The bulk bismuth used as charge was of purity 99.999% (Johnson Mathey Chemicals Ltd, London) and was evaporated from a molybdenum dimpled boat after initial degassing. The source-to-substrate distance was 20 cm and the film dimensions were 2.5 cm x 4 cm x 25 nm. The substrate temperature was measured using an iron–constantan thermocouple. The thickness of the films was controlled using a quartz crystal thickness monitor *in situ*.

Immediately after the formation, each of the bismuth films was heated *in situ* at a uniform rate of 2.5 K min^{-1} to a temperature of about 473 K, held there for about 1/2 h, and then cooled back. Some of the bismuth films were heated a second time to the same temperature and cooled. During this heating and cooling process, the vacuum was maintained at 2 to 3×10^{-5} torr and the resistance of the film was continuously monitored. The maximum temperature of heating was chosen by trial experimentation and corresponded to a temperature above which resistance of the film increased steeply due to grain growth, recrystallization and agglomeration and consequent discontinuities in the film [15, 16]. Hence, the films, both as-deposited and after heating and annealing were continuous, and the resistances were of the order of a couple of hundred ohms.

The films deposited at the above substrate temperatures and heated at 473 K for 1/2 h were examined by X-ray diffractometry after cooling to room temperature. The X-ray diffractograms showed that the films were all polycrystalline, but, with a strong fibrous texture, the texture improving slightly with the increase in the substrate temperature during growth, as evidenced by the strong (0 0 3), (0 0 6) and (0 0 9) reflections (of the hexagonal lattice). No other strong peaks of bismuth were observed. Also, no additional peaks indicating any oxide formation during growth or heat treatment could be observed in the diffractograms (Fig. 1).

TABLE I Band gap values E_g of bismuth films (25 nm thick) determined from Fig. 3

Substrate temperature (K)	Band gap, E_g (meV)
323	27.2
348	25.0
363	28.7
383	24.9

3. Results

Figs. 2a to d show the resistivity against temperature plots for the bismuth films of thickness 25 nm deposited at substrate temperatures 50, 75, 90 and 110° C during the heating–cooling cycle. It is seen from the figures that the resistivity variation with temperature during heating and cooling do not coincide even though in both cases the resistivity decreases continuously with increasing temperature. This is because, during heating, frozen-in defects are eliminated or at least reduced [15, 16]. As a consequence, the resistivity of the film during cooling is lower than that during heating at all temperatures. As mentioned, in some cases the films were subjected to a second cycle of heating and cooling. It was found that during the second cycle, the first cycle cooling curve was reproduced. This indicated that the film, after the first heating, was well annealed and hence there was no further removal of defects during the second heating as the maximum temperature of heating during this cycle was not above that in the first cycle [15, 16]. The interesting observations from the figures are that well annealed bismuth films (cooling curve) all show a continuously decreasing resistivity with increasing temperature in the range studied, and there is no resistivity minimum at any intermediate temperature.

Figs. 3a to d show log ρ against $1/T$ plots for the films of Fig. 1 obtained from the cooling curves and hence show the behaviour of well-annealed bismuth films. It is seen from the figures that the plots are linear in all cases. The band gap values calculated from the slopes of these plots are shown in Table I. It is seen that the band gap is nearly constant within about ± 2 meV.

4. Discussion

As mentioned, the important observations made were the semiconducting behaviour of thin bismuth films and the absence of a resistivity mini-

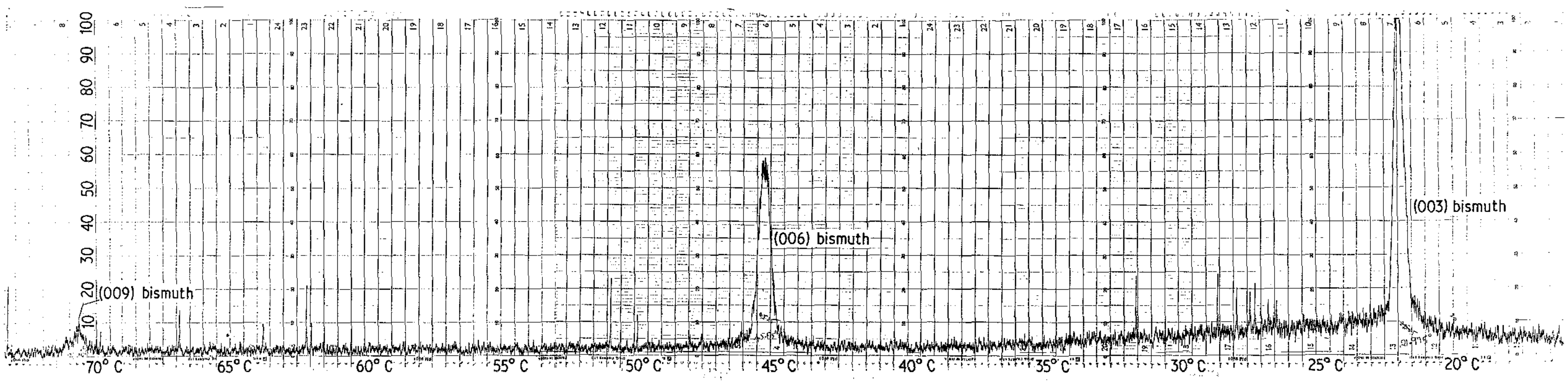

Figure 1 Typical X-ray diffractogram of bismuth films showing (003), (006) and (009) peaks (see text).

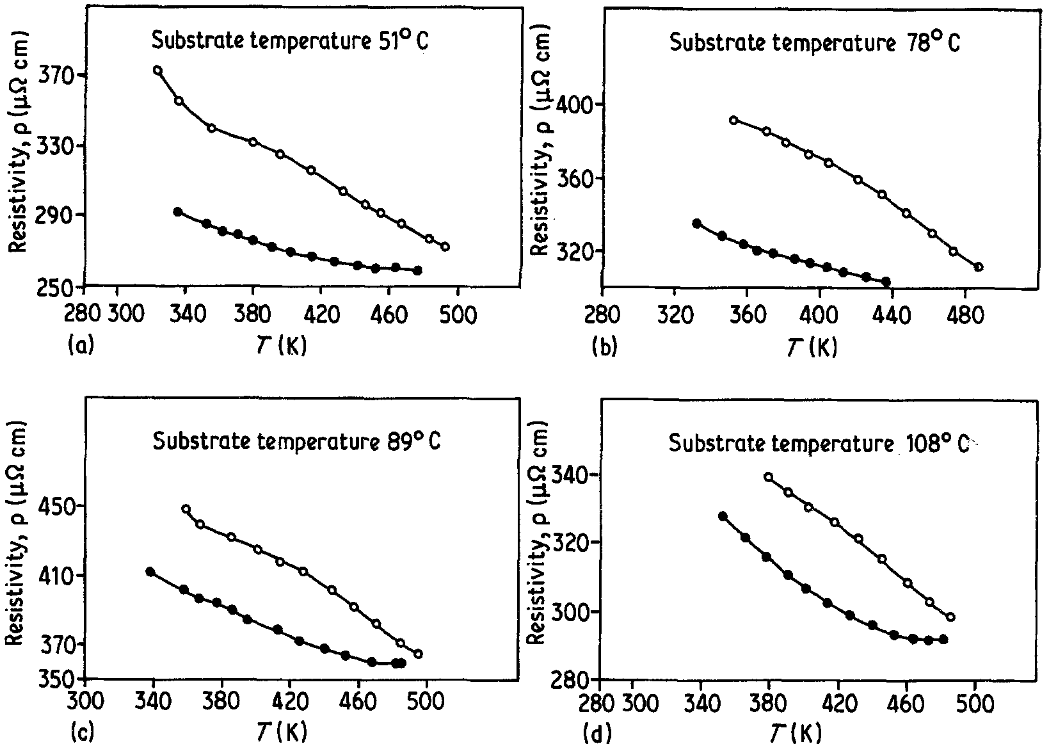

Figure 2 Resistivity against temperature plots of thin bismuth films (thickness 25 nm) deposited at: (a) 323, (b) 348, (c) 363, and (d) 383 K during heating and cooling. (The upper curves are due to heating and the lower ones are due to cooling.)

mum in the temperature range studied, in the case of all the films deposited at different substrate temperatures. The latter observation is in contrast to the observations of Damodara Das and Jayaprakash [1] on thicker (~ 70 nm thick) bismuth films as outlined earlier.

The present observations can be explained on two counts on the basis of the fact that the present films are very much thinner, (almost 3 times thinner than those of Damodara Das and Jayaprakash [1]) and consequently, they have a larger band gap and smaller crystallite size.

According to Sandomirskii [10, 11], the band gap produced due to the quantum size effect is inversely proportional to the square of the film thickness and hence the present, thinner, 25 nm thick, thin films have band gaps larger than those of 70 nm thick films of Damodara Das and Jayaprakash [1]. (They had not evaluated the band gap of their films but had assumed a value of 10 meV for the interpretation.) Even experimentally, we find a band gap of 25 to 26 meV for our films. Hence, the carrier concentration variation with temperature will be about 4 times more rapid in the case of our films as compared to theirs.

Secondly, as the film thickness is smaller in the present case, the grain size of the films will also be smaller [17–19]. Of course, as the substrate temperature increases, the grain size will also increase for a film of given thickness [17–19]. However, this variation of grain size with temperature will not be large enough, compared to the variation as a function of thickness, especially in the case of a thinner film. This is because the grain size increases nearly linearly with thickness, while it increases more slowly with an increase in the substrate temperature [17–19].

Damodara Das and Jayaprakash [1] and the present authors [14] had explained the appearance of the resistivity minimum and its changing magnitude and position with substrate temperature and thickness respectively by considering the exponential increase of carrier concentration with temperature, inverse temperature dependence of the mean free path, and the limitation of the mean free path by the grain size of the films at low temperatures. In the present case however,

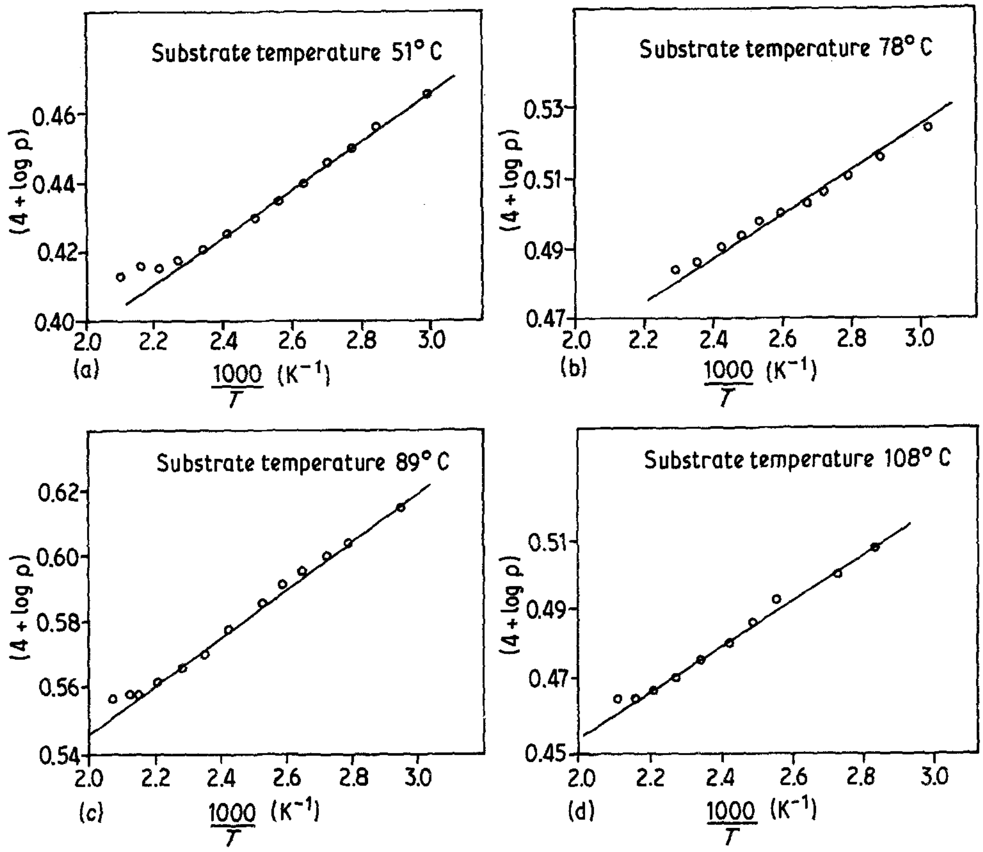

Figure 3 Log ρ against $1/T$ plots for bismuth films of Fig. 2 after annealing (during cooling). Substrate temperature during deposition: (a) 323, (b) 348, (c) 363, and (d) 383 K.

because of the thinness of the film, the grain size is small and even when the film is prepared at a higher substrate temperature, the increase in grain size is not sufficient as explained above. Therefore, the mean free path is limited by the smaller grain size of the film even at the highest temperature of ~ 500 K for all the films, and hence, at lower temperature also, the mean free path will be the same and equal to the average grain size because of limitation by the grains. So, in the entire temperature region studied, the mean free path remains constant, limited by the grain size. Thus, the resistivity variation with temperature in the entire temperature region should be solely due to the carrier concentration variation with temperature, and hence, should be exponential, as observed (c.f. Figs. 3a to d). Thus, no resistivity minimum should be observed because in the present case of 25 nm thick bismuth thin films, because of the larger band gap, the carrier concentration varies at a much steeper rate with temperature, and because of the smaller thickness, the grain size of the films prepared at all the substrate temperatures is much smaller and sufficiently small to make the mean-free-path limited by the grain size in the entire temperature region studied so that it is independent of temperature. This reasoning is supported by the fact that the plots of log ρ against $1/T$ for all the films are linear in the entire temperature region (c.f. Figs. 3a to d) unlike the plots for higher thickness bismuth films reported earlier [14], which were linear only in a limited temperature range, the linearity range decreasing with increasing thickness.

The slight variation of band gap observed for films prepared at different substrate temperatures can be attributed to slightly varying thicknesses (± 2 nm) of the films due to the error involved in the measurement of the thickness of the films by the quartz crystal monitor at different substrate temperatures, due to temperature effects and other errors in the measurements.

5. Conclusions

Thin bismuth films in the present study, even though they show a semiconducting behaviour, do not show any resistivity minimum as observed earlier [1]. This has been explained by the fact that the present films, being thinner, are small-grained and hence, (1) the mean free path of the electrons is independent of temperature in the entire region studied because of the limitation by the grains, and, (2) the band gap is larger and hence the carrier concentration variation with temperature is steeper. It is also found that the effect of substrate temperature in increasing the grain size is not sufficient enough to alter the mean free path limitation temperature.

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