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OPTICAL BAND GAP STUDY OF $Bi_{1-x}Sb_x$ (x = 0.10, 0.15 & 0.20) THIN FILMS

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The solid-liquid interface of $Bi_{1-x}Sb_x$ crystal growth is very favorable for investigations of electron- phonon phenomena. Bismuth is a semimetal with high electron and hole mobilities. When Bi is doped with Sb in the range of 7 to 22 atomic percentage, it undergoes semimetal-semiconductor transition. Interest in Bi-Sb materials system has recently been stimulated due to promise of a new generation of thermoelectric materials based on these alloys. The starting materials used in this study, Bi and Sb, were both of 99.999 % purity $Bi_{1-x}Sb_x$. Thin Films were grown using the thermal evaporation technique on a (001) face of NaCl crystal as a substrate at room temperature. The optical absorption was measured in the wave number range 500 cm^{-1} to 4000 cm^{-1}. From the optical absorption data the band gap has been evaluated and the results indicate absorption through direct interband transition. The absorption spectra were obtained for films of various thicknesses. The band gap was found to increase with decreasing thickness, the dependence being inverse of square of thickness. The effect is most pronounced for thicknesses below 150 nm and is indicative of the quantum size effect. The estimate of the de Broglie wavelength of the carriers confirms this. The detailed results have been reported.

Keywords: *ABSORBANCE, BAND GAP, FILM THICKNESS, SIZE EFFECT.*

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1. INTRODUCTION

Considerable attention has been given recently to the alloys of bismuth and antimony because they not only possess unusual thermoelectric and thermo magnetic effects at cryogenic temperatures but also possess semi conducting properties. Several research groups have investigated the use of Antimony as a surfactant during the growth of III-V compound semiconductors. Bismuth and antimony have rhombohedral structures at low antimony concentration, the alloy has metallic nature and becomes more and more semimetal with antimony concentration exceeding about $x = 0.1$. It is found that the Fermi energy of the alloy decreases with the increase in antimony concentration. The $Bi_{1-x}Sb_x$ alloy system can be either a semiconductor or a semi-metal depending on Sb concentration [1-8]. They have small energy band overlap between the conduction and valence bands, high carrier motilities, and a small effective mass. Because of these characteristics, Bi and Sb have frequently been used for quantum-size effect studies. Hardness testing is one of the mechanically properties to check nature of the metal and nonmetal materials. There have been various studies on the bulk and thin film characteristics of Bi-Sb including optical, electrical and mechanical properties [1-8]. However, there is no report on the band gap variation with

thickness of $Bi_{1-x}Sb_x$ ($x = 0.10$, 0.15 and 0.20) thin films. We hereby report the thickness dependence of optical band gap of $Bi_{1-x}Sb_x$ thin films, with $x = 0.10$, 0.15 and 0.20.

2. EXPERIEMENTAL

Bismuth and Antimony each of 99.999 % purity (5N purity) were purchased from Nuclear Fuel Complex, Hyderabad, India. The stoichiometric amounts of the materials were weighed accurately up to 10 micrograms using a semi-microbalance and filled in a quartz ampoule of about 10 cm length and 1 cm diameter. The quartz tube was then vacuum-sealed at a pressure of about 10^{-4} Pa and it was kept in the alloy-mixing furnace. In this mixing unit, the material was mixed in the molten state for about 48 hours by rotating the tube at 10 rpm at 630 °C for thorough mixing. The rotation of the tube was stopped and the material was further kept in the molten state for further 24 hours in order to ensure homogenization and complete reaction in the molten charge. It was then slowly cooled to room temperature. This process usually produces fairly homogeneous compound. The ingot so prepared was subjected to growth by zone melting.

The $Bi_{1-x}Sb_x$ ($x = 0.10$, 0.15, 0.20) alloys prepared as discussed above were used for growing single crystals by zone melting method. The starting ingot was about 6 cm in length and 0.8 to 1 cm in diameter. First the ingot was zone leveled. The temperature gradient across the two solid – liquid interfaces was obtained to be about 65 °C/cm by controlling the furnace temperature within $\pm$ 1 °C, giving a zone length of about 1-2 cm.

To level off impurities, 10-25 passes in alternate directions were given and finally the last pass was used to obtain self-nucleated single crystals. To obtain good quality crystals, it was found necessary to give sufficient time to the first molten zone before starting the zone travel to achieve stable conditions. Single crystals grown by the zone melting method after 25 zone leveling passes at the growth speed of 0.35 cm/hr were used for the micro hardness study. The crystals have good planar cleavage along (111) and the tests were carried out on the freshly cleaved (111) surfaces of the crystals. The indentations were performed at a very slow rate and for all indentations, care was taken to see that the rate was nearly the same. Also, between two neighboring indentation marks on the same surface, a separation of at least three indentations was maintained to avoid interference.

Thin films were prepared from the material so obtained, on (001) face of NaCl crystal as the substrate using thermal evaporation method under a pressure of 10^{-4} Pa at room temperature, i.e., 313 K, using the vacuum coating unit model 12A4 (Hind Hivac, Bangalore). The thickness of the film was measured using Tolansky's [9] multiple beam interferometric technique. For optical study, the films coated on NaCl were used in the sample chamber of a FTIR spectrophotometer (Bomem, Canada) with wave number resolution 4 cm^{-1}.

3. RESULTS AND DISCUSSION

The optical absorption was measured in the wave number range 500 cm^{-1} to 4000 cm^{-1}. The absorption coefficient α was calculated as a function of photon energy $h\nu$ from absorbance versus wave number curve. The plots of $(\alpha h\nu)^2$ versus hν ıwere used to evaluate the optical gaps. The extrapolation of the linear portion on the high energy range to zero abscissa gives the band gap [10].

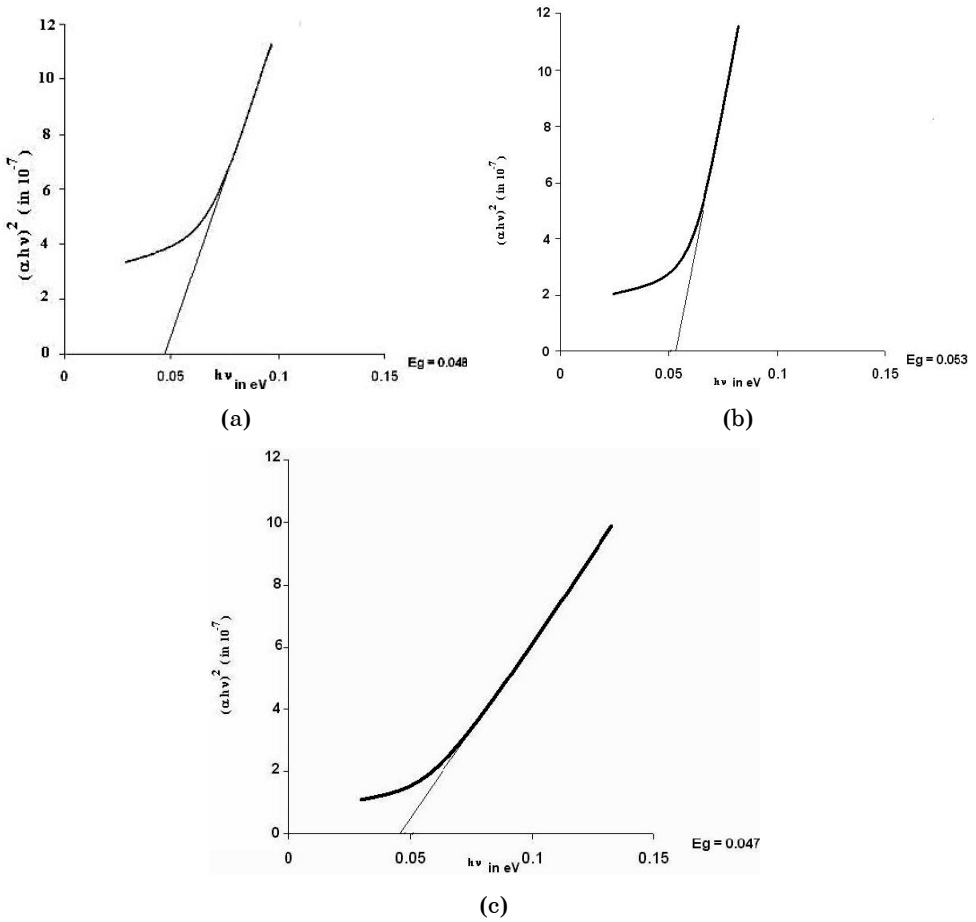

Fig. 1 *– Plot of* $(\alpha h\nu)^2$ *versus* $h\nu$ *:* $Bi_{90}Sb_{10}$ *(a),* $Bi_{85}Sb_{15}$ *(b) and* $Bi_{80}Sb_{20}$ *(c)*

The typical plots are shown in Fig. 1a, b, c for films of $Bi_{0.9}Sb_{0.1}$, $Bi_{0.85}Sb_{0.15}$ and $Bi_{0.8}Sb_{0.2}$ with thicknesses 180 nm, 150 nm and 160 nm obtained at 313 K, respectively. It can be seen that the plot is linear in the region of strong absorption near the fundamental absorption edge. Thus, the absorption takes place through direct transition. The band gaps E_g were evaluated in this way for films of different thicknesses t. The band gap variation with film thickness follows the relation [11]

$$E_z = \frac{\hbar^2\pi^2}{2m^*t^2}$$

where m* is the effective mass of the charge carrier, t is the thickness of the film and E_z is the kinetic energy contribution due to motion normal to the film plane. Accordingly, the plot of E_z vs. $1/t^2$ is found to be linear (Fig. 2 a, b and c).

This variation can be explained in terms of quantum size effect. This is usually defined as the dependence of certain physical properties of a solid on

its characteristic geometric dimensions when these dimensions become comparable to the de Broglie wavelength of the charge carriers [11-14], the concept basic to the nanoscience. Because of the finite thickness of the film,

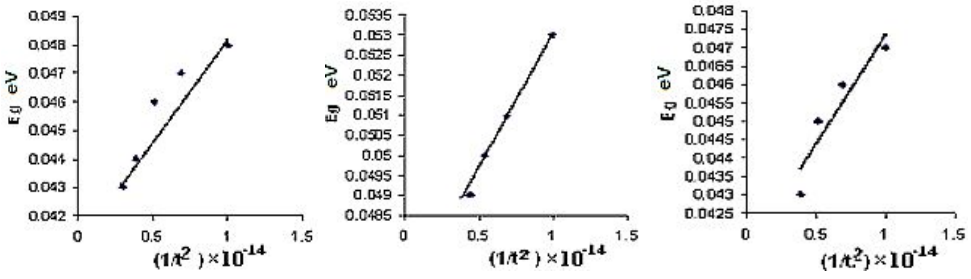

Fig. 2 *– Plot of E_z versus $1/t^2$: $Bi_{90}Sb_{10}$ (a), $Bi_{85}Sb_{15}$ (b) and $Bi_{80}Sb_{20}$ (c)*

the transverse component of quasimomentum is quantized. Therefore the electron/hole states assume quasidiscrete energy values in a thin film. As a consequence, the separation of valence and conduction bands increases by an amount E_z given by the above relation. The effective mass of holes calculated from the slope of the E_g vs. $1/t^2$ plot (assuming electrons to be heavy) is found to be $4.7 \times 10^{-4}\ m_0$, where m_0 is the electron rest mass. The de Broglie wavelength of the holes, estimated by taking the Fermi energy to be half of the average band gap, turns out to be about 210 nm. Thus a quantum size effect is expected to be exhibited by the films, in the thickness range used, viz., 100 nm to 1800 nm, particularly in the lower part of the range.

Films were also deposited at different substrate temperatures ranging from room temperature to 413 K. However, the band gap did not exhibit any variation in the average value of 0.044 eV, the average being over the films of different thickness.

4. CONCLUSIONS

The following main conclusions can be drawn from the present study.

1. Thin films of $Bi_{0.9}Sb_{0.1}$, $Bi_{0.85}Sb_{0.15}$, and $Bi_{0.8}Sb_{0.2}$ are observed to have direct band gaps of about 0.048, 0.053 and 0.047 eV, respectively, in close agreement with the studies done by Cho, DiVenere, et al. [15].
2. The films with thicknesses of about 103 nm or less exhibit the quantum size effect with respect to optical absorption.
3. The deposition temperature does not have a substantial effect on the optical band gap of these films.

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