Optostructural and electrical studies on chemically deposited Bi_2Se_3 thin films

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Abstract **- Bismuth selenide films are deposited by arrested precipitation technique at optimized preparative parameters using Bi-TEA and Na_2SeSO_3 as sources of Bi^{3+} and Se^{2-}. Bi_2Se_3 is p-type semiconductor and room temperature electrical conductivity is 1.88 $ohm^{-1}cm^{-1}$.The films are polycrystalline in nature. Optical absorption coefficient revealed a high absorption coefficient, with a direct type of transition. Composition measured by microprobe analysis is close to Bi_2Se_3.**

Keywords- Thin films; semiconductors; electron microscopy

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1. INTRODUCTION

Thin films of Bi_2Se_3 and its alloys find many applications such as in small scale thermoelectric power generator, thermopile, thermoelectric refrigerators, thermoelectric cooler, thermoelectric and optical recording materials [1]. Malhotra et al. [2] have observed that Bi_2Se_3 films are good contenders for phase change optical media and that the amorphous phase of these films is stable, their optical properties remain unaffected by normal environmental conditions. Several methods such as reactive evaporation [3], electrodeposition [4], solvothermal [5],SILAR [6] have been used for Bi_2Se_3 film preparation. A few reports are available on the preparation of Bi_2Se_3 thin films by chemical deposition [7,8]. M. Gracia et al. [9] reported chemical deposition method using different selenide ion releasing sources such as N, N –dimethyl selenourea.

In the present investigation, preparative parameters are optimized in order to obtain high-quality and well reproductive Bi_2Se_3 thin films. In this communication we report preliminary results on optical, structural and electrical properties of the Bi_2Se_3 films.

2. EXPERIMENTAL DETAILS

2.1. Preparation of bismuth selenide thin films

Bismuth selenide thin films have been prepared by an arrested precipitation technique [10] by allowing the Bi-TEA complex to react with Se^{2-} ions, which are released slowly by the dissociation of Na_2SeSO_3 in alkaline medium at pH 10.4. Glass slides of dimensions 75 mm x 25 mm x1.35 mm were used as substrates, the substrates were cleaned well subsequently using chromic acid, detergent, distilled water and dried prior to film deposition. Thoroughly cleaned glass substrates were mounted on a specially designed substrate holder. The substrate holder was attached to constant speed gear motor. The parameters such as time (90 min.), temperature of deposition bath (45 ^oC) and speed of substrate rotation (60 rpm) were optimized. After deposition, samples were taken out, washed with distilled water and kept in dark desiccators. The as-deposited Bi_2Se_3 films are specularly reflective and black in appearance when observed in white light.

2.2 Characterization of sample

After synthesizing the films, their optical, structural, morphological and electrical characterizations were performed. The optical study was performed in the range of wavelength between 350 to 850 nm using spectrophotometer (Hitachi model 330, Japan) at room temperature. X- ray diffraction (XRD) analysis was carried out using a Philips PW-1710 X-ray diffractometer for the 2θ ranging from 0^0 to 100^0 with Cu K_α line used as a beam ($\lambda = 1.5418A^0$)

The electrical conductivity of the films was studied by using two point D. C. probe method. As the contact resistance of the film is very low compared to film resistance, the two probe method is accurate and hence used for electrical conductance measurements. The area of the film was defined and silver was applied to ensure good electrical contact to the films. The working temperature was recorded using a Chromel-Alumel thermocouple. The potential drop across the film was measured with the help of Meco 801 digital multimeter and current passed through the sample was noted with a sensitive 4 digit picoammeter (Scientific equipment, Roorkee DPM 111).The measurements were carried out by keeping the film system in a light tight box, which was kept at room temperature.

Thermoelectric power measurement is carried out under the condition of maximum temperature difference and minimum contact resistance. The thermoelectric voltage was measured with digital Testronix micro voltmeter. A JEOL-JSM- 6360A electron microscope with an energy dispersive X-ray analysis (EDS) attachment is used to record the scanning electron microscopy micrograph (SEM) and EDS spectrum of the sample.

3. RESULTS AND DISCUSSION

3.1. Optical Studies

Optical absorbance measurement of the film was used to estimate the band gap energy from the position of absorption edge. Optical absorption coefficient (α) of the material is of the order of 10^4 cm^{-1}. Near the absorption edge α is given by

□ = A (h□ – E_g) $^{n/2}$ / h□

Where A is an energy dependent constant, hν is photon energy and n=1 for direct band gap materials. The optical absorption data was used to plot a graph of $(\alpha h\nu)^2$ vs. hν.□The plot of $(\alpha h\nu)^2$ vs. hν yielded straight line at higher energies indicating direct type of transition. Extrapolation of the plot to the x-axis gives the energy band gap of the deposited film as shown in figure 1. The band gap determined from $(\alpha h\nu)^2$ vs. hνplots is found to be 1.73 eV. This is in good agreement with the literature data [9].

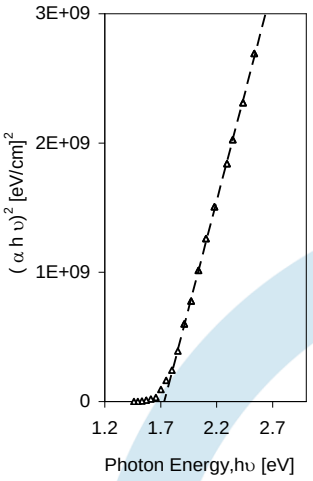

Fig.1. Determination of band gap.

3.2 XRD Studies

Figure 2 shows XRD patterns of the as deposited Bi_2Se_3 thin film. The deposited layers exhibited polycrystalline nature which is explained by the presence of (221) and (130) peaks. The plane indices are obtained by comparing the intensities and positions of the peaks with JCPDS data [11].

Table 1. Comparison of observed and standard 'd' values of Bi_2Se_3 film.

Standard 'd' values (A°)	Observed 'd' values (A°)	Reflection Plane (hkl)	I / I_{max} (%)
3.7341	3.7707	(130)	37.1
2.9112	3.0024	(221)	100

The structural analysis of the thin film indicates that the material crystallizes in the orthorhombic structure. The crystallite size of the film is calculated using Scherrer formula

Grain size= 0.9 λ / β cos θ

Where λ is the wavelength of the X-ray radiation used, β is the full width at half maximum and θ is Bragg angle. The crystallite size calculated for (221) reflection is 35.8 nm.

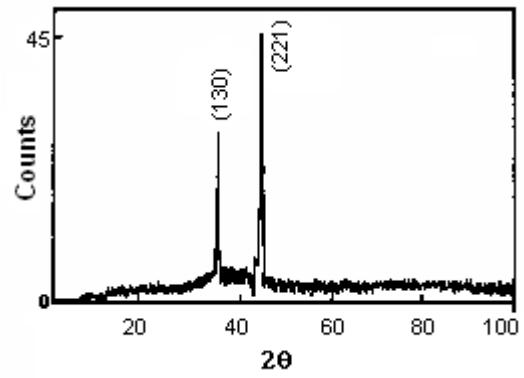

Fig. 2. X-ray diffraction pattern of as-deposited Bi2Se3 film.

3.3 SEM/ EDS studies

Figure 3 shows scanning electron micrograph of Bi_2Se_3 film in the as-grown condition. The microstructure of the films observed by SEM shows that the films are uniform, crack free and covered all over the surface area. The SEM micrograph of the sample shows more grain formation and well-defined particle edges. Some regions of overgrowth were also observed. All grains

having average size (970 nm) are composed of single type small densely packed crystals. The grains show an agglomerated morphology and appear very homogeneous.

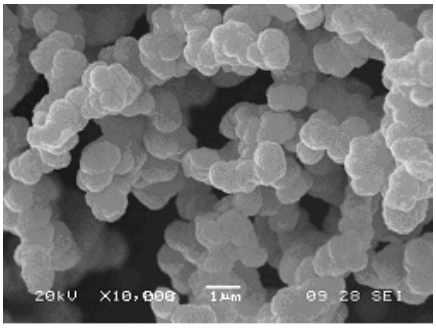

Fig.3. SEM micrograph of as deposited Bi_2Se_3 film.

To find the stoichiometry, atomic and elemental wt% of as deposited Bi_2Se_3 film was found by EDS. Figure 4 shows EDS spectrum of the as deposited Bi_2Se_3 thin films giving the elemental compositions of the samples. It contains 45.45% Bi and 54.55% Se.

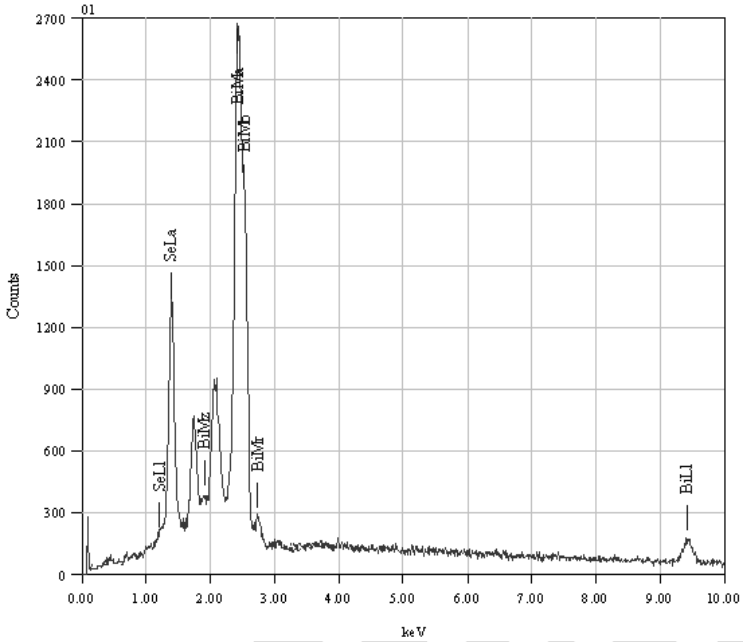

Fig.4. EDS spectrum of as deposited Bi_2Se_3 film.

3.4 Electrical / TEP studies

To examine the temperature dependence of the electrical conductivity in more detail, electrical conductivity measurement was made in the temperature range 300 K to 500 K under constant voltage (5 volt). The temperature dependence of electrical conductivity of the semiconducting thin films is given by,

$$\square = \square_{\square} e^{(-Ea/\square T)}$$

Where E_a is conductivity activation energy, κ is Boltzmann constant and σ_0 is the temperature independent part of the conductivity. The variation of log $\square$ with 1 / T in the temperature range 300 K to 500 K is shown in figure 5.The linear variation of the plot confirms the semiconducting nature of the film. The plot reveals that there two regions: one below 445 K, where the conductivity varies slowly with 1 / T and other above 445 K, where the conductivity varies abruptly with temperature. The activation energy for conduction in low temperature region is the energy required to take place between the defect level and valence bond or conduction band. At sufficiently high temperature intrinsic conductivity starts and electron conduction from valence bond to conduction band take place. From the slopes of linear plots, activation energy for conduction was calculated for two temperature region. The activation energy for low temperature region 0.369 eV and in high temperature region is 0.863 eV.

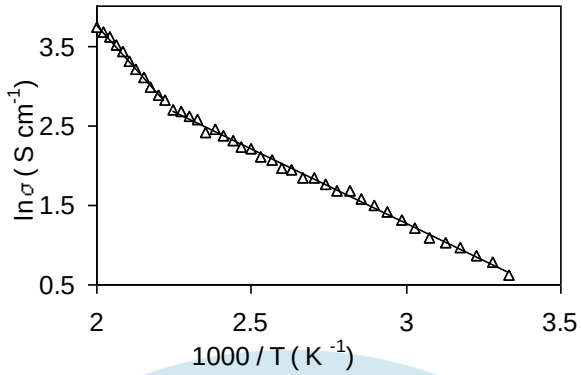

Fig.5. Temperature dependence of the d. c. conductivity for Bi_2Se_3 film.

The n-type character is most common in most of the bismuth selenide based compounds [12] while rarely p-type material is reported [13,14] . The Seebeck coefficient of Bi_2Se_3 thin films is quite high, positive and increases with increasing temperature. The positive sign stems from a dominance of p-type charge carriers. The temperature dependence the Seebeck coefficient of as deposited Bi_2Se_3 film is shown in Figure 6.

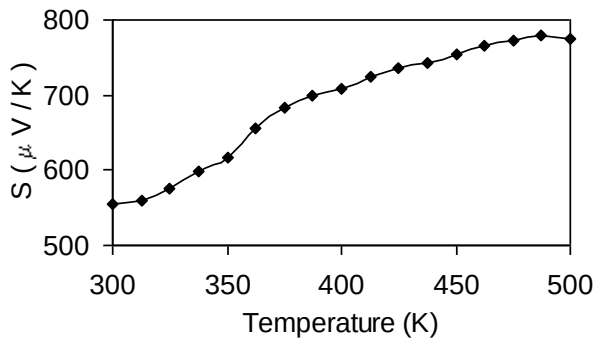

Fig.6. Temperature dependence of the Seebeck coefficient of Bi_2Se_3 film.

4. CONCLUSION

Good quality films of thickness 0.34 μm containing Bi and Se in an approximately 2:3 atomic ratio have been deposited successfully by arrested precipitation technique. The technique is simple and requires less monitoring. X-ray diffraction patterns confirmed the proper phase formation of the material. The films are mechanically stable since no cracks are observed in the low magnification image (10,000 X). Activation energy is different for low and high temperature. Bi_2Se_3 exhibits a p-type semiconducting behavior with a low electrical conductivity and very high thermopower.

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