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Growth of multilayer Bi_2Se_3-Sb_2Se_3 thin films by SILAR technique

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The successive ionic layer adsorption and reaction (SILAR) technique is well suited for producing large area thin films, as they are required in solar energy related applications. It is applied for the growth of multilayer Bi_2Se_3-Sb_2Se_3 thin films onto glass substrates. The preparative parameters are optimized to get multimonolayers of Bi_2Se_3-Sb_2Se_3 of terminal thickness ~ 0.185 µm. Structure, surface morphology, optical band gaps and electrical resistivity of the Bi_2Se_3-Sb_2Se_3 thin films are studied. Structural study by X-ray diffraction shows that multilayer Bi_2Se_3-Sb_2Se_3 thin film formation is possible by SILAR technique. Scanning electron microscopy and atomic force microscopy studies show that films formed are nanocrystalline. The optical band gap was estimated to be 1.57 eV using optical absorption studies, which lies between the individual band gaps of Bi_2Se_3 and Sb_2Se_3. The dark electrical resistivity is found to be of the order of 10^5 Ω-cm.

Compounds of the column V-B (As, Sb, Bi) and VI-B (S,Se,Te) elements in the periodic table with chemical formulas $M^{V\text{-}B}{}_2\ N^{VI\text{-}B}{}_3$ basically have the crystal structure of antimony sulphide. The energy gap of these compounds has been found to range from 1.88 eV for Sb_2Se_3 to 0.16 eV for the Bi_2Te_3 [1,2]. As the atomic number of the compound increases, the energy gap decreases. These materials act as semiconductors. Some of their compounds have been of interest in the study of photosensitivity, photoconductivity and thermoelectric power[3-5]; Bi_2Se_3 and Sb_2Se_3 compounds are the members of the above group of materials. Number of methods have been employed for the deposition of Bi_2Se_3[6-9] and Sb_2Se_3[10-12] compound thin films. The band gap of single crystalline Bi_2Se_3 was reported earlier as E_g=0.35 eV[13] which lies in the near infrared region (within the wavelength range of 850-2000 nm). To make it in the visible region (within wavelength of 350-850 nm) of solar spectrum, another compound like Sb_2Se_3, whose band gap is E_g = 1.88 eV[2] is mixed with Bi_2Se_3, so that the combination of two gives better results in application such as photosensitivity and photoconductivity. Hence, efforts are made to deposit Bi_2Se_3-Sb_2Se_3 thin films by simple and less expensive successive ionic layer adsorption and reaction (SILAR) technique. Reports are available on such thin film combinations as CdS-Cu_xS[14], PbS-Cu_xS[15] and Bi_2S_3-Cu_xS[16] and have illustrated or suggested their applications in the area of energy conservation and solar energy utilization[17, 18].

In the present investigation, it is our interest to use SILAR method to the growth of multilayer Bi_2Se_3-Sb_2Se_3 thin films. The preparative parameters such as concentration, immersion cycle, immersion time etc. are optimized to get good quality and well adherent thin films. Optimised films are characterised by means of X-ray diffraction, scanning electron microscopy, atomic force microscopy, optical absorption and electrical measurements.

Experimental Procedure

Materials

S. D. fine analytical reagent grade bismuth nitrate pentahydrate [$Bi(NO_3)_3.5H_2O$], potassium antimony tartrate [$K(SbO)C_4H_4O_6$], triethanolamine (TEA) [$N(CH_2C(H_2OH)_3$], anhydrous sodium sulphite (Na_2SO_3) of analytical reagent quality products Loba, and sodium selenosulphite [Na_2SeSO_3], prepared in our laboratory following the method reported earlier[19], were used in the deposition of thin films. Corning glass microscope slides of 76 mm × 26 mm × 1 mm were used as substrates. The substrates were cleaned well using detergent, double distilled water and finally by ultrasonic cleaner.

Deposition procedure

For the deposition of Bi_2Se_3 - Sb_2Se_3 thin films the deposition of single layer of Sb_2Se_3 over Bi_2Se_3 repeatedly was followed.

For the deposition of Bi_2Se_3 cationic precursor solution was 0.01 mol. L^{-1} bismuth nitrate complexed with TEA. The *p*H of the precursor solution was 8. The source for anionic pressure was 0.1 mol. L^{-1} sodium selenosulphite with *p*H ~ 8.5. For the deposition of Bi_2Se_3 thin films, well cleaned substrates were immersed in cationic precursor solution (bismuth nitrate) for 60 s. Bismuth ions get adsorbed on the substrate surface. The substrate was rinsed in flowing distilled water for 40 s to remove loosely bound or excess bismuth ions. The conductivity of rinsing water was under 1 $\mu\Omega^{-1}cm^{-1}$ and flow rate was 400 mL. min^{-1}. Then the substrate was immersed in anionic precursors solution (sodium selnosulphite) for 60 s. The selenide ions reacted with pre-adsorbed bismuth ions to form a layer of Bi_2Se_3. The unreacted or unabsorbed Se^{2-} ions or powedery Bi_2Se_3 material was separated out by rinsing the substrate again in the flowing water for 40 s. This completes one Bi_2Se_3 layer formation. Over this Bi_2Se_3 layer , by performing similar procedure, Sb_2Se_3 layer was formed , which resulted into the formation of Bi_2Se_3-Sb_2Se_3 layer. Such SILAR cycles were repeated by using subsequent Bi_2Se_3 and Sb_2Se_3 one over another for 350 times, multilayer Bi_2Se_3-Sb_2Se_3 film of terminal thickness ~ 0.185 μm was obtained. The experiment was performed at room temperature 300 K. The adsorption, reaction times were optimized experimentally. The deposition occurred layerwise and resulted in homogeneous thin film structure. The optimized conditions used for multilayer Bi_2Se_3-Sb_2Se_3 are depicted in Table 1.

Characterization of films

The Bi_2Se_3-Sb_2Se_3 thin films were characterized by means of XRD, SEM, AFM, optical absorption and electrical resistivity measurement techniques.

X-ray diffraction pattern of the film was recorded on a Philips – PW 3710 model X-ray diffractometer in the range of scanning angles 10-100° (2θ) with Cu-K_α radiation. The wavelength used was 1.5406 Å. The surface morphology of the film was scanned by using the SEM unit. (LEICA S 440 i) and AFM unit (digital nanoscope). The optical absorption spectra of the films were recorded on Hitachi 330 (Japan) UV-VIS-NIR spectrophotometer. The electrical resistivity measurement of the film was carried out using a d.c. two point probe method. The film area (~ 0.5 cm^2) was defined and a silver paste was applied to ensure good ohmic contact to the film. A chromel alumel thermocouple was used to measure the temperature.

Table 1—Optimized deposition conditions for the preparation of multilayer Bi_2Se_3-Sb_2Se_3 thin film.

Parameters	Bi_2Se_3		Sb_2Se_3	
	Cationic	Anionic	Cationic	Anionic
Sources	bismuth nitrate	sodium seleno-sulphite	potassium antimony tartrate	sodium seleno-sulphite
Concentration	0.01	0.1	0.2	0.1
*p*H ~	8	8.5	5	8.5
Immesion time (s)	60	60	60	60
Ringing time (s)	40	40	40	40
Temperature (K)	300	300	300	300

Results and Discussion

Growth rate

Multilayer thin film Bi_2Se_3-Sb_2Se_3 was grown onto glass substrate under optimized deposition conditions shown in Table 1. Fig. 1a shows the plot of thickness versus growth cycle of SILAR grown multilayer Bi_2Se_3-Sb_2Se_3 thin film. The film thickness increases linearly up to 350 cycles of Bi_2Se_3-Sb_2Se_3 . Film formation starts after 50 cycles, and reaches a maximum value at 350 cycles, this maximum value of thickness may termed as 'Terminal thickness' Upto 350 cycles, the inner compact layer of Bi_2Se_3-Sb_2Se_3 film formation takes place giving a terminal thickness and after 350 cycles the thickness goes on decreasing due to the formation of outer porous layer of Bi_2Se_3-Sb_2Se_3 . The nominal growth per one cycle was 0.55 nm $cycle^{-1}$ during the first 200 cycles which decreases slightly for further deposition cycles (Fig. 1b).

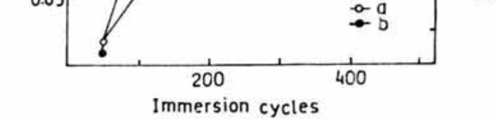

Fig. 1(a)—Variation of thin film thickness with number of immersion cycles for Bi_2Se_3-Sb_2Se_3 thin film and (b) The normal growth rate versus growth cycle for Bi_2Se_3-Sb_2Se_3 multilayer thin film.

Structural studies

X-ray diffraction pattern of as grown thin film of about 185 nm thick Bi_2Se_3-Sb_2Se_3 layer onto glass substrate is shown in Fig. 2. The higher base line from 15-35° is due to the amorphous glass substrate. Detected reflections are hexagonal (006) Bi_2Se_3 and orthorhombic (520) Sb_2Se_3 as compared with standard '*d*' values[20,21]. This confirms multilayer Bi_2Se_3-Sb_2Se_3 film formation by SILAR technique, of rather mixed or a ternary system. This type of multilayer CdS/ZnS film formation is reported earlier by Valkonen *et al.*[22] by the SILAR technique. The Bi_2Se_3-Sb_2Se_3 , films obtained are amorphous or consisting of fine grains.

Surface morphology

Scanning electron microscopy and atomic force microscopy studies are well suited for surface morphological studies.

Fig. 3 shows the scanning electron micrograph of the Bi_2Se_3-Sb_2Se_3 film at magnification 20,000 ×. Films are found to be nanocrystalline. The estimated grain size was between 50 –55 nm by using Cottrell's method[23].

Fig. 4 shows the tapping mode AFM (TM AFM) image of the Bi_2Se_3-Sb_2Se_3 film onto glass substrate. The grain shape is found to be spherical one. The average grain size was calculated as 60-70 nm which gives support to grain size estimated from SEM study.

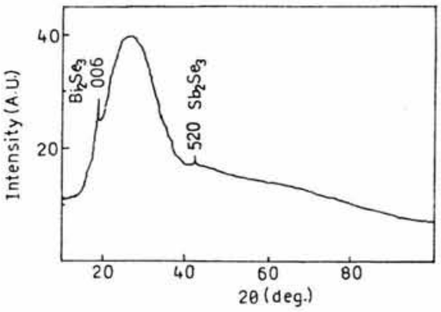

Fig. 2—XRD pattern of as deposited Bi_2Se_3-Sb_2Se_3 thin film onto glass substrate.

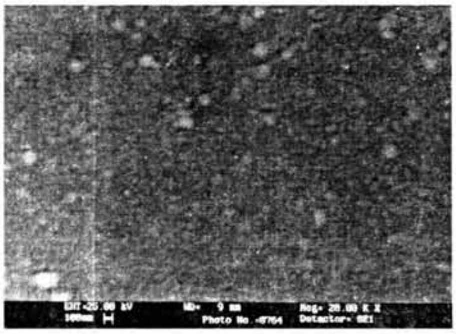

Fig. 3—Scanning electron microphotograph of Bi_2Se_3-Sb_2Se_3 thin film at magnification 20,000 X.

Optical absorption studies

Optical study of multilayer Bi_2Se_3-Sb_2Se_3 film onto glass substrate has been carried out within the wavelength range 350-2000 nm. The variation of absorption coefficient against wavelength is shown in Fig. 5 in the 350-850 nm wavelength range. The absorption coefficient is of the order of 10^{-4} cm $^{-1}$. The variation of $(\alpha h\nu)^2$ against $h\nu$ is depicted in Fig. 6 The straight line portion of the plot indicates band allowed transition. On extrapolating the straight line to the energy axis at $\alpha = 0$, gives band gap energy E_g = 1.57 eV. The band gap of Bi_2Se_3-Sb_2Se_3 obtained is

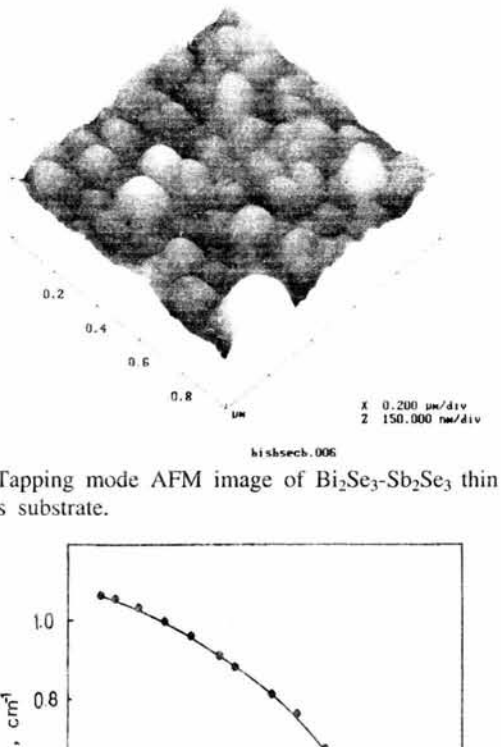

Fig. 4—Tapping mode AFM image of Bi_2Se_3-Sb_2Se_3 thin film onto glass substrate.

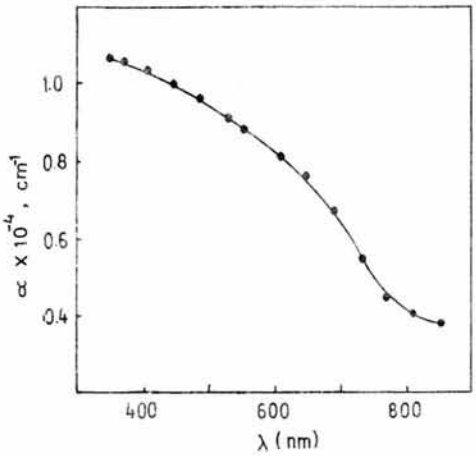

Fig. 5—Plot of absorption coefficient against wavelength for Bi_2Se_3-Sb_2Se_3 film onto glass substrate.

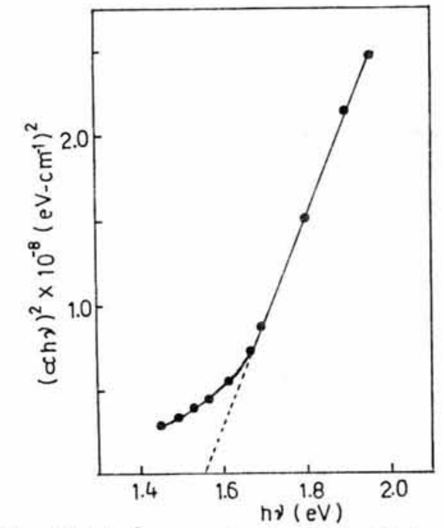

Fig. 6—Plot of $(\alpha h\nu)^2$ versus $h\nu$ for Bi_2Se_3-Sb_2Se_3, thin film [derived from Fig. 5]

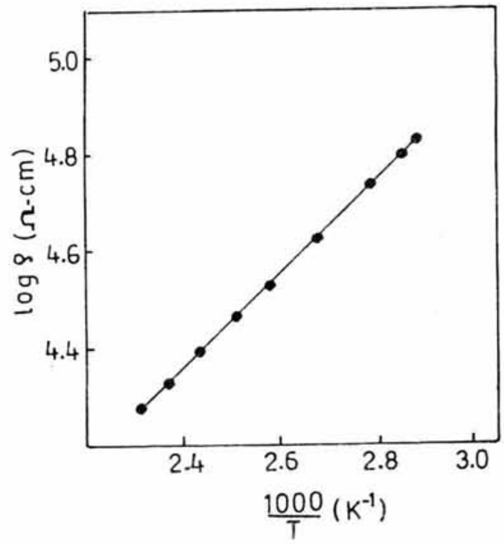

Fig. 7—Plot of log of resistivity with ($1/T$) for Bi_2Se_3-Sb_2Se_3 thin film.

in between the reported value of Sb_2Se_3 (1.88 eV)[2] Bi_2Se_3 (0.35eV)[13] and lies in the visible spectrum of solar energy.

Electrical resistivity

The dark electrical resistivity measurement was carried out in the temperature range 323-448 K using a d. c. two point probe method, since above 448 K temperature, loss of appreciable amount of selenium is observed, similar to the selenium loss observed for vacuum deposited In_2Se_3 [24-26] films as reported earlier. The room temperature resistivity of Bi_2Se_3-Sb_2Se_3 films is of the order of 10^5 Ω-cm. Variation of log of resistivity with inverse of temperature is shown in

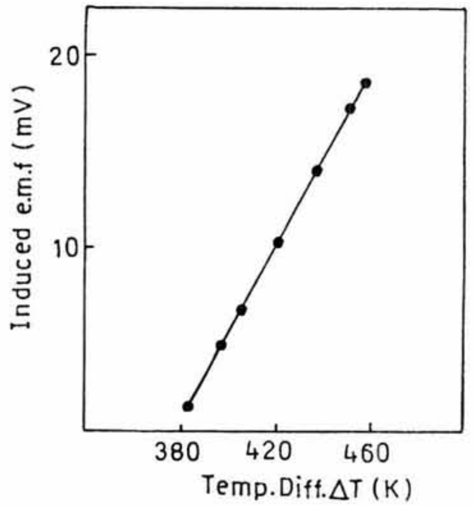

Fig. 8—Plot of induced emf against temperature difference (ΔT) for Bi_2Se_3-Sb_2Se_3 thin film.

Fig. 7. The decrease in electrical resistivity with increase in temperature suggests semiconducting behaviour of Bi_2Se_3-Sb_2Se_3 film. The activation energy is found to be 0.17 eV. The activation energy represents the average energy of carriers with respect to the fermi-energy, if carriers can move only at the bottom or top of the well defined bands.

Thermo e.m.f.

Fig. 8 shows that the thermo e.m.f. (electromotive force) generated in the film varies linearly in the temperature range (323-448 K). Positive polarity of the generated thermoelectric voltage suggests that the conduction in the film is *n* type, which is in good agreement with the conductivity of Bi_2Se_3[9] and Sb_2Se_3[27] thin films. The observed value of TEP is 4.13 mV/K.

Conclusions

Multilayer Bi_2Se_3 - Sb_2Se_3 film formation is possible by simple and less expensive successive ionic layer adsorption and reaction (SILAR) technique, as seen from XRD study. SEM and AFM images show that the films are nanocrystalline in nature. The optical band gap (1.57eV) lies between individual band gaps of Bi_2Se_3 and Sb_2Se_3 . The dark electrical resistivity is of the order of 10^5 Ω -cm, with *n*-type electrical conductivity.

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