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Studies on Electrical and Optical Properties of Annealed and Unannealed Nanocrystalline Bismuth Sulphide Thin Films Prepared by Chemical Bath Deposition

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ABSTRACT

Thin films of nanocrystalline bismuth sulphide were deposited on a chemically cleaned glass substrate from solution containing bismuth nitrate, triethanolamine (TEA) and thioacetamide. The mixture solution was heated at 318 K for 20 min and the resultant solution changes to dark brown. Characterization of the prepared films was carried out by XRD, optical absorption, electrical conductivity and hot probe measurement. XRD studies revealed that bismuth sulphide films consisted of nanocrystalline grains. Average crystallite size calculated from the XRD spectra of both annealed and unannealed films were found to be 24 and 21 nm, respectively. The optical band gap obtained from the absorption spectra of annealed and unannealed Bi_2S_3 films was found to be 2.05 and 2.1 eV, respectively. With an increase in grain crystallite size of Bi_2S_3, a shift of 0.05 eV in the optical band gap energy E_g was observed. From log (σ) vs 1/T curve, the activation energies at low and high temperatures for annealed films were found to be 0.463 and 3.39 eV and for unannealed films were found to be 0.455 and 2.94 eV, respectively. The electrical conductivity was found to be in the order of 10^{-3} Ω^{-1} m^{-1}. The films were found to be n-type as determined by hot-probe method.

Key words: Nanocrystalline, bismuth sulphide, XRD, electrical conductivity, optical absorption

INTRODUCTION

Recently, research on nanocrystalline semiconducting thin films has been considerably increased due to their potential applications in solar cells and other electronic devices. The optical and electrical properties of the materials changes by changing grain size. These unique properties are required for the development of modern electronic devices. Among the various semiconductor compounds, Bi_2S_3 is considered as an important material because of its unique properties. Bi_2S_3 belongs to group V-VI compound semiconductor with wide band gap energy 1.7 eV which lies in the visible solar energy spectrum (Lokhande, 1991) and could be increased to higher energy by reducing the grain size. Several researchers have reported for the preparation of nanocrystalline Bi_2S_3 thin films using different techniques such as cathodic electrodeposition (Lokhande and Bhosale, 1990) anodic electrodeposition (Miller and Heller, 1976), vacuum evaporation (Mahmoud, 1996), solution gas interface (Pawar and Bhosale, 1986; Pawar *et al.*, 1983), spray pyrolysis (Killedar *et al.*, 1996) and chemical deposition (Cullity, 1978; Sonawane and Patil, 2007; Lokhande *et al.*, 1997; Sheng-Cong *et al.*, 2006). Among the above mentioned techniques chemical bath deposition is preferred because it is simple, economic and convenient for large area deposition

and does not require sophisticated instruments. In this process, the film growth can take place by ion-by-ion condensation of the material on the substrates or by adsorption of the colloidal particles from the solution onto a substrate (Sonawane and Patil, 2007). The films obtained in this process are smooth and more adherent to the glass substrate.

In the present study, Bi_2S_3 thin films have been prepared at 318 K by chemical bath deposition technique using TEA as complexing agent. In this study we report the structural, electrical and optical properties of the annealed and unannealed Bi_2S_3 thin films.

MATERIALS AND METHODS

For the preparation of Bi_2S_3 thin films, 5 mL of 0.5 M bismuth nitrate dissolved in 2 mL of TEA was used as Bi^{+3} sources and 4 mL of 1 M thioacetamide solution was used as S^{-2} sources. Both the solution were mixed together and stirred for few minutes to get uniform mixture solution. Finally, distilled water was added to the resultant solution to obtain a total volume of 50 mL. Before deposition of the films, the glass substrates were chemically cleaned using Nitric acid and iso-propanol and finally ultrasonically cleaned in distilled water for 1 h. The chemically cleaned glass substrates were treated in 0.05 wt% of tin chloride solution for 20 min, rinsed in distilled water and heated at 473 K in oven. The treated glass substrates were dipped vertically in the resultant solution and heated at 318 K for 20 min. The resultant solution changes from brown to dark brown colour which indicates the initiation of Bi_2S_3 films formation. The solution was kept at room temperature for 2 h for further deposition. The Bi_2S_3 films were removed from the solution and washed with distilled water several times. The films were coated on both side of the glass substrate. The films facing towards the wall of the beaker were retained for further studies and the other sides were removed with dilute nitric acid. The average thickness of the film was measured by the Tolansky method. For this a highly reflecting film of 'Al' is vacuum deposited on the glass substrate containing the film whose thickness is to be determined, so that it overcoats a part of the film and covers a part of the bare glass substrate thus making a step. The height of the step is the thickness of the film. The glass substrate supporting the film with a step is placed on a specially designed holder inclined with another glass plate carrying a semi-transparent film, thus forming a wedge-shaped air film between the two plates. When parallel monochromatic light is allowed to fall normally, dark fringes with displacement or stepper can be observed with a microscope. Thus, the film thickness is calculated from the equation:

$$t = \frac{\lambda D}{2d} \tag{1}$$

where, D is the fringe shift and d is the fringe width and λ is the wavelength of sodium light. The structural characterization of Bi_2S_3 thin films was carried out by analyzing the X-ray Diffraction (XRD) patterns obtained using a XPERT PRO Philips (λ = 1.5405 A° for Cu K_α radiation). X-ray Fluorescence Study (XRFS) was done using AXIOS spectrometer (DY 840) for elemental analysis of the as prepared films. For electrical conductivity measurement 'Al' electrodes in a co-planar configuration separated by a small gap were evaporated in vacuum on the surface of the Bi_2S_3 thin films. A constant voltage was applied across the sample and the current was noted using a Keithley electrometer. The type of electrical conductivity was determined by hot probe technique (Golan *et al*., 2006).

RESULTS AND DISCUSSION

Structural analysis: The X-ray diffraction patterns of the annealed and unannealed Bi_2S_3 thin film prepared at bath temperature 318 K are shown in Fig. 1. The observed 'd' spacings corresponding to the prominent peak (020) (120) (310) (211) (221) (410) (420) (431) and (631) planes are in good agreement with the JCPDS (ASTM data file No. 17-320) data. Therefore, it has been concluded that the deposited Bi_2S_3 thin films are polycrystalline in nature with orthorhombic structure. From the Fig. 1 the intensity of (310) peak is higher as compared with other intensities peaks. This indicates that the orientation of the grain growth is preferably along (310) direction. The average crystallite size were calculated using the Scherrer's formula (Cullity, 1978):

$$d = \frac{0.94\lambda}{\beta\cos\theta} \tag{2}$$

where, λ is the X-ray wavelength used, β is the angular line width at half maximum intensity and θ is the Bragg's angle. The average crystallite size of the annealed and unannealed Bi_2S_3 films were found 24 and 21 nm, respectively.

X-ray fluorescence: XRF spectra give the confirmation of presence of Bi and S in the unannealed Bi_2S_3 films as shown in Fig. 2. The presence of Bi is indicated by the distinct peaks $Bi_{M\alpha}$ and $Bi_{M\alpha 1}$ and S is indicated by $S_{K\alpha}$. The figure also shows another peak for the presence of 'Cl' which is believed to be due to the glass substrate.

Optical studies: Optical absorption study provides some characteristics on the band structure of the materials. In the present investigation optical absorption of annealed and unannealed Bi_2S_3 thin films were studied in the wavelength range of 360 to 900 nm as shown in Fig. 3a. The optical absorption edge of annealed sample shows a red shift. This indicates that the crystallite size increased after annealing. The nature of the transition (direct or indirect) is determined by using the known relation (Pankove, 1971):

$$\alpha = \frac{A(h\upsilon - E_g)^n}{h\upsilon} \tag{3}$$

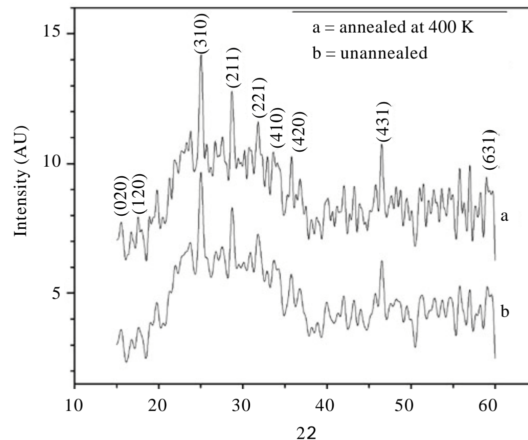

Fig. 1: X-ray diffractogram of annealed and unannealed Bi_2S_3 thin film

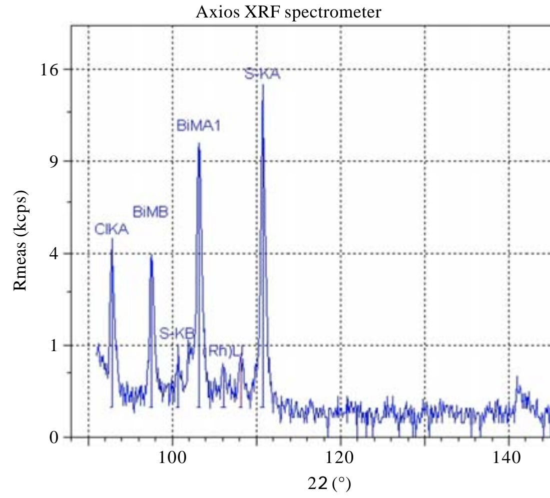

Fig. 2: X-ray fluorescence of unannealed Bi_2S_3 thin film

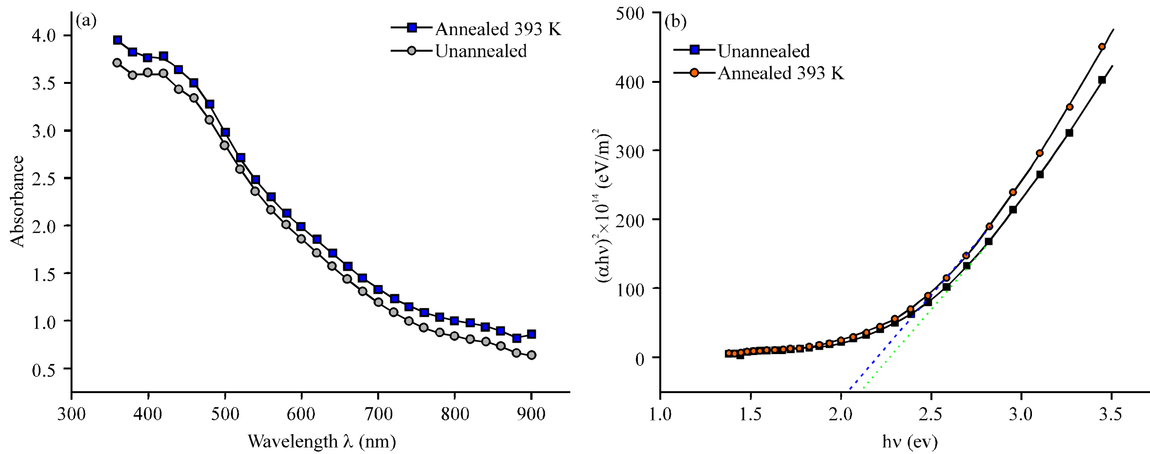

Fig. 3(a-b): (a) Plots of optical absorption (αt) vs. wavelength (λ) for unannealed and annealed Bi_2S_3 thin film and (b) Plots of $(\alpha h\nu)^2$ vs. hν for unannealed and annealed Bi_2S_3

where, hν is the photon energy, E_g is the band gap, A and n are constant. For allowed direct transition n = ½ and for allowed indirect transition n = 2. The plots of $(\alpha h\nu)^2$ vs. (hν) of the two sample of Bi_2S_3 thin films are shown in Fig. 3b. The linear nature of the plots indicates the existence of the direct transitions. The band gap E_g is determined by extrapolating the straight portion of the plot to the energy axis. The band gap determined from the Fig. 3b is found to be 2.05 and 2.1 eV for annealed and unannealed Bi_2S_3 thin films respectively. This is because of improvement in crystallinity and decrease in the defects levels of the Bi_2S_3 films after annealing.

Electrical conductivity: The electrical conductivity in dark of the annealed and unannealed Bi_2S_3 thin films using Al electrode was studied in the temperature range of 300 to 423 K. Figure 4 shows the variation of log (σ) vs. 1000/T plots for both films. The electrical conductivity of both the

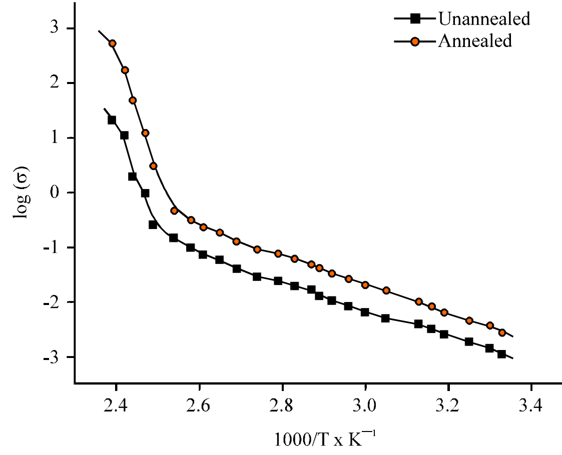

Fig. 4: Plots of log (σ) vs. 1000/T for unannealed and annealed Bi_2S_3

Table 1: Electrical conductivity, activation energy, crystallite size and band gap values of Bi_2S_3 thin films

	Activation energy (eV)				
Sample	High temperature region	Low temperature region	Room temperature electrical conductivity (Ω^{-1} m^{-1})	Crystallite size (nm)	Band gap (eV)
Annealed Bi_2S_3 thin film	3.39	0.46	2.735×10^{-3}	24	2.300
Unannealed Bi_2S_3 thin film	2.94	0.45	1.088×10^{-3}	21	2.403

films at room temperature was found to be of the order of 10^{-3} Ω^{-1} m^{-1}. The thermal activation energy was calculated using the relation (Hussain *et al*., 2010):

$$\sigma = \sigma_o e^{\frac{-E_a}{2kT}} \tag{4}$$

where, E_a is the activation energy, σ_o is a constant, k is the Boltzman's constant and T is the absolute temperature. The calculated activation energies in the lower and higher temperature of both the annealed and unannealed Bi_2S_3 films were shown in Table 1. These energy levels are thought to be associated with defect levels within the band gap. From thermo EMF measurements it was found that the polarity of the thermally generated voltage at the hot end was positive, indicating that the Bi_2S_3 thin films was n-type.

CONCLUSION

From the results reported, nanocrystalline Bi_2S_3 thin films were successfully prepared by chemical bath deposition technique. The crystallite size and electrical conductivity of the annealed films increases in comparison with the unannealed films. The optical bandgap decreased from 2.1 to 2.05 eV on annealing. The prepared films were of n-type as determined by the hot probe method. The electrical conductivity of both the films at room temperature was found to be of the order of 10^{-3} Ω^{-1} m^{-1}.

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