OPTICAL AND ELECTRICAL STUDIES ON THERMALLY EVAPORATED Sb_2S_3 THIN FILMS

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Sb_2S_3 (Antimony Sulphide) thin films were grown on pure glass and Indium Tin Oxide (ITO) coated glass substrates at room temperature by thermal evaporation technique. The optical and electrical properties of the Sb_2S_3 thin films were influenced by the thermal treatment. Optical transmission spectra in the spectral range 860 - 330nm before and after heat treatment have been used to study the optical properties of these films. The estimated direct band gap energies for as-deposited and annealed (473K, 523K) films of Sb_2S_3 on glass are 2.43eV, 1.97eV, 1.58eV respectively. Band gap energy for as-deposited Sb_2S_3 film on ITO is 2.19eV. The investigations on dielectric properties and impedance analysis have been done in the frequency range 100 KHz – 10MHz for Sb_2S_3 films on glass substrates and the influences of both temperature and frequency on these properties evaluated.

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Keywords: Sb_2S_3, Antimony Sulphide, ITO, Thermal Evaporation, Annealing, Optical studies, Electrical studies, Band Gap.

1. Introduction

Antimony Sulphide is a semiconducting chalcogenide of the V_B and VI_B groups of elements. Due to its attractive photo conducting properties and high thermoelectric power, Sb_2S_3 has wide industrial applications such as target material in television camera, microwave devices, switching devices and optoelectronic devices [1]. Some physical properties like photoelectric properties [2] and the conduction and charge carrier transport mechanism [3] have been reported in literature. The optical properties of amorphous and annealed chalcogenides have been observed and investigated by N. Tigau et al. [4] Nicolae Tigau [5] and R. S. Mane et al. [6]. In recent years, the manufacture of photovoltaic cells, solar cells and photoelectrochemical cells has increased dramatically due to the growing need for renewable energy sources. The band gap of the material determines what portion of the solar spectrum absorbs by these cells. Absorption take place only if the photon energy is greater than the energy gap ($h\nu > Eg$). The electrical property of semiconductors depends on the chemical composition and the structural features. Dielectric measurements of amorphous chalcogenide semiconductors have been used to understand the conduction process in these materials.

In this paper we report the investigations on the optical properties of as-deposited and annealed Sb_2S_3 thin films of thickness 17nm coated on pure glass and of thickness 300nm on Indium Tin Oxide (ITO) coated glass substrates and electrical properties and impedance analyses of Sb_2S_3 thin films of thickness 300nm coated on pure glass substrates. The present study has two purposes: to observe the band gap changes with two temperatures and to compare the optical properties of Sb_2S_3 on pure glass and on Indium doped Tin Oxide (ITO) coated glass substrates.

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2. Experimental

Thin films of Sb_2S_3 have been prepared onto glass and Indium doped Tin Oxide (ITO) coated glass substrates (Resistivity: < 12 ohm-cm, thickness: 150nm, MACWIN India) by physical vapour deposition technique from high purity polycrystalline powder (99.999% purity, Sigma-Aldrich), using a coating unit. The vacuum pressure was maintained at 10^{-5} torr and the substrates were rotated during the deposition process. The substrate temperature was maintained at 300K during the deposition. The film thickness and deposition rate of the prepared film were controlled by quartz oscillator thickness monitor. X-ray diffraction analysis revealed the amorphous nature of the structure of the films prepared at room temperature and the polycrystalline nature of the films annealed for 1h at 523K in vacuum with the pressure of 10^{-6} torr. The optical properties of the films were determined from the transmission spectra by using a dual beam UV-VIS-NIR spectrometer (Perkin Elmer Model Lambda 950). The optical transmittance of the samples was measured at room temperature with unpolarised light at normal incidence in the wavelength range 330 to 860nm. By using Impedance analyzer, a. c. measurements have been done for as-deposited films in the frequency range 100 KHz – 10MHz.

3. Results and discussion

3.1 Optical properties

Fig.1 shows the transmission spectra of the as-deposited and annealed films of lower thickness (17nm). It is clear from the figure that the film transmittance in the spectral region 450-860nm decreases with thermal treatment and similar result has been reported by N. Tigau et al. [7]. The decrease of transmittance may due to: i) the precipitation of the sb excess and to the high absorption coefficient of sb in this spectral region, ii) the increase of crystallite size and an improvement of the film crystallinity and iii) the increased roughness of the heat-treated films. Increased roughness plays an important part in the drastic decrease of optical transmittance because the destructive interference of the light transmitted through the high and irregular grains of the samples which form non-leveled surfaces.

Optical parameters such as absorption coefficient α, extinction coefficient (k) and band gap were determined from the transmission data obtained by following the method of Swanepoel [8]. We have calculated the extinction coefficient (k) using the formula,

$$k = \frac{2.303 \log (1/T) \lambda}{4\pi t} \qquad (1)$$

where T is the transmittance, λ is the corresponding wavelength, t is the thickness of the film. The absorption coefficient α, calculated using,

$$\alpha = 4\pi k / \lambda \qquad (2)$$

where λ is the wavelength, k is the extinction coefficient. Fig.2 shows the variation of the extinction coefficient, k as a function of photon energy. The extinction coefficient, k increases with photon energy as well as with temperature.

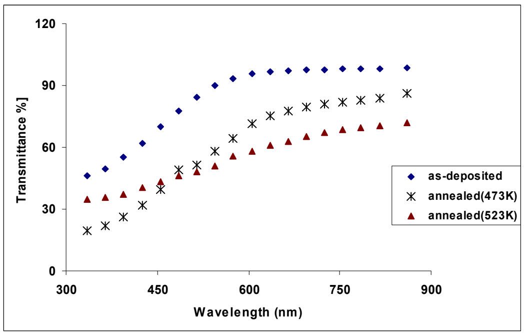

Fig. 1. Transmission spectra of the Sb_2S_3 film (thickness=17nm)

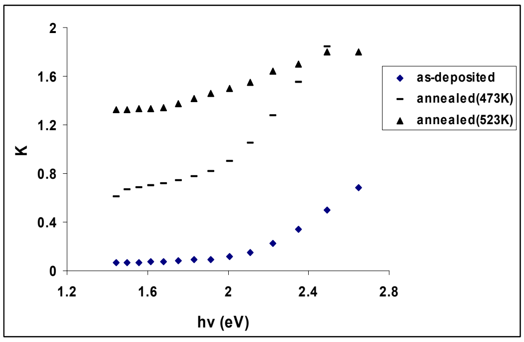

Fig.2. Variation of extinction coefficient (k) with photon energy (hν) for Sb_2S_3 film(thickness=17nm).

The type of optical transition can be explained by observing the dependence of absorption coefficient, α on the photon energy, hν. The electron excitation from valence band to conduction band is known as fundamental absorption and which can be used to determine the nature and value of the optical band gap. The optical band gap, Eg of the semiconductor is determined from the dependence of absorption coefficient values (α) on the photon energy, using Tauc's relation [4],

$$(\alpha h\nu) = B\,(h\nu - Eg)^n \tag{3}$$

where B is a parameter that depend on the transition probability, Eg is the optical band gap energy of the material, hν is the photon energy and n is an index that characterizes the optical absorption process and is theoretically equal to 2 and ½ for indirect and direct allowed transitions respectively.

The variation of the absorption coefficient, α as a function of photon energy, hν is presented in fig 3. As can be seen from the figure, the absorption coefficient of the films increases with annealed temperatures is due to the change in the films' structure. For higher values of photon energy, the energy dependence of absorption coefficient ($\alpha > 10^4$ cm^{-1}) suggests the occurrence of direct electron transitions.

For direct allowed transitions n has the value 1/2 (eqn.2) and it is observed from the plot of $(\alpha h\nu)^2$ versus hν (fig.4). The band gap values for as-deposited and annealed films are 2.43eV, 1.97eV and 1.58eV, respectively. The value of the direct optical transition for as-deposited film is in good agreement with the reported results of N. Tigau et al. [4] for Sb_2S_3 thin films prepared by thermal evaporation. It is evident from figure 4 that band gap decreases with heat treatment.

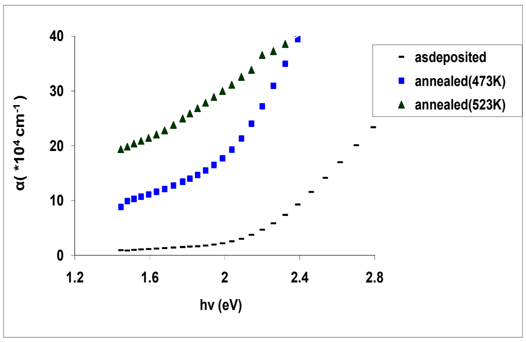

Fig.3-Variation of absorption coefficient (α) with photon energy (hν) for Sb_2S_3 film(thickness=17nm)

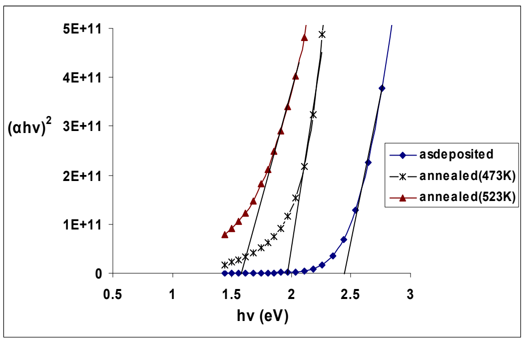

Fig.4-Variation of $(\alpha h\nu)^2$ with photon energy (hν) for Sb_2S_3 film(thickness=17nm).

ITO can be used as a transparent electrode. The attractiveness of ITO is related to the low sheet resistance and high optical transmittance from visible to near infrared light. Here we have done an investigation and a comparative study on the optical properties of Sb_2S_3 film of thickness 300nm on glass and ITO coated glass substrates. Optical band gaps of Sb_2S_3 films on different substrates were obtained from plots of $(\alpha h\nu)^2$ against photon energy hν, of direct transitions as shown in fig.5. The direct band gap of Sb_2S_3 on glass is 1.93eV and of Sb_2S_3 on ITO glass substrate is 2.19eV. The direct band gap of Indiun coated Tin Oxide glass substrate is also observed and it is shown as 2.76eV. There is a difference in the band gaps of Sb_2S_3 on pure glass plate (1.93eV) and on ITO coated glass plate (2.19eV).

Fig. 6 shows the transmittance spectra of Sb_2S_3 films (thickness=300nm) on glass and ITO coated glass substrates. As it is clear from the figure that transmittance of Sb_2S_3 film on glass is less than Sb_2S_3 film on ITO, especially in the wavelength region 500-700nm. The variations of the extinction coefficient, k and absorption coefficient, α as a function of photon energy for the films of Sb_2S_3 on glass and ITO coated glass substrates are shown in figs.7 and 8.

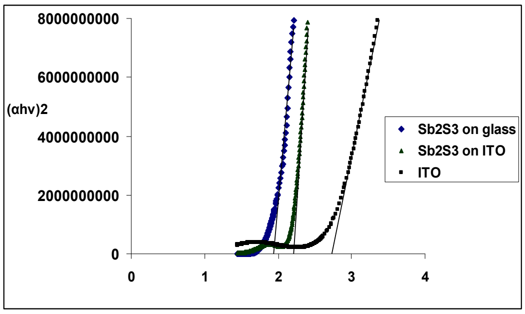

Fig.5 - Variation of $(\alpha h\nu)^2$ with photon energy (hν) for ITO film and Sb_2S_3 films (thickness=300nm).

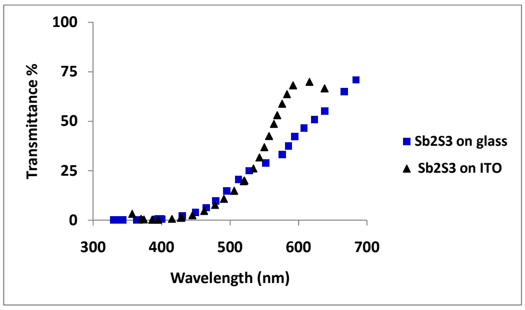

Fig.6 – Transmission spectra of Sb_2S_3 films (thickness=300nm).

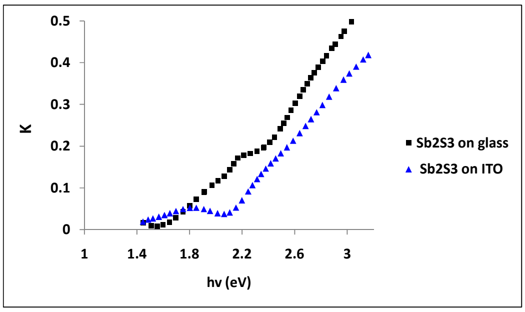

Fig.7- Variation of extinction coefficient (k) with photon energy (hν) for Sb_2S_3 films(thickness=300nm).

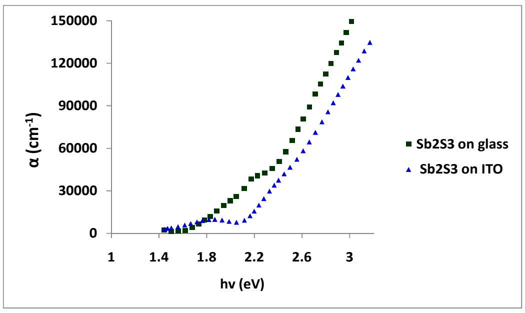

Fig.8- Variation of absorption coefficient (α) with photon energy (hν) for Sb_2S_3 films(thickness=300nm).

3.2 Dielectric properties and impedance analysis

The variation of capacitance with frequency for as-deposited and annealed Sb_2S_3thin films of thickness 300nm in the frequency range 100 KHz to10 MHz is presented in Fig. 9. The capacitance decreases with increasing frequency and attain a constant value at higher frequencies. From this it can be concluded that the as deposited films have many defects and impurities such as voids, grain boundaries dislocations, stresses etc. Annealing in vacuum improves the dielectric properties.

Fig. 10 indicates the variation of dielectric constant (ε) with frequency. The dielectric constant decreases with increasing frequency and increases with increasing temperature. Dielectric constant decreases with frequency may be attributed to the fact that the orientational polarization decreases when the frequency is increased [9]. The value of dielectric constant attains a constant value at high frequency due to interfacial polarization. A. M. Farid and A. E. Bekheet [10] give the reason for the increase of dielectric constant with increasing temperature that, orientation of the dipoles facilitated with higher temperature and this increases the orientational polarization.

Fig. 11 shows the variation of the real part of impedance (*Z*′) with frequency for the as-deposited and annealed thin films of Sb_2S_3. It is clear from the graph that the magnitude of *Z*′ decreases with the increase in both frequency as well as temperature. Similar results have been reported by C. K. Suman et al. [11]. The variation of the imaginary part of impedance (*Z*″) with frequency for the as-deposited and annealed temperatures is given in fig.12. This also indicates the magnitude of *Z*″ decreases with the increase in frequency. But the variation is less in *Z*″ with the increase of temperature.

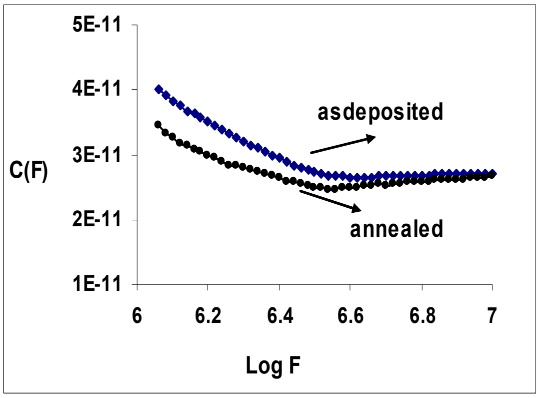

Fig.9-Variation of capacitance with frequency

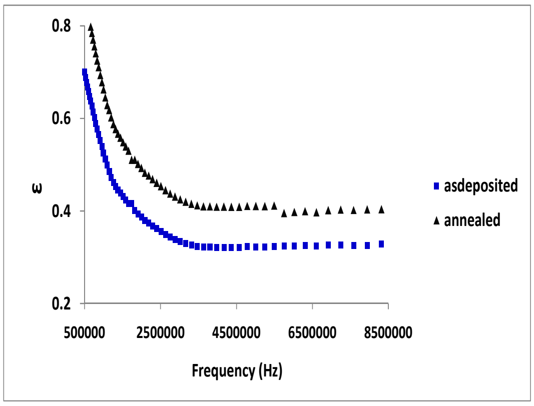

Fig.10- Variation of dielectric constant with frequency

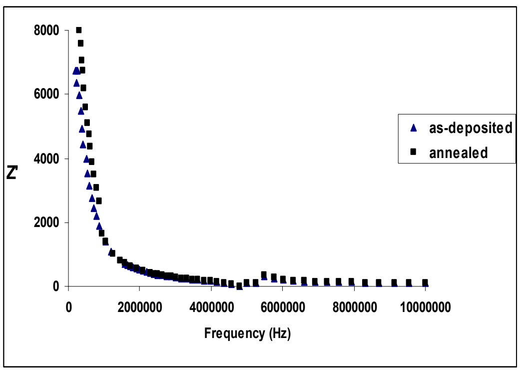

Fig.11- Variation of impedance (Z′) with frequency

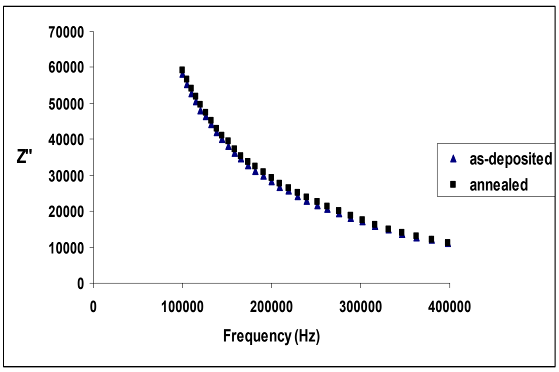

Fig.12- Variation of impedance (Z″) with frequency

4. Conclusions

Thermally evaporated Sb_2S_3 thin films were deposited onto pure glass and ITO coated glass substrates. The transmittance data were used to observe the optical characterizations. The influence of the post deposition thermal treatment on the optical and electrical properties of the prepared films has been studied. The observed optical band gaps due to direct transitions for the as-deposited and annealed (473K, 523K) films of Sb_2S_3 on glass are 2.43eV, 1.97eV, 1.58eV respectively. Direct band gap energy for as-deposited Sb_2S_3 film on ITO is obtained as 2.19eV. The dielectric constant and capacitance are found to be frequency and temperature dependant. The dielectric constant decreases when frequency increases from 500 KHz to 4 MHz and the values remain constant at very high frequencies.

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