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INVESTIGATIONS ON THE Se DOPED Sb_2S_3 THIN FILMS

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Thin films of Sb_2S_3 and $(Sb_2S_3)_{0.9}Se_{0.1}$ were prepared on microscope glass slides at room temperature by thermal vacuum evaporation and electron beam deposition techniques, respectively. The effect of Selenium doping on the structural, optical and electrical properties of Sb_2S_3 thin films is investigated. As-deposited films of Sb_2S_3 and $(Sb_2S_3)_{0.9}Se_{0.1}$ do not show any peak in the XRD patterns, while peaks appeared in the powder samples. The observed direct band gaps of Sb_2S_3 and $(Sb_2S_3)_{0.9}Se_{0.1}$ are 2.21 eV and 2.61 eV, respectively. The studies on dielectric properties and impedance analysis have been done in the frequency range 100 KHz – 10MHz for Sb_2S_3 and $(Sb_2S_3)_{0.9}Se_{0.1}$ films on glass substrates and the influences of both temperature and frequency on these properties evaluated.

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1. Introduction

Binary and ternary chalcogenides of Sb_2S_3 are very promising materials because of their attractive physical properties which can be controlled by changing the chemical composition, which makes these materials useful for technological applications. It has been found that these chalcogenides are useful semiconductors, which find application in the electronic devices especially in photoconductive targets for the videocon type of television camera tubes, microwave, switching and optoelectronic devices [1]. The addition of a third elemental impurity in the Sb-S compound has a special effect on structural, optical, electronic and thermal properties of chalcogenide glassy semiconductors. The effects due to the impurity element in various chalcogenide glasses have been reported by several workers: for e.g. B. Frumarova et al. [2] prepared Sm^{3+} doped Sb_2S_3 thin films, A.M. Fernandez and J.A. Turner [3] developed Cu-Sb-Se films, Liudi Jiang et al. [4] conducted XPS studies on Ge-Sb-S thin films etc. But the preparation of Sb-S-Se thin films can be seen in the published papers of Sarah Messina et al. [5-6] and D.Y. Suarez-Sandoval et al. [7] by heating thin films of Se-Sb_2S_3, deposited sequentially by the chemical bath method. The effect of impurities depends strongly on the composition of the glass, the chemical nature of the impurity and the method of doping. Some of the physical properties also found to be improved by the addition of certain impurities. The efficiency of different devices is determined by the structural, electrical and optical studies of the films. The optical and electrical studies of these films provide important information about the internal electronic structure of the deposited non-crystalline materials. This information supports the industrial application.

The present work deals with the preparation of Selenium doped Antimony Sulfide thin films by electron beam evaporation technique and the structural, optical and electrical characterizations of the as-deposited films. Also in this paper we compare the results of structural,

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optical and electrical characterizations of Sb_2S_3 thin film with that of the $(Sb_2S_3)_{0.9}Se_{0.1}$ thin film. To the best of our knowledge nobody has performed the work on the preparation and characterization of $(Sb_2S_3)_{0.9}Se_{0.1}$ thin films by electron beam evaporation technique using newly prepared powder by the doping of Se on Sb_2S_3 (both in powder form).

2. Experimental

Thin films of Sb_2S_3 were prepared via thermal vacuum evaporation technique from high purity polycrystalline powder (99.999% purity, Sigma-aldrich), using a coating unit under vacuum at 10^{-5} torr. The newly prepared powder sample by the doping of 10% of Se (99.999% purity) on 90% of Sb_2S_3, was evaporated by electron beam technique. Evaporation takes place under high vacuum, 10^{-5} torr. Chemically cleaned microscope glass slides were used as substrates in both deposition techniques. In order to get uniformly coated films, the pre-cleaned substrates were placed in a rotative sample-holder at room temperature during deposition. Deposition rate and film thickness were controlled during deposition by quartz oscillator thickness monitor. The substrate temperature was maintained at 300K during the deposition. The structural characterization of Sb_2S_3 and $(Sb_2S_3)_{0.9}Se_{0.1}$ films and powder samples were made using X-ray diffractometer with CuK_α radiation (λ = 1.5406Å). The room temperature transmission spectra of the as -deposited films were taken 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. A blank glass slide was placed as reference and the spectra for thin films were recorded. Dielectric measurements were taken for as-deposited films in the frequency range 100 KHz – 10MHz by using Impedance analyzer.

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows the X-ray diffractograms of the as-deposited $(Sb_2S_3)_{0.9}Se_{0.1}$ thin film and powder sample. The as-deposited film is appeared as amorphous in nature. The position of peaks appeared in the diffractogram of the powder sample lie very near to those listed in the PDF for Sb_2S_3 (PDF 42-1393) and Sb_2Se_3 (PDF 15-0861). The XRD patterns of as-deposited Sb_2S_3 thin film and powder sample are shown in fig. 2. As it is clear from the figure, the film formed at room temperature has amorphous nature, which agrees with the previous observations reported by N. Tigau et al. [8-9].

The structural features are consistent with an orthorhombic cell. The orthorhombic crystal structure of the powder sample $(Sb_2S_3)_{0.9}Se_{0.1}$ with cell parameters, a = 1.132nm, b = 1.117nm and c = 0.382nm has been found out from XRD powder data. These values lie in between those of Sb_2Se_3 (PDF 15-0861) and Sb_2S_3 (PDF 42-1393). The hkl indices are common for both Sb_2S_3 and Sb_2Se_3. No other peaks due to impurities or other phases were observed within the sensitivity of the instruments. The peaks (211) and (310) were found to have the highest intensities. In an X-ray diffraction experiment the peak intensities of various reflections are controlled by atom types and their distribution in the unit cell. A measurement of these intensities allows the crystallographers to work out the structure of the crystalline material which produced them.

3.2 Optical properties

Fig. 3 shows the optical transmission spectra of Sb_2S_3 and $(Sb_2S_3)_{0.9}Se_{0.1}$ thin films in the wavelength range 330-960nm deposited at substrate temperature 300K. It is observed from the figure that film transmittance of $(Sb_2S_3)_{0.9}Se_{0.1}$) is lesser than of Sb_2S_3 thin films and similar result can be observed in the research work of Sarah Massina et al. [5].

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 [10]. We have calculated the extinction coefficient (k) using the formula,

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

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

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

where λ is the wavelength, k is the extinction coefficient. Fig.4 shows the variation of the extinction coefficient, k as a function of photon energy. Here we can observe the increase of extinction coefficient, k with photon energy.

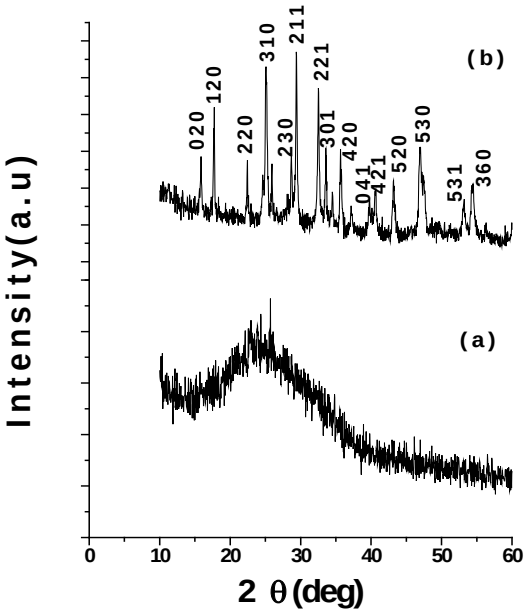

Fig 1-XRD patterns of as-deposited thin film (a) and powder sample (b) of $(Sb_2S_3)_{0.9}Se_{0.1}$

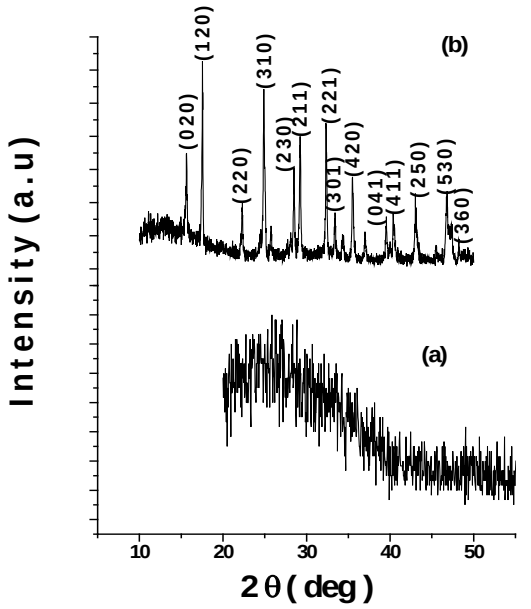

Fig 2-XRD patterns of as-deposited thin film (a) and powder sample (b) of Sb_2S_3

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 [11],

$$(\alpha h\nu) = B\,(h\nu - Eg)^n \quad (3)$$

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 dependence of the absorption coefficient, α, on photon energy, hν for Sb_2S_3 and $(Sb_2S_3)_{0.9}Se_{0.1}$ as-deposited films is presented in fig 5. As can be seen from the figure, the absorption coefficient of Sb_2S_3 films is greater than of $(Sb_2S_3)_{0.9}Se_{0.1}$ thin films.

The direct allowed band gap values for as-deposited Sb_2S_3 and $(Sb_2S_3)_{0.9}Se_{0.1}$ thin films obtained by using the value 1/2 for n (eqn.2) and it is observed from the plot of $(\alpha h\nu)^2$ versus hν (fig.6) as 2.21 eV and 2.61eV, respectively. The value of the direct optical transition for as-deposited Sb_2S_3 film is in agreement with the reported results of A.M. Salem and M. Soliman Selim [12] for Sb_2S_3 thin films prepared by thermal evaporation.

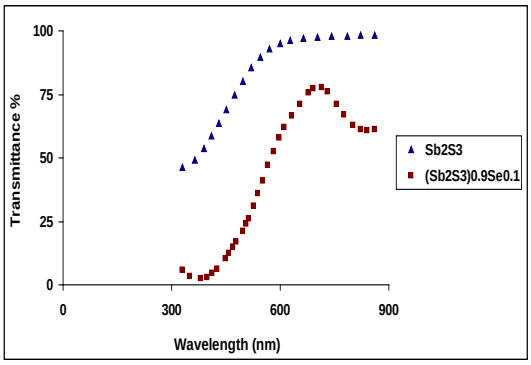

Fig 3-Variation of transmittance (T) with wavelength (λ)

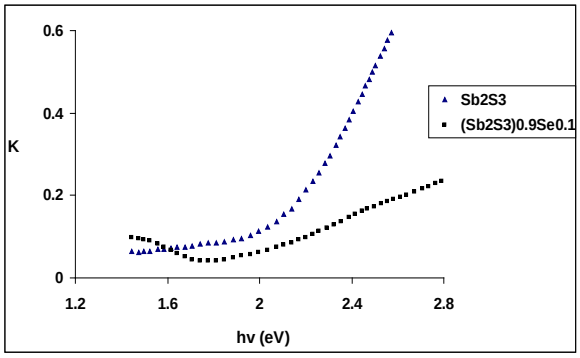

Fig 4 - Variation of extinction coefficient (k) with photon energy (hv)

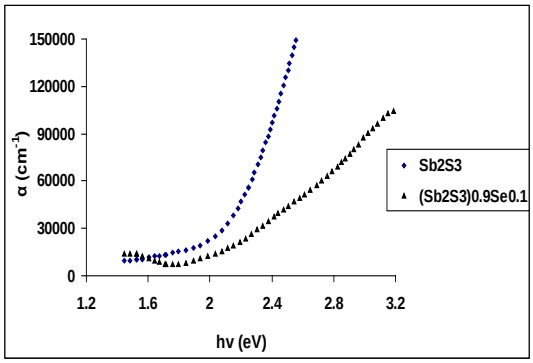

Fig 5- Variation of absorption coefficient (α) with photon energy (hv)

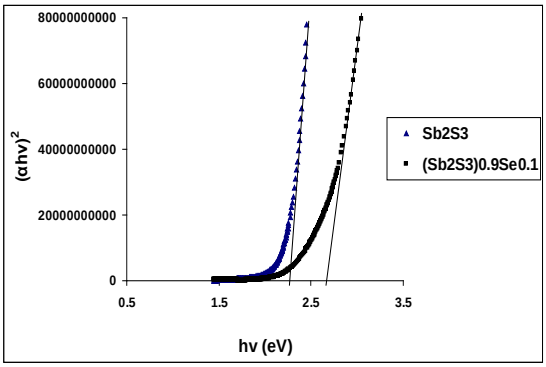

Fig 6-Variation of $(\alpha h\nu)^2$ with photon energy (hv)

3.3 Dielectric properties and Impedance Analysis

Fig.7 shows the variation of capacitance with frequency for as-deposited Sb_2S_3 and $(Sb_2S_3)_{0.9}Se_{0.1}$ thin films in the frequency range 100 KHz to10 MHz. The capacitance decreases with increasing frequency and attain a constant value at higher frequencies. The as-deposited films have many defects and impurities such as voids, grain boundaries dislocations, stresses etc.

The variation of dielectric constant (ε) with frequency for the as-deposited Sb_2S_3 and $(Sb_2S_3)_{0.9}Se_{0.1}$ thin films is presented in fig. 8. The dielectric constant decreases with increasing frequency. This decrease may be due to fact that the orientational polarization decreases when the frequency is increased [13]. The value of dielectric constant attains a constant value at high frequency due to interfacial polarization.

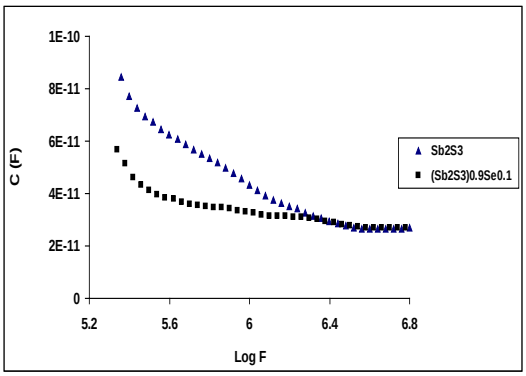

Fig 7-Variation of capacitance with frequency

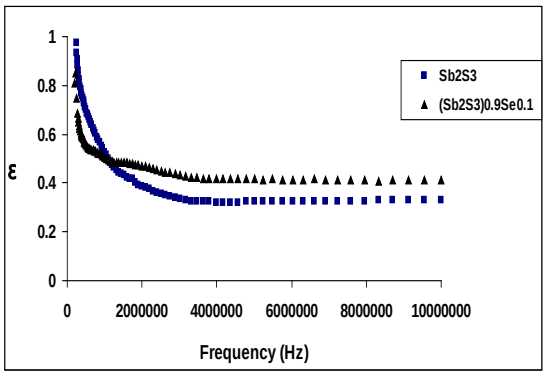

Fig 8- Variation of dielectric constant with Frequency

The variation of the real part of impedance (Z') with frequency for the as-deposited Sb_2S_3 and $(Sb_2S_3)_{0.9}Se_{0.1}$ thin films is shown in fig.9. It is clear from the graph that the magnitude of Z' decreases with the increase of frequency. This result is in agreement with the reported results published by C. K. Suman et al. [14]. The variation of the imaginary part of impedance (Z'') with frequency of the as-deposited Sb_2S_3 and $(Sb_2S_3)_{0.9}Se_{0.1}$ thin films is given in fig.10. This also indicates the magnitude of Z'' decreases with the increase of frequency.

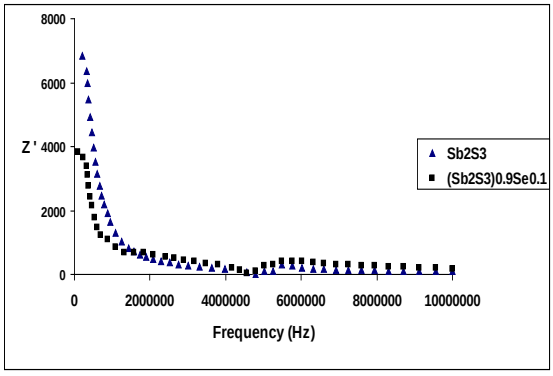

Fig 9- Variation of impedance (Z') with frequency

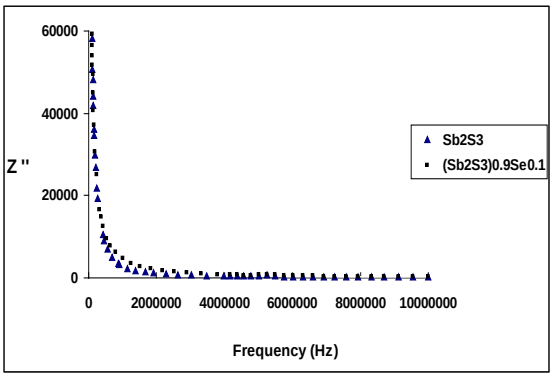

Fig 10- Variation of impedance (Z'') with frequency

4. Conclusions

In this paper we presented a methodology that used to prepare $(Sb_2S_3)_{0.9}Se_{0.1}$ powder by the doping of Se on Sb_2S_3 and structural, optical and electrical characterizations have been done on Sb_2S_3 and $(Sb_2S_3)_{0.9}Se_{0.1}$ thin films. Thermally evaporated Sb_2S_3 thin films have been prepared as the base material for the studies. The as-deposited thin films of both were appeared as amorphous in nature and peaks appeared in the XRD patterns of the powder samples $(Sb_2S_3)_{0.9}Se_{0.1}$ and Sb_2S_3. To calculate optical parameters of as-deposited Sb_2S_3 and $(Sb_2S_3)_{0.9}Se_{0.1}$ thin films the optical transmission spectra in the wavelength range 330-860nm has been used. While comparing the direct band gaps of Sb_2S_3 (Eg=2.21 eV) and $(Sb_2S_3)_{0.9}Se_{0.1}$ (Eg=2.61eV), it can be seen that the band gap increased due to the doping of Se. Dielectric constant decreases with increasing frequency and remain constant at high frequencies.

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