

STRUCTURAL AND OPTICAL ANALYSIS OF PLASMA EXPOSED AND ANNEALED Sb₂S₃ THIN FILM

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ABSTRACT

Sb₂S₃ thin films were prepared by thermal evaporation method. The film thickness was measured using a quartz crystal thickness monitor in the coating unit. In the present work thin films are exposed to glow discharge plasma for various time intervals at pressure 0.2mb, breakdown voltage 350 V and electrode distance 3 cm. The films were also annealed at 250° C for 2hrs. Plasma exposed and annealed Sb₂S₃ thin films were characterized and studied by XRD analysis and optical analysis. The as-deposited films were amorphous, while the plasma treated and annealed films have an orthorhombic microcrystalline structure.

Keywords: Plasma treatment, Antimony trisulfide, thin films, Structural and Optical analysis.

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INTRODUCTION

Industrial appliances of binary compound semi-conductors stimulate the investigation of the physical properties of amorphous and crystalline systems. The relation between the physical properties and local structure is of great interest in non- crystalline materials where the preparation techniques and composition can affect the short and medium range order.¹

Metal chalcogenides (sulfides, selenides and tellurides) are significant materials for uses in photoconducting cells, photovoltaic cells and other optoelectrical devices. Among the group V-VI compounds, antimony tri sulfide film is a gifted nominee as a target material in television cameras², microwave devices³, switching devices and various optoelectronic devices.⁴⁻⁷ Antimony tri sulfide has received a little interest as a possible aspirant in solar energy conversion⁸.

Low temperature plasma is a partially ionized, neutral gas component and characteristics are different from the normal gas. Plasma of different ionization extents can be produced with the help of an electrical discharge. Since the plasma temperatures are comparatively low, the active species in plasma simply drop their temperature once reacting with the material. It has been used in a broad range of engineering applications. It is also a restricted and reproducible way to clean, activates, etch or modify the surface of textiles, plastics, metals or ceramic materials.

From the survey of literature, it is seen that almost no effort has been made to study plasma exposed Sb₂S₃ thin films. Numerous researchers have also worked on plasma surface modification of textiles, polymer thin films and have got excellent results because of their increase in water repellent, water absorbance, increasing surface roughness, adhesion, contact angle and surface free energy which are also dependent on the nature of gas used.

The aim of the present study is to look at the effects of optical and structural properties of plasma treated Sb₂S₃ thin films.

EXPERIMENTAL

Antimony trisulfide thin films were prepared by thermal vacuum evaporation technique onto a glass substrate, at vacuum of 5*10⁻⁵ torr using Hind Hivac coating unit. Powdered material of Sb₂S₃ having

99.99% purity (Sigma –Aldrich) was heated in a quartz crucible to temperature near the melting point of Sb_2S_3 (650°C) evaporated and condensed on glass substrates. The glass substrates had been previously cleaned and were kept at room temperature ($T_s=295\text{ K}$) during the deposition. The substrates were mounted directly over the quartz crucible about 15cm from the sample boat. The rate of deposition was maintained at $2\text{ \AA}/\text{sec}$. The thickness of the film was measured using inbuilt quartz crystal monitor and it was found to be 1000 \AA .

After deposition the Sb_2S_3 thin films were exposed to plasma. The thin film samples were loaded in the substrate holder inside the plasma chamber. The coated side of the thin film was kept facing to the cathode. The pressure inside the chamber was maintained at 0.2 mb and the applied voltage was 350 V. The distance between the electrodes was kept at 3 cm and the distance between the cathode and sample holder was 1cm. We estimate that the temperature of the sample was undoubtedly below 100°C during the treatment because the film should have disintegrated over a long exposure at the temperature higher than that. The Sb_2S_3 thin films were also annealed at 250°C for two hours.

Untreated, annealed and plasma treated thin films were analyzed by structural and optical studies. The structure of the films was examined by using Shimadzu XRD-6000 X-ray diffractometer. Samples mounted on the specimen holder using silica gel were scanned at a rate of $5^\circ/\text{min}$ with $\text{CuK}\alpha$ radiation ($\lambda=1.5406\text{ \AA}$). All the films were analyzed in the $10^\circ - 80^\circ$ (2θ) scale angle range. The optical transmissions spectra of as-deposited, plasma exposed and annealed films were recorded using JASCO-UV/VIS/NIR (JASCO v-570) double beam spectrophotometer in the range 190 - 2500nm. The observed transmittance data were corrected relative to optically identical uncoated glass substrate.

RESULTS AND DISCUSSION

Structural analysis

The X-ray diffraction pattern of as-deposited, plasma treated film for various treatment times and annealed Sb_2S_3 thin films are shown in Figure-1. The X-ray diffraction pattern of as-deposited film shows an amorphous nature. After the plasma treatment and annealing process it was seen that the amorphous nature has changed into microcrystalline nature. The major diffraction peaks are indexed and compared with the standard Joint Commission of Powder Diffraction Standards (JCPDS 75-1310) data and are shown in the Table-1. The interplanar spacing values d were also calculated by using the formula,

$$d = n \lambda / 2 \sin \theta \quad (1)$$

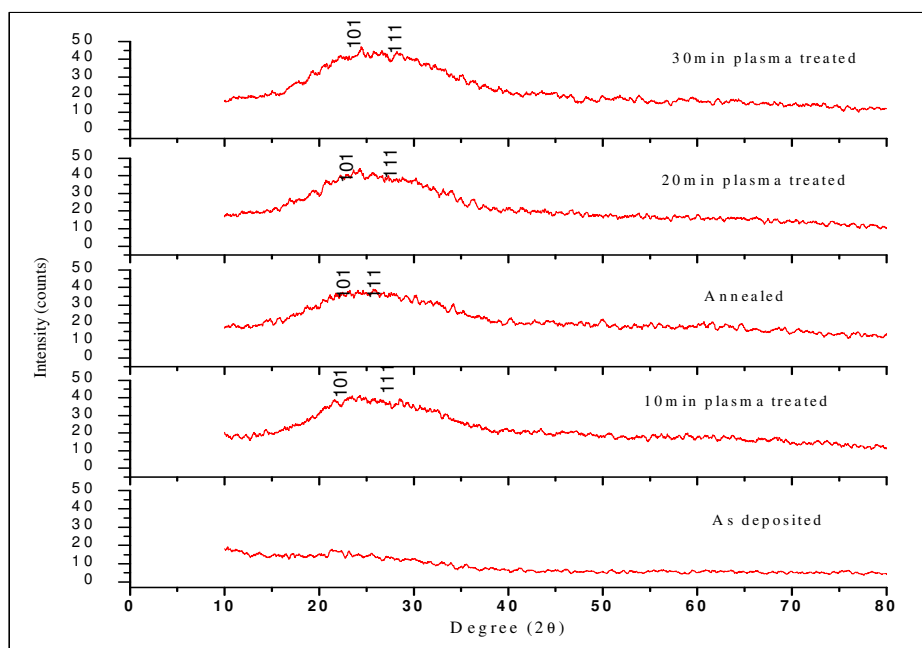


Fig.-1: XRD pattern of Sb_2S_3 thin film

During plasma treatment process, the electrons from the cathode move towards the anode meanwhile it also ionizes the surrounding gas particles. The presence of electron temperature due to electrons, ion temperature due to ions and the ambient temperature due to the applied electric potential between the electrodes will impart energy to the thin films, which causes the grain size to grow. This causes the change from amorphous nature to microcrystalline nature.⁹

While plasma exposed, there is not only a change in the surface properties; also an extremely thin, active layer is also formed below surface of the film. The thickness of this layer, the modified depth, depends on the chemical nature of the materials (linear or branch chains, functional groups, crystalline), as well as on the type of the reactor, distance between film and the electrode, treatment time and type of gas used. The thickness of the modified layer is several hundreds of Å, and it is possible that the plasma treatment has an influence on the structural and optical properties.

Table-1: JCPDS and Observe data and band gap energy of the plasma and annealed Sb₂S₃ thin films

Samples	JCPDS Data			Observed		Band Gap (eV)
	2θ	h k l	d _{hkl}	2θ	d _{hkl}	
Untreated	-	-	-	-	-	3.81
10mins treated	24.532	1 0 1	3.626	24.469	3.635	2.66
	25.778	1 1 1	3.453	25.789	3.452	
20mins treated	24.532	1 0 1	3.626	24.389	3.647	2.40
	25.778	1 1 1	3.453	25.748	3.457	
30mins treated	24.532	1 0 1	3.626	-	-	2.37
	25.778	1 1 1	3.453	25.789	3.450	
Annealed at 250° C for 2hr	24.532	1 0 1	3.626	24.229	3.670	2.47
	25.778	1 1 1	3.453	25.830	3.445	

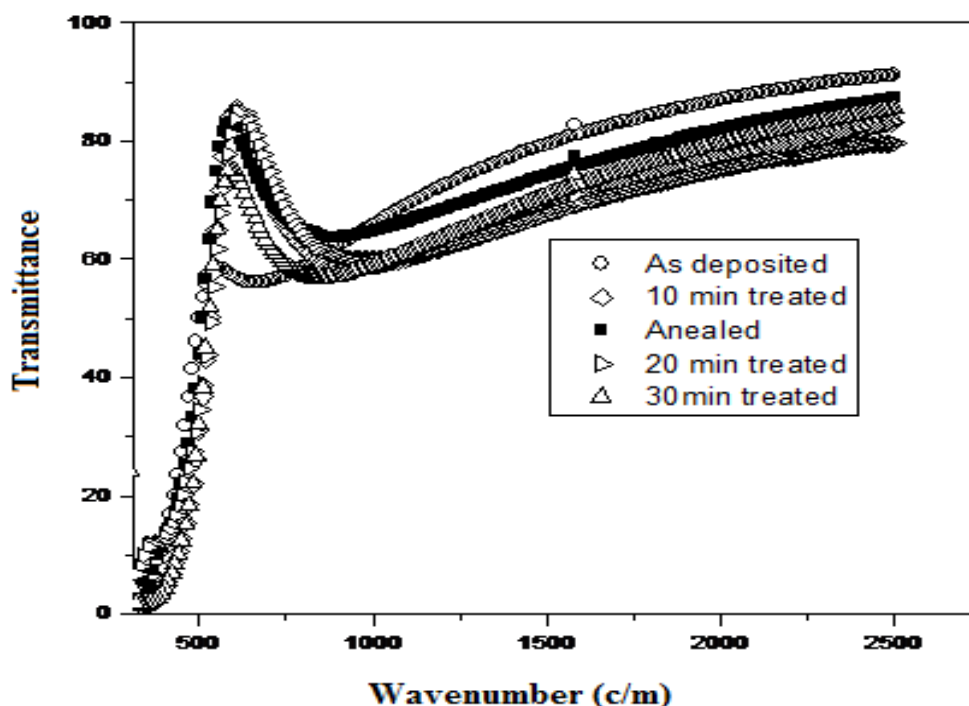
The Sb₂S₃ thin films treated with plasma for 10mins possess microcrystalline nature with a predominant peak (101) positioned near 24.5°. When the treatment time is increased to 20mins and 30mins, the predominant peak intensity has been decreased, and a new peak (111) has been formed. The decrease in the peak intensity suggests that lattice planes tend to random orientation and further the new peak formation may be due to explains re-orientation of lattice planes to (111).¹⁰

Figure-1 shows the X-ray diffraction spectrum of Sb₂S₃ thin film annealed at 250° C for two hour. It is observed that the structure of Sb₂S₃ film posses microcrystalline nature. They exhibit higher orientation at 2θ = 24.53° corresponding to (101) plane and 2θ = 25.778° corresponding to (111) plane. This increase in diffraction intensity may be due to increase in grain size during annealing process.^{11, 12} Since the graph shows microcrystalline nature, it is not possible to calculate grain size accurately.

Optical properties

The optical properties of Sb₂S₃ thin films have strong modification with the grain dimension and residual stress and hence the stress generated in the film should also affect their optical spectra. The intrinsic structural inhomogeneities in the films result in local fluctuations in the potential and hence in the band gap energies of the disordered system. The normalized optical transmittance spectra (the transmittance loss due to the substrate has been eliminated by keeping the uncoated glass substrate as a reference) were recorded in 190-2500nm range of the X-ray diffraction electromagnetic JASCO-UV/VIS/NIR (JASCO v-570) double beam spectrophotometer in order to study the modification in the optical properties due to plasma exposure.

Figure-2 shows the optical transmittance spectra of the as deposited and plasma exposed Sb₂S₃ thin film. The decrease in transmission could arise due to the creation of localized energy levels between the valance band and conduction band.

Fig.-2: Transmittance spectrum of Sb_2S_3 thin films

In polycrystalline materials the nature of optical inter band transmission near the absorption edge can be determined by the relation between absorption coefficient(α) and the optical energy gaps(E_g) using the standard expression for direct transition between two parabolic band $(\alpha h\nu)^2 = A(h\nu - E_g)$, the band gap of both as-deposited, plasma treated and annealed films was estimated. The value of E_g is determined from an intercept on the energy axis of $(\alpha h\nu)^2$ versus $h\nu$ plot as shown in Fig.-3 and the values are given in Table-1. The band gap energy decreases gradually with increase in plasma treatment time.

The extrapolation of the linear part of the curves indicates the Tauc optical band gap.⁶ The optical band gap is the minimum energy required to excite an electron from the valence band to the conduction band by an allowed optical transition¹⁴. From the graphs which is seen that the value of band gap decreases after plasma treatment. The band gap decreases from 2.61 eV to 2.37 eV with increase in treatment time and are shown in Table-1. The band gap energy values agree well with values reported by A.M. Saleem et al⁸. From the optical analysis, the value of band gap energy of the plasma treated Sb_2S_3 thin films is lesser than the annealed one.

This decrease in band gap is due to the change of as- deposited Sb_2S_3 thin film to microcrystalline structure and the same is seen in XRD analysis. The change from amorphous nature to microcrystalline nature may be due to the increase in the grain size during plasma treatment.

Surface morphology analysis of Sb_2S_3 thin films

The Sb_2S_3 thin films surface morphology has been studied by scanning electron microscopy. The Scanning electron micrographs show that the as-deposited thin film and annealed thin film have amorphous structure. Several small grains are found to agglomerate and form a few larger grains (Fig.-4a). Due to thermo- annealing, too many small grains are combined together and found to be a bigger grains.

Figure-4a shows that as deposited Sb_2S_3 thin film is more number of tiny and little irregular spherical boundaries of grains are clearly seen. In Figure-4b shows that 10 min plasma treated thin film, the tiny spherical boundaries are combined together and get bigger grain comparing with as deposited one. For 20

min plasma treatment, the film is getting spread and their shape is changed. The Scanning electron microscopic photograph of 30 min plasma treated film shows that the spherical grain shape disappears and spreads. Figure-4d shows the SEM micrographs of surface morphologies of the annealed Sb_2S_3 thin film (250°C for 1 hour). It is seen that the morphology of the Sb_2S_3 thin films is strongly affected by thermal treatment. The SEM micrograph of annealed film clearly shows smooth surface of Sb_2S_3 .

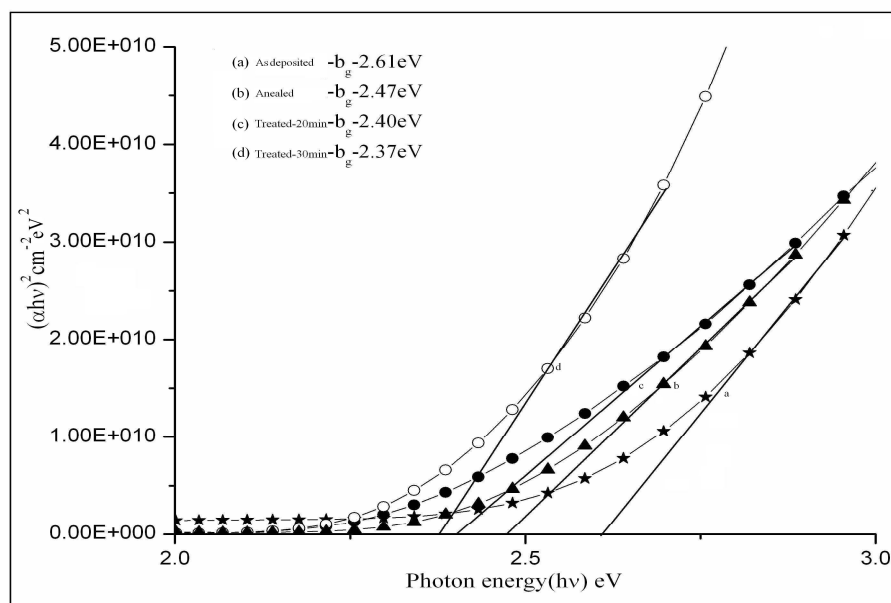


Fig.-3: Band gap energy graph for Sb_2S_3 thin film

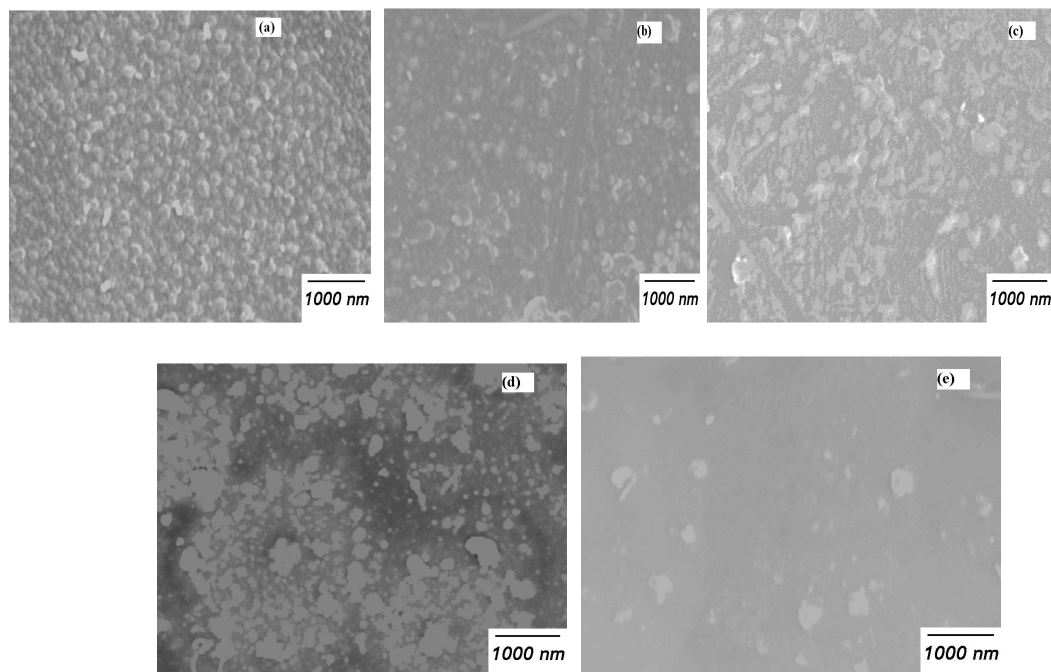


Fig.-4: SEM micrographs of (a) deposited (b) 10min plasma treated (c) 20 min plasma treated (d) 30min plasma treated (e) annealed Sb_2S_3 thin films

CONCLUSION

From the above results it can be conclude that plasma treatment can be used instead of annealing process. XRD analysis reveals that the as-deposited films were in amorphous nature, where as plasma treated and annealed films microcrystalline. From the optical analysis the band gap energy decreases with increasing plasma treatment time. Plasma treatment is more beneficial since it need less time compared to annealing process.

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[RJC-1725/2017]