STRUCTURAL CHARACTERIZATION AND OPTICAL PROPERTIES OF ANNEALED Sb$_2$S$_3$ THIN FILMS

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The influence of thermal annealing on the structure and optical properties of antimony trisulfide (Sb$_2$S$_3$) thin films deposited by thermal evaporation under vacuum onto glass substrate was studied. The structural investigation performed by means of X-ray diffraction (XRD) and atomic force microscopy (AFM) showed that the ad-deposited films have an amorphous structure. After thermal annealing at temperature of 500 K the Sb$_2$S$_3$ thin films becomes polycrystalline in structure. The values of some important parameters of studied films as absorption coefficient and optical band gap energy are determined from transmission spectra. The indirect optical band gap of amorphous film was found to be 1.53 eV and the direct optical band gap of polycrystalline film was found to be 1.71 eV.

Key words: Antimony trisulfide, thin films, structural properties, optical band gap.

1. INTRODUCTION

In recent years a large number of studies have devoted to the physical properties of chalcogenides thin films due to their wide applications in optoelectronic devices [1–5]. Among the available chalcogenides, pure and doped Sb$_2$S$_3$ thin films are used in solar energy conversion, thermoelectric cooling technologies and as photoconductive target for vidicon type of television camera [6, 7]. Many workers have obtained Sb$_2$S$_3$ thin films by various technique as the chemical bath deposition [8, 9], the sol-gel method [10], vacuum evaporation method [6, 11] and have studied the effect of deposition conditions on the physical properties of the thin films.

In a series of previous paper [12–14], we have studied the structural, electrical and optical properties of Sb$_2$S$_3$ thin films deposited at different substrate temperature. In this paper the influence of annealing in air on the optical properties of Sb$_2$S$_3$ thin films deposited by thermal vacuum evaporation technique is investigated.


2. EXPERIMENTAL

Sb$_2$S$_3$ thin films, with thickness $d = 1.25$ μm were deposited onto glass substrates with a rectangular shape of 16 mm × 30 mm, by thermal evaporation under vacuum of Sb$_2$S$_3$ polycrystalline powder. The Sb$_2$S$_3$ powder was placed in quartz ampoule which was around with molybdenum heating coil and heating up to 565°C under pressure of 2 × 10$^{-5}$ torr. The glass substrates were maintained at substrate temperature of 300 K. As-deposited Sb$_2$S$_3$ thin films were annealed in air at 500 K for 1 h.

Structural analysis was performed before and after annealing using a Dron 3 X-ray diffractometer with the Cu K$_{α}$ radiation ($λ = 1.5418$ Å). The film surface morphology was analyzed by atomic force microscopy (AFM) in non-contact mode. Also, the AFM investigation was utilized to determine the roughness of the surface films.

The transmittance measurements in the visible and near-infrared region were performed at room temperature to calculate the absorption coefficient and optical band gap energy. The transmission spectra in the spectral range from 500 to 1400 nm were recorded at normal incidence using a PMQ-II spectrophotometer.

3. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) analysis previously reported [12–14] revealed that the Sb$_2$S$_3$ thin films deposited at substrate temperature of 300 K are of amorphous structure (Fig. 1a). After annealing process in air at 500 K the Sb$_2$S$_3$ thin films becomes polycrystalline as showed in Fig. 1b.

The XRD pattern of the annealed films shows that the film is crystallized in the orthorhombic phase and presents a preferential orientation along (310) plane.

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Fig. 1 – XRD patterns of Sb$_2$S$_3$ thin films: a) as-deposited, b) annealed.
parallel with the substrate. The (220), (211), (221), (240), (431) and (132) peaks were also observed at \(2\theta = 22.84^\circ, 29.72^\circ, 32.86^\circ, 36.11^\circ, 47.31^\circ\) and \(54.50^\circ\) respectively but these peaks are much lower intensity than the intensity corresponding reflection to (310) plane. The grain size, \(D\), can be estimated using the Scherrer’s formula:

\[
D = \frac{k\lambda}{\beta\cos\theta}
\]

where \(k\) is the shape factor with value in the neighborhood of 0.94 and \(\beta\) is the full-with at half-maximum (FWHM) of the (310) diffraction expressed in radians. The average size of crystallites was estimated about 30 nm.

From the XRD pattern (Fig. 1b) the interplanar spacing \(d_{hk\ell}\) was calculated from (310) plane using the Bragg’s relation:

\[
d_{hk\ell} = \frac{n\lambda}{2\sin\theta}
\]

where \(\lambda\) is the X-ray wavelength, \(n\) is the order number and \(\theta\) is the Bragg’s angle.

The \(d_{hk\ell}\) calculated values, for the annealed Sb\(_2\)S\(_3\) thin films, are compared with the standard card (ASTM no 6-674) in Table 1. It is observed that the experimental interplanar distances, \(d_{hk\ell}\), are in good agreement with the standard values. The calculated lattice parameters of orthorhombic unit cell were \(a = 11.235\,\text{Å}, b = 11.294\,\text{Å}\) and \(c = 3.836\,\text{Å}\).

<table>
<thead>
<tr>
<th>(hk\ell)</th>
<th>(2\theta) (deg.)</th>
<th>(d_{hk\ell}) (Å)</th>
<th>(I) (%) (XRD)</th>
<th>(I) (%) (standard)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(220)</td>
<td>22.84(^\circ)</td>
<td>3.975</td>
<td>3.987</td>
<td>26.16</td>
</tr>
<tr>
<td>(310)</td>
<td>25.41(^\circ)</td>
<td>3.563</td>
<td>3.558</td>
<td>100</td>
</tr>
<tr>
<td>(211)</td>
<td>29.72(^\circ)</td>
<td>3.048</td>
<td>3.053</td>
<td>40.30</td>
</tr>
<tr>
<td>(221)</td>
<td>32.86(^\circ)</td>
<td>2.756</td>
<td>2.764</td>
<td>30.91</td>
</tr>
<tr>
<td>(240)</td>
<td>36.11(^\circ)</td>
<td>2.519</td>
<td>2.525</td>
<td>25.23</td>
</tr>
<tr>
<td>(431)</td>
<td>47.31(^\circ)</td>
<td>1.935</td>
<td>1.940</td>
<td>32.01</td>
</tr>
<tr>
<td>(132)</td>
<td>54.50(^\circ)</td>
<td>1.697</td>
<td>1.691</td>
<td>21.02</td>
</tr>
</tbody>
</table>

The effect of the post-deposition annealing process on surface morphology of Sb\(_2\)S\(_3\) thin films was also investigated. The 3D-AFM images (5 \(\mu\text{m} \times 5 \mu\text{m}\)) of surface corresponding of as-deposition and annealed Sb\(_2\)S\(_3\) thin films are presented in Fig. 2a and Fig. 2b, respectively.
The surface morphology of Sb$_2$S$_3$ thin films is significantly changed by thermal annealing process at 500 K. The AFM observation also revealed that the growth of bigger crystallites, around 90 nm, was started in some portions of the as-deposition films (Fig. 2a). The 3D-AFM image corresponding of as-deposition film revealed the surface to be extremely smooth with the root-mean-square (RMS) roughness of about 1.38 nm. After annealing process the Sb$_2$S$_3$ thin films shows a denser microstructure. In this case conical features clearly seen on the surface are the cause of the surface roughness. The annealed film has an average grain size of 30 nm with the RMS roughness about 5.63 nm. These results are in good agreement with that obtained by XRD study.

In Fig. 3 the transmission spectra, relative to uncovered glass substrate, in the wavelength range of Sb$_2$S$_3$ fundamental edge (500–1400 nm) for Sb$_2$S$_3$ thin film deposited at 300 K and annealed film are presented. From Fig. 3, it can be seen that for annealed Sb$_2$S$_3$ thin film, the transmittance decrease drastically. This can be attributed to structural transformation, increasing grain size and roughening [15].

The variation of the absorption coefficient, $\alpha$, as a function photon energy are presented in Fig. 4. The values of the absorption coefficient are in order 10$^4$ cm$^{-1}$ in the investigation spectral range.

The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the nature and value of the optical band gap, $E_g$. The relation between the absorption coefficient, $\alpha$, and the incident photon energy, $h\nu$, can be written as [16]:

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

Fig. 3 – Transmission spectra of Sb$_2$S$_3$ thin films.
where $A$ is an constant depending on the transition probability and $n$ is an index that characterizes the optical absorption process and is theoretically equal to $1/2$, 2, 1/3 or 2/3 for indirect allowed, direct allowed, indirect forbidden and direct forbidden transition, respectively.

The usual method to calculate the band gap energy is to plot a graph between $(\alpha h\nu)^n$ and photon energy, $h\nu$, and find the value of the $n$ which gives the best linear graph. This value of $n$ decides the nature of the energy gap or transition involved. If an appropriate value of $n$ is used to obtain linear plot, the value of $E_g$ will be given by intercept on the $h\nu$-axis. To apply the relation (3) for as-deposited and annealed Sb$_2$S$_3$ thin films the dependences $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^2$, $(\alpha h\nu)^3$ and $(\alpha h\nu)^{2/3}$ versus $h\nu$ were plotted. For as-deposited Sb$_2$S$_3$ thin film, the best plot that covers the widest range of data and intercept the $h\nu$-axis is obtained only for the $(\alpha h\nu)^{1/2} = f(h\nu)$ dependence, while for annealed Sb$_2$S$_3$ thin film, the best plot is obtained for the $(\alpha h\nu)^2 = f(h\nu)$ dependence (Fig. 5).

The obtained value, $n = 1/2$, characterizes an indirect allowed optical transition for the amorphous as-deposited thin films [17] and $n = 2$, corresponding of annealed film, characterizes a direct allowed optical transition which occur in polycrystalline films [18]. The value of indirect band gap energy for amorphous Sb$_2$S$_3$ thin film was found to be 1.53 eV while the value of direct band gap corresponding of polycrystalline Sb$_2$S$_3$ thin film was found to be 1.71 eV. These results are in good agreement with the reported values in literature for Sb$_2$S$_3$ thin films prepared by different methods [6, 8–11].
4. CONCLUSIONS

Using the thermal vacuum evaporation technique, Sb$_2$S$_3$ thin films with amorphous structure were deposited at substrate temperature of 500 K. By XRD studies it was established that the annealed Sb$_2$S$_3$ thin films becomes polycrystalline in nature having an orthorhombic structure. AFM study showed smooth surface morphology of as-deposited film and columnar features in case of annealed Sb$_2$S$_3$ thin film. Also, from AFM images was calculated the RMS roughness of surface thin films before and after annealing treatment. It was found that the RMS roughness increase from 1.38 to 5.63 nm after annealing process.

The absorption coefficient and optical band gap were determined from the transmission spectra recorded in the visible and near infrared range. It was found that the transmittance of the annealed Sb$_2$S$_3$ thin films decrease drastically due to the phase transition from the amorphous to the crystalline state. The as-deposition thin film exhibited an indirect optical transition while the annealed film exhibited a direct optical transition that occurs between the valence and conduction band of Sb$_2$S$_3$.

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Fig. 2 – 3D-AFM images of surface Sb$_2$S$_3$ thin films: a) as-deposited, b) annealed.