

Nickel Antimony Sulphide Thin Films for Solar Cell Application: Study of Optical Constants

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Abstract

Chemical bath deposition technique has been used to deposit Ni-doped Sb_2S_3 thin films onto glass substrate. Doping was carried out by adding 1, 3 and 5 wt% of Ni. Bath temperature was kept as 10°C and films were annealed at 250°C under vacuum. Polycrystalline nature of films with an orthorhombic phase was analyzed by X-ray diffraction technique. Scanning electron microscopy was used for morphological study which shows that grains are spherical. Optical measurements using transmittance data indicated that films have a direct band gap of 1.00 - 2.60 eV with an absorption coefficient of $\sim 10^4 \text{ cm}^{-1}$ in visible range. The average value of electrical conductivity was calculated as 1.66, 1.11 and $1.06 (\Omega\cdot\text{cm})^{-1}$ for as-deposited films and 1.90, 2.08 and $1.15 (\Omega\cdot\text{cm})^{-1}$ for annealed films while refractive indices were found as 2.18 - 3.38 and 1.91 - 3.74 respectively. The obtained films can be used for solar cell applications due to their good absorbing properties like higher absorption coefficient and refractive index values.

Keywords

Ni Doped, Optical Constants, Sb_2S_3 Thin Films, Chalcogenides, Solar Cells

1. Introduction

Thin films of chalcogenide family (sulphides, selenides, tellurides) are gaining much attention these days due to their wide applications in optoelectronic devices [1]. One of the members of chalcogenide family, antimony

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sulphide (Sb_2S_3) is under intense consideration for its use in thin film solar cells [2]. Some of the properties of Sb_2S_3 which signify its large scale applicability in optoelectronics are their high refractive index, absorption coefficient of the order of 10^5 cm^{-1} , band gap of 1.7 eV and well-defined quantum size effects [3]. Apart from all the above mentioned properties, Sb_2S_3 has problem of high resistivity and low optical transmission, which hinder its applications at large scale [4]. Based on the recent literature survey on the current research trends in the field of design and development of Sb_2S_3 thin films, a two-way approach has been used so far for the alteration of properties. One is the use of various deposition techniques and the other is the modification of properties of Sb_2S_3 by the addition of different dopants. Various techniques are used to deposit amorphous and crystalline Sb_2S_3 thin films such as chemical bath deposition [5], electro-deposition [6], spray pyrolysis [7], vacuum thermal evaporation [8] and dip and dry method [9]. Similarly, different dopants like carbon, tin, lead, bismuth, copper and silver are used to improve the structural, optical and electrical properties of material [10] [11]. Annealing of the films after deposition changes their optical properties due to change in their structure [11].

Both the already mentioned approaches alter the structural and the morphological properties which in turn affect the optical transmission and reflectance of thin films based on their thickness variations. Going through the detailed literature survey on the deposition and properties of thin films, the approach of studies up till now is mostly focused on the phase evolution, grain size and structure and their effects on the transmission properties and band gap values. Although the thorough studies of the optical constants like refractive index, absorption coefficient, extinction coefficient and electrical properties like dielectric constant and electrical conductivity are important for the use of material as an absorbing material in solar cells. Very few reports are found on the studies of optical constants on the bare Sb_2S_3 and their doped derivatives.

The objective of this research is to study the effect of Ni doping on Sb_2S_3 thin films grown by chemical bath deposition (CBD) technique at substrate temperature of 10°C . The important characteristic of it is that large area films can be deposited regardless of shape and morphology of the substrate without any sophisticated instrumentation.

2. Experimental Details

Nickel antimony sulphide thin films were prepared by chemical bath deposition technique onto glass substrate. The solution was prepared using 650 mg of SbCl_3 (Merck, 99%) dissolved in 10 ml of Acetone and CH_3COCH_3 (Merck, 99%) with 25 ml of 1M $\text{Na}_2\text{S}_2\text{O}_3$ (Aldrich, 99%) dissolved in 65 ml of distilled water. The solution was prepared in 100 ml beaker with 1, 3 and 5% of NiCl_2 . Orange-yellow solution turned dark orange when kept for 15 to 20 minutes. The glass substrates were cleaned using ethyl alcohol, chromic acid and distilled water. The substrates were kept vertically in solution beaker. The deposition was made at a substrate temperature of 10°C for 2 hours. The films were annealed for 2 hours at 250°C under low vacuum condition to improve their crystallinity.

Crystal structure of films was obtained by X-ray diffraction technique using PANalytical XPert Pro (Holland). $\text{CuK}\alpha$ radiation with a wavelength of 1.54\AA was used. Scanning electron microscopy (JEO1, JSM-5910) was used for surface morphology of annealed Ni-doped films. Optical transmittance spectra were measured at room temperature in the wavelength range of 400 - 800 nm using Perkin Elmer Lambda 25 spectrophotometer.

3. Results and Discussion

X-ray diffraction measurements were carried out in the range $2\theta = 20^\circ - 70^\circ$ to analyze the crystal structure and grain size of Ni-doped Sb_2S_3 thin films. The comparison of the patterns is done taking standard pattern of orthorhombic Sb_2S_3 (ICSD code: 001-0538) as a reference material [5], as shown in Figure 1. Grain size (D), lattice parameters (a , b and c), unit cell volume (V_{cell}) and X-ray density were determined using the following equations [12]:

$$D(\text{nm}) = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (2)$$

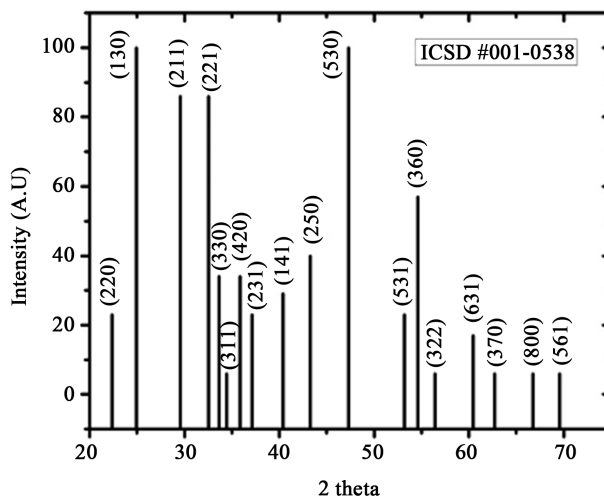


Figure 1. Standard XRD pattern for Sb_2S_3 (ICSD # 001-0538).

$$V_{\text{cell}} = abc \quad (3)$$

$$\rho_{\text{X-ray}} = \frac{ZM}{V_{\text{cell}}N_A} \quad (4)$$

where β is full width at half maximum of the peak intensity, λ is the wavelength of incident X-ray (1.54 Å), k is the shape factor with a value of 0.9, d is the d-spacing value between the planes, hkl are miller indices, Z is number of molecules per formula unit which has a value 4 for the orthorhombic crystal system, M is the molecular weight and N_A is the Avogadro's number. X-ray diffraction patterns for Ni-doped Sb_2S_3 thin films with varying concentrations of Ni which are deposited at 10°C and annealed at 250°C are shown in **Figure 2**.

A comparison of 2θ and d-spacing values of the deposited samples with the standard sample is given in **Table 1**.

The XRD patterns of the deposited samples were compared with standard pattern of Sb_2S_3 (ICSD code: 001-0538) with lattice parameters; $a = 11.20$ Å, $b = 11.28$ Å, $c = 3.83$ Å, $V_{\text{cell}} = 483.87$ Å³ and $\rho_{\text{X-ray}} = 4.63$ g/cm³. It can be seen that films are polycrystalline with an orthorhombic stibnite phase. The preferential plan for 1% Ni-doped film was found at $2\theta = 22.31^\circ$ corresponding to hkl plane (220) while for 3% and 5% Ni-doped films it was shifted towards $2\theta = 24.92^\circ$ with hkl plane (130). The calculated lattice parameters in comparison with un-doped sample [13] are given in **Table 2**. The lattice parameters for 1% and 3% are in good agreement with un-doped Sb_2S_3 thin film sample with the grain size increasing from 21 nm to 63 nm while for 5% Ni-doping, a drastic increase in grain size can be seen, *i.e.*; grain size was found as 24 μm. The increase in grain size can be attributed to increase in film thickness with higher Ni concentrations as observed during experimental work and the change in lattice parameters for 5% doping shows that there may be formation of any other phase of NiSbS.

Scanning electron micrographs for 1%, 3% and 5% Ni doped Sb_2S_3 thin films are shown in **Figure 3**. It can be seen that grains are solid and spherical with well-defined boundaries for all the films. The grains are distributed randomly on the surface for 1% and 5% Ni doping while the inter-grain distance for 3% Ni doped film is very small. The growth of particles with increase of Ni concentration can be seen from SEM micrographs. Since the boundaries are clear so we can calculate grain size from SEM micrographs using the mean linear intercept method by the formula:

$$D = \frac{1.5L}{Nm} \quad (5)$$

where, L is line length on the micrograph, N is the number of grains crossed by that line, m is magnification of micrograph and 1.5 is called as the shape factor.

The grain size calculated as 180, 360 and 360 μm for 1%, 3% and 5% Ni doped films respectively. The obtained values are greater than the values calculated by XRD due to the reason that XRD gives average information about entire film thickness while SEM extracts the surface analysis in micrometers.

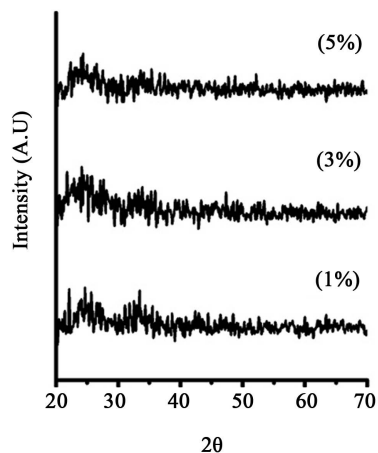


Figure 2. XRD patterns for Ni-doped Sb_2S_3 thin films with varying concentrations of Ni.

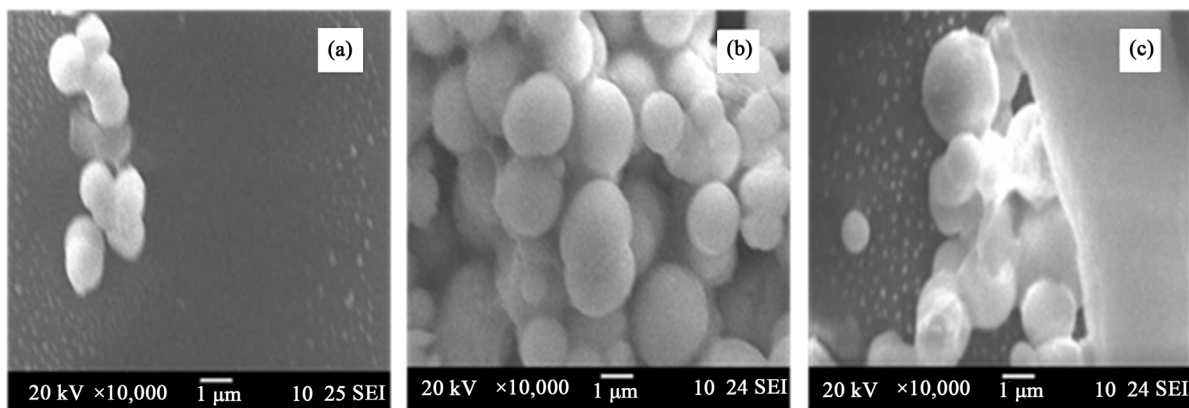


Figure 3. Scanning electron micrographs for Ni-doped Sb_2S_3 thin films with varying concentrations: (a) 1%; (b) 3% and (c) 5%.

Table 1. Comparison of 2θ and d_{hkl} values of deposited films with standard pattern of Sb_2S_3 .

ICSD # 001-0538 (Sb_2S_3)			1% Ni		3% Ni		5% Ni	
2θ	d_{hkl}	hkl	2θ	d_{hkl}	2θ	d_{hkl}	2θ	d_{hkl}
22.37	3.970	220	22.12*	4.017	21.78	4.079	22.82	3.897
24.92*	3.570	130	24.70	3.604	24.54*	3.626	24.82*	3.587
-	-	-	25.91	3.437	-	-	-	-
33.66	2.660	330	33.90	2.667	-	-	-	-
35.89	2.500	420	-	-	-	-	35.41	2.534
47.30	1.920	530	-	-	47.26	1.923	-	-
53.21	1.720	531	-	-	52.30	1.749	-	-
54.58	1.680	360	54.30	1.689	-	-	-	-
-	-	-	-	-	65.26	1.429	-	-
69.58	1.350	561	-	-	-	-	69.34	1.355

*Peak with maximum intensity.

Table 2. Lattice parameters and grain size of annealed Ni-doped Sb₂S₃ thin films.

% Ni	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> _{cell} (Å ³)	<i>ρ</i> _{X-ray} (g/cm ³)	<i>D</i> (nm)
0%	11.47	11.22	3.81	490	4.60	21
1%	11.21	11.42	3.98	509	4.43	45
3%	11.40	11.60	3.79	501	4.50	63
5%	11.50	10.50	5.40	652	3.46	2413
Sb ₂ S ₃ *	11.20	11.28	3.83	483	4.63	-

*Standard values.

UV/vis spectra of both the as-deposited as well as annealed were taken for the determination of optical constants like refractive index, absorption coefficient, extinction coefficient and electrical properties like dielectric constant and electrical conductivity. The optical absorbance spectra for as-deposited Ni-doped Sb₂S₃ thin films are shown in **Figure 4**.

The absorbance was calculated in wavelength range of 400 - 800 nm. It can be seen that the high absorbance region for 1% Ni-doped films can be found in the range 500 - 700 nm while for 3% Ni-doped films maximum value of absorbance can be seen at wavelength of 600 nm. The decreasing values for absorbance can be observed in the wavelength range 450 - 600 nm for 5% Ni doping. Absorbance spectra of the annealed Ni doped thin films were also taken for comparison. These spectra are given in **Figure 5**.

The absorption coefficient, α can be calculated by transmittance data using following relation

$$\alpha = \frac{1}{d} \ln \frac{(1-R)^2}{T} \quad (6)$$

where d is thickness of film and R is the reflectance. The average value of α was found in the range of 10^4 cm^{-1} in visible region for all of the as-deposited as well as annealed Ni-doped thin films (**Table 3**). The high absorption value $\sim 10^4 \text{ cm}^{-1}$ has a significant effect on solar conversion efficiency. Gracia *et al.* have suggested that scattering losses could be the reason for increase in absorbance due to overgrowth of particles on the surface of film [14]. The growth of particles can be seen from SEM images. The increase in grain size also supports the high absorption coefficient value.

The optical band gap of Ni-doped Sb₂S₃ thin films can be determined using Tauc's relation.

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (7)$$

where A is constant which depends on transition probability, E_g is band gap energy between bottom of conduction band and top of valence band, n is an index parameter with the values 2 and 1/2 for indirect and direct band gap respectively. The band gap values can be obtained by plotting graph between $(\alpha h\nu)^{1/n}$ and $h\nu$ as shown in **Figure 6** and **Figure 7** both for as-deposited and annealed samples. The best linear fit were obtained for $n = 1/2$ which shows that the dominant transition is direct transition here. The extrapolation of linear portion towards $h\nu$ gives the value for band gap shown in **Table 3**. There could be different reasons for band gap variation like morphology of films, deposition parameters and environment and grain boundaries, etc.

The extinction coefficient k was found using following relation:

$$k = \frac{\alpha \lambda}{4\pi} \quad (8)$$

The variation of extinction coefficient values can be depicted from **Table 3**. It can be seen that the values ranges from 0.10 - 0.27 and 0.04 - 0.24 for as-deposited and annealed films, respectively. The low value of extinction coefficient for both as-deposited and annealed thin films shows the smoothness and homogeneity of deposited films. The refractive indices for Ni-doped Sb₂S₃ thin films were calculated using the following relation.

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1+R)^2} - k^2} \quad (9)$$

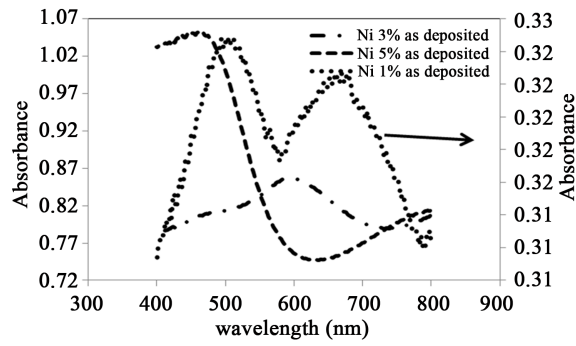


Figure 4. Absorbance spectra of as deposited Sb_2S_3 films with varying Ni concentrations.

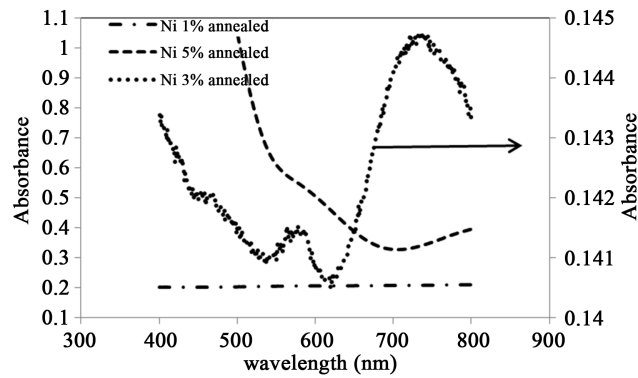


Figure 5. Absorbance spectra of annealed Sb_2S_3 films with varying Ni concentrations.

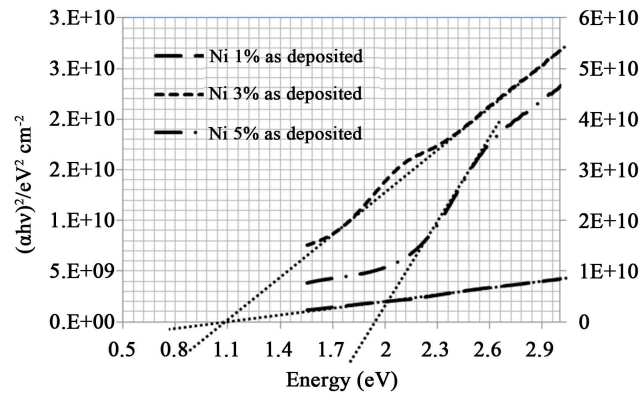


Figure 6. Band gap values obtained for the as deposited samples.

Table 3. Optical parameters for as-deposited and annealed Ni-doped Sb_2S_3 thin films.

Parameters	As-deposited							
	N	k	ϵ	α (cm^{-1}) $\times 10^4$	E_g (eV)	σ_e ($\Omega \cdot cm$) $^{-1}$	σ_o (s^{-1}) $\times 10^{14}$	σt (W/K·m) $\times 10^{-8}$
1%	2.18	0.10	05.21	2.21	1.00	1.66	1.15	12.14
3%	3.26	0.26	12.36	5.65	1.10	1.11	4.40	08.11
5%	3.38	0.27	13.34	5.96	1.90	1.06	4.87	07.77
Annealed								
1%	1.91	0.06	03.91	1.43	1.00	1.90	0.65	13.87
3%	1.73	0.04	03.18	1.00	1.50	2.08	0.41	15.25
5%	3.74	0.24	22.90	5.84	2.60	1.15	8.13	08.41

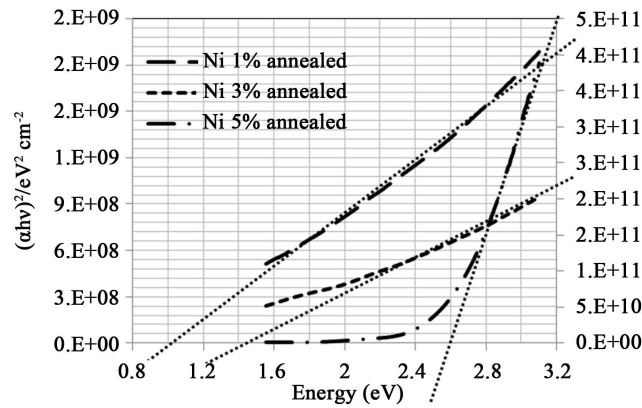


Figure 7. Band gap values obtained for the annealed samples.

The different values of refractive index were calculated in the wavelength range 400 - 800 nm. The average values are given in **Table 3**. The high refractive index values can be attributed to increase in crystal quality and grain size. The dielectric constant values were calculated using the relation

$$\varepsilon = (n - ik)^2 \quad (10)$$

The maximum value of dielectric constant was found for 5% Ni-doped Sb_2S_3 thin films as 13.34 and 22.90 for as-deposited and annealed films, respectively; which show that doping has remarkable effect at higher concentration. The response of optical conductivity σ_o was seen using the relation.

$$\sigma_o (s^{-1}) = \frac{\alpha nc}{4\pi} \quad (11)$$

Both the as-deposited and annealed Ni-doped Sb_2S_3 thin films have high optical conductivity response $\sim 10^{14} s^{-1}$ in wavelength range 400 - 800 nm. The average value for each sample is given in **Table 3**. Electrical conductivity values were measured using

$$\sigma_e (\Omega \cdot \text{cm})^{-1} = \frac{2\pi}{\lambda nc} \quad (12)$$

It can be observed from **Table 3** that all the samples have values of the electrical conductivity in the range for semi-conductors, which is $10^{-12} - 10^2 (\Omega \cdot \text{cm})^{-1}$ [15]. Thermal conductivity measurements were made using the relation [15]:

$$\sigma_T (\text{W/m} \cdot \text{K}) = LT\sigma_e \quad (13)$$

where L is Lorentz number with a value of $2.45 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$ and T is temperature. The values for optical constants are given in **Table 3**.

4. Conclusion

Ni-doped Sb_2S_3 thin films have been deposited using chemical bath deposition technique. Doping was carried out using 1, 3 and 5 wt% of Ni. Polycrystalline orthorhombic crystal structure of films was analyzed using XRD technique. Scanning electron microscopy showed that grains are solid and spherical. The band gap values were calculated in the range 1.0 - 2.6 eV with an absorption coefficient value $\sim 10^4 \text{ cm}^{-1}$. The electrical conductivity values were found in limit of values for semiconductor. High absorbance properties confirm its use for solar cell application.

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