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Effect of Thermal Annealing on the Structural and Optical Properties of Sb_2Se_3 Thin Films

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Abstract. In this paper the effect of thermal annealing on the structural and optical properties of Antimony Selenide (Sb2Se3) is investigated. Sb2Se3 powder is evaporated on clean amorphous glass substrates at room temperature under high vacuum pressure (4.5×10^{-6} mbar) to form thin films. The structural investigation was done with the aid of X-ray diffraction (XRD) and atomic force microscopy (AFM). The amorphous to polycrystalline transformation of these thin films was shown by X-ray diffraction analysis after thermal annealing. These films' morphology is explained. (UV-Vis) spectra in ranges from 300 to 1100 nm was used to examine the optical properties of the films .The absorption coefficient and optical energy gap of the investigated films are calculated using transmission spectra according to UV-visible absorption spectra. The optical band energy gap is measured using as-deposited Sb2Se3 thin films at room temperature and annealed Sb2Se3 thin films at 473K and 573 K.

Keywords. (Sb_2Se_3) Thin Films, Structural properties, Optical properties , Thermal evaporation , Thermal annealing.

INTRODUCTION

Chalcogenide materials continue to pique interest, owing to their vast range of technological use [1] .Antimonselite (Sb2Se3) is a V2 -VI3 binary chalcogenide with a (Pnma 62) space group and an orthorhombic crystal structure. It's a layered compound with staggered layers made up of parallel 1D (Sb4 Se6) n ribbons held together by weak van der Waals forces [2]. A thorough understanding of the optical characteristics of Sb2Se3 is required to better design the device configuration and increase device performance. The bandgap of amorphous Sb2Se3 (a-Sb2Se3) is greater than that of polycrystalline Sb2Se3 (c-Sb2Se3) [3,4]. Sb2Se3 films exhibit a high absorption coefficient of $> 10^5$ cm^{-1} for photon energies greater than the bandgap (hv > Eg), according to experimental data. As a result, Sb2Se3 films as thin as 800 nm are capable of absorbing photons in the 400–1000 nm wavelength range [5]. the melting point of Sb2Se3 is 608C^o [6]. low toxicity and relatively earth-abundant constituents. All these features merit its exploration for photovoltaic application [7].

The aim of this research is to focus on the effect of thermal annealing on the structural and optical properties of Antimony Selenide (Sb2Se3) thin films and the correlation between these parameters. Furthermore, to explore the effect of thermal annealing on the performance of photovoltaic devices.

EXPERIMENTAL DETAILS

For growing the Sb_2Se_3 crystals, Sb_2Se_3 in bulk form was prepared by melting stoichiometric amounts of the elements antimony (Sb) and Selenium (Se) of 99.99% purity to yield the Sb_2Se_3 crude ingot. Antimony and Selenium powders have been put into a quartz ampoule that has been vacuum sealed at (10^{-3} mbar). This ampoule

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was sealed and placed in a furnace. the tube's temperature was increased slowly (300 C/h) to avoid any possibility of explosions because of Selenium high vapor pressure, sustaining the melt at 700 C for 3 h will result in a complete homogenization of the sample. The tube is then allowed to cool slowly to avoid cracks due to the melt's thermal expansion during solidification. Grinding the initial ingot yields the crude material for vacuum thermal evaporation .Sb2Se3 films were deposited on amorphous glass substrates by thermal vacuum evaporation under approximately ($4.5x10^{-5}$ mbar) vacuum at room temperature. Using the weighing approach, a (Precisa-Swiss) microbalance was used to determine the thickness of the films. and found to be about (500∓20) nm, with deposition rate about (1) nm/sec. using (Edwards-Unit 306) system. The annealing process was carried out by (VECTOREEN model) oven at different temperatures (473,573) K for one hour . X-ray diffraction was used to examine The crystal structure of these films. The (SHIMADZU Japan -XRD600) automated diffractmeter was used to extract the (XRD) patterns, which were obtained using CuKα radiations (λ=1.54059 Å) with a voltage of (40 kv) and (8 deg/min) scanning speed in the range of 2θ between 10° and 80°.Optical transmission measurements were performed with (UV/Visible 1800 spectrophotometer). (SPM model AA 3000 Angstrom Advanced Lns., USA) was used to carry out Atomic force microscopy (AFM) measurements to determine the crystalline topography and grain size of the films.

RESULTS AND DISCUSSION

The XRD pattern of grown Sb2Se3 crystals is shown in Fig. 1(a). The noted pattern is analogous with the Sb2Se3 peak which has an orthorhombic structure [JCPDS file No. 15–0861]. Also, the powder's XRD pattern symbolize strong peak corresponding to (240) reflections at a diffraction angle of 34.1683º. The X-ray diffraction (XRD) analysis shows that, The as deposited Sb_2Se_3 films an amorphous structure Fig. 1(b). The thin films show a polycrystalline structure after annealing at 473K and 573K Fig. 1(c)(d). d(hkl) (interplanar spacing) was calculated with Bragg's equation [8] .

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

Where (θ) is the diffraction angle, (n) is an integer which represents the order of the reflection, and (λ) is the wavelength of the X-ray beam used (λ=1.54059 Å). Calculated d_{hkl} values for Sb2Se3 thin films at 473 K and 573K are consistent with the standard values as shown in Table (1). Films that have been annealed at this temperature are crystallized in the orthorhombic phase, with a preferential orientation along the (240) plane. These results agree with the researcher [9].

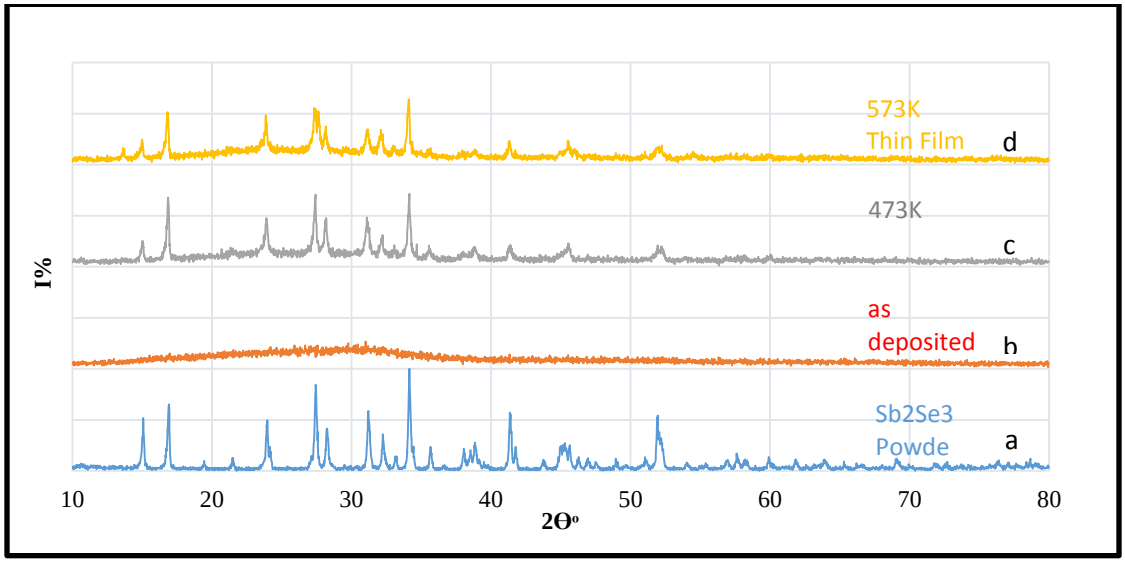

FIGURE 1. (XRD) pattern of Sb_2Se_3 .

TABLE 1. Experimental d_{hkl} with standard values for Sb2Se3.

Sample	2θ Stander	2θ Observed	d(A°)Standard	d(A°)Observed	(hkl) Standard
Sb2Se powder	27.3944	27.4656	3.2530	3.24481	(230)
	31.1593	31.2443	2.8680	2.86046	(221)
	34.0745	34.1683	2.6290	2.62207	(240)
	51.8776	51.9520	1.7610	1.75870	(061)
Sb2Se3 Thin film	16.8738	16.8315	5.2500	5.26323	(120)
Annealing at 473K	27.3944	27.3714	3.2530	3.25577	(230)
	31.1593	31.1083	2.8680	2.87266	(221)
	34.0745	34.1056	2.6290	2.62674	(240)
	51.8776	51.9457	1.7610	1.75046	(061)
Sb2Se3 Thin film	16.8738	16.8613	5.2500	5.25400	(120)
Annealing at 573K	27.3944	27.4269	3.2530	3.24930	(230)
	31.1593	31.1570	2.8680	2.86828	(221)
	34.0745	34.0972	2.6290	2.62737	(240)
	51.8776	51.9474	1.7610	1.75884	(061)

The crystalline size 'C.S' value of the films was estimated from the Debye-Scherrer equation[10] from the full width at half maximum (FWHM) of the preferred orientation (240):

$$C.S = \frac{K\lambda}{\beta_{FWHM}\cos\theta} \quad (2)$$

Where θ is the Bragg angle , β is the full width at half maximum of diffraction peak measured in radians units, K (the Scherrer constant), and λ is the X-ray wavelength used (λ=1.54059 Å). The dislocation density (δ) has been calculated using the equation, which is defined as the length of dislocation lines per unit volume of the crystal [11]:

$$\delta = \frac{1}{(C.S)^2} \quad (3)$$

the crystal layers number ($N_\circ$) calculated by using relation[12]:

$$N_\circ = \frac{t}{(C.S)^3} \quad (4)$$

Where t(nm) is the thickness of thin film . Table (2) shows that when the annealing temperature rises, the crystalline size increases from 36.737 nm to 41.629 nm. As the annealing temperature rises, the number of crystals and dislocation density decrease.

TABLE 2. The values of the structural calculations of the prepared films at (473 K) and (573 K).

Sample	C.S(nm)	δ(1/cm^2)	N°(1/cm^2)
473 k	36.7371	7.4095E+10	1.0084E+12
573 k	41.6296	5.7703E+10	6.9304E+11

AFM is a high-resolution non-optical imaging technique , to study the change in the surface topography of the films, Multiple scans of the surface topography were carried out Fig. 2. AFM images were used to estimate the (R.M.S) root-mean-square roughness and grain size of the samples and the results have been shown in table (3). The grain size or particle size of Sb2Se3 rises with increasing annealing temperature, as seen in Table (3) of AFM investigation. As a result of the fusion of tiny grains to generate larger grains, which leads to the structural development of the thin films, these results are consistent with XRD results.

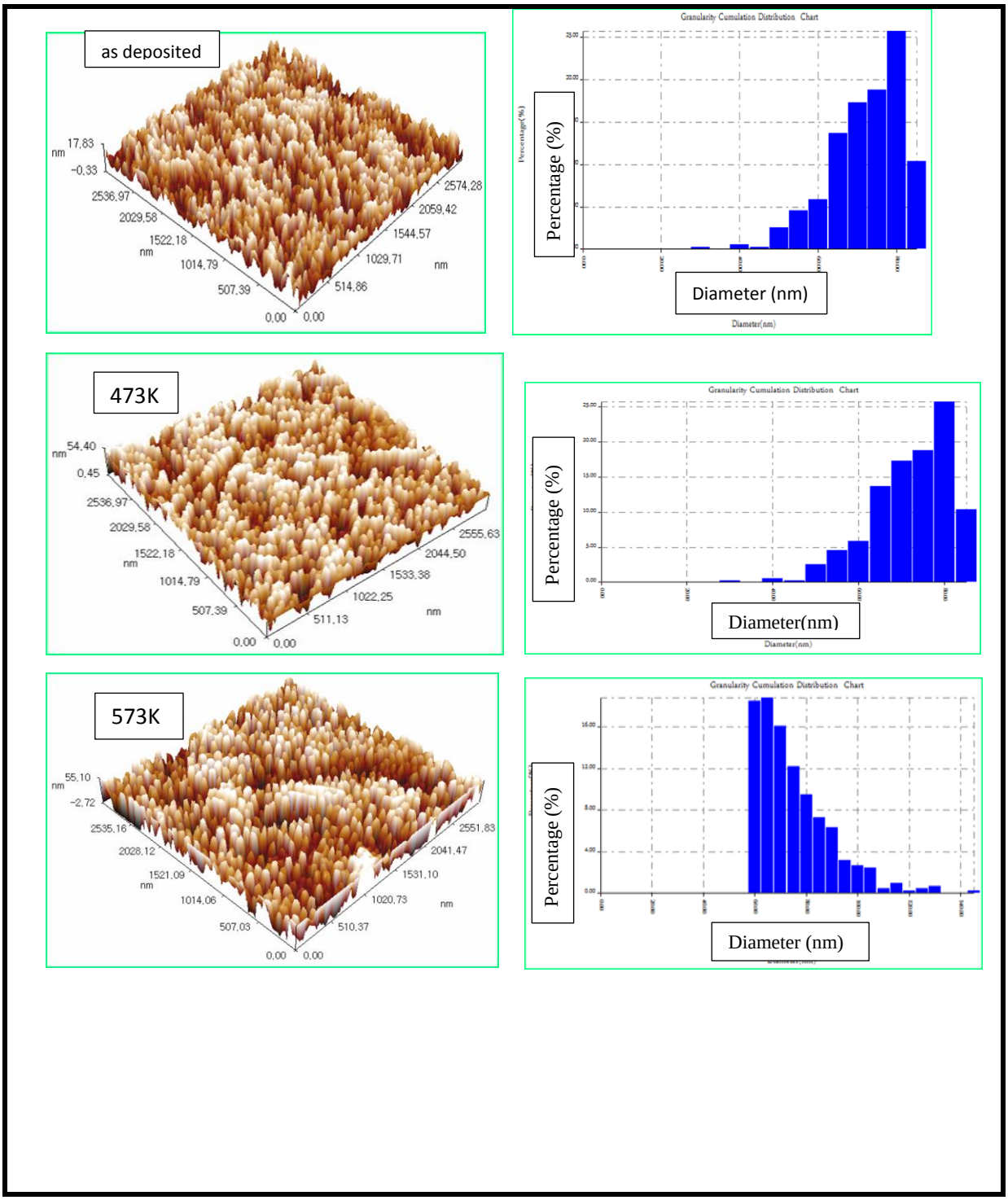

FIGURE 2. AFM surface topography images of Sb_2Se_3 thin films .

TABLE 3. AFM Report for Sb2Se3 thin films at room temperature and different annealing temperatures.

Sample	Avg.Diameter (nm)	Roughness(nm)	R.M.S (nm)
As deposited Sb2Se3 films	69.77	4.07	4.7
473 K	70.74	12.3	14.4
573 K	72.64	14.5	16.7

The transmittance spectra were measured as a function of wavelength in the spectral region (300-1100) nm at 500 nm thickness for (Sb_2Se_3) films at room temperature and for annealing at (473 , 573) K as presented in Figure (3). Energy gap and band structure understanding of both amorphous and crystalline materials are done through optical absorption spectra analysis. Figure (4) displays the presence of an absorption edge and shows that the optical absorption coefficient (α) is a function of photon wavelength. As all films have high values ($\alpha > 10^4$ cm^{-1}) indicating that a direct transition has occurred. the absorption edge is shifted toward longer wavelengths . This variation could be related to the variation of the crystallinity . The energy gap (Eg) of the Sb_2Se_3 thin films is calculated using the expression [13]:

$$\alpha h\upsilon = \eta(h\upsilon - Eg)^{r} \quad (5)$$

Where η is constant, α (cm^{-1}) is the absorption coefficient , Eg (eV) is the energy gap , (hν)(eV) is the photon energy. (r) is determined by the optical transition involved in the absorption process. The photon energy axis was intersected by the straight line of the curve $(\alpha h\upsilon)^2$ versus (hυ) plot, yielding the energy gap as Shown in Figure(5). The optical band gap as a function of temperature was found to be (1.6) eV at room temperature, and as the annealing temperature rises from (473 K) to (573 K), the optical band gap drops from (1.3) eV to (1.25) eV, with allowed direct transition. the effect of increasing the temperature of annealing on the energy gap can be noted from the Table (4). At higher temperature, When the amorphous structure in the annealed Sb2Se3 thin films transforms to polycrystalline, the decrease in band gap energy is attributed to the improvement in grain size and quantum confinement effect due to the increase in the crystallites size. Similar type of observations in the Sb2S3 thin films have been reported earlier 14]. Reported optical band gap values of Sb_2Se_3 thin films prepared using various methods are consistent with These values [15,16].

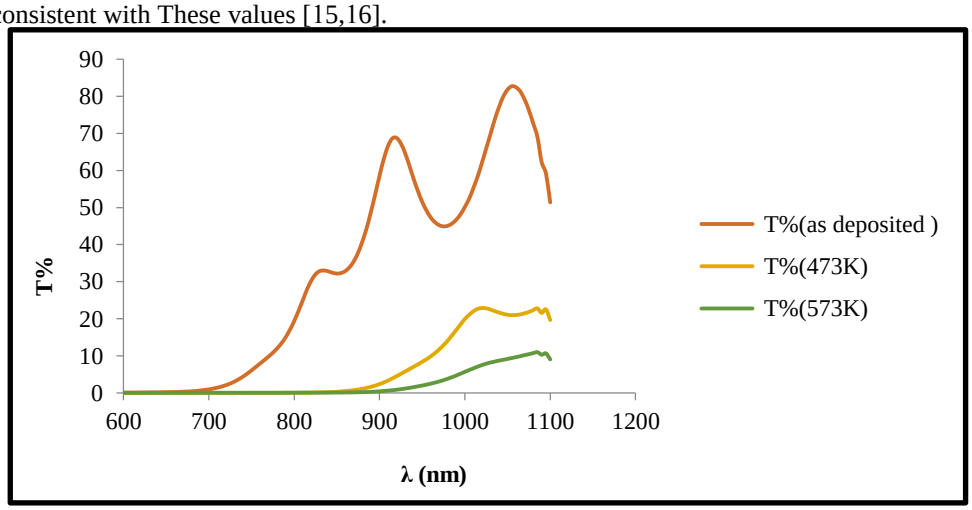

FIGURE 3. The transmittance as a function of wavelength for Sb2Se3 films at room temperature and the annealing at (473,573) K.

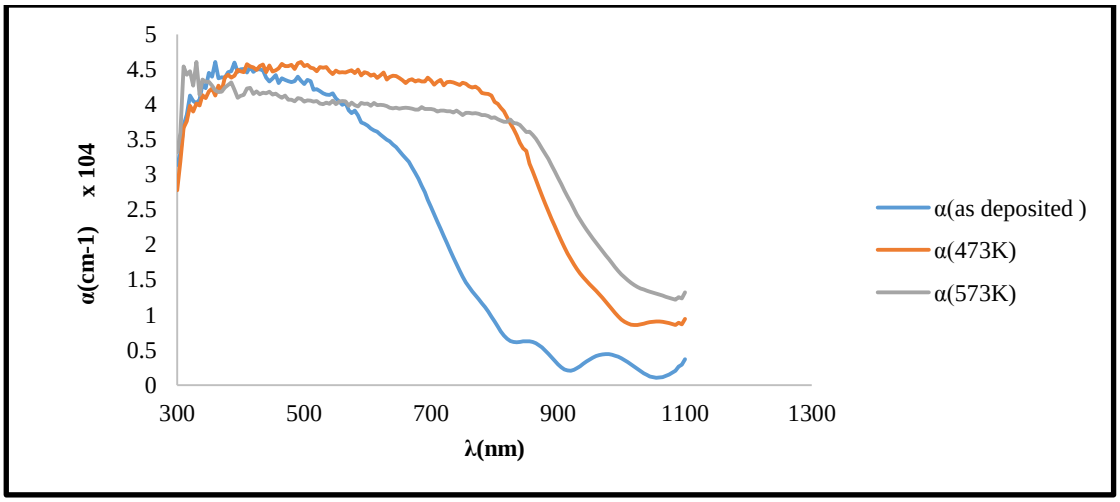

FIGURE 4. Absorption coefficient (α) as a function of wavelength.

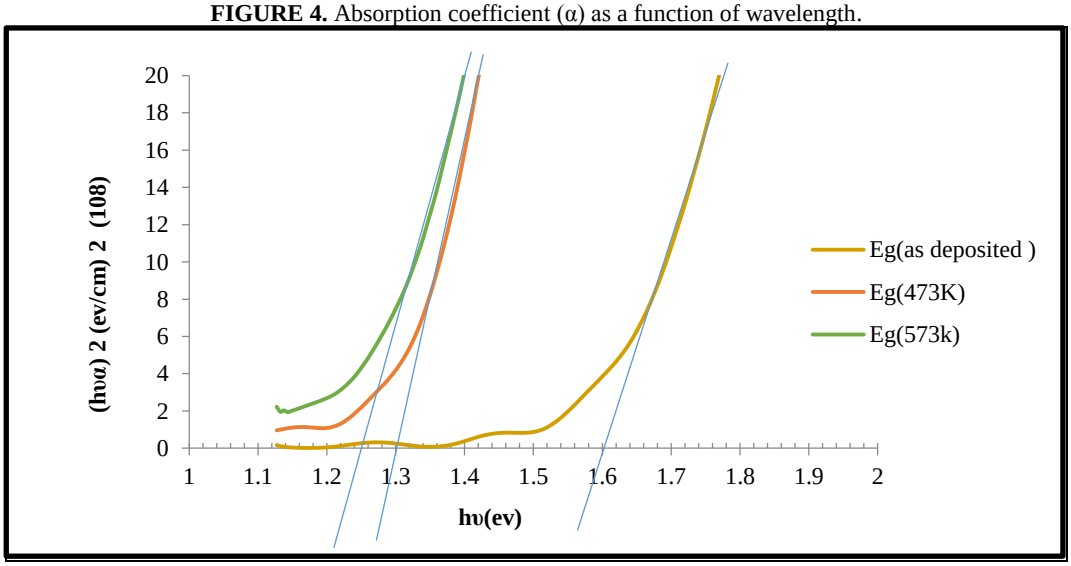

FIGURE 5. $(\alpha hv)^2$ as a function of photon energy of Sb2Se3 films with various annealing temperatures.

TABLE 4. Band gap (Eg) of as-deposited and thermally treated.

Sample	Eg (eV)
as deposited	1.6
475k	1.3
575k	1.25

CONCLUSIONS

In summary , Sb2Se3 powder was prepared successfully and we found that our Sb2Se3 thin film prepared at room temperature has an amorphous structure and changes to a polycrystalline with orthorhombic structure at 473 K and 573K , with a preferential orientation along the (240) plane. The absorption coefficient is greater than 10^4 (cm^{-1}) .The correlation between structural properties and morphology of the films have shown that the grain size increases with increasing annealing temperature ·At room temperature, the optical energy gap is (1.6) eV, and at (473,573) K, it is (1.3, 1.25) eV respectively.

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