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THE INFLUENCE OF HEAT TREATMENT ON THE ELECTRICAL CONDUCTIVITY OF ANTIMONY TRIOXIDE THIN FILMS

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Antimony trioxide (Sb_2O_3) thin films were prepared by thermal vacuum evaporation technique onto glass substrates kept at 300 K. Film structure, grains size, morphology and roughness of surface were determined by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The obtained films are polycrystalline with face centered cubic symmetry and lattice constant a=11.16 Å. The electrical conductivity of the Sb_2O_3 films increases from 3.10×10^{-10} to 2.97×10^{-8} $\Omega^{-1}cm^{-1}$, after heat treatment.

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1. Introduction

Transparent and electrically conductive antimony trioxide (Sb_2O_3) films are widely used for a variety of applications, including electrodes for flat panel displays, light emitting devices, solar cells, spectrally selective coating, gas sensors and heat mirrors [1]. Pure single and cubic Sb_2O_3 crystal has very high electrical resistance with a band gap of about 4 eV [2]. The intrinsic conducting electron density at room temperature of undoped polycrystalline Sb_2O_3 thin films is about 10^{25} m^{-3} [3]. This high conducting electron density is caused by deviations from the ideal single crystal structure: e.g. oxygen vacancies interstitial atoms and dislocations act as conductive electron donors, producing a wide band gap in the range 3.17-3.29 eV [4]. In the last few years, several reports have been published on the electrical properties of oxide glasses containing Sb_2O_3 as glass formers have beenpublished [5,6]. The presence of Sb_2O_3 in silicate glasses leads to interesting electrical behavior of these materials at a temperature around 300 K.

Post deposition annealing in air changes the conductivity and structural properties of polycrystalline Sb_2O_3 thin films, and is one of the methods employed to improve their usability. The heat treatment increased film conductivity [7].

The objective of this work was to study the effect of heat treatment on a minute timescale and below crystallization temperature on the structural properties and conductivity of polycrystalline Sb_2O_3 thin films. Comparisons of the structural and electrical properties of films before (as-deposited) and after (post-deposited) the annealing treatment have been discussed. Average grain diameter, energy bandgap and electrical conductivity have been analyzed.

2. Experimental

Thin films of Sb_2O_3 were deposited by thermal evaporation under vacuum at about 10^{-5} torr of polycrystalline powder of 99.99% purity on glass substrates. The substrate temperature, T_S, was kept

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constant during the film growth at 300 K. The thickness of the films (d = 0.8 μm) was measured by interferometric method [8] using a MII-4 type Linnik microscope.

After preparation, the samples were heat-treated by annealing, in air at rate of 6.66 K/min from room temperature to final 500 K, which was maintained for 30 min. Then the samples were cooled down at the same rate.

The structure of the films before and after the heat-treatment was investigated by standard X-ray diffraction (XRD) technique using CuK_α radiation (λ = 0.15418 nm) and electron microscopy investigations (TEM and SEM). A transmission electron microscope (Philips CM 120), operating with a calibration resolution 0.4 nm, was used for the microstructural study.

The surface morphology of the thin films was investigated by means of Atomic Force Microscopy (AFM) both before and after thermal treatment. Digital Instruments Nanoscope AFM was used for the analysis at a tapping mode. The scanned area was 5 μm, at a scanning rate 1.969 Hz.

For the electrical measurements, samples with planar geometry have been used. Vacuum deposited aluminum thin films were used as electrodes. The measurements were made in ambient atmosphere. The electrical conductivity, σ, was determined according to the relation $\sigma = \ell / Rdb$ [9], where $\ell = 3\,mm$ is the distance between the electrodes, $b = 1\ cm$ is the width of the film and R represents the electrical resistance of the film, measured by a standard d.c. method, using a KEITHLEY 6517 A electrometer.

3. Results and discussion

3.1 Structural properties

The cystallinity of antimony trioxide (Sb_2O_3) thin films was investigated with the XRD (Fig. 1) and TEM (Fig. 2) measurements. The XRD data reveal that both as-deposited and annealed thin films are single phase and polycrystalline in nature. The structure of the film has been found to be cubic with lattice parameter a = 11.16 Å and do not vary significantly with the heat treatment. The crystallites are preferentially oriented with the (222) planes parallel to the glass substrate. The peak (551) is evidenced after annealing.

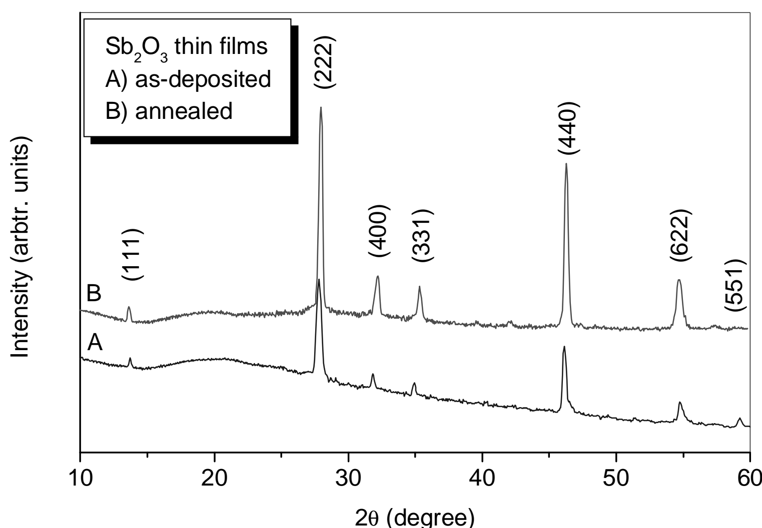
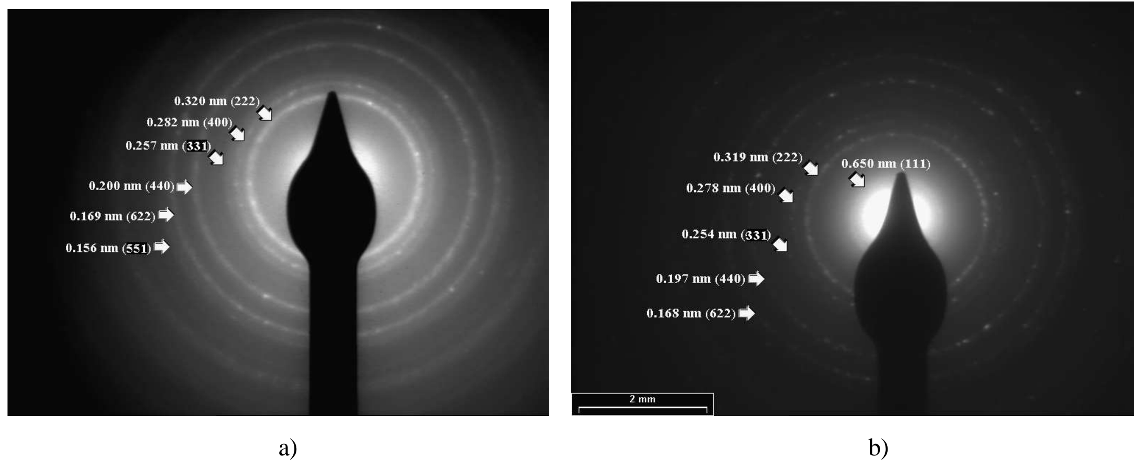


Fig.1. XRD pattern of Sb_2O_3 thin film.

In Table 1 are compared the interplanar distances calculated from XRD patterns and TEM patterns, for the as-deposited and annealed Sb_2O_3 thin films.



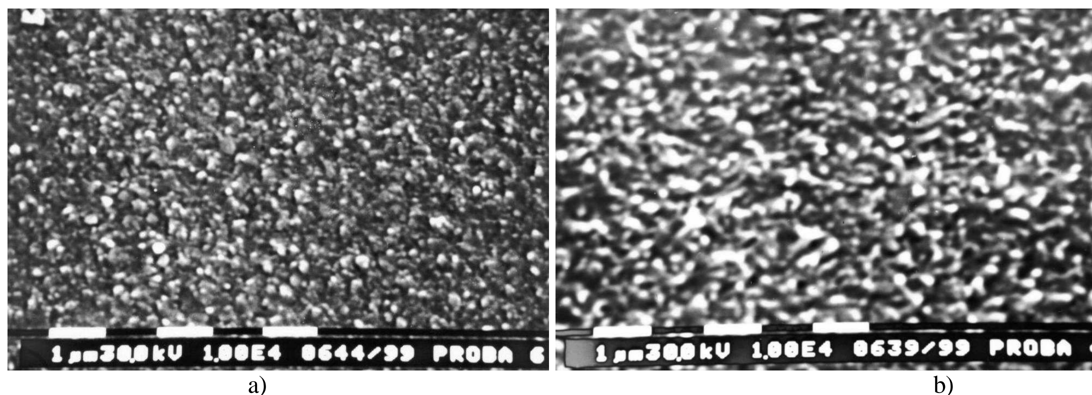
a) b)

Fig. 2. TEM patterns of Sb_2O_3 thin films a) as-deposited and b) annealed.

Table 1.

hkl	$d_{hk\ell}$ (nm) –XRD patterns		$d_{hk\ell}$ (nm) –TEM patterns		$d_{hk\ell}$ (nm)
	as-deposited	annealed	as-deposited	annealed	standard
(111)	0.644	0.649	0.644	0.650	0.643
(222)	0.320	0.318	0.320	0.319	0.321
(400)	0.280	0.278	0.282	0.278	0.278
(331)	0.256	0.254	0.257	0.254	0.214
(440)	0.196	0.196	0.200	0.197	0.197
(622)	0.167	0.168	0.169	0.168	0.168
(511)	0.156	-	0.156	-	0.156

The average grain size was found to increases from 75.22 to 85.44 nm after heat treatment. This observation is confirmed by scanning electron micrographs (SEM) shown in Fig. 3. Fine grains and good homogeneity is observed.



a) b)

Fig. 3. SEM micrographs of Sb_2O_3 thin films a) as-deposited and b) annealed.

Atomic force microscopy (AFM) was used to examine the surface morphology of Sb_2O_3 thin films. Fig. 4 shows the AFM micrographs (5×5 μm^2) for studied samples before and after heat treatment. The grain-like morphology can be seen in both samples and the topography of samples was

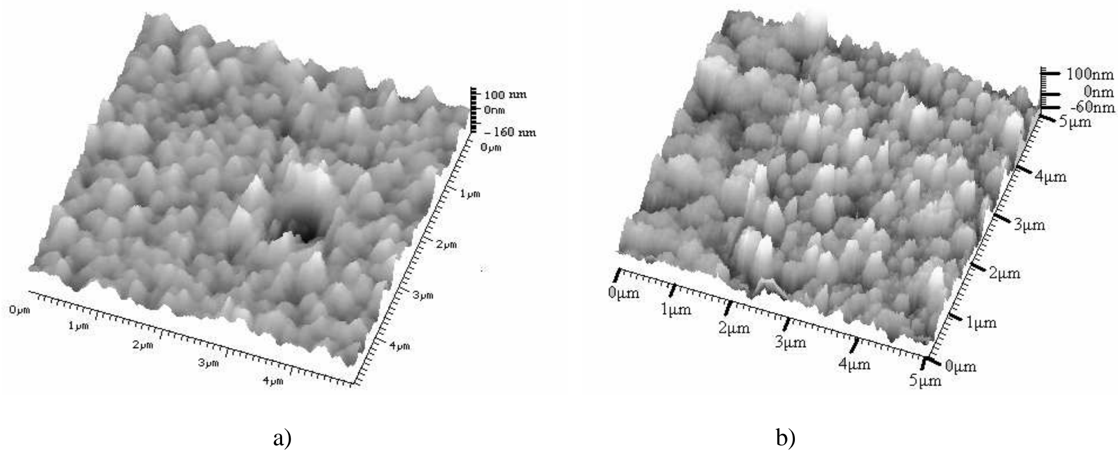
not changed after heat treatment. However, the root mean square (RMS) roughness value decreases from 41.995 to 27.485 nm after heat treatment at 500 K. It is generally known that the annealing of polycrystalline films results in reduction of surface roughness [10]. According to the definition, the root mean square is given as [11]:

$$RMS = \frac{1}{\sqrt{n}} \sqrt{\sum_{i=1}^{n} (x_0 - x_i)^2} \tag{1}$$

where x_i are the individual AFM data point, n is the number of data points and x_0 is their mean value given by:

$$x_0 = \frac{\sum_{i=1}^{n} x_i}{n} \tag{2}$$

The root mean square value for the scanned surfaces was automatically calculated.



a) b)

Fig. 4. AFM micrographs (5×5 μm^2) of Sb_2O_3 thin films a) as-deposited and b) annealed.

3.2 Electrical properties

The current voltage characteristics of structures Al-Sb_2O_3-Al (Fig. 5) are perfectly symmetric with respect to the polarity of applied voltage. The I–U characteristics indicates lower electrical conductivity of thin films of Sb_2O_3. This is due to weak intermolecular interaction forces of the Van der Waals type among Sb_2O_3 molecules. At room temperature, the density of free charge carriers is extremely low, which prevents electrical conduction.

When low voltage (U<1V) is applied the contacts Al-Sb_2O_3 are ohmic. This is because due to the low concentration of intrinsic carriers, the conductivity of semiconducting film will be determined by the concentration of injected carriers. The current becomes nonlinear ($I \sim U^n$) above 1V. For as-deposited Al-Sb_2O_3–Al structures n =3.6 and after heat treatment n=2.3. We may conclude that there exists a possible region of carrier injection due to the relatively low height of the forbidden band (E_g=4 eV). This fact leads to a relatively low height of the potential barrier at the metal - semiconductor contact. There are indications that in Sb_2O_3 polycrystalline layers the conduction mechanism is characteristic of space–charge–limited current (SCLC), based on the assumption of exponential trap distribution and described by the relation [12]:

$$I = ct.\frac{U^n}{d^{\ell}} \tag{3}$$

with $n=m+1$ and $\ell = 2m+1$, where $m=T_c/T$, ($T_c > T$). T_c is the characteristic temperature of distribution relating the rate at which the trap density change with energy, T the temperature and d is the thickness of dielectric layers.

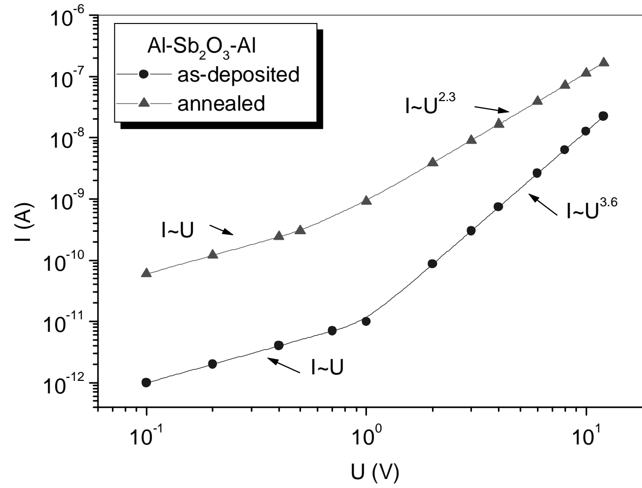


Fig. 5. Current-voltage characteristics of Al-Sb_2O_3–Al structures.

From the mean value of *m*, we determined T_c = 644 *K* and the distribution factor kT_c = 0.55 eV. The value of kT_c, in evaporated polycrystalline films of different inorganic molecular compounds, in the range 0.03-0.15 eV, is nearly the same as in single crystals [13]. These results are consistent with a trap distribution whose density decreases exponentially as the energy from the band edge increases.

The temperature dependence of the electrical conductivity has been investigated for Al-Sb_2O_3-Al thin films prepared at 300 K. An exponential increase of the electrical conductivity with the temperature was observed for all investigated temperature ranges.

The dependence can be written as [14]:

$$\sigma = \sigma_0 \exp(-E_a / kT) \tag{3}$$

where E_a denotes the thermal activation of electrical conduction, σ_0 is a parameter that depends on the semiconductor nature and *k* is the Boltzmann's constant.

Fig. 7 shows the temperature dependence of electrical conductivity, for samples prepared at substrate temperature T_S = 300 K. The samples were subjected to two successive heating and cooling.

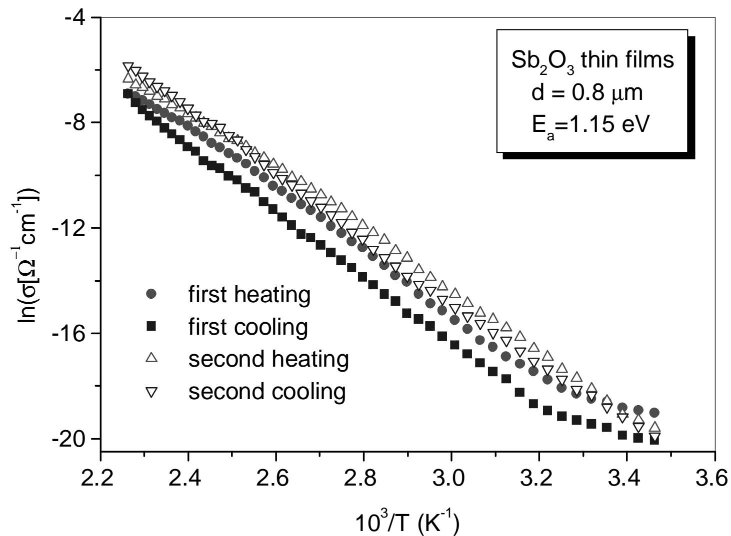


Fig. 6. Plot ln σ versus (10^3/T) for Sb_2S_3 thin films deposited at substrate temperature T_S = 300 K.

It can be observed that after second heating, the temperature dependence of the electrical conductivity becomes reversible. This fact indicated the stabilization of the film structure.

The activation energy E_a calculated from the slope of the dependence $ln\sigma = f(10^3/T)$ is indicated in Table 2. The calculations were carried out taking into account the relationship (3). The values of the characteristic parameters are given in Table 2: *d*-film thickness, T_S-substrate temperature, σ_c-electrical conductivity at room temperature before the heat treatment, σ_T-electrical conductivity at room temperature after the heat treatment, ΔT-temperature range in which the treatment of the samples was performed.

Table 2. The characteristic parameters of the films.

Sample	d (μm)	T_S (K)	σ_c ($\Omega^{-1}cm^{-1}$)	σ_T ($\Omega^{-1}cm^{-1}$)	ΔT (K)	E_a (eV)
Sb_2O_3	0.80	300	3.10×10^{-9}	2.97×10^{-8}	300-500	1.15

The lower values of σ for thin films might be explained by the presence of the crystallites with smaller size in respective sample. The obtained results lead to the conclusion that the polycrystalline structure of the investigated sample plays an important role in the electronic transport properties. For polycrystalline samples it is possible to use the models elaborated for explaining the mechanism of electrical conduction in the films with discrete structure [15].

5. Conclusions

Using the vacuum evaporation technique, Sb_2O_3 thin films with crystalline structure were prepared. The XRD and TEM study reveal that the films, freshly-deposited and annealed at 500 K, have the polycrystalline nature corresponding to a FCC phase with lattice parameter a=11.16 Å.

The grain size depends on the heat treatment. It was found that the grain size increases from 75.22 nm, for as-deposited films, to 85.4 nm after heat treatment. Also, the root mean square (RMS) roughness decreases from 41.995 to 27.485 nm.

The temperature dependence of electrical conductivity indicates a typical semiconducting behavior. From the $\ln\sigma = f(10^3 T)$ dependence, the values of the thermal activation energy of electrical conduction, were determined: E_a=1.15 eV. As the temperature increases from 300 to 500 K, the electrical conductivity of the Sb_2O_3 thin films increases from 3.1×10^{-9} $\Omega^{-1}cm^{-1}$ to 2.97×10^{-8} $\Omega^{-1}cm^{-1}$.

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