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The Influence Of Antimony-Doping Contents On The Structure And Optical Properties Of Tin Oxide Thin Films Prepared By Spray Pyrolysis Technique

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***Abstract*— In the existing work, Nanostructure SnO2 films have been deposited on glass at substrates temperatures 3500C at different Sb contents (1, 3, 5 and 7%wt.) with thickness (250±10nm), by chemical spray pyrolysis technique. The structural properties of films have been studied by using X-ray diffraction, which show that the prefer orientation is (110) and structures of film have a polycrystalline in nature and had a tetragonal structure for samples of contents (0, 1, 3%wt.), except the films for Nanostructure SnO2:Sb with (5 and 7% wt.) offers an amorphous structure. And we found that the grain size increases with the increasing of doping percentage. The lattice constants, micro strain, dislocation density and number of crystals per unit area, were calculated. The optical properties of the films have been studied by using UV-VIS spectrophotometer in the range from 290-1100nm, The all films showed excellent optical transparency, close to 87% with 0% wt. of antimony doping, in the visible region and has a maximum average transmittance of un-doped SnO2 films are about 97% in the near infrared region of the electromagnetic spectrum.**

Keywords—SnO₂, XRD, Nanostructure, Grain Size, Transmittance, Energy gap.

Introduction

Is a well-known as transparent conductive oxide, which belongs to the wide-band gap semiconductor family. It is a promising material for a variety of applications, and seems to be the most appropriate material for different applications in optoelectronic devices such as solar cells, optical filters, high stability resistors, displays and Electro chromic devices**,** covering layers of fiber optical systems, photovoltaic devices. Owing to their specific combined electrical, optical and chemical properties have dominated the present scientific world of thin films and gas sensing [1-4]. In addition, they exhibit low electrical resistivity and high optical transmittance. Various techniques have been applied to study tin dioxide films such as chemical vapor deposition [5], thermal evaporation [6], sol–gel coating [7], laser pulse evaporation [8], magnetron sputtering [9], electron beam evaporation [10] and spray pyrolysis [11]. Among these methods, the spraying technique is a simple, economic and commonly used method and it is well suited for the preparation of tin dioxide thin films because of its simple and inexpensive experimental arrangement, ease of adding various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings [12]. In addition, the tin dioxide prepared by the spraying technique is also physically and chemically resistant against environmental effects and adheres strongly to different substrates.

Experimental

The SnO_2 were prepared by using acetone solution of tin chloride ($SnCl_4.5H_2O$) with (0.1Molari) dissolved in acetone, $SnCl_4.5H_2O$ used for England (CAS number 10026-06-9) is a solid material which has a white color and its molecular weight is (350.59 g/mol) has been dissolved in 100ml for acetone. For calculating mass of ($SnCl_4.5H_2O$) in the current experiment the following equation was used:-

$$M = \frac{W_t}{M_{wt}} \times \frac{1000}{V} . \quad (1)$$

Where: M: concentration of molarities, W_t: weight of ($SnCl_4.5H_2O$),

M_{wt}: molecular weight of $SnCl_4.5H_2O$, V: volume of acetone (100 ml).

Weight for tin chloride ($SnCl_4.5H_2O$) is measured by the sensitive electrical balance and is analyzed in acetone solution has been prepared depending on the equation (1). By heating the glass substrate at a temperature (350℃) and SnO_2 will be deposited on substrates glass. The Sb was prepared by using acetone solution of antimony chloride ($SbCl_3$) with (0.1Molari) dissolved in acetone, $SbCl_3$ used from Germany (Re diel de hien). Is a solid material which has a colorless and its molecular weight is (228.11 g/mol) has been dissolving in 50ml for acetone. For calculating mass of ($SbCl_3$) in the current experiment the following equation was used equation (1):Where: M: concentration of molarities, W_t: weight of ($SbCl_3$),M_{wt}: molecular weight of ($SbCl_3$), V: volume of acetone (50 ml).

Weight for antimony chloride ($SbCl_3$) is measured by the sensitive electrical balance and is analyzed in acetone solution has been prepared. The (X-ray) diffraction instrument type (Shimadzu 6000) made in Japan is used with the following specifications:-

- **Target: Cu kα radiation of Wavelength =1.54 Å. Current: 30 mA. High voltage: 40 kV. Range: 2000** counts/s. Scanning speed = 5deg/min. Incident angle from 20 to 60 degrees. And the optical properties was analysis by using UV-VIS spectrophotometer, type (SHIMADZU) (UV-1650/1700 series).

Results and discussion

XRD pattern of nanostructure SnO_2:Sb films with different concentration of antimony (0, 1, 3, 5, 7% wt.) prepared by chemical spray pyrolysis technique at a substrate temperature of (350°C) has been shown in fig. (1), It is seen that the peaks are more broadened and shifted toward the decrease when the increase of antimony doping.

The x-ray diffraction spectra of nanostructure (SnO_2:Sb) films for different antimony doping rates, it can be observed that the films are polycrystalline with (110) as a preferred growth orientation. The (110) peak is the strongest peak observed in all the films, the presence of other peaks such as (101), (200) and (002) have also been detected but with substantially lower intensities. The increase of antimony doping concentration does effect the structural properties of the films and the decrease in the intensities of the main XRD peaks, and then will be converted from polycrystalline (tetragonal shape) to amorphous when increase the antimony concentration more than 3%wt., as specified in percentages 5 and 7%wt. [13]. Indicating that the (O) atoms are replaced by (Sb) atoms in the nanostructure SnO_2:Sb films because the atomic radius for antimony larger than the atomic radius for tin oxide [14].The observed d-values are presented in table (1) and are compared with the standard ones from the (JCPDS) data files. The matching of the observed and standard d-values confirms that the deposited films are of tin oxide with tetragonal structure. Figure (1) represents the X-ray diffraction of nanostructure SnO_2:Sb films at deposited temperatures (350°C) for different antimony doping.

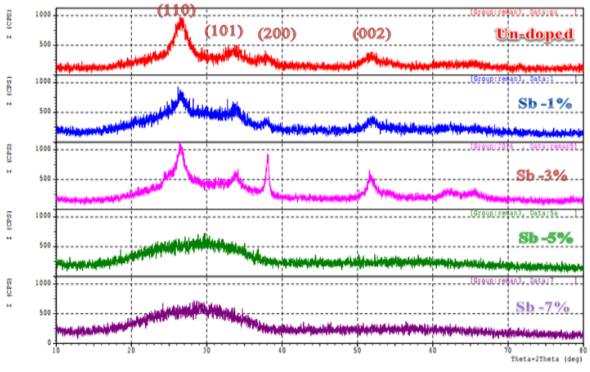

Figure (1) XRD image of Sb-doped SnO_2 nanostructure.

Table (1) the obtained result of the structural parameters from XRD for nanostructure SnO_2:Sb Films with different antimony doping.

Wt.%	2θ (deg)	FWHM (deg)	d_{hkl} EXP.(A)	$_{hkl}$ Std	hkl	phase	G.S (nm)	Card No.
Pure	*26.5433*	*1.89*	*3.35543*	*3.347*	*(110)*	*Tetragonal*	*4.525*	*00-041-1445*
Sb -1%	*26.5284*	*1.32*	*3.35728*	*3.347*	*(110)*	*Tetragonal*	*6.493*	*00-041-1445*
Sb -3%	*26.4583*	*1.21*	*3.36602*	*3.347* 4	*(110)*	*Tetragonal*	*7.24*	*00-041-1445*

The values of full width at half maximum (FWHM) of the preferred orientation (110) of antimony doped tin oxide thin films are obtained from (XRD) pattern. The (FWHM) decrease with increasing antimony doping in the films. This indicates that crystallization of the nanostructure SnO_2:Sb progresses gradually as the antimony increases as shown in Table (1).

Average Grain Size (G.S)

The average grain size has been calculated using Scherer formula:

$$G.S = \frac{0.94\,\lambda}{\beta\,cos\theta}\ .\ (2)$$

Where:λ: X-ray wavelength (1·542 Å).

β: the full width at half maximum of peak measured FWHM (in degree), θ: Bragg diffraction angle of the XRD peak (degree), and the resultant values the prepared samples are listed in the table (1). Figure (1) exhibits the effect of antimony doping concentrated on the average grain size, it clearly appear that the average grain size has been increased with increase in concentration. Which in turn is responsible for the changes in the crystallite size, and it was maximum ~7nm for the preparation at 3%wt. Transmission of films depends in general on the thickness of the film, and the nature of the surface and the kind of material, and its crystal structure, and the degree of heat-substrate, as well as the algebraic sum of the absorbency and the reflectivity of these films.

Transmission is measured for all films at room temperature by UV-VIS spectrophotometer in the range from 290-1100nm. The variation in the transmission of nanostructure SnO_2:Sb films depends on the method of preparation of the films. The transmittance spectra of the nanostructure SnO_2:Sb films doped with different concentration of Sb are shown in fig. (2). The all films showed excellent optical transparency, close to 87% with 0% wt of antimony doping, in the visible region and has a maximum average transmittance of un-doped SnO_2 films is about 97% in the near infrared region of the electromagnetic spectrum [15].

It is seen that the transmittance of the nanostructure SnO_2:Sb films decreases with increasing antimony doping in the films, and the average transmittance in the visible region (at 550 nm) has been found (87, 80.64, 80.5, 83.9 and 83.71%wt) for the un-doped and antimony doping (0, 1, 3, 5, 7%wt.) respectively [16].

But when you continue to increase the ratio of doping we find the increase of transmittance of nanostructure SnO_2:Sb thin films with increasing antimony doping concentration is caused by the decrease of surface roughness that leads to the decrease of optical scattering in the films. We observed the films were very transparent, which may be attributed by the formation of the Fermi level in the conduction band. As the ripples shown in the transmittance spectra may resulted from the interference of light, since they show wave forms that are characteristic of the interference light, also to the homogeneity of films significantly [17].

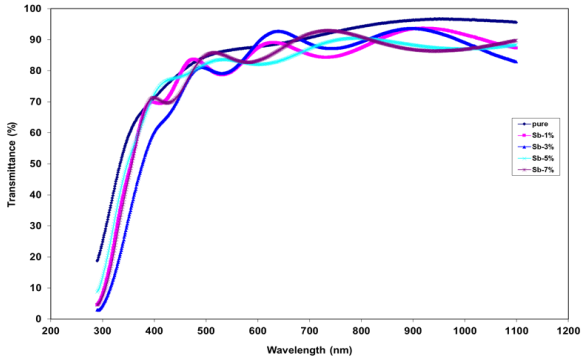

Figure (2) The optical transmission of nanostructure SnO_2:Sb thin film with different concentration of antimony.

Absorption Coefficient (α)

The optical absorption coefficient determined from absorbance measurements. The absorption coefficient of nanostructure SnO_2:Sb films decreased in the UV/VIS boundary (or at lower photon energy), and then increases gradually in the visible region (or at high photon energy) because it is inversely proportional to the transmittance. We calculated the absorption coefficient (α) as a production of photon energy of nanostructure SnO_2:Sb films with different concentration of antimony. Figure (3) presents the absorption coefficient (α) of nanostructure SnO_2:Sb films increases with the increasing of photon energy. The absorption coefficient is decreasing with the antimony doping increasing the absorption coefficient value depends on absorbance nanostructure SnO_2:Sb films has a value of absorption coefficient ($\alpha > 10^4$ cm^{-1}) which causes the increase of the probability of the occurrence of direct transitions.

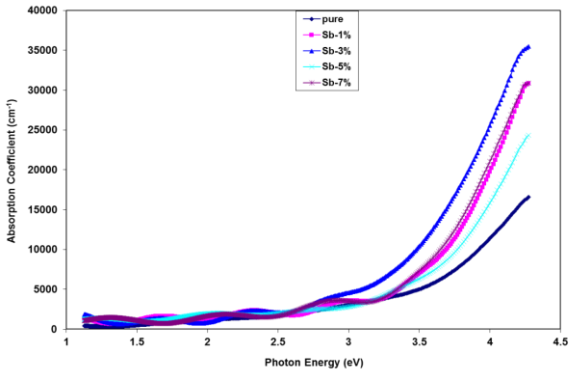

Figure (3) Absorption coefficient as a function of photo energy nanostructure SnO_2:Sb thin film with different concentration of antimony.

Optical energy gap (Eg)

The optical band gap (Eg) of nanostructure SnO_2:Sb films was evaluated from the transmission (or absorption) spectra and optical absorption coefficient (α) near the absorption edge for allowed direct transitions is given by the equation:

$$\alpha h\upsilon = B'(h\upsilon - Eg)^{1/2} \quad (3)$$

The relation is drawn between $(\alpha h\upsilon)^2$, $(\alpha h\upsilon)^{1/2}$ and photon energy (hυ), as in fig (4) illustrates allowed direct transition electronic and fig (5) illustrates allowed indirect transition electronic.

Equation (3) which can produce the band gap Eg, when the straight portion of $(\alpha h\upsilon)^2$ and $(\alpha h\upsilon)^{1/2}$ versus hυ plot is extrapolated to the point α = 0.

Figure (4) shows the variation of the direct band gap with different concentration of antimony. Nanostructure SnO_2:Sb thin films grown here have a direct band gap in the range (3.94 eV- 3.82 eV) and have an indirect bang gap in the range (3.08 eV- 3.0 eV) in figure (5) which shows in table (2). These values are decreasing with the increasing concentration of antimony. There is possibility of structural defects in the films due to their preparation this decrease in energy gap can be due to the prohibited impurities that led to the formation of donor levels within the energy gap near the conduction band. This will absorb photons of low energy [18].

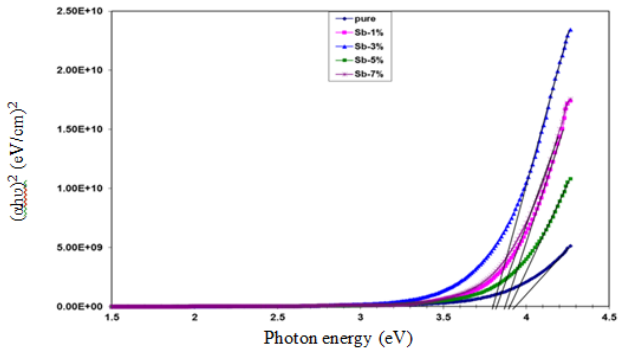

Figure (4) shows the variation of the direct band gap of nanostructure SnO_2:Sb thin film with different concentration of antimony.

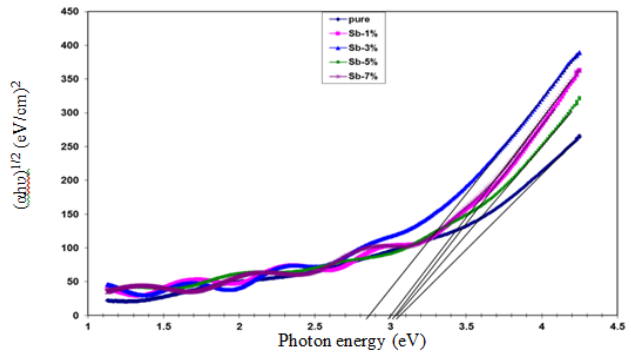

Figure (5) shows the variation of indirect band gap of nanostructure SnO_2:Sb thin film with different concentration of antimony.

Table (2) the values of optical direct and indirect band gap for nanostructure SnO_2:Sb thin film with different concentration of antimony.

content	*Allowed direct band gap (eV)*	*Allowed indirect band gap (eV)*
SnO_2-Pure	*3.94*	*3.08*
Sb- (1%)	*3.87*	*3.04*
Sb- (3%)	*3.8*	*2.86*
Sb- (5%)	*3.9*	*3.05*
Sb- (7%)	*3.82*	*3.0*

Figure (6) shows the variation of optical conductivity as a function of photon energy for different antimony doping of nanostructure SnO_2:Sb films. The optical conductivity is calculated by using an equation:

$$\sigma = \frac{\alpha nc}{4\pi}. \quad (4)$$

From the figure can see that the optical conductivity growths with increasing photon energy. This suggests that the increase in optical conductivity is due to electron excited by photon energy, and the optical conductivity of the films increases with increasing antimony doping of the films.

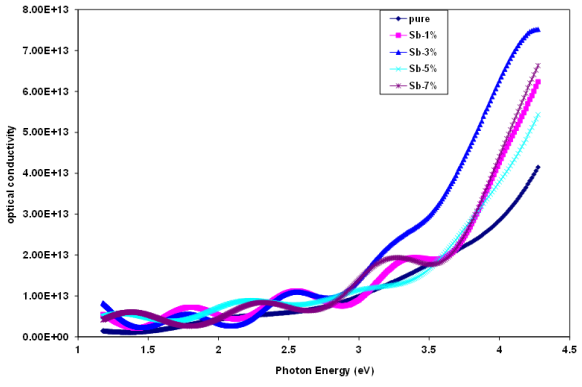

Figure (6) Optical conductivity as a function of photon energy for nanostructure SnO_2:Sb thin films with different concentration of antimony.

Conclusion

The XRD result shows that the films are polycrystalline is nature with a tetragonal structure and the preferred orientation is along (110) plane for pure SnO_2 and rate 1% and 3% antimony doping. But the increase of antimony doping concentration dose effects the structural properties of the films and the decrease in the intensities of the main XRD peaks, and then will be converted from polycrystalline (tetragonal shape) to amorphous when increase antimony concentration more than 3%wt, as specified in percentages 5 and 7% wt. The antimony doping (3%wt.) has a higher average grain size of about (7.24 nm) while the pure SnO_2 has a minimum average grain size of about (4.52 nm). Transmittance for all films decrease with increasing antimony doping in the films. The all films showed excellent optical transparency, and have a maximum average transmittance of un-doped SnO_2 films about 97% in the near infrared region. As for the energy gap we note that it decreases with the increase of the antimony doping concentration. Also, we observe from the measurements that the nanostructure SnO_2:Sb has two energy gaps, first of which is directly within the range of (3.94- 3.82 eV) and the other is indirect and within the range (3.08-3.0 eV).

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