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Influence of Structural Properties of Nanostructure SnO_2:Sb Thin Films Deposited By Spray Pyrolysis Technique

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***Abstract*—In the existing work, Nanostructure SnO2 films have been deposited on glass substrates at 350 oC temperature 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 films structures have a polycrystalline in nature and had a tetragonal structure for samples at contents (0, 1, 3%wt.), except the films for 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, microstrain, dislocation density and number of crystals per unit area, were calculated.**

Keywords—SnO_2, XRD, Nanostructure, lattice constants, number of layers, texture coefficient.

INTRODUCTION

Transparent conducting oxide (TCO) films are widely used in a variety of optoelectronic devices such as solar cells, displays and electrochromic devices. In recent years, there has been growing interest in the application of TCO films as electrodes in solar cell devices. Among the TCO films, the most appropriate material for the application seems to be tin oxide films, which are chemically inert, mechanically hard and heat resistant. In addition, they exhibit low electrical resistivity and high optical transmittance. Either doped or non-doped tin oxide thin films can be fabricated by a number of techniques: chemical vapor deposition [1], sputtering [2], spray pyrolysis [3-5]. The sol–gel method has such advantages as cheap cost and flexible deposition technique. Such properties can be improved by doping the tin oxide with, for example, antimony (Sb), indium (In) or fluorine (F).

Tin dioxide (SnO_2) is widely used as the active component of solid state gas sensors, and also has application in heterogeneous catalysis [6]. The basis for these applications is the reducibility of the oxide. The changes in conductivity of this n-type semiconductor resulting from surface processes are the basis for the material's gas-sensing characteristics. Because of this, it has long been a goal of fundamental research to characterize the structural, physical and chemical properties of SnO_2 surfaces. In the present work, Nanostructure tin oxide and antimony doped tin oxide thin films deposited on glass substrate where prepared by the chemical spray pyrolysis technique. The study investigated the structural properties of thin films characterized by X-ray diffraction (XRD). The purpose of the present work was to undertake a detailed examination of the effects of antimony contents on the structural properties of antimony-doped tin oxide thin films.

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 from 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 dissolving in 100mL for acetone. For calculating mass of ($SnCl_4.5H_2O$) in the current experiment the following equation was used:-

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

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 temperature (350±5) and SnO_2 will be deposited on substrates glass.

The Sb where 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.

X-ray diffraction (XRD) analysis is used to recognize the crystal structure of un-doped and antimony doped tin oxide thin films. When incident beam of (X-ray) diffractometer from a certain wavelength on film surface this will exhibit peaks on limit angels for each material because of Bragg's reflection on parallel crystalline surface, 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.

Results and discussion

Structural properties

X-ray Diffraction

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 substrate temperature of (350℃) has been shown in fig. (1), It is seen that the peaks are more broadened and shifted toward the decrease when 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 for 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. [7]. Indicating that the (O) atoms are replaced by (Sb) atoms in the nanostructure (SnO_2:Sb) films because the atomic radius for antimony large than the atomic radius for tin oxide [8].

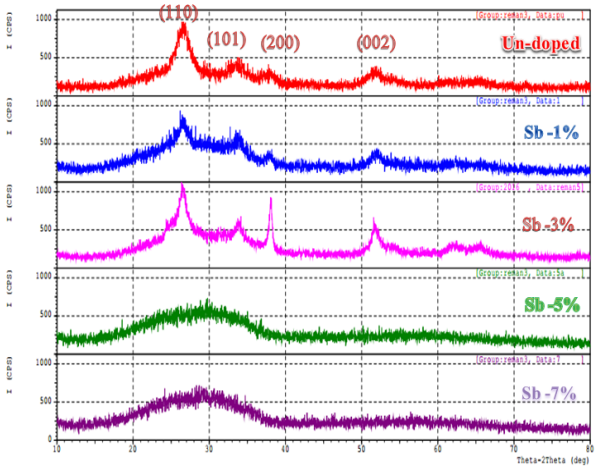

Figure (1) XRD image of Sb-doped SnO_2 nanostructure.

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) represent the X-ray diffraction of nanostructure SnO_2:Sb films at deposited temperature (350℃) for different antimony doping.

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)	d_{hkl} Std	hkl	phase	Card No.
Pure	*26.5433*	*1.89*	*3.35543*	*3.347*	*(110)*	*Tetragonal*	*00-041-1445*
Sb -1%	*26.5284*	*1.32*	*3.35728*	*3.347*	*(110)*	*Tetragonal*	*00-041-1445*
Sb -3%	*26.4583*	*1.21*	*3.36602*	*3.347*	*(110)*	*Tetragonal*	*00-041-1445*

Full Width at Half Maximum (FWHM) (β)

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 [9]:

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

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 (2). Figure (1) exhibits the effect of antimony doping concentration on the average grain size, it is 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 prepared at 3%wt.

Table (2) the obtained result of the structural parameters from XRD for nanostructure SnO_2:Sb Films with different antimony doping.

Wt.%	*Stress*	*Strain*	*Texture Coefficient T_c (hkl)*	*Dislocation Density (δ) x10^{16} m^2*	*G.S (nm)*
Pure	*0.07303*	*0.0313*	*0.80*	*4.88*	*4.525*
1%	*-0.2775*	*0.9413*	*0.89*	*2.37*	*6.493*
3%	*-0.352*	*0.125*	*0.91*	*1.90*	*7.24*

Texture Coefficient (Tc)

The values of texture coefficient (Tc) of the thin films are listed in table (2). The texture coefficient is calculated using the relation [10]:

$$Tc(hkl) = \frac{[(I(hkl)/I_o(hkl)]}{[Nr^{-1}\sum I(hkl)/I_o(hkl)]} \ldots\ldots\ldots\ldots (3)$$

Where: I (h k l) is the measured intensity, I_o (h k l) taken from the JCPDS data, (Nr) the number of diffraction peaks and (h k l) is Miller indices, for crystal

plane (110), the values of texture coefficient increase with increasing of antimony doping concentration as shown in fig. (1).This is a usual result because increase of antimony doping concentration causes an decrease in the surface roughness. It is clear that the texture coefficient Tc values are <1 for less than 3%wt. films indicating that there are numerous grains in the (110) favorite direction.

Number of Crystallites per unit area (N_o)

By using the film thickness and grain size of the films prepared on glass substrate the number of crystallites per unit area is calculated and listed in table (3), the values of the number of crystallites per unit area decreases with increase antimony doping concentration, using the relation [11]:

$$N_o = \frac{t}{G.S^3} \quad \text{..... (4)}$$

Dislocation Density (δ)

The dislocation density (δ), which represents the amount of defects in the film, is calculated using equation [12]:

$$\delta = \frac{1}{G.S^2} \quad \text{..... (5)}$$

The calculated values of dislocation density (δ) are varies between (4.88×10^{16} to 1.90×10^{16} m^2) observed for all the films along plane (110) with increase in antimony content in the films shown in table (2).

Number of Layers (N_ℓ)

The number of layers evaluated from film thickness it's listed in table (3). The variation of layer number varies with antimony doping in random way. It is thought that the substrate temperature varies and quantity of drop play a great role in this random change. The value of the number of layers decreases with increase antimony doping concentration is calculated using equation [13]:

$$N\ell = \frac{t}{G.S} \text{..... (6)}$$

Stress

The calculation of the film stress is based on the strain model. The values of the film stress decrease with increasing antimony doping in the film as shown in table (2). The residual stress (σ) in SnO_2:Sb films can be expressed as [12]:

$$\sigma = \frac{2C_{13}^2 - C_{33}(C_{11}+C_{12})}{2C_{13}} \times \frac{C - C_\circ}{C_\circ} \quad \text{..... (7)}$$

Where (C) and ($C_\circ$) are the lattice parameter of the thin film obtained from JCPDS respectively. The value of the elastic constant (C_{ij}) from single crystalline SnO_2 are used C_{11}=208.8 GPa, C_{33}=213.8 GPa, C_{12}=119.7 GPa and C_{13}=104.2 GPa [14].

Micro Strain

The micro strain depends directly on the lattice constant (c), and its value related to the shift from the JCPDS standard value which could be calculated using the relation [15]:

$$S = \left[\frac{|C_{ASTM} - C_{XRD}|}{C_{ASTM}}\right] \times 100\% \quad \text{..... (8)}$$

No important effect of un-doped SnO_2 and various doping concentration for Sb is recorded on the c-parameter, as seen in table (2). The value of the number of micro stain varies with increase antimony doping concentration.

Lattice Constant (a, c)

The lattice constant (a) and (c) of the nanostructure SnO_2:Sb thin films deposited on glass substrate at different antimony doping have been calculated using equation [16]:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad \text{..... (9)}$$

Where: d: was the distance between adjacent plane in the set (hkl), hkℓ: Miller (indices), (a, c): lattice constants

The lattice constant (a), (c) belong to the (110) plane as a preferred orientation have been listed in table (3), when found to be in a good agreement with the reported and the standard (JCPDS) values And this result that's agreement with the result of Archana Gupta in his study [17]. It is also found that the lattice

constant (a) increases slightly with increasing antimony doping in the films, and lattice constant (c) increases with increasing antimony doping.

Table (3) the obtained result of the structural parameters from XRD for Nanowire SnO_2:Sb Films with different antimony doping.

Wt.%	*Lattice Constant a(Å) EXP*	*Lattice Constant a (Std)*	*Lattice Constant EXP c (Å)*	*Lattice Constant c (Std)*	*Number of Layers (N_ℓ)*	*Number of Crystallines Per unit area(N) x 10^{18} (m^2)*
Pure	*4.745*	*4.7382*	*3.186*	*3.1871*	*167.88*	*8.199*
1%	*4.747*	*4.7382*	*3.190*	*3.1871*	*117.64*	*2.79*
3%	*4.760*	*4.7382*	*3.191*	*3.1871*	*113.89*	*2.17*

Conclusion

Nanostructure SnO_2:Sb films prepared by chemical spray pyrolysis (CSP) technique at substrate temperature (350℃) on glass substrate and different antimony doping (0, 1, 3, 5 and 7% wt.). The XRD result show 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 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 antimony concentration more than 3%wt, as specified in percentages 5 and 7% wt. The antimony doping (3%wt.) has highest average grain size of about (7.24 nm) while the pure SnO_2 has minimum average grain size of about (4.52nm).

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