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Solution molarity effect on electrical properties of SnO_2 thin films

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ABSTRACT

Tin oxide thin films of different molarities were successfully deposited by spray pyrolysis technique on preheated glass substrates at a temperature of 500°C. the Effect of molarity concentration on film properties was investigated. All deposited films were characterized by various techniques such as X-ray diffraction for structural characterizations, weight difference density method for thickness measurement, the two probe conductivity measurements for electrical characterization. The X- ray diffraction (XRD) patterns showed that the film of 0.1 M tin chloride pentahydrate has amorphous structure. With increasing the molarity concentration of the films to 0.3 M and 0.5 M the patterns showed a polycrystalline structure with preferential orientation along (110) direction. Results showed that the resistivity increases remarkably as the molarity increases. The variation of electrical conductivity as a function of temperature increases with increasing temperature, and tend to decrease with increasing the molarity concentration to 0.5 M. The activation energies increased with increasing the molarity concentration. Hall measurements showed that all films are n-type. The charge carrier concentration, Hall mobility, drift velocity, and mean free path decreases with increasing molarity concentration.

KEYWORDS

SnO_2;
Spray pyrolysis;
Electrical properties;
Thin films.

INTRODUCTION

Transparent conducting oxide (TCO) thin films have attracted considerable attention from scientific and technological point of view due to their unique properties of high electrical conductivity and high optical transmittance[1,2]. They are used for photovoltaic devices, phototransistors, liquid crystal displays, optical heaters, gas sensors, solar cells, transparent electrodes and other optoelectronic devices[3-8].

Among these TCOs, SnO_2 films are inexpensive, chemically stable in acidic and basic solutions, thermally stable in oxidizing environments at high temperatures and also mechanically strong, which are important attributes for the fabrication and operation of solar cells[9,10]. Their property is resulted from its n-type semiconductor behavior and wide band gap E_g=3.6–4.0 eV[11,12].

Thin films of SnO_2 can be produced by various techniques, such as chemical vapor deposition[13,14], beam evaporation[20] and spray pyrolysis[21,22]. Among these techniques that used to form SnO_2 films spray pyrolysis technique is the best, it is simple and inexpensive ex-

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perimental arrangement, ease of adding various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings[23]. The aim of this work is to investigate the effect of solution molarity effect on electrical properties of SnO_2 films produced by spray pyrolysis technique.

EXPERIMENTAL DETAILS

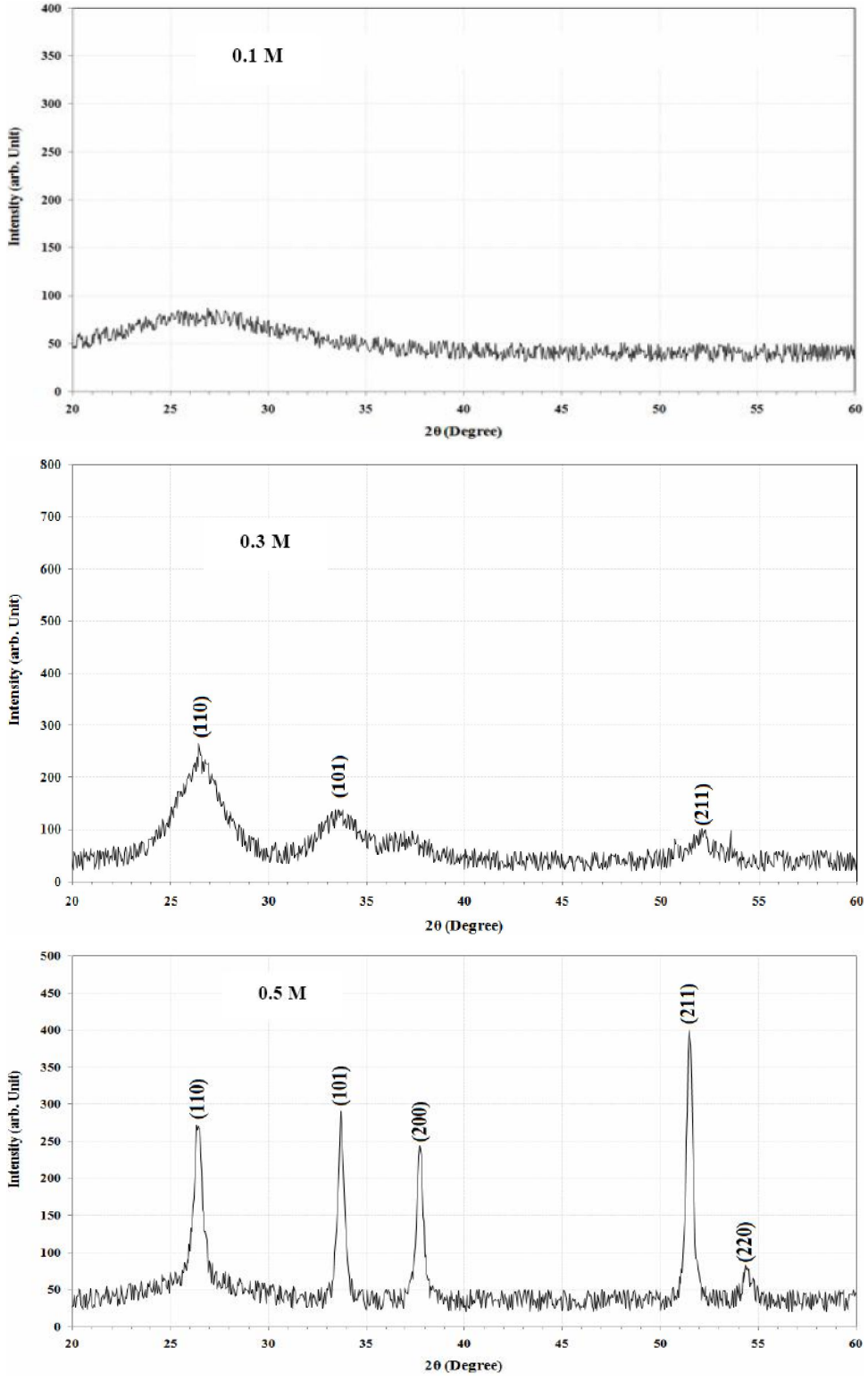

Figure 1 : X-ray diffraction pattern of SnO_2 films with different molarity

Thin films of tin oxide SnO_2 with different molarities have been prepared by spray pyrolysis technique. The spray pyrolysis was done by using a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at a temperature of 500°C, The deposition was carried out for different molar concentration of the solution varied from 0.1M to 0.5M of tin (IV) Chloride Pentahydrate $SnCl_4.5H_2O$ from Fluka Germany, this material was dissolved in deionized water and ethanol, few drops of HCl were added to speed up the dissolving, formed the final spray solution and a total volume of 50 ml was used in each deposition. With the optimized conditions that concern the following parameters, spray time was 10 Sec lasted by two minutes to avoid excessive cooling and the spray interval (3min) was kept constant. The carrier gas (filtered compressed air) was maintained at a pressure of 10^5 Nm^{-2}, distance between nozzle and the substrate was about 28 cm ±1 cm, solution flow rate 5 ml/min. The samples were weighted before and after spraying to determine the mass of the films[24]. Knowing the dimensions of the used substrates, the thicknesses can be determined by the following equation[25].

$$d = \frac{\Delta m}{\rho_m \, l \, L} \qquad (1)$$

Where Δm is the difference between the mass after and before spraying, ρ is the density, l the width and L the length. Thickness of the films was found to be around 300 nm. XRD patterns for SnO_2 films were carried out using a Phillips X–ray diffractometer system which records the intensity as a function of Bragg angle. The source of radiation was CuK_α with wavelength λ = 1.5405 Å, the current was 20 mA and the voltage was 30 kV. The scanning angle 2θ was varied in the range of (20–60) degree with speed of 2 $cm.min^{-1}$.

RESULTS AND DISCUSSION

Structure properties

X-Ray diffraction (XRD) analysis has been performed onto certain the crystal structure and the crystal orientation. The XRD spectra of SnO_2 thin films with various molar concentrations (0.1,0.3 and 0.5) M recorded in 2θ angle in the range of 20-60 are depicted in Figure 1. It can be seen that the film obtained with a concentration of 0.1M tin chloride pentahydrate has amorphous structure. By increasing the molarities of the films to 0.3M and 0.5M one may observe a strong diffraction Peak for [110] direction, which is characteristic for the tetragonal structure of the SnO_2 thin films. Also, the [101] direction yields the second most important diffraction peak. This [101] peak is shown in the figures which reveal the polycrystalline structure of these films. Mean crystallite
size was calculated for the [110] diffraction peak using Debye–Scherrer formula:

$$\mathbf{D = \frac{k\lambda}{\beta \cos\theta}} \qquad (2)$$

Comparison between observed and standard d-values for 0.1M and 0.5M SnO_2 thin films are listed in TABLE 1.

Electrical properties

The variation of resistivity of SnO_2 thin films as a

TABLE 1: Gives the interplaner distance d, I/I_O, a, and D for 0.3M and 0.5M samples in comparison with the standard values as in ASTM card

Solvent Volume of SnO_2	2θ (degree)	d_{exp} (Å)	$(I/I_O)_{exp.}$	(hkl)	FWHM Degree (SnO_2)	D×10^{-4} (μm)	N×10^{14} (m^{-2})	δ×10^{13} (Lines/m^2)	S×10^{-4}
3%	26.423	3.370	100	110	2.75	3.617294	10563	7642.4	95.82714
	33.895	2.642	42	101	1.0875	22.4724	440.57	198.01	15.42492
	50.792	1.796	36	211	0.314	26.21634	277.49	145.43	13.22209
	54.897	1.67	8	220	0.1917	61.15883	21.857	26.735	5.667783
5%	26.404	3.372	100	110	0.4618	21.38889	510.98	218.58	16.20630
	33.7016	2.657	89	101	0.400	31.42857	161.06	101.23	11.0293
	51.5359	1.7719	65	211	0.374	32.91442	140.22	92.305	10.53140
	54.514	1.6819	12	220	0.275	54.98669	30.074	33.073	6.303981

function of temperature in the range of (303-473) ºK at different solution molarity is shown in Figure 2. It's clear from the figure that the resistivity shows the negative temperature coefficient of resistance for all deposited films. Also, the resistivity increases markedly as the molar concentration of films increases.

The variation of electrical conductivity as a function of temperature for SnO_2 films at different molarity concentration is shown in Figure3. It's clear from this figure that the conductivity for all deposited films increases with increasing of the temperature.

Also, it can be seen that the conductivity decreases with the increasing of molarity concentration of the films. This decrease in the conductivity can be understood on the basis of the fact that the conductivity generally decreases when the carrier concentration of the heavily doped semiconductor increases[26]. For example,which is attributed to the strong scattering or absorption of photons by the increased number of carrier concentration resulted from the defects created in the lattice[27]. In this study, when the solvent volume increases, the spray flux density decreases, which make the growth rate slow and thereby, the carrier concentration increases.

In order to study the conductivity mechanisms, it is convenient to plot logarithm of the conductivity (lnσ) as

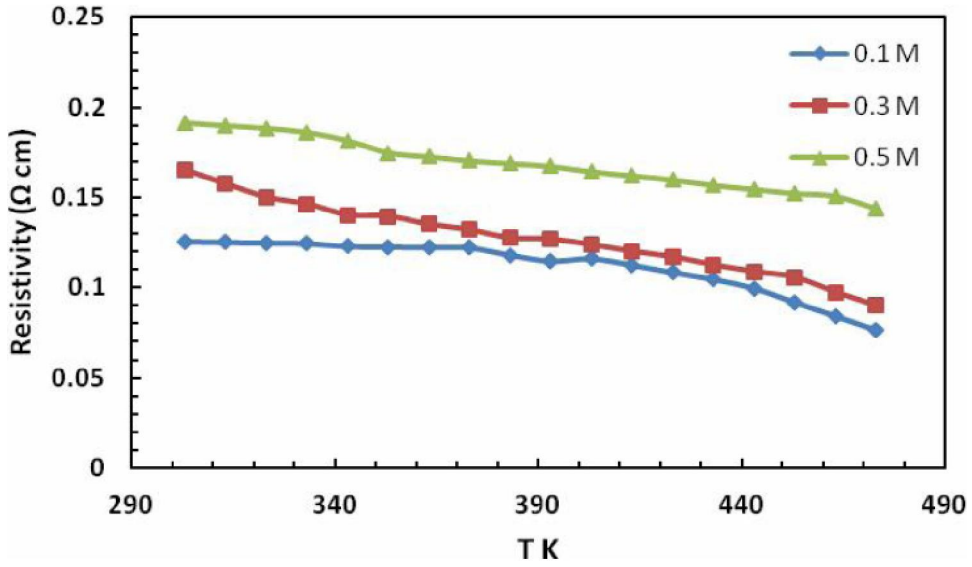

Figure 2 : Variation of resistivity versus temperatures for SnO_2 films with different molarity

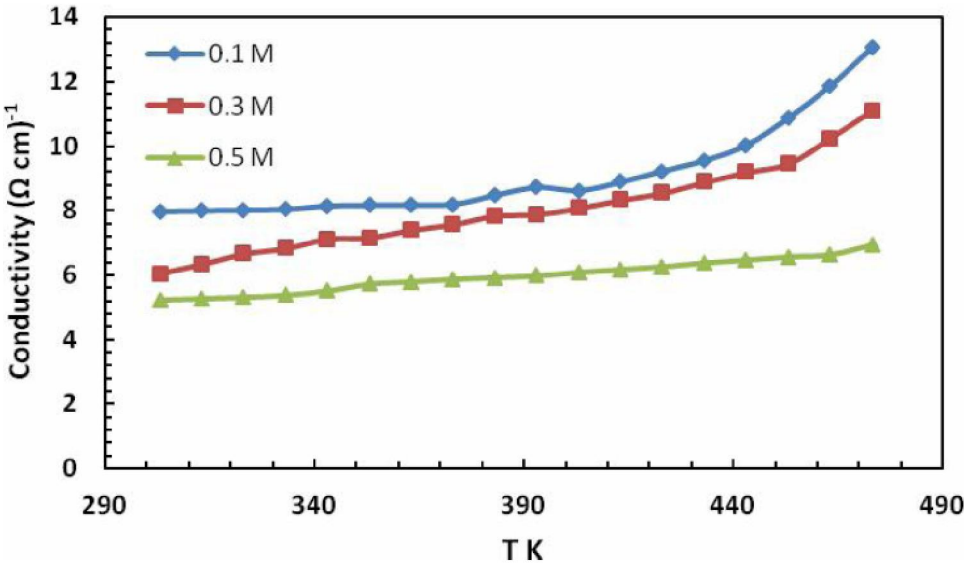

Figure 3 : Variation of $\sigma_{D.C}$ with temperatures for different molarity SnO_2

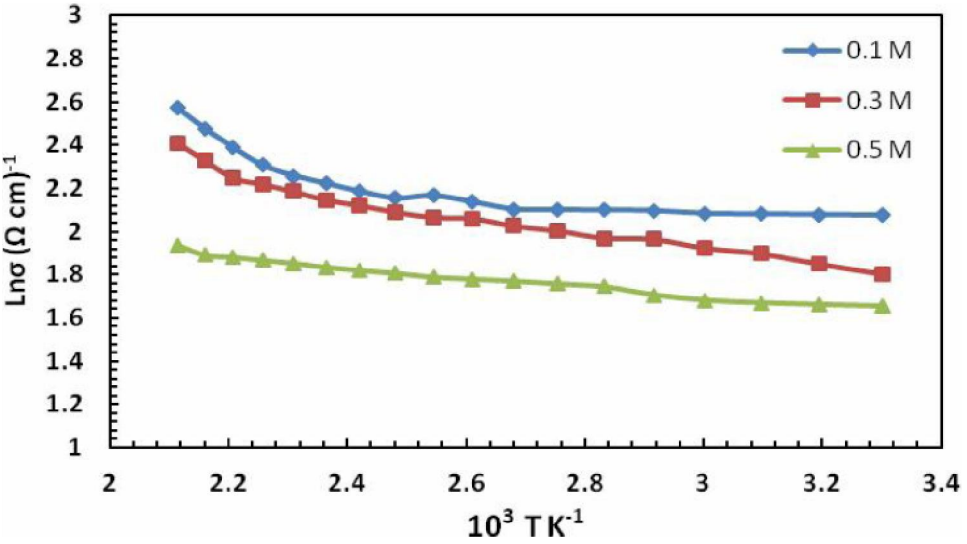

Figure 4 : Lnσ versus 1000/T for SnO_2 films with different molarity

TABLE 2 : Carries concentration, Hall mobility, V_d, Ea_1 and Ea_2 for SnO_2 films with different molarity.

Solvents volume (ml) SnO_2	$\sigma_{R.T}\times10^{1}$ $(\Omega.cm)^{-1}$	$R_H\times1^{-2}$ cm^2/C	$\rho\times10^{-2}$ (Ω.cm)	$\mu_H\times10^{2}$ $(cm^2/V.s)$	$v_d\times10$ (cm/s)	$N\times10^{19}$ $(1/cm^3)$	Type of con.	Ea_1 (eV)	Ea_2 (eV)
0.1	4.05	57.4	2.466	5.3	5.56	2.36	n-type	0.0043	0.095
0.3	2.93	8.49	3.4	2.49	2.61	7.35	n-type	0.032	0.103
0.5	2.02	1.45	4.9	0.59	0.619	42.8	n-type	0.0336	0.121

a function of 1000/T for SnO_2 films for different molarities, as shown in Figure 4. It is clear from this figure that there are two transport mechanisms, giving rise to two activation energies E_{a1} and E_{a2}. The conduction mechanism of the activation energy (E_{a2}) at the higher temperatures range (403-503)ºK is due to carriers excitation into the extended states beyond the mobility edge and at the lower range of temperatures (303-373)ºK, the conduction mechanism is due to carriers excitation into localized state at the edge of the band.

Hall measurements of SnO_2 thin films

Hall mobility, carrier type and concentration were measured from Hall coefficient (R_H) data and D.C conductivity. The complete data of μ_H, N, σ, ρ, V_d, Ea_1 and Ea_2 with different molarities are tabulated in TABLE (2). The results indicate that the materials under study are n-type semiconductor possibly due to the donor formation by O_2 vacancies, these results correspond to the published literatures. From the table, it can be seen that the carrier mobility decreases with increasing of the carrier concentration which is due to increase in the solvent volume. The interpretation of this decrease is attributed to the increase in the localized state near band edge, and also increase in carrier concentration,which leads to decrease in μ_H.

CONCLUSIONS

From the obtained results, we can conclude the following. The structural study of the films showed that an amorphous state may exist in the material as in the films with molarity 0.1M. With increasing the molarity to 0.3M and 0.5M a polycrystalline structure with preferred orientation along [110] direction with strong diffraction Peak has been observed. The variation of resistivity of the films with different molarities as a function of temperature showed the negative temperature coefficient of resistance. The resistivity increases remarkably as the molarity increases. The variation of electrical conductivity as a function of temperature increases with increasing temperature, and tend to decrease with the increasing of molarity concentration to 0.5 M. The results indicate that the materials under study are n-type semiconductor possibly due to the donor formation by O_2 vacancies. The carrier mobility decreases with increasing of the carrier concentration which is due to

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