Influence of substrate temperature on structural and optical properties of SnO_2 films

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Abstract

Tin Oxide (SnO_2) films have been deposited by spray pyrolysis technique at different substrate temperatures. The effects of substrate temperature on the structural, optical and electrical properties of SnO_2 films have been investigated. The XRD result shows a polycrystalline structure for SnO_2 films at substrate temperature of 673K. The thickness of the deposited film was of the order of 200 nm measured by Toulansky method. The energy gap increases from 2.58eV to 3.59 eV when substrate temperature increases from 473K to 673K .Electrical conductivity is $4.8*10^{-7}(\Omega.cm)^{-1}$ for sample deposited at 473K while it increases to $8.7*10^{-3}$ when the film is deposited at 673K

Key words
Tin Oxide,
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تأثير درجة حرارة الأرضية على الخواص التركيبية والبصرية لأغشية SnO_2الرقيقة

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الخـــلاصـــة

تم ترسيب اغشية (SnO_2) بطريقة الرش الكيميائي عند درجات حرارة ارضية مختلفة وقد تمت دراسة تاثير تغيير تلك الدرجات الحرارية على تركيب الاغشية وخصائصها البصرية والكهربائية. أظهرت نتائج حيود الاشعة السينية ان الاغشية المحضرة عند درجة حرارة ارضية (673K) كانت ذات تركيب متعدد البلورات. كان سمك الاغشية المحضرة بحدود (200nm) وقد تم قياسها بطريقة تولانسكي(Toulansky). ازدادت فجوة الطاقة البصرية من 2.58 الى 3.59 الكترون-فولت .كما ان التوصيلية الكهربائية ازدادت من $4.8*10^{-7}(ohm.cm)^{-1}$ الى $8.7*10^{-3}$ $(ohm.cm)^{-1}$ عند زيادة درجة حرارة الارضية من 473K الى 673K.

Introduction

Tin oxide (SnO_2) semiconducting films has been intensively used in the field of microelectronics and stable gas sensors, especially in recognition of volatile organic compound(VOC).The film is highly trans parent, chemically inert, and mechanically hard. Application of the tin oxide films are not limited to the research laboratory but are used commercially in environmental monitoring, industrial electronic sensor, liquid crystal displays etc[1].Owing to its low resistivity and high transmittance, tin oxide thin films are as a window layer in solar cells[2].It is gas sensor for different gases like CO,NOx,H_2S,CH_4 and CNG etc[3-5]. Doped or undoped tin oxide films can be deposited by several methods such as thermal evaporation [6], Chemical vapor deposition[7], R. F. Magnetron Co-sputtering[8],Laser pulse Deposition[9] and Spray pyrolysis[10].Among all technique spray pyrolysis has been used extensively being less expensive ,large area deposition and chemically viable technique. Nano structures Sb doped SnO_2 thin films presents high electrical conductivity even in the presence of high porosity[11].Direct energy gap is 3.7 eV[12].The influence of oxidation of SnO_2 thin films depletion

layer, electronic parameters and film conductance has been studied by means of computer simulations[12].The 3-coating layers $SiO_2/SnO_2/TiO_2$ exhibited super hydrophilicity (self-cleaning effect)under UV irradiation for 30min[13]. Flourine-doped tin oxide(FTO) films deposited on heated surfaces showed twinned crystalline properties [14].Tin oxide affected with glass surface preparation, with materials like sodium, titanium and Alumina[15].

Experimental

The films were prepared on glass substrates, which were placed on the surface of substrate heater when they were sprayed. The substrate heater was on electrically controlled block furnace. The spraying solution used was of 0.1M concentration of high purity stannous chloride $SnCl_2.H_2O$=225.63 (As 99.98 BDH,England). Then the starting solution was sprayed onto the hot substrate kept at a distance of 30cm below the spray gun nozzle using air as carrier gas. Substrate temperature is measured using an Iron-constantan thermocouple. The solution is sprayed (from a reservoir) by means of the carrier gas, incidentally to the substrate. The spraying solution consists of an aqueous solution of Tin chloride-$SnCl_2.H_2O$, dissolved in distilled water. The flow rate of solution was 8 ml/min. The structure of SnO_2 films were analyzed by x-ray differactometer (XRD) with $CuK_{\alpha 1}$ radiation with λ=1.54A^0 the optical properties of SnO_2 films were +carried out with a double beam spectrometer (ELICO-159) ,in the UV-VIS regions. The optical transmittance and absorbance at normal incidence was recorded in the wavelength range of (200-900) nm to evaluated the energy gap. The photoluminescence spectra of SnO_2 films are plotted using (SL 174 SPECTROFLUOROMETER) covering a range at (200-900) nm.

Results and Discussion

The X-Ray diffraction pattern of the prepared films is plotted in Fig.(1). It is obvious there is no diffraction peaks of the films deposited at 473K and 573K which indicates the amorphous structures in contrast to the films deposited at 673K which revealed many peaks indicating the polycrystalline structure, thus increasing substrate temperature to 673K transforms the structure of the prepared films from amorphous to polycrystalline, Table (1) illustrate the values of d, I/I0 and hkl of polycrystalline SnO_2 films.

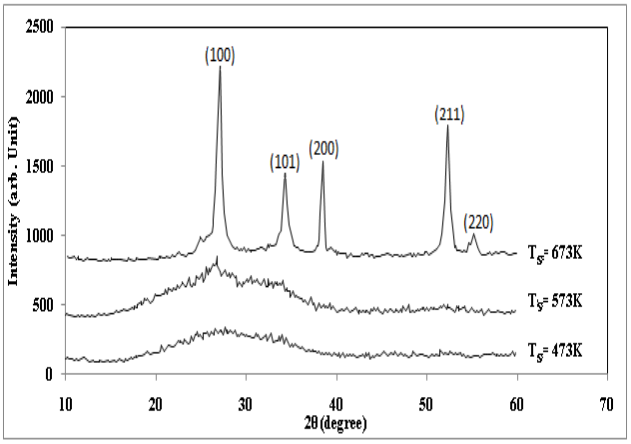

Fig.1:XRD of SnO_2 films deposited at different substrate temperature

Table 1: Comparison between experimental and standard d_{hkl} , I/I_o and hkl

2θ Exp.	d [Å] Exp.	I/I_0 Exp.%	d [Å] std.	I/I_0 std.	hkl
26.96	3.3072	100	3.35	100	110
34.2	2.6219	44	2.64	78	101
38.35	2.3469	49	2.37	21	200
39.26	2.2951	76	2.31	36	111
52.17	1.7533	68	1.76	58	211
55.07	1.6676	14	1.67	14	220

In Fig. 2 the transmittance spectrum as a function of the wavelength For SnO_2 films at different substrate temperatures are presented. The percentage of transmittance (%T) value in the visible region was found to be increase with the increase of substrate temperature. Maximum transmittance behavior is observed for the SnO_2 films prepared at 673K and comparatively lower transmittance values were recorded for the films prepared at 473K and 573K.

The increase in T% is attributed to the well adherent and crystalline nature of the film throughout the coated area, which is obtained due to uniform oxidation and improvement in lattice arrangements, resulting in better optical properties.

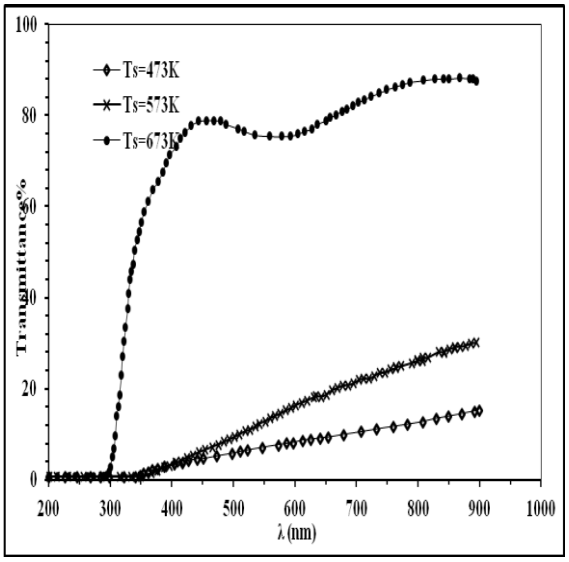

Fig.2: Transmission Spectrum of SnO_2 thin films

It should be noted that the polycrystalline SnO_2 films showed both PL peaks and the absorption edges at the same which energy band gap Fig. 3.

The absorption coefficient of the films was found to be of the order of 10^4 cm^{-1}, where it follows the relation:

$$\alpha = [A(h\upsilon - E_g)^{1/2}]/h\upsilon$$

where A is a constant and E_g the optical energy gap. Plots of $(\alpha h\upsilon)^2$.vs. the photon energy ($h\upsilon$) in the absorption region near the fundamental absorption edge indicate direct allowed transition in the film material, as shown in Fig.4.

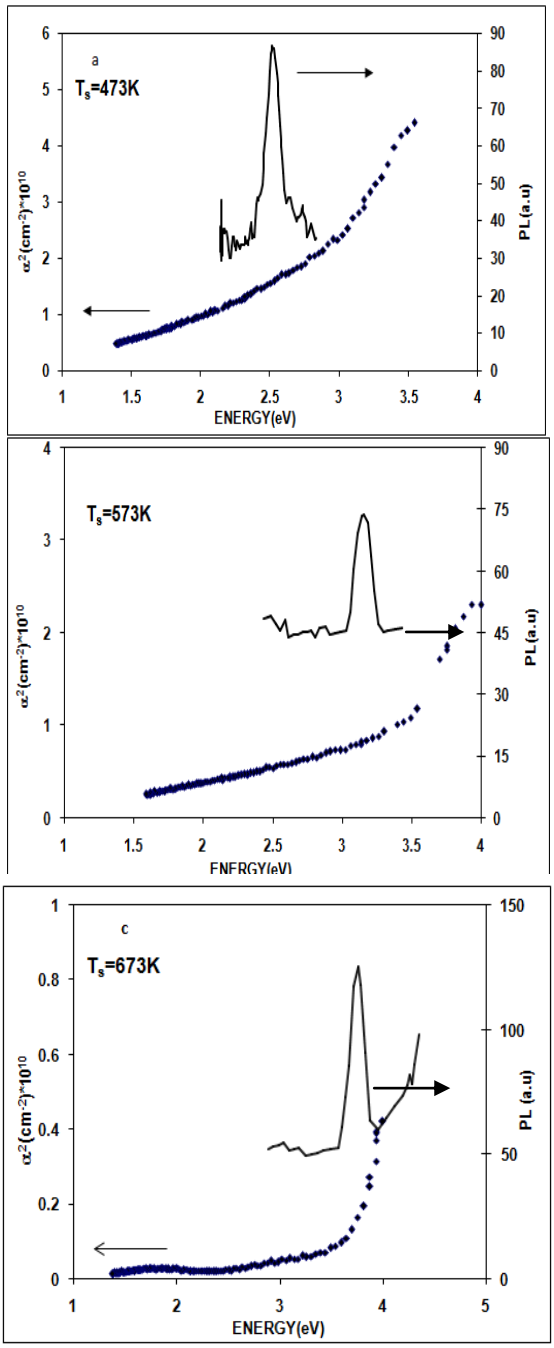

Fig.3: Photoluminescence(PL) and absorption spectra of SnO_2 thin films.

The optical energy gap was estimated from the extrapolation of the linear portion of the graph to the photon energy axis, and its dependence on substrate temperature is illustrated in Fig.5. The values of energy gap with

substrate temperature are shown in Table2.

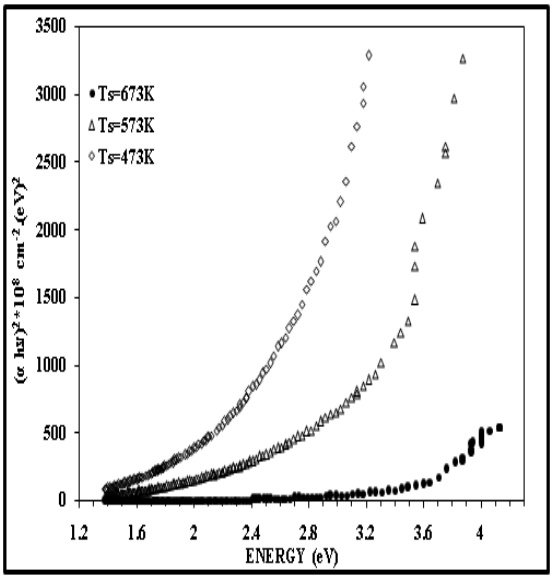

Fig.4: Tauc plot of $(\alpha h\upsilon)^2$ with photon energy in SnO_2 thin films

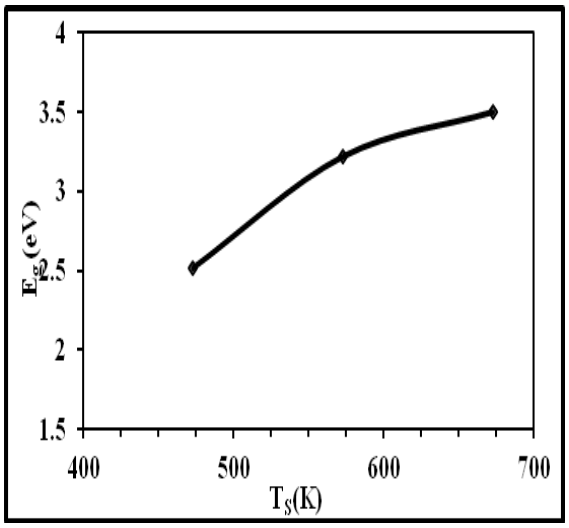

Fig.5: Optical energy gap vs. substrate temperature of SnO_2 films

The high dc electrical resistance, in order of Mohm(MΩ), observed for SnO_2 films at room temperature (303K) can be attributed to the large density of extrinsic traps at the grain boundaries due to oxygen chemisorptions.

These traps deplete the grains and result in a charge carrier barrier at the grain boundaries [16].This effect can be more relevant for small grain size.

The inverse absolute temperature dependence of the electrical conductivity of the films is shown in figure 6.For all the films, the conductivity is found to increase with the increase of temperature as well as substrate temperature in the range 300-450K.

The increase in conductivity is related to the increase in carrier concentration resulting from activation of deep and shallow donors which may arise due to native defects such as interstitial Sn atoms and oxygen vacancies [17].

The activation energy was obtained using the relation

$$\sigma=\sigma_0 \exp(-E_a/kT)$$

where σ is the electrical conductivity at any temperature, σ_0 is a constant, E_a is the activation energy for conduction, k is the Boltzman constant and T is the absolute temperature.

The conductivity of studied films shows that all the films exhibit two activation energies at different temperature regions. These two activation energies vary with substrate temperature and are listed in table 2.The first activation energy E_{a1} indicates that the conduction is by tunneling mechanism near Fermi level and the second activation energy E_{a2} is by hopping mechanism at localized states. Both of these mechanisms depend on substrate temperature, and are found to decrease with increasing substrate temperature.

Table 2 Variation of activation energy with substrate temperature for SnO_2 thin films

T_s(K)	λ(nm)	E_g(PL)	E_g(eV)	E_{a1}(eV)(303-393K)	E_{a2}(eV)(393-473K)	$\sigma_{R.T}(\Omega.cm)^{-1}$
473	494	2.51	2.58	0.065	0.202	$4.81*10^{-7}$
573	395	3.139	3.279	0.053	0.181	$5.82*10^{-7}$
673	330	3.757	3.591	0.19	0.149	$8.73*10^{-3}$

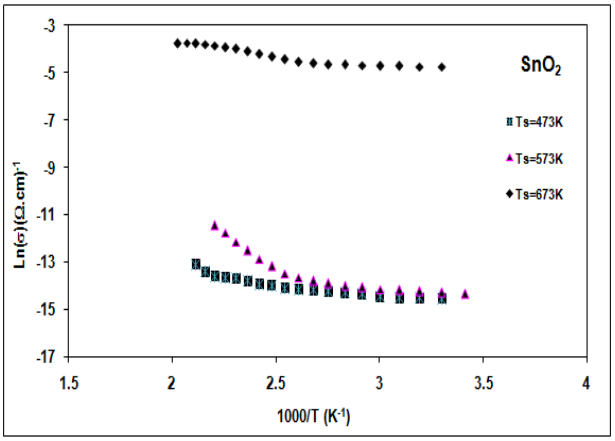

Fig.6:Plot of lnσ vs 100/T for the films of different substrate temperatures

Conclusions

The wide band gap Tin oxide samples were prepared by spray pyrolysis technique. Polycrystalline structure has been observed for film deposited at 673K.Optical measurements indicated that direct transition happen in SnO_2 films. The PL spectrum of Tin oxide shows the appearance of direct band gap transition and the deep level defect transition. We found that SnO_2 films with T_s=673K has 80% in transmittance in the wavelength range (200-900 nm) and the conductivity increases about four orders in magnitude , this temperature is suitable for using this material as a window for solar cell devices.

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