

## PREPARATION OF NANOCRYSTALLINE SnO<sub>2</sub> THIN FILMS FOR MICRO GAS SENSORS

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Recently interest in transparent electrically conducting Tin oxide films has been revived because of their prospective application in photovoltaic solar cells. Chemical vapor deposition and reactive sputtering are the methods generally employed for the deposition of oxide films. Metal oxide films deposited by hydrolysis of metal chloride (SnCl<sub>4</sub>.5H<sub>2</sub>O) have been extensively studied where as only a few reports have appeared on films deposited by Oxidation of metal chloride (SnCl<sub>2</sub>.2H<sub>2</sub>O). Even though the later method is relatively inexpensive. In this paper we report the influence of the deposition temperature and RPM of the substrate on the uniformity and the mean grain size of the films deposited by oxidation. The aim of this study was to establish the deposition parameters for obtaining nanocrystalline films with the best uniformity and the largest mean grain size

(Received September 28, 2010; accepted October 14, 2010)

*Keywords:* SnO<sub>2</sub> thin films, sol-gel process, spin coating, XRD, SEM, UV

### 1. Introduction

Tin oxide films possess very interesting physical properties namely high electrical conductivity coupled with fairly large optical transmission in the visible region Tin oxide films have found many technological applications among them as catalysts for oxidation of organic compounds and as solid state sensors.[2-5] Tin oxide films are being used as transparent windows and anti reflective coatings on conventional silicon p-n junction solar cells. Tin oxide film preparation can be achieved by sol-gel and co-precipitation methods. Typically in the sol-gel method, Tin tetrachloride hydrate is dissolved in distilled water and to this is added ammonium hydroxide to cause gellation. Advani G.N et al (1) prepared tin oxide by a sol-gel method that obviates the need of a precipitating reagent. The gellation took place spontaneously from aqueous and an alcoholic solution of tin tetrachloride hydrate avoiding the presence of foreign ions in the solution was central to the success of the method. In this paper we describe the Preparation of tin oxide thin films by soft chemistry route using an aqueous solution of tin dichloride dripped onto the preheated spinning substrate.

### 2. Experimental

#### 2.1 Sol preparation

Tin II chloride dihydrate was dissolved in isopropyl alcohol and kept under stirring at room temperature for two days. The yellow solution obtained (3.3g/l of Sn) was diluted to give a solution with 0.8 g/l tin concentration and kept at room temperature. With time this solution becomes increasingly cloudy and after some days, a gelatinous suspension was formed with slowly settled to the bottom of the container. The gel was separated from the solution and diluted with isopropyl alcohol for coating on glass substrates. The coating was carried out by an indigenously designed spin coating system.

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## 2.2 Spin coating technique

The experimental setup consists of stainless steel substrate holder attached to a universal motor. A 2Kw heater coil is used to heat the substrate holder and the set up is isolated from the surrounding with a chamber made up of heat insulator fiberglass. This is again surrounded by glass wool insulation. The spinning rate of the substrate is monitored by a stroboscope arrangement, which enables to optimize the system for uniform thickness and repeatability and the thickness of the films. The solution has been taken in the burette at the level of 10 ml height, by which the solution drip rate is maintained. The cleaned glass substrate has been kept on the stainless steel base of the furnace and the furnace is switched ON to obtain the equilibrium set temperature. After reaching the steady set-temperature in the controller, the substrate has been given rotation by motor arrangement. The stroboscope flash lamp is used to set the RPM of the substrate as shown in fig [1]. After reaching a steady set-RPM, the stopper in the burette tube is opened for dripping the solution onto the substrate.

For achieving good quality transparent conducting films the following process parameters have been studied. Temperature of the substrate, RPM of the substrate and Time of coating.

Spin hydrolysis involves optimization of these process parameters. Better control on the physical properties of the films can be achieved, with the investigation of the influence of

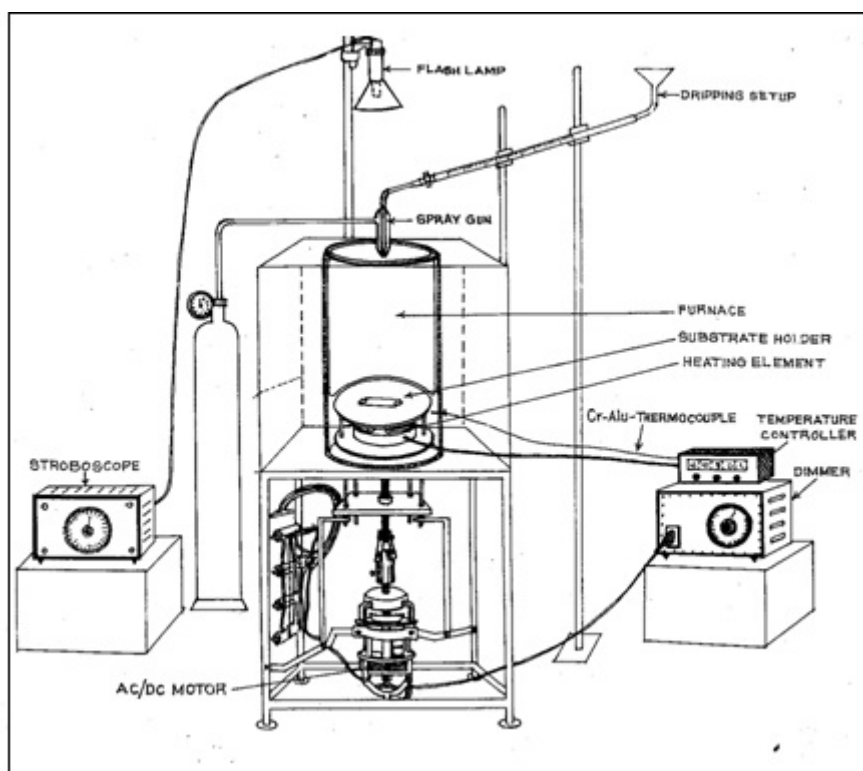


Fig. 1. Schematic Diagram of Spin cum spray Coating system

each process parameter on the film properties. Spin deposition has been carried out on glass substrates at different substrate temperatures (350-500°C) for achieving oxidation. Uniform spreading of the alcoholic metal solution is achieved by spinning the substrate. The influence of rate of rotation per minute on the film thickness and uniformity are analyzed. Trial and error method is employed for getting good quality transparent conducting films by varying the RPM starting from few hundreds of RPM to 2500 RPM. The influence of time of coating on the rate of oxidation, and the thickness are analyzed for getting transparent conducting films.

### 3. Results and discussion

Substrate temperature is one of the main parameters, which determine the stoichiometry and structural properties of the films. Fig. [2] shows the x-ray diffractogram of SnO<sub>2</sub> films grown at different substrate temperatures. From the figure, it is seen that the films are polycrystalline in nature. The poly crystalline film with preferred growth direction along [110] is seen from the graph. Other peaks corresponding to the directions [101], [200], [211] are also seen. The peaks positions are in agreement with ASTM card values. The crystalline size of the tin oxide films calculated from Debye-Scherer's equation which is given by

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

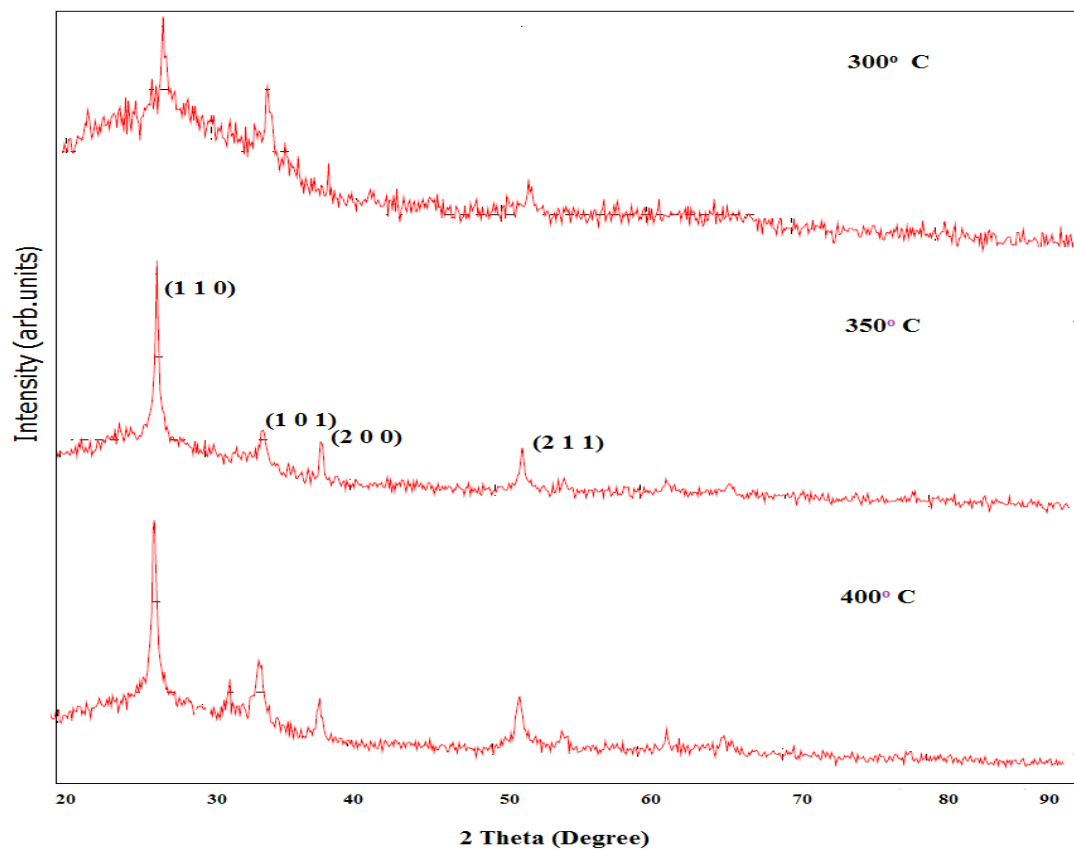


Fig.2. XRD pattern of Spray coated tin oxide nanocrystalline thin films

Where  $\lambda$  is the wavelength of X-ray used,  $\beta$  is the full width half maximum (FWHM) of the peak and  $\theta$  is the glancing angle. The lattice constant of the spray coated Tin oxide films calculated using the formula,

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

Where 'd' is the interplanar distance, (h k l) are the Miller indices and 'a' and 'c' are the lattice constant for the tetragonal structure.

Table.1. Structural parameters of spray coated SnO<sub>2</sub> with 2500 RPM

Substrate temperature	h k l	d (Å)	2θ	FWHM (β)	D (Å)	c (Å)	a (Å)
300° C	1 1 1	3.32692	26.7750	3.8500	21	9.84	4.45
	1 0 1	2.66639	33.5833	3.1667	26		
	2 0 0	3.88036	22.9000	5.4666	14		
350° C	1 1 1	3.33899	26.6764	0.35020	233	6.57	4.79
	1 0 1	1.76143	51.8655	0.32620	270		
	2 0 0	3.28775	27.1000	0.48000	170		
400° C	1 1 1	3.34051	26.6640	0.51460	158	7.49	4.31
	1 0 1	2.64143	33.9102	0.68710	120		
	2 0 0	1.76272	51.8246	0.58720	151		

The calculated crystalline size (D) and lattice constant (a and c) of spray coated Tin oxide with RPM of 2500 are tabulated in table 1. It is observed that the film prepared at 300°C seems to be less crystalline size (1-2 nm). The crystallinity improves with increasing substrate temperature with average particle size of 22 nm evident from XRD pattern. Further increasing substrate temperature, the high intensity peaks observed (400°C) which indicates that the smooth and uniform surface of as-prepared films and have the crystalline size of 12-15 nm.

### 3.2. Morphological studies

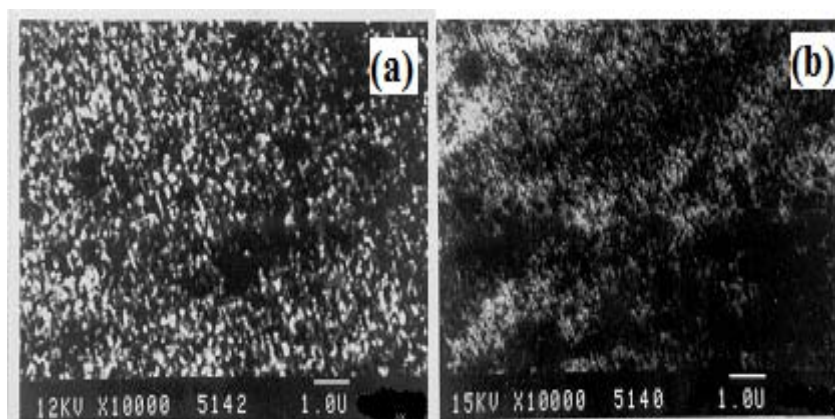


Fig.3. SEM images of SnO<sub>2</sub> films with 2500 RPM (a) and 1000 RPM (b) at 400° C

The morphological studies on as prepared SnO<sub>2</sub> films carried out Scanning Electron Microscopic technique. The films prepared at 400° C under goes with the RPM of 2500 and 1000 are shown in figure 3. It is observed that the films with 2500 RPM shows uniform and smooth surface as it is evident from the XRD intensity whereas the non uniform surface accrued at films prepared at 1000 RPM.

### 3.3. Optical studies on SnO<sub>2</sub> thin film

The absorption and optical band gap of the grown films with different substrate temperature at 2500 RPM are shown in figure (4-5). The analysis of optical absorption Spectra is

one of the most productive tools for understanding and developing the band structure and energy band gap,  $E_g$ . Optical absorption of as prepared films (fig.4) shows the

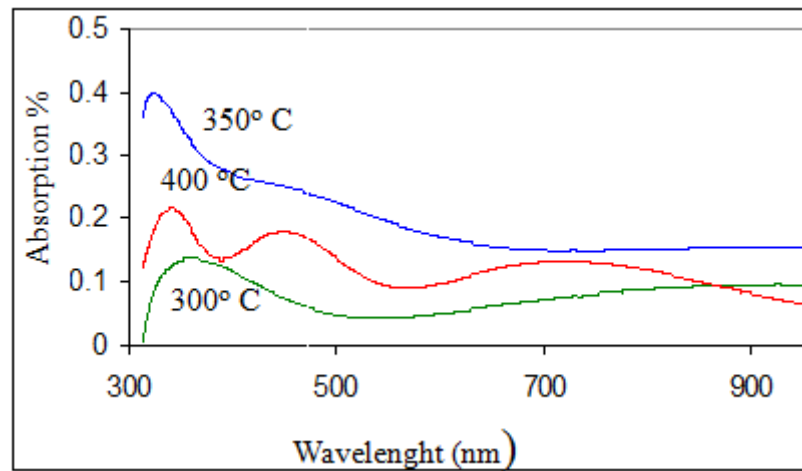


Fig.4. Absorption spectra of spray spin cum spray coated  $\text{SnO}_2$  with 2500 RPM

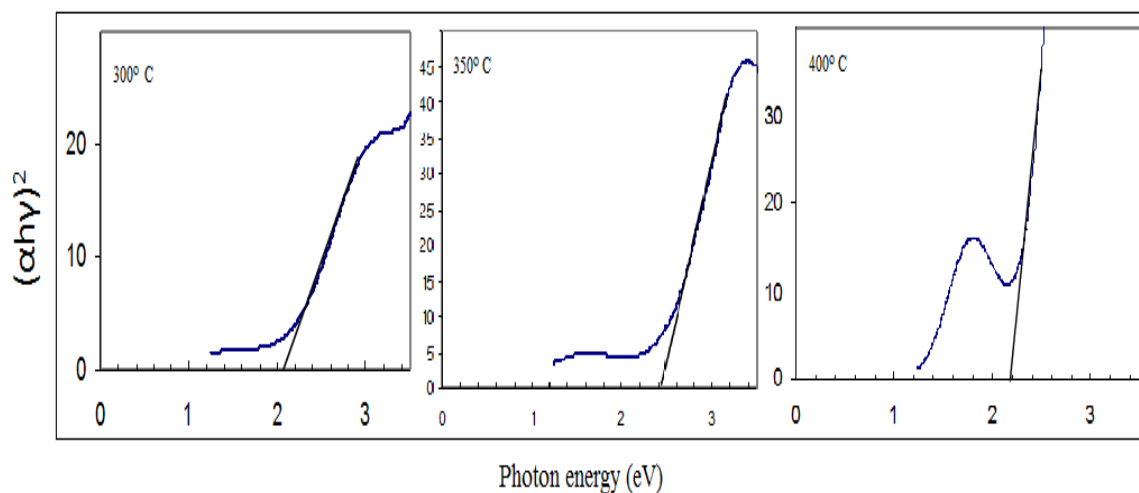


Fig.5. Optical band gap of  $\text{SnO}_2$  with different substrate temperature at 2500 RPM.

absorption shift towards blue which indicates the nanocrystalline effect of the films. It is also evident that the films have more absorption peaks when the substrate temperature increases. To find the suitability of the device formation with silicon substrate was studied by calculating its band gap of  $\text{SnO}_2$  at various temperatures. The band gap value could be obtained from the optical absorption spectra by using Tauc's relation [12],

$$\alpha = \frac{A}{h\nu(h\nu - E_g)^n} \quad (3)$$

Where  $\alpha$  is the absorption coefficient,  $(h\nu)$  is the photon energy and A is a constant. The direct band gap semiconductor can be obtained from the relation,

$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}} \quad (4)$$

Fig.5. shows the variation of  $(\alpha h\nu)^2$  versus  $(h\nu)$  for the  $\text{SnO}_2$  thin film. The straight nature of the films over the wide range of photon energy indicates the direct type of transition. The

optical gap has then been determined by extrapolation of the linear region on the energy axis shown in fig.5. The optical band gap of 2.1 eV was observed in films prepared at 300° C at 2500 RPM. When increasing substrate temperature to 350° C and 400° C the direct band gap of 2.4 eV and 2.2 eV observed respectively and also there is a splitting of band gap at 1.2 eV was observed in films prepared at 400° C indicates the nanocrystalline nature of the films.

#### 4. Conclusions

Tin oxide films were grown on different substrate temperature at 2500 and 1000 RPM using spin cum spray pyrolysis method. With the increase in substrate temperature, the particle size, the crystallinity of the SnO<sub>2</sub> films increases. The increase in crystallinity at higher substrate temperature beyond 300°C is attributed to improved stoichiometry or reduction of chlorine impurity or both. The increase in transmission of these films with increase in the substrate temperature and RPM may be due to reduced grain boundary scattering (enhanced crystallinity and uniform spreading due to centrifugal force). Varying the thickness by viewing through the stroboscope flash lamp can alter the electro-optic properties of the Tin Oxide films, the colour change due to increasing thickness can be optimized with time factor. The absorption shift towards blue wavelength indicates the presence of nano particle on grown films with increasing the substrate temperature which provides information on future potential applications.

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