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Effect Of Temperature On The Structural And Optical Properties Of Spray Pyrolysis Sno_2 Thin Films

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Abstract: - SnO_2 thin films were synthesized at 300-500^{0}C temperature by spray pyrolysis method using tin chloride pentahydrate, acetic acid, ammonia solution. The films were characterized by XRD, SEM and UV-Vis-NIR. XRD analysis of nanocrystals prepared with three different temperatures which shows the crystalline nature, structure as well as particle size of the prepared SnO_2 particles. From the peaks position of XRD shows that the deposited films possess tetragonal structure with most prominent reflection along (200) plane. The Parameters such as crystalline size, strain and dislocation density has been analyzed. Surface morphology and film composition have been analyzed using scanning electron microscopy, the images of SnO_2 nanoparticles showed their morphology, particle size and crystalline respectively. From the structural and SEM analysis it has been confirmed that phase change can be achieved by varying the temperature. The band gap of the prepared nanoparticles is found to be in the range 2.7 to 2.95eV, it is clear that by increases the temperature, energy gap was decreased.

Keywords: - *Spray pyrolysis thin film, XRD, EDAX, SEM and Optical properties.*

I. INTRODUCTION

In recent years, there has been considerable interest in use of thin films in solar cells devices. Tin oxide is a semiconductor with an energy band gap of 2.7eV and the electrical properties can be suitably controlled by altering the deposition conditions. These materials are important in the fields of catalysis, photograph, electronics, photonics, data storage, optoelectronics, biological labeling, imaging and bio sensing. Tin Oxide (SnO_2) films have been successfully used for many applications including use in gas sensor devices, pure and Cd doped SnO_2.

SnO_2 films can be prepared by different techniques such as Spray pyrolysis, successive ionic layer adsorption reaction (SILAR), electro deposition, RFsputtering, pulse laser evaporation, physical vapour deposition, screen printing, metal organic vapour phase expitaxy (MOVPE)/metal organic chemical vapour deposition (MOCVD) and chemical bath deposition (CBD) method.

In this paper tin oxide material is fabricated by Spray pyrolysis method, the purpose of this work was to investigate the effects of the growth condition for various temperatures from 300-500^{0}C.

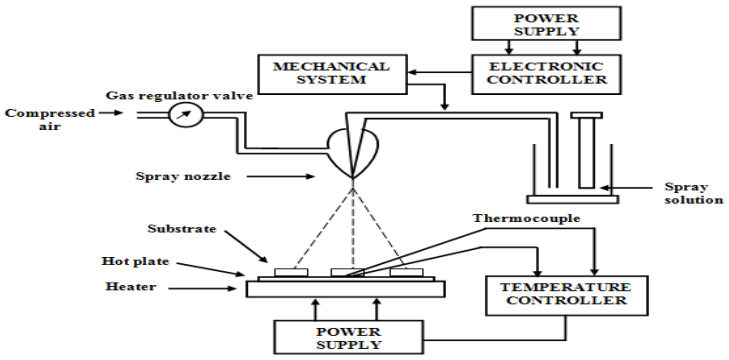
II. MATERIALS AND METHODS

2. Experimental work

SnO_2 thin films were deposited by the CSP technique. In this deposition technique a starting solution, containing Sn precursors, was sprayed by means of a nozzle, assisted by a carrier gas, over a hot substrate. When the fine droplets arrived at the substrate, the solid compounds reacted to become a new chemical compound. SnO_2 thin films were deposited into ultrasonically cleaned glass substrates using the spray pyrolysis method at different substrate temperature was varied from 300 to 500 ± 3°C which was controlled by thermo controller.

2.1. Fabrication of SnO_2 thin film sample

The Substrates were heated to required temperature for film deposition by an electrical heater. The first precursor solution was 0.1M tin (IV) Chloride prepared by the dissolving in deionized water. A few drops of acetic acid were added to aqueous solutions to prevent the formation of hydroxides. The nozzle was kept at a distance of 5cm from the substrate during deposition. The solution flow rate was held constant at 0.5ml/min. Air was used as the carrier gas, at the pressure of 3bar. When aerosol droplets came close to the substrates, a pyrolysis process occurred and highly adherent SnO_2 films were produced.
The scheme of the spray Pyrolysis setup used in this study is presented in Figure.



The various process parameters in the film deposition are listed in Table 1.

Deposition rate	0.5ml/min
Substrate temperature(°C)	300, 400, 500°C
P^H of the solution	7
Deposition time (minutes)	10 minutes
Nozzle to substrate distance	5cm
Carrier gas pressure	30Pa

In the present study, the P^H of the bath was measured using digital P^H meter. SnO_2 thin films were deposited using aqueous solutions of 0.1M of tin (IV) chloride maintaining the P^H value in between 7 using ammonia solution. If the value is increased above 8 the bath became cloudy due to the precipitation of cadmium acetate. Hence the optimum P^H value of 7±0.2may is chosen for all depositions. The films were deposited at bath temperatures 300, 400, and 500 °C for deposition. The dissociation is greater and gives higher amount of Sn^{4+} ions. The deposition time was optimized as 10 minutes, as which uniform and adherent films were obtained. Then the glass substrates were treated for 15 minutes with ultrasonic waves in a bath of is propane and then rinsed with acetone. The thickness of the substrate was measured using **"Stylus profilometer"** At various points on the substrate and their average was taken as the film thickness.

2.2. Characterization of SnO_2 material

The deposited thin films were characterized by Xray diffraction (XRD), scanning electron microscopy (SEM), and optical absorption spectra. X-ray diffraction pattern was recorded on Diffractometer (Miniflex Model, Rigaku,Japan) using CuKα radiation with a wavelength λ = 1.5418 °A at 2θ values between 20◦ and 80◦. The average crystallite size (D) was estimated using the Scherrer equation [12] as follows: $D = 0.9\lambda/\beta \cos\theta$, where λ, β, and θ are the X-ray wavelength, the full width at half maximum (FWHM) of the diffraction peak, and Bragg's diffraction angle, respectively. The optical absorption spectra of the films were measured in the wavelength range of 200–700nm on a Shimadzu UV-2450 spectrophotometer.

III. RESULTS AND DISCUSSION

SnO_2 thin films were deposited by the CSP technique. The transparency of thin films so formed depends on parameters like substrate temperature and concentration of the precursor solution. Also other parameters such as spray duration, flow rate, pressure etc.

Structure Analysis:

The X-ray diffraction patterns of the SnO_2 thin films deposited at different substrate temperature 300,400 and 500º C are shown in fig (1, 2&3). The most intense peak was observed in XRD at (200) plane and additional peaks along (110), (101),(200), (211), (002), (310), and (112) planes were also observed. The

preoperational orientation (200) plane of SnO_2 thin films were found to gradually increase with the increase in substrate temperature 300 to 500ºC. It revel that the film is polycrystalline in nature with tetragonal structure. Inter planar spacing "d" were calculated and compared with standard valued of JCPDS 88-0287. It was found that at higher temperature intense diffraction peaks well – crystallized film were formed.

The sharper peak (200) was found by x-ray diffraction pattern for SnO_2 thin films deposited at higher temperature and small FWHM data were indicated in table. The lattice constants **(a,c)** was calculated using a equations for the SnO_2 films as follow

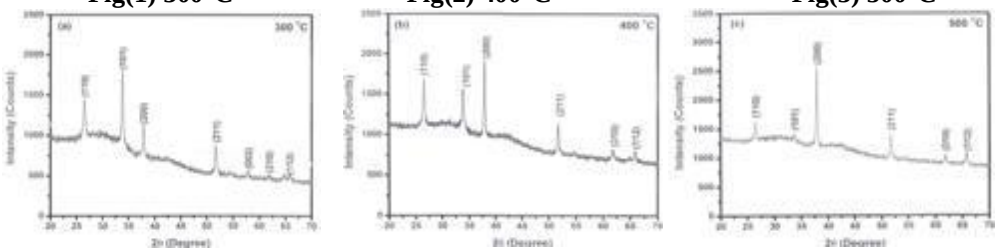
$$\frac{1}{d^2} = (h^2+k^2)/a^2+l^2/c^2$$

It is observed that the lattice constants **(a,c)** value were slightly decreases with the increased the temperature. The lattice constants, crystalline size and its thickness for various temperatures are shown in table.By using Debye – Scherer formula the crystalline size are calculated,

$$D = 0.9\lambda/\beta\cos\theta$$

where, D is the mean crystalline size, β is the full width at half maximum of the diffraction line, θ is diffraction angle and λ is the wavelength of the x-radiation. The variation of crystalline size and micro strain with substrate temperature. SnO_2 films increases with increase in substrate temperature and attains the maximum 67nm.

Fig(1) 300^{0}C **Fig(2) 400^{0}C** **Fig(3) 500^{0}C**

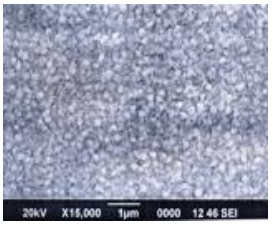


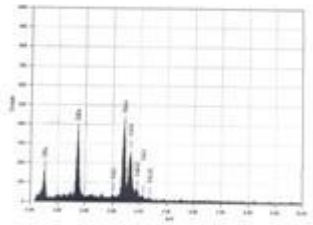
Variation of lattice constants and crystalline size with substrate temperature for the SnO_2 thin films.

Temperature	2θ	d spacing (Aº)	FWHM	(hkl)	Standard Lattice Constant (a) Aº	Experimental lattice Constant (c) Aº	Crystalline size(nm)
300	26.49	3.364	0.187	110	4.7455	3.1583	45.571
	33.792	2.652	0.093	101			92.721
	37.852	2.376	0.224	200			39.078
	51.629	1.77	0.187	211			49.277
	57.817	1.594	0.448	2			21.118
	61.775	1.501	0.897	310			10.771
	65.872	1.416	0.547	112			10.062
400	26.553	3.357	0.187	110	4.7507	3.1307	45.577
	33.822	2.65	0.187	101			46.364
	37.896	2.374	0.187	200			46.900
	51.661	1.769	0.224	211			41.069
	61.816	1.5	0.299	310			32.324
	65.898	1.416	0.41	112			26.086
500	26.464	3.368	0.149	110	4.7486	3.1352	56.961
	33.763	2.655	0.448	101			19.319
	37.901	2.374	0.131	200			67.002
	51.623	1.771	0.187	211			49.275
	61.871	1.499	0.299	310			32.333
	65.829	1.417	0.274	112			36.115

Chemical composition:

Fig. Shows the EDAX spectrum of SnO_2 thin film deposited at 400°C. The strong peaks for Sn and O were found in the spectrum, the silicon (Si) peak is due to the glass (parts of the glass component is Si) substrate and no other impurities were detected confirming high purity of the SnO_2thin film.





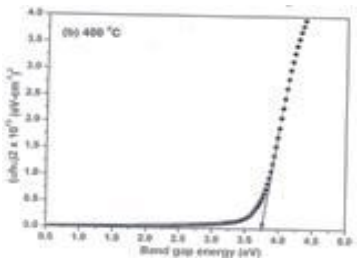
Surface Morphology:

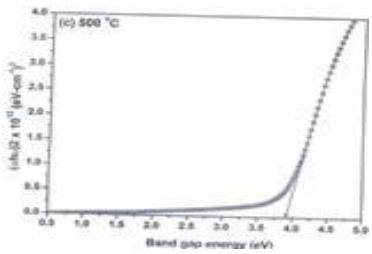
The Surface Morphologies of the SnO_2 thin films were observed through a scanning electron microscopy (SEM). The surface of the film is smooth and covers to the glass Substrates well are shown in Fig. The surface of the films is found to be uniform and many pallets like grains are observed. By varying the temperature from 300 to 500 ^{0}C the structure of the films and the grain size estimation base are depicted in fig. The average grain sizes are in the range of 350 to 400nm.

Optical properties:

The energy band gaps of these films were calculated with the help of the absorption spectra. To determinate of the energy band gap, we plotted $(\alpha h\upsilon)^2$ versus $h\upsilon$. Where α is the absorption coefficient and $h\upsilon$ is the photon energy. The absorption coefficient α is proportional to

$$\alpha h\upsilon = A(h\upsilon - E_g)^h$$





The band gap of films was found to be increased by increasing temperature from 3.7 to 3.95 eV for SnO_2. Our results are in agreement with this literature.

IV. CONCLUSION

In this investigation SnO_2, thin films were grown on glass substrates by CSP and the effects of growth conditions such as the molarities of the constituents, growth temperature on structural and optical properties were studied. The major findings are

1. The structural study from X-ray diffraction indicate the best crystalline with tetragonal structure. It revealed that the grain size of the SnO_2 films increases with the increase in temperature.
2. The SEM micrograph shows that the film is uniform and many pallets like grains to the substrate. The average grain size of the grains are in the range of 350to 400nm.
3. The stoichiometric compound is confirmed by the EDAX measurements.
4. The Optical absorption study reveals that SnO_2 thin films have allowed direct transitions. The optical band gap energy varies from 3.7 eV to 3.95 eV with temperature.

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