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Growth, Structural, Optical, Morphological Studies of SnO2 Thin Films Prepared by Spray Pyrolysis Technique

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ABSTRACT: Tin dioxide (SnO_2) thin films have been deposited using chemical spray pyrolysis on non- conducting glass substrates at temperature 400^oC with different solution concentration from 0.2M to 0.5M.The structural , optical and surface morphological properties of deposited films were studied using scanning electron microscope (SEM), X-ray diffraction (XRD), UV-Vis spectrometry techniques. SEM studies reveal that SnO_2 films exhibited the irregular grains over the surface and the amount of grain increases with increase in the solution concentration. The XRD studies reveal that films are crystalline and structure of tetragonal phase. Micro structural parameters such as crystallite size, micro strain, and dislocation density are calculated and found to depend on solution concentrations. The optical band gap of SnO_2 thin films is calculated using transmittance and reflectance data using UV-Vis spectrometry. From the data, energy band gap lies between 2.72 eV to 2.95eV. And refractive index of the thin film is decreases with decrease in solution concentration.

KEYWORDS: Spray pyrolysis, SnO_2 Thin films, SEM, XRD, UV-Vis spectrometry

I. INTRODUCTION

Studies of dioxide films are quite important because of their possible technological applications. Among the various dioxide, tin dioxide (SnO_2) is promising one and receiving ever-increasing attention owing to its potential uses in a wide variety of applications. It belongs to the II-VI family of semiconducting material owing to energy band gap value about 3 eV. This material is used as the transparent conductive coatings for liquid crystal displays, flat panel displays, plasma displays, touch panels, electronic ink applications, organic light- emitting diodes, solar cells, antistatic coatings and EMI shielding, gas sensing process and also for the fabrication of the optoelectronic devices such as blue-emitting diodes, electroluminescent devices, optical coating, n-window layers for thin film hetrojunction solar cells, photo conductor, photovoltaic devices. It is a good reflector and also dielectric filters due to the high refractive index and high transmittance in the visible range. Tin dioxide (SnO_2) is the most important material for use in gas sensing applications. It is the dominant choice for solid state gas detectors in domestic, commercial and industrial settings due to the low operating temperatures, high sensitivities, mechanical simplicity of sensor design and low manufacturing costs. Tin dioxide is an n-type semiconductor, where the sensor conductivity increases in the presence of a reducing gases (such as CO), and decreases in the presence of an oxidizing gas (such as O_2). SnO_2 sensor response is due to surface interactions between the tin oxide and the surrounding gases [1].

II. MATERIALS AND METHODS

Several techniques have been used to produce SnO_2 films such as thermal evaporation[2], spray pyrolysis[3], molecular beam epitaxy[4], sputtering[5], chemical bath deposition(CBD)[6-11]. Among them, the spray pyrolysis technique is particularly attractive because of its simplicity in comparison with required vacuum conditions or complex equipments. The method have been made to prepare SnO_2 thin films by simple and low cost chemical spray pyrolysis technique. In this work it is concentrated the growth and different characterisation of SnO_2 thin film prepared by spay pyrolysis

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technique. The films have been characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and optical measurement techniques and the result have been discussed.

III. EXPERIMENTAL

Various solution concentration of SnO_2 thin films are prepared using spray pyrolysis instrument by depositing onto glass substrates. The spray solution was prepared by mixing the appropriate quantity of $SnCl_2.2H_2O$ dissolved in a mixture of methanol/ distilled water (volume ratio 9:1). A few drops of hydrochloric acid were added to increase the solubility of the solution. The hot substrate provides the thermal energy for the thermal decomposition and subsequent recombination of the constituent species. SnO_2 thin films of different molar concentrations (0.2 to 0.5 M) are prepared by keeping the constant substrate temperature (400 ^{0}C).

The structural characterization of the thin films was carried out by analyzing the XRD pattern obtained using Bruker AXSDS Advance X-ray diffractometer with Cu k α radiation (λ = 0.154056 nm).Surface morphological was carried out using a scanning electron microscope (JEOL Model, JSM-6390LV). Optical measurements were carried ot UV-Vis technique using instrument VARIAN make, model CARY 5000 with a spectral range of 200-1200 nm.

IV. RESULT AND DISCUSSION

X-ray diffraction pattern recorded for the spray deposited SnO_2 films on glass substrates at various solution concentrations from 0.2M, 0.3M, 0.4M, and 0.5M are shown in fig.1. It is observed that, in all the XRD pattern contains the characteristic SnO_2 orientations along the preferred direction (200). The presence of other peaks such as (110), (101), (211), (220), (310) and (301) has also been detected but with substantially lower intensities. The intensity of (200) peak increases progressively as the concentration increases. The increase in (200) peak intensity may be attributed to the continuous increase in film thickness from 181.50 to 190.90 nm. At lower concentration (0.2 M), large number of small nuclei are formed at pyrolysis temperature 400˚ C. The growth of each nucleus has taken place separately with different orientations and finally the crystal growth along (200) plane is dominant. With increasing solution concentration (0.2 to 0.5 M), initially formed large number of small nuclei might have agglomerated (coalescence) and relatively small number of large nuclei might have formed, which might have caused minor peaks to suppress or disappear and growth along (200) plane is further dominated.

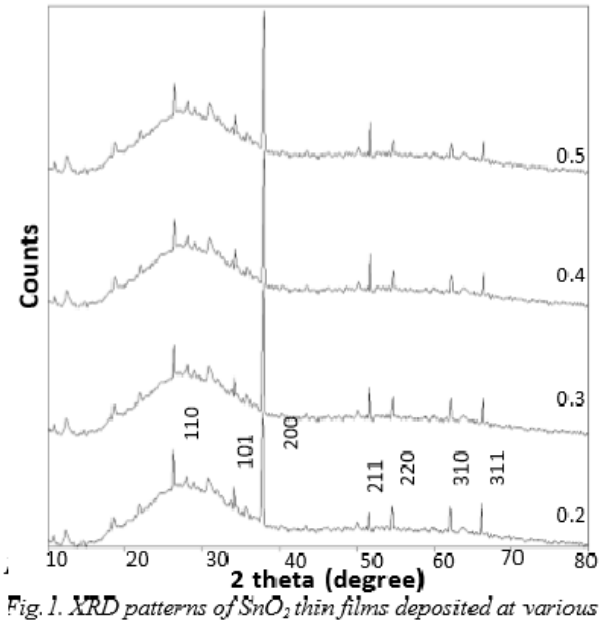

Fig. 1. XRD patterns of SnO_2 thin films deposited at various solution concentrations

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It is found that grain size increases from 30.7 to 39.4 nm as solution concentration increases. Increase in crystallinity and crystallite size (D) with spraying concentration is due to the optimum rate of supply of ions for recrystallisation with substrate temperature. Since dislocation density (δ) is the measure of amount of defects in a crystal, the small values of δ obtained in the present study confirmed the good crystallinity of the tin oxide thin films deposited using the spray pyrolysis. The structural parameters of SnO_2 thin films at various solution concentrations are given in Table.1.

Spraying solution concentration (M)	D (nm)	δ (× 10^{14}) (lines /m^2)
0.2	30.7	10.6
0.3	32.5	9.46
0.4	36.3	7.50
0.5	39.4	6.44

Table.1.Structural parameters of SnO_2 thin films

Scanning electron microscope (SEM) studies were carried out for evaluating surface morphology of the SnO_2 films deposited on glass substrate at 0.2M and 0.5M solution concentrations is shown in fig2(a) and (b).In film with 0.2M solution concentration, it is observed that the film exhibit a very smooth surface, devoid of asperity and pinholes and no well-defined crystallites seen. This evinces that the film is uniform and forces to believe on the uniform distribution of larger number of small nuclei. As solution concentration increases resulted in agglomeration of these nuclei (initially formed) to form cluster. This may be due to different atomic rearrangement process involved during the pyrolytic decomposition of the sprayed droplets on the hot substrates are responsible for the difference in observed surface topography of 0.5 M SnO_2 films. In film with 0.5M solution concentration, lot of irregular grains with different shapes were observed. Also some triangular shaped grains can be seen which are as imbedded in the clusters. From the morphological observations it is conclude that the change in morphology with change in solution concentration.

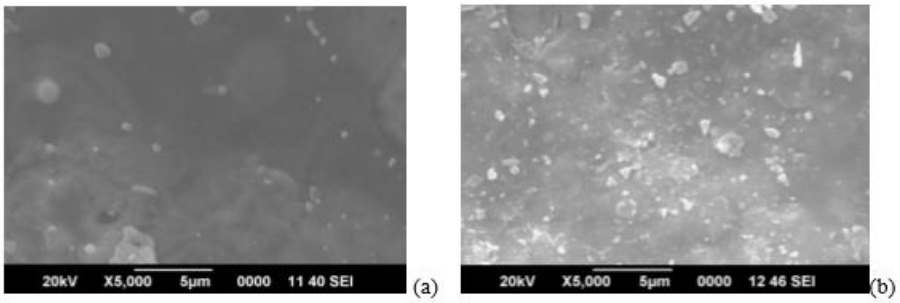

Fig.2. (a) . Microstructure of 0.2M SnO_2 thin film. (b). Microstructure of 0.5 M SnO_2 thin film

Optical transmittance of the thin films were used to estimate the band energy from the position of the absorption coefficient edge. The absorption coefficient can be calculated the relation.

$$\alpha = \beta(h\upsilon - E_g)^2 / h\upsilon$$

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Where β is the corresponding absorption constant and E g is the energy gap. From the estimated value of the absorption coefficients a plot of $(\alpha h\upsilon)^2$ versus h υ, where h υ is the photon energy. Extrapolation of the x-axis gives the band gap energy of the SnO_2 thin films deposited at different solution concentrations shown in fig.3. The band gap energy of the SnO_2 films deposited at various solution concentrations is found to lies in the range between 2.72eV to 2.95eV.

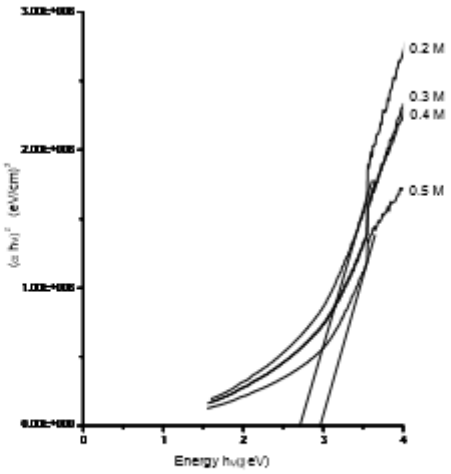

Fig .3. Variation of $(\alpha h\nu)^2$ Vs. hυ for SnO_2 thin films at various solution concentration

Figure 4(a) and (b) shows the transmittance and reflectance versus wavelength for SnO_2 films of different concentrations. From the Fig. 4.(a), it is observed that for the films of all concentrations the transmittance value increases with increase in wavelength and highly transparent over the visible region. Among them film of concentrations, 0.2 M exhibits higher transmittance. This may be attributed to less carrier concentration, smooth surface and small crystallite size observed in 0.2 M SnO_2 thin film produce less scattering effects and results higher transmittance.

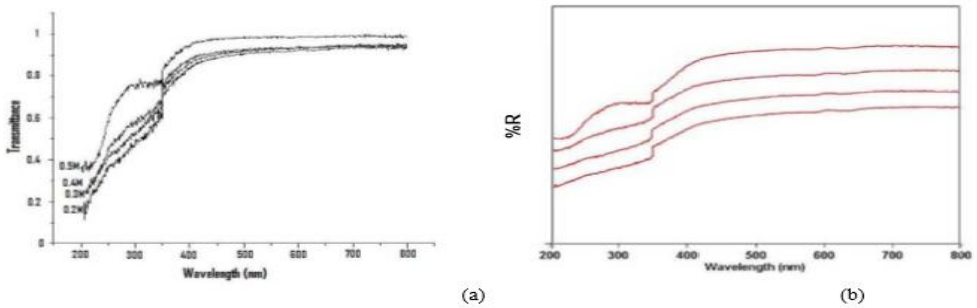

Fig 4. (a).Transmittance spectra of SnO_2 thin films. (b). Reflectance spectra of SnO_2 thin films

From the Fig. 4.(b) It is seen that the reflectivity of 0.2 M SnO_2 film exhibits a lower value compared to 0.5 M. It is due to the fact that the reflectivity is low and there is no (or less) absorption due to transfer of electrons from valence band to conduction band owing to optical interference effects. This possible to maximize the transmission of film (0.2 M) in the visible region.

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Refractive index for tin dioxide thin films were evaluated from the transmittance and reflectance measurements and its variation with wavelength are shown in Fig. 5. From the plot, it is clear that the refractive index decreases with decrease in solution concentration. For all films, the refractive index is found to decrease in the wavelength region 200 nm to 450 nm and thereafter remains more or less constant. The refractive index lies between 1.68 and 1.89 for 0.2 M SnO_2 films and 1.73 and 1.94 for 0.5 M SnO_2 films. This may be due to solution concentration, mobility and coarse surface effect of thin films.

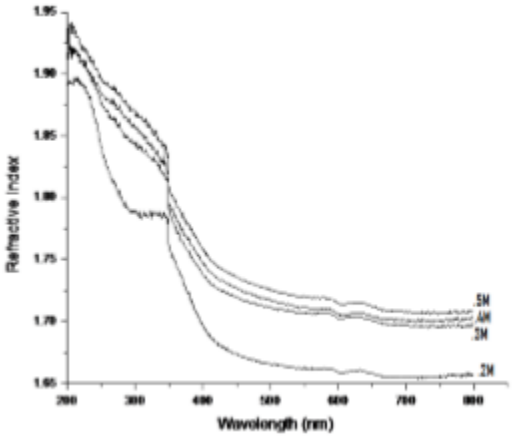

Fig.5. Variation of refractive index of SnO_2 thin films

V. CONCLUSION

The SnO_2 thin films were successfully deposited on glass substrate at various solution concentrations 0.2M, 0.3M, 0.4M and 0.5M using spray pyrolysis technique. X-ray diffraction analysis confirmed that the deposited SnO_2 films were crystalline and tetragonal structure. Various structural parameters such as crystalline size, dislocation density are calculated and found to depend upon various solution concentrations. SEM studies reveal that irregular grains were increased with respect to the increase in solution concentration. The surface morphology of the thin films changes with change in solution concentrations. Optical transmittance measurements indicate that the deposited thin films have band gap energy lies in the range between 2.72 eV to 2.95eV which confirm these are good semiconducting films.

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