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Physics

ROLE OF ANNEALING TEMPERATURE ON THE STRUCTURAL, MORPHOLOGICAL AND OPTICAL CHARACTERIZATIONS OF SnO2 THIN FILMS SYNTHESIZED BY SPIN-COATING METHOD

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ABSTRACT The influence of annealing temperature on the structural, morphological, and optical properties of SnO_2 thin films prepared by spin-coating method has been studied. The samples were thermally annealed at 673 K and 773 K for 2 hrs. Powder XRD analysis of the thin films annealed at 673 and 773 K shows less intense and broad diffraction peaks. The size of the grains found to increase with annealing temperature. The grain size of the synthesized film is enhanced due to increasing annealing temperature upto 773 K. The grains are well agglomerated for films annealed at the higher temperature of 773 K. The transmission spectra of SnO_2 thin films annealed at the temperatures of 673 and 773 K was analyzed. The percentage of transmittance found to increase from 56 to 91% with an increase in the annealing temperature from room temperature to 773 K. The bandgap energy value (Eg) was calculated and it increases from 3.25 to 3.35 eV with the increase in annealing temperatures.

KEYWORDS : Spin Coating, annealing temperature, XRD, SEM.

INTRODUCTION

In recent years, thin film research and experimental work for successful application of its properties in engineering and different branches of science and technology are greatly expanding in different parts of the world. During the last five decades, a great deal of research work has been carried out on thin films of metals, semiconductors, insulators and ceramic materials. A thin film in a layer of material ranging from fractions of nanometer (monolayer) to several micrometers in thickness [1]. Thin films find large applications in the field of opto-electronic devices, photoconductive panels, photovoltaic applications, solid-state layer devices, electro-luminescent displays, smart window coating, electro-chromic coatings, photo-chromic, thermo-chromic coating, solar absorbing layer *etc*. [2-5]. Numerous works has also been undertaken for the search of new coating materials related to electro-optical properties [6-8]. These include transparent conducting coating, spectrally selective coating, antistatic coating on instrument panels, heating elements, electrical contact in liquid crystals and to fabricate and structure of the devices.

Transparent conducting oxides (TCO) are materials with wide band gap energy, a higher optical transmittance, excellent electrical conductivity and high thermal stability. They are suitable for application in the area of solar cell, gas sensor and can be used as interfacial layer for diodes. The important TCO materials are ZnO, SnO_2 and TiO_2which are used in various electronic and optoelectronic device fabrication [9-11]. Fabrication of thin films by vacuum and non-vacuum techniques yield films of different nature, but the basic principles of condensation and nucleation of the films from its vapor phase are the same in the initial film growth stage. Since chemical spray deposition, chemical bath deposition and drop chemical methods are non-vacuum techniques and can operate in open atmosphere. To have a good quality film requires a stern quality imposed on the films prepared by these methods. Our aim is to prepare films in chemical methods such as spray pyrolysis, chemical bath and drop chemical deposition techniques.

Spin coating is used for many applications [12-14] where flat small substrates or objects need to be coated with thin layers of material. For example, several cathode ray tube (CRT) manufacturers use this method to make anti-glare or anti-reflection coatings. In spin coating, the material to be coated is first dissolved or dispersed into a solvent, then deposited onto the surface and then spun off to leave a uniform layer for subsequent processing stages and ultimate use.

MATERIALS AND METHODS

Glass substrate dimensions of 2.5 × 2.5 cm were cleaned well with acetone and isopropyl alcohol kept in an ultrasonic water bath around 15 min. The substrates were further washed with distilled water, acetone and isopropanol and then dried well at room temperature.

By employing spin-coating technique, SnO_2 thin films were coated on glass substrates. The precursor solution was prepared by dissolving 0.1 M stannous chloride pentahydrate ($SnCl_2{\cdot}5H_2O$) in 10 ml of ethanol. Homogeneous solution was obtained after stirring at 333 K for 24 hrs in an ambient condition. The glass substrate is fixed onto the sample holder of spin coater. A drop of clear solution was poured over the glass substrate with a fine nozzle and the substrate was allowed to rotate at a spin rate of 2500 rpm for 30s. The solution-processed spin-coated thin films were thermally annealed at two different temperatures 673 K and 773 K, for almost 1 hr during annealing; the temperature was increased by 4–5 K per min.

RESULTS AND DISCUSSION

X-ray diffraction analysis

The X-ray diffraction (XRD) analysis is an illustrious method for the characterization of bulk and thin film samples. It is a powerful tool to determine the crystal structure of materials. Both pristine and annealed SnO_2 samples were subjected to powder XRD analysis. During the analysis, the sample is exposed to X-rays, which diffracts off the atomic planes of the crystal structure. Constructive interference patterns occur when the atomic spacing is an integer multiple of the X-ray wavelength, resulting in a characteristic diffraction peak. By moving the detector and source over different angles with respect to the sample, diffraction patterns can be obtained.

Recorded XRD pattern of both pristine and annealed SnO_2 thin films in the temperature of 673 and 773 K are depicted in Fig. 1. Both non-annealed and annealed thin films have no diffraction peaks attributable to the amorphous nature. XRD patterns of the thin films annealed 673 and 773 K shows a broad diffraction peaks at 2(°)= 26.5, 33.0, 37.8, 51.6 and 54.6 and can be indexed to (110), (101), (200), (211) and (220), respectively. The observed diffraction peaks correspond to tetragonal SnO_2 crystal structure and space group *P42/mnm* according to the JCPDS Card no.41-1445. Annealing temperature enhances the formation of nano crystalline structure in the prepared samples and the intensity of the diffraction peaks was enhanced with an increase in the annealing temperature.

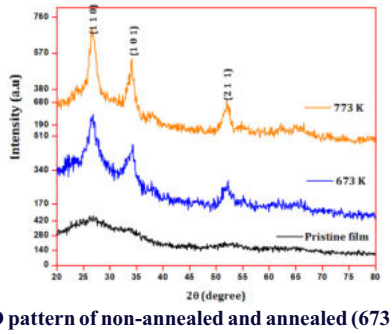

Fig. 1. XRD pattern of non-annealed and annealed (673 and 773K) SnO_2thin films

The crystallite size of the samples was calculated using Debye-Scherrer's formula [15-16] $D = \frac{0.89\lambda}{\beta\cos\theta}$, where 0.89 is the shape factor, β is the full-width at half the maximum of the diffracted peak, λ is the wavelength of the X-ray radiation source ($CuK\alpha_1$) and θ is the diffraction angle in degrees. It has been observed that the D value varies from 23.56 to 49.69 nm for the predominant peak (1 1 0) of the SnO_2 thin films.

SEM analysis

Scanning electron microscopy (SEM) is a well-suited and versatile tool for studying surface morphology of the thin and bulk samples. It provides the information about surface or near surface region. The surface morphology and grain growth of the pristine and annealed SnO_2thin films were analyzed by SEM analysis.

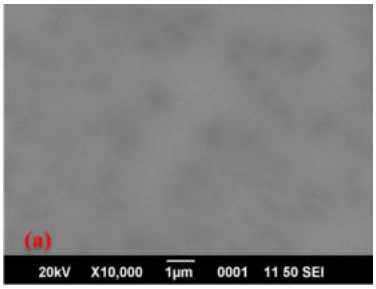

Fig. 2. SEM image of pristine SnO_2 sample

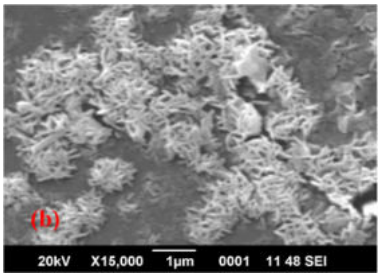

Fig. 3. The SEM image of annealed SnO_2 sample at 673K

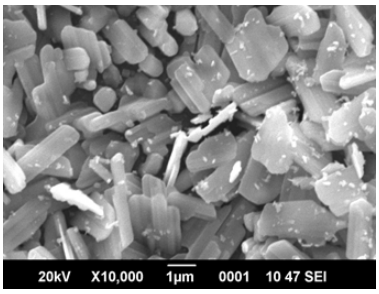

Fig.4. The SEM image of annealed SnO_2 sample at 773K

The SEM image of pristine SnO_2 sample is shown in Fig.2. A smooth film surface with no visible grain growth has been observed in the case of pristine film. The SEM image of annealed SnO_2 sample at 673K is shown in Fig.3. The grain growth was evident at the annealing temperature 673 K. The presence of randomly oriented rod like grain at the surface is visible at this temperature. The SEM image of annealed SnO_2 sample at 773 K is shown in Fig.4. Sub-microsized plate like grain distribution with increasing grain size is observed at annealing temperature 773 K. Hence, it is obvious that the annealing temperature influences the grain growth of SnO_2 clusters, which supports the results of XRD patterns.

UV-visible spectral analysis

The UV-Vis spectroscopy is the traditional analytical technique deals with the measurement of outcome of interaction of electromagnetic radiation in the UV-visible regions with the absorptions of atoms, molecules or ions [17]. The equilibrium charge carrier distribution in any material can be altered by its exposure with electromagnetic radiation of suitable energy. Absorption of photons of sufficient energy tends to transfer the electrons from valance band to conduction band giving absorption maxima. Thus, the optical absorption spectrum of a pure semiconductor exhibits a fundamental absorption edge at a certain incident photon energy, which can be ascribed to the excitation of electrons from valence to conduction band separated by energy equal to the band gap energy (E_g).

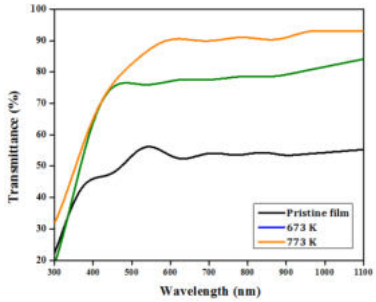

Fig. 5. Transmittance spectra of Pristine and annealed SnO_2 thin films

The optical responses of the pristine and annealed thin films were analyzed using UV-visible analysis in the wavelength range from 300 to 1100 nm and are shown in Fig. 5. It shows the maximum transmittance for the SnO_2 film annealed at 773K is about 90 % in the entire visible region. The percentage of transmittance increases from 56 to 91% with an increase in the annealing temperature from room temperature to 773 K. Generally, increase in transmittance can be attributed to a reduction in grain boundary scattering. The thickness of the pristine SnO_2 thin film is 348 nm and annealed films thicknesses are varied from 320 to 302 nm.

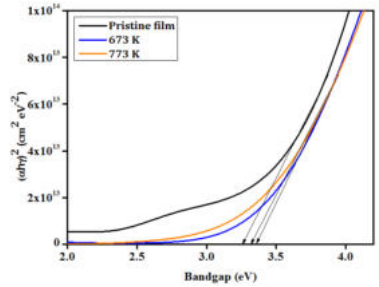

Fig. 6. The $(\alpha h\nu)^{1/2}$ versus hν spectra of the pristine and annealed 773 and 773K of SnO_2

The band gap energy was calculated using Tauc's relation [18]

$$(\alpha h\gamma)^{1/y} = A\left(h\gamma - E_g\right)$$

The $(\alpha h\nu)^{1/2}$ *vs* hν graph is shown in Fig. 6. The band gap energy (E_g) values are extracted from this graph which indicates that an indirect band gap for all the SnO_2 films. It has been observed that there is an increase in band gap energy from 3.25 to 3.35 eV.

CONCLUSION

Tin oxide (SnO_2) thin films were prepared by sol-gel spin coating method. The prepared films were annealed from 673 to 773 K. From the XRD analysis, the phase tetragonal SnO_2 crystal structure was observed. The crystallite size (d) of the prominent peaks increases from 23.56 to 49.69 nm which depends on the annealing temperature of SnO_2 thin films. The SEM micrographs reveal that non-annealed SnO_2 thin films shows smooth surface. With the increase of annealed temperature the grain size was increased. The plate like structure was observed for 773 K annealed SnO_2 thin films. The transmittance values were increased for annealed film from 56 to 91%. The bandgap energy was calculated from Tauc plot, which shows that the bandgap has been increased from 3.25 to 3.35 eV with the increase of annealing temperature.

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