CHEMICAL BATH DEPOSITION AND CHARACTERIZATION OF PVP CAPPED TIN OXIDE THIN FILMS

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Chemical bath deposition of transparent conducting tin oxide (SnO_2) thin films has been carried out within the pores of polyvinylpyrrolidon (PVP). The bath for the deposition of SnO_2 is made up of $SnCl_4$, NaOH and PVP solution. The deposition was maintained at a temperature of 65ºC for 6hours. In this present work, these films were annealed at different temperatures and characterized for the structural and optical properties. These properties were studied by means of x-ray diffraction (XRD) and optical spectrophotometer. The composition of the film was determined by Rutherford back scattering. The optical properties revealed the presence of direct band gaps with energy in the 1.5 to 2.2eV range. The films show high transmittance of 60% and above in the VIS and near infrared regions of the solar spectrum.

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1. Introduction

Low electrical resistivity and high visible transmittance are the key elements for solar cells [1]. Among the various transparent and conducting oxides (TCO), tin oxide films are most promising. They have been intensively used in the field of microelectronics and stable gas sensors [2]. The film is highly transparent, chemically inert, and mechanically hard along with low electrical resistivity and has good optical transmittance [2]. Owing to these properties, tin oxide serves as a window layer in solar cells [2]. TCO coatings can also act as heat mirrors due to their high reflectivity in infrared region. Application of tin oxide films are not limited to the research laboratory but are used commercially in environmental monitoring, industries, electronic sensor and liquid crystal displays etc.

Doped and undoped tin oxide films have been deposited by several researchers by various methods such as sputtering, chemical vapour deposition, spray pyrolsis, thermal evaporation, laser pulse evaporation [3, 4]. Among all these techniques, chemical bath deposition technique is credited with several advantages such as its how cost since no expensive and sophisticated vacuum equipment are required, ease of handling and ease of application to many compounds such as sulphides and selenides which includes ZnS, CdS, PbS, CdSe and CuS.

2. Experimental details

SnO_2 thin film has been successfully deposited on glass slide using chemical bath deposition (CBD) method at of 65ºC for 6 hours. Prior to deposition, the glass slides were cleaned by degreasing them in dilute HNO_3 for 24hours, thoroughly washed in detergent solution, rinsed in distilled water and dried in air.

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The cleaned glass surface provided nucleation centre for growth, good adhesion and uniform deposition of the films. The bath for the deposition of SnO_2 thin films is made up of $SnCl_4$, NaOH and polyvinylpyrrolidon (PVP). The PVP solution was prepared by dissolving 4.0g of solid PVP in 400ml of distilled water. This was stirred (without heating) in a magnetic stirrer until the solution became homogenous. In a typical deposition set up, the bath was composed of 8ml of 1mole $SnCl_4$, 3ml of 1mole NaOH and 35ml of PVP solution added in that order and stirred thoroughly.

The glass slides were dipped inside the bath covering 2/3 of its length and left for 6 hours at a temperature of 65ºC. After deposition, the coated slide was rinsed with distilled water and dried in air. The films were annealed in oven at a temperature of between 200ºC and 300ºC.

The deposited SnO_2 films were characterized by x-ray diffraction (XRD), optical microscopy and spectrophotometer. The composition of the film was determined by Rutherford backscattering (RBS). The absorption coefficient (α) and the band gap of the films were determined by using the absorbance and transmittance measurement from UNICO UV-2102PC spectrometer at normal incident of light in the wavelength range of 200 – 1100nm.

3. Results and discussion

3.1 Elemental Composition

The elemental composition as analyzed by RBS is given in figure 1 below and it shows that the film comprises of oxygen and tin with no impurity content.

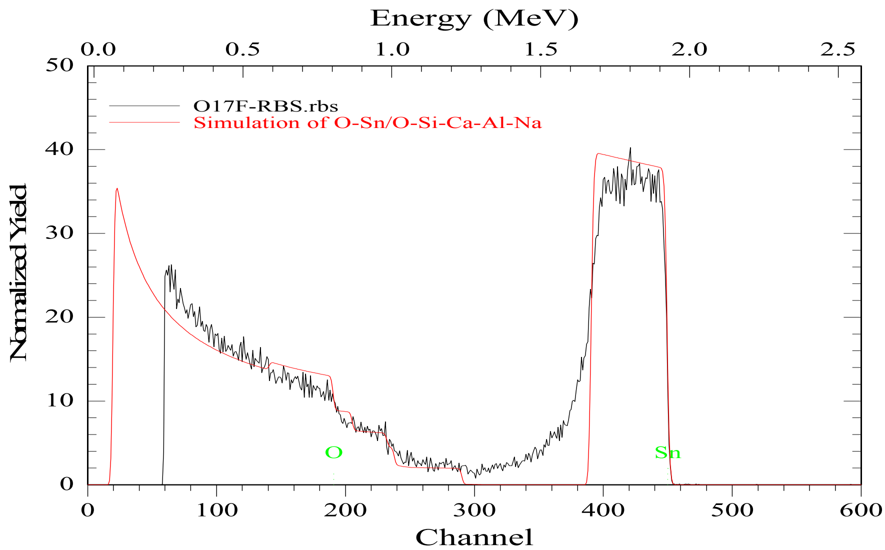

Fig 1. RBS result for tin oxide.

3.2 Structural studies

Structural analysis of the CBD deposited SnO_2 films were carried out by using CuKα radiation source having wavelength of 1.5408Å. The x-ray diffraction pattern of the film is shown in figures 2 and 3

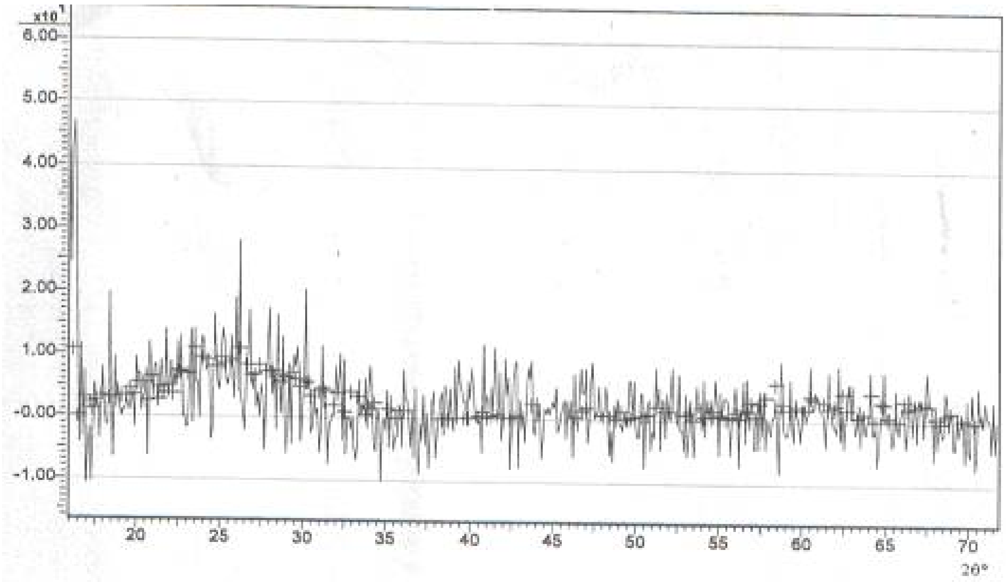

Fig. 2: XRD of the as-grown SnO_2 thin film.

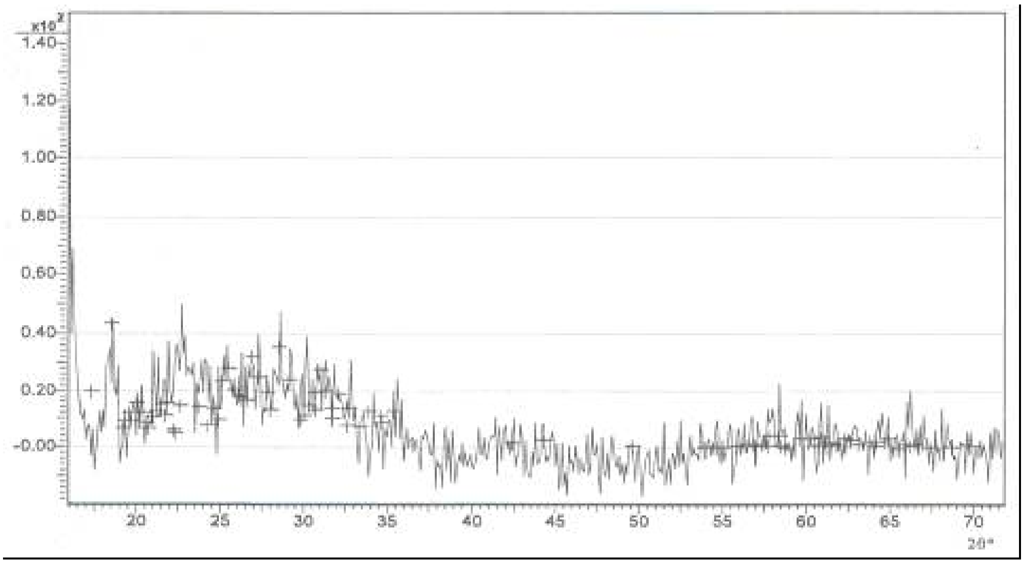

Fig. 3:XRD of SnO_2 thin film annealed at 300^oC

Peak broadening has been observed in recorded diffraction patterns, which shows the formation of crystalline thin films. The diffraction lines appearing at 2θ values of 26.81^o and 54.65^o correspond to (110) and (220) planes respectively, (JCPDS 05-0640) [1]. However, the noise in the diffractograms is attributable to the glass substrate used for the deposition.

The average crystallite size of the films was calculated from the recorded XRD patterns using Debye Scherrer formula:

$$D = 0.89\ \lambda/\beta \cos\theta,$$

where D is the average crystallite size, λ is the wavelength of the incident X-ray, β is the full width at half maximum of X-ray diffraction and θ is the Bragg's angle. The average crystallite size for the thin film of SnO_2 was found to be 23.54nm.

3.3 Optical and Solid State Studies

The optical absorption spectra of the films deposited onto glass surface were studied in the wavelength range of 200 – 1100nm. The variation of absorbance with wavelength for the samples annealed at different temperatures and the as-grown is shown in fig 4.

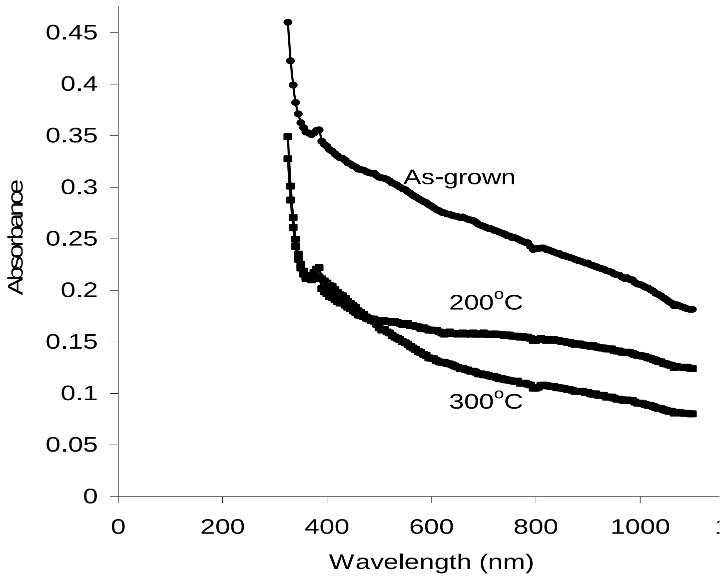

Fig.4: Absorbance vs. wavelength for SnO_2 thin films annealed at different temperature

A close observation of figure 4 shows that the films have low absorption in the visible spectrum, which decreases as the wavelength increases towards the NIR region. The figure also reveals that annealing the films in the oven tends to lower the absorbance of the films. However, the reverse is the case for the plot of transmittance against wavelength. In this case, the transmittance of the films increase with annealing temperature, as displayed in the figure 5. The transparency varies from 60 to 85% in the visible and NIR region of the solar spectrum.

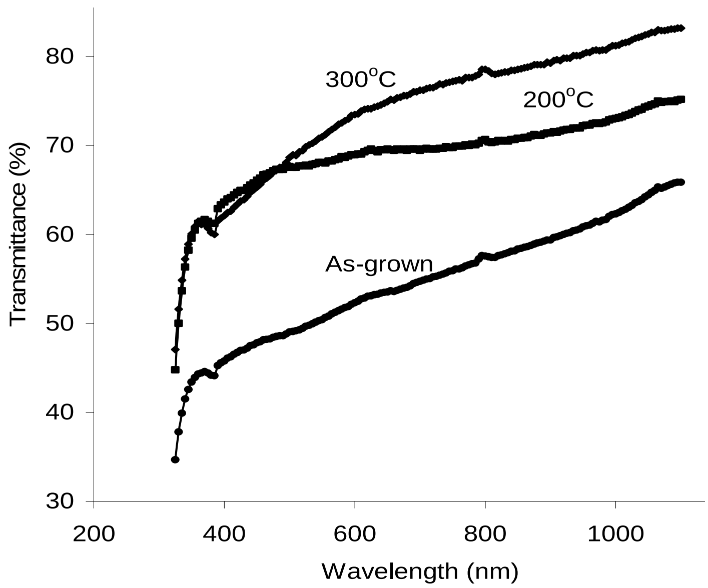

Fig. 5. Transmittance vs. wavelength for SnO_2 thin films annealed at different temperature

Fig. 6 shows a plot of reflectance against wavelength for thin films of tin oxide deposited and annealed at different temperature. The films show a reflectance of less than 20% in the VIS and NIR regions of the solar spectrum.

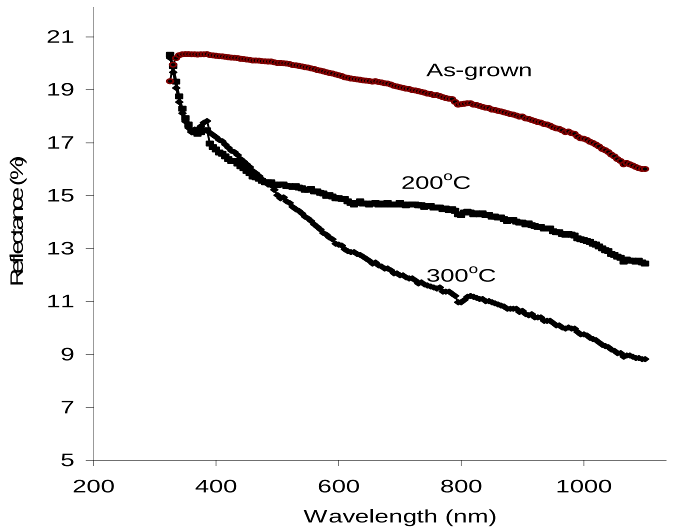

Fig. 6. Reflectance vs. wavelength for SnO_2 thin films annealed at different temperature

The thin films with high transmittance and low reflectance are good material for antireflection coatings of solar thermal devices. It has been shown that high transmittance and low reflectance properties of thin films in the visible region are the desired properties for their application in solar thermal control coatings [5]. The application of solar energy as a source of heat in chick breeding requires thin films with high transmittance in the NIR with moderate reflectance. The property of high transmittance in the NIR exhibited by these films therefore make them good materials for the construction of poultry roofs and walls. This has the potential to minimize the cost of energy consumption associated with the use of electric bulbs, heater, stove etc and the hazards associated with them, while at the same time protecting the chicks from UV radiation.

The details of the mathematical determination of the absorption coefficient (α) can be found in literature [6] while the plots of absorption coefficient against photon energy is shown in fig. 7.

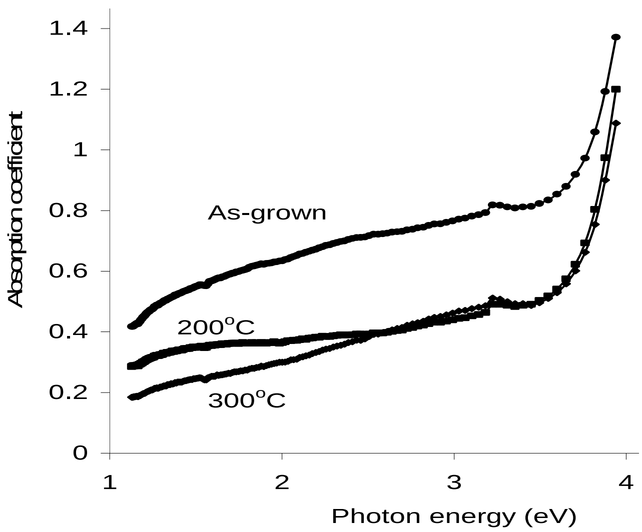

Fig.7. Absorption coefficient vs. photon energy for SnO_2 thin films annealed at different temperature

These absorption spectra, which are the most direct and perhaps the simplest method for probing the band structure of semiconductors, are employed in the determination of the energy gap, E_g. The E_g was calculated using the following relation: $\alpha = A(h\nu - E_g)^n / h\nu$

Where A is a constant, hν is the photon energy and α is the absorption coefficient, while n depends on the nature of the transition. For direct transitions n = ½ or ⅔, while for indirect ones n = 2 or 3, depending on whether they are allowed or forbidden, respectively.

The best fit of the experimental curve to a band gap semiconductor absorption function was obtained for n = ½. The calculated values for the direct energy band gap, from fig.8 lie in the range of 1.5 to 2.2eV. Annealing the sample in the oven lowers the value of coefficient of absorption of the films and thus increases the band gap energy. The band gap energies obtained here are low compared with values in the literature.

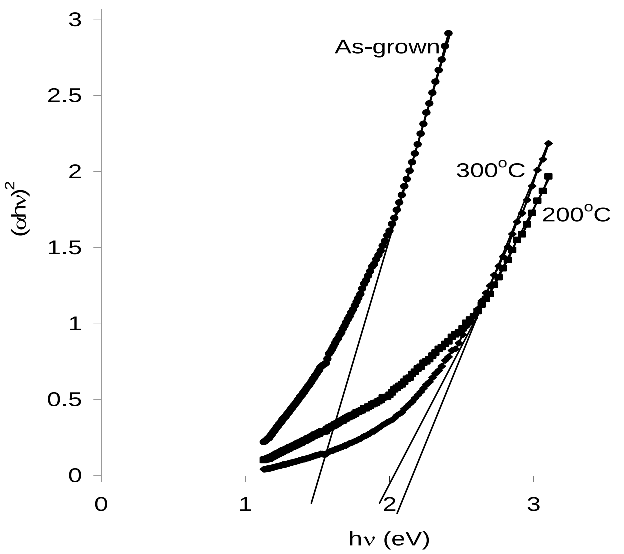

Fig.8. $(\alpha h\nu)^2$ vs. hν for SnO_2 thin films annealed at different temperature

4. Conclusions

This study focuses on direct deposition of thin films of SnO_2 at a temperature of 65°C by simple and inexpensive chemical bath deposition technique. The films were deposited and annealed at different temperature. XRD study reveals better crystallization of the films at a higher thermal annealing temperature. XRD pattern shows that the SnO_2 thin films have a preferred orientation in the (110) plane. Optical studies and band gap analysis show that thermal annealing has significant effect on these properties. The properties of high transmittance in the NIR exhibited by these films make them good materials for the construction of poultry roofs and wall. Thin films also have potential application in solar cell architecture.

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