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Optical Characteristics of Nanocrystaline Thermal Annealed Tin Oxide (SO_2) Thin Film samples Prepared by Chemical Bath Deposition Technique

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ABSTRACT

A tin oxide thin film was prepared by chemical bath deposition technique, deposited on glass substrates using 5mls of 1m of $SnCl_2 2H_2O$ and 1ML of 1M of NaOH solution with triethanolamine (TEA) as the complexing agent. The films were subjected to post deposition annealing under various temperatures, 100, 150, 200,300 and 399^{0}C. Found to be firmly adhered to the substrate and resistant to chemicals wear. The transmittance is between 57% and 95% while the reflectance is between 4% and 19%. The band gaps obtained under various thermal treatments are between 1.40eV and 3.2eV. The refractive index is between 0.00 and 3.00. The thickness achieved is in the range of 0.12-0.14μm. These properties of the oxide film make it suitable for application in solar cell fabrication, gas sensor devices, transparent electrodes for panel displays, etc.

Keywords: Thin Film, Tin Oxide, Chemical Bath Deposition, Optical Properties, Thermal Annealing, complexing agent.

INTRODUCTION

Tin oxide ($Sn0_2$) is one of the transparent conductive oxides (TCOs). The oxide films are stable, strongly adherent to the substrate, mechanically hard and resistant to moisture and acids [1]. In recent times, techniques like atmospheric chemical vapour deposition (APCVD) system [1] Femtosecond pulsed laser deposition [2], chemical vapour deposition [3] etc, have been used in depositing tin oxide films. Band gap range of 1.40 – 3.2 eV has been reported using these techniques. Transparent conductive oxides (TCOs) are unusual materials that are both electrically conductive and visually transparent [4, 5]. Tin oxide films have large transmittance in the visible region of the electromagnetic spectrum as a consequence of the large band gap [3]. Owing to its outstanding electrical, optical and electrochemical properties, $Sn0_2$ is extensively used in many applications such as catalytic support materials, transparent electrodes for flat panel displays and solar cells and gas sensors. In particular, $Sn0_2$ thin films have drawn much

interest because of their potential application in microsensor devices [2,5-7] They are widely used in high and low technical applications such as antistatic coatings instrument panels, on heaters, electrical contacts in liquid crystals, electrochronic and electroluminescent displays and optical coatings [1,4].

The deposition of thin Tin oxide films using chemical bath deposition technique and post deposition thermal annealing on the optical properties of the oxide film are successfully looked into in this paper.

MATERIALS AND METHODS

The tin oxide ($Sn0_2$) thin films were prepared using chemical bath deposition technique. The chemical bath system was prepared using 5mls of 1M of $SnCl_2 2H_2O$, 1ml of 1M of sodium hydroxide (NaOH), triethanolamine (TEA) or Ammonia (NH_3) as complexing agent, prepared polyvinyl alcohol (PVA), 50ml beakers and 76 mm x 26mm x 1mm glass microscope slides which were used as depositing substrates. The glass slides as the substrates for depositing SnO2 films were prepared by ultrasonically cleaned by acetone, followed by ethanol and finally, de-ionized water for 5mins respectively and allowed to air dry. The PVA solution was first prepared by adding 450mls of distilled water to 0.9g of solid PVA $(-C_2H_4O)_n$ (where n = 1700), and stirred by a magnetic stirrer at 90^0C for 1hour. The solution was aged until the temperature drops to room temperature. Uniform films were obtained in the process. In each case, the substrate was suspended vertically in the reaction bath after stirring the solution properly for homogeneity. The equation of reaction is:

$SnCl_2 + TEA \leftrightarrow [Sn(TEA)]^{2+} + 2Cl^-$
$[Sn(TEA)]^{2+} \leftrightarrow Sn^{2+} + TEA$
$2NaOH + 40H^- \leftrightarrow 2Na^+ + 30^{2-} + 3H_20$
$Sn^{4+} + 20^{2-} \rightarrow Sn0_2.$

The films were removed and washed after various periods of deposition and allowed to dry in air. The thin film samples were deposited at the temperature between 60^0C – 75^0C, some of them were subjected to post deposition annealing between the temperatures of 100^0C and 399^0C. The optical Absorbance/transmittance of the samples were investigated in the spectral range of 200 – 1000nm (UV-VIS-NIR regions) using Unican Helios Gamma UV - Visible spectrophotometer

RESULTS AND DISCUSSION

Chemical bath deposition techniques were successfully used to deposit Tin oxide (SnO_2) thin films on glass substrate. The films are very transparent, firmly adhered to the substrates and resistant to both trioxonitrate (v) acid and hydrochloric acid.

Fig 1: Transmittance against Wavelength for Tin oxide thin film at different annealing temperature

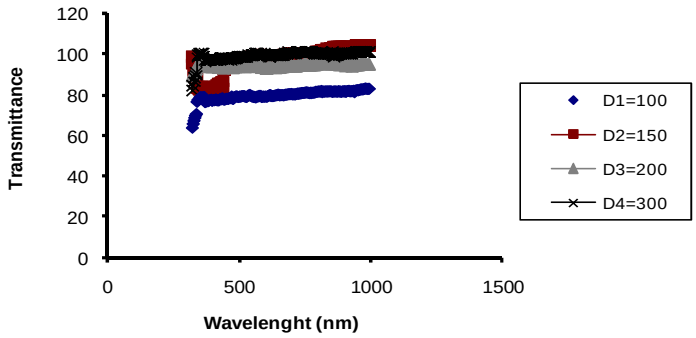
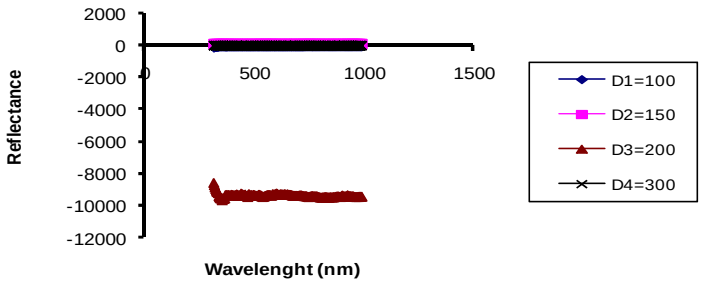


Fig 2a: Reflectance against Wavelength for Tin oxide thin film at different annealing temperature



Thermal annealing does not affect the physical nature of the films rather it the thermal treatment streamlined the properties of the oxide films. The range of thickness of the films deposited is 0.010 - 0.148μm. Figures 1 and 2 show plots of transmittance and reflectance as functions of wavelength. It was noted from the graphs that the properties of the films become more defined with increase in the annealing temperature. All Thermal annealed films show very high degree of transmittance and very low degree of reflectance in the entire spectral regions.

The films as grown and those annealed at lower temperature (100^0C – 150^0C) show transmittance in the range of above 80% to nearly 100% and reflectance in the range of below 0% to nearly 10%. There is depreciation in transmittance and improvement on reflectance on those annealed at higher temperature. The range is now from below 60% to nearly 90% and below 0% to nearly 10% respectively. As shown in figure 2b, it is seen that the transmittance rises with increasing wavelength while reflectance decreases with increasing wavelength

Maximum and minimum values of refractive index, 0.60 and 0.90 respectively were obtained for the $Sn0_2$ films. The values decrease with increasing wavelength as shown in figure 3. The rate of decrease increases with the annealing temperature.

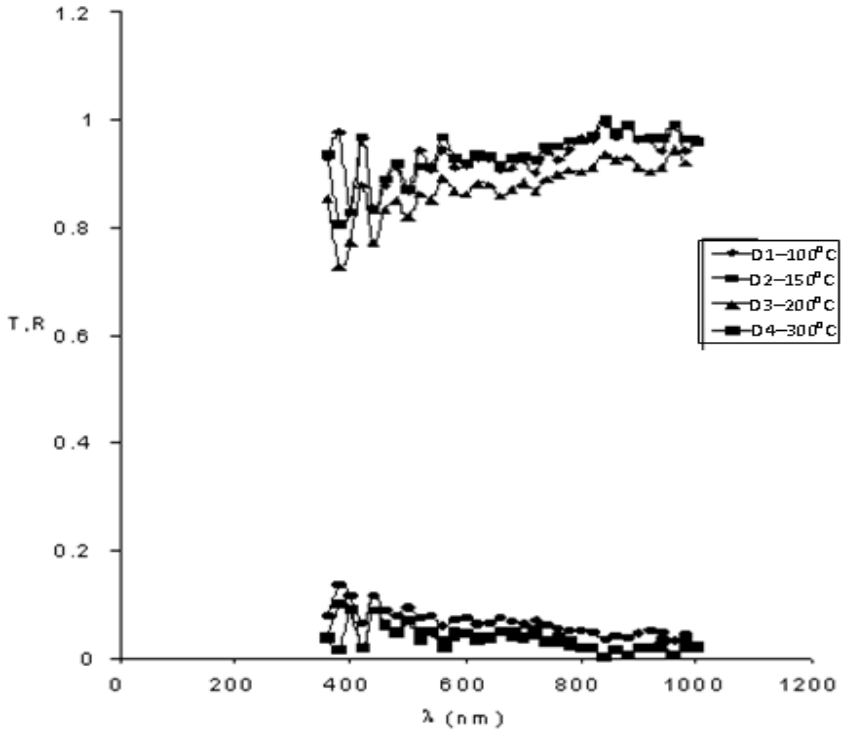
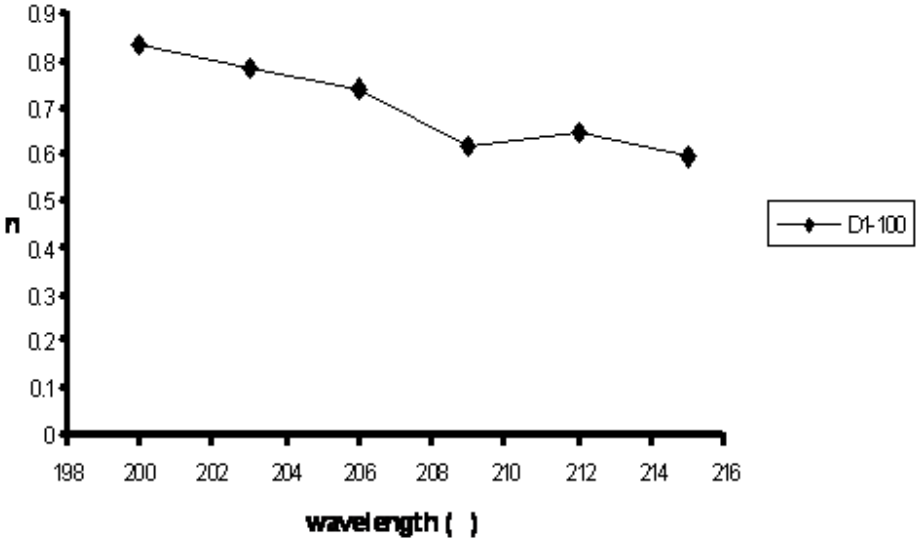


Fig 2b: Transmittance (T) and Reflectance (R) as function of wavelength (λ) under

Fig 3: refractive index (n) as a function of wavelength (λ) various annealing temperature



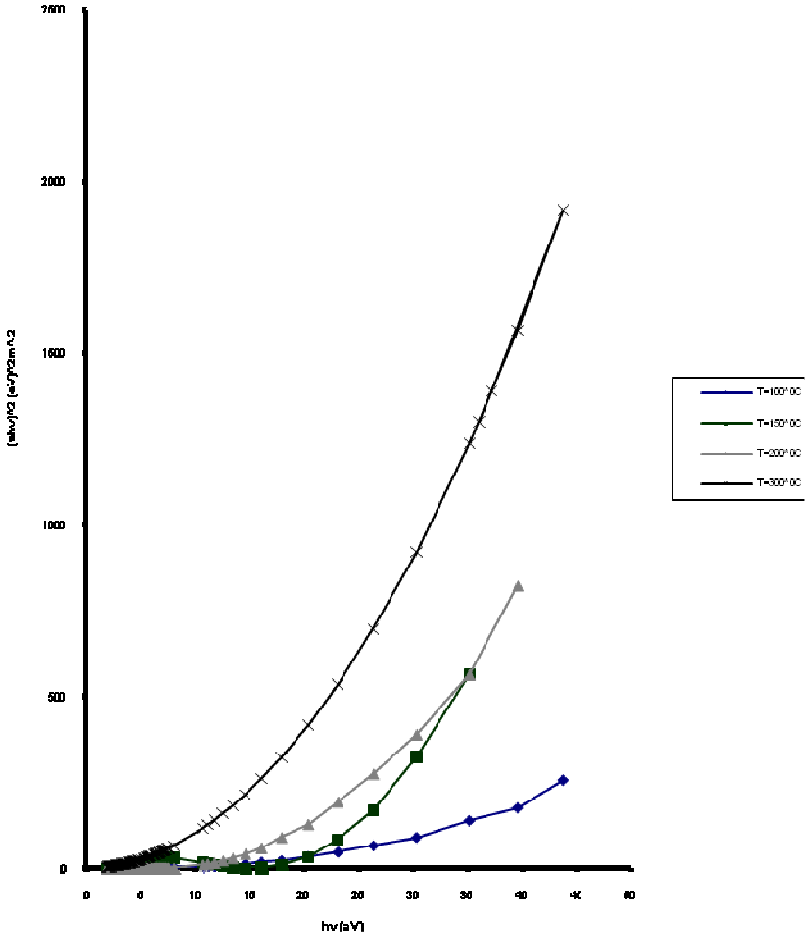
In order to determine the optical band gap of the semiconductor, the following dependence of the absorption coefficient, α on the photon energy equation [5, 8, and 9] is used $(\alpha h\nu)\ \alpha\ (h\nu - E_g)^n$ Where E_g is the direct transition band gap and n=1/2 for direct allowed transition Figure 4 shows

a plot of $(\alpha h\nu)^2$ against the photon energy, hν. The band gap obtain for various annealing temperature are shown in the table below. The table αshows a decreasing band gap with increasing temperature. Even the decreased values of Eg still remain wide.

Band gap of SnO under various annealing temperatures

Sample	Annealing temp	Band Gap (eV)
D_1	100	3.20
D_2	150	2.80
D_3	200	2.60
D_4	300	2.40
D_5	399	1.60

Fig 4: A plot of $(\alpha h\nu)^2$ as a function of photon Energy (hv) for SnO_2



Various authors in their separate reports had reported band gap ranging from 3.0ev to 4.2ev in agreement with the wide band gap reports under a deposition temperature slightly above the

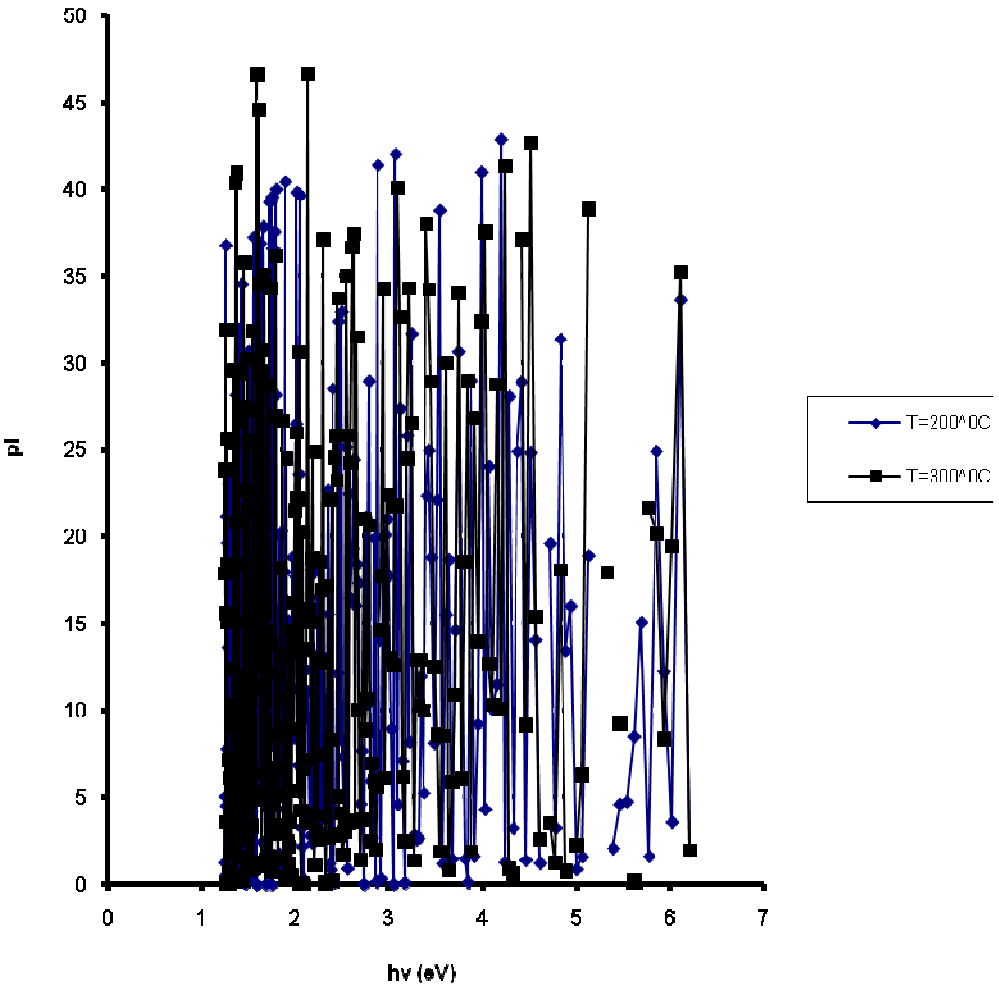
room temperature. In this case, a nearly lower ranger of 1.6 – 3.2eV band gap where obtained at a deposition temperature far above room temperature as reported.

The optical conductivity is given by [10] $\sigma = \frac{\alpha nc}{4\pi}$ where α is the absorption co-efficient, n the refractive index, c is the velocity of light and σ_0 the optical conductivity. Plots of optical conductivity as a function of photon energy are shown in figure 5.

At 200^0C, the rate of random increase of $\boldsymbol{\sigma_0}$ with increasing photon energy was very steep. However at 300^0C, the rate of increase was equally steep but slower. Both maximum values decrease and minimum values increase with increase in photon Energy.

Minimum and maximum values of $0.00s^{-1}$ and $4.20x10^{12}s^{-1}$ respectively are shown the figure.

Fig 5: A plot of optical conductivity as a function of photon Energy (hv) for SnO_2



CONCLUSION

Tin oxide (Sn02) thin films have been deposited by chemical bath deposition technique using $SnCl_2$ and Na0H solution. Post deposition annealing of the films at temperatures 100,150,200, and 300^0C sharpened the properties of the films. $Sn0_2$ film is a transparent oxide film. It has very high transmittance in all the regions of electromagnetic spectrum. The transmittance increase from UV-NTR regions up to over 90% The reflectance is generally low and decrease within the same region.

Band gap of 1.60 – 3.20 eV were obtained for the oxide film under various annealing temperatures. The values are in agreement with theoretical values. Values of the refractive index are within the range 0.00 to 3.00. The outstanding properties of the oxide films show them as good materials for solar cells, gas sensors, transparent electrodes for panel displays, etc.

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