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Effects of Thermal Annealing on the Optical Properties of Titanium Oxide Thin Films Prepared by Chemical Bath Deposition Technique

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Abstract: A titanium oxide thin film was prepared by chemical bath deposition technique, deposited on glass substrates using TiO_2 and 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 399ºC. The thermal treatment streamlined the properties of the oxide films. The films are transparent in the entire regions of the electromagnetic spectrum, firmly adhered to the substrate and resistant to chemicals. The transmittance is between 20 and 95% while the reflectance is between 0.95 and 1%. The band gaps obtained under various thermal treatments are between 2.50 and 3.0 ev. The refractive index is between 1.52 and 2.55. The thickness achieved is in the range of 0.12-0.14 µm.These properties of the oxide film make it suitable for application in solar cells: Liquid and solid dye-sensitized photoelectrochemical solar cells, photo induced water splitting, dye synthesized solar cells, environmental purifications, gas sensors, display devices, batteries, as well as, solar cells with an organic or inorganic extremely thin absorber. These thin films are also of interest for the photo-oxidation of water, photocatalysis, electro chromic devices and other uses.

Key words: Complexing agent, chemical bath deposition, optical properties, thermal annealing, thin film, titanium oxide

INTRODUCTION

Titanium oxide (TiO_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 (Matsui, 2000; Chopra, 1983). In recent times, techniques like atmospheric chemical vapour deposition (APCVD) system (Matsui, 2000). Femtosecond pulsed laser deposition (Dominguez *et al*., 2001), chemical vapour deposition (Eze and Okeke, 1997) and other method of deposition had been carried out at various places. Transparent conductive oxides (TCOs) are unusual materials that are both electrically conductive and visually transparent (Jeong *et al*., 2004; Thangaraju, 2000). The transmittance of the titanium increases in the visible region of the electromagnetic spectrum as a consequence of the large band gap.

Owing to its outstanding electrical, optical and electrochemical properties, $Sn0_2$ is extensively used in many applications such as photo-induced water splitting dye synthesized solar cells, environmental purifications, gas sensors, display devices, batteries (Regan and Gratzel 1991; Bach *et al*., 1998), as well as, solar cells with an organic or inorganic extremely thin absorber (Tennakone *et al*., 1995; Siebentritt *et al*., 1997). These thin films are also of interest for the photo- oxidation of water (Pozzo *et al*., 1997), photocatalysis (Kang *et al*., 1988), electro chromic devices (Paz *et al*., 1995) and other uses (Eya *et al*., 2005).

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 in this paper.

MATERIALS AND METHODS

The titanium oxide (TiO_2) nanoparticles thin films were prepared using chemical bath deposition technique. The chemical bath system was prepared with titanium chloride $TiCl_4$, titanium tetraoxosulphate (iv) ($TiSO_4$), sodium Hydroxide (NaOH) as complexing agent, 50ml beakers and 76 x 26 x 1 mm^3 glass microscope slides which were used as depositing substrates. The substrates were degreased in Aqua Regia (3:1 of conc. HCl: HNO_3) solution for 24 h, washed clean in detergent solution rinsed out in distilled water and allowed to air dry. Solution of the same concentration were prepared and used in arriving at the optimum combination and depositing film of various thicknesses on different five glass slides. 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:

$$TiCl_4 + TEA \leftrightarrow [Ti(TEA)]^{2+} + 4Cl^-$$
$$[Ti(TEA)]^{2+} \leftrightarrow Ti^{2+} + TEA$$
$$2NaOH + 4OH^- \leftrightarrow 2Na^+ + 3O^{2-} + 3H_2O$$
$$Ti^{4+} + 2O^{2-} \rightarrow TiO_2.$$

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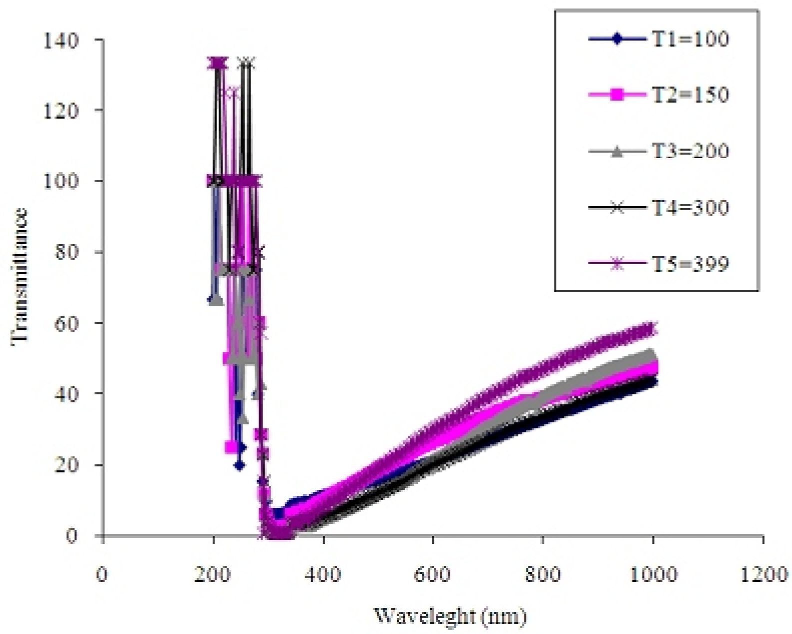

Fig. 1: Transmittance against Wavelength for titanium oxide thin film at different annealing temperature

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 of 39-30ºC slightly above the room temperature, some of them were subjected to post deposition annealing between the temperatures of 100 and 300ºC. The optical Absorbance/ transmittance of the samples were investigated in the spectral range of 200 - 1000 nm (UV-VIS-NIR regions) using Unican Helios Gamma UV - Visible spectrophotometer

RESULTS AND DISCUSSION

Titanium oxide (TiO_2) thin films were successfully deposited on glass substrate using chemical bath deposition technique. The films are very transparent, firmly adhered to the substrates and resistant to both trioxonitrate (v) acid and hydrochloric acid. Thermal annealing does not affect the physical nature of the films. The range of thickness of the films deposited is 0.12-0.14 µm. Figure 1 and 2 show plots of transmittance and reflectance as functions of wavelength. The graphs show that the properties of the films become more defined with increase in the annealing temperature. Generally, the 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 (100-150ºC) show transmittance in the range of 90% -<100% and reflectance in the range of 0-10%. On the other hand, those annealed at higher temperature (above 200ºC) show depreciation in transmittance and on reflectance. The range is now ~60% -90% and 0% - (-0%), respectively. The transmittance rises with increasing wavelength while reflectance decreases with increasing wavelength.

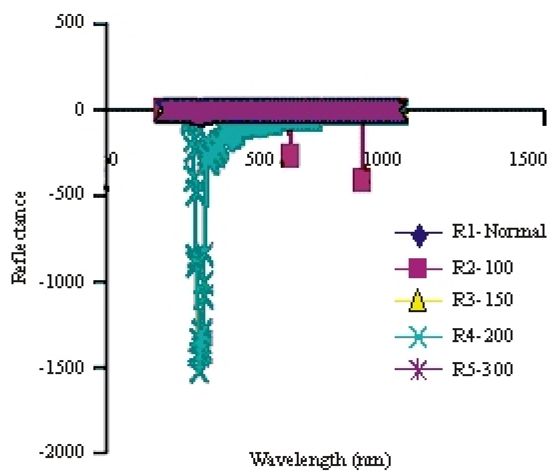

Fig. 2: Reflectance against Wavelength for titanium oxide thin film at different annealing temperature

Maximum and minimum values of refractive index, 0.00 and 3.50, respectively were obtained for the TiO_2 films. The values maintained a random increase and decrease with increase wavelength as shown in Fig. 3. The values have no effect with the increase in the annealing temperature.

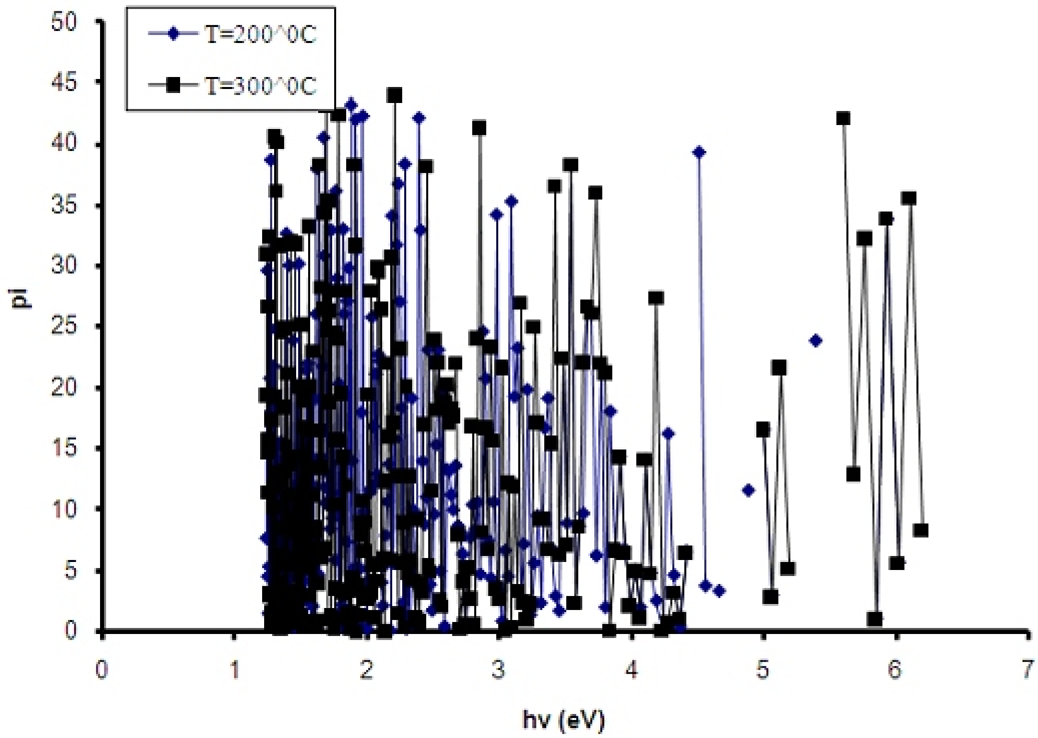

Fig. 3: Refractive index (n) as function of wavelength (λ) under various thermal treatments (that is annealing temperature)

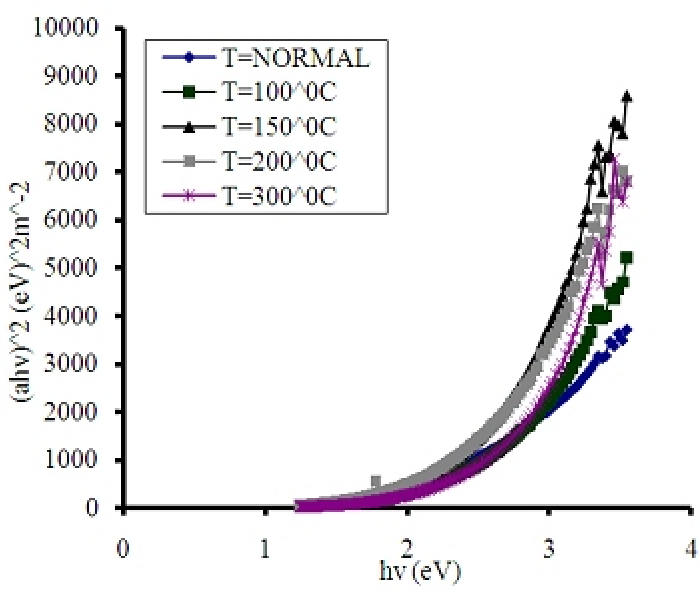

Fig. 4: A Plot of $(\alpha hv)^2$ as a function of photon Energy (hv) for TiO_2

In order to determine the optical band gap of the semiconductor, the following dependence of the absorption coefficient, α and the photon energy equation(Thangaraju, 2000; Pankove, 1971; Tanusevski, 2003) is used (αhu). i.e., $\alpha = (hu\text{-}E_g)^n$

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 1. The table shows a

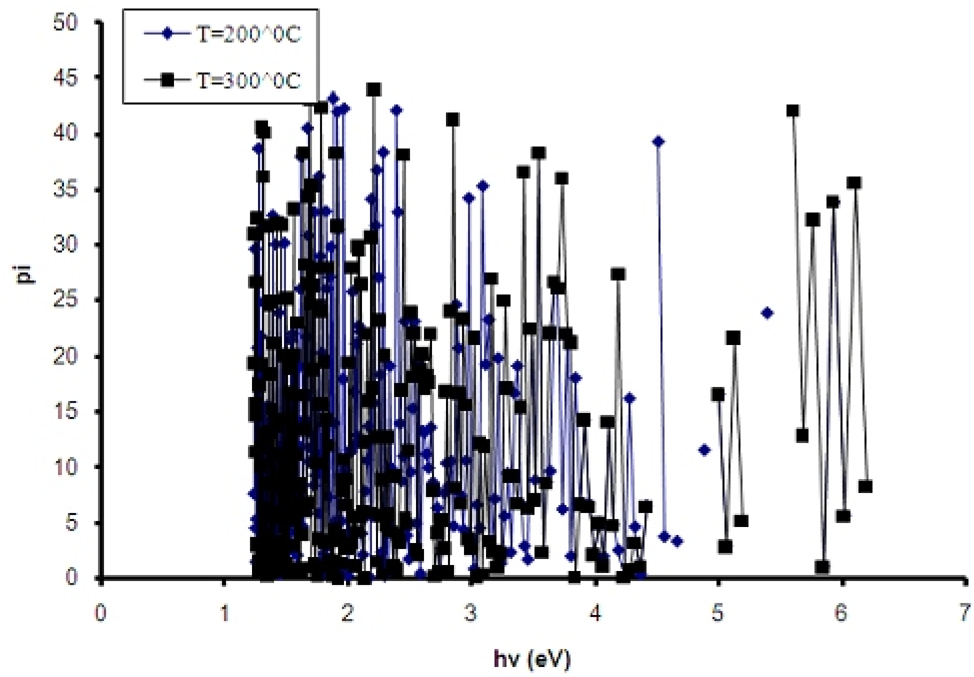

Fig. 5: A plot of optical conductivity as a function of photon Energy (hv) for TiO_2

Table 1: Band gap of SnO under various annealing temperatures

Sample	Annealing temp	Band gap (eV)
A_1	Normal	2.90
A_2	100	2.80
A_3	150	2.60
A_4	200	2.40
A_5	300	2.20

decreasing band gap with increasing temperature. Even the decreased values of Eg still remain wide.

Various authors in their separate reports had reported band gap ranging from 3.0 to 4.2 ev in agreement with the wide band gap reports.

Table 1 The band Gap gap of SnO under various annealing temperature. The optical conductivity is given by Pankove (1971):

$$\sigma = \frac{\alpha nc}{4\pi}$$

where α is the absorption co-efficient, n the refractive index, c is the velocity of light and s_0 the optical conductivity.

Plots of optical conductivity as a function of photon energy are shown in Fig. 5.

At 200ºC, the rate of increase and decrease of σ_0 with increasing photon energy was very random and reduces as photon energy increased steep. However at 300ºC, the rate of increase and decrease was equally random but reduces more slowly.

Minimum and maximum values of 0.00 s^{-1} and $4.4x10^{12}s^{-1}$ respectively are shown the Fig. 4.

CONCLUSION

Titanium oxide (TiO_2) 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 300ºC sharpened the properties of the films. $Ti0_2$ 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 2.20-2.90 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 3.50. The outstanding properties of the oxide films show them as good materials for dye synthesized solar cells, gas sensors, display devices, etc.

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