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Optical Characterization and Surface Morphology of Sno_2 Thin Films Prepared By Spin Coating Technique

Jonathan O. Ajayi [1] , David B. Agunbiade [2]
[1,2]*Ladoke Akintola University of Technology, Ogbomoso, Nigeria,*

Abstract- Investigation of optical properties and surface morphology of SnO_2 thin films was carried out in this study. The effects of precursor concentration on the thin film properties were also studied. SnO_2 was synthesized from anhydrous $SnCl_2$ dispersed in Methanol and Acetic acid. The metallic oxide (SnO_2) films deposited were characterized using the UV Spectrophotometer and the Scanning Electron Microscope (SEM). From the absorption spectra, absorption increases with decrease in precursor concentration. Absorbance in the VIS region is lower than 0 % at higher concentration. The optical transmission spectrum shows that transmission increases as the concentration of precursor decreases and the maximum transmission in visible region is about 90% for films prepared with 0.2 M. Also, there is increase in the reflectance of thin films as concentration of precursor increases. The films have high transparency (more than 85%) and low reflectance (less than 40%) in the VIS region. Investigation showed that the direct band gap value increased from 3.79eV, to 3.82eV as the precursor concentration decreased from 0.6 M to 0.2 M. Average direct bandgap energy for all the tin oxide films was estimated to be 3.80eV. The effect of precursor concentration was directly observed in crystal outgrowth and surface particle densification. They were found to increase proportionately with higher concentration. The low reflectance at low concentration makes the thin film a good material for anti-reflective coatings and the wide band gap makes these films good material for optoelectronic applications.
Keywords— Morphology, precursor, anhydrous, spectrophotometer, crystal outgrowth, densification

I. INTRODUCTION

The application of thin films in technology cuts across all areas of electronics, optoelectronics, photo-voltaic, photo-thermal, photo electromagnetic, photo-electrochemical and photo-bio chemical [10]. The wide variety of electronic and optical properties of metal oxides makes them preferred materials for basic research and technological applications. Oxides have a wide range of electrical properties from wide band-gap insulators to metallic and superconducting. Tin oxide (SnO_2) belongs to a class of materials called Transparent Conducting Oxides (TCO), constituting an important component for optoelectronic applications [6]. Tin oxide thin films have beneficial properties, such as transparency for visible light, reflectivity for infrared light and a low electrical sheet resistance, rendering them suitable for a wide variety of applications as in solar cells, light emitting diodes [22], anti reflective coatings [10], transparent electrodes in electroluminescent lamps and displays [7], transistors[1], photovoltaic cell [9], gas sensors [8], Protective and wear resistant coating on glass containers [24]), Infrared reflectors for glass windows [20].

Tin Oxide is a tetragonal n-type semiconductor with high energy band gap (3.71 eV) [3] where inherent oxygen vacancies act as an n-type dopant. It has high transmittance in the region of visible spectrum due to high band gap. In practice, deposited tin oxide layers contain a reasonable number of oxygen vacancies, making electrons available for conduction. As a result of these, doped and un-doped tin oxide thin films are of great importance to researchers for various applications. In this study, Tin (II) Chloride was used as the starting material, it was preferred due to its low cost as precursor [31], methanol was used as solvent and acetic acid was used as the chelating agent. With these a transparent solution of tin oxide was achieved and deposited on a glass substrate by the spin coating technique.

II. EXPERIMENTAL DETAILS

A. Preparation Of Solution

All reagents were analytical grade and used as received. Anhydrous Tin (II) chloride ($SnCl_2$) was dissolved in methanol and acetic acid in a conical flask [30]. The solution was gently stirred by a magnetic stirrer until a transparent and homogeneous solution is achieved. Solvent volume was varied to achieve the different concentrations. The concentrations achieved are 0.2M, 0.4M and

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0.6M.

B. Substrate Cleaning

The glass slides were washed thoroughly with a cotton wool, cleaning soap and distilled water. After cleaning, the glass slides were placed in a glass jar with a picker. The glass jar was filled with Acetone and placed in an Agitator for 15 minutes. This was done to remove all other micro particles. Afterwards, the glass slides were ultrasonically bathed with ethanol for another 15 minutes. This is done for further cleaning and removal of all organic particles and solution droplets. Finally, the glass slides were dried in a micro analysis oven at a temperature of 200^0 C for 10 minutes. At this point the substrates were ready for deposition. A very thin area of the glass surface was masked for deposited surface and sample identification.

C. Spin Coating

The spin coater used was a Model WS – 400BZ – 6NPP/ AS and the process was carried out under a stream of compressed air. An amount of 1ml of solution was spun on a piece of glass substrate. Table 2.2 shows the deposition parameter control for each cycle. The total duration of coating for a cycle is 60 seconds.

STEP	SPEED (RPM)	DURATION (S)
Spin Up	200	10
Spin Off	1000	20
Evaporation	2000	30

Table 1: Deposition Cycle Program

D. Characterization

Optical properties of the tin oxide thin film from the interference fringes of the transmission spectrum was carried out by using UV spectrophotometer (Model – AvaSpec- 204B) in the wavelength range 200nm to 1000nm. Micro-structural analysis of the films was carried out by obtaining the SEM micrographs from the Scanning Electron microscope (Model ASPEX 3020).

III. RESULTS

A. Absorption Spectra

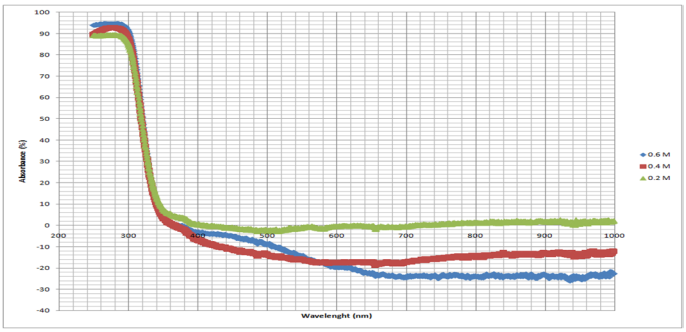

Fig 1: The Absorbance spectra of SnO_2 films as a function of wavelength

B. Transmittance Spectra

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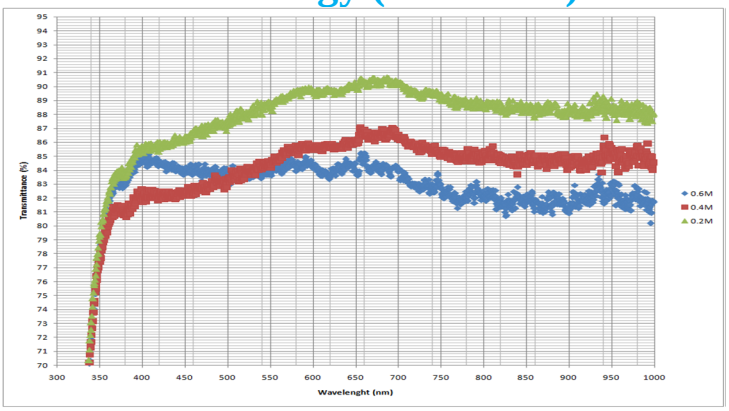

Fig 2: The Transmission Spectra of SnO_2 films as a function of Wavelength.

C. Reflectance Spectra

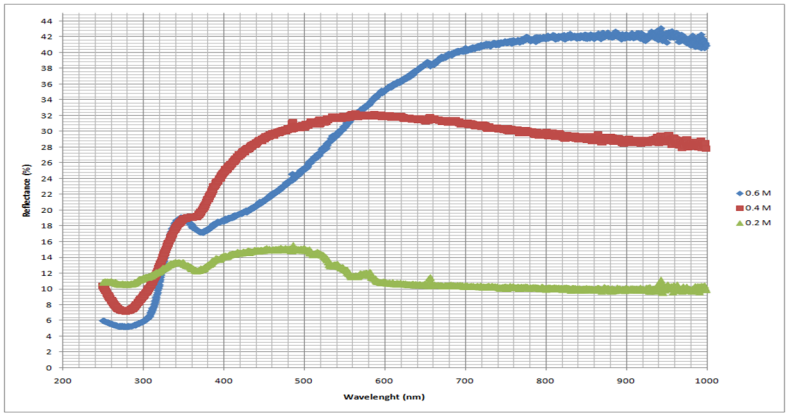

Fig 3: The Reflectance Spectra of SnO_2 films as a function of Wavelength.

D. Absorption Coefficient

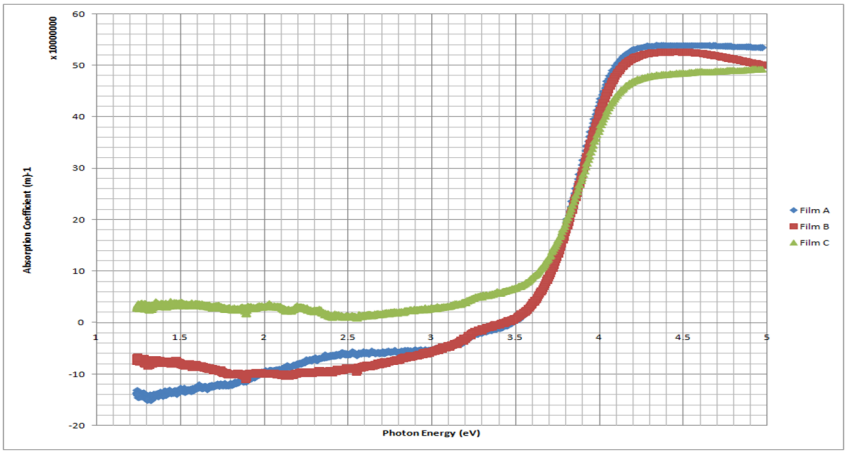

Fig 4: The Absorption Coefficient of SnO_2 films as a function of Photon energy.

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E. Direct Bandgap Energy

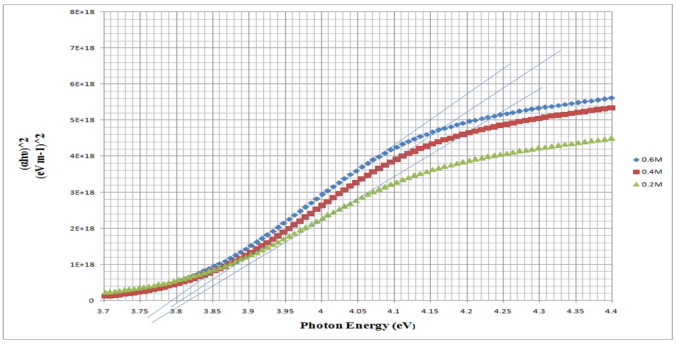

Fig 5a: The Optical Energy Gap for the Direct Allow Transition of SnO_2 films.

F. Indirect Bandgap Energy

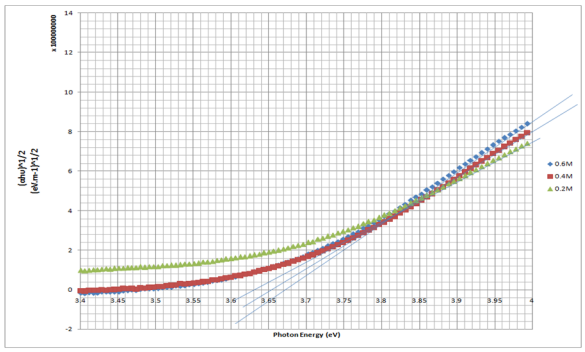

Fig 5b: The Optical Energy Gap for the Indirect Allow Transition of SnO_2 films.

G. Photomicrograph Of Thin Films

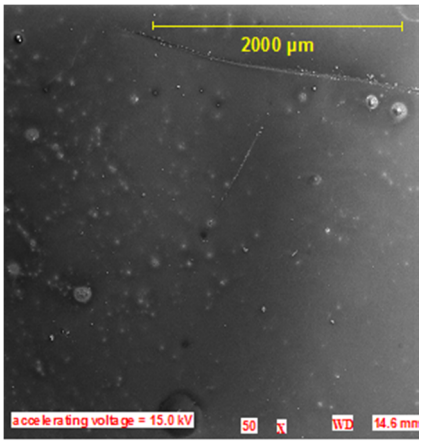

Figure 6a: SEM image for Sample at 0.6 M

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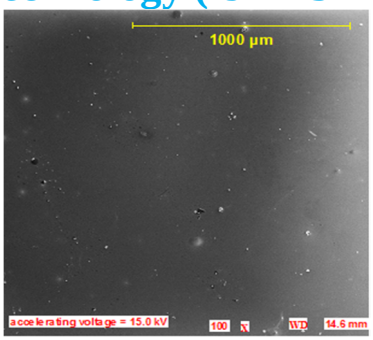

Figure 6b: SEM image for Sample at 0.4 M

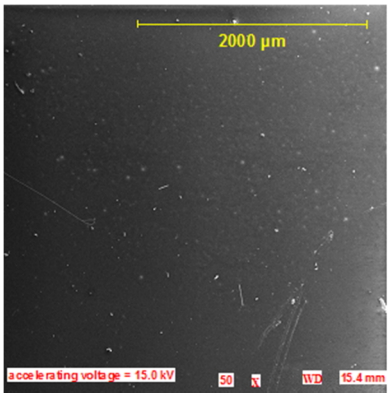

Figure 6c: SEM image for Sample at 0.2 M

IV. DISCUSION

The absorbance spectrum of films with different concentration is shown in figure 1. The spectra pattern is similar for the grown films. For all the films, absorbance at UV region is very high, lowest absorbance occurred in the VIS region (negative values all in most cases). Absorbance increased slightly at the NIR region and afterwards became steady. Absorbance increased as precursor concentration decreases for the thin films.The transmittance spectrum of films with different concentration is shown in figure 2. The spectra pattern is similar for films with lower concentration. For all the films, transmittance at UV region is very low, highest transmittance occurred in the VIS region (>80% in all cases). Transmittance reduces slightly at the NIR region and afterwards became steady. Transmittance increases as precursor concentration decreases for the thin films. The reflectance spectrum of films with different concentration is shown in figure 3. There is significant difference in the reflectance spectra pattern of the films. For all the films, reflectance is lower at UV region. For film C, average reflectance is lowest with a slight increase around the band gap energy. Average reflectance increases with increase in precursor concentration. The absorption coefficient (α) of SnO_2films with different concentration is shown in figure 4. The absorption coefficient of SnO_2 films were determined from the absorbance measurements, (α) was calculated using the following equation:

$$\alpha = \frac{2.303\,A}{t}$$

where α is the absorption coefficient, A is the absorbance and t is the thickness of the film. [23].
The absorption coefficient of films was plotted against the photon energy. A similar pattern for all the films is observed. The films have good absorption at short wavelength region where absorption decreases with increase in wavelength. Increase in absorption occurred when the photon energy becomes equal to the value of the energy gap. At this point electronic transfer between the valance and the conduction band begins. The absorption co-efficient for the films is same at a value of (25 x 10^5 m^{-1}) corresponding to

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Photon energy of 3.75eV. Absorption co-efficient is minimum in the low photon energy region because of the low probability of electrical transfer between the valance band and the conduction band.

The optical energy gap for the direct allowed and indirect transition between valence bands and conduction bands of SnO_2 thin films were shown in figure 5a and 5b. The direct and indirect optical band gap energy of the films was extrapolated from the plot of αhv^2 and $\alpha hv^{\frac{1}{2}}$ against photon energy (eV) respectively. A linear fit was performed for the curve and the values were estimated from the intercept with the energy axis. There is slight effect of concentration on the both the direct allow and indirect band gap energy. The estimated direct allow bandgap energy for the thin films are 3.79eV, 3.81eV and 3.82eV respectively. These results are in agreement with previously reported value [3, 35]. The wide direct band gap makes these films good material for potential applications in optoelectronic devices such as multilayer dielectric filters and solar cell. The estimated indirect allow bandgap energy for the thin films are 3.65eV, 3.63eV and 3.60eV respectively. Figure 6a-c shows the micrographs of the film prepared at films A, B and C at concentration of 0.6 M, 0.4 M and 0.2 M respectively. The surface is apparently compact, adhesive and slightly rough. The particle size distribution is even across the surface and existence of some agglomerates of small rounded particles is evident. There is evidence of granularity which is a feature seen in crystalline films. [30]. This could be associated with the super-saturation of the tin oxide ions in the methanol solution. The tin oxide presents a spherical geometry that is evenly dispersed on its surface. Further examination of the micrographs showed that the size, numbers and the densification of the particles increases with higher concentration.

V. CONCLUSION

Tin Oxide (SnO_2) thin films have been successfully deposited using the spin coating technique with deposition duration as little as 2 minutes. Films were prepared by varying the concentration of the precursor solution. Absorbance spectra showed that the films have low absorbance while the transmission spectra analysis showed that the films are highly transparent. It was observed that the prepared films have wide direct energy gap, the estimated value of the energy gap is in agreement with the reported values. The high values of absorbance in UV region and low in VIS-NIR region allows the thin film to screen off UV radiation and admits visible radiation which could be utilized for prevention of house warming in buildings. The low reflectance at low concentration makes the thin film a good material for anti reflective coatings and the wide band gap makes these films good material for optoelectronic applications.

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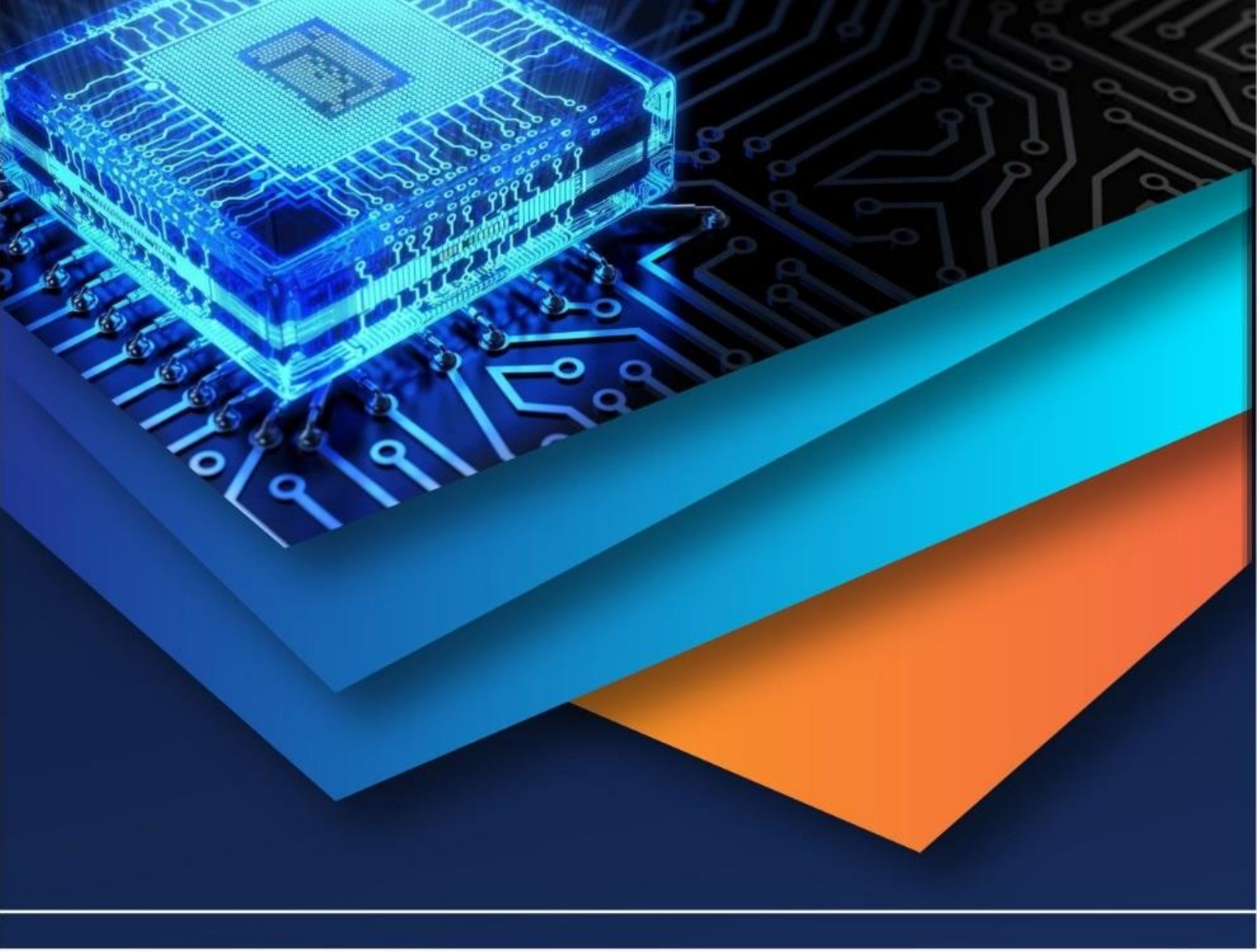

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