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CHARACTERIZATIONS OF TiO_2 THIN FILMS PREPARED FROM METAL-ORGANIC LIQUID PRECURSOR AT DIFFERENT DEPOSITION TEMPERATURE

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Abstract: Thin films of TiO_2 were prepared on glass substrates at varied deposition temperature using metal-organic liquid precursor by simple chemical vapor deposition technique. The deposition process was carried out at 350, 380, 420 and 480°C for samples TiOT1, TiOT2, TiOT3 and TiOT4, respectively. Characterizations of the films were carried out using UV-Vis-NIR spectrophotometry, field emission scanning electron microscopy (FE-SEM), energy dispersive x-ray spectroscopy and Sign at one four-point probe coupled with Keithley source meter 2400. The uv-visible optical studies revealed that the films transmitted between 65 and 85% mainly in the visible region. Hence, depending on deposition temperatures, energy band gap values between 1.53 and 3.26 eV were obtained. Refractive indices were also estimated between 2.55 and 3.50. Estimating from the sectional FE-SEM analysis, slight differences in the film thickness was observed. Film thickness in the range of 131.11–132.01 nm was determined. Sheet resistivity of the films ranged between 596.32 to 7694.79 Ωm.

Keywords: Titanium dioxide, thin films, MOCVD, coatings, micrograph, optical properties

Introduction

Titanium oxide (TiO_2) thin film is found to be stable, strongly adherent to the substrate, mechanically hard and resistant to moisture and acids (Matsui *et al.*, 2000). It is one of the transparent conductive oxides (TCOs). Mainly, due to the present quest for fabrication of cheap devices for application in the area of optoelectronics, simple and inexpensive techniques are required for the deposition of thin film of titanium oxide. Studies have shown that the optical properties of thin film depend largely on deposition method (Savaloni *et al.*, 2003; Ajenifuja *et al.*, 2012; Ajenifuja *et al.*, 2016). Thus, the ease of production of TiO_2 single layer makes it suitable for several applications such as low-loss, low-scatter optical coating for visible and near infrared optics (Vorotilov *et al.*, 1992), electrical devices (Babelon*et al.*, 1998), gas sensors (Castaneda *et al.*, 2002), high stability against mechanical abrasion, chemical attack, and high temperatures. These applications have encouraged a considerable amount of activity in the fabrication of dielectric films with high refractive indices, transparency and low absorption in the visible light (Banakh *et al.*, 2002). Besides the deposition technique, growth parameters such as deposition condition, substrate temperature (Ida and Toraya, 2002), gas flow rate (Enzo *et al.*, 1989), film thickness (Savaloni *et al.*, 2004; Adeoye *et al.*, 2015) and dopant properties also have significant effects on morphology and surface distribution of thin films. Effect of deposition temperature on the optical behaviour of TiO_2 has been widely studied and enhanced film transmittance and high photo-response has been observed in the visible region of the electromagnetic spectrum.

In this study, titanium peroxide (titanium peroxo-complex) was used as titanium oxide source while simple, efficient and affordable MOCVD method was used for the deposition of thin films on soda lime substrates. Microstructure, optical and some electrical properties of the TiO_2 films are hereby presented based on the varied deposition temperature.

Materials and Methods

Precursor synthesis

The experiment was carried out inside the glove box following Schlenk procedure. Liquid precursors were prepared from purchased analytical grade reagents in a two-step process. In the first process, titanium isopropoxide, ethanol and citric acid were reacted together in the ratio 1:12:1 by volume to yield Ti-peroxo complex $[Ti(O_2)(OH)_3]^+$. The chemical complex was then reacted with citric acid and ammonia solution to form Ti $(H_8C_6O_7)$ $(O_2)_3^+$[10] which is the precursor for the work. The reaction was catalyzed by a few drops of carboxylic acid.

Preparation of TiO thin films

Prior to the deposition, soda-lime glass substrates were cleaned in an ultrasonic bath comprising distilled water, ethanol and acetone. The substrates were then dried in an oven at 120°C for about 30 min. Hence, to enhance the adequate surface adhesion to the films, substrates were etched with a solution containing 10 mL HF and 15 mL HNO_3, while the etchants were cleaned of with distilled water. Liquid precursor was pre-heated at 85°C for few minutes before attaining the final deposition temperatures. The TiO_2 films were deposited on glass substrates from the liquid precursor using metal organic chemical vapor deposition (MOCVD) technique (Ajayi, 1970). The deposition temperature ranged between 300 and 480°C, while the flow rate of the carrier gas was 2.0 dm^3/min. Each film growth process took 2 h only.

Characterization techniques

Carl Zeiss EVO-MA 10 model field emission scanning electron microscope (FESEM) coupled with energy dispersive x-ray (EDX) detector was used to examine the microstructure of the deposited films. Elemental composition was obtained with full scale EDX scan at beam kinetic energy of 20 KeV. Optical properties were studied with a dual beam spectrophotometer (Jenway model 6405) in the spectral region of 200 nm to 1100 nm. FESEM was used to estimate the thickness of the films in sectional geometrical position. Slight differences in the thickness were shown. Electrical resistivity and conductivity of the prepared films were investigated by using sign at one four-point probe coupled with Keithley source meter 2400.

Results and Discussion

Elemental characterization

The EDX spectra showing the elemental composition of the precursor is shown in Fig. 1 and that of the deposited film representative in Fig. 2. The prominent peak of titanium is shown in the figure, likewise that of chlorine, carbon and oxygen. Whereas the detected aluminium and chlorine can be traced to the sample holder and the starting reagents, respectively. From the quantitative analysis of the EDX results, the atomic percentages for Ti and O are found to be 34% and 64%, respectively. Silicon peak was detected in the film spectra which is due to the sodalime glass substrate. Other elements form the substrate are also visible.

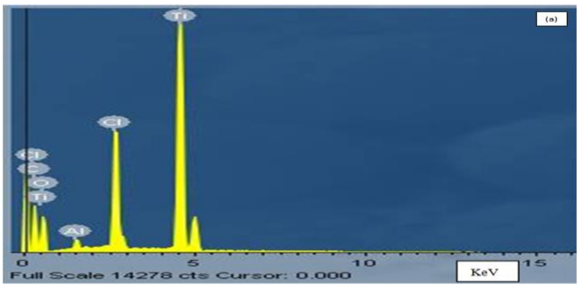

Fig. 1: EDX spectrum showing the elemental composition of Ti-O complex precursor

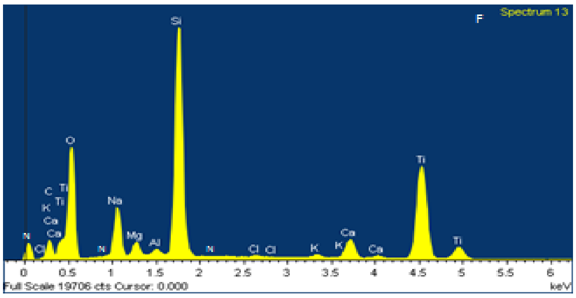

Fig. 2: Representative EDX spectra of the deposited films

Microstructural studies

Based on the deposition temperature, films were prepared from the synthesized liquid precursor between 300 and 480ºC. At 350ºC, the film appears more uniform and with highest relative thickness as observed from SEM analysis. However, at higher deposition temperature (> 350 ºC), a slight decrease in thickness is observed due to the fact that the rate of decomposition and vaporization of the metal organic precursor before or on the substrate is higher.

The surface morphology of TiO_2 thin film obtained from SEM in (Fig. 3) shows 'blocs' image. The images revealed smooth, dense, uniform surface and adhere to the substrate of the films. Also, there are no major differences in surface distribution of the images despite variation in growth temperature, this implies that deposited TiO_2 films do not undergo phase separation. The presence of scantily distributed little voids in films indicates a well-developed structure with medium-sized grain. An estimated grain size varies between 20 and 100 nm was obtained with image-J software. The columnar structure transformed from a discontinuous and thicker feature into a continuous and thinner one as revealed from micrograph (Vanessa *et al.*, 2014) and is as a result of an increase in the temperature which promotes crystal growth that is attributed to the dissolution-recrystallization effect resulting in a reduction of carbonaceous matter within the coating. At higher temperature, sinuous and continuous channels were observed from deposited films therefore, it implies that temperature range used along with other growth criteria can produce relatively good and uniform films. The size increased with increasing deposition temperature as observed from the micrographs and each grain is a cluster of several smaller grains. This may also be due to the formation of stresses by differences in ion size between Ti and O (Jin-Cherng *et al*., 2006). EDX analysis gave the percentage composition of Ti and O with respect to temperature as in Table 1.

From the spectra obtained as in (Fig. 2), the peaks of Ti and O can be clearly seen as a major composition of deposited films. Other elements such as Si, Ca, K, Al, Mg, Na and V can be attributed to soda-lime glass substrate analyzed before deposition. Quantitative data extracted from EDX spectra showed that atomic percentage of oxygen increases with increase in temperature, which closely in agreement with the stoichiometric composition of titanium oxynitride thin film reported earlier (Ogunmola, *et al.*, 2015).

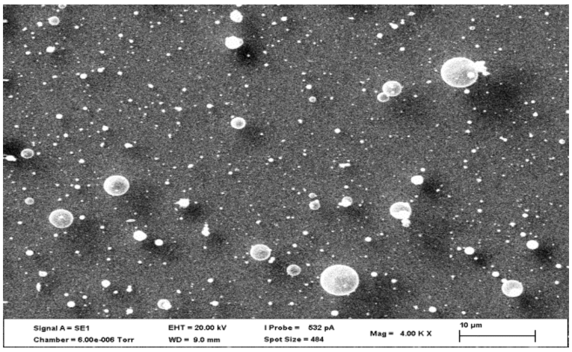

Fig. 3a: FESEM micrograph of sample TiOT1 deposited at 350°C

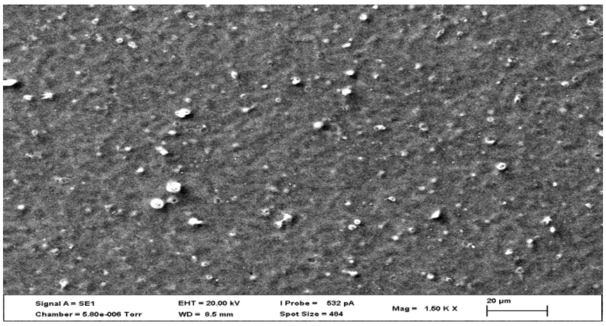

Fig. 3b: FESEM micrograph of sample TiOT2 deposited at 380°C

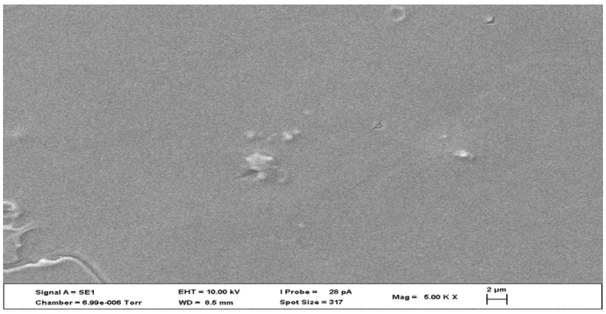

Fig. 3c: FESEM micrograph of sample TiOT3 deposited at 420°C

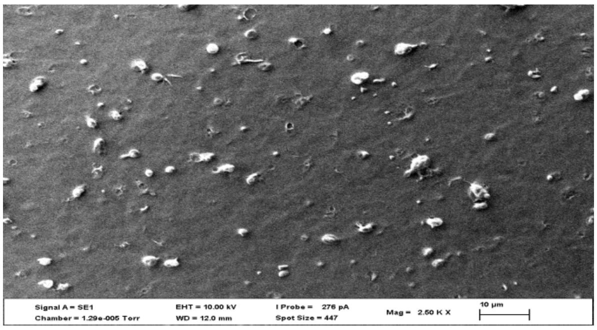

Fig. 3d: FESEM micrograph of sample TiOT4 deposited at 480°C

Table 1: Atomic composition (%) of Ti and O, average electrical resistivity, average electrical conductivity, sheet resistance and thickness of Ti-O thin films

S/N	TiO thin Films samples °C	Elements Atomic (%)		Thickness of TiO Thin films d(nm)	Average Electrical Resistivity ρ (Ωm)	Average Electrical Conductivity σ(1/Ωm) x10^{-3}	Average Sheet Resistance Rs (Ω)
		O K	Ti K				
1	350	30.11 ± 2.75	4.80 ± 0.15	132.01	596.32	1.68x10^{-3}	131.58
2	380	50.21 ± 0.96	4.10 ± 0.11	131.12	643.43	1.68x10^{-3}	141.98
3	420	52.38 ± 2.52	2.82 ± 0.09	132.00	7694.79	5.65x10^{-5}	3904.41
4	480	54.59 ± 1.01	7.99 ± 0.12	131.11	4605.69	2.17x10^{-4}	1016.26

Optical properties

Optical transmittance of TiO_2 thin films on soda-lime glass substrate were recorded in the UV-Visible near IR region (λ= 200 – 1190 nm) with unpolarized light at room temperature using blank soda-lime glass as a reference sample. Within the visible region and above, film's transmittance is high and consistent, therefore no significant interference fringe was observed. The spectra are quite similar to each other except for the displacement of the absorption edge towards the visible region. An increase in absorption intensity was observed as shown in (Fig. 4a) in the range of 370 nm and near-IR region. Also one can remark that the elemental ratio has a substantial effect on the film properties by comparing the transmittances in the visible region (Fig. 4a) with elements atomic (%) in Table 1. The study further shows that the transmittance of the films decreases with increase in deposition temperature relative to film thickness. The energy band gap was evaluated from optical absorption data using equation (1) below (Pal *et al.*,1989). The plots indicate the films have indirect allowed transition.

$$\frac{\propto hc}{\lambda} = Ai(\frac{hc}{\lambda} - E_g)^2 \quad \dots\dots\dots\dots\dots\dots\dots 1$$

Where, A_i is a photon energy independent parameter, α is the absorption coefficient, (hc/λ) is the incident photon energy and E_g is the band gap energy. Using the plot of $(\alpha hc/\lambda)^{1/2}$ vs (hc/λ), the corresponding energy band gap was estimated by extrapolating the linear part to the energy axis (Fig. 4b). The values achieved range between 1.53 - 3.26 eV which can be attributed to various deposition temperatures and crystalline. An energy band gap of 3.24 and 3.20 eV was achieved for films deposited at 350 and 380ºC, respectively, and this correspond to anatase phase of TiO_2 previously mentioned (Tang *et al.*, 1993). It was of the view that other values might be due to the presence of impurities or possible interference with photon absorption. Also, this result is indicative of a control of the deposition mechanism by the absorption edge charge transfer at low energy band while high energy band corresponds to interband transition (Kiran *et al.*, 2008). It must also mention that increase in free electrons with respect to a deposition temperature could be ascribed to decrease in peak transmittance and the increase in the reflectivity of the films (Niyomsoan *et al.*, 2002). Durusoy and his group (Durusoy *et al.*, 2003) have reported that an increase in titanium oxide thin film's transparency within infrared region is due to increasing non-stoichiometry.

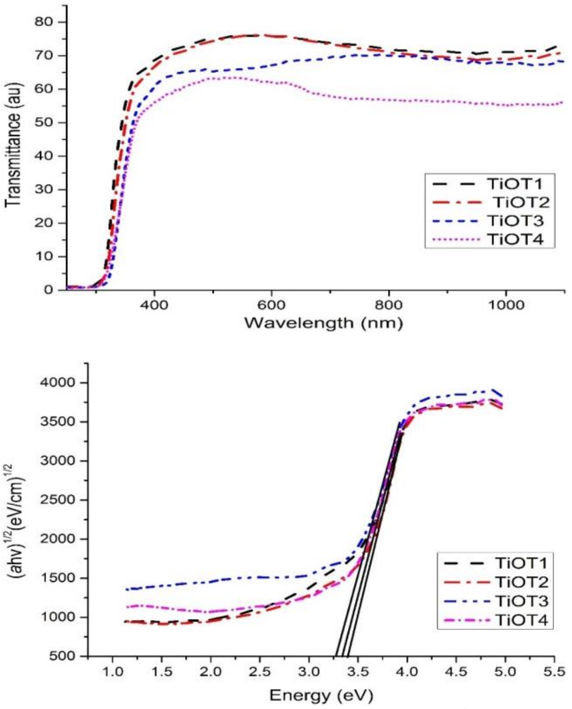

Fig. 4: (a) Ultraviolet-visible transmission spectra for a TiO_2 thin films; (b)Energy band gap determination of TiO_2 thin film

Electrical properties

The resistivity is given by Eq. (2) when the spacing (s) is far greater than the thickness (d) of the film (Deite, 2006).

$$\rho = 4.532 \left(\frac{V}{I}\right) x \; d \dots\dots\dots\dots\dots\dots\dots 2$$

The electrical conductivity and sheet resistance of the films can be calculated by equation (3) and (4), respectively (Maissel and Glang, 1970);

$$\sigma = \left(\frac{1}{\rho}\right) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 3$$

$$Rs = \left(\frac{\rho}{d}\right) \dots\dots\dots\dots\dots\dots\dots\dots\dots 4$$

Table 1 shows sheet resistance, electrical conductivity and average electrical resistivity with respect to different thicknesses. The results show that increase in thickness of the films lead to decrease in resistivity as well as conductivity. Similarly, average sheet resistance decreases with increase in film thickness. This indicates that the thickness of as-deposited TiO_2 film decreases, the electron collisions with surfaces become important, such confinement effect are due to film thickness and is clearly observed in thin films whose electrical resistivity values are higher than bulk.

Conclusion

Titanium oxide thin films have been successfully deposited on a glass substrate between 300 and 480^0C by MOCVD technique via solution precursor. The mole ratio of oxygen to titanium was 1.98: 1. High deposition rate was observed during pyrolysis, this indicated a considerable amount of activation and/ or decomposition of precursor which resulted in high film thickness.

There is significant variation in the energy band gap of TiO$_2$ films with variation in deposition temperature and it lies in the range of 1.53 - 3.26 eV. All optical properties and surface structure showed thickness dependence. There were good agreement between elemental composition and optical properties. Reflectance properties and optical band gap of the films are proportional to the oxygen content in TiO$_2$ composition and were estimated to be between 1.53 and 3.87 eV varied with deposition temperature. The energy band gaps achieved and the possibility of preparing thin films of these materials suggest that it may be possible to apply them for preparing electronic devices.

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References

Adeoye AE, Ajenifuja E, Taleatu BA, & Fasasi YA 2015. Rutherford Backscattering Spectrometry Analysis and Structural Properties of Znxb1$-x$ Thin Films Deposited by Chemical Spray Pyrolysis. *Journal of Materials, 2015*, 8.

Ajayi OB1970. Electrical and Optical Properties of Pyrolytically Deposited Indium Oxide. (M.Sc.Thesis).

Ajenifuja E, Fasasi AY & Osinkolu GA 2012. Sputtering-Pressure Dependent Optical and Microstructural Properties Variations in DC Reactive Magnetron Sputtered Titanium Nitride Thin Films. *Transactions of the Indian Ceramic Society,* 71(4): 181-188.

Ajenifuja E, Osinkolu GA, Fasasi AY, Pelemo DA & Obiajunwa EI 2016. Rutherford backscattering spectroscopy and structural analysis of DC reactive magnetron sputtered titanium nitride thin films on glass substrates. *J Mater Sci: Mater Electron,* 27: 335.

Babelon P, Dequiedt AS, Mostesa-Sba H, Bourgeois S, Sibillot P & Sacilotti M 1998. *Thin Solid Films,* 322: 63.

Banakh O, Schmid PE, Sanjines R & Levy F 2002. Electrical and optical properties of TiOx thin films deposited by reactive magnetron sputtering. *Surf. Coat. Techn.,* 151-152, 272-275.

Castaneda L, Alonso JC, Ortiz A, Andrade E, Saniger JM & Banuelos JG 2002. Spray pyrolysis deposition and characterization of titanium dioxide thin films. *Material Chemical Physiccs,* 77: 938.

Deite SK 2006. *Semiconductor Material and Device Characterization.* (3. Edition, Ed.)

Durusoy HZ, Duyar O, Aydinli A & Ay A 2003. Influence of substrate temperature and bias voltage on the optical transmittance of TIN Films. *Vacuum,* 70: 21-28.

Enzo S, Fagherazzi G, Benedetti A & Polizzi S 1989. A profile-fitting procedure for analysis of broadened X-ray diffraction peaks. I. Methodology. *J. Appl. Cryst.,* 22: 184.

Ida T& Toraya H 2002. Deconvolution of the instrumental functions in powder X-ray diffractometry. *J. Appl. Cryst., 35*, 58.

Jin-Cherng H, Paul WW & Cheng-Chung L 2006. X-ray photoelectron spectroscopy study of thin TiO2 films cosputtered with Al. *Applied Optics,* 45(18): 4303-4309.

Kiran MS, Ghanashyam KD & Padmanabhan KA2008. *Appl. Surf Sci.,* 255: 1934-1941.

Maissel LI & Glang R 1970. *Hand book of thin film Technology.* New York, USA: MC Graw Hill co.

Matsui V, Yamamoto Y & Takeda S 2000. Stability in electrical properties of ultra thin tin oxide films. *Mat. Res. Symp. Proc.,* 621: 4.9.1-4.9.6.

Niyomsoan S, Grant W, Olson DL & Mishra B 2002. Variation of color in titanium and zirconium nitride decorative thin films. *Thin Solid Films, 415*, 187-194.

Ogunmola ED, Famojuro AT, Olofinjana B, Akinwunmi O, Ojo IA & Ajayi EOB 2015. Synthesis and Properties of Titanium Nitride Thin Films Prepared by Metal Organic Chemical Vapour Deposition Technique. *Int. J. Materials Chem. & Phy.,* 1(3), 308-322.

Pal U, Saha S, Chaudhury AK, Rao VV & Banerjee HD 1989. Some optical properties of evaporated zinc telluride films. *J. Phys.,* D(22): 965.

Savaloni H, Khojier K & Alaee MS2003. characteristics of nanostructure and electrical properties of Ti thin films as a function of substrate temperature and film thickness. *J. Mater. Sci., 42*, 2603.

Savaloni H, Taherizadeh A & Zendehnam A 2004. Residual stress and structural characteristics in Ti and Cu sputtered films on glass substrates at different substrate temperatures and film thickness. *Physica B,* 349: 44.

Tang H, Berger H, Schmid PE, Levy F, Gritsyna VT & Shirley DA 1993. Photoluminescence in TiO 2 anatase single crystals. *Solid state Commun.,* 87: 847.

Vanessa GV, Yudith OL, Jesús SG, Alejandro LO& Virginia HC-M 2014. TiO2 Films Synthesis over Polypropylene by Sol-Gel Assisted with Hydrothermal Treatment for the Photocatalytic Propane Degradation. *Scientific Res., Green & Sustainable Chem.,* 4: 120-132.

Vorotilov KA, Orlova EV & Petrovsky VI 1992. Sol-gel TiO2 films on silicon substrates. *Thin Solid Films,* 207: 180.