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Advances in Applied Science Research, 2012, 3 (1):599-604

ISSN: 0976-8610
CODEN (USA): AASRFC

Temperature effect on the thickness and optical properties of Core-Shell TiO_2/ZnO crystalline thin films

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ABSTRACT

Novel TiO_2/ZnO core-shell thin film has been deposited onto a glass substrate by the chemical bath deposition technique. The films were annealed in the temperature range of 373k and 673K in order to investigate the effect of annealing on the optical properties and thickness of the film. The films were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM),Rutherford backscattering (RBS) and spectrophotometer. Our results showed that there is more crystallization and more orientation of the crystal growth with increase in temperature. The results also revealed that most of the optical properties were significantly affected by the annealing process. The calculated thickness shows that the films are nanocrystalline in nature. The optical band gap decreased with increase in temperature and are in the range of 2.17eV- 2.68eV.

Keywords: Chemical bath Deposition, Thin films, Thermal annealing, optical properties.

INTRODUCTION

Transparent conducting oxides (TCOs) have long been an interesting area of research. This is largely due to its unique properties and diverse applications. Some of these TCOs include titanium oxide, tin oxides, cadmium oxides, ferrous oxide, cuprous oxides etc. Titanium oxide (TiO_2) has been one of the most studied oxides because of its role in various applications, namely photo induced water splitting, dye synthesized solar cells,solar cells environmental purifications, gas sensors, display devices batteries etc[1] Znic oxide (ZnO) belongs to member of the hexagonal wurtize class, it is semiconducting, piezoelectric and optical waveguide material with a variety of applications. Znic oxide has been extensively studied as a promising material for blue and ultraviolet light emitting devices because of its wide band gap and large binding energy [2]. The development of new materials, blends, composites and advanced materials is a necessity for modification of mechanical, electrical, optical and thermal properties of thin films to fulfil the demand for improved materials in industries. The development runs parallel with the intense series of studies aiming at describing the structure-property relationship of the modified materials. Many studies have been reported on electrical and thermal properties of some core shell thin films [3]

The study of semi conducting thin film are being pursued with increasing interest on the account of their proven and potential applications in many semiconductor devices such as solar energy converters, optoelectronics devices etc.[4] In the last decades, there has been a great deal of interest in the production of inexpensive thin films, due to its high varying characteristics. Such characteristics include high resistivity, heat reflecting windows, catalytic properties, photo thermal and photovoltaic[3]. Practical applications of thin oxide films are in house hold, electronics, recording heads, memory and microwave devices. Most oxide thin films can also be applied in highly reproducible gas and humidity sensor materials [5,10] Oxides thin film materials have been one of the most attractive research topics in physics and material science. Materials like Fe_3O_4, CrO_2, manganese pervoskites, double and layered pervoskites, $BiFeO_3$ and more recently transition metal doped semiconductors thin films such as TiO_2, ZnO, MnO to mention but a few have been reported and have received new and exciting attentions [1,5]

Thin films of TiO_2 and ZnO oxide film are some of the metal oxide semiconductors which have been found to be very useful as a UV detector [5,15]. As important group II-IV semiconductor thin films with versatile characters, these films possess wide applications in various field: such as gas sensors, transducers, catalysis, secondary batteries and super capacitors [6]. In recent years, the development of core/shell structured materials on a nanometer scale has been receiving extensive attention [7,8]. The shell can alter the charge, functionality, and reactivity of surface, or improve the stability and dispersive ability. Furthermore, catalytic, optical, or magnetic functions can be imparted to the core particles by the shell material. In general, the synthesis of core/shell structured material has the goal of obtaining a new composite material having synergetic or complementary behaviours between the core and shell materials. Many studies on the synthesis of composites, i.e. TiO_2 [9], $CaCO_3$ [10], Fe_2O_3 [11,13] and Ag coated with SiO_2 shells have been reported. Optical characterization of thin films gives information about other physical properties like band gap energy and band structure, optically active defects etc. It is therefore of permanent interest for different applications. The widely used envelope methods have been adopted for measurement of transmittance and this can be used to evaluate the refractive index, extinction coefficient and absorption coefficient. Generally, the optical band gap E_g and the absorption coefficient α could be calculated from the transmittance or absorbance spectra [14]. Many properties of thin films have been shown to depend on the thickness of the film. For instance, the reflectance, the transmittance, the resistivity to mention but a few depends to a large extent on the film thickness.

In this paper, the effect of annealing on the optical properties and thickness of novel core-Shell TiO_2/ZnO crystalline thin films are reported.

MATERIALS AND METHODS

The chemical bath used for the preparation of the thin films in PVA matrix in this work was prepared in the following order. First the PVA solution was prepared by adding 900ml of distilled water to 1.8g of solid PVA and stirred at 363K for 60mins. The solution was aged until the temperature dropped to room temperature. To obtain the deposition of TiO_2, the chemical bath was composed of 12 mls of 1M $ZnCl_2$, 12mls of 1M $NH4Cl_4$, 12mls of 10M NH_3 and 13 mls of PVA solution put in that order in 100ml cleaned and dried beaker. Four (4) clean glass slides were then inserted vertically into the solution. The deposition was allowed to proceed at a temperature of 338K for 3hrs in an oven after which the coated substrate were removed, washed with distilled water and allowed to dry. To obtain the TiO_2/ZnO core-shell, the TiO_2 already formed (core) was inserted in a mixture containing 12mls of 1M $ZnCl_2$, 12mls of IM NH_4Cl, 12mls of 10M NH_4OH and 40mls of PVA in 100ml beaker. Deposition was allowed to proceed at same temperature and duration. Two of the deposited films were annealed in an oven at 473K and 673K respectively for 1hr. One of the samples was left unannaeled to serve as the control. Structural analysis of the films was carried out using X-ray diffraction (XRD) method within the range of 15- 75^0 on a computer controlled Phillips pin 1500 X-ray diffractometer of CU-Kα wavelength (1.5408Å). The composition of the films was determined using Rutherford back scattering (RBS) ,while the optical properties of the CBD deposited films were measured at room temperature from Unico-UV-2102PC Spectrophotometer at normal incident of light in the wavelength range of 200-1200nm. From the absorption spectra, optical band gaps of the samples were determined.

RESULTS AND DISCUSSION

The chemical status and the elemental composition of the film analysed by using RBS method is presented in fig.1.The analysis showed that the samples is made up of 6.0% of titanium (Ti), 6.1% of znic (Zn) and 88.0% of oxygen. This implies that the crystalline film is almost pure.

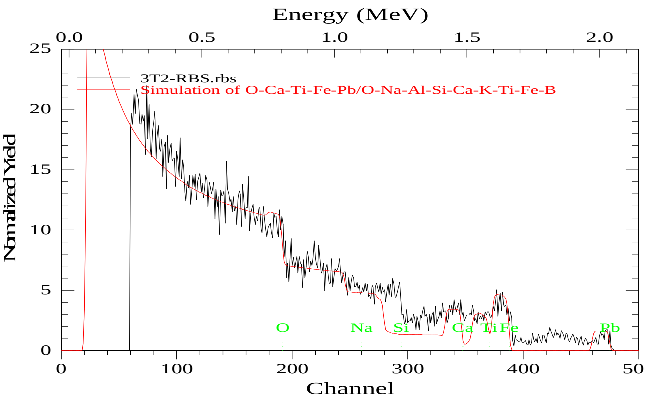


Fig.1 RBS of TiO_2/ ZnO thin film

(hkl)	2θ	d(Å)
1 0 1	20.87	4.516
1 1 3	21.46	4.080
1 0 4	32.11	2.854
3 2 1	43.89	2.273
3 2 4	47.20	2.213
0 1 11	49.04	1.468
3 3 0	52.65	1.440
5 1 4	59.68	1.430
1 1 9	69.54	1.420

The crystalline structure and orientation of the TiO_2/ZnO thin films deposited were investigated by X-ray diffraction (XRD) pattern. The X-ray diffraction spectrum is shown in fig.2a, b and c for as-deposited, thermally annealed at 373K and 673K respectively. The figures indicate that the film is polycrystalline in nature. A close look at the two diffractograms show several peaks. Prominent among them are peaks at 2θ values of around 20.87^0, 32.11^0, 69.54^0 corresponding to diffraction lines produced by (101), (104) and (119) plane (JCPDS 35-0D88) respectively. A close look at figures 2a to c shows an improvement in the crystallinity of the films. A comparison among the spectra of figures 2a,b and c show that there is more crystallization and more orientation of the crystal growth in the case of film annealed at 673K. The peaks at 2θ values of 25.68^0 and 59.99^0 are attributed to orthorhombic TiO_2 (JCPD -29-1360) with lattice parameter a=b=c=4.120 Å. These were assigned to the diffraction line produced by (111) and (123) planes. However the additional peaks at an angle of 34.89 and 48.01 are identified to be ZnO (JCPD –29-0902) and are assigned diffraction line produced by (110) and (024) planes of the $ZnTiO_3$ (pyrophanite) phase. These results suggest that the thin films deposited in this are a mixture of oxides of zinc and titanium. The existence of this high pressure magnetic phase implies that the film can be used as magnetic resonance element. The crystalline grain size was calculated using the Scherer formula: $D=0.89\lambda/\beta\cos\theta$ (1)

Where D is the average crystalline 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 crystallite size for the annealed film at 373K and 673K are 18.31nm and18.03nm respectively while the calculated crystallite size for as-deposited film is 14.12nm. The 2θ and d values are given in table 1.

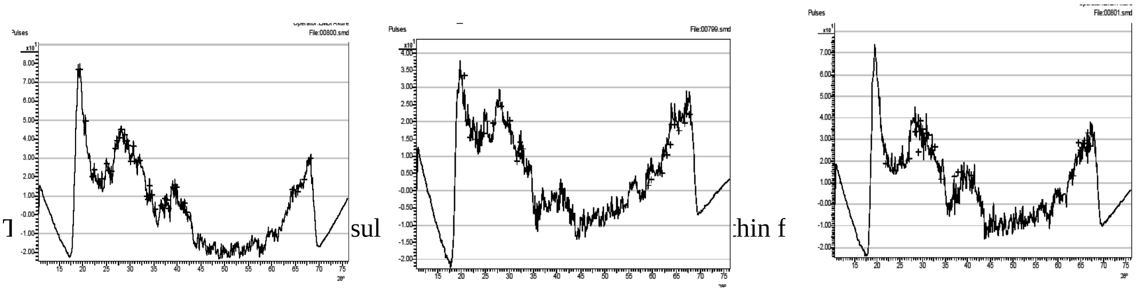


Fig.2: XRD for TiO_2/ZnO at (a) as-deposited (b) annealed at 373K (c) annealed at 673K

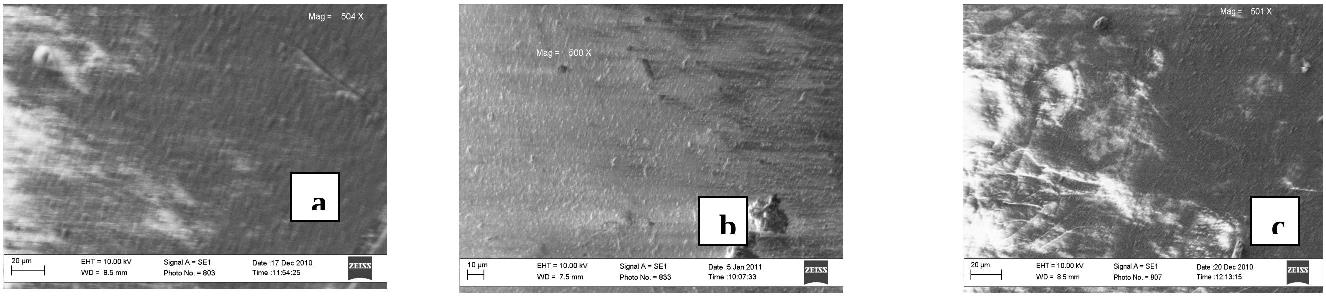


Fig.3 SEM micrograph for TiO_2/ZnO core shell thin film (a) as-deposited, (b) annealed at 373K and (c) annealed at 673K

The SEM of the as-deposited, thermally annealed at 373K and 673K are displayed in figures 3a, b and c respectively. The SEM show an increase in grain size as annealing temperature increases due to effects of evaporation of absorbed water and reorganization of the grain. Uniform distribution of the grain is also observable with the gradual fading in colour from grey to yellowish brown.

Figs. 4 and 5 are plots of transmittance against wavelength and absorbance against wavelength respectively for TiO_2/ZnO core shell oxide films deposited in this work. From fig.7, we deduce that the transmittance increases with wavelength for all the samples. This is due to the increase in crystalline size associated with higher densifications of the film. The figure also shows high transmittance of the film in the NIR region of the solar spectrum. The plots also show that in the UV region, samples exhibit low transmittance. Thin film of TiO_2/ ZnO of displays high absorbance values in the IR region and virtually non-absorbing in the UV-VIS at all temperatures.

The spectral absorbance and transmittance displayed in figures 4 and 5 shows that TiO_2/ ZnO thin films could be used as spectrally selective window coatings in cold climate to facilitate transmission of VIS and NIR while suppressing the UV portion of the solar radiation. The thin film can be used for coating eyeglasses for protection from sunburn caused by UV radiations.

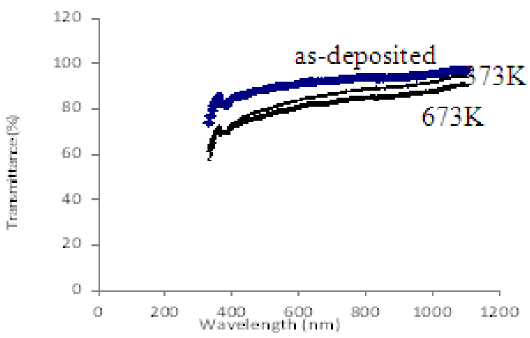


Fig.4: Transmittance against wavelength for TiO_2/ ZnO thin films

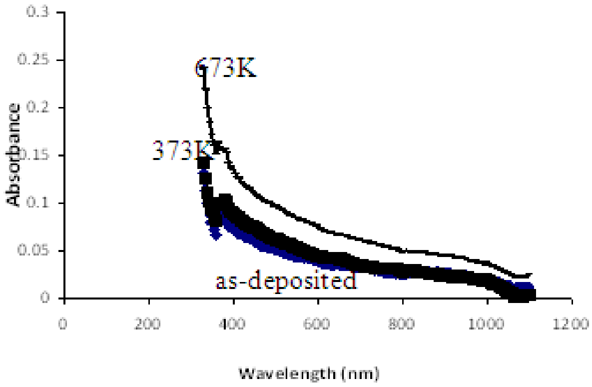


Fig. 5: Absorbance against wavelength for TiO_2/ ZnO thin films

The extinction coefficient k can be obtained from the experimental expression [14]:

$$K = \frac{\alpha\lambda}{4\pi d} \qquad (2)$$

And $$\alpha = -\frac{1}{t} In \frac{(n-1)(n-n_s)[\ [T\max/T\min]+1]^{0.5}}{(n-1)(n+n_s)[\ [T\max/T\min]-1]^{0.5}} \qquad (3)$$

where α is the absorption coefficient and t is the thickness of the film. The optical constants such as refractive index n and extinction coefficient k were determined from the transmittance and absorbance spectra. The variation of n and k is as displayed in figures 6 and 7 respectively.

The film thickness was calculated using the relation [14]

$$t = \frac{\lambda_1\lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \qquad (4)$$

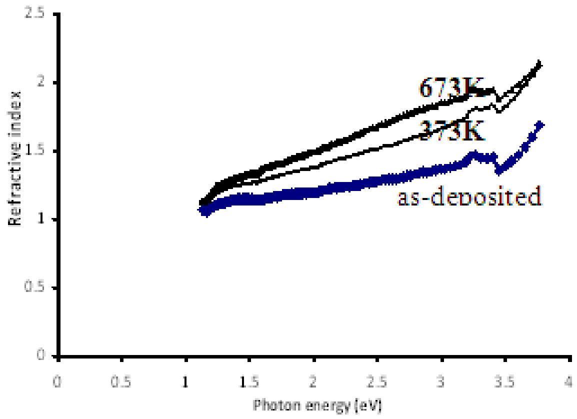
where n_1 and n_2 are the refractive indices corresponding to wavelength λ_1 and λ_2 respectively. The thicknesses of the films are 75.48nm, 85.16nm and 97.51nm for as-deposited, thermally annealed at 373K and 673K respectively. This shows that high temperature annealing has significant effect on the thickness of the deposited film. The result shows that as the annealing temperature increases, the thickness increases. The result also indicates that the deposited thin films are nano in size. The absorption coefficient was determined using the relation:

$$\alpha = 2.303\frac{A}{t} \qquad (5)$$

where A is the absorbance. The optical absorption edge was analyzed using the equation [11,12]

$$\alpha h\nu = B(h\nu - E_g)^{1/2} \qquad (6)$$

where B is a constant.



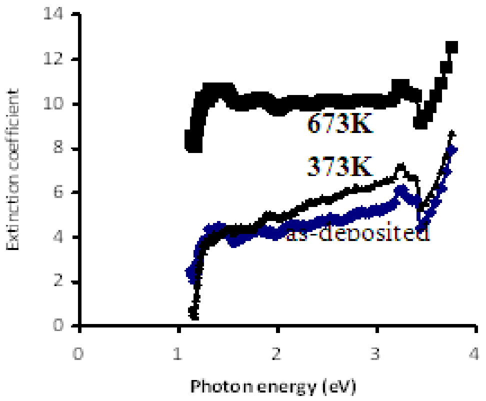


Fig.6: Refractive index vs hυ for TiO_2/ ZnO thin films **Fig. 7: Extinction coefficient Vs hυ TiO_2/ ZnO thin films**

The variation of $(\alpha h\upsilon)^2$ with photon energy in joule is shown in fig.8. The plot shows that the band gaps are 2.62eV, 2.68eV and 2.17eV for the as deposited, thermally annealed at 373K and 673K respectively. The above suggests that annealing the sample in oven lowers the values of the band gap. This may be a consequence of the increase in crystalline size associated with high temperature annealing.[12,14].

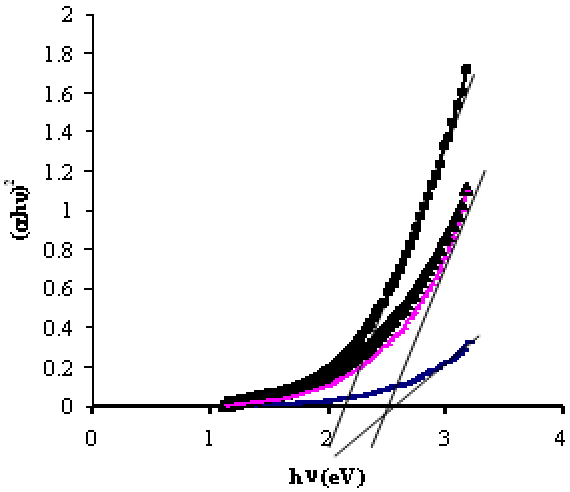


Fig.8: $(\alpha h\upsilon)^2$ vs hυ for TiO_2/ZnO thin films

According to [15], a change in energy band gap depends inversely on the particle radius R. Therefore as R increases due to the increase in the crystalline size associated with temperature annealing the value of ΔE_g will decrease.

CONCLUSION

In conclusion, this communication demonstrates that novel nanocrystalline core/shell oxide thin film of the form T-iO$_2$/ZnO films have been successfully deposited onto a glass slide using the CDB technique. XRD study reveals better crystallization of the films and band gap analysis show that high temperature annealing has pronounced effect on the properties of the deposited film. The formation of TiO$_2$/ZnO composite has considerably modified the optical properties of the independent thin film.

REFERENCES

1. M. Habib, Y.K. Woo, D.J. Kwang, J. Oh-Shim, *J. Applied surfaces Science*. **2005**, 72-76.
2 J. Zhang, Z. Liu, B. Han, Z. Li, G. Yang, J. Li, J. Chen, *J.Supercrit. Fluids* 36, **2006**, 194–201.
3. H. Bala, Y. Zhang, H. Ynag, C. Wang, M. Li, X. Lv, Z. Wang, *Colloids Surf.* A 294 **2007**, 8–13.
4 V. Maurice, T. Georgelin, J.M. Siaugue, V. Cabuil, **J**. Magn. Magn. Mater.321, **2009**, 1408–1413.
5. K.S. Chou, C.C. Chen, *Mesopor. Mater*. 98, **2007,** 208–213.
6 S.C Ezeugwu, , F.I Ezeama, and P.U Asogwa,. *J. Chalcogenide Letters,* 7(5). **2010,** 369-376.
7 A. Cai, L.Muth,. Mat.Res.soc. symp.Proc. **2007**. P.C3.21.1- C3.21.6
8. F.I.Ezeama, S.C.Ezeugwu, R.U.Osuji, B.A Ezekoye, A.B.C.Ekwealor, M.P.Ogbu, J**.** Non-oxide Glasses, **2010,** 45-50.
9. Khetre, S.M. Jadhav, H.V. Jagadale, P.N. Kulal, S.R. and Bamane, S.R. *Adavances in Applied Science Research,* 2011, 503-511
10. Dipalee, J.D. Shaeed, S. Farha, S. Arindam G. Ravikiran B. Anil, G. Ramphal, S. *Adavances in Applied Science Research,* 2011, 417-425
11. J.I. Pankove. Optical processes in Semiconductors. Prentice-Hall .**1971**.
12. M. Popa, V.Lisca, M .Stancu, E.Buda, T.Pentia, ***J.*** *Botila, Optoelectro. Adv. Mater*. **2006**, 46.
13 L.M. Marzan, M. Giersig, P. Mulvaney, Langmuir 12, **1996**, 4329–4335.
14. Ilican, S. Caglar, M.Caglar, Y. Materials Science-Poland, **2007**, 710-714
15. H .B. Lee, Y.M. Yoo, Y.H. Han, *Scripta Mater*. 55, **2006**, 1127–1129.