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POST-DEPOSITION SINTERING ON THE RBS, MORPHOLOGICAL AND ELECTRICAL PROPERTIES OF TiO_2/CoO CORE-SHELL THIN FILMS

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Abstract

The Rutherford backscattering (RBS), spectrophotometer analysis, morphological and electrical properties of TiO_2/CoO core-shell thin films were studied and reported in this paper. This study was within the ultraviolet, visible and near infrared regions of electromagnetic spectrum. The films' structural properties, morphological, electrical and optical properties were analysed using X-ray diffraction, scanning electron microscope (SEM) analysis, four point probe and spectrophotometer. The films' composition and the dependence of surface morphology or microstructure and electrical properties of the films on the annealing temperatures were of particular interest in this paper. RBS results showed that the films have no impurities and there was no quantum size effect. SEM results showed that post-deposition sintering yielded better morphology films with better surface coverage and higher nanocrystalline character, suitable for gas sensing. Electrical resistivity measurement from the four point probe showed there was a decrease in electrical resistivity of the films from 1.532×10^4 Ωm to 1.320×10^4 Ωm when the annealing temperature was increased from 373-673K. This confirmed the semiconducting properties of TiO_2/CoO thin films.

***Keywords*:** Film Composition, Morphology, Resistivity, Sintering

1.0 Introduction

Titanium dioxide [TiO_2] is a white solid inorganic substance that is thermally stable, non-flammable, poorly soluble and not classified as hazardous [1]. TiO_2 is one of the most widely studied oxide thin films due to its wide range of applications such as; photoactivated catalyst for water and air purification, window layers for photovoltaic cells, coatings, electrochromic material and an electron accepting electrode for dye-sensitized solar cells [2-8]. Photo-degradation of hydrocarbons can be done in water or in air using suspended small particles or thin films of TiO_2 [2]. High dielectric constants of titanium dioxide thin films make them suitable materials for capacitors in microelectronics and insulator gate in metal-insulator-semiconductor [MIS] structures [9].

Transition metal oxides such as TiO_2, NiO, ZnO and CoO etc are the most attractive research topics in thin film technology in the recent times. Cobalt oxide [CoO] is a transition metal oxide that is very suitable for charge storage and with a band gap of 2.1eV, CoO has suitable properties for photovoltaic applications [10] and it is a p-type semiconductor. The synthesized and characterized Co_3O_4 thin film has its dc electrical conductivity increased with increase in annealing temperature [11]. CoO, Co_3O_4 and TiO_2 have been synthesized using a variety of methods such as chemical bath deposition technique, laser chemical vapour deposition, sol-gel spin coating technique and R.F. sputtering etc.

In the literature survey, studies of core-shell oxide materials or thin films have been sparse especially TiO_2/CoO films. Therefore, in the present study, investigations of the post-deposition sintering on the Rutherford backscattering spectrometry [RBS], morphological and electrical properties of TiO_2/CoO core-shell thin films were carried out. This study was done within the UV, visible and NIR regions of the electromagnetic spectrum.

2.0 Materials and Methods

2.1 Experimental Details

Chemical bath deposition [CBD] technique was used in this study. Five samples of TiO_2/CoO core-shell thin films were obtained once in a bath. Four samples were sintered or annealed in an oven, model GZX-DH 30 x 31. Sintering time was 1 hour per sample and the range in annealing temperature was 373 – 673K while the deposition temperature was 338K. Other experimental details not included here, have been published elsewhere [3, 10].

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2.2 Thin Film Characterization

The synthesized and deposited TiO_2/CoO core-shell thin films were characterized using various techniques and analysis. Rutherford backscattering spectrometry [RBS] analysis was used to study the chemical compositions of the thin films, Energy dispersive spectrum [EDS] analysis was used to investigate the crystalline quality, scanning electron microscopy [SEM] analysis was used in studying the morphology of the films, X-ray diffraction [XRD] analysis was used for the structural properties of the films, spectrophotometer analysis was used to determine the optical and solid state properties and QUARDPRO-301 auto calculating four point probe was used to determine the electrical resistivity of the films. Nevertheless, only the dependence of post-deposition sintering on the RBS, morphological and electrical properties of the films were investigated and discussed in this paper.

3.0 Results and Discussion

3.1 RBS Analysis

Rutherford backscattering spectrometry [RBS] is an ion scattering technique used for compositional thin film analysis. It is based on collision between atomic nuclei. It involves measuring the number and energy of ions in a beam which backscatter after colliding with atoms in the near – surface region of a target sample [12]. RBS is ideally suited for determination of trace elements heavier than the major constituents of the substrates. The RBS for plane glass substrate and TiO_2/CoO thin films are shown in Figures 1(a) and (b) while the chemical compositions are shown in tables 1(a) and (b) respectively.

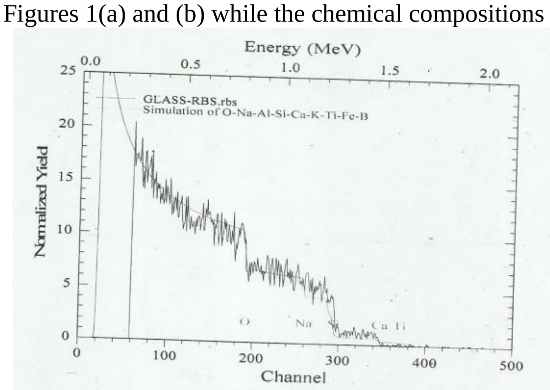

Fig. 1a: RBS for plane glass substrate

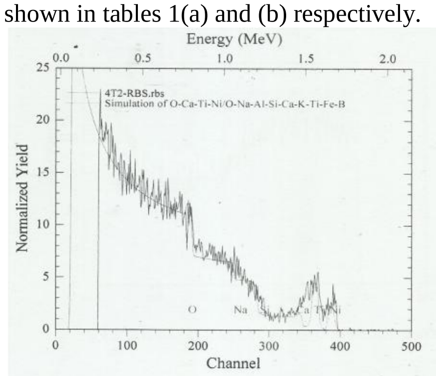

Fig. 1b: RBS for TiO_2/CoO core-shell thin film annealed at 473K

Table 1a: Chemical compositions of plane glass substrate

Element	O	Na	Al	Si	Ca	K	Ti	Fe	B
Glass	0.603	0.158	0.084	0.114	0.005	0.003	0.003	0.003	0.026

Table 1b: Chemical compositions of TiO_2/CoO core-shall thin film

Element	O	Ti	Na	Al	Si	Ca	K	Fe	B	Co
Glass	0.662	0.003	0.125	0.037	0.115	0.022	0.006	0.003	0.025	
Film	0.576	0.242								0.182

Comparing the two tables (1a and b) TiO_2/CoO contained no impurities. Thus available quantum states were not altered. No new energy levels appeared in the films. Hence, there was no quantum size effect [QSE] [2]

3.2 Scanning Electron Microscopy [SEM] Analysis

The surface morphological studies of the thin films were done using scanning electron microscopy [SEM] analysis. The scanning electron microscope uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimen [13]. SEM analysed the microstructure of the thin films. Figures 2(a) and (b) show the SEM results for the film samples annealed at 473K and 673K respectively.

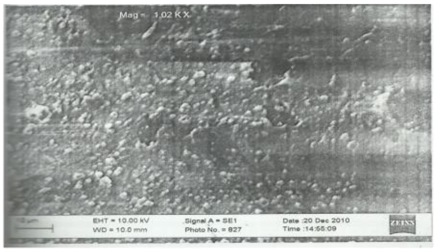

Fig. 2a. SEM for TiO2/CoO thin film annealed at 473K

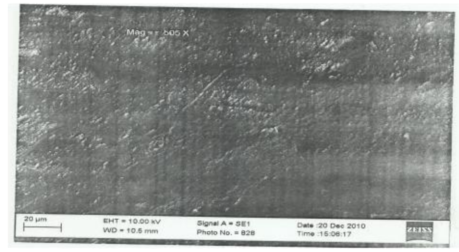

Fig. 2b. SEM for TiO2/CoO thin film annealed at 673K

In Figure 2(a) and (b), the films covered the substrates well in each sample. Some coax parts seen in Figure 2(a) disappeared after annealing/sintering at higher temperature in Figure 2(b). Absence of cracks in these two Figures showed high mechanical stability of the films. Smooth surface appeared in the sample annealed at higher temperature. Grains became well crystallized at higher annealing temperature, 673K. The increase in post-deposition sintering yielded better morphology thin films, better surface coverage and higher nanocrystalline character of the thin films. Absence of cracks and good surface coverage are ideal properties of thin films for gas sensing.

3.3 Electrical Resistivity [ρ]

The study of electrical resistivity [ρ] was done using QUARDPRO 301 – auto calculating four point probe and the purpose was to measure the resistivity [ρ] of the thin films. The resistivity [ρ] of a material and its conductivity [σ] are reciprocal quantities so that at the simplest relationship between these two quantities is given in equation [1].

$$\rho = \frac{1}{\sigma} \qquad (1)$$

Both quantities in equation [1] are microscopic quantities because they have values at every point in a given material or object [14]. The resistivity of an intrinsic or pure semiconductor is given by

$$In\rho = \frac{E_g}{2k_BT} + InA \qquad (2)$$

Where E_g is the energy gap, k_B is the Boltzmann constant, T is absolute temperature and A is a constant. Equation [2] clearly indicates that in a semiconductor, the higher the temperature the lower the resistivity [15]. Also equation [2] suggests an alternative method of determining the energy gap of an intrinsic material including thin films. Table 3 shows the resistivity values for TiO_2/CoO core-shell thin films at various sintering temperatures.

Table 3: Resistivity values for TiO_2/CoO thin films at various post-deposition temperatures

Film sample	Sample label	Deposition temperature [K]	Post-deposition temperature [K]	Resistivity [Ωm)
TiO_2/CoO	3T	338	Nil	1.532 x 10^4
[5 samples]	$3T_1$	338	373	1.511 x 10^4
	$3T_2$	338	473	1.481 x 10^4
	$3T_3$	338	573	1.352 x 10^4
	$3T_4$	338	673	1.320 x 10^4

In table 3, the resistivity of the thin films decreased with the increase in annealing/sintering temperatures. Similar results were obtained by other scholars for other thin films [11, 16, 17]. The inverse variation of resistivity with the annealing temperature indicates the semiconducting property/nature of the films. Carrier concentration and mobility of the thin films increased with increase in annealing temperature, thus resulting in the decrease in resistivity of the thin films. Therefore, the electrical quality of TiO_2/CoO core-shell thin films is enhanced by sintering. The films are good materials for efficient electroluminescence because of their semiconducting properties.

4.0 Conclusion

Studies on the post-deposition sintering on the RBS, morphological and electrical properties of TiO_2/CoO core-shell thin films have been concluded. The study was within the UV, visible and NIR regions of electromagnetic spectrum. The films contained no impurities. The samples have high mechanical stability and there was no quantum size effect in the films. The resistivity of the thin films decreased with the increase in the annealing/sintering temperature. The increase in post-deposition sintering yielded better morphology thin films, better surface coverage and enhanced the electrical quality of thin films. TiO_2/CoO core-shell thin films are good materials for gas sensing and electroluminescence devices.

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REFERENCES

[1] European Chemical Industry Council [2012] About Titanium Dioxide pan@efic.be www.cefic.org

[2] Eufinger, K., Poelman, D., Poelman, H., De Gryse, R. and Marin, G.B. [2008] TiO_2 thin films for photocatalytic applications. *Thin Solid Films, Process and Applications,* ISBN: 978-81-7895-314-4, 189-227.

[3] Onah, D.U. and Uguru, E.H. [2016] Investigation of optical parameters of Nanocrystalline TiO_2/CoO core-shell thin films. *International Journal of Current Research,* 8[11], 41674-41677.

[4] Onah, D.U., Ekpe, J.E., Elebe, M.A. and Nnaji, E. [2013] Optical characterization of chemical bath deposited nanocrystalline TiO_2 thin films. *Journal of the Nigeria Association of Mathematical Physics,* 24, 361-364.

[5] Dakka, A., Lafait, J., Abd-Lefdil, M. and Sella, C. [1999] Optical study of titanium dioxide thin films prepared by R.F. sputtering. *M.J. Condensed Matter,* **2,** 153-156.

[6] Niu, W., Wang, G., Liu, X., Tang, J. and Bi, X. [2015] Preparation and Electrochronic Performance of TiO_2 Thin Film. *International Journal of Electrochemical Science,* **10,** 2613-2620.

[7] Alvarez, A., González-Garcia, L., Romero-Gómez, P., Rico, V., Cotrino, J., González-Elipe, A.R. and Palmero, A. [2011] Theoretical and experimental characterization of TiO_2 thin films deposited at oblique angles. *Journal of Physics D: Applied Physics,* **44,** [38], 22-25.

[8] Igor, Y.D. and Mari, I.F. [2010] Nanocrystals: A review of high nanoparticles concentration composites; semiconductor and high refractive index materials. Sciyo Publishers, Croatia, 139 – 140.

[9] Mardare, D. and Rusu, G.I. [2004] Comparison of the dielectric properties for doped and undoped TiO_2 thin films. *Journal of Optoelectronics and Advanced Materials,* **6,** [1], 333- 336.

[10] Onah, D.U., Okeke, C.E., Osuji, R.U., Ezekoye, B.A., Ekpe, J.E., Ibeh, G.F., Ekwealor A.B.C. and Ezema, F.I. [2013] Study of the effects of thermal annealing on the optical bandgap of nanocrystalline CoO thin films prepared by chemical bath deposition. *Chemistry and Materials Research,* **3,** [1], 43-51.

[11] Patil, V., Joshi, P., Chougule, M. and Sen, S. [2012] Synthesis and characterization of Co_3O_4 thin films. *Soft Nanoscience Letters,* **2,** 1-7.

[12] Evans, Analytical Group [2012] Material characterization. http://www.eagtabs.com/mc.rutherford-backscattering-spectrometry.html

[13] Goldstein, J. [2003] Scanning electron microscope and X-ray microanalysis. Klumer Academic/Plenum Publishers, New York, 689 – 690.

[14] Halliday, D. and Resnick, R. [1978] Physics parts 1 and 2, third edition, John Wiley & Sons. New York. 679 – 680.

[15] Pillai, S.O. [2010] Solid state physics [new revised sixth edition] New Age Techno. Press, New Delhi, 528 – 536.

[16] Patil, V., Pawar, S., Chougule, M., Godse, P., Sakhare, R., Sen S. and Joshi, P. [2011] Effect of Annealing on structural, Morphological, Electrical and Optical Studies of Nickel Oxide Thin Films. *Journal of Surface Engineered Materials and Advanced Technology,* **1,** 35-41.

[17] Rusu, R.S. and Rusu, G.I. [2005] On the electrical and optical characteristics of CdO thin films. *Journal of Optoelectronics and Advanced Materials,* **7,** [3], 1511-1516.