Journal of NAMP 70, (2025) 95-102

The Nigerian Association of Mathematical Physics

Journal homepage: https://nampjournals.org.ng

ON THE ELECTROLUMINESCENCE, OPTICAL AND ELECTRICAL PROPERTIES OF TIO_2/NIO CORE-SHELL THIN FILMS

[1]Daniel U. Onah, [2]John E. Ekpe, [3]Edwin H. Uguru, [4]Rufus O. Ijeh and [5]Stephen Eze

[1]*Department of Industrial Physics, Ebonyi State University, Abakaliki – Nigeria*
[2]*Department of Physics, Alex Ekwueme Federal University, Ndufu Alike-Ikwo (AE-FUNAI)*
[3]*Department of Industrial Physics/Astronomy, David Umahi Federal University of Health Sciences, Uburu.*
[4]*Department of Physics, University of Delta, Agbor Delta State.*
[5]*Department of Physics, FCE (Technical) Ekiadolor Benin City, Nigeria.*

ARTICLE INFO

Article history:
Received 20/5/2025
Revised 13/6/2025
Accepted 24/6/2025
Available online 17/7/2025

Keywords:
Electroluminescence, annealing reflectance, extinction coefficient, resistivity.

ABSTRACT

The electroluminescent properties, some optical and electrical properties of nanocrystalline TiO_2/NiO core-shell thin films were studied and reported in this paper. The study was within the ultraviolet, visible and near infrared regions of electromagnetic spectrum. The films' structural properties, microstructure, optical and electrical properties were analysed using X-ray diffraction, scanning electron microscope [SEM] analysis, spectrophotometric analysis and the four-point probe. In this paper, the dependence of reflectance, extinction coefficients and resistivity of the thin film samples on the annealing temperatures were particularly highlighted. Increasing the annealing temperatures from 373K to 673K resulted in the decrease in resistivity from 1.683 x $10^4\Omega m$ to 1.121 x $10^4\Omega m$. The films have low reflectance values ranging from 10% to 20%, and the increase in the annealing temperatures increased and enhanced the electroluminescent property of the studied core-shell thin films.

1. INTRODUCTION

Titanium dioxide [TiO_2] thin film is a very important functional material and its preparation, performance and application have become hot topics in recent years [1]. Due to the smaller size of primary particles and higher surface area, TiO_2 as a nonamaterial allows the manufacture of various catalysts of enhanced activity [2]. Numerous applications of TiO_2 include photonic devices [3], dye-sensitized solar cell [4], photoactivated catalysts and UV absorbers [2,5] and insulator gate in metal-insulator – semiconductor [MIS] structures [6]. According to the United Nations' [UN] Globally Harmonized System of classification and labelling of chemicals [GHS]. TiO_2 is not harzardous. Also as nanomaterials, TiO_2 is more effective as UV absorbers or photocatalysts and its transparency makes it a suitable material as a protective ingredient for sunscreens [7].

*Corresponding author: DANIEL U. ONAH
E-mail address: daniel.onah@ebsu.edu.ng
https://doi.org/10.60787/jnamp.vol69no2.527

The use of nanocrystalline TiO_2 as an electron accepting electrode for dye-sensitized solar cells has shown an overall power conversion efficiency as high as 10% [8]. Several and simple deposition techniques such as; chemical bath deposition [CBD] technique, site – selective deposition [SSD] method, RF magnetron sputtering, Sol-gel methods and direct current [d.c] magnetron sputtering etc, have been used to deposit metal oxide thin films of TiO_2, NiO, ZnO, CoO and Co_3O_4 etc [1, 5, 9 – 12].

Nickel oxide [NiO] is an attractive material due to its excellent chemical stability as well as optical, electrical, magnetic and catalystic properties [10, 13]. NiO thin films have been shown to be very useful as optically active counter electrodes for window layer applications and the optical quality of NiO thin films is improved by annealing [14]. NiO thin films are very suitable as positive electrodes and can be used in asymmetric devices with cobalt oxide thin films [15, 16]. Study of optical and electrical properties of NiO thin films has shown that NiO has higher absorbance of 77.7% and electrical conductivity of 1.3×10^{-5} $(\Omega cm)^{-1}$ [17].

A relatively new and novel dimension in thin film technology is the development of core-shell thin films for various device applications. Synthesis of Ag@SnO core-shell structure nanoparticle thin films has been carried out using a soft-chemical technique in aqueous phase at 60^oC [18]. ZnO/CdSe core-shell nanorod array films synthesized via a two-step method have been used as solar cell photoanodes [19]. However, reports on metal oxides core-shell thin films have not been made extensively in the literature.

Electroluminescence is a process that converts an electrical input into a light output and it was first discovered by Round around 1907 in a silicon carbide substrate contact [20]. Direct and wide energy gap materials are good candidates for efficient electroluminescence, and ZnO: In thin film with a direct band gap of 3.44eV has been reported to be a good material for electroluminescent devices [20, 21]. Thin film electroluminescent [TFEL] can provide light sources for a variety of purposes in which planar or linear sources of lithographically determined dimensions of high radiance are wanted [22]. The use of glass substrates facilitates high temperature processing that optimized the luminescent properties of the thin films [23]. The electroluminescent properties, dependence of reflectance, extinction coefficients and resistivity of TiO_2/NiO core-shell thin films on the annealing temperatures are particularly emphasized and highlighted in this paper.

The Objectives of this study are; to:

(i) deposit core-shell thin films of TiO_2/NiO on Sail Brand Microscopic slides Cat. No. 7102 of 76.2 x 25.4 x 1.1mm, using chemical bath deposition [CBD] technique.
(ii) investigate the electroluminescent properties and
(iii) highlight the dependence of reflectance, extinction coefficients and resistivity of the thin films on the annealing temperatures.

2.0 MATERIALS AND METHODS

The materials used for the synthesis of the core [TiO_2] include titanium trichloride [$TiCl_3$], sodium hydroxide pellets [NaOH], polyvinyl alcohol [PVA] while the shell [NiO] was synthesized using nickel sulphate [$NiSO_4$], potassium chloride [KCl], water [H_2O] and ammonia [NH_3]. Chemical bath deposition [CBD] technique was used in this experiment because it is highly specific, cost effective and convenient. More experimental details have been reported, showing that TiO_2/NiO thin film samples have direct wide band gaps ranging from 2.3eV to 2.5eV [24].

2.1 Thin Films Characterization

The thin films' structural properties, morphology, optical and electrical properties were analysed using X-ray diffraction, scanning electron microscope [SEM] analysis, spectrophotometric analysis and the four-point probe. The electroluminescent properties, some optical and electrical properties reported in this paper were studied in the temperature range from 373 – 673K for TiO_2/NiO core-shell thin films and reported in the wavelength range from 200 – 1200 nm of the electromagnetic spectrum. Four samples of the films were annealed before characterization. These samples are labelled $5T_1$ – $5T_4$ respectively while the sample not annealed [as – deposited] is labelled 5T.

RESULTS AND DISCUSSION

3.1 Reflectance [R]

The reflectance of a thin film is the ratio of the light reflected to incident light energy. The total energy reflected, absorbed and transmitted per unit area per second is equal to the incident energy in the same time over the same area. It is an intrinsic optical property of thin films and can be used to determine other properties of thin films such as colour, transparency and dielectric or polarization characteristics [24]. Figure 1, shows the graphs of reflectance against wavelength for the thin film samples.

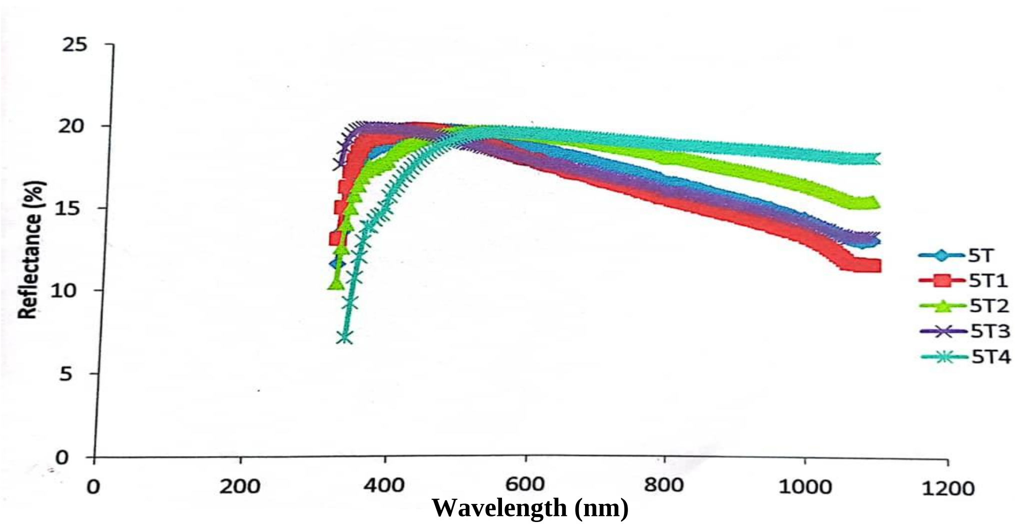

Fig. 1: Reflectance vs. wavelength for TiO_2/NiO core-shell thin films

It can be observed in Fig. 1, that the values of reflectance for the thin film samples increased sharply from 10% to 20% for the as-deposited sample [5T] and also for the samples annealed at 373K [$5T_1$] and 573K [$5T_3$] respectively. This occurred within the NIR [300 nm] and visible [400 nm] regions. Beyond 400nm [401 – 1100 nm], the reflectance of these film samples decreased gradually. The sample annealed at 673K [$5T_4$] has its reflectance increased from 6% to 20% within the ultraviolet to visible regions [270 – 500 nm]. The maximum value of reflectance [20%] for this sample remained constant in the wavelength range from 500 – 1100 nm [i.e within the visible and infrared regions]. The low values of reflectance [6 – 20%] could enhance both the short- circuit current and open circuit voltage of TiO_2/NiO core-shell thin films as photovoltaic materials like solar cells, regulate light transmission and temperature, display technologies and energy efficience [25].

3.2 Extinction Coefficients

Extinction coefficient is a macroscopic constant though it is really not at all constant because it varies with frequency or photon energy [26]. The extinction coefficients of these thin film samples were determined using transmittance and reflectance measurements. The graphs of extinction coefficients of the film samples versus photon energy are shown in Figure 2.

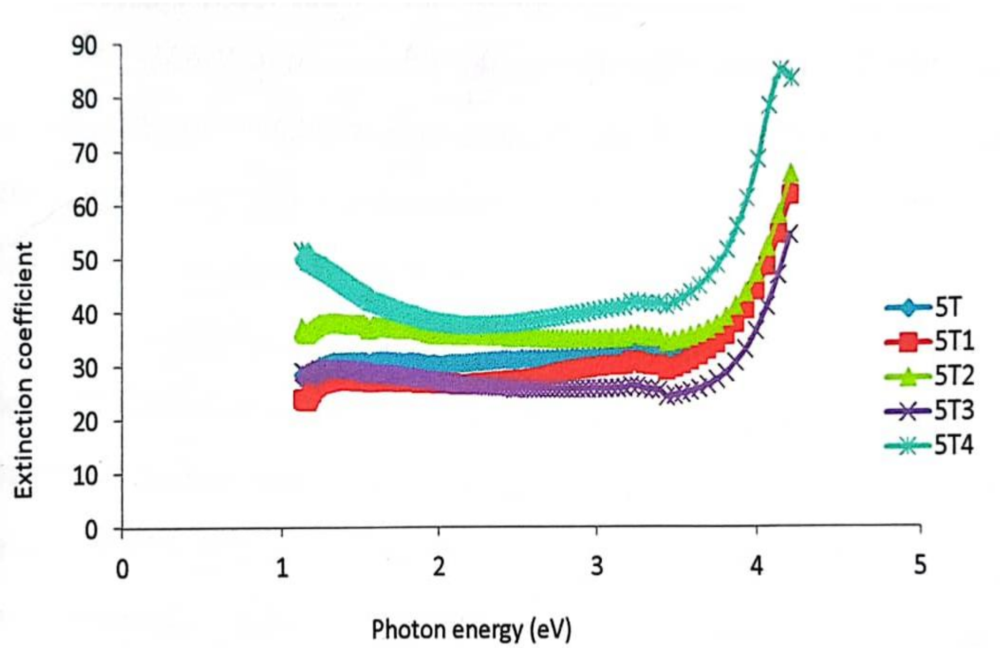

Fig. 2: Extinction coefficient vs. photon energy for TiO_2/NiO core-shell thin films

From Fig. 2, the sample annealed at 673K, [$5T_4$] has the highest value of extinction coefficient which decreased from 50 to 40 between 1 to 2eV. Between 2 to 3.5eV, the value of extinction coefficient 40, remained constant but sharply increased to a maximum value of 80 at a photon energy greater than 3.5 eV. The sample annealed at 573K [$5T_3$] has lowest value 25, of extinction coefficient which remained constant between 1 – 3.5eV of photon energy. The value increased to 50 in the energy range from 3.5 – 4.0eV. The as – deposited sample [5T] and the samples annealed at 373 – 473K temperatures, have nearly the same extinction coefficient which increased from 30 to a maximum value of 55 each, between 3.5 – 4.0eV of photon energy. With these trends, the values of extinction coefficients of the thin film samples cannot be said to be explicit functions of the annealing temperatures. This result does not agree with the one obtained for variation of extinction coefficient with annealing temperature for ZnO: Al thin films [27].

3.3 Electrical Resistivity [ρ]

The electrical resistivity of TiO_2/NiO core-shell thin films was studied in air by using QUARDPRO 301 – auto calculating four-point probe. Four-point probe is the most common method for measuring resistivity. The values of the resistivity of the thin film samples at different annealing temperatures are shown in table 1.

Table 1: Resistivity value of TiO_2/NiO core-shell thin films at different annealing temperatures

Film sample	Annealing temperature [K]	Resistivity ρ [Ωm]
5T	Nil (as-deposited)	1.683×10^4
$5T_1$	373	1.465×10^4

$5T_2$	473	1.203×10^4
$5T_3$	573	1.156×10^4
$5T_4$	673	1.121×10^4

Comparing the values of the resistivity of the studied thin film samples, the values of ρ decreased with the increase in the annealing temperatures as shown in table 1. This clearly indicates the semi-conducting nature of the thin films. Increase in the post-deposition heat treatment of the films resulted to better crystallization, greater grain size of the thin films and decrease defects density so that the resistivity of thin films decreased. Similar results were reported on the studies of electrical properties of other thin films [14, 28, 29].

3.4 Electroluminescent Property

Chemical bath deposition technique is a low temperature method of synthesizing a high luminance thin film electroluminescent [TFEL] device on [Sail Brand] microscopic slides Cat. No. 7102 of 76.2 x 25.4 x 1.1mm. Post deposition sintering at the temperature ranging from 373K to 673K was used to enhance electroluminescent emission of TiO_2/NiO core-shell thin films since high temperature increased the density of the active luminescent centres of the thin films [24, 30]. The relatively high bandwidth or energy gap [direct, E_g > 2.0eV], simple fabrication, low cost, low deposition temperature dependence, high mechanical stability [23], are some of the properties of TiO/NiO core-shell thin films that make them suitable light sources [24, 30, 31].

Conclusions

We have deposited and characterized the core-shell thin films of TiO_3/NiO using the chemical bath deposition [CBD] technique. Four samples of the thin film were annealed or subjected to pest – deposition sintering. The thin films have low reflectance ranging from 10% to a maximum of 20%. The extinction coefficients of the thin films were not explicit functions of the annealing temperatures. The resistivity of the films decreased with increase in the post deposition heat treatment or annealing temperatures. Annealing temperature increased and enhanced the electroluminescent property of the core-shell thin films of TiO_2/NiO.

Acknowledgements

Authors are grateful to Nanoscience Research Group, University of Nigeria Nsukka. We extended our thanks to Prof. F.I. Ezema and also to the technologists in: Obafemi Awolowo University Ile Ife and Federal University of Technology Akure.

Conflict of Interest

The Authors hereby declare no conflict of interest.

REFERENCES

[1] Niu, W., Wang, G., Liu, X., Tang, J. and Bi, X. [2015] Preparation and electrochromic performance of TiO_2 thin film. *International Journal of Electrochemical Science,* **10,** 2613-2620.

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

[3] Onah, D.U., Nwofe, P.A. and Uguru, E.H. [2016] Influence of post-deposition heat treatments on the optical properties of chemically deposited nanocrystalline TiO_2 thin films. *Research Journal of Applied Sciences, Engineering and Technology,* **13** [3], 253-256.

[4] Hisashi, F., Yoshihiro, I., Seiogo, N. and Shigeru, N. [2009] Synthesis of High-K titanium oxide thin films formed by metalorganic decomposition. *Electrochem. Solid State Lett.* **12** [5], E5.

[5] 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.

[6] 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.

[7] Titanium Dioxide Manufacturers Association [2012] About Titanium Dioxide. European Chemical Industry Council, Belgium. 1-8.

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

[9] 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 Nigerian Association of Mathematical Physics,* **24,** 361-364.

[10] Chen, H., Lu, Y. and Hwang, W. [2005] Characterization of sputtered NiO thin films. *Surface & Coatings Technology,* **198,** 138-142.

[11] Masuda, Y. [2010] Morphology control, self-assembly and site-selective deposition of metal oxide nanocrystals. Nanocrystals Sciyo Publishers, Croatia, 1-3.

[12] Haniam, P., Kunsombat, C., Chiangga, S. and Songsasen, A. [2014] Synthesis of cobalt oxides thin films fractal structures by laser chemical vapour deposition. *The Scientific World Journal,* **2014,** 1-4.

[13] Gamo, M.N., Gamo, H., Nakagawa, K. and Ando, T. [2010] Chemical structure and surface potential of nickel and nickel-oxide thin film surfaces studied by High-Resolution Monochromated X-ray Photoelectron Spectroscopy and Scanning Kelvin Force Microscopy. Toppan Printing Co. Ltd, Japan, 84-85.

[14] Vikas, P., Shailesh, P., Manik, C., Prasad, G., Ratnak, S., Shashwati, S. and Pradeep, J. [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,** 35-38.

[15] Venkat, S. and John, W.W. [2001] Capacitance studies of cobalt oxide films formed via electrochemical precipitation. *Journal of Power Sources,* **108,** 20-23.

[16] Han, S.Y. and Lee, D.H., Chang, Y.J., Ryu, S.O., Lee, T.J. and Chang, C.H. [2006] "The growth mechanism of nickel oxide thin films by room-temperature chemical bath deposition". *Journal of Electrochemical Society,* **153** [6], C382 – 383.

[17] Ahmed, J.H. [2014] Study of optical and electrical properties of nickel oxide [NiO] thin films deposited by using spray pyrolysis technique. *Journal of Modern Physics,* **5**, 18, 1-7.

[18] Tripathy, S., Jo, J., Song, H. and Yu, Y. [2011] Fabrication and optical study of Ag@SnO core-shell structure nanoparticle thin films. *Applied Physics A: Materials Science & Processing,* **104**[2], 601 – 603.

[19] Xu, Y. [2009] ZnO/CdSe core-shell nanorod array films synthesized via a two-step method. *Journal of Electrochemical Acta,* **54** [10], 2742 – 2747.

[20] Islam, S.S. [2006] Semiconductor Physics and Devices, Oxford University Press, New Delhi. 428-429.

[21] Severiano, F., Garcia, G., Castaňeda, L., Gracia-Jimẻnez, J.M., Gỏmez-Pozos, H. and Luna-Lỏpez, J.A [2014] Electroluminescent devices based on junctions of indium doped zinc oxide and porous silicon. *Journal of Nanomaterials.* http://dx.doi.org/10.1155/2024/409493, 1 – 7.

[22] Mueller-Mach, R., Mueller, G.O., Alinsog, E. and Helbing, R. [1999] High Luminance from thin film electroluminescence devices. Semiconductors and Semimentals, **65**, 27 – 105

[23] Tsakonas, C., Wakeham, S., Cranton, W.C., Thwaites, M., Boutaud, G., Farrow, C., Koutsogeorgis, D.C. and Ranson, R. [2015] Transparent and Flexible Thin Film Electroluminescent Devices Using HitUS deposition and Laser processing fabrication. *Journal of the Electron Devices Society.* **4** [1], 22-29.

[24] Onah, D.U., Okeke, C.E., Ezema, F.I., Ekwealor, A.B.C., Osuji, R.U. and Ezekoye, B.A. [2012] Synthesis, structural and optical properties of novel core-shell oxide materials by chemical bath deposition. *Journal of Ovonic Research.* **8** [5], 105-111.

[25] Sonia, S., Reshmi, S., Girish, M.G., Ajith, K., Sriram, K.V. and Bhottacharjee, K. [2021] Low reflectance of Carbon nanotube and nanoscroll – based thin film coatings: a case study. Nanoscale Advances: *Journal © The Royal Society of Chemistry,* **11**, 3184 – 3198.

[26] Smith, F.G. and King, T.A. [2000] Optics and Photonics: An Introduction. John Wiley New York, 217-218.

[27] Pallai, S.O. [2010] Solid State Physics (New Revised Sixth edition) New Age International Publishers, New Delhi, 694-695.

[28] Baydogan, N., Ozdurmusoglu, T., Cimenoglu, H. and Tugrul, A.B. [2013] Refractive index and extinction coefficient of ZnO: Al thin films derived by sol- gel dip coating technique. Defect and Diffusion Forum. **334-335**, 290-293.

[29] 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 – 1512.

[30] Fuh, A., Gallinger, R.P., Schuster, P., Adolph, J. and Caporaletti, O. [1992] "The effects of post-deposition annealing on ZnS;Mn film crystalline structure and electroluminescent characteristics." *Thin Solid Films*, **20**7, [1-2], 202-205.

[31] Galal, A.M., El-Moiz, A.B. and Rashaed, M. [2005] Li-doping effects on the electrical properties of ZnO films prepared by chemical-bath deposition method. *Journal of Physics B*, **370**, 158-159.