European Journal of Material Science
Vol.8, No.2, pp.1-9, 2021
Print ISSN: ISSN 2055-6551(Print),
Online ISSN: ISSN 2055-656X (Online)

THERMAL ANNEALING ON THE EDS AND OPTICAL PROPERTIES OF TIO_2/CUO CORE-SHELL THIN FILMS

[1]Daniel U. Onah, [2]Peter E. Agbo, [3]Mary O. Nwodo, [4]Rufus O. Ijeh, [5]Edwin H. Uguru and [5]Omeje, Conelius U.

[1,2,5]Department of Industrial Physics, Ebonyi State University, Abakaliki – Nigeria.
e-mail: d_onah@yahoo.co.uk
[3]Department of Science Education, Ebonyi State University, Abakaliki
[4]Department of Physics, University of Delta, Agbor.
[5] Department of General Studies and Entreprenuership
Enugu State Polytechnic, Iwollo, Enugu State, Nigeria

ABSTRACT: *Studies of thermal annealing on the energy dispersive spectrometer (EDS) analysis and some optical properties of TiO_2/CuO core-shell thin films were carried out in the visible, infrared and UV regions. In this study, the optical properties such as reflectance, absorption and extinction coefficients in relation to the annealing temperatures were particularly investigated. Results of this study showed that: the films are crystalline and contained no impurities as EDS analysis indicated, the as – deposited thin film has the lowest values of reflectance ranging from 5 – 12% within 400 – 1100nm (visible – NIR) regions. Low reflectance values of the films improved their qualities as photovoltaic materials. The sample annealed at 473K has the highest value of absorption coefficient in the UV (0.29 – 0.35μm) region. The films are good materials for UV sensors. The variations of the reflectance, absorption and extinction coefficients of the films with the annealing temperatures cannot be said to be in; a direct or any defined proportion.*

KEY WORDS: Thermal annealing, reflectance, EDS, absorption and extinction coefficients

INTRODUCTION

Transition metal oxides (TMO) in recent times are attracting the attention and interests of many scholars and researchers due to their numerous and potential applications in many device domains. Examples of these oxides include TiO_2, CuO, NiO, ZnO, CoO, Co_2O_3, Co_3O_4, etc. TiO_2 is a wide band gap semiconductor which has become well known as photoactivated catalyst for water and air purification and cleaning surfaces (1). The maximum value of the energy gap determined for TiO_2 is 2.2eV, and this is within the range suitable for application in photovoltaic devices and also in related photonic applications (2). The energy gap of transition metal oxide thin films like Co_3O_4 films decreases with increasing annealing temperatures (3). Cobalt oxide can exist in three different forms such as CoO, Co_2O_3 and Co_3O_4 and each type can be prepared in bulk and thin films on different substrates (4).

@ECRTD-UK https://www.eajournals.org/
https://doi.org/10.37745/ejms.2014

Zinc oxide (ZnO) thin film is typically unintentionally doped n-type material when grown, due to a stoichiometry imbalance that results in oxygen vacancies (5). ZnO has a direct wide band gap which makes it suitable for a variety of potential applications. The increase in annealing temperatures increased the extinction coefficient of the ZnO:Al film (6). Nickel oxide (NiO) like other transition metal oxide thin films can be grown using various deposition techniques such as sol-gel method, chemical bath deposition technique, d.c. sputtering technique and laser chemical vapour deposition etc (5, 7 – 10). NiO thin films have direct wide band gap which decreased from 3.86 – 3.47eV after annealing, so that the optical quality of NiO thin films is improved by annealing (11).

Copper oxide (CuO) thin films can be synthesized using low-cost methods like successive ionic layer adsorption and reaction (SILAR) method and solution growth technique (12, 13). CuO has been used as a shell in TiO_2/CuO indirect transitions after post-deposition heat treatments or thermal annealing (14). Studies on core-shell oxide thin films have remained relatively scarce. Therefore, the aim of this paper is to report or present the effects of thermal annealing on the EDS, reflectance, absorption and extinction coefficients of TiO_2/CuO core-shell thin films prepared using solution growth or chemical bath deposition technique.

MATERIALS AND METHODS

Details of the materials used, synthesis and growth of TiO_2/CuO core-shell thin films using the chemical bath deposition technique have been reported. The bath temperature was between 75 – 80^oC and the deposition time was 4 hours (14). After deposition, four samples of the films were annealed at different temperatures ranging from 373 – 637K. Annealing the thin films was done before characterization. Annealing enhanced the crystallinity of thin films (15). The as – deposited thin film sample is denoted by 6T while the samples annealed at 373 – 673K are denoted by $6T_1$ – $6T_4$ respectively.

Thin Film Characterization

The optical characterization of the thin films was done at Federal University of Technology Akure. XRD or structural analysis and Rutherford Backscattering for compositional analysis were done at the Centre for Energy Research and Development, Obafemi Awolowo University Ile Ife, Nigeria. Energy dispersive spectrometer (EDS) analysis, scanning Electron Microscopic (SEM) analysis and the conductivity test (four points probe) were done at Sheda Science and Technology Complex (SHESTCO), Abuja – Nigeria. Nevertheless, only EDS, reflectance absorption and extinction coefficients were reported here.

RESULTS AND DISCUSSION

Energy Dispersive Spectrometer (EDS) Analysis

The EDS is a suitable technique to determine the crystalline quality and the presence of impurities in the thin films and also exciton fine structure. Qualitative analysis (i.e. determination of the concentrations of the elements present) involved measuring line intensities for each element. Thus EDS provided a quantitative analysis of the films' surface compositions. The EDS for TiO_2/CuO core-shell thin films annealed at 573K is shown in Figure 1.

European Journal of Material Science
Vol.8, No.2, pp.1-9, 2021
Print ISSN: ISSN 2055-6551(Print),
Online ISSN: ISSN 2055-656X (Online)

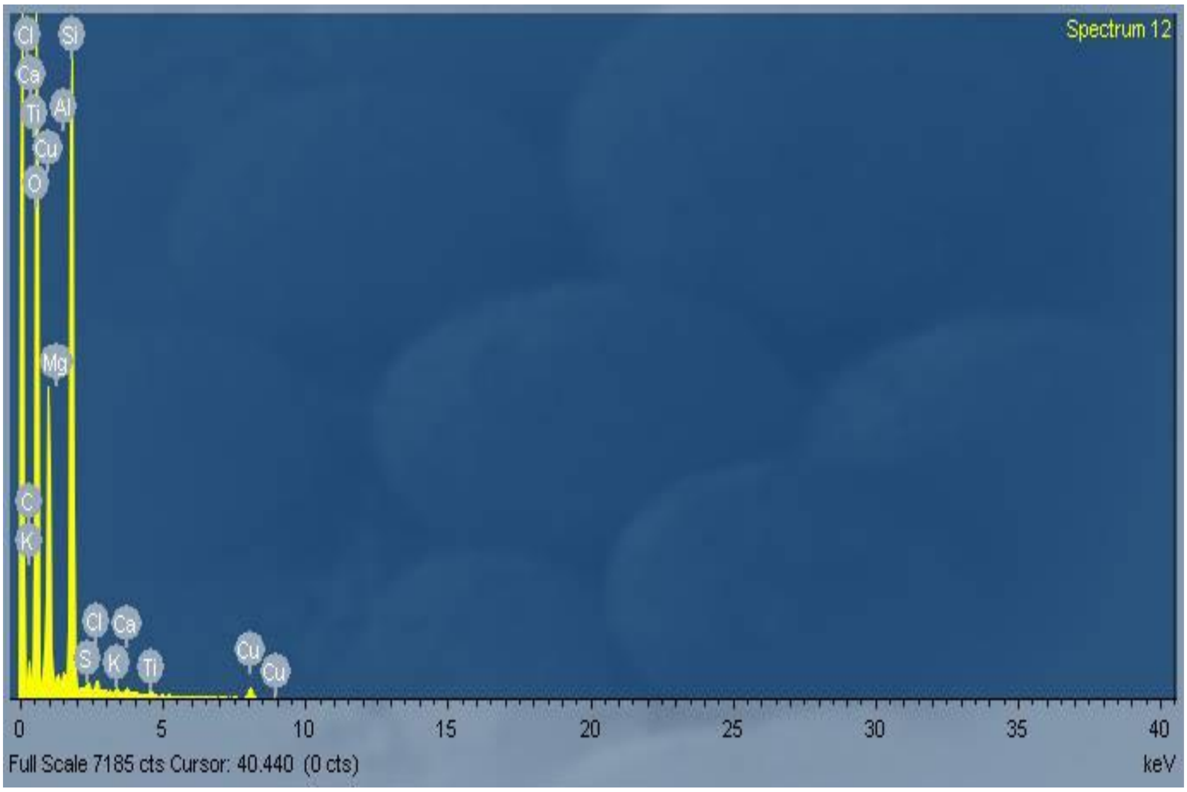

Fig. 1: EDS for T_iO_2/C_uO core-shell thin film annealed at 573K

In Figure 1, strong and sharp emission peaks are noticed at the energy range from 0 – 2KeV. These are indications that there was no crystalline defects during films' growth. Also there is noisy background in Figure 1. This is an indication that the films are crystalline (16).

Reflectance (R) of the Thin Films

Reflectance is a directional property that depends largely on the surface qualities of the films. It is the amount of reflection in terms of energy and is usually expressed in percentage. The limiting value of reflectance is known as reflectivity (17). Reflectivity can give detailed information on the electronic systems of a given thin film material. The graph of reflectance versus wavelengths for TiO_2/CuO core-shell thin films is shown in Figure 2.

@ECRTD-UK https://www.eajournals.org/
https://doi.org/10.37745/ejms.2014

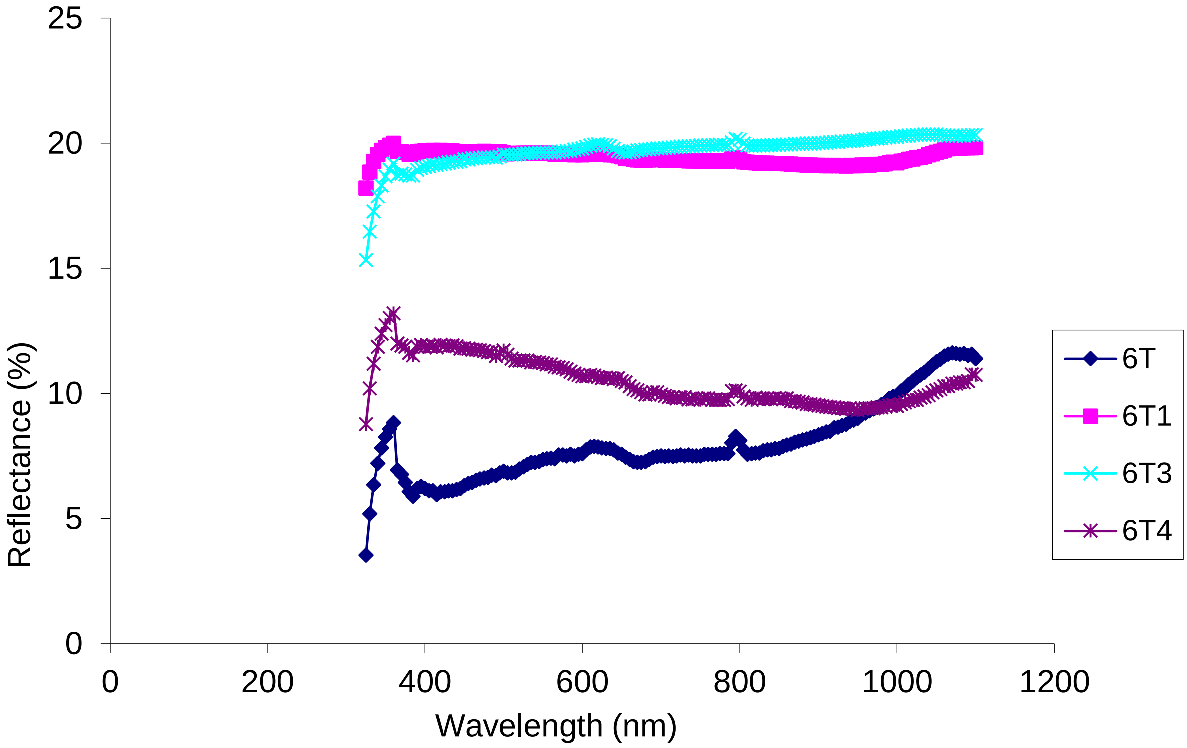

Fig. 2: Reflectance vs. wavelength for TiO_2/CuO thin films

In Figure 2, the as – deposited sample (6T) has the lowest values of reflectance ranging from 5 – 12%. The variable values in reflectance with wavelengths occurred in the as – deposited sample more than in the annealed samples ($6T_1 – 6T_4$). The sample annealed at 673K ($6T_4$) has reflectance of 10% while the samples annealed at 373K and 573K both have reflectance of 20%. Though the reflectance increased with the annealing temperatures, the relationship cannot be said to be in a direct or any defined proportion.

Absorption Coefficient (α)

Optical absorption is induced by either the excitation of vibrational modes or the promotion of electrons from a given set of energy states to other states of higher energy (18). Absorption coefficient (α) equals the relative change in light intensity per unit length covered by the light traversing an absorbing medium, and the relationship among absorption coefficient, extinction coefficient and wavelength is shown in equation (1).

$$\alpha = \frac{4\pi k}{\lambda} \qquad (1)$$

where λ is wavelength and k is extinction coefficient or attenuation index (19). Absorption coefficient (α) can also be calculated from the transmission (T) using equation (2).

$$T = (I - R)^2 \, exp^{(-\alpha x)} \qquad (2)$$

where R is the reflection coefficient and x has dimension of length (20). On further simplification of equation (2), absorption coefficient can as well be evaluated using equation (3).

$$\alpha = \frac{2}{x} ln \left(\frac{I-R}{T}\right) \tag{3}$$

Near the absorption edge, the absorption coefficient can be expressed using equation (4).

$$\alpha = \left(h\nu - E_g\right)^n \tag{4}$$

where $h\nu$ is photon energy, E_g is the band gap and $n = {}^1/_2, {}^3/_2$ and 2 for allowed direct, forbidden direct and indirect transitions (21). The graph of absorption coefficients versus photon energy for the thin film samples is shown in Figure 3.

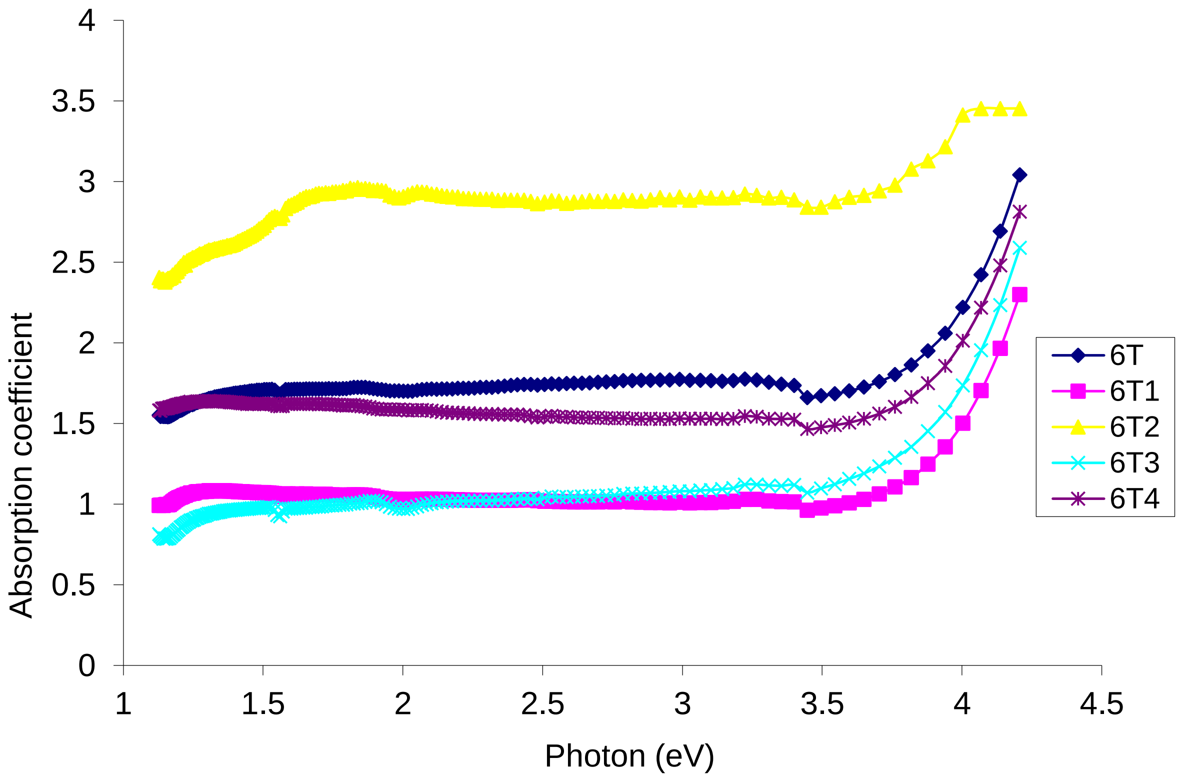

Fig. 3: Absorption coefficient vs. photon energy for TiO_2/CuO thin films

In Figure 3, the absorption coefficient increased sharply with the increase in photon energy between 3.50 – 4.25eV (i.e within the near infrared region) of the electromagnetic spectrum. The sample annealed at 473K has the highest absorption coefficient ranging from 2.5 – 3.0 in the UV region and gradually reduced to a constant value of 2.8 within the visible region till the sharp edge or absorption edge, (or long-wavelength cut off λ_c). Beyond the λ_c, the absorption

@ECRTD-UK https://www.eajournals.org/
https://doi.org/10.37745/ejms.2014

coefficient increased from 3.0 to 3.5 in the NIR region. For wavelengths longer than λ_c, absorption coefficient (α) is always too small due to very small or negligible absorption. The band gap of the thin film is therefore determined by the beginning of the absorption coefficient value immediately after the absorption edge (20). However a moderate absorption has been observed after the absorption edge due to charge carrier absorption (4).

The samples annealed at 373K and 573K, ($6T_1$, $6T_3$) both have a constant value of 1.0 for α before the sharp edge. The as – deposited sample (6T) has the value of α increased from 1.3 to 1.7 within the infrared region, before increasing sharply to 3.0 after the sharp edge. All the samples of the thin films have sharp increase in α after the sharp edge (i.e between 3.50 – 4.25eV). The relation between absorption coefficient and annealing temperature is therefore not a sharply or well defined one.

Extinction Coefficient (k)

Extinction coefficient or attenuation coefficient is a measure of the decrease of energy in electromagnetic wave that propagates through a material due to influence of microscopic electric fields (18). Energy from the wave is removed due to displacement of ions which impart energy to electrons near the Fermi level, in a process called acoustic attenuation. The spectra of extinction coefficient of thin films cannot easily be directly measured, but can be determined indirectly from measurable quantities which depend on it, such as reflectance and refractive index. The extinction coefficient is a macroscopic optical constant though it varies with frequency or photon energy. It shows how an external electromagnetic disturbance travelling with the velocity of the light in vacuum is exactly cancelled out and replaced in the substance by the secondary disturbance travelling with an approximately smaller velocity $^{c}/_{n}$ (19) where n is refractive index of the material and c is the velocity of light in a vacuum. Though extinction coefficient (k) and absorption coefficient (α) are related by equation (1), the former is a function of wave intensity whereas the later is a function of the wave phase. Graphs of extinction coefficient versus photon energy for five thin film samples are shown in Figure 4.

@ECRTD-UK https://www.eajournals.org/
https://doi.org/10.37745/ejms.2014

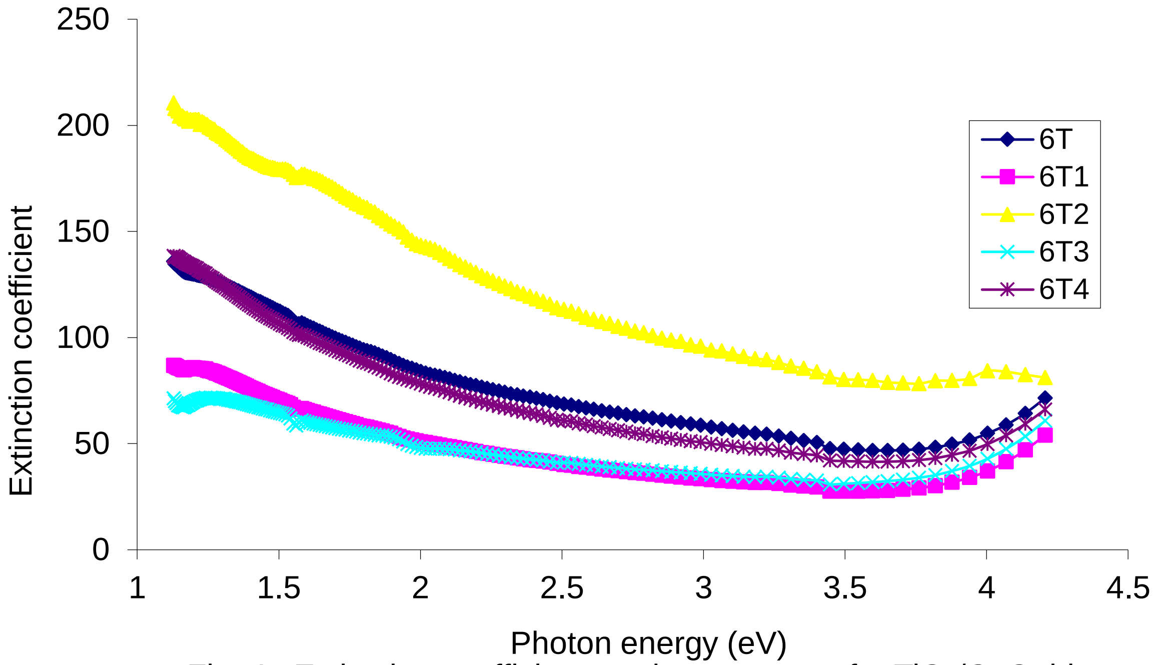

Fig. 4: Extinction coefficient vs.photon energy for TiO_2/CuO thin films

From Figure 4, the sample annealed at 473K ($6T_2$) has the highest extinction coefficient decreasing from 2.0 – 0.8. The samples annealed at 373K and 573K have the same value of extinction coefficient decreasing from 0.7 to 0.4 before the absorption edge (between 1.1 – 3.4eV of photon energy). The as – deposited thin film sample (6T) and the sample annealed at 673K have the same value of k, decreasing from 1.4 – 0.6 (between 1.1 – 3.4eV of photon energy). It is very obvious from these results that the relationship between the extinction coefficients of the thin films and the annealing temperatures is not a clearly defined one. This result agreed with the ones obtained by other scholars (22).

CONCLUSION

The TiO_2/CuO core-shell thin films were deposited on glass substrates using the chemical bath deposition technique. The effects of annealing temperatures on reflectance, absorption and extinction coefficients were investigated. Also EDS analysis showed that the films are crystalline and contained no impurities. The thin films have low reflectance values thereby making them good candidates or materials for photovoltaic devices. High absorption coefficients of the films in the UV region implied that the films are good materials for UV sensors. The relationships or the variations of the reflectance spectra, absorption and extinction coefficients with the annealing temperatures were not clearly defined in this study.

Acknowledgement

I appreciate the assistance of the workers in the Laboratory of the Federal University of Technology, Akure – Nigeria. I also thank the Nanoscience Research Group, University of Nigeria Nsukka.

References

1. 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.
2. Onah, D.U., Nwofe, P.A. and Uguru, H.E. (2016) Influence of Post-deposition Heat Treatments on Optical Properties of Chemically Deposited Nanocrystalline TiO_2 Thin Films. *Research Journal of Applied Sciences, Engineering and Technology*. **13**(3), 253.
3. Patil, V., Joshi, P., Chougule, M. and Sen, S. (2012) Synthesis and Characterization of Co_3O_4 Thin Film. *Soft Nanoscience Letters*. **2**, 1.
4. Mordi, C.U., Eleruja, M.A., Taleatu, B.A., Egharevba, G.O., Adedeji, A.V., Akinwunmi, O.O., Olofinjana, B., Jeynes, C. and Ajayi, E.O.B. (2009) Metal Organic Chemical Vapour Deposited Thin Films of Cobalt Oxide Prepared via Cobalt Acetylacetonate. *J. Mater. Sci. Technol.* **25,** 1, 85.
5. Sönmezoğlu, S. and Akman, E. (2014) Improvement of Physical Properties ZnO thin films by tellurium doping. *Applied Surface Science*, **318**, 319.
6. 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.
7. Onah, D.U., Okeke, C.E., Ugwu, E.I. and Ekpe, J.E. (2015) Study of the effects of thermal annealing on the optical and solid state properties of nanocrystalline TiO_2/NiO core-shell thin films. Nanoscience and Nanotechnology: *An International Journal,* **5**(2), 22.
8. 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.
9. Mardare, D. and Rusu, G.I. (2000) On the Structure of Titanium Oxide thin films http://stoner.phys.uaic.ro, 201.
10. 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*, htt://www.hindawi.com/journals/tswj/2014/685270/, 1.
11. Patil, V., Pawar, S., Chougule, M., Godse, P., Sakhare, R., Sen, S. and Joshi, P. (2011) Effects of Annealing on Structural, Morphological, Electrical and Optical Studies of Nickel Oxide Thin Films. *Journal of Surface Engineered Materials and Advanced Technology*. **1,** 35.
12. Mageshwari, K. and Sathyamoorthy, R. (2013). Physical properties of nanocrystalline CuO thin films prepared by SILAR method. *Journal of Material Science in Semiconductor Processing*, **16** (2), 337.
13. Onah, D.U., Ugwu, E.I. and Ekuma, B.O. (2008) Solution Growth and Characterization of Copper Oxide Thin Films. *Nigerian Journal of Physics*, **20** (2), 251.

14. Onah, D,U., Ugwu, E.I. and Ekpe, J.E. (2015) Optical Properties of Nanocrystalline TiO_2/CuO Core-Shell Thin Films by Thermal Annealing. *American Journal of Nano Research and Applications*, **3** (3), 62.
15. Bube, R.H. and Fahrenbruch, A.L. (1983) Fundamentals of Solar Cells: Photovoltaic Solar Energy Conversion. Academic Press, London, 352.
16. Nishad, G.D., Jagdish, C.V. and Ramphal, S. (2008) Preparation and Characterization of Nanocrystalline Tin Oxide Films Deposited at Room Temperature. *Journal of Thin Solid Films*, **516**, 8591.
17. Smith, F.G. and King, T.A. (2000) Optics and Photonics: An Introduction, John Wiley, New York, 217.
18. Pillai, S.O. (2010) Solid State Physics, New Age International Publishers, New Delhi, 368.
19. Born, M and Wolf, E. (1993) Principles of Optics, Pergamon Press, New York, 71.
20. Islam, S.S. (2006) Semiconductor Physics and Devices. Oxford University Press, New Delhi, 205.
21. Sze, S.M. (1981) Physics of Semiconductor Devices, John Wiley & Sons, Singapore, 40.
22. Benno, G. and Joachim, K. (2003) Optical Properties of Thin Semiconductor Films http://home.fnal.gov/~jkopp/tum/pd/F/hl spekt.pdf

@ECRTD-UK https://www.eajournals.org/
https://doi.org/10.37745/ejms.2014