COMPOSITION AND OPTICAL CHARACTERIZATION OF ZnO/NiO MULTILAYER THIN FILM: EFFECT OF ANNEALING TEMPERATURE

A.E. AJUBA, S.C. EZUGWU[*], P.U. ASOGWA, F.I. EZEMA
Department of Physics and Astronomy, University of Nigeria Nsukka

ZnO/NiO multilayer thin films were obtained using chemical bath deposition method. The precursor solution used were nickel sulphate and zinc nitrate. The effect of annealing temperature on the optical properties and band-gap energy were studied by annealing the deposited films at different temperatures of $100^{o}C$ and $300^{o}C$. Optical properties such as absorbance and transmittance were determined using Unico UV-2102 PC spectrophotometer, at normal incidence of light in the wavelength range of 200-1000nm. The band-gap energy was discovered to lie between 2.00-2.50 eV. The composition of the deposited firm was also obtained.

1. Introduction

NiO is a transition metal oxide that has several potential applications, such as solar thermal absorber, electrodes for battery and photoelectron-catalysts [1]. Nickel oxide (NiO) thin films are promising materials with excellent electrochromic properties [2]. Other important application of Nickel oxide films includes preparation of alkaline batteries (as cathode material), antiferomagnetic layers and P-type transparent conducting films [2]. Nickel oxide (NiO) can be synthesized by thermal decomposition with $Ni(OH)_2$ thin film precursor [3]. The appealing electronic properties of NiO such as large band-gap energy of (≈4.00) eV, and high thermal stability, make it a favourable material for electronic device applications [3].

Zinc oxide (ZnO) on the other hand is one of the versatile and technologically important semi conducting material because of its typical properties such as transparency in the visible range, high electrochemical stability, direct band gap (3.37)eV, absence of toxicity, abundance in nature etc. [4]. Nickel oxide (NiO) and Zinc oxide (ZnO) thin films have been prepared by various techniques, such as thermal evaporator, sputtering, sol-gel, spray pyrolysis, chemical vapour deposition and chemical bath deposition (CBD). For instance, work has been done on the microstructure, electrical and optical properties of $ZnO-NiO-SiO_2$ nanocomposite synthesized by Sol-Gel Technique [6]. Other work carried out in this area includes synthesis and characterization of ZnO-NiO composite nano particles by solution method etc [7]. Among all these different techniques for deposition, chemical bath deposition was successfully used to obtain ZnO/NiO multilayer thin films due to its relative simplicity, low cost and potential application for large area deposition [5]. The deposited firms were characterized with regards to its optical properties, band gap energy and its composition.
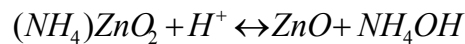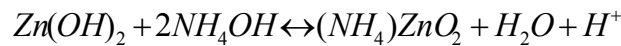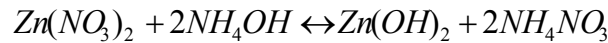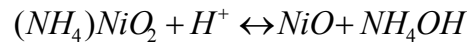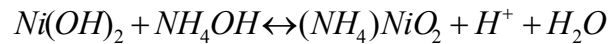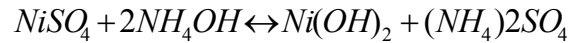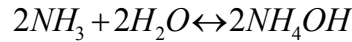
[*]Corresponding author: sabroec@gmail.com

2. Experimental details

The chemical bath for zinc oxide (ZnO) deposition was prepared by mixing 10ml, 0.5M zinc nitrate $Zn(NO_3)_2$, NH_4OH and 35ml of distilled water, put in that order. The deposition of ZnO thin film on clean microscope slide lasted for 4 hours in the oven set at 70^oC. The deposited film was allowed to drip dry and then used as the substrate for the formation of ZnO/NiO multilayer.

Thin film of nickel oxide (NiO) was deposited on glass-ZnO system by using a deposition bath composed of nickel sulphate ($NiSO_4$), the source of cation, ammonia solution as a complexing agent and PVA solution. Earlier, the PVA solution was prepared by adding 900ml of distilled water to 1.8g of solid PVA ($-C_2H_4O)_n$ (n = 1700). The temperature of the homogeneous solution was then allowed to drop to 25^oC. The formation of ZnO/NiO multilayer thin film lasted for 6 hour in the oven at 65^oC. Two of the deposited films were annealed at different temperature of 100^oC (sample B3) and 300^oC (sample B5) to determine the effects of the annealing temperature on the deposited thin film.

The ionic reactions involved are

$$2NH_3 + 2H_2O \leftrightarrow 2NH_4OH$$

$$NiSO_4 + 2NH_4OH \leftrightarrow Ni(OH)_2 + (NH_4)2SO_4$$

$$Ni(OH)_2 + NH_4OH \leftrightarrow (NH_4)NiO_2 + H^+ + H_2O$$

$$(NH_4)NiO_2 + H^+ \leftrightarrow NiO + NH_4OH$$

$$Zn(NO_3)_2 + 2NH_4OH \leftrightarrow Zn(OH)_2 + 2NH_4NO_3$$

$$Zn(OH)_2 + 2NH_4OH \leftrightarrow (NH_4)ZnO_2 + H_2O + H^+$$

$$(NH_4)ZnO_2 + H^+ \leftrightarrow ZnO + NH_4OH$$

Accurate knowledge of the absorption co-efficient, optical bandgap and refractive index of semiconductors is indispensable for the design and analysis of various optical and opto-electronic devices [8]. As such, the optical properties and bandgap energy of ZnO/NiO multilayer thin films deposited in this work were calculated using the absorption and transmittance measurement determined by Unico-UV-2102 PC Spectrophotometer at normal incidence of light in the wavelength range of 200-1000mm. The composition of the film was determined by Rutherford Back Scattering (RBS).

3. Results and discussion

The elemental composition and chemical states of sample B_5 (film annealed in the oven at 300^oC) was analyzed by Rutherford Backscattering (RSB) at Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria. The results are presented in figure 1. From the film composition presented in Table 1, we can deduce that sample B_5 comprises Zn, Ni and O. The result from RBS analysis also shows that the deposited film has a thickness of 590nm.
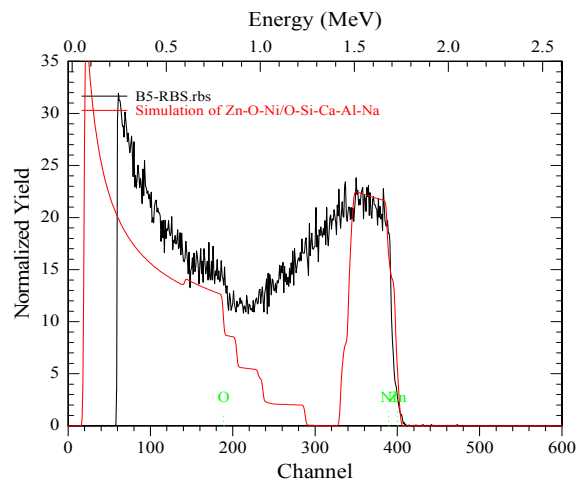
Fig.1: RBS of ZnO/NiO multilayer thin film

Table 1: The composition of substrate and ZnO/NiO multilayer thin film from RBS analysis

	Oxygen	Zinc	Nickel	Silicon	Calcium	Aluminium	Sodium
ZnO/NiO Multilayer thin film	0.696	0.186	0.119	-	-	-	-
Glass substrate	0.550	-	-	0.120	0.050	0.050	0.230

Figs. 2 and 3 are plots of absorbance vs. wavelength and transmittance vs. wavelength for ZnO/NiO multilayer thin films deposited in this work.
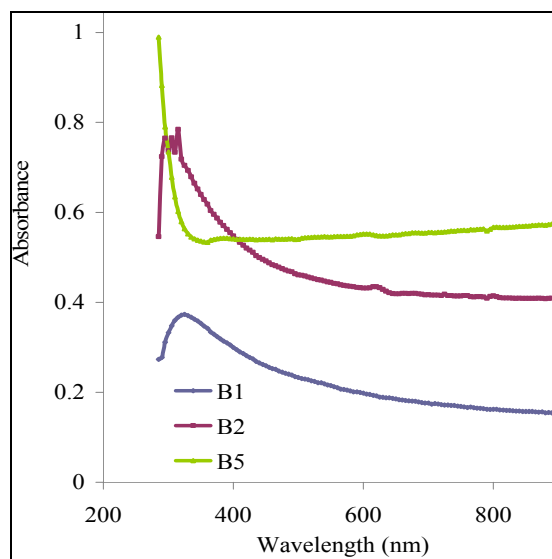

Fig.2: Absorbance vs. wavelength for ZnO/NiO multilayer thin films.

The absorbance of B1 and B3 were observed to decrease with wavelength through VIS-NIR regions. However the film annealed in the oven at 300°C showed absorbance that decreased sharply within the UV region and remain almost constant through the VIS-NIR regions. In general, the figure shows that heat treatment increases the absorbance value of the ZnO/NiO films.
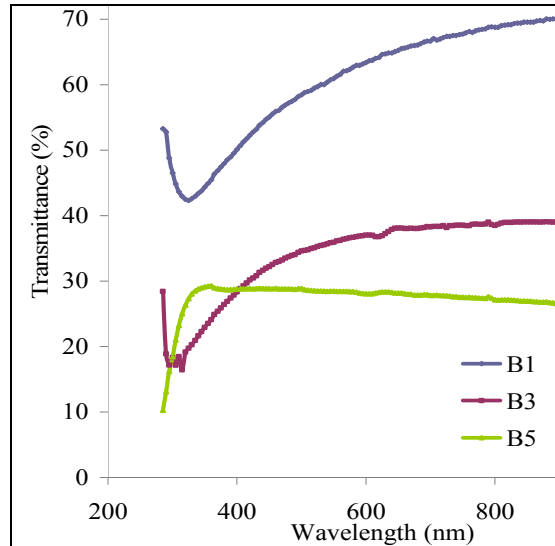

Fig.3: Transmittance vs. wavelength for ZnO/NiO multilayer thin films.

For transmittance spectra, it is observed that the as-grown film has the highest transmittance of 70% at the wavelength of 900nm. The transmittance of the film decreases with annealing temperature.

Fig. 4 is a plot of reflectance as a function of wavelength for ZnO/NiO multilayer thin film deposited in this work. The film shows an average reflectance of 20% in the wavelength range of (300 - 900) nm. With regards to relatively low reflectance of sample B5, the film can serve as an anti-reflecting coating material.
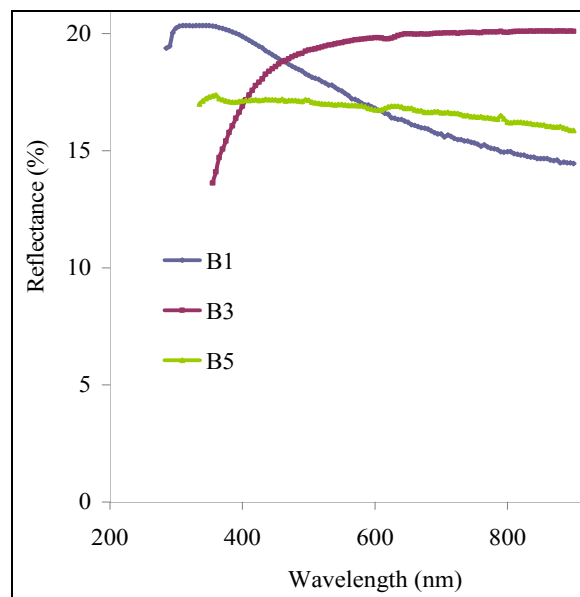

Fig.4: Reflectance vs. wavelength for ZnO/NiO multilayer thin films

Fig. 5 is a plot of refractive index vs. photon energy of ZnO/NiO multilayer thin film. The refractive index of samples B3 and B5 decreased with increasing photon energy.
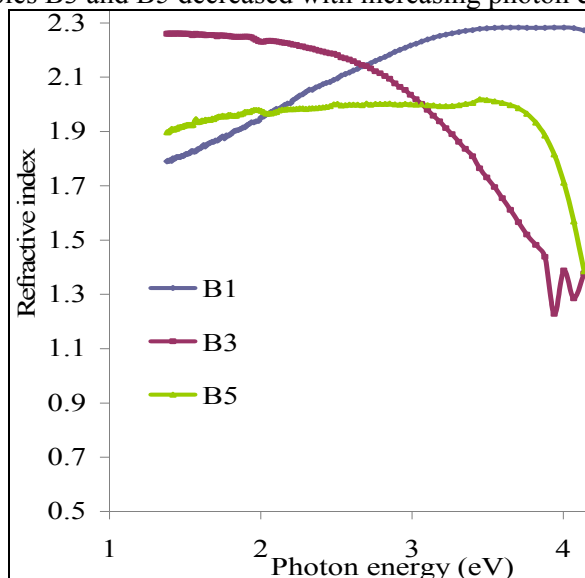

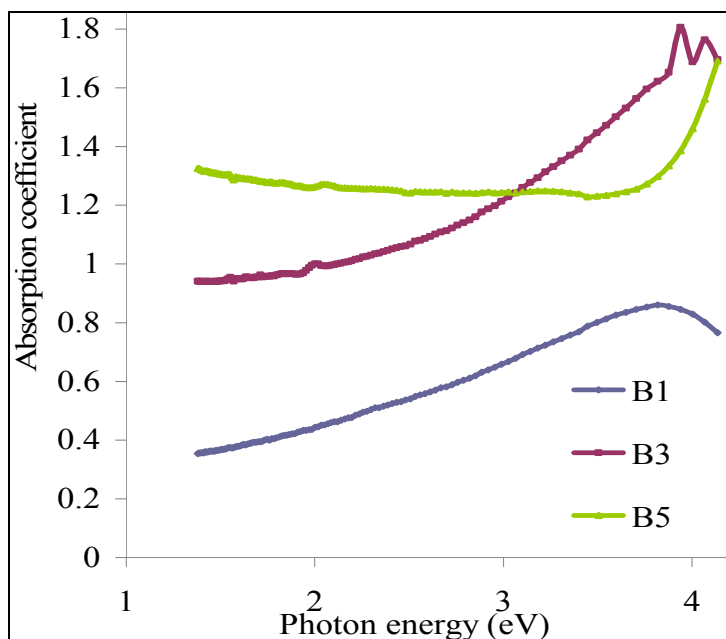*Fig.5: Refractive index vs. photon energy for ZnO/NiO multilayer thin films.*

Fig.6: Absorption co-efficient vs. photon energy for ZnO/NiO multilayer thin films.

The details of the mathematical determination of absorption coefficient (α) can be found in literature [10] while the plots of absorption coefficient against photon energy is shown in fig. 6. The region of higher values of α, that is $\alpha > 10^4$ cm^{-1} correspond to transition between extended state in both valence and conduction bands while the lower values, that is $\alpha \leq 10^4$cm^{-1} is the region where absorption present a rough exponential behaviour. Fig. 7 is a plot of $(\alpha h\upsilon)^2$ vs. photon energy (hυ) for ZnO/NiO multilayer thin film. The band gap energy obtained here lie in the range

of 1.40 - 2.50eV. A close observation of figure 7 shows that the band gap energy decreases with increase in the annealing temperature. This is possibly due to evaporation of water molecules off the films and/or reorganization of the films. However, band-gap energy may be affected by the thickness of the film and its crystallite size [9]. Furthermore, thin film materials with band gap energy above 1.9eV can be used as a window layer. Hence the multilayer thin films deposited in this work can serve as a window layer since its band gap energy lie within the prescribed range. The band gap energy of the film annealed at 300°C is close to the value reported in literature for ZnO-NiO-SiO$_2$ nanocomposite [6].
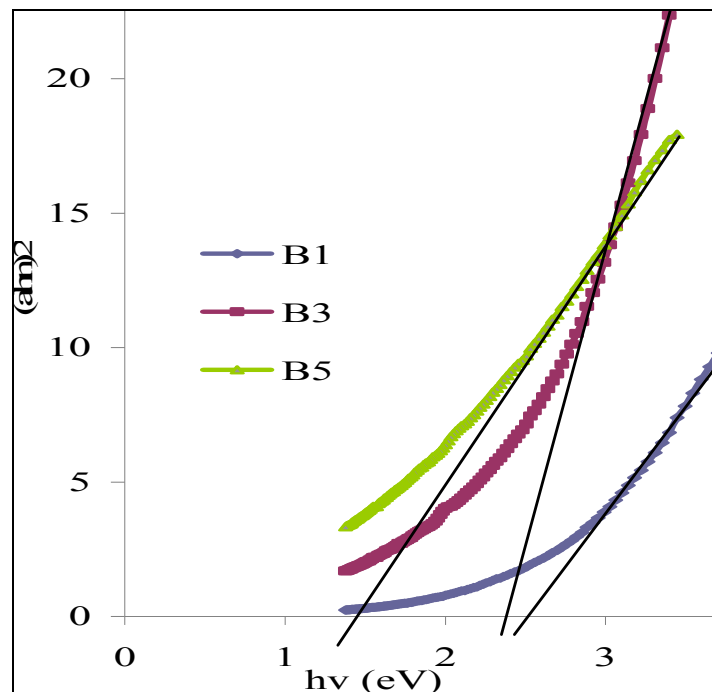

Fig.7: Plot of $(\alpha h\upsilon)^2$ vs. $h\upsilon$ for ZnO/NiO multilayer thin films

4. Conclusions

ZnO/NiO multilayer thin films were deposited using CBD method. The optical properties and composition of the films were characterized. Annealing temperature influences the optical properties and bandgap energy of the film. The bandgap energy lies in the range of 1.40-2.50eV. Thin film material with the bandgap energy above 1.9eV can be used as a window layer in solar cell fabrication. Again, thin films with high transmittance in the NIR are employed in construction of poultry houses to allow enough intra-red to warm the very young chicks during the day. Some of the films grown in this work could therefore be applied in the construction of poultry roots and wall. This helps to reduce the cost of energy consumption through stoves, heaters, electric bulbs and the hazards associated with them while at the same time protecting the chicks from UV radiation [10]. It is also discovered that the bandgap energy decreases with increase in annealing temperature.

References

[1] S.V. Han, D.H. Lee, V.J. Chang, S.O. Ryu, T.J. Lee, C.H. Chang. Journal of the Electrochemical Society, **153(6)**, 382 (2006)

[2] B.N. Wang, O.Y. Li, Z.R. Nie, Z.H. Wang, Q. Wei, Journal of Colloid and Interface Science, **320**, 254 (2005)

[3] K.S.R. Krish, M. Liberati, V.M. Grazioli, S. Turchini, P. Luches, S. Vateri, C. Carbone, J. of Magnetism and magnetic Materials, **310**, 8 (2007).

[4] V.R. Shinde, C.D. Lokhande, R.S. Mane, H. Sung-Hwan, Applied Surface Science, **245**, 407 (2005).

[5] M.A. Vidales-Hurtado, A. Mendoza-Galvan, Materials Chemical and Physics, **107**, 33 (2008).

[6] A.C. Canan, A. Ayse, Turkish Journal of Science and Technology, **4(2),** 121 (2009).

[7] V. Mohammad, Theories and Applications of Chemical Eng., **14(2)** (2008)

[8] A. Abu El-Fadl, G.A. Mohamad, A.B. Abd EL-Moiz, M. Rashad, Physica B, **366**, 44(2005).

[9] C.D. Lokhande, E.H. Lee, K.D Jung, O.S, Joor, Material Chemical and Physics, **91**, 200 (2005).

[10] S.C. Ezugwu, F.I. Ezema, R.U. Osuji, P.U. Asogwa, A.B.C. Ekwealor, B.A. Ezekoye, Optoelectron. Adv. Mater.-Rapid-Comm., **3**(2)**,** 141 (2009)