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Comprehensive Studies on the Optical Properties of ZnO-Core Shell Thin Films

P. E. Agbo and P. A. Nwofe.*

Division of Materials Science and Renewable Energy, Department of Industrial Physics, Ebonyi State University, Abakaliki, P.M.B 053, Ebonyi State, Nigeria.

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Abstract: In this study, we report on the optical properties of ZnO-core shell thin films deposited by chemical bath technique. The core-ZnO was first deposited before the shells were deposited upon it. UV-spectrophotometer was used to study the optical parameters. The variation of the transmittance, reflectance, absorbance and refractive index against wavelength has been investigated for the deposited films. Our result showed that highest transmittance of about 80% is displayed by ZnO/NiO while ZnO/MnO displayed the lowest value of transmittance. The highest and lowest value of absorbance are 2.5 and 0.2 as displayed by ZnO and ZnO/NiO respectively. These values are within the range suitable for use as window layers in solar cell devices and in other photonic and opto-electronic applications. The study reveals that the shell has profound influence on some of the optical properties of ZnO.

Keywords: Chemical bath, refractive index, transmittance, absorbance, reflectance, zinc oxide, core shell.

1 Introduction

The semiconductor- ZnO has gained substantial interest in the research community in part because of its large exciton binding energy (60 meV) which could lead to lasing action based on exciton recombination even above room temperature. Even though research focusing on ZnO goes back many decades [1], the renewed interest is fueled by availability of high-quality substrates and reports of *p*-type conduction and ferromagnetic behavior when doped with transitions metals, both of which remain controversial. It is this renewed interest in ZnO which forms the basis of this review. As mentioned already, ZnO is not new to the semiconductor field, with studies of its lattice parameter dating back to 1935 by Bunn [2], and more recently by Özgür et al [3]. ZnO is an important II–VI compound semiconductor material due to its direct energy gap and large excitation binding energy at room temperature. It has the unique optical and electrical properties which can be used in a variety of applications, such as high transmittance conductive oxide coatings for solar cells, gas sensors, UV photodetectors, and bulk acoustic wave resonators. It has direct bandgap energy of 3.37 eV, which makes it transparent in visible light and operates in the UV to blue wavelengths. Manganese oxide are important materials in many application such as catalyst, electrodes, high density magnetic storage media, ion exchangers, sensors, molecular absorption and electronics. Particularly, Mn_3O_4 is known to be efficient catalyst in the decomposition of waste gas $–NO_2$, and reduction of nitrobenzene. It has been widely used in Li-Mn-O electrodes for rechargeable lithium batteries and for soft magnetic materials such as manganese zinc ferrite [3,4]. In recent years, many researchers have focused on cadmium oxide (CdO) due to their application in several areas of research, specifically in optoelectronic and other applications, including solar cells [5, 6], phototransistors [4], photodiodes [7], transparent electrodes and gas sensors [6,7]. In this communication, the comprehensive study of the optical properties of core- shell thin films of the form; ZnO/MnO, ZnO/NiO and ZnO/CdO is reported. The chemical bath technique was employed because of its inherit advantages. Nickel Oxide is a transition metal oxide with excellent chemical and thermal stability [8-11]. It has potential applications in such areas like electro-chromic displays devices, anti-ferromagnetic layers etc.

*Corresponding author e-mail: ekumaagbo@gmail.com

2 Experimental Procedures

2.1. Substrate preparation

Soda lime glass procured from the Xin Yan Technology LTD, Hong Kong were used as substrates. The glass substrates were first cleaned by degreasing in hydrochloric acid, and then cleaned with detergent/cold water and then rinsed with distilled water. The glass slides were then further cleaned with an ultrasonic machine. The zinc oxide (core) was then deposited on the glass substrate.

2.2. Film deposition and reaction mechanism

The reaction mechanism that led to the deposition of the films is possible through the reactions of the appropriate precursors thus: ZnO solution was prepared by adding 60 ml of 0.l M Zinc nitrate hexahydrate $Zn[NO_3]_2.6H_2O$, 28 ml of aqueous NH_3, with continuous heating and stirring. Four (4) clean glass slides, held with synthetic foam were immersed vertically into the solution. The deposition was allowed for a temperature of 333 K for 1 h in an oven after which the coated substrates were removed, rinsed with distilled water and dried in air. To obtain ZnO/MnO core/shell, the ZnO (core) film already deposited was inserted in a mixture containing 10 ml of 0.l M of $MnCl_2H_2O$, 4 ml of analytical grade of NH_3 (ammonia) and 46 ml of distilled water in 100 ml beaker. Deposition was allowed for a temperature of 313 K for 2 h in an oven, after which the films were removed, rinsed with distilled water and dried in air. To obtain ZnO/CdO thin film, the core was inserted vertical in a bath consisting of 4mls of 1M $CdSO_4$, 2mls of NH_3 solution and 35mls of H_2O. The bath was allowed to stand for 360 minutes at a temperature of 348K. The bath used in depositing ZnO/NiO consist of 40mls of 0.5M of NiS, 1% PVA solution, 10ml of 1M NH_3 solution and 50ml of distilled water.

In the literature, it has been established that film deposition on a substrate occurs in two steps of nucleation and particle growth. In chemical bath deposited films, nucleation and film growth mostly occur due to an inter-play of other processes such as: simple-ion cluster mechanism, simple hydroxide cluster mechanism, complex ion-by-ion decomposition mechanism, and the complex-cluster decomposition mechanism. As discussed in the literature, the simple ion process could diffuse to the substrate to initiate nucleation and the nucleated layers then grow by adsorption of ions in the solution and or nucleation of new crystals [12]. The films formed by the crystals are mostly held together by weak forces (Van der Waals forces). Comprehensive analyses of the film growth and nucleation processes are discussed extensively in the literature [12, 13, 14].

2.3. Structural and Optical characterisation of the deposited thin films

The characterisation of the films was done as follows; a PANalytical (XPERT=PRO) D8 advance X-ray diffractometer with a CuKα radiation source (λ = 1.5406 Ǻ) was used for the structural characterisation and for the optical characterisation: absorbance (A), (transmittance (T) and reflectance (R) versus wavelength measurements) was done using a UV spectrophotometer. The wavelength scan range was done between 200 nm to 1000 nm.

3 Results

Fig.1 and Fig. 2 gives a typical transmittance and absorbance versus wavelength plots for ZnO, ZnO/NiO, ZnO/MnO and ZnO/CdO thin films grown between 60 minutes. As shown in Fig. 1.ZnO/NiO thin film showed the highest transmittance in the UV region. This followed by ZnO/CdO, while ZnO and ZnO/MnO did not show any significant transmittance in the UV region. Optimum transmittance of about 45% was recorded by ZnO and ZnO/CdO thin films at the far infrared portion of the spectrum. The trend in transmittance suggest that the coating of the core by the shell can greatly affect the transmittance values of ZnO thin films. The transmittance values as displayed, shows that the shell of NiO on ZnO had the highest influence on the transmittance behaviour of ZnO thin films. The sharp rise in the transmittance of ZnO/NiO thin films is an identification of good crystallinity of the film. Films with less transmittance in the UV region will lead to increase in the optical bandgap and it may be attributed to small grain size. Fig. 2 and Fig. 3 show the absorbance and the reflectance spectrum of the deposited thin films. The plot shows that ZnO/CdO and ZnO/NiO thin films were almost non-absorbing at all wavelength while ZnO and ZnO/MnO have absorbance which decreases with wavelength with optimum value of about 0.9. However, ZnO had a peak absorbance value of 2.4. The absorbance trend showed that coating the core-ZnO with shells of CdO, NiO and MnO decreases the absorbance. This trend could be attributed to the substitution of Zn^{2+} with Mn^{x+} , Ni^{x+} and Cd^{x+} where x represent the various oxidation states of the element in question. The reflectance and absorbance curve shows that ZnO, ZnO/CdO and ZnO/MnO are good optical devices [10, 15, 16, 17].

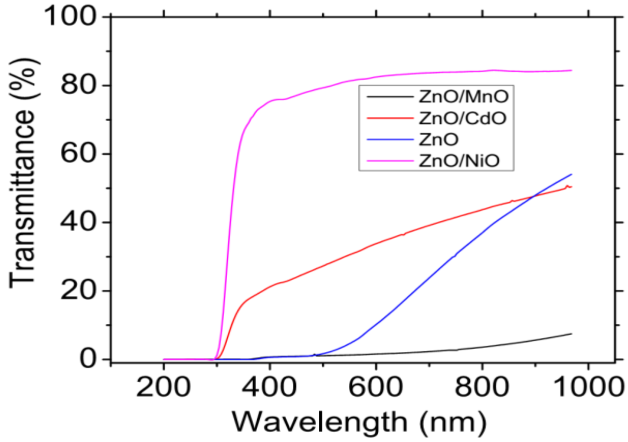

Fig.1 Transmittance vs. Wavelength spectrum of the deposited thin films

The data extracted from the reflectance and absorbance measurements were used to extract some useful optical constants such as refractive index, n. The plot of refractive index against wavelength is displayed in Fig. 4. Maximum refractive index of about 1.34 is displayed by the ZnO thin film which is in close agreement to that obtained by Baydogan *et al* [11]. The plot shows that coating the ZnO thin film with NiO, CdO and MnO has profound effect on the refractive index either by decreasing the index of refraction or by increasing it. This behaviour could be attributed to the filling of zinc vacancies by the manganese, nickel and cadmium ions, resulting to either in the increase or reduction of the grain size [11, 15].

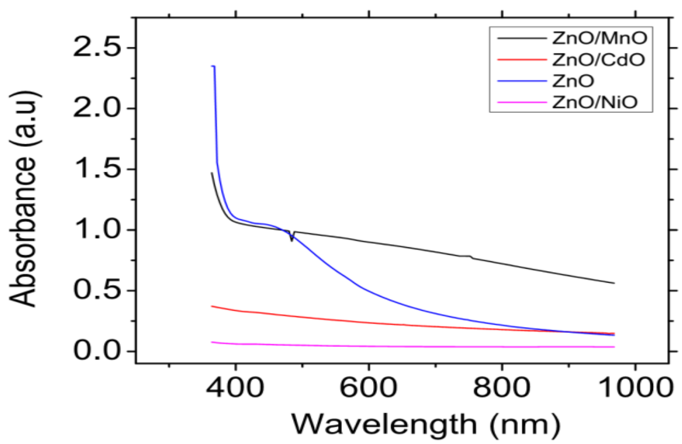

Fig.2 Absorbance vs. Wavelength spectrum of the deposited thin films

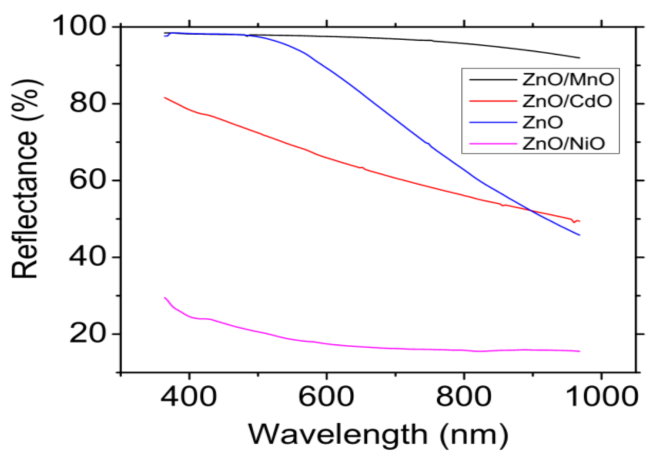

Fig.3 Reflectance vs. Wavelength spectrum of the deposited thin films.

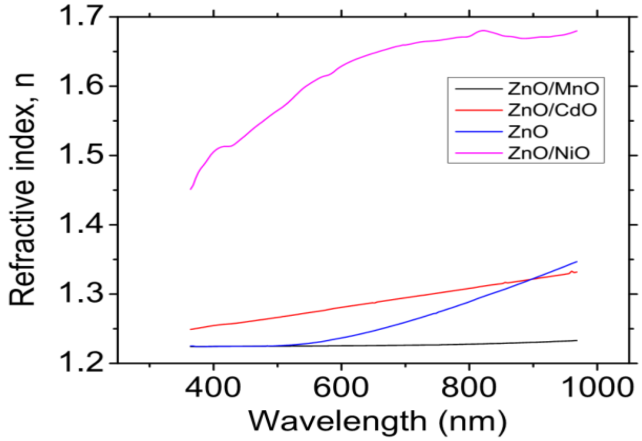

Fig.4 Refractive index vs. Wavelength spectrum of the deposited thin films

In the literature [9, 10, 18, 19, 20, 21], it has been established that the optical reflectance is related to the refractive index as:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad (1)$$

Where n is the refractive index and R is the optical reflectance.

4 Discussion

ZnO thin film as the core and ZnO/MnO,ZnO/NiO and ZnO/CdO as core shell thin films were grown using the chemical bath technique. Optical characterisation and study, revealed that the transmittance, absorbance and refractive index of the core is affected by the shell. The study also showed that NiO as the core has greater influence on the optical properties of the core.

5 Conclusions

In this study the optical properties of core shell thin films with ZnO as the core is investigated. The variation of the transmittance, reflectance, absorbance and refractive index against wavelength has been investigated for the deposited films and our result showed that highest transmittance of about 80% is displayed by ZnO/NiO while ZnO/MnO displayed the lowest value of transmittance. The highest and lowest value of absorbance are 2.5 and 0.2 as displayed by ZnO and ZNo/NiO respectively. The highest index of refraction of about 1.69 is displayed by ZnO/NiO thin film while ZnO/MnO thin film has the lowest value of refractive index that is almost constant with wavelength. Some of these values are within the range suitable for use as window layers in solar cell devices and in other photonic and opto-electronic applications.

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