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Influence of cadmium ion (Cd^{2+})concentration on the optical properties of electrodeposited CdO-NiO thin films.

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Abstract: *CdO-NiO thin films were successfully deposited on glass substrates using electro-deposition technique. Cadmium chloride salt provided source of cadmium ion, citric acid as oxidizing agent, nickel chloride as source of nickel ion, and sodium hydroxide as pH adjuster. The films were deposited at various concentrations. The optical properties were investigated using UNICO-UV-2012 PC spectrophotometer. The optical results showed that the films exhibited interference patterns based on the variation of the transmittance with growth parameter. The maximum transmittances are 63%, 65%, 60% and 64% for 0.01M, 0.05M, 0.07M and 0.1M samples of CdO/NiO thin films respectively. The band-gaps were found to be between 2.38eVand 2.50 eV as the concentrations were varied and have extinction coefficient of that fluctuates between maxima and minima. The properties of high transmittance in the visible region and wide direct band gap of the films suggest that they can be used as window layers in a heterojunction solar cell as well as in optoelectronic applications.*

Keywords: *electro-deposition, band gap, transmittance, concentration, optical*

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I. Introduction

Cadmium oxide is one of the widely studied transparent conducting oxide because of their simultaneously high transparency in the visible spectrum and low resistivity [1, 2].CdO is a degenerate semiconductor with wide band gap that varies from 2.2 to 2.9 eV with increasing carrier density [3]. It shows high n-type conductivity due to the presence of interstitial Cd atoms and oxygen vacancies which both act as donors [3]. Nickel oxide is one of the most exhaustively investigated metal oxide. Reason being that, it is a well suited anode material for Ni-Cd, Ni-Fe, Ni-air secondary batteries, Fuel cells as well as super capacitor applications [4]. Nickel oxide exhibit high capacitive values and are being investigated for miniaturized devices because of their cost effectiveness as compared to activated carbon based electrodes in organic electrolytes [5]. Metal oxides like nickel oxides have found wide application in materials applications such as sensors [6], transparent electrode [7], efficient control of energy inflow-outflow of buildings or automobiles and aerospace [7, 8], large scale optical switching glazing and electronic information display [9].CdO and NiO binary thin films have been prepared using various deposition techniques such as sputtering [10, 11], sol–gel [12, 13], spray pyrolysis [14, 15], chemical bath deposition [16-18], chemical vapour deposition [19, 20] and thermal evaporation [21, 22].Chemical bath deposition method is one of the most widely used techniques in thin film deposition because it offers high quality films with low cost equipments and can easily be tailored to suit different device designs [23].

Currently, the development of core-shell structured materials have been receiving extensive attention due to the potential of tailoring both the lattice parameters and the band gap by controlling depositions parameters [24, 25]. The shell can alter the charge, functionality, and reactivity of surface, or improve the stability and dispersive ability. Furthermore, catalytic, optical, or magnetic functions can be imparted to the core particles by the shell material [26]. In general, the synthesis of core/shell structured material has the goal of obtaining a new composite material having synergetic or complementary behaviours between the core and shell materials [26]. Extensive study on the synthesis of core-shell thin films using chemical bath deposition techniques have been made by different researchers [27-33].

In this present study, CdO-NiOthin films were synthesized using electro-deposition method at variousconcentrations with fixed pHvalue. The optical properties of the films such as transmittance, bandgap and extinction coefficientswere evaluated.

II. Experimental

A conventional three electrode electrochemical cell was used in this research work. It consists of a saturated calomel electrode (SCE) as the reference electrode, platinum foil electrode as the counter electrode and conductive indium Tin Oxide (ITO) glass substrate as the working electrode. A Dazheng DC – power supply, PS – 1502A model and two digital multimeters DT9201A CE were used to set up the deposition apparatus.Before deposition of the thin films, the electrochemical cell bath, without the electrodes was first degreased by dipping it into ethanol. It was next scrubbed with soft rubber sponge in a cold detergent solution. Finally, it was rinsed in distilled water and dried, ready to be used. The electrodes [working electrodes (ITO), the counter electrode (platinum foil) and the reference electrode (saturated calomel electrode)] were polished with 0.05 μm α-alumina powder on a polishing micro-cloth and washed twice with distilled water. The polished and washed conductive surface of the working ITO electrodes provided nucleation centers for the growth of the films thereby producing highly adhesive uniform deposits. The core-CdO films were first deposited from a chemical bath containing 20ml of (0.01M, 0.05M, 0.07M and 0.10M) of $CdCl_2$ corresponding to S_7, S_8, S_9 and S_{10} respectively, 20ml of 0.05M citric acid, 4ml of 1.0M NaOH and 4.5ml of TEA. To deposit CdO/NiO thin films, five samples of CdO thin films were inserted into a chemical bath containing 20ml of 0.01M $NiCl_2.6H_2O$, 20ml of 0.05M citric acid, 4.5ml of 1.0M NaOH and 4.5ml of TEA. The possible chemical reaction for the deposition of CdO thin films proceeded as follows:

$$CdCl_2.H_2O + \text{TEA} \rightarrow \left[Cd(\text{TEA})\right]^{2+} + 2Cl^- + H_2O$$

$$\left[Cd(TEA)\right]^{2+} \rightarrow Cd^{2+} + TEA$$

$$2NaOH + 2Cl^- \rightarrow 2NaCl + 2(OH)^-$$

$$Cd^{2+} + 2(OH)^- \rightarrow CdO + H_2O$$

The kinematics of the chemical reaction for the formation of NiO films proceeded as follows:

$$NiCl_2.6H_2O + TEA \rightarrow \left[Ni(TEA)\right]^{2+} + 2Cl^- + 6H_2O$$

$$\left[Ni(TEA)\right]^{2+} \rightarrow +Ni^{2+} + TEA$$

$$NaOH + 2Cl^- \rightarrow +NaCl + OH^-$$

$$Ni^{2+} + 2OH^- \rightarrow +NiO + H_2O$$

The transmittance measurement was done using UNICO-UV-2012 PC spectrophotometer from which other optical and solid state properties of the films were calculated using mathematical relations.

III. Results and Discussion

The elemental components of Cd, Ni and O were quantitatively obtained from RBS analysis as shown in the RBS micrographs in figures 1 and 2 for CdO and NiO thin films respectively. Other elements present could have come from the glass substrate and some impurities.

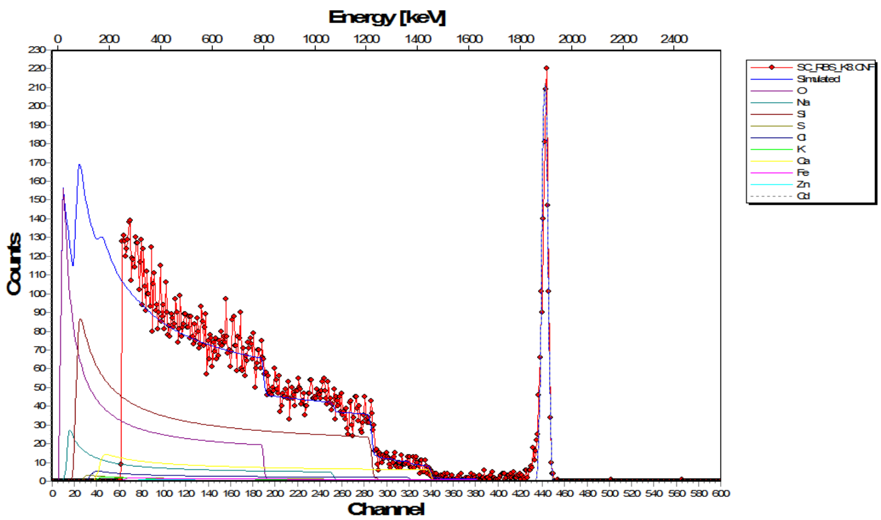

Fig.1: RBS micrograph of CdO thin films

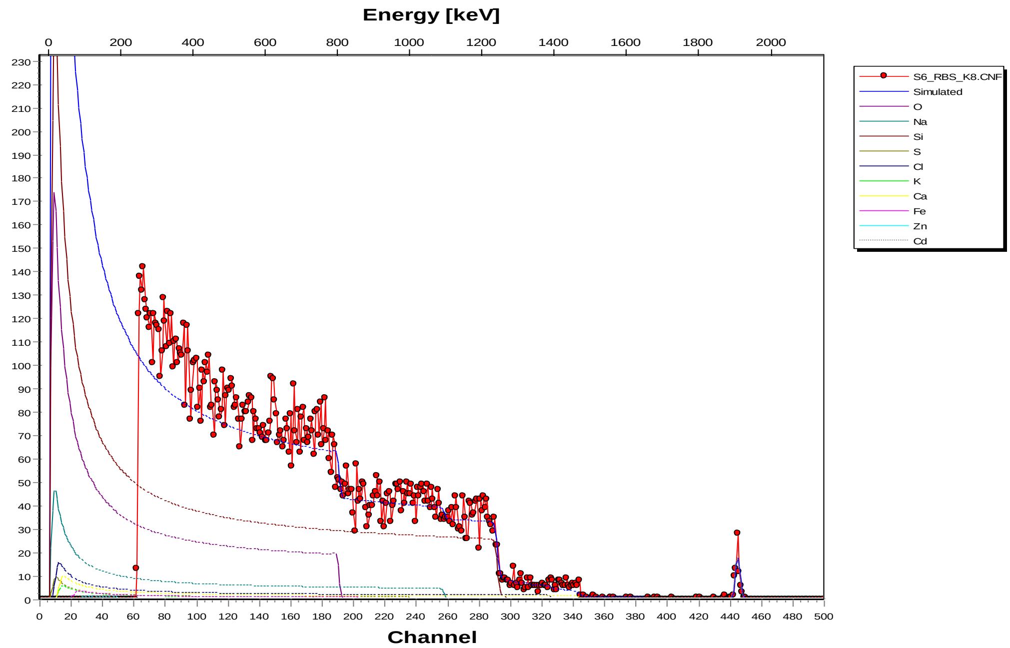

Fig.2: RBS micrograph of NiO thin films

Fig. 3 is the transmittance spectra of CdO-NiO thin films for various concentration of Cd^{2+}. The films showedirregular variation of transmittance with wavelength in the visible region of electromagnetic spectrum. All the samples exhibited maximum transmission of solar radiation in the visible region at 470m. With respect to changes in concentration, the transmittance showed no trend with the growth parameter. The maximum transmittances are 63%, 65%, 60% and 64% for S_7, S_8, S_9 and S_{10} samples of CdO/NiO thin films respectively.A steady decrease in transmittance of the films were observed within 800-1000 nm which indicates poor absorbance and reflectance of solar radiation by the thin films. The film with concentration of 0.05M exhibited the highest transmittance of 65%.The transmittance spectra of the deposited films showed some observed interference pattern. This may be due to the difference in the refractive index of the film and the substrate used. The interference pattern displayed by the transmittance spectra showed that the films deposited in this research work are homogenous.This property makes it good material for solar thermal application in flat-plate-collectors, and house heating for solar chick brooding[34, 35]. The transmittance of thin films can be greatly modified by different growth parameters. In the literature, the variation of transmittance with annealing temperatures [27-33, 36-40], concentration [41-43], deposition time [44-48] and P^H [49-52] have been reported.

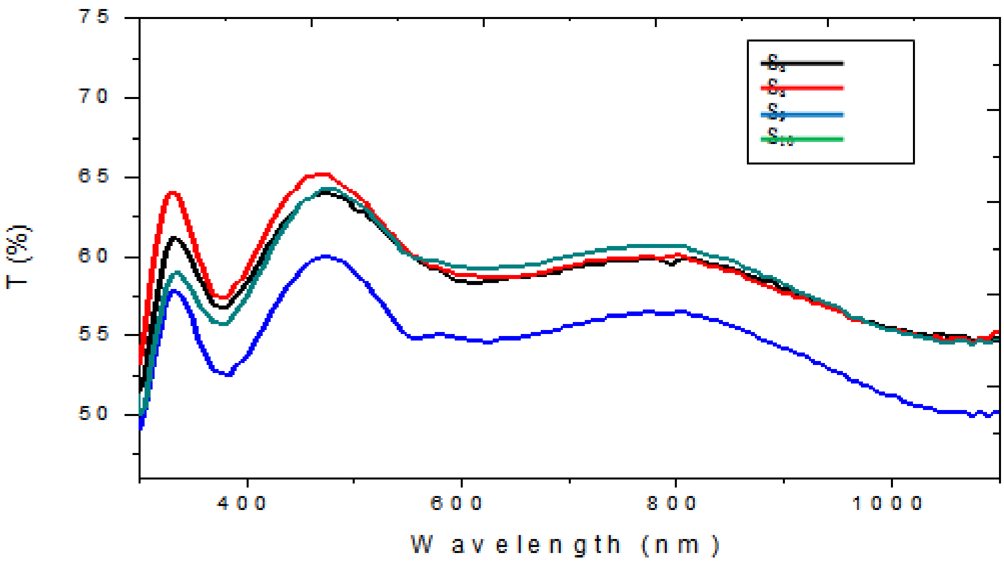

Fig. 3: Plot of transmittance vs wavelength of CdO-NiO

Fig.4 depicts the graph of $(\alpha h\upsilon)^2$ as function of photon-energy hυ for the determination of energy band gap of the grown films. The approximate straight portion of the curve is extrapolated to the horizontal axis where the band-gap energiesare read. The energy band gap values are 2.38eV, 2.50eV, 2.40eV and 2.48eV for $S_{7,}$ S_8, S_9 and S_{10} samples respectively. Clearly, the energy band gap varied with parametric variation of concentration of the principal precursor solutions. The energy band gap of CdO thin films as widely reported are 2.45-2.55eV [53], 2.35-2.50eV [54] and 2.54-2.58eV [55]. Accordingly, our values are within the range reported in the literature for binary CdO thin films, indicating that the coating of NiO films on CdO thin films has no significant effect on the energy band gap. The energy band gap values are in the range suitable for applications as window layers in heterojunction solar cell. The primary function of a window layer in a heterojunction is to form a junction with the absorber layer while admitting a maximum amount of light to the junction region and the absorber layer [56].

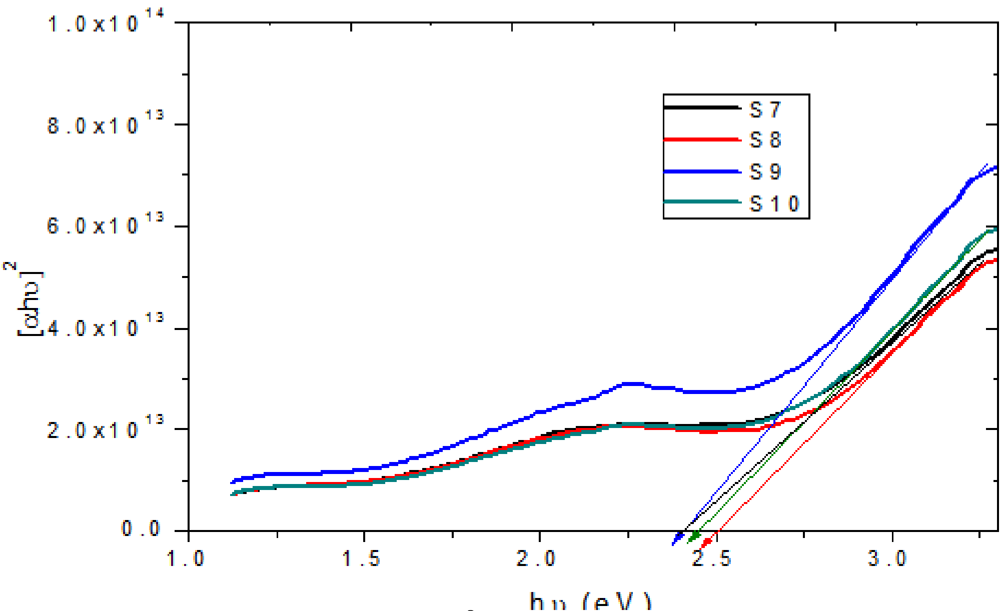

Figure 4: Plot of agraph of $(\alpha h\upsilon)^2$ as function of photon-energy (hυ)

The plot of extinction coefficient versus photon energy is shown in fig.5. The extinction coefficient generally fluctuates between maxima and minima. The film sample, $S_{9,}$ has the maximum value of about 0.254.

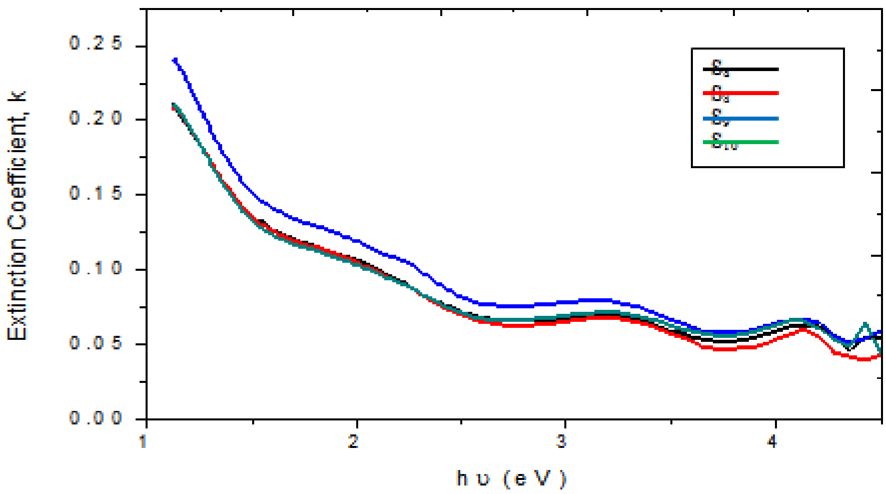

Figure 5: Plot of extinction coefficient vs hυ

IV. Conclusion

Thin films of CdO-NiO have been deposited on ITO glass substrates by electro-deposition method. The elemental components of Cd, Ni and O were quantitatively obtained from RBS analysis confirming the formation of CdO-NiO thin films. The optical properties of the films within the UV-VIS-NIR indicates that the transmittance varied with concentration of the principal precursor solution. The maximum transmittances are 63%, 65%, 60% and 64% for S_7, S_8, S_9 and S_{10} samples of CdO/NiO thin films respectively. The energy band gap values are 2.38eV, 2.50eV, 2.40eV and 2.48eV for $S_{7,}$ S_8, S_9 and S_{10} samples respectively. Based on the exhibited properties of the films, it can be concluded that they are suitable materials for the construction of poultry houses, solar cell fabrication as well as in optoelectronic devices.

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