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RESEARCH ARTICLE

EFFECT OF DEPOSITION VOLTAGE ON THE OPTICAL PROPERTIES OF NICKEL COBALT OXIDE NANOFILMS DEPOSITED BY ELECTRODEPOSITION METHOD

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ABSTRACT

Nickel cobalt oxide nanofilms were grown by electrodepositing method using heptahydrated nickel tetraoxosulphate (VI) salt as source of nickel ion, Citric acid as oxidizing agent, hexahydrated cobalt chloride salt as source of cobalt ion, and Sodium hydroxide as pH adjuster. The deposition voltage was varied from 8.5V to 14.5V in intervals of 1.5V. Results of the study show that the films exhibit low absorbance and low reflectance in all the regions of electromagnetic spectrum; and high transmittance in the regions. The optical properties viz, absorbance, reflectance, refractive index, extinction coefficient, are directly proportional to the deposition voltage while percentage transmittance is inversely proportional.

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INTRODUCTION

This research is aimed at growing Nickel cobalt oxide nanofilms at various deposition voltages with cobalt as dopant; and studying the effects on the optical properties with a view to ascertaining the possible applications. Metal oxides, such as nickel oxides have found wide material applications such as glazing and electronic information display (Yu *et al.,* 1987), sensors (Mutschall *et al.,* 1996), transparent electrode (Fantini and Gorenstein, 1987), efficient control of energy inflow-outflow of buildings, automobiles and aerospace (Fantini and Gorenstein, 1987; Carpenter *et al.,* 1987), large scale optical switching, Nickel oxide thin films could be deposited by different methods such as evaporation, sputter deposition, sol gel, electrochemical and chemical techniques (Mutschall *et al.,* 1996; Berkat *et al.,* 2005). Hufner (1994) in his work electronic structure of Nio and related 3d-transition metal compounds obtained a bandgap of 4.3ev (Hufner, 1994). In their work spectroscopic ellipsometry characterization of electrochromic tungsten oxide and nickel oxide thinfilms made by sputter deposition Valyukh *et al.* (2010) obtained direct bandgaps of 3.95ev, 3.97ev, 3.63ev for Nickel oxide (Valyukh *et al.,* 2010). NiO thin film has a direct bandgap which decreases from 3.90eV to 2.10eV as the film thickness increases (Ezema *et al.,* 2008). Wide bandgap semiconductors are materials that have bandgap significantly greater than those of Silicon 1.1ev and as such allow power electronic components to be smaller, faster, more reliable, and more efficient than their silicon (Si)-based counterparts. They are high-efficiency data centres and show promise as compact power supply for consumer electronics (Department, 2013). Being lightly doped with cobalt, $NiCo_2O_4$ is a dilute magnetic semiconductor. Dilute magnetic semiconductors are ideal materials for spintronics (Zheng Nan, 2008). It has been found that nickel oxide (NiO) is nearly transparent wide band-gap semiconductor and shows p-type semi-conducting behavior. A slightly nonstoichiometric composition in NiO thin film occurs due to acquisition of an excess of oxygen (which is compensated by the oxidation of some Ni2+ to Ni3+) and is responsible for the p-type semi-conducting behaviors. The p-type semiconductor transparent conducting oxide is important for the fabrication of transparent conducting p-n junction for many optoelectronic devices (Hiromichi Ohta *et al.,* 2000). The conductivity of NiO thin films has dependence on the formation of micro-structural defects such as nickel vacancies and interstitial oxygen in NiO (Antolini, 1992).

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MATERIALS AND METHODS

The substrates used in the deposition were Indium tin oxide (ITO), which were prepared by washing with detergent.

They were rinsed three times with distilled water, and soaked in acetone for fifteen minutes to degrease them. The substrates were then rinsed in distilled water three times without any body contact to avoid contamination, then immersed in a beaker almost half-full of distilled water and put inside Shanghai ultrasonics (SY-180) for ultrasonic bath for ten minutes. Thereafter, they were brought out using clean forceps, put in another clean dry beaker, and put inside the oven for ten minutes for drying. The clean substrates ready for use were handled with clean forceps to avoid contamination. The precursors for deposition of nanofilms of $NiCo_2O_4$ at various deposition voltages are Heptahydrated nickel tetraoxosulphate (vi) salt as source of nickel ion, Citric acid as oxidizing agent, Hexahydrated Cobalt Chloride salt as source of cobalt ion and sodium hydroxide as pH adjuster. The deposition was carried out at room temperature of 303K, pH of 8.6, deposition time of ten minutes, percentage doping of 8%, constant concentrations and volumes of Citric acid, Sodium hydroxide, $NiSO_4.7H_2O$ and $CoCl_2.6H_2O$ and varying deposition voltage as shown in the Table 3.2. The deposited films were annealed at 200^0C for thirty minutes.

Where α = absorption coefficient and λ = wavelength (Bakr Nabeel *et al.,* 2011)

3.1.3: Refractive index (n)

The refractive index of the films was calculated using the relation:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \qquad \text{.................................(3)}$$

Where R = reflectance (Rubby Das and Suman Pandey, 2011)

3.1.4: Absorption coefficient (α)

The absorption coefficient α, is a property of a material which defines the amount of light absorbed by it (Katarzyna Skorupska, 2014)

The absorption coefficient of the films was calculated using the relation as given by:

Table 1. Variation of deposition voltage for $NiCo_2O_4$ nanofilms

Reaction bath	$NiSO_4.7H_2O$		Citric acid		$CoCl_2.6H_2O$		NaOH		Deposition voltage(V)	pH	% Doping	Time (mins)
	Conc.(M)	Vol.(ml)	Conc.(M)	Vol.(ml)	Conc.(M)	Vol.(ml)	Conc.(M).	Vol.(ml)				
N_6	0.046	15	0.05	30	0.004	15	1	6	8.5	8.6	8	10
N_1	0.046	15	0.05	30	0.004	15	1	6	10.0	8.6	8	10
N_7	0.046	15	0.05	30	0.004	15	1	6	11.5	8.6	8	10
N_8	0.046	15	0.05	30	0.004	15	1	6	13.0	8.6	8	10
N_9	0.046	15	0.05	30	0.004	15	1	6	14.5	8.6	8	10

3.0: Theory

3.1: Analysis of optical properties

The optical properties of the films were analysed using the following mathematical tools.

3.1.1: Reflectance

Reflectance is the fraction of incident electromagnetic power that is reflected at an interface (Klein Miles and Furtak Thomas, 1986). The mathematical tool used in analysis of the reflectance of the films is

$$R = 1 - A - T \qquad \text{.......................... (1)}$$

Where A = absorbance, T = transmittance (Rubby Das and Suman Pandey, 2011), However the Absorbance and transmittance were obtained by the spectrophotometer characterization. In optics and spectroscopy, transmittance is the fraction of incident light (electromagnetic radiation) at a specified wavelength that passes through a sample (Verhoeven, 1996)

3.1.2: Extinction coefficient (k)

The extinction coefficient is a measure of the fraction of light lost due to scattering and absorption per unit distance of the penetration medium.

Extinction coefficient thus:

$$k = \frac{\alpha\lambda}{4\pi} \qquad \text{...........................(2)}$$

$$\alpha = A/\lambda \qquad \text{................................(4)}$$

Where A = Absorbance and λ = wavelength

3.1.5: Photon energy (hυ)

Photon energy is given by:

$$E = h\upsilon \qquad \text{...................................(5)}$$

Where h = Planck's constant = 6.63×10^{-34}Js, υ = frequency of photon (Nadeem and Waqas Ahmed, 2000)

$$\text{However } \nu = \frac{c}{\lambda} \qquad \text{.........................(6)}$$

Where c = velocity of light = $3\text{x}10^8$m/s and λ = wavelength, Therefore Photon energy can be calculated by the relation:

$$E = \frac{hc}{\lambda} \qquad \text{...........................(7)}$$

In terms of electron volt, $1eV = 1.602 \times 10^{-19}J$,

Planck's constant $h = \frac{6.63\times10^{-34}Js}{1.602\times10^{-19}J} \approx 4.14 \times 10^{-15}eV$

∴ Photon energy $E = \frac{4.14\times10^{-15}eV\times3\times10^{8}m/s}{\lambda(m)}$ = …..eV

3.2: Structural analysis

3.2.1: Average crystallite size (D)

Using the Debye-Scherrer formular, the average crystallite size is calculated by

$$D = \frac{k\lambda}{\beta cos\theta} \quad \text{…………………………(8)}$$

Where shape factor k ≈ 0.9 , λ = wavelength of the X-ray radiation, β= full width at half maximum (FWHM) of the diffraction path, θ = diffraction angle

3.2.2: Dislocation density (δ)

The dislocation density is calculated by Williamson and Smallman's formular thus:

$$\delta = \frac{1}{D^2} \text{ (lines/m}^2\text{)} \quad \text{…………………(9)}$$

3.2.3: Microstrain (ε)

The microstrain is calculated using the relation,

$$\varepsilon = \frac{\beta cos\theta}{4} \quad \text{…………………………..(10)}$$

RESULTS

3.3: Bandgap (Eg)

The bandgap of the film is obtained by a graph of square of absorption coefficient against the photon energy. The straight part of the graph is extrapolated to the photon energy axis (horizontal axis), and the bandgap is the energy value corresponding to zero value of absorption coefficient squared (zero value of vertical axis).

Variation of absorbance with deposition voltage for Nickel cobalt oxide nanofilms (Fig. 1)

Absorbance of the film increases with increasing deposition voltage. However beyond 10 V, the film over thickens, peels off from the slide and starts building up afresh. This occurrence creates new trend of direct proportionality starting from 11.5V.

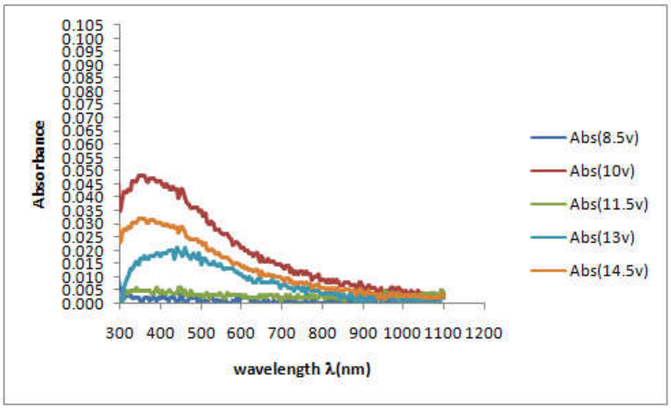

Figure 1. Variation of absorbance with deposition voltage for $NiCo_2O_4$ nanofilm

Variation of transmittance with deposition voltage for Nickel cobalt oxide nanofilms (Fig. 2)

Transmittance of the film decreases with increasing deposition voltage. However, peeling off effect creates a new trend of inverse proportionality starting from 11.5V.

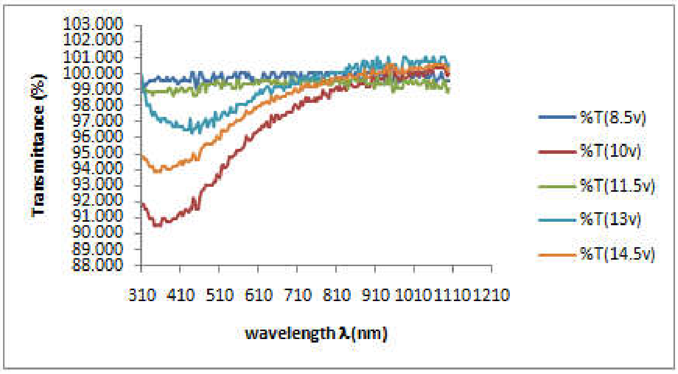

Figure 2. Variation of transmittance with deposition voltage for $NiCo_2O_4$ nanofilm

Variation of reflectance with deposition voltage for Nickel cobalt oxide nanofilms (Fig. 3)

Reflectance of the film increases with increasing deposition voltage. However due to peeling off effect at voltages beyond 10V, a new trend of direct proportionality occurs starting from 11.5V.

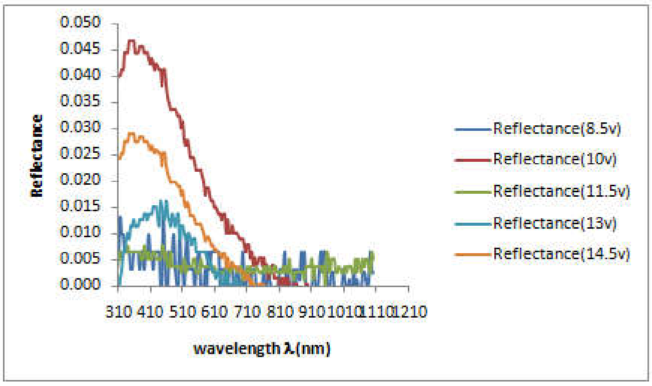

Figure 3. Variation of reflectance with deposition voltage for $NiCo_2O_4$ nanofilm

Variation of Refractive index with deposition voltage for Nickel cobalt oxide nanofilms (Fig. 4)

Refractive index of the film increases with increasing deposition voltage. Beyond 10V, peeling off effect occurs resulting to a new trend of direct proportionality starting from 11.5V.

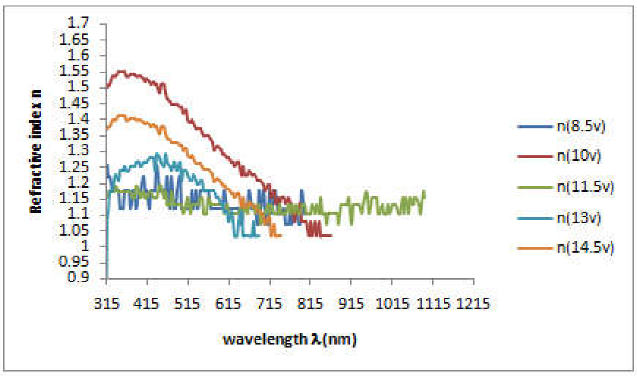

Figure 4. Variation of refractive index with deposition voltage for $NiCo_2O_4$ nanofilm

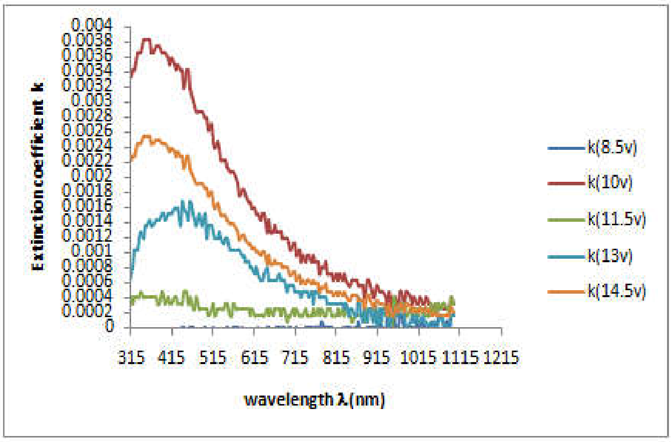

Figure 5. Variation of extinction coefficient with deposition voltage for $NiCo_2O_4$ nanofilm

Variation of Extinction coefficient with deposition voltage for Nickel cobalt oxide nanofilms (Fig. 5)

Extinction coefficient of the film increases with increasing deposition voltage. However due to peeling off effect at voltages beyond 10V, a new trend of direct proportionality occurs starting from 11.5V.

Bandgap of Nickel cobalt oxide naofilm at deposition voltage of 10V (Fig. 6)

The film has a direct allowed bandgap of 2eV

Morphorlogical analysis of Nickel cobalt oxide nanofilm (Fig. 7)

The micrograph reveals that the film is polycrystalline.

Structural analysis of Nickel cobalt oxide nanofilm (Fig. 8)

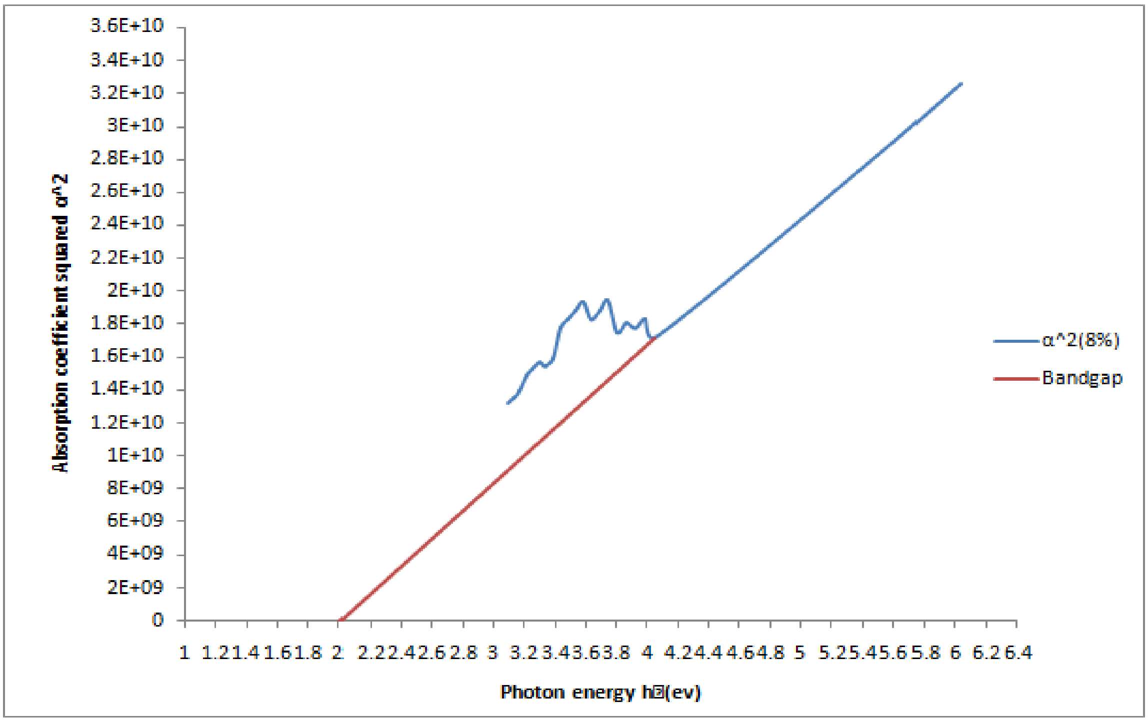

Figure 6. Graph of absorption coefficient squared versus Photon energy for Nickel Cobalt oxide nanofilm (Deposition voltage 10V)

Figure 7. Optical micrograph of $NiCo_2O_4$ nanofilm

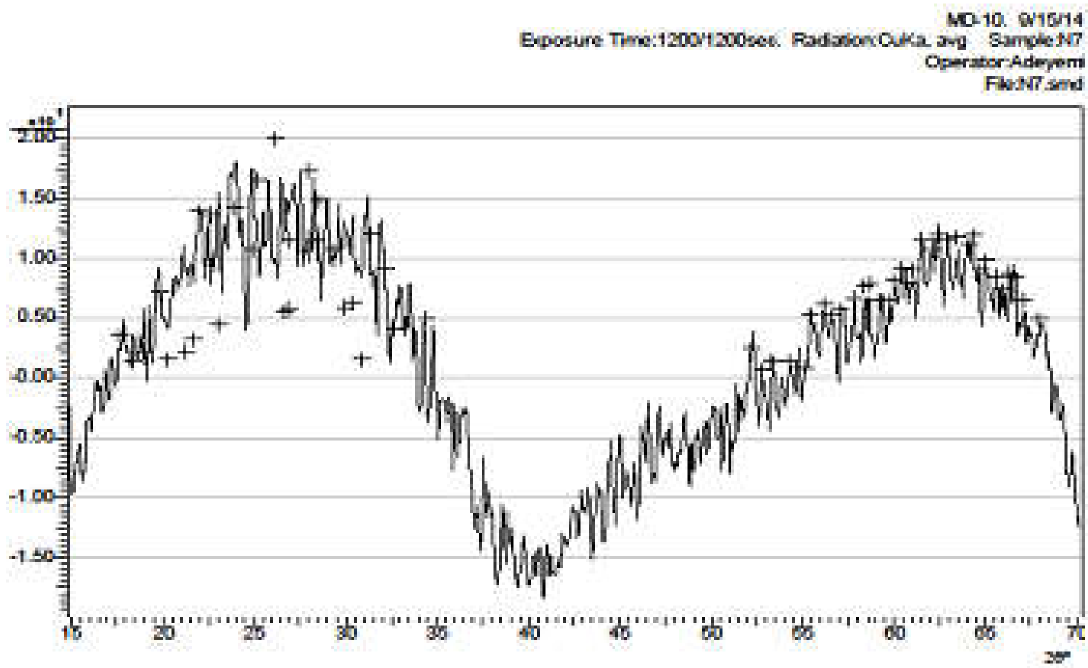

Figure 8. XRD Pattern of $NiCo_2O_4$

DISCUSSION

As shown in Figure 1, absorbance of the films is generally low in all the regions of electromagnetic spectrum; maximum of 0.045 = 4.5% in the UV region and decreases to zero in near infra red region. Absorbance of the film is directly proportional to the deposition voltage. Result from Figure 2 shows that the film has high transmittance in all the regions of electromagnetic spectrum; minimum of 90.5% in UV region and tends to 100% in NIR. Transmittance of the film is inversely proportional to the deposition voltage. These properties of low absorbance and high transmittance in all the regions, makes the film a good material for solar cell, photothermal application and phosphors. Figure 3 shows that the reflectance of the film is generally low in all the regions; maximum of 0.047=4.7% in UV region and tends to zero in NIR region. The reflectance is directly proportional to deposition voltage. This makes the film a good material for antireflection coating. Low reflectance in NIR region makes the film a good material for cold mirror. As shown in Figure 4, the film has maximum refractive index of 1.5 in UV region. Voltages beyond 10V have lower refractive index due to peeling off effect. The refractive index is directly proportional to deposition voltage. Extinction coefficient of the film is directly proportional to the deposition voltage. As shown in Figure 6, the film has a wide bandgap.

This property makes it a veritable material in light emitting diodes, satellite communications, high frequency, and high power radar, sensors. It also makes power electronic components to be smaller, faster, more reliable, and more efficient than silicon based counterparts. Wide bandgap-based power electronics could also accelerate development of high-voltage DC power lines which will operate more efficiently than existing high-voltage AC transmission lines and has tolerance for higher operating temperatures (Pursuing the Promise, 2013). Result of structural analysis show that the film is cubic in structure with average crystallite size of 1.278nm, dislocation density of 0.673 and microstrain of 0.2797.

Conclusion

Nickel cobalt oxide nanofilm could be grown by electrodeposition method. The optical properties viz: absorbance, reflectance, refractive index, extinction coefficient are directly proportional to the deposition voltage while transmittance is inversely proportional. The film is a wide bandgap semiconductor.

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