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EFFECT OF COBALT DOPING 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 percentage doping was varied from 3% to 23% in intervals of 5%. Results of the study show that optical properties viz absorbance, reflectance, refractive index, extinction coefficient, are directly proportional to percentage doping with cobalt while percentage transmittance is inversely proportional. However, the films exhibit low absorbance and reflectance in all the regions of electromagnetic spectrum and high transmittance in the regions.**
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***Index Terms*— D: Optical properties; A: semiconductors; A: nanostructures; B: Crystal growth**

I. INTRODUCTION

This research is aimed at growing Nickel cobalt oxide nanofilms at various percentages doping with cobalt and studying the effects on the optical properties with a view to ascertaining the possible applications. Deposition of Nickel oxide thin film could be achieved by different methods such as evaporation, sputter deposition, sol gel, electrochemical and chemical techniques [1, 2]. Metal oxides, such as nickel oxides have found wide material applications such as efficient control of energy inflow-outflow of buildings, automobiles and aerospace [3, 4], large scale optical switching, glazing and electronic information display [5], sensors [1], transparent electrode [3]. 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 [6]. Hufner (1994) in his work electronic structure of Nio and related 3d-transition metal compounds obtained a bandgap of 4.3ev [7]. NiO thin film has a direct bandgap which decreases from 3.90eV to 2.10eV as the film thickness increases [8].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 [9]. Being lightly doped with cobalt, NiCo2O4 is a dilute magnetic semiconductor. Dilute magnetic semiconductors are ideal materials for spintronics [10]. 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 conductivity of NiO thin films has dependence on the formation of micro-structural defects such as nickel vacancies and interstitial oxygen in NiO [11].The p-type semiconductor transparent conducting oxide is important for the fabrication of transparent conducting p-n junction for many optoelectronic devices [12].

II. MATERIALS AND METHOD

Indium tin oxide (ITO) used as deposition substrates were washed with detergent and rinsed three times with distilled water. They were soaked in acetone for fifteen minutes to degrease them, and then rinsed in distilled water three times without any body contact to avoid contamination. The substrates were immersed in a beaker almost half-full of distilled water and put inside Shanghai ultrasonic's (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 NiCo2O4 at various percentages of Cobalt dopant 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, and deposition voltage of 10V. Fixed concentrations and volumes of Citric acid and Sodium hydroxide were used while the concentrations of NiSO4.7H2O and CoCl2.6H2O were varied in accordance with their percentage doping as shown in the table 1 below. The deposited films were annealed at 2000C for thirty minutes. Characterization of absorbance and percentage transmittance of the films was done with UV/Visible spectrophotometer while other optical properties were calculated accordingly. Characterization of structural property was done by X-Ray diffraction (XRD) while compositional characterization was done with X-Ray fluorescence (XRF) spectrometer. Optical micrograph of the film was done with Olympus microscope.

Table1. Variation of percentage doping with cobalt

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_{10}	0.049	15	0.05	30	0.001	15	1	6	10	8.6	3	10
N_1	0.046	15	0.05	30	0.004	15	1	6	10	8.6	8	10
N_{11}	0.043	15	0.05	30	0.006	15	1	6	10	8.6	13	10
N_{12}	0.041	15	0.05	30	0.009	15	1	6	10	8.6	18	10
N_{13}	0.039	15	0.05	30	0.011	15	1	6	10	8.6	23	10

3.0: Theory

3.1: Analysis of optical properties

The following mathematical tools were employed in the analysis of the following optical properties

3.1.1: Reflectance

Reflectance is the fraction of incident electromagnetic power that is reflected at an interface [13]

The Reflectance of the films were calculated using the relation

………………………..(1)

Where A = absorbance, T = transmittance [14], 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 [15]

3.1.2: Refractive index (n)

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

…………………………….(2)

Where R = reflectance [14]

3.1.3: Absorption coefficient (α)

The absorption coefficient α, is a property of a material which defines the amount of light absorbed by it [16]

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

……………………………(3)

Where A = Absorbance and □ = wavelength

3.1.4: 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:

………………………..(4)

Where α = absorption coefficient and □ = wavelength [17]

3.1.5: Photon energy (h□)

Photon energy is given by:

E = h□ ………………………………(10)

Where h = Planck's constant = Js, □ = frequency of photon [18]

However ……………………(11)

Where c = velocity of light = 3x108m/s and □ = wavelength, Therefore Photon energy can be calculated by the relation:

………………………(12)

In terms of electron volt, ,

Planck's constant

Photon energy = …..eV

3.2: Structural analysis

3.2.1: Average crystallite size (D)

The average crystallite size of the films was calculated using the Debye-Scherrer formular thus:

…………………………(13)

Where shape factor k ≈ 0.9 , □ = wavelength of the X-ray radiation, , θ = diffraction angle

3.2.2: Dislocation density (δ)

This can be evaluated from Williamson and Smallman's formular thus:

(lines/m2) …………………(14)

3.2.3: Microstrain (ε)

This can be calculated using the relation,

…………………………..(15)

3.3: Bandgap (Eg)

To obtain the bandgap of the film, square of absorption coefficient is plotted against the photon energy. The straight part of the graph is extrapolated to the photon energy axis (horizontal axis), and the energy corresponding to zero value of absorption coefficient squared (zero value of vertical axis) is noted as the bandgap.

III. RESULTS AND DISCUSSION

4.1: **Variation of absorbance with percentage doping with cobalt for Nickel cobalt oxide nanofilms**

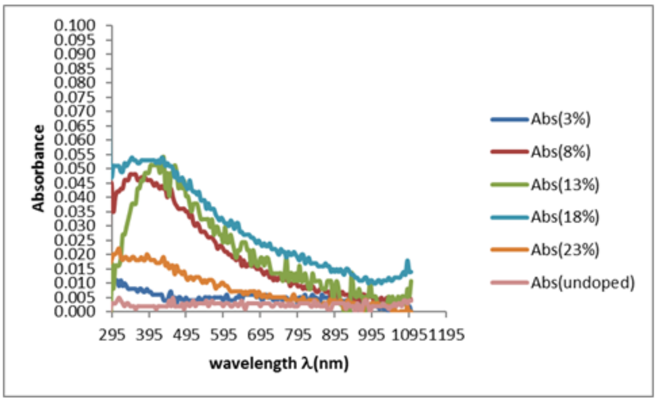

Figure 1: Variation of absorbance with percentage doping for NiCo2O4 nanofilm

The result as shown in figure 1 shows that the absorbance of Nickel cobalt oxide nanofilm is very low. The films have highest absorbance in the UV region (with the highest absorbance of 0.053=5.3% in the UV region) and tends to zero in the near infra red region of the electromagnetic spectrum. However the absorbance increases with increasing percentage doping, not minding the case of 23% doping which deviated from the trend due to peeling off effect from the slide as it over thickened and started depositing afresh. The absorbance of the undoped film is very low in all the regions.

4.2: variation of transmittance with percentage doping with cobalt

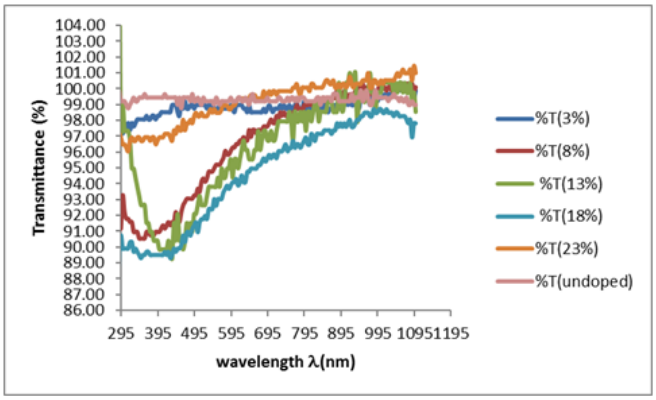

Figure 2: Variation of percentage transmittance with percentage doping for NiCo2O4 nanofilm.

Result from figure 2 shows that transmittance of the film is minimum (89.31% for 18%) in the UV region and maximum(≈100%) in the near infra red region of the electromagnetic spectrum. However, the transmittance decreases with increasing percentage doping, not minding the peeling off effect, which caused the deviation of 23% from the trend.

4.3: variation of Reflectance with percentage doping with cobalt

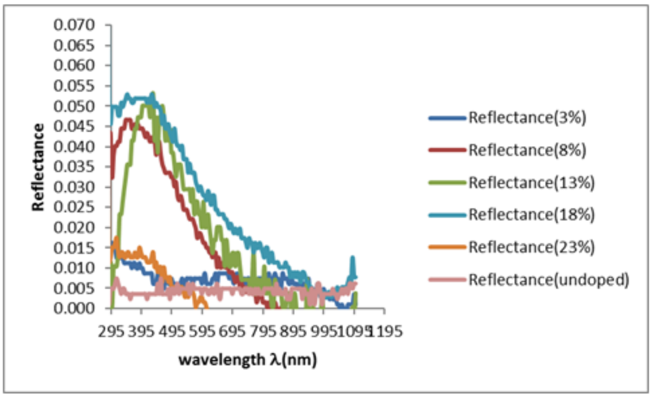

Figure 3: Variation of Reflectance with percentage doping for $NiCo2O_4$ nanofilm.

From figure 3, the films generally have very low reflectance. They have maximum reflectance (0.053≈5.3%) in the UV region which decreases to zero in the near infra red region of the electromagnetic spectrum. However the reflectance increases with increasing percentage doping, not minding 23% which deviated due to peeling off effect.

4.4**: variation of Refractive index with percentage doping with cobalt**

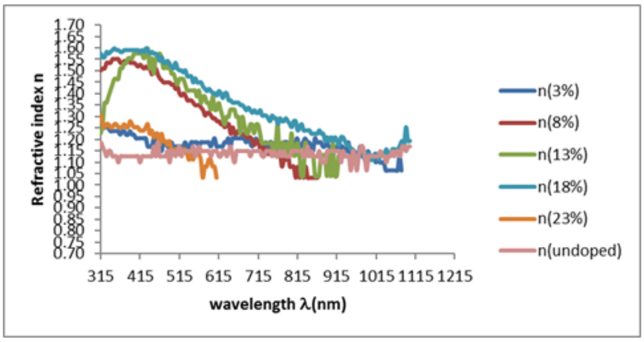

Figure 4: Variation of Refractive index with percentage doping for NiCo2O4 nanofilm.

From figure 4, the film 18% doping has the maximum refractive index (1.58) in the UV region and decreases to minimum(1.16) in the NIR region. 3% doped film has maximum refractive index of 1.25 in UV region and decreases to minimum (1.07) in NIR. The undoped film has the minimum refractive index (1.15) in the UV region. However, the refractive index increases with increasing percentage doping, not minding 23%, which deviated from the trend due to peeling off effect as the film over thickens.

4.5: Variation of extinction coefficient with percentage doping with cobalt

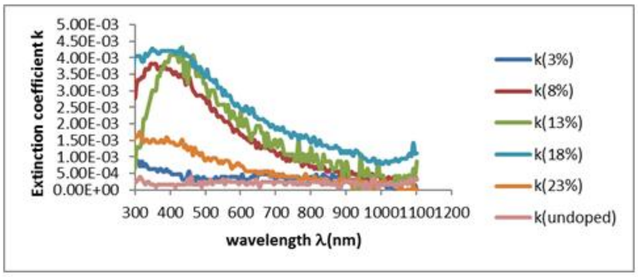

Figure 5: Variation of extinction coefficient with percentage doping for NiCo2O4 nanofilm.

Result from figure 5 shows that18% doped film has the maximum extinction coefficient 4.22E-03 in the UV region and minimum 8.75E-04 in the NIR, 3% doped film has maximum of 7.16E-04 in the UV region and tends to zero in the NIR region. The extinction coefficient of undoped film is 1.59E-04 in UV and tends to zero in NIR.The extinction coefficient increases with increasing percentage doping not minding 23%, which deviated from the trend due to peeling off effect of the film as it, became thicker.

4.6: BANDGAP

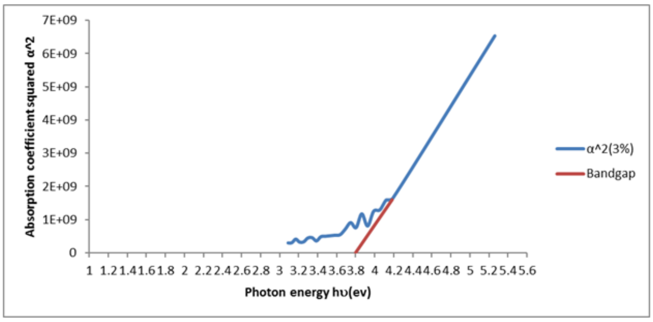

Figure 6: Graph of absorption coefficient squared versus Photon energy for Nickel Cobalt oxide nanofilm.(3% doping with cobalt).

From figure 6, 3% cobalt doped nickel oxide nanofilm has a direct allowed bandgap of 3.8ev.

4.7: MORPHORLOGICAL ANALYSIS

Figure 7: Optical micrograph of NiCo2O4 nanofilm

The micrograph as shown in figure 10 reveals that the film is polycrystalline and uniformly deposited on the slide

4.8: COMPOSITIONAL ANALYSIS

Table 2: Compositional analysis for Nickel cobalt oxide nanofilm

N10	3	76.3067	21.3333	2.3600
N1	8	72.3046	21.3321	6.2933
N11	13	68.4399	21.3334	10.2267
N12	18	64.5099	21.3301	14.1600
N13	23	60.5745	21.3322	18.0933

4.9: Structural analysis

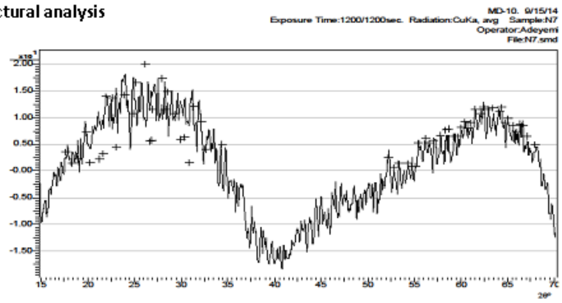

Figure 8: XRD Patterns for Nickel cobalt oxide nanofilms

IV. DISCUSSIONS

Result from figure 1, shows that the absorbance of the films is generally very low. It has maximum in the second half of UV region (0.053=5%) and decreases to zero in the NIR region of electromagnetic spectrum. The absorbance of the films is directly proportional to the percentage doping with cobalt. The deviation of 23% from the trend is due to peeling off effect whereby the film over thickened, peeled off from the slide and started building up again. This development made the film less thick like the lightly doped ones. This low absorbance property makes the film a good material for Solar cell, Photothermal heating. From figure 2, the transmittance of the films is generally high in the UV-VIS-NIR regions . The minimum trasmittance of the films is 89.5% in the UV region and increases to maximum 100% in the NIR region. This property makes the films useful in photothermal application, Phosphors and Solar cell. However, the transmittance of the films is inversely proportional to the percentage doping with cobalt. As shown in figure 3, the reflectance of the films is very low in all the regions, maximum of 0.053= 5.3% in the UV region, and decreases to zero in the near infra red region of the electromagnetic spectrum. This property makes the film good material for antireflection coating. The reflectance increases with increasing percentage doping with cobalt, not minding 23% which deviated from the trend due to peeling off effect as the film gets thicker. Low reflectance in the Infrared region makes the film a good material for cold mirror. As shown in figure 4, the films exhibit maximum refractive index in the UV region, and decrease to minimum in the NIR. The lower percentage doped film and undoped have low refractive indices while the higher percentage doped have average refractive index in the UV region.. The film could be good material for multilayer antireflection coating in the visible region and in film stalk for colour selective coatings. Extinction coefficient the films are directly proportional to the percentage doping. The films have maximum extinction coefficient in the UV region and decrease to zero in the NIR. 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.

As a dilute magnetic semiconductor, NiCo2O4 nanofilm finds good application in Spintronics, hard disks, magnetic discs, micro drive. As wide bandgap semiconductor, it is applicable 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 [19]

V. CONCLUSION

Cobalt doped Nickel oxide nanofilm could be prepared by electrodeposition method. The optical properties viz; absorbance, reflectance, refractive index, extinction coefficient, are directly proportional to percentage doping with cobalt while percentage transmittance is inversely proportional. The film is a wide bandgap semiconductor.

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