Effects Of Deposition Voltage On The Optical Properties Of Cadmium Cobalt Oxide Nanofilms Deposited By Electrode Position Method

Umeokwonna N.S, Ekpunobi A.J.

Department of Industrial Physics Chukwuemeka Odumegwu Ojukwu University Uli
Department of Physics and Industrial Physics Nnamdi Azikiwe University Awka
nicksunny87@yahoo.com

Abstract: Cobalt doped Cadmium Cobalt Oxide nanofilms were deposited by electrodeposition method using hexahydrated Cobalt Chloride salt as source of Cobalt ion, hydrated Cadmium Chloride salt as source of Cadmium ion, Citric acid as oxidizing agent, 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 work show that the optical properties viz; absorbance, reflectance, and refractive index are directly proportional to the deposition voltage while transmittance is inversely proportional. The film exhibits high transmittance in all the regions of electromagnetic spectrum but low absorbance and reflectance in the regions. It is a wide bandgap semiconductor

KEY WORDS: Nanofilms; Doping; Optical properties; Bandgap

1 INTRODUCTION

This aim of this work is to deposit Cadmium cobalt oxide nanofilms by electrodeposition method and determine the effect of deposition voltage on the optical properties with a view to ascertaining the possible applications. Many method abound for the deposition of Cadmium oxide thin films such as solution growth [3], radio frequency sputtering [2] and spray pyrolysis[1]. Nanostructures of CdO have been prepared by many methods like DC magnetron sputtering [7], spray pyrolysis [4] and sol-gel method [6]. Many attractive properties associated with CdO includes high transmission coefficient in visible spectral domain, large energy bandgap, remarkable luminescence characteristics etc. This semiconductor has been widely studied for applications in photovoltaic device [10], photodiodes [11], optoelectronic applications in transparent conducting oxides (TCO) [8], solar cells [9]. Other areas of application includes low-emissive windows, thin-film resistors,[13], Infra red heat mirror, gas sensors [12], As a result its applications, specifically in the field of optoelectronic devices such as solar cells [14], photo transistors and diodes, transparent electrodes, and gas sensors [15] there has been focused research on the semiconductor in recent years.

2.0 MATERIALS AND METHOD

I TO Used as deposition substrate were washed with detergent and rinsed three times with distilled water. They were soaked in acetone for fifteen minutes to degrease them. They were again rinsed in distilled water three times without any body contact to avoid contamination. They were immersed in a beaker almost half-full of distilled water and put inside Shanghai ultrasonics (SY-180) for ultrasonic bath for ten minutes. They were again brought out using clean forceps and put in another clean dry beaker and put inside the oven for ten minutes for drying. The slides ready for use were always handled with clean forceps to avoid contamination. The precursors for deposition of nanofilms of $CdCo_2O_4$ at various deposition voltages are hydrated Cadmium Chloride salt as source of Cadmium 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, $CdCl_2.2\frac{1}{2}H_2O$ and $CoCl_2.6H_2O$ and varying deposition voltage as shown in the table 1. The deposited films were annealed at 200^0C for thirty minutes.

***Table 1**: Variation of deposition voltage for $CdCo_2O_4$ nanofilm*

Reaction bath	$CdCl_2.2\frac{1}{2}H_2O$		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_{32}	0.046	15	0.05	30	0.004	15	1	6	8.5	8.6	8	10
N_{28}	0.046	15	0.05	30	0.004	15	1	6	10	8.6	8	10
N_{33}	0.046	15	0.05	30	0.004	15	1	6	11.5	8.6	8	10
N_{34}	0.046	15	0.05	30	0.004	15	1	6	13	8.6	8	10
N_{35}	0.046	15	0.05	30	0.004	15	1	6	14.5	8.6	8	10

3.0 THEORY/CALCULATIONS

3.1 Analysis of optical properties

Mathematical tools applied in the analysis of the optical properties are as follows;

3.1.1 Refractive index (n)

By the mathematical relation as given by Rubby et al (2011) [16], the refractive index of the films was calculated using the relation:

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

Where R = reflectance

3.1.2 Reflectance

Using the relation according to Rubby et al (2011) [16]: the reflectance is calculated thus;

$$R = 1 - (A + T) \qquad (2)$$

Where A = absorbance, T = transmittance, However the Absorbance and transmittance were obtained by the spectrophotometer characterization.

3.1.3 Absorption coefficient (α)

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

$$\alpha = \frac{A}{\lambda} \qquad (3)$$

Where A = Absorbance and λ = wavelength

3.1.4 Photon energy (hυ)

Nadeem et al (2000) [17], Photon energy is given by:

$$E = h\upsilon \qquad (4)$$

Where h = Planck's constant = 6.63×10^{-34}Js, υ = frequency of photon,

$$\text{However } v = \frac{c}{\lambda} \qquad (5)$$

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

$$E = \frac{hc}{\lambda} \qquad (6)$$

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

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

$$\therefore \text{Photon energy } E = \frac{4.14\times10^{-15}\text{eV}\times3\times10^{8}\text{m/s}}{\lambda(\text{m})} = \text{.....eV} \qquad (7)$$

3.2 Structural analysis

3.2.1 Average crystallite size (D)

Debye-Scherrer formular is employed in calculation of the average crystallit size thus;

$$D = \frac{k\lambda}{\beta\cos\theta} \qquad (8)$$

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 of the film is evaluated using Williamson and Smallman's formular thus;

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

3.2.3 Microstrain (ε)

This is calculated using the relation,

$$\varepsilon = \frac{\beta\cos\theta}{4} \qquad (10)$$

3.3 Bandgap (E_g)

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

4.0 RESULTS

4.1 Variation of Optical properties with deposition voltage for $CdCo_2$ O4 nanofilms

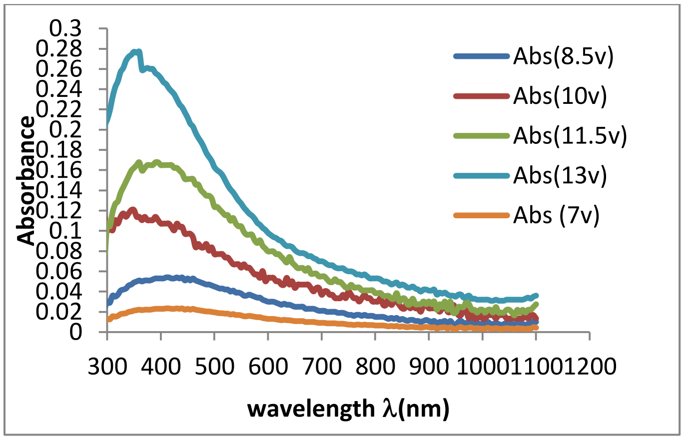

Fig. 1: *Variation of absorbance with deposition voltage for $CdCo_2O_4$ nanofilm*

The absorbance of the film increases as deposition voltage increases.

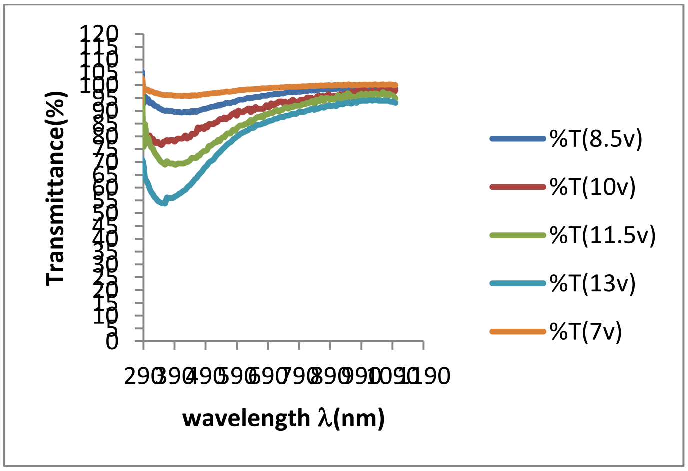

Fig. 2: *Variation of transmittance with deposition voltage for $CdCo_2O_4$ nanofilm*

The transmittance of the film decreases as deposition voltage increases.

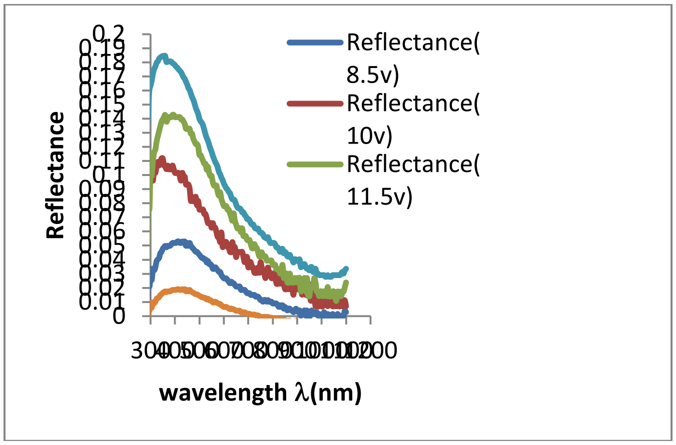

Fig. 3: *Variation of reflectance with deposition voltage for $CdCo_2O_4$ nanofilm*

The Reflectance of the film increases as deposition voltage increases.

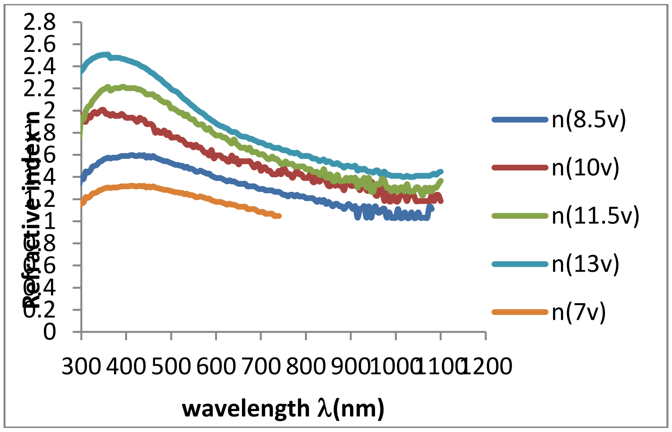

Fig. 4: *Variation of refractive index with deposition voltage for $CdCo_2O_4$ nanofilm*

The Refractive index of the film increases as deposition voltage increases.

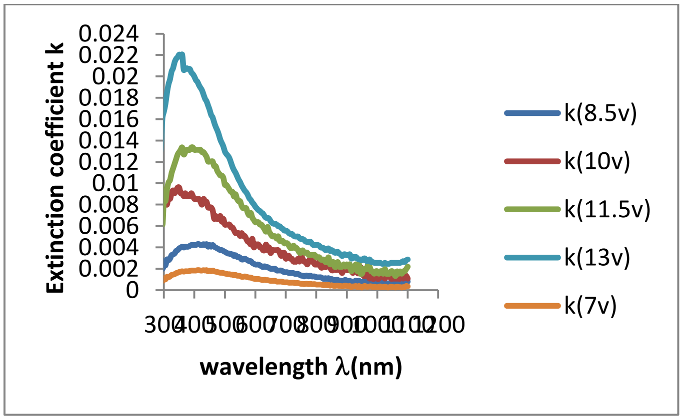

Fig.5: *Variation of extinction coefficient with deposition voltage for $CdCo_2O_4$ nanofilm*

The extinction coefficient of the film increases as deposition voltage increases.

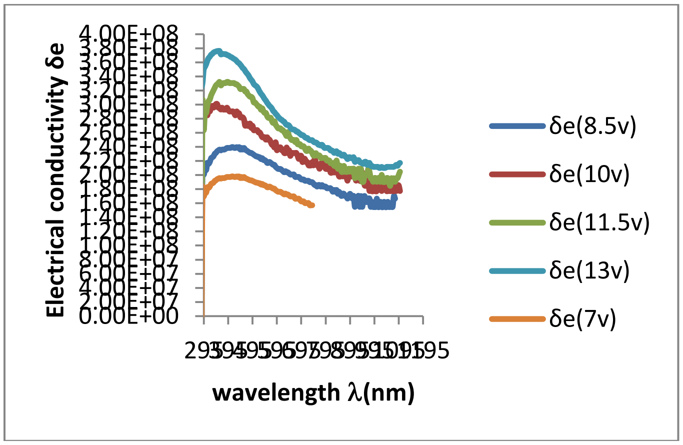

Fig. 6: *Variation of electrical conductivity with deposition voltage for $CdCo_2O_4$ nanofilm*

The electrical conductivity increases as deposition voltage increases.

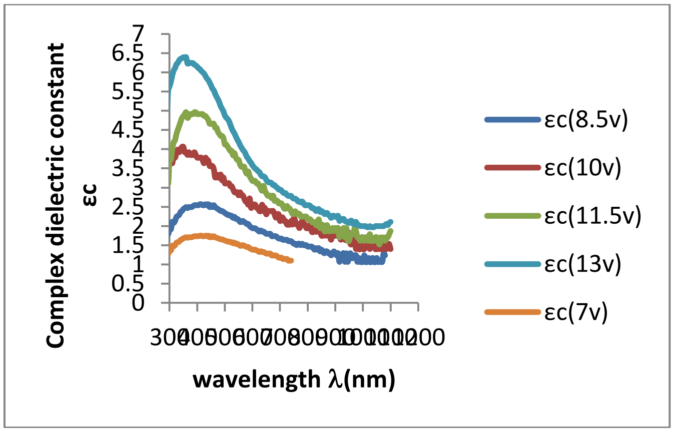

Fig. 7: *Variation of Complex dielectric constant with deposition voltage for $CdCo_2O_4$ nanofilm*

The complex dielectric constant of the film increases as deposition voltage increases.

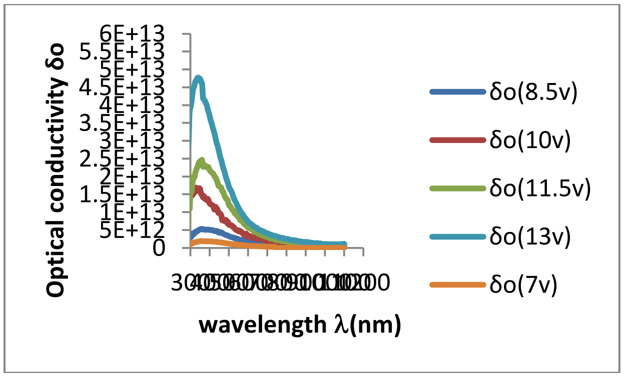

Fig. 8: *Variation of Optical conductivity with deposition voltage for $CdCo_2O_4$ nanofilm*

The optical conductivity of the film increases as deposition voltage increases.

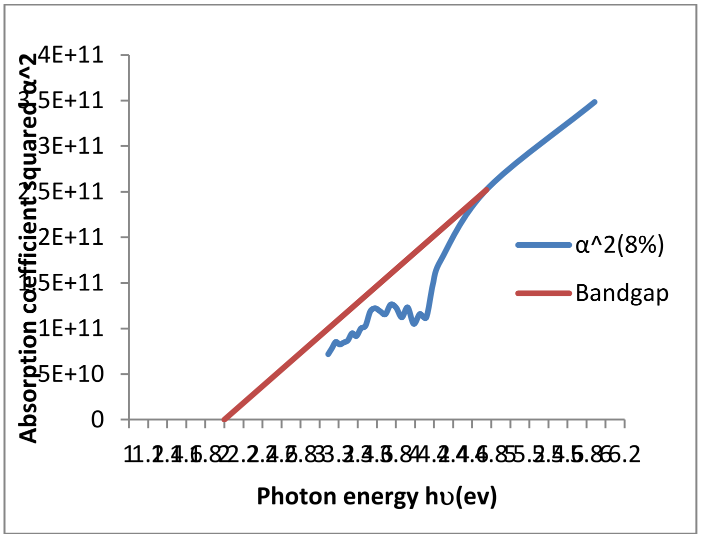

Fig.9: *Absorption coefficient squared versus Photon energy*

The film has a wide direct bandgap of 2eV

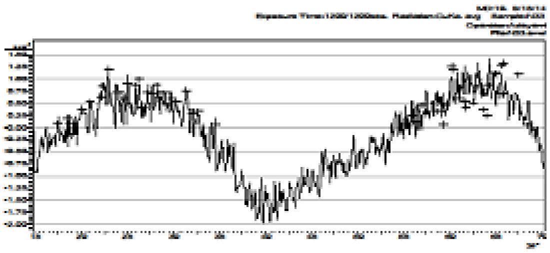

Fig.10: *XRD patterns of* $CdCo_2O_4$

6.0 Discussions

As shown in figure 1, absorbance of the films is generally low in all the regions of electromagnetic spectrum; maximum of 0.274 = 27.4% in the UV region and tends to zero in the NIR region. Absorbance of the film is directly proportional to the deposition voltage. From figure 2, transmittance of the films is high in all the regions of electromagnetic spectrum; minimum of 53.84% and maximum of 96.3% in the UV region and tends to 100% in NIR region. Transmittance of the films is inversely proportional to the deposition voltage. Low absorbance and high transmittance in the regions makes the film a good material for solar cell, phosphors and photothermal applications. Figure 3 shows that the reflectance of the films is generally low in all thr regions of electromagnetic spectrum; maximum of 0.186 = 18.6 % in the UV region. Reflectance of the films is directly proportional to the deposition voltage. This property makes the film a veritable material for antireflection coating and cold mirror. Figure 4 shows that refractive index o the film low in the UV region at low deposition voltages; 1.32 for 7V, however at higher voltages the refractive index is high; 2 , 2.5 for 10V and 13V respectively. The film is a good material for multilayer antireflection coating. Refractive index of the film is directly proportional to deposition voltage. As shown in figure 9, the film has a bandgap of 2eV . According to US department of energy 2013, as wide bandgap semiconductor, the films find good application as enabling material for high density power application, satellite communications, high power radar. It is applicable in LED that can produce10times more light than incandescence bulbs and last longer by 30 times or more. It allows power electronic components to be smaller, faster, more reliable and more efficient. It also permits devices o operate at much higher temperature, voltage and frequency. XRD analysis reveals that the film is monoclinic in structure, with average crystallite size of 1.988nm, dislocation density of 0.259/nm^2 and microstrain of 0.176.

7.0 REFERENCES

[1] R.L Mishra , A.K. Sharma , S.G. Prakash , " Gas sensitivity and characterization of cadmium oxide semiconducting thin film deposited by spray pyrolysis technique," Digest Journal of Nanomaterials and Biostructures, Vol.4, no.3,pp. 511-518, 2009

[2] N. Veda , H. Meada , H. Hosono and H. Kawazoe , "Band-gap widening of CdO thin films," Journal of Applied Physics, Vol. 84, pp. 6174, 1998

[3] K. Gurumurugan , D. Mangalraj and S.K. Narayanandas, "Correlations between the optical and electrical properties of CdO thin films deposited by spray pyrolysis," Thin Solid Films, vol. 251, pp. 7, 1994

[4] P. C. Shindov, "CdO thin films deposited by spray pyrolysis," Electronics, pp. 22-24, 2004

[5] H. Khallaf, C. Chen, L. Chang, O. Lupan, A. Dutta, H. H. A. Shenouda, L. Chow, "Investigation of chemical bath deposition of CdO thin films using three different complexing agents," Applied Surface Science, vol. 257, pp. 9237–9242, 2011

[6] S. Sakthivel , D. Mangalaraj , "Cadmium Oxide Nano Particles by Sol-Gel and Vapour-Liquid-Solid Methods," Nano Vision, vol. 1, no. 1, pp. 47-53, 2011

[7] T.K. Subramanyam , N.B. Srinivasulu , S. Uthanna, "Studies on dc magnetron sputtered cadmium oxide films," Applied Surface Science, vol.169, no. 170, pp. 529-534, 2001

[8] D.L. Zhiyong Zhao , C.S. Morel Ferekides, "Electrical and optical properties of tin-doped CdO films deposited by atmospheric metalorganic chemical vapor deposition," Thin Solid Films, vol. 413, pp. 203–211, 2002

[9] A.M. Baranov , Y.A. Malov , D.F. Zaretsky, S.A. Tereshin, "Solar cells based on the heterojunction a-C/p-Si," Solar Energy Materials & Solar Cells, vol. 60, pp. 11-17, 2000

[10] C.H. Champness, K. Ghoneim, J.K. Chen, “Optimization of CdO layer in a Se-CdO Photovoltaic cell,” Canadian Journal of Physics, vol. 63, pp.767, 1985

[11] R. Kondo , H. Okhimura , Y. Sakai, “Electrical properties of Semiconductor Photodiodes with Semitransparent films,” Japan Journal of Applied Physics, vol. 10, pp. 176, 1971

[12] R.L. Mishra , A.K. Sharmaa , S.G. Prakash , “Gas sensitivity and characterization of cadmium oxide (CdO) semi conducting thin film deposited by spray pyrolysis technique,” Digest Journal of Nanomaterials and Biostructures, vol. 4, no. 3, pp. 511–518, 2009

[13] D.O. Gomez, R.A. Arias-Carbajal, J. Campos, M.T.S. Nair, P.K. Nair, “Formation of Conductive CdO Thin Films on Photoconductive CdS thin films for Window Layer Applications in Solar Cells,” Mod. Phys. Lett. B, vol. 17, pp. 609-612, 2001

[14] D.M. Galicia , R.C. Perez, O.J. Sandoval, S.J.S. Sandoval and C.I.Z. Romero, “High transmittance CdO thin films obtained by the sol-gel method,” Thin Solid Film,vol. 371, pp. 105-108, 2000

[15] R.S. Mane, H.M. Pathan , C.D. Lokhande and S.H. Han, “An effectve use of nanocrystalline CdO thin films in dye-sensitized solar cells,” Solar Energy, vol. 80, pp. 185-190, 2006

[16] D. Rubby and S. Pandey, “Comparison of optical properties of bulk and nano crystalline thin films of CdS using different precursors,” Intrenational Journal of Material Science, vol. 1, no. 1, pp. 35-40, 2011

[17] M.Y. Nadeem and W. Ahmed, “Optical properties of ZnS thin films,” Turk Journal of Physics, vol. 24,pp. 651-659, 2000

[18] US.Department, “Wide bandgap Semiconductors: Pursuing the Promise,” 2013