Effects of Cobalt Doping on the Optical Properties of Cadmium Cobalt Oxide Nanofilms Deposited by Electrodeposition Method

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Abstract: Cobalt doped Cadmium Cobalt Oxide nanofilms were grown by electrodeposition method using 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 percentage doping was varied from 3% to 23% in intervals of 5%. Results of the work show that the absorbance, reflectance, and refractive index are directly proportional to percentage doping with cobalt while transmittance is inversely proportional. The film exhibits low absorbance and reflectance while transmittance is generally high in all the regions of the electromagnetic spectrum.

KEY WORDS: Doping; Optical properties; Nanofilms; Bandgap

1. INTRODUCTION

This research is aimed at growing Cadmium cobalt oxide nanofilms by electrodeposition method and determining the effect of cobalt doping on the optical properties with a view to ascertaining the possible applications. Cadmium oxide thin films can be prepared by various techniques viz spray pyrolysis[1], radio frequency sputtering [2], and solution growth [3]. A Variety of techniques has been employed to prepare CdO nanostructure such as spray pyrolysis [4], chemical vapour deposition [5], sol-gel method [6] and DC magnetron sputtering [7]. CdO has many attractive properties such large energy bandgap, high transmission coefficient in visible spectral domain, remarkable luminescence characteristics etc. This material has been widely studied for optoelectronic applications in transparent conducting oxides (TCO) [8], solar cells [9], photovoltaic device [10], photodiodes [11] as well as other types of applications like Infra red heat mirror, gas sensors [12], low-emissive windows, thin-film resistors, etc [13]. In recent years, researchers have focused on cadmium oxide (CdO) due to its applications, specifically in the field of optoelectronic devices such as solar cells

[14], photo transistors and diodes, transparent electrodes, and gas sensors [15]

2. MATERIALS AND METHODS

ITO slides 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, 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 ultrasonics (SY-180) for ultrasonic bath for ten minutes. They were brought out using clean forceps, and put in another clean dry beaker, and dried in the oven for ten minutes. The substrates ready for use were handled with clean forceps to avoid contamination. The precursors for deposition of nanofilms of $CdCo_2O_4$ with various percentages of Cobalt dopant 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, and deposition time of ten minutes. The deposition voltage was maintained at 10V. Constant concentrations of Citric acid and Sodium hydroxide were used but varied in $CdCl_2.2\frac{1}{2}H_2O$ and $CoCl_2.6H_2O$ in accordance with the percentage doping as shown in the table 1. The deposited films were annealed at 200^0C 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 by X-Ray fluorescence (XRF). Optical

Micrograph of the film was done with Olympus microscope.

Table 1: Variation of percentage doping for Cadmuim cobalt oxide 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_{27}	0.048	15	0.05	30	0.001	15	1	6	10	8.6	3	10
N_{28}	0.046	15	0.05	30	0.004	15	1	6	10	8.6	8	10
N_{29}	0.044	15	0.05	30	0.006	15	1	6	10	8.6	13	10
N_{30}	0.041	15	0.05	30	0.009	15	1	6	10	8.6	18	10
N_{31}	0.039	15	0.05	30	0.011	15	1	6	10	8.6	23	10

3.0: THEORY/CALCULATIONS

3.1: Analysis of optical properties

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

3.1.1: Reflectance

The Reflectance of the films was calculated using the relation according to Rubby *et al* (2011) [16]:

$R = 1 - (A + T)$

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

3.1.2: Refractive index (n)

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

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

Where R = reflectance

3.1.3: Absorption coefficient (α)

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

$\alpha = \frac{A}{\lambda}$

Where A = Absorbance and λ = wavelength

3.1.4: Photon energy (hυ)

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

E = hυ

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

However $\nu = \frac{c}{\lambda}$

Where c = velocity of light = $3x10^8$m/s and λ = wavelength, Therefore Photon energy is calculated by the relation:

$$E = \frac{hc}{\lambda}$$

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)

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

$D = \frac{k\lambda}{\beta cos\theta}$

Where shape factor k ≈ 0.9 , λ = wavelength of the X-ray radiation,

$\beta = full\ width\ at\ half\ maximum (FWHM) of\ the\ diffraction\ path$

, θ = diffraction angle

3.2.2: Dislocation density (δ)

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

$\delta = \frac{1}{D^2}$ (lines/m²)

3.2.3: Microstrain (ε)

This is calculated using the relation,

$\varepsilon = \frac{\beta cos\theta}{4}$

3.3: Bandgap (E_g)

To obtain the bandgap of the film, square of absorption coefficient was plotted against the photon energy. The straight part of the graph was 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.

4. RESULTS AND DISCUSSIONS

4.1: Absorbance

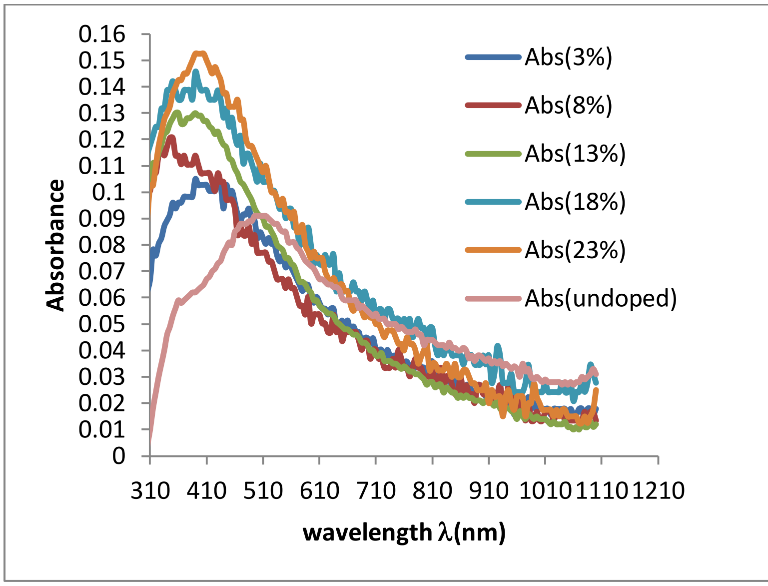

Fig. 1: Variation of absorbance with percentage doping for $CdCo_2O_4$ nanofilm.

From figure 1, absorbance of the films is generally very low. The absorbance of the doped film is maximum in the UV region (0.15 = 15%) while the undoped has maximum in the visible region (0.089 = 8.9%) and decreases to minimum in the NIR region of electromagnetic spectrum. Absorbance of the film is directly proportional to the percentage doping with cobalt.

4.2: Transmittance

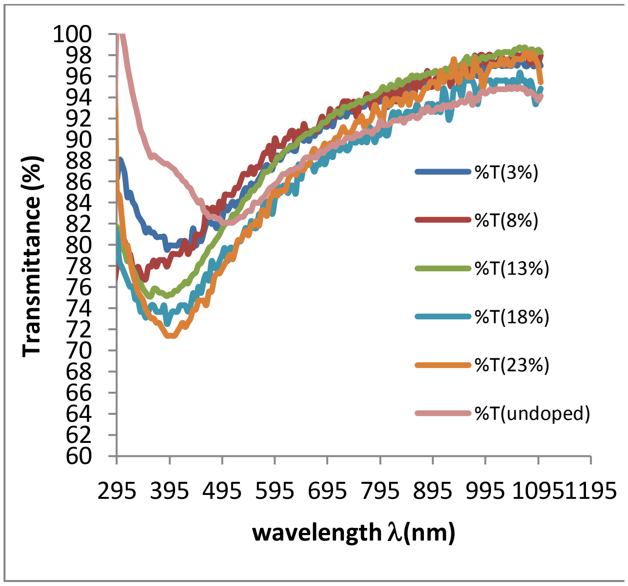

Fig.2: Variation of transmittance with percentage doping for $CdCo_2O_4$ nanofilm.

By the result as shown in fig. 2, the transmittance of the films is generally high in all the regions of electromagnetic spectrum. Transmittance of the doped film is minimum in the UV region (71.39%) while the undoped has minimum (82.5%) in the visible region and tend to 100% in the NIR . Transmittance of the film is inversely proportional to the percentage doping with cobalt.

4.3: Reflectance

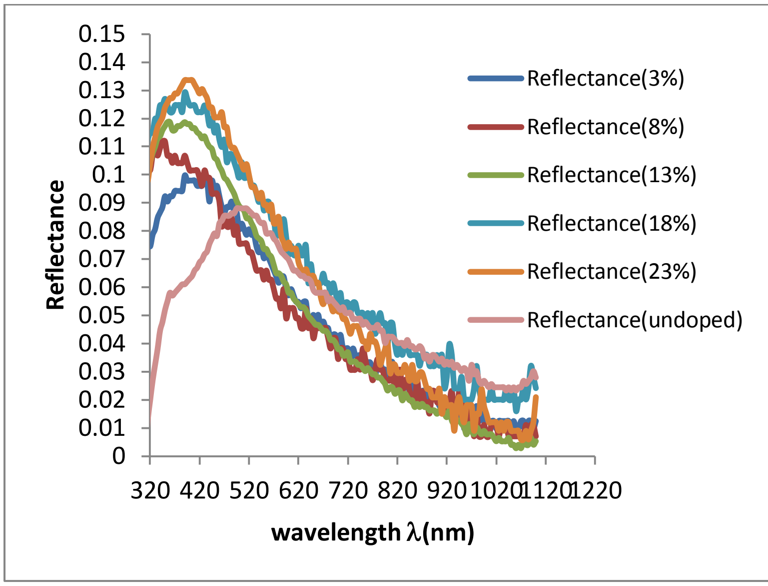

Fig.3: Variation of Reflectance with percentage doping with cobalt for $CdCo_2O_4$ nanofilm.

From figure 3, the film generally has very low reflectance in all the regions of electromagnetic spectrum. Reflectance of the doped film is maximum in the UV region (0.13 = 13%) while the undoped has maximum in the visible region (0.085 = 8.5%) and decreases to minimum in the NIR region of electromagnetic spectrum. Reflectance of the film is directly proportional to the percentage doping with cobalt.

4.4: Refractive index

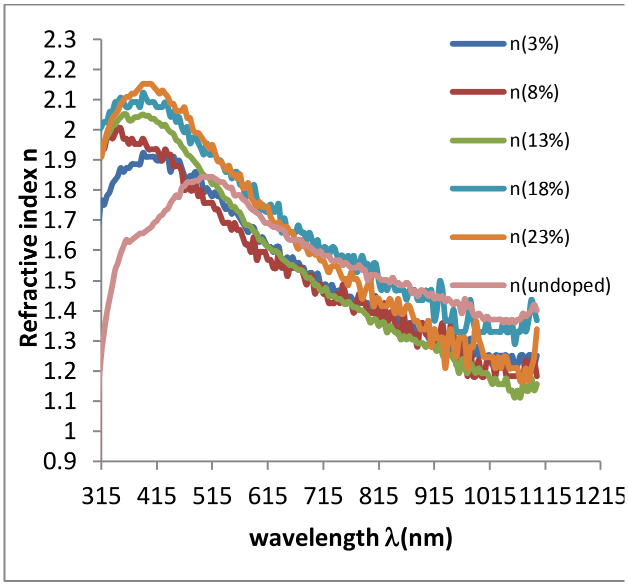

Figure 4: Variation of refractive index with percentage doping for $CdCo_2O_4$ nanofilm

Result as shown in figure 4 indicates that generally the film has high refractive index in the UV region. Refractive index of the doped film is maximum in the UV region (2.15) while the undoped has maximum in visible region (1.78) and decreases to minimum in the NIR region of electromagnetic spectrum. Refractive index of the film is directly proportional to the percentage doping with cobalt.

4.5: BANDGAP

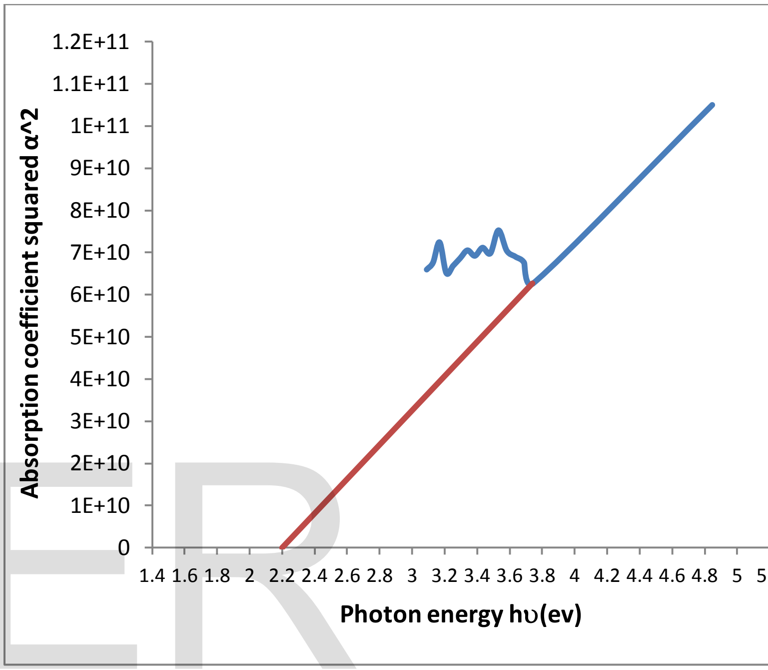

Figure 5: Graph of absorption coefficient squared versus photon energy for 3% Cobalt doped Cadmium Cobalt oxide nanofilm.

From the graph as shown in figure 5, 3% cobalt doped Cadmium Cobalt oxide nanofilm has a direct allowed bandgap of 2.2ev.

4.6: COMPOSITIONAL ANALYSIS

The compositional analysis of the film is shown in table 2

Table 2: Compositional analysis for Cadmium Cobalt Oxide nanofilm

Sample	Percentage doping	Cd	O	Co	Ge
N27	3	84.8739	12.5000	2.6250	0.0011
N28	8	80.4963	12.5019	7.0000	0.0018
N29	13	76.1217	12.5011	11.3750	0.0019
N30	18	71.7467	12.5021	15.7500	0.0012
N31	23	67.3735	12.5007	20.1250	0.0008

The film contains Germanium as impurity

4.7: Structural analysis for Cadmium cobalt oxide nanofilm

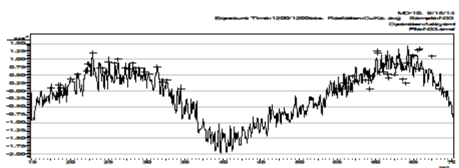

Fig.6 : XRD patterns for $CdCoGe_2O_6$ nanofilm

Ge is present as impurity

5.0 DISCUSSIONS

As shown in figure 1, the films, generally have low absorbance in all the regions of electromagnetic spectrum, with maximum in the UV region (0.15=15%) and decreases to minimum in the NIR . The 23% doped, has the maximum absorbance of 0.15, which attenuates down the VIS, NIR regions. The absorbance of the films is directly proportional to the percentage doping with cobalt. Figure 2 shows that transmittance of the films is generally high in all the regions, with minimum in the UV region (71.39% for 23% doped) and increases to maximum in the NIR (<94.7% for undoped , < 98.7% for 13% doped). This property makes the film a good material for solar cell, phosphors, and photothermal application. Transmittance of the films is inversely proportional to the percentage doping with cobalt. From figure 3, the reflectance of the films is generally very low in all the regions, with the doped films having maximum of 0.13=13% in the UV and the undoped having 0.085=8.5% in the visible region which attenuates down to NIR regions. This property makes the film a good material for anti reflection coating. Reflectance of the film is directly proportional to the percentage doping with cobalt. Figure 4, shows that refractive index of the doped films is generally high in the UV region (2.15 maximum) while undoped has maximum of 1.78 in the visible region which decreases to minimum in the NIR. High refractive index makes the film applicable in multilayer film stack for anti reflection coating. The refractive index is directly proportional to the percentage doping with cobalt. As dilute magnetic semiconductor $CdCo_2O_4$ nanofilm finds good application in Spintronics, hard disks, magnetic discs, micro drive. As wide bandgap semiconductor, it is applicable in ultra high efficiency 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. [18]. XRD result shows that the film has monoclinic structure and contains Germanium, though as impurity. Results of analysis of the XRD data also reveal that the film has mean crystallite size of 1.988nm, dislocation density of 0.0259lines/nm^2 and microstrain of 0.176.

6.0 CONCLUSIONS

Cadmium cobalt oxide nanofilm could be grown by electrodeposition method. The optical properties viz; absorbance, reflectance, refractive index, of the films are directly proportional to the percentage doping with cobalt while the transmittance is in inverse proportion. The film is a wide bandgap semiconductor.

7.0 REFERENCES

[1] Mishra RL, Sharma AK, Prakash SG, Gas sensitivity and characterization of cadmium oxide semiconducting thin film deposited by spray pyrolysis technique, *Digest Journal of Nanomaterials and Biostructures*, (2009), **4**(3), 511-518

[2] Veda N, Meada H, Hosono H and Kawazoe H, Band-gap widening of CdO thin films, *Journal of Applied Physics*, (1998), **84**, ,6174

[3] Gurumurugan K, Mangalraj D and Narayanandas SK, Correlations between the optical and electrical properties of CdO thin films deposited by spray pyrolysis,*Thin Solid Films*, (1994), **251**, 7

[4] Peter Chritov Shindov, CdO thin films deposited by spray pyrolysis, *Electronics*; (2004), 22-24

[5] Hani Khallaf, Chia-Ta Chen, Liann-Be Chang, Oleg Lupan, Aniruddha Dutta, Helge Heinrich A. Shenouda, Lee Chow, Investigation of chemical bath deposition of CdO thin films using three different complexing agents, *Applied Surface Science*, (2011),**257**, ,9237–9242.

[6] Sakthivel S , Mangalaraj D, Cadmium Oxide Nano Particles by Sol-Gel and Vapour-Liquid-Solid Methods, *Nano Vision*, (2011),**1**(1), ,47-53.

[7] Subramanyam TK, Srinivasulu Naidu B, Uthanna S, Studies on dc magnetron sputtered cadmium oxide films, *Applied Surface Science*, (2001),**169**(170), ,529-534.

[8] Zhiyong Zhao DL , Morel Ferekides CS, Electrical and optical properties of tin-doped CdO films deposited by atmospheric metalorganic chemical vapor deposition, *Thin Solid Films*, (2002), **413**, , 203–211.

[9] Baranov AM , Malov YA , Zaretsky DF, Tereshin SA, Solar cells based on the heterojunction a-C/p-Si, *Solar Energy Materials & Solar Cells*. (2000),**60**, ,11-17.

[10] Champness CH , Ghoneim K , Chen JK, Optimization of CdO layer in a Se-CdO Photovoltaic cell,*Canadian Journal of Physics,* (1985),**63**, ,767.

[11] Kondo R, Okhimura H, Sakai Y, Electrical properties of Semiconductor Photodiodes with Semitransparent films, *Japan Journal of Applied Physics*, (1971),**10**, ,176.

[12] Mishra RL , Sharmaa AK , Prakash SG, Gas sensitivity and characterization of cadmium oxide (CdO) semi conducting thin film deposited by spray pyrolysis technique, *Digest Journal of Nanomaterials and Biostructures*, (2009),**4**(3), ,511–518.

[13] Gomez Daza O , Arias-Carbajal Readigos A, Campos J , Nair MTS,Nair PK, Formation of Conductive CdO Thin Films on Photoconductive CdS Thin films for Window Layer Applications in Solar Cells, *Mod. Phys. Lett. B*, (2001), **17**, ,609-612.

[14] Galicia DM, Perez RC , Sandoval OJ , Sandoval SJS ,and .Romero CIZ, High transmittance CdO thin films obtained by the sol-gel method, *Thin Solid Film,* (2000),**371**, ,105-108.

[15] Mane RS, Pathan HM, Lokhande CD and Han SH, An effectve use of nanocrystalline CdO thin films in dye-sensitized solar cells, *Solar Energy*, (2006), **80**, ,185-190.

[16] Rubby Das and Suman Pandey, Comparison of optical properties of bulk and nano crystalline thin films of CdS using different precursors, *Intrenational journal of material science,* (2011) , ***1****(1), ,35-40*

[17] Nadeem MY and Waqas Ahmed,Optical properties of ZnS thin films, *Turk journal of physics*, (2000),**24**, , *651-659*

[18]. US.Department(2013):Wide bandgap Semiconductors: Pursuing the Promise