Effect of Cobalt Doping on Optical Properties of Silver Cobalt Oxide Nanofilms Deposited by Electrodeposition Method

N.S. Umeokwonna[*a], A.J. Ekpunobi[b], P.I. Ekwo[b]

a. Department of Industrial Physics Chukwuemeka Odumegwu Ojukwu University, Uli, Anambra State, Nigeria

*Corresponding author: nicksunny87@yahoo.com

b.Department of Physics and Industrial Physics Nnamdi Azikiwe University, Awka, Anambra State, Nigeria

Abstract

Cobalt doped Silver Oxide nanofilms were grown by electrodeposition method using Silver trioxonitrate (v) salt as source of Silver 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 inversely proportional to the percentage doping with cobalt while transmittance is directly proportional. The film is a wide bandgap semiconductor.

Key words: **Doping, Electrodeposition, Nanofilm, Optical properties.**

1 INTRODUCTION

This research is aimed at growing nanofilms of Silver cobalt oxide by doping with cobalt at various percentages using electrodeposition method. The films are to be analyzed for their optical properties with a view to ascertaining the effect of doping and ascertain possible applications.Silver oxide exists in different defined compounds namely; AgO, Ag_2O, Ag_2O_3, Ag_3O_4, Ag_4O_4 and Ag_4O_3. The most thermodynamically stable among them is Ag_2O. The oxide Ag_2O has a simple cubic structure at room temperature [1]. Silver oxide thinfilms can be prepared by various techniques such as chemical

vapour deposition [2],thermal evaporation [3], electron beam evaporation [4], thermal oxidation of silver films[5], DC sputtering[6], pulsed laser deposition [7], RF sputtering [8] and electrodeposition[9]. Silver oxide nano crystals and thinfilms have been intensively pursued for promising applications as a catalyst for ethylene and methanol oxidation [10], as a sensor for the detection of carbon monoxide and ammonia [11] and as photovoltaic materials [12]. Silver oxide films also act as a mask layer in magneto-optical disk to enhance the magneto-optical signal. [13]

2 MATERIALS AND METHODS

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 then 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. The substrates were again brought out using clean forceps, put in another clean dry beaker, and put inside the oven for ten minutes for drying. The slides ready for use were handled with clean forceps to avoid contamination. The precursors for deposition of nanofilms of $AgCoO_2$ with various percentages of Cobalt dopant are Silver trioxonitrate (v) salt as source of Silver 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 forty-five seconds and deposition voltage of 0.5V. Constant concentrations and volumes of Citric acid and Sodium hydroxide were used while concentrations of $AgNO_3$ and $CoCl_2.6H_2O$ were varied 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 with X-Ray fluorescence (XRF) spectrometer. Optical micrograph of the film was done with Olympus microscope.

Table 1: Variation of percentage doping for $AgCoO_2$ nanofilm

Reaction bath	AgNo3		Citric acid		CoCl2.6H2O		NaOH		Deposition voltage(V)	pH	% Doping	Time (secs)
	Conc.(M)	Vol.(ml)	Conc.(M)	Vol.(ml)	Conc.(M)	Vol.(ml)	Conc.(M)	Vol.(ml)				
N40	0.048	15	0.05	30	0.001	15	1	6	0.5	8.6	3	45
N41	0.046	15	0.05	30	0.004	15	1	6	0.5	8.6	8	45
N42	0.043	15	0.05	30	0.006	15	1	6	0.5	8.6	13	45
N43	0.041	15	0.05	30	0.009	15	1	6	0.5	8.6	18	45
N44	0.038	15	0.05	30	0.011	15	1	6	0.5	8.6	23	45

3 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 were calculated using the relation according to Rubby *et al* (2011) [18]:

$$R = 1 - (A + T)$$

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) [14], 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) [22], Photon energy is given by: E = hυ

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

υ = frequency of photon,

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

Where c = velocity of light = 3×10^8m/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 $h = \frac{6.63 \times 10^{-34}Js}{1.602 \times 10^{-19}J} \approx 4.14 \times 10^{-15}eV$

$\therefore$ Photon energy $E = \frac{4.14 \times 10^{-15}eV \times 3 \times 10^8 m/s}{\lambda(m)}$ = ...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 $k \approx 0.9$, 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:

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

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.

4.0 RESULTS AND DISCUSSIONS
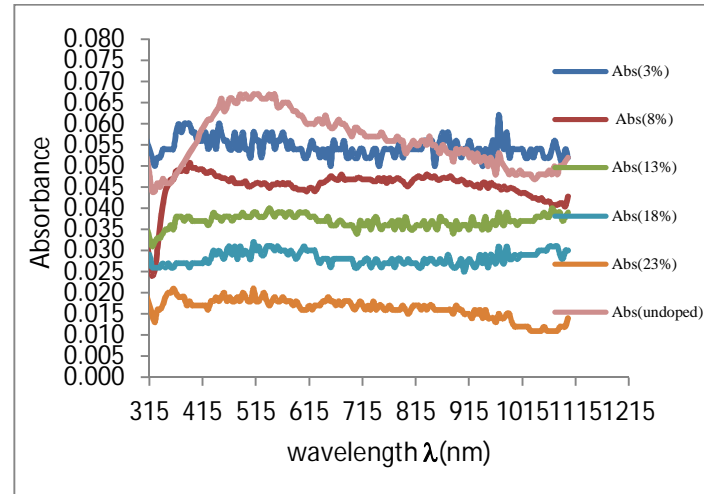
4.1 Absorbance

Fig. 1: Variation of absorbance with percentage doping

for AgCoO$_2$ nanofilms.

From figure 1, the films generally have very low

absorbance in all the regions (maximum of 0.60 = 6% for

doped film and maximum of 0.067 = 6.7% for the

undoped film). Each doped film exhibites almost same

level of absorbance in all the regions. The undoped has

maximum absorbance in the UV region (0.067 = 6.7%)

and decreases to minimum in the NIR region.

The absorbance of the films decreases with increasing

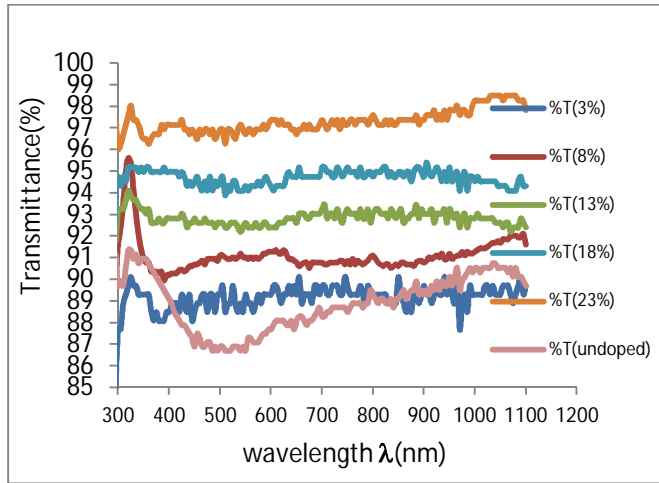percentage doping with cobalt

4.2 Transmittance

Fig. 2: Variation of transmittance with percentage doping

for AgCoO$_2$ nanofilms

As shown in figure 2, the transmittance of the films is generally high ($\leq$87.7% to $\geq$98.5%) for doped films .Each of the doped film exibits almost same level of transmittance in all the regions. The undoped film has minimum transmittance   (86.7%) in the visible region and increases to maximum (90.5%) in the NIR region. However, the transmittance of the film increases with percentage doping with cobalt.
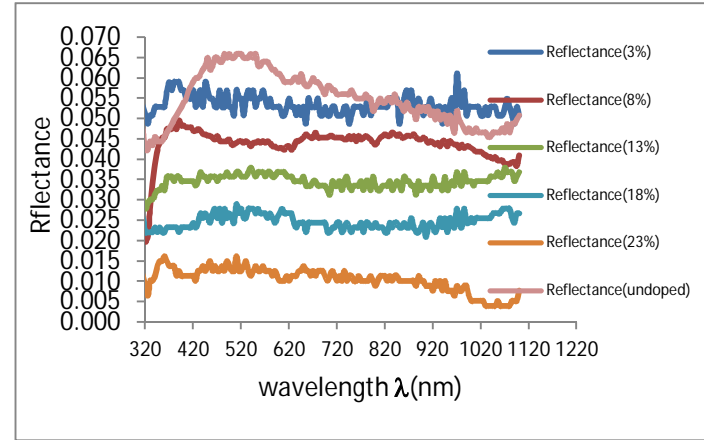
4.3 Reflectance

Fig. 3: Variation of reflectance with percentage doping

for AgCoO$_2$ nanofilm.

Reflectance of the films as shown in figure 3 is generally very low (maximum of 0.059 = 5.9%) for doped films. Each percentage of doped film exihits almost same level of reflectance in all the regions. The undoprd film has maximum reflectance (0.066 = 6.6%) in the visible region and decreases to minimum in the NIR region .

However, the reflectance of the film decreases as percentage doping increases.
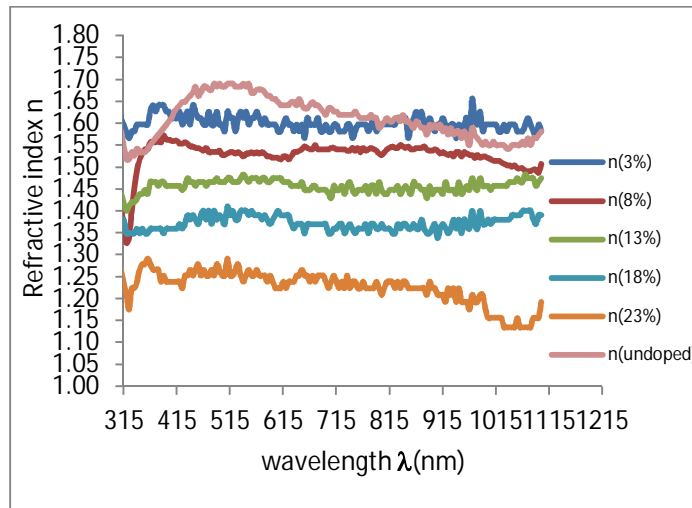
4.4 Refractive index

Fig. 4: Variation of refractive index with percentage doping for AgCoO$_2$ nanofilm.

From figure 4, refractive index of lower percentage doping (3% to 8%) is high ($\leq$ **1.52** to $\geq$1.63) but that of higher percentage doping (13% to 23%) is low ($\leq$ **1.14** to $\geq$ **1.47**) . Each of percentage doping has almost same refractive index in all the regions.

The undoped film has maximum refractive index (1.69) in the visible region and decreases to minimum in the NIR region.

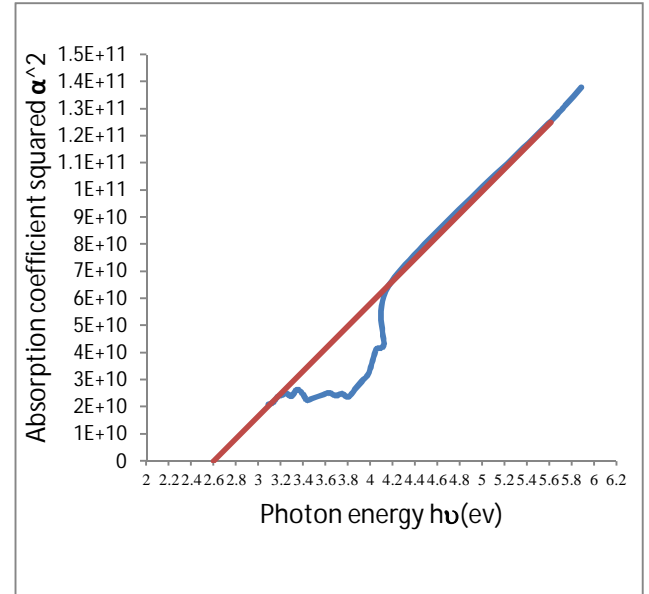The refractive index of the film decreases with percentage doping with cobalt.

4.5 BANDGAP

Fig. 5: Absorption coefficient versus photon energy for 3% AgCoO$_2$ nanofilm.

From figure 5, 3% Cobalt doped Silver Cobalt Oxide nanofilm has direct allowed bandgap of 2.6eV.

4.6 MORPHOLOGICAL ANALYSIS

Fig. 6: Optical micrograph of AgCoO$_2$ nanofilm

The micrograph reveals the film as uniformly deposited and polycrystalline

4.7 COMPOSITIONAL ANALYSIS

Compositional analysis of the film is shown in table 2.

Table 2: Compositional analysis of Silver cobalt oxide nanofilm

Sample	Percentage doping	Ag	O	Co
N40	3	90.3103	6.8966	2.7931
N41	8	85.6550	6.8967	7.4483
N42	13	80.9999	6.8959	12.1042
N43	18	76.3462	6.8952	16.7586
N44	23	71.689	6.8961	21.4149

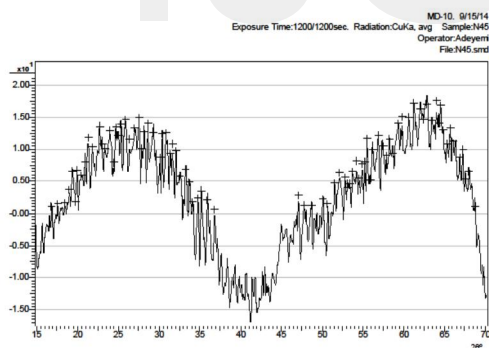## 4.8 Structural analysis of Silver cobalt oxide nanofilm

Fig. 7: XRD pattern of $AgCoO_2$ nano film

5.0 DISCUSSIONS

From figure 1, the films have generally have very low absorbance in all the regions (UV,Visible and NIR). For the doped films, maximum absorbance is 0.06=6% and 0.067=6.7% for the undoped. The absorbance of each doped film is almost the same in all the regions. The undoped film has maximum absorbance (6.7%) in the UV region and decreases to minimum in the NIR. Absorbance of the films is inversely proportional to the percentage doping with cobalt. This is attributed to the fact that Silver is the best conductor of electricity, so replacing the atom(s) with another element decreases the conductivity and so less deposition on the substrate. The more it is doped, the less conductive it becomes, hence less deposit is obtained. The absorbance of a film increases with increasing film thickness and decreases with decreasing film thickness [15]. As shown in figure 2, transmittance of the films is generally high; for the doped, minimum of 87.7% (for 3% doping) and maximum of 98.5% (for 23% doping). The undoped film has minimum of 86.7% in visible region and increases to maximum(90.5%) in the NIR. Their excellent light transmission makes the film good material for UV laser application, Solar cell, Phosphors and other photothermal applications. Transmittance of the films is directly proportional to percentage doping with cobalt.

Figure 3, shows that the reflectance of the films is generally very low in all the regions; maximum of 0.059=5.9% for the doped. Each doped film exhibits almost same level of reflectance in all the regions. The undoped has maximum reflectance of 0.066=6.6% in the visible region and decreases to minimum in the NIR. This low reflectance property makes the film a veritable material for antireflection coating. Reflectance of the films is inversely proportional to the percentage doping with cobalt. From figure 4, the lower percentage doping have high refractive indices while higher percentage doping have low refractive indices. 3% doping has refractive indices in UV(~1.64) ,VIS (~ 1.67), NIR (~1.61). 8% doping has ~1.57 , 13% has in UV (~1.47) ,VIS (~1.48), NIR (~1.46). 18% has in UV (~1.39) , VIS (~1.39) , NIR (~1.40) , 23% has in UV (~1.28) , VIS (~1.27), NIR(~1.19).The undoped film has maximum refractive index (1.69) in the visible region and decreases to minimum (1.51) in the NIR. This property makes the film good material for multilayer antireflection coating and in film stack for colour selective coating. The refractive index of the films is inversely proportional to the percentage doping with cobalt. The optical properties viz; absorbance, reflectance,and refractive index of the films are inversely proportional to the percentage doping with cobalt while transmittance is directly proportional. As dilute magnetic semiconductor, $AgCoO_2$ finds good application in Spintronics, hard disks, magnetic discs, micro drive. As wide bandgap semiconductor, it is applicable in light emitting diodes, sensors and can enable electronic equipment to operate at higher temperatures and voltage [16]. The XRD result shows that the film is rhombohedral in structure with mean crystallite size of 1.8418nm, dislocation density of $0.2948lines/nm^2$ and microstrain 0.1882

6.0 CONCLUSIONS

Cobalt doped Silver oxide nanofilm can be grown by electrodeposition method.

The optical properties viz; absorbance, reflectance and refractive index, of the films are inversely proportional to the percentage doping with cobalt while transmittance is directly proportional. The film is a wide bandgap semiconductor.

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