INFLUENCE OF PRECURSOR CONCENTRATION ON STRUCTURAL AND OPTICAL PROPERTIES OF Co_xO_y THIN FILMS

A.N.C. AGBOGU, A.B.C EKWEALOR* F.I. EZEMA
Department of Physics and Astronomy, University of Nigeria, Nsukka

In this paper is presented the influence of precursor concentration on the structural and optical properties of Co_xO_y thin films synthesized in the pores of PVP by chemical bath deposition technique. XRD analysis results revealed the films to be cobalt oxyhydroxide, CoO(OH) nanocrystals of size range 28.04nm – 65.65nm. Studies of the optical properties using absorption spectra in UV–VIS–NIR regions showed that the optical parameters (including constants) increased with increase in precursor concentration in an irregular manner. The energy band-gap of the films ranged from 2.70eV to 3.62eV which makes them possible materials for use as window layer in solar cell.

(Received July 1, 2014; Accepted September 30, 2014)

Keywords: Cobalt oxyhydroxide, Precursor concentration, CBD, Band gap, Structural and optical properties.

1. Introduction

Hydroxides and oxides of cobalt constitute an important class of materials characterized by good electrochemical, catalytic and optical properties [1]. Generally, cobalt oxide exists in three different crystalline forms; namely CoO, Co_2O_3 and Co_3O_4 [2, 3]. It is classified as one of the most versatile oxide materials among the transition metal oxides [4]. Cobalt oxyhydroxide, CoO(OH), has a hexagonal structure, in which the divalent metal cation is located in the octahedral site coordinated by six hydroxy groups [1]. It has been proposed as an alternative material for CO detection at low temperatures [5]. It is a promising material for fuel cells [6] and capacitors [7].

Cobalt oxide thin films are promising candidates for various applications such as ion-storages [8], chemical sensors [9], solar thermal energy collectors [10] and electrochromic (EC) devices [11, 12]. Because of its optical, semiconducting, magnetic and electrochemical properties, black cobalt is a promising material among transition metal oxides, which renders it attractive for solar photochemical applications and electrochemical devices as a counter electrode [13]. It has been reported that cobalt oxide has desirable optical properties to harvest the solar energy in an efficient way, when used as the selective coating in photothermal devices [14].

Cobalt oxide thin films have been produced by different approaches. Cobalt oxide films have been grown by glancing angle deposition (GLAD) [15], chemical vapor deposition (CVD) [16], spray pyrolysis [17], sol-gel [18], and electrodeposition [19, 20] techniques. However, not much has been reported on oxyhydroxides produced by chemical bath deposition (CBD) technique. In this paper, a report on the result of investigation into variations of optical and structural properties with precursor concentration of cobalt oxyhydroxide films deposited by CBD method is presented.

* Corresponding author: abcekwealor@yahoo.com

2. Experimental Details

2.1 Synthesis of Cobalt Oxide Co_xO_y Films

The glass substrates and bath vessels for this were thoroughly washed clean and dried. Five different baths (samples CX1 – CX5) with varied concentrations of cobalt salt were prepared as follows: Sample CX1 was obtained by mixing 5ml of 0.1M $CoCl_2$, 5ml of 1M Triethanolamine (TEA), 1ml of 13.4M NH_3 and 40ml of PVP in a 100 cm^3 beaker. Samples CX2, CX3, CX4 and CX5 were obtained as in sample CX1, but with the concentration of $CoCl_2$ increased to 0.25M, 0.50M, 0.75M and 1.00M respectively. Substrates were then immersed in the baths of these samples and covered with synthetic foams. These were now put in an oven at 333K for five hours to allow for substantial deposits; after which they were removed, rinsed in distilled water and annealed at 473K in an oven for two hours.

2.2 Optical Characterization of Co_xO_y Thin Films

Using absorption spectra in UV–VIS–NIR regions obtained from Unico UV – 2102 PC spectrophotometer at normal incidence of light within the wavelength range 200nm – 1200nm, the optical properties of the films were studied.

2.3 Results and Discussion

In fig 1 which gives a plot of absorbance against wavelength, it can be observed that whereas samples CX1, CX3 and CX5 have very low absorbance in the visible regions which gradually decreased to the near infrared region, samples CX2 and CX4 have high absorbance in the VIS which decreased to the NIR region. This shows that the absorption of the films, though increased, has no sequential variation with increase in the concentration of the precursor. However, the films generally show moderate absorption in the visible region of radiation spectrum.

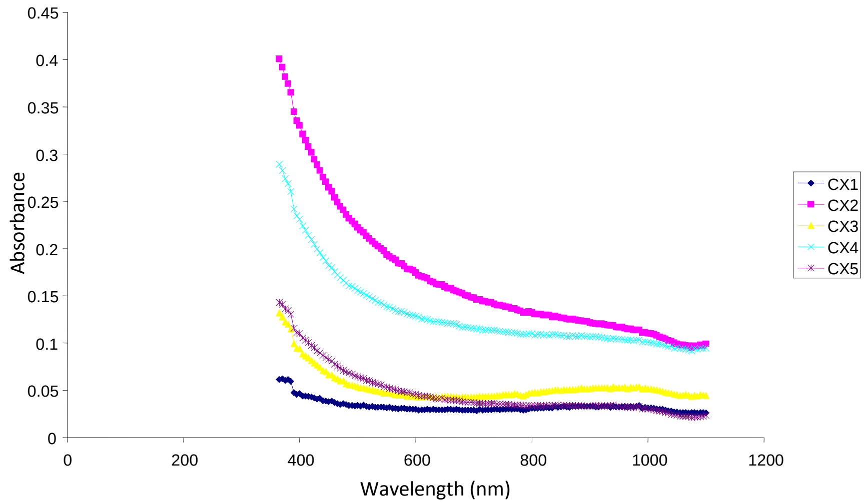

Fig 1. Absorption Spectra for Co_XO_Y thin films with varying precursor concentration

The transmittance of samples CX1, CX3 and CX5 is high in the VIS region and increased slightly in the NIR region. However, sample CX2 and CX4 have moderate transmittance in the VIS region and increased in the NIR region. These are observed in fig 2 which is a plot of transmittance against wavelength. Again, the transmittance of the films, though increased, varies irregularly with increasing precursor concentration. However, the transmittance of the films is in general above 60% in the visible and infra red regions of solar spectrum. This makes them promising materials for use as electrochromic material in smart windows devices. The sensitive of human eye is known to lye only in the range 400 – 700nm with its peak at 500nm [21]. Some of these films met this condition in window coatings; thus making them suitable for window coatings. It is in literature that thin films with high transmittance in the NIR are employed in construction of poultry houses to allow enough infrared to warm the very young chicks during the day [22]. Some of the films synthesized in this work could therefore be applied in the construction of poultry roofs and wall.

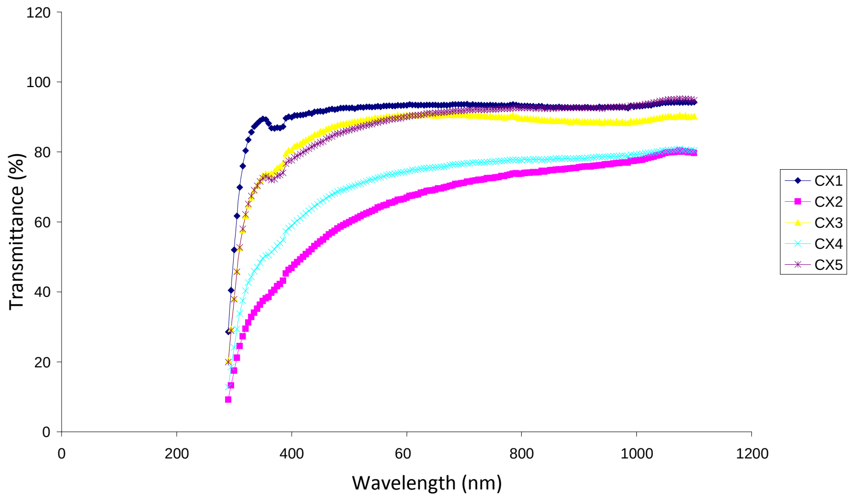

Fig 2: Transmittance spectra for Co_XO_Y thin films with varying precursor concentration

Fig 3 gives a plot of reflectance against wavelength; it also shows that the reflectance of samples CX1, CX3 and CX5 is low in the VIS region and decreased into NIR region. Samples CX2 and CX4 however, have higher reflectance in the VIS region which also decreased into NIR region. Here again, the reflectance shows an irregular increase with increase in precursor concentration

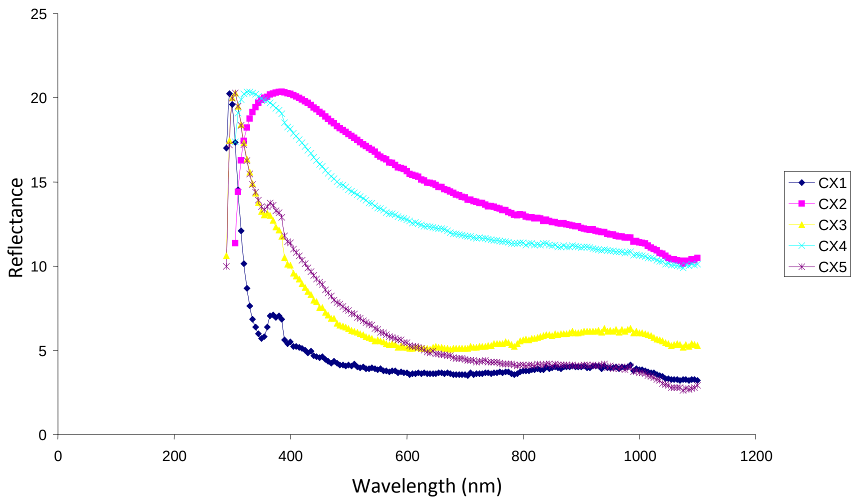

Fig 3: Reflectance spectra for Co_XO_Y thin films with varying precursor concentration

Tauc plots of $(\alpha h\nu)^2$ vs hν are shown in fig 4. Extrapolations of the curves gave intercepts on the x-axis which ranged from about 2.70eV – 3.62eV as the energy band gap for direct allowed transition. The band gap had values E_g = 3.09eV – 3.62eV for films with lower precursor concentration, but had lower values of $E_g \leq$ 3.00eV for films with higher concentrations. These could be as a result of the increase in crystallite size for films with high precursor concentrations [23]. It has been shown in literature that processes that increase the particle size decreases the band gap of most thin films [24]. It can therefore be inferred that the films deposited at lower concentration had small crystallite size. The large band gap energy makes the films possible materials for use as window layer in solar cell and for application in photoelectrochemical (PEC) solar cells.

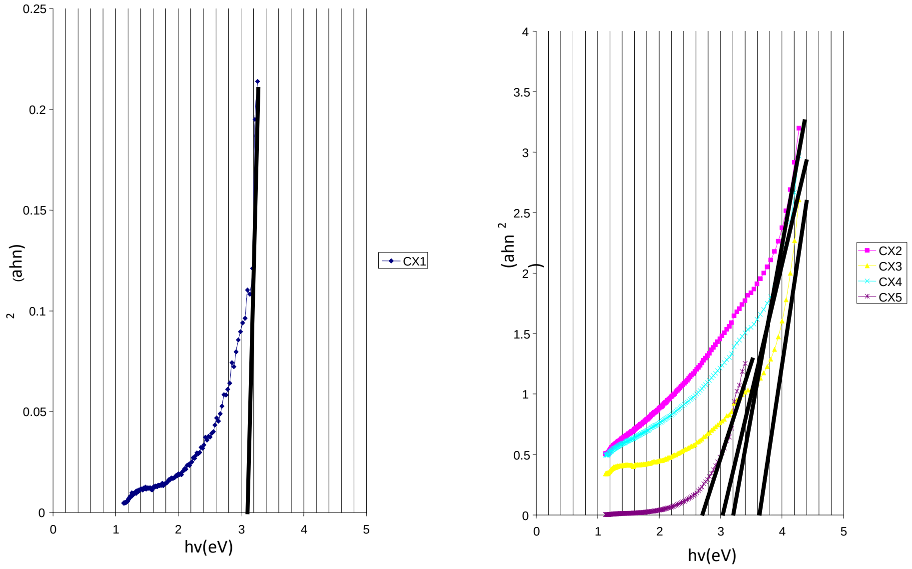

Fig 4: Band-gap spectra for Co_XO_Y thin films with varying precursor concentration

The absorption coefficient versus photon energy plots are shown in fig 5. Here, it can be seen that the absorption coefficient, though increased, has an irregular variation with increase in precursor concentration of the films. However, its value is low < 0.5 for energy values < 3.00eV, but increased to values between 0.1 – 2.5 for photon energies > 3.00eV.

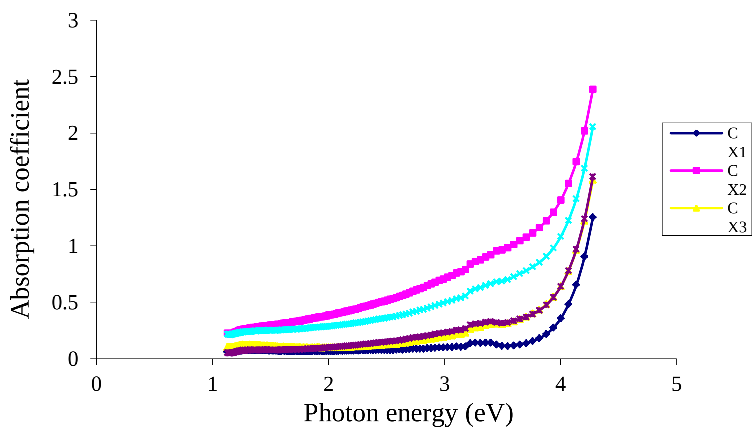

Fig 5: Absorption coefficient spectra for Co_XO_Y thin films with varying precursor concentration

The refractive index versus photon energy plots given by fig 6, show that the refractive index of deposited films increased, but has irregular variation with increase in precursor concentration. The value ranges from about 1.10 – 2.30 for photon energies < 4eV. These values obtained for the refractive index, agree fairly with those reported in the literature for cobalt oxide [25]. Variations of the refractive index for CoO reported in the literature can be explained by the preparation method of the films [26]. Films with refractive index lower than 1.9 could be employed as anti-reflecting material and could improve the transmittance of glass from 0.91 to 0.96 [27]. This shows that the films can also be used for this purpose.

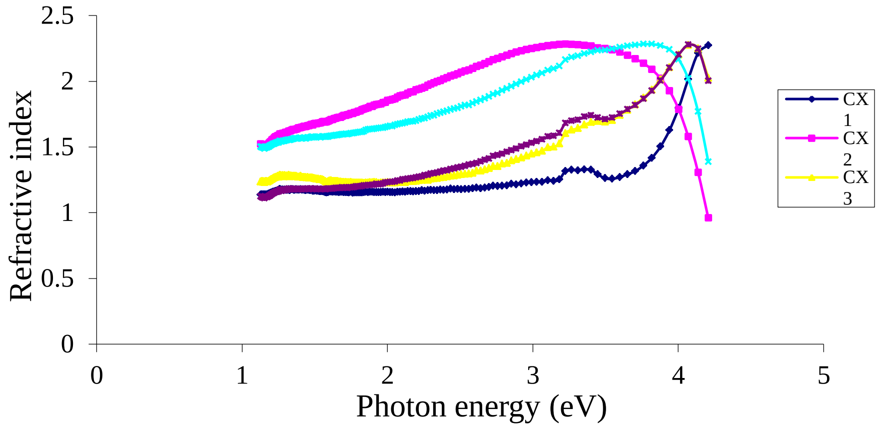

Fig 6: Refractive index spectra for Co_XO_Y thin films with varying precursor concentration

Although the extinction coefficient of the films, was low, it increased with increase in precursor concentration. It actually had an irregular increase with the increase in precursor concentration. This is evident in fig 7, which gives the spectral plots of extinction coefficient against photons of incident radiation.

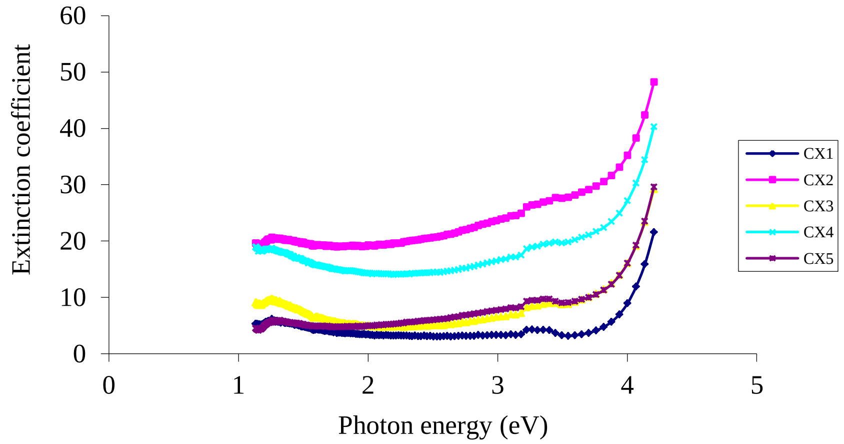

Fig 7: Extinction coefficient spectra for Co_XO_Y thin films with varying precursor concentration

2.4 Structural Characterization of Co_xO_y Thin Films

Figs 8 – 10 give the XRD spectra for the synthesized Co_XO_Y films with varying concentration. It was deduced from these that the film deposited is Cobalt OxyHydroxide, CoO(OH); Hetrogenite-3.

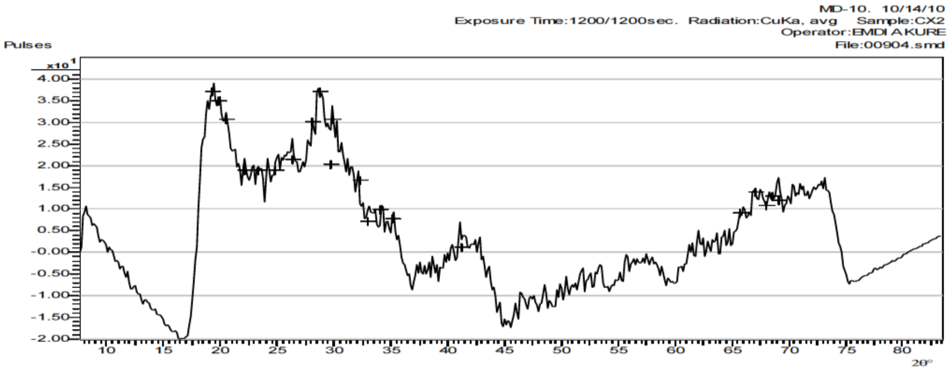

Fig 8: XRD diffractogram for CoO(OH) films with precursor concentration of 0.25M

From fig 8, which is the spectra for film with precursor concentration (0.25M), peaks were obtained at 2θ = 41.20º, 68.50º, and 69.30º; corresponding to diffraction lines produced by (006), (018) and (113) planes respectively.

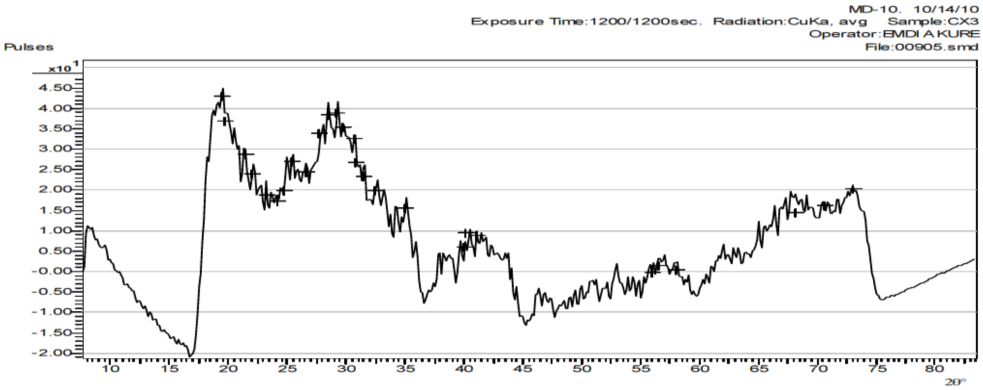

Fig 9: XRD diffractogram for CoO(OH) films with precursor concentration of 0.50M

For fig 9, which is the spectra for film with precursor concentration (0.50M), peak was obtained at 2θ = 41.20º; corresponding to diffraction line produced by (006) plane.

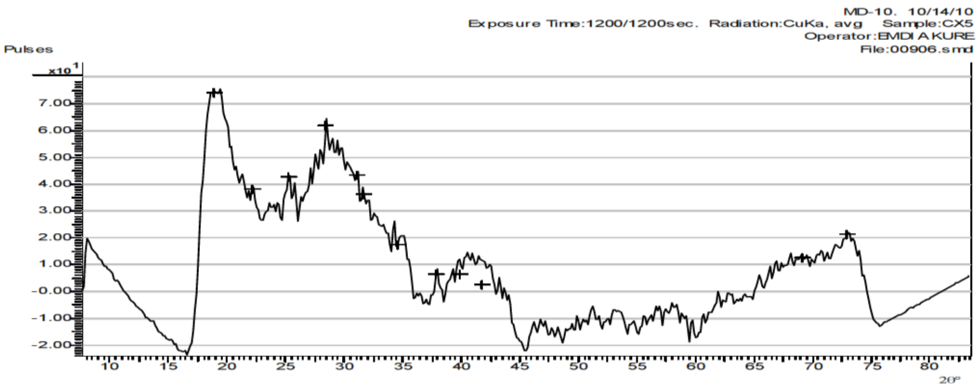

Fig 10: XRD diffractogram for CoO(OH) films with precursor concentration of 1.00M

Fig 10, which is the spectra for film with precursor concentration (1.0M), shows peak at 2θ = 69.30º which corresponds to diffraction line produced by (113) plane.

2.5 Determination of Film Size

Using the Scherer's formula given by [28] $D = \frac{0.9\lambda}{\beta \cos\theta}$, where λ is wavelength of the x-ray, β is full width at half maximum (FWHM) of the peak with highest intensity and θ is the diffraction angle, the grain sizes were obtained to be of range 28.04nm – 65.65nm.

3. Conclusion

Nanocrystalline thin films of CoO(OH) were successfully deposited on glass slide using chemical bath deposition technique. XRD studies revealed that the CoO(OH) nanocrystalline thin films have orientations in the (006) and (113) planes. The crystallite size range was found to be from 28.04nm–65.65nm. Optical studies and band gap analysis show that variation of precursor concentration has significant effect on these properties. Their energy band gaps ranging from 2.70eV – 3.62eV, make them suitable for many applications. Their high transmittance in the VIS region makes them suitable in solar cell applications.

References

[1] I. Kelpšaitė, J. Baltrušaitis, E. Valatka, Materials Science (Medžiagotyra), **17**, No. 3. (2011).
[2] S.G. Kandalkar, C.D. Lokande, R.S. Mane, S.H. Hun, Appl. Surf. Sci. **253**, 3952 (2007).
[3] A. Louardi A. Rmili, F. Ouachtari, A. Bouaoud, B. Elidrissi, H. Erguig, Journal of Alloys and Compounds **509**, 9183 (2011).
[4] P.S. Patil, L.D. Kadam, C.D. Lokhande, Thin Solid Films, **272**, 29 (1996).
[5] R. J. Wu et al, Sensors Actuators B: Chem., **120**, 104 (2006)
[6] C. Mansour, T. Pauporté, A. Ringuedé, V. Albin, M. Cassir, Journal of Power Sources 156, 23 (2006).
[7] H. Zheng, F. Tang, M. Lim, T. Rufford, A. Mukherji, L. Wang, G. Lu, Journal of Power Sources 193, 930 (2009)
[8] S.G. Kandalkar, C.D. Lokhande, R.S. Mane, S.-H. Han, Appl. Surf. Sci. **253**, 3952 (2007).
[9] A. Cao, J. Hu, H. Liang, W. Song, L. Wan, X. He, X. Gao, S. Xia, J. Phys. Chem. B **110,** 15858 (2006).
[10] B. Pejova, A. Isahi, M. Najdoski, I. Grozdanov, Mater. Res. Bull. **36**, 161 (2001).
[11] C.G. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier, Amsterdam, 1995.
[12] P.M.S. Monk, R.J. Mortimer, D.R. Rosseinsky, Electrochromism: Fundamentals and Applications, VCH, Weinheim, 1995.
[13] G.Toghdori, S.M.Rozati, N. Memarian, M. Arvand, M.H. Bina, World Renewable Energy Congress, Sweden (2011).
[14] E. Barrera-Calva, J.C. Martinez-Flores, L. Huerta, A. Avila, M. Ortega-Lopez, Solar Energy Materials & Solar Cells **90**, 2523 (2006).
[15] D. Schmidt, A. C. Kjerstad, T. Hofmann, R. Skomski, E. Schubert, and M. Schubert, J. Appl. Phys. **105**, 113508 (2009)
[16] D Barreca, A Gasparotto, O. I. Lebedev, C. Maccato, A. Pozza, E. Tondello, S. Turnerc G. Van Tendelooc, CrystEngComm, **12**, 2185 (2010).
[17] P.S. Patil, L.D. Kadam, C.D. Lokhande, Solar Energy Materials and Solar Cells **53**, 229 (1998).
[18] R. Drasovean, S. Condurache-Bota, N. Tigau, Journal of Science and Arts, **2**(13), 379 (2010).
[19] G.Toghdori, S.M.Rozati, N. Memarian, M.Arvand, M.H.Bina, World Renewable Energy Congress 2011 – Sweden, Solar Thermal Applications (STH) Sweden.
[20] V. Srinivasan, J. W. Weidner, Journal of Power Sources **108**, 15 (2002).
[21] F.I. Ezema, P. U. Asogwa, A.B.C. Ekwealor, P.E. Ugwuoke, R. U. Osuji, J. University of

Chemical Technol. and Metall. **42**(2) 217 (2007).
[22] S. C. Ezugwu, F. I. Ezema, R. U. Osuji, P. U. Asogwa, A. B. C. Ekwealor, B. A. Ezekoye Optoelectron. Adv. Mater. – Rapid Commun. **3(**2), 141 (2009).
[23] S. Erat, H. Metin CP899, Sixth International Conference of the Balkan Physical Union, edited by Cetin S.A. and Hikmet I., 249 (2007).
[24] A. Djelloul, K. Bouzid, F. Guerrab, Turk J. Phys. **32**, 1 (2008).
[25] D. Gallant, M. Pezolet, and S. Simard J. Phys. Chem. B **110**, 6871 (2006).
[26] M. Ando, K. Kadono, K. Kamada, K. Ohta, Thin Solid Films, **446**, 271 (2004**)**,.
[27]. R.B. Petit, C. J. Brinker, Solar Energy Materials **14**, 269 (1986).
[28] V. Elena, et al, Thin Solid Films. **365**, 12 (2000).