Volume 4, Issue 1, 2020 ISSN: 2617-3522
DOI: https://doi.org/10.31058/j.mana.2020.41002

Synthesis and Characterization of Manganese Doped Cadmium Oxide Thin Films by Electrodeposition Method

Mafiana Edward Udoka[1], Ezenwaka Laz Nnadozie[2], Ottih Ifeyinwa Euphemia[2], Okoli Nonso Livinus[3*]

[1] National Engineering Design Development Institute, Nnewi, Anambra State, Nigeria
[2] Department of Industrial Physics, Chukwuemeka Odumegwu Ojukwu University Uli, Anambra State, Nigeria
[3] Department of Physics, Legacy Univeristy, Okija, Anambra State, Nigeria

Email Address
okolinonsolivinus@gmail.com (Okoli, Nonso Livinus)
*Correspondence: okolinonsolivinus@gmail.com

Received: 31 December 2019**; Accepted:** 4 April 2020**; Published:** 8 July 2020

Abstract:
The electrodeposition of Manganese doped Cadmuim Oxide ($CdMnO_2$) thin films on conducting Indium Tin Oxide (ITO) glass was done successfully at room temperature of 302 K at varying time of deposition. The grown films were subjected to optical, crystal structure surface structural and compositional characterization to determine their properties and possible applications. The results revealed that absorbances of the films were high in VIS region but decreases towards the NIR region. Transmittance of the films is low in VIS region but increases towards the NIR region. The deposited films have optical band gap energies range from 2.80 eV to 3.85 eV. The deposited films have low reflectance and refractive index obtained ranged from 2.64 to 1.01. Average optical thickness of the deposited films revealed that the films have optical depth between 1.35 µm and 0.05 µm. X – ray diffraction result of the films obtained confirm that the films are of CdO with cubic crystal structure. Crystallite sizes of the films deposited range from 28.54 nm to 97.05 nm. The average microscopic particle sizes of the films were analyzed using ImageJ and values obtained range between 2.98 nm and 33.81 nm. Thickness of the films obtained in atom / cm^2 ranges from 2,02 x 10^{18} atom/cm^2 to 3.22 x 10^{18} atom/cm^2.

Keywords:
Transparent Semiconducting Oxides, Metal Oxides, Cadmium Oxide, Electrodeposition, Thin Films

1. Introduction

A thin film is microscopically thin layer of material (less than about one micron) that is deposited on to a metal, ceramic, semiconductor or plastic base material. According to [1], a thin film is a material created by the random nucleation and growth processes of individually condensing, reacting atomic, ionic, molecular species on a substrate. Today thin film technology itself is a separate branch of material science and technology and has evolved into a set of techniques used to fabricate many products. Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic, and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices. Thin films are commonly applied to improve the surface properties of solids such as transmission, reflection, absorption, hardness, abrasion resistance, corrosion, permeation and electrical behavior and other properties [2].

Cadmium oxide (CdO) is an n-type semiconductor with nearly metallic conductivity [3], with a direct and indirect band gap of 2.2 – 2.5 eV and 1.36 – 1.98 eV, respectively [4,5]. Cadmium oxide is one of the promising transparent conducting oxides from II to VI group of semiconductors having high capacity for absorption and emission of radiation [6]. Additionally, CdO is a favorable material for solar cell applications due to its high electrical conductivity and optical transmittance in the visible region of the solar spectrum [7].

The major optical transition at the higher energy and the values are both dependent on the defect concentration due to the Burstein-Moss effect [8].The combination of high transparency in the visible range of the electromagnetic spectrum, high electrical conductivity and high carrier concentration (even in non-doped samples because of inherent non-stoichiometry) of this material has prompted its use in CdO/CdTe heterostructure solar cells, [9]. CdO/Cu_2O solar cells [10], photoelectrochemical devices [11], phototransistors [12], photodiodes [13] and gas sensors [14].

Many empirical studies have revealed the importance of transparent semiconducting metal oxide due to the numerous industrial applications. Cadmium oxide (CdO) being one of the various transparent semiconductors possess low band gap compare to other transparent semiconducting oxide. To get rid of this drawback, CdO band gap could be widen without altering its electrical properties by doping the CdO thin film with metallic impurities. In general, it was observed that doping of CdO with metallic ions having ionic radius smaller than that of Cd^{2+}, could improve its electrical conduction and increase its optical band gap. Using Manganese (Mn^{2+}) which serves as dopant atom, and has ionic radius of 91 picometer (pm) compared to 95 picometer (pm) ionic radius of Cd^{2+} will lead to improvements in the properties of CdO material system.

Therefore, we optimized the deposition time in the preparation of manganese doped cadmium oxide ($CdMnO_2$) nanocrystalline thin films by electrodeposition method.

2. Material and Methods

Reagents used for electrodeposition of diluted magnetic semiconducting metal oxide of $CdMnO_2$ are Cadmium tetraoxosulphate (vi) monohydrate ($CdSO_4$. H_2O), Mangenese (ii) tetraoxosulphate (vi) monohydrate ($MnSO_4$. H_2O, Sodium Hydroxide (NaOH) and Distilled water. The eletro-deposition set-up is a three-electrode system (Reference electrode, Working electrode and Counter electrode). In the experimental set – up, the reference electrode used was Saturated Calomel Electrode (SCE), Indium doped Tin Oxide (ITO) glass slide served as the working electrode and platinum foil served as counter electrode. Prior to fabrication of the films, the substrates (ITO) were subjected to distinct pre-treatment to ensure the presence of catalytic surface to improve the adhesion of the films to the substrates particularly as film thickness increases. The cleaning processes involved washing the ITO substrates with detergents, soaked in acetone for 15 minutes for degreasing, ultrasonicated the substrates for about 10 minutes in an ultrasonic bath and finally dried in an electronic oven for 10 minutes at a temperature of 60°C. Five sets of pre-treated indium thin oxide (ITO) conducting glass substrates were used. Each of the five beakers used for experiment contained various volumes of the reagents mentioned above. The five slides were labeled 1 min, 2 mins, 3 mins, 4 mins and 5 mins. Each of the baths for deposition of $CdMnO_2$ contains 10 mls of $CdSO_4.H_2O$, 5 mls of $MnSO_4.H_2O$ and 10 mls of sodium hydroxide. $CdSO_4.H_2O$ was firstly measured using a 10 mls syringe, transferred to 100 mls beaker, then 5 mls of $MnSO_4.H_2O$. Lastly, 10 mls of sodium hydroxide was also measured and transferred to the 100 mls beaker, the mixture was stirred for 5 minutes to obtain a homogeneous mixture. After the stirring of the mixture, all the three electrodes were immersed into the beaker containing the reagents. A wooden guide was used to hold the three electrodes erect onto the beaker. The DC voltage supply was then put on and the deposition voltage was set at 5 Volts. The deposition time of 1 minute, 2 minutes, 3 minutes, 4 minutes and 5 minutes were recorded for the five different variations. The other four films deposited have similar stoichiometric compositions and presented in Table 1.

Table 1. *Time Optimization of Electrodeposited $CdMnO_2$ Thin Film.*

Bath Name	**$CdSO_4 . H_2O$ (0.05 M)**	**$MnSO_4 . H_2O$ (0.05 M)**	**NaOH (0.05 M)**	**Working Voltage**	**Working Current**	**Depostion Time**
	Volume (mls)	Volume (mls)	Volume (mls)	(volts)	(amp.)	(mins)
1 min	10.00	5.00	10.00	0.75	0.02	1.0
2 mins	10.00	5.00	10.00	0.75	0.02	2.0
3 mins	10.00	5.00	10.00	0.75	0.02	3.0
4 mins	10.00	5.00	10.00	0.75	0.02	4.0
5 mins	10.00	5.00	10.00	0.75	0.02	5.0

The electrodeposited manganese doped cadmium oxide ($CdMnO_2$) films were characterized for optical properties using spectrophotometer (StellarNet UV – VIS – NIR spectrometer; Blue – Wave Miniature; Model: UVNb) at UV laboratory, structural properties using X – Ray Diffractometer (Bruker D8 Advance X – ray Diffractometer), surface microstructure using Digital Optical Microscope (Celeston LCD Digital Microscope; Model: 44348) and elemental composition using Rutherford Backscattering Spectroscopy (RBS).

3. Results and Discussions

3.1. Optical Properties

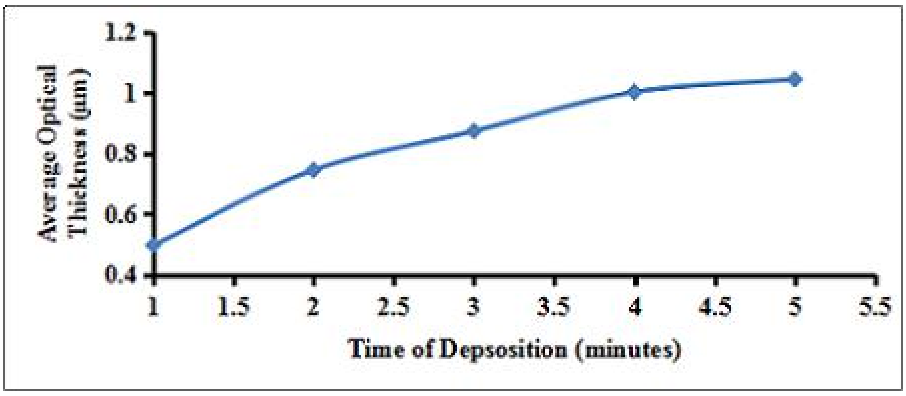

Figure 1. *Plot of average optical thickness versus time of deposition (minutes).*

The optical thickness of the deposited films shown in Figure 1 reveals an increase in the optical thickness as time of deposition increases. Film grown at 5 minutes has peak thickness of 1.04 µm while film grown at 1 minute has optical thickness of 0.50 µm. This increase in film thickness as time of deposition increases may be due to formation of more film layer caused by more implantation of the ions on the surface of the substrates. This result suggests that films with lesser thickness could be obtained in a timeless than 1 minutes of deposition and films of thickness greater than 1.04 µm could be obtained in much time greater than 5 minutes.

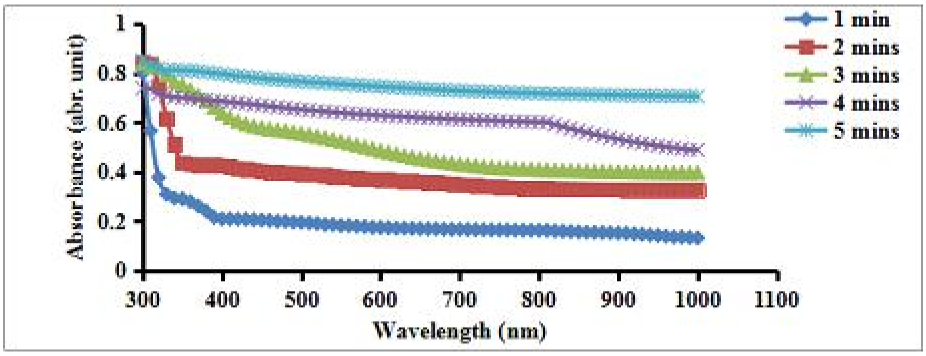

Figure 2. *Plot of absorbance (abr. unit) versus wavelength (nm) of CdMnO2 Thin films at various time of deposition.*

Figure 2 reveals a decrease in absorbance as wavelength increases also, the absorbance increases as time of deposition increases. Figure 3 reveals an increase in transmittance as wavelength increases also, the transmittance decreases as time of deposition increases. The high optical transmittance in the visible region suggest that the film could be used for solar cell fabrication.

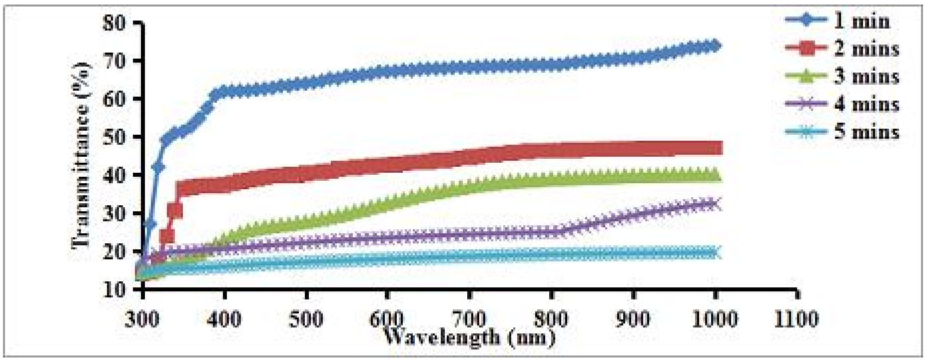

Figure 3. *Plot of transmittance versus wavelength (nm) of CdMnO2Thin films at various time of deposition.*

Figure 4 shows an increase in reflectance as wavelength increases within UV region but remain the same within VIS – NIR regions expect for films deposited at 1 minute and 4 minutes. Figure 5 shows an increase in refractive index as wavelength increases within UV region but remain the same within VIS – NIR regions expect for films deposited at 1 minute and 4 minutes.

Figure 6 shows that the band gap energy of the films decreases as time of deposition increases. Band gap energy between 2.8 eV - 3.85 eV was obtained. This shows that the deposited film is a wide band gap material. The value of the energy band gap obtained in this work is in line to band gap of 3.85 eV obtained by [15] and slightly higher than band gap value of 2.77 eV obtained by [16].

Volume 4, Issue 1, 2020 ISSN: 2617-3522
DOI: https://doi.org/10.31058/j.mana.2020.41002

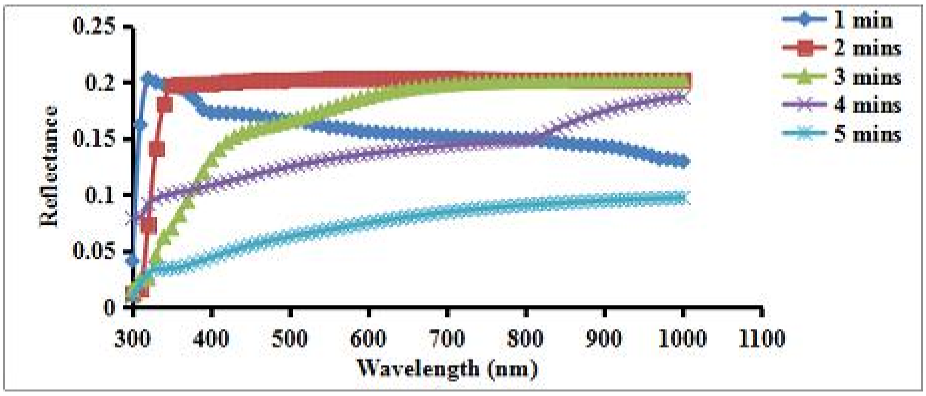

Figure 4. *Plot of reflectance versus wavelength (nm) of CdMnO2Thin films at various time of deposition.*

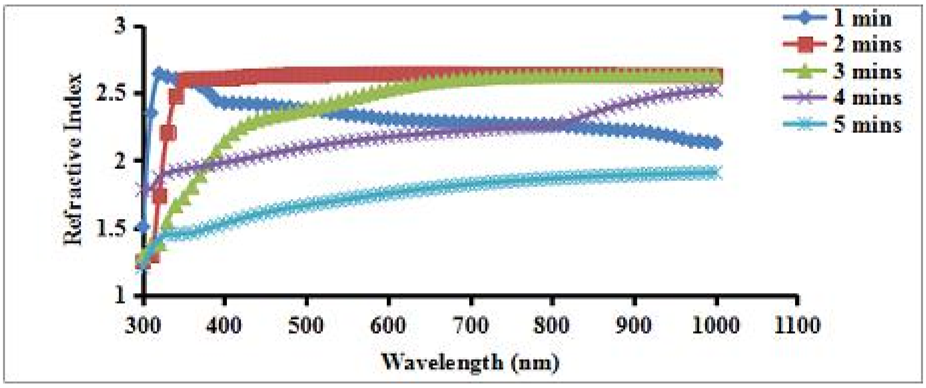

Figure 5. *Plot of refractive index versus wavelength (nm) of CdMnO2Thin films at various time of deposition.*

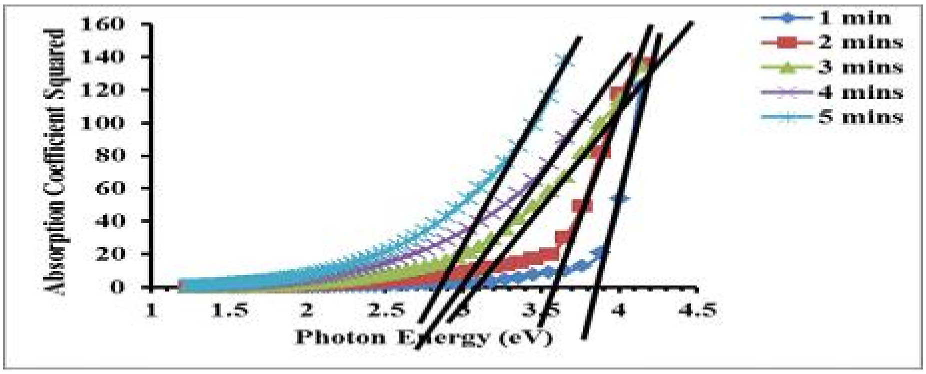

Figure 6. *Plot of absorption coefficient squared versus wavelength (nm) of $CdMnO_2$Thin films at various time of deposition.*

3.2. X − ray Diffraction Analysis

Figure 7 and Figure 8 show the x – ray spectra pattern of the films deposited at 2 and 4 minutes respectively. The x – ray diffraction results show that the films manganese doped cadmium oxide films deposited have Monteponite phase of Cadmium oxide. Figure 7 shows the x –ray spectra of $CdMnO_2$ thin film deposited within 2 minutes. The spectra has miller indices of (111), (200), (220), (31)] and (222) with corresponding 2θ angles of 32.95°, 38.28°, 55.68°, 65.30° and 70.10°. Figure 4.8 shows the x –ray spectra of $CdMnO_2$thin film deposited within 4 minutes. The spectra has miller indices of (111), (200), (220), (311) and (222) with corresponding 2θ angles of 32.99°, 38.33°, 55.60°, 65.31° and 69.98°.

Volume 4, Issue 1, 2020 ISSN: 2617-3522
DOI: https://doi.org/10.31058/j.mana.2020.41002

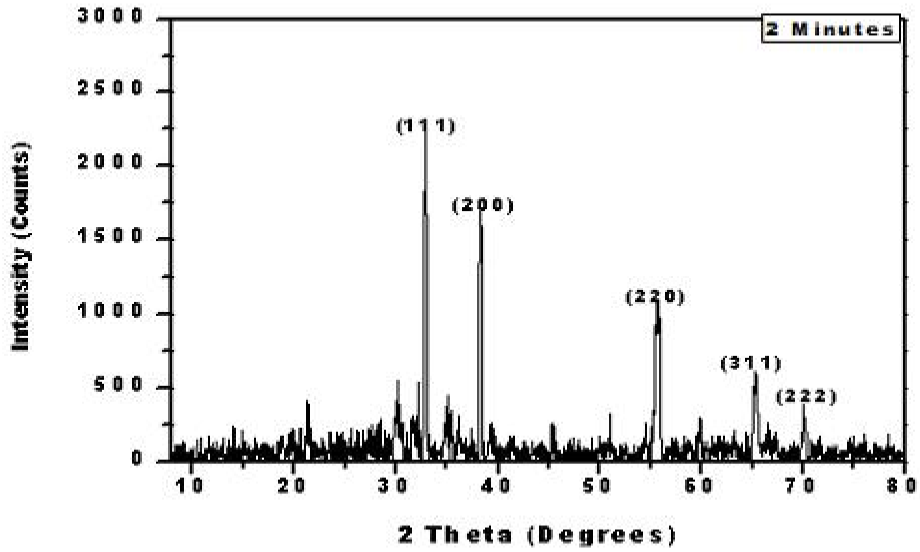

Figure 7. *X – Ray Diffraction pattern of CdMnO2 Thin film deposited at 2 minutes.*

All the peaks correspond to the peaks presence in the standard Powder Diffraction File (PDF) card number 73 – 2245 of JCPDS – ICDD (The Joint Committee on Powder Diffraction Standard - International Centre for Diffraction Data) no peaks corresponding to starting materials such as Cd ion and Mn ion precursors or their oxides were found in the pattern. This purely revealed that the reactant was stoichiometrically mixed to give the desired phase of cadmium manganese oxide and that doping CdO with Mn^{2+} ion does not affect the crystal structure of CdO. The matching of the calculated d_{hkl} values and the standard ones confirms that all the deposited films crystallize well in the cubic structure with preferential orientation of the crystallites along the (111) direction with 2 theta angles of 32.90° for film deposited at 2 minutes, 32.93° for film deposited at 4 minutes. Crystallite sizes of the deposited films obtained using Debye-Scherrer's equation given in equation by [17, 18, 19] ranged from 28.54 nm to 97.05 nm.

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

This range of crystallite sizes confirmed that the deposited films are nano-films of Manganese doped Cadmium oxide ($CdMnO_2$). The result obtained is in line with result obtained by [20].

3.3. Microstructural Properties of Manganese Doped Cadmium Oxide thin Films

The micrograph images of the deposited Cadmium Manganese Oxide ($CdMnO_2$) films taken from digital optical microscope showed that the crystallites are of varying sizes and orientation. This property suggests that the grown films are polycrystalline in nature. ImageJ for Microscopy Image Analysis [21] software was used to determine the average particle sizes and particle counts of the films from the micrograph images. Figures 9 shows the time optimized $CdMnO_2$ films. Average particle sizes and number of counts of the particle in each of the micrograph obtained for time optimized $CdMnO_2$ is shown in Table 2. Figure 10 shows the plot of average particle sizes of deposited films plotted against deposition time. The particle sizes increase as deposition time increases.

Volume 4, Issue 1, 2020 ISSN: 2617-3522
DOI: https://doi.org/10.31058/j.mana.2020.41002

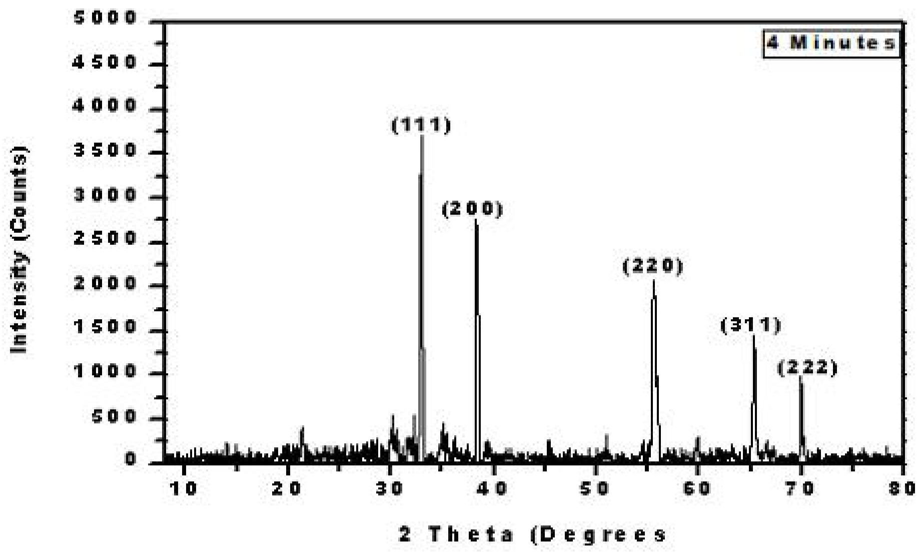

Figure 8. *X – Ray Diffraction pattern of CdMnO2 Thin film deposited at 4 minutes.*

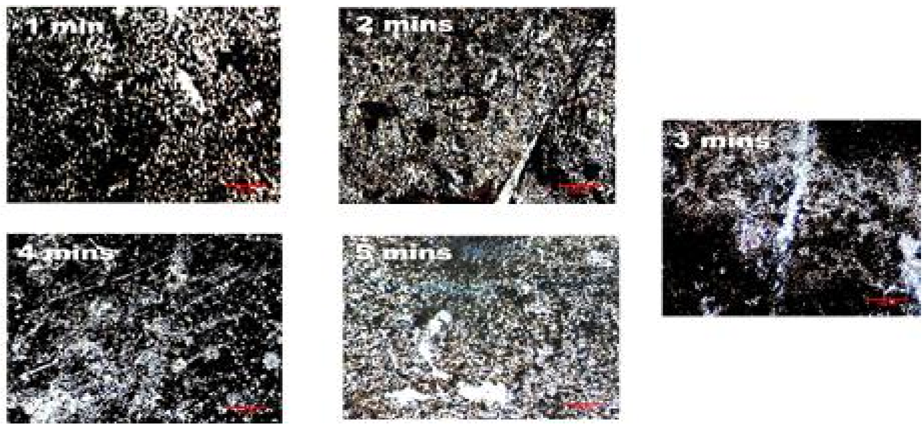

Figure 9. *Micrograph image of Manganese doped Cadmium oxide deposited at varying time.*

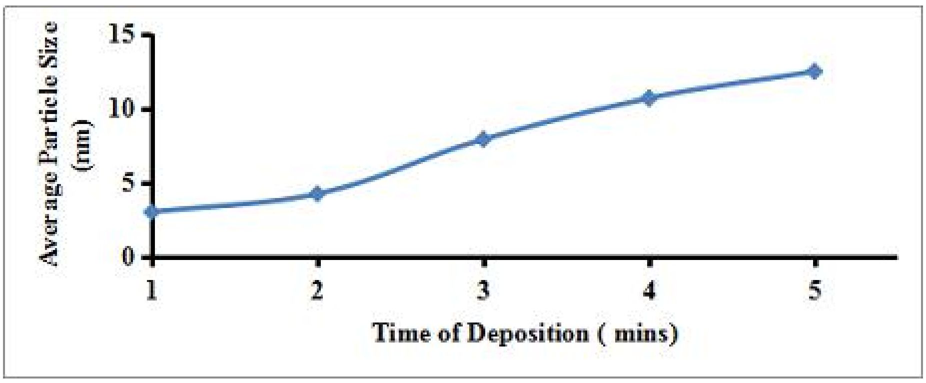

Figure 10. *Plot of Average Particle Sizes of Deposited Films against Deposition Time.*

Table 2. *ImageJ Analysis of Time Optimized Cadmium Manganese Oxide.*

Time (minutes)	Particle Count	Average particle Size (nm)
1	19144	2.98
2	14535	4.21
3	13306	7.89
4	12809	10.65
5	10219	12.45

3.4. Elemental Composition

Figure 11 and Figure 12 represent the Rutherford Backscattering Spectrometry (RBS) graphs of $CdMnO_2$ film deposited at 2 minutes and 4 minutes respectively. These results as shown in Table 3 revealed the percentage composition of the elements in each of the deposited samples of manganese doped cadmium oxide studied. The Rutherford Backscattering Spectrometry (RBS) results of the films clearly show that the samples contain all the elements required for the formation of the desired films of manganese doped cadmium oxide films. Two layers were observed by the RBS machine, layer 1 and layer 2. Layer 1 represents the layer of the film deposited while layer 2 represents the layer of the substrate used for the experience. The thickness of the films measured in atoms/cm^2 shows that film deposited at 2 minutes has thickness of $2.02 \times 10^{18}\, atoms/cm^2$. Film deposited at 4 minutes has thickness value of $3.22 \times 10^{18}\, atoms/cm^2$. This result confirms the formation of $CdMnO_2$in the deposited films. The nature of the thickness obtained here is in line with the nature of the optical thickness obtained in the Figure 1 above. Table 3 shows the elemental composition and thickness in atom/cm^2.

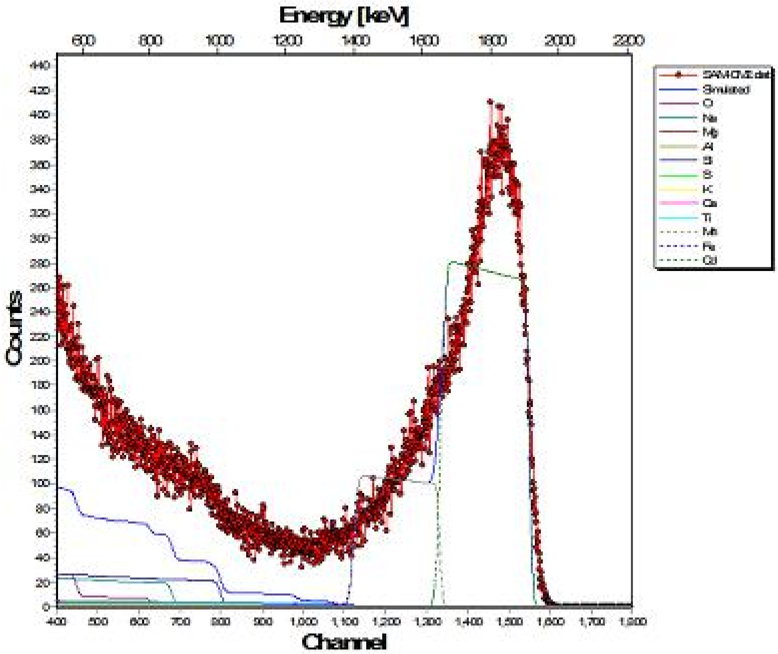

Figure 11. *Elemental Composition of Sample Deposited in 2 minutes obtained using RBS Techniques.*

Table 3. *Elemental composition and thickness (atom/cm^2) of the deposited $CdMnO_2$ Thin films.*

Samples	**LAYER 1:**				**Thickness (Atoms/cm^2)**
	Composition	**Cd**	**Mn**	**O**	
2 minutes	Elemental Weight (%)	30.28	40.92	28.80	2.02×10^{18}
4 minutes	Elemental Weight (%)	32.66	40.52	26.82	3.22×10^{18}

Volume 4, Issue 1, 2020 ISSN: 2617-3522
DOI: https://doi.org/10.31058/j.mana.2020.41002

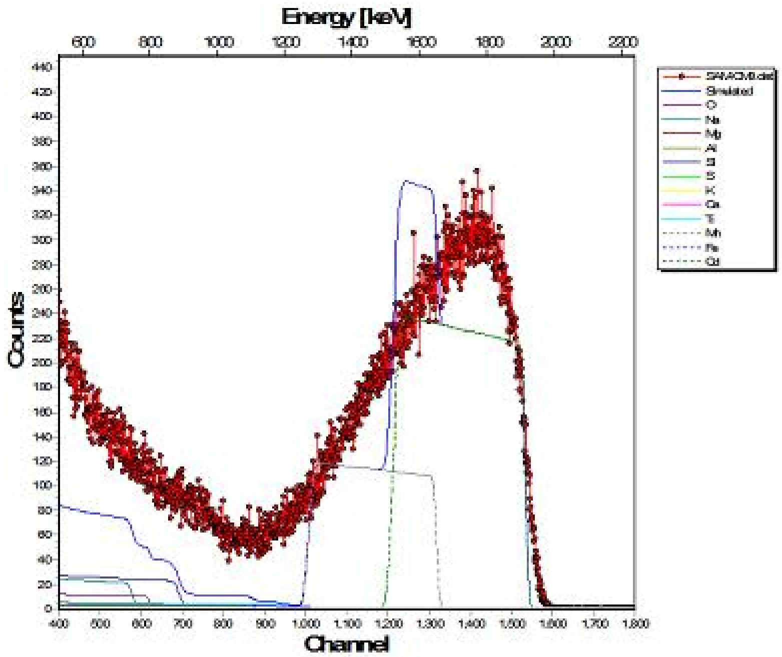

Figure 12. *Elemental Composition of Sample Deposited in 4 minutes obtained using RBS Techniques.*

4. Conclusion

The results revealed that absorbances of the films were high in VIS region but decreases towards the NIR region. Transmittance of the films is low in VIS region but increases towards the NIR region. The deposited films have optical band gap energy ranging from 2.80 eV to 3.85 eV. The deposited films have low reflectance and refractive index obtained ranged from 2.64 to 1.01. Average optical thickness of the deposited films revealed that the films have optical depth between 1.35 µm and 0.05 µm. X – ray diffraction result of the films obtained confirm that the films are of CdO with cubic crystal structure. Crystallite sizes of the films deposited range from 28.54 nm to 97.05 nm. The average microscopic particle sizes of the films were analyzed using ImageJ and values obtained range between 2.98 nm and 33.81 nm. Thickness of the films obtained in atom/cm2 ranges from $2.02 \times 10^{18}\mathrm{atom/cm^2}$ to$3.22 \times 10^{18}\mathrm{atom/cm^2}$. These results confirm that possibilities of using the deposited films in solar cells, low emissive windows, optical communications, flat plat display and transparent electrode.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Author Contributions

Conceptualization: M.E.U.; E.L.N.; O.I.E.; Methodology: M.E.U.; O.N.L.; Software: M.E.U.; O.N.L.; Validation: E.L.N.; O.I.E.; Formal analysis: M.E.U.; O.N.L.; Investigation: M.E.U.; O.N.L.; Resources: M.E.U.; Data Curation: M.E.U.; O.N.L.; Writing – original draft preparation: M.E.U., O.N.L.; Writing – review and editing: M.E.U.; E.L.N.; O.I.E.; O.N.L.; Supervision: E.L.N.; O.I.E.; Project administration: M.E.U.; E.L.N.; O.I.E.; O.N.L.; Funding acquisition: M.E.U.

Funding

This research received no specific grant from any funding agency in the public, commercial or not-for-profit sectors.

Acknowledgments

The authors would like to acknowledge the lecturers in the solid state physics, department of Industrial Physics, Chukwuemeka Odumegwu Ojukwu University Uli, Anambra State, Nigeria for their positive criticism of this work.

Reference

[1] Chopra, K.L.; Paulson, P.D.; Dutta, V. Thin-Film Solar Cells: An Overview. *Prog. Photovolt: Res. Appl.* 2004, 12, 69-92.

[2] Frey, H. Applications and Developments of Thin Film Technology. In: Frey H., Khan H.R. (eds) Handbook of Thin Film Technology. 2015, Springer, Berlin, Heidelberg. DOI: https://doi.org/10.1007/978-3-642-05430-3_1.

[3] Rahman, A.; Shahjahan, M.D.; Khatun, M. H. Structural, Optical and Electrical Properties of Al Doped CdO Thin Films Deposited by Spray Pyrolysis Method. *IOSR Journal of Applied Physics (IOSR-JAP)*, 2019, 11(6), 9-14.

[4] Dong, W.; Zhu, C. Optical properties of surface modified CdO nanoparticles. *Optical Materials*, 2003, 22, 227-233.

[5] Vinodkumar, R.; Lethy, K.J.; Arunkumar, P.R.; Krishnan, R.R.I; Pllai, N.V.; Pillai, V.P.M.; Philip, R. Effect of cadmium oxide incorporation on the microstructural and optical properties of pulsed laser deposited nanostructured zinc oxide thin films. *Material Chemistry and Physics,* 2010, 121, 406-413.

[6] Balu, A.R.; Nagarethinam, V.S.; Suganya, M.; Arunkumar, N.; Selvan, G. Effect of the solution concentration on the structural, optical and electrical properties of SILAR deposited CdO thin films. *Journal of Electronics Devices,* 2012, 12, 739-749.

[7] Mane, R.S.; Pathan, H.M.; Lokhande, C.D.; Han, S.H. An Effective Use of Nanocrystalline CdO Thin Films in Dye-Sensitized Solar Cells. *Solar Energy*, 2006, 80(2), 185-190.

[8] Kawamura, K.; Maekawa, K.; Yanagi, H.; Hirano, M.; Hosono, H. Observation of carrier dynamics in CdO thin films by excitation with femtosecond laser pulse. *Thin Solid Films,* 2003, 445(2), 182-185.

[9] Chu, T.L.; Shirley, S.C. Degenerate cadmium oxide films for electronic devices. *Journal of Electronic Materials*, 1990, 19(9), 1003-1005.

[10] Hames, Y.; San, S.E. CdO/Cu_2O solar cells by chemical deposition. *Solar Energy*, 2004, 77(3), 291-294.

[11] Makuta, D.; Poznyak, S.K.; Kulak, A.I. Hole diffusion transport and photocurrent generation in the degenerate n – CdO/electrolyte Junction. *Solid State Communications.,* 1990, 76(1), 65-68.

[12] Su, L.M.; Grote, N.; Schmitt, F. Diffused planar InP bipolar transistor with a cadmium oxide film emitter. *Electronics Letters,* 1984, 20, 716-717.

[13] Ortega, M.; Santana, G.; Morales-Acevedo, A. Optoelectronic properties of CdO/Si photodetectors. *Solid State Electronics.* 2000, 44, 1765-1769.

[14] Mishra, R.L.; Sharmaa, A.K.; Prakash, S.G. Gas sensitivity and characterization of cadmium oxide (CdO) semiconducting thin film deposited by spray pyrolysis technique. *Digest Journal of Nanomaterials and Biostructures,* 2009, 4(3), 511-518.

[15] Ezenwa, I.A.; Ezeobele E.E.. Fabrication and Optical characterization of CdO thin films deposited by chemical bath method. Proceedings of the 1st African International Conference / Workshop on Application of Nanotechnology to Energy, Health and Environment at University of Nigeria, Nsukka, Nigeria, 2014, 23-29, March.

[16] Mohandas, T.; Thiagaragan, R.; Srinivasan D. Optical Characterization of Manganous doped Cadmium Oxide Thin Films deposited by Spray Pyrolysis method. *Der Chemica Sinica,* 2018, 9(3), 746-749.

[17] Ezenwaka, L.N.; Umeokwonna, N.S.; Okoli, N.L. Optical, structural, morphological, and compositional properties of cobalt doped tin oxide (CTO) thin films deposited by modified chemical bath method in alkaline medium. *Ceramics International*, 2020, 46(5), 6318-6325.

[18] Okoli N.L.; Nkamuo C.J.; Elekalachi, C.I. Effect of Dip Time on Electrodeposited Zinc Oxide Nanofilms. *American Journal of Materials Synthesis and Processing*, 2018, 3(2), 7-11.

[19] Ravindranah, K.; Prasad, K.D.V.; Rao, M.C. Spectroscopic and luminescent properties of Co^{2+} doped tin oxide thin film by spray pyrolysis. *Aims Mater. Sci.,* 2016, 3(3), 796-807.

[20] Amutha, S.; Chandiramouli, R.; Jeyaprakash, B.G. Microstructural and electrical properties of Mn doped nanostructured CdO thin films. *Journal of Applied Sciences,* 2012, 12, 1641-1645.

[21] Abramoff, M.D.; Magalhaes, P.J.; Ram, S.J. Image processing with ImageJ. *Biophotonic International,* 2004, 11(7), 36-42.