Effects of Annealing Temperature on CdO Thin Films Produced by Using Electro Deposition Method under Magnetic Field

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Abstract: ***For obtaining to CdO thin film, electrochemical deposition method was used under magnetic field at different annealing temperature and the results was reported in this paper. It was understood that there are effects of annealing temperature on the CdO structural and physical properties of the samples. The structure of CdO samples was analyzed by X-ray diffraction. It is realized that crystal structures of the samples was polycrystalline and they have several peaks of cubic face structure. The, microstrain, dislocation density, crystallite size and number of dislocations of the CdO thin film were calculated and listed. Optical band gap decreases from 2.31 eV to 1.95 eV with increase in annealing temperature. it is evident that the SEM images are consisted of the CdO nanocrystalline grains along with some spongy clusters. The spongy cluster increases as annealing temperature increases.***

Keywords: CdO, magnetic field, spongy cluster, annealing temperature

1. Introduction

Because of the fact that CdO thin films have high optical transmittance, low electrical resistivity and high carrier concentration it is importance for electronic device applications, and it has low band gap and in the visible region of the solar spectrum [1,2]. CdO has a direct energy band gap ~2.3 eV and two indirect transitions at lower energies. [3]. CdO has attracted considerable attention for various applications such as solar cells, photodiodes phototransistors, liquid crystal displays and IR detectors. Until now somewhat methods have been used to synthesize the assorted nanostructures, including the plasma-assisted approach [4–6], chemical bath deposition method [7], solvothermal condition [8] and thermal evaporation method [9,10], radio frequency magnetron sputtering [11], molecular beam epitaxy [12], sol–gel process [13], chemical vapour deposition [14], spray pyrolysis [15] and electro deposition [23-27]. The method of electro deposition presents low cost, a simple and quick method for the obtaining of CdO nanostructure. Moreover, many researchers investigated the effect of annealing temperature on the optoelectronic, structural and electrical properties of nanocrystalline CdO thin films [16,17] investigated structural, optical and electrical properties of thermal evaporated annealed CdO films [18].

In this work, electrodeposition method under variable magnetic field was used to deposit thin films of CdO on ITO substrates after various annealing temperatures. The deposited films were characterized structurally, morphologically and optically. The effects of annealing temperatures on the properties of the films were studied and their respective possible applications based on these properties were presented.

2. Preparation of CdO thin films

Electrodeposition method was employed for thin films of CdO in aqueous solution (100ml in volume) of 0.01 M $Cd(NO_3)_2$ and 0.1 M KCl. KCl as to be supporting electrolyte. The pH of the electrolyte was fixed at 7 in this deposition. Deposition of the CdO thin films was carried out using chronoamperometry method with a standard three electrode system. ITO is used as working electrode, saturated calomel electrode as reference electrode and platinum wire as counter electrode here. In all experimentally the cathodic potential is fixed at -0.69 V and the time deposition is 45 minutes. Schematic diagram of electrochemical deposition system demonstrate in Figure 1 was used all experiment [24]. The magnetic field was applied perpendicular to the surface of the ITO during the depositions. The frequencies of the magnetic field were adjusted to 50Hz. Pending the depositions temperatures were hold at 80 ± 2°C. Deposition solutions were mixed at 550 rpm. After the deposited thin films was annealed in air at a range of 425°C to 525°C for 30 minutes to transform the hydroxide phase to the oxide. The depositions contexts are shortened in Table 1.

Table 1: The deposition conditions of the CdO thin films

Experiments	Concentration of $Cd(NO_3)_2$ (M)	Deposition time (min)	Cathodic Potential (V)	Magnitude of Magnetic field (mT)	Deposition temperature (°C)	Annealing Temperature (°C)	pH
A1	0.01	45	-0.69	3.25	80± 2	525	7
A2	0.01	45	-0.69	3.25	80 ± 2	475	7
A3	0.01	45	-0.69	3.25	80± 2	425	7

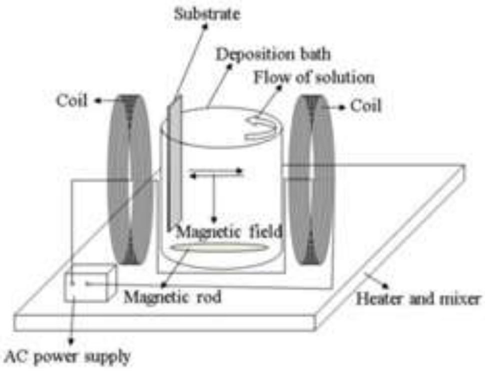


Figure 1: Schematic illustration of electrodeposition mechanism [24]

3. Sample Characterization and measurements

The crystalline phase of annealed samples was characterized by recording the X-ray Diffraction spectra in the range of 20–80°. The scanning electron microscopic (SEM) picture of the CdO films was taken using Zeiss SUPRA 40VP model. JASCO V–530 UV-vis device was used to record the optical transmission for CdO thin films after annealing in the range (300 – 600 nm).

4. Results

4.1 Optical studies of CdO thin films

Fig.2 shows the optical spectra of CdO thin films. Absorbance measurements are estimated to calculate optical characteristics of the CdO thin films. When annealing temperature of the sample was 525°C, the absorbance was nearly 0.75. Besides when annealing temperature decreased up to 425°C the absorbance was nearly 1.7. The film thicknesses are related to annealing temperature. Consequently, the absorbance depends on the film thickness and the film thicknesses depend on the annealing temperature of the CdO films.

The optical band gap, Eg was anticipated by extrapolating the linear part of Tauc's [25] plot of $(\alpha h\nu)^2$ as a function of hν in Figure 3. The intercept of the energy axis gives the value of Eg which increased from 1.95 eV to 2.31 eV. Thence, if the annealing temperature decreased, the energy band gap of the CdO films was reduced.

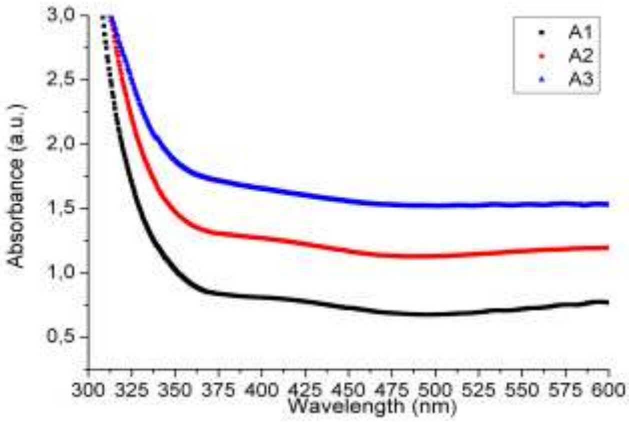


Figure 2: Absorption spectra of CdO thin films acquired at different annealing temperature

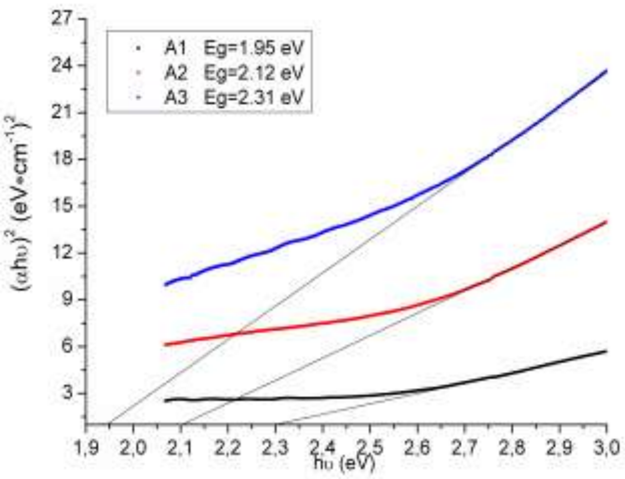
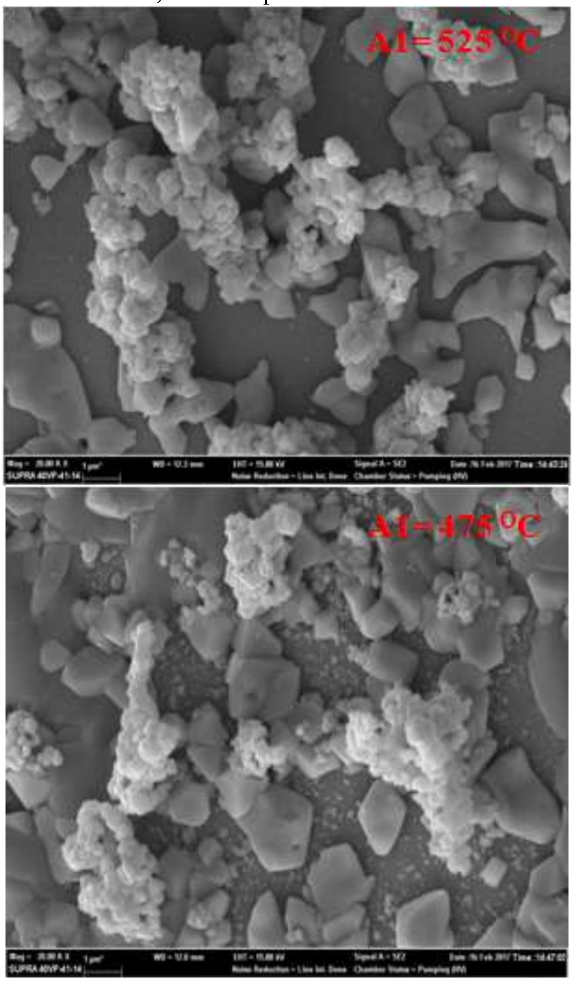


Figure 3: Tauc plots and band gaps of CdO thin films acquired at different annealing temperature

4.2 Surfaces of CdO thin films

The surface morphological study of the CdO films for different annealing temperature was carried out using 20000 times magnified surface SEM images as demonstrated in Figure 4. From the micrographs, it is evident that the samples are composed of the CdO nanocrystalline grains along with some spongy clusters. The spongy cluster reduces as annealing temperature reduces. Also, it is not seen on these surfaces that crack, voids or pinholes.



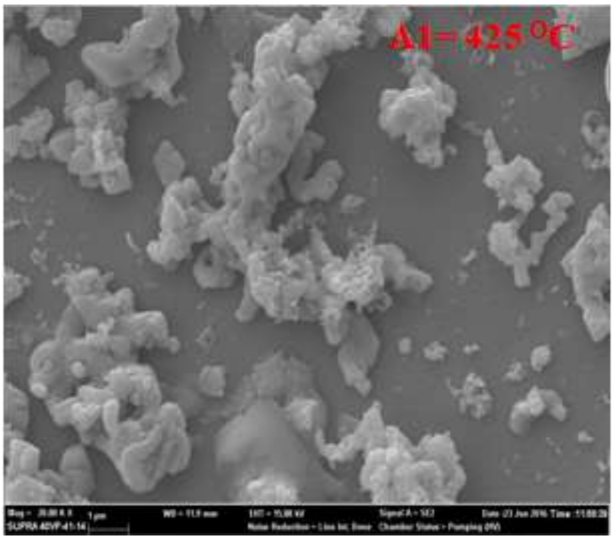


Figure 4: SEM images of the CdO films thin films acquired at different annealing temperature magnified 20000 times.

4.3 XRD of the CdO thin films

The XRD patterns revealed that are the position of the all the films diffraction peaks fit well with the cubic structure of (98-005-0848) corresponding to (1 1 1), (0 0 2), (0 2 2), (1 1 3) and (2 2 2) planes.

The texture coefficient TC (h k l) was used to determine preferred orientation and it obtained by using following formula [26]:

$$TC = \frac{I_{(hkl)}/I_{0(hkl)}}{\frac{1}{N}\sum_N \left(\frac{I_{(hkl)}}{I_{0(hkl)}}\right)} \quad (1)$$

where I(hkl) is the measured relative intensity of a plane (hkl), I_0(hkl) is the standard intensity of the plane (hkl) taken from ASTM card and N is the reflection number. The calculated texture coefficients were demonstrated in Table 2. It has been reported that all films have 3 texture coefficient values larger than 1 concern with different planes. As a result, it is thought that all films which was produced to be random.

The crystallite size of the films for all plane was calculated using the Scherrer formula

$$cs = \frac{0.089 * 180 * \lambda}{314 * \beta * \cos\theta_C} \text{nm} \quad (2)$$

It is observed that the crystallite size is significantly high for A1 sample whose annealing temperature is high. Confirming the fact that crystallization improves as the annealing temperature increases.

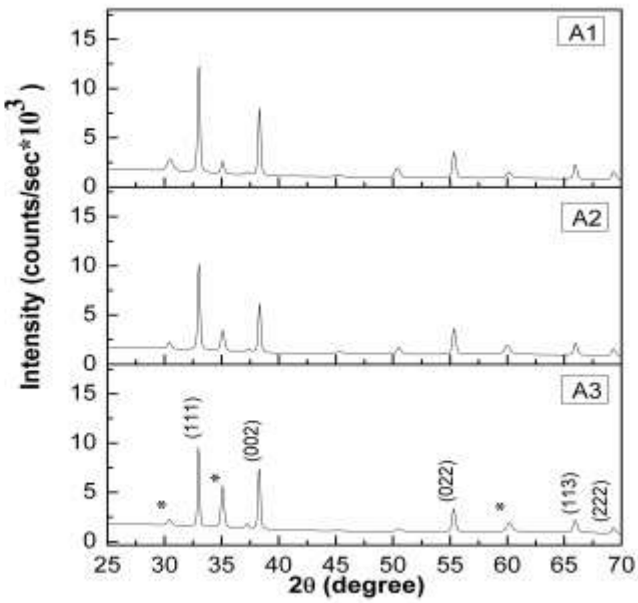


Figure 5: X-ray diffractograms of CdO thin films acquired at different annealing temperature

Calculated film thicknesses which using gravimetric method was given in Table 2. While the thicknesses of the CdO films were decreased as the annealing temperature were decreased.

The constant of the lattice for cubic rock salt structure is given bellow as is [27].

$$a = d\sqrt{(h^2 + k^2 + l^2)} \quad (3)$$

where h, k and l are the Miller indices and d is the interplanar distance. Intercalarity average stress and micro strain were calculated by using Equation 4 and 5 respectively and they are demonstrated in Table 3.

$$\varepsilon = (a_0 - a)/a_0 \quad (4)$$

$$S = \varepsilon Y/(2\sigma) \quad (5)$$

where a and a_0 are the corrected value of lattice parameter and lattice parameter of the bulk sample of CdO thin films respectively. The Y and σ are in order of the Young's modulus and Poisson's ratio of the bulk crystal. The value of Y and σ is 141,67 GPa and 0.33 for cubic CdO thin films respectively [28].

The Nelson–Riley plots presented that the corrected values of lattice parameters of which is demonstrated in Figure 6, Figure 7 and Figure 8 [29]. The declination of the corrected lattice constant (a) from the strain of bulk sample (a_0 = 4.695 nm) indicates that the obtained films were under strain [30]. In ordinarily, the dislocation density detected as the length of dislocation lines per unit volume, has been conjectured using the Equation 6 and offered in Table 3 [31].

$$\delta = \frac{1}{(cs)^2} \quad (6)$$

With respect to Table 4, the micro strain and average stress for the CdO samples are significantly is high for A1. The dislocation density is significantly is low for A1.

Table 2: The intensity, texture coefficient, and film thickness of the CdO thin films acquired at different annealing temperature

Experiment	2θ	Intensity (Count/ Seconds)	I / I_O	TC	(hkl)	Film Thickness (nm)
A1	32,9666	9575,163	100	4,65	(111)	441
	38,2669	7080,927	64,05	2,98	(002)	
	55,2761	3313,542	25,18	1,17	(022)	
	65,9175	2191,786	13,76	0,64	(113)	
	69,2572	1424,958	7,43	0,35	(222)	
A2	32,996	9224,437	100	4,58	(111)	429
	38,2968	5076,797	60,85	2,79	(002)	
	55,2995	3631,377	32,46	1,49	(022)	
	65,9401	2179,339	15,78	0,72	(113)	
	69,2707	1559,467	9,12	0,42	(222)	
A3	32,9842	11783,42	100	3,03	(111)	368
	38,2874	6876,181	64,94	1,97	(002)	
	55,2955	3585,151	25,93	0,79	(022)	
	65,92	2277,868	17,09	0,52	(113)	
	69,2734	1556,493	8,28	0,25	(222)	

Table 3: The crystalite size, dislocation densities, lattice parameter, micro strain values, and average stress values of the CdO thin films acquired at different annealing temperature

Experiment	2θ	Crystalite Size (nm)	Latice Parameter a (Verified) (Å)	Mikro Strain$*10^{-3}$	Dislocation Density (lines/m^2) $*10^{15}$	Average Stress (10^8N/m^2)
A1	32,9666	63	4,7993	22,2	2,52	47,7
	38,2669	43	4,7041	1,95	5,49	4,18
	55,2761	34	4,7006	1,20	8,59	2,57
	65,9175	29	4,6999	1,04	12	2,24
	69,2572	49	4,6996	0,99	4,17	2,12
A2	32,996	42	4,7021	1,51	5,66	3,23
	38,2968	43	4,7006	1,19	5,49	2,56
	55,2995	34	4,6988	0,81	8,59	1,73
	65,9401	36	4,6985	0,74	7,70	1,58
	69,2707	37	4,6988	0,82	7,41	1,76
A3	32,9842	42	4,7037	1,85	5,66	3,98
	38,2874	43	4,7017	1,43	5,49	3,07
	55,2955	34	4,6991	0,87	8,59	1,87
	65,92	48	4,6998	1,01	4,33	2,17
	69,2734	37	4,6987	0,79	7,41	1,70

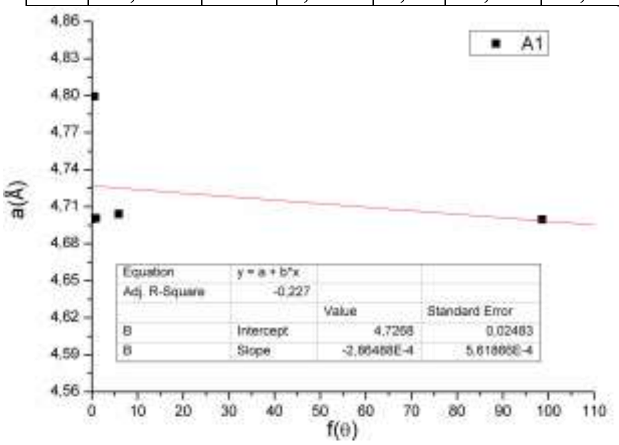


Figure 5: Nelson–Riley plots of CdO thin films acquired at 525 °C annealing temperature

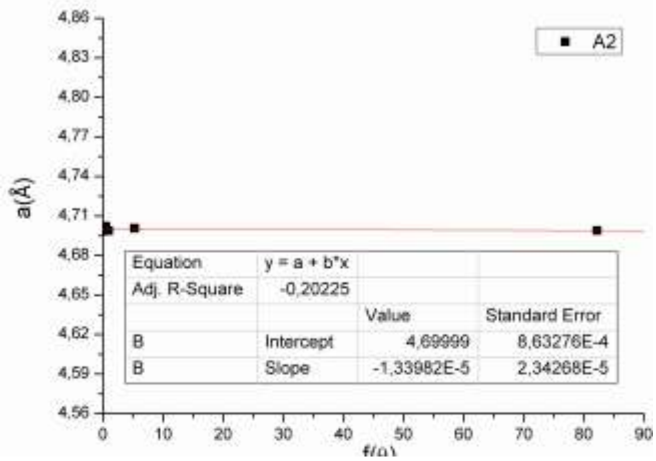


Figure 6: Nelson–Riley plots of CdO thin films acquired at 475 °C annealing temperature

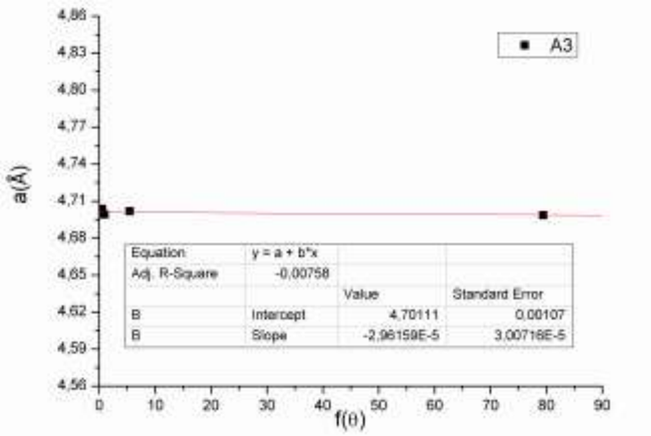


Figure 6: Nelson–Riley plots of CdO thin films acquired at 425 °C annealing temperature

5. Conclusion

In this study, electrodeposition method was used for depositing of CdO thin films. It is reported that when annealing temperature was increased, the absorbance level and energy band gap were decreased. Energy band gap was decreased from the 2.31 eV to the 1.95 eV as annealing temperature was increased from the 425 °C to the 525°C. The structures of the samples were investigated by using an X-Ray diffractometer. When film thicknesses were taken into consideration, it was seen that all films gave the same intensity. Surface morphologies were investigated by using a SEM and they revealed the spongy cluster increases as annealing temperature increases.

6. Acknowledgement

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References

[1] J.Santos-Crua, G.Torres-Delgado, R.Castanedo-Perez, S.Jimenez-Sandoval, J.Marquez-Marin, O.Zelaya-Angel, Influence of the growth parameters of p-CdTe thin films

on the performance of Au–Cu/p-CdTe/n-CdO type solar cells Sol. Energy, 80, 142-147, (2006).

[2] A.R. Balu, V.S. Nagarethinam, M.Suganya, N.Arunkumar, G.Selvan, Nanocrystalline NiO Thin Films prepared by a low cost simplified spray technique using perfume atomizer J. Electron Devices 12, 739-749, (2012).

[3] F. A. Benko and F. P. Koffyberg, " Quantum efficiency and optical transitions of CdO photoanodes , " Solid State Commun., 57, (1986) 901 - 903.

[4] U. Cvelbar, K. Ostrikov, M. Mozetic, Nanotechnology 19 (2008) 405605–405611.

[5] K. Ostrikov, A.B. Murphy, J. Phys. D: Appl. Phys. 40 (2007) 2223–2241.

[6] M. Mozetic, U. Cvelbar, M.K. Sunkara, S. Vaddiraju, Adv. Mater. 17 (2005) 2138–2142.

[7] D.S. Dhawale, A.M. More, S.S. Latthe, K.Y. Rajpure, C.D. Lokhande, Appl. Surf. Sci. 254 (2008) 3269–3273.

[8] Y.C. Zhang, G.L. Wang, Mater. Lett. 62 (2008) 673–675.

[9] X.L. Liu, S. Li, S. Han, J. Han, C.W. Zhou, Appl. Phys. Lett. 82 (2003) 1950–1952.

[10] H.B. Lu, L. Liao, H. Li, Y. Tian, D.F. Wang, J.C. Li, Q. Fu, B.P. Zhu, Y. Wu, Mater. Lett. 62 (2008) 3928–3930.

[11] Z. Zhao, D.L. Morel, C.S. Ferekides, Electrical and optical properties of tin-doped CdO films deposited by atmospheric metalorganic chemical vapor deposition, Thin Solid Films 413 (2002) 203.

[12] S. Sadofev, S. Blumstengel, J. Cui, J. Puls, S. Rogaschewski, P. Schafer, Visible band-gap ZnCdO heterostructures grown by molecular beam epitaxy, Appl. Phys. Lett. 89 (2006) 201907.

[13] G. Torres-Delgado, C.I. Zuniga-Romero, O. Jimenez-Sandoval, R. Castanedo-Perez, B. Chao, S. Jimenez-Sandoval, Percolation mechanism and characterization of (CdO)y(ZnO)1 y thin films, Adv. Funct. Mater. 12 (2002) 129.

[14] F. Wu, L. Fang, Y.J. Pan, K. Zhou, Q.L. Huang, C.Y. Kong, Effect of substrate temperature on the structural, electrical and optical properties of ZnO:Ga thin films prepared by RF magnetron sputtering, Physica E 43 (2010) 228.

[15] H. Tabet-Derraz, N. Benramdane, D. Nacer, A. Bouzidi, M. Medles, Investigations on ZnxCd1 xO thin films obtained by spray pyrolysis, Sol. Energy Mater. Sol. Cells 73 (2002) 249.

[16] M. Santamaria, P. Bocchetta, F. D. Quarto, "Room temperature electrodeposition of photoactive Cd(OH)

[17] Kıyak Yıldırım, A. and Altıokka, B. (2017). An investigation of effects of bath temperature on CdO films prepared by electrodeposition. Applied Nanoscience. doi: 10.1007/s13204-017-0591-x

[18] Kıyak Yıldırım, A. and Altıokka, B. (2017). Effects of concentration on CdO films grown by electrodeposition. Applied Nanoscience. 7:131–135. doi:10.1007/s13204-017-0552-4

[19] Altıokka, B. and Kıyak Yıldırım, A. (2018). Effects of pH on CdO films deposited onto ITO coated glass substrates by electrodeposition. Int. J. Surface Science and Engineering, 12(1), pp.13-22.

[20] Kıyak Yıldırım, A. and Altıokka, B. (2016). CdO Films Obtained by Electrodeposition at -0.5 V and -0.7 V Potentials Range Journal of Materials Science and Engineering A 6 (9-10) 249-253 doi: 10.17265/2161-6221/2016.9-10.006

[21] M. AzizarRahman, M.K.R.Khan, Effect of annealing temperature on structural, electrical and optical properties of spray pyrolytic nanocrystalline CdO thin films, Materials Science in Semiconductor Processing 24(2014) 26–33

[22] A.A.Dakhel,F.Z.Henari,Cryst.Res.Technol.38(2003)979–985.

[23] J.S.Cruz,G.T.Delgado,R.C.Perez,S.J.Sandoval,O.J.Sandoval,C.I.Z.Romero,J.M.Marın,O.Z.Angel,ThinSolidFilms493(2005)83–87.

[24] Altıokka B. and Kıyak Yıldırım A., 2015 Effects of External Alternating Magnetic Field on ZnO Films Obtained by ElectrodepositionArab J Sci Eng., DOI 10.1007/s13369-015-1980-7

[25] J. Tacu, Amorphousand liquid. Semiconductors, Pelenum, NewYork, 1974.

[26] T. Sivaraman, A.R. Balu, V.S. Nagarethinam, CdS thin films Fabricated by a simplified Spray technique from different Substrate Temperatures – Structural, Morphological, Optical and Electrical analysis Mater. Sci. Semiconductor Processing, 27 915–923, (2014).

[27] Gadave, K.M., Jodgudri, S.A. and Lokhande, C.D. (1994). Chemical deposition of PbS from an acidic bath. Thin Solid Films, Vol. 245, pp.7–9.

[28] JemmyCinthia A., Sudhapriyang G., Rajeswarapalanichamy R., Santhosh M., 2014, Structural, Electronic and Elastic Properties of ZnO and CdO: A First-Principles Study Procedia Materials Science Volume 5, Pages 1034-1042

[29] Soonmin, H.O. Kassima, A. Weetee, T. (2013). The role of Bath Temperature in aqueous Acidic Chemically PbS Films. Journal of Basic and Applied Scientific Research, Vol. 3(11), pp.353-357.

[30] A. Antony, K.V. Murali, R. Manoj, M.K. Jayaraj , Materials Chemistry and Physics 90, 106 (2005).

[31] Bilgin, V., Kose, S., Atay, F., Akyuz, I., 2005. The effect of substrate temperature on the structural and some physical properties of ultrasonically sprayed CdS films. Mater. Chem. Phys. 94, 103–108.

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