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Effects of Percentage of the Volume of the Electrolyt on CdO Thin Films Growth by Using Electro Deposition Method Under Magnetic Field

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Abstract: ***This work presented that percentage of the volume of the electrolyte effect on CdO thin films obtained by electrodeposition. The crystal properties were investigated by using an X-Ray diffractometer (XRD). The XRD results showed that polycrystalline structures of CdO were formed which have cubic face form. Besides, the dislocation densities, crystallite sizes and micro strains were calculated via XRD results. It is observed that when percentage of the volume of the $Cd(NO_3)_2$ was decreased, the intensity of the films diffraction peaks were increased. The energy band gaps of the samples were varied from the 2.56 to the 2.16 depends on increasing annealing temperature. The surfaces of the CdO samples were analyzed SEM photographs and these photographs showed that there are striated like CdO structure, CdO nanocrystalline grains along with some spongy clusters and CdO nanocrystalline grains on the surfaces of some films. Moreover, the spongy clusters were decreased as $CdCl_2$ volume in the final solution was reduced.***

Keywords: CdO nanocrystalline grains, magnetic field, spongy cluster, striated like structure

1. Introduction

Thin films of CdO are used electronic devices because of the fact that it shows low electrical resistivity and high carrier concentration. Besides it has low band gap and shows high transmittance in the visible region [1,2]. CdO crystals have direct transition and average energy gap ~2.3 eV [3]. There are various application areas such as photodiodes, phototransistors, solar cells, IR detectors and liquid crystal displays. In the literature, there are various technique for growing CdO such as plasma-assisted approach [4–6]. solvothermal condition [7] chemical bath deposition method [8] and radio frequency magnetron sputtering [9] thermal evaporation method [10,11] molecular beam epitaxy [12], sol–gel process [13], spray pyrolysis [14], chemical vapour deposition [15] and electro deposition [16-20]. Among these methods electrodeposition is simple, quick and low costs

The effects of percentage of the volume of the electrolyte on CdO films were investigated. In all experiments, the deposition was carried out under alternating magnetic field. The indium tin oxide (ITO) coated glass substrates were used as to be working electrodes. The structural, optical and morphological effects of annealing temperature were presented.

2. Preparation of CdO thin films

Thin films of CdO were prepared by electrodeposition method according to percentage of the volume of the $Cd(NO_3)_2$ and $CdCl_2$ aqueous solutions and they are demonstrated in Table 1. The experiments named as ON1, ON2, ON3, ON4, and ON5 and ON6. KCl was selected for the supporting electrolyte. The deposition solution pH was ranged from 9.7 to 6.5. Producing of the CdO thin films was relaized using chronoamperometry method with a standard three electrode system. ITO is operated as working electrode, saturated calomel electrode as reference electrode and platinum wire as counter electrode for this system. In all producing the cathodic potential and the time deposition are fixed at -0.73 V and 45 minutes, respectively. Schematic diagram of electrochemical deposition system represent in Figure 1 [20]. The alternating magnetic field was perpendicularly to the surface of the working substrates. In the experiments, 50 Hz was chosen as to be frequency of magnetic field. The final solutions were heated up to 84 ± 2°C. Deposition electrolytes were stirred with 550 rpm. After the deposited thin films was annealed by using an oven.

Table 1: The deposition requirements of the CdO thin films

Experiments	Volume of $CdCl_2$ (0.022M) mL	Volume of $Cd(NO_3)_2$ (0.022M) mL	Deposition time (min)	Cathodic Potential (V)	Magnitude of Magnetic field (mT)	Deposition temperature (°C)	pH
ON1	0	90	45	-0.73	3.25	84± 2	6.5
ON2	15	75	45	-0.73	3.25	84 ± 2	7.3
ON3	30	60	45	-0.73	3.25	84± 2	7.7
ON4	60	30	45	-0.73	3.25	84± 2	8.3
ON5	75	15	45	-0.73	3.25	84± 2	8.9
ON6	90	0	45	-0.73	3.25	84± 2	9.7

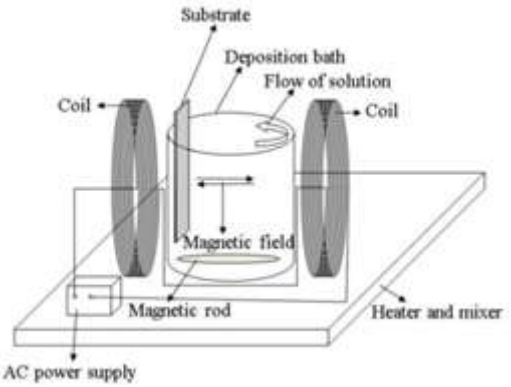


Figure 1: Schematic illustration of electrodeposition mechanism [20]

3. Sample characterization and measurements

The XRD peaks were recorded in range of 20–80° by using an X-ray diffractometer. A Zeiss SUPRA 40VP model scanning electron microscope was employed to obtain surface photographs. A JASCO V–530 UV-vis spectrophotometer was used to obtain optical absorbance 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. If percentage of the volume of the electrolyte was investigated, we could report that the absorbance was significantly high for ON6. Besides, when volume of the electrolyte of the sample was changed, the absorbance was decreased. Therefore, the film thicknesses increased on the absorbance of CdO films and they are related to percentage of the volume of the electrolyte. The Tauc's plots were used to estimate energy gap of the samples [21] $(\alpha h\nu)^2$ versus $h\nu$ plots were obtained and the intercept of the $h\nu$ axis gives the value of Eg. The energy gaps of the films were varied between 2.56 eV and 2.16 eV. Thus, if the percentage of the volume of the $Cd(NO_3)_2$ are decreased, the energy band gap of the CdO films was increased proportionally.

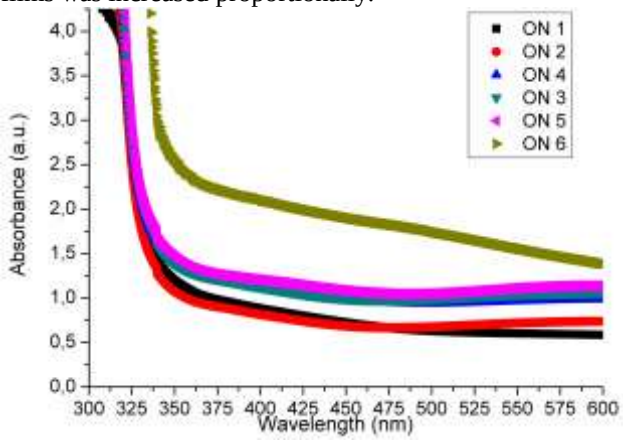


Figure 2: Absorption spectra of CdO thin films carried at percentage of the volume of the electrolyte

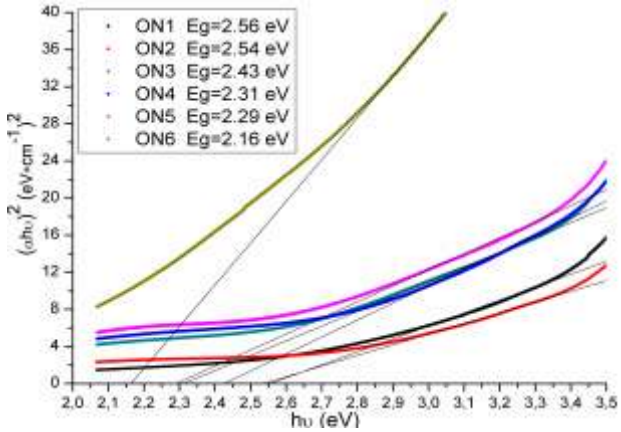
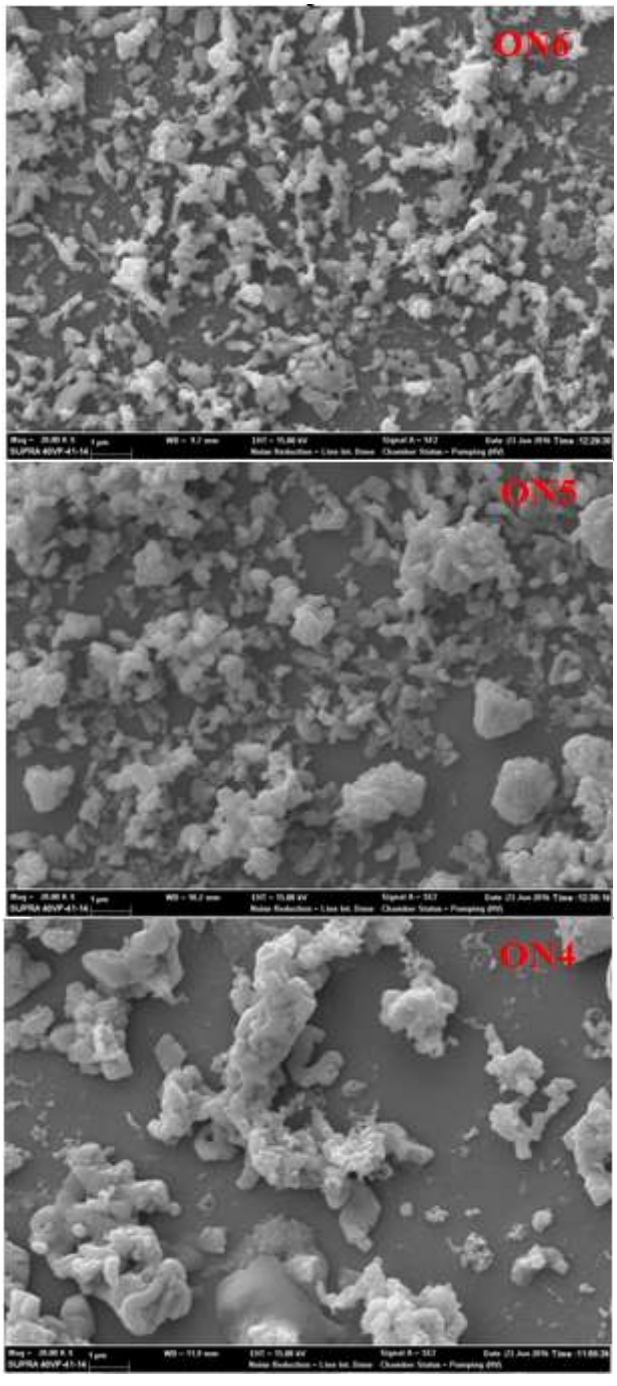


Figure 3: Tauc plots and band gaps of CdO thin films carried at different percentage of the volume of the electrolyte

4.2 Surfaces of CdO thin films

The surface morphological study of the CdO films for percentage of the volume of the electrolyte was made using 20000 times magnified surface SEM images as displayed in Figure 4 and Figure 5. It is observed that there are striated like structure on the surface of the sample obtained ON1. From the micrographs of ON2, ON3 and ON4, it is evident that the samples are composed of the CdO nanocrystalline grains along with some spongy clusters. The spongy clusters were reduced as $CdCl_2$ volume in the final solution was decreased. Moreover from the micrographs of ON5 and ON6 there are no spongy clusters on the surface. These two surface CdO are composed of the CdO nanocrystalline grains and these grains are bigger than the grain whose obtained at ON2, ON3 and ON4. Also it is not seen on all CdO films surface that crack, voids or pinholes.



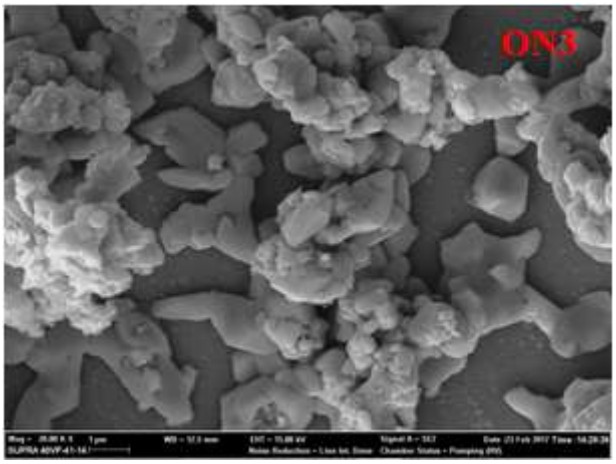


Figure 4: SEM images of the CdO films thin films carried at different percentage of the volume of the electrolyte magnified 20000 times

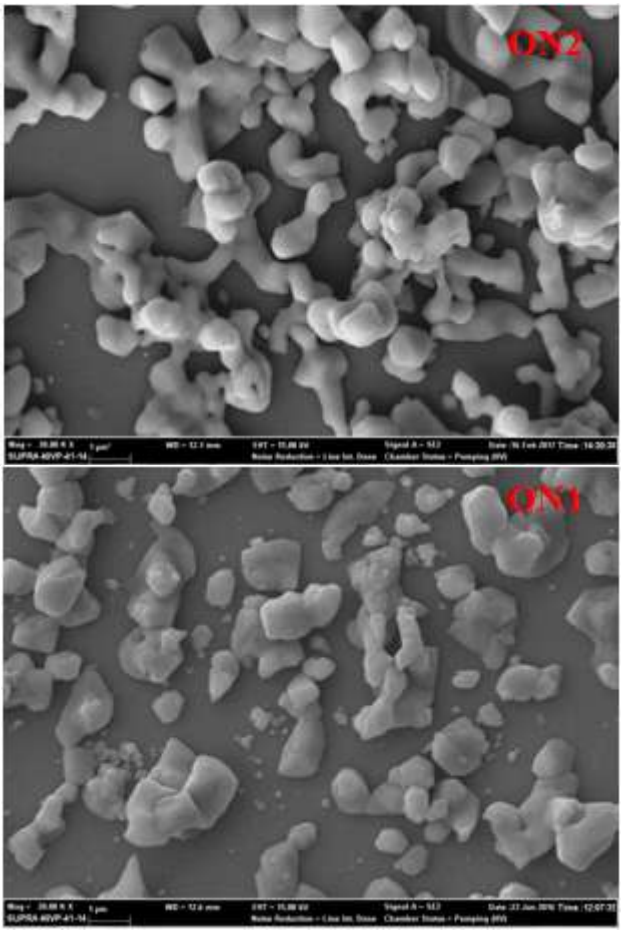


Figure 5: SEM images of the CdO films thin films carried at different percentage of the volume of the electrolyte magnified 20000 times.

4.3 XRD of the CdO thin films

According to the (1 1 1), (0 0 2), (0 2 2), (1 1 3) and (2 2 2) planes of the ASTM cards (98-005-0848), the structure well matches cubic structure of CdO. It is reported that when percentage of the volume of the $Cd(NO_3)_2$ was decreased, the intensity of the films diffraction peaks were increased. The texture of a particular plane can be represented by the texture coefficient TC (h k l) which can be calculated from X-ray data using the formula [22]:

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

where I_0(hkl) is the standard intensity of the plane (hkl) obtained from ASTM card I(hkl) is the measured relative intensity of a plane (hkl) and N is the reflection number. For this work the calculated texture coefficients were presented in Table 2. For obtained samples, there are tree texture coefficient larger than 1. Thus, it is not said that the films have not one preferred orientation.

The Scherrer formula which given in Equation 2 was employed to calculate crystallite sizes of the CdO films.

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

It is observed that the crystallite size is significantly high for ON2 sample whose percentage of the volume of the $Cd(NO_3)_2$ is higher than $CdCl_2$. Confirming the fact that crystallization improves that percentage of the volume of the is $Cd(NO_3)_2$ and $CdCl_2$.

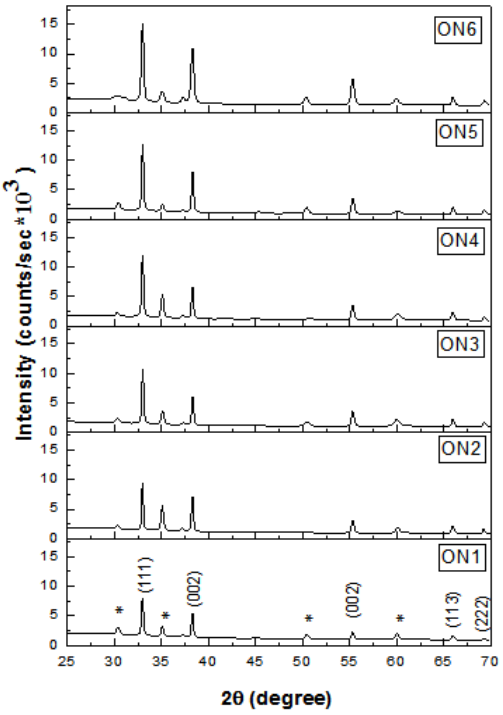


Figure 5: X-ray diffractograms of CdO thin films acquired at different percentage of the volume of the electrolyte

The gravimetric method was used to calculate film thicknesses and calculated values were given in Table 2. While the thicknesses of the CdO films were increased as the percentage of the volume of the $CdCl_2$ increased.

The lattice constant for cubic rock salt structure is given in Equation 3 [23].

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

where d is the interplanar distance and h, k and l are the Miller indices. Equation 4 and 5 was used for calculating average stress and micro strain respectively and they given in Table 3.

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

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

where a_0 and a are lattice parameter of the bulk sample and the corrected value of lattice parameter of CdO thin films respectively. The σ and Y are Poisson's ratio of the bulk crystal and in order of the Young's modulus. The value of Y and σ is 141.67 GPa and 0.33 for cubic CdO thin films respectively [24].

The Nelson–Riley plots were employed to determine the corrected values of lattice parameters and they given in Figure 6, Figure 7, Figure 8, Figure 9, Figure 10 and Figure 11 [25]. The corrected lattice constant (a) were deviated from the strain of bulk sample (a_0 = 4.695 nm). Thus, it can be said that the crystals were under strain [26]. The dislocation density is length of dislocation lines per unit volume and it calculated by using Eq.6 and values were given in Table 3 [27].

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

In accordance with Table 4, the micro strain and average stress for the CdO samples are significantly is high for ON1 whose percentage of the volume of the $Cd(NO_3)_2$ is highest. The dislocation density is significantly is high for ON6 sample whose percentage of the volume of the $CdCl_2$ is highest.

Table 2: The intensity, texture coefficient and film thickness of the CdO thin films acquired at different percentage of the volume of the electrolyte

Experiment	2θ	Intensity (Count/ Seconds)	I / I_O	TC	(hkl)	Film Thickness (nm)
ON1	32.962	8072.111	100	4.75	(111)	423
	38.2638	5402.485	64.1	3.05	(002)	
	55.2772	2173.732	19.19	0.91	(022)	
	65.9355	1554.392	10.99	0.52	(113)	
	69.279	1123.96	5.22	0.25	(222)	
ON2	32.9683	9549.611	100	4.52	(111)	433
	38.2668	7217.109	62.88	2.84	(002)	
	55.2819	3080.975	23.17	1.05	(022)	
	65.9221	2170.91	14.09	0.64	(113)	
	69.2232	1596.899	10.53	0.48	(222)	
ON3	32.9926	9756.987	100	4.52	(111)	483
	38.298	6111.119	57.73	2.61	(002)	
	55.2966	3561.475	30.19	1.37	(022)	
	65.9241	2170.91	17.66	0.80	(113)	
	69.2671	1683.82	10.58	0.48	(222)	
ON4	32.9726	11847.29	100	4.64	(111)	496
	38.2696	6622.096	51.33	2.38	(002)	
	55.2773	3476.604	23.91	1.11	(022)	
	65.9047	2296.456	14.38	0.67	(113)	
	69.2501	1529.31	7.75	0.36	(222)	
ON5	32.9844	12138.89	100	4.64	(111)	502
	38.2879	8028.106	63.02	2.93	(002)	
	55.2978	3608.907	25.26	1.17	(022)	
	65.9373	2084.521	13.63	0.63	(113)	
	69.2761	1540.044	7.65	0.36	(222)	
ON6	32.9721	15055.76	100	4.68	(111)	613
	38.2631	11029.78	60.63	2.84	(002)	
	55.2854	5812.475	31.46	1.47	(022)	
	65.9422	2793.157	12.5	0.59	(113)	
	69.2854	2025.537	6.76	0.32	(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 percentage of the volume of the electrolyte

Experiment	2θ	Crystalite Size (nm)	Lattice Parameter a (Verified) (Å)	Mikro Strain $*10^{-3}$	Dislocation Density (lines/m^2)$*10^{15}$	Average Stress (10^8N/m^2)
ON1	32.962	41	4.7068	2.51	5.87	5.39
	38.2638	43	4.7045	2.02	5.49	4.34
	55.2772	34	4.7005	1.18	8.59	2.53
	65.9355	36	4.6988	0.80	7.70	1.72
	69.279	37	4.6984	0.72	7.41	1.54
ON2	32.9683	63	4.7059	2.32	2.52	4.98
	38.2668	43	4.7041	1.95	5.49	4.18
	55.2819	34	4.7002	1.10	8.59	2.36
	65.9221	36	4.6996	0.99	7.71	2.11
	69.2232	49	4.7017	1.42	4.17	3.06
ON3	32.9926	42	4.7025	1.60	5.66	3.45
	38.298	43	4.7005	1.16	5.49	2.50
	55.2966	34	4.6990	0.85	8.59	1.83
	65.9241	48	4.6995	0.96	4.33	2.05
	69.2671	37	4.6991	0.87	7.41	1.87
ON4	32.9726	42	4.7053	2.20	5.66	4.72
	38.2696	43	4.7038	1.88	5.49	4.03
	55.2773	34	4.7005	1.17	8.59	2.52
	65.9047	36	4.7007	1.22	7.71	2.61
	69.2501	49	4.7001	1.08	4.17	2.33
ON5	32.9844	41	4.7037	1.84	5.87	3.96
	38.2879	43	4.7017	1.42	5.49	3.04
	55.2978	34	4.6989	0.84	8.59	1.79
	65.9373	48	4.6986	0.77	4.33	1.66
	69.2761	37	4.6985	0.75	7.41	1.62
ON6	32.9721	40	4.7054	2.21	6.36	4.74
	38.2631	27	4.7046	2.04	13.9	4.39
	55.2854	29	4.6999	1.04	12.2	2.2
	65.9422	45	4.6983	0.71	4.87	1.52
	69.2854	31	4.6980	0.64	10.5	1.36

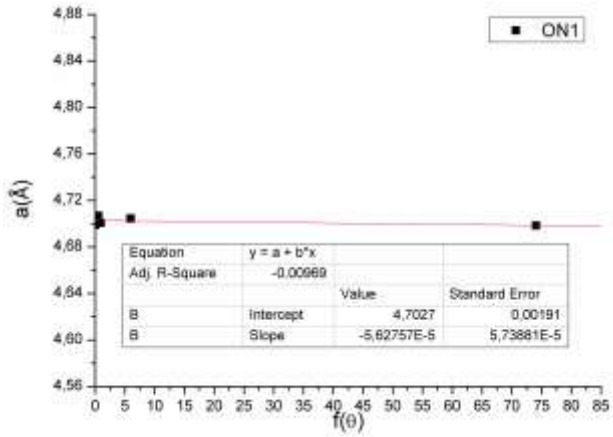


Figure 6: Nelson–Riley plots of CdO thin films acquired at ON1

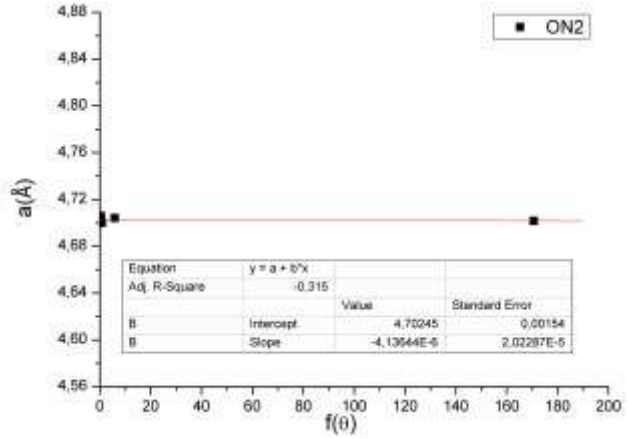


Figure 7: Nelson–Riley plots of CdO thin films acquired at ON2

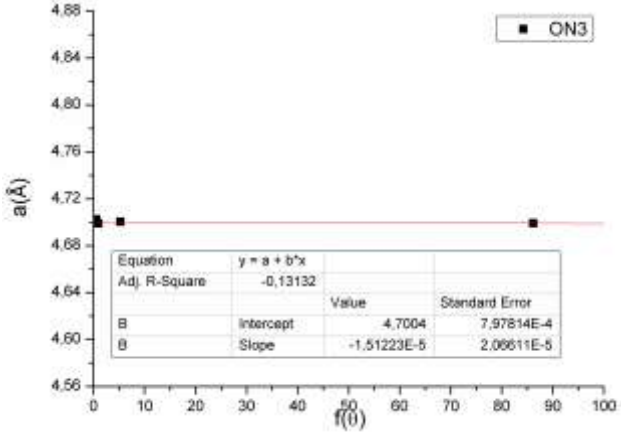


Figure 8: Nelson–Riley plots of CdO thin films acquired at ON3

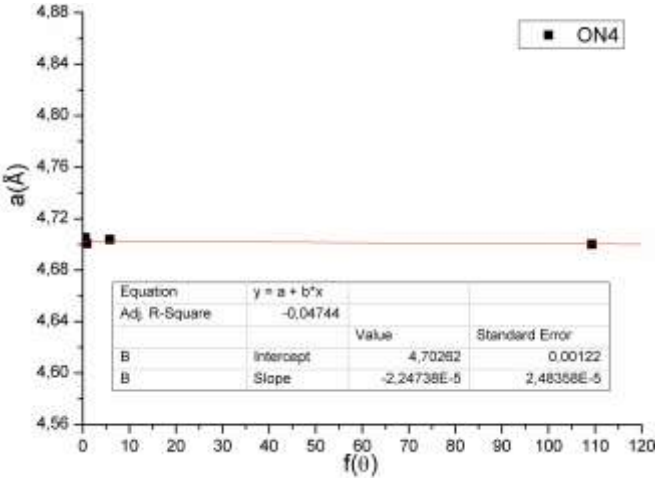


Figure 9: Nelson–Riley plots of CdO thin films acquired at ON4

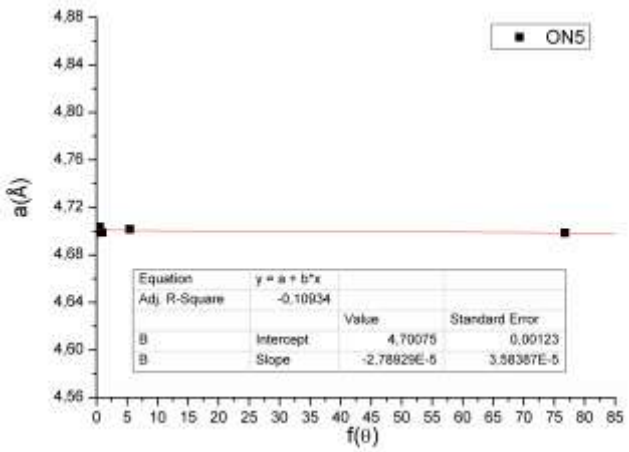


Figure 10: Nelson–Riley plots of CdO thin films acquired at ON5

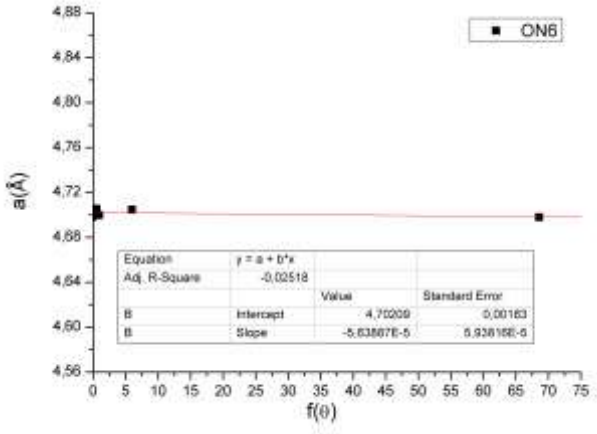


Figure 11: Nelson–Riley plots of CdO thin films acquired at ON6

5. Conclusion

In this study, electrodeposition method was used for depositing of CdO thin films. It is reported that when percentage of the volume of the $Cd(NO_3)_2$ was increased, the absorbance level and film thickness were decreased. Moreover, the percentage of the volume of the $Cd(NO_3)_2$ was increased, the energy band gap were decreased from the 2.56 eV to the 2.16 eV. The structures of the samples were investigated by using a X-Ray diffractometer. When film thicknesses were taken into consideration, it was seen that when the the intensity of the films diffraction peaks were increased, the percentage of the volume of the Cd(NO3)2 was decreased. Surface morphologies were investigated by using a SEM and it is revealed that the samples are composed of the striated like CdO structure, CdO nanocrystalline grains along with some spongy clusters and CdO nanocrystalline grains. Moreover, the spongy clusters were reduced as $CdCl_2$ volume in the final solution was decreased.

6. Acknowledgement

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Author Profile

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