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Studying the Optical and Structural Properties of Cadmium Oxide Thin Films Prepared by Successive Ionic Layer Adsorption and Reaction (SILAR) Technique

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Abstract

Cadmium oxide CdO thin films were prepared by successive ionic layer adsorption and reaction (SILAR) technique at varying number of dippings. The CdO thin films were prepared from a source material of Cadmium acetate and ammonium hydroxide solution deposited on glass substrate at 95℃. The prepared thin films were investigated by X-ray diffraction (XRD), Atomic force microscopy (AFM), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR), and UV-Visible spectrometry. The XRD analysis reveals that the films were polycrystalline with cubic structure having preferential orientation along (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes. While the tests of the scanning electron microscopy and the atomic force microscopy indicate that the thin films are homogeneous and free of voids.

Keywords: thin films, SILAR, X-ray diffraction, optical and structural properties.

دراسة الخصائص البصرية والتركيبية لأغشية اوكسيد الكادميوم المحضرة بطريقة تفاعل وامتزاز الطبقات الايونية المتعددة SILAR

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الخلاصة :

تم تحضير غشاء اوكسيد الكادميوم بطريقة الغطس الايوني المتعاقب لدورات ترسيب متفاوتة , غشاء اوكسيد الكادميوم حضر بواسطة محلول خلات الكادميوم المائية وهيدروكسيد الامونيوم على قواعد من الزجاج عند 95 درجة سيليزية. تم فحص الاغشية الرقيقة المحضرة عن طريق حيود الاشعة السينية, (XRD) والفحص المجهري للقوة الذريةAFM) الاشعة السينية, والفحص المجهري الالكتروني ,(SEM) وتحويل فوريية للأشعة تحت الحمراء ,(FTIR) ومقياس الطيف المرئي للأشعة فوق البنفسجية . كشف تحليل حيود الاشعة السينية (XRD) أن الاغشية المحضرة كانت متعددة البلورات ذات بنية مكعبة ذات اتجاهات دورانية (1 1 1) ,(2 0 0),(2 2 0), (3 1 1). بينما تشير فحوصات المجهر الالكتروني الماسح ومجهر القوة الذرية ان الغشاء متجانس وخالي من الفراغات

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Introduction

Cadmium Oxide (CdO) is an n-type degenerate semiconductor with a simple cubic structure having direct band gap of 2.5 eV and indirect gap of 1.18 eV [1]. CdO has a reddish brown color and is generated when Cd is burned in air. In addition, it has high conductivity and high transmission. Cadmium oxide (CdO) is a promising transparent conducting oxide from the II-VI compounds [2]. It has been used in many applications like photodiodes [3], phototransistors [4], photovoltaic cell [5], transparent electrodes [6] etc. CdO thin films can be prepared by several techniques including: sol-gel [7], pulsed laser deposition [8], chemical bath deposition [9], spray pyrolysis[10], electron beam evaporation [11] and successive ionic layer adsorption and reaction (SILAR)[12].

The SILAR technique is a modified version of the chemical bath sedimentation method. It has many advantages like low cost, low-temperature. The SILAR technique is basically a two-step chemical bath deposition method. In SILAR technique the substrate is sequentially immersed into separate cation and anion precursor solutions and rinsed with purified water after each immersion. Unlike the closed vapor deposition method, in the SILAR method, the deposition rate and the thickness of the film can easily be controlled over a wide range by changing the deposition cycles (the number of dipping). In this work, CdO thin films were prepared by SILAR method for different number of dipping (10, 20 and 30) at pH = 7.2.

Experimental methods

The following steps were followed in preparing cadmium oxide

i) Glass substrates were cleaned with chromic acid and rinsed with distilled water for 15 min in an ultrasonic bath.

ii) certain weight of cadmium acetate cadmium acetate $Cd(CH_3COO)_2.2H_2O$ (BDH-England) (which is a colorless), soluble in water, with a molecular weight (266.52) g / mol(99% e-Merck) at molar concentration (0.3 mol / l)) was gradually dissolved in(100)ml. distilled water with a magnetic mixer for two hours, a homogeneous clear solution was obtained. The relationship below was used to prepare the solutions:

$$M= M_{wt}\times 1000/V \text{ x } W_t \quad (1)$$

Where:

M: molar concentration.

W_t: Molecular weight of aqueous cadmium acetate.

V: volume of distilled water.

M_{wt}: Powder weight of aqueous cadmium acetate to be prepared.

iii) Aqueous ammonia with a molecular weight of 17.03 gm/mol was gradually added to the aqueous solution of aqueous cadmium acetate to reach the pH of 7.2; and in this process, cationic solution was obtained. The temperature of the cationic solution was raised to 95℃, and then the glass substrates were immersed in the cationic solution for 30 seconds; the substrates were immersed in a water bath whose temperature reaches the boiling point of an anionic solution; this process was repeated several times, then the glass substrate was annealed at a temperature of 150 ℃ [13]:

$$Cd(CH_3COO)_2 + NH_3 \rightarrow [Cd(NH_3)_2]^{+2} \quad (2)$$

$$[Cd(NH_3)]^{+2} + H_2O_2 \rightarrow Cd(OH)_2 \quad (3)$$

$$Cd(OH)2 \ (\overset{\Delta}{\rightarrow}) \ CdO + H_2O \quad (4)$$

The prepared CdO thin films were characterized using different analytical techniques like X-ray Diffraction (XRD), FTIR spectroscopy, Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), in addition to optical measurements and calculations.

Results and Discussion

A. Thickness Film:

Thickness of the prepared films was measured using a helium neon laser (He-Ne) of continuous optical power of 1 m. watt. Eq. (5) was used to calculate the thickness(t) of the prepared films:

$$t= \lambda/2\ \Delta x/x \quad (5)$$

Where: Δx is the distance between two fringes, x is the width of a bright fringe and λ= 632nm is the wavelength of the Helium-Neon laser. The film thickness for 10, 20 and 30 dipping were 118nm,136nm and 158nm, respectively.

B .X-Ray Diffraction Analysis:

The XRD patterns of pure CdO thin films obtained by the SILAR technique at different number of dipping are shown in Figure 1.

All the peaks of the CdO thin films XRD patterns correspond to the standard CdO peaks of JCPDS- ICDD card no-0640. It indexed the CdO thin films to be polycrystalline face centered cubic structure (FCC). The grown CdO thin film exhibited good trend along (1 1 1) plane. It showed reflections at (2 0 0), (2 2 2) and (3 1 1) planes. It can be noted, from Figure 1, that the highest peaks intensity is for CdO thin film obtained with 30 dipping. This indicates that the polycrystalline membrane is cubic face centered. The polycrystalline size can be calculated by Scherer formula (Eq.6) as follows:

$$D= \frac{\kappa\lambda}{\beta \cos\theta} \quad (6)$$

Where: K is a constant taken to be 0.94, λ is the wavelength of the X-ray used (λ=1.54 Å), β is the full width at half maximum (FWHM) of the preferential plane, and θ is the Bragg angle.

The dislocation density (δ) is defined as the length of dislocation lines per unit volume, it changes with crystallite size D, was estimated using Eq. (7) [14]

$$\delta = 1/D^2 \quad (7)$$

The average micro strain developed in the prepared thin films is define as the disarrangement of lattice and was calculated using Eq. (8):

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (8)$$

All the results are listed in Table (1)

Table 1: the structural parameters of the prepared CdO thin films with different number of dipping

No. of dipping	FWHM β $\times 10^{-3}$ Radian	Bragg angle(2θ)Deg	Miller indices (h k l)	Observed values (Å)	Strain $\varepsilon \times 10^{-3}$	Crystallite Size (nm)	$D_{Avg.}$ (nm)	$\delta \times 10^{14}$ lines/cm^2
10	7.27	32.88	(1 1 1)	2.72	4.28	33.7	25.16	8.7
	7.26	38.18	(2 0 0)	2.35	2.22	21.2		22.2
	7.97	55.08	(2 2 0)	1.66	1.75	20.6		23.5
20	6.73	32.84	(1 1 1)	2.72	1.59	22.7	21.2	19.4
	7.29	38.13	(2 0 0)	2.35	1.71	21.1		17
	8	55.07	(2 2 0)	1.66	1.67	20		23.7
30	6.02	32.95	(1 1 1)	2.71	1.42	25.3	24.3	30.5
	6.09	38.25	(2 0 0)	2.35	1.43	25.2		15.7
	7.27	55.15	(2 2 0)	1.66	1.60	22.6		19

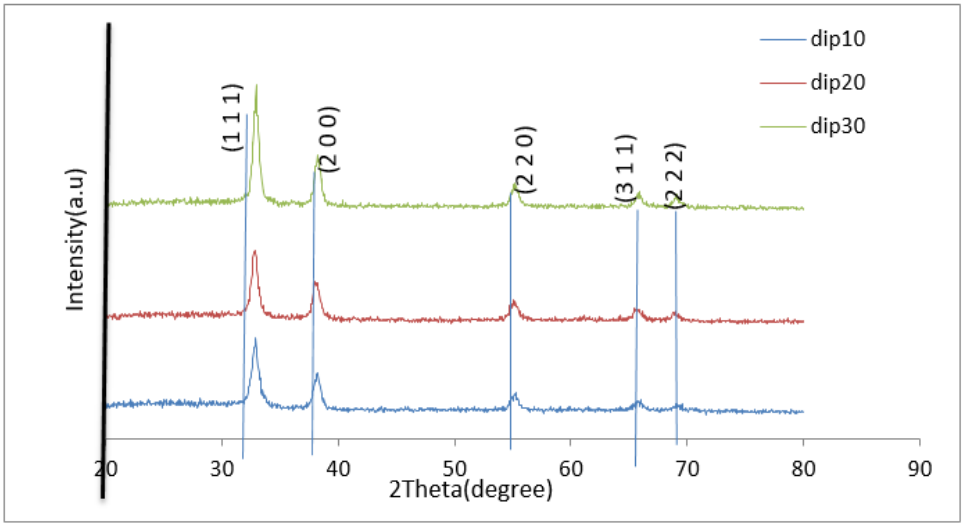

Figure 1: XRD patterns of CdO thin films at 0.3 M, PH=7.2 for different number of dipping.

Optical properties:

Figure(2) shows the absorption spectra of pure CdO thin films, which were prepared by SILAR technique for different number of dippings, as a function of wavelength at (300-900)nm range. It can be noticed that the number of dippings significantly affects the optical properties of the deposited films. Also, theCdO thin film showed high transmittance,as shown in Figure(3), that gradually decreased with increasing the number of dippings. This decrease may be due to an increase in the thickness of the films. It was also observed that there was a slight shift in the edge of the optical absorption towards the red region with the increase of the number of dippings.

The optical absorption coefficient can be calculated from the following relationship [14]:

$$\boldsymbol{\alpha} = \frac{2.303 * A}{t} \quad (9)$$

Where: A is the optical absorbance, t is the sample thickness.

The direct band gap of the films was estimated utilizing the relation introduce by Tauc [15]:

$$\alpha h\upsilon = C(h\upsilon - E_g)^n \quad (10)$$

where α is the absorption coefficient, hυ is the photon energy, E_g is energy gap, C is a constant related to the effective masses associated with band gap, n = 1/2, 2, 3/2, and 3 n, depending on the type of transition, corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively**.**

Figure (4) shows the variation of $[(\alpha h\upsilon)]^2$ as a function of photon energy, and from this figure, by extrapolating the linear part of the absorption edge one can find the intercept with hυ which gives the value of the energy band gap. As can be noticed from the figure, the energy band gap value increases as the number of dipping increases. It is equal to 1.6, 1.9, and 2.5 eV for 10, 20 30 dippings, respectively.

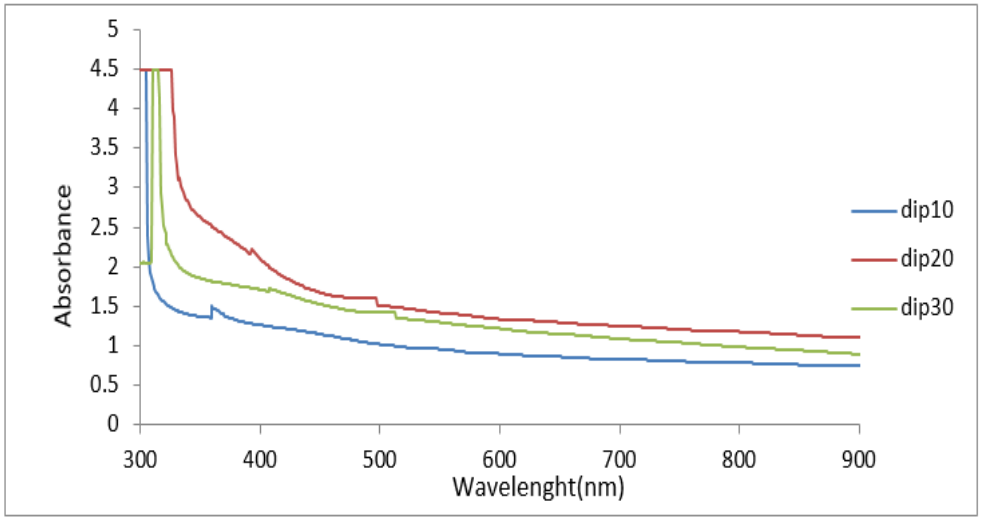

Figure 2: Absorbance as a function of wavelength of pure CdO thin films (0.3 M and pH=7.2) for different number of dipping.

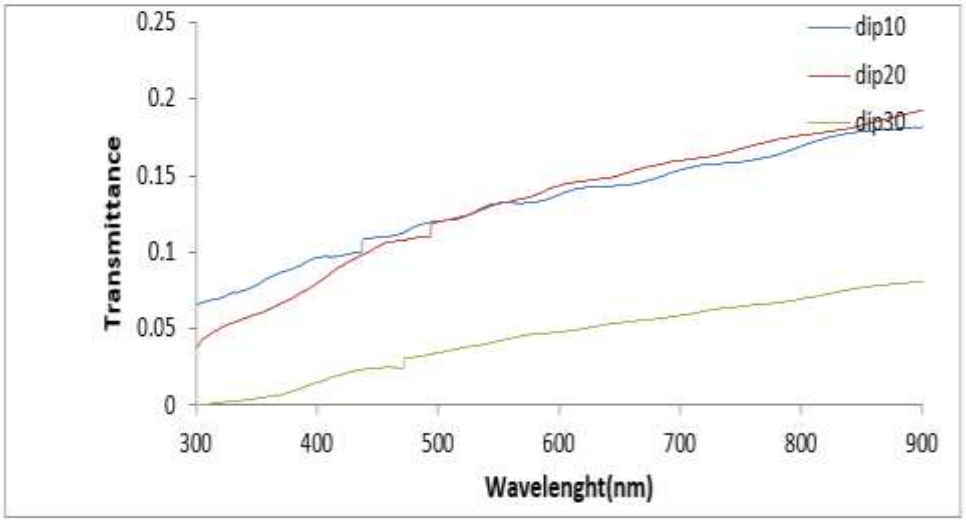

Figure 3: Transmittance as a function of wavelength of CdO thin films (0.3 M and pH=7.2) for different number of dipping.

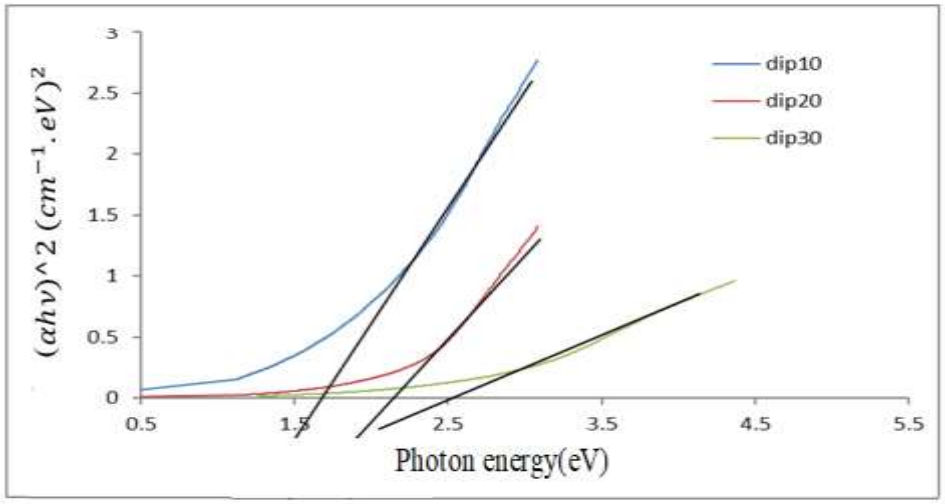

Figure 4: Optical energy gap of pure CdO thin films (0.3 M and pH=7.2) for different number of dipping.

Scanning Electron Microscopy Images:

Scanning electron microscope images of CdO thin films prepared by the SILAR technique of different number of dipping are shown in Figures (5,6, and 7). The membrane surface was noted to be covered with small porous masses, which became more evident at 30 number of dipping. The size of the particles seen in Figure (5) was less than the size of the particles seen in Figures(6 and 7), implying that the number of particles has increased with the increase of the number of dipping.

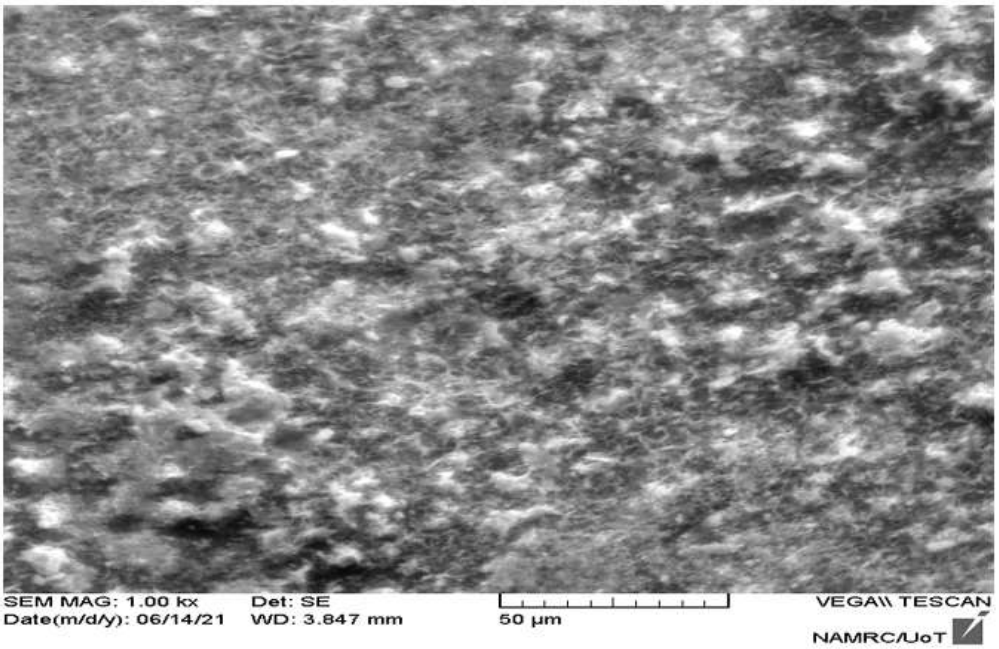

Figure 5: An electron microscope image of pure CdO thin films (0.3 M and pH=7.2) of 10 dipping.

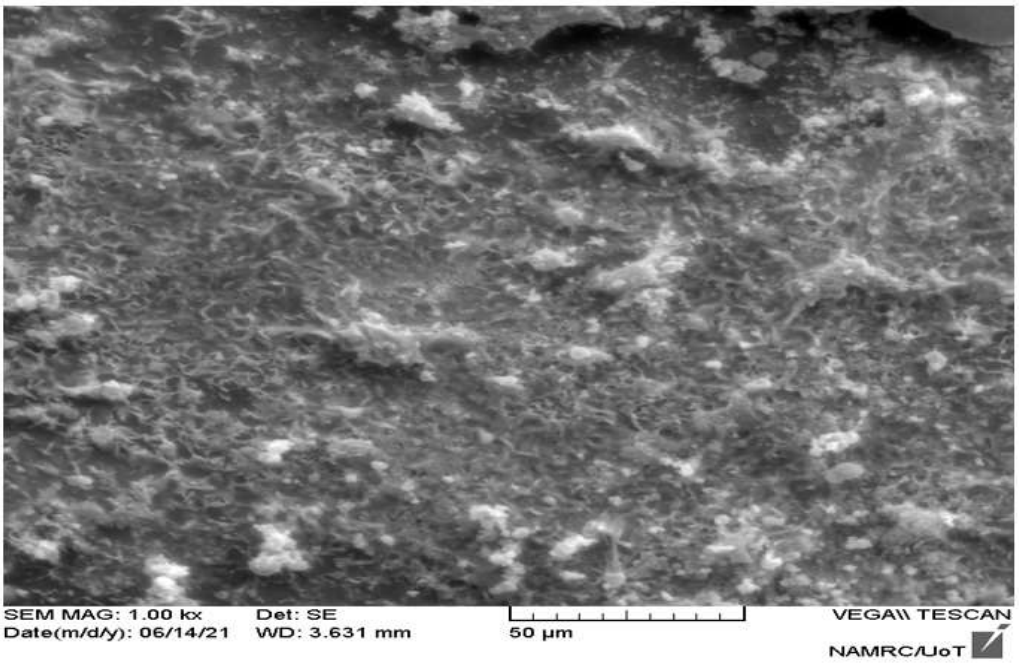

Figure 6: An electron microscope image of pure CdO thin films (0.3 M and pH=7.2) of 20 dipping.

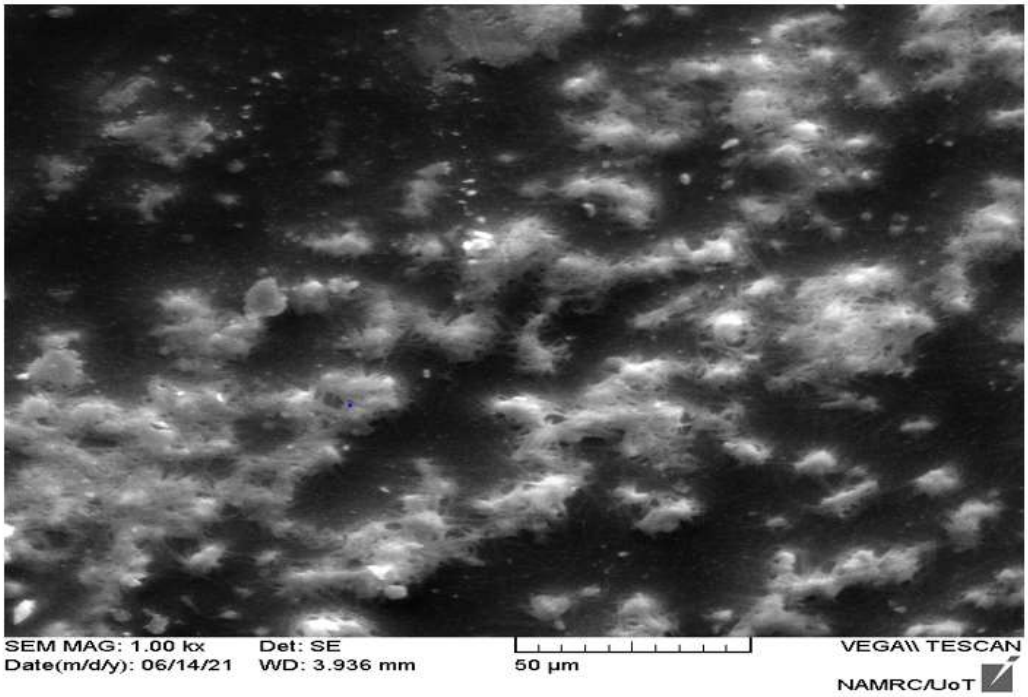

Figure 7: An electron microscope image of pure CdO thin films (0.3 M and pH=7.2) of 30 dipping.

Atomic Force Microscopy (AFM) Study:

Figures (8,9 and 10) show the atomic force microscope images of pure CdO thin films from which roughness, rate square root for roughness rate values and grain size averages can be estimated. From these calculations, it was concluding that the prepared films have nanostructures.

Table 2: Average diameter size, Roughness and Root Mean Square of pure CdO membrane.

Average Diameter (nm)	surface Roughness (nm)	Root Mean Square(nm)	No. of dipping
76.55 nm	4.92	5.8	10
82.42 nm	4.74	5.47	20
84.58 nm	4.49	5.37	30

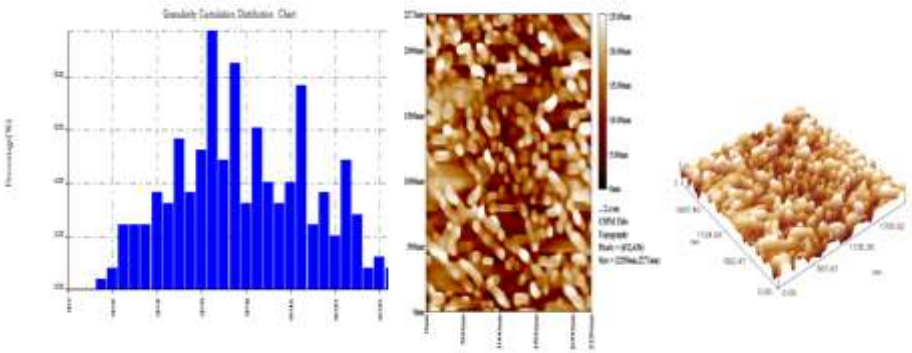

Figure 8: AFM of CdO thin films of 10 dipping.

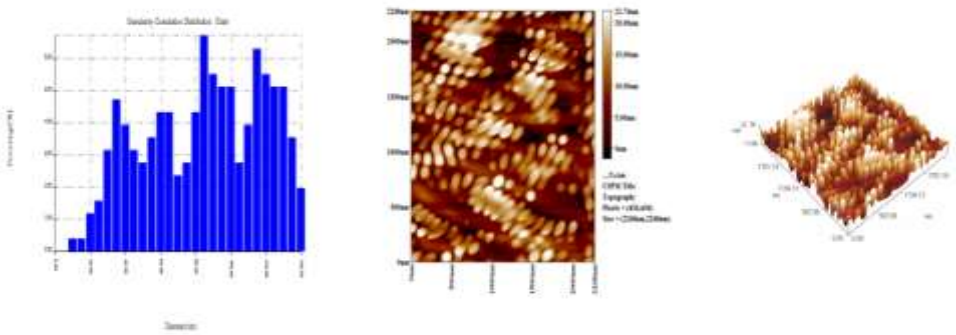

Figure 9: AFM of CdO thin films of 20 dipping.

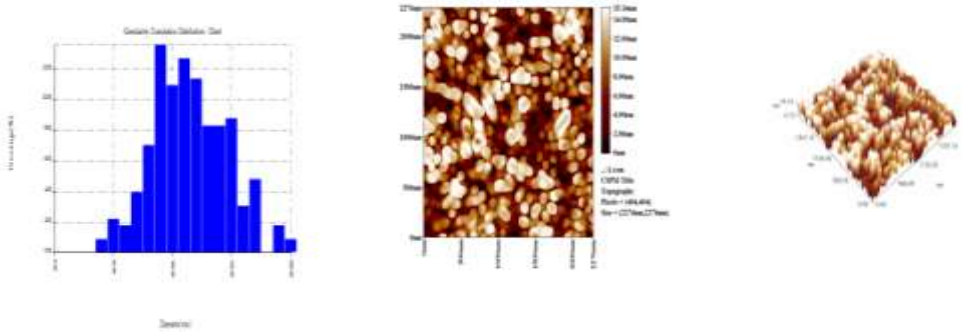

Figure 10: AFM of CdO thin films of 30 dipping.

Fourier Transforms infrared(FTIR) analysis:

Figure 11 (a, b and c) shows the FTIR spectra CdO nanoparticles prepared by (SILAR) for different number of dippings. From the figures, the chemical bond O-H and C-H were determined by their vibration sites in the infrared spectrum. Table 3 shows the type of bond and its corresponding frequency. From the spectra, it can be noted that the infrared transmittance increases with the increase in the number of dippings. It was equal to 621.08, 626.87, and 634.85 cm^{-1} for 10, 20, and 30 dippings, respectively.

Table 3: The type of bond and the corresponding field for each frequency.

bond type	Vibration field$(cm)^{-1}$	No. of.dipping
symmetric and asymmetric vibration frequencies of Cd and O bond(cd-O).	621.08,669.3,719.45 ,858.32, 1130.29, 1386.82	10
	466.77,626.87,725.23,856.39, 1390.68, 1458.18	20
	484.48,634.55,763.81, 856.39, 1388.82, 1425.4	30
C-O stretching vibration band	1423.47,1595.13,1627.9	10
	1560.41,1639.49	20
	1506.41,1550.77,1637.56	30
C-H	2362.8,2924.09	10
	2453.45,2987.74	20
	2314.58,2924.09	30
the formation of O-H in the adsorbed water molecule	3446.79	10
	3454.5	20
	3421.72	30

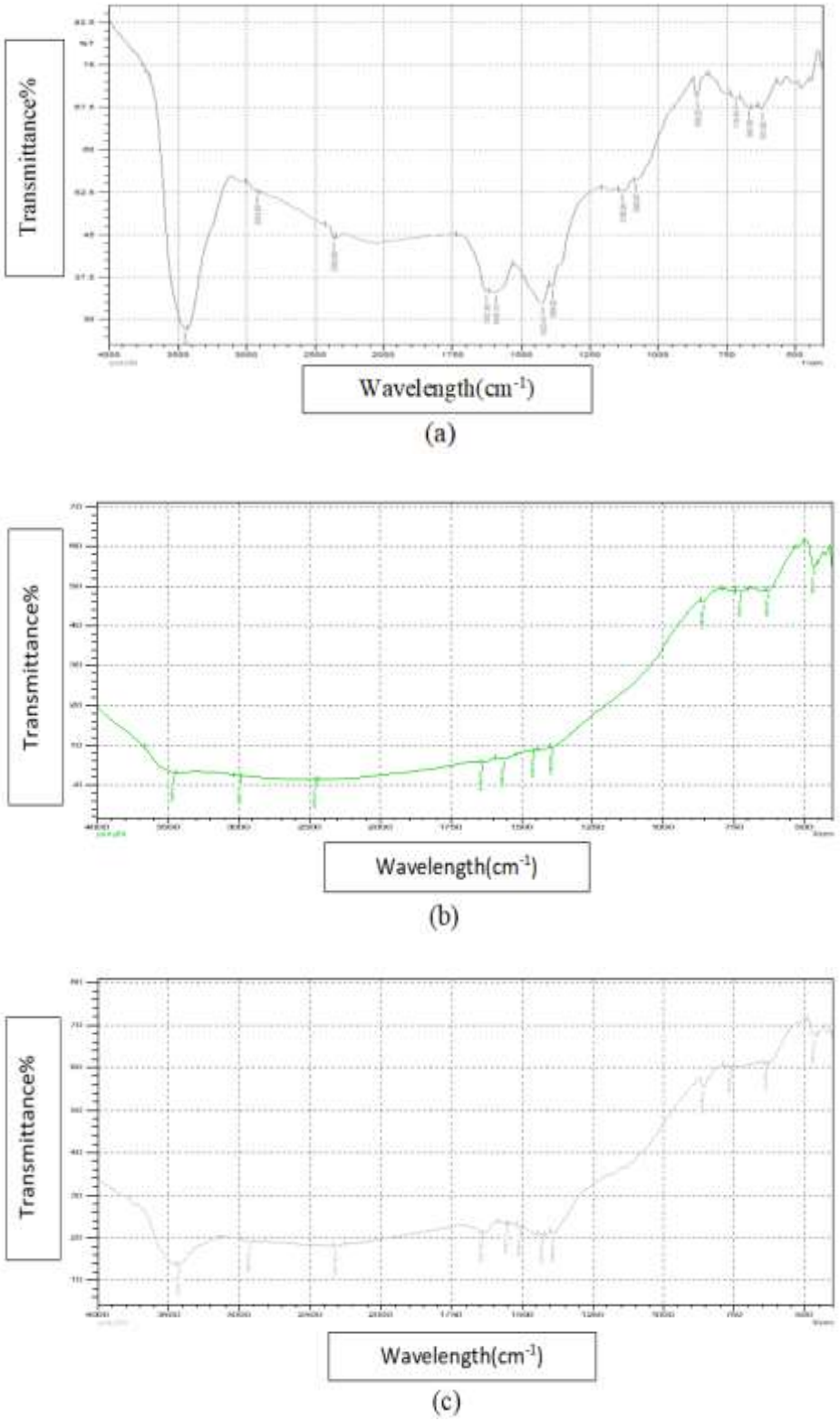

Figure 11: FTIR spectra of CdO thin films for: a)10 dipping, b)20 dipping, c)30 dipping.

Conclusion

From the obtained results in this research, it was concluded that a homogeneous polycrystalline CdO films can be produced using a simple chemical method: successive ionic

and layer adsorption reaction (SILAR) method. Scanning electron microscope images showed that the thin film was free of voids. XRD studies revealed that the CdO thin film deposited on glass substrate at 95℃ is cubic polycrystalline phase. AFM micrographs of the nanostructure film indicated the homogeneity of the thin film. The optical band gap of the CdO film was 2.5 eV when the number of dipping was 30.

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