JOURNAL OF KUFA–PHYSICS
www.uokufa.edu.iq/journals/index.php/jkp | ISSN: 2077–5830

Study the Structural Properties and Surface Morphology of CdO Thin Films Prepared by Chemical Spray pyrolysis

Karrar Mahdi Saleh

Ashur Secondary School ,Directorate of Education Baghdad Rusafa first, Ministry of Education, Baghdad-Iraq

*Corresponding Author E-mail: Amaramar123h@gmail.com

ARTICLE INF

Article history:
Received: 5 JAn., 2020
Reviced:25 FAB., 2020
Accepted: 10 MAR., 2020
Available Online: 14 DEC, 2020

Keywords:

CdO
CSP
Structure properties
Surface Morphology

ABSTRACT

CdO films were prepared using a chemical spray paralysis (CSP) method on the glass substrate at a temperature of 350 ° C and thickness (260 ± 15 nm), and study the effect annealing time (0, 1, 1.5, 2, 2.5) h at annealing temperature 450 °C on structural properties.

The X-ray diffraction pattern the results showed that all CdO thin films have a polycrystalline structure and a prevalent growth in the direction (111), and the average grain size (G) in this direction ranges (29.80 - 33.23) nm. It generally increases in value while the agitation values, extraction density, number of crystals decrease by increasing the annealing time (0-2)h at annealing temperature 450 ° C of thin films. From the resulted of the atomic force microscope (AFM), the surface roughness, medium square root (RMS) and average grain size increase with the increasing of the annealing time (0-2) h, at annealing temperature 450 ° C. The thin film with annealing time 2.5 h at annealing temperature 450 °C . We note a slight decrease in the values of the coefficients (XRD and AFM) Due to the changes in the crystal structure of thin films and beginning of cracks and crystal defects generated on the surface of the thin film during the annealing process. It has been observed in practice that the increase in the annealing time to 3 h at annealing temperature 450 ° C. led to the separation of the thin film from the substrates.

DOI: http://dx.doi.org/10.31257/2018/JKP/2020/120201

دراسة الخصائص التركيبية والتشكيل السطحي لأغشية CdO الرقيقة المحضرة بالرش الكيميائي الحراري

كرار مهدي صالح

مدرسة أشور الثانوية، مديرية تربية بغداد الرصافة الأولى، وزارة التربية، بغداد- العراق

الـــخُـــلاصـــة

تم تحضير أغشية CdO باستخدام طريقة الرش الكيميائي الحراري(CSP) على قواعد زجاجية عند درجة حرارة ٣٥٠ درجة مئوية وسمك (٢٦٠ ± ١٥ نانومتر) ، ودراسة تأثير

الكلمات المفتاحية:

أوكسيد الكادميوم
الرش الكيميائي الحراري
الخصائص التركيبية

التشكيل السطحي

زمن التلدين (٠ ، ١ ، ١.٥ ، ٢ ، ٢.٥) ساعة عند درجة حرارة التلدين ٤٥٠ درجة مئوية على الخصائص التركيبية.

نمط حيود الأشعة السينية أظهرت النتائج أن جميع أغشية CdO الرقيقة لها بنية متعددة البلورات ونمو سائد في الاتجاه (١١١) ، ومتوسط حجم الحبوب (G) في هذا الاتجاه يتراوح (٢٩.٨٠ - ٣٣.٢٣) نانومتر. تزداد قيمته بشكل عام بينما تنخفض قيم المطاوعة وكثافة الانخلاعات وعدد البلورات بزيادة وقت التلدين (٠-٢) ساعة عند درجة حرارة التلدين ٤٥٠ درجة مئوية للأغشية الرقيقة. نتيجة مجهر القوة الذرية (AFM) ، تزداد خشونة السطح ، الجذر التربيعي المتوسط (RMS) ومتوسط حجم الحبوب مع زيادة زمن التلدين (٠-٢) ساعة ، عند درجة حرارة التلدين ٤٥٠ درجة مئوية. مع وقت التلدين ٢.٥ ساعة عند درجة حرارة التلدين ٤٥٠ درجة مئوية. نلاحظ انخفاضًا طفيفًا في قيم المعامِلات (XRD و AFM) بسبب التغيرات في التركيب البلوري للأغشية الرقيقة وبداية الشقوق والعيوب البلورية المتولدة على سطح الغشاء الرقيق أثناء عملية التلدين. لقد لوحظ في الممارسة العملية أن الزيادة في وقت التلدين إلى ٣ ساعات عند درجة حرارة التلدين ٤٥٠ درجة مئوية أدت إلى فصل الغشاء الرقيق عن القواعد.

1. INTRODUCTION

A thin film is described as a layer or several layers of atoms of a particular substance with a thickness not exceeding one micrometer. As the thin films layer is very thin, which means that it can be easily broken, so it is deposited on certain materials that differ according to the nature of the study and use and these materials are called the substrate such as: glass, quartz, silicon, aluminum and others [1]. Cadmium oxide is one of the chemical compounds of the cadmium element, as it dissolves in water or in the bases but dissolves in acids and ammonia salts, It can be obtained from the intense heating of cadmium [2]. Cadmium oxide belongs to the second-sixth group (II-VI) of the periodic table, a dark brown substance with a viscous crystalline structure (F.C.C.) that resembles the crystal structure of sodium chloride (NaCl)[3] .

Cadmium oxide is a negative semiconducting material (n-Type) and has been classified as a Transparent Conductive Oxides (TCO) group because of its different physical properties such as high permeability in the visible area of the electromagnetic spectrum and the movement of high charge carriers and the large energy gap [4].

On this basis, cadmium oxide has been used as thermal transparent materials for vehicle and aircraft windows, and as window layers in the Hetrojunction Solar Cell as well as used in the manufacture of solar cell systems [5], because of its laboratories High absorption that enables it to be used as Absorbent Compound Selective in solar thermal complexes and as a gas sensor [6]

Chemical Spray pyrolysis is a low – cost method of preparation and its equipment is less complex. The thin films prepared in this way is good thin films and has important applications in many fields such as scientific studies and some technological and industrial applications[7].

The research aims to improve study the structural properties and surface morphology of CdO thin films prepared by chemical spray pyrolysis.

2. Materials and Methods

The $Cd(CH_3COO)_2.2H_2O$ cadmium acetate material used by BDH-England was used, which is a colorless, soluble substance in water with a molecular weight (266.52) g / mol at molar concentration (0.1 mol / l), where a certain weight has been dissolved Of cadmium acetate in distilled water gradually using a magnetic mixer for (15-20) minutes. We obtain a homogeneous clear solution according to the relationship [8]:

$$M = \frac{W_t}{M_{Wt}} \times \frac{1000}{V} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where:

M: molar concentration.

W_t: The weight required to melt.

V: Volume of distilled water.

M_{wt} :molar weight of matter.

After dissolving and obtaining the appropriate solution, the solution is left for an appropriate period of time to ensure that no residue is present. Then, it is placed in the tank of the spray device. After the spraying process, the gases evaporate by heat. CdO thin films remain on the glass substrate for the following chemical formula

$$(CH_3COO)_2\ Cd.2H_2O + H_2O \longrightarrow CdO + 2H_2O + 2CH_3COOH$$

The thickness of the prepared thin films (t) was measured using a weight-difference method using a sensitive electronic scale Sartorius of 10^{-4} g of German origin using the following relationship [9]:

$$t = \frac{\Delta w}{\rho \times S} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where :

t: thin films thickness.

Δw: difference in base weight before and after the film is deposited,

ρ: the density of the thin films material,

S: the area of the substrates glass on which the film is deposited.

3. Results and Discussion

Results of X-Ray Diffractions

Diagnostic results (XRD) showed that all prepared thin films are thin CdO films with a polycrystalline cube type (cubic). This is consistent with the results of published research [9].

We see three distinct peaks (220), (200), (111) and a prevalent growth towards (111), and that annealing process for annealing time (0,1, 1.5, 2, 2.5) h. It did not affect the nature of crystallization but led to an increase in the intensity and intensity of the peaks (decrease of FWHM) while continuing to grow in the direction (111), This indicates increased crystallization as shown in figures(a-1) (b-1) (c-1) and (d-1).The effect time of annealing on increasing the degree of crystallization of thin films in direction (111) is consistent with the findings of O. Vigil et. al [10] prepared thin films CdO with Chemical Spray pyrolysis at temperatures annealing at 450ºC for time of annealing 0.25h, 0.5h, 1h and 1.5h with air.

Continued increase in annealing time to 2.5h resulted in a decrease in peak strength as shown in figure (e-1).This may be due to the possibility thermodynamic properties or the possibility of cracks in the thin films formed.

It was observed that increasing the annealing time treatment to 3h resulted in completely separating the CdO thin film from the substrate.

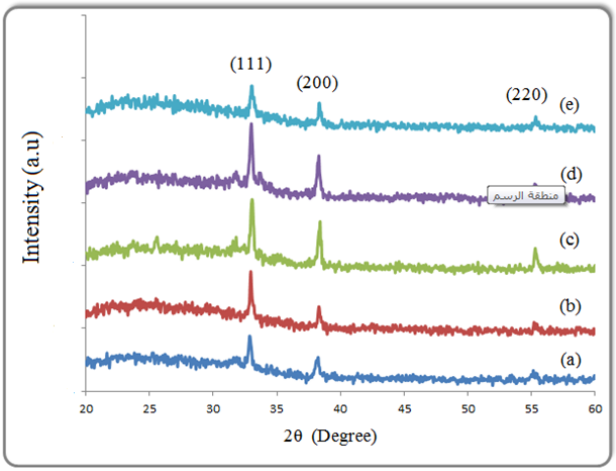


Fig. (1) (XRD) spectra of thin films Cdo prepare at annealing temperatures 450ºC for annealing time: (a) 0h, (b) 1h, (c) 1.5h, (d) 2h, (e) 2.5h.

Depending on the results of X-ray diffraction, a number of the following structural properties and parameters were calculated:

1) Interatomic spacing (d)

The distance between the crystalline levels (d) of thin films CdO before and after annealing time was calculated at annealing temperatures 450 ° C and annealing time (0,1, 1.5, 2, 2.5) h and compared with the results obtained from X-ray diffraction data for all membranes using Brack method by applying the following equation: [11]:

$$2d\sin\theta = n\lambda \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where :

d: distance between crystalline levels

θ: angle of fall confined between the falling beam and the reflector surface.

The Order of the

λ: Single wavelength x-ray beam.

The values of (d) thin films (CdO) decrease with increasing annealing time except annealed thin films for annealing time 2.5h We note a slight increase in their value as shown in figure 2 and table 1.

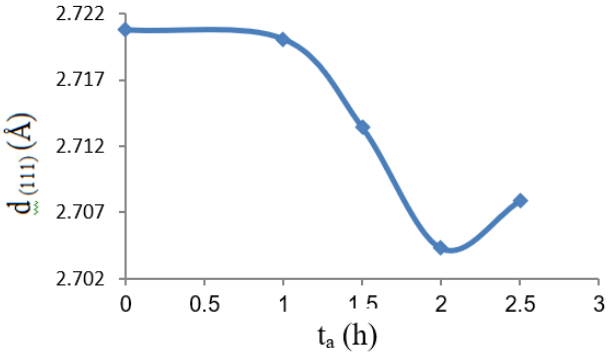


Fig. (2) Interval as a function the annealing time.

2) Lattice Constant (a_0)

Lattice constant a_0 for the preferred level (111) was calculated by applying the following equation [12]:

$$a_0 = d_{hkl}(h_2 + k_2 + l_2)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots (4)$$

Where:

a_o: lattice constants in Cubic structure.

d_{hkl} :Interval of levels (hkl).

hkl : Miller coefficients.

It was generally found that the a_o value for CdO thin films prepare and annealing temperatures at 450ºC and annealing time (0,1, 1.5, 2, 2.5) h is approximate to the lattice constant a_o = 4.695Å obtained from the ASTM card.

The values of ao decrease with thin films annealing time. This may be due to mechanical stresses, changes in the crystal structure of thin films, or cracks and defects, especially for thin films 450ºC for 2.5h as shown in the figure . 3 and table 1.

This corresponds to the results of published research [10] to decrease the value of a_o from 4.696Å to 4.689Å by increasing annealing time from 0.25h to 2h for CdO thin films prepared by Chemical Spray pyrolysis and temperatures annealing at 450ºC with air.

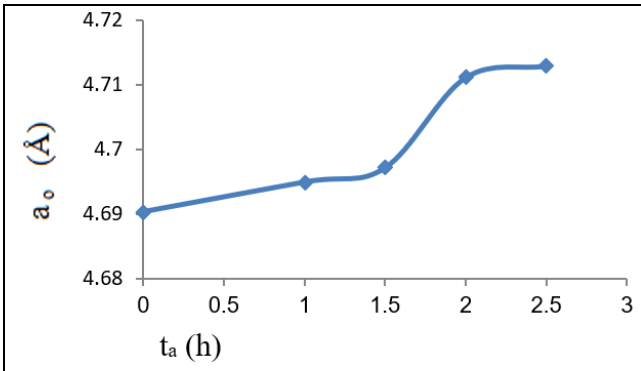


Fig. (3) Fixed relationship of the lattice with the annealing time.

3) Crystallite Size (G):

To determine the improvement in the crystal structure, it is necessary to calculate the crystallite size of all thin films of the characteristic directional peak (111) by measuring the full width of the curve at the mid-peak of the diffraction (FWHM) using the Scherer's equation (Scherer's)[13].

$$G = \frac{k\lambda_x}{\beta \cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where:

k: constant close to one and found that its value is 0.94 for polycrystalline thin films [14].

λ_x : fallen wavelength of the X-ray diffraction.

β: full width at the middle of the diffraction peak and measured in radial angles.

θ: Brack angle measured in degrees.

Generally, the increase in the annealing time at the annealing temperature 450 ° C from (0 to 2)h, resulted in an increase in the average grain size from 29.80 nm to 33.23 nm due to a decrease in the curve width at mid-peak (β), indicating an improvement in crystallization Thin films CdO, which is consistent with O. Vigil et. al [10], then the G value decreases when the annealing time is increased to 2.5 h.

This is due to an increase in the curve width at the midpoint of the point (β) as shown in table 1. As shown in figure 4

From this it can be said that annealing at a temperature of 450 ° C for annealing time less than 2.5 h allows better granular growth by maintaining the high level trend (111).

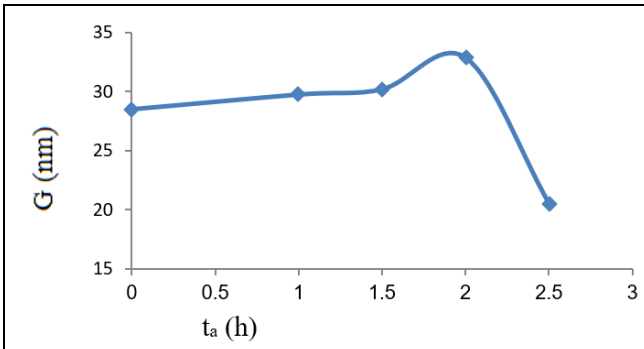


Fig. (4) relationship of the Crystallite Size with the annealing time.

4) Texture Coefficient(T_C):

The texture coefficient (TC) represents the preferential direction of the diffraction level (hkl) in polycrystalline thin films. TC was calculated using equation [15]:

$$T_c(hkl) = \frac{I(hkl)/I_0(hkl)}{N^{-1}\sum_N I(hkl)/I_0(hkl)} \quad \ldots\ldots\ldots\ldots (6)$$

where :

N : The number of peaks in X- ray diffraction.

$I_{(hkl)}$:The relative intensity measured for the level (hkl).

$I_{o\ (hkl)}$: Standard intensity (hkl) from ASTM.

The results shown in table (1) show that all values are not less than one for the direction (111), This indicates that all CdO films prepared at the time of different annealing have a predominant growth towards the diffraction level (111).

5) Strain (Є)

It can be calculated according to the following relationship [15]:

$$Є = \frac{\beta \cos\theta}{4} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

The results shown in table (1) generally showed a decrease in the value of Є by increasing the thin films of annealing time from(0-2)h, which indicates the relaxation of the stresses on the thin films after the heat treatment process. This is consistent with published research results [16,10],The increase of time of annealing to 2.5h resulted in an increase in the value of Є as shown in table (1), indicating an increase in defects at the granular boundaries, increasing dislocations and decreasing the particle size of the thin films. As shown in figure 5.

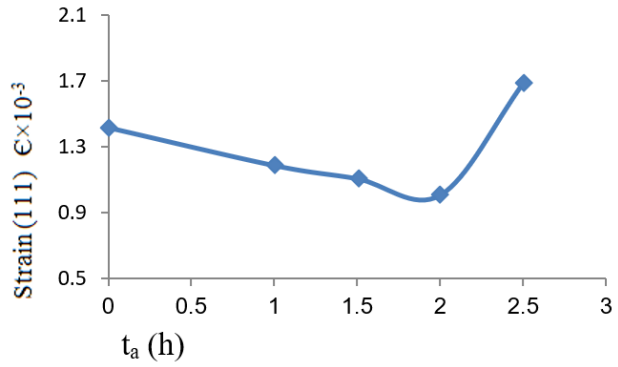


Fig. (5) relationship of the strain with the annealing time.

6) Dislocation Density (δ)

It represents the number of lines of extraction that cut a unit of area in that crystal, The dislocation density of all thin films of the preferred level (111) was calculated using equation (8) and calculated from the following relationship [15]:

$$\delta = \frac{1}{G^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

It was found that the dislocation density (δ) decreases from 1.13 × 10^{15}lines / m^2 to 0.91 × 10^{15}lines / m^2 when the annealing time (ta) decreases from (0- 2)h. and then 2.34 × 10^{15} lines / m^2 when annealing time (ta) increased to 2.5 h. The increase in the value of δ may be attributed to the change in the chemical equivalence of the thin film and to the emergence of new crystalline defects that led to a decrease in crystal size as well as an increase in dislocation density when the annealing time increased to 2.5h. As shown in figure 6, the results are shown in table (1).

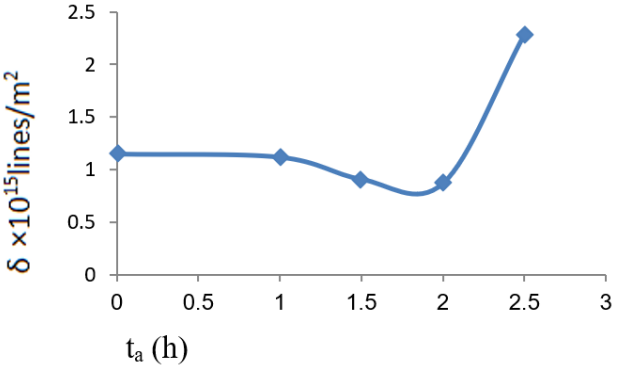


Figure (6) Relationship of the Dislocation Density With the annealing time.

7) Number of Crystals (N_C):

It was calculated by the relationship [17]:

$$N_C = \frac{t}{G^3} \; / \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

t : the thickness of the thin film.

It was found that the increase in the annealing time value (t_a) from (0-2)h led to a decrease in N_C value, this may be due to a decrease with the thickness and Increasing the crystallite size (G) by increasing annealing time, However, the increase in ta to 2.5h led to an increase in N_C due to the decrease in the average crystallite size (G). As shown in the results shown in fig. 7 and table 1.

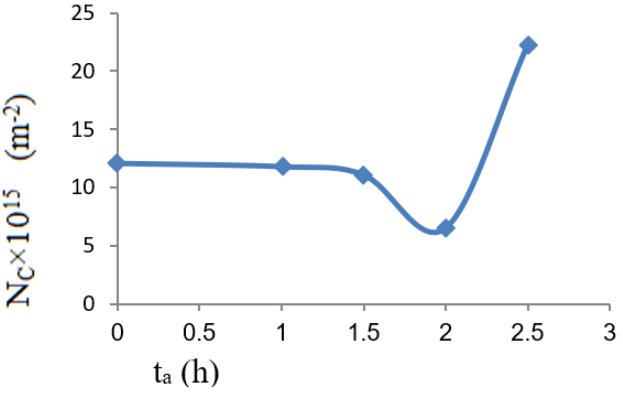


Fig. (7) Relationship of the number of crystals with the annealing time.

8) Number of Layers) (N_L)

The number of deposited layers are calculate by relationship [18]:

$$N_L = \frac{t}{G} \quad \text{.....(10)}$$

It was found that the value of N_L decreases by increasing ta from(0-2)h and then increasing the annealing time to 2.5h. This may be due to the effect of heat treatment on the crystal size and thin films thickness. The results are shown in figure. 8 and table 1.

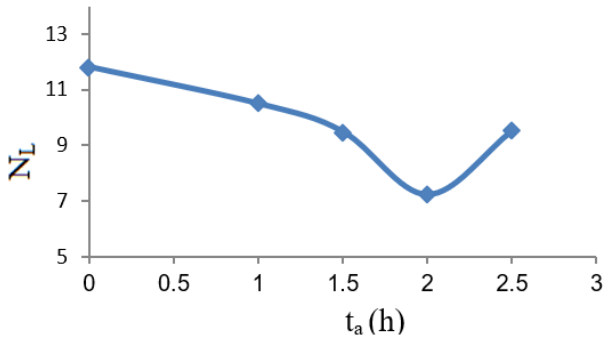


Fig. (8) Relationship of the number of crystals with the annealing time.

Table (1) Results of (XRD) of CdO thin films with changing time of annealing

shown in Table 2 and Figure 9, from the images

Sample		ASTM	0h	1h	1.5h	2h	2.5h
$d_{(111)}$ (Å)		2.71	2.7208	2.7201	2.7134	2.7043	2.7079
Lattice Constants $a_\circ$(Å)	(111)	4.695	4.69.03	4.6949	4.6971	4.7111	4.7129
2θ (deg)		-	32.982	32.989	33.054	32.991	33.059
β ×10^{-3}(rad)		-	5.27	5.16	5.06	4.54	5.71
(G) nm	(111)	-	28.51	29.76	30.21	32.89	20.51
Tc(hkl)	(111)	-	1.197	1.257	1.258	1.106	1.162
Strain Є×10^{-3}		-	1.42	1.19	1.11	1.01	1.69
δ×10^{15} (Lines/m^2)	(111)	-	1.15	1.12	0.91	0.87	2.29
N_C×10^{15} (m^{-2})	(111)	-	12.07	11.79	11.09	6.51	22.26
N_L	(111)	-	11.82	10.50	9.49	7.22	9.51

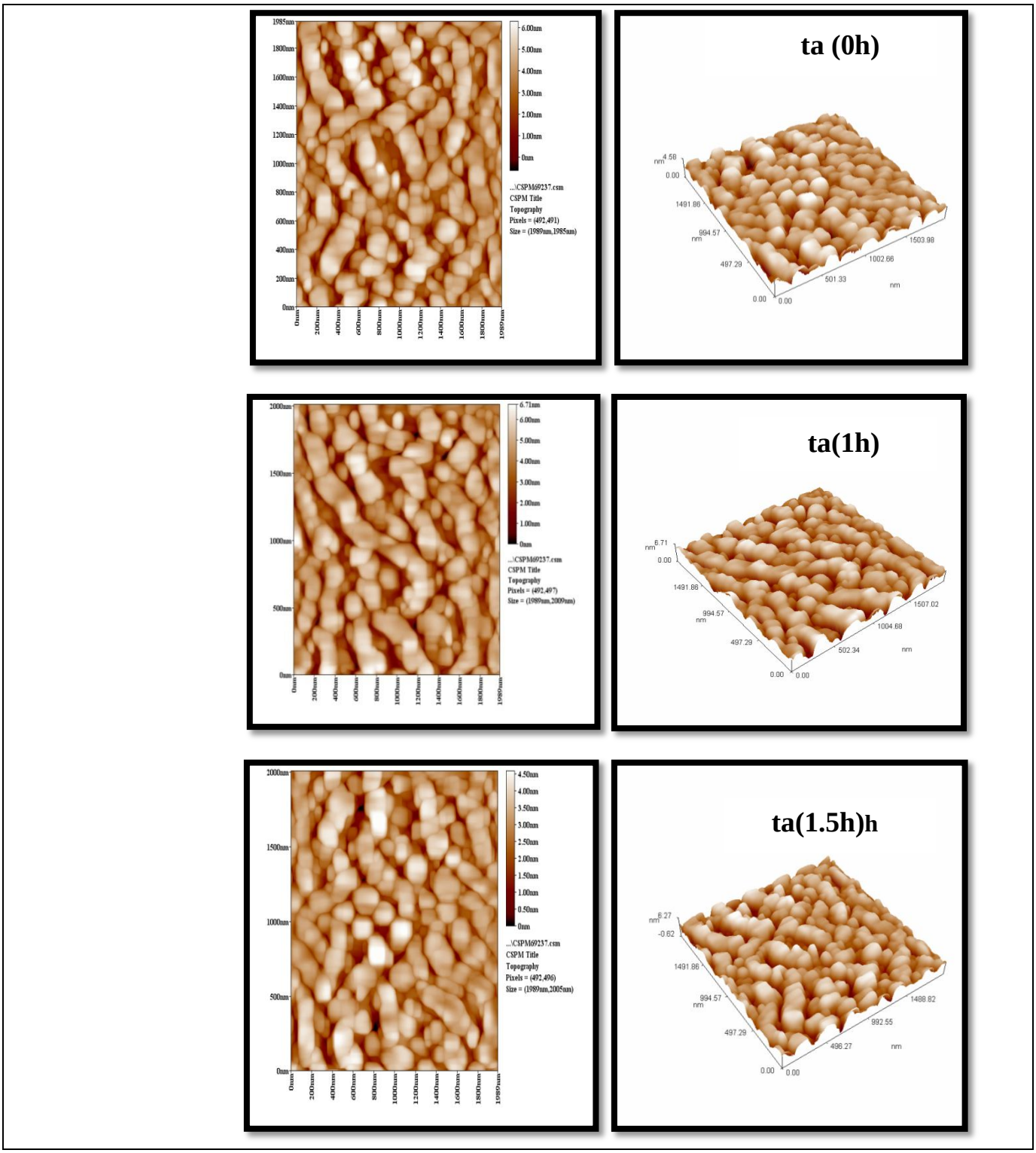
1. Result of Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is used to study terrain changes in the surface formation of thin films and has the ability to analyze these surfaces and explain the amount of their homogeneity, while giving the particle distribution values Very accurate values for the average grain size, surface roughness and root mean square (RMS) [19].

The images for CdO thin films with thickness (260 ± 15 nm) which was measured by before and after annealing at temperature 450 ℃ and annealing time (0,1, 1.5, 2, 2.5) h . These images are used to confirm XRD notes as observed in figure 9 that all thin CdO films do not have holes or island structures, that is, they are homogeneous.

We note from table (2) that the average grain size, root mean square and surface roughness increase with increasing of annealing time, Expect for melting thin films at temperatures 450 ℃ and for the annealing time 2.5h note decrease slightly may be the possibility of an occurrence the cracks- free of the thin films component. The distribution of molecules on the surface of the thin films is a measure of the roughness of these CdO surfaces.

There is a difference in the grain size measurement from the AFM and XRD measurements, as the AFM measurement only visualizes the surface grain without looking at the degree of structural defects [20], while the XRD scale depends on the size of the empty grain with the presence of structural defects [21]



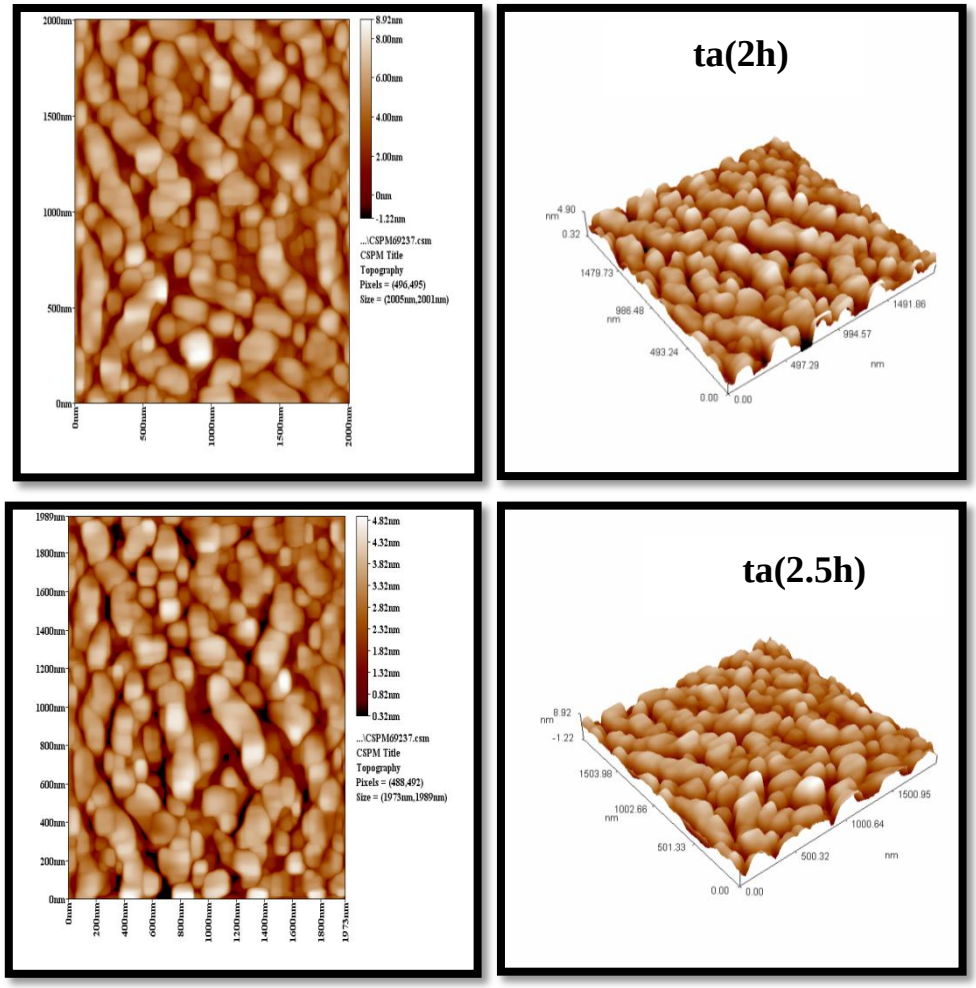


Figure (9) shows the AFM image after and before annealing at temperatures annealing 450°C and time annealing (1, 1.5, 2, 2.5) h for the CdO thin films.

Table (2): The values of the average grain size, surface roughness and root mean square (RMS) for CdO thin films.

ta(h)	Surface Roughness (nm)	RMS (nm)	Grain Size (nm)
0	10.11	12.454	46.32
1	11.239	14.242	49.77
1.5	26.418	22.734	51.33
2	36.069	37.506	56.67
2.5	35.529	33.762	41.63

CONCLUSION

All CdO thin films have a polycrystalline crystalline structure of the cubic type and the highest intensity was at the crystal level (111) which represents the preferred direction of thin films growth. An improvement in the crystalline nature of the thin films and an increase in the rate of granular size in the direction (111) ranging between (28.58 - 33.23) with a decrease in the values of emotions, the density of extraction, the number of crystals and the number of crystalline levels annealing thin films (1-2) h. The possibility of obtaining Nano films free of cracks and smooth and homogeneous and coherent well by the chemical Spray pyrolysis method. The increase annealing time to 3 hours separated the CdO thin film completely from the substrate. The Annealing time at a temperature of 450 ° C for less than 2.5 hours allows better granular growth by maintaining the high level trend (111).

4. REFERENCES

[1] K. Chopra and A. Maini, "Thin Films and Their Applications in Military and Civil Sectors", (2010).

[2] ج. هوليدي " الكيمياء اللاعضوية الحديثه " ترجمة د. وسام إبراهيم عزيز والسيد أدريس عبد القادر خطاب (مطبعة الموصل)(1980).

[3] Z.M. Jarzberzki, "oxide Semiconductors", Pergamon Press London, (1973).

[4] A. Varkey , " Transparent Conducting Cadmium Oxide Thin Films Prepared by A solution Growth Technique " , Journal of Thin Solid Films ,Vol. 239 , P. 211 , (1994) .

[5] C. Stravani and RW. Miles , Journal of Crystal Growth ,Vol.185 , P.1031 , (1998) .

[6] A. H. Omran , " A study of Optical and Electrical Properties of CdO, CuO , Thin Films and Their Mixture Prepared by Chemical Spray Pyrolysis ", M. SC. Thesis , Al-Mustansiriya University, (1998) .

[7] H. A. Macleod, "Thin Film Optical Fillers", 3rd Ed., (2001).

[8] أ. د., "الكيمياء اللاعضوية العامة "ترجمة د. حبيب عبد الاحد, مطبعة الموصل(1986).

[9] P. Perumal, A. Manohari, S.Valanarasu, A. Kathalingam, Jin-Koo Rhee, N.Soundaram and R.Chandramohan, "Influence of Deposition Time on the Microstructure and Transport Properties of CdO Thin Films Prepared by Chemical Bath Deposition", Journal of Surface Engineered Materials and Advanced Technology, V.2 (2012) pp. 71-75.

[10] O. Vigil, F. Cruz, A. Morales-Acevedo, G. Contreras-Puente, L. Vaillant and G. Santana, "Structural and Optical Properties of Annealed CdO Thin Flms Prepared by Spray Pyrolysis", Materials Chemistry and Physics, V.68 (2001) pp. 249-252.

[11] C. Kittel , "lnfroduction to Solid State Physics", 8th edition, John Wiley and Sons (2005).

[12] Y. Waseda, E. Matsubara and K. Shinoda, "X-Ray Diffraction Crystallography", Springer-Verlag Berlin Heidelberg (2011) .

[13] Faizullah, M. Khan and M. Rahman, "Pyrolized Growth of (Al, N) Dual Doped CdO Thin Films and Study of Structural, Surface Morphology and Opto-electrical Properties", International Journal of Materials Science and Applications, V.2, N.4 (2013) pp. 124-127.

[14] M. Zaien, K. Omar and Z. Hassan, "Growth of Nanostructured CdO by Solid-Vapor Deposition", International Journal of the Physical Sciences, V.6, N.17 (2011) pp. 4176-4180.

[15] M. Barote, "Structural and Morphological Properties of Spray Deposited CdO Thin Films," Indian Journal of Applied Research, V.3, N.9 (2013) pp. 514-516.

[16] B. Gokul, P. Matheswaran and R. Sathyamoorthy, " Influence of Annealing on Physical Properties of CdO Thin Films Prepared by SILAR Method", J. Mater. Sci. Technol., V.29, N.1 (2013) pp. 17-21.

[17] Balu, V. Nagarethinam, M. Suganya, N. Arunkumar and G. Selvan, "Effect of the Solution Concentration on the Structural, Optical and Electrical Properties of SILAR Deposited CdO

Thin Films", Journal of Electron Devices, V.12 (2012) pp. 739-749.

[18] H. Kadhim and J.Al-Ogili, "Effect of Thickness to the Structure Properties of CdO Thin Films", Eng. and Tech. Journal V.29, N.8 (2011) pp. 1536-1544.

[19] S. M. Ahmad, "The effect of thickness on the optical and structural properties of copper oxide the nano-grain size", M.Sc. Thesis, AL-Mustansiriyah University, (2010).

[20] Raid A. Ismail; Abdulrahman, K. Ali and Khaleel,I. Hassoon. (2013). "Preparation of a silicon heterojunction photodetector from colloidal indium oxide nanoparticles". Optics & Laser Technology, 51: 1–4.

[21] Spolenak, R.; Ludwig, W.; Buffiere, J. Y. and Michler, J. (2010). In-situ elastic strain measurements – diffraction and spectroscopy. MRS Bulletin, 35(5): 368-374.