Optimizing the Structural Properties of CdO Nanoparticle Thin Films as a Function of Temperature

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Abstract:

A thin film on glass substrates of cadmium oxide (CdO) nanoparticles was prepared by thermal vacuum technique. The films were annealed at (300, 350 and 425) °C for 2 h. The impact of thermal treatment change on the structure and micro-structural properties was observed. XRD and AFM analysis confirms that the CdO films are a polycrystalline cubic structure and the preferred growth orientation along (111) plane, which it has a texture coefficient at 1.261, 1.310, 1.355 and 1.124 values for before and after annealing the films. The grain size increases from 73.79 nm to 86.17 nm as annealing temperature increases. The result of scanning electron microscopy (SEM) was proved of presence nanostructures with homogeneous a characteristic nano-grain size and different shapes for all the films.

Keywords: Annealing, Grain size, Nanostructured CdO, Texture coefficient, XRD.

1. Introduction

Transparent conducting oxides (TCO) have attracted to various research activities due to their unique optical, electrical and structural properties, especially after the revolution in the discovery of the nanoscale size for atoms of materials. Therefore, the researchers have been recently interested in studying nano-sized semiconductors extensively as a result of wide range of technical applications because of the unique properties possessed also by nanoparticles (NPs) through the deviation of chemical and physical properties from the bulk materials. The cadmium oxide nanostructure was demonstrated as one of the most popular materials for various applications. It is considered one of the most promising semiconductors oxides in the development of photovoltaic devices, especially in photovoltaic diodes, solar cells and gas sensors, with other important applications being manufactured from cadmium oxide films.[1,2,3]

Cadmium oxide thin films have been prepared on a large scale using several of the techniques, such as: solid-vapor [4], successive ionic layer adsorption and reaction (SILAR) [5], sol gel [6], chemical bath deposition (CBD) [7], spray pyrolysis [8], layer adsorption [9], sputtering [10] and mechanochemical [11]. Thermal vacuum technology is one of the important methods for preparing the membrane because it has good sedimentation properties, the most important are: (i) the good adhesion for the films with substrate, (ii) the deposition of multiple and very thin layers for different the materials [2].

Cadmium oxides (CdO) have high structure and optical properties and an n-type. It is that has lower the electrical of conductivity and the band-gap energy of (2.2 - 2.6) eV at room temperature (RT) [12, 13]. The optimization of optical and electrical properties in general consist on improvement the structural properties, which is very important in the applications of technological devices.

The main objective of this work is to reach the improvement of the structural properties of the nano-sized CdO films by studying the impact of the thermal treatment (deposition and annealing) on the prepared films, which was analyzed of the structural and surface morphological from results of the lattice parameters, texture coefficient and grain size.

2. Experimental

The thin films of cadmium (Cd) powder nanoparticles (Fluka CO., A.G/Germany), purity (99.95%), were prepared by vacuum thermal evaporation technique by placing cadmium powder in a boat of the element molybdenum (Mo). Cd powder nanoparticles was deposited on glass substrates with dimensions (76 x 26) mm, which were cleaned thoroughly with alcohol and distilled water using Ultrasonic device at 15 minutes for

each of liquid separately. The distance between the boat and the glass substrate was taken as 12 cm, at a thermal pressure of (5×10^{-5}) Torr.
Four samples of Cd nanoparticles were deposited and exposed to an oxygen flow of 3 L/min at RT (27°C) for half an hour. After that, three of the CdO films were exposed to different annealing temperatures at (300, 350 and 425)˚C, by a tube furnace under an oxygen flow of 2 L/min for 1 hour at a heating and cooling rate of 5°C/min. The thickness of the samples was ~250 ±5 nm, which was measured by weighting method. The micro-structural and surface morphological properties of CdO thin films NPs were studied, by X-ray diffraction (XRD 6000-7000) Shimadzu, Japan, and Atomic Force Microscopy (AFM) (AA 3000 - Angstrom Advanced Inc) USA, in the University of Technology. As for the surface morphology of the films as well, it was done by scanning electron microscopy (SEM) images of a type (FEI CO. / Holland) in Al-Nahiri University.

3. Results and Discussion

The results obtained from X-ray patterns determined the structural properties of the CdO films prepared before and after annealing treatment as in Figure 1. This result were studied and analyzed of the structural properties for films prepared at different temperatures with fixed thickness. Comparing XRD results with reference data for cubic structure (NaCl) with the lattice parameters CdO of the crystalline phases (JCPDS standard card No. 050640), it can be observed a number of characteristic peaks (111), (200) and (222), and other peaks for (220) and (311) planes were found to be slightly increased.
This means there is an improvement in the structural properties of the films due to increased crystallization because the thermal treatment leads to reduce the crystal defects and re-crystallization of the material lead to re-stability of the atoms [10, 14, 15]. Therefore, it is the surface morphology and crystallinity change with thermal treatment. Whereas, the orientation (111) is more prominent with strong, sharp intensity and the higher value it has

compared to other peaks because the film surface density energy for this direction is less than the energies of other crystal directions. [3, 13, 16]

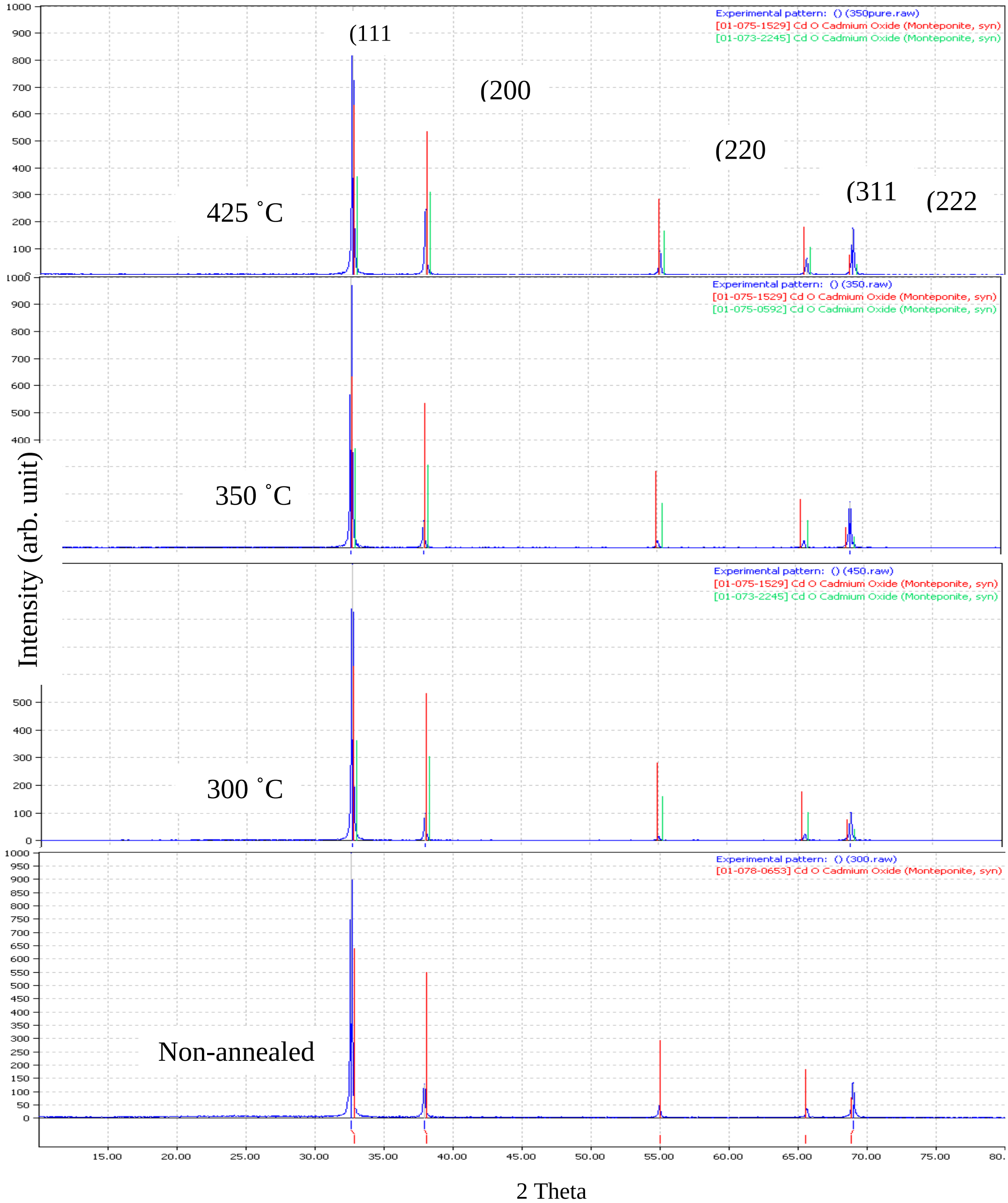


Figure 1: XRD analysis of the CdO nanoparticles films for all samples.

The average crystal size corresponding to the CdO thin film is calculated, using Scherer's formula [17]

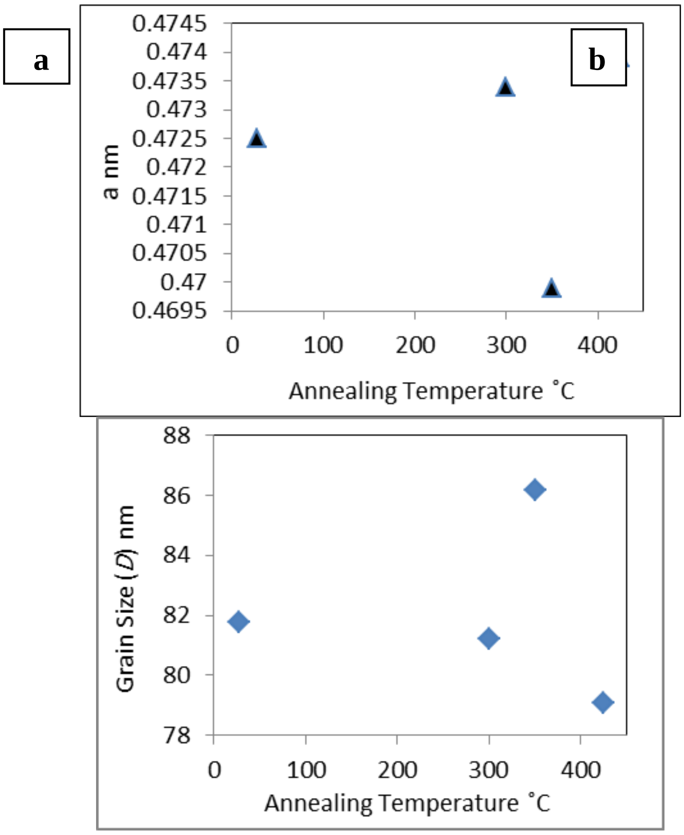
$$D = \frac{K\lambda}{\beta \cos\theta} \qquad \ldots\ldots\ldots\ldots\ldots (1)$$

where: K is 0.89 for CdO, λ is wavelength of CuKα = 0.15418 nm, θ is the diffraction angle, and β is full width at half maximum (FWHM) in XRD analysis.

Scherer's formula is using for calculate grain size for various annealed films by the FWHM values for (111), (200} and (222) peaks. The annealing temperature increase led to an increase in the rate of grain size, as in Table 1

The average grain size also increases by annealed process consequent relaxation in the tensile strain for the deposited films; which leads an improvement in the structural properties of the film (nanocrystallin), because the display curved at the full width at half maximum inversely proportional to grain size, as in equation 3. Thus, the decrease FWHM leads to an increase in the grain size. Noted that from the Table 3 most of the values that are calculated responsive to this proportionality.[13, 18, 19, 20, 21]

Table 1 shows also the significant values for (111) peak in terms of lattice constant (a) and grain size. It can be concluded that the main influence of vacuum evaporation is associated the increase in grain size and lattice constant, where the intensity of the diffracted peaks is preserved with low FWHM in general, and the lattice constant (a) in particular [14, 20], as shown in Figure 2.



Figures 2: The dependence of annealing temperature of CdO thin film for (111) plane on a)Lattice constant (*a*) and b) grain size (*D*) for all samples.

The preferential crystallographic orientation of CdO films was specified by the texture coefficient (TC) from Equation:[22]

$$TC_{(hkl)} = \frac{I_{(hkl)}/I_{0\,(hkl)}}{N^{-1}\ \sum_N I_{(hkl)}/I_{0\,(hkl)}} \qquad \ldots\ldots\ldots\ldots\ldots (2)$$

where N is reflections number for identified Bragg peaks; $I_{(hkl)}$ is intensity measured for thin film sample and $I_{0\,(hkl)}$ is intensity measured from standards of (JCPDS)..

From Table 1, found that more valuable calculated values of TC(hkl) are greater than 1, especially those corresponding to (111) and (222) planes. The value of the direction TC(111) is 1.557 obtained at 425 °C, as shown in Figure 3.

This means that the film considered as a tightly film oriented towards the preferred crystal orientation (111) which is the largest direction along the diffraction plane. But the value which is less than one is a polycrystalline with the direction not uniform, such as (200) plane. These changes in TC (111) of the films were due to the nano-sized cadmium oxide recrystallization process and in agreement with [14, 20, 23] results.

Therefore, the temperature of annealing has the effect to improve texture coefficient and increasing the directivity of the film because the texture coefficient is a recipe for directional material. [24]

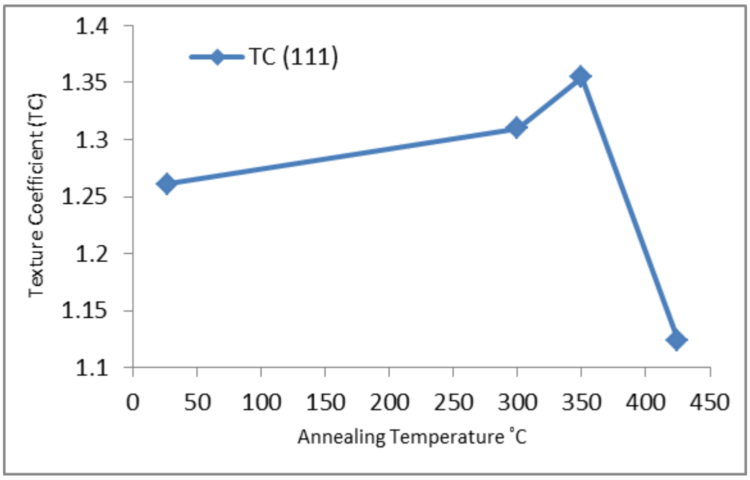


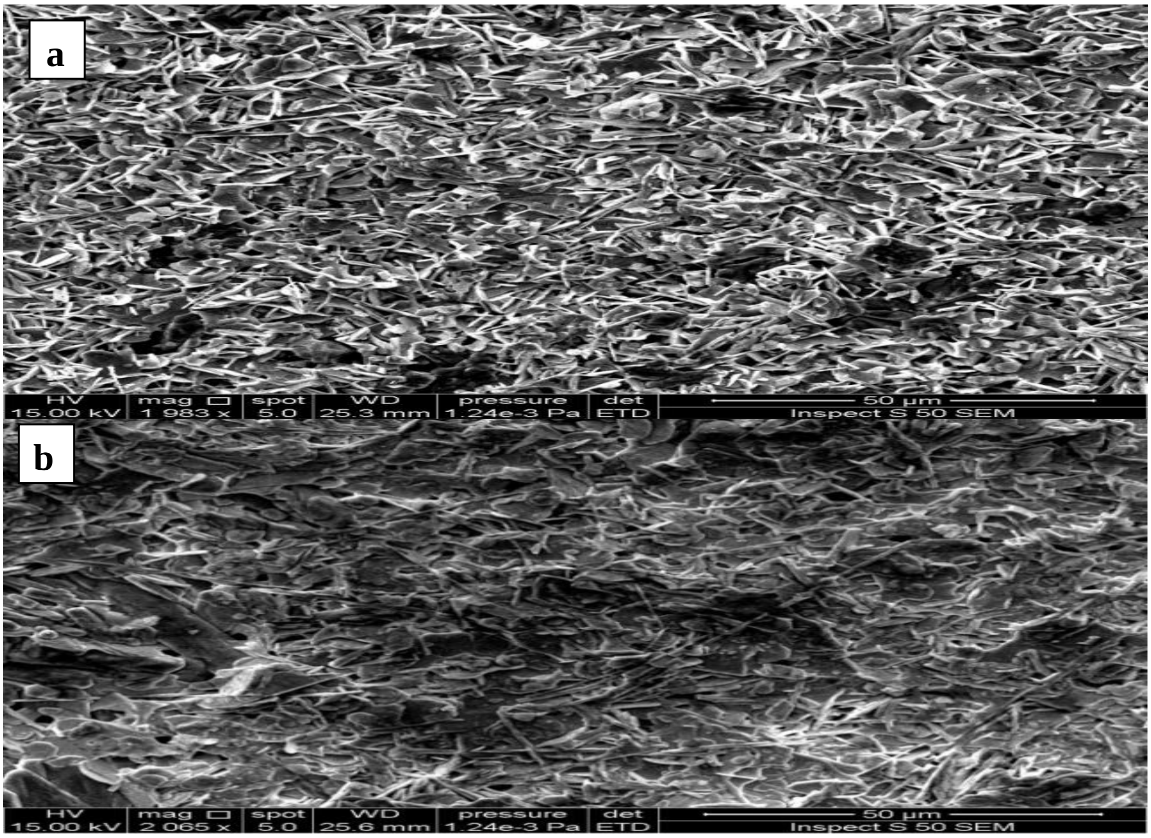
Figure 3: The texture coefficient for (111) plane of CdO thin film for all samples.

Table 1: XRD analysis of CdO nanoparticales films for structural, morphological and surface values from the results of lattice parameters, texture coefficient and grain size.

Annealing Temperature °C	**(hkl)max. XRD**	**2*θ***	**FWHM (Deg.) XRD**	***d* (nm) XRD**	***a* (nm) XRD**	**TC**	***D* (nm)**
Non-annealed	**(111)**	**32.638**	**0.1748**	**0.2728**	**0.4725**	**1.261**	**81.75**
	(200)	**37.927**	**0.1850**	**0.2363**	**0.4726**	**0.186**	**78.39**
	(222)	**68.943**	**0.1978**	**0.1364**	**0.4725**	**1.586**	**89.66**
300	**(111)**	**32.737**	**0.1759**	**0.2733**	**0.4734**	**1.310**	**81.21**
	(200)	**38.015**	**0.1952**	**0.2365**	**0.4730**	**0.179**	**73.95**
	(222)	**69.053**	**0.2076**	**0.1359**	**0.4708**	**1.511**	**80.55**
350	**(111)**	**32.706**	**0.1658**	**0.2713**	**0.4699**	**1.355**	**86.17**
	(200)	**38.006**	**0.1727**	**0.2350**	**0.4700**	**0.185**	**83.96**
	(222)	**69.019**	**0.1878**	**0.1355**	**0.4694**	**1.463**	**88.57**
425	**(111)**	**32.701**	**0.1734**	**0.2736**	**0.4739**	**1.124**	**79.07**
	(200)	**37.981**	**0.1800**	**0.2367**	**0.4734**	**0.319**	**73.79**
	(222)	**68.998**	**0.1972**	**0.1360**	**0.4711**	**1.463**	**84.37**

The micrographs for SEM show that the microstructures for CdO are influenced by the annealing treatment of the films prepared, as in Figure 4. The SEM image showed of high nanoparticales concentration for all specimens which thin plate-like and needle-like structural. The films appeared having some voids with more porosity. While many grain boundaries of films on the substrate can also be seen, especially for samples *b* and *c*, due to large lattice mismatch which may be in turn lead to an increase in granule size, as in Table 1.

The difference in the distribution and size of grains on the surface of the samples indicates the effect of ion exchange and the chemical interaction of O_2 and nano-Cd^{2+} on the morphology of the prepared samples [25] and upon it this results showed there is a bonding between the grains, which is important to obtain a homogeneous density, which results in a better structural. It was showed that strength development of grain or granular morphology relates to the microstructure due to fabric of the film as in good texture coefficient values for (111) plane [5, 10, 26]. This corresponds to the values obtained from by XRD or AFM analysis.



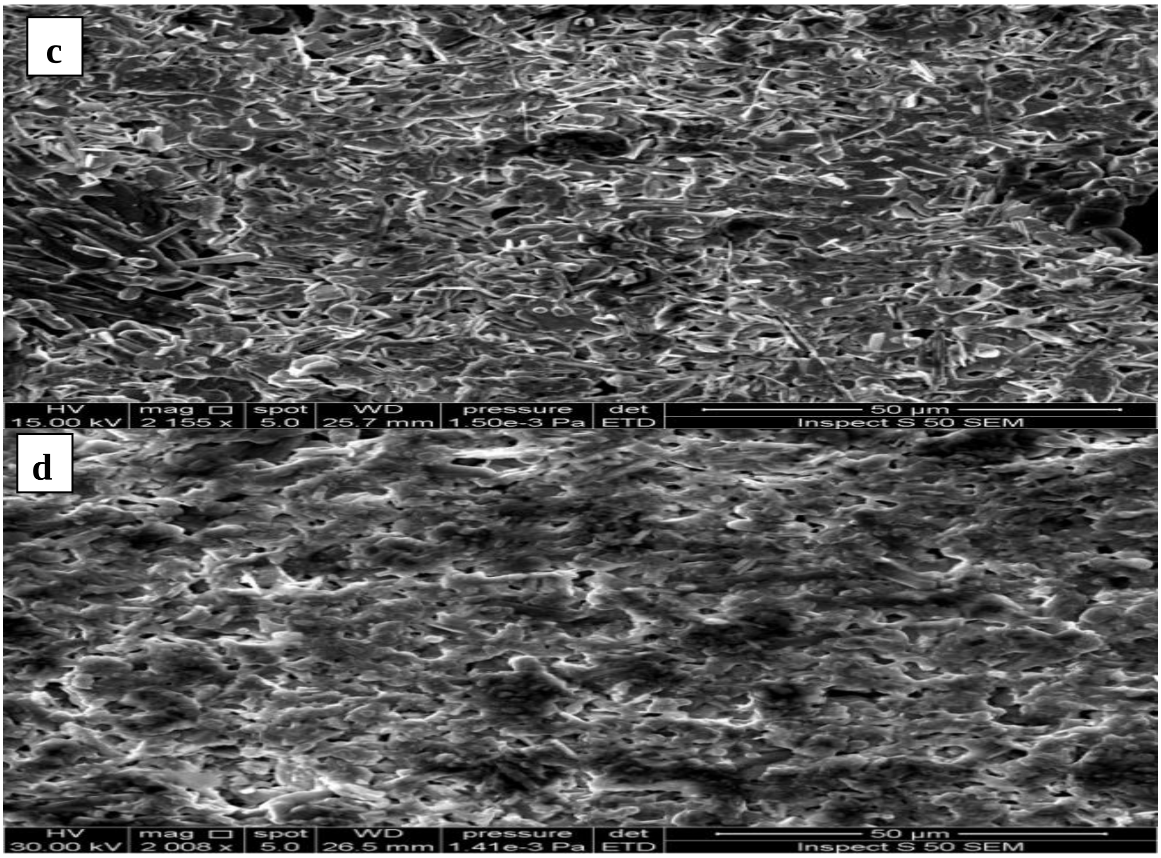


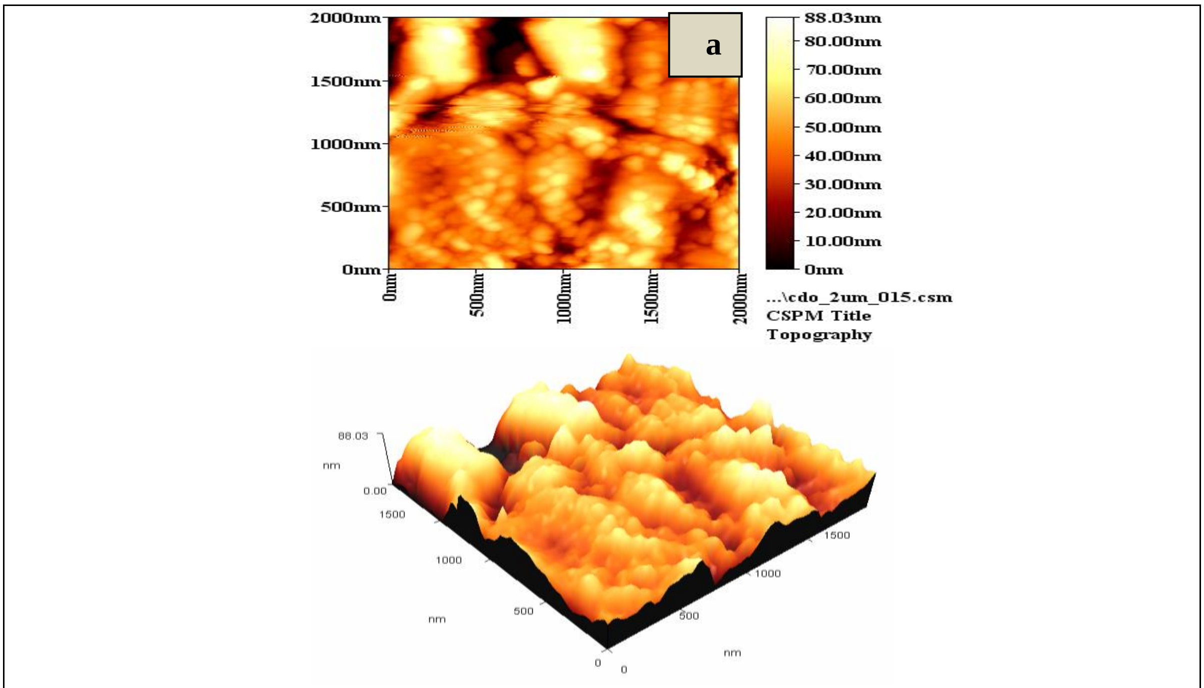
Figure 4: SEM images of CdO nanopartical films for all samples, a) Non-annealed b) 300˚C c)350˚C d) 425˚C.

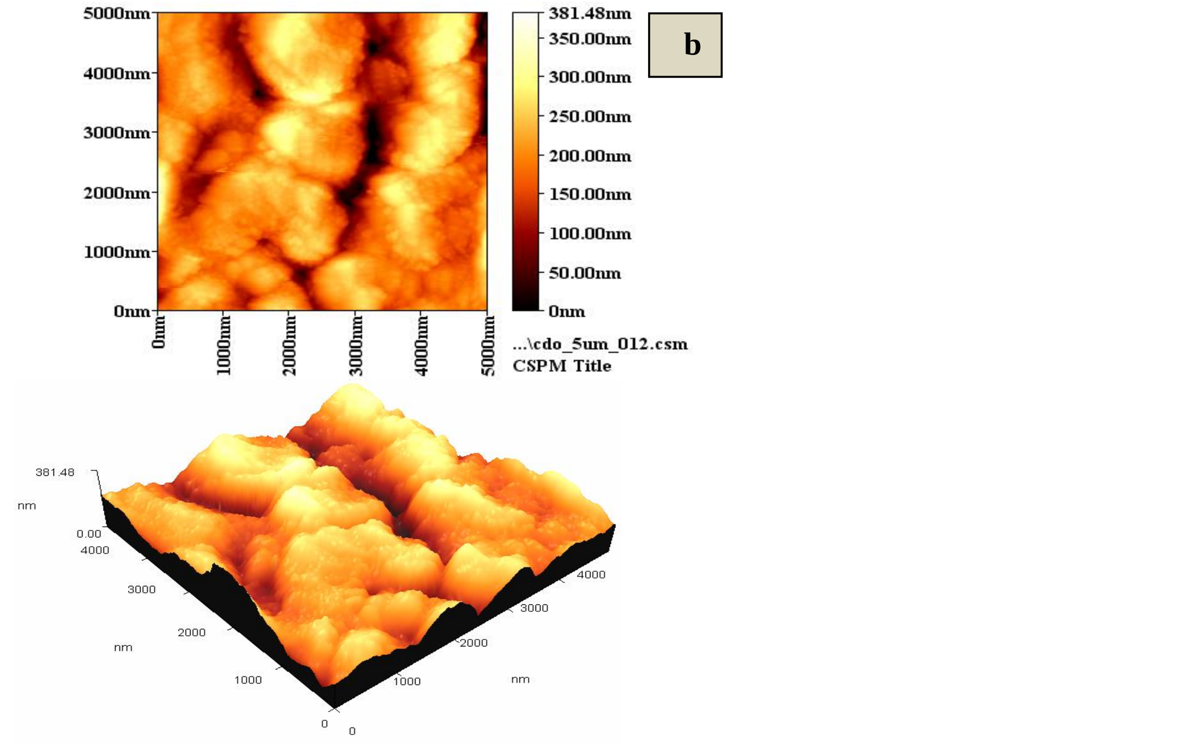
AFM image of CdO nanofilms as shown in Figure 5, which is exposes a spherical and rod-like shape, with an average diameter ranging from 78 nm to 95 nm. Mean Roughness (RA) and Root Mean Square Deviation (RMS)
AFM image for CdO films which is reveals spherical shape and rod-like, with average diameter between from 78nm to 95nm. The roughness average (RA) and root mean square deviation (RMS) of the highest value are 48.36 nm and 61.72 nm respectively, for all samples, as in Table 2.
The AFM image was showed that the topography of the films prepared have surfaces that are similar in composition. This is depends on the chemical composition for obtaining CdO and the stress that take place between the molecules consequent to the heat (annealing) applied to the film. Therefore, the thermal treatment (annealing) also led to an increase in the surface roughness resultant to increased grain growth [15, 21]. Thus, this is leads to

an increase in the amount of stress as the proportionality between the two is directly proportional. Therefore, the difference in the grains size of the nanoparticles between from D value by XRD analysis and the diameter decrease for AFM values are explained by the different epitaxial growth modes for the surface with strong chemical bond or weak physical interaction with substrate. [27, 28, 29]

Table 2. AFM parameters of the deposited CdO film for all samples.

Annealing Temperature°C	Roughness Average nm	Root Mean Square nm	Avg. Diameter nm
Non-annealed	29.91	37.54	78
300	46.38	58.88	88
350	48.36	61.72	92
425	40.53	51.02	95
D_{avg} (hkl)	**D_{avg} (111)**	**D_{avg} (200)**	**D_{avg} (222)**
XRD	82.02	77.52	85.79

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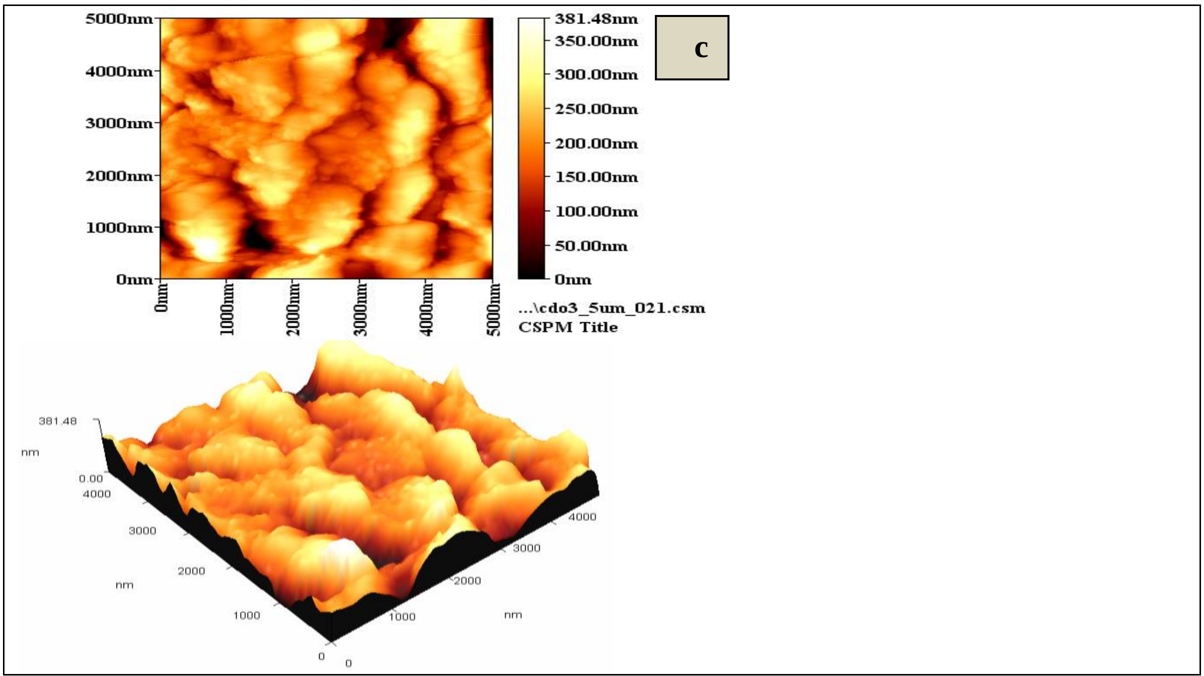
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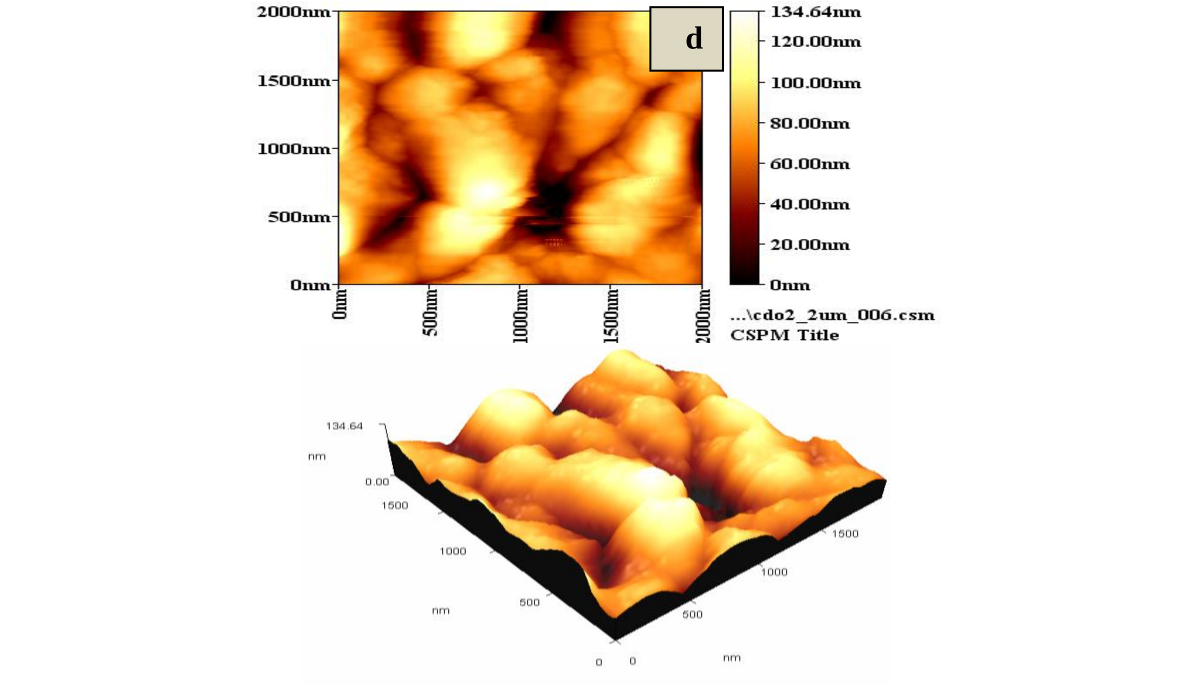

Figures 5: AFM images for CdO nanopartical films for all samples, a) Non-annealed b) 300˚C c) 350˚C d) 425˚C.

4. Conclusion

The structural properties of nanostructures CdO thin films that have good adhesion with the glass substrate were optimized which it was deposited by thermal vacuum technique. XRD shows that these films have a polycrystalline shape with cubic structure and preferred orientation along (111) planes with an increase in grain size due to the annealing temperature increases which was confirmed by AFM and SEM analyses. The average grain size value for the preferential orientation (111) is 82.02 nm. The crystal structure of the film is homogeneous at different annealing temperatures as is evident at (350 and 425) °C. The surface roughness has increased due to the appropriate increase in grain size along that (111) plane upon thermal treatment of all prepared films.

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كدالة الى درجة النانوية CdO تحسين الخصائص الهيكلية لأغشية رقيقة للجسيمات الحرارة

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مستخلص البحث:

تم تحضير غشاء رقيق على قواعد زجاجية من جزيئات أكسيد الكادميوم النانوية بتقنية الفراغ الحراري. تم تلدين الأغشية عند (300, 350 and 425) درجة مئوية لمدة ساعتين. لوحظ تأثير تغيير المعالجة الحرارية على الخصائص التركيبية والتركيب المايكروي. حيث يؤكد تحليل حيود الأشعة السينية (XRD) ومجهر القوى الذرية (AFM) أن أغشية أوكسيد الكادميوم (CdO) عبارة عن هيكل مكعب متعدد التبلور وأتجاه النمو المفضل على طول مستوى (111), والتي له معامل نسيج (TC) عند القيم (1.261, 1.310, 1.355 and 1.124) قبل وبعد تلدين الأغشية. يزداد حجم الحبوب من 73.79 نانومتر إلى 86.17 نانومتر مع زيادة درجة حرارة التلدين. أثبتت نتيجة الفحص المجهري الإلكتروني (SEM) وجود هياكل نانوية متجانسة ذات حجم حبيبات نانوية مميز وأشكال مختلفة لجميع الأغشية.

الكلمات المفتاحية: التلدين ، الحجم الحبيبي، أوكسيد الكادميون (CdO) ذو البنية النانوية ، معامل النسيج، حيود الأشعة السينية (XRD).