Characterization of CdO film AFM and XRD Diffraction Using Rietveld Refinement

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Received in 19 September 2012 , Accepted in16 January 2013

Abstract

Nano particles of Cadmium Oxide (CdO) thin films were prepared by spray pyrolysis technique. The synthesized film is annealed at (200 , 300, 450) ^{o}C for 3 hours . The XRD and AFM for the analysis of its structural and micro-structural characteristic has been preformed. The average grain size was found to be about 32.50 nm .There is a preferred orientation along (200) plane with texture coefficient 1.79, 1.644, 1.763 and 1.792 for deposited and annealed films, corresponding to grain size 57,58 ,51 and 51 nm. The variations of stress with temperature is ranged from 0.157 - 0.376 GPa .

Keywords: Spray pyrolysis , Preferred orientation, Rietveld Refinement , Grain size, Nano CdO

Introduction

Among the IIB-VI compound, CdO is of special interest .While other members of Cd and Zn based on tetrahedral of metal cations in wurtzite and zinc blende structure, this compound adopts a face –centered-cubic rock salt structure based on octahedral coordination around (Cd).It has important electronic, structural and optical properties. Its occur naturally as the rare mineral monteponite, [1] and has special features such as high conductivity, high transmission and low band gap made it applicable in photodiodes, phototransistors, photovoltaic cell , transparent electrodes , liquid crystal displays, IR detectors and anti reflection coatings [2].

Thin film technologies play the pivotal role specifically in the field of microelectronics such as cadmium plating baths, electrodes for storage batteries, cadmium salts, catalyst ceramic glazes, phosphors, optical coating, integrated optics and superconductors etc. In the last ten years, the CdO thin films were prepared by various techniques such as spray pyrolysis, oxidation of cadmium films, chemical vapour deposition etc. It was experimentally established that its properties are very sensitive to the film structure and deposition conditions [3,4].

The properties of CdO depend on their chemical composition and microstructure (volume fraction of crystalline and amorphous, type, shape, and size of the crystals), and also on the magnitude and type of residual stresses that arise on cooling below the glass transition region. These residual stresses result from the superposition of macroscopic stresses caused by temperature gradients across the sample cross section during the cooling process, the so-called thermal tempering stresses, with microscopic stresses due to the mismatch between the thermal and elastic properties of the crystalline and amorphous phases [5].

The phases, cell parameters and particle size are the important parameters that influence physical properties of material. Several techniques could be used for the investigation of them. However, the particle size determination can be based on direct observation of particles by atomic force microscopy (AFM) or scanning electron microscope (SEM) techniques. In this case, we can also receive the important information on the size and shape of particles. Data on particle size can be obtained by X-ray diffraction (XRD) technique as the particle size is related to the diffraction peak broadening. It is important to note that XRD and AFM methods allow not only to measure the particle size, but also to identify crystalline phases, were analyzed by the Rietveld refinement technique. [6]

Rietveld refinement is a technique devised by Hugo Rietveld for using in the characterization of crystalline materials. The neutron and x-ray diffraction of powder samples result in a pattern characterized by reflections (peaks intensity) at certain positions. The height, width and position of these reflections can be used to determine many aspects of the materials structure. The Rietveld refinement is a well-known and useful tool for structure determination; it allows the determination of lattice parameters, atom positions, occupation parameters, isotropic and anisotropic temperature parameters. The method may also be used for quantitative phase analysis. Because the Rietveld refinement is a universal and convenient procedure of powder data analysis, it was decided to use it for resolving other problems like the determination of crystallite size.

During the refinement the whole X-ray diffraction pattern is analyzed and the profile parameters describe the whole pattern. The value of the Bragg reflection full-width at half-maximum (FWHM) is a function of θ, but the shape, model of asymmetry, character of the "tails of the diffraction lines" are the same for the whole diffraction pattern. In the classical way of crystallite size determination, it is necessary to analyze the individual reflection profile fitting. In spite of these differences, the usefulness of the Rietveld refinement for crystallite size determination was tested [7,8]. CdO thin films are characterized by different authors. Their XRD is associated with presences of (111), (200), (220), (311), and (222) planes of the cubic structure as it is compared with standard of bulk CdO. In literature one can observe

difference in the reported data about the peak of maximum intensity .Most authors [9-13] refer to (111) as plane of prefer orientation and texture coefficient ,while [14] reported the plane (200) for prefers orientation.

So, in this work, we presented synthesis a nano particles CdO thin films with (200) plane of prefer orientation. Then, characterized, its structure, morphology and microstructure at different annealing temperatures by using Rietveld refinement in order to provide us accurate values of the lattice parameters in the respective phases can be related to CdO .

Experimental work

CdO thin films were prepared by spray pyrolysis technique on a glass substrate using a homemade spray system . The subsequent reaction on the heated substrates produces the CdO thin films products by using cadmium nitrate hydrate $(Cd(NO_3)_2.4H_2O)$ material to produce thin films. The solution of cadmium nitrate hydrate with concentration (0.2M) is prepared according to the following relation;

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

Where: M: concentration molarity , V: volume of water , W_t: weight of solution.

M_{wt} :molecular weight of $(Cd(NO_3)_2.4H_2O)$ material

After the solution is cooled locate in the spray system to spray on the glass substrate, we can get the CdO thin films according to the chemical equation :

$$2Cd(NO_3)_2 \xrightarrow{Heat} 2\,CdO + 4NO_2 \uparrow + O_2 \uparrow \quad \text{.....(2)}$$

It has been found that the following deposition parameters give films with good transparency and uniform surface at:

(1) Substrate Temperature is once 550 °C, (2) Spray rate 8 cm^3/min , and (3) Distance between sprayer nozzle and substrate of 28±1 cm

The glass substrates are placed on the hot plate for about (25 min) before spraying process, so the glass substrates are nearly at the same temperature as the hot plate. Each spraying period lasts for about (20s) followed by about (5 min) waiting period to avoid excessive cooling of the hot substrates due to the spraying. The thicknesses of the sprayed samples were in the range of (10±0.3 µm) which was measured by weighting method. The films were clear, transparent, brown colored having very good adhesive properties with smooth surface free from pinholes.

Results and Discussion

X-ray characterization

The X-ray diffraction patterns were obtained in a (Shimadzu XRD-6000) goniometer using copper target (Cu K_α, 1.5418 Å), (40 kV, 30 mA). The thin films were mounted in an aluminum sample holder. Step-scan data were collected from range 20°-100° with a step width of 0.02° and a counting time of 5 sec/step. The divergence, scattering , and receiving slits are 1.0°, 1.0° , 0.30 (mm) respectively with monochromator was used. X-ray diffraction patterns of CdO thin film is shown in Fig .1. Its exhibited three strong diffraction peaks at (38.336°,33.040°, 55.336°) associated with planes (200) (111), (220) and other peaks for (311), (222), (400),(331) and (420) planes. These indications are for polycrystalline nature with cubic structure (JCPDS 05-0640).

Texture Coefficient (TC) is used to quantify the preferential orientation of the film deposited using the following relation [13]:

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{N^{-1}\sum_n I(hkl)/I_0(hkl)} \quad \text{.....(3)}$$

Where I is the measured intensity, I_o is the standard intensity, Joint Committee on Powder Diffraction Standards, (JCPDS) and N is the number of diffraction peaks.

The prepared films of CdO have (200) plane as preferred orientation. This shows a good agreements with the discussion of [14]with respect to their film deposited on glass substrate . For fcc, high lattice point density on (200) plane refer to low surface energy on it ,then the growth along that plane is so easy . According to , table 1, the calculated lattice parameter(4.69184 Å) of this film, very close to that of the bulk CdO 4.6958 Å .This indicates ,that the prepared films were formed in an effective equilibrium state. Due to high crystalline state a little pit difference in lattice parameter is observed for annealing the sample at different temperature. The effect of line broadening is primarily due to the micro-residual stress and decrease in the grain size [l].

Morphology

AFM (AA 3000 , Angstrom Advanced Inc.) analysis of CdO thin film (Fig. 2) shows that the surface is composed of crystallites with an approximate size of 32.50 nm grouped together into larger agglomerates, the RMS surface roughness is found to be 3.53 nm. Mean crystallite size corresponding to the CdO thin film is calculated, using Scherrer's formula [15].

$$D = K\lambda / B\cos\theta \qquad \ldots\ldots\ldots\ldots\ldots(4)$$

Where *D* is the average crystallite size, λ is the wavelength of the X-ray radiation ($Cu_{K\alpha}$ = 0.15418 nm), K is a constant taken as 0.94 , θ is the diffraction angle and B is the full width at half maximum height.

Texture coefficient for (200) plane is 1.79,1.644,1.763 and 1.792 (corresponding to grain size 57, 58 ,51 and 51 nm) for room temeperature,200,300 and 450 °C respectively. Its seem so high as it is compared with 0.899,1.086,0.999 and 1.086 for (111) plane (corresponding to grain size 55,56 ,49 and 49 nm) at the same temperatures. This gives us an indication of preferred orientation of the films along the (200) diffraction plane. Which is associated with increase of average grains size from 52nm for(111) up to 56 nm along (200)plane. The above result shows good agreements with Balu et al [2] for his sample at 0.2 M.

Rietveld Refinement and Microstructural details

Structural analyses of as-deposited and the annealed films were carried out by X-ray diffraction patterns. Their XRD patterns on glass substrate are shown in Fig. 3. It can be seen that the nano particles displays the structure with high crystalline as it is compared with the standard diffraction pattern of cadmium oxide. The figure shows the change of intensity and peak angle of material before and after annealing temperatures (200 , 300, 450) ^{o}C for 3h . Its also shows the Rietveld plots (carried out by fullprof software)[16] for the different samples studied in this work. Rietveld Refinement was performed for all samples and the results are given in table 1. It is clear that, intensity is maximum for (200) plane for all the films deposited at different annealing temperatures., its sharp XRD peaks refer to grow the nanostructure at random orientation [4].

In figure 4 for raw x-ray data, the peak position shifts to lower angle for 300°C and 450°C . Shifting of peak to lower angles indicates the increase in lattice constant, but for 200°**C** shifted to higher angle values. This may be due to a uniform compressive or tensile strain (macrostrain) ,while a non-uniform tensile and compressive strain results in broadening of diffraction lines (microstrain)[17].Also figure 4 shows the small shift in XRD peaks of the films annealed relative to the CdO film peaks is attributed to the mechanical micro stress produced by different resources like; impurities, defects and vacancies reside in the film even after annealing.[13]

The error in d (d_{error} %) [18] , elastic stress (σ) and Strain are calculated from the following equations and their results are presented in table 2;

$$d_{error}(\%) = \frac{|d_H - d|}{d} * 100\% \quad \ldots\ldots\ldots\ldots\ldots(5)$$

Where d_H , d are the measured and standard inter planer spacing , respectively.
The elastic stress (σ) and Strain of the films can be determined from Hoffman's relation [19]:

$$\sigma = -232.75 \ \frac{(c-c_0)}{c} \ [GPa] \quad \ldots\ldots\ldots\ldots\ldots(6)$$

$$\text{Strain } (\%) = \frac{(c-c_0)}{c} * 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

Where the c, c_0 are the measured and stress-free c-axis lattice constants, respectively.
Microstrain analysis: Figure 4 shows XRD pattern for peaks (111),(200) and (220) to deposited film and annealed films at different temperatures. Its depicted the peak shift and the lines broadening as a function of diffraction angle. This indicates the presence of microstrain rather than macrostrain [13]. As seen from table 2, the microstrain and the corresponding stress are varied from 0.067 to 0.161 and 0.157 to 0.376 GPa respctively with annealing temperature. Then ,the stress is decreased with the grain size increase as shown in figure.5.

Conclusion

Thin film of CdO on glass substrate is prepared by homemade spray pyrolysis unit. XRD shows the films have fcc crystal structure with lattice parameter a = 4.69±0.01 Å according to Retiveld refinement and XRD pattern confirm CdO phase with preferential orientation along (200) plane. The average grain size was found to be about 32.50 nm .There is preferred orientation along (200) plane for deposited film and annealed films , this is indicated to the increase of grains along that plane. The peaks show shift and the lines are broadened as the function of diffraction angle. This indicates the presence of microstrain rather than macrostrain.

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Table No.(1):Micro structural analysis using Rietveld analysis

(hkl)	Unannealed			200°C			300°C			450°C		
	d(Å)	2Θ(°)	I(a.u)	d(Å)	2Θ(°)	I(a.u)	d(Å)	2Θ(°)	I(a.u)	d(Å)	2Θ(°)	I(a.u)
(111)	2.7088	33.040	159.5	2.7085	33.045	213.1	2.7063	33.072	174.0	2.7066	33.068	186.6
(200)	2.3459	38.336	303.8	2.3456	38.342	268.0	2.3437	38.374	255.7	2.3440	38.369	255.1
(220)	1.6588	55.336	68.5	1.6586	55.344	66.3	1.6573	55.393	64.3	1.6575	55.385	64.1
a(Å)	4.69184			4.69123			4.69197			4.69189		
D(nm) (111)	55			56			49			49		
D(nm) (200)	57			58			51			51		

Table No.(2) The microstrain , σ(GPa) , $d_{error\%}$ and TC are measured as a function of temperature treatment

(hkl)	Unannealed		Annealed at200°C		Annealed at 300°C		Annealed at 450°C	
	$d_{error\%}$	TC	$d_{err\%}$	TC	$d_{error\%}$	TC	$d_{error\%}$	TC
(111)	0.118	0.899	0.129	1.056	0.210	0.990	0.199	1.025
(200)	0.132	1.79	0.145	1.644	0.225	1.761	0.212	1.792
(220)	0.132	0.734	0.398	0.774	0.223	0.829	0.211	0.807
Strain%	0.067		0.080		0.161		0.145	
σ(GPa)	0.157		0.187		0.376		0.338	

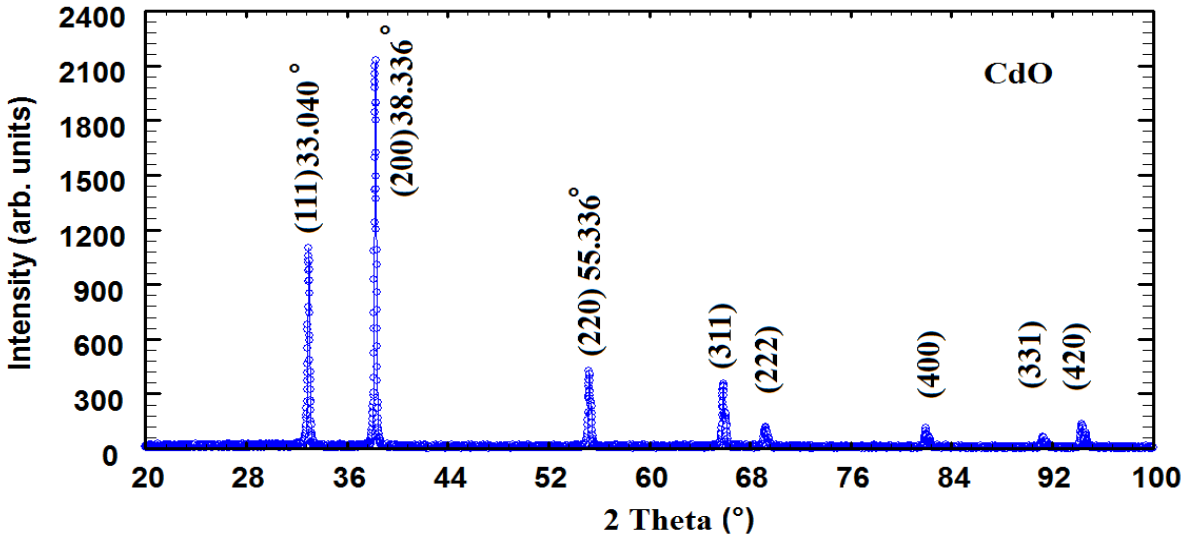

Figure No.(1) X-ray diffraction pattern of CdO thin film as- prepared

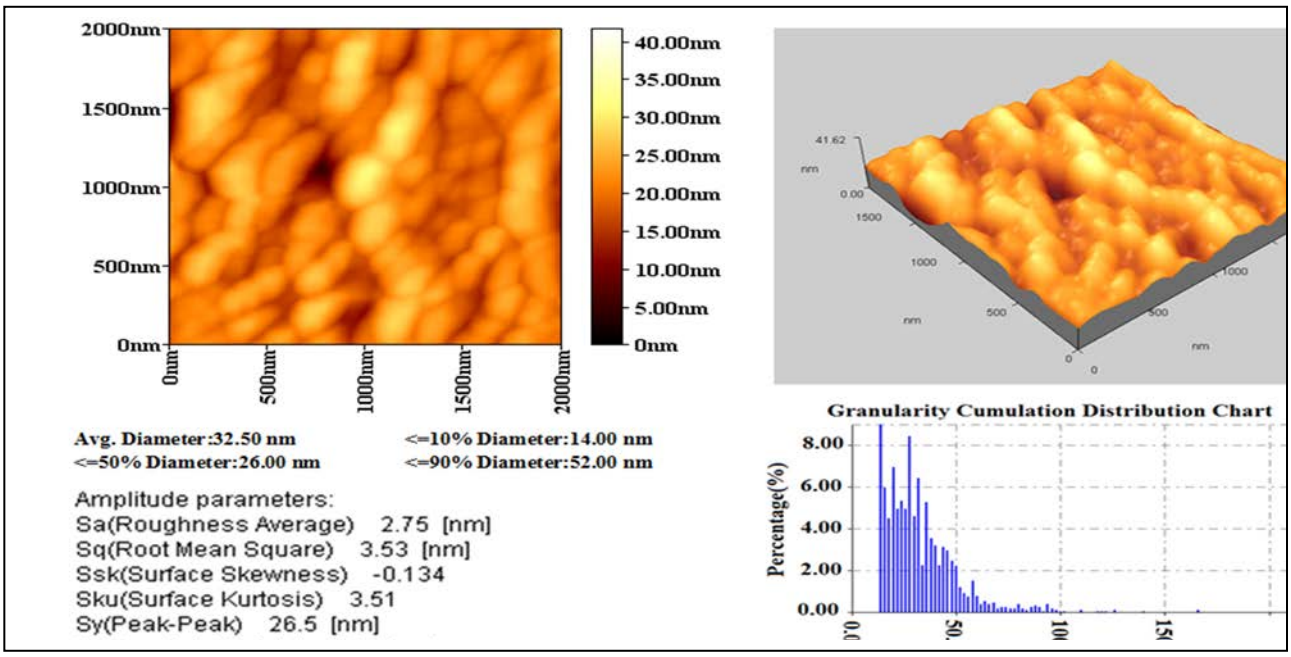

Figure No.(2) AFM image of CdO thin film and granularity cumulation distribution report .Sample area is 2µm by 2µm**.**

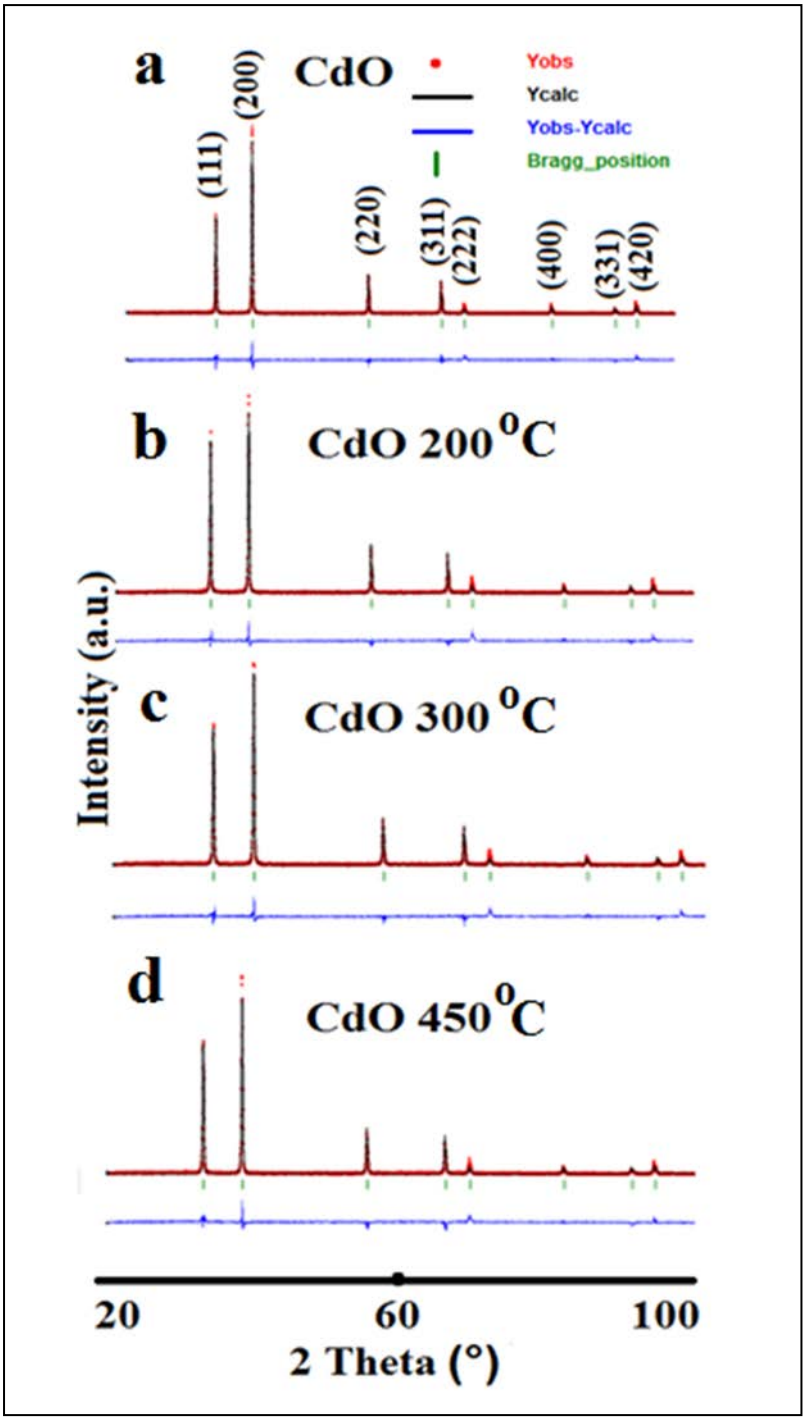

Figure No.(3) Rietveld refinement pattern of CdO thin films. a)unannealed , b)annealed at 200 °C , c) 300 °C , d) 450 °C

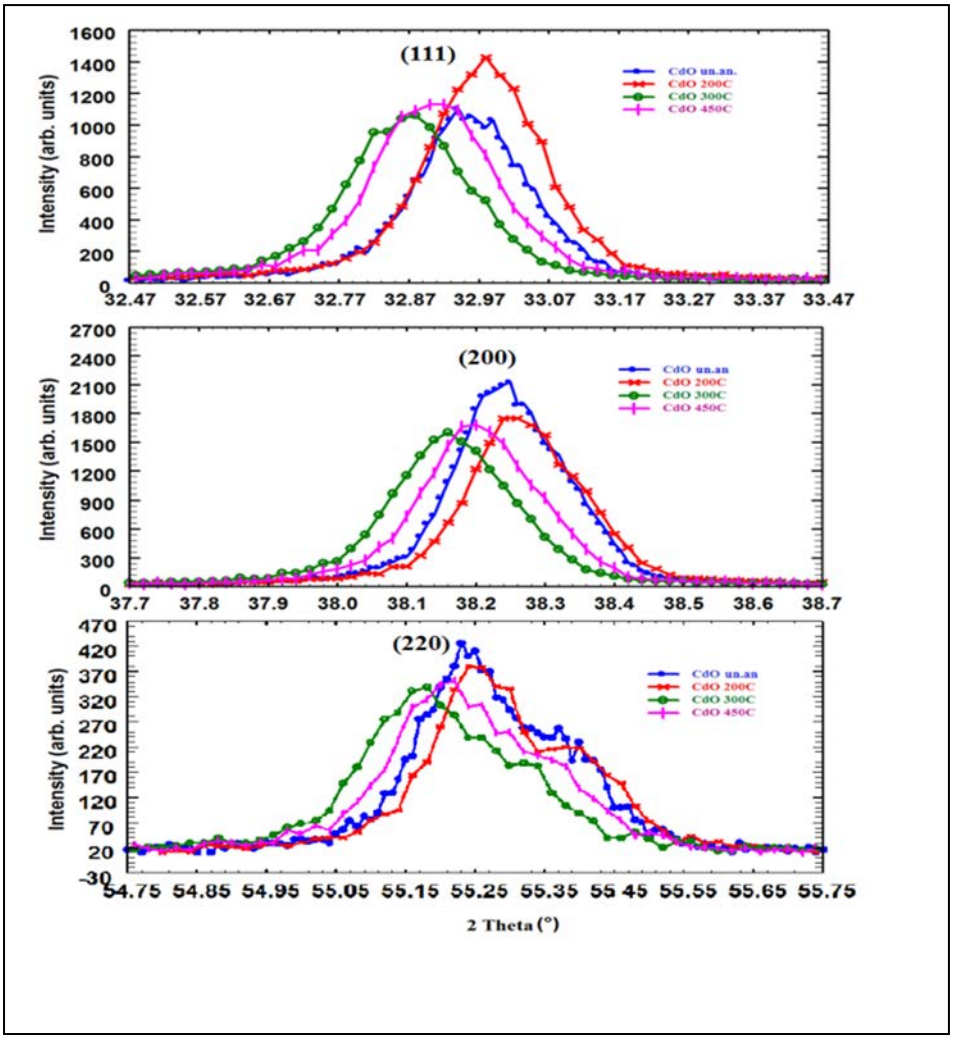

Figure No.(4) Peaks (111),(200),(220) for CdO thin films a)unannealed , b)annealed at 200 °C , c) 300 °C , d) 450 °C

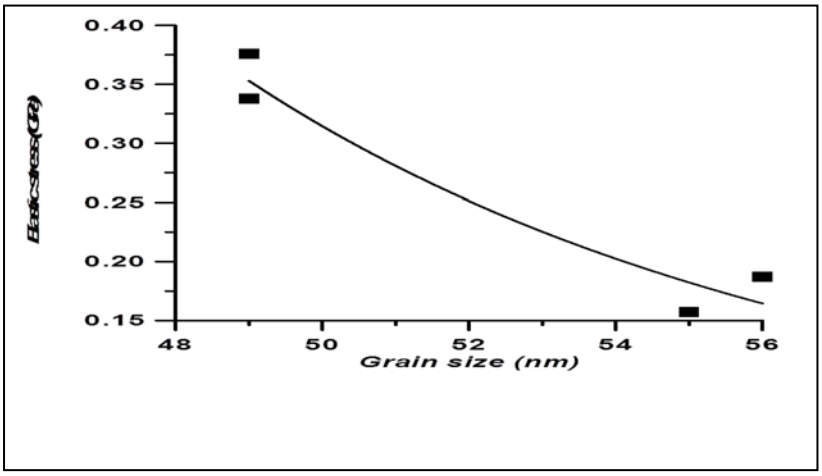

Figure No.(5): The variation of grain size with elastic stress (σ)

ميزات غشاء اوكسيد لكادميوم بوساطة مجهر القوة الذرية وحيود الاشعة السينية بإستخدام تصفية ريتفيلد

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استلم البحث 19 ايلول2012 ، قبل البحث في 16 كانون الاول 2013

الخلاصة

حضرغشاء نانوي من اوكسيد الكادميوم بتقنية التحليل الحراري. وتم تلدينه الى 200 و300 و450 درجة مئوية لثلاث ساعات .استعمل AFM وXRD لتحليل التركيب والتركيب المايكروي . وجد ان معدل الحجم الحبيبي 32.5nm ، وان التوجيه التفضيلي على طول السطح (200) والمعامل TC هو 1.79 للغشاء المحضر. أما TC للاغشية الملدنة فمناظرة لدرجات حرارة التلدين وهي 1.79 ،1.763,1.644 و 1.79 على التوالي . والحجم الحبيبي المناظر 51,58,57 و51 وحسب تغير الاجهاد مع درجة حرارة التلدين وكان ضمن المدى 0.157-0.376 GPa.

الكلمات مفتاحية : التحليل الحراري ، توجيه تفضيلي،تصفية ريتفيلد ، حجم حبيبي ، أوكسيد الكادميوم النانوي