*Structural Properties of Nano (CdO) Semi Conduction Thin Film Deposited by Spray Pyrolysis Technique

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Abstract

In this paper CdO films of 160 nm thickness were deposited onto glass substrates by spray pyrolysis technique at 400 ^{o}C temperature. The structure of films where studied , where X-ray measurements showed that the polycrystalline film and have a grain size of 14.63 nm. As shown images of atomic force microscope that the film surface roughness of 3.26 nm .The photo of Scanning electron microscope show that the film high and free from cracks and holes have a superficial homogeneity. The energy-dispersive X-ray analysis show that the film containing the pure and elemental cadmium and oxygen only signifying purity film prepared.

Keywords: Spray pyrolysis technique, cadmium oxide , Structural properties , Thin films ,XRD, AFM, SEM.

الخلاصة

في هذا البحث تم ترسيب أغشية اوكسيد الكادميوم النانوية بسمك 160 نانومتر على قواعد من الزجاج باستخدام تقنية الرش الكيميائي عند درجة حرارة 400 درجة سيليزية . اختبرت الخصائص التركيبية للأغشية المحضرة حيث أظهرت قياسات الأشعة السينية إن الغشاء متعدد التبلور ويملك حجم حبيبي 14.63 نانومتر. كما بينت صور المجهر الالكتروني الذري إن الأغشية ذات خشونة سطحية 3.26 نانومتر. وأظهرت صور المجهر الالكتروني الماسح إن الغشاء يملك تجانس سطحي عالي وخالي من التشققات والثقوب. وبين فحص التشتت بواسطة أشعة اكس إن الأغشية تحتوي على عنصري الكادميوم والأوكسجين فقط مما يدل على نقاوة الغشاء المحضر.

1.Introduction

The preparations of nanometer size crystallites open the opportunity of observing the evolution of physical properties of the materials with sizes. The reduction of sizes with which the bulk properties change remarkably and provide the possibility of observing novel behaviors such as size-dependent structural, electrical and optical properties. The physics associated with these properties of nanocrystallites of II–VI semiconductors have been very interesting because of thinking the phenomena in a new point of view with the properties exhibited by them. Nanocrystalline semiconductors have attracted much attention due to their novel properties and varieties of promising potentials in extensive applications **[1,2]**. Numerous technical advancements in the field of nanostructured materials have stimulated the wide range of research interest in

recent years because of various new properties exhibited by them. Recently, nanostructured semiconductors are widely used to design a rich varieties of device for microelectronics. One-dimensional nanostructured materials have gained special interest in the assembly of nanodevices **[1,2]**. Nanometer-scale electronics have been predicted to play an important role in device technology**[3,4]**. Quantum wires of semiconductors**[5]** and metallic alloys **[6]** have found to exhibit interesting magnetic and electrical properties. The nanostructured transparent conducting oxides have also gained tremendous importance due to their size dependent optical properties and possible applications in near future. Recently, various research groups around the world are working on the synthesis of several II–VI n-type transparent semiconducting oxide thin films by different processes. Previously, thin films of cadmium oxide (CdO) have been synthesized by various techniques, including activated reactive evaporation **[7]**, spray pyrolysis **[8,9]**, solution growth **[10]**, MOCVD **[11]**, PLD **[12]**, rf sputtering **[13]** etc. Recently, Fdoped CdO thin film has been reported **[14]** via sol–gel process. The preparation of ZnO quantum dots **[15]** , nanowires and nanorods **[16,17]** etc. have been studied widely. In this study the structural properties of CdO will studies.

2.Experimental

2.1.Solutions Preparation:

CdO thin films was prepared by spraying an aqueous solution of $Cd(CH_3COO)_2.2H_2O$ [which is a powder of white color, it's molecular weight (266.53 gm/mol)] in 100 ml distilled water. The dissolving weight (W_t) of the materials $[Cd(CH_3COO)_2.2H_2O]$ was determined by using the following equation **[18]** :

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

Where:

M: is the molar concentration, equal {0.1M materials $[Cd(CH_3COO)_2.2H_2O]$ M_{wt} : molecular weight, V : volume of distilled water. The weights of $[Cd(CH_3COO)_2.2H_2O]$ were measured by using electrical balance sensitive (Metller. A.K -160) four digits (10^{-4} g). The solutions leaving for 24 hours to make sure that no residues were left and to ensure the homogeneity of the resultant solution. The resultant solution was sprayed on preheated glass substrates to prepare nano (CdO) thin film. When the solution is sprayed, the reaction takes place at the surface of the heated substrate, the equations (2) show the reaction. The resulting film were stable, whitish downhill to yellow in color, transparent, free from pinholes and have good adhesive properties .

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

$$Cd(CH_3COO)_{2(s)} \longrightarrow CdO_{(s)} + CH_3COOH_{3(g)} + CO_{2(g)}$$

2.2.The Parameters to Preparation Films

Asimple homemade spray pyrolysis experimental setup was employed to prepare nano (CdO) thin film on glass substrates (35× 25 ×1.35 mm^3) at a substrate temperature of 400 °C. Spray solution and a total volume of 25 ml was used in each deposition. The deposition parameters such as spray nozzle-substrate distance (30 cm), ,spray time

(4 s) and the spray interval (1 min) were kept constant. The carrier gas (filtered compressed air) flow rate was maintained at 6 l/min at a pressure of 6.5×10^4 Nm^{-2}. XRD ,AFM ,SEM and EDX analysis were used to recognize the crystal structure properties of nano (CdO) thin film.

3.Results and Discussion

3.1.X-Ray Diffraction Analysis

The X-ray Diffraction investigation has been carried out for the prepared thin film of (CdO) in Fig. (1), for range from 20^o-70^o in 2θ. According to (ASTM) cards, the structure of these film showed a polycrystalline. The XRD shows peaks whose position were shifted slightly from the data of (ASTM) card Increased by 0.03. The interplanner spacing (d_{hk1}) was determined using the Bragg relationship (3) **[19]** :

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

Where n is an integer that indicates the order of the reflection, θ is Bragg angle, and λ is the wavelength of the X-ray beam. By measuring the Bragg angle θ, the interplanar distance d can be obtained if the wavelength of the X-ray beam is known **[20].**

From Fig. (1) the five diffraction peaks observed were identified as the reflections from (111)*, (200)*, (220)*, (311)* and (222)* planes of cubic CdO phase with a lattice parameter of 4.6948 Å [ICDD PDF file No:75-591]. The most prominent peak was the reflection from the (111)* plane. The diffraction peaks corresponding to (111)* and (200)* planes were sharp in comparison to those from(220)* , (311)* and (222)* planes.

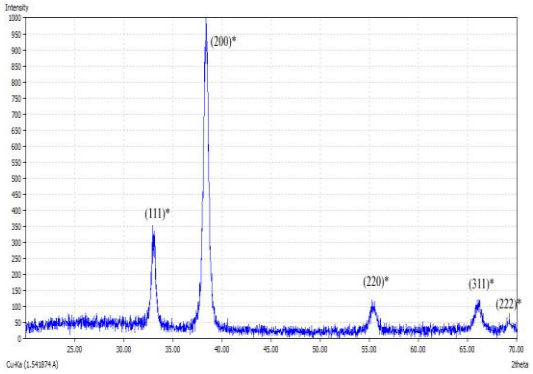

Fig.(1): The X-ray diffraction patterns of the CdO films.

For all film, the grain size (G.s) was calculated from the full width at half maximum (FWHM) (β) of the preferred orientation diffraction peak by using the Debye-Sherrer' s equation, **[20]** :

$$D = \frac{0.9\,\lambda}{\beta\cos\theta} \quad \cdots\cdots\cdots\cdots (4)$$

Where:

λ: is the X-ray wavelength (Å) ,

β: FWHM (radian). ,

θ: Bragg diffraction angle of the XRD peak (degree).

Larger G.s and smaller β values indicate better crystallization of the materials According to Table (1) .

Table (1): X-ray diffraction data for nano (CdO) thin films.

Sample	(hkl)	Θ (deg)	d (nm)	FWHM (deg)	G.S (nm)	Ave. G.S (nm)
CdO	(111)*	16.4	0.27	0.37	22.3	14.6
	(200)*	19.1	0.23	0.555	15.1	
	(220)*	27.6	0.16	0.9259	9.68	
	(311)*	33.0	0.14	0.8333	11.3	

3.2.Atomic Force Microscope (AFM)

Figure (2) show two-dimensional , three-dimensional, granularity normal distribution and appearance, graphic granular aggregates formed in the film and grain boundaries of nano (CdO) thin film. The white regions in this figure represent the formation of agglomerated grains one on the top of the other. For these regions, we think that neighbouring grains come together forming large clusters. So grains in the white regions are larger in size as compared to others. From all of these interpretations, the film growth mechanism is thought to be formed firstly layer by layer and then island growth type .Figure (2.a) shows the three-dimensional images of the CdO film where the note topographic surface and appearance of grains formed on the surface of the film, and from these images, we found that surface thickness equal 27.53nm ,this value represents the thickness of the film surface roughness, which account for the highest crystalline granular tops on the surface, as we note regularity in the grow film and note that granules with a vertical arrangement on the crystal axis and equal heights. Figure (2.b) shows the Analytical CdO thin film topographic image of the two-dimensional surface roughness and found that average roughness equal 12.8 nm . As it turns out that the value of root mean square equal 14.8nm , it represents (total highs surface and lows squared divided by the sum of the number are all under the square root) and this value is interpreted and describes the surface roughness rate higher the average square root of the value indicated by the increase of surface roughness of the film conversely rate, and can take advantage of that in how to get the morphology of the surface the film according to the required applications. Figure (2.c) shows the graph on the distribution of granular aggregates on the surface of CdO film. It was found that average diameter equal 72.11nm ,the graph diagram shows how the distribution of sizes grain aggregates on the surface of the film a certain percentage. Figure (2.d) shows the morphological appearance of the granular aggregates formed in the film and grain boundaries.

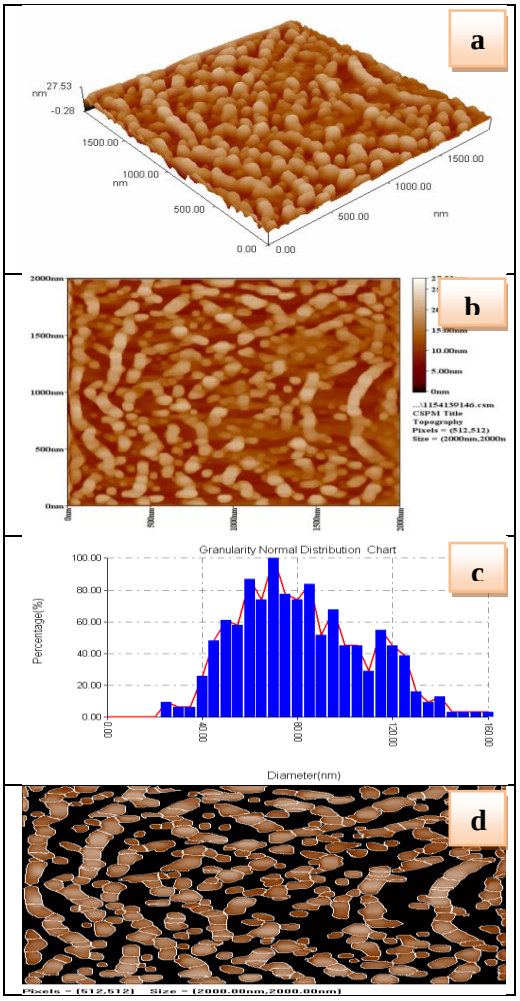

Fig.(2): AFM images of CdO thin film.

Table (2): AFM data for (CdO) thin film.

Sample	RMS (nm)	Rough. (nm)	Total Grain No.	Aver. Diameter (nm)
CdO	3.8	3.26	354	72.11

3.3.Scanning Electron Microscopy (SEM)

Fig.(3) shows the scanning electron microscope images of (CdO) thin film grown on glass substrates at 400^{o}C of which consists of a uniform distribution of spherical shaped of nanostructured grains . This structure throughout the materials with closely packed to each other indicating good adhesiveness of film with the substrate.

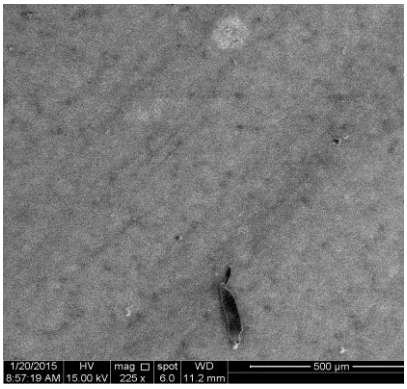

Fig.(3): The SEM image of the CdO thin film.

3.4.Elemental Analysis

The energy-dispersive X-ray analysis (EDX) spectra of the CdO thin films deposited on a glass substrate at 400 ^{o}C by spray pyrolysis technique was given in Fig. (4). Which show that the film contain the elements (Cd , O) as expected, indicating formation of the (CdO) film with high purity and it reveals that the compound percentage for the (Cd) and (O) are (86.96036) and (13.03964) respectively.

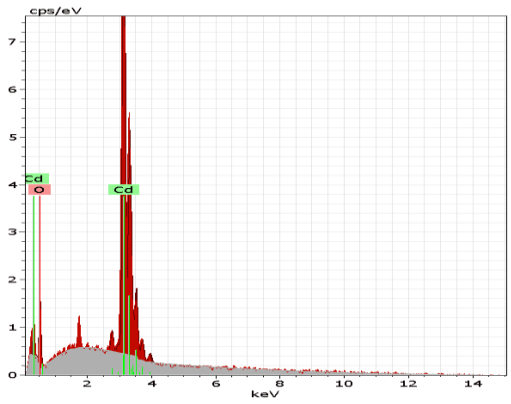

Fig. (4): EDX spectra of the CdO thin film.

4.Conclusion

The nano CdO thin film deposited through spray pyrolysis method on glass substrate shows better structural properties at substrate temperature 400 ^{o}C , The average grain size of CdO thin film has been calculated 14.63 nm , surface roughness of 3.26 nm and has high purity film.

References

[1] Bachtold A., P. Hadley, T. Nakanishi and C. Dekker, Science **294**, 1317 (2001).

[2] Huang M.H., S. Mao, H. Feick, H.Q. Yan, Y.Y. Wu, H. Kind, E. Weber, R. Russo and P.D. Yang, Science **292**, 1897 (2001).

[3] Pease R.F. Kirk W.P. and Reed M.A. eds, Nanostructures andMesoscopic Systems , Academic, NewYork, p. 37,(1992).

[4] Schon J.H., O. Schenker and B. Batlogg, Thin Solid Films **385**, 271 (2001).

[5] Lee S.T., Y.F. Zhang, N. Wang, Y.H. Tang, I. Bello, C.S. Lee and Y.W. Chung, J. Mater. Res. **14**, 4503(1993).

[6] Blythe H.J., V.M. Fedosynk, O.I. Kasyutich and W. Schwarzacher, J. Magn. Magn. Mater. **208** , 251 (2000).

[7] Phatak G. Quadri S.B., E.F. Skelton, D. Hsu, A.D. Dinsmore, J. Yang and R. Lal, Thin Solid Films **245**, 17(1994).

[8] Gurumurugan K., D. Mangalaraj and S.K. Narayandass, . Thin Solid Films **251**, 7.(1994)

[9] Sanatana G., A.M. Acevedo, O. Vigil, F. Cruze, G. Contreraspuente and L. Vaillant, Superficiesy Vacio **9**, 300(1999).

[10] Verkey A. and A.F. Fort, Thin Solid Films **239**, 211(1994).

[11] Freeman A.J., K.R. Poeppelmeier, T.O. Mason, R.P.H. Chang and T.J. Marks, MRS Bull. **25**, 45(2000).

[12] Yan M., M. Lane, C.R. Kannewurf and R.P.H. Chang, Appl. Phys. Lett. **78**, 2342 (2001).

[13] Ueda N., H. Meada, H. Hosono and H. Kawazoe, J. Appl. Phys. **84**, 6174(1998).

[14] Ghosh P.K., R. Maity and K.K. Chattopadhyay, Sol. Energy Mat. Sol. Cells **81**, 279 (2004).

[15] Mahamuni S., K. Borgohain, B.S. Bendre, V.J. Leppert and S.H. Risbud, J. Appl. Phys. **85**, 2861 (1999).

[16] Guo L., Y.L. Ji, H. Xu, P. Simon and Z. Wu, J. Am. Chem. Soc. **124**, 14864(2002).

[17] Liu B. and H.C. Zeng, . J. Am. Chem. Soc. **125**, 4430 (2003).

[18] R. Kumaravel, V. Krishnakumar, K. Ramamurthi, E. Elangovan and M. Thirumavalavan, Thin Solid Films **515**, 4061 (2007).

[19] S. M. Sze, John Wiley and Sons ,(1981).

[20] H. Hosono, Y. Yamashita, N. Ueda and H. Kawazoe, Appl. Phys. Lett.**68** , 661 (1996).