Structure and Morphological Properties of Cadmium Oxide Nanostructure Prepared By Oblique Angle Deposition Method

The 5th International scientific Conference on Nanotechnology& Advanced Materials Their Applications (ICNAMA 2015) 3-4 Nov, 2015

Dr.Wafaa K. Khalef
Applied science Department, University of technology,/Baghdad
Email:drwafaa1980@gmail.com
Dr. Sariya D.AL. ALgawi
Applied science Department, University of technology,/Baghdad
Sura R. Mohammed
Applied science Department, University of technology,/Baghdad

ABSTRACT

Oblique angle deposition technique (OAD) can generate nanostructures and has attracted the interest of many researchers. In this article we use this technique to investigate the morphological and structure properties of obliquely evaporated Cd films deposited onto glass substrates at different angles (0^o, 50^o, and 70^o),and then oxidized in air at (573 K) for 1:30 h to produce (CdO) nanostructure. The influences of deposition angle on the structural and morphological properties of cadmium oxide thin films were investigated. X-ray diffraction pattern shows, that all prepared films are cubic structure with preferred orientation along (111) plane with peak intensity increased with increasing incident angles .The AFM results demonstrate that the film deposition at higher oblique angle (70^o) has higher surface roughness and the values of (G.s) decreased as the oblique angle deposition angle increases (112 to 267) nm. Scanning electron microscopy shows that the films had microstructure with columns that are progressively inclined as the incident angle was increased.

Keywords: CdO thin films, Oblique incident, OAD technique.

الخصائص التركيبية والسطحية لاغشية اوكسيد الكادميوم النانوي التركيب المحضر بتقنيه التريسيب المائل بالفراغ

الخلاصة

تم استخدام تقنية الترسيب المائل oblique angle deposition technique لدراسة الخصائص التركيبية لاغشية اوكسيد الكادميوم من خلال ترسيب معدن الكادميوم على شرائح من الزجاج بالتبخير العمودي والتبخير المائل , ومن ثم اكسدته بالهواء عند درجة حرارة (573) كلفن وزمن اكسدة ساعه ونصف باستخدام الفرن التقليدي كمصدر للاكسدة . تم دراسة تأثير زاوية الترسيب على الخصائص التركيبية و السطحية لاغشية اوكسيد الكادميوم. لدراسه الخصائص البلورية للاغشية المرسبة، استخدمت تقنية حيود الاشعة السينية للقياس، وظهر ان الاتجاهية المفضلة لغشاء اوكسيدالكادميوم كانت (111) وشدة القمة تزاداد مع زيادة زاوية الترسيب .من خصائص مجهر القوة الذرية اتضح ان الخشونة تمتلك اكبر قيمه لها عند زاوية ترسيب 70 وان الحجم الحبيبي يقل مع زيادة زاوية الترسيب وخصائص المجهر الالكتروني الماسح اظهرت التركيب العمودي النانوي للاغشية المحضرة.

الكلمات المرشدة: أغشية اوكسيد الكادميوم، الترسيب المائل، ،الترسيب الزاوي المائل

https://doi.org/10.30684/etj.2015.117449
2412-0758/University of Technology-Iraq, Baghdad, Iraq

INTRODUCTION

In recent years, researchers have focused on cadmium oxide (CdO) due to its applications, specifically in the field of optoelectronic devices such as solar cells [1, 2] photo transistors and diodes, transparent electrodes, gas sensors [3, 4] etc. (CdO) is an n-type semiconductor with a rock-salt crystal structure (F.C.C) and possesses a direct band gap of (2.2-2.5) eV [5].Various techniques have been employed to prepare CdO thin films such as spray pyrolysis [6] sputtering [7, 8] solution growth [9] activated reactive evaporation [10] pulsed laser sputtering [11] and sol-gel method [12]. The glancing angle deposition (GLAD) technique is the extension of the commonly used oblique angle deposition (OAD) in thin film deposition community which has been practiced for many years [13]. In the state of obliquely deposited thin films, it is noticed forms like high density rod or needles, separated by low density voids [14]. Then the film density less than the material density in its bulk and the film density decreases with increasing deposition angle (Θ^{o}) [15].The oblique deposition produces columnar structures due to the shadowing effect and random fluctuations during film growth [16]. The shadowing effect favors the growth of longer Nano rods that causes decrease in the number density of Nano rods. Also, the fluctuations in the deposition fluxing Unstable deposition rates or angular spreads of the incoming particles) make the growth of uniform nanostructures even more difficult therefore, large clusters of tilted rods mixed with smaller and shorter rods are common topologies produced [17]. The idea of this work is study the effect of deposition angle $\Theta°$ on the structure and morphological properties of (CdO) films prepared by normal and oblique thermally evaporated cadmium thin films.

Experimental part

Cadmium thin films were normally and obliquely deposited at different angle θ = (0◦, 50◦ and 70◦) onto a glass substrate by thermal evaporation type (thermionic Laboratory Inc.) German Production Company. The (Cd) material was placed in tungsten (W) boat in a vacuum chamber at a pressure of ($7x10^{-}5$) torr. The distance between source and substrate was kept (15) cm for all samples to obtain homogenous and uniform film thickness of large area. The Pisces of glass substrate (2cm x2cm) were washed in acetone and ethanol for 15 minute in ultrasonic treatment (Transistor/UL Transonic T-7), rinsed using deionized water, and then dried with nitrogen gas. The slides finally were dried by magnetic stirrer with hot plate device at 150C. All the samples were annealed in a furnace type KSL-1100X at temperature equal 573 K for 1:30hour to produce of cadmium oxide. Film thickness is measured by optical interferometer method. The method is based on interference of the light beam reflection from thin film surface and substrate bottom. He – Ne Laser (632.8 nm) is used and the thickness is determined using the formula [18].

$$d = \frac{\Delta x}{x} \cdot \frac{\lambda}{2} \quad \dots (1)$$

Where: x is fringe width, Δx is the distance between two fringes and λ is the wavelength of the laser light. The crystallinity of the films was determined by X-ray diffraction (with Cukα radiation (λ =1.54 Å) with Current= 30 mA, Voltage = 40 KV and Scanning speed =5 cm/min). To determine the nature of the growth films and the structural characteristics of (CdO) films, X – ray diffraction measurement has been done and compared with the ASTM [19, 20] (American Society of Testing Materials) card Scanning electron microscopy (SEM) (Tescon Vega III) was used to examine the film morphology of normally and obliquely (CdO) films . To determine the grin size and surface roughness, used atomic force microscopy (AFM) (type NT-MDT spm ntegra).

Results and dissections

Thicknesses results

The film thickness for normal ($\theta=0^o$) and oblique ($\theta=50^o$ and70^o) deposited films respectively shows in the table below. It is clear from table 1 that the deposition film thickness decreases with increasing deposition angle and this results agreement with paper [21]. This is due to shadowing effect and geometrical consideration in oblique deposition, also increasing the deposition angle will decreases the deposited materials per unit area.

Table (1) Film thickness of CdO thin films deposited at different angles ($\theta=0^o$, $\theta=50^o$ and70^o).

Deposition angle θ_d (deg)	Film Thickness (nm)
0^o	630
50^o	618
70^o	611

Thickness measurement by fringes method

The thickness of normally and obliquely deposited (CdO) thin film and prepared at different oxidation temperature (573) K was measured by using an optical interferometer fringes method and in the flowing is explained in details :

If dropping a bundle of laser helium-neon (He-Ne) has a wavelength (632.8) nm on the surface of the (CdO) film it was reflected from the surface of film package is received and then collected by the lens and drop it in the end, on a white screen containing equal divisions of the lines are calculated thickness of film of a relationship (1). According to the schedule shown, it clears film thickness decreases with increasing in all oxidation temperature, due to geometrical consideration in oblique deposition technique. It’s clear that the same behave of the (CdO) film thickness in this method with the thickness measuring using measuring device.

Table (2) Film thickness of (CdO) thin films deposited at different angles (θ=0°, θ=50° and70°) and prepared at oxidation temperatures (573) K and time (1:30) hour.

θ_d (deg)	T (K)	Thickness (nm)
0°	573	348
50°		316
70°		275

X-ray diffraction results

The XRD patterns of the (CdO) thin film deposited on glass substrate at different angles (θ=0°, θ=50° and70°) shows in figure (1- a, b and c) respectively .It's clear from figures, that all normal and oblique samples have the sharp and strong peak observed at diffraction angle (2θ) of (33°) corresponded to the (111) planes (preferred orientation), and the intensity of the (111) plane increases with increasing incidence angle θ, and becomes more intense with angle (70◦) . In addition, for normal angles (0◦) we observe the presence of a weak peak assigned to the (222), (200) reflection appearing at 2Θ◦= (69°, (38°) respectively, and the, (222), (200) peaks was absent in fig 1 (b) at incident angle (50°) and presence of a sharp peak assigned to the (111) reflection appearing at (2Θ◦= 33.30) in oblique incident (θ=50°) this results agree with paper [22]. Also, one can observe that figures (1, a) show polycrystalline structure, while become single crystal as deposition angles θ= (50° and 70°) as shows in figure (1, b and c).This shows an improvement in the structural properties observed which have better degree of crystallinity. Therefore, deposition at this angle presents the advantage to get homogeneous and more films crystalline. Through peaks shows us the effect angle on the intensity of the peaks where the larger incident angle increased the intensity of peaks and become sharper. These peaks also corresponded to these observed for (CdO) (JCPDF File No. 03-065-2908). Structure properties (hkl) and inerplaner distance of (CdO) listed in table (3), The XRD patterns of (CdO) obtained indicated, that oblique incident shows an improvement in the structural properties observed which have better degree of crystallinity as compared with normal incident, therefore deposition angle has a great effect on the structural properties of these films which means that it has a great effect on the optical properties and other properties. Also, it is clear that the deposition method and preparation conditions had a great effect on films structure prepared in this research closer to a single crystal.

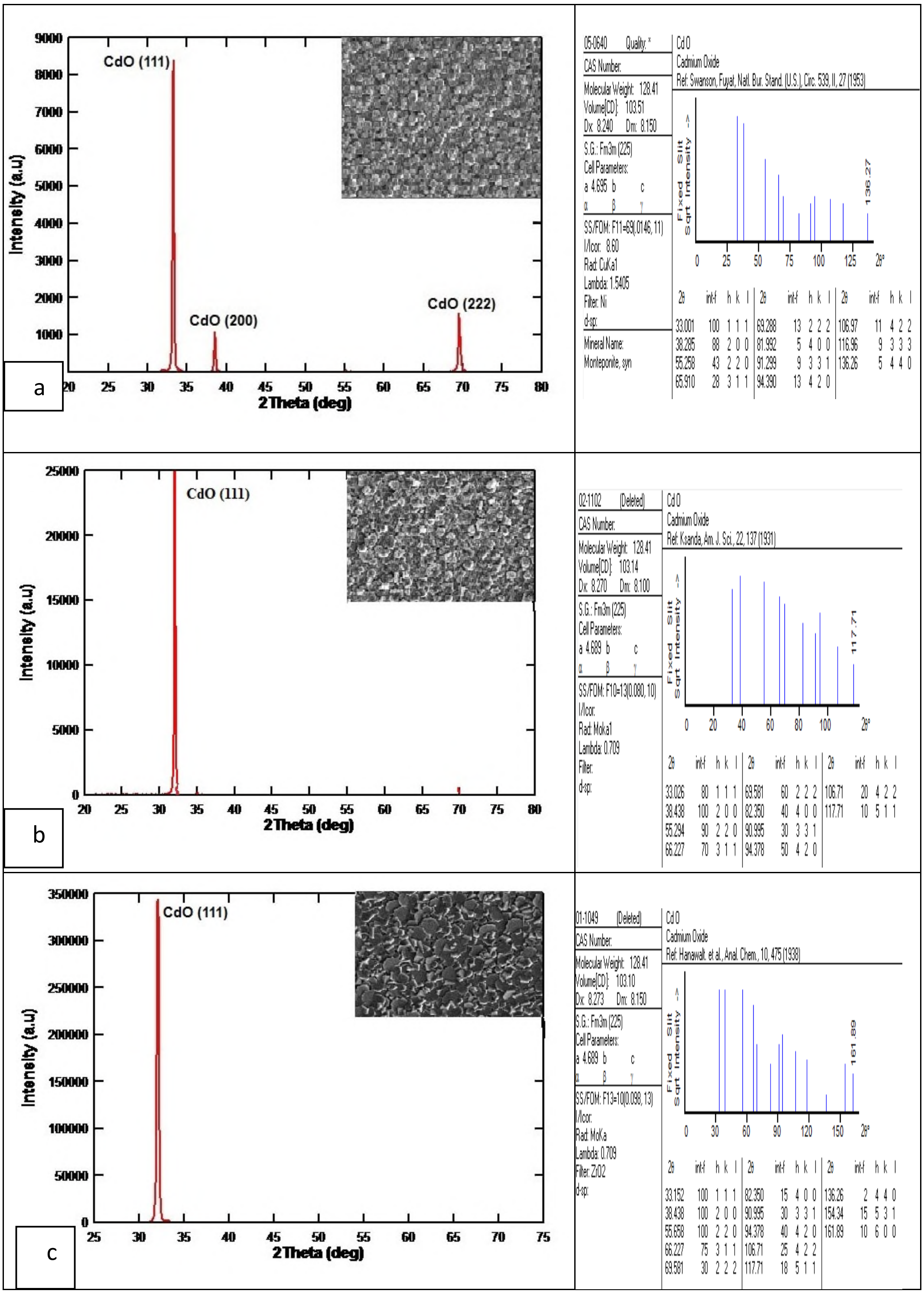


Figure (1a, b and c) shows XRD of (CdO) films deposited normally and obliquely ($\theta=0^{o}$, $\theta=50^{o}$ and70^{o}) respectively.

From the X-ray diffraction the planes orientation as a function of deposition angle were determined; also grain size (G.s), number of layers (Nℓ) and micro-Strain (s%) and other parameter of cadmium oxide (CdO) metal were also calculated and listed in table (3).

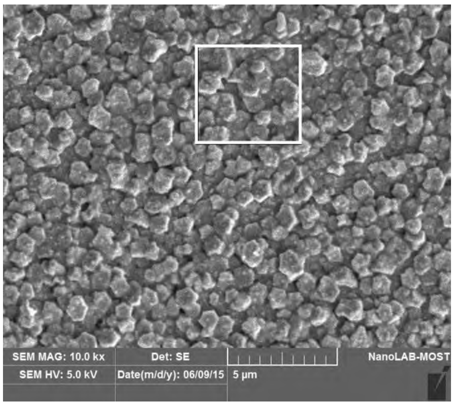
Table: (3) structure properties of (CdO) thin films deposited at different angles ($\theta=0^o$, $\theta=50^o$ and70^o).

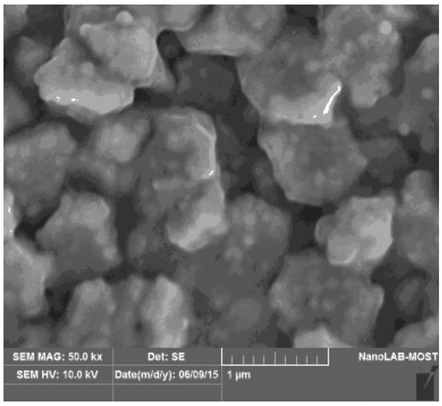
T C°	θ_d°	2θ°	hkl	FWHM	d_{ASTM}	d_{XRD}	α_{XRD}	G.s nm	T_c	N_L	%s
300	0°	33.297	111	0.1983	2.7000	2.6886	4.656	43.67	3.34	12	0.68
		38.563	200	0.2006	2.3400	2.3327	4.679	50.65	2.56	12	0.20
		69.531	222	0.1994	1.3500	1.3508	4.665	43.82	0.49	13	0.50
	50°	33.301	111	0.2226	2.7000	2.6882	4.656	38.90	1	10	0.70
	70°	33.089	111	0.3428	2.7120	2.7870	4.827	25.25	1	11	0.74

From during table (3) The lattice constants obtained are found to be in good agreement with ASTM data (CdO) metal sample, it is clear that the variation in lattice constant with deposition angle, for all angles the lattice constant value for the preferred orientation (111) is less than its value of ASTM, (cubic (CdO), $a^o=c^o$ = 4.656 Å). Hence, we think that the samples are under tensional stress (+). Also it is clear that the lattice constant decreases with increasing angle. This fact is attributed to the surface effect, which leads to the shrinkage in the a-lattice distortion and decreases the lattice parameter [23]. This has larger effect on the structure properties of the films. While The FWHM gives indication of the existence of dislocations in the material [24]. It is equal to the width of the line profile (in degrees) at half of the maximum intensity [25, 26]. From table (3) and for preferred orientation (111) of (CdO) thin films, it is clear that the FWHM increases with increasing deposition angle, although thickness decreases with increasing angle. As the mean grain size decreases as shown in the same table .also this is more probably due to a better crystallization of deposited films .The FWHM of XRD depends on the crystalline quality of each grain and distribution of grain orientation. And Micro Strain (δ٪) the micro strains are caused during the growth of thin films, and will be raised from stretching or compression in the lattice to make a deviation in the a-lattice constant of the cubic structure from chart value of ASTM. So the strain broadening is caused by varying displacements of the atoms with respect to their reference lattice position [21, 27]. The micro strain depends directly on the constant (a), and its value is related to the shift from the ASTM standard value, from above table, it's clear that the micro strain increases with increasing deposition angle and this may be caused by defects like dislocation and stacking faults in the film deposited [24] While Texture coefficient, (Tc) is the best indication of preferred orientation, (which may be defined simply as a condition in which the distribution of crystal orientation is nonrandom) [25, 28]. Table (3) shows the influence of deposition angle on (Tc) of (CdO) thin films prepared at oxidation temperatures (573) K at 1:30 hour .The results indicate that the Tc obtained results decrease with increasing deposition angle for preferred orientation (111).This is attributed to the changing in the surface morphology of (CdO) thin films which produce by oblique deposition technique. And It is clear from the table (3) for the preferred orientation (111) that decrease in the average grain size With increases deposition angle of (CdO) prepared at oxidation temperatures (573) K. This is due to linear dependence of grain size on film thickness [29]. By comparing with FWHM results shown in table (3), it is clear that the behavior of grain size is the inverse of FWHM.

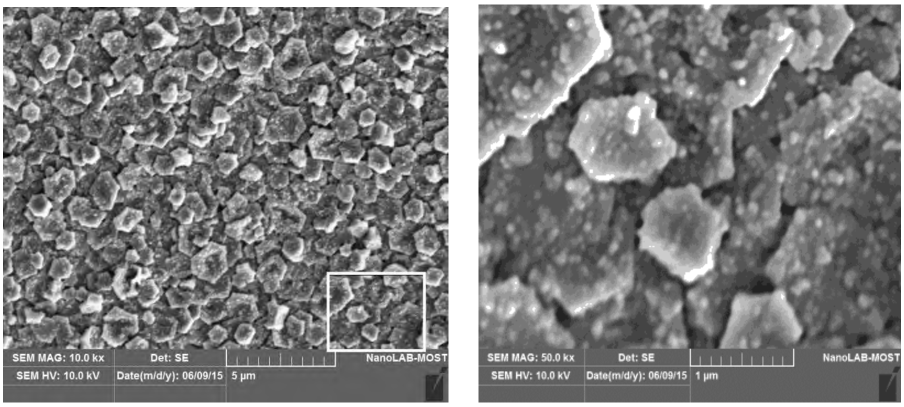
Scanning Electron Microscopy (SEM) results

Figure: (2-a, b and c) shows SEM images of cadmium oxide films deposited at various angles of incidence. Figure: (2-a) shows a film deposited at normal angle of incidence. A dense film with a range of submicron particle sizes from approximately 100 to 500 nm can be observed. Figure: (2-b and c) show images of cadmium oxide films deposited at (50^o and 70^o) angle of incidence. From the images, it can be observed that at higher angles of incidence nanoporous films have been obtained. The microstructures of these films are considerably different from the film deposited at the normal angle of incidence Figure: (2-a). The particles size of (CdO) is the structure is very compact and that the (CdO) consists of a few small particle in normal film (**$\theta = 0^o$**) and many large particles in case of oblique incident (50º, 70º) as shows in figure (2- b, c) ,duo to columnar structure. Which it is a result of the shadowing effect due to: (i) the incident flux does not arrive wholly perpendicular to the surface and (ii) the incident particles of a material that come to the surface with an oblique angle [30]. From the images, it is apparent that angular deposition at a higher angle can significantly change the porosity and morphology of the film. The effect of surface morphology on gas sensitivity has been reported elsewhere [31].

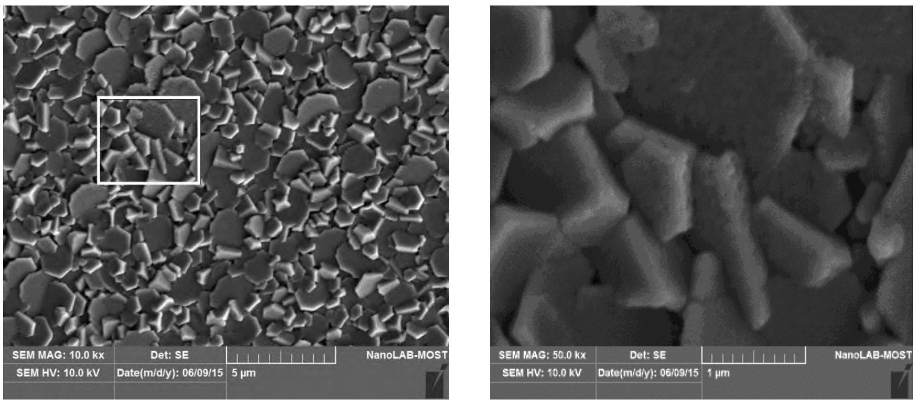




(a)



(b)



(c)

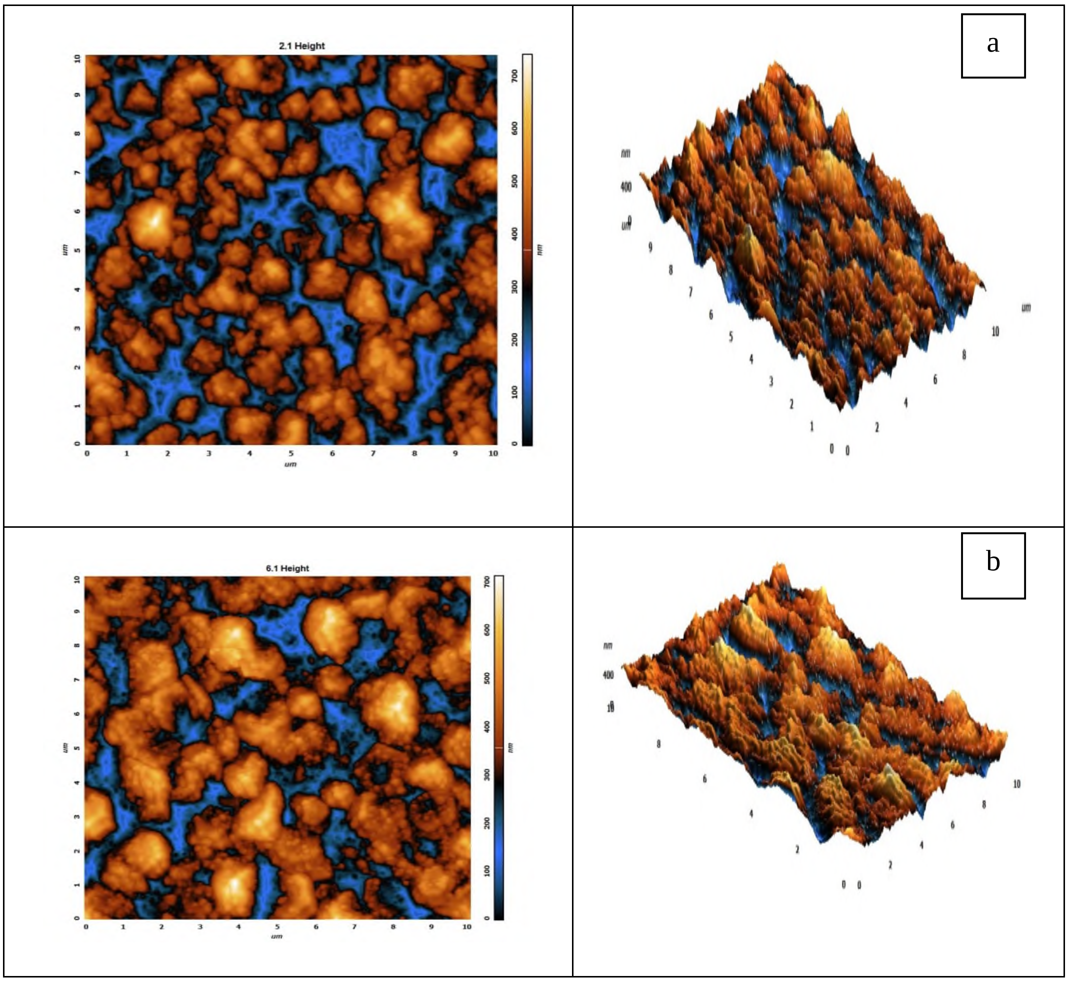
Figure (2) SEM images of cadmium oxide nanofilm evaporated at (a) normal 0º (b) 50º and (c) 70º angles of incidence.

Atomic Force Microscope (AFM) results

AFM was used to characterize the topography of the (CdO) thin film. AFM images indicate changes in surface behavior of the film. Also us information about the average size and size distribution of the islands and provides information about the shape of the island [32]. The results provide proof that the oblique deposition greatly affect the final surface morphology of Cadmium oxide thin films as can be shown in Figure (3 -a, b and c) for scan area (10×10µm). The porosity of the films was found to increase with increasing deposition angle which is consistent with the SEM results discussed above. During deposition of the films, the particles cluster together forming bigger grains with grain boundaries clearly shown between particles and also between grains. From the results of AFM, the values of (G.s) and the values of roughness (R_{rms}, R_a) were calculated, as it is shown in the table (3). The general output concluded is that a change in deposition angle leads to change in film microstructure.

Table (3) Grain sizes of cadmium oxide film deposited between 0° and 70° angles of incidence, determined from AFM scans.

Deposition angle (deg)	Roughness high (R_a) (nm)	Grain size G.S (nm)
0°	188.02	267
50°	273.94	118
70°	485.62	112



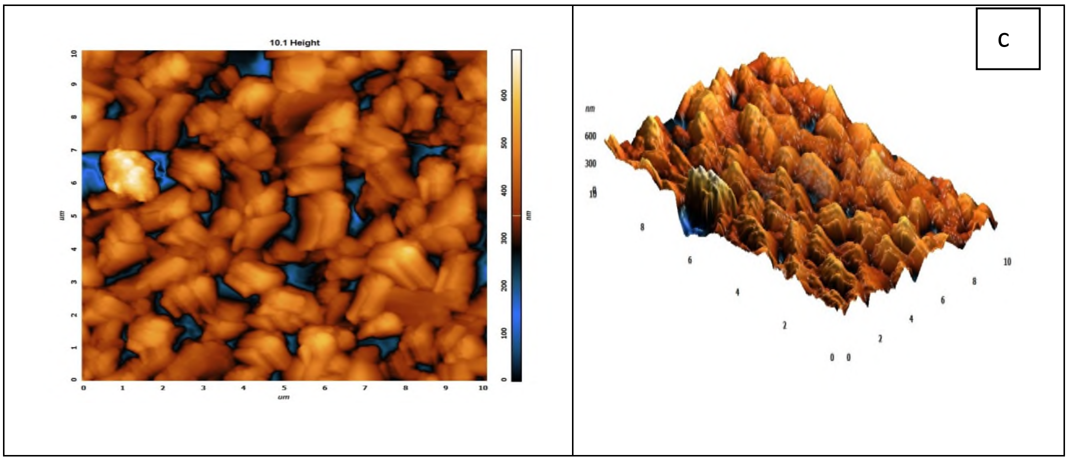


Figure (3) AFM images of evaporated thin films deposited at (a) 0°, (b) 50° and (c) 70° angles of incidence.

CONCLUSION

In conclusion, we have presented experimental study of the growth of (CdO) thin films using oblique angle deposition. XRD studies show that all the films having preferential orientation along (111) plane and intensity increases with increasing deposition angle. SEM picture show that the films have microstructures with columns that are progressively inclined as the incident angle was increased. The AFM images of the normal and oblique deposition films reveal the formation of a porous granular surface, while the surface roughness values are in the range between 112 nm and 267 nm and change in deposition angle leads to change in film microstructure

REFERENCE

[1] P.A.Radi, A.G.Brito, J.M.Madurro, and N.O.Dantas "Characterizationand properties of CdO nanocrystals incorporated in polyacrylamide" Brazilian Job Physics, 36, 412-414, (2006).

[2] Dr. Selma Mohammed H. Al-Jawad,HadiaKadhimJ.Alogili "Investigation of optical and electrical properties of chemically deposited nanocrystalline CdO thin film" College Journal of Basic Education (2011).

[3] R.S.Mane, H.M.Pathan,C.D.Lokhande and S.H.Han , "An effective use of Nano crystalline CdO thin films in dye-sensitized solar cells" Solar Energy, 80,185-190, 2006.

[4] P. Sinatirajah "Formation of CdO films from chemically deposited Cd $(OH)_2$ films as a precursor", Applied Surface Science, 254(13), 3813 – 3818 (2008)

[5] Senthil K, Tak Y, Soel M, Yong K "Synthesis and Characterization of ZnO Nanowire-CdO Composite Nanostructures" J. Nanoscale Res. Lett., 4: 1329–1334 (2009).

[6] M. D. Uplane, P. N. Kshirsagan, B. J. Lokhande, C. H. Bhosale, " Characteristic analysis of spray deposited Cadmium oxide thin films" Materials Chemistry and Physics Volume 64, Issue, Pages 75–78, (2000)

[7] Osvaldo Vigil et.al "Structural and optical properties of annealed CdO thin films prepared by spray pyrolysis" Elesvier (2001).

[8] G. Anil Kumar et.al "Structural and Optical Properties of CdO Thin Films Deposited by RF Magnetron Sputtering Technique" Thapar University, Patiala, Punjab, India, AIP Conf. Proc. 1591, 1009 (2014).
[9] A. J. Varkey, A. F. Fort, Thin Solid Films 239, 211 (1994)
[10] K. T. Ramakrishna Reddy, C. Sravani, R. W. Miles, J. Cryst. Growth 184/185, 1031 (1998)
[11] I. I. Shagnov, B. P. Kryzhanovskii, V. M. Dubkov, Sov. J. Opt. Technol. 48, 280 (1981)
[12] Lecturer Fatima I. Sultan "Study the effect oxidation time on physical properties of CdO thin films prepared by thermal evaporated" College Journal of Basic Education No.86-20 (2014).
[13] Y.-P.Zhao*a, D.-X. Yeb, G.-C. Wangb, and T.-M. LubaDepartment of Physics and Astronomy, University of Georgia, Athens, GA 30602-2451(Designing Nanostructures by Glancing Angle Deposition) and Astron., Rensselaer Polytechnic Institute, Troy, NY, 12180-3590 (2003).
[14] Matthew M. Hawkeye Department of Electrical and Computer Engineering, University of Alberta, Edmonton,Alberta T6G 2V4, Canada (Glancing angle deposition: Fabrication, properties, and applicationsof micro- and nanostructured thin films).J. Vac. Sci. Technol. A 25„5 (2007)
[15] K. Robbie, M.J. Brett: J. Vac. Sci. Technol. (Advanced techniques for glancing angle deposition) J. Vac. Sci. Technol. B 16„3 (1998).
[16]Dr .Ali M .Mousaat.el "Study the Effect of Deposition Angle on Structural Properties of Zn thin films" Department of Applied Sciences, University of Technology issn: 18120380 page 666-690 (2012).
[17] AbdolahzadehZiabaria A. and Ghodsia F.E. "Optical and Structural Studies of SolGel Deposited Nanostructured CdO Thin Films: Annealing Effect" Acts Physical Polemical, Vol 120 No.3 (2011)
[18] M.MahaboobBeevia ,M.Anusuyab, V.Saravananc* IACSIT Member "Characterization of CdO Thin Films Prepared By SILAR Deposition Technique" International Journal of Chemical Engineering and Applications, Vol. 1, No. 2010 ISSN: 2010-0221.
[19] ASTM X-ray Powder Diffraction Data File, Card 05-640.
[20] Standard X-ray Diffraction Powder Patterns: Section 1. Data for 46 Substances
[21] Lalitha,S. R. Sathyamoorthy , S. Senthilarasu , A. Subbarayan, K. Natarajan,"Characterization of CdTe thin film – dependence of structural and optical properties on temperature and thickness", Sol. Energy Mater. Sol.Cells 82 (2004) Page 187-199
[22] Dr .Ali M .Mousa, Assist, Dr. Muslim F.Jawad, Assist.Lacture.Wafaa K. 2012
[23]A. SINAOUI et.al "Investigation Of The effect Of Obliquely Incident Deposition On Structural, Morphological And Optical Properties Of CuInS2 Thin Films" Materials Science and Chemistry Vol. 2, Issue 1, 2013, Pages 1-17.
[24] J. Lintymer et.al "Glancing angle deposition to modify microstructure and properties of sputter deposited chromium thin films" Surface and Coatings Technology 174–175 (2003) 316–323
[25] M.J.PETERSON, F.H.COCKS "The preparation of texture Te thin films with pounced acicular morphology and concomitant high absoribity ""journal of materiel sincere 14(1979)2702-2712.
[26] Raad Saied Abed et.al (Effect of deposition angle on optical properties of Selenium thin films) ISSN 2319 – 4847 Volume 2, Issue (2013)

[27] A.J.AL-Jabiry,”Studying the Effect of Molarity on the Physical and Sensing Properties of Zinc Oxide Thin Films Prepared by Spray Pyrolysis Technique", ph.D.Thesis, Applied Science Dep. University of Technology, 2006

[29] A.R. Balu et al "Studies on the Physical Properties of three Potentially important TCO Thin Films fabricated by a Simplified Spray Technique under same Deposition conditions" Int.J. ChemTech Res.2014, 6(1), pp 705-718.

[30]A. Abdolahzadeh Ziabaria and F.E. GhodsibDepartment of Physics, Faculty of Science, University of Guilan, Namjoo Av., P.O. Box 413351914, Rasht, Iran (2011).

[31] T. Tesfamichael a,*, Nunzio Motta a, Thor Bostrom b, J.M. Bell c:"Development of porous metal oxide thin films by co-evaporation" Applied Surface Science 253 (2007) 4853–4859.

[32] Dr.Wafaa K. Khalef "Preparation and Characterization of CdO Thin Films Obtained by Oxidation of Obliquely Evaporated Cd Thin Films" Journal of Al-Nahrain University Science Vol.71 (4), December, 4174, pp.711-771 (2014).