Preparation and Characterization of CdO Thin Films Obtained by Oxidation of Obliquely Evaporated Cd Thin Films

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Abstract

In this work, oblique angle deposition technique (OAD) was used to grow cadmium thin films onto glass substrates at different angles (٠° and ٧٠°), and then oxidized in air at (٥٠٠ °C) for ١ hour by conventional furnace as the oxidation source. The effect of deposition angle on the structural, morphology, optical and electrical properties of cadmium oxide thin film were studied. XRD technique used to study the crystalline structure of these films confirm the polycrystalline nature of these films and the higher intensity accompanied that deposited with (٧٠˚) with preferred orientation (١١١). Some structural parameters such as grain size was calculated. The surface morphology shows an improvement with higher incident angle. The optical properties shows that the transmition decreasing with increases deposition angle and the optical energy gap (Eg) values are (٢،٤ and ٢،٨) eV for normal and oblique deposition respectively. The dark current increases linearity with applied voltage and deceases with increasing deposition angle at the fixed applied voltage (ohmic behavior) with activation energy found to be (٠،١٥٤٤ - ٠،٣٣٢٣) (eV) for normal and oblique deposition respectively .

Keywords: Oblique deposition, Cadmium thin films, GLAD Method, Oblique angle deposition.

Introduction

Thin films deposited from oblique angles (>٧٠°) by physical vapor deposition (PVD) exhibit highly underdense columnar morphologies, [١, ٢] which are due to atomic shadowing effects under limited adatom mobility conditions. By this technique it has been possible to produce zigzags [٢], pillars [٣], chevrons [٤], spirals [٥] and other film microstructures from various materials including metals, insulators and semiconductors [٦]. Potential applications include optical polarizers, high birefringence biaxial films, thin-film wave plates, optical humidity sensors, magnetic storage media, nanoemitters, and actuators. The self-shadowing effect and limited surface diffusion are two dominant mechanisms determining the tilting angle β, the microstructure and the average separation of nanorods. Unfortunately, these three parameters are coupled in oblique angle deposition such that they cannot be changed separately to meet the specific requirements of a desired application. In addition, the number density of nanorods (the number of nanorods per unit area) changes with deposition time due to the competitive nature of oblique angle growth [٧,٨]. The shadowing effect favours the growth of longer nanorods that causes a decrease in the number density of nanorods. Also, the fluctuations in the deposition flux (e.g. 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 [٩]. The objective of this work is study the effect of deposition angle θ° on the physical properties of thermally evaporated CdO films.

Cadmium Oxide Preparation and Characterization

After the glass samples were cleaned, thermal evaporation technique (Balzers coating unit model B٥١٠) was used to deposit Cd material at different angles, normal (θ°=٠°) and oblique (θ°=٧٠°) on the glass substrate, where (θ°) the angle between the normal to the substrate and direction of incidence of the evaporated atoms. After the evaporation process was carried out, oxidation films in air at (٥٠٠°C) and oxidation time (١hour) using conventional furnace (٠-١٠٠٠°C) as the oxidation source. Glass slides were used as the substrate for depositing the films which held at an angle to the direction of evaporation source. The evaporation was carried out on the substrates at room temperature in a vacuum of about (١*١٠$^{-٤}$) Torr from a molybdenum boat heater, which cleaned, and located at a distance of ١١ cm from the substrate. Deposited material thickness was measured using an optical interferometer method employing He-Ne laser (٠,٦٣٢μm) with incident angle ٤٥°. The film thickness found to be (٣٠٠ and ٢٧٦) nm for normal and oblique deposition respectively. It is clear that the deposition film thickness decreases with increasing deposition angle. Due to increasing the inclination angle of deposition will decreases the deposited materials per unit area. The structural properties of the layers were investigated using X-ray diffraction system (LabX-XRD-٦٠٠٠/Shimadzu) which has the following characteristics: source: radiation of CuKα and with waelengvth ١,٥٤A°, scanning speed (٢٠degree/min), and incidence angle (٠–٨٠) degree. From the X-ray diffrograms, the crystallite size (grain size) (D) were calculated using the Scherrer formula from the full-width at half-maximum (FWHM)(□△)[١٠]:

$$D = \left(\frac{0.94\lambda}{\Delta \cos\theta} \right) \text{ .... } (١)$$

Where λ is wavelength of the X-rays and θ° is Bragg angle. The average particle size and size distribution were characterized with atomic force microscope AFM scanning probe microscope (SPM). The optical measurements were done by measuring spectral transmission of the samples as a function of the wavelength in (λ=٣٠٠-٩٠٠ nm) range by using Ultraviolet-Visible spectrophotometer (Phoenix-٢٠٠٠V/ UV-VIS spectrophotometer/ (Biotech Engineering Management Co., Ltd-UK). The energy gap was calculated as for both normal and oblique incidence. Electrical measurements were carried by measure the electrical current under dark with different bias voltage. Current – voltage curves were measured using a dc power supply (Farnell Instrument LTD, England), supplying (٠-٣٥٠ volt), and (٠-١٠٠ mA), and the output current is measured by Keithly Electrometer solid state ٦٠٢. The conductivity of the samples evaluate from the following equation [١١]:

$$\sigma = \frac{1}{\rho} \text{ .... } (٢)$$

The activation energy (Ea) of both normal and oblique deposited films evaluated from the following equation [١٢]:

$$б = б_o \exp(-Ea/KT) \text{ .... } (٣)$$

Where б: electrical conductivity, бo: minimum electrical conductivity, Ea: activation energy, K: Boltzmann constant and T is the absolute temperature.

Results and Discussions

A) XRD measurements

Fig.(١) (A and B) shows the XRD patterns of the CdO films deposited on glass substrate for normal and oblique incident respectively .It shows presence of different strong diffraction peaks which confirm polycrystalline cubic CdO phase formation. All the diffraction peaks of the films are indexed to (١١١), (٢٠٠) and (٢٢٠) as compared with standard bulk CdO [JCPDS: ٠٥-٠٦٤٠], in both normal and oblique deposition. It’s clear from figures, that Bragg’s peaks more intense for oblique deposition film as compared with normal deposition. The observed diffraction peaks (١١١), (٢٠٠) and (٢٢٠) for CdO thin films are in good agreement with the reported data [١٣]. It can be seen also that the prepared thin films (oblique and normal) are highly oriented in the (١١١) direction .Also as it is clear from Table (١), there are very little differences between observed d-values and the standard d-values, this refers to small strength in the interplane distance in oblique deposition and normal incidence. These differences may arise from the defects which occur during the deposition. Also, it s clear from table ١ that the values of grain size calculated from scheerer formula decreases with increasing deposition angle and this result agreement with the AFM results shown below.

Table (١)
Comparison between experimental and standard d_{hkl}, grain size (nm) and hkl of preferred orientation (١١١) of CdO thin films deposited normally and obliquely.

Deposition angle (θ°)	*٢θ (deg)*	*d_{hkl} Exp.(Å).*	*d hkl) standard((A°)*	*Miller indices (hkl)*	*G.S (nm) For (١١١) by Scherrer formula*
Normal (θ°=٠°)	٣٣,٥٨٠	٢,٦٦٦٦	٢,٧١٠	١١١	٥٠
	٣٨,٦٢٠	٢,٣٢٩٤	٢,٣٤	٢٠٠	
	٥٥,٧٨	١,٦٣٦٠	١,٦٦	٢٢٠	
Oblique (θ°=٧٠°)	٣٣,٦٥٠	٢,٦٦٨١	٢,٧١٠	١١١	٤٨,٥
	٣٨,٦٦	٢,٣٢٧١	٢,٣٤	٢٠٠	
	٥٥,٧٧	١,٦٤٦٧	١,٦٦	٢٢٠	

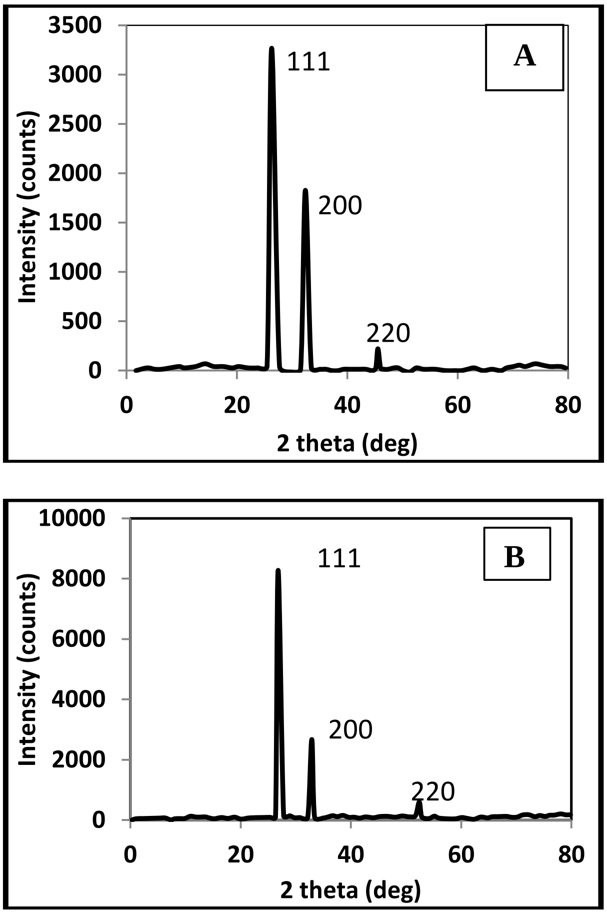

Fig.(١) XRD pattern of normal deposition CdO thin films A) Θº = ٠ and B) Θº = ٧٠ oxides at ٥٠٠ C.

B) Atomic force microscope

The surface morphology, and hence particles size distribution of the cadmium oxide thin film deposited normally and obliquely shows in Fig.(٢) (A and B) respectively. As it is clear from figure, the crystallinity of the samples has been improved by incidence angle and a drastic change in grain shape is observed. Furthermore, it's clearly seen that at normal deposition the mean size of nearly circular shaped grains is about ٩٨ nm Fig.(٢) (A) larger than that of oblique deposition (٨٠) nm shows in Fig. (٢) (B). The decreases of the grain size in oblique deposition as compared with normal deposition. may be due to the proportional of the grain size with film thickness [١٤]. This technique confirms the crystalline structure improves in oblique angle deposition of as deposited film and it shows the faceted columnar microstructure of the film is perpendicular to the surface and this result agreement with Kooy et al [١٥]. From the results of AFM (listed in Table (٢)), found that the values of (R_{rms}) increased as the oblique angle deposition is increased. This behavior is due to the aggregation of the native grains into larger clusters [١٦]. The CdO thin film deposition by oblique angle (θ° = ٧٠°), has larger clusters and becomes rougher. This result is in good agreement with those in literature [١٧-١٨]. This may be due to in columnar structure of films produce by oblique deposition technique accompanied by self shadowing effect and film thickness [١٩].

Table (٢)
Characterizing parameter of the surface CdO thin film morphology.

Deposition Angle (degree)	*Film Thickness t (nm)*	*A Grain size (D)nm by (AFM)*	*RMS (nm)*
٠° normal	٣٠٠	٩٨	١,٩٥
٧٠° oblique	٢٧٦	٨٠	٣,١٧

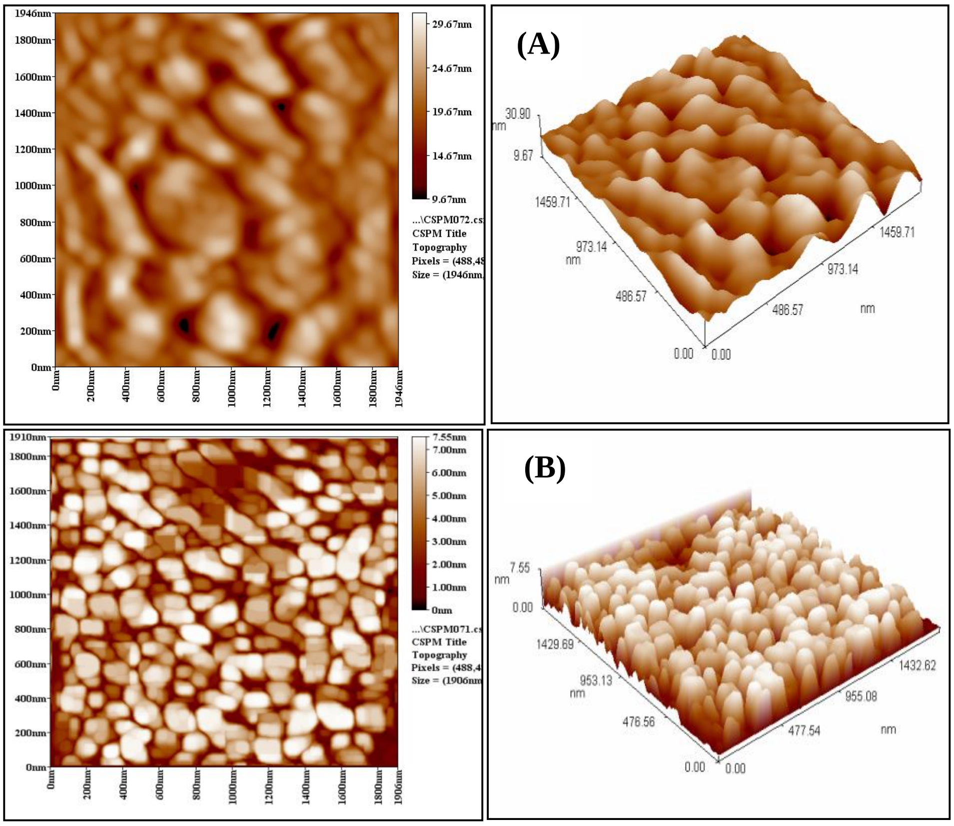

Fig. (٢) AFM image of the CdO thin films with A) normal and B) oblique deposition.

Optical Properties

The relation between transmittance and wavelength of cadmium oxide thin films deposited at normally and obliquely (٠° and ٧٠°) shows in Fig.(٣). It is clear from figures, that at normal deposition, the curve shows high transmition about (٨٥٪) of different wave length, while in oblique deposition, curve show lower transmition about (٤٣%) although film thickness decreases with increasing deposition angle. This is resulted from roughness increases, due to columnar growth with needle and rod like shape formation in case of oblique deposition θ°=٧٠° [٢٠]. The energy gap values depend in general on the films crystal structure, the arrangement and distribution of atoms in the crystal lattice. The usual method for determining the value of Eg involves plotting a graph of $(\alpha h\nu)^r$ versus photon energy hν, if an appropriate value of r is used to linearize the graph then the value of Eg will be given by intercept on the hν axis when $(\alpha h\nu)^r$ = ٠[٢٠]. Fig.(٤) shows the optical band gap (Eg) of cadmium oxide thin films deposited normally (θ°=٠) and obliquely (θ°=٧٠°) at oxidation time (١ hour). It's clear from figure that the energy band gap increasing with increasing deposition angle. Angle deposition process of thin film led to increasing in the film crystallites as shows previously and decreasing in the structure defects which led to increasing in energy band gap (Eg) eV, also is due to crystal size decreases shows previously, a certain limiting size, associated with its exciton Bohr diameter. The spacing between levels in the bands becomes larger so that the energy structure changes from aquascontinuum band to discrete quantized levels and the band gap increases, [٢١]. An increase in the band gap related to decrease in film thickness (in oblique deposition, where θ°=٧٠□), structural changes, on the other hand, accompany the change in optical constants besides the change in bandgap and hence these effects can be useful for devices, such as optical memory applications [٢٢]. This results shows in Table (٣).

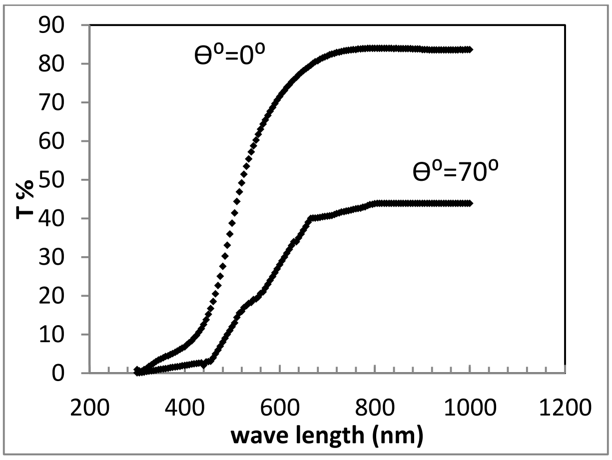

Fig.(٣) Transmittance as a function of wavelength of cadmium oxide thin film deposited at different angles Θ°= ٠°, Θ° = ٧٠°.

Table (٣)
Energy gap (eV) of Cadmium Oxide films as a function of deposition angle.

Sample	*Incident Angle θ°*	*Temperature of Oxidation(□C)*	*Time of Oxidation (Sec)*	*Energy gap (eV)*
CdO	٠°	٥٠٠	١ hour	٢,٤
	٧٠°			٢,٨

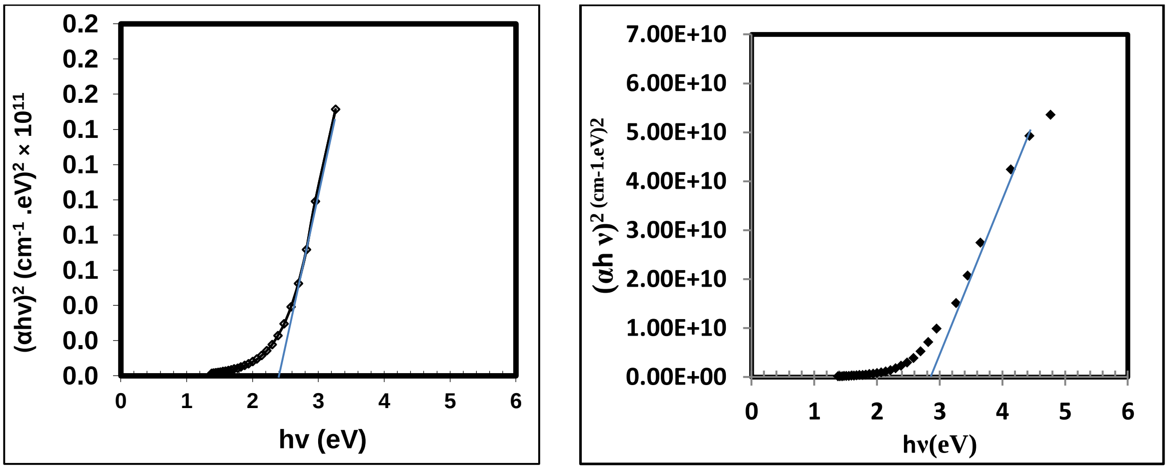

Fig.(٤) The optical band gap of normal (٠□) and oblique (٧٠□) CdO films.

Electrical properties of CdO thin films

Dark currents for normal (θ°=٠°) and oblique (θ°= ٧٠□) cadmium oxide thin films shows in Fig.(٥). It is clear that the dark current increases linearity with applied voltage and deceases with increasing deposition angle at the fixed applied voltage (ohmic behavior). This is attributed to the columnar structure in the film, which leads to increase the sheet resistance with increasing angle [١٥]. The increase in surface resistance with deposition angle, due to anisotropic columnar growth, which leads to inhomogoneity in electrical properties, especially for larger angles, when the voids between columns become larger [١٥].

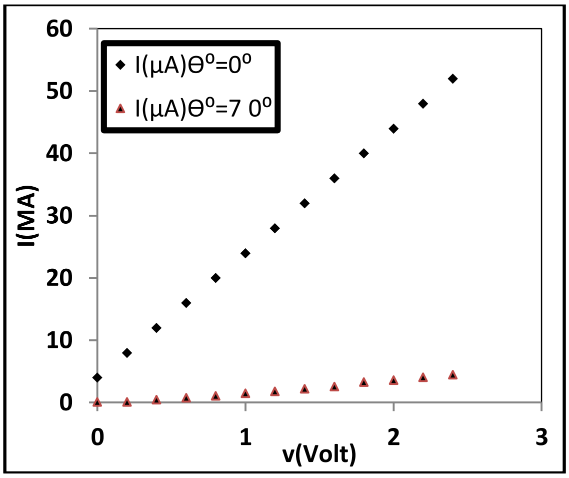

Fig. (٥) I-V characters in drake for normal and oblique deposition CdO thin films deposited at different angles.

The conductivity of both normal and oblique CdO films increases with temperature increasing where this behavior agrees with semiconductor nature and can be observed through Fig.(٦) which represent the variation of electrical conductivity which was calculated by using equation (٢) of normal and oblique CdO films as a function of temperature. This increasing of conductivity due to the increasing of carrier transition from valance band to conduction band. The effect of the deposition angle on the electrical conductivity (σ), measured at room temperature of cadmium oxide material worthy to note that there is a decrease in the conductivity, with increasing deposition angle θ°. The decrease in the conductivity with θ° is mainly due to significant modifications of the film's morphology [٢٣]. Also this is correlated with changes in the grain boundaries, mainly in the column borders. The column borders behave as a potential barrier, which decreases the probability of electron transmission. An increase in the strength of that potential, describes the decrease of this probability and consequently the decrease of conductivity [٢٣]. Fig.(٧) indicates the relationship between lnб and ١٠٠٠/T for normal and oblique films. From this Figure the activation energy can be calculated using relation (٣). The activation energy is found to be (٠,١٥٤٤ eV) for normal deposited film, whiles the activation energy of oblique deposited film is (٠,٣٣٢٣ eV). We noticed that the value of Ea for oblique film larger than in the case of normal as a consequence of quantum size effect and the increasing in the energy gap for oblique deposited film.

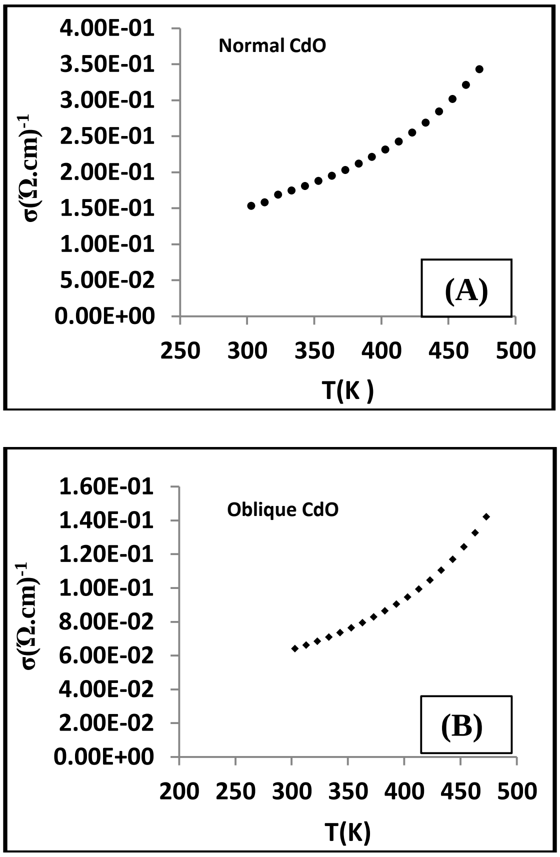

Fig. (٦) Electrical conductivity vs. temperature for different incident angles (A) normal (θ° = ٠°) and (B) oblique deposition (θ□ = ٧٠□).

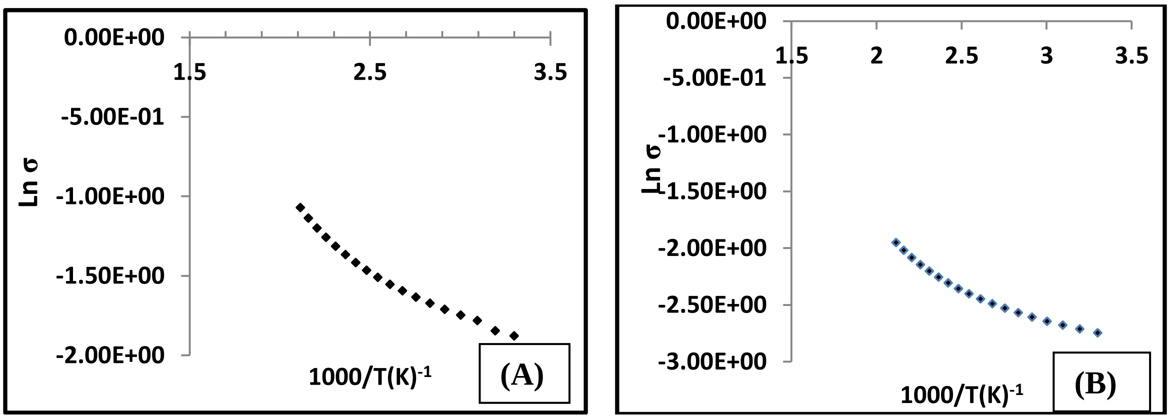

Fig. (٧) Plots of lnσ with ١٠٠٠/T ($K^{-١}$) for CdO films for (a) normal deposition CdO (b) oblique deposition CdO.

Conclusions

This is very important because the OAD method can be used to enhance the physical properties of the CdO films only by varying the obliquely incident angle.

١- The optical transmission of CdO films were decreased from ٨٥٪ value for normal deposition CdO to ٤٣٪ for oblique deposition.
٢- The derived band gap changed from ٢,٤ eV (For Normal CdO) to ٢,٨eV (For Oblique CdO) as a result of quantum confinement.
٣- The low conductivity of oblique deposition CdO as compared with normal deposition is due to decreases crystalline size and columnar growth in oblique deposition.
٤- Dark current deceases with increasing deposition angle and the activation energy is found to be (٠,١٥٤٤ and ٠,٣٣٢٣) ev for normal and oblique deposited films respectively.

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الخلاصة

في هذا البحث، تم استخدام تقنية الترسيب المائل oblique angle deposition technique لترسيب اغشية الكادميوم على شرائح من الزجاج بزوايا مختلفة (٠°,٧٠°)، ومن ثم اكسدته بالهواء عند درجة حرارة ٥٠٠ درجة سيليزية وزمن اكسدة ساعه باستخدام الفرن التقليدي كمصدر للاكسدة. تم دراسة تأثير زاوية الترسيب على الخصائص التركيبية، السطحية، البصرية والكهربائية على اغشية اوكسيد الكادميوم ثم استخدمت تقنية حيود الاشعة السينية لقياس الخصائص التركيبية، وظهر ان غشاء اوكسيد الكادميوم هو من النوع المتعدد البلورات وان الاتجاهية المفضلة كانت ١١١. بالإضافة إلى ذلك فقد تم حساب بعض الخصائص التركيبيه مثل الحجم الحبيبي بدلاله تغيير زاوية الترسيب وتأثير ذلك على هذه الخصائص. زيادة زاوية الترسيب ادت الى نقصان النفاذية، اضافة الى ذلك قيم فجوة الطاقة كانت (٢.٤–٢.٨) إلكترون فولت للترسيب بالوضع العمودي والمائل على التوالي. ان خصائص تيار جهد، اظهرت السلوك الاومي لتيار الظلام مع زياده الجهد المسلط، ولكنه يقل مع زيادة زاوية الترسيب. قيم طاقة التنشيط كانت (٠,١٥٤٤-٠,٣٣٢٣) للاغشية المرسبة عموديا ومائلا على التوالي.

الكلمات المرشدة: الترسيب المائل، اغشية الكادميوم الرقيقة، تقنية GLAD، الترسيب الزاوي المائل.