Investigation of optical and electrical properties of chemically deposited nano-crystalline CdO thin film

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Abstract

nano crystalline CdO films have been deposited by chemical bath deposition technique, where the cadmium acetate salt ($Cd(CH_3COO)_2$) used as a source of cadmium ions. The spectral transmission and the optical energy band gap increase from 8٤% and 2.47eV (for bulk CdO) to 95% and 2.92 eV(for nano CdO) respectively. This has been obtained as a result of quantum confinement with low values of conductivity and carriers mobility.

Key ward: nano – crystalline, CdO thin film, chemical bath deposition.

1. Introduction

Nanoparticals have attracted great interest in recent years because of their unique physical and electronic properties, which are different from those of either the bulk materials or single atoms [1].

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[2,3], photo transistors and diodes, transparent electrodes, gas sensors[4,5], etc. These applications of CdO are based on its specific optical and electrical properties. For example, CdO films show a high transparency in the visible region of the solar spectrum, as well as a high ohmic conductivity. The intensity of optical and electrical effect of CdO depends on the deviations from the ideal CdO stoichiometry, as well as on the size and shape of the particles. However, nanostructure CdO is particularly interesting because it can serve as electrode for nanoscale light – emitting diodes, lasers, and be applied in other devices [6].

It is an important study structure, optical, and electrical properties of CdO thin films especially films prepared by a promising technique as (CBD). This technique produces CdO thin films having special and unique feature such as high conductivity, high transmission, and wide band gap energy. All these properties made up appropriate films for different applications especially in fabrication of solar cells and other optoelectronic devices [7, 8].

2. Experimental work

Chemical deposition refers to the deposition of films on a solid substrate from a reaction occurring in a solution [9].In general, the process involves the application of controllable chemical reaction which proceeds at allow rate in an aqueous solution containing the various reactants, and the substrates are immersed in this solution.

The deposition of CdO films is achieved using cadmium acetate solutions, consist of 3ml of 1M cadmium acetate ($Cd(CH_3COO)_2$) with 5ml of 14.4M ammonium hydroxide solution (NH_4OH) (NH_3 after mixing with water) was used as a complex agents ,and the solution volume was ultimately fixed at 50ml by adding deionized water .Deposition was preformed at 50-55C$^{\circ}$.

Films were deposited on glass slides by using ($Cd(CH_3COO)_2$) as a source of Cd^{2+} ions with (NH_4OH) solution (with molarities and volumes as above mentioned) ,where mixed slowly with deionized water at room temperature with continuous stirring . Substrates were then immersed vertically in a beaker containing the reaction mixture. The beaker was placed in a water bath at temperature (50 ± 3 C$^{\circ}$). The solution was stirred with a magnetic stirrer type (LMS-1003) .Then, it was heated with continuous stirring to the required temperature of deposition, the pH measured by pH meter type (HANA, pH211 Digital); where as the measure pH in the start of the deposition process takes place was (11). Substrates were then taken out after a suitable time; they were washed with distilled water, and then dried. The white film of cadmium hydroxide ($Cd(OH)_2$) which converted to CdO film after the annealing process, due to the removal of H_2O vapor from the film structure.

3. Measurements

3.1. Electrodes Deposition:

In order to measure the electrical properties, ohmic contacts were needed. It was obtained by under vacuum of indium wire evaporation with high purity (99.99%). The evaporation process was started at a pressure of 10^{-5} Torr. Ohmic contact from indium wire on CdO film was made through a metal mask made aluminum (Al) foil.

3.2. X. Ray Diffraction Spectra

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 (American Society of Testing Materials) cards (see Table (3-2)), using (lab X-XRD 6000/shimad2u) of = 1.54 $\mathring{A}$ from Cu - K. The average grain size (G_S) of the polycrystalline material can be calculated from the X - Ray spectrum by means of Full Width at Half Maximum (FWHM) method (Scherrer relation)[10]:

$$GS = \frac{A\lambda}{\Delta\theta \cos\theta} \qquad (1)$$

Where $\Delta\theta$ is the full – width at half maximum of the XRD peak appearing at the diffraction angle θ, A represents the shape factor, the value of which depends on the crystalline shape, is 0.94 and generally it is(1).

3.3. Thickness Measurement:

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:-

$$d = \frac{\Delta x}{x} . \frac{\lambda}{2} \qquad (2)$$

Where: x is fringe width, Δx is the distance between two fringes and λ is the wavelength of the laser light.

3.4. Transmission Measurements

UV-VIS, Phoenix-2000V device was used to record the optical transmission for CdO/glass thin films in the range (380 – 900 nm). The data from transmission spectrum can be used in the calculation of the absorption coefficient (α) for CdO films, according to the following equation **[**11]:

$$\alpha = \frac{1}{d} \ln \frac{1}{T} \qquad (3)$$

Where d is the thickness of thin film, and T is the transmission. The value of extinction coefficient (K) was calculated using the following equation:

$$K = \frac{\alpha\lambda}{4\pi} \qquad (4)$$

The nature and value of band gap (Eg) were determined from the graph of

$(\alpha h\upsilon)^2$ versus $(h\upsilon)$ for the thin film.

Both transmittance (T) and absorbance (A) were converted to reflectance values (R), in terms of (R+A+T=1).

The reflectance can be expressed in terms of optical constants, (n) and (K) as [11] :

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \qquad (5)$$

Where n is the refractive index and (K) is the extinction coefficient. In the range of frequencies in which the films are weakly absorbing $K^2 << (n-1)^2$ so that:

$$R = \frac{(n-1)^2}{(n+1)^2} \quad \text{, or} \quad n = \frac{(1+R^{1/2})}{(1-R^{1/2})} \qquad (6)$$

Values of refractive index were calculated using equation (6).For non magnetic materials, the square of refractive index is the dielectric constant .The complex dielectric constant is given by the following equation [12] :

$$\varepsilon = \varepsilon_r + \varepsilon_i = (n+iK)^2 \qquad (7)$$

Where ε_r , and ε_i are the real and the imaginary parts of ε and $(n+iK)^2$ is the complex refractive index . From equation (7) we obtain:

$$\varepsilon_r = n^2 + K^2, \text{ and } \varepsilon_i = 2nk \qquad (8)$$

This equation was used in calculating the real and imaginary dielectric constants.

3.5. Resistivety Measurements

The electrical resistively of CdO films is a very important parameter for all applications .It can be calculated from the current - voltage measurements .Also can be measured through the change of thin film resistance with temperature. This was done by putting the samples inside the (electrical blast dry box, model WG 20), and it attached with a thermocouple (Digital Multiter) to measure the film temperature ,also the sample was connected to hp 343A,Multimeter device to record the current through the film, and then resistivity was determined by equation [13] :

$$\rho = R\frac{bd}{l} \qquad (9)$$

Where □□□□is the electrical resistivity of CdO film and l, b and d are the length, width and thickness of the film respectively and thus the resistance of the film can then evaluate the conductivity from the following equation (10):

$$\sigma = \frac{1}{\rho} \qquad (10)$$

3.6. Hall Measurements

The type of conductivity of the CdO films is deduced using Hall Effect measurement. The shape of CdO film is square; four (In) electrodes are deposited on its sides. When the magnetic field (B=0.538KG) is applied perpendicular to the electric field, it yields a current (I) then the transverse electric magnetic field is called Hall voltage (V_H), which set a cross up the sample, hence the Hall coefficient (R_H) is given by [14]:

$$R_H = \frac{1}{nq} \qquad (11)$$

Where q is the electron charge, n is the carrier density related to the Hall voltage by the following equation:

$$n = \frac{B}{qd} \cdot \frac{I}{V_H} \qquad (12)$$

Where d is the thickness of the film. And the mobility of carriers □$_e$ is calculated by

$$R_H = \frac{\mu_e}{\sigma_e} \qquad (13)$$

Where

$$\sigma_e = nq\mu_e \qquad (14)$$

The sign of the Hall coefficient (R_H) determines the type of the semiconductor that is under investigation [15].

3.7. Annealing Treatments

All the samples were annealed in a furnace type England, S30 2AU at temperature equal 573 K for 15 min.

4. Results and discussions

4.1. X-Ray diffraction

Figure (1) shows XRD pattern of film was deposited by using cadmium acetate as a source of Cd^{2+} ion with deposition time 75 min and pH=11 on the glass substrate. From the pattern can be notice that the preferential crystal orientation at 2θ=33.02° corresponding to reflected from C(111) peak ,with two minor peaks for C(200) and C(220) crystalline planes. They have large width indicating to the small grain size (nanocrystal) of CdO film .The average grain size was calculated from the full width of half maximum of preferential orientation by using Sherrer equation (1) is 4.8 nm, this result agree very well with literature [16], where K.S.Ramaiah et al. used the cadmium acetate to obtaining to the nanocrystal of CdS thin film.

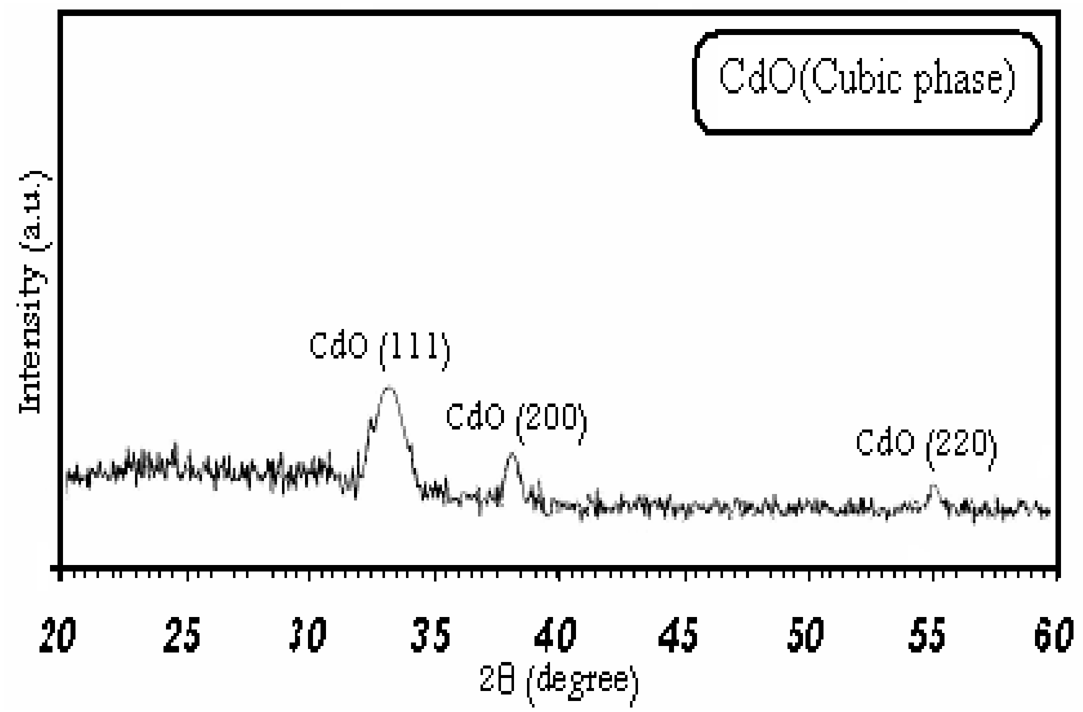

Fig.(1): The X-ray diffraction of CdO thin films by using cadmium acetate .

The chemical nature and the composition of acetate due to low deposition rate which causes the low growth rate to the grains even with deposition time increasing and hence low terminal thickness [17], where the thickness of CdO film is about 57 nm.The low deposition rate give more chance to the obtaining to small grains which constituting the CdO film .This nature of the structure will be reflected to all properties of the film.

4.2. Transmission and Absorption:

The results of optical transmission spectrum of CdO thin films which were deposited by using cadmium acetate ($Cd(CH_3COO)_2$) as a source of Cd^{+2}. It can be observed from Figure (2a) that the increase in optical transmission for noncrystalline CdO in comparison with bulk CdO film which was prepared with deposition time about (5) hours. The maximum value of transmission of bulk CdO was about 84% while increased to 95% for nano structure of CdO at a wavelength of 900 nm.

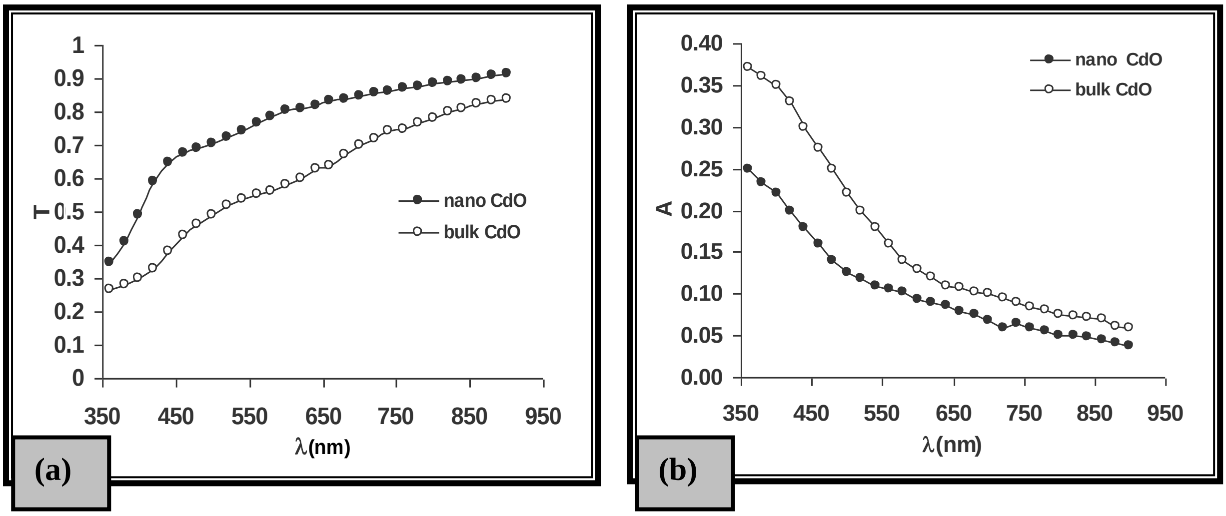

Fig. (2): Optical properties of bulk and nano structure of CdO thin films prepared by using $Cd(CH_3COO)_2$.
(a) Transmission spectra as a function of wavelength of CdO thin films.
(b) Absorption spectra as a function of wavelength of CdO thin films.

This behavior may be due to the decreasing of the average grain size which provided by using cadmium acetate [17] and ammonium hydroxide solution (NH_4OH) as complex agent, as well as because of small thickness of the film. The same behavior is reflected on the spectral absorption as shown in Figure (2b).

4.3. Absorption coefficient:

The date from transmission spectrum was used to calculate absorption coefficient by using equation (3). The behaviors of absorption coefficient for the bulk and nanocrystalline CdO thin films are shown in Figure (3). The maximum value of bulk and nano films are ($2.85 * 10^5$ cm^{-1}) and ($1.8 *10^5$ cm^{-1}) respectively at low wavelength. These values gradually decrease even reach to minimum value at longer wavelengths. The values of absorption coefficient of bulk CdO larger than for nanocrystalline CdO as a result of high degree of crystalline and because of low transmission values according to relation (3).

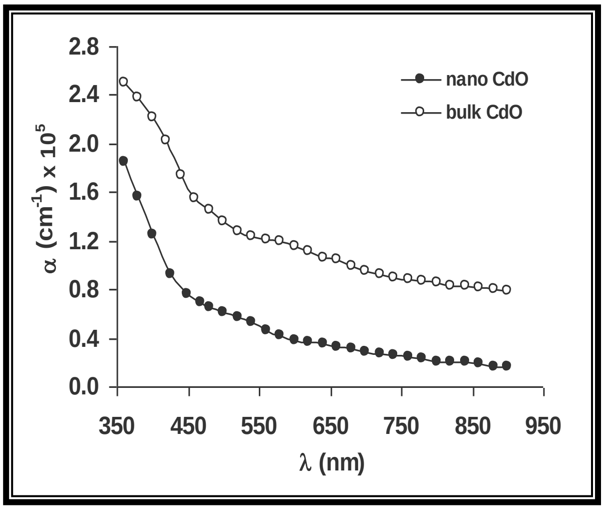

Fig. (3): Optical absorption coefficient of bulk and nano structure of CdO thin films prepared by using $Cd(CH_3COO)_2$.

As the crystal size decreases, there is a blue shift of the absorption edge (i.e. shift towards short wavelengths) which is a signature for the size quantization effect. This result is in good agreement with result of literature [18].

4.4. Optical band gap:

The optical energy gap is estimated from the plots of $(\alpha h\upsilon)^2$ versus (hυ) and shown in Figure (4), where it has a change in the band gap from 2.47eV to 2.92eV (nanocrystalline). This increase is due to crystal size decreases below 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 aquas – continuum band to discrete quantized levels and the band gap increases.

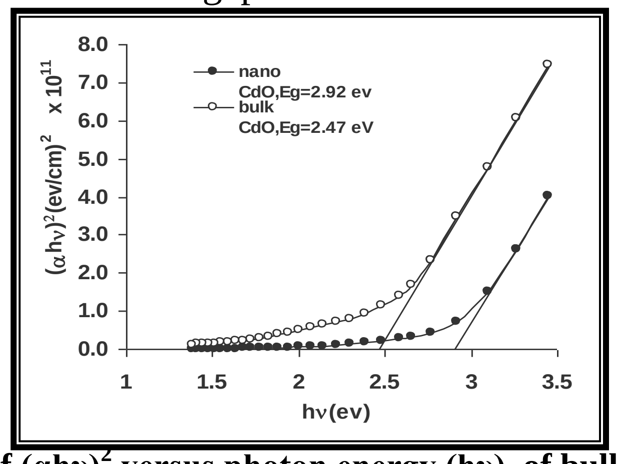

Fig.(4): Plots of $(\alpha h\upsilon)^2$ versus photon energy (hυ) of bulk and nano structure of CdO thin films prepared by using $Cd(CH_3COO)_2$.

The preparation of CdO film by CBD with using cadmium acetate as a source of Cd^{+2} ions give arise of the size quantization effect with wide energy gap reach to 2.9٢eV, in comparison with that nanocrystalline CdO films prepared by other techniques such as the nanocrystalline CdO film prepared by electrodeposited method, where it has energy gap in around 2.4eV [19].

According to the effective mass approximation; can use the energy position to estimate the average grain size, by using equation [1, 20].

$$E_{gn} = \left[E_{gb}{}^{2} + 2\hbar E_{gb} \left(\pi / R \right)^{2} / m^{*} \right]^{1/2} \qquad (9)$$

Where E_{gb} is the band gap for the bulk semiconductor, *R is* the particle radius, and m^* the effective electron mass, where m_e is the mass of a free electron and E_{gb} = 2.47 eV. We notice that the value of average grain size by using above relation equal 2.76 nm, Comparison with 4.8 nm in the case of using Scherrer relation (1).

4.5. Electrical Properties

To study the electrical properties of nanocrystalline CdO films which deposited using cadmium acetate as a source of Cd^{2+} ions, where the nano structure have value of electrical conductivity equal $3(\Omega.cm)^{-1}$,compared with standard films (which also prepared by using cadmium acetate) which have $15(\Omega.cm)^{-1}$ at room temperature .The low conductivity of the nanostructure film is due to the small crystalline size 4.8nm .The change in crystalline size will mainly affect the mobility of carrier and so change the conductivity. However, low carrier density and mobility simultaneously means low conductivity .Therefore, the relative high conductivity for standard films as a result of large grain size and reduce the ratio of crystalline boundaries within the structure of the film. The conductivity of both nano and standard CdO films increases with temperature increasing where this behavior agrees with semiconductor nature and can be observed through Figure (5) which represent the variation of electrical conductivity (which was calculated by using equation(10))of nano and bulk CdO films as a function of temperature. This increasing of conductivity due to the increasing of carrier transition from valance band to conduction band .Figure (6) indicates the relationship between lnσ and 1000/T for standard and nanocrystalline films. From this Figure the activation energy can be calculated using relation [8]:

$$б=б_o \exp(-E_a / KT)$$

The activation energy is found to be 0.15377eV for standard film while the activation energy of nanocrystalline film is 0.334eV. We noticed that the value of Ea for nano films larger than in the case of standard as a consequence of quantum size effect and the increasing in the energy gap for nanocrystalline film.

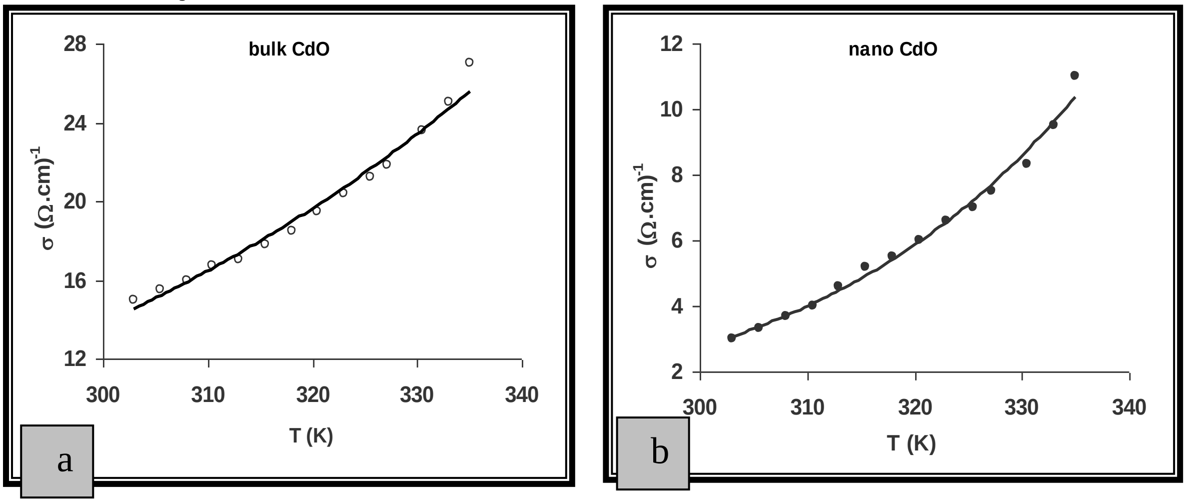

Fig.(5): The variation of conductivity with temperature for CdO films for (a)bulk CdO and (b) nano CdO.

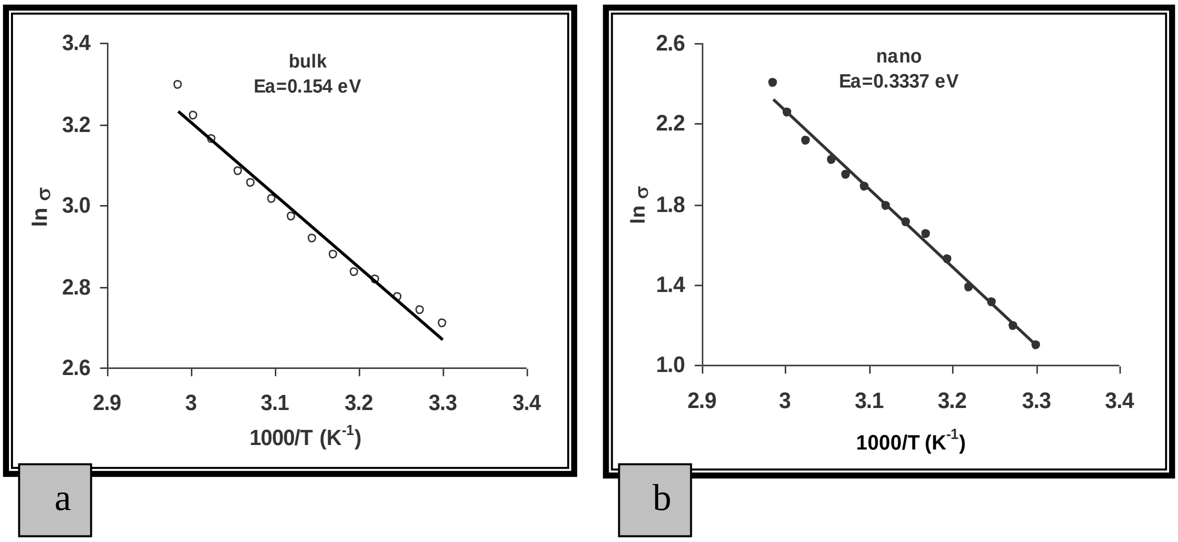

Fig. (6): Plots of lnσ with 1000/T(K^{-1}) for CdO films for (a)bulk CdO (b)nano CdO.

When using cadmium acetate as a source of cadmium ion concentration, we found that the bulk and nano CdO films have n-type conductivity. This is concluded from the relationship of Hall voltage and electric current. As the cadmium oxide is an n-type semiconductor the carriers are electrons. Figure (7) shows these results for bulk and nano structure of CdO films.

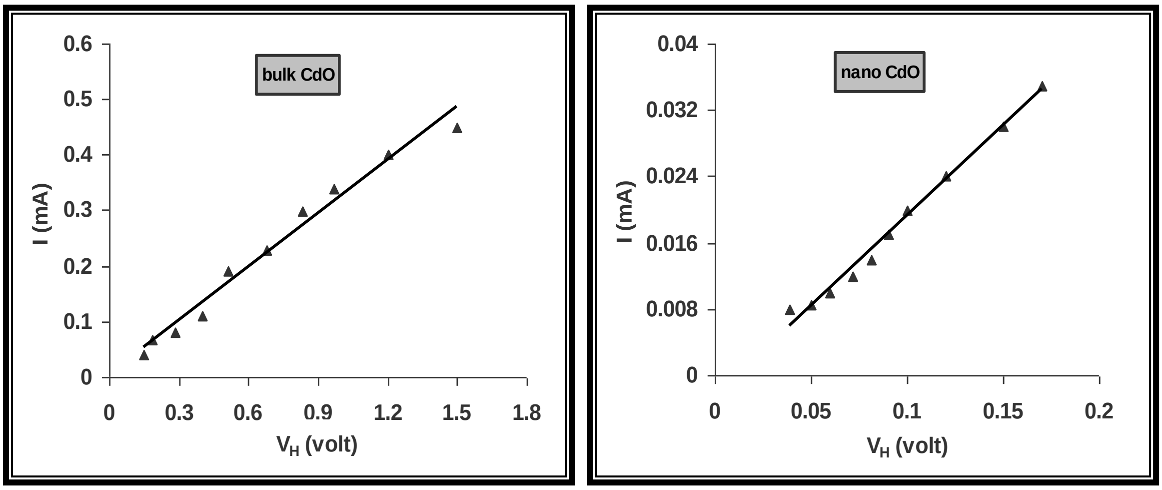

Fig. (7): The relationship between the Hall voltage and electrical current for CdO films with and without KCN.

Table (1) explains the carriers concentration and mobility of bulk and nano CdO films .From this table it can be observed that the carriers mobility of nano CdO film were lower than bulk CdO film as a result of small grain size and high density of crystalline boundaries.

Table (1): The experimental results.

Deposition conditions	Carriers concentration (cm^{-3})	Carriers mobility ($cm^2/V.cm$)
Bulk CdO	$0.722*10^{19}$	12.98
Nano CdO	$1.282*10^{19}$	1.46

CONCLUSIONS:

1- Nano crystalline CdO films was obtained by using cadmium acetate $Cd(CH_3COO)_2$ as a source of Cd^{+2} ion, deposition time of 75 min.Comparison with bulk CdO film which was prepared with deposition time about (5) hours.

2- The optical transmission of nanocrystalline CdO was increased from maximum value for bulk CdO 84% to 95% at a wavelength of 900 nm.

3- The derived band gap changed from 2.47 eV (for bulk CdO) to 2.92eV, as a result of quantum confinement.

4- The nano structure has value of electrical conductivity equal $3(\Omega.cm)^{-1}$, compared with standard film which has $15(\Omega.cm)^{-1}$ at room temperature .The low conductivity of the nanostructure film is due to the small crystalline size (4.8nm).

5- The change in crystalline size will mainly affect the mobility and concentration of carriers.

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دراسة الخواص البصريه والكهربائيه لاغشية اوكسيد الكادميوم النانويه المرسبه كيميائيا.

د.سلمى محمد الجواد **م.م هديه كاظم العكيلي**

قسم الهندسه الكهروميكانيكيه **قسم العلوم التطبيقيه**

الجامعة التكنولوجيه

الخلاصه :-

تم تحضيرالاغشيه النانويه لاوكسيد الكادميوم بواسطة تقنية الترسيب بالحمام الكيميائي ،حيث استخدم ملح خلات الكادميوم كمصدرلايونات الكادميوم . النفاذيه البصريه وفجوة الطاقة البصريه ازدادت من ٨٤% و٢,٤٧ الكترون فولت (لاغشية اوكسيد الكادميوم الكتلويه) الى٩٥ % و ٢,٩٢ الكترون فولت (لاغشية اوكسيد الكادميوم النانويه) على التوالي مع قيم واطئه لكل من التوصيليه الكهربائيه وتحركية الحاملات. وهذه النتيجه التي حصلنا عليها هي بسبب ظاهرة التكمم الحجمي.