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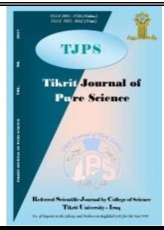

Effects of increasing molar concentration on cadmium dioxide (CdO) nanoparticles prepared by chemical Bath deposition (CBD)

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ABSTRACT

Polycrystalline thin films were prepared from CdO nanoparticles in the chemical Bath deposition (CBD) with different molar concentrations at (0.01, 0.03, 0.05, 0.07) M.

In order to obtain the best results, the structural and optical properties of CdO films were studied under the influence of increasing molar concentration, the results of the absorbance measurements there showed a change in the absorbance spectrum of the (CdO) films upon the increase in the molar concentration in the deposition, The value of the absorbance is within the limits of short wavelengths and where the absorbance increases at the wavelength ($\lambda \leq 550$ nm), and we note that it increases with the decrease in the wavelength and that the increase in the molar concentration in the deposition leads to an increase in thickness where the greater the absorbance increases the thickness. All samples of the prepared films were examined using scanning electron microscopy (SEM) at 2,000x magnification in order to identify the nature of the surface of the prepared films and to note the change in particle size with increasing molar concentration in the deposition. Experimental results showed that the grain size increases its crystal growth with increasing molar concentration, and this was shown by X-ray, AFM measurements.

1- Introduction

In recent years, the chemical bath deposition (CBD) method has been used to prepare nanostructures from cadmium oxide (CdO) films, as it is a simple method that does not require complicated devices and is relatively inexpensive, and is suitable for preparing thin films with a large area and various shapes [1]. The chemical bath deposition (CBD) method is one of the chemical solution deposition (CSD) methods that are used to precipitate semiconductor compounds on a solid base through the reaction that takes place inside the aqueous solution, and this method is analogous to chemical vapor deposition (CVD) [2,3]. Among II-VI semiconductors, polycrystalline CdO thin films are a representative materials with many applications such as solar cells and large-area electronic devices, and it has a wide direct energy gap equal to (2.42 eV) so it has been used as a window material containing many semiconductors such as CdTe and Cu_2S. Interest in CdO thin films also stems from their piezoelectric properties and potential laser applications [4, 5, 6]. Several techniques have been reported in the deposition of CdO thin films. These include chemical bath deposition (CBD), evaporation, spraying, molecular beam epitaxy (MBE) technology, photochemical precipitation, successive ionic layer adsorption and reaction method (SILAR) [7-11]. In all these deposition methods, there are some problems in all of them, for example, it is difficult to obtain chemical CdO thin films using chemical bath technology and high temperature annealing [12,13]. CdO thin films have been widely used and it was found that the physical properties depend on the preparation technique [14,15].

In this work, the structural and optical properties of polycrystalline cadmium oxide nanostructures as a function of molar concentration increase were studied.

2. Experimental part

2.1. Materials and method of work

Cadmium oxide thin films are prepared by chemical bath deposition technique by slow release of positive cadmium ions (Cd^{+2}) and negative hydroxide ions

(OH^{-2}) in a chemical bath solution, Calcium Chloride ($CdCl_2.2H_2O$), cadmium acetate Cd(CH_3COO)$_2$.($2H_2O$) and cadmium nitrate $Cd(NO_3)_2.(4H_2O)$. When cadmium nitrate is used as a source of cadmium ions, the reaction product is as follows [16]:

$Cd(NO_3)_2 \longrightarrow Cd^{+2} + 2NO_3^-$ .....(1)

And potassium hydroxide solution (KOH) is added to the cadmium nitrate solution so that it is one of the catalysts and to adjust the value of (pH) and the source of negative hydroxide ions (OH^{-2}), the reaction is as follows[17]:

$2KOH \longrightarrow 2OH^- + 2K^+$ .....(2)

A reaction occurs between ions (Cd^{+2}) and ions (OH^{-2}) at a temperature of (80 ℃) by the availability of hydrogen peroxide (H_2O_2) as a catalyst to accelerate the reaction process [5,6] and by the force of Vander Waals, the ions are attracted to the surface of the sample and precipitation occurs as in the following interaction[18]:

$[Cd(NH_3)_4]2Cl + H_2O_2 \rightarrow CdO_{2\downarrow} + 2NH_4Cl + 2NH_4O$ .....(3)

Through the above reactions, we see that the use of cadmium chloride salts in the presence of H_2O_2 and at a high concentration (30%) will obtain mono crystal line CdO_2 instead of CdO (300 ℃), some of the peroxide is converted to oxide and we get a CdO membrane, as in the following reaction [19]:

$CdO + ½\, O \longrightarrow CdO_{2\downarrow 2}$ ..... (4)

3. Results and discussion

3.1. Structural properties

3.1.1. X-ray diffraction

Figure (1) shows the X-ray diffraction measurement of cadmium oxide (CdO) films prepared by chemical bath deposition (CBD) technique, where it represents the precipitated films at a different molar concentration in the deposition. Cadmium oxide (CdO), which has a polycrystalline structure of hexagonal type, has the best crystalline orientation (100) at the angle 2ɵ = 30.22°. And that the appearance of additional peaks (CdO) at the angles 32.94° and 38.96° for the levels (111), (200) with the other peaks of the hydroxide represents the phase of cadmium oxide (CdO), this is consistent with the sources [20], [21]. shows Figure (2) we note that the difference in molar concentration in the deposition of the films leads to the appearance of four levels: (100), (111), (200) and (220), and the prevailing pattern is at the level (111), the patterns of the films show a polycrystalline structure of a cubic type. And when the molar concentration differs in the deposition, the intensity of the peaks is more severe, and this is evidence of an increase in the rate of grain size, which indicates that the hydroxide phase is fading and the concentration of the ion (Cd^{+2}) is excess in the solution[22], while the (XRD) results of the (CdO) film pattern showed up Deposition of sharp peaks at the highest intensity of the pure (CdO) phase. Generally, the peaks of the (CdO) film are of wider structures in case of different deposition pattern.

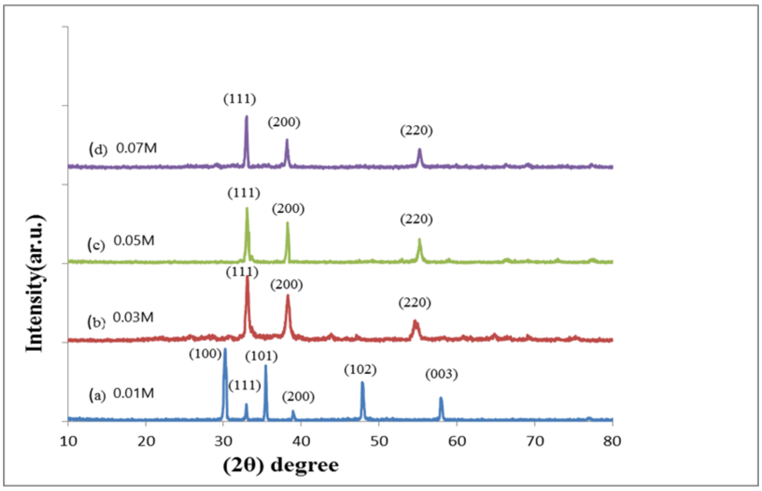

Fig. 1: X-ray diffraction spectrum of the molar concentration difference in the deposition.

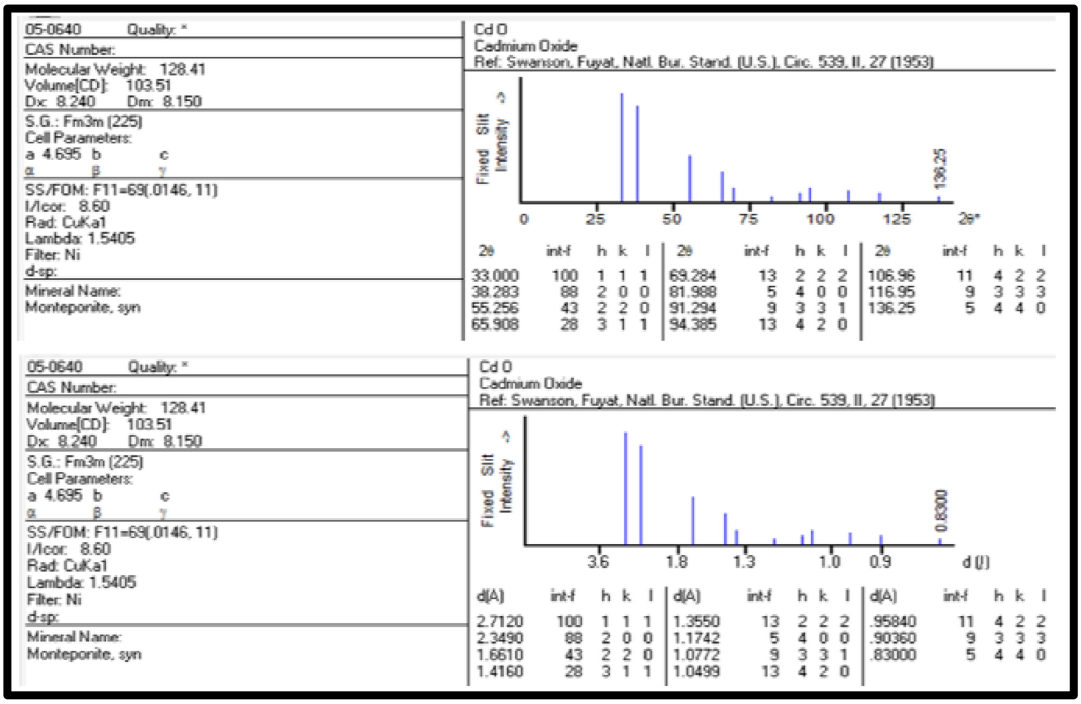

Fig. 2: (ASTM) card for (CdO) numbered (05-0640)[23].

3.1.2. Scanning Electron Microscope (SEM) Examination

Figure (3) shows the (EDS) analysis of the proportions of the elements in the prepared films, we notice from Figure (3) (a,b,c,d) the appearance of the elements cadmium and oxygen, which represents cadmium oxide (CdO). Figure (4), we can observe the images and that the increase in the molar concentration in the deposition had a significant impact on the formation of features and the shape of the surface structure of the prepared films. All the prepared films have uniformly distributed grains, and by increasing the molar concentration in the deposition, the surface of the pure (CdO) film is more homogeneous and uniform, and the quality of the prepared films for the same samples is improved. And that the increase in the molar concentration in the deposition leads to an increase in the particle size as a result of the effect of cadmium atoms in the composition of the material, and we also note that the higher the molar concentration in the deposition, the greater the homogeneity of the surface of the prepared films, and this is consistent with the results of X-ray diffraction (XRD) tests.

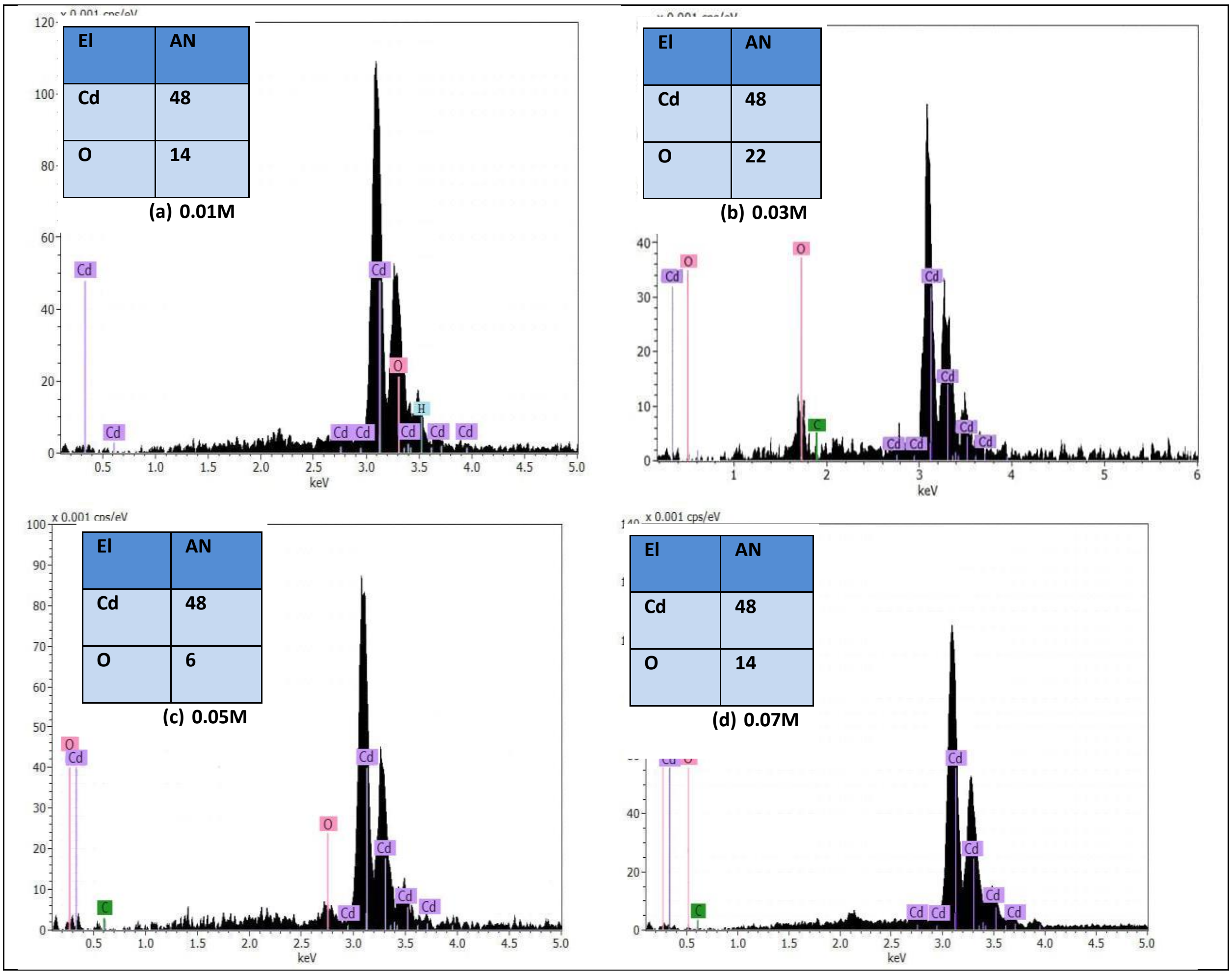

Fig. 3: shows the EDS analysis of the prepared films

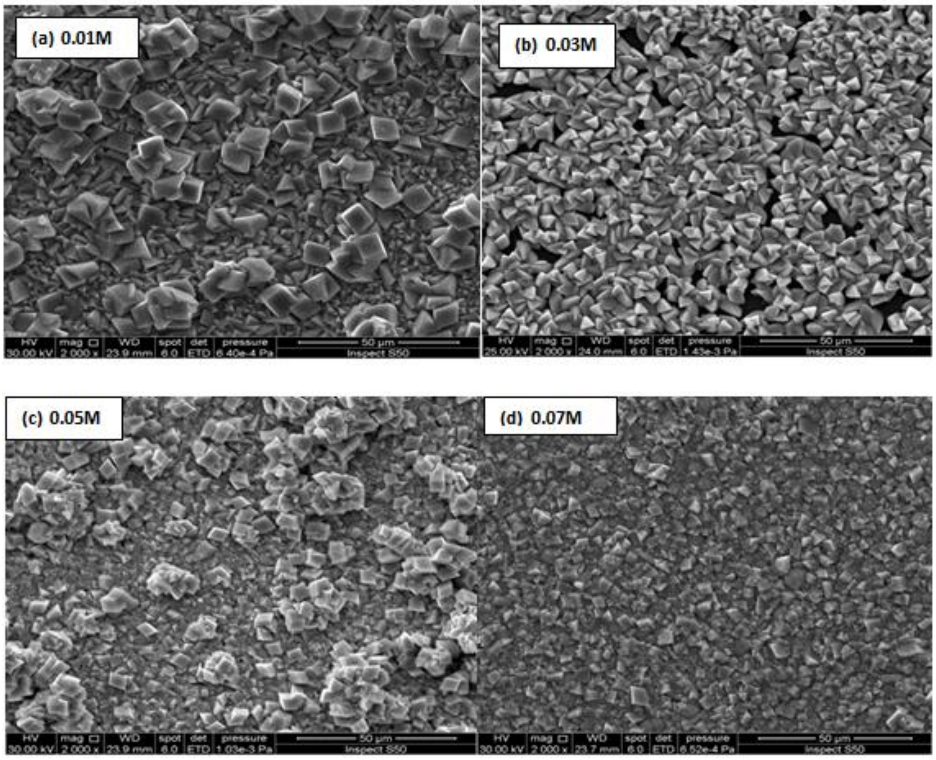

Fig. 4: SEM images of (CdO) films deposition at molar concentrations. (a)0.01M,(b) 0.03M,(c) 0.05M,(d) 0.07M

3.1.3. Atomic force microscopy (AFM)

The results of atomic force microscopy were studied and discussed when increasing the molar concentration in the deposition of the prepared CdO films, measured with a magnification area (2000×2000) nm in two dimensions (2D) and in three dimensions (3D) and the average grain diameter of the surface topography of the film with concentration (0.01 M), as The value of the average square root is (5.21) nm and the value of the average membrane roughness is (4.45) nm where we notice an increase in the roughness rate of the membrane surface and an increase in the value of the average square root leads to an increase in the average surface roughness and vice versa. And the highest surface height is (19.54) nm and the rate of the diameter of the particles is (77.58) nm we notice when the concentration is increased to (0.03 M) where the film was heat treated for a period of 60 min. The average roughness of the membrane surface, therefore, we find that the increase in the value of the mean square root indicates the increase in the roughness rate of the membrane surface and vice versa. The highest surface height is (2.54) nm and the average diameter of the particles is (69.01) nm. When the molar concentration in the precipitate increases to (0.05 M), we notice that there is an increase as for the surface topography of the membrane, the average surface roughness becomes (0.585) nm, the mean value of the square root is (0.689) nm, the highest height is 2.50 nm, and the average grain diameter is 71.75 nm. When the concentration is increased to (0.07 M), we see a regularity in the arrangement of atoms, growth in size, and the beginning of the appearance of nanostructures similar to this bad translation , or nanoparticles, with the increase in the rate of topographic characteristics in the surface of the membrane, so that the rate of roughness of the surface of the membrane becomes 1.77nm, and the value of the average square root is 2.05 nm, and the highest height is (7.01) nm and the average diameter of the particles is (81.96) nm ,shows the Table (1).

Table 1: AFM microscopy results for as-prepared films upon increasing molar concentration in the deposition.

Deposition Condition	Roughness (nm)	RMS (nm)	Ten point height (nm)	Avg. Diameter (nm)
0.01M	4.45	5.21	11.6	77.58
0.03M	0.319	0.388	1.51	69.01
0.05M	0.585	0.689	2.49	71.75
0.07M	1.77	2.05	7.26	81.96

3.2. Optical properties

3.2.1 Optical transmittance

The transmittance spectrum was measured at specific wavelengths between transmittance and at specific wavelengths between (300-900 nm), as it was shown from Figure (5) that the value of the transmittance of the precipitated film is more than 70% and the transmittance decreases with increasing molar concentration in the deposition and that the transmittance decreases at wavelengths ($\lambda \leq 550$ nm).The increase in the molar concentration in the deposition does not affect the behavior of the curve, but the transmittance value decreases. And the annealing leads to an increase in the transmittance. The reason is due to the reduction of structural defects representing deposition zones in the incident beam[24].

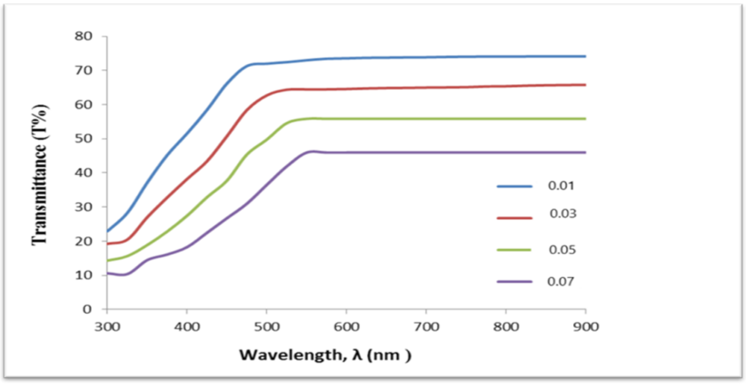

Fig. 5: The transmittance spectrum as a function of the wavelength of the CdO films for deposition at different molar concentration.

3.2.2. Absorbance

The absorbance was calculated and it was shown from Figure (6) that there was a change in the absorbance spectrum of (CdO) films upon the increase in the molar concentration in the deposition and that the value of the absorbance is within the limits of short wavelengths and where the absorbance increases at the wavelength ($\lambda \leq 550$ nm). It increases with the decrease of the wavelength and that the increase in the molar concentration in the deposition leads to the increase in the thickness as the more thickness the absorbency increases.

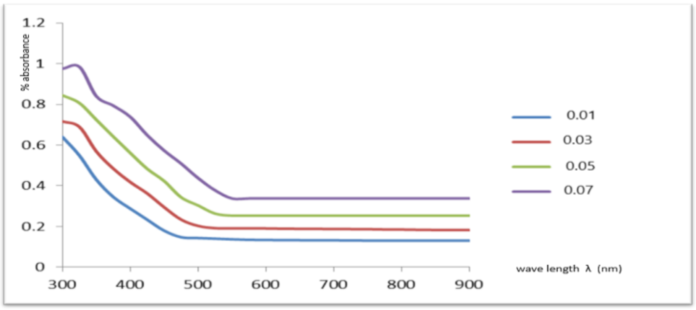

Fig. 6: The absorbance spectrum as a function of the wavelength of CdO films at different molar concentration deposition

3.2.3. Absorption coefficient

The absorption coefficient was calculated for all the prepared films by means of the equation $\alpha = (2.303)\,\frac{A}{t}$ [25]. Figure (7) shows the change of the absorption coefficient with the photon energy of the (CdO) films prepared by (CBD), where the absorption coefficient increases with the increase in the molar concentration in the deposition and its value is (α>104 cm^{-1}). And that the value of the absorption coefficient increases with the increase in the energy of the photon, and this leads to the occurrence of direct transfers. that the high value indicates the occurrence of direct electronic transmissions.

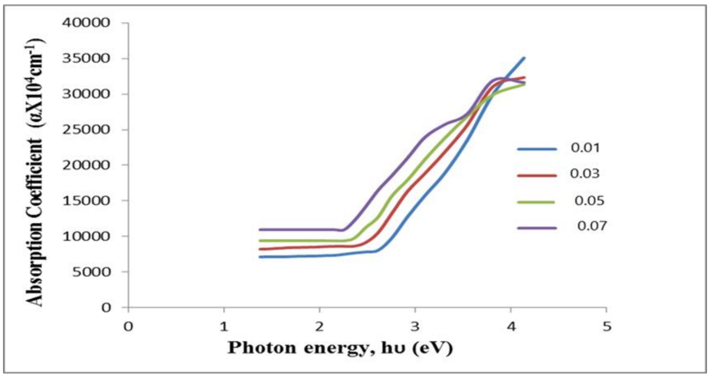

Fig. 7: the absorption coefficient as a function of the photon energy for CdO films of different molar concentrations

4.2.3. Optical energy gap

The energy gap was calculated and the relationship between $(\alpha h\nu)^2$ and (hν)was drawn through the intersection of the straight line with the x-axis ($(\alpha h\nu)^{1/2}=0$). shows the Figure (8) The effect of the concentration of cadmium ions (Cd^{+2}) on the energy gap, as the increase in the molar concentration in the deposition leads to an increase in thickness as a result of increasing the grain size rate and improving the crystal structure of the films, as with increasing thickness the energy gap decreases and it ranges between (2.24-2.63) eV. We obtain the pure phase of the CdO film with an energy gap of 2.41 eV through the improvement in the crystal structure of the film due to the increase in the grain size and the decrease in the energy gap value. And that the dominant transmission is of the direct Allowed type.

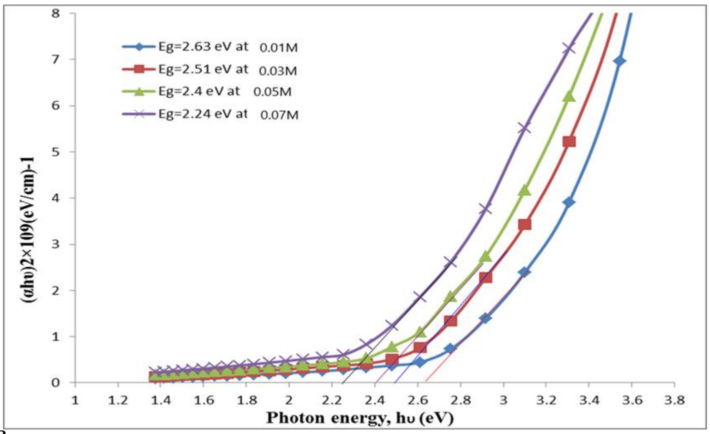

Fig. 8: values of $(\alpha h\nu)^2$ with the incident photon energy of (CdO) films at different molar concentrations in the deposition

4. Conclusions

1- The pure cadmium oxide (CdO) Nano films by chemical bath deposition (CBD) were of a polycrystalline crystalline structure of cubic type and with a growth advantage towards (111), and this corresponds to the card (JCPDS: 005-0640).

2- When examining the prepared films by XRD, it was found that the particle size decreases with the decrease in the molar concentration ratio. Also, the increase in the molar concentration led to a shift of the diffraction angle (2θ) in the X-ray diffraction curve.

3- When conducting AFM atomic force microscope examinations on the prepared films, it was found that these films have a smooth and homogeneous surface, and the surface roughness varies with the increase in the molar concentration ratios, and the ionic diameter rate decreases with the increase in the concentration ratios.

4- The increase in molar concentration led to a decrease in optical transmittance and absorption coefficient and an increase in absorbance and optical energy gap.

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تأثير زيادة التركيز المولاري في اغشية اوكسيد الكادميوم (CdO) ذو التركيب النانوي والمحضرة بالترسيب الحمام الكيميائي (CBD)

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الملخص

تم تحضير اغشية رقيقة متعددة البلورات من مادة اوكسيد الكادميوم CdO النانوية بالترسيب الحمام الكيميائي (CBD) بتركيز مولاري مختلف M= 0.07,0.05,0.03,0.01 مولاري.

لغرض الحصول على أفضل النتائج تمت دراسة الخصائص التركيبية والبصرية لأغشية CdO تحت تأثير زيادة التركيز المولاري, أظهرت نتائج قياسات الامتصاصية هناك وجود تغير في طيف الامتصاصية لأغشية (CdO) عند الزيادة في التركيز المولاري في الترسيب، أن قيمة الامتصاصية هي بحدود الاطوال الموجية القصيرة وحيث تزداد الامتصاصية عند الطول الموجي (λ≤550 nm), ونلاحظ أنها تزداد مع قلة الطول الموجي وأن الزيادة في التركيز المولاري في الترسيب يؤدي الى الزيادة في السمك حيث كلما يزداد السمك تزداد الامتصاصية. تم فحص جميع النماذج للأغشية المحضرة باستخدام المجهر الإلكتروني الماسح (SEM) وعند قوة تكبير x2,000 وذلك لغرض التعرف على طبيعة سطح الأغشية المحضرة وملاحظة التغير في الحجم الحبيبي مع زيادة التركيز المولاري في الترسيب. أوضحت النتائج العملية أن الحجم الحبيبي (grain size) يزداد أنماءه البلوري بزيادة التركيز المولاري وهذا ما تبين من قياسات X-ray, AFM .