Iraqi Journal of Physics, 2022
DOI: 10.30723/ijp.v20i1.975

Vol.20, No.1, PP.63-71
P-ISSN:2070-4003
E-ISSN:2664-5548

Effect of pH on the Structural and Optical Properties of Cadmium oxide Thin Films Prepared Using the Successive Ionic Layer Adsorption and Reaction (SILAR) Method

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Abstract

Cadmium oxide (CdO) thin films were deposited using the sequencing ion layer adsorption and reaction (SILAR) method. In this study, the effect of the pH value of an aqueous solution of cadmium acetate at a concentration of 0.2 mol of the cadmium oxide film was determined. The solution source for the cadmium oxide film was cadmium ions and an aqueous ammonia solution. The CdO films were deposited on glass substrates at a temperature of 90 ℃. The cadmium oxide film thickness was determined by the weight difference method at pH values (7.2, 8.2). X-ray diffraction (XRD) and scanning electron microscopy (SEM) showed that the size of the crystals increased with the increase in the solution (pH). While the UV-visible spectra of the films revealed that the optical band gap energy decreases with increasing (pH) of the CdO solution. The absorbance spectrum of the cadmium oxide film was recorded in the wavelength range (300 – 900) nm. The change in the pH of the cadmium acetate aqueous solution from the energy gap and X-ray diffraction calculations showed that the film had an optical band gap energy and that the highest intensity was at (111) and that the membrane is n-type, as shown by studies to prepare the cadmium oxide membrane using the SILAR method.

Article Info.

Keywords:
CdO, thin-film, SILAR technique, pH, optical properties.

Article history:
Received: Jan. 09, 2022
Accepted: Feb. 15, 2022
Published: Mar. 01,2022

1. Introduction

The films of transparent conducting oxide (TCO) have a lot of potential in optoelectronics and other solid-state technologies. CdO thin films have attracted a lot of attention in recent years due to their unique optical, electrical, and structural properties [1]. Cadmium oxide is a transparent conducting oxide material that has high optical transparency and electrical conductivity in the visible region of the electromagnetic spectrum [2].

Cadmium oxide is a reddish substance with a cubic crystalline structure comparable to sodium chloride (F.C.C.) [3]. It belongs to the second-sixth group (II-VI) of the periodic table [4]. Cadmium oxide is a cadmium-based chemical that dissolves in acids and ammonium salts but not in liquid or bases [5]. Accordingly, it is being used in smart windows, flat panel displays, solar cells, and other optoelectronic applications [6]. To make thin films of cadmium oxide, researchers have used thermal evaporation metal-organic deposition [7], chemical bath deposition [8], spray-pyrolysis [9], sequential ionic layer adsorption, reaction (SILAR) method, and other methods[10].

SILAR method is a two-beaker system. Changing the number of cycles as well as the pH, the thickness required for the cadmium oxide film can be obtained.

The purpose of this study is to create a 0.2g/cm^3 cadmium oxide film using the SILAR method due to its high absorbance in the visible spectrum region and to study the effect of pH at values of 7.2 and 8.2 on the film structural and optical properties.

2. Experimental work

2.1. Preparation of thin films

Cadmium acetate (purchased from BDH-England company) with the molecular formula $Cd(CH_3COO)_2$. $2H_2O$ (99% e-Merck) and of a molecular weight of 266.35 g/mol with a concentration of 0.2 gm/cm^3(Weight difference method) was used in the form of a water-soluble powder. The weight of the cadmium acetate material was determined according to the relationship below [11]:

$$[M] = \frac{Wt}{Mwt} \times \frac{1000}{v} \quad (1)$$

where [M] is the molar concentration of the cadmium oxide film, W_t is the weight of aqueous cadmium acetate powder needed to dissolve, V is the amount of distilled water in a given volume, and M_{wt} is the molecular weight of cadmium acetate powder in g/mol.

In addition, aqueous ammonia with the molecular formula NH_3 alkali (pH=7) and distilled water (d.w.) was also used. The used glass substrates were first rinsed with distilled water, then dipped in dilute chromic acid for 1 hour, then placed in an ultrasonic bath for 20 minutes, and finally dried in an oven.

Cadmium acetate aqueous powder at a concentration of 0.2 g/cm^3 was gradually dissolved in 100 ml of distilled water using a magnetic stirrer for two hours with increasing the temperature of the magnetic mixer to reach 90°C, during which ammonia was gradually dropwise added to increase the pH and, in this way, the cadmium oxide membrane chemical bath was prepared.

The clean glass substrate was immersed in becker1 containing the aqueous cadmium acetate solution, representing a cationic solution, for 30 seconds, and when the glass substrate was withdrawn after the duration of the immersion period has ended, it was dipped for 15 seconds in a water bath of becker 2 at the boiling point, representing an ionic solution. These dipping steps were repeated 10 times. Finally, the sample on which the cadmium oxide film was deposited was air blow-dried to get rid of moisture and then annealed at a temperature of 150 degrees Celsius. During the dipping process, cations representing positive charges and anionic charges representing negative charges are formed on the glass substrate. The complexing agent ammonium hydroxide was used to stabilize the crystallite size. The thin films thickness (t) was determined using a weight-difference method on a sensitive electronic scale (Sartorius 10^{-4} g of German origin), as follows [12]:

$$t = \frac{m}{A\rho} \quad (2)$$

where *m* is the weight gain, ρ is the density of the CdO thin film, and A is the coated film area.

3. Results and discussion

3.1 X-Ray diffraction

Fig. 1 shows the XRD patterns of CdO thin films deposited at two pH values of 7.2 and 8.2. It illustrates a cubic crystal structure of CdO, which can be indexed for all diffraction peaks in the XRD pattern and is consistent with the standard data for CdO

(JCPDS, Data File No. 0640). This would be in line with reports of CdO thin films produced utilizing the SILAR method. Due to the significant orientation in the (1 1 1) plane, as well as the reflections in the (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes, the polycrystalline membrane is thus revealed in the highest peak. The presence of many peaks revealed the polycrystalline structure of the CdO films. Three prominent diffraction peaks were observed in the patterns that can be indexed to (1 1 1), (2 0 0), and (2 2 0) planes by the ASTM standards. Peaks corresponding to (3 1 1) and (2 2 2) planes were also observed. The crystallites in a polycrystalline material normally have a crystallographic orientation different from that of their neighbors. This orientation of the crystallites named the preferential orientation may be distributed randomly according to some selected frame of reference. Comparing XRD patterns of the thin film prepared at pH=7.2 with that prepared at pH=8.2, it is clear that the Bragg peaks for pH 7.2 were more intense, showing a clear improvement in the grain size (calculated using Scherrer, Eq. (3)) [13]:

$$\mathbf{D = \kappa\lambda / \beta\cos\theta} \qquad \mathbf{(3)}$$

where K is a constant of 0.9 for polycrystalline membranes, λ is the wavelength of X-ray radiation, β is the full-width at half maximum measured in radial angles in the center of the diffraction peak, and θ represent Bragg angle (measured in degrees). Table 1 summarizes the XRD parameters of CdO thin films.

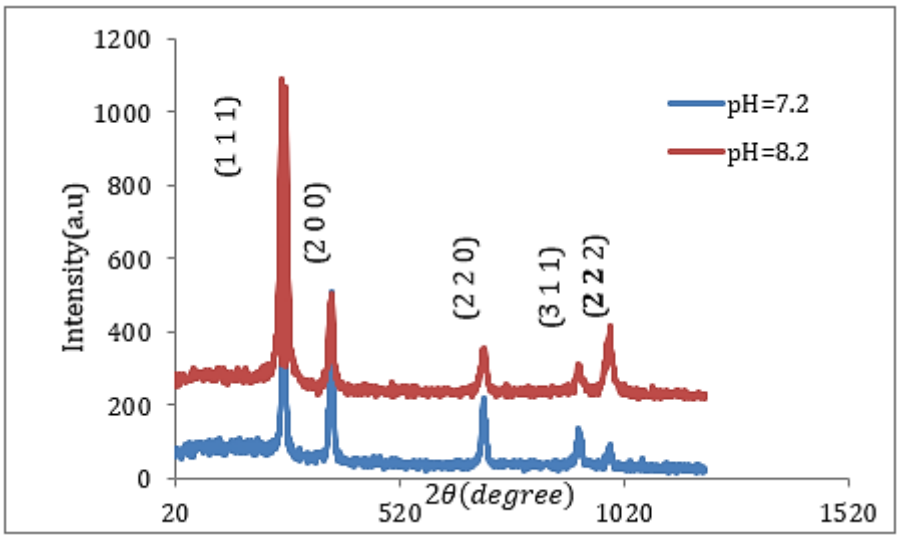


Figure (1): XRD patterns of cadmium oxide films at the two pH values.

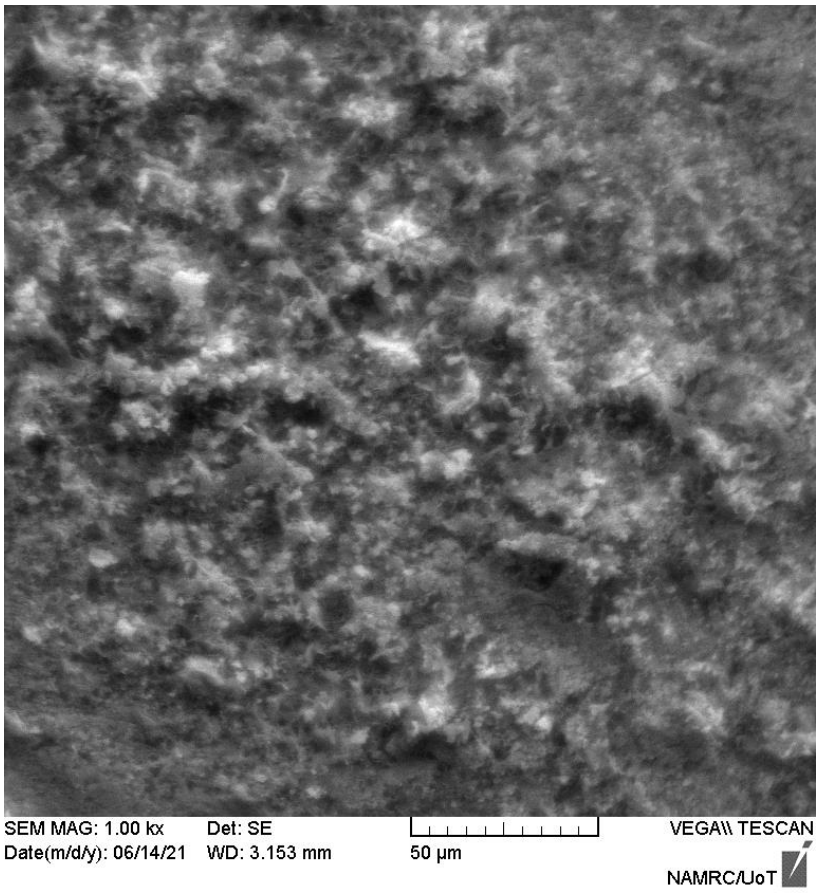
Table 1: XRD parameters of CdO thin films of the two pH values at a concentration of 0.2 M.

2θ(deg)	FWHM (deg)	(h k l)	No. of dipping	Observed values (Å)	*Crystallite size (nm)*	pH	Thickness (nm)
32.8653	0.78700	(1 1 1)	10	2.7	1.93	7.2	182.4
32.8927	0.68040	(1 1 1)	10	2.7	2.2	8.2	197.4

The films of cadmium oxide were deposited on a clean glass slide using SILAR method for two pH values were taken to support the XRD data. Figs.2 and 3 show the images of (SEM) which illustrate the surface topography of the precipitated CdO films. The higher pH of the cadmium oxide thin films showed a heterogeneous distribution on the surface and inter-grain assemblies as in Fig.2(a,b) compared with Fig.3(c,d). This method confirms that the crystal structure of the precipitated layer improves when

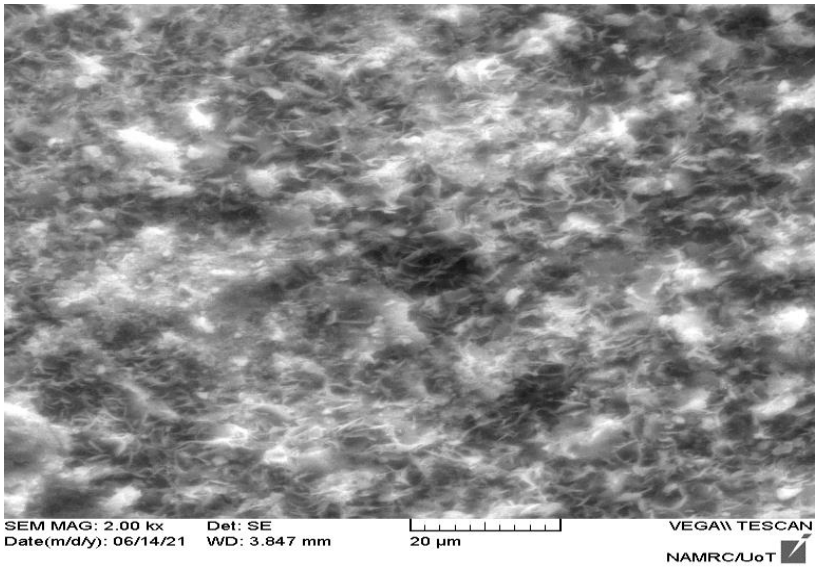
the pH of the cadmium acetate solution is low due to the effect of basic ammonia on the solution on the one hand. On the other hand, the addition is considered as an impurity that affects the structural properties of the film. From the results of XRD of the prepared film with 0.2M, at a pH of 7.2, the solution has micro-granules of 1.93 nm size distributed all over the surface. As for the thin films with a pH of 8.2, the grains appear larger. It was found to be equal to 2.2 nm.

Fig. 4 appear the absorbance spectra of CdO thin films prepared at two values of pH by the SILAR technique as a function of wavelength range (300-900) nm. This figure describes optical absorption showing that film absorption decreases with increasing wavelength. All films deposited at both pH values showed high transparency in the visible region with little or no difference in optical transparency. The absorbance was higher at the higher pH, that is, the precipitated layer with pH = 8.2 shows higher absorbance compared to that deposited at pH = 7.2.



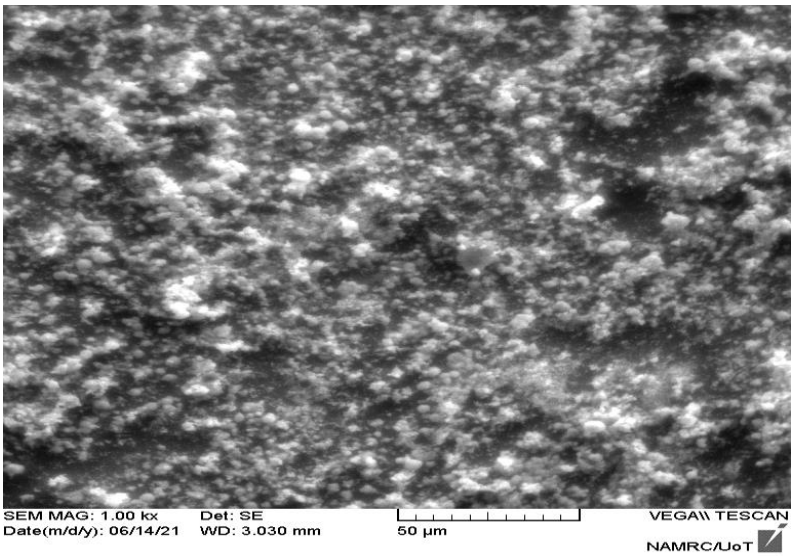
(a)

Figure 2(a): SEM image of 0.2gm/cm^3 of CdO thin film for pH=7.2.

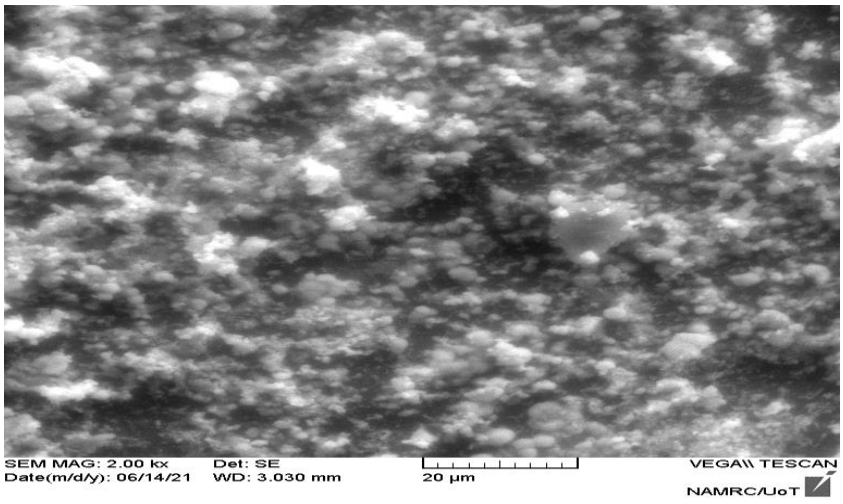


(b)

Figure 2(b): SEM image of 0.2gm/cm^3 of CdO thin film for pH=7.2.



(c)



(d)

Figure 3 (c, d): SEM image of 0.2 gm/cm^{3}of CdO thin film for pH=8.2.

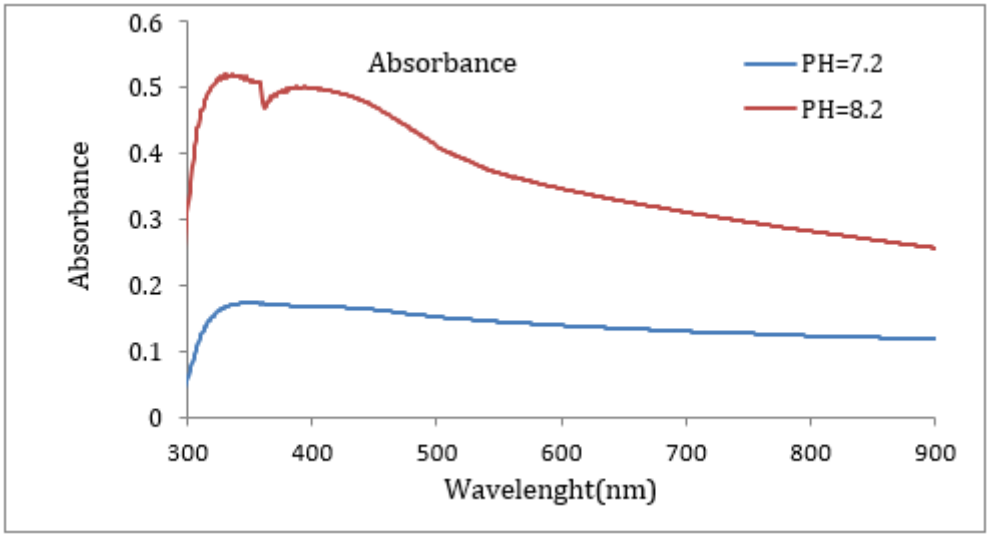


Figure 4: Absorbance spectra of CdO thin films.

Equation (4) was used to calculate the absorption coefficient [14]:

$$\alpha = \frac{2.303\ A}{t} \qquad (4)$$

where t is the film thickness and A is the optical absorbance. The incident photon energy (hν) and the absorption coefficient (α) are related by equation (5) [15]:

$$(\alpha h\nu)^2 = B(h\nu - E_g) \qquad (5)$$

where Eg is the energy gap and B is constant. Typical plots of $(\alpha h\nu)^2$ versus hν for CdO thin films with pH 7.2 and 8.2 deposited on glass substrates are shown in Figs.5 and 6. As noted from the figures, increasing the pH of the solution from 7.2 to 8.2 has no discernible effect on the band edge in the visible region. This means that the fundamental crystal structure remains unchanged. It was observed that the increase in the pH of the CdO precursor solution led to a slight decrease in the optical bandgap from 2.3ev to 2.2ev and this is within the energy gap of the direct CdO film transitions.

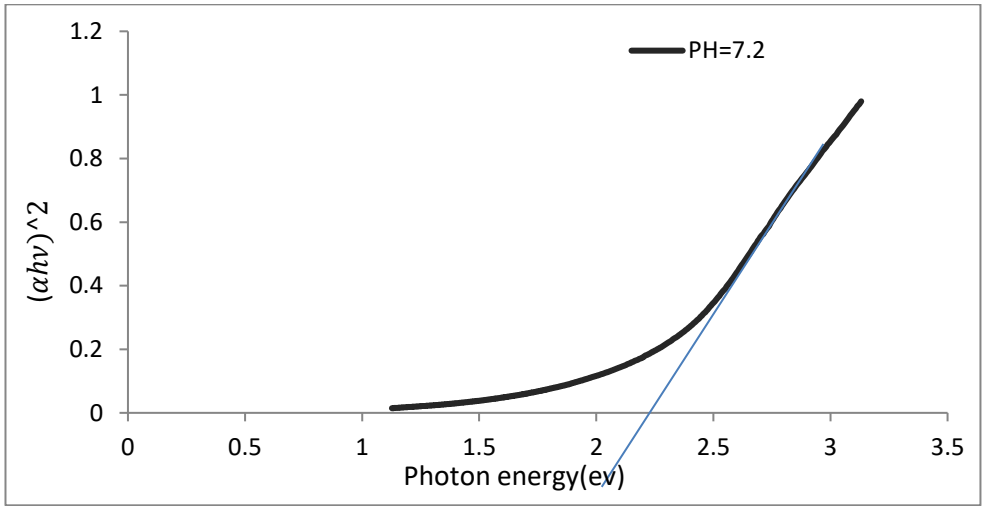


Figure 5: The optical energy gap CdO thin film at pH=7.2.

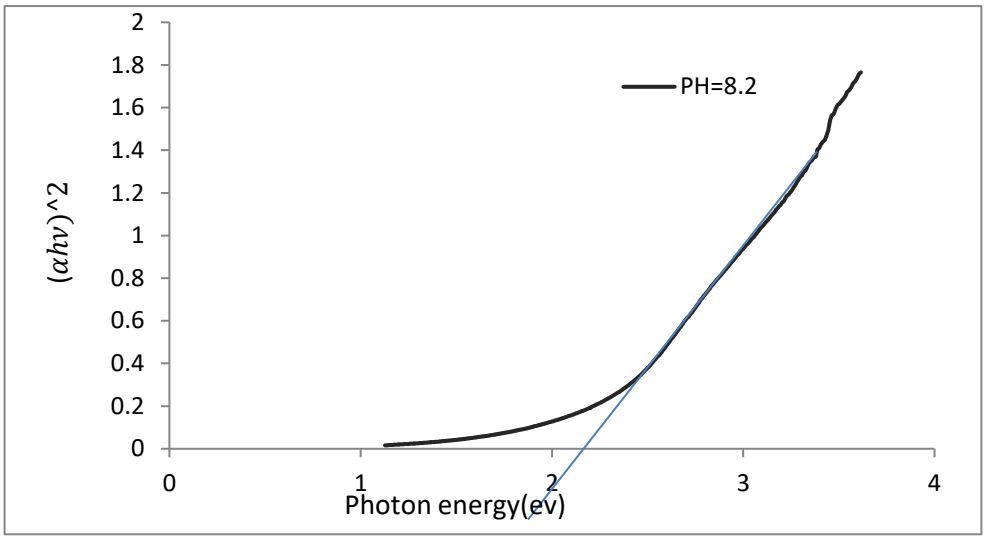


Figure (6): The optical energy gap CdO thin-film pH =8.2.

4. Conclusions

The cost-effective modified SILAR method was employed successfully to prepare transparent conducting cadmium oxide thin films. XRD study indicates that all of the films were polycrystalline, with a cubic structure that preferentially aligned along with the (111) plane. The optical energy gap value of the film remained constant when the pH was decreased. Scanning electron microscope images show that the membrane has voids and is of a porous structure. Optical studies of the films revealed that the film deposited at the high pH has a high transmittance and a low adsorption nature. It can be concluded from the results obtained for the cadmium oxide film that the energy gap did not change with the change of pH, which can be used in optoelectronic applications such as solar cells.

Acknowledgments

The authors would like to express our gratitude to the Department of Physics (Laser and Molecular) at the University of Baghdad for allowing us to use the laboratory to accomplish this work.

Conflict of interest

The authors declare that they have no conflict of interest.

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تاثير الأس الهيدروجيني على خواص أغشية أكسيد الكادميوم المحضرة باستخدام طريقة الامتزاز والتفاعل المتتالي للطبقة الأيونية(SILAR)

فهمي كاظم جواد[1] و نذيرة عباس علي التميمي[1]
قسم الفيزياء، كلية العلوم، جامعة بغداد، بغداد، العرا ق

الخلاصة

تم ترسيب أغشية رقيقة من أكسيد الكادميوم (CdO) بواسطة امتزاز وتفاعل الطبقة الأيونية المتعاقبة (SILAR). في هذه الدراسة، تم تحديد تأثير الرقم الهيدروجيني للمحلول المائي من أسيتات الكادميوم بتركيز 0.2 مول من غشاء أكسيد الكادميوم. كان مصدر المحلول لغشاء اوكسيد الكادميوم هو ايونات الكادميوم ومحلول أمونيا المائي. تم ترسيب الغشاء على ركائز زجاجية عند درجة حرارة 90 درجة سيليزية .تم تحديد سمك غشاء اوكسيد الكادميوم بطريقة الفرق بالوزن للفيلم المحضر عند قيمة pH (7.2، 8.2). يظهر حيود الأشعة السينية والمسح المجهري الإلكتروني أن حجم البلورات يزداد مع زيادة (الرقم الهيدروجيني) للمحلول. بينما أظهر الطيف المرئي للأشعة فوق البنفسجية للأغشية أن طاقة فجوة البصرية تقل مع زيادة (الرقم الهيدروجيني) لمحلول أكسيد الكادميوم. أظهر التغير في الرقم الهيدروجيني للمحلول المائي لخلات الكادميوم من فجوة الطاقة وحسابات حيود الأشعة السينية أن الغشاء له طاقة فجوة بصرية وأن أعلى شدة كانت عند (111) وان الغشاء هو النوع n كما بينت ذلك الدراسات لتحضير غشاء اوكسيد الكادميوم باستخدام طريقة سيلر.