Effect of Thickness to the Structure Properties of CdO Thin Films

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Abstract

In this paper CdO thin films were prepared by using chemical bath deposition method. Three different thicknesses of CdO films (84.1nm, 165.1nm, 194.23nm) were used .x-ray diffraction technique has confirmed the formation of cadmium oxide, where reveals the changes in films structure with thickness increase. Many structural properties and constants have been studied and calculated by using the formation from XRD patterns and ASTM chart such as grain size, FWHM, integral breadth, shape factor, texture coefficient, and number of layers .These structural constants were plotted as a function of the films thicknesses. The results indicate that the high grain size (21.557nm) which was calculated for crystalline plane (111) was corresponding to the high film thickness (194.23nm), while larger number of layer obtained for the film thickness 165.2nm.

Keywords: CdO thin film, chemical bath deposition, structure properties.

تأثيرالسمك على الخصائص التركيبيه للاغشيه الرقيقة لاوكسيد الكادميوم

الخلاصه

في هذا البحث تم تحضيرالاغشية الرقيقه لاوكسيد الكادميوم باستخدام طريقة الترسيب بالحمام الكيميائي ,حيث ان الغشاء المستخدم كان بثلاثة اسماك مختلفه وهي (194.23, 165.1, 84.1 نانومتر), اثبتت تقنية حيود الاشعه السينيه تكون غشاء اوكسيد الكادميوم حيث اظهرت التغيرات الحاصله في البنيه التركيبيه للغشاء مع زيادة السمك. بواسطة المعلومات المستحصله من مخططات حيود الاشعه السينيه والبطاقة الخاصه بالاوكسيد تم دراسة وحساب العديد من الخواص والثوابت التركيبيه مثل (الحجم الحبيبي, اعظم عرض لمنتصف القمه, عرض الاتساع ,عامل التشكيل, معامل الخشونة ,عدد الطبقات) ,هذه الثوابت التركيبيه رسمت كدالة لاسماك الاغشيه. النتائج اشارت الى ان اعلى حجم حبيبي (21.557 نانومتر) كان للغشاء بسمك (194.23 نانومتر) هذا بالنسبه للمستوي البلوري (111). بينما اكبر عدد للطبقات كان للغشاء الذي بسمك (165.2 نانومتر).

1. Introduction

Semiconductors have considerable technical interest in the field of electronic and electro optical devices. In general, it is difficult to prepare these materials in bulk form; however, synthesis can be achieved in case of thin films [1]. The commonly used methods of preparation thin films of

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semiconductors are vacuum thermal evaporation, spray pyrolysis, sputtering, sol gel and molecular beam epitaxy, and the most of these techniques are expensive and require high vacuum and controlled formation conditions [2, 3, 4]. Chemical bath deposition (CBD) represents less common technique but inexpensive and convenient method for large preparation of thin films at low temperatures [5, 6]. The semiconductors oxide such as CdO, ZnO, BaO, Fe_2O_3, BiClO and Cu_2O thin films have studied extensively as a result of wide range of technical applications, specifically in the field of photovoltaic solar cells and other optoelectronic devices [7,8] , cadmium oxide (CdO) one of these important semiconductors oxide which has high optical properties. According to these properties it has vast applications. Where it show high transparency in the visible region of solar spectrum and has high electrical properties which were represented low ohmic resistance [9]. Although it is difficult to obtain simultaneously a high transmission coefficient and good conductivity these properties of CdO thin films have been carried out [10, 11].

2. Experimental

2.1 Substrate Preparation

Substrate used for the deposition of CdO is borosilicate glass slides, which were first cleaned in distilled water in order to remove impurities and residuals from their surfaces, followed by rinsing in sulphuric acid (H_2SO_4) (for two days), to introduce functional groups called nucleation and / or epitaxial centers, which formed the basis for the thin films growth [12]. Then the samples were washed repeatedly in deionized water, after that dried and kept to be used in time.

2.2 Solution preparation

Cadmium Oxide films were prepared from cadmium nitrate which were provided from (SEELZE-HANNOVER) with 99.99% pure. The deposition of CdO films is achieved by using cadmium nitrate solutions, consist of 20ml of 0.2M cadmium nitrate ($Cd(NO_3)_2$), 20ml of 0.5M potassium hydroxide (KOH), 2ml hydrogen peroxide (H_2O_2) and deionized water were mixed slowly at room temperature. KOH acted as both a complexing agent and a pH stabilizer in the alkaline medium, and it represented as a source of (OH^-) ions, while the role of H_2O_2 is to avoid the spontaneous precipitation of any solid phase in the reaction.

2.3 Deposition of the CdO Films

The substrates were immersed vertically in a beaker containing the above reaction mixture. The beaker was placed in a water bath at temperature ($80 \pm 3\ C^{\circ}$). 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); whereas the value pH in the start of the deposition process takes place was (9). Substrates were then taken out after a suitable time; they were washed with distilled water, and then dried. After KOH was added to the solution the color of solution becomes milky. The value of pH of the solution in the case of KCN added is (10.5). By heating the solution, the ions of Cd^{2+} (from cadmium nitrate solution) and OH^- ions (from potassium hydroxide solution) will react with each other to form the white

film of cadmium hydroxide $Cd(OH)_2$ which convert to CdO film after the annealing process, due to the removal of H_2O vapor from the film structure .

3. Measurements

3.1 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:-

$$d = \frac{\Delta x}{x} \cdot \frac{\lambda}{2} \qquad \text{..... (1)}$$

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

3.2 Structure Measurement

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, using (lab X-XRD 6000/shimad2u) of λ= 1.54 A° from Cu - K□α. The average grain size (g) of the polycrystalline material can be calculated from the X - Ray spectrum by means of Full Width at Half Maximum (FWHM) method (Scherrer relation)[13]:

$g = (0.94\,\lambda)/[\Delta_{(2\theta)} \cos\theta]$ ..... (2)

Where:

λ: is the x-ray wavelength (Å)

$\Delta_{(2\theta)}$: FWHM (radian) .

θ : Bragg diffraction angle of the XRD peak (degree) .

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?

4. Results and discussionXRD Patterns

Figure (1) represents the structural changes of CdO films, where obviously it can be notice that the diffraction patterns are consistent with the presence of pure polycrystalline CdO thin film with cubic (NaCl) structure, showing a number of characteristic peaks assigned for every value of thickness. For 194.23nm, there are eight peaks at 2θ=29.3941°, 32.9864°, 38.2839° ,48.9484° ,52.31° ,55.2136° ,56.096° ,and 58.757° which corresponding to diffraction from H(100) ,C(111) ,C(200) , H(102), H(110) , C(220) ,H(111) ,and H(003) planes respectively. The three peaks C(111) ,C(200) ,and C(220) refer to cubic phase of polycrystalline CdO films ,while the others reflected from hexagonal phase of $Cd(OH)_2$. These peaks were produced of the excess growth of grains with decreasing of thickness value and not all the water vapor could be released from the film structure. As to the pattern of the film which deposited at 165.2nm reveals three peaks at 2θ=33.0261°,38.3071°, and 55.3135° corresponding to crystalline planes C(111) ,C(200) ,and C(220) .All three peaks refer to cubic phase of polycrystalline CdO films .

The last pattern represents the XRD pattern of the film which deposited with 84.1nm. There is a special case, where the pattern contain one clear peak only at 2θ=33.0414° reflected from C(111) peak with other four peaks have very low intensity at 2θ=29.499° ,38.584° ,48.8121° ,and 55.513° for H(100) ,C(200) ,H(102) ,and C(220) respectively.

The two minor peaks for C(200) and C(220) represented the peaks of CdO films which were disappeared to the very low intensity at this pH value. This can be attributed to the reverse relation between growth rate and pH value while others refer to hydroxide phase which reside in the film even after annealing and causes clear increasing in average grain size .The average grain size showed have an inverse relationship to the thickness value, therefore the preferred orientation of CdO films at ($2\theta = 33^{\circ}$) are due to the controlled nucleation process associated with the low deposition rate. In other words when thickness values increases the growth are decreased due to more (OH^-) ion concentration which gives colloidal precipitation during heating (because of high (OH^-) ion concentration leading to high and fast reaction to produce $Cd(OH)_2$ as a precipitate in solution during heating). Therefore the reaction life is short with low growth rate, and this gives low thickness of film as follows small grain size with low diffraction intensity.

From comparing our results with those given in the (ASTM data card 5-0664), one could conclude that the deposition films are having the cubic structure of CdO. Significant changes, observed in the X-ray diffraction patterns, manifest themselves in increase of peak intensity corresponding to (111) crystal plane and a decrease in the peak intensity corresponding to other planes. Figure (2) shows the linear dependence of the (111) plane intensity peak on thickness cadmium oxide films.

4.2 FWHM (Δ)

The results of the (FWHM) for all samples point that have values close together for lower thickness and decrease for higher thickness. For thickness (84.1, 165.2) nm value is (about 0.5 deg.) while for (194.23) it is about (0.3 deg.) as in table (1).

4.3 **Integral Breadth (β)**

There are two branches of line profile analysis:-

a- Broadening.

b- Shape of diffraction line.

The first one is caused by non ideal optics of the instrument, wavelength, dispersion, and structural imperfections of the specimen, also this branch is subdivided and size broadening (which is caused by the finite size of domains), and strain broadening (which is caused by varying displacements of the atoms with respect to their reference-lattice positions). The second is frequently characterized by means of one or two breadth measures FWHM, and **β.**

The integral breadth of the samples were obtained from the XRD pattern sheets and using the relation (3) [14].

$$\beta = \text{Area} / I_o \quad \text{…...……..…. (3)}$$

Where Area: area under peak.

I_o: maximum intensity.

Our results indicate that increasing the thickness leads to increasing in the integral breadth; they are recorded in the table (1) below.

4.4 Shape Factor (Φ):

The shape factor determined the line profile resulting from the XRD patterns, which

Was calculated using the following relation (4) [13].

$\Phi = \Delta / \beta$ ……...……. **(4)**

The results show that the shape factor had decreased with increasing thickness of the thin films.

4.5 Average Grain Size (g)

The average grain size was calculated using Scherrer's formula (2) the values of average grain size listed in the Table (2) show an increases with thickness of the films. Increasing of thickness cause to increase the average grain size, as shown in Figure (3). It may be due to the combined effect of increase in Cd incorporation, increase in growth rate and reorientation effect.

4.6 Texture Coefficient (T_c)

Texture coefficient (T_C) of fabricated CdO thin film was calculated using relation (5) [13].

$$T_C(hkl) = [(I(hkl) / I_o(hkl)] / [N_r^{-1} \sum I(hkl) / I_o(hkl)] \quad \text{…….(5)}$$

Where I: is the measured intensity.

I_o: the ASTM standard intensity.

N_r: the reflection number.

(hkl): Miller indices

The results indicate that (T_c) increase with increasing thickness. This is a usual result because increased thickness causes an increase in the surface roughness. This result is in a good agreement with that in the literature [1].

Figure (4) shows the texture coefficient and the number of layers as a function of thickness. The increase of number of layers causes to reduce gaps between grains, then increase the smoothness or reduce the roughness and then minimize the texture of the film surface.

4.7 Number of Layers (N_t)

The number of layers was evaluated by using the relation (6) [13, 14].$d = g * N_t$ **...…… …..……..… (6)**

Where g: is a mean crystallite size or average grain size.

In table (3) the variation of layer number varies with thickness in a random way, where can be notice that the higher thickness have number of layer less than the thickness (165.2 nm) .This result may be due to the values of grain size and the rate of growth of the film with thickness (194.23 nm).

Conclusions

We describe bellow summarization of our work:

1- The deposition films are having the polycrystalline structure of cadmium oxide with cubic type.
2- The pure phase of CdO was obtained with film thickness of 165.23nm.
3- The intensity of x-ray diffraction was proportional with the film thickness.
4- The texture Coefficient and number of layers were increased with increasing of film thickness, unless for the film with thickness 165.2nm.
5- The other structural constants were altering in randomly way.

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Table (1): The FWHM, Integral Breadth (β) and shape factor *planes of different* Thicknesses of CdO thin films.

Thickness T(nm)	Crystal plane (hkl)	Full width of half maximum FWHM(deg.)	Integral breadth B(deg.)	Shape factor Φ
84.1	**111**	0.4825	0.01	48.25
165.2	**111**	0.52270	0.0161	32.46
194.23	**111**	0.30490	0.0080	38.11

Table (2): The grain size and number of layers of different thicknesses of CdO thin film.

Thickness T(nm)	Grain size G_s (nm)	Crystal plane (hkl)
84.1	17.946	111
165.2	16.564 16.322 14.77	111 200 220
194.23	21.557 39.159 79.93	111 200 220

Table (3): The grain size and number of layers of different thicknesses Of CdO thin film.

Thickness T(nm)	Crystal plane (hkl)	no. of layer NL
84.1	111	4.68
165.2	111 200 220	9.97 10.123 11.187
194.23	111 200 220	9.01 4.96 2.43

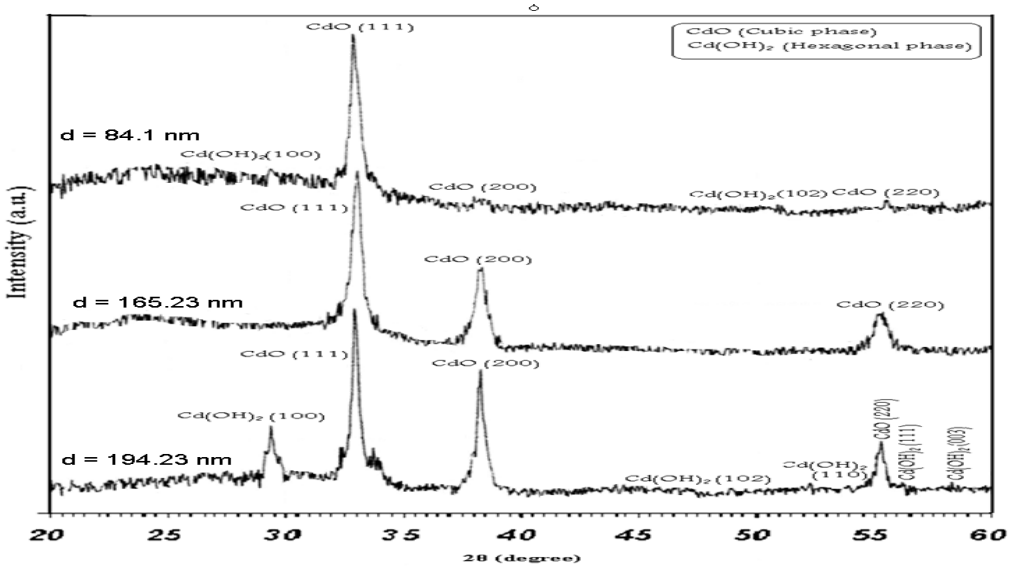

Figure (1): The X-ray diffraction of CdO films for different thickness (d).

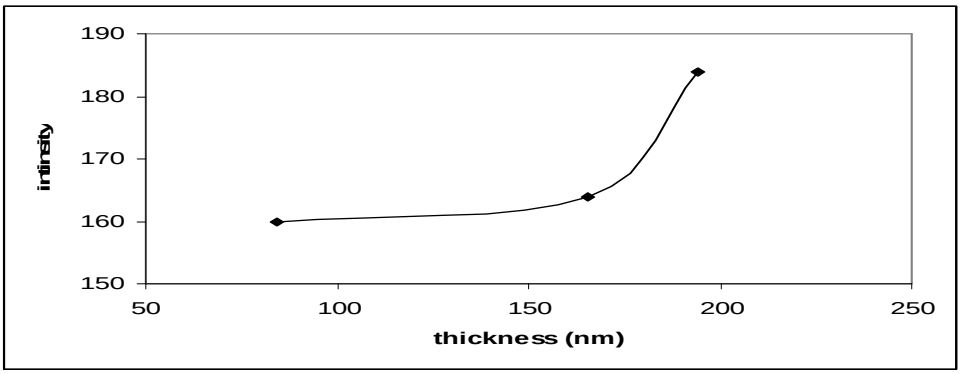

Figure (2) Effect of thickness on the relative intensity of investigated peak (111)

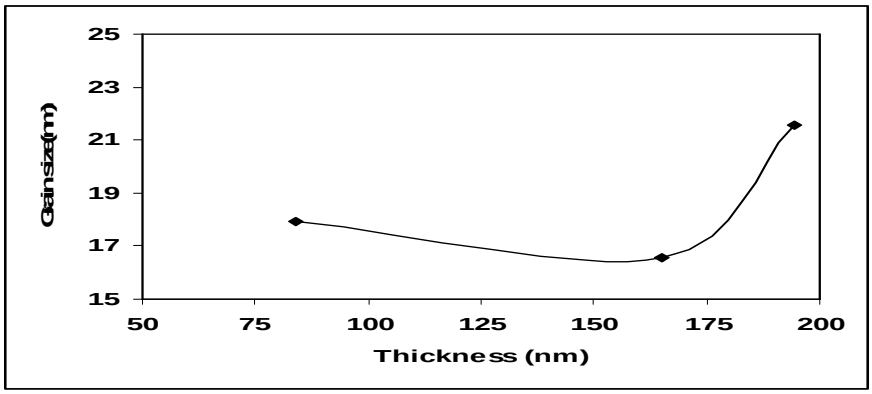

Figure (3): The average grain size of CdO films as a function of thickness

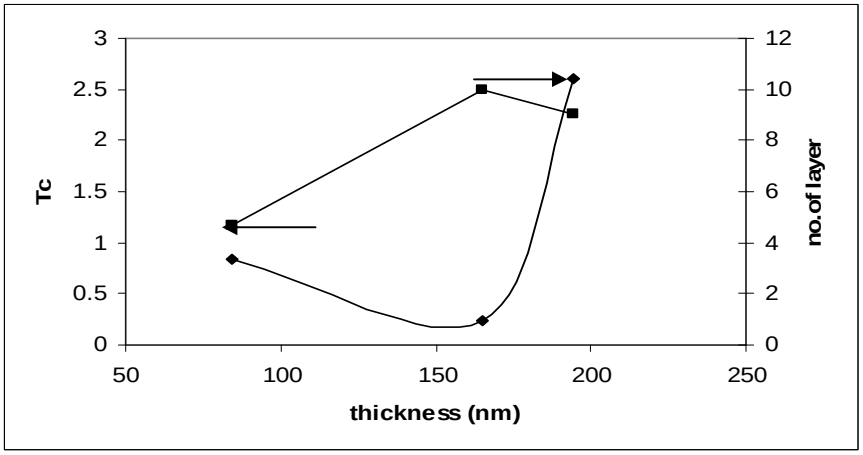

Figure (4) Texture coefficient & number of layers as a function of thickness