Growth Kinetics of Chemically Deposited CdO Thin Films

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Abstract

In this work CdO films were prepared by using chemical bath deposition technique where the cadmium nitrate salt was used as a source of cadmium ions. The effect of different bath parameters has been considered in this work, namely, cadmium ion concentration, deposition time, temperature of solution and pH value, on the rate of deposition and terminal thickness. Annealing process in air at temperature 573K° and time of 15min. are carried out for the conversion of cadmium hydroxide film to oxide film. X-Ray diffraction technique has confirmed the formation of cadmium oxide (CdO).

Keywords: CdO, Thin film, Chemical Bath Deposition, Growth Kinetics

ميكانيكية النمو لأغشية اوكسيد الكادميوم ألمرسبه كيميائيا

الخلاصه

في هذا البحث تم تحضير اغشية اوكسيد الكادميوم باستخدام تقنية الترسيب بالحمام الكيميائي حيث استخدم ملح خلات الكادميوم كمصدر لايونات الكادميوم . تم دراسة تاثير مختلف ظروف الحمام وهي تركيز ايون الكادميوم ,زمن الترسيب ,درجة حرارة المحلول و قيمة ألداله الحامضيه على معدل الترسيب والسمك النهائي للغشاء.عملية التلدين اجريت في الهواء بدرجة حراره 573 كلفن ولزمن يساوي 15 دقيقه من اجل تحويل غشاء هيدروكسيد الكادميوم الى اوكسيد الكادميوم. تم اثبات تكون غشاء اوكسيد الكادميوم بواسطة تقنية حيود الاشعه السينيه.

Introduction

Semiconductors are of considerable technical interest in the field of electronic and electro optical devices [1].The commonly used methods of preparation of semiconductors thin films are vacuum thermal evaporation, spray pyrolysis, sputtering, sol gel and molecular beam epitaxy. 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 technique involves the application of controllable chemical reaction; the reaction rate can be controlled by the adjustment of pH, temperature, and the relative concentration of various reactants in the solution. The semiconductor oxides such as CdO, ZnO, BaO, Fe_2O_3, BiClO, and Cu_2O thin films have been studied extensively as a result of wide range of technical applications [7, 8]. Cadmium Oxide (CdO) is one of these important semiconductors oxides, which has high optical

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properties, shows high transparency in the visible region of solar spectrum, and has high electrical conductivity [9]. Although it is difficult to obtain simultaneously a high transmission coefficient and good conductivity these properties of CdO thin films preparation has been carried out [10].

Theoretical part:

Although there are different pathways that can occur in the (CBD) process, the kinetics can vary widely from one deposition another, in other words from film deposition to another. Regarding the time taken for the deposition, some depositions can be completed in a few minutes less, while others can proceed for days and still be far from terminated.

The deposition consists of different phases:-

ί) Nucleation (Induction): The initial step is usually a high activation energy, in which reactive centers are formed as reaction catalyst, and where no observed grow.

ίί) Termination step , in which the reagent becomes depleted and the reaction begins to slow and eventually step [11] .

This type of growth kinetics often occurs regardless of the deposition mechanism. For the ion- by - ion growth, the deposition begins only when the negative ion concentrations are high enough to allow nucleation to occur, while the induction time corresponds to build up of negative ion concentration. Growth occurs on these initial nuclei, along with new nucleation, approximately linear region of growth. As the limiting reactant is used up, growth will start to slow down and eventually stop due to depletion of the reactant. For the cluster mechanism, the hydroxide cluster can start to be adsorbed on the substrate immediately after immersion of the substrate in the deposition solution. Yet experiment has shown that the film growth often does not occur for some time. If the reaction is allowed to proceed until the termination stage is reached, the terminal thickness of many (CBD) films is typically several hundred nanometers, although it may reach a micron or more in some cases .This terminal thickness depends to a large extent on the deposition parameters [12]. The parameters are implying the pH value, Cadmium ion concentration, deposition time, and deposition temperature. The rate of reaction and deposition depend on the super saturation (S), which represented the ratio (IP/SP=S), (that defines the super saturation of the ions; where (IP) is the ionic product of the reactant ions, which must exceed the solubility product (SP) of compound material [13]. The lower super saturation involves the formation which will be slower. The more concentration of $[OH^-]$ in terminal thickness of many (CBD) film is typically several hundred nanometers, although it may reach a micron or more in some cases .This terminal thickness depends to a large extent on the deposition parameters. The parameters are implying the pH value, Cadmium ion concentration, deposition time, and deposition temperature [14, 15].

Experimental part:

Cadmium Oxide films were prepared from cadmium nitrate, provided from (SEELZE-HANNOVER) with 99.99% pure. The deposition of CdO films is achieved by using cadmium nitrate solutions, consisting of 20ml cadmium nitrate ($Cd(NO_3)_2$) ,20ml of 0.5M potassium hydroxide (KOH), 2ml hydrogen peroxide (H_2O_2), and deionized water. They 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. The reactants were mixed slowly at room temperature with continuous stirring. 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 or epitaxial centers water, after that washed and dried for use. Substrates were then immersed vertically in a beaker containing the reaction mixture. The beaker was placed in a water bath. The solution was stirred with a magnetic stirrer type (LMS-1003) as illustrated in Figure (1).Then, it was heated with continuous stirring to the required temperature of deposition, the pH measured by pH meter type (HANA, pH211 Digital), where the measure of pH is at the start of the deposition process. Substrates were then taken out after a suitable time; they were washed with distilled water, and then dried. After wards KOH was added to the solution, the color of solution become milky. 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 is converted to CdO film after the annealing process, due to the removal of H_2O vapor from the film structure .Film thickness is measured by optical interferometer method. 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. X-ray measurements were performed using (lab X-XRD 6000/shimad2u) of λ= 1.54 A° from Cu - Kα.

Results and discussion:

X-Ray Diffraction

To study the annealing effect for film, which has been deposited under optimum conditions with a temperature of 353K° and pH= 9, M=0.2, and deposition time of 30min, the annealing is preformed in air at temperature of 573K for 15 min. The XRD pattern of as deposited and annealed films onto glass substrate are shown in Figure (2), which shows the change of film after annealing. From the pattern of as- deposited film, it can be observed that peaks at 2θ= 29.449 ,35.546 ,38.371 ,48.964 ,and 52.31° appear, which correspond to diffraction from H(100) ,H(101) ,H(002) ,H(102) ,and H(110) crystalline planes respectively. These values of 2θ and its crystal planes are comparable with standard data from $Cd(OH)_2$ ASTM card , and confirm that the diffraction is from hexagonal phase of polycrystalline $Cd(OH)_2$, while the XRD pattern of annealed film, reveals the diffraction peaks at 2θ=33.0261°, 38.307°1, and 55.3135° corresponding to diffraction from C(111) , C(200) , and C(220) planes respectively , implying diffraction from cubic phase of polycrystalline CdO .

Kinetics of Growth.

1-Cadmium Ion Concentration Effect.

Figure (3) shows the growth is strongly influenced by the molarity of cadmium nitrate. The deposition rate increases with increasing cadmium ion concentration ,the terminal thickness first increases, passes through a maximum value, and then approximately saturate, with increasing cadmium ion concentration (as above 0.2M) .The increase in deposition rate infers that in any chemical reaction the reaction rate is proportional to the concentration of the reacting species .In the case, when the cadmium ion concentration is low ,the number of (Cd^{2+}) ions insufficient to combine with all the available (OH^-) ions ,but in the case of high concentration more (Cd^{2+}) ions become available to form $Cd(OH)_2$ that lead to greater thicknesses .

2- Deposition Time Effect:

The effect of deposition time on the terminal thickness is very obvious in Figure (4), which explains the growth of CdO films with deposition time at (80C°) and 0.2M of $Cd(NO_3)_2$. The deposition thickness increases with increasing deposition time especially in the first 25min where the deposition rate is much faster with a rate (5.88 nm/min), while for longer deposition time the rate decreases to (3.13 nm/min). Therefore, the variation in thickness with longer time is very low, so the value of (188.52 nm) could be regarded as the terminal thickness. In the first 25 min, the film thickness increases linearly with time initially but saturates after some time at some terminal thickness. The leveling of the film thickness is due eventual reduction in the ionic product of $Cd(OH)_2$ in the solution to values about the solubility product and coagulation of colloidal particles of $Cd(OH)_2$ to form larger particles which cannot be adsorbed .This is an agreement with the results of many literatures[16,17,18].

3- Temperature Effect:

CdO thin films will be deposited if the ionic product (IP) of (Cd^{2+}) and (OH^-) exceeds the solubility product (SP) of $Cd(OH)_2$. Figure (5) shows the growth kinetics of CdO films with the deposition time at four different temperatures. Throughout the Figure, we can observe that the terminal thickness increases with increasing bath temperature, where the heating of the solution helps the decomposition of the reactants and produces the ions which are very necessary for film formation .In addition to that, it provides kinetic energy to the ions, resulting in increased number of collisions and hence combination to form $Cd(OH)_2$ leading to increase in terminal thickness with increasing bath temperature .

4- pH Effect

From Figure (6) it can be observed that the terminal thickness decreases with increasing [pH] values where the maximum value of [pH] is (11.9). A minimum terminal thickness is obtained opposite to the [pH] value of (8.1). On the other hand, a decrease takes place in thickness due to rapid reaction, and only precipitation will occur. When the [pH] of the solution increases further most of the (Cd^{2+}) and (OH^-) ions spontaneously react to form $Cd(OH)_2$ in the bulk of the solution, and hence to lower terminal thicknesses at high [pH] values of the bath[1]. That the deposition thickness decreases with increasing in pH value. Therefore throughout Figure (7) it can be noted as the (KOH) concentration increases, the (Cd^{2+}) ions are generated very slowly, therefore the rate of precipitation is very much higher.

Conclusions:

1. By annealing process, the hydroxide phase of as-deposited film is converted to oxide phase.
2. The terminal thickness and deposition rate of CdO thin films increases with increasing of cadmium ion concentration.
3. The terminal thickness of CdO films increases with increasing deposition time and then saturate with (188 nm) at 30min as a result of reduction in the ionic product from the solution.
4. The terminal thickness and reaction rate increases with increasing bath temperature.
5. The thickness and deposition rate of CdO films pH value of preparation solution.
6. The optimum conditions for prepared CdO films by CBD technique and by using cadmium nitrate salt with potassium hydroxide as a complex agents are 0.2M, 30min, 80C, and pH equal 9.

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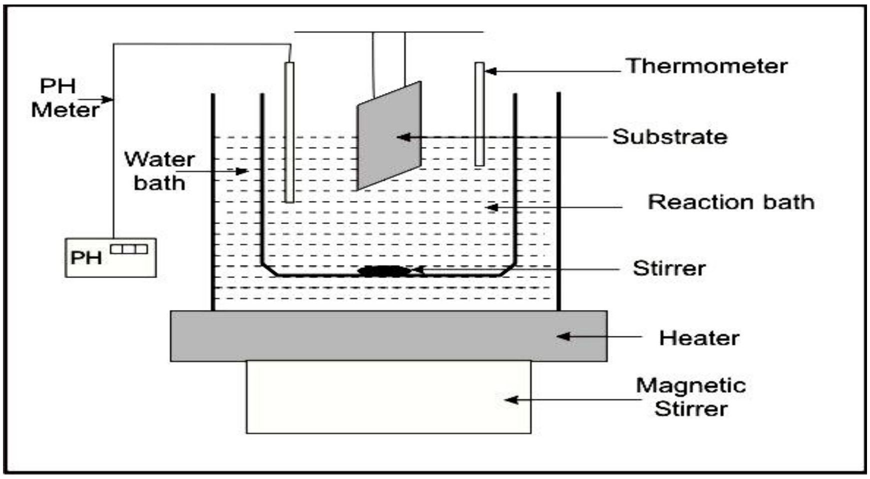

Fig. (1) Experimental arrangement for the deposition of CdO films.

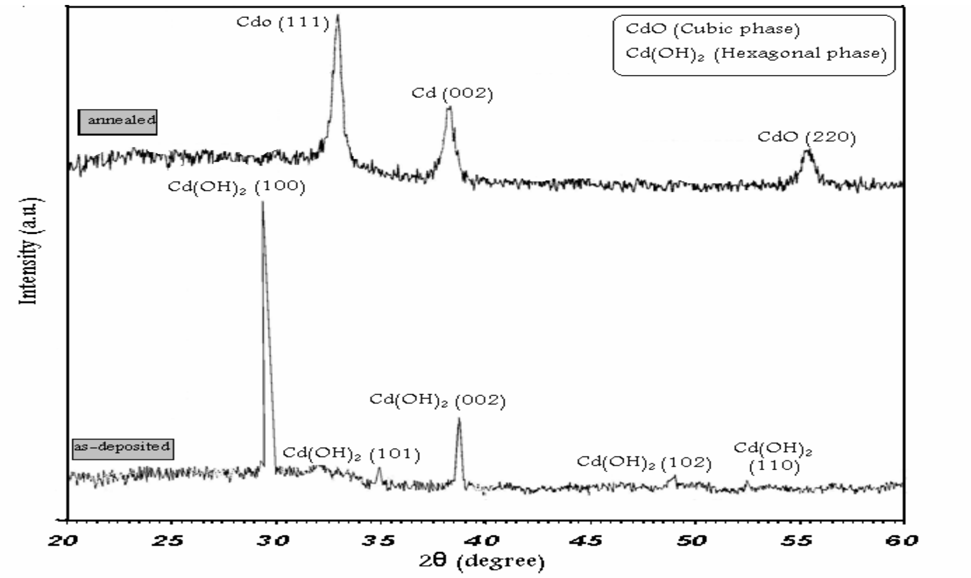

Fig. (2): The X-ray diffraction of as-deposited and annealed CdO films

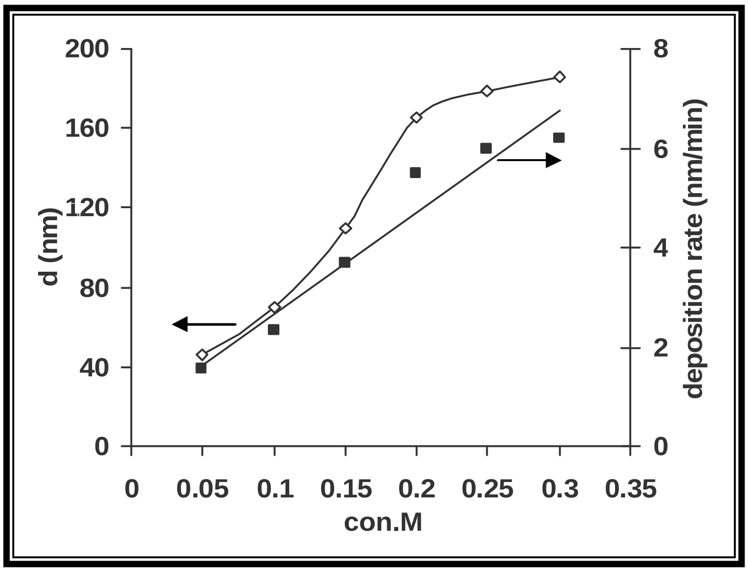

Fig. (3): Terminal thickness and rate of deposition of CdO films as a function molarity value at 353K°.

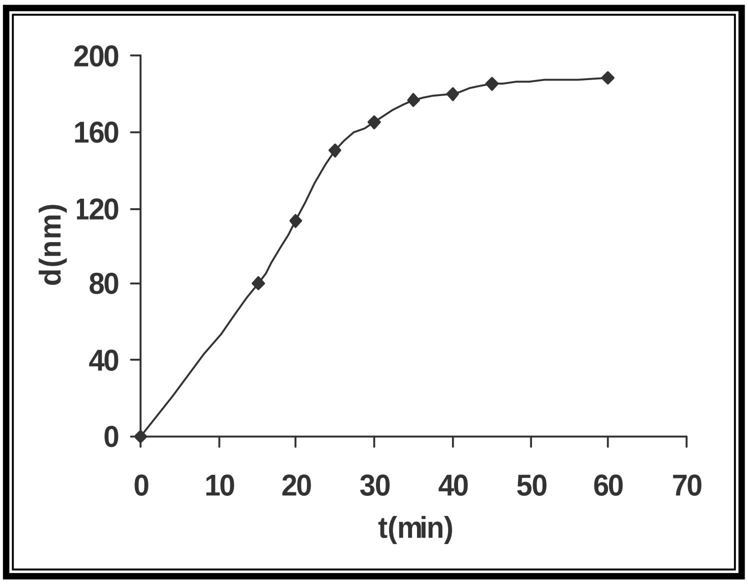

Fig.(4) :Thickness of CdO thin film as a function of deposition time .

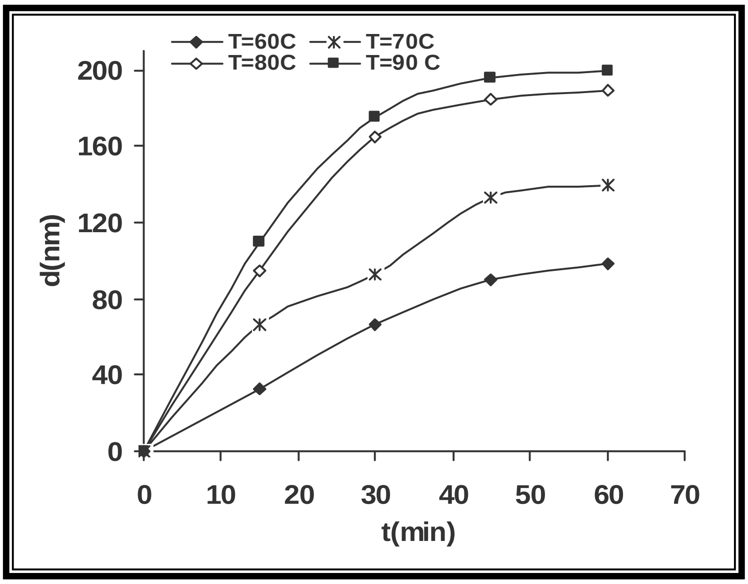

Fig. (5): **Thickness of CdO thin film as a function of deposition time at different deposition temperatures with M=0.2.**

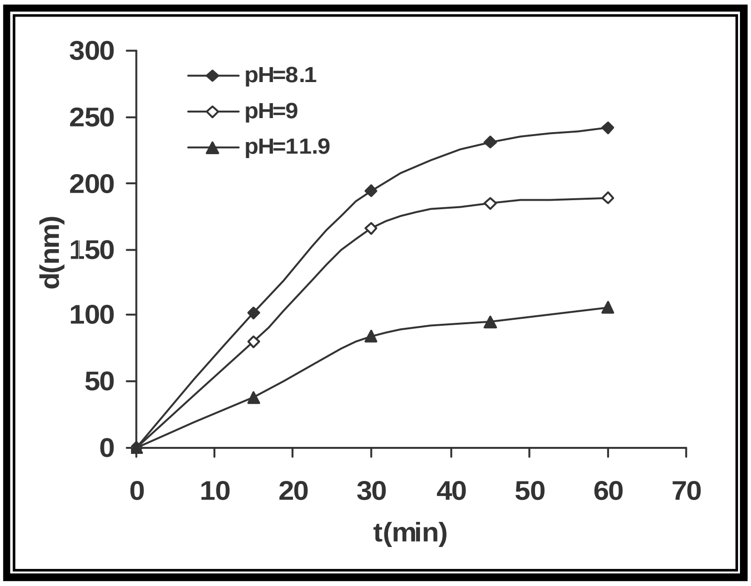

Fig. (6): Thickness of CdO thin as a function of deposition time at different [pH] values with M=0.2, and 353K°.

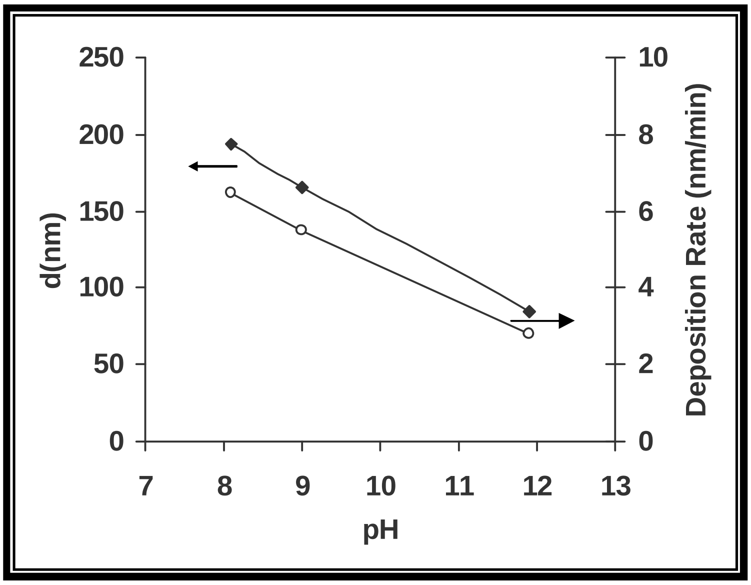

Fig. (7): Terminal Thickness and rate of deposition of CdO thin film as a function of [pH] values M=0.2, and 353K°.