# Affect The Precipitation Times on The Prepared Nanocystals of CdS by Chemical Bath Deposition

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**Abstract:** The nanocrystals of Cadmium sulfide (CdS) are synthesized via chemical bath technique and deposited onto  glass substrates commercial plates at different time (60,120,180and 240 )minute respectively ,then annealing at 300°C to enhance the adhesion and recrystallization the films . The results confirmed that the structural features the examined by X-ray diffraction(XRD) are wurtzite structures for all samples  while the atomic force microscope( AFM ) examinations give prefect analyses and proved that  increasing  the precipitation times effect on the morphological surfaces become clear to be more homogenies and compact , the roughness increased on  the surface with increasing the deposition time expect at 240 mintue decrease , therefore ;  can be notice that  average roughness around (1.83, 2.99,3.24 and 3.13)nm series . The absorbance spectra of the deposited CdS nanocrtysals illustrate   high absorbance in visible region, on the other hand observes that the optical energies gaps increase slightly for all films with increasing the deposition times of the samples and register about (2.3, 2.4, 2.5 and 2.65) eV respectively. So note that the colors of  solutions is yellow and remain temperature at   (80)°C during period preparation in the bath and value of PH is 10.5 of solutions.

**Keywords**: chemical bath technique, structural and optical properties , Cadmium sulfide, nanocrystal , deposition time**.**

## 1.Introduction

The different features of Cadmium sulfide (CdS) and the preparation of methods are studied by many researches for several years since 1990. CdS has direct energy gap 2.42 eV, belongs to II-VI chalcogenide semiconductor, which makes CdS a more suitable semiconductor for absorbing visible light. [1]. Recently the Semiconductor such as CdS nanocrystals (NCs) become the most important subject as regards their marvelous properties in electronic, optical and other features that can lie among the  bulk semiconductor crystals ,the molecules and atoms [2] .CdS thin films are employed in various aspects widely in technological applications such as , in lasers [3] , photo electrochemical cells[4], thin film solar cells [5-8] to improve the efficiency, biological imaging[9] , electrochemical cells[10], light emitting diodes [11], optical waveguides, gas sensors, optical switching and single electron transistors ,and photo electrochemical water splitting [12] .Several techniques are utilized for deposition thin films of CdS, such as SILAR method [13], sputtering [14], molecular beam epitaxy [15], chemical bath technique [16], chemical spray pyrolysis [17], and close space sublimation (CSS)and so on. In order to get on the film structure with high quality must be varied pH value during the growth [18]. Some the studies found that CBD technique prepares CdS thin films  with exist

EDTA ligand (ammonia and/or ethylenediamine) at variation concentrations  to controll on quality of the structure [18].Others authors used two substances diethylenetriamine (DETA) and ethyl alcohol (EtOH) in Mixed Solvothermal Strategy to get on the highest energy facet of CdS nonoflowers ,the facet preferred is (002 )in wurtize CdS ,this facet to the enhancement  the photocatalytic activity [19] in the present paper, investigates us CdS nanocrystals were synthesized via CBD route  on glass substrate under various precipitation time at  same the preparation conditions ,the paper explains influence increasing the deposition time on  the optical and structural features for the films with comparison the results among them , this method suitable or useful for making thin films in the solar cell.

## 2. Experimental Work

In the current work, the deposited films of cadmium sulfide on the glass substrates after the cleaned very well and utilized the chemical bath deposition route (CBD) to deposition, this technique offers the deposition of a thin uniform film with a minimal thickness on the substrate surface. Also can use the methanol and acetone to clean the glass substrate for 10 minute by an ultrasonic cleaner then use deionized water after that dried. Aqueous solutions of 240 ml each of 0.384gm of Cadmium Chloride $CdCl_2$ as a source of cadmium, and 0.768gm of Thiourea $CS(NH_2)_2$ as a sulfur source was employed . First, 240 ml of $CdCl_2$ solution placed in a 500 ml beaker under vigorous stirring (about quarter o'clock). Then add sodium hydroxide to solution of cadmium chloride   drop by drop with continuous  strongly stirring and keep  value of pH is (10.5) to obtain on the colorless solution .Then under continuous stirring, 240 ml of $CS(NH_2)_2$ solution was added to $CdCl_2$ solution with added distilled water to complete 500ml with continuous stirring about 20 min . The glass substrate hang vertically into the solution in beaker with maintain the temperature inside the solution about 80±5 where the growth on the glass slide. The deposition time was change from (60,120, 180 and 240) minute, after that the color becomes yellow, the deposited films were pulled out the bath then  washed by using the distilled water and  dried .  The CdS films that obtain from this route  are  good films because it was homogenous and had high adhesion  on commercial glass slides. Finally, all films of CdS annealing at (300°C) about (45 min). The SP-3000NANO optima (UV-Vis spectrophotometer) used to study the transmission and absorbance of nanocrystals of CdS at (200-1100) nm, whereas SHIMADZU-6000  (Cu Kα with $\lambda$1.54056 Å) measured the crystals structures of films with comparison by XRD standard .As well as, the topographical of surfaces or atomic force microscope( AFM) are recorded by scanning probe microscope AA3000  supplied by Angstrom Advanced Inc.

## 3. Results and Discussion

### 3.1. *Structural Properties*

The analyses via XRD as in the fig.(1) illustrates the crystalline structure of the CdS nanocrystals are prepared by CBD route at  constant temperature of bath at 80 °C along period of deposition on the glass substrate  with varying  deposition time  (60,120,180 and 240)minute respectively. The results of these  films found that the hexagonal structure exists in all the polycrystalline films that have diffraction peaks Compatible with (JCPDS no. 77-2306) as ref. [19]. The plane (002) has high intensity of all samples the CdS nanocrstyls with (001) plane as preferent Orientation for wurtize CdS [20] .The lattice constants of these samples are   a=b= 4.1409A° and   c= 6.7198 Å, also the grains size average (D) of nanocrystals about (22.3nm) are calculated from FHWM at 2Θ = 24.93° using Scherr´s equation as in [21].

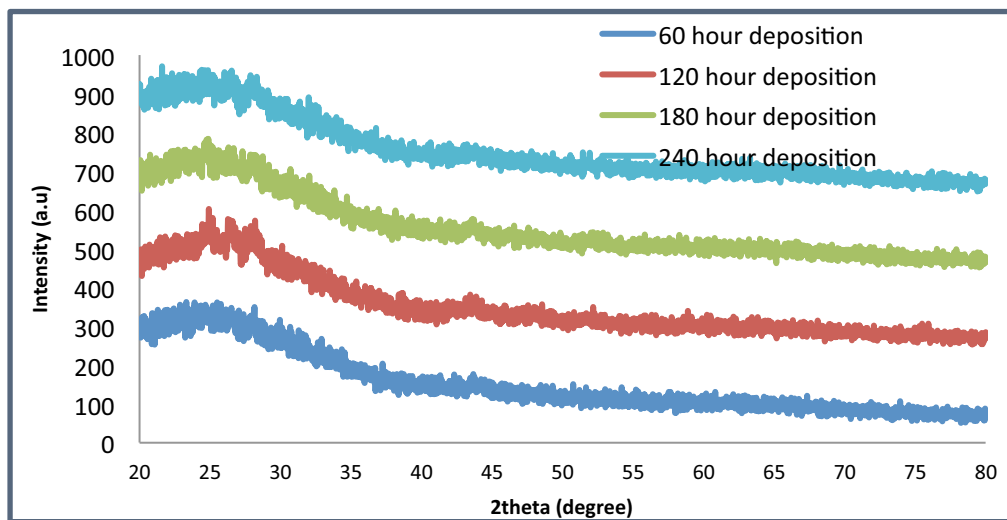**Figure .1** Thin films of CdS precipitated onto glass substrates by CBD for various time

$$D = \frac{0.9\lambda}{\boxed{}\,Cos\theta}........(1)$$

D is the grain size average of nanocrystals, all parameters in above equation mentioned in [22]. This obvious that nanocrystal particles are formed on the films this agrees with [22]. The 2θ locates between 20˚ to 80˚. At most the CdS has many structures are zincblide (cubic), wurtize (hexagonal) and third is the rock salt, the wurtize structures are more stability and more favorable in made solar cells [2,8] according to the route which used to prepare Cadmium Sulfide[ 6]. CdS can be transfer from zinc blend (ZB) to wurtize phase due to formation of defects and stacking faults inside the materials [7]. The2theta 24.93,26.59,28.19,43.44,52.168,58.88 and (75.44) and the reflection planes (100), (002), (101), (110), (201), (202) and (105) of CdS thin films for various deposition time that confirm the structures were the hexagonal structure, can observe that the intensity increasing for thin films of CdS with deposition time increase from 60 min. gradually to 240 min. This indicates that the deposition for 240 min. is the optimized precipitation time for which the crystallinity of the samples so as to reach the maximum [22] , also the broadening of the peaks belong to formation the nanocrystals of the CdS samples. The CdS nanocrytsals strongly depending on the conditions of preparation, deposition time, the bath temperature, heated treatment, PH value and concentration of the reactants .In some the studies of XRD on Cadmium sulfide substrates interfaces have illustrated that the films which have the good quality may form on ITO substrates or glass but not on substrates from silicon as in [23]. When the material of CdS annealing at 300 °C will be the wurtize phase is more stable and predominant than the cubic phase [24]

3.2. *Atomic Force Microscope*

    The atomic force microscope of the prepared of CdS nanocysrals by CBD at different time of deposition (60,120,180 and 240) minute, has the high resolution and accuracy in the measurements can use to show the morphological surfaces of all films of the CdS prepared. The films grow apparently on glass substrates this agree with [2] .The surfaces were more homogenous and had continuous structure after increasing the time until reach at 4 hours. The images of AFM on the surface are taken at different regions, from the images, 3- Dimenations of AFM as shown in Figure.2 ( e, f ,g, and h) respectively,found that the average grains diameters of all samples are uniform and compact and the average of roughness to films are augment as shown in the Table 1 below, is relation between the deposition Times ,and other parameters mention in the table, can notice that high roughness surface with roughness average (1.83,2.99 ,3.24 and 3.13) nm , as well as large peaks number occur the magnitudes of root mean square (2.17,3.35, 3.81and 3.66) nm ,respectively, found that the values of the roughness average and root mean square increased clearly when the deposition time of films increasing as a result of growth rate of Cadimum sulfide nanocrystals on glass, which

may due to high growth rate of all samples or may be influence of the growth solution on the films accompaniment to increase in homogeneity of the surfaces with increasing in roughness average values as appears in **Table 1** ,therefore the root mean square values  refer to increase the summits height.  It is important to know difference that touches in roughness values of samples at all hours as result of the homogeneous distribution of surfaces and the solution concentration of growth are increasing.
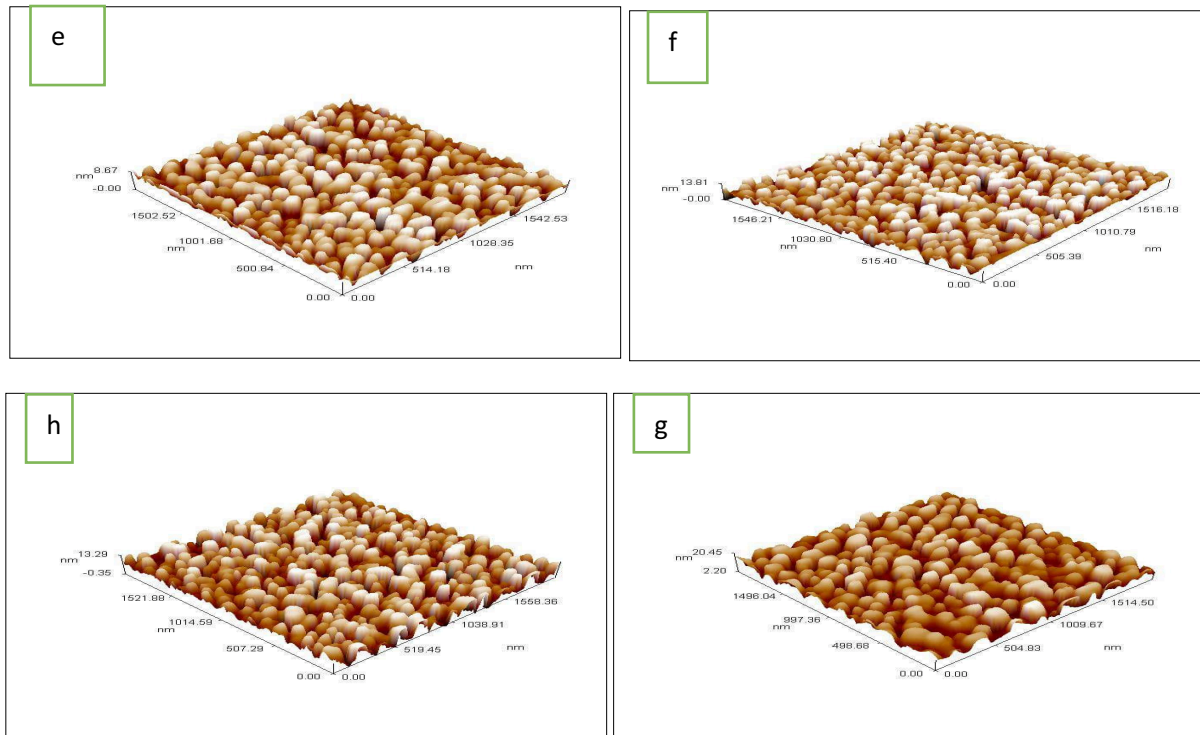


**Figure 2.** AFM of theCdS nanocrystals at various deposition times ,e- at 60 min. deposition , f- at 120min .deposition time in(3D)image ,g- at 180 min.deposition time in(3D)image , h- at 240 min. deposition time in(3D)image.

The surface skewness (SsK) is one of the important parameters of amplitude, it expresses from the asymmetry of distributions the height in histogram for the samples in 2-D images. SsK has two values positive or negative in this work appears only the value of negative because of the positive values point to flat surface while the CdS samples at different deposition time (60,120,180and 240) min. are given negative values of this parameter which refer to the surface can be bearing with holes, also there another parameter is the kurtosis surface (Sku) that depict summits for the topography surfaces have found that all films fall within surface distribution of Platykurtic which point at the flat distribution with reason the values of surface kurtosis were minimize from 3 but the nearest value to 3 is near to be more flat as observed in (60,120 and180)min. with 2.27,2.17and 2.02 respectively, while the sample at (240) min. illustrates  the least value as evidence  to the distribution of minimum due to the inhomogeneity covering . Peak-Peak (Sy) represents the lowest or highest values of peaks on surface CdS samples at different deposition time on glass substrate where the sample at deposition for one hour registered the less value of Peak-Peak is 8.67nmas proof on the stability distribution and the homogeneous, whereas the deposition time at 3 hours of CdS appears the Sy as height value because of the high peaks and valleys on the surface of sample and this agree with results of roughness [25]. The final factor of amplitude is Ten-point height (Sz) define that the distinction among the five summits the highest and lowest, to optimize the average of the peaks height. The Sz values as in Table

(1) the below, the mentioned values from the expected results of Sz , low value of Sz is registered for films at deposition time 60min. which is evident of the low roughness of surface with value5.5nm.

**Table** .1 The relation between the deposition time, Amplitude parameters and average diameter of CdS thin films by CBD.

| deposition Time (min.) | Average roughness [Sa] (nm) | Root Mean Square Sq(nm) | Surface Skewness [Ssk] | Surface Kurtosis [Sku] | Top Ten Height [Sz] | Peak-Peak [Sy] (nm) | Average diameter (nm) |
|---|---|---|---|---|---|---|---|
| 60 | 1.83 | 2.17 | -0.462 | 2.27 | 5.5 | 8.67 | 67.01 |
| 120 | 2.99 | 3.35 | -0.37 | 2.17 | 13.8 | 13.8 | 97.30 |
| 180 | 3.24 | 3.81 | -0.263 | 2.02 | 8.4 | 16.4 | 83.71m |
| 240 | 3.13 | 3.66 | -0.241 | 1.96 | 7.73 | 13.6 | 97.88 |

*3.3.Optical Properties-Absorption spectrum &Energy Gaps*

From absorbance Measurements asdepicts in Fig (3) of CdS thin films at various deposition time (60,120,180 and 240 hours) by CBD .  It can be found that the energies band gap values the CdS nanocrysals from absorbance spectrum as function of wavelength lead to appear four peaks at 551,517,496and 467 nm, respectively, for all samples. This reveals that the shift in the
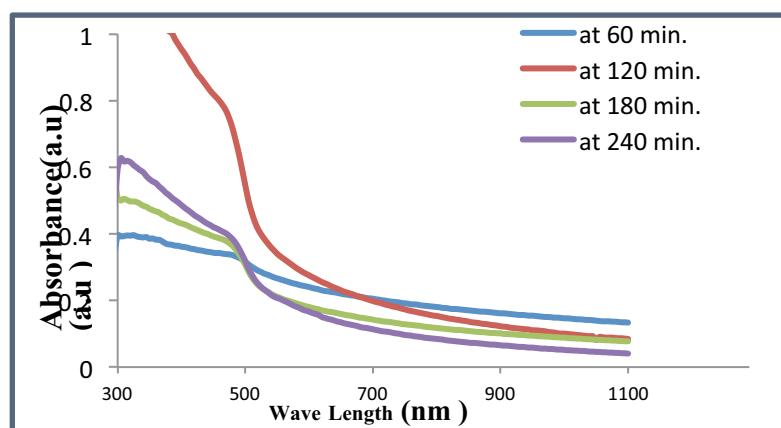


**Figure3**.Absorbance spectrum of the CdS nanocrystals at various  deposition time  (60,120,180and 240min.) on glass substrate.

Absorbance edge toward a blue shift. Where the peaks at 496 and 467 nm illustrate influence quantum confinement due to the formation of CdS nanoparticles [26-31]. All thin films of CdS nanostructures at different deposition time was shown that the shift in the absorbance peak toward the highest energy

or (the lowest wavelength) as compared to that of the bulk CdS (516 nm) at room temperature [32-33]. Therefore the results give high absorbance in the visible region of all films for CdS .As result of vary electron confinement in material leads to appear different shapes of CdS nanostructure and therefore the peak absorption is changed [32] The optical energy gaps magnitudes were calculated by extrapolating the linear $(\alpha h\upsilon)^2$ vs. photon energy in the abscissa (x axis) plots derived from the Stern relation [31]as in

$$\alpha h\upsilon = A\sqrt{(h\upsilon - Eg)} \ldots\ldots\ldots 2$$

 Where Eg represents the energy gap , h Planck's constant ,while A as constant , the band gaps of CdS are estimated  to be a little higher than the mentioned magnitude from the bulk material of CdS [37] Fig (4),which indicates a direct optical transition. The optical energies gaps values of the CdS nanocrysals   were found increases from (2.3, 2.4, 2.5 and 2.65) eV with increasing disposition times at (60,120,180 and 240) min., respectively. This behavior is identical to the results of previous research [34 , 35] as results of decrease sizes of crystals under a specific size, be associated with their exciton Bohr diameters. The levels between the bands have space being to be larger for this reason the energy structure varies from aquas continuum band to discontinuous or that named discrete and as a result of this the gaps increase [36].
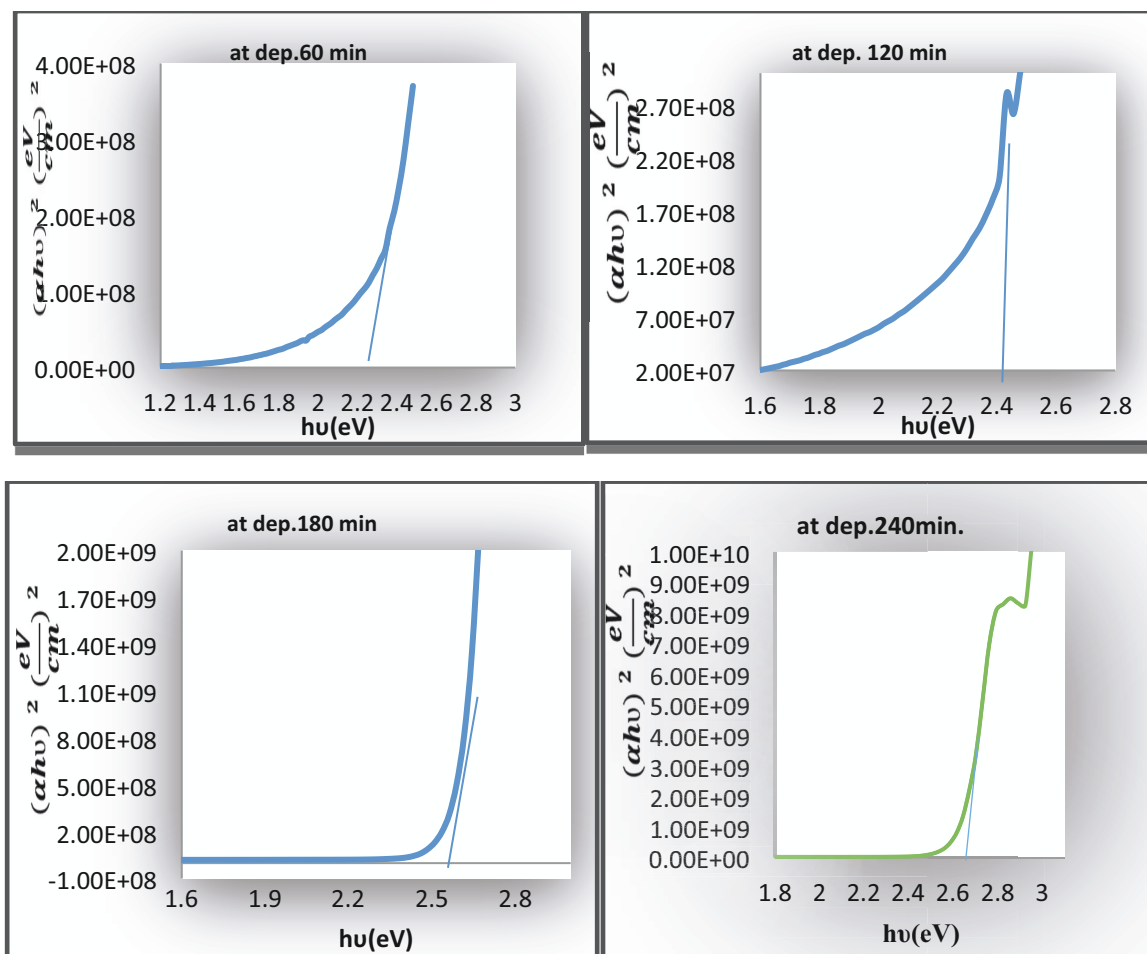


**Figure 4** .The values of energy gaps  for  as prepared CdS nanocrystals vai CBD at various deposition times .

## 4. Conclusions

The chemical bath deposition route utilized to prepare the nanocrytsals of CdS thin films at various deposition times (60,120,180 and 240 hours) respectively on glass substrate was easy an inexpensive and low hazard technique. XRD found that all structures of these films are hexagonal structures (Wurtize). The energy gap of all films increase gradually at  different the deposition time which  have values in the range from 2.3 eV (for deposition  time 1hour) toward 2.65eV (for deposition Time 4hour),small deferent in values due to quantum confinement. also can be employed these nonocrystals as thinfilms in solar cells as window layer.

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