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Effect pH on Structural and Optical Properties of Nanostructure CdS Films Prepared by Chemical Bath Deposition Technique

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A R T I C L E I N F O

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A B S T R A C T

Nanostructures CdS films were prepared by chemical bath deposition technique on glass substrates, where the cadmium nitrate salt was used as a source of cadmium ions and thiourea (SC(NH2)2) as a source of sulphide ions(S-2). The deposition were carried out at different pH values. Structure of these films was characterized by X-ray diffraction and atomic force microscope (AFM). CdS films deposited have cubic(zinc blende) structure and the grain size of nanoclusters decreases with increasing pH value in solution. The optical properties study by transmission spectra and the films have highly transmittance in visible region of spectrum and reach to more than 86%. The CdS films have band gap increase from 2.42 to 2.58 eV with increasing pH value in solution.

Introduction

Nanostructured materials are attractive and interesting materials for optoelectronic applications because of their unique chemical and physical properties, which differ from those of bulk materials or single atoms[1].

Cadmium sulphide(CdS) is an n-type semiconductor with a direct bandgap of 2.42 eV that can be employed in a large variety of optoelectronic devices, such as highly efficient CIGS and CdTe solar cells and photodetectors, as well as gas sensors, field effect transistors, and LEDs [2].

There are various methods employed for deposition of CdS thin films such as spray pyrolysis, pulsed laser deposition,chemical vapour transport ,vacuum evaporation, electrodeposition, sputtering , successive ionic layer adsorption reaction and chemical bath deposition [3-10].

Particularly, the CBD technique is an easy low-cost process, and useful for large-area industrial applications, reason for which it has been very used in the current days. CBD is a process to achieve high quality films, which are obtained by adjusting the pH, temperature and reagent concentrations. Normally, for obtaining CdS thin films by chemical bath deposition in aqueous solution a cadmium salt is used as the Cd ion source, thiourea as the sulfur source, a base to adjust the pH of solution, and a ligand to control the precipitation of chalcogenides and hydroxides. As far as we know, CdS thin films have been mainly obtained through CBD with ammonia and/or ethylenediamine (Lewis base) ligand [11]. In CBD, the nucleation and particle growth to form CdS film on a substrate is limited with two processes involved in hydrolysis and deposition of material on the substrate immersed in the solution. To overcome the harmful influences of hydrolysis, and for better quality surface CdS thin films, optimal processing parameters and additive complexing agents for metal ions should be chosen. Indeed, the CdS films that were prepared via the solution route have a nanostructured surface with grain dimensions less than 100 nm in diameter or are

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nanocrystalline CdS thin films consisting of needle-shaped grains [12,13]. Beside this, films that are flat, homogeneous, green-yellowish, transparent with very good adherence to the substrate, and possess a preferential orientation, were also reported [14]. In the present work, we report the chemical bath deposition of nanostructure CdS thin films and their characterization. The effect of pH on structural, morphological and optical properties of these films is investigated with the objective to optimize the conditions of the deposition process

Experimental

Cadmium sulfide thin films have been deposited on glass substrates using the chemical bath deposition technique. Glass slides (75×25×1 mm) were used as substrates. The substrates were degreased in HCl, washed in detergent and rinsed in distilled water dried in oven at 80oC. The CdS films was grown on glass substrate by using the cadmium nitrate salt[Cd(NO3)2 .4H2O] in molarity of 0.05 M as a source of cadmium ions(Cd+2) and 0.05 M thiourea [SC(NH2)2] as a source of sulphide ions (S2-). Ammonia hydroxide solution (NH4OH) 30 % was added slowly to adjust pH from 9 to11. The solution was stirred to ensure homogeneous dissolve about 15 minutes. The bath temperature was kept at 75°C for 2h and under unstirred condition. After the deposition, the CdS films were washed with methanol ultrasonically to remove the loosely adhered CdS particles on the film and annealed in air at 673 K for 1h using furnace model Yamato FM 27. Film thickness is important parameter in the study of film properties. For thickness measurement, gravimetric weight difference method with the relation t=m/(ρ×A) where, m is the mass of the film deposition on the substrate in gram,A the area of the deposited film in cm2 and ρ the density of the deposited material (CdS=4.69g/cm³)in bulk form[15]. The maximum thickness for CdS thin film was 532 nm. The X-ray diffraction(XRD) analysis was carried out using X-ray 6000(Shimadzu) diffractometer with Cukα radiation (α-1.541 Å) at 40 kV and 30 mA . The surface morphology, grain size and surface roughness were analyzed by CSPM AA3000 (Angstrom Advanced Inc) atomic force microscope (AFM).The optical transmission spectra were investigated by UV-Visible Spectrophotometer (Cintra 5) GBC-Astrural).

Results and discussion

Reaction Mechanism

In the growth of the CdS thin film from chemical bath, ammonia as the complex agent to bind the Cd^{2+} ions. Formation of complex ion is essential to control the rate of the reaction and to avoid the immediate precipitation of the compound in the solution. The metal complexes hydrolyses slowly to generate the Cd^{2+} in the solution. Thiourea furnishes the necessary S^{2-} ions by hydrolysis. The reaction mechanism for the formation of CdS could be understood as follows[16].

Ammonia hydrolyzes in water can give out OH^-:

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^- \quad \text{..... (1)}$$

The source of Zn^{2+}:

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

Cd^{2+} and NH_3 form a complex species of cadmium $[Cd(NH_3)_4]^{2+}$ (to slowly release Cd^{2+}):

$$Cd^{+2} + 4NH_3 \longrightarrow [Cd(NH_3)_4]^{2+} \quad \text{.....(3)}$$

Then

$$Cd^{2+} + 2OH^- \longrightarrow Cd(OH)_2 \text{ ..... (4)}$$

Thiourea hydrolyzes in alkaline solution to give S^{2-}(The source of S^{2-}):

$$CS(NH_2)_2 + 2OH^- \longrightarrow S^{2-} + CN_2H_2 + 2H_2O \text{ ....(5)}$$

Cadmium sulfide is formed:

$$[Cd(NH_3)_4]^{2+} + + S^{2-} \longrightarrow CdS + 4NH_3 \quad \text{.....(6)}$$

The pH of the reaction mixture is controlled by the addition of NH_4OH. The addition of NH_4OH increases the presence of NH_3 in the solution and there

by increases the concentration of metal complex $Cd(NH_3)_4^{2+}$ (equ. 3) .At the same time the addition of NH_4OH increases the OH^- ion concentration in the solution and thereby favours the hydrolysis (eqn.4) of the chalcogen precursor. In the presence of sufficient NH_3, Cd^{2+} ions exist in the solution mainly as $Cd(NH_3)_4^{2+}$. The deposition of CdS occurs when the ionic product of Cd^{2+} and S^{2-} exceeds the solubility product. At a given temperature the rate of formation of CdS is determined by the concentration of Cd^{2+} provided by $Cd(NH_3)_4^{2+}$ and the concentration of S^{2-} by the hydrolysis of $(NH_2)_2CS$.Ammonium hydroxide solution(NH_4OH) is added to the chemical bath to adjust the pH from 9 to 11under the control of a pH meter. Layer thickness is estimated by the weight method. Fig.1 shows the variation of CdS film thickness as a function of the pH value. The thickness decreases from 532 to 370 nm when the pH increases respectively from 9 to 11.

X-Ray Diffraction

Fig. 2(a ,b and c) shows X-ray diffraction pattern of nanostructure CdS thin films deposited on glass substrate at different pH values(9 to 11), where obviously can be notice that the diffraction patterns are consistent with the presence of pure polycrystalline CdS thin film with cubic (NaCl) structure, showing a number of characteristic peaks assigned for every value of pH**.** Fig.2(a) for pH=9, there are three peaks at 2θ=26.85 ˚,44.42 ˚ and 52.78˚, which corresponding to diffraction from (111) , (220) and (222) , planes respectively**.** Fig.2(b) shown the pattern of the film which deposited at pH of 10 reveals three peaks at at 2θ=26.72 ˚,44.18 ˚ and 52.54 ˚, corresponding to crystalline planes (111),(220) and (222). Fig.2(c) shows the XRD pattern of the film which deposited with pH value of 11 , we can be observed appearing peaks at 2θ= 26.41 ˚ ,44.07 ˚ and 52.49˚ which correspond to diffraction from (111) ,(220) and (222) crystalline planes respectively. All the above mention planes refer to the polycrystalline CdS with cubic phase. The diffraction intensity decreases with increasing pH value in solution. These values of 2θ and its crystal planes are comparable with standard data from CdS matches well (JCPD file no .10-0454). Similar results have been observe by CBD as reported in literatures[17,18].

The grain size (D) of the nanocrystalline films was estimated using Debye-Scherrer's formula,.

$$D = \frac{k\lambda}{\beta\cos\theta} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

where *k* is a constant taken to be 0.94, λ is the X-ray wavelength ,β is the full-width at half-maximum (FWHM) of the peak, and θ is the reflection angle[19].The equation (1) was used for the calculation of the crystallite sizes. The average grain size showed have an inverse relationship to the pH value, therefore the preferred orientation of CdO films at (2θ=26) are due to the controlled nucleation process associated with the low deposition rate. In other words when pH values increases the film thickness and 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 .The grain sizes of the CdS films decrease from 35 nm to13 nm with increasing pH value in solution .These results agree with those of many studies[20,21].

Force Microscope (AFM)

Figures (4, 5 and 6) show 2D and 3D AFM images of CdS films prepared at different pH values(9 to 11),respectively. As seen in Figures, the

CdS films is formed from nanoclusters. The average grain size of nanoclusters CdS film was obtained from AFM analysis software found decrease from 104 nm to 81 nm with increasing pH value in solution . This is in good agreement with XRD results which are mentioned previously. The root mean square (RMS) of roughness of nanoclusters CdS film was 10.7nm for film prepared at pH =9 and was 12 nm for film prepared at pH =10, also was 8.07nm for film prepared at pH =11. No colloidal of CdS particles was observed in AFM investigation.

Optical Properties

Fig.7 shows the effect pH value on the transmission spectra in for the range 400 – 800 nm. The average transmittance o f the CdS films in the visible region was found to be with a transmittance of more than 86%.We have found film transmission increases with increasing pH value in solution, where increasing pH value in solution causes an decrease of grain size as a result of decreasing the film thickness and consequence transmission increases .This behavior appreciably a constant procedure for all films were prepared by CBD as reported in literatures [22].

Optical band gap (E_g) of film was estimated from transmittance data. The photon energy (hν) and absorption coefficient (α) for direct optical transition are related by the following equation[23].

$$(\alpha h\nu) = B(h\nu - E_g)^{1/2} \quad \text{.....(8)}$$

Where hυ is the photon energy, α is the absorption coefficient, E_g is the optical band gap and B is a constant. For calculation of the optical band gap of CdS film, the curve of $(\alpha h\upsilon)^2$ vs. hυ was plotted. The E_g value of the CdS film was determined from Fig. 8 and it was found increases from 2.42 eV to 2.58 eV with increasing pH value in solution . The optical band gap of CdS film prepared at pH =11 is larger than that for pH =9 and pH =10 . These energies are slightly higher than earlier reported by [24-26] this can be attributed to the effect of grain size and the crystal quality was decreases with increasing pH value in solution [27].

Conclusions

CdS Nanostructure thin films are prepared by low cost chemical bath deposition technique with different pH values. The present method is simple, economic and easily reproducible for cadmium Sulphide. The XRD measurements indicate that the structure of the CdS thin films is cubic(zinc blende) . AFM measurements show the CdS films is formed from nanoclusters and the average grain size decrease with increasing pH value in solution. The optical transmittance measurement showed that the CdS films has flat surface, a high average transmittance over 86% in the visible region with presence of direct band gaps increase from 2.42 to 2.58 eV with increasing pH value in solution is a promising material to be used in photovoltaic devices, solar cells and detectors

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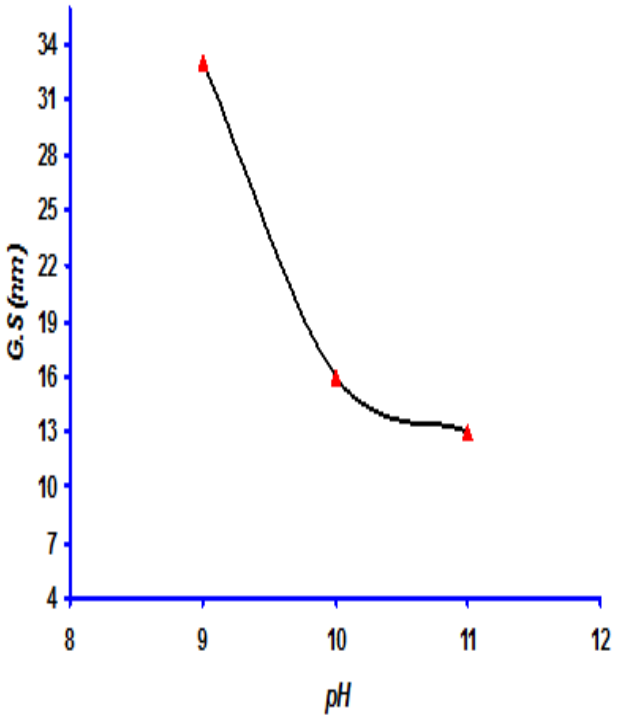
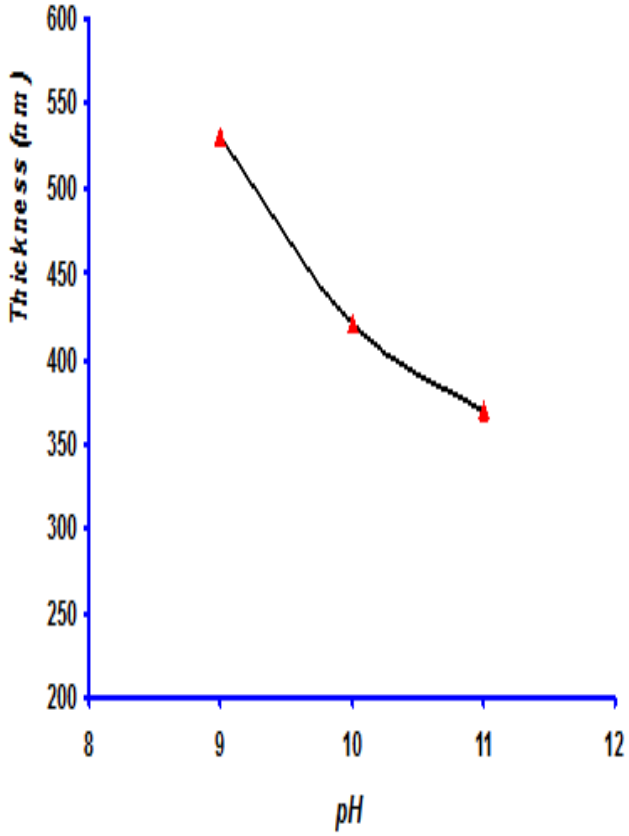


Fig. 1 .Terminal thickness of CdS films as a function of the pH value.



ig.3. The average grain size of CdS films as a function of pH of solution.

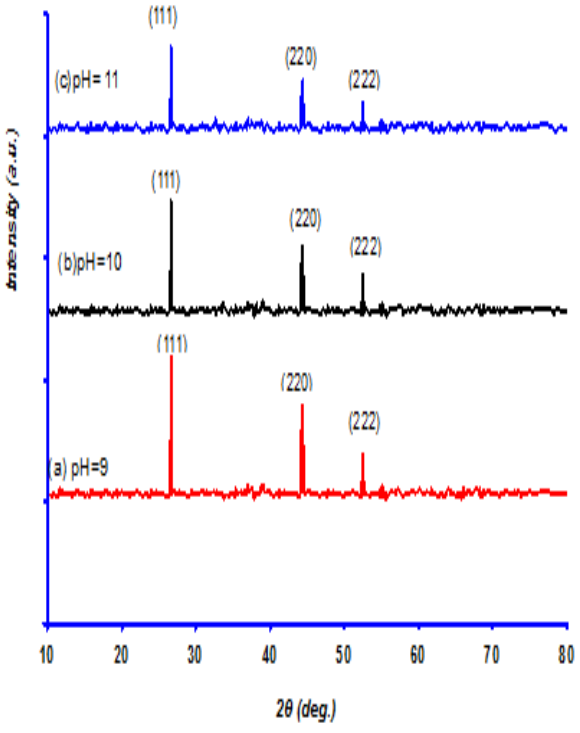


Fig. 2. The X-ray diffraction patterns of CdS thin films at different pH values.

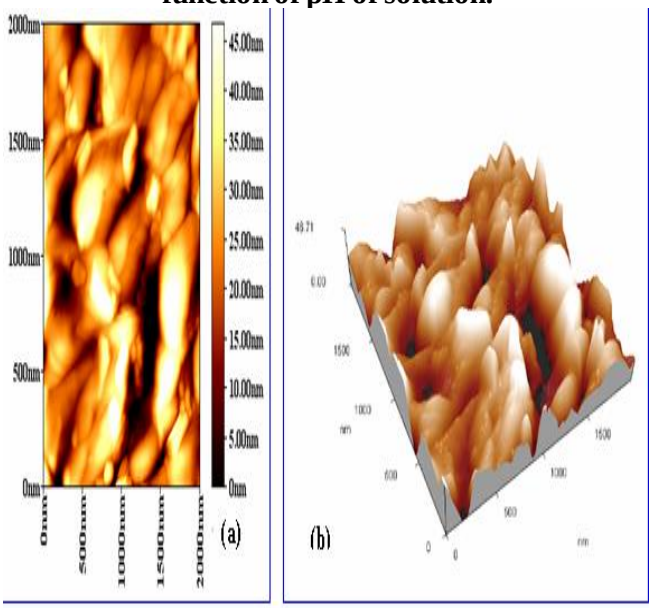


Fig.4: Atomic force microscopy images of CdS thin films at pH=9 M (a)2D and (b)3D.

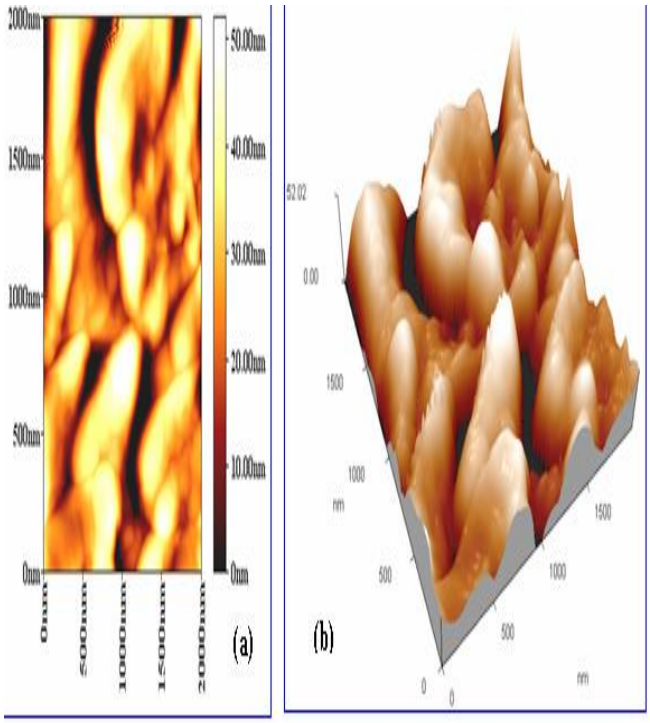


Fig.5: Atomic force microscopy images of CdS thin films at pH=10 M (a)2D and (b)3D .

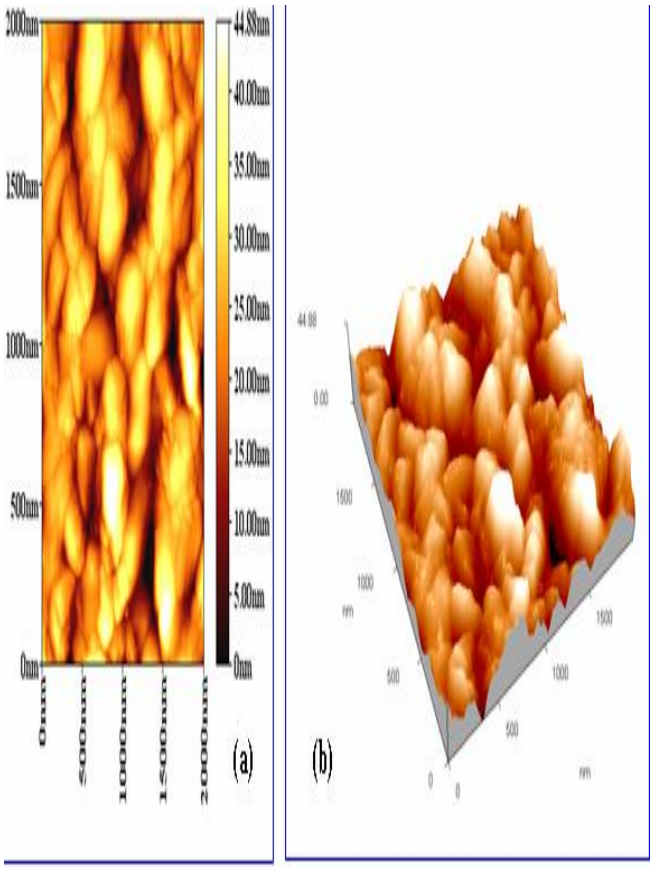


Fig.6: Atomic force microscopy images of CdS thin films at pH=11 M (a)2D and (b)3D.

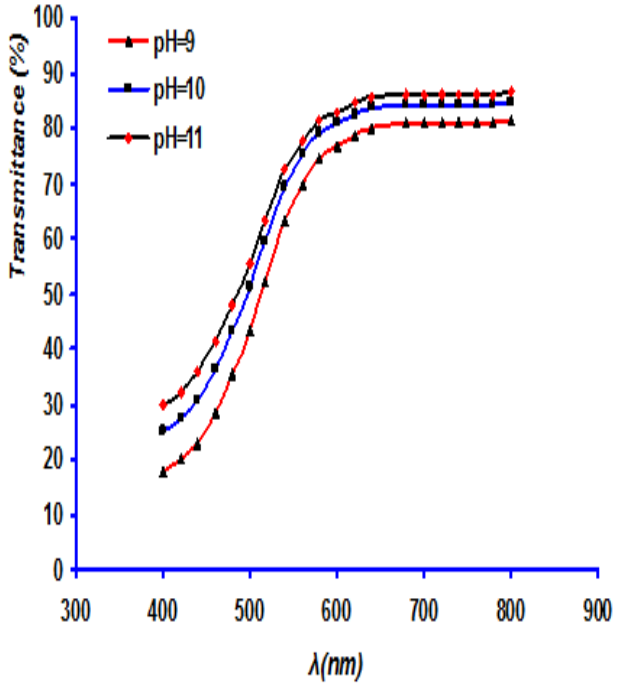


Fig.7. The optical transmission spectra as a function of wavelength of CdS thin films at different pH values.

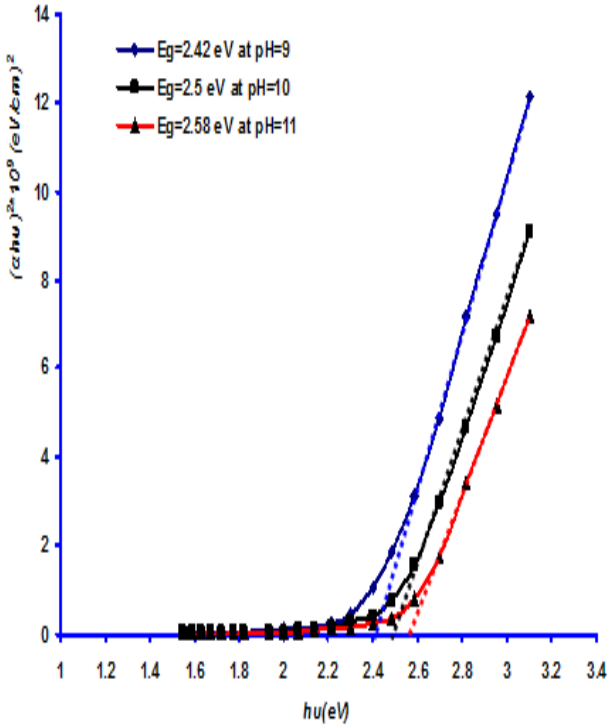


Figure (8): A plots of (αhυ)2 versus (hυ) of CdS thin films at different pH values.

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تأثير الدالة الحامضية (pH) على الخصائص التركيبية البصرية لأغشيه CdS نانويه التركيب المحضرة بتقنية ترسيب بالحمام الكيميائي

هاني هادي احمد عبدالله سليم خزعل فارس صالح عطاالله

الخلاصة

تم ترسيب تراكيب نانوية (Nanostructure) من أغشية CdS على أرضيات زجاجية بتقنية ترسيب بالحمام الكيميائي، حيث استخدام ملح نترات الكادميوم كمصدر لايونات الكادميوم الموجبة والثيوريا كمصدر الايونات الكبريت.وأجريت عملية الترسيب عند قيم مختلفة للدالة الحامضية(pH).الخصائص التركيبية لهذه الأغشية شخصت بواسطة حيود الأشعة السينية(XRD) ومجهر القوة الذري(AFM)، حيث بينت إن أغشية CdS المرسبة تمتلك تركيب مكعب(مشبك الخارصين) ومعدل الحجم الحبيبي للعناقيد النانوية يقل مع زيادة قيمة الدالة الحامضية (pH) في المحلول. الخصائص البصرية درست باستخدام أطياف النفاذيه ، حيث بينت إن أغشية CdS لها نفاذيه عالية في المدى المرئي من الطيف وتصل إلى أكثر من 86 %. أغشية CdS تمتلك فجوة طاقة تزداد من 2.42 eV إلى 2.58 eV مع زيادة قيمة الدالة الحامضية (pH) في المحلول.