

EFFECT OF DEPOSITION RATE ON THE MORPHOLOGY OF CdS FILMS DEPOSITED IN AN AMMONIA FREE SOLUTION

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Cadmium sulphide semiconductor thin films have been deposited by chemical bath technique (70°C) on HfO₂ substrates. The effect of pH on deposition rate was studied to determine the optimum condition for deposition. CdS films were deposited at pH ranging from 10 to 11.9 in an ammonia-free CBD process employing sodium citrate dihydrate and potassium hydroxide as complexing agents. The increase of pH reduced the deposition rate due to higher complexation and slow generation of Cd²⁺, improving the morphology of CdS films. X-ray diffraction studies showed hexagonal crystalline phase of CdS with an optical band gap around 2.4 eV as determined by UV-Vis absorption. Fourier transform infrared spectroscopy showed more presence of impurities on CdS films deposited at low deposition rate-high pH.

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1. Introduction

A II–VI compound semiconductor deposition from aqueous solution has become increasingly popular because it has economical advantages and capability of large-area deposition [1-2]. Cadmium sulphide (CdS) is the most studied chalcogenide with a bandgap of 2.4 eV (in bulk) [3], and it was studied as the semiconductor active layer during the early development of TFTs [4]. Also the application of CdS films as window layers in high efficiency solar cells based on CdTe and Cu(In,Ga)Se₂ (CIGS) has recently increased the interest and studies on this material [5].

CdS thin films have been prepared by variety of methods (both physical and chemical) like electrostatic deposition [6], gas evaporation [7], micelles [8], CBD [9] and etc. The CBD process is a simple and inexpensive technique to obtain homogeneous, hard, adherent, transparent and stoichiometric CdS films. Typically, chemically CdS films are formed from the reaction between a cadmium salt and thiourea in an ammoniacal alkaline solution. The main role of ammonia in the CBD process is as complexing agent for the cadmium ions in the reaction solution. It is clear that the preparation of CdS films by CBD for large scale for example in solar cell production represents a serious environmental problem because the employment of large amounts of ammonia, which is toxic and is highly volatile and harmful for the environment [10]. Efforts

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have been dedicated to the investigation of CBD processes for the synthesis of good quality CdS films, which reduce this environmental problem. One of the main approaches is the substitution of ammonia as the complexing agent of cadmium ions in the CBD process.

In the present work we studied the effect of pH on the properties of CdS films deposited by an ammonia-free CBD process employing sodium citrate dihydrate and potassium hydroxide as complexing agents instead of ammonia. CdS films were deposited in a pH range from 10 to 11.9. Low pH produces a high concentration of free Cd^{2+} affecting the quality of the films. The increase of pH reduces the deposition rate due to a high complexation and slow generation of Cd^{2+} , improving the morphology of CdS films. CdS films were characterized through Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques to study thin film composition, structure and morphological characteristics respectively. Less impurity on CdS films deposited at low deposition rate-high pH were found through FTIR. X-ray diffraction studies showed the hexagonal crystalline phase of CdS with an optical band gap ~ 2.4 eV as determined by UV-Vis absorption.

2. Experimental details

a) Substrate preparation

The CdS films were deposited on 90 nm thick HfO_2 [11]. The HfO_2 was deposited using atomic layer deposition at 100°C on heavily doped Si wafers (p-type: boron; <0.005 ohm-cm). The HfO_2/Si substrates were cleaned in an ultrasonic bath with acetone followed by isopropanol and finally rinsed with distilled water and dried with N_2 .

b) Cadmium sulphide deposition

The CdS films were deposited by immersion of the substrates in a CBD solution prepared from cadmium chloride (CdCl_2), sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), pH 10 borates buffer, potassium hydroxide (KOH), and thiourea ($\text{SC}(\text{NH}_2)_2$) in a volumetric ratio of 9 ml (0.05M): 9 ml (0.5 M): 3 ml: 1 ml – 5 ml (0.5 M): 4.5 ml (0.5M). The total reaction volume was adjusted with water to 60 ml. The temperature of the solution was maintained at $70^\circ\text{C} \pm 1^\circ\text{C}$ for 25 minutes. After deposition, the CdS films were cleaned in an ultrasonic bath with methanol followed by distilled water rinse and dried with N_2 .

The crystalline structure of the CdS films was analyzed in a Rigaku Ultima III X-ray diffractometer with $\text{CuK}\alpha$ (λ) = 1.54 \AA , operated at 40kV and 44mA. The 2θ scan rate was $0.5^\circ/\text{min}$. The morphology was studied in a SEM Zeiss SUPRA 40 with operating voltage of 5 kV. FTIR Spectra was recorded with Nicolet Magna- IR 560 spectrometer from 200 to 3500 cm^{-1} and the optical properties were studied using an Ocean optics UV-Vis spectrophotometer.

3. Results and discussions

In the chalcogenide films growth by chemical bath deposition, the thin film formation relies on the reaction mixture pH which depends on OH ions presence.

In our experimental conditions CdS thin films were grown on HfO_2 in a pH range from 10 to 11.9. The deposition rate as a function of pH was studied. While deposition rate normally increases with increase in pH for the standard bath [12], in our studied conditions the opposite behaviour was obtained. Increasing pH results in two opposing effects: thiourea decomposition increase while Cd^{2+} concentration decreases. An excess of OH^- should shift the reaction to the right to complete precipitation of $\text{Cd}(\text{OH})_2$. This is a general effect, but the conclusions are not always valid [4], the reason is that OH^- can form a complex with Cd^{2+} ($\text{Cd}(\text{OH})_4^{2-}$), thus removing free Cd^{2+} from solution and reducing the degree of precipitation. This effect is showed in the Figure 1, where the variation of deposition rate with pH can be observed.

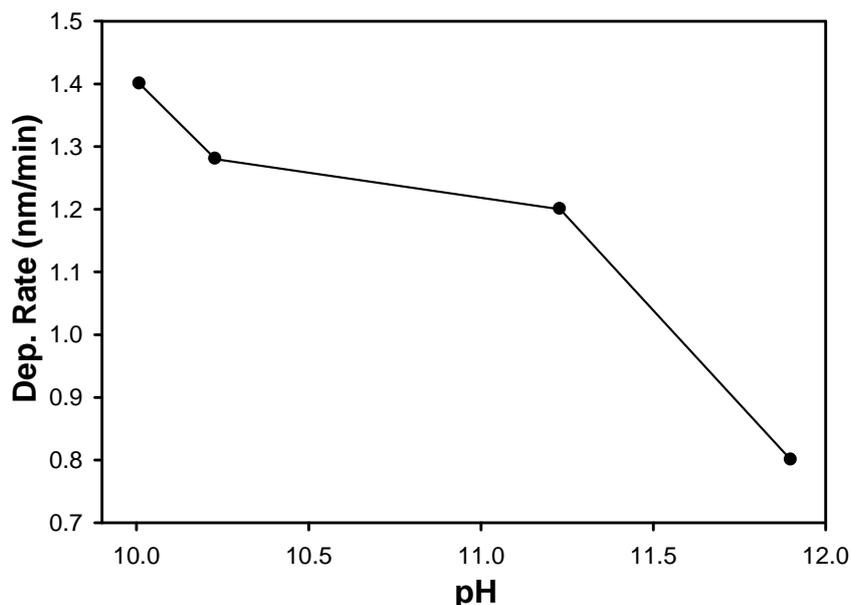


Fig. 1. Variation of deposition rate with pH for CdS films. CdS films deposited at pH ranging from 10 to 11.9.

In the chemical bath the CdS deposition takes place at the surface of the substrate. The cadmium complexes and the thiourea diffuse to the active sites of the substrate, where CdS formation takes place and then the film growth occurs. The X-ray diffraction patterns in the Figure 2a show the crystallinity of the films deposited at different pH. As the pH increases from 10 (low pH) to 11.9 (high pH), the degree of crystallinity of as deposited CdS thin films increases. The X-ray diffraction peak at $2\theta = 26.5^\circ$ evidenced the preferential orientation along the (002) hexagonal plane. The broad hump in the 2θ range of 20–35 is due to the substrate. The increase in the cadmium metal ions concentration at low pH, increases the heterogeneous reaction that leads to the formation of colloidal CdS precipitates in the growth solutions. The increase of pH promotes the formation of a complex between Cd^{2+} and OH^- ($\text{Cd}(\text{OH})_4^{2-}$) reducing the availability of free cadmium metal ions for the reaction and therefore homogeneous reaction in the vessel is controlled. Homogeneous reaction in the vessel can promote an increase in the degree of crystallinity of CdS films as is showed in Figure 2a.

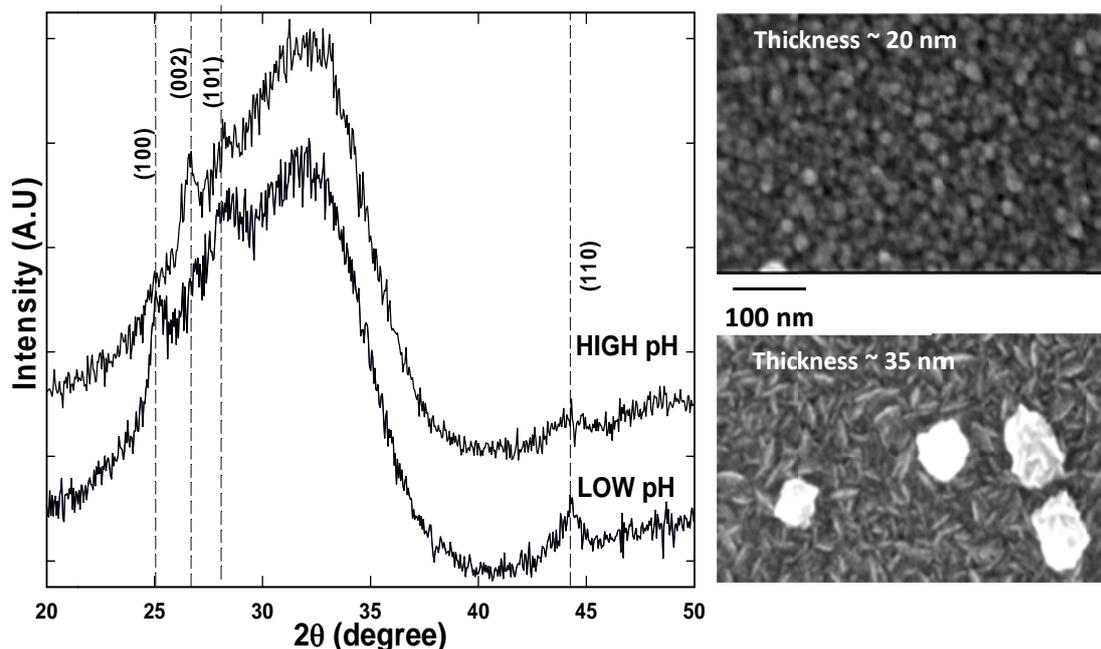


Fig. 2. a) XRD patterns and b) SEM for CdS films deposited at different pH.

SEM yields microscopic information of the surface (Figure 2b). This technique was helpful to identify the growth mode, determining the pH effect on the film morphology. Average CdS thicknesses were obtained by cross-section SEM. Film deposited at low pH showed more irregular morphology with some clusters on the surface due to the high deposition rate. At low pH the free Cd^{2+} concentration is higher due to low Cd^{2+} complexation resulting in high deposition rate. At high pH the free Cd^{2+} concentration is lower due to high complexation. However free S^{2-} concentration increases, which can be attributed to the anion generation being relatively slow, preventing sudden precipitation. Thus, a homogeneous process take place which then results in a lower film thickness.

IR Spectra of CdS films are presented in Figure 3. The band at 3300 cm^{-1} is due to O-H stretching vibration and the band at 1587 cm^{-1} is due to H-O-H bending vibration, both vibrations belong to water molecules [13]. Medium strong bands positioned in the range from 1340 cm^{-1} to 1400 cm^{-1} , are possibly due to stretching vibrations of sulphate groups [14-15]. The band at $\sim 2000\text{ cm}^{-1}$ corresponds to N-H stretching vibrations, due to incomplete hydrolysis of thiourea at low pH [16]. CdS film deposited at low pH showed more impurities. Sulphate vibration is more intense than CdS in the film deposited at low pH, this is probably due to incomplete hydrolysis of thiourea. CdS films also showed two stretching bands of Cd-O at 1060.4 and 1180.21 cm^{-1} [11-17], this is likely due to oxidation of $\text{Cd}(\text{OH})_2$ present at the solution. At 608 cm^{-1} there is a medium strong band which has been assigned to Cd-S stretching [18-19]. The vibration absorption peak of CdS band is situated at 240 cm^{-1} and this is more intense in CdS film deposited at high pH.

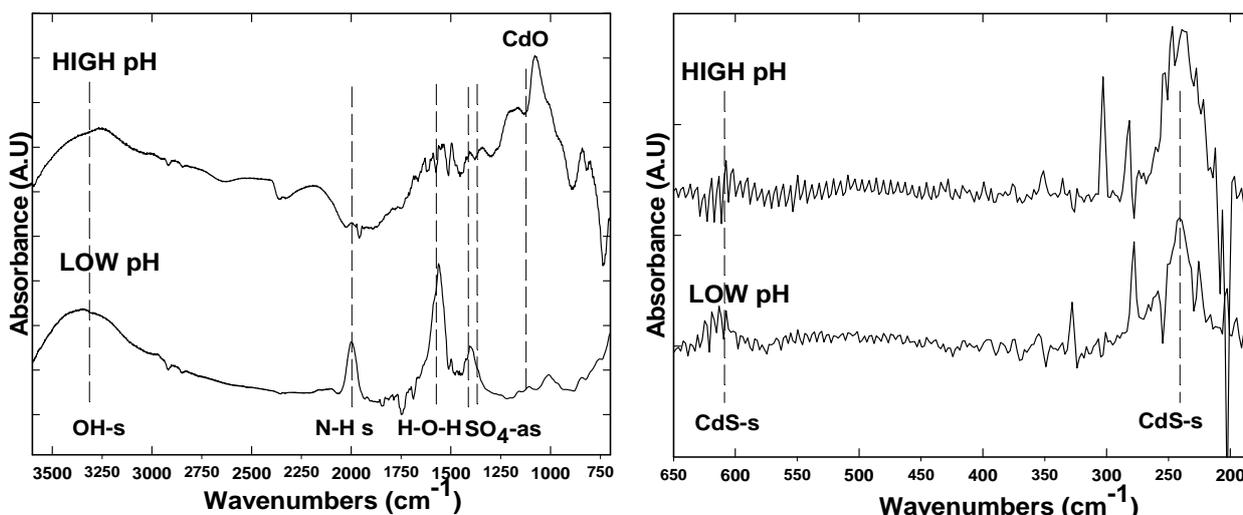


Fig. 3. IR Spectra for CdS films deposited at different pH for a) Mid-IR-CdS and b) Far-IR-CdS.

A method for band gap determination of the semiconductor compound (CdS thin film) is to study the absorption spectra of the samples. To do this, CdS films were grown onto an optically transparent substrate. The absorption measurement at various wavelengths (UV-Vis) of the CdS film deposited on glass substrate was used to estimate the optical band gap. A plot of $(OD \times E)^2$ versus E is shown in the Figure 4.

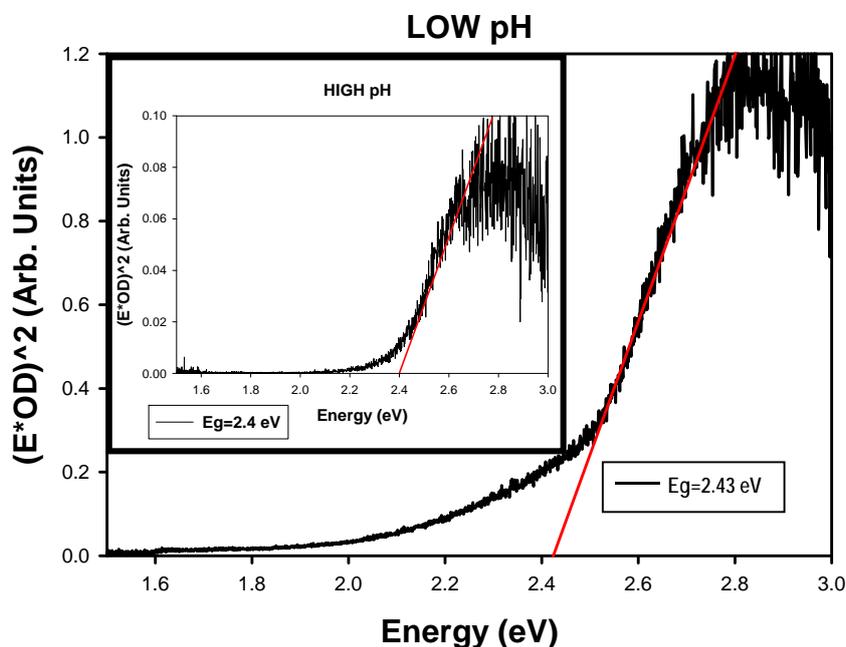


Fig. 4. Estimated band gap from optical absorption spectrum of CBD CdS thin films grown on a glass slide at different pH.

Here, OD is the optical density and E is the photon energy. Extrapolation of the linear portion of the curve to $(E^*OD)^2=0$, gives the estimated optical band gap ~ 2.43 eV for CdS film deposited at low pH and 2.4 eV for CdS film deposited at high pH. The latter suggests an increase of pH in the chemical bath does not affect the optical band gap. Measured band gap values are comparable with previously reported values (2.43 eV) [20-21].

4. Conclusions

In the present work, the CdS thin films chemical bath deposition conditions, such as, pH and deposition rate to yield a uniform deposition have been optimized from an ammonia free solution. Low pH of the solution produces a high concentration of cadmium ions affecting the quality of the film. At high pH the free cadmium ions concentration was low due to high complexation, thus reducing the degree of precipitation and yielding on resulting homogeneous deposition process.

CdS film deposited at low deposition rate was found to be polycrystalline with a hexagonal phase and an optical band gap of around 2.4 eV. Through FTIR it was also found low presence of impurities at high pH. These characteristics in the CdS films make them a suitable candidate for various optoelectronic and device applications.

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