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Electrodeposition of CdS Thin Films at Various pH Values

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The effects of pH value on CdS thin films fabricated by using electrodeposition were investigated in detail. The pH values of the final solutions were adjusted between 1 and 5. Aqueous solutions of HCl and NaOH were used to adjust the pH. The reaction rates were changed by the pH due to the fact that the pH affected the rate of release of sulphide from sodium thiosulfate. The structural, optical and morphological properties of the films were analyzed by using X-ray diffraction, Ultraviolet-visible spectroscopy and scanning electron microscopy, respectively. Compact films with good crystallinity were obtained at pH value of 4 and 5.

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I. INTRODUCTION

Among the II-VI semiconductor such as CdS, ZnS, CdSe, and ZnSe, CdS is the most commonly used buffer layer in photovoltaic devices. Thus, CdS (cadmium sulphide) thin films have been used widely as window layers in solar cells with an absorber layer of CdTe, Cu_2S, or $CuInSe_2$ [1]. CdS is a direct *n*-type semiconductor with a band gap of about 2.4 eV and a large absorption coefficient of 4×10^4 cm^{-1} [2]. CdS thin films are generally obtained using various techniques, such as chemical bath deposition and chemical vapour deposition. CdS can also be deposited electrochemically from organic or aqueous solutions [3]. Electrodeposition of semiconducting materials is significant not only from the academic point of view but also in relation to the economy because this method presents appealing characteristics, such as low cost, a large area, and generally lower temperature and soft processing of materials [4].

If CdS films are obtained from an aqueous solution containing Cd^{2+} and $Na_2S_2O_3$ (sodium thiosulfate), the problem is that the CdS formation reaction on the electrode will not be clear [3]. When $Na_2S_2O_3$ dissolves in water, the reaction will be [5].

$$\mathrm{Na_2S_2O_3 + H_2O \rightarrow S_2O_3^{2-} + Na_2O + 2H^+}. \qquad (1)$$

Lowering the pH below 3 causes the decomposition of $S_2O_3^{2-}$, where sulphur will be generated as follows [5]:

$$\begin{aligned} \mathrm{S_2O_3^{2-}} &\rightarrow \mathrm{S + SO_3^{2-}}, & (2)\\ \mathrm{S}_{(s)} + 2e^- &\rightarrow \mathrm{S}^{2-}_{(aq)}. & (3) \end{aligned}$$

S and S^{2-} may react with Cd and Cd^{2+}, respectively to generate CdS as is in chemical bath deposition. Reducing the pH causes the numbers of S^{2-} ions in the solutions to increase. When free S^{2-} ions are present in the solutions, CdS crystals may be precipitated via chemical bath deposition; thus, CdS clusters may be formed. This is not desirable because of the fact that clusters may not adhere well to the surface of the substrate; thus, the obtained film may not be compact.

This study has been designed to find a solution to the cluster-formation problem mentioned above. In some experiments, the pH value was increased above 3; thus, the numbers of sulphur atoms and sulphur ions in the final solution were decreased to a minimum levels. However, the absence of sulphur atoms and sulphur ions does not stop the following reaction [6] from occurring.

$$\mathrm{Cd^{2-} + S_2O_3^{2-} + 2e^- \rightarrow CdS + SO_3^{2-}}. \qquad (4)$$

Thus, all CdS formation on the surface takes place nearly as given in Eq. (4). Electrodeposition of CdS thin films has been investigated widely, but no studies have been done on the effects of pH values above 3. In this work, the effects of pH values between 1 and 5 were investigated. The pH was reduced by using HCl and was increased by using NaOH. Redundant varying pH cause to the number of free S^{2-} ions in the solutions to vary and, thus, the reaction rates to vary.

II. EXPERIMENTAL PROCEDURE

This study adresses electrodeposition of polycrystalline CdS films from aqueous electrolyte solutions con-

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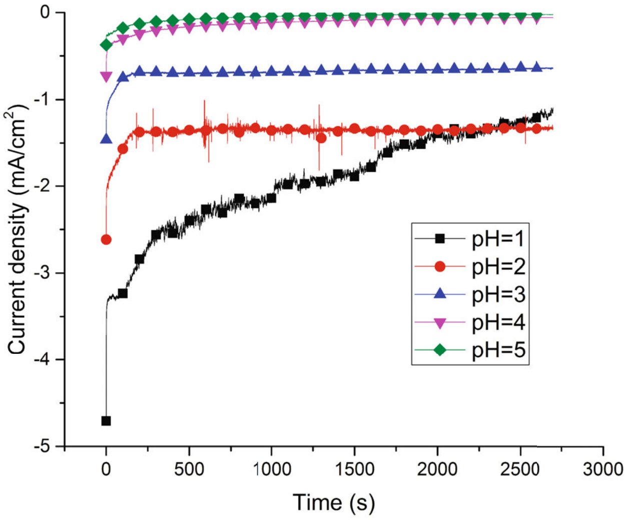

Fig. 1. (Color online) Current densities during the CdS depositions for various values of the pH.

Table 1. Experimental conditions.

Experiments	p1	p2	p3	p4	p5
Concentration of $CdCl_2$ (M)	0.2	0.2	0.2	0.2	0.2
Concentration $Na_2S_2O_3$ (M)	0.01	0.01	0.01	0.01	0.01
Deposition time (s)	2700	2700	2700	2700	2700
Cathodic potential (V)	−0.6	−0.6	−0.6	−0.6	−0.6
Temperature (°C)	90 ± 2	90 ± 2	90 ± 2	90 ± 2	90 ± 2
pH	1	2	3	4	5

taining 0.2-M $CdCl_2$ and 0.01-M $Na_2S_2O_3$. For depositions, an IVIUM Vertex potentiostat/galvanostat, which consisted of a conventional three-electrode cell, such as a silver/silver chloride, a platinum wire, an indium-tin-oxide (ITO)-coated glass substrate the reference, a counter electrode, and a working electrode, was employed. The depositions were completed in a time of 2700 s, and the temperatures of the final solutions were kept at 90 ± 2 °C. The pH of the final solution was measured as 3.5 without any additives, and it was reduced to 1, 2 and 3 by using 5% ww hydrochloric acid, and increased to 4 and 5 by using a 0.5-M aqueous solution of NaOH. The final solutions were stirred at 300 rpm by using a heater and a stirrer. The conditions of the depositions are given in Table 1.

X-ray diffreaction (XRD) PANalytical Empyrean (X-ray diffractometer) was used to determine the structures of the films. The optical analysis was performed using a JASCO V-530 UV-vis spectrometer at wavelengths from 350 nm to 600 nm. Surfaces were magnified 50,000 times by using a Zeiss SUPRA 40VP scanner electron microscope (SEM) to understand the morphologies.

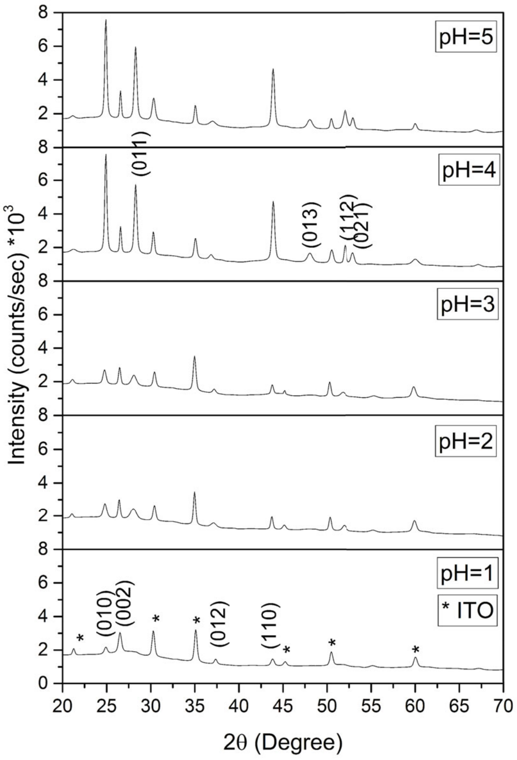

Fig. 2. XRD spectra of electrodeposited CdS samples for various values of the pH.

III. RESULTS AND DISCUSSION

1. Structural characteristic of the CdS thin films

As the temperature approached 90 °C, the color of the final solutions whose pH values were 1, 2 and 3 turned from colorless to yellowish. This result indicated that CdS particles might have been as in chemical bath deposition. On the other hand, when the pHs of the final solutions were 4 and 5, the colors were not yellowish. Thus, one might conclude that the forming of CdS clusters can be prevented partly by increasing the pH to 4 and 5. CdS crystals were not formed as the value of the pH approached to 6.

Plots of the current densities are given in Fig. 1. The current densities decreased as the pH increased. This result was expected due to the fact that the numbers of S atoms and S^{2-} ions decreased as the pH increased. Naturally, the decreasing current densities reduced the reaction rate and the films thickness. The thicknesses of the films were obtained by using the gravimetric method and were calculated by using the current densities according to.

$$d = \frac{jMt}{nF\rho}, \tag{5}$$

where d is the film's thickness, M is the molecular weight

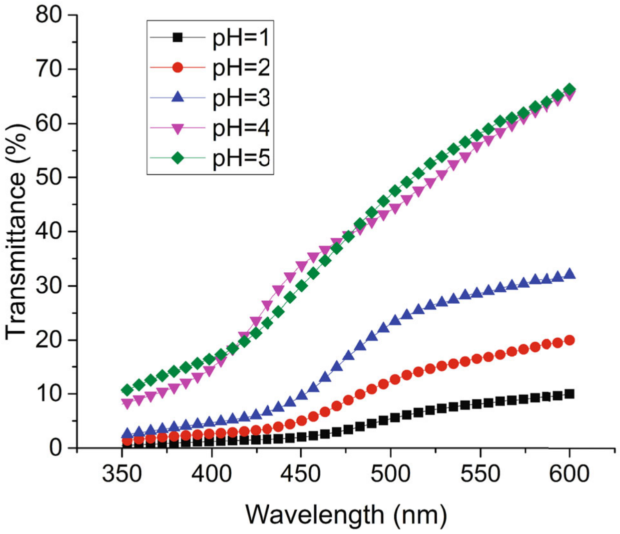

Fig. 3. (Color online) Transmittances of CdS thin films versus wavelength for various values of the pH.

Table 2. Thicknesses, crystallite sizes and band gaps of the obtained CdS thin films.

Experiment	p1	p2	p3	p4	P5
Thickness Gravimetric (nm)	470	305	231	124	108
Thickness Calculated (nm)	807	620	412	186	153
Crystallite size (nm)	36	32	29	15	17
Band gap (eV)	2.22	2.40	2.47	2.64	2.58

(g), n is the number of electrons, t is the deposition time (sec), j is the current density (mA/cm^2), ρ is the CdS density (4.84 g/cm^3) and F is the Faraday constant (96500 C) [2]. The results for the thicknesses are shown in Table 2. The thicknesses of the films measured by using the gravimetric method were lower than the thicknesses calculated from the current densities due to the fact that the efficiency is not 100%. The thicknesses decreased as pH increased because of the fact that the numbers of free S atoms and S^{2-} ions decreased as pH increased. When pH was reduced, the numbers of free S^{2-} ions in the final solutions were increased; therefore, reaction rate was increased.

The XRD patterns of the CdS films are presented in Fig. 2 for various values of the pH. All samples were formed in a hexagonal structure but when pH was reduced to 1, 2 and 3, the peak intensities also decreased whereas the thicknesses of these films were higher than these of the other two film (pH 4 and 5). These results indicate that when the reaction rate was reduced, well crystallized films were obtained. The intensity of the peak due to the (011) plane increased as the pH of the final solution was increased and was nearly the same as that of the peak due to the (010) plane in the films obtained at pH 4 and 5.

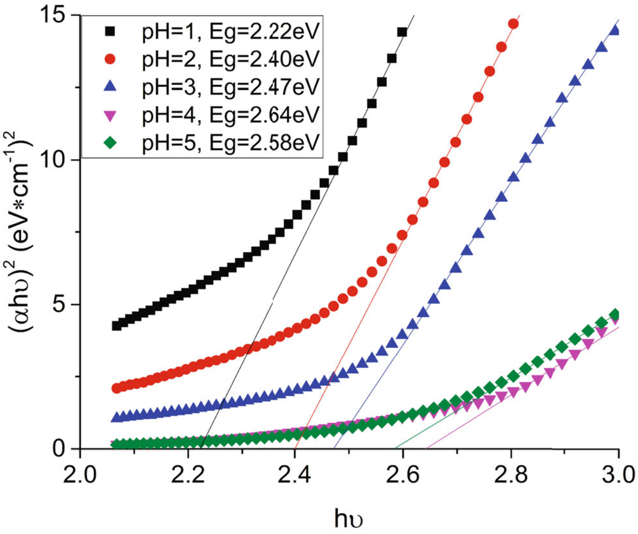

Fig. 4. (Color online) $(\alpha h\nu)^2$ versus $h\nu$ plots and band gaps of the electrodeposited CdS thin films.

To calculate the crystallite sizes, we used the Debye Scherr's equation:

$$\mathrm{cs} = \frac{0.089 \times 180 \times \lambda}{314 \times \beta \times \cos\theta_C}\ \mathrm{nm}, \tag{6}$$

in which $2\theta_C$ is the peak center, β is the full width at half maximum, and λ is the wavelength of X-ray radiation (1.54056 Å). β and $2\theta_C$ were calculated by fitting the XRD peak profile [7]. In Table 2, we present the calculated crystallite size. From the thicknesses of the films, the crystallite size decreased from 36 nm to 15 nm as a result of the decreasing reaction rate. There is a strong relationship between the crystallite size and the band gap. This was due to the fact that when the numbers of the atom are increased, the overlap of the orbitals increases and, therefore, the bandwidths increase.

2. Optical characteristic of the CdS films

To understand the optical properties of the films, we recorded the absorbance values at wavelengths between 350 nm and 600 nm. Because the ITO substrates had a very strong absorbance at wavelengths < 300 nm [8], the absorbance measurements were ended at 350 nm. The transmittance values calculated from the absorbance measurements, and the results are given in Fig. 3. While the films obtained at pH 1, 2 and 3 demonstrated transmittances of 10 - 15% on average, the other films obtained at pH 4 and 5 demonstrated a transmittance of 50%. We conclude that the relatively high transmittance resulted from the less thickness, good crystallization, and lower surface roughness because a low roughness caused less scattering of the incident light beam. The increasing transmittance might make these thin films suitable for are in solar cells.

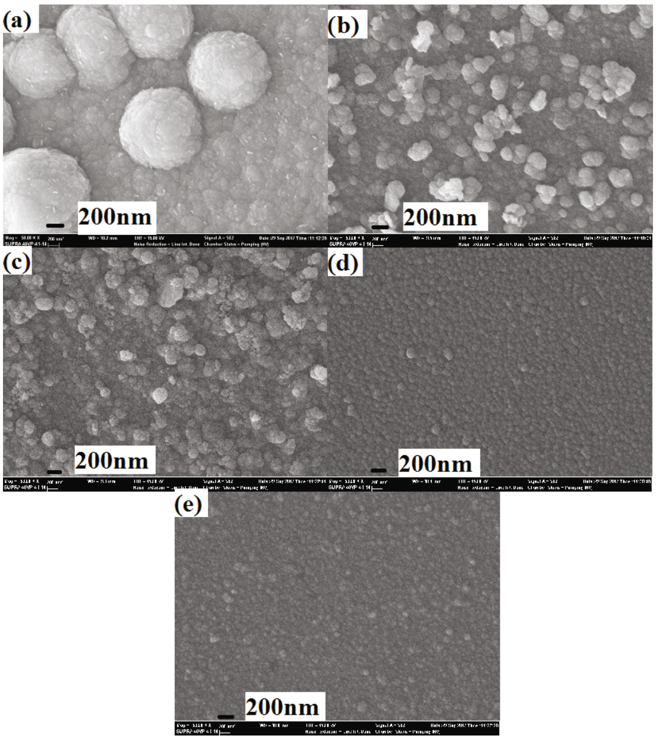

Fig. 5. SEM images of electrodeposited CdS thin films for pH value of (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5.

The optical energy gaps were estimated from the absorbance measurements by extrapolating the linear portions of the $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ plots based on the relation

$$(\alpha h\nu)^2 = A(h\nu - E_g), \tag{7}$$

where α is the optical absorption coefficient, A is a constant for a direct transition, $h\nu$ is the photon energy, and E_g is the optical band gap [9–11]. $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ plots and estimated optical band gaps are given in Fig. 4 and Table 2. In the literature, CdS thin films produced at pH 1.8 are reported to exhibit a band gap of 2.33 eV [12]. In this study, the band gaps of the films were 2.22 eV and 2.40 eV at pH 1 and 2. This result is consistent with the value reported in the literature. On the other hand, when the pH was increased to 4 and 5, the estimated band gaps increased to 2.58 eV and 2.64 eV. These results indicate that band gap depends on the pH because of the fact that the pH affects the crystallite size and the reaction rate. A strong relationship was found between the band gap and the crystallite size.

3. Morphologic characteristic of the CdS films

The CdS surfaces were magnified 50,000 times by a SEM, and the resulting images given in Fig. 5 for pH values of 1, 2, 3, 4 and 5. The clusters seen on the surfaces of the films were obtained at pH 1, 2 and 3. Information about these surfaces can be found in the literature [13]. The number of cluster decreased as the pH increased. These results indicate that pH affects the formation of clusters due to the fact that when the pH is reduced, the numbers of sulphur atoms and sulphur ions are increased, and CdS is formed by a chemical reaction. Figures 5(d) and 5(e) show images of the surfaces of the films obtained at pH 4 and 5. These surfaces appear very smooth, as sheet-like surfaces. Moreover, the surfaces of these films were very compact and dense. Thus, we are able to conclude that the smooth surfaces might be result of the reactions similar to the reactions in electrodeposition.

IV. CONCLUSION

This report presented the effects of pH on CdS films produced by using chronoamperometry of electrodeposition. The fact that the pH was reduced by using HCl and H_2SO_4 had been investigated, but no studies had been done on increasing the natural pH of the final solution. In this study, the natural pHs of the final solutions were increased by using an aqueous solution of NaOH. Although the film's thickness decreased, the peak intensities were increased by nearly three times according to the XRD patterns. This indicated good crystallization.

According to the absorbance measurements, when the pH was increased to 4 and 5, the transmittance values were increased three times on average. This is important for solar cells due to the fact that the *n*-layer of the solar cell should be transparent. While the band gaps of the films obtained at pH 1, 2 and 3 varied between 2.22 eV and 2.47 eV, these of the films obtained at pH 4 and 5 varied between 2.58 eV and 2.64 eV. We conclude that decreasing the crystallite size caused an increase in the band gap. The surfaces of the films were analyzed by using SEM images. Clusters of CdS were seen on the surfaces of the films produced at pH 1, 2 and 3. The presence of S and S^{2-}, which resulted from the decomposition of $S_2O_3^{2-}$ at pH < 3, might have caused cluster formation. On the other hand, when the pH was greater than 3, no clusters were found on the film's surfaces, and the surfaces were very smooth. Moreover, the formed surfaces were very compact and dense.

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