



Study of the Optimal Conditions and Mechanism of CdS Thin Layers Formation by Chemical Bath Deposition Method

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In recent years, it has been considerable interest in thin film semiconductors for use in solar cells or photovoltaic devices and thin film transistors for flat panel displays. Cadmium sulfide has been one of the promising materials. Cadmium sulfide is a II-VI group compound semiconductor with a direct band gap of 2.42 eV at room temperature. Cadmium sulfide exists in two crystalline forms *i.e.*, hexagonal phase and cubic phase. It is possible to grow CdS films in both phases. Among several methods of CdS thin film deposition, chemical bath deposition is a suitable one. In chemical bath deposition, the structure of the film is influenced by the composition of the bath, temperature and pH of the solution. Determination of optimum conditions in chemical bath deposition-CdS thin film formation on a substrate, as for pH, temperature, reagent concentrations, *etc.* can be guided by a detailed knowledge of bath reactions mechanism. Decrease in the band gap CdS with increasing thickness and optical and electrical properties can be due to the influence of these parameters. In this work the hydrolysis mechanism of sulfide ion producing agents [thiourea and thioacetamide] and cadmium ion complexation and CdS saturation condition in the bath solution is observed and discussed mainly by UV-VIS spectroscopy.

Key Words: Thin film, Cadmium sulfide, Chemical bath deposition, Solar cell, Electrical devices.

INTRODUCTION

The study of semiconductor nano particles has been widely studied during past few years because of their novel optical and electrical properties. These unique properties are responsible for the many new application areas, such as their use in solar cells, photo detectors, light-emitting diodes and switches. Among metallic nano particle sulfides in thin film preparation, CdS have received considerably more attention than others. CdS has many commercial and potential applications in photovoltaic solar cells or other photoelectric devices^{1,2}. Chemical bath deposition is well known as a prevalent low-temperature aqueous technique for depositing large-area thin films of semiconductors and has been recognized as one of the simplest methods^{3,4}. Good quality, adherent, uniform CdS films were obtained by chemical bath deposition method. One of the advantages of the chemical bath deposition CdS layer in photovoltaic devices is deposition of very thin layers (< 50 nm) in a conformal manner on the substrate surface⁴. The deposition of cadmium sulfide by chemical bath deposition requires the presence of reagents that act as a source of chalcogen ions (often thiourea or thioacetamide) a source of metal ions (often cadmium chloride) and complexation of the metal ion of interest^{5,6}. A chelating agent (such as ammonium

solution or EDTA) is added to control the hydrolysis of the metal ion and to avoid the formation of excess Cd(OH)₂ precipitate^{5,6}. The controlling physiochemical factors for successful chemical bath deposition thin layer formation are the supersaturation of the solution and the kinetics of the growth process^{5,6}. Super saturation is defined as the meta stable condition whereas the concentration of a substance in solution exceeds the equilibrium concentration with respect to its precipitate⁶. Super saturation of the bath with respect to Cd(OH)₂ is necessary for the deposition of good quality films. The importance of Cd(OH)₂ in the growth mechanism of CdS has become clear even in conditions where no observable macroscopic precipitate is present⁷⁻¹¹. During chemical bath deposition film growth, two processes can take place: a heterogeneous reaction (ion by ion) upon the substrate surface occurring between absorbed ionic species and those in the solution, resulting a very adherent layer¹²⁻¹⁵; and a homogeneous reaction (cluster by cluster) yielding colloidal particles nucleated in solution. The non-adherent clusters are deposited on the bottom of the reaction beaker as precipitate. The layer deposition process can be subdivided into three periods: 1) induction period, with nucleation center formation, 2) the layer growth period by ion by ion mechanism, 3) the layer growth

period by cluster by cluster mechanism. The reaction rate and deposition rate of CdS are determined by parameters such as the proportion of the chelating agent and metal ions, the pH of the solution, the temperature and the deposition time.

EXPERIMENTAL

All chemicals used were of analytical grade. Thioacetamide (Fluka 99 %), thiourea (Merck, 99 %), cadmium chloride (Aldrich, 99.99 %), EDTA (Merck, 99 %), isopropyl alcohol (Merck, 99 %), silver nitrate (titrisol, 0.10 M) were used without further purification. Double-distilled water was used during this study. The pH of the solutions was adjusted to a desired value using sodium hydroxide (Merck, 99 %) or ammonium and hydrochloric acid (Merck, 37 %) solutions.

A double-beam UV-VIS spectrophotometer model Perkin Elmer Lambda 25 supplied by Philips company was used for absorbance measurements. The pH values were measured with a pH meter model E39613 supplied by Metrohm Co. (Swiss). A Mettler DL40 GP memotitrator was equipped with DM141 (Ag/Ag₂S coated) electrode and 0.01 N alcoholic AgNO₃ as the titrant. Isopropyl alcohol was treated by purging NH₃ gas for 10 min and then used as the titration solvent in all potentiometric titrations. For all CdS deposition studies, the hot plate equipped with magnetic stirrer and water bath system were needed.

Procedure A: To study the hydrolysis of thioacetamide and thiourea, the stock solutions of 0.1 M thioacetamide and thiourea in deionized water were prepared. The aqueous standard solutions of 0.01, 0.001, 0.0001 M of the sulfide ion producing agents were also prepared. The pH of these solutions was maintained at a desired value of 10-11 and 2 using NaOH or NH₃ and HCl solutions, respectively. Absorbance of solutions at ambient temperature, 80 °C (under reflux condition) indifferent time increments was determined by UV-visible spectrophotometer. Thioacetamide can exist in two tautomeric forms, that is called lactum-lactim tautomerism. In order to analyze these species quantitatively, an aqueous solution of 0.10 and 0.01 M of thioacetamide were prepared and immediately titrated, potentiometrically by 0.01 N standardized silver nitrate solution. The solutions were made up with 40 mL isopropyl alcohol before titration.

Procedure B: To study the changes of concentrations of cadmium ion in deposition CdS, stock solution 0.1 M cadmium chloride in water was prepared. From this, various solutions at different concentrations were also prepared by dilution of the stock solution. After adjusting the pH of solutions at 10.5 (with 2 M ammonium solution), 0.01 M thiourea or thioacetamide was gradually added and the formation of yellow deposits on the substrate (one clean glass slide) was placed in a solution. When the observation of yellow sediment is not possible, the absorbance of these solutions were shown at $\lambda = 400.7$ nm by spectrophotometer.

Procedure C: To study the effect of pH and the effect of complexing agent concentrations, the related experiments were done in two steps. In first step, a solution of 0.1 M cadmium chloride was prepared in water, so that the pH of solution was determined instantly during addition of ammonia or NaOH solutions. Therefore, gradual increases in the pH of the solution

were carefully carried out during good mechanical stirring and the process was followed to obtain the white cadmium hydroxide precipitation.

In the second step, various concentrations of thioacetamide as complexing agent were added to form yellowish CdS. In both steps, the formation of white and yellow precipitations observed on the substrate which was manually placed in the solution.

Procedure D: In order to optimizing different parameters affective on quality of the deposited layer, the bath was adjusted at 80, 85 and 90 °C by controlling heater temperature. During deposition of CdS, the magnetic stirrer was switched on to ensure uniform profile of heating through out water bath. The glass slides were cleaned by 0.10 M sulfuric acid 0.10 M acetone, methanol and double distilled water for thin layer deposition. These slides were used into the solution bulk immediately after drying. Deposition of CdS thin layer were done in solutions with ratio of 1:1, 2:1, 3:1 (thioacetamide/or thiourea to cadmium ion) at pH = 9, 10, 11, 12 on substrate. The pH of solutions was maintained by using NaOH or NH₃ solution.

RESULTS AND DISCUSSION

Study on hydrolysis rates of thioacetamide and thiourea:

To investigate the hydrolysis rates of thioacetamide or thiourea and tautomer of thioacetamide, spectroscopic studies in different pH and temperature were performed for a certain concentration of these sulfide generator agents. Fig. 1 shows UV/VIS spectra of the alkaline solutions of 0.10 M thioacetamide in different temperatures.

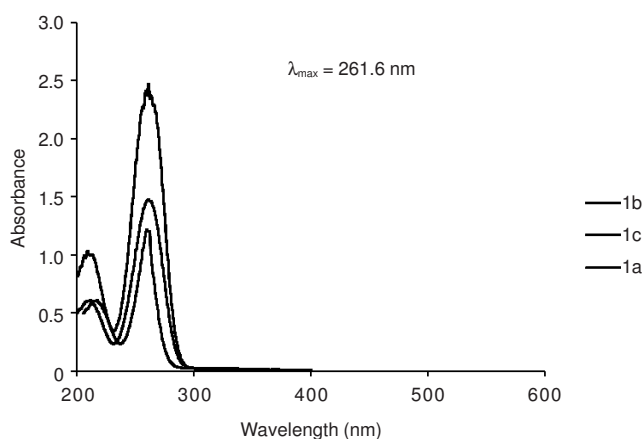
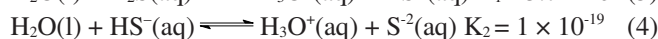
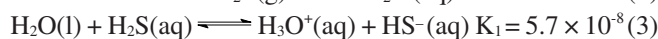
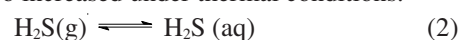


Fig. 1. UV/VIS spectrum of 0.10 M thioacetamide in a) pH of 2.0 at 25 °C; b) pH of 10.5 at 25 °C) pH of 10.5 at 80 °C

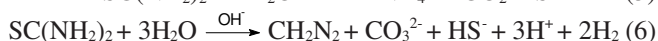
According to the following reactions, two possible paths are for the hydrolysis of thioacetamide in basic solutions¹⁶⁻¹⁹.

$$\text{CH}_3\text{-CSNH}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{NH}_3\uparrow + \text{H}_2\text{S}\uparrow \quad (1)$$

Reaction (1) can catalyze by acid or base and the rate of hydrolysis can also increased under thermal conditions.



Similarly, the reactions for the hydrolysis of thiourea in basic solutions are given as follows^{6,20}:



Both thioacetamide and thiourea show well-defined peaks at 261.6 and 238.0 nm (λ_{max}), respectively due to their electronic absorbance in the ultraviolet region (Figs. 1 and 2). For comparing, the results are summarized in Table-1.

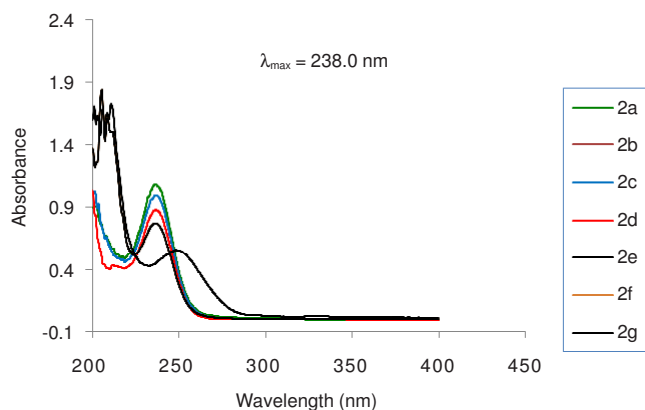


Fig. 2. UV/VIS spectrum of 0.10 mM thiourea at pH of 2

TABLE-1
SPECTROSCOPIC RESULTS OF 0.1 M THIOACETAMIDE SOLUTION IN DIFFERENT pH AND TEMPERATURE

No	pH	Temperature (°C)	Absorbance at $\lambda_{\text{max}} = 261.6$ nm
1	2.0	25	2.79
2	10.5	25	2.473
3	10.5	80	1.475

As the absorbance is proportional to concentration, a linear decrease in maximum absorbance of thiourea/thioacetamide was observed owing to decrease in concentrations of these species. In basic solutions, this reduction is greater than the acidic one. It means that the rate of hydrolysis of thioacetamide or thiourea in basic solution is significantly greater than the rate of their hydrolysis in acidic solution. Besides, the results show that the hydrolysis of thioacetamide is faster than that of thiourea.

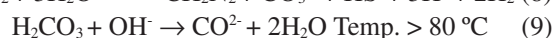
The absorbance of 1×10^{-4} M thiourea in different conditions is given in Table-2.

TABLE-2
SPECTROSCOPIC RESULTS FOR 1×10^{-4} M THIOUREA SOLUTIONS AT 25 °C

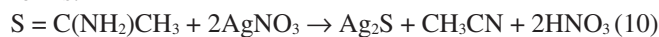
No	pH	Time (min)	Absorbance at $\lambda = 238$ nm
1	2	0	1.084
2	2	20	0.914
3	2	111	0.90
4	2	273	0.876
5	10-11	20	0.809
6	10-11	111	0.761
7	10-11	273	0.761

The results reveal that the pH of solution has more pronounce effect on hydrolysis progress in comparison with the reaction time.

The following reactions show also carbonate ions are removed as carbon dioxide gas is released the chemical bath. The thiourea hydrolysis rate is enhanced as the temperature increases:



Thioacetamide reacts to silver nitrate in two tautomeric forms:



The XRD studies revealed that the black Ag_2S precipitation is a marker for the reaction between the tautomery form A and silver nitrate. Fig. 3 shows X-ray diffraction of the precipitation resulting from titration of thioacetamide with 0.01 N silver nitrate solution.

The formation of the crystalline Ag_2S nanoparticles is established from the XRD pattern (Fig. 3). The diffraction peaks at $2\theta = 11.9\theta$ and 20.9θ correspond to the monoclinic crystal system of silver sulfide ($\beta\text{-Ag}_2\text{S}$). According to Scherrer's equation, $D_{\text{hkl}} = k\lambda \times 57.3/\beta \cos\theta$, where D is the average diameter of the crystals in \AA , λ is the X-ray wavelength ($\lambda = 1.5418\text{\AA}$), κ is the shape factor ($\kappa = 0.89$), θ is the Bragg angle in degrees, β is the line broadening measure and the half-height in radians. When the reflecting peaks of Ag_2S in Fig. 3 are chosen for calculating the crystal size of Ag_2S , the average size of the Ag_2S nano particles is about 15 nm.

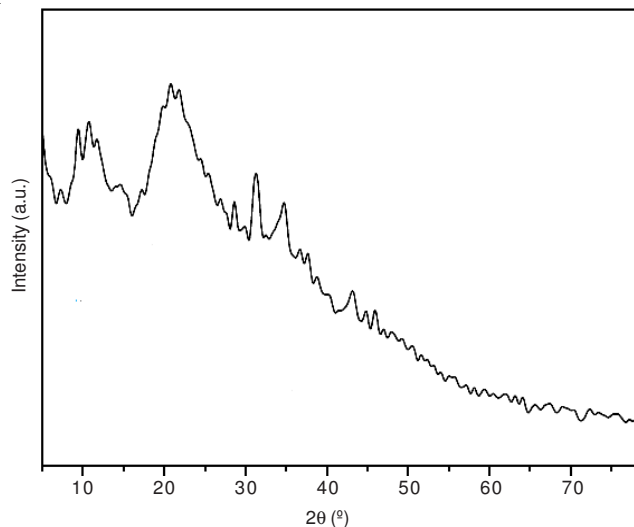


Fig. 3. XRD spectrum of black Ag_2S precipitate

Effect of cadmium ion concentration on type and appearance of deposited products: The concentration of S^{2-} can be calculated from the ratio of the two solubility products⁹.

$$\frac{K_{\text{sp}}\text{CdS}}{K_{\text{sp}}\text{Cd}(\text{OH})_2} = \frac{[\text{Cd}^{2+}][\text{S}^{2-}]}{[\text{Cd}^{2+}][\text{OH}^-]^2} = \frac{[\text{S}^{2-}]}{[\text{OH}^-]^2} = 5 \times 10^{-15} \quad (14)$$

Calculation of the maximum concentration of free metal ion, $[\text{M}^{+2}]$ follows us to determine the super saturation of the system:

TABLE-3
RESULTS AT DIFFERENT CONCENTRATIONS OF Cd²⁺, (0.01 M THIOUREA), (K_{sp} Cd(OH)₂ = 1.2 × 10⁻¹⁴, K_{sp} CdS = 7.2 × 10⁻²⁷ AT pH 10.5

No.	Dilution factor of cadmium solution	Observation	[Cd ²⁺] (M)	[Cd ²⁺][OH ⁻] ² (M ³)	[Cd ²⁺][S ²⁻] (M ²)
1	-	Excess of Cd(OH) ₂ , thiourea: yellow solution after 10 days	0.059	5.87 × 10 ⁻⁹	2.95 × 10 ⁻²³
2	10	First white colloid particles, thiourea: yellow solution after 2 hours	5.87 × 10 ⁻³	5.87 × 10 ⁻¹⁰	2.95 × 10 ⁻²⁴
3	100	White colloid particles (2 days), thiourea: yellow solution after several hours	5.87 × 10 ⁻⁴	5.87 × 10 ⁻¹¹	2.95 × 10 ⁻²⁵
4	1000	No white colloid particles thiourea: yellow solution after several hours	5.87 × 10 ⁻⁵	5.87 × 10 ⁻¹²	2.95 × 10 ⁻²⁶
5	1 × 10 ⁵	No white or yellow colour	5.87 × 10 ⁻⁷	5.87 × 10 ⁻¹⁴	2.95 × 10 ⁻²⁸
6	1 × 10 ⁷	No white or yellow colour	5.87 × 10 ⁻⁹	5.87 × 10 ⁻¹⁶	2.95 × 10 ⁻³⁰
7	1 × 10 ⁹	No white or yellow colour	5.87 × 10 ⁻¹¹	5.87 × 10 ⁻¹⁸	2.95 × 10 ⁻³²
8	1 × 10 ¹¹	No white or yellow colour	5.87 × 10 ⁻¹³	5.87 × 10 ⁻²⁰	2.95 × 10 ⁻³⁴
9	1 × 10 ¹³	No white or yellow colour	5.87 × 10 ⁻¹⁵	5.87 × 10 ⁻²²	2.95 × 10 ⁻³⁶
10	1 × 10 ¹⁵	No white or yellow colour	5.87 × 10 ⁻¹⁷	5.87 × 10 ⁻²⁴	2.95 × 10 ⁻³⁸

$$[M^{2+}]_T = \alpha[M^{2+}]_f, \alpha = 1 + \sum_L \sum_{n=1}^{n_L} \beta_{L,n} [L]_n \quad (15)$$

where, α : coefficient which is a function of pH; [L]: ligand concentration; n: coordination number; $\beta_{L,n}$: stability constant of the corresponding complex; $[M^{2+}]_T$: total metal ion concentration; $[M^{2+}]_f$: free metal ion concentration.

Making super saturation condition in chemical bath deposition, depends on the concentrations of three species: free metal ion, hydroxide ion which depends on pH and complexing agent. These conditions have been studied as the following:

At pH = 10.5, if ionic products of cadmium ion and hydroxide ion was close to solubility product of cadmium hydroxide {it means $S = 1$, $S =$ ion product (IP)/solubility product (SP)}; As distinguishing white colloidal particles of Cd(OH)₂ is difficult, the observation of absorption spectrum of substrate that was placed in solution will prove the existence of Cd(OH)₂ peak in 298 nm (Figs. 4 and 5):

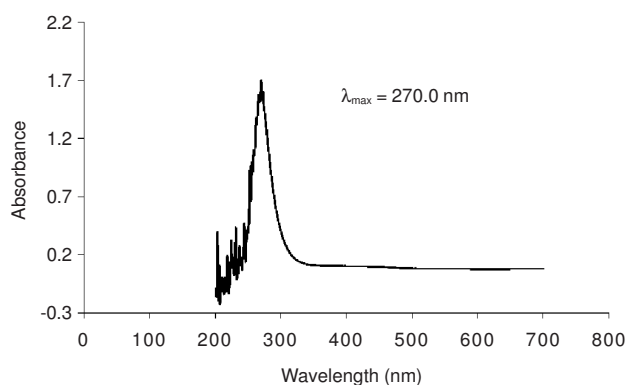


Fig. 4. UV/VIS spectrum of Cd(OH)₂ on the substrate

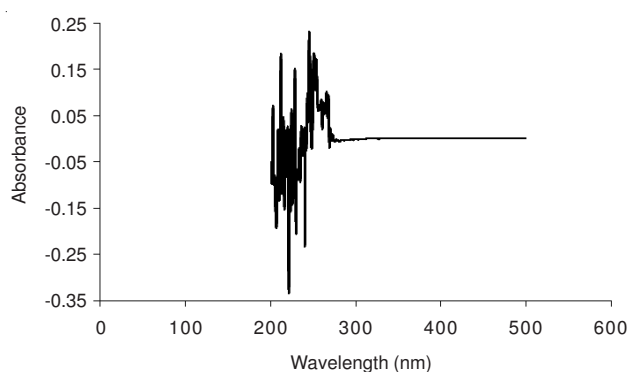


Fig. 5. UV/VIS spectrum of without Cd(OH)₂ on the substrate

Although low cadmium ion concentration causes CdS formation, but it is not suitable for thin film deposition. In this condition, the reaction becomes slow and finally terminates. In chemical bath deposition, the rate of deposition could not be constant because the concentration of reagents was decreased gradually and therefore, the reaction rate was reduced too.

If absorbance of prepared solutions were plotted against their corresponding cadmium ion concentrations, the graph will be like below (Fig. 6).

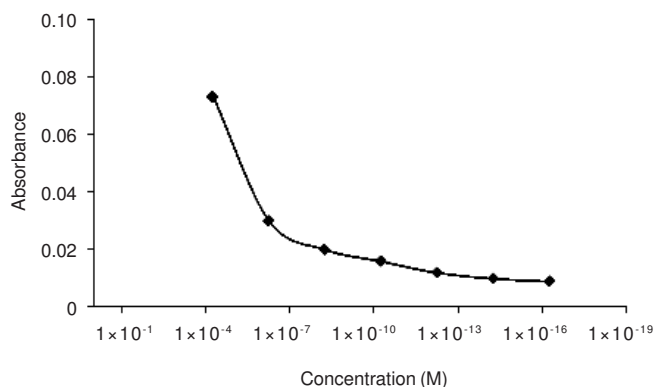
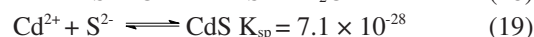
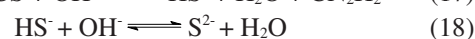
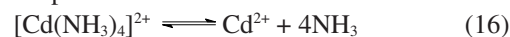


Fig. 6. Spectrum of UV/VIS of cadmium ion solutions after adding thiourea at $\lambda = 400.7$ nm

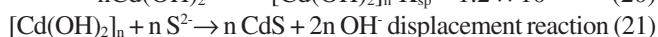
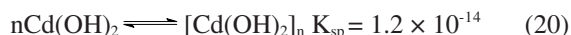
As cadmium ion concentration was gradually reduced, the formation of cadmium sulfide become more difficult, then the absorbance at maximum wavelength 400.7 nm (correspond to cadmium sulfide precipitate, yellow region) is reduced until cadmium sulfide is not produced.

Effect of pH and concentration of complexing agent:

There are two suggested mechanisms in the bath solution which are well documented⁹; a) *ion by ion*: The presence of ammonia solution in the reaction serves to provide the OH⁻ ions required for the hydrolysis of thiourea that gives S²⁻ and controlling the amount of Cd²⁺ ions in the bath through the reaction of the tetraamine complex. The mechanism consists of a slow generation of the Cd²⁺ and S²⁻ ions by decomposition of [Cd(NH₃)₄]²⁺ complex.

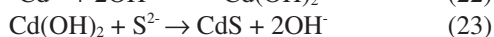


b) Simple cluster



These conditions have been studied as follows:

Studies at pH = 9-10 and 2 M ammonium solution and complexing agent concentration relative to cadmium ion concentration is low: It was found that $\text{Cd}(\text{OH})_2$ precipitate will be formed on the substrate in this condition so that it leads to the creation of initial nuclei of CdS and growth of nuclei and deposition of the CdS film. The resulting thin film has good adherence on the substrate and heterogeneous precipitation occurs in the solution according to the following reactions:



In this respect sulfide ion replaced hydroxide ion easily as the K_{sp} of CdS is smaller than the K_{sp} of $\text{Cd}(\text{OH})_2$.

Studies at pH = 9-10 and 2 M ammonium solution and complexing agent concentration relative to cadmium ion concentration is high: In contrast with early condition, it prevents the formation of $\text{Cd}(\text{OH})_2$ precipitate. In this case, thin film formed on the substrate has no adherence because of CdS particles already precipitate in the solution and the absorbance spectrum of this substrate is similar to absorbance spectrum of non-precipitate substrate (Fig. 5).

Studies at pH = 11, 12, 13 and complexing agent concentration relative to cadmium ion concentration is high: Under these conditions, $\text{Cd}(\text{OH})_2$ precipitates on the substrate and CdS film has a good adherent to the glass substrate (Fig. 7).

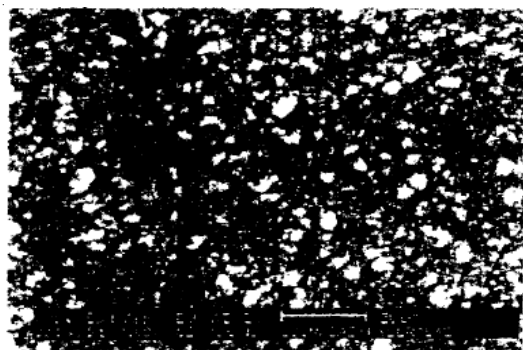


Fig. 7. SEM image of CdS thin film on a special support

The graining of layers is almost distributed evenly and no hole is observed on the surface of them.

Studies at pH = 12, 13 and complexing agent concentration relative to cadmium ion concentration is low: In this condition, there is an excess of $\text{Cd}(\text{OH})_2$ precipitate in the solution and a predominantly homogeneous reaction often happens. Furthermore, the resulting film would grow by the absorption of colloids and thin film formed has no good adherence to the substrate. Due to lack of enough adhesion to the substrate, the thickness was unreadable by SEM.

Formation of CdS nanoparticles was confirmed by UV absorption spectra and TEM images. As shown in Fig. 8, the size of the CdS nanoparticles was varied from 10 to 25 nm, in correlation with the increase of amount of cadmium salt in the test solutions, which was also confirmed by a red shift in the UV spectra.

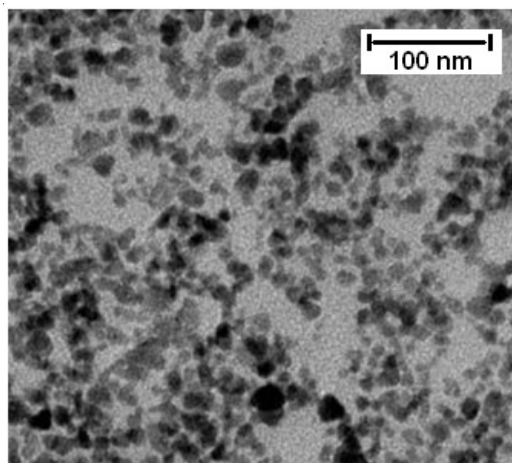


Fig. 8. TEM image of CdS thin film on a special support

Conclusion

Sulfide ion is provided by the hydrolysis reactions of thiourea or thioacetamide in the bath solution. The use of suitable pH, temperature of about 80 °C in basic bath solution (especially this temperature is useful for better hydrolysis thiourea) and with adequate complexing agent and cadmium ion concentration in the bath solution, formation of $\text{Cd}(\text{OH})_2$ precipitate on the substrate is not stopped. This precipitate then becomes the matrix which paves the way to the formation of an adherent CdS thin film on the substrate in the bath solution.

In the right conditions predominantly heterogeneous reaction happens in the chemical bath solution. It is recommended to avoid more basic values of pH when complexing agent concentration is low and with lower values of pH, high complexing agent concentration is required.

REFERENCES

- R. Zhai, S. Wang, H. Xu, H. Wang and H. Yan, *Mater. Lett.*, **59**, 1497 (2005).
- G. Sasikala, P. Thilakan and C. Subramanian, *Solar Energy Mater. Solar Cells*, **62**, 275 (2000).
- C. Voss, Y.-J. Chang, S. Subramanian, S. O. Ryu, T.-J. Lee and C.-H. Chang, *J. Electrochem. Soc.*, **151**, C655 (2004).
- I. Kaur, D.K. Pandya and K.L. Chopra, *J. Electrochem. Soc.*, **127**, 943 (1980).
- M.A. Martínez, C. Guillén and J. Herrero, *Appl. Surf. Sci.*, **136**, 8 (1998).
- I.O. Oladeji and L. Chow, *J. Electrochem. Soc.*, **144**, 2342 (1997).
- E. Pentiaz, V. Draghici, G. Sarau, B. Mereu, L. Pintilie, F. Sava and M. Popescu, *J. Electrochem. Soc.*, **151**, G729 (2004).
- J.M. Dona and J. Herrero, *J. Electrochem. Soc.*, **144**, 4081 (1997).
- J. Herrero, M.T. Gutiérrez, C. Guillén, J.M. Doña, M.A. Martínez, A.M. Chaparro and R. Bayón, *Thin Solid Films*, **361-362**, 28 (2000).
- P. Nemeč, I. Nemeč, P. Nahálková, Y. Nemečová, F. Trojánek and P. Malý, *Thin Solid Films*, **403**, 9 (2002).
- D.S. Boyle, A. Bayer, M.R. Heinrich, O. Robbe and P. O'Brien, *Thin Solid Films*, **361-362**, 150 (2000).
- P.O. Brien and J. McAleese, *Mater. Chem.*, **8**, 2309 (1998).
- H. Zhang, X. Ma, J. Xu and D. Yang, *J. Crystal Growth*, **263**, 372 (2004).
- M. Ortego-Lopez, A. Avila-Garcia, M.L. Albor-Aguilera and V.M. Sanchez-Resendiz, *Mater. Res. Bull.*, **38**, 1241 (2003).
- S. Herrera, C.M. Ramos, R. Patiño, J.L. Peña, W. Cauich and A.I. Oliva, *Brazil. J. Phys.*, **36**, 1054 (2006).
- O.M. Peeters and C.J. de Ranter, *J. Chem. Soc. Perkins Trans II*, **2**, 1832 (1974).
- D. Rosenthal and T.I. Taylor, *J. Am. Chem. Soc.*, **79**, 2684 (1957).
- E.A. Butler, D.G. Peters and E.H. Swift, *Anal. Chem.*, **30**, 1379 (1958).
- O. Portillo-Moreno, H. Lima-Lima, R. Lozada-Morales, R. Palomino-Merino and O. Zelaya-Angel, *J. Mater. Sci.*, **40**, 4489 (2005).
- E.H. Swift and E.A. Butler, *Anal. Chem.*, **28**, 146 (1956).