

Electrochemical Studies on the Cathodic Electrodeposition of n-type semiconductor CdS thin film from Thiosulfate Acidic Aqueous Solution

M Akif Shikhan Aliyev¹ and Mahmoud El-rouby^{*2,3}

¹ Institute of chemical problems, National Academy of sciences of Azerbaijan, AZ 1143 Baku, Azerbaijan

² Chemistry Department, Faculty of Science, Sohag University, 82524 Shag, Egypt

E-mail: dr_mahmoudelrouby@hotmail.com

Received: 6 Jul. 2013, Revised: 11 Jul. 2013; Accepted: 11 Aug. 2013

Published online: 1 Sep. 2013

Abstract: The cathodic electrodeposition of CdS from aqueous solutions of Cd²⁺ and S₂O₃²⁻ at 40 °C, has been achieved using a combination of cyclic voltammetric and potentiostatic techniques. The voltammetric responses of the investigated thiosulfate, Cd²⁺ both individually as well as with each other are achieved and hence the optimum conditions for the electrodeposition of CdS were determined. Interesting data was obtained and discussed in this work. The mechanism of the electrode reactions for the investigated substance have been evaluated and proposed. X-ray diffraction investigations demonstrate that the electrodeposited CdS is hexagonal polycrystalline in nature. Furthermore, the electrodeposited CdS is of n-type semiconductor was investigated by Mott-Schottky test and from it, donor concentration (N_D) is also determined.

Keywords: CdS, Cathodic Electrodeposition, Aqueous Acidic Media, hexagonal crystal, Mott-Schottky test

1. Introduction

II-VI semiconductors such as CdS is used as buffer layers in Cu(In,Ga)(S) (CIGS) photovoltaic devices. CdS n-type semiconductor is with a band gap of 2.42 eV at room temperature. Thus, CdS thin films have been used widely as window layers in solar cells with an absorber layer of CdTe, Cu₂S₂ or CuInSe₂. Therefore it is still under consideration of the researchers till now. So far, CdS thin films have been deposited by various methods, e.g. vapor deposition, spray pyrolysis, chemical bath deposition, and electrochemical deposition. Electrochemical deposition is an attractive method for preparation of thin films in commercial quantities because it uses relatively cheap equipment, enables the deposition in large area and easy control of growth parameters through applied potential, current, pH and temperature of the bath. Many works have been reported for studying the mechanism of an electrochemical deposition of CdS from aqueous [1-6].

Cadmium sulfide has been formed from the anodization of the metal in alkaline sulfide solution [7] and in buffered sulfide solution [8, 9]. It has been deposited cathodically from a solution containing cadmium and thiosulfate ions [1, 10]. CdS has also been deposited on ITO-coated glass potentiostatically [11].

Where an aqueous solution of 0.2M $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.01M $\text{Na}_2\text{S}_2\text{O}_3$ adjusted to a pH in the range of 2–3 using HCl was used with a bath temperature of 90 °C.

The aim of the present work is to study the optimal conditions for simple and fast cathodic electrodeposition method for obtaining of n-type hexagonal crystal structure of CdS. Also determination of N_D of CdS from the Mott-Schotky test.

2. Materials And Methods

2.1. Apparatus

Electrochemical experiments were carried out using an Ivium Sat potentiostat /galvanostat at controlled thermostated desired temperature. A conventional three-electrode cell was used. The cell has a slot for purging the nitrogen gas and a magnet for mixing the solutions; hence the cell is set on a stirrer. A silver/silver chloride ($\text{Ag}/\text{AgCl}/\text{KCl}_{(\text{sat.})}$) and platinum sheet were used as reference and auxiliary, respectively. Platinum wire (0.25 cm^2) and Nickel sheet (0.5 cm^2) were used as working electrodes. The working electrode was cleaned with a solution contains 1:1 concentrated H_2SO_4 and H_2O_2 followed by acetone and rinsed with deionized water before performing the experiment.

The pH value of the solution was adjusted to the desired value with H_2SO_4 by a digital calibrated pH-meter.

2.2. Reagents

Cadmium sulfate $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, Sodium thiosulfate $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, Thiourea $(\text{NH}_2)_2\text{CS}$ and sulfuric acid H_2SO_4 are of analytical grade from Merck, and BDH were used without further purification. All solutions were prepared freshly with deionized water.

3. Results and Discussion

3.1. Cyclic voltammetric behavior

Cyclic voltammetry was used to determine the electrode potential mechanism for the electrodeposition of CdS and to determine the peak location of CdS electroreduction.

Cyclic voltammetry of $\text{S}_2\text{O}_3^{2-}$

At first $\text{Na}_2\text{S}_2\text{O}_3$ solution was investigated to get information relating to its cathodic reaction as in Fig. 1. It shows the cyclic voltammogram of 0.005 M $\text{Na}_2\text{S}_2\text{O}_3$ solution containing sulfuric acid at pH = 2.5, room temperature and scan rate = 0.05 V s^{-1} . In the voltammogram the cathodic peak was observed around -0.66 V. It has a similar behavior, irreversible, that was obtained in other literatures. But in the later, the reduction peak was observed around -0.8 V on Ti electrode [12]. This difference may be attributed to the difference of hydrogen over potential and the electrocatalytic activity between Ti and Pt.

The number of electrons that consumed in this electrochemical reduction reaction can be determined to know the mechanism of the reaction by the following equation [13];

$$\left| E_p - E_{p/2} \right| = \frac{1.857RT}{\alpha nF} = \frac{47.7}{\alpha n} \quad \text{mV} \quad (1)$$

In addition, the peak separations confirm that there is a totally irreversible two electron transfer process at the main cathodic peak on the working electrode according to the previous relation.

Cyclic voltammetry of Cd^{2+}

Fig. 2. shows the cyclic voltammogram of 0.01 M Cd^{2+} solution containing sulfuric acid at pH = 2.5, at 22 °C and at scan rate = 0.05 V s⁻¹. In the voltammogram the cathodic peak was observed around -0.85 V.

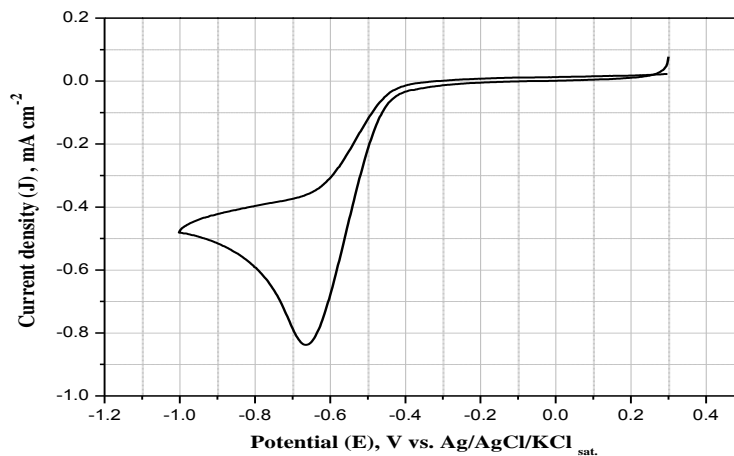


Figure 1: Cyclic Voltammogram of 0.005-M $\text{Na}_2\text{S}_2\text{O}_3$ at 0.05 V s⁻¹, at pH = 2.5 on Pt- electrode at 22 °C at pH = 3 and t =22 °C.

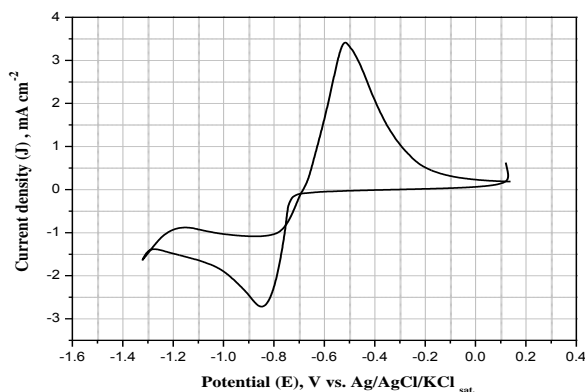


Figure 2: Cyclic Voltammogram of 0.01-M Cd^{2+} at 0.05 V s⁻¹, at pH = 2.5 on Pt- electrode at 22 °C at pH = 3 and t =22 °C.

While the oxidation peak appeared at a potential of -0.53 V, the redox process is considered to be quasi-reversible with two electrons transfer. It seems that the peaks are commonly associated with reduction process of the Cd (II) to Cd(0), as confirmed by other researches [14,15].

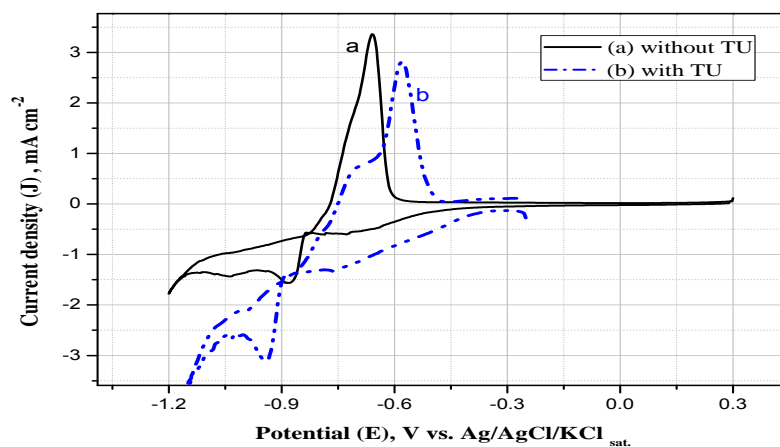


Figure 3 : Cyclic Voltammogram of $0.01\text{-M Cd}^{2+} + 0.1 \text{ S}_2\text{O}_3^{2-}$ without TU (a) and with TU (b) at 0.02 V s^{-1} , at $\text{pH} = 2.5$ on Pt-electrode at $40 \text{ }^\circ\text{C}$ at $\text{pH} = 3$ and $t = 22 \text{ }^\circ\text{C}$.

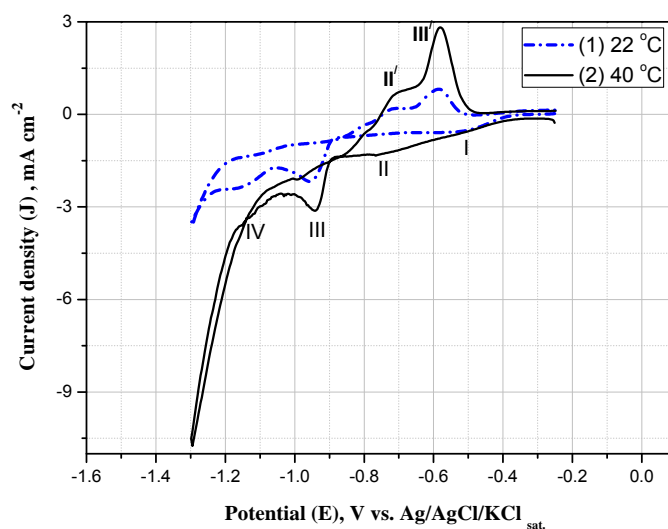


Figure 4: Cyclic Voltammogram of $0.01\text{-M Cd}^{2+} + 0.1 \text{ S}_2\text{O}_3^{2-} + (\text{NH}_2)_2\text{CS}$ at 0.02 V s^{-1} , at $\text{pH} = 2.5$ on Pt-electrode at (1) at $22 \text{ }^\circ\text{C}$ and (2) $40 \text{ }^\circ\text{C}$ at $\text{pH} = 3$ and $t = 22 \text{ }^\circ\text{C}$.

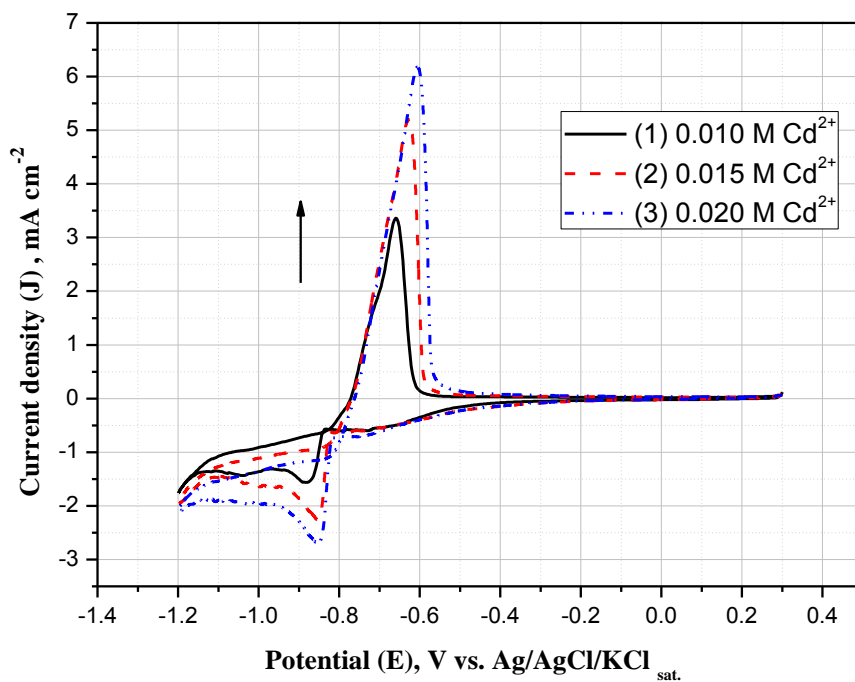


Figure 5: Cyclic Voltammogram of $M Cd^{2+} + 0.1 S_2O_3^{2-}$ at (1) 0.01 M Cd^{2+} , (2) 0.015 M Cd^{2+} , (3) 0.02 M Cd^{2+} at $0.02 V s^{-1}$, at pH = 2.5 on Pt- electrode at $40 ^\circ C$ at pH = 3 and $t = 22 ^\circ C$.

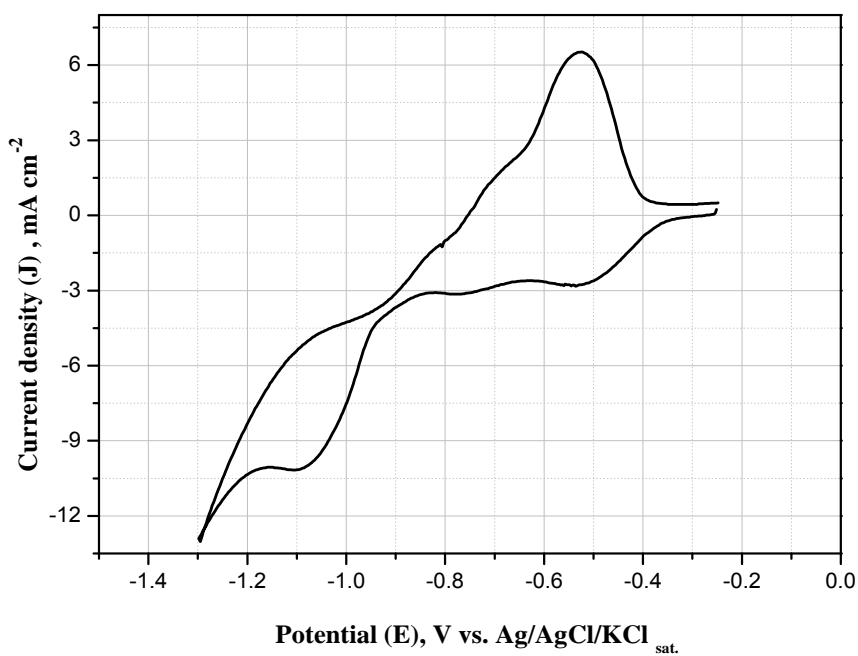


Figure 6: Cyclic Voltammogram of $0.01-M Cd^{2+} + 0.1 S_2O_3^{2-} + (NH_2)_2CS$ at $0.02 V s^{-1}$, at pH = 2.5 on Ni- electrode at $40 ^\circ C$. at pH = 3 and $t = 22 ^\circ C$.

- *Cyclic voltammetry of $\text{Cd}^{2+} + \text{S}_2\text{O}_3^{2-}$*
- *Thiourea effect*

Fig. 3 shows the cyclic voltammograms of a Pt electrode in 0.01 M $\text{Cd}^{2+} + 0.1 \text{ M S}_2\text{O}_3^{2-}$ without and with 0.1 M thiourea (TU) at 40 °C. The addition of TU gave a little hinder effect on the cathodic peak potential (shifted to more negative potential) of Cd^{2+}/Cd while a significant increase in the cathodic peak current density was observed.

In aqueous solutions, there are mainly two ways for the additives to affect the deposits during the electroplating. One is carried through making a complex with the metal ions and the other by the adsorption on the electrode surface and/or the electrodeposits. So, there are change in the cathodic current density and in the location of the cathodic peaks potential [16,17].

- *Temperature effect*

It is found in this work, the optimum condition for the electrodeposition of CdS (confirmed by XRD analysis below) as described in Fig. 4(2). Figure 4 shows the cyclic voltammograms of a Pt electrode in 0.01 M $\text{Cd}^{2+} + 0.1 \text{ M S}_2\text{O}_3^{2-} + 0.1 \text{ M thiourea (TU)}$ at room temperature (22 °C) and at 40 °C. The increase of temperature increases the cathodic peak current density of the electrodeposition process.

The first cathodic peak (I) (~ -0.55 V) is attributed to the electroreduction of the colloidal sulfur which dissociated from thiosulfate at these conditions. While The electroreduction cathodic peak potential of sulfur is observed at ~ -0.65 V in Fig. 1., this difference due to the difference in temperature and concentrations in the two experiments and the presence of thiourea. The second cathodic peak potential (II) (~ -0.75 V) is attributed to the electrodeposition of CdS (confirmed by XRD);

$\text{S (colloidal)} + 2\text{e}^- \rightarrow \text{S}^{2-}$ (adsorbed at the electrode surface) (first peak, I)

S^{2-} (adsorbed) + $\text{Cd}^{2+} = \text{CdS}$ (adsorbed at the electrode surface)..... (second peak, II)

At the third cathodic peak potential, III, (~ -0.93 V) free unreacted Cd^{2+} ions are discharged into Cd(0). But the electroreduction peak potential of Cd^{2+} is observed at ~ -0.87 V as in Fig. 2. This difference is due to the presence of thiourea which makes a complex with Cd^{2+} ion that hinders the electroreduction process and also the difference in the temperature of each experiment. Also it can be confirmed by addition of Cd^{2+} as shown in Fig. 5.

Fig. 5. shows the cyclic voltammetry of Pt electrode in a solution of $\text{M Cd}^{2+} + 0.1 \text{ M S}_2\text{O}_3^{2-}$ at pH = 2.5 and temperature of 40 °C. It is observed that, by increasing the concentration of Cd^{2+} ions the third peak increases. This emphasizes that the third peak is attributed to the electroreduction of Cd^{2+} ions into Cd(0).

The fourth cathodic peak, IV, (~ -1.15 V) is attributed to the electroreduction decomposition of the electrodeposited CdS on the electrode surface resulting Cd(0) and S^{2-} ;

$\text{CdS} + 2\text{e}^- = \text{Cd} + \text{S}^{2-}$

Fig. 6. shows the cyclic voltammetry of Ni electrode in a solution of $0.01\text{M Cd}^{2+} + 0.1 \text{ M S}_2\text{O}_3^{2-}$ at pH = 2.5 and temperature of 40 °C. This behavior looks like the behavior on Pt electrode. So Ni can be used as a substrate for the electrodeposition of CdS. Moreover, because of Ni is more available and cheaper than

Pt, so it can be introduced as a substrate for the analysis such as XRD, ...etc of the electrodeposited CdS on its surface.

From the previous data of cyclic voltammetric measurements, the optimum conditions for the electrodeposition of CdS thin film are; by using a solution of a composition $0.1 \text{ M S}_2\text{O}_3^{2-} + 0.01 \text{ M Cd}^{2+} + 0.1 \text{ M thiourae (TU)}$ at $\text{pH} = 2.5$, $t = 40 \text{ }^\circ\text{C}$ and the electrodeposition potential is in between the range $-0.75 > E > -0.85$ for a certain time.

3.2. XRD analysis

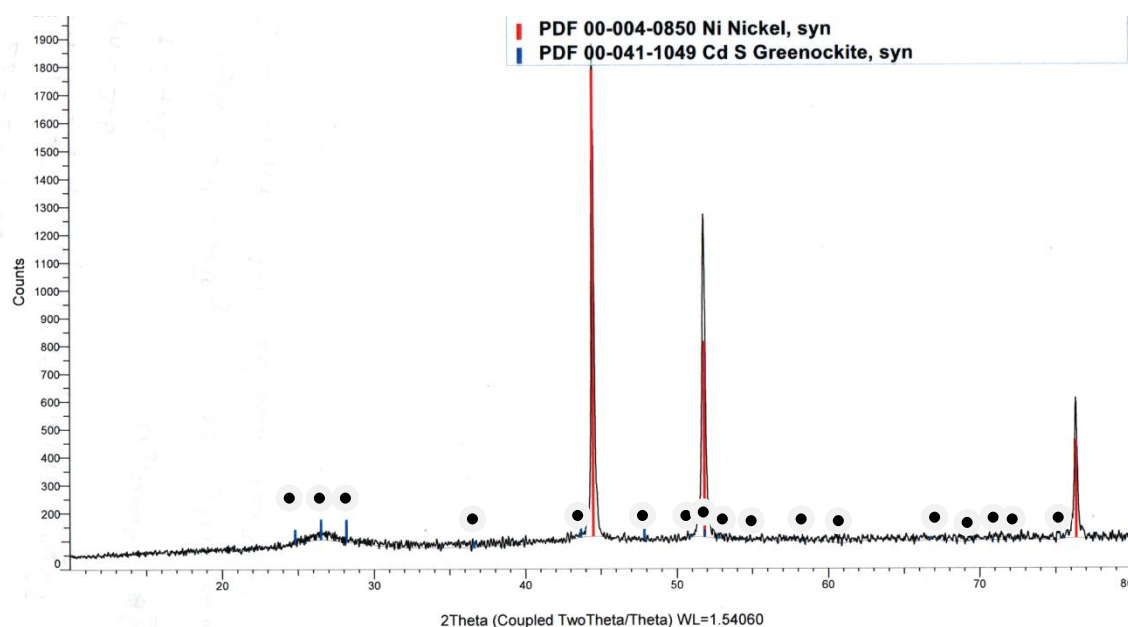


Figure 7: XRD patterns for the CdS thin film • obtained at $E = -0.80 \text{ V}$ for two hours at Ni substrate. Conditions are as in Fig. 4(2).

Fig. 7 shows the XRD patterns of the electrodeposited CdS film deposited at potential $= -0.80 \text{ V}$ (the potential at which the CdS film is electrodeposited, second cathodic peak II, Fig. 4) for two hours from solution contains $0.1 \text{ M S}_2\text{O}_3^{2-} + 0.01 \text{ M Cd}^{2+} + 0.1 \text{ M (NH}_2)_2\text{CS}$ on Ni substrate at $\text{pH} = 2.5$ and $t=40 \text{ }^\circ\text{C}$. The XRD data reveals that, at these conditions polycrystalline hexagonal CdS is obtained. The XRD data is listed in Table 1 and show a mixed phases similar to those reported by other workers for hexagonal crystalline CdS [18-20].

Table 1: Experimental XRD data related to CdS films as in Fig. 6.

2 θ	d($^{\circ}$ A)	I	hkl
24.81	3.59	63	100
26.51	3.36	94	002
28.18	3.16	105	101
36.62	2.45	30	102
43.68	2.07	50	110
47.84	1.90	51	103
50.88	1.79	10	200
51.83	1.76	30	112
52.80	1.73	16	201
54.58	1.68	5	004
58.28	1.58	3	202
60.84	1.52	3	104
66.77	1.40	14	203
69.26	1.36	5	210
70.86	1.33	7	211
72.40	1.30	4	114
75.48	1.26	8	105

From XRD data, it is illustrated that when the deposition potential is fixed at potential of -0.80 V (second cathodic peak II, Fig. 4), the CdS is only deposited on the electrode surface, but when the deposition potential is fixed at -1.2 (fourth cathodic peak IV) CdS and Cd(0) are electrodeposited as shown in Fig. 8.

Fig. 8 shows the XRD patterns of the electrodeposited CdS film deposited at potential = -1.2 V for two hours from solution contains 0.1 M $S_2O_3^{2-}$ + 0.01 M Cd^{2+} + 0.1 M $(NH_2)_2CS$ on Ni substrate at pH = 2.5 and t=40 $^{\circ}C$.

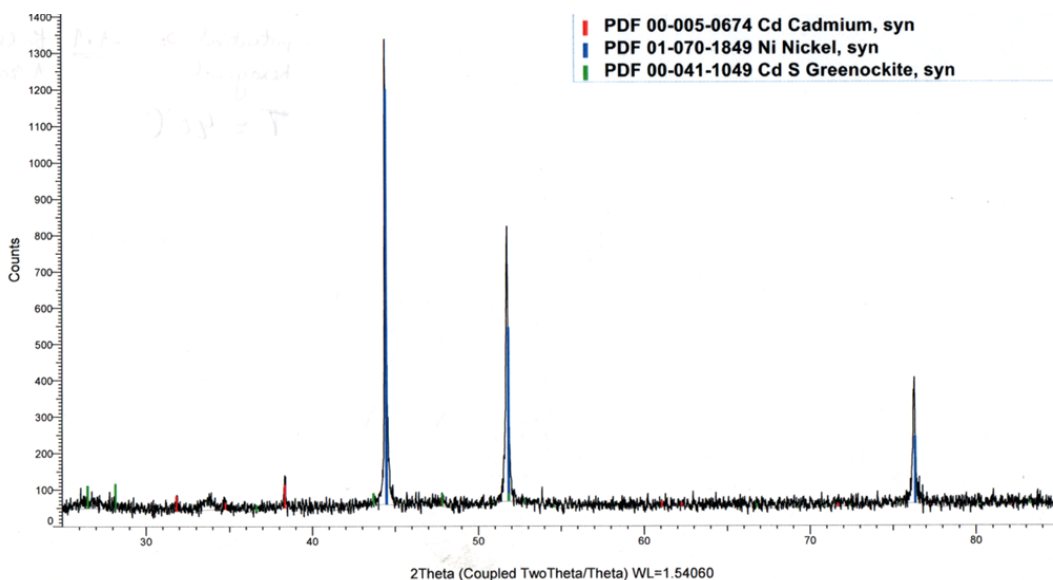


Figure 8: XRD patterns for the CdS thin film obtained at $E = -1.20$ V for two hours at Ni substrate. Conditions are as in Fig. 4(2).

3.3. Mott-Schottky test

Mott-Schottky plot ($1/C^2$ vs. V) is studied using 0.5 M Na_2SO_4 as supporting electrolyte.

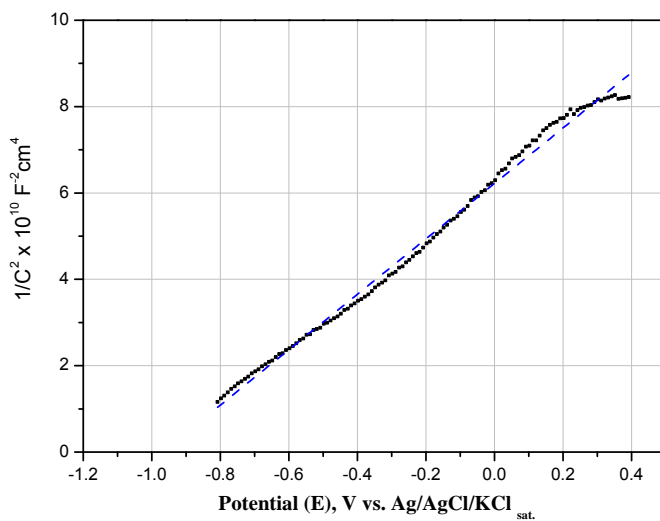


Figure 9 : Mott-Schottky plot of the electrodeposited CdS, Conditions of the electrodeposition are as in Fig. 4(2).

Figure 9 exhibits the Mott-schottky plot for the electrodeposited CdS thin film prepared at the condition as described in Fig. 4(2). The capacitance measurement was carried out at 5000 Hz within the potential range from + 0.4 to - 0.8 V in the cathodic direction. The nature of the plot indicates n-type behavior. Extrapolation of the plot to the potential axis gives a flat band potential V_{fb} of -1.0 V (Ag/AgCl). The

value of the carrier density (N_D) can be determined from the slope of the plot with the aid of Mott-Schottky equation [21];

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon^0 e N_D} (V - V_{fb} - kT/e)$$

where e is the elementary charge (+ e for electrons and $-e$ for holes), ϵ is the dielectric constant, ϵ^0 the permittivity in vacuum, N_D is the acceptor or donor concentration, V is the applied potential, and V_{fb} , the flat band potential.

The N_D value is around $1.0 \times 10^{17} \text{ cm}^{-3}$. This value agrees with that obtained from other reports [22]

4. Conclusion

- The electrodeposition of n-type hexagonal crystals of CdS thin films can be accomplished by applying a fixed potential at -0.8 V vs. Ag/AgCl/KCl (sat.) for two hours in a bath contains $0.1 \text{ M S}_2\text{O}_3^{2-} + 0.01 \text{ M Cd}^{2+} + 0.1 \text{ M (NH}_2)_2\text{CS}$ at $\text{pH} = 2.5$ and $t=40 \text{ }^\circ\text{C}$ on Ni or Pt substrates.
- XRD analysis reveals that the obtained electrodeposits are pure CdS hexagonal crystals.
- Mott-Schottky test confirms that the electrodeposited CdS is of n-type semiconductor and has N_D value of around $1.0 \times 10^{17} \text{ cm}^{-3}$.

References

- [1] E. Fatas, R. Duo, P. Herrasti, F. Arjona et. al. Electrochemical Deposition of CdS Thin Films on Mo and Al Substrates. *J. Electrochem. Soc.* 1984. Vol. 131. pp. 2243.
- [2] S. Dennison. Studies of the Cathodic Electrodeposition of CdS from Aqueous Solution. *Electrochim. Acta.* 1993.vol. 38. pp. 2395.
- [3] G. Sasikala, R. Dhanasekaran, C. Subramanian. Electrodeposition and Optical Characterisation of CdS Thin Films on ITO-coated Glass. *Thin Solid Films.* 1997. vol. 302. pp. 71.
- [4] S.J. Lade, M.D. Uplane, C.D. Lokhande. Photoelectrochemical properties of CdX (X=S, Se, Te) films electrodeposited from aqueous and non-aqueous baths. *Mater. Chem. Phys.* 2001. Vol. 68. pp. 36–41.
- [5] M.N. Mammadov, A.Sh. Aliyev, M. Elrouby. Electrodeposition of cadmium sulfide. *Int. J. Thin Film Sci. Tec.* 2012. Vol. 1. No. 2. pp. 43-53.
- [6] A. Sh. Aliyev. Electrodeposition of thin layers CdS from sulfuric acid electrolyte. *Azerb. Chem. J.* 2005. no. 3. pp. 156-160.
- [7] B. Miller, S. Menezes, A. Heller. Anodic Formation of Semiconductive Sulfide Films at Cadmium and Bismuth Rotating Ring-Disk Electrode Studies. *J. Electroanal. Chem.* 1978. Vol. 94. pp. 85.
- [8] L. M. Peter. The Electrocrystallisation of Cadmium Sulphide Films on Cadmium. *Electrochim. Acta.* 1978. vol. 23. pp. 165.
- [9] L. M. Peter. The Photoelectrochemical Properties of Anodic Cadmium Sulphide Films. *Electrochim. Acta.* 1978. vol. 23. pp.1073.
- [10] G. P. Power, D. R. Peggs, A. J. Parker. The Cathodic Formation of Photoactive Cadmium Sulfide Films from Thiosulfate Solutions. *Electrochim. Acta.* 1981. vol. 26. pp. 681.
- [11] G. Sasikala, R. Dhanasekaran, C. Subramanian. Electrodeposition and Optical Characterisation of CdS Thin Films on ITO-coated Glass. *Thin Solid Films.* 1997. vol. 302. pp. 71.
- [12] T. Yukawa, K. Kuwabara, K. Koumoto. Electrodeposition of CuInS₂ from aqueous solution Part I. Electrodeposition of Cu-S film. *Thin Solid Films.* 1996. Vol. 280. pp. 160-162.

- [13] A.J. Bard, L.R. Faulkner. *Electrochemical methods: fundamentals and applications*. 2001. Wiley, New York.
- [14] A. Dolati, A. Afshar, H. Ghasemi. A kinetic study on the electrodeposition of cadmium with the presence of organic agents in sulfate solutions, *Mater. Chem. Phys.* 2005. Vol. **94**. pp. 23–28.
- [15] T.S.N. Sankara Narayanan. Influence of quaternary ammonium ions the electrodeposition of cadmium. *Met. Finish.* 1999. Vol. 97. pp. 94.
- [16] G.T. Rogers, M.J. Ware. The Incorporation of Sulfur in Electrodeposited Nickel, Using Thiourea as a Brightener and Leveler, *J. Electrochem. Soc.* 1960. Vol. **107**. pp. 677.
- [17] H. Yang, X. Guo, N. Birbilis, G. Wu, W. Ding. Tailoring nickel coatings via electrodeposition from a eutectic-based ionic liquid doped with nicotinic acid. *Appl. Surf. Sci.* 2011. vol. **257**. pp. 9094.
- [18] H. Uda, S. Ikegami, H. Sonomura. Structural and Electrical Properties of Chemical-Solution-Deposited CdS Films for Solar Cells, *Jpn. J. Appl. Phys.* 1990. Vol. **29**. pp. 30.
- [19] D. Bhattacharya, M.J. Carter. Effect of substrate on the structural and optical properties of chemical-bath-deposited CdS films. *Thin Solid Films.* 1996. vol. **288**. pp. 176.
- [20] N. Razik. Use of a standard reference material for precise lattice parameter determination of materials of hexagonal crystal structure. *J. Mater. Sci. Lett.* 1987. Vol. **6**. pp. 1443.
- [21] S.R. Morrison. *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*. 1980. Chap. 5, Plenum Press, New York.
- [22] Y. Ramprakas, V. Subramanian, R. Krishnakumar, A. S. Lakshmanan, V. K. Venkatesan, photoelectrochemical study of screen-printed cadmium sulphide electrodes. *J. Power Sources.* 1988. vol. **24**. pp. 4.