

***Dedicated to Professor Valer Fărcășan
at his 85th anniversary***

ELECTRODEPOSITION OF CdS THIN FILMS

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ABSTRACT. CdS thin films were obtained by potentiostatic electrodeposition on platinum and ITO electrodes from solutions containing CdSO₄ and Na₂S₂O₃ at concentration ratios higher than 1. The influence of deposition time, temperature and Cd²⁺/S₂O₃²⁻ ratio on CdS thin film electrodeposition on platinum electrodes, as well as the film composition were investigated electrochemically, by stripping voltammetry. The morphology and the composition of CdS films obtained on ITO supports were determined by SEM and EDS. It was concluded that the CdS film formation is favored by the increase of electrodeposition duration and electrolyte temperature, as well as by acid media (pH 3) and high Cd²⁺/S₂O₃²⁻ ratios (200/1).

Keywords: CdS electrodeposition, Pt and ITO electrodes, stripping voltammetry.

INTRODUCTION

The electrochemical deposition of thin films of metallic chalcogenides represents a subject of great interest, due to the semiconducting properties of these materials. Among these, CdS has gained considerable attention, being an n-type semiconductor with an optical band gap of 2.4 eV at room temperature. Thin films of CdS are used as detectors of light and window materials for CdS/CdTe solar cells of high efficiency (more than 7%) [1].

The electrodeposition represents a successful way to prepare CdS, being a low-cost process, well suited to the manufacture of film solar cells. Recently, several papers have been published referring to the CdS electrodeposition conditions and to methods of its electrochemical characterization [2, 3].

The electrodeposition of thin films of metallic chalcogenides can be realized in many ways, but the most successful methodologies are:

(i) co-deposition, where both elements are deposited at the same time from the same solution. Stoichiometry is maintained by having the more noble element as the limiting reagent, and poisoning the potential where the less noble element will be underpotentially deposited only on the more noble element [4-7].

(ii) precipitation, which consists in electrochemical generation of the precursor of one of the elements, the other being in solution. The reaction takes place in homogeneous phase, but because one of the reactants is forming directly on the electrode surface, the greatest part of the product precipitates on the surface and the thickness of the deposited film is controlled by the quantity of electrogenerated forerunner.

In both cases, the electrodeposition of CdS films on conductive substrates is a process difficult to control and frequently the quality of the obtained film is relatively poor [2, 8]. Moreover, there is a tendency towards the incorporation of some minority components from solution into the CdS film, which can result in greatly altered solid-state properties [9].

In this context, in order to optimize the obtaining of CdS films on different supports, the aim of this work was to investigate the influence of deposition time, temperature, pH, and $\text{Cd}^{2+}/\text{S}_2\text{O}_3^{2-}$ ratio on the characteristics of the thin CdS films prepared by potentiostatic electrodeposition on platinum and on indium tin oxide (ITO) electrodes.

Stripping voltammetry was used to estimate the nature and the amount of the film components, being one of the methods that could furnish interesting information about the phase composition of chalcogenides, particularly of sulfide materials. On the other side, it gives the possibility to discriminate between the electrochemical processes associated with transformation of the metal and that of metallic sulfides [3]. The electrochemical behavior of sulfides depends on their nature (Gibbs energy, crystal lattice energy, chemical interaction with electrolyte solutions) and the greater the crystal lattice energy, the more positive potential is required for the compound oxidation.

The morphology and the structure of CdS films were investigated using Scanning Electron Microscopy (SEM) and Energy Dispersive X Ray Spectroscopy (EDS).

EXPERIMENTAL SECTION

Reagents

Chemically purified 3 M CdSO_4 , 2.7 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.1 M H_2SO_4 were obtained at "Raluca Ripan" Institute of Chemistry Cluj-Napoca. Na_2SO_4 was purchased from Chimopar, Bucharest.

CdS film electrodeposition

In a first step, the deposition process was achieved in solutions containing CdSO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ ($\text{Cd}^{2+}/\text{S}_2\text{O}_3^{2-}$ ratios of 2/1 and 200/1), at pH 3, using a thermostated parallel plates cell equipped with a Pt cathode and a Pt anode. The deposition potential was chosen in the range corresponding to very low cathodic currents, where Cd nucleation starts, and the rate of deposition process is small. This condition assures the limitation of atoms number, which are deposited in a defined time range, as well as atoms diffusion on the surface towards optimum incorporation positions in crystalline network [4].

Next, the electrodeposition was achieved on ITO glass previously cleaned by ultrasonation during 15 minutes, in a 1:1 acetone-ethanol mixture.

Electrochemical measurements

The electrodeposited CdS film was cathodically stripped. Stripping voltammetry measurements were carried out in a conventional three-electrode electrochemical cell by recording the voltammogram corresponding to the previously

electrodeposited CdS, after replacing the solution used during deposition by 0.5 M Na₂SO₄ (pH 3). A saturated calomel electrode (SCE) and a coiled Pt wire served as reference and counter electrode, respectively. The cell was connected to a computer-controlled voltammetric analyzer (Autolab-PGSTAT10, Eco Chemie, The Netherlands). The scan rate was 50 mV s⁻¹.

Characterization of electrodeposited CdS films

Morphological examination of CdS deposits on ITO prepared in the parallel plates cell, was carried out with a Cambridge S 250 scanning electronic microscope (SEM). The chemical composition of the samples was obtained by using a Princeton Gamma Tech. energy dispersive X-ray analyzer coupled with the SEM.

RESULTS AND DISCUSSION

Influence of deposition time

The electrodeposition was achieved at potentials placed in the equilibrium proximity (-750 mV vs. SCE), where the deposition rate is low and the exchange current density is high, the numbers of atoms that are deposited being a little greater than those which are dissolved in a certain time range.

In each solution, the deposition was performed at the above mentioned potential, during 30 and 60 minutes. The cathodic current decay observed during the electrodeposition time proves that a resistive film is formed on the electrode surface.

For electrochemical characterization of deposited films, a cathodic stripping (Figure 1) of CdS covered electrodes, immersed in a solution of 0.5 M Na₂SO₄ (pH 3), was used.

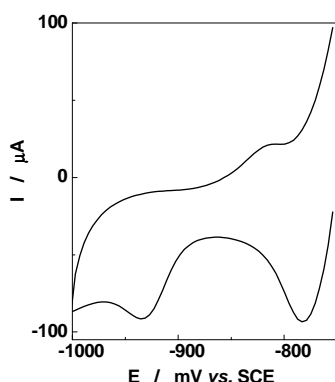
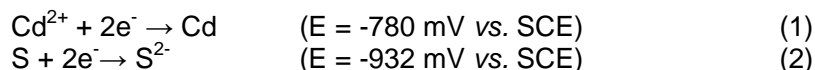


Fig. 1. Cathodic stripping of previously electrodeposited CdS film on Pt electrode. Experimental conditions: 0.5 M Na₂SO₄ (pH 3); scan rate, 50 mV s⁻¹; deposition electrolyte, 0.2 M CdSO₄ + 0.1 M Na₂S₂O₃ (pH 3); deposition potential, -750 mV vs. SCE; deposition time, 30 min.; working temperature, 20° C.

The two peaks observed during the cathodic scanning, were attributed to the following processes:



The first peak appears because, during the CdS deposition on Pt electrode, beside CdS, metallic Cd was deposited, too. In contact with the Na₂SO₄ solution (pH 3) the electrodeposited metallic Cd is partially dissolved, and is subsequently redeposited during the cathodic scanning. This fact was experimentally confirmed by the increase of this peak height after Cd²⁺ addition in the Na₂SO₄ solution (results not shown).

The second reaction is the result of S₂O₃²⁻ decomposition in acid medium, when elemental sulphur, able to be reduced to S²⁻, is formed [1]. The corresponding voltammetric peak appears as well on the cyclic voltammogram recorded on Pt electrode in a Na₂SO₄ solution of pH 3 containing only thiosulphate (results not shown).

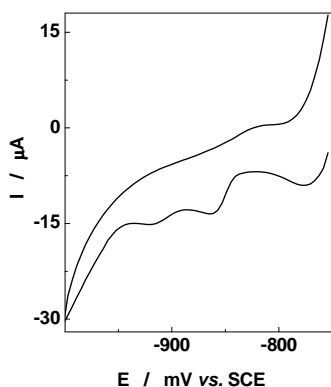


Fig. 2. Cathodic stripping of previously electrodeposited CdS film. Experimental conditions: Pt electrode; deposition time, 60 min; for the other conditions, see Fig. 1.

As it can be seen from Figure 2, the increase of deposition time from 30 to 60 minutes led to the appearance of a supplementary peak (placed between the two peaks already discussed) during the cathodic stripping. This supplementary reduction peak (placed at E = -860 mV vs. SCE) was attributed to the CdS reduction following the reaction:



CdS formation is favored by the increase of the deposition time.

A supplementary proof supporting this conclusion is the fact that, when CdS (prepared from CdSO₄ solution by precipitation with Na₂S, followed by filtration and drying) was mechanically immobilized on a graphite electrode, the corresponding cyclic voltammogram exhibited a single reduction peak at -875 mV vs. SCE (results not shown).

Influence of temperature

CdS formation is favored by the temperature increase [3], when the superficial diffusion of adatoms (which is slow at ambient temperature) is enhanced. The results obtained by stripping of deposits obtained on Pt electrode, at temperatures around 90°C from solutions of 0.2 M CdSO₄ + 0.1 M Na₂S₂O₃

(pH 3) presented in Figure 3, confirm this affirmation. Thus, during cathodic stripping only one peak appears, at a potential of about -880 mV vs. SCE, being ascribed to CdS reduction. A comparison of this stripping voltammogram with that recorded in the same solutions at room temperature, allowed to conclude that CdS formation is clearly favored by the temperature increase.

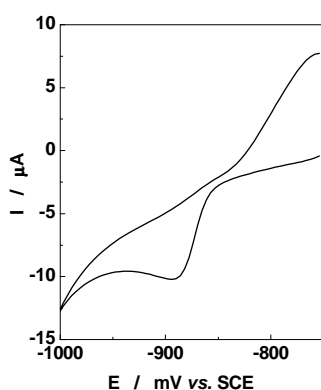


Fig. 3. Cathodic stripping of previously electro-deposited CdS film at high temperature. Experimental conditions: Pt electrode; deposition time, 30 min.; working temperature, 90⁰ C; for the other conditions, see Fig. 1.

Influence of Cd²⁺/S₂O₃²⁻ ratio

High concentrations of S₂O₃²⁻ favor the formation of colloidal S, which disturbs the reduction of S to S²⁻ and contribute to the obtaining of CdS films of poor quality [1].

In this context, the influence of Cd²⁺/S₂O₃²⁻ ratio upon the CdS film formation was initially examined at room temperature.

Comparing the stripping voltammogram recorded for CdS film deposited when the Cd²⁺/S₂O₃²⁻ ratio was 200/1 (results not shown) with that obtained in the same experimental conditions, but for a Cd²⁺/S₂O₃²⁻ ratio of 2/1 (Figure 1), it was noticed that the peak corresponding to CdS reduction becomes visible only in the first case. The fact that high Cd²⁺/S₂O₃²⁻ ratio is beneficial for CdS film formation was more evident, examining the results obtained at 90⁰C and 60 minutes deposition time (Figure 4).

Based on the above mentioned experiments it was concluded that the best conditions for CdS film deposition on Pt electrode were the following: deposition electrolyte, 0.2 M CdSO₄ + 1 mM Na₂S₂O₃, pH 3; deposition time, 60 minutes; working temperature, 90⁰ C. Extrapolating these results, ITO glass was used as substrate for CdS film deposition.

Morphology of electrodeposited CdS films

The morphology of CdS films obtained on ITO glass at 90⁰ C, 60 minutes deposition time and Cd²⁺/S₂O₃²⁻ ratio of 200/1 was investigated by SEM. In these conditions, in the absence of any previous activation of ITO glass, the CdS film consisted of insular growths on the electrode surface, suggesting the existence of a limited number of active sites on the ITO surface (Figure 5A). Consequently,

an activation treatment of the ITO support was performed before electrodeposition, by cathodic polarization at -300 mV vs. SCE, during 10 s, in a 0.1 M H₂SO₄ solution. As expected, the CdS deposits become more uniform and small grained (Figure 5B).

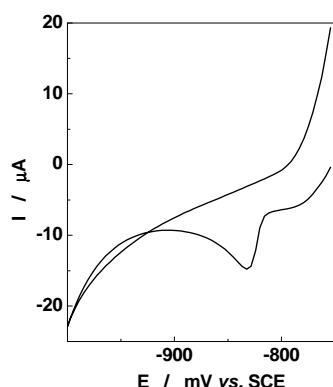


Fig. 4. Cathodic stripping of electrodeposited CdS film. Experimental conditions: Pt electrode; deposition solution, 0.2 M CdSO₄ + 1 mM Na₂S₂O₃ (pH 3); deposition time, 60 min.; working temperature, 90⁰ C; for the other conditions, see Fig. 1.

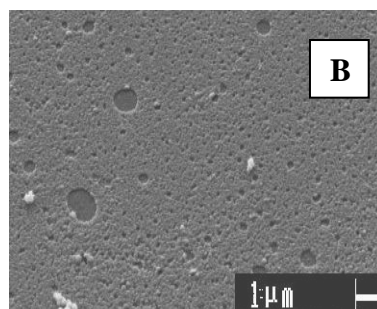
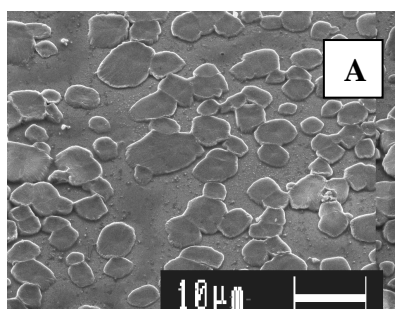


Fig. 5. SEM micrographs of CdS film electrodeposited on ITO electrode unactivated (A) and previously activated by cathodic polarization (B). Experimental conditions: activation potential, -300 mV vs. SCE; activation time, 10 s; supporting electrolyte, 0.1 M H₂SO₄; deposition solution, 0.2 M CdSO₄ + 1 mM Na₂S₂O₃ (pH 3); deposition time, 60 min.; working temperature, 90⁰ C; deposition potential, -750 mV vs. SCE.

The EDS spectrum recorded for CdS deposited film (Figure 6) pointed out to a chemical composition of ~50% Cd and 50% S, with a slight excess of S (Table 1).

Table 1.
Chemical composition corresponding to EDS spectrum of the electrodeposited CdS film on ITO electrode. Experimental conditions, as in Fig. 6.

Element	Composition		χ^2	P:B Ratio
	Wt%	At%		
Cd	77.2	49.2	4.4	8.2
S	22.8	50.8	2.1	8.0
Total	100.0	100.0	-	-

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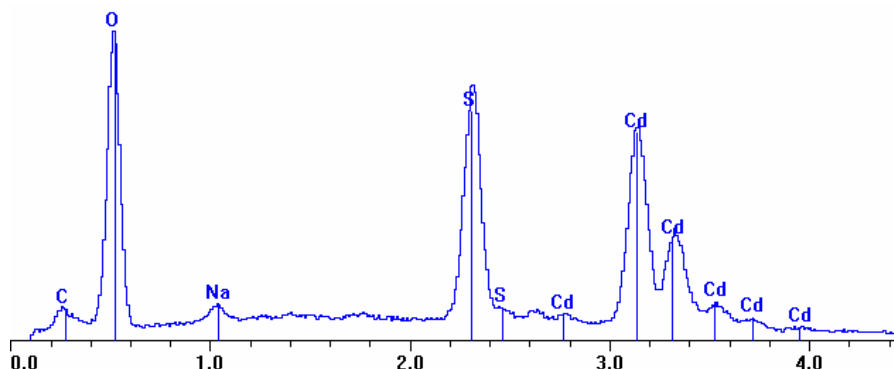


Fig. 6. EDS spectrum of CdS film electrodeposited on unactivated ITO electrode. Experimental conditions: electrodeposition conditions as in Fig. 5; live time, 100.00; beam voltage, 10.00; count rate, 2841; beam current, 1.00; dead time, 24.36 %; takeoff angle, 38.84.

CONCLUSIONS

Based on the obtained results, the following conclusions can be formulated:

- CdS film electrodeposition is promoted by temperatures around 90⁰ C, acid media (pH 3), long electrodeposition time (1h) and high Cd²⁺/S₂O₃²⁻ ratios (200/1).
- The morphology and the structure of the CdS films obtained on ITO electrodes without a previous activation of the support indicates the existence of a limited number of active sites on the surface, but a short cathodic polarization significantly improves the CdS film quality.

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