Improved electrodeposition of CdS layers in presence of activating H$_2$SeO$_3$ microadditive

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**A B S T R A C T**

CdS thin films were deposited electrochemically onto indium tin oxide (ITO)/glass substrates from aqueous solutions containing 0.01 M CdCl$_2$, 0.05 M Na$_2$S$_2$O$_3$ and 0.02 M Edta-Na$_2$ at $-1.2$ mV versus saturated sulfate reference electrode. Depositions were carried out at various temperatures (20, 50 and 80 °C) and different pH (2.5, 3.5 and 4.5) in a three electrode electrochemical cell. All above mentioned electrochemical syntheses were reproduced in presence of H$_2$SeO$_3$ microadditive to compare resulted CdS layers. Electrodeposited CdS thin films were characterized by different instrumental techniques to know the influence of deposition conditions on the quality of the obtained layers. It was found that the presence of 0.05−0.5 mM of H$_2$SeO$_3$ in the electrolyte changes the mechanism of the CdS film formation that facilitates nucleation and a growth of a more dense and uniform polycrystalline CdS film. Addition of 0.5 mM of H$_2$SeO$_3$ into the initial solution allowed us to obtain nearly stoichiometric (sulfur content ~52 at%) CdS films at reduced temperature value of 50 °C vs. higher temperature values used in a conventional electrodeposition process of CdS layers. No Se-containing phases were detected by EDX, Raman and XRD analyses in the CdS films. The presence of H$_2$SeO$_3$ tends to rearrange polytype crystalline structure of CdS to more stable hexagonal structure. The band gap value of CdS was increased from 2.3 eV to 2.5 eV as a result of H$_2$SeO$_3$ addition.

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1. Introduction

Cadmium sulfide is one of the most attractive semiconductors for application in solar cells [1] and other optoelectronic devices [2,3] due to its appropriate properties: wide band gap of about 2.5 eV at 300 K, n-type conductivity, Hall mobility of electrons ~10$^4$ cm$^2$/V s, and optical transmittance > 70% [4]. CdS thin films are produced using different techniques such as chemical vapor deposition [5], chemical bath deposition [6], spray pyrolysis [7], sputtering [8], and electrodeposition [9,10]. CdS can be deposited electrochemically from ionic liquids [9], aqueous [10] and organic solutions [11]. Electrodeposition is a relatively simple and inexpensive technology which allows the control of film properties through the change of growth parameters such as applied potential, pH, temperature and composition of the electrolyte. Generally, the use of specific additives in aqueous solutions may shift the optimal potential of electrodeposition [12], helps to refine grain size, and controls surface morphology, influencing crystalline structure and electrical properties of the layers [10]. In the electrodeposition of metals the presence of H$_2$SeO$_3$ shifts the reduction reaction of metals to lower current densities, and influences the polarization of the electrode, affecting the current efficiency and energy consumption of the electrodeposition process [13,14]. The studies concerning the properties of CdS thin films by the electrodeposition method [15,16] were held by different groups, though there are few reports on the influence of additives in the solution on the properties of CdS films.

In this work we show the effect of the H$_2$SeO$_3$ microadditive on the growth mechanism. Improvement of morphology, crystalline structure, and optical properties of the electrodeposited CdS thin films were observed at lower deposition temperature.

2. Experimental

CdS layers were electrodeposited onto indium tin oxide (ITO) coated glass substrates (15 Ω sq$^{-1}$) in a potentiostatic mode using a Voltalab PGZ100 potentiostat/galvanostat. All the electrochemical experiments were carried out in a conventional three-electrode cell. Platinum wire was used as a counter electrode (CE), an ITO/glass as a working electrode (WE), and a saturated sulfate reference electrode (SSE) as a reference. The glass/ITO substrates were cleaned in heated concentrated sulfuric acid, then rinsed with deionized Millipore water.
An initial solution was prepared in Millipore water by using reagent grade anhydrous cadmium chloride (CdCl₂, 99.0%, Alfa-Aesar), ethylenediaminetetraacetic acid disodium salt concentrate (EDTA-Na₂, Sigma-Aldrich) and sodium thiosulfate pentahydrate (Na₂S₂O₃·5H₂O, > 99.0%, Alfa-Aesar) in concentrations 0.01 M, 0.02 M and 0.05 M, respectively. The CdS films were electro-deposited at −1.2 V vs. SSE from the initial solution at the temperatures of 20, 50 and 80 °C. As growth rate is usually temperature-dependent, we used different electro-deposition times at different temperatures (20 °C – 60 min, 50 °C – 30 min, 80 °C – 20 min) to obtain films with a comparable thickness. The pH of the electrolyte was adjusted by addition of 0.1 M H₂SO₄ up to the values of 2.5, 3.5 and 4.5. The H₂SeO₃ microadditive was added into the initial solution in the concentration range of 0–0.5 mM.

The composition of the deposited CdS films was determined by energy-dispersive X-ray microanalysis (EDX) method using Bruker Esprit 1.8 system. Due to very thin CdS layers minimum acceptable accelerating voltage of 7 kV was used. Quantification of the EDX results was performed by the help of interactive PB-ZAF standardless method. For determination of the presence of Se in film 4 kV accelerating voltage was used. Phase composition was studied using Micro Raman spectroscopy (Horiba LabRam HR spectrometer). X-ray diffractometer (Rigaku Ultima IV diffractometer with Cu-Kα radiation) was applied to analyze the crystalline nature and phase composition of the deposited films. The average crystallite size was calculated from the full width at half maximum (FWHM) intensity of the preferred peak using the Scherrer equation (11), where D is the average crystallite size, K is the constant related to crystallite shape (normally taken as 0.9), λ is the X-ray wavelength, β is the FWHM, and θ is the angle of the diffraction. Morphology and thickness of the films was imaged using high-resolution scanning electron microscopy (HR-SEM, Zeiss ULTRA 55). The surface topography of the prepared CdS thin films as well as surface roughness and average grain size were investigated by atomic force microscopy (AFM, Bruker Multimode 8.0 with application module based on Nanoscope V controller). Optical properties were measured using the SHIMADZU UV-1800 UV-vis spectrophotometer in the wavelengths region of 300–800 nm. Optical transmission and reflection data were used to determine the absorption coefficient of the deposited CdS thin films. Based on the Tauc relation [17], the values of E₈ were estimated by extrapolating the linear portion of (αhv)² versus hν plot.

$$D = \frac{(K\lambda)}{(\beta \cos \theta)}$$  

3. Results and discussion

3.1. Mechanism of electrochemical formation of CdS

Electrochemical formation of CdS thin film in acidic medium takes place according to the sequential reactions (3.1–3.3) on the surface of the WE [10].

$$\text{S}_2\text{O}_3^{2-} + 6 \text{H}^+ + 4\text{e}^- \rightarrow 2\text{S(s)} + 3\text{H}_2\text{O} \quad (E^0 = 0.465 \text{ V, SHE}) \quad (3.1)$$

$$\text{S(s)} + 2 \text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{S}_{\text{ads}} \quad (E^0 = 0.141 \text{ V, SHE}) \quad (3.2)$$

$$\text{H}_2\text{S}_{\text{ads}} + \text{Cd}^{2+} \rightarrow \text{CdS} + 2\text{H}^+ \quad (3.3)$$

Initially, thiosulfate anions reduce to sulfur on the surface of the WE (3.1), where SHE is the saturated hydrogen electrode, and then sulfur reduces to hydrogen sulfide H₂Sₕads (3.2). The molecules of H₂Sₕads react with Cd cations and form CdS (4). Because metallic cadmium can be reduced at the potential of −0.45 V vs. SHE (3.4), we used EDTA-Na₂ as a complexing agent in order to shift the deposition potential of Cd to a more negative region.

$$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd} \quad (E^0 = −0.451 \text{ V, SHE}) \quad (3.4)$$

In parallel with electrochemical reactions, chemical disproportion reaction of the thiosulfate anions (3.5) can occur at pH lower than 5 [14]. There is a high probability that sulfur in a form of nanoparticles could be incorporated into the CdS film during the deposition process.

$$\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{S(s)} + \text{SO}_3^{2-} \quad (3.5)$$

A small amount of selenious acid added into the initial solution influences the mechanism of electrodeposition and may cause changes in the chemical, structural and optical properties of CdS films [13,16]. According to our assumption, Se reduces from H₂SeO₃ under a more positive potential (3.6) than sulfur from the thiosulfate ions (3.1). Se contributes to the formation of a larger number of nucleation centers on the surface of the WE. This may promote the growth of a denser film with smaller grain size. Then Se can be reduced to H₂Se at the cathodic potential of 0.40 V vs. SHE (3.7). H₂Se may react with Cd²⁺ ions forming CdSe as nucleation centers (3.8) or return back into the electrolyte. Then Se may be replaced by S with following formation of CdS layer.

$$\text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{Se(s)} + 3\text{H}_2\text{O} \quad (E^0 = 0.740 \text{ V, SHE}) \quad (3.6)$$

$$\text{Se(s)} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{Se} \quad (E^0 = −0.40 \text{ V, SHE}) \quad (3.7)$$

$$\text{H}_2\text{Se} + \text{Cd}^{2+} \rightarrow \text{CdSe} + 2\text{H}^+ \quad (3.8)$$

3.2. Electrodeposition from Se-free solution

The temperature and pH of an electrolyte have a great influence on the growth rate and morphology of the CdS films during the electrodeposition [16,18]. The changes of sulfur content in the films as a function of a pH from 2.5 to 4.5 in the initial solution at 80 °C are shown in Fig. 1 (curve a). Nearly stoichiometric CdS films with the sulfur content ~55 at% were obtained at the pH 2.5. When the pH increases from 3.5 to 4.5 the content of sulfur in the films raises from ~59 at% to ~75 at%, respectively.

Changes of the film stoichiometry as a function of deposition temperature (20–80 °C) at the pH 3.5 are shown in Fig. 1 (curve b). The pH 3.5 was chosen due to the electrolyte stability in the range of pH from 2.8 to 4.0 and because at higher pH values a poor adhesion of CdS to the ITO/glass substrate was observed [19].

![Fig. 1. Content of sulfur in CdS films electrodeposited from initial Se-free solution at −1.2 V vs. SSE at a) pH 2.5 – 4.5, 80 °C, b) 20 °C – 80 °C, pH 3.5.](image-url)
Sulfur content decreases from ~80 at% to ~72 at% by raising the deposition temperature from 20 °C to 50 °C. In terms of stoichiometry (53–55 at%), the best films deposited from Se-free initial solution were obtained at the highest temperature of 80 °C at the pH values of 2.5 and 3.5. However, in terms of stability of aqueous solution a lower temperature of 50 °C is preferable.

3.3. CdS electrodeposited from Se-containing solutions

In order to study the influence of H$_2$SeO$_3$ on the electrodeposition of CdS, a micromolar concentration of H$_2$SeO$_3$ (0, 0.05, 0.1, 0.5 mM) was added into the initial solution. The properties of the CdS films deposited at different H$_2$SeO$_3$ concentrations were studied as a function of pH and temperature. More stoichiometric CdS films were obtained at lower pH values 2.5 and 3.5 (Fig. 2(a)), which is in an agreement with the data obtained for CdS electrodeposited from the Se-free solution (Fig. 1). The decrease of the pH from 4.5 to 2.5 reduces the excess of sulfur from ~63 at% to 54 at%, while addition of H$_2$SeO$_3$ lowers deviation in the composition of the deposits.

The raise of the solution temperature decreases the deviation of composition, and improves the stoichiometry of the deposited CdS films (Fig. 2(b)). At 20 °C the addition of 0.01 mM of H$_2$SeO$_3$ diminishes the excess of sulfur from 80 at% to 70 at%, whereas higher concentrations of the H$_2$SeO$_3$ (0.1, 0.5 mM) increase it back. S-rich composition of the CdS thin films obtained at 20 °C may be caused by slow diffusion of the Cd$^{2+}$ ions towards the WE at low temperature. At higher temperatures the content of sulfur is decreased by the addition of H$_2$SeO$_3$ from ~70 at% to ~56 at% and from ~53 at% to ~52 at% at 50 °C and 80 °C, respectively. We can conclude that the presence of H$_2$SeO$_3$ microadditive allows to obtain nearly stoichiometric CdS at lower deposition temperature (50 °C).

The elementary analysis of the CdS films deposited from the solution with maximal concentration of H$_2$SeO$_3$ (0.5 mM) at the pH 3.5, at ~1.2 V vs. SSE, at 50 °C for 30 min is shown in Fig. 3. Strong peaks corresponding to Cd at L$_\alpha$ of 3.13 keV and S at K$_\alpha$ of 2.307 keV were observed (Fig. 3-a). Composition of the CdS films was found to be nearly stoichiometric with a ratio of Cd:S equal to 1:1.08. Small excess of sulfur may occur as a result of sulfur nanoparticles trapping in the CdS layer. Peaks of indium and oxygen appear from ITO. As no detectable L$_\alpha$ Se peak at 1.419 keV was revealed (Fig. 3-b), it is reasonable to assume that Se is absent or very low (less than 0.3 m%) in the deposits. Similar compositional results were obtained for all the CdS thin films deposited from the solutions Se-free and containing 0.05–0.5 mM of H$_2$SeO$_3$.

Raman spectra of the CdS films deposited at various concentrations of H$_2$SeO$_3$ are shown in Fig. 4. Peaks at 300 cm$^{-1}$ and 600 cm$^{-1}$ are attributed to longitudinal optical (LO) phonon vibrational modes of CdS [20], whereas peaks at 91, 128, 170 and 561 cm$^{-1}$ correspond to sulfur vibrational modes [21]. Peak at 300 cm$^{-1}$ is the dominant for CdS, and its intensity increases with addition of a higher concentration of H$_2$SeO$_3$ to the working solution. A small peak at 188 cm$^{-1}$ appears only for the CdS thin films deposited with the presence og 0.5 mM of H$_2$SeO$_3$ in the electrolyte. According to literature, this peak is attributed to

![Fig. 2. Content of sulfur in CdS films as function of H$_2$SeO$_3$ concentration (CM) deposited from initial solution at a) different pH at 80 °C and; b) various temperatures at pH 3.5.](image)

![Fig. 3. EDX elemental microanalysis of CdS film deposited at pH 3.5, ~1.2 V vs. SSE, 50 °C for 30 min from initial solution with 0.5 mM of H$_2$SeO$_3$ measured at accelerating voltage of (a) 7 kV and (b) 4 kV.](image)
surface optical (SO) phonon modes of CdSe or to vibrational modes of pure S and S-Se [22,23]. H$_2$SeO$_3$ microadditive seems to promote the inclusion of Se into the crystalline structure of electrodeposited CdS thin films without forming Se-containing phases.

XRD analysis (Fig. 5) confirms the absence of Se-containing phases (or very low amount, in the frames of accuracy (~1%) of XRD measurement) in CdS thin films deposited from Se-containing solution. The CdS thin films deposited from Se-free solution exhibit both hexagonal and cubic structures with peaks (100), (002), (101), (110), (112) corresponding to the hexagonal structure, and (111), (220) and (311) planes related to the cubic structure [24]. All diffraction peaks were identified by using ICDD database [25,26]. With addition of 0.5 mM of H$_2$SeO$_3$ into the working solution, dominant hexagonal crystalline structure of the CdS thin films can be observed (Fig. 5). Transformation of the main peak at around 26.5° from mixed-phase to the hexagonal structure was detected. In order to study this transition the XRD pattern in the 2θ region 25.5–27.5° (Fig. 5-inset) was magnified. In both cases the peak at around 26.5° does not clearly belong to any of (111) and (002) planes. The diffraction peak at 2θ = 26.49° is shifted towards the higher angle side equal to 26.61° with addition of 0.5 mM of H$_2$SeO$_3$ to the working solution. This may be attributed to the lattice distortion due to changes in the stacking order. Crystalline modifications in the CdS thin films may be influenced with a Se-modified growth mechanism of the film related to the surface and interface energy. In addition, lattice constants of the CdS film increase from a = 4.13 Å to a = 4.14 Å and from c = 6.67 Å to c = 6.69 Å. The average crystallite size decreases from 15 nm to 8 nm with addition of 0.5 mM of H$_2$SeO$_3$. These changes in the crystal lattice support our assumption of Se inclusion into the CdS lattice.

Thus H$_2$SeO$_3$ microadditive in the solution tend to rearrange the usual mixed-phase [27,28] structure of CdS film to hexagonal. Moreover, it seems that the transformation tendency of the mixed-phase structure to a more hexagonal in the obtained CdS layers is connected with the initial formation of Wurtzite-hexagonal nuclei of CdSe [29,30], where Se is replaced with S as described in part 3.1.

HR-SEM and AFM micrographs of the CdS films deposited from the solutions with 0.1 mM and 0.5 mM of H$_2$SeO$_3$ were analyzed and compared to the reference film obtained from the Se-free solution (Fig. 6). The average thickness of the CdS films is in the range of 70–100 nm. The film deposited from the initial Se-free solution consists of grains and covers the ITO/glass substrate uncontinuously (Fig. 6(a)). On the other hand, the CdS films deposited from the initial solution with H$_2$SeO$_3$ microadditive are denser with smaller grains uniformly distributed on the substrate surface (Fig. 6(b) and (c)). Improved density of CdS films deposited from Se-containing solution may be explained by larger number of initial nucleation centers generated by the H$_2$SeO$_3$ microadditive.

The AFM 3D topographical images (Fig. 7) taken over the area of 2 × 2 μm$^2$ have a good correlation with the HR-SEM images (Fig. 6). The average surface roughness and grain size values were analyzed using the Nanoscope software with corresponding two dimensional images. The analysis was performed at different places. It can be seen from the AFM images that the surface of the CdS deposited from the Se-free solution covers the substrate unevenly.
with distinctly smaller grains that are loosely packed, and at particular regions grow as agglomerated islands, thus z-scale is higher (Fig. 7(a)) than for the CdS thin films deposited in the presence of Se (Fig. 7(b) and (c)). The average surface roughness was 11, 17 and 9 nm for the CdS films deposited at the H₂SeO₃ concentrations of 0, 0.1 and 0.5 mM, respectively. The reported average roughness values are relatively dependent on the thickness of the film. With increase of the H₂SeO₃ concentration in the solution, the average grain size decreases from 77 nm to 46 nm in the electrodeposited CdS films.

Changes in CdS density are reflected in the optical properties as well. The optical transmittance (Fig. 8) of the CdS thin films decreases from 81% to 75% with addition of H₂SeO₃ microadditive into the initial solution, the optical band gap value slightly increased from 2.3 eV to 2.5 eV (Fig. 8-inset), and the red shift of the absorption edge is observed. The decrease in the transmittance may be due to the scattering effects, deviations in composition stoichiometry and/or changes in thickness. The second slope at ~400 nm may be attributed to the presence of oxides or/and to the size confinement effect in nanocrystalline CdS films [31,32], which can be responsible for the formation of localized states in band gap. The increase of sub-band gap with addition of H₂SeO₃ can be explained by the decrease of the average crystallite size. Generally, nano-size particles have higher surface area due to increase of band bending at grain boundaries, and also the changes in stacking order of the structure results in the sub-band gap states as per the quantum mechanical considerations [33,34]. The obtained band gap results are consistent with our XRD analysis.

4. Conclusions

We investigated the influence of H₂SeO₃ microadditive on the properties of the CdS thin films deposited electrochemically from the acidic medium at different pH and temperatures. Thickness of the obtained CdS thin films is in the range of 70–100 nm. Nearly stoichiometric CdS thin films with sulfur content of 52 at% were deposited from Se-containing solution at the lower temperature of 50 °C at the pH 3.5, while the most appropriate temperature for the electrodeposition of CdS from Se-free solution is ≥ 80 °C. Addition of micromolar concentration of H₂SeO₃ into the working solution influences the mechanism of CdS formation promoting the transformation of the mixed-phase crystalline structure to a more hexagonal.

In addition, it promotes the decrease of the average grain size and surface roughness from 77 nm to 46 nm and from 11 nm to 9 nm, respectively. Resulted CdS thin films deposited from Se-containing solution are denser and cover uniformly the underlying substrate. With addition of 0.5 mM H₂SeO₃ the band gap value increases from 2.3 eV to 2.5 eV.

Although no Se-containing phases were detected by Raman or XRD analyses in the electrodeposited CdS films from Se-containing solutions. The main XRD peak C(001)/H(002) at around 26.5° is shifted towards the 20 value corresponding to the pure hexagonal structure, the lattice parameter is slightly increased from 4.13 Å to 4.14 Å. All these changes indicate to the inclusion of Se into the CdS lattice. The reason of Se inclusion into CdS may be CdSe nuclei formation during the electrodeposition process, where Se did not exchange to S.

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References
