Electrosynthesis and characterization of Hg$_{1-x}$Cd$_x$Se films

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Abstract. An electrodeposition process from an aqueous bath of CdSO$_4$, SeO$_2$ and Hg$_2$Cl$_2$ at pH 2.3 was performed to synthesize two Hg$_{1-x}$Cd$_x$Se alloys with $x \geq 0.8$ onto TiO$_2$. In order to establish an intimate contact between Hg$_{1-x}$Cd$_x$Se and the TiO$_2$ substrate, electrodeposition of Hg$_{1-x}$Cd$_x$Se films was investigated. Reduction processes of H$_2$SeO$_3$ and Cd$^{2+}$ to produce CdSe and Hg$_{1-x}$Cd$_x$Se were studied by cyclic voltammetry. Initially, deposition of selenium allows codeposition of Cd$^{2+}$ and Hg$^{2+}$. Hg$_{1-x}$Cd$_x$Se film was obtained by holding the electrode at a constant potential. The characterization of the films was performed by GIXRD, FESEM, and the chemical composition of the film was obtained by energy-dispersive X-ray spectroscopy, photoluminescence and Raman spectroscopy.

1. Introduction
In recent years, pseudobinary II–VI chalcogenide semiconductors have received a lot of attention because of their potential applications in optoelectronic devices, solar cells and photocatalysts [1]. Hg$_{1-x}$Cd$_x$Se is a ternary semiconductor/semimetal chalcogenide which can be tuned across the infrared spectrum by controlling the Hg and Cd molar fractions. These materials can be synthesized by numerous preparation methods in the form of thin polycrystalline films. In particular, cathodic electrodeposition has several advantages over vapor phase techniques because it is a potentially low-cost, non-vacuum, high-rate deposition process that can easily deposit uniform film on different conducting substrates at low temperature [1]. Himei and Muto [2] reported the preparation of Hg$_{1-x}$Cd$_x$Se films onto ITO substrate by varying the Hg content, whereas Singh and Tanveer [3,4] published the electrochemical formation of Hg$_{1-x}$Cd$_x$Se films on titanium foils. Although, Hg$_{1-x}$Cd$_x$Se films exhibited photoresponse [3,4], composition of the electrodeposits was not determined. In order to study chemical composition of Hg$_{1-x}$Cd$_x$Se alloys, in this study several measurement were performed: FESEM-EDS, photoluminescence and Raman spectroscopy. In addition, to the best of our knowledge, the mechanism of Hg$_{1-x}$Cd$_x$Se electrodeposition from aqueous solutions containing Hg(II), Cd(II) and Se(IV) have not been investigated. In an effort to further elucidate this question, we have performed cyclic voltammetric studies.

2. Materials and methods

1. Electrosynthesis
The electrodes employed were made from a 99.99 % purity Alfa-Aesar Ti rod embedded in Teflon, and with a 0.07 cm$^2$ circular area left uncovered. Prior to the electrochemical experiments Ti was
polished with a series of silicon carbide emery papers, subsequently obtaining a mirror-like finish with 50 nm alumina powder and washed successively with acetone, distilled water and etched in 10% (v/v) HF. The experiments were carried out using a conventional three-electrode cell with a graphite rod as counter electrode and a reference electrode Ag/AgCl/3 M KCl (0.210 V vs NHE). All potentials in this work are given with respect to this reference electrode. Electrochemical experiments were performed with a potentiostat Autolab PGSTAT 302N (Eco Chimie, Utrecht, The Netherlands) and NOVA software. Cyclic voltammetry studies were recorded in negative direction at 100 mV/s⁻¹. Before electrodeposition, nitrogen was purged through the bath for 20 min to remove oxygen from the solution. The solutions were prepared from Millipore Milli-Q grade water and analytical-grade reagents (99% purity, Merck). The pH of solution was adjusted at 2.3 with H₂SO₄. Depositions were carried out from the aqueous solutions containing 50 mM CdSO₄, 10 mM SeO₂, 1 mM and 10 mM Hg₂Cl₂. The films used in the characterization were grown on Ti foils by imposing a potential of -0.60 V during 1800s.

2.1 Crystalline structure
Grazing incidence X-ray diffraction measurements were made using a Bruker D8-Discover diffractometer working at 40 kV with the Cu Ka radiation in a glancing geometry and incidence angle fixed at 2°.

2.2 Morphology and chemical analysis
The morphology of Hg₁₋ₓCdₓSe films was investigated by field emission scanning electron microscopy FESEM, QUANTA FEG 650.

2.3 Composition
Energy dispersive spectroscopy (EDS) was used to study atomic composition with a FESEM, QUANTA FEG 650 scanning electron microscopy, Noran detector and analysis system TN-5400. Furthermore, photoluminescence and Raman were measured at 291K with a LabRam Evolution Horiba spectroscope. A laser wavelength of 532nm and 785nm were used to obtain photoluminescence and Raman spectra, respectively. Gaussian peaks models were implemented to analyse photoluminescence and Raman spectra and Summers-Broerman relation for band gap [5] and Miranda et. al. model for phonons in Hg₁₋ₓCdₓSe alloys [6] were implemented to achieved alloy composition, respectively.

3. Results and discussion
In order to investigate the mechanism of Hg₁₋ₓCdₓSe electrodeposition onto TiO₂ substrate, the electrochemical behavior of Ti electrode in solutions of individual components of the electrolyte bath was studied. In addition, cyclic voltammetry was used to study the electrochemical reactions in solution containing 50 mM CdSO₄, 10 mM SeO₂, and 1 mM Hg₂Cl₂ at pH 2.3. All voltammetry curves were initiated in the negative-going direction. The background current of TiO₂/H₂SO₄ interface is observed in figure 1 (aI); it is very small compared to those currents obtained from the Cd(II) and Se(IV) within the potential window studied. Typical cyclic voltammograms for 50 mM CdSO₄ is displays in figure 1 (aII). In the forward scan, a visible silver gray film appear on the surface of working electrode at a potential about -0.70 V, confirming that the increase of current is due to the cadmium reduction. In the backward scan, the anodic peak corresponding to oxidation of metal Cd is about -0.5 V. The currents on the inverse scan are higher than those on the forward scan, thereby appearing on reverse scan a crossover potential. This behavior is described in the literature as a nucleation-loop phenomenon [7] and it has provided direct experimental evidence to diagnose a process nucleation-controlled. Hence, reduction of cadmium ions occurs more easily on the cadmium surface than that on the TiO₂ surface.
A cathodic peak with onset about -0.4 V can be observed in figure 1 (aIII) where the wide cathodic peak corresponds to the irreversible reactions (1) and (2) [8].

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\begin{align*}
H_2SeO_3^+ + 4H^+ + 4e^- &= Se + 3H_2O & (1) \\
Se + 2H^+ + 2e^- &= H_2Se + 3H_2O & (2)
\end{align*}
\]

Figure 1. Typical cyclic voltammograms obtained on TiO\textsubscript{2} for aI) 0.1 M H\textsubscript{2}SO\textsubscript{4}, aII) 50 mM Cd\textsuperscript{2+}, aIII) 10 mM SeO\textsubscript{2}, b) 50 mM Cd\textsuperscript{2+} + 10 mM SeO\textsubscript{2} and c) 50 mM Cd\textsuperscript{2+} + 10 mM SeO\textsubscript{2} + 1 mM Hg\textsuperscript{2+}. Different inversion potentials values were applied to the substrate. Scan rate \(v = 0.1 \text{ V s}^{-1}\).

The electrodeposition of Hg\textsubscript{1-x}Cd\textsubscript{x}Se is very similar to CdSe, figure 1 (b) and (c), as such streamlining of mercury in the solution is very low. In this deposition process when a suitable potential is applied between the electrodes, the ions undergo the discharge process and the deposits of Hg\textsubscript{1-x}Cd\textsubscript{x}Se is formed. The potential range reported in the literature for obtaining the chalcogenide compounds on TiO\textsubscript{2} is about of -0.62 V, hence, Se must be initially deposited on TiO\textsubscript{2}, thereby Hg and Cd are codeposited to form Hg\textsubscript{1-x}Cd\textsubscript{x}Se alloy.

The identification of Hg\textsubscript{1-x}Cd\textsubscript{x}Se was confirmed with XRD measurements, figure 2. Diffraction peaks exhibit the characteristic reflections (111), (220), (311) and (400) of Cd\textsubscript{0.733}Hg\textsubscript{0.267}Se phase (PDF 000-48-1450). The peaks ratios shown the deposited film has a preferential orientation in (111) direction in contrast with non-oriented alloys in which not preferences in an orientation are obtained. [9]

The surface morphology of the films is shown in figure 3. The deposits are compact and exhibit cauliflower morphology. The quantitative analysis of the film was carried out by EDS, to determine the stoichiometry of the films. The elemental analysis was carried out only for Cd and Se, the average atomic percentage; it was found that the film deposited is Hg\textsubscript{0.1}Cd\textsubscript{0.9}Se.
Figure 2. X-ray powder diffraction profile of electrodeposited Hg$_{1-x}$Cd$_x$Se film from 50 mM Cd$^{2+}$ + 10 mM SeO$_2$ + 1 mM Hg$^{2+}$. Asterisk (*) indicate peak from the Ti support.

Figure 3. Scanning electron micrograph of electrodeposited Hg$_{0.1}$Cd$_{0.9}$Se (a) 5000X, (b) 80000X and (c) Hg$_{0.2}$Cd$_{0.8}$Se, 80000X.

Photoluminescence and Raman spectra are shown in figures 4 and 5, respectively. Raman spectra were modeled by three Gaussian peaks at 150 cm$^{-1}$, 199 cm$^{-1}$ and 204 cm$^{-1}$. Miranda et. al. model [6] applied to Raman peaks suggest the electrodeposited alloy are conformed by two phases: Hg$_{0.1}$Cd$_{0.9}$Se and CdSe. Otherwise, photoluminescence spectra were modeled by fourth Gaussian peaks at 1.3 eV, 1.4 eV, 1.5 eV and 1.8 eV that can be associated to band gap of Hg$_{0.1}$Cd$_{0.9}$Se alloy, 1.4 eV [5] and impurity and band to band transitions. The suggestion of impurity transition is based in the presence of low energetic peak and the expectation of impurities in the material due to fabrication process. The band to band transition is proposed to explain the more energetic peak that cannot be associated with band gap, i.e. 1.5 eV and 1.8 eV.
4. Conclusions

Hg$_{1-x}$Cd$_x$Se thin films have been successfully electro-synthesized. Cyclic voltammetry studies revealed that deposition of selenium allows codeposition of Cd$^{2+}$ and Hg$^{2+}$, furthermore, the reduction processes of H$_2$SeO$_3$ and Cd$^{2+}$ allows deposition of CdSe and Hg$_{1-x}$Cd$_x$Se. Electron microscopy, DRX, EDS, photoluminescence and Raman studies show that electrochemically films are globular and polycrystalline with two dominant phases: Hg$_{0.1}$Cd$_{0.9}$Se and CdSe.

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