Composition control by bath temperature and use of supporting electrolyte in electrodeposited mercury cadmium selenide thin films

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Abstract. In continuation of our previous studies for electrodeposition of mercury cadmium selenide thin films, we have now focused on the improvement of the composition of film to obtain single-phase of chalcogenide. The bath temperature dependence of the composition of Hg₁₋ₓCdₓSe thin films electrodeposited on titanium substrate from an aqueous solution containing Hg²⁺, Cd²⁺, H₂SeO₃ and supporting electrolyte has been investigated. The photoluminescence results demonstrated that by increasing the bath temperature and using supporting electrolyte a single phase of Hg₁₋ₓCdₓSe is deposited. Crystallinity is enhanced by annealing treatment and a smooth surface is observed without cracking of the film.

1. Introduction
Weng and Cocivera were the first to report the electrodeposition of mercury cadmium selenide (CdₓHg₁₋ₓSe) thin films [1]. They reported that, as the electrodeposition proceeded, the mercury concentration in the bath was depleted, and hence they suggested adding mercuric salt to maintain its concentration constant. In a recent work [2], we show that the experimental procedure proposed by Singh [3,4], which involves potentiostatic deposition of Hg₁₋ₓCdₓSe on titanium under quiescent conditions in absence of supporting electrolyte at ambient temperature, result in a mix of CdSe and Hg₀.₁Cd₀.₉Se. This could be ascribed to the Hg²⁺ ion depletion in the diffusion layer with electrodeposition time. Thus, here we use supporting electrolyte in order to prevent undesirable effects as migration, and we applied elevated temperature to accelerate the diffusion of the reactants during the electrodeposition process, and thereby improve the film-forming characteristics.

2. Experimental

2.1 Chemical and solutions
All chemical reagent used were analytical grade and used without further purification. All solutions were prepared just before electrochemical experiments using deionized water from a Milli-Q ultrapure water system (18.2MΩcm). The electrolyte solution was prepared with 50mM CdSO₄·8H₂O, 10mM SeO₃, 1mM HgCl₂ and adding either 100 or 250mM Na₂SO₄ as supporting electrolyte. A similar solution was prepared in absence of supporting electrolyte. The pH was adjusted at 2.3 with sulfuric acid. The dissolved oxygen was removed by bubbling the solution with nitrogen for 20min.
2.2 Preparation of electrodes

Ti disk (6.0 mm in diameter) or titanium plates (thickness 0.25 mm, size 15 mm × 30 mm), 99.5% of purity in both cases, were polished with alumina, cleaned ultrasonically with ethanol and acetone, and rinsed with deionized water. Before each electrochemical measurement the surface of working electrode was etched in 10% HF aqueous solution, and rinsed with deionized water.

2.3 Electrochemical experiments

Cyclic voltammetry was performed in a conventional three-electrode cell, provided with a jacket for the control of temperature of the cell, using an Autolab PGSTAT 302N potentiostat/galvanostat. The counter electrode was a graphite rod, a Ag|AgCl|3M KCl was used as reference electrode, and a Ti disk was used as working electrode. The experimental setup for electrochemical deposition was a Ti plate used as working electrode—exposed dimensions (when placed in the solution) 15 mm × 10 mm, a 304 stainless steel plate was used as auxiliary electrode. Electrochemical deposition of Hg1-xCdxSe was carried out by holding the potential at -0.65V vs Ag/AgCl.

2.4 Characterization of chalcogenide film

Morphology of electrodeposited films were observed by field emission scanning electron microscopy (FESEM, Quanta 650 FEG). Crystal structure and photoluminescence spectra of films were measured by grazing incidence X-ray diffraction using a Bruker D8-Discover diffractometer and a fluorimeter (PTI, Quanta Master Spectrofluorometer, QM-40), respectively.

3. Results and discussion

In previous studies [3,4], a potential-step deposition method was used to prepare Hg1-xCdxSe films on titanium substrates from aqueous solutions composed of 0.05M CdSO4, 0.01M SeO2, and variable concentration of HgCl2 in the range 10^-5 to 10^-3 M. These potential step depositions were performed in absence of supporting electrolyte in a quiescent condition at ambient temperature. Typically, at sufficiently long times, linear diffusion to the electrode surface dominates the deposition rate [5], and the current flowing at the electrode in the current−time transient curve can be described by the Cottrell equation (1)

\[ i(t) = \frac{nFAD^{1/2}c_0}{\pi^{1/2}t^{1/2}} \]  

where \( n \) is the number of electrons involved in the reaction, \( F \) is Faraday’s constant, \( A \) is the electrode area, \( c_0 \) is the bulk ion concentration, and \( D \) is the diffusion coefficient for electroactive species. Thus, a linear region is expected from the Cottrell equation for log(current) vs log(time), with a slope of (-1/2) typical of semi-infinite linear diffusion. However, figure 1 shows that, in aforementioned conditions, the lack of supporting electrolyte in the solution affects the current transient response, because a markedly non-Cottrellian diffusion response is observed. This anomalous current−time behavior is sometimes referred to as “Frumkin Effects” [6], which is result of the distortion of the electric field at interface and the resistance of the medium [7]. Indeed, the point where the slope changes drastically around 50 s, in figure 1(b), corresponds to the time when the diffusional control is reached; hence, a depletion layer of the electroactive species can extend into the solution.

Application of an electric field across the interface in poorly supported media can produce concentration gradients which result in regions of depleted and enriched ionic concentration [6]. Therefore, deviations from film stoichiometry [2] in the synthesis proposed by Singh and Tanver [3,4] are attributed to variations in the conductivity of the solution (Ohmic drop). In order to minimize concentration gradients of reactants that can cause formation of impurity phases on the Hg1-xCd_xSe surface, electrodeposition was performed using Na2SO4 as supporting electrolyte. Besides, temperature of the electrolyte was changed between 22°C and 60°C while keeping the pH at 2.3 and all other variables constant.
Figure 1. Current transients of the potential step in (a) current vs time and in (b) log (current) vs log (time) scale for the deposition of Hg$_{1-x}$Cd$_x$Se on titanium in absence of supporting electrolyte at ambient temperature. Potential was stepped from open-circuit potential to −0.65V vs Ag/AgCl for 30 min. Aqueous solution (quiescent): 50mM CdSO$_4$·8H$_2$O, 10 mM SeO$_2$ and 1 mM HgCl$_2$.

Figure 2 shows typical electrochemical behavior of HgCdSe electrodeposition. On the sweep initiated in negative-going direction, a peak C1 corresponding to reduction of selenious acid (Equation (2)) is registered. At potential around the peak current, codeposition of mercury(II) and cadmium(II) occurs (Equation (3)). At more negative potential a rise of cathodic current corresponds to cadmium(II) reduction (Equation (4)), which is related to the stripping of the cadmium in the backward sweep (peak A1).

\[
\begin{align*}
H_2SeO_3 + 4H^+ + 4e^- &\rightarrow Se + 3H_2O \quad (2) \\
Hg^{2+} + Cd^{2+} + Se + 2e^- &\rightarrow (HgCd)Se \quad (3) \\
Cd^{2+} + 2e^- &\rightarrow Cd \quad (4)
\end{align*}
\]

Figure 2. Cyclic voltammograms (ν=0.1 Vs$^{-1}$) obtained on Ti in 50mM CdSO$_4$·8H$_2$O, 10 mM SeO$_2$, 1 mM HgCl$_2$ and 250 mM Na$_2$SO$_4$·12H$_2$O solution (pH 2.3) at different temperatures: (a) 22°C, (b) 30°C, (c) 40°C, (d) 50°C and (e) 60°C.

The temperature dependence of the cyclic voltammetry curves for the electrodeposition of Hg$_{1-x}$Cd$_x$Se onto a Ti disk electrode are shown in figure 2. As the temperature was increased from 22°C to 60°C, the current for deposition of Hg, Cd and Se increases, as a consequence of thermal convection.
The increase in bath temperature produces a more compact diffusion layer and thus increases the current response. A series of experiments were conducted to establish the experimental conditions for obtaining the thin film of desired features on the Ti substrate. The effects of temperature, concentration of supporting electrolyte and electrodeposition time were studied. The highest concentration of supporting electrolyte studied (250mM Na$_2$SO$_4$) was chosen because with the lowest concentration (100mM Na$_2$SO$_4$) were obtained films with sulfate impurities (not shown). In addition, a temperature of 40°C was chosen because the results were similar to those obtained at higher temperatures.

Morphology of the films obtained at various times was observed, as shown in figure 3. Films showed typical cauliflower-shaped structures. The higher deposition time, the higher grain size, leading to an increase in thickness according to equation (5)

$$c = \exp(4,47244 + 0.00683 t - 3,21605 \times 10^{-6} t^2)$$

where $c$ is the thickness of the film in µm and $t$ is the deposition time. Thus, the greatest thickness obtained was about 3 µm.

Backscattered electron image of figure 4 shows that annealed film has very similar elemental composition throughout the surface and its roughness is lower than that of as-deposited film. Diffractograms (figure 5) exhibit the characteristic reflections of HgCdSe (PDF 010-71-4138). The broadening of diffraction peaks for as-deposited film indicates lower crystallite size than that annealed. In addition, the degree of crystallinity increases with annealing.

The photoluminescence spectra (figure 6) show that band gap for as-deposited an annealed film have a band gap of about 1.48 eV. The narrow peak of annealed crystal evidence fewer surface defects. It is noteworthy that the spectra of figure 6 show a single peak, indicating a single phase was obtained, thereby improving the results obtained previously [2].

4. Conclusions

Hg$_{1-x}$Cd$_x$Se films were prepared in an aqueous solution by using potentiostatic deposition. A smooth surface and uniform grain sizes were obtained at -0.65 V vs Ag/AgCl/3MKCl. The bath temperature and the concentration of supporting electrolyte affect the stoichiometry of electrodeposited Hg$_{1-x}$Cd$_x$Se films. Supporting electrolyte is necessary to prevent issues associated with electrode potential gradients and Ohmic drop in the solution. In addition, thermal convective flow increased mass transfer of the electroactive species to the electrode surface, producing a film composed of a single phase.
Figure 5. X-ray diffractograms of (a) as-deposited and (b) N$_2$-annealed Hg$_{1-x}$Cd$_x$Se thin films. The triangle (▲) indicates the XRD peaks from the Ti substrate.

Figure 6. Photoluminescence spectra of Hg$_{1-x}$Cd$_x$Se films (a) before and (b) after the annealing.

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6. References
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