



## Electrodeposition of In–Se and Ga–Se Thin Films for Preparation of CIGS Solar Cells

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An approach was developed for electrochemical codeposition of In–Se and Ga–Se films with high repeatability and controllable In/Se and Ga/Se molar ratios to prepare precursor layers for copper indium gallium diselenide (CIGS) film formation by two-stage processes. Full potential of complexation was used for the first time by using aqueous electroplating solutions containing complexing agents at alkaline regime. It was found that tartrate and citrate were suitable complexing agents to solubilize In and Ga ions at high pH, respectively. Because no appreciable complexation of Se occurred, Se reduction potential could be independently controlled by the amount of dissolved Se. Use of alkaline solutions also reduced hydrogen bubble generation and related defects. © 2009 The Electrochemical Society. [DOI: 10.1149/1.3079481] All rights reserved.

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Cu(In,Ga)Se<sub>2</sub> (CIGS) is one of the most advanced absorber materials for thin-film solar cells due to its direct bandgap, high absorption coefficient, and ability to yield good quality devices. CIGS-based solar cells have yielded the highest conversion efficiencies of all thin-film solar cells to date, reaching up to about 20%.<sup>1</sup> One technique used to form CIGS layers is a two-stage approach which involves deposition of a precursor layer on a substrate followed by a high-temperature activation step that converts the precursor layer into solar-cell-grade CIGS. The precursor layers employed in two-stage processes may be in the form of stacks containing Cu, In, and Ga species. Some examples of such stacks are Cu/In/Se, Cu–Ga/In/Se, Cu/In/Ga–Se, Cu/In–Se, Cu/In–Se/Ga–Se, etc. Although various techniques such as evaporation and sputtering have been employed to prepare precursor layers for CIGS film formation, electrodeposition is especially attractive due to its low cost, efficient utilization of raw materials, and scalability to high-volume manufacturing. While electrodeposition of In–Se and its possible application to solar cells has been previously studied, no prior publications were found on Ga–Se electrodeposition. Most of these studies, however, concentrated on acidic electrolyte compositions. Hirono,<sup>2</sup> for example, electrodeposited In layers out of acidic solutions that contained a suspension of fine Se particles. Because this method forms a composite layer comprised of electroplated In and mechanically trapped Se particles without any electrochemical reduction reaction of Se on the cathode surface, the technique is not expected to be very repeatable for electronic device fabrication applications. Igasaki and Fujiwara<sup>3</sup> electrodeposited In–Se material out of an electrolyte containing hydrochloric acid which was used to adjust the pH value of the solution to a range of 1.0–1.7. Massaccesi et al.<sup>4</sup> used another acidic solution based on sulfuric acid. This solution had a pH value of 3.45. Bhattacharya and co-workers<sup>5</sup> electrodeposited In–Se layers using acidic baths comprised of In ions and H<sub>2</sub>SeO<sub>3</sub>. Kampmann et al.<sup>6</sup> reported In<sub>2</sub>Se<sub>3</sub> alloy electrodeposition from an acidic electrolyte with a pH value of 2.4. Gopal et al.<sup>7</sup> and Hermann et al.<sup>8</sup> employed In<sub>2</sub>Se<sub>3</sub> plating electrolytes with a pH of about 1.5. All the codeposition approaches listed above utilized simple acidic electrolytes with pH values less than 7. Formation and precipitation of In and Ga hydroxides and oxides are the main concerns with the alkaline plating solutions. However, as will be detailed in this paper, these problems can be avoided by using suitable complexing agents and optimization of the plating chemistries. In addition, alkaline solutions offer significantly less hydrogen generation and ability to bring electrodeposition potentials of metallic elements closer. This way, a viable electrochemical method to deposit (In,Ga)Se films can be materialized to prepare precursor layers to form CIGS films employing two-stage processes. In the present work, we investigated

utilization of high-pH electrolytes containing complexing agents for electrochemical codeposition of In–Se and Ga–Se layers.

### Experimental

Electrochemical experiments and plating studies for In–Se or Ga–Se deposition were conducted in aqueous solutions containing indium chloride or gallium chloride, selenious acid, and 0.7 M of complexing agent. Potassium sodium tartrate and trisodium citrate were used as complexing agents for In and Ga, respectively. The pH of the solutions was adjusted by NaOH. Potentiodynamic polarization curves were obtained at a scan rate of 1 mV/s using a Princeton Applied Research potentiostat/galvanostat 263A. The substrate was stainless steel. One surface of the substrate was coated with a 500 nm thick sputtered Mo layer. Electrodeposition experiments were carried out on Cu or In films coated over the Mo layer, because, as explained in the background section, the material stacks of interest include Cu/In/Ga–Se, Cu/In–Se, Cu/In–Se/Ga–Se, etc. The Cu and In films were deposited by either sputtering or electroplating. The counter and reference electrodes were a Pt mesh and a saturated calomel electrode, respectively. The solutions were magnetically stirred with a speed of about 300 rotations per minute during the electroplating experiments. There was no stirring during the polarization measurements. All of the experiments were carried out at room temperature.

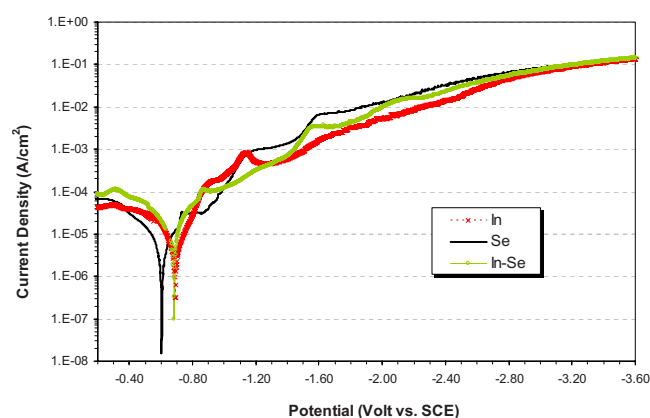
Electrodeposition of In–Se and Ga–Se was studied using a factorial design with three factors, namely, the molar ratios of In/Se or Ga/Se in the solution, the solution pH, and the deposition current density. Surface areas of the substrates were between 10 and 30 cm<sup>2</sup> in all studies. The compositions of the plated films were measured using X-ray fluorescence analysis (XRF, Fischer Technology, Fischerscope XAN-DPP energy-dispersive XRF) and the surface morphology of the films was examined with scanning electron microscopy (SEM, JEOL JSM-6390 scanning electron microscope). The surface roughness of the films was measured with a NewView 6 K white-light interferometry tool from Zygo Corp.

### Results and Discussion

Figure 1 shows the potentiodynamic polarization curves obtained for In, Se, and In–Se film depositions on In-coated substrates from solutions containing 0.05 M indium chloride, 0.1 M selenious acid, and 0.05 M indium chloride + 0.1 M selenious acid, respectively. The pH of all the solutions was adjusted to about 10 and they all contained 0.7 M potassium sodium tartrate. We were able to obtain cathodic efficiencies up to about 95% for In and up to about 85% for Se in these studies when these materials were electroplated separately. For indium electrodeposition, the initial peak at around –1.1 V is due to the reduction of a thin indium oxide layer on the In-coated substrate that might have formed in air or during anodic polarization. This peak is not seen in In and In–Se plots as the surface is covered by a Se-rich film at potentials more positive than –1.1 V. As can be seen from Fig. 1, the cathodic current for Se

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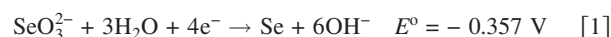


**Figure 1.** (Color online) Potentiodynamic polarization curves for In, Se, and In-Se deposition at a pH of 10 with a scan rate 1 mV/s. The working electrode had an In surface.

deposition increased swiftly from about 1.38 to 5.5 mA/cm<sup>2</sup> as the potential was changed from  $-1.4$  to  $-1.57$  V. Within the same voltage range the current increased slowly for pure In deposition. The In-Se deposition also showed a sharp increase, suggesting that Se-rich films could be plated in this potential range. At cathodic potentials more negative than  $-1.6$  V, Se plating current increased slowly but In current increased significantly. Therefore, this is the potential regime where In-rich In-Se films could be obtained. At potentials between about  $-1.6$  and  $-2.2$  V, accumulation of H<sub>2</sub> bubbles on the cathode surface caused irregularities in the In polarization curve. As the potential was reduced further down, bubbles gradually became larger and detached from the surface. Because the deposition surface area changed with the release of the bubbles, current increased. For the In-Se deposition, at potentials between about  $-1.85$  and  $-2.1$  V, both Se and In are deposited with increasing rates. There was also appreciable H<sub>2</sub> gas generation on the cathode surface in this potential range, generating a rapid increase in the measured In-Se current. The limiting current for Se was reached at about  $-2.1$  V, which led to an In-rich plated surface, thereby reducing the H<sub>2</sub> generation and decreasing the total current in the potential range between  $-2.1$  and  $-2.3$  V. At more negative potentials, all three curves merged, because hydrogen gas generation became the dominating cathodic reaction.

The tartrate in the In-Se solution forms soluble complexes with In<sup>3+</sup> ions at neutral and alkaline pH regimes, preventing indium ions from precipitation as In(OH)<sub>3</sub>. Selenium, on the other hand, may not form any complexes with the tartrate salts. Selenium is already soluble in basic baths in the form of SeO<sub>3</sub><sup>2-</sup>. If the electrodeposition

potentials of Se and In are very different from each other, the co-electrodeposition process to deposit In-Se on a cathode surface becomes very sensitive, i.e., a small change in the process parameters causes a large variation in the deposited layer composition, uniformity, and microstructure. The chemical baths developed in the present study are capable of bringing the deposition potentials of these species close to each other. In a neutral or basic aqueous solution, selenite species, SeO<sub>3</sub><sup>2-</sup>, may be reduced at the cathode surface according to the following reaction

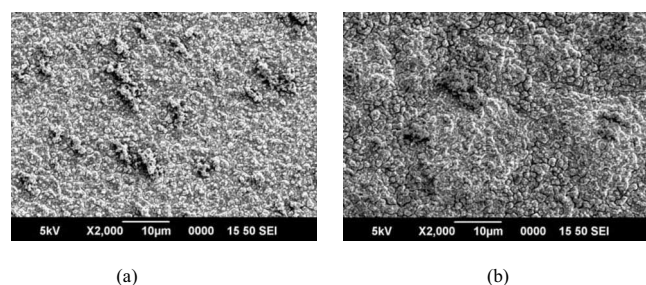


This standard potential<sup>9</sup> is almost the same as the standard reduction potential of In ( $E^\circ_{\text{In(III)/In}} = -0.34$  V). By contrast, the same SeO<sub>3</sub><sup>2-</sup> reduction in an acidic solution requires a standard potential of 0.885 V, according to the same reference cited above. This suggests that the co-electrodeposition can be successful in an alkaline solution but difficult in an acidic aqueous solution due to the large difference between the reduction potentials of the two species. Similarly, Ga has a standard potential of  $E^\circ_{\text{Ga(III)/Ga}} = -0.52$  V. Therefore, it can also be codeposited with Se in an alkaline aqueous solution.

Table I gives the results of the factorial design experiments for In-Se alloy plating on the In-coated substrates. The same experiments were also carried out on the Cu surfaces and similar findings were obtained. Table I tabulates the compositions of the resultant alloy films and the cathodic current efficiencies for comparison at different plating conditions. As can be seen from this data, it was found that tests 1, 4, and 7 resulted in a composition with an In/Se ratio close to 2/3. It was also observed that lower molar ratios of (In/Se) in the plating solution produced more Se-rich alloys or mixtures. Higher pH values reduced the Se amount in the deposited layers. Higher plating current densities increased the amount of In in the In-Se films. These results demonstrate that the method and the high-pH chemistry of the present work have the capability to produce In-Se films with a wide range of compositions by simply adjusting the concentrations of ionic species in the electrolyte, or by varying the plating current density, or by varying the pH value. Through these variables codeposited In-Se films with various In/Se ratios may be obtained. Surface morphologies of the electroplated In-Se films were examined using SEM. Figure 2 shows SEM pictures of the In-Se films from tests 7 and 2 with In/Se ratios of 4/5 and 7/6 in the electrodeposited films, respectively. While films have mostly smooth areas, agglomerations of material are distributed over the surface of both films. Some fissures and cracks separating 1–2 μm sections of the film were also detectable. These are believed to arise from the underlying In structure. Comparatively, the film with an In/Se ratio of 4/5 has a smoother surface and compact structure. Average roughness of this film was measured to be 250 nm using the Zygo white-light interferometry tool, while the

**Table I.** In-Se film electrodeposition process conditions and results.

Test no.	In/Se ratio in the solution (mol/L)	pH	<i>i</i> (mA/cm <sup>2</sup> )	In/Se ratio in the electrodeposited film	Cathodic efficiency (%)
1	0.05/0.1	11.5	10	2/3	42
2	0.05/0.1	10	10	7/6	63
3	0.1/0.05	13	10	9/1	68
4	0.05/0.1	10	5	4/7	44
5	0.05/0.1	13	5	7/2	47
6	0.05/0.2	13	5	4/3	56
7	0.05/0.2	10	5	4/5	51
8	0.05/0.2	11.5	20	7/5	64
9	0.05/0.1	13	20	5/1	47
10	0.1/0.05	10	20	2/1	23
11	0.1/0.05	11.5	5	1/1	41
12	0.05/0.2	13	10	1/1	51



**Figure 2.** SEM pictures of (a)  $\text{In}_4\text{Se}_5$  film (test 7) and (b)  $\text{In}_7\text{Se}_6$  film (test 2).

film with an In/Se ratio of 7/6 was measured to have an average roughness of about 800 nm. In the preparation of the In–Se baths, in addition to potassium sodium tartrate, other related tartrate compounds and salts can also be used. These include alkaline and alkaline earth metallic salts of tartrates, ammonium salts of tartrates, and organically modified tartrates such as alkyl or dialkyl tartrates.

A similar methodology was used to develop electrolytes for Ga–Se codeposition. In these studies, citrate was determined to be a more suitable complexing agent than tartrate for Ga–Se electrodeposition, as higher plating efficiencies were obtained in electrolyte solutions with citrate. Similar to In–Se deposition, Ga was complexed with citrate while there was no complexation of Se in the solution. The solutions at pH values from 5 to 14 were investigated in this case. It was found that the electrodeposition of Ga–Se thin films was much more challenging than In–Se because of much lower deposition potential of Ga compared to In, and that the composition of a Ga–Se film dramatically depended on the solution pH value. At a low pH value such as at pH 5, Se dominated the film, allowing very little Ga to be plated. At high pH values such as a pH of 13.5, the film contained more than 90% Ga with little Se. It was determined that Ga–Se films could be successfully deposited at a narrow pH range between 7 and 8.5. While cathodic current efficiencies as high as 35% were obtained, the film composition was found to be very sensitive to the deposition current density. Selenium-rich films were obtained at lower current densities while higher current densities resulted in Ga-rich films. More work is underway to increase the cathodic efficiencies and the film quality of Ga–Se using alternate

complexing agents. Indium, gallium, and selenium can also be codeposited using the chemical compositions similar to those developed for In–Se and Ga–Se films described above. In such solutions, a blend of tartrate and citrate can serve as the complexing agents. Results of these efforts will be the subject of future publications.

### Conclusions

The electrochemical codeposition of In–Se and Ga–Se thin films from solutions containing complexing agents was studied. Tartrate was used in In–Se solutions while Ga–Se solutions were prepared with citrate as the complexing agent. Potentiodynamic polarization studies indicated that high current densities favored In or Ga-rich films. The influences of the pH, concentrations of the metal salts, and the deposition current density on the codeposition were investigated with a factorial design statistical method. The results revealed that the selenium ratios in the alloy films increased with the higher selenium concentration in the bath, lower pH, and lower current densities. The cathodic current efficiencies obtained in the In–Se codeposition were between 40 and 70%. SEM examination of the surface morphology showed that In–Se films with a reasonably flat surface and compact structure could be obtained. The electrochemical codeposition of Ga–Se alloy was more challenging compared to In–Se. The control of the composition of the Ga–Se films was easier at pH values between 7 and 8.5 with modest deposition current densities.

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