Electrodeposition of CuGaSe₂ from Thiocyanate-Containing Electrolytes
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We report electrodeposition of CuGaSe₂ from electrolytes that contain thiocyanate (SCN⁻) as a complexing agent to cathodically shift the reduction potential of Cu(II). In the presence of thiocyanate, the peak reduction currents for Cu(I) and Ga(III) during cyclic voltammetry occur at potentials that differ by only 80 mV, even though the standard reduction potentials of the uncoupled species differ by about 870 mV. Stoichiometric CuGaSe₂ deposits are obtained by the induced codeposition mechanism at −300 mV vs SCE and pH 2.75 from electrolytes with Cu/Ga ratios ranging from 0.5 to 1.5. The stoichiometry is controlled by the thermodynamic driving force associated with stable compound formation, as illustrated by the anodically shifted reduction peak obtained in cyclic voltammograms of electrolytes containing all three elemental species. Oxygen incorporation into the electrodeposited film is observed, because electrodeposition of stoichiometric CuGaSe₂ appears to be immediately followed by Ga oxidation. Methods for removing oxygen from the electrodeposited film are discussed.

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CulnGa₃Se₅ (CIGS) thin film solar cells have been reported with efficiencies up to 18.8% due to the high optical absorption coefficient, modest blueshifting with 20–30% Ga incorporation, beneficial effects of Na incorporation, and low interfacial recombination velocities. Thin film solar cells promise significant economic benefits, because the optical absorber need only be as thick as the optical penetration depth. CIGS thin films are typically formed either by coevaporation of elemental sources or by selenization of metal alloy precursors. However, electrochemical deposition methods may be significantly less expensive for scale-up of thin film solar cells, leading to significant interest in electrodeposition of CIGS.

A significant challenge in CIGS electrodeposition is the widely spaced reduction potentials of the different elements, with standard reduction potentials of +0.340, −0.338, and −0.529 for uncoupled Cu, In, and Ga, respectively. The presence of four elements with widely differing reduction potentials makes it difficult to control the deposit stoichiometry, because the deposition of no species can be mass transport limited. One approach to this problem has been demonstrated for CuInSe₂ electrodeposition, where complexing agents are chosen that bind much more strongly to Cu than to In, thus shifting the Cu reduction potential in the cathodic direction toward that of In.

We report electrodeposition of CuGaSe₂ from electrolytes containing thiocyanate (SCN⁻) to cathodically shift the reduction potential of Cu(II). For a window of electrolyte compositions at pH 2.75, a cathodic peak is observed for CuGaSe₂ electrodeposition at −300 mV vs saturated calmel electrode (SCE) that is anodically shifted relative to the cathodic peaks for electrodeposition of the individual elements. The thermodynamic driving force to form the CuGaSe₂ compound thus aids in obtaining the ideal 1:1:2 stoichiometry. Electrodeposition of stacked thin films of CuGaSe₂, CulnSe₂, and/or CIGS, followed by subsequent annealing, has been proposed as a method to form CIGS absorber films. To the best of the authors’ knowledge, only one report has previously appeared of CuGaSe₂ electrodeposition.

Experimental

Glass slides with a 100 nm Au film atop a 5 nm Ti adhesion layer were purchased from Evaporated Metal Films (Ithaca, NY). CuSO₄ and Ga₂(SO₄)₃ were purchased from Alfa Aesar, while H₂SeO₃ and NaSCN were purchased from Sigma Aldrich. Reagent grade chemicals and double distilled water were used for all experiments. The pH was adjusted by addition of dilute NaOH. Prior to each experiment, the Au surface was cleaned by acetone, isopropanol, Alconox, and double distilled water. Voltammetry experiments were conducted statically and controlled with an EG&G PAR model 273A potentiostat/galvanostat. Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) measurements were made with a JEOL model 7400F field emission scanning electron microscope. For SEM and EDX analysis, CuGaSe₂ electrodeposition was performed using a rotating disc electrode at 200 rpm.

Results and Discussion

The primary electrolyte studied for CuGaSe₂ electrodeposition contains 5 mM CuSO₄, 5.68 mM Ga₂(SO₄)₃, 20 mM H₂SeO₃, and 2.0 M NaSCN at pH 2.75. The use of SCN⁻ as a complexing agent has previously been reported for CuInSe₂ electrodeposition but not for CuGaSe₂ electrodeposition. Figures 1-3 show voltammograms for the Au electrode in this electrolyte containing SCN⁻ and either Cu, Ga, or Se, respectively. Figures 1 and 2 show the typical cathodic peaks for diffusion limited electrodeposition of Cu and Ga, with these peaks overlapping with the cathodic current from hydrogen evolution. Figure 3 shows a series of cathodic peaks, with the highest current peak at −770 mV. The cathodic peak potential for Cu electrodeposition is about −700 mV, while that for Ga electrodeposition is about −780 mV. Thus the difference in cathodic peak potentials for Cu²⁺ and Ga³⁺ is about 80 mV, whereas the difference in standard reduction potentials for the uncoupled species is about 870 mV.

Figure 4 shows the voltammogram for the Au electrode in the full electrolyte containing Cu, Ga, and Se precursors. A cathodic peak is observed at about −300 mV vs SCE that is anodically shifted from the cathodic peaks observed for only Cu or Ga electrodeposition. As discussed above, this corresponds to the deposition of stoichiometric CuGaSe₂, and the anodic shift arises from the thermodynamic driving force for stable compound formation. Such an anodic shift has previously been reported for CuInSe₂ electrodeposition from electrolytes containing SCN⁻, glycine, and citrate complexing agents, but not for CuGaSe₂. Such results have been attributed to an induced codeposition mechanism, where a subsequent reaction of an initially deposited species is thermodynamically driven by CulnSe₂ or CuGaSe₂ compound formation.

At −300 mV vs SCE, the CuGaSe₂ deposition rate is about 0.42 μm/min. Thick CuGaSe₂ films formed cracks, but this could be prevented by limiting the deposit thickness to about 1.25 μm. Subsequent analysis by SEM and EDX was performed on CuGaSe₂.
films about 1.25 μm thick. Figure 5 shows an SEM micrograph of a CuGaSe2 film deposited at −300 mV from the electrolyte described above.

The composition of electrodeposited CuGaSe2 films was studied using EDX as a function of deposition potential, pH, and electrolyte composition. The starting point for these studies is the film electrodeposited at a constant potential of −300 mV vs SCE from the primary electrolyte containing 5 mM CuSO4, 5.68 mM Ga2(SO4)3, 20 mM H2SeO3, and 2.0 M NaSCN at pH 2.75. At this potential, where the cathodic peak is observed in Fig. 4, the Cu:Ga:Se atomic ratio in the deposit is about 1:1.03:1.93. Within the accuracy of EDX measurements, this corresponds to stoichiometric CuGaSe2. For the induced codeposition mechanism, the deposit stoichiometry at this potential is expected to be largely independent of the exact solution phase composition. This is a significant advantage for commercial applications, because the process becomes less sensitive to the depletion of reactants, and to the compositional gradients arising from inadequate mass transfer. Figure 6 shows the atom fraction of Cu, Ga, and Se at ratios of Cu to Ga ranging from 0.5 to 1.5. X-ray diffraction studies of different samples indicate no peaks due to either chalcopyrite CuGaSe2 or any metallic phase. This suggests an amorphous deposit containing a stoichiometric ratio of Cu:Ga:Se.

The formation of stoichiometric CuGaSe2 depends on both the electrolyte pH and the deposition potential. As the pH is raised above 2.75, the fraction of Ga in the deposit initially increases, but little or no deposit is obtained at pH 3.75. As the pH is reduced below 2.75, the amount of Ga in the deposit also decreases. At potentials cathodic to −300 mV vs SCE, the ratio of Cu:Ga decreases well below unity. At more anodic potentials, no cathodic current is observed and no deposit is obtained.

As discussed above, the CuGaSe2 stoichiometry was consistently observed for the electrodeposits at a potential of −300 mV and a pH of 2.75. However, oxygen incorporation was also consistently observed, with the O:Ga ratio ranging from 2.4 to 2.8, which may correspond to formation of Ga2O3. Oxygen was omitted from the atomic ratios reported in Fig. 6 for clarity. At pH and potential values where no Ga is incorporated into the electrodeposits, no O peak is observed in the EDX spectrum. This demonstrates that oxygen incorporation does not arise during sample transfer between the
due to the strong affinity of Ga for O, several research groups have reported oxygen incorporation into electrodeposited CuGaSe$_2$ or CIGS films. Recently Lai et al. reported that the presence of Ga in electrodeposited CIGS films results in the formation of either oxides or hydroxides. They also reported that annealing the CIGS films in a H$_2$S atmosphere simultaneously removed oxygen while improving the deposit crystallinity. Because annealing, rapid thermal processing, or anodic bonding of CIGS films is required anyway to improve the deposit crystallinity, this is not an overarching concern.

Conclusions

We report electrodeposition of CuGaSe$_2$ from electrolytes that contain thiocyanate as a complexing agent to cathodically shift the reduction potential of Cu(II). In the presence of thiocyanate, the peak reduction currents for Cu(II) and Ga(III) during cyclic voltammetry occur at potentials that differ by only 80 mV, even though the standard reduction potentials of the uncomplexed species differ by about 870 mV. When Cu, Ga, and Se are all present in the electrolyte, a cathodic peak at ~300 mV is observed that is shifted anodically relative to the cathodic peaks that are observed in the presence of only Cu or Ga. Stoichiometric deposits are obtained at ~300 mV vs SCE and pH 2.75 from electrolytes with Cu:Ga ratios ranging from 0.5 to 1.5. This excellent stoichiometry is explained by the induced codeposition mechanism, whereby the thermodynamic driving force for stable compound formation induces a subsequent reaction of the initial species deposited. Oxygen incorporation into the electrodeposited CuGaSe$_2$ is observed, because electrodeposition of stoichiometric CuGaSe$_2$ appears to be immediately followed by Ga oxidation.

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