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Edited by Loucas Tsakalakos, Henry Ji and Binxian Ren

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Solution-Based Processes

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Analysis and Control of Plating Baths in the Electrodeposition of Copper Indium Gallium Selenide (CIGS) Films with Ion Chromatography

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ABSTRACT

Cu(In,Ga)Se₂ (CIGS) is one of the most advanced absorber materials with conversion efficiencies reaching up to about 20%. Electrodeposition of CIGS precursors is highly attractive due to its low cost, efficient utilization of raw materials and scalability to high-volume manufacturing, however, a strict chemistry control of the plating baths is required in a manufacturing environment to ensure a consistent plating process with high yields. In the present study, we tested the use of ion chromatography (IC), for the quantitative analysis of both the cationic and anionic species in a variety of aqueous alkaline electroplating solutions we developed for the fabrication of CIGS precursors. Using ion chromatography we were able to precisely determine the concentrations of several key anions commonly employed in the plating baths including chloride, sulfate, selenite, selenate, tartrate, citrate, gluconate, and ethylenediaminetetraacetate. Our results indicated IC might not be a suitable method to determine the cationic concentrations for Cu, In, Ga ions when complexing species, such as ethylenediaminetetraacetate, are present in the electroplating solutions. We determined that inductively coupled plasma optical emission spectroscopy (ICP-OES) could be used instead for the precise determination of the cationic concentrations.

INTRODUCTION

CIGS is an advanced absorber material with a direct bandgap and a high absorption coefficient. CIGS-based solar cells have yielded the highest conversion efficiencies of all thin film solar cells, reaching up to about 20% [1]. One of the techniques 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. Although various techniques such as evaporation and sputtering have been employed to prepare precursor layers, electrodeposition is especially attractive due to its low cost, efficient utilization of raw materials and scalability to high-volume manufacturing.

A wide range of processing approaches employing electrodeposition has been explored for CIGS film formation during the last two decades. The reader is referred to Lincot and coworkers [2] for a detailed review. It should be noted that most of the previous approaches concentrated on acidic electrolyte compositions. Moreover, they were generally aimed at growing CIS layers rather than CIGS films. This is partly due to the fact that addition of Ga into electrodeposited films is challenging because of the high negative plating potential of Ga compared to Cu, In and Se. Such high plating potential gives rise to excessive hydrogen evolution on the cathode surface during plating of the films out of aqueous electrolytes. Hydrogen evolution reduces the plating efficiency of Ga and causes defects such as pinholes in the grown layers since the small gas bubbles stick to the surface of the growing film and prevent proper deposition at that location. Development of specialized electrolytes with long term stability and ability to control the

crucially important Cu/(In+Ga) and Ga/(Ga+In) molar ratios are of utmost importance for the successful industrial application of electrochemistry to CIGS film growth. Previously efficiencies close to 13.8 % was demonstrated on small area ($\sim 0.5 \text{ cm}^2$) cells on flexible stainless steel substrates [3,4]. Recently, we achieved cell efficiencies over 14 % on 12 cm^2 lab-size cells (Figure 1). We also obtained efficiencies up to 13% on 120 cm^2 cells and aperture efficiencies up to 12.1% for our lightweight flexible modules from our roll-to-roll manufacturing line. More detailed results from our roll-to-roll electroplating approach for the fabrication of flexible cells were given in some recent publications [5,6].

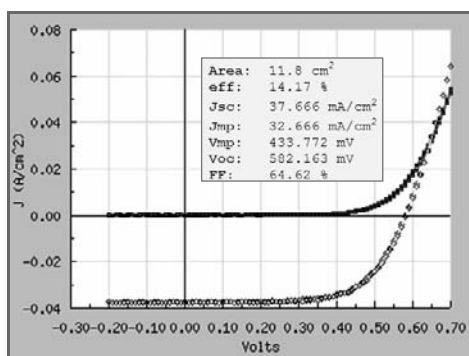


Figure 1. Illuminated and dark I-V characteristics of an 11.8 cm^2 area CIGS solar cell with an efficiency of 14.17%.

In one of our earlier studies, we reported on an alkaline electroplating bath with the capability to deposit In-Se as well as Ga-Se layers [7]. In a later study we demonstrated electrochemical deposition of a metallic copper-indium-gallium alloy films from aqueous alkaline electroplating solutions [8]. In addition to these, we have plated several other formulations capable of depositing numerous alloy layers as well as the entire CIGS layer in a single plating step. The analysis of the electroplating solutions used for electrochemical synthesis of the CIGS precursor is of extreme importance since only a robust control over the electroplating bath chemistry will ensure high efficiency CIGS solar cells with high yield in the manufacturing environment. In the present study, we tested the use of ion chromatography and inductively coupled plasma optical emission spectroscopy methods for the quantitative analysis of the anionic and cationic chemical constituents in our aqueous alkaline electroplating solutions used for the fabrication of CIGS precursors.

EXPERIMENTAL DETAILS

Although the exact formulations of the plating solutions are proprietary, it might be sufficient to state that common complexing species such as ethylenediaminetetraacetic acid (EDTA), maleic acid, oxalic acid, ethylenediamine, tartaric acid, gluconic acid, triethanolamine, citric acid, and glycine, etc. are employed to chelate the metal ions in the baths. Since the affinity of a particular complexing agent might be different for each metal, a blend of complexing agents

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might be necessary to provide a complete chelation of all the Cu, In and Ga ions in the plating electrolyte. No appreciable complexation occurs between Se and the complexing agents. Therefore, Se reduction potential could be independently controlled by the amount of dissolved Se in the Se-containing solutions. In addition to complexing agents, it might be advantageous to include organic additives in electrolytes to refine the grains, improve the adhesion, provide leveling, reduce surface tension and minimize corrosion and pitting of molybdenum layer or stainless steel substrate. The pH of the solution in the alkaline regime (pH 9-13) can be adjusted by addition of sodium hydroxide, potassium hydroxide or ammonium hydroxide. Alkaline buffer couples are also employed to maintain a fixed pH range. Conductivity of the electrolytes can be increased by the addition of salts, preferably in the form of ammonium nitrate, potassium sulfate or sodium chloride. In the experiments used for testing the capabilities of IC and ICP-OES methods, analytical grade reagents of copper sulfate, indium chloride and gallium chloride, selenious acid, tartaric acid, citric acid, ethylenediaminetetraacetic acid and sodium gluconate were used to prepare the test solutions. The pH was adjusted to the desired level with concentrated NaOH solution.

Ion chromatography measurements were carried out using a Dionex ICS-3000 system. For the determination of transition metals, pyridine-2,6-dicarboxylic acid (PDCA) obtained from Dionex was used as the eluent and delivered to the IC system by a gradient pump at a flow rate of 0.3 mL/min in an isocratic mode. The separation columns were IonPac CS5A Analytical and CG5A Guard obtained from Dionex. The post-column reagent was prepared by dissolving 120 mg of 4-(2-Pyridylazo)resorcinol (PAR) in 1L of (Metpac post-column diluent), both obtained from Dionex. This reagent was dosed at a rate of 0.15 mL/min with a PC-10 post-column pneumatic delivery system. The eluent and the post-column reagent were mixed into a 375 μ L reaction coil. The detection of the different transition metals was achieved with a UV-VIS detector (ICS-VWD) at 530 nm in an 11 μ L PEEK cell. The injection volumes used for transition metal determination varied from 10 to 50 μ L with the use of an AS-3000 auto-sampler. The determination of anions in the plating bath solutions was carried out using an AS17 and IonPac AG17 columns with an ASRS suppressor, all obtained from Dionex. KOH gradient was used as the eluent with a concentration profile of 4mM to 30mM for 0-10 minutes, 30mM to 54mM for 10-15 minutes, 4mM for 15-20 minutes. The eluent flow rate was 1 mL/min, while the temperature of the column was maintained at 30 $^{\circ}$ C, the injection volume was 25 μ L. The anion concentration was determined by a suppressed conductivity detector. Because all of the organic acids dissociate under such a high pH environment, the anions can be well separated and detected.

ICP-OES measurements were carried out using a Perkin Elmer Optima 2100 DV. Diluted calibration solutions of Cu, In, Ga and Se for the ICP-OES were prepared from standard solutions (1000 \pm 4 mg/L) obtained from Perkin Elmer. For IC measurements, we first prepared standards at a concentration of 20 mg/L for chloride, sulfate, selenite, selenate, tartrate, citrate and higher concentrations for ethylenediaminetetraacetate and gluconate. Diluted calibration solutions were prepared from these concentrated standard solutions.

RESULTS AND DISCUSSION

Ion chromatography results of transition metals calibrations are shown in Figure 2. As it can be seen from this figure, the sensitivity of the UVW detector at 530 nm with the PAR post-column reagent was very high for Cu and In while it decreased greatly for Ga. The calibrations in

Figure 2 was obtained from the chromatograms in Figure 3a. The inset in Figure 3a shows that there was an increase in the baseline after the Ga peak was obtained at the highest concentration level. The retention times for Ga, Cu and In were determined as 4.34 ± 0.02 , 7.62 ± 0.03 and 8.48 ± 0.08 minutes, respectively. Good separations were observed for Ga and Cu, but there was only a small change difference in retention times between Cu and In. At high Cu concentrations, the column can saturate, which causes shouldering of the Cu peak into the In peak. This is typically observed when injection volumes are higher than $50 \mu\text{L}$.

Figure 3b shows the chromatograms for the CIGS electroplating solution containing Cu, In, Ga cations as well as anions including chloride, sulfate, selenite, selenate, tartrate, citrate and ethylenediaminetetraacetate. As can be seen from this figure, the Ga and In peaks were absent and only the Cu peak was detected. The Cu peak height decreased with the decreasing concentration as expected. It was found that complexation of Ga and In with EDTA masked their signals in the IC measurements. Figure 3c shows the chromatograms of plating solutions without EDTA. In the absence of EDTA, Cu, Ga and In were separated on the IonPac CS5A. The efficiency of separation is expected to be dependent on the complexation of each transition metal with the PDCA as compared to complexation with the chelating agents in the electroplating bath. Staff and coworkers [9] observed that Ga extraction was only about 50% from Ga-EDTA solutions. This was likely due to the high stability constant for the Ga-EDTA complex ($10^{22.01}$) compared to that of Ga-citrate ($10^{10.02}$). Similarly, the stability constant for the EDTA-In complex is high compared to that for EDTA-Cu ($10^{24.95}$ versus $10^{18.8}$, respectively) [10]. This difference in the stability constants is expected to be the main reason for repression of Ga and In signals.

Instead of IC, ICP-OES was found to be a more preferred method for the analysis of cationic concentrations in the electroplating solutions. In ICP-OES measurements the metal ion concentration is not dependant on the chelating agent. However, since the overall intensity of the spectra can be perturbed by the matrix in which the metal ions are diluted, matrix effects should be taken into account to improve the precision [11]. We established that ICP-OES, with appropriate standards, can measure the cationic species and total dissolved Se in the electrodeposition baths with less than 5% variation on a regular basis. With improvements in the sample preparations, especially with accurate dilutions, this error percentage might be brought below 3%.

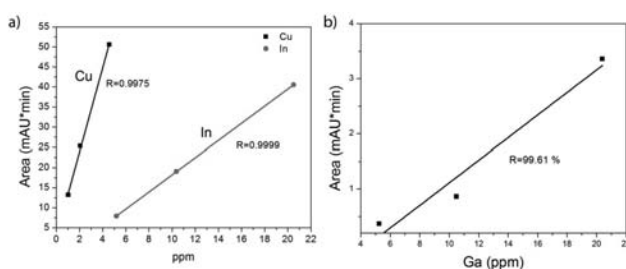


Figure 2. Calibration curves and linear fits for (a) Cu and In (b) Ga.

Anion separations in IC measurements were successfully achieved with well separated peaks. The retention times for gluconate, chloride, selenite, tartrate, sulfate, selenate, citrate and

ethylenediaminetetraacetate were obtained as 2.16 ± 0.02 , 3.167 ± 0.01 , 5.40 ± 0.01 , 5.81 ± 0.02 , 6.40 ± 0.02 , 6.89 ± 0.02 , 11.44 ± 0.04 and 14.71 ± 0.07 minutes, respectively, as shown in Figure 4a. Figure 4b displays the chromatographs of the CIGS solutions showing a sample diluted 1000 and 10,000 times (scaled up 10 times) while calibration curves for the different anions are shown in Figure 5. Calibration for the anions showed fairly good fits but in the case of EDTA there was a need to 'spike' the solution with a background amount of 50 ppm due to its low detection limit. The sample-to-sample measurement error was less than 1.5 % in the anionic measurements.

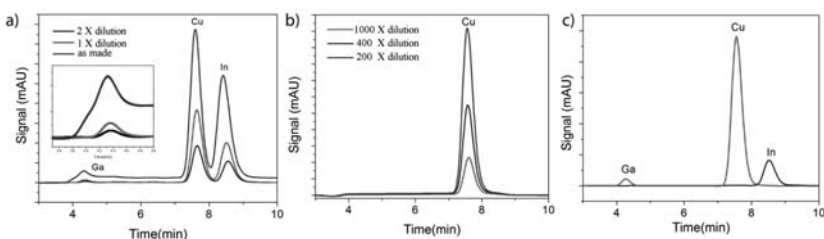


Figure 3. Chromatograms of (a) Ga, Cu and In calibration standards at different dilutions (b) CIGS solution at 1000, 400 and 200 times dilution. (c) modified CIGS solution Ga, Cu and In without EDTA.

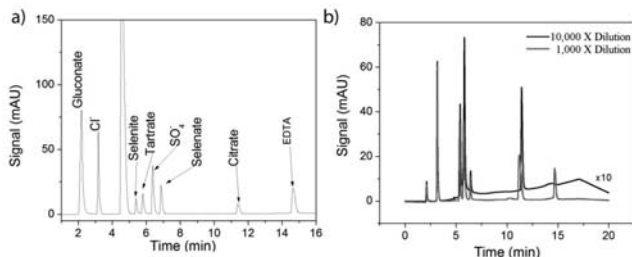


Figure 4. Chromatograms for (a) calibration standards for anions (b) anions in the CIGS plating solution sample.

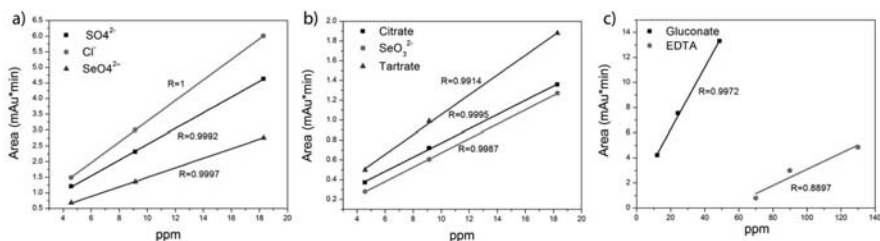


Figure 5. Calibration curves for anions and linear fits for (a) SO₄²⁻, Cl⁻ and SeO₄²⁻, (b) citrate, tartrate and SeO₃²⁻ (c) gluconate and EDTA.

CONCLUSIONS

We found that IC can be successfully used to determine the anionic concentrations in the plating baths with a sample-to-sample measurement error below 1.5 %. IC was able to determine the precise concentrations of both inorganic ions and organic complexing species and distinguish between selenite and selenate ions. However, IC measurements might not be suitable for cationic measurements for solutions containing complexing agents. In such solutions, the strong binding of metallic ions to some of the complexing agents might lead to erroneous measurements. ICP-OES was proven to be a useful method for the determination of Cu, In, Ga and Se in the electroplating bath with less than 5% error. However ICP-OES is not capable of determining the amounts of organic anions such as citrate and tartrate and distinguishing between elemental selenium, SeO_4^{2-} or SeO_3^{2-} . Its use is limited to simple anions such as Cl⁻. In a manufacturing environment, on-line chemical monitoring systems might be adapted to measure the samples withdrawn from the plating lines at a desired periodicity. Once anionic and cationic concentrations are measured by IC and ICP-OES, respectively, necessary chemical additions can be made to maintain the bath chemistry at the specified concentration ranges.

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Pore-opening Process in Nanoporous AAO Membranes for Electrodeposition of Semiconducting Nanowires

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ABSTRACT

The fabrication of nanoporous aluminum oxide (Al_2O_3) membranes for large scale production of nanowires is performed at room temperature by a two-step anodization of commercially available aluminum foil tapes. During the anodization process, an oxide barrier layer is formed at the interface with aluminum. In the present work, the removal of the barrier is performed by (i) ramping down the voltage with a rate in the range of 0.5 V per 60s to 2 V per 60s and (ii) immersing the substrate in 50% phosphoric acid for up to 5 minutes. Depending on the removal conditions, several morphologies at the oxide-aluminum interface are observed by Scanning Electron Microscopy (SEM). Ramping down the voltage at less than 0.3 V per 15s combined by immersion in 50% phosphoric acid for less than 3 minutes is found to open the barrier layer of the nanopores. The pores have root-like structure with branches as small as few nanometers due to the slow voltage ramping. Several amorphous anodized Al_2O_3 (AAO) templates with pore diameter ranging from 30 to 40 nm and with length up to 25 μm were prepared by two-step anodization for the cathodic electrodeposition of photoactive nanowire semiconductors such as copper indium diselenide and cadmium sulfide.

INTRODUCTION

Nanoporous membranes have shown great potential in areas of inclusion chemistry, guest-host synthesis, molecular manipulations and reaction in the nanoscale for making nanoparticles, nanowires [1-6] and nanotubes [7, 8] with their unusual physical properties. High aspect-ratio (HAR) nanostructured materials have attracted great interests for nanoscale device applications in microelectronics, non-linear optics and optoelectronics [9]. In particular, solar devices based on photoactive HAR semiconductors are predicted to exhibit higher efficiency when compared to planar thin-film solar cells due to enhanced optoelectronic properties by quantum confinement effects and larger effective surface area. In order to develop a large-scale production approach of HAR nanostructure solar devices, the HAR semiconductors are fabricated by a well-established bottom-up strategy integrating low cost and non-vacuum electrochemical techniques. In general, such nanofabrication requires a conducting substrate and a chemically inert template with well-ordered nano-channels in which the semiconductor material is directly deposited. In our strategy, the HAR nanostructures are fabricated by electrodepositing the materials inside the nano-channels of anodized aluminum oxide membranes using the remaining aluminum foil as a conducting electrode. This approach leads to

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homogeneous HAR nanostructure diameter due to the limitation of the semiconductor growth by the nanopore dimension.

EXPERIMENT

Commercially available aluminum foil tapes with acrylic adhesive layer are cut into one square inch sample specimens for the two-step anodization process at room temperature. The electrolytic bath is a 200 mL aqueous solution containing 0.3 M oxalic acid. The tapes are first anodized at voltage of 20 V for 10 minutes. The anodization is stopped abruptly without voltage ramping. The anodized tapes are cleaned in deionized water and dried by blowing air. The removal of the first aluminum oxide layer containing disordered pores is performed for one minute in 15 ml of hot (100°C) mixed acid solution containing 5% phosphoric acid and 2% chromic acid followed by a cleaning step in deionized water and drying step by blowing air. After the first anodization process, dimples in a honeycomb arrangement are formed in the aluminum tapes. The dimple arrangement served as imprint for the growth of well-ordered nanopores during the second anodization process at voltage of 40 V for 15 minutes and up to 3.5 hours to obtain nanoporous layer of less than 2.5 and 25 μm thick, respectively. After the current reached 0.3 or 0.6 of the maximum current recorded initially, the voltage is first ramped down to 10V with a constant rate of 2V/min and then to 1V with a rate in the range of 0.5V/min to 2.4/min as shown in figure 1. The power is turned off when 1V is reached. After ending the 2nd step anodization, the membranes are cleaned in deionized water and dried by blowing air. An additional step is performed by immersing the membranes in 50% phosphoric acid for up to 5 minutes at room temperature to remove residual thin barrier. Finally after removing the acrylic tape by immersing the membranes in acetone for several minutes, the membranes are annealed at 230 °C in air for several hours in order to remove the unwanted residuals like hydroxides that are detrimental to the deposition of semiconducting materials in the nanopores.

DISCUSSION

In order to fabricate HAR nanostructures by either constant applied current or constant applied voltage cathodic electrodeposition, it is critical that (i) the nano-channels in which the materials is to be deposited are open and (ii) the electrolyte is flowing inside the nano-channels. Thus, capillarity or surface tension effect inside the nano-channels should not be inhibiting the liquid flow within the nanopores. In this work, opening the pore at the oxide-metal interface has particularly attracted our interest in either membranes of less than 2.5 μm thick for photovoltaic micro-devices or membranes of 25 μm thick for high aspect ratio nanostructure fabrication.

Pore opening in 2.5 μm thick AAO membranes

In the case of short templates of less than 2.5 μm thick, we recently showed that a smaller initial “pore dimple” nanoprint from the first step is required for less “dissolution time” for pore-opening in the second step anodization. Consequently, a low voltage of 20V is applied in the first step anodization in oxalic acid media. This led to a better surface quality and a highly ordered 2D nanoporous template than applying identical voltage in both steps [2]. In 0.3 M oxalic acid media, the anodization produced membranes with average pore diameter of 30 nm for an applied voltage of 40 V [3]. In addition, the approximate pore density, estimated from SEM pictures was about $2.5 \times 10^{10} \text{ cm}^{-2}$ [3]. Using a programmable power supply, the voltage at the end of the anodization step is ramp down with the rates shown schematically in figure 1. The profile of the