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Electrochemical studies of the electrodeposition of copper-zinc-tin alloys from pyrophosphate electrolytes followed by selenization for CZTSe photovoltaic cells

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ABSTRACT

Ternary copper-zinc-tin coatings have been prepared by a one-step electrodeposition on molybdenum sputtered soda-lime glass (SLG) (20×20 mm^2) from an aqueous pyrophosphate electrolyte at room temperature. The plating bath contains copper(II), zinc(II), tin(II) and potassium pyrophosphate at pH = 10. The influence of pyrophosphate as a complexing agent is characterized by speciation simulation, cyclic voltammetry and linear sweep voltammetry. The electrolyte and deposition conditions were adjusted to deposit ternary coatings with the appropriate copper-poor and zinc-rich composition (Cu/(Zn + Sn) = 0.89 and Zn/Sn = 1.04), making them suitable for preparing kesterite absorber films for photovoltaic applications. The composition is influenced by variation of the deposition potential, pH, temperature, composition of the electrolyte and control of the mass transport. The morphology, composition and structure of the as-deposited and selenized films were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), inductively coupled plasma optical emission spectroscopy (ICP-OES) and X-ray diffraction (XRD). Dense, closed, homogeneous films of ternary copper-zinc-tin alloys with a mirror-bright gray appearance were deposited from the pyrophosphate electrolyte. After selenization, the coatings were matte gray and consisted of micrometer sized grains of pure CZTSe reaching over the complete thickness with only a few voids near the molybdenum back contact.

1. Introduction

In recent years, research on thin film photovoltaic cells is focusing on the development of inexpensive, earth abundant and environmentally benign materials [1–7]. CZT(S,Se) ($Cu_2ZnSn(S,Se)_4$) thin films meet this unlike the present commercial photovoltaic thin films CIG(S,Se) ($Cu(In,Ga)(S,Se)_2$) and CdTe. The crystal structure of CZT(S,Se) is obtained by replacing half of the indium and/or gallium in CIG(S,Se) by zinc and the other half by tin, which are both more earth-abundant materials than indium and gallium [8,9]. CZT(S,Se) has a direct band gap of 1.0 eV ($Cu_2ZnSnSe_4$) to 1.5 eV (Cu_2ZnSnS_4) and a large absorption coefficient of over $10^4\ cm^{-1}$ [10]. CZT(S,Se) thin films have previously been prepared by evaporation [11–14], sputtering [15–18], sol-gel deposition [7,19–21], pulsed laser deposition [22–24], spray pyrolysis [25–27], screen-printing [28,29] and electrodeposition [30–51]. Wang et al. recently reported a record power conversion efficiency of 12.6% (CZTSSe) by a hydrazine-based solution process [52,53], which is highly toxic and reactive. This new record encouraged many researchers to search for production techniques that are more environmentally benign.

In this view, electrodeposition is a promising technique because it is a low-cost method that allows fast and continuous production on large substrates with good control over the composition and morphology. Three approaches are commonly used to deposit the precursors: successive deposition of copper, tin and zinc or binary alloys of these metals [30–36], co-electrodeposition of copper, zinc and tin [37–43] and co-electrodeposition of copper, zinc, tin and sulfur/selenium [44–51]. After deposition of these coatings, an annealing step is required to sulfurize/selenize the metallic

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precursors and/or improve the crystallinity of the Cu-Zn-Sn-S/Se coatings.

Deposition of *stacked elemental layers* (SEL) of copper, tin and zinc enables control of the ratio of the three metals in the final crystal structure, but still this method is accompanied by several issues hindering further deployment [54]. For example, plating and cleaning/rinsing procedures are required for each metal, resulting in multiple process steps. Moreover, some steps are troublesome. For example, displacement reactions on immersion in tin solutions result in loss of zinc. Difficulties with uniformly depositing tin from tin(IV) electrolytes are reported as well [30]. Perhaps the most important problem is the complex annealing sequence. Tin sulfides and elemental zinc are known to evaporate during sulfurization [31,55,56]. The loss of these elements can be minimized by the sequence of the metal coatings, or by an additional soft-annealing in an inert atmosphere before sulfurization/selenization [32–34,57], but the process becomes more complicated and the advantage of accurately controlling the ratio of the three metals in the final crystal structure by controlling the charge of each separate metal coating, is lost.

A one-step electrodeposition of all four elements counteracts the problems encountered in the SEL approach. Obviously, the number of process steps is minimized. Furthermore, the compounds are mixed on a microscopic scale before annealing, resulting in the absence of volume expansion during this step. In 2010, a one-step electrodeposition of copper-zinc-tin-sulfur precursors was described for the first time from a citrate/tartrate-based solution followed by an annealing step [51]. Although a one-step electrodeposition of the four elements would be ideal, the stoichiometric deposition of the quaternary coating is difficult to control and an additional annealing step to obtain the right ratio of the chalcogenide and to improve the crystallinity is still required. Furthermore, most researchers use thiosulfate as the sulfur source in acidic citrate/tartrate-based electrolytes, which is unstable and precipitates as sulfur [44,48–51].

Because of these disadvantages, electrodeposition of ternary copper-zinc-tin alloys followed by sulfurization/selenization is more suitable [37–43]. Most electrolytes used for the electrodeposition of copper-zinc-tin alloys contain citrate as a complexing agent [37–40]. Araki et al. prepared a CZTS solar cell by a 20 min electrodeposition of ternary Cu-Zn-Sn from a citrate electrolyte followed by sulfurization [40]. The as-deposited ternary films were rather rough and consisted of pillar-shaped grains. Mixtures of tartrate and citrate as complexing agents were also reported [41]. Although the electrodeposition of copper-zinc-tin alloys from pyrophosphate electrolytes was already described in 1987 [58], the application of this complexing agent for the electrochemical production of CZTS thin films was reported for the first time in 2009. Copper-zinc-tin alloys were deposited with copper(II), zinc (II) and tin(IV) salts in a pyrophosphate electrolyte in presence of other (undefined) complexing agents and additives. The resulting CZTS photovoltaic cell showed an efficiency of 3.6% [43]. Khalil et al. reported the electrodeposition of rough films of a ternary copper-zinc-tin alloy from a pure pyrophosphate-based electrolyte. Their electrolyte was based on that of Ennaoui et al. [43] with copper(II), zinc(II) and tin(IV) salts, but using only pyrophosphate as complexing agent. Sulfurization of the coatings did not decrease the roughness of the films [42].

A tin(II) salt is used instead of a tin(IV) salt in this work because of several advantages. Because of the valence of the two tin species, electrodeposition of tin from a tin(II) electrolyte requires half of the energy required to deposit the same amount of tin from a tin(IV) electrolyte. In tin(IV) electrolytes, adequate growth rates are only obtained at elevated temperature, typically above 60 °C, while tin (II) electrolytes are operated at ambient temperature [59]. Furthermore, rather rough copper-zinc-tin films are deposited from pyrophosphate electrolytes containing tin(IV) salts [42]. By using a tin(II) salt in this work, dense, closed, homogeneous films are obtained. The coatings consist of fine grains and show a good adhesion to the molybdenum substrate. The main disadvantage of using tin(II) electrolytes is the tendency of tin(II) to oxidize to tin (IV) by dissolved oxygen in the electrolyte or at the counter electrode during electrodeposition. In order to minimize the dissolved oxygen concentration, the electrolyte is deaerated after preparation and after each deposition. By using a 1000 mL electrolysis cell, the potential decrease of the tin(II) concentration by oxidation to tin(IV) does not influence the composition of the deposits because each set of experiments is performed from a fresh electrolyte in which tin(II) is added shortly before the start of each set. These measures have shown to efficiently inhibit significant changes of the tin(II) concentration because of the good repeatability of the composition and morphology of the ternary coatings. The oxidation to tin(IV) can be highly inhibited by using a soluble counter electrode or even better by using a membrane cell [60], but this is not investigated in this work.

In this work, dense, closed, homogeneous, mirror-flat films of ternary copper-zinc-tin were obtained in one electrodeposition step from a pure pyrophosphate-based electrolyte with tin(II) instead of tin(IV) salts as the tin precursor. The composition of the film approaches ratios of $Cu/(Zn+Sn) = 0.8$ and $Zn/Sn = 1.1$, which are the targeted ratios for obtaining the kesterite structure after annealing. In order to obtain these ratios, the composition of the electrolytes was adjusted by studying the speciation of the ionic species in solution and the electrochemical properties of the metal-pyrophosphate complexes. Finally, the coatings were selenized in a H_2Se atmosphere to produce CZTSe thin films.

2. Experimental

2.1. Chemicals

Electrochemical experiments were performed at room temperature from an aqueous electrolyte containing 15 mmol dm^{-3} copper(II) pyrophosphate ($Cu_2P_2O_7{\cdot}3H_2O$, Sigma-Aldrich), 100 mmol dm^{-3} zinc(II) pyrophosphate ($Zn_2P_2O_7$, in-house synthesis, vide infra), 8 mmol dm^{-3} tin(II) pyrophosphate ($Sn_2P_2O_7$, Sigma-Aldrich 98%) and 500 mmol dm^{-3} potassium pyrophosphate ($K_4P_2O_7$, Sigma-Aldrich 97%). All chemicals were used as purchased. In order to obtain stable electrolytes, the potassium pyrophosphate and the copper(II) and zinc(II) salts were dissolved before the tin(II) salt was added. By complexation of copper(II) before the addition of tin(II), the oxidation of tin(II) to tin(IV) and the reduction of copper(II) to copper during preparation of the electrolyte are inhibited [59]. The pH of the solution was adjusted to pH = 10 with ortho-phosphoric acid (H_3PO_4, Carl Roth ≥ 85% pro analysis). After dissolution and adjustment of the pH, the electrolyte was deaerated with nitrogen for 15 min. Deaeration was repeated after each deposition.

Zinc(II) pyrophosphate was synthesized by the reaction of zinc (II) sulfate ($ZnSO_4{\cdot}7H_2O$, Acros Organics > 99.5%) with potassium pyrophosphate. The products were dissolved in separate beakers and added dropwise to a third beaker filled with water under vigorously stirring. A white precipitate was immediately formed. Because of the high solubility of zinc(II) sulfate (3.57 mol dm^{-3}), potassium pyrophosphate (5.66 mol dm^{-3}) and potassium sulfate (0.64 mol dm^{-3}) [61], it is expected that only $Zn_2P_2O_7$ precipitated. The precipitate was washed with water, dried at 55 °C for 72 h, ground with a mortar and pestle, washed again until no more sulfates were detected, dried at 55 °C for 72 h and further dried at 150 °C for 4 h. The presence of sulfates in the washing water was tested by adding a few drops of 0.1 mol dm^{-3} barium nitrate ($Ba(NO_3)_2$, Alfa Aesar 99%).