

Morphology and Thickness Control of Thin Copper Films Prepared by Electrochemical Deposition onto Mo-sputtered Stainless Steel Substrates

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Chalcopyrite thin film solar cells of copper (Cu), indium (In), gallium (Ga) and selenium (Se) (CIGS) are receiving much attention, because they show high efficiency and long-term stability.¹ Methods to prepare CIGS light absorber layers include co-evaporation of elemental sources,² physical vapor deposition,³ printing and electrochemical deposition.⁴ Among those, electrochemical deposition is considered as an excellent technique for large area processing with good uniformity, low cost, and high material yield.⁵

Electrodeposition of CIGS precursor films can be performed by using either single step or multistep process. Although Bhattacharya et al. have reported the development of a 15.4% efficiency CIGS cell by employing a single-bath electrochemical deposition following physical vapor deposition,⁶ no other laboratory has reproduced it. The multistep process can be two or three stage process; some examples of such stacks are like Cu/In/Ga, Cu-Ga/In/Se, Cu/In/Ga-Se, Cu/In-Se/Ga-Se, *etc.*⁷⁻⁹ For successful industrialization of CIGS solar cells, control of metal layers is required in morphology, thickness, and production speed. The objective of this study was to fabricate the targeted copper thin film onto Mo/SUS substrates by electrochemical deposition for CIGS thin film solar cell precursor. Morphology and thickness of copper thin film onto the Mo/SUS are very important factors because film's surface condition can affect electrochemical deposition of the next layers of In, Ga, and Se before thermal selenization process. In this work, we wish to report our preliminary work on the electrochemical conditions that can produce a uniform thin copper metal layer onto the Mo sputtered stainless steel (Mo/SUS) flexible substrate for short time (sec). Mo/SUS substrate has the advantages of weight lighter than soda lime glass, of installation to the building integrated photovoltaic and of roll-to-roll manufacturing leading to substantial cost reductions due to enhanced productivity.

All chemicals were analytical grade. Double-distilled water was used throughout. The electrochemical experiment was performed in a freshly prepared 0.1, 0.5 and 1 M CuSO₄ baths containing various concentrations of (0.1, 0.5, 1, 1.5 M) H₂SO₄. Two-electrode configurations were used for deposition of Cu thin film. Hull cell test was performed in order to find the current density. The 100 × 100 mm² Mo/SUS substrate and mesh-Pt were used as a working electrode and a counter electrode, respectively. The Mo film on the

stainless steel was ~500 nm thick and was deposited by DC sputtering. A 430 CSP stainless steel was used because it has high tension. No organic additives were used in the present experiments.¹⁰ First, Hull cell was used to find the different current densities of the various thicknesses of Cu films at designated locations of Mo/SUS substrates in aqueous sulfuric acid solutions of copper, and then electrodeposition of the Cu film was confirmed in a vertical cell of the both working and counter electrodes for short time (within 10 sec). All of the experiments were performed at room temperature. A COXEM CX-100 scanning electron microscopy (SEM) and a Bruker 410-M energy dispersive spectrometer with computer control were used to analyze surface, thickness and components of thin films.

Sulfuric acid was used as an electrolyte; morphologies of electrodeposited copper film changed depending on the electrolyte concentration. At the given deposition time, copper films did not adhere strongly to Mo/SUS substrates and even peeled off when they were electrodeposited in higher ratios of sulfuric acid to copper concentrations. The activity of Mo as a substrate depends on the pH of the electrolyte. In aqueous acidic conditions, Mo initially dissolves as Mo³⁺ before becoming passivated by a layer of MoO₂ or MoO₃, which may prohibit effective nucleation of Cu and cause to produce a non-adherent, powdery form.¹¹ Figure 1 shows that the copper films with good uniformity could be electrodeposited in the

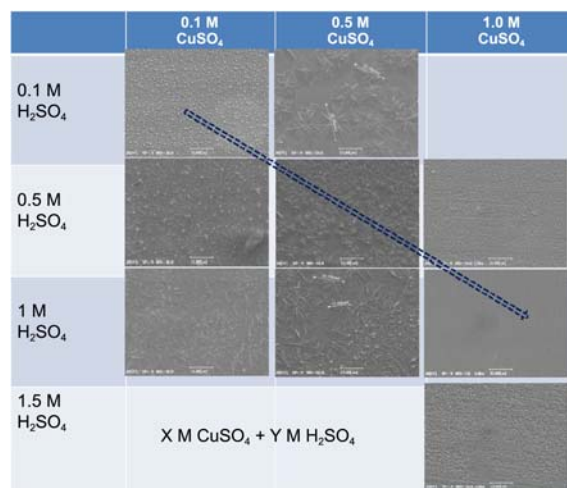


Figure 1. SEM images of Cu films. Electrolytic solutions: X M CuSO₄ (0.1 < [X] < 1.0 M) and Y M H₂SO₄ (0.1 < [Y] < 1.5 M).

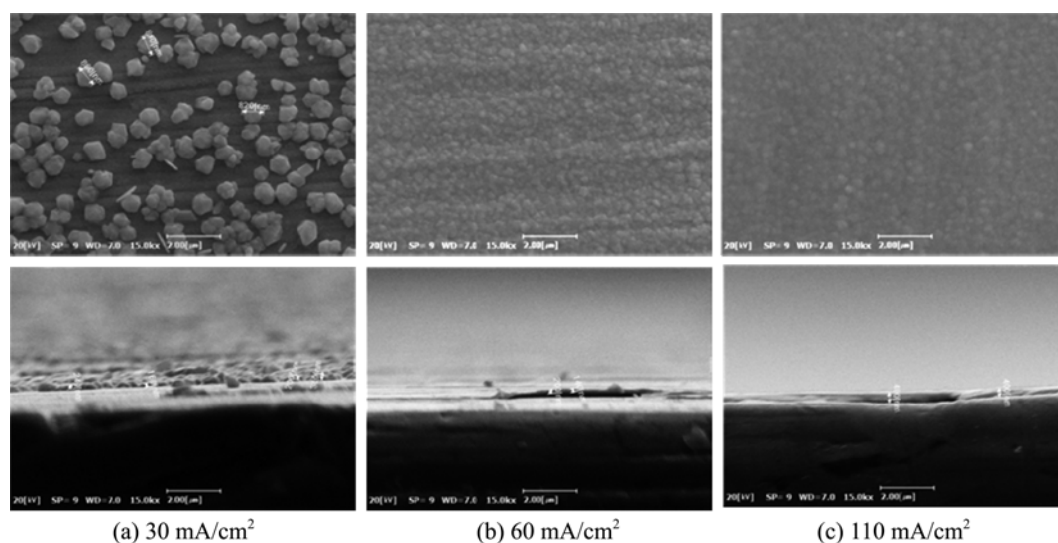


Figure 2. Top and side SEM images of Cu films electrodeposited onto the Mo sputtered-stainless steel at different current densities of two-electrode parallel system: (a) 30 mA/cm² (b) 60 mA/cm² (c) 110 mA/cm²; Electrolytic solution: 1 M CuSO₄ and 1 M H₂SO₄.

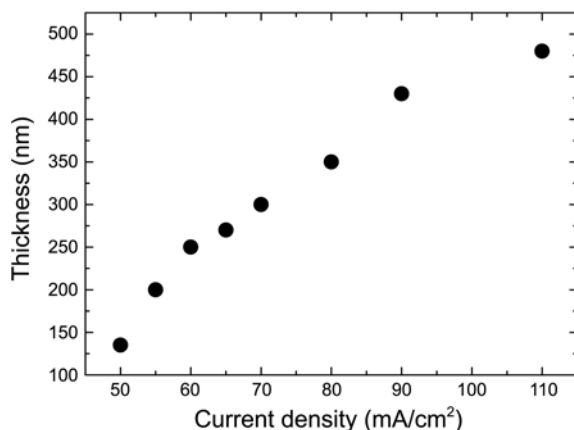


Figure 3. Plots of thickness against current density for Cu films prepared at the given time.

condition of 1 (H₂SO₄):1 (CuSO₄) molar concentration ratio.

Hull cell test was hired in order to investigate the optimal electrochemical conditions to produce copper layer. At the given time of electrodeposition, the size of copper particles decreased with uniformity increased at higher current density or at shorter distance in the Hull cell, while the Mo surface was exposed with increasing particle size at lower current density. Flower-shaped copper seeds deposited onto Mo surfaces have been shown at low concentration of copper and at low current density, which are not desirable for the industrial purpose of producing solar cells. Manufacturing solar cells in less time is better for the industrial purpose because it will result in a higher production speed and improve manufacturer's productivity. In the present experiment, we succeeded in producing targeted copper thin films by using larger concentrations of copper at high current densities in shorter time (< 10 sec). Figure 2 shows the SEM images of copper film deposited by two electrodes placed vertically. The Cu films were obtained by changing the current densities and were analyzed by SEM. Summary data in Figure 3 shows that the thickness of the copper film increased in

proportion to current density. The proper thickness range of copper films is between 300 nm and 400 nm. Those thicknesses are optimal for the CIGS solar cell precursor of 1-2 μm fabricated by layer-by-layer stacked electrochemical deposition. Therefore, current density between 70 and 90 mA/cm² is the optimal range to produce copper films for the thin film solar cells in the current experimental conditions.

In summary, we succeeded in producing copper thin films suitable for industrial purpose. Work is in progress to find the mechanistic aspect of Cu film formation and the electrodeposition conditions of other elements (In, Ga, and Se) as well with high speed for commercialization of CIGS solar cells.

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