Hydrazine solution-processed CuIn(Se,S)₂ thin film solar cells: Secondary phases and grain structure

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Abstract

We have carried out microstructural studies of secondary phase formation at the Mo/CuIn(Se,S)₂ interface, and of grain structure in hydrazine solution-processed CuIn(Se,S)₂ films. The CuIn(Se,S)₂ layers were deposited on Mo-coated glasses followed by thermal annealing under a nitrogen ambient. In our previous work, we identified [Cu₆S₄]²⁻ and \[In₅(Se,S)₄\]²⁻ as the two major molecular species present in hydrazine CuIn(Se,S)₂ precursor solutions. The CuIn(Se,S)₂ films prepared by the precursor solution containing only above two molecular complexes exhibited the undesired secondary interfacial phases such as CuSe and CuIn₅S₈. It is likely that the reactions between the Mo bottom electrode with sulfur in \[Cu₆S₄\]²⁻ can result in the formation of a MoS₂ phase, triggering the phase separation of CuIn(Se,S)₂ into CuSe and CuIn₅S₈. To make matters worse, the final CuIn(Se,S)₂ films contain a lot of voids that reduce the structural and electrical integrity of the device. The addition of polyselenide molecules \[Se₂\] into the above CuIn(Se,S)₂ precursor solutions introduced MoSe₂ rather than MoS₂ at the back interface which in turn allows sulfur to remain in \[Cu₆S₄\]²⁻ complexes. As a result, only the desired phases, CuIn(Se,S)₂ and MoSe₂, were formed near the back interface. Furthermore, the formation of voids within the film can be also prevented by adding \[Se₂\] into the CuIn(Se,S)₂ precursor solution, leading to the formation of a dense film structure.

Keywords: Thin film solar cells, CuIn(Se,S)₂, Hydrazine, Secondary phases, Grain structure

1. Introduction

While crystalline silicon technology occupied approximately 85% of the photovoltaic market in 2010, these modules are still more expensive than fossil fuels largely because of the costly silicon wafers, impeding the wide-spread use of solar cells as an energy source [1]. Therefore, thin film solar cells, including cadmium telluride, copper chalcopyrite, polycrystalline silicon, and amorphous silicon have been extensively researched to reduce the fabrication cost of solar modules [2]. Among them, Cu(In,Ga)₅(Se,S)₈ solar cells have attracted a lot of attention due to their highest power conversion efficiency (PCE) of around 20% among thin film solar cells [3,4]. Achievement of such high PCE can be largely ascribed to the excellent optoelectronic properties of the absorber layer such as an Ohmic contact with the back electrode, long minority carrier life time, and optimized energy band gap. These desirable properties can be partially ascribed to the formation of a MoSe₂ phase at the Mo/absorber interface [5], large grain size in the absorber film [6], and partially replacement of indium and/or selenium by gallium and/or sulfur, respectively [3–6]. These properties are readily delivered by co-evaporation techniques by precisely controlling the atomic flux of each element and the composition of film over the entire deposition period [3,4].

However, the use of vacuum facilities in the preparation of the absorber layer has still caused difficulty in the low-cost and large area production of solar modules. Therefore, a number of research efforts have been dedicated to the development of non-vacuum deposition methods for the preparation of the absorber layer in an effort to reduce the cost of producing these devices [7–12]. Almost all reported non-vacuum methods demonstrating reasonable PCE values require a post selenization and/or sulfurization step which typically uses vacuum facilities as well as toxic gases such as H₂Se and/or H₂S. Furthermore, an undesirable redistribution of indium, gallium, and sometimes sulfur upon post selenization/sulfurization makes it difficult to optimize the final energy band gap profile of the absorber layer.

Several years ago, Mitzi et al. developed hydrazine solution processed chalcogenide absorber layers including Cu(In,Ga)₅Se₈ (CIGS) and Cu(In,Se,S)₈ (CISS) as a simple and high throughput process with no need for post selenization treatment [13–16]. Hydrazine processed CISS solar cells have been demonstrated with PCE values of 12.2% that are comparable to the record values of vacuum processed CuInS₂, CuInSe₂ and Cu(In,Se,S)₈ solar cells [14]. Furthermore, these hydrazine processed CIGS solar cells currently hold the highest published PCE value of 15.2% among...
purely solution processed thin films solar cells despite its early stage of the development [16]. CIGS films used in the best solution-processed devices also exhibit a MoSe₂ phase at the Mo/CIGS interface, large grain size in the absorber film, and an adjustable energy band gap.

In our previous work, we reported hydrazine processed 7.4% efficiency CISS thin film solar cells [17]. In this study, we report microstructure formation mechanism of hydrazine solution-processed CISS films mainly aiming to understand secondary phase formation at the Mo/CISS interface and the resulting grain structure of the CISS films. In order to do this, we have directly probed secondary phases at the Mo/CISS interface using Raman spectroscopy and used scanning electron microscopy (SEM) to observe the grain structure of the CISS films. While [Cu₆S₄]²⁻ and [In₂Se₄]²⁻ are known to be two molecular complexes present in hydrazine CISS precursor solutions that are essential in forming the chalcopyrite CISS phase, the presence of excess selenium in the form of polymeric [Se]ₙ structures appears to be vital to the fabrication of high efficiency photovoltaic devices. Here we focus on the role of polyselenide molecules [Se]ₙ in achieving the desirable microstructure within the deposited CISS films and the resulting grain structure of the CISS films. In order to directly probe the microstructural properties of the CISS absorber layer based on the this information, we have demonstrated a roughly absolute 2% improvement in the PCE of hydrazine solution processed CISS thin films solar cells.

2. Experimental details

Photovoltaic devices with the structure MgF₂/Al/Ni/ITO/i-ZnO/CdS/CISS/Mo/Glass were prepared on Mo-coated soda lime glasses by sequentially depositing the CISS absorber layer using hydrazine solution processing, the cadmium sulfide (CdS) buffer layer by chemical bath deposition, the bi-layered window layer consisting of intrinsic zinc oxide (i-ZnO) and indium tin oxide (ITO) by radio frequency sputtering, the bi-layered metal grid composed of nickel (Ni) and aluminum (Al) by thermal evaporation, and the magnesium fluoride (MgF₂) anti-reflection coating by thermal evaporation.

The CISS precursor solutions were prepared by mixing Cu-precursors containing Cu₂S and sulfur with In-precursors composed of In₂Se₃ and selenium and/or sulfur (Fig. 1). The details of solution precipicator preparation can be found elsewhere [18,19], CISS films were deposited by spin-coating the hydrazine CISS precursor solutions at a spin-speed of 3000 rpm for 50 s. The coating was repeated to prepare ~1.5 μm-thick layer to effectively absorb the solar spectrum. Between each coating step, the films were annealed at 300 °C for several minutes, and finally annealed at 550 °C for 15 min using rapid thermal annealing. Caution: hydrazine is highly toxic and should be handled with appropriate protecting equipment to prevent contact with either the vapors or liquid. The CdS layer was deposited from an aqueous bath containing cadmium acetate, thiourea, ammonium hydrosulphide and ammonium acetate at 65 °C. The i-ZnO layer was deposited at a relatively mild sputtering condition with a deposition rate below 0.25 Å/s so as not to damage the devices. The ITO film was deposited at conditions of approximately 1% oxygen to argon working gas flow to achieve both high optical transmittance (> 90%) and low sheet resistance (~ 35 Ω/sq).

Completed CISS films were mechanically exfoliated and flipped over onto 3 M tape. The images of exposed Mo surface and a flipped over CISS film were taken by optical microscope. Raman spectroscopy was performed on the prepared CISS films and the exposed Mo surface in a confocal backscattering configuration at room temperature using a Renishaw InVia model with a 514.5 nm argon laser as a light source. The scanning electron microscope images were taken on a Jeol JSM-6700F electron microscope. The current density-voltage characteristics of the photovoltaic devices were measured using a Keithley 2400 power supply under a 100 mW/cm² simulated AM1.5G spectrum provided by an Oriel 91191 solar simulator.

3. Results and discussion

The presence of a thin layer of MoSe₂ at the Mo/absorber interface has been reported to provide Ohmic back contact which is important for achieving high performance photovoltaic devices [20]. MoSe₂ phase can be typically formed by flowing selenium vapor or H₂Se gas onto substrates held at temperatures above 400 °C during or after growth of the absorber layers [4,21]. In the hydrazine solution process, absorber layers are generally deposited at room temperature followed by high temperature annealing under nitrogen ambient. In other words, this process does not contain a continuous flux of selenium vapor or molecules containing selenium impinging on the substrate while it is held at high temperature. Thus, molecular species containing selenium atom(s) in precursor solutions must be responsible for MoSe₂ phase formation.

[In₂Se₄]²⁻, [Cu₆S₄]²⁻, and polyselenide molecules [Se]ₙ have been identified in hydrazine CISS precursor solutions [18]. We employed two different kinds of CISS precursor solutions for the study on microstructural properties of the resulting CISS films. One contains only two kinds of molecular species, [Cu₆S₄]²⁻, and [In₂Se₄]²⁻ which are essential to form CISS phase, and the other additionally contains polyselenide molecules [Se]ₙ (Fig. 2). A pale yellow color and dark green color of the CISS precursor solutions originate from [Cu₆S₄]²⁻ complexes, and polyselenide molecules [Se]ₙ, respectively.

In order to directly probe the microstructural properties of the prepared CISS films near the Mo surface, completed CISS films were mechanically exfoliated and flipped over onto 3 M tape (Fig. 3 a). Fig. 3 b and c show optical microscopy images of the exposed Mo surface and a flipped over CISS film on 3 M tape. Raman spectra were obtained from the exposed Mo surface, and the top and bottom surface of the CISS films marked as (1), (2) and (3), respectively, in Fig. 3 and Fig. 4.

In the CISS films prepared using CISS precursor solutions containing only the [Cu₆S₄]²⁻ and [In₂Se₄]²⁻ molecular complexes,
several secondary phases other than CISS including MoS$_2$, CuSe, and CuIn$_5$S$_8$ were observed on the exposed Mo surface while only the CISS chalcopyrite single phase was detected from both the back and front surface of the film (Fig. 4a). The Raman spectra revealed a MoS$_2$ peak at 400 cm$^{-1}$ [22–24], CISS peaks at 176 cm$^{-1}$ and 292 cm$^{-1}$ [25], a CuSe peak at 263 cm$^{-1}$ [24,26–28], broad peaks related to the CuIn$_5$S$_8$ phase in the 320–380 cm$^{-1}$ range [22,23,29], and an un-identified peak at 223 cm$^{-1}$ which can be related to the existence of copper rich phases [24]. Nonetheless, the overall composition of this film of In/Cu$\approx$1.2 falls into the expected range of the thermodynamically stable chalcopyrite phase, both the copper rich phase (CuSe) and indium rich phase (CuIn$_5$S$_8$) coexisted with CISS phase at back interface, implying the phase separation of CISS into CuSe and CuIn$_5$S$_8$. The presence of several secondary phases resulting from the phase separation of CISS at the back interface will negatively affect the photovoltaic performance of any resulting devices.

MoS$_2$ formation can be attributed to the reaction of sulfur in [Cu$_6$S$_4$]$^{2-}$ with the Mo electrode. The [Cu$_6$S$_4$]$^{2-}$ complex is relatively unstable during thermal treatment compared with [In$_2$Se$_4$]$^{2-}$ [19,30]. Thus, it can be assumed that the Cu–S

Fig. 2. Two different kinds of CuIn(Se,S)$_2$ precursor solutions. Left one contains only two molecular species, [Cu$_6$S$_4$]$^{2-}$, and [In$_2$Se$_4$]$^{2-}$. Right one additionally contains polyselenide molecules [Se]$_n$. A pale yellow color and dark green color of the CuIn(Se,S)$_2$ solutions originate from [Cu$_6$S$_4$]$^{2-}$ ions, and polyselenide molecules [Se]$_n$, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Raman spectra taken from the exposed Mo surface, and the top and bottom surface of the CuIn(Se,S)$_2$ films marked as (1), (2) and (3), respectively. The spectrum intensity from exposed Mo surface is amplified by 10 or 3 to provide for easier viewing. (a) The CuIn(Se,S)$_2$ films prepared using the precursor solutions containing only [Cu$_6$S$_4$]$^{2-}$ and [In$_2$Se$_4$]$^{2-}$ exhibits several secondary phases including MoS$_2$, CuSe, and CuIn$_5$S$_8$ near the back interface. (b) In contrast, the CuIn(Se,S)$_2$ films prepared by the precursor solutions containing polyselenide molecules [Se]$_n$ in addition to [Cu$_6$S$_4$]$^{2-}$ and [In$_2$Se$_4$]$^{2-}$ show only MoSe$_2$ peaks at the back interface. A distinct CuIn(Se,S)$_2$ single phase peak can be observed from both the front and back surface of the CuIn(Se,S)$_2$ film in both cases.

Fig. 3. (a) Completed CuIn(Se,S)$_2$ films are mechanically exfoliated and flipped over onto 3 M tape. Optical microscopy images of (b) the exposed Mo surface and (c) a flipped over CuIn(Se,S)$_2$ film on 3 M tape.
interactions in $[\text{CuS}_4]^{2-}$ ions are significantly weaker than the In-Se interactions in $[\text{InS}_4\text{Se}_4]^{2-}$ ions [19]. It is thus likely that the Mo bottom electrode preferentially reacts with sulfur in $[\text{CuS}_4]^{2-}$ rather than with selenium in $[\text{InS}_4\text{Se}_4]^{2-}$ ions. Thus, out-diffusion of sulfur from $[\text{CuS}_4]^{2-}$ into the Mo may leave free copper atoms or copper rich complexes, triggering an inhomogene-ous distribution of molecular precursors which in turn can lead to the phase separation of CISS into CuSe and CuIn$_5$S$_8$. This is one possible explanation for the observation of co-existence of the MoS$_2$, CuSe, CuIn$_5$S$_8$ and CISS phase at the Mo/CISS interface.

In contrast, Raman spectra of the CISS film prepared by CISS precursor solutions containing polyselenide molecules $[\text{Se}]_n$ in addition to $[\text{CuS}_4]^{2-}$ and $[\text{InS}_4\text{Se}_4]^{2-}$ show only MoSe$_2$ peaks [31] at 168 cm$^{-1}$, 237 cm$^{-1}$, 251 cm$^{-1}$, 286 cm$^{-1}$, and 347 cm$^{-1}$ from the Mo surface, and a distinct CISS phase peak at 175 cm$^{-1}$ from both the front and back surface of the CISS film (Fig. 5a). A potential mechanism for the dramatically different back contact structure is as follows. In the presence of polyseleni-dioxide molecules $[\text{Se}]_n$, the Mo film preferentially reacts with selenium in $[\text{Se}]_n$, to form MoSe$_2$ rather than with the sulfur in $[\text{CuS}_4]^{2-}$ complexes because polyselenide molecules $[\text{Se}]_n$ are not bound to metal atoms. The preferential formation of MoSe$_2$ would allow sulfur atoms to stay in $[\text{CuS}_4]^{2-}$ ions, maintaining a homogeneous precursor mixture during film formation and ultimately stabilizing the CISS phase near the back interface.

We have also investigated the effects of the presence of polyselenide molecules $[\text{Se}]_n$ in CISS precursor solutions on the grain structure of the resulting CISS films. A large grained film structure can typically be achieved by supplying a large amount of selenium vapor to substrates held at high temperatures ($\geq 500$ °C). Hydrazine solution processing, however, cannot simply borrow pre-developed techniques from other deposition methods in achieving large grained film structure due to its unique deposition method. The resulting grain structures of hydrazine solution processed CISS films are shown in Fig. 5. In the CISS film prepared by the precursor solutions without $[\text{Se}]_n$ (Fig. 5a), the formation of voids can be clearly observed within the film. In contrast, much smaller number of voids as well as a larger overall grain size are observed in the CISS film prepared by the precursor solutions with $[\text{Se}]_n$ (Fig. 5b). While the reaction between the $[\text{CuS}_4]^{2-}$ and $[\text{InS}_4\text{Se}_4]^{2-}$ complexes forms the CISS chalcopyrite phase, polyselenide complex $[\text{Se}]_n$, play a critical role in obtaining a dense and large grain structure. To explore the impact of $[\text{Se}]_n$ and their resulting improvements in film structures on device performance, we fabricated two cells with the structure MgF$_2$/Al/Ni/ITO/i-ZnO/CdS/CISS/Mo/Glass based on absorber deposited using CISS precursor solutions both with $[\text{Se}]_n$ and without $[\text{Se}]_n$. The thicknesses of the CISS films were adjusted to be approximately 1.5 μm in each type of photovoltaic devices. The power conversion efficiency was improved from 8.9% to 11.1% by adding $[\text{Se}]_n$ into the precursor solutions. We fabricated more than ten samples for each condition. The addition of polyselenide molecules $[\text{Se}]_n$ in CISS precursor solutions lead an average of ~2% absolute efficiency improvement. The $[\text{Se}]_n$-based cell shows improvement in every major photovoltaic device parameters, including short circuit current density ($J_{SC}$), open circuit voltage ($V_{OC}$), and fill factor (FF) under AM1.5G illumination (Fig. 6). We characterized parasitic resistance components of two devices to clearly elucidate the role the secondary phases on the back contact. The shunt resistance between two devices showed negligible difference. In contrast, the addition of polyselenide molecules $[\text{Se}]_n$ lowered the series resistance value from 1.3 Ω cm$^2$ to 0.3 Ω cm$^2$ which most likely led to the improvement in FF from 64.4% to 70.5%. The lower series resistance in the $[\text{Se}]_n$-based cell can be ascribed to an increasingly Ohmic back contact formed by the presence of a MoSe$_2$ layer at the Mo/CISS interface.

We believe that the improved device performance is largely due to the more desirable microstructural properties in the $[\text{Se}]_n$-based CISS absorber layer by avoiding the formation of secondary phases and voids that are generally known to degrade the device performances.

4. Conclusions

The microstructural properties of CISS absorber layers are important to achieve high efficiency solar cells. Stability of the chalcopyrite phase and the careful control of chemical reactions with adjacent layer are key issues in achieving the desired microstructure in the CISS absorber layers. While $[\text{CuS}_4]^{2-}$ and $[\text{InS}_4\text{Se}_4]^{2-}$ play important roles in forming the CISS chalcopyrite phase, the presence of $[\text{Se}]_n$ are vital for obtaining desirable microstructure in the resulting CISS film, including MoSe$_2$ formation at the CISS/Mo interface and a dense and large grain structure within in the CISS films. In the absence of $[\text{Se}]_n$, molecules, potentially detrimental secondary phases at the Mo/CISS interface such as CuSe and CuIn$_5$S$_8$ are formed as well as a numerous of voids in the final films. The addition of polyselenide molecules $[\text{Se}]_n$ into the CISS precursor solution resulted in not only the formation of a beneficial MoSe$_2$ phase at the back interface which is helpful for achieving an Ohmic back contacts but also the formation of a CISS phase with a dense grain structure. More
refined control of molecular precursor species and their bonding environments may be possible as a result of this observation, and at present we have produced an increase in photovoltaic device performance of roughly 2% absolute from 8.9% to 11.1% through the appropriate application of selenium complexes in our CISS precursor solutions to further improve photovoltaic device performance.

References


