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Hydrazine-based deposition route for device-quality CIGS films

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ABSTRACT

A simple solution-based approach for depositing CIGS (Cu–In–Ga–Se/S) absorber layers is discussed, with an emphasis on film characterization, interfacial properties and integration into photovoltaic devices. The process involves incorporating all metal and chalcogenide components into a single hydrazine-based solution, spin coating a precursor film, and heat treating in an inert atmosphere, to form the desired CIGS film with up to micron-scaled film thickness and grain size. PV devices (glass/Mo/CIGS/CdS/i-ZnO/ITO) employing the spin-coated CIGS and using processing temperatures below 500 °C have yielded power conversion efficiencies of up to 10% (AM 1.5 illumination), without the need for a post-CIGS-deposition treatment in a gaseous Se source or a cyanide-based bath etch. Short-duration low-temperature (T<200 °C) oxygen treatment of completed devices is shown to have a positive impact on the performance of initially underperforming cells, thereby enabling better performance in devices prepared at temperatures below 500 °C.

1. Introduction

Low-cost processing techniques for photovoltaic (PV) device fabrication—especially for the active absorber layer—are critically needed to enable PV technology to become cost competitive with conventional electricity generation [1]. $Cu_{1-z}In_{1-x}Ga_xSe_{2-y}S_y$ (CIGS) represents one of the leading absorber layer candidates for achieving a cost competitive (on a $/W basis) thin-film technology, primarily because of the demonstrated potential for high power conversion efficiencies (up to ~20%) and for incorporating relatively high levels of device performance into a variety of useful form factors (e.g., building materials and mechanically flexible devices) [2,3]. Despite offering great promise, the complicated nature of this material generally renders the deposition process quite complex and therefore time consuming/costly. Most high-efficiency CIGS PV devices are deposited using multistep vacuum-based deposition processes (e.g., sputtering or evaporation) [4–6]. While reasonably low-cost CIGS solar modules can be produced using the vacuum-based techniques, the high initial capital investment for implementing these processes, coupled with uniformity issues over larger-scale substrates, has triggered a growing interest in developing potentially lower-cost solution-based CIGS deposition approaches [6–15].

Several solution-based approaches have been demonstrated for CIGS deposition, including electrochemical [7–9], spray or spin coating of organometallic precursors [10,11], screen printing of CIGS or component metal pastes [12,13], and printing of nanoparticle-based precursors [14,15]. A number of processing issues arise in these approaches, however, including: 1) removing undesirable film impurities that derive from the selected precursor and solvent (e.g., O, C, Cl), 2) getting rid of the need for a high-temperature post-deposition treatment in a gaseous selenium source (e.g., H_2Se) or in a cyanide-based bath, 3) simplifying or reducing the number of steps required to deposit high quality films, and 4) improving the compositional control and quality of the solution-processed CIGS films so that higher efficiency devices can be achieved. Here we focus on a new hydrazine-based precursor approach for depositing CIGS and related chalcogenide-based absorber layers [16]. Deposition involves dissolving the elements in a hydrazine-based solvent, spin coating the precursor solution into thin-film form, and heat treating the precursor film in an inert atmosphere to yield the targeted CIGS layer [16–19], with no need for high-temperature post-deposition selenization treatment [4] or a cyanide bath etch step [20] to correct phase purity, stoichiometry and grain size. In contrast to our earlier report [16], which focused on initial PV device results for films processed above 500 °C, this report will provide more detailed characterization of the CIGS films and interfaces, as well as demonstrate how low-temperature treatment in an oxygen atmosphere can improve the performance of the solution-deposited CIGS devices with processing temperatures constrained to T<500 °C.

2. Experimental details

All CIGS film processing was performed in a nitrogen-filled glove box with water and O_2 levels maintained below 1 ppm. Note that hydrazine is highly toxic and should be handled using appropriate protective equipment to prevent contact with either the vapors or liquid.

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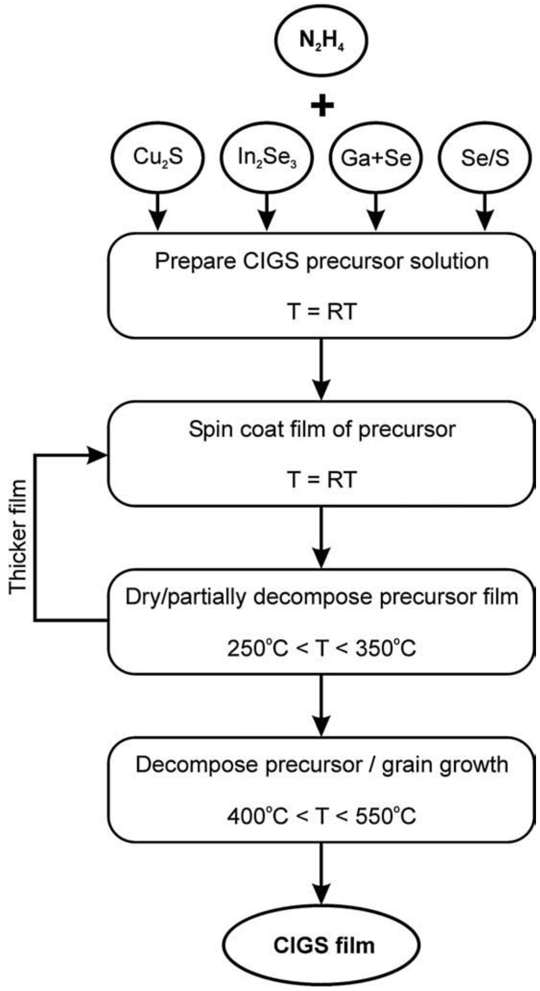

Fig. 1. Schematic flow diagram for the hydrazine-based CIGS deposition process.

2.1. Thin-film formation

CIGS ($Cu_{1-z}In_{1-x}Ga_xSe_{2-y}S_y$) precursor solutions were prepared by dissolving the components (i.e., Cu_2S, In_2Se_3, Ga, S, Se) in hydrazine at room temperature, as described in more detail in [16]. Extra Se was generally included in the solution to improve film morphology and to control the S:Se ratio in the resulting film. CIGS films were spin coated onto molybdenum-coated 2.5 cm×2.5 cm soda lime glass substrates (0.1 cm thickness) using the precursor solutions. The films were immediately dried and partially decomposed for 5 min at 290 °C on a preheated hot plate, followed by a final heat treatment at a selected temperature of between 400 and 500 °C. When thick (μm-scaled) films were desired for device structures, sequential layers were deposited using the same solution for each layer (typical film thickness per deposition layer is ~100 nm) [16].

2.2. Device fabrication

The device structure was formed on Mo-coated (~700-nm-thick layer) soda lime glass employing a ~1.3-μm-thick CIGS absorber layer, deposited as described above using 12 deposition cycles and a final heat treatment at 490 °C for 30 min. The device was completed with ~50 nm of chemical bath deposited CdS, 70 nm of sputtered intrinsic ZnO, followed by 200 nm of sputtered ITO (indium tin oxide). The sheet resistance of the ITO layer (on a glass slide without the other layers) was 50–60 Ω/sq, as measured using a 4-point probe method, and the transparency in the visible spectral range was >80%. Finally, a patterned Ni (50 nm)/Al (2 μm) grid was deposited on the top of the device to facilitate collecting the photo-generated carriers. Each device (0.45 cm^2 total area) was separated from neighboring devices (four per substrate) by mechanical scribing. Selected completed devices were further processed by annealing in a tube furnace at 180 °C under flowing O_2 for between 2 and 20 min to examine the effect of this treatment on device performance.

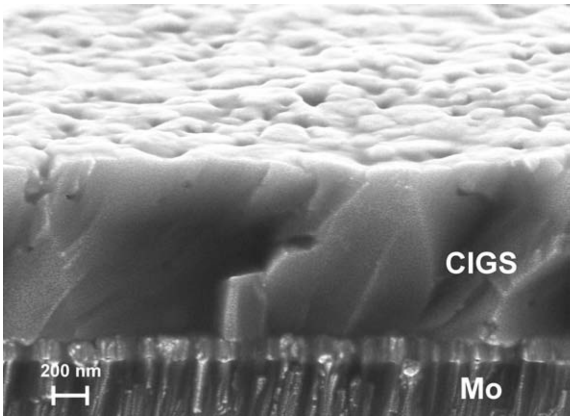

Fig. 2. Cross-sectional SEM image of a CIGS film, processed using 8 deposition cycles and a final 45 min heat treatment at 450 °C. Nominal film composition, as measured using RBS and PIXE, is $CuIn_{0.7}Ga_{0.3}Se_{1.9}S_{0.2}$. The experimental uncertainty in stoichiometry for each element is ~0.05.

2.3. Characterization

For all device depositions, corresponding CIGS films deposited on oxidized silicon using the same spin-coating solution and deposition conditions were analyzed by a combination of RBS (Rutherford Backscattering Spectrometry) and PIXE (Particle Induced X-ray Emission) to verify that the targeted composition was obtained. RBS was performed using an NEC 3UH Pelletron, with a beam current of 20 nA at 2.3 MeV, while PIXE was performed using the same machine with 1.1 MeV protons. The PV devices were electrically tested using a Hewlett-Packard 4145B semiconductor analyzer under ambient temperature/atmosphere conditions. Simulated sunlight was applied using a 300 W (Xe lamp) Oriel Solar Simulator with AM1.5 filter. The light source was calibrated to 100 mW cm^{-2} using a NIST-calibrated Eppley thermopile, as well as an Oriel reference solar cell (NREL calibrated).

3. Results and discussion

3.1. Hydrazine-based deposition process

The first step of the hydrazine-based deposition process (shown schematically in Fig. 1) consists of dissolving each component metal

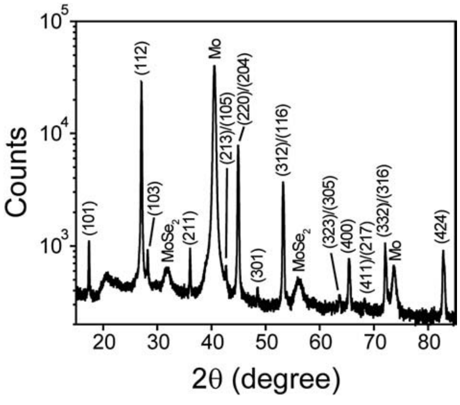

Fig. 3. Powder X-ray (Cu Kα radiation) diffraction from the solution-deposited CIGS film shown in Fig. 2, with reflection indices indicated for the CIGS phase.