Chalcopyrite thin films and solar cells prepared by using selenoamide as a selenium source

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ABSTRACT

$CuInSe_2$ (CIS) and $Cu(In,Ga)Se_2$ (CIGS) thin films were prepared by selenizing stacked Cu–In and In–CuGa metal layers, respectively, with selenoamide in a tube furnace at 400 °C at atmospheric pressure for solar cell fabrication. Chalcogen amides can allow safe transportation and handling of chalcogen sources that can produce chalcogen hydrides at reasonably low temperature. Selenoamide used in this study is stable at room temperature and decomposes into H_2Se below 150 °C. Towards the bottom of the CIS thin films, In segregation was observed particularly during selenization and it was concluded to be due to diffusion of released liquid In towards the bottom of the films and upward diffusion of Cu driven by $Cu_{2-x}Se$ formation on the surface during the process. Homogenizing In in CIS thin films was realized by carrying out post-selenization annealing without the presence of Se at 500 °C for various time periods. On the other hand, Ga accumulated to the bottom of the CIGS thin films upon selenization creating a bandgap profile, which benefits collection of the minority carriers. The post-selenization annealing applied to CIGS thin films favored further intermixing between In and Ga while some degree of the bandgap profile was preserved. Solar cells fabricated with a soda–lime glass/Mo/CIS/CdS/ZnO/ZnO:Ga/Al structure exhibited power conversion efficiencies up to 1.6% without any further optimization.

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1. Introduction

Chalcopyrite $Cu(In,Ga)(Se,S)_2$ material system has been extensively investigated for solar cell applications since its parent material $CuInSe_2$ (CIS) was first synthesized in 1953 [1,2]. Their adjustable direct bandgap and high absorption coefficient make the chalcopyrites ideal absorber materials for thin film solar cells [2,3], and power conversion efficiencies of ~15% and ~20% have been achieved for thin film CIS [4] and $Cu(In,Ga)Se_2$ (CIGS) [5,6] solar cells in the laboratory, respectively. Although up to 14% power conversion efficiencies have been demonstrated with non-vacuum processed CIGS absorbers [7], higher efficiencies have been obtained by using vacuum-based thin film deposition methods. Typical vacuum-based processes are performed by either co-evaporation of the constituent elements in the vacuum chamber [6,8] or by selenizing predeposited metal layers at a temperature up to 600 °C [9–16]. For the selenization process, Se can be provided either as a layer deposited on top of the metal layers [9,10] or as a gas-phase precursor such as a vapor of elemental Se [11,12], H_2Se gas [13,14], and a vapor of diethylselenide [15,16]. When H_2Se is used, the endothermic dissociation of H_2Se results in H_2 and polymeric Se_x species, and both H_2Se and Se_x can react with the predeposited metal layers to form chalcopyrite compound [17]. Selenization by H_2Se has the advantage of reducing the consumption of Se compared to the amount of Se needed during a co-evaporation process [18] and removing the excess oxygen by hydrogen during chalcopyrite growth providing an option for an atmospheric pressure process [2,19]. However, high toxicity and the air reactivity of H_2Se create issues in its mass production, transport and handling [2,15,20]. As a safer alternative to direct use of H_2Se, selenoamide ($RC(=Se)NR_2$) can be synthesized and used as a Se-containing precursor which can liberate H_2Se upon its thermal decomposition that only occurs during the selenization process. Selenoamide is a solid material at room temperature (RT) and expected to be safer than H_2Se under typical handling and storage conditions. A family of selenoamides has been used as precursors for the synthesis of Se-containing heterocyclic compounds which draw attention due to their bioactivity and pharmacological activity. Reaction of nitrile with a selenating reagent, such as H_2Se or NaSeH, is one of the methods commonly used to synthesize selenoamides [21–23]. In a similar context to the selenoamide, chalcogen amides, in general, can be used in various

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thin film chalcogenization processes. For example, H_2S used for sulfurization reaction and for bandgap grading of the already selenized absorber is a hazardous gas with similar handling issues as H_2Se [2], and the authors have sulfurized stacked Cu–In metal thin films into CuInS$_2$ thin films using thioacetamide as an alternative to H_2S [24]. Although telluroamide is known to be relatively instable in air and hence rare [25], it is an intriguing thought to utilize the full series of chalcogen amides including thio-, seleno-, and telluroamide in synthesizing chalcopyrite compounds with different bandgaps for fabricating multijunction devices.

Phenylselenocarboxamide synthesized in this study decomposes below 150 °C liberating H_2Se (Fig. 1) according to thermogravimetric analysis (not shown). It was used to selenize stacked Cu–In and In–CuGa metal thin films into CIS and CIGS thin films, respectively, in an atmospheric pressure tube furnace at 400 °C. Vertical compositional inhomogeneity was observed in both CIS and CIGS thin films, and the effect of post-selenization annealing on In and Ga re-distribution, respectively, in CIS and CIGS thin films was investigated. Homogenous In distribution and larger grain size in CIS thin films, and improved intermixing between In and Ga in CIGS thin films were obtained by the post-selenization annealing at 500 °C. Finally, working CIS solar cells were fabricated with CIS absorbers prepared by using phenylselenocarboxamide.

2. Experimental details

2.1. Selenoamide preparation

Phenylselenocarboxamide was synthesized by a reaction between arylnitriles and NaSeH according to a previously published study [22]. Phenylselenocarboxamide at the end of its synthesis appeared as a yellow color solid compound at RT and it was stored under vacuum until its use for the selenization process. Standard laboratory protective clothes, i.e. coat, gloves, and dust mask, were always used for unknown hazards while handling. Although spontaneous oxidation of phenylselenocarboxamide under air was possible and can be recognized by its color change from yellow to brown, the oxidation rate seemed very slow at RT and its handling before the selenization process did not require an inert atmosphere. The full chemical analysis on its oxidation process is still necessary, if the extensive use of phenylselenocarboxamide is intended, and the authors recommend handling the precursor under a fume hood.

2.2. Cu–In bilayer deposition

First, 0.8–0.9 μm thick Mo back contact layer was deposited on clean 1″ × 1″ soda–lime glass (SLG) (microscope slide from Fisher) substrates by a home-built RF sputtering system. Base pressure was 1.6×10^{-3} Pa and working pressure was maintained at ~1.3 Pa during Mo deposition. An NRC thermal evaporator was used for the Cu and In sequential deposition to prepare 1.4–1.5 μm thick Cu–In bilayers with a target Cu/In ratio of 0.9 on SLG/Mo substrates. Cu and In (both 4N pellets from Kurt J. Lesker) were evaporated from tungsten boats (Kurt J. Lesker) at a rate of 1–2 Å/s which was controlled by a quartz crystal monitor, and the base pressure was 6.7×10^{-4} Pa before the evaporation was started. Depositions were made without intentional substrate heating.
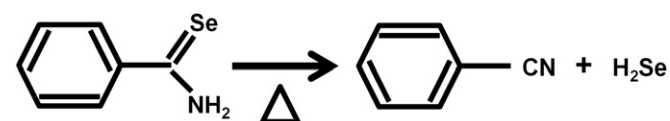

Fig. 1. Thermal decomposition of phenylselenocarboxamide.

2.3. In–CuGa bilayer deposition

Mo, In and CuGa layers were sequentially deposited on 1″ × 1″ SLG substrates by a sputtering system (DMS CO., Republic of Korea) without breaking the vacuum. The base pressure was $\sim 1.3 \times 10^{-5}$ Pa and the working pressure was maintained at ~1.3 Pa during the deposition of all layers. Thickness of Mo layer and In–CuGa bilayer was 0.8–0.9 μm each. A CuGa alloy target with Cu/Ga ratio of 3.6 was used for CuGa layer deposition. Targeted Cu/III and Ga/III ratios of the bilayer were ~1 and ~0.28, respectively, because optimum composition of CIGS absorbers yielding high efficiency solar cells has been Cu-poor with Ga/III ratio of ~0.3 so far [5,6,8,26].

2.4. Selenization process

The bilayers were selenized in a quartz tube furnace which comprised the substrate zone (SubsZ) and the selenium zone (SeZ) heated by a coil furnace (Zircar Ceramics, Inc.) and a heating tape, respectively (Fig. 2). After the bilayer was placed into the tube furnace, ~0.3 g phenylselenocarboxamide was weighed under ambient conditions and placed into the SeZ in an alumina crucible. Flange of the tube furnace was then placed and it was purged with ultra-high purity Ar flowing at 300 sccm for at least 15 min, before the furnace temperature was raised. Temperature of the SubsZ and the SeZ was controlled independently, and while the SubsZ temperature was measured at the middle of the coil furnace where the bilayer was located, the SeZ temperature was measured at the front of the SeZ which is the closest side of the SeZ to the SubsZ. Because the SeZ temperature was slightly affected when the SubsZ was heated, distance between the two zones was maintained such that the temperature of the SeZ stayed under the decomposition temperature of phenylselenocarboxamide before the selenization step was started by raising the SeZ temperature. Ar was kept flowing at the same rate of 300 sccm throughout the process including the substrate cooling period. The tube furnace was placed under a fume hood and its outlet was connected to, first, a cold trap and then to two scrubbers containing an aqueous solution of 3 M NaOH.

Selenization process (Fig. 3) was started with an isothermal pre-selenization annealing (PA) at 400 °C for 30 min (ramping rate: 20–30 °C/min) to homogenize the bilayer. At the end of the PA step, temperature of the SeZ usually reached 65–70 °C without intentional heating. Once the PA was complete, the temperature of the SeZ was raised up to ~145 °C (ramping rate: ~10 °C/min) supplying H_2Se to the bilayer in the SubsZ at 400 °C for 30 min (PSe). Since there was a temperature gradient along the SeZ due to the unintentional heating from the SubsZ, the temperature of the SeZ was increased by 10 °C in every 6–7 min up to 175 °C during the PSe to utilize the entire selenium precursor placed in the crucible. The PSe was finally followed by four different processes (P0–P3). In P0, the substrate was naturally cooled down to RT after the PSe. In the other three processes, SubsZ temperature was increased to 500 °C (ramping rate: 10–15 °C/min) right after the PSe for a post-selenization annealing without the supply of Se. Post-selenization annealing was performed for 1 h (P1), 2 h (P2) or 3 h (P3), and then the substrate was naturally cooled down to RT. While CIS thin films were prepared by all processes shown in Fig. 3, only P0 and P3 processes were used for CIGS thin film preparation.

2.5. Solar cell fabrication

An 80 nm CdS buffer layer and a 50 nm ZnO/500 nm ZnO:Ga window layer were deposited on CIS and CIGS absorbers by chemical bath deposition and RF sputtering (SNTEK), respectively. Front contact was 1 μm-thick Al deposited by electron beam evaporation (MEP5000, SNTEK). Device isolation was done by mechanical scribing. Resulting structure of the solar cells was SLG/Mo/(CIS or CIGS)/CdS/ZnO/ZnO:Ga/Al, and the output characteristics were characterized under AM1.5 using a solar simulator (K3000LAB, McScience) at RT.