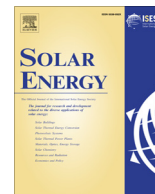




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Selective thin film synthesis of copper-antimony-sulfide using hybrid ink

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ABSTRACT

In the copper-antimony-sulfide (Cu-Sb-S) system, four major phases (CuSbS₂, Cu₃SbS₃, Cu₃SbS₄, Cu₁₂Sb₄S₁₃) exist and are known to have good potentials as absorbers. To form thin films of Cu-Sb-S using a non-vacuum hybrid ink, Cu and Sb precursors were coated and sulfurized with a rapid thermal annealing (RTA) process. According to the ratio of Cu and Sb (Cu/Sb), different Cu-Sb-S thin films (CuSbS₂ vs. Cu₃SbS₃, Cu₃SbS₄, Cu₁₂Sb₄S₁₃) were easily obtained and confirmed by X-ray diffraction (XRD). However, although the Cu/Sb ratio of the hybrid ink was the same, different phases (Cu₃SbS₃, Cu₃SbS₄, Cu₁₂Sb₄S₁₃) were observed depending on the reaction temperature, time, and pressure. It was shown that the reaction temperature, time, and pressure were also important factors for obtaining thin films. The sulfurized conditions to achieve thin films with a target phase were compared against different Cu/Sb ratios, reaction temperatures, reaction times, and chamber pressures.

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1. Introduction

Copper-based semiconducting chalcogenides have been investigated to address the needs in a wide range of research areas, such as capacitors (Ramasamy et al., 2015) and solar cells (Jackson et al., 2011). In particular, in the photovoltaic research area, Cu(In,Ga)Se₂ (CIGS) and Cu₂ZnSnSe₄ (CZTS) compounds are well-known because CIGS absorbers have reported efficiencies of over 21% (Clean Technica, 2014) using vacuum-based processes (co-evaporation). However, due to the high production costs and toxic material waste from vacuum-based processes, CIGS and CZTS absorbers using non-vacuum processes have also been studied despite their low conversion efficiencies. This environmental-friendly research approach using low-cost and easily accessible processes has accelerated the search for potential photovoltaic absorbers meeting specific requirements.

In recent years, ternary copper-antimony-sulfide (Cu-Sb-S) materials have received significant attention in solar cell research as alternative absorbers due to their low-toxicity and earth-abundant elements (Tablero, 2014; Yu et al., 2013; Ramasamy et al., 2014) instead of doping Sb to CIGS or SnS (Garskaite et al.,

2012; Ali et al., 2015). Cu-Sb-S compounds consist of four phases, i.e., CuSbS₂ (chalcostibite), Cu₃SbS₃ (skinnerite and wittichenite), Cu₃SbS₄ (famatinitite), and Cu₁₂Sb₄S₁₃ (tetrahedrite), and have high absorption coefficients (Yu et al., 2013), as well as suitable band gaps as absorbers (Yu et al., 2013; Ramasamy et al., 2014).

The band gaps of CuSbS₂, Cu₃SbS₃, Cu₃SbS₄ are known to be 1.38–1.56 eV, 1.60–1.89 eV, 0.46–0.98 eV, respectively (Rodriguez-Lazcano et al., 2005; Yu et al., 2013; Tablero, 2014). On the other hand, the band gap of Cu₁₂Sb₄S₁₃ is unclear because of the multiplicity of cation and anion sites in the structure. Cu₁₂Sb₄S₁₃ can be represented by (Cu⁺)₁₀(Cu²⁺)₂Sb₄S₁₃ with mixed Cu(I)/Cu(II) ions (Ramasamy et al., 2014), differing from other compounds with only the Cu(I) ion. However, this mixed Cu(I)/Cu(II) ion ratio in Cu₁₃Sb₄S₁₂ can be changed; thus, the band gap of Cu₁₂Sb₄S₁₃ is affected due to the variation of the number of valence electrons per unit cell (Jeanloz and Johnson, 1984). According to previously reported papers, the band gap of Cu₁₃Sb₄S₁₂ is 1.6–1.9 eV (Jeanloz and Johnson, 1984; Ramasamy et al., 2014; Tablero, 2014).

In terms of the chemical composition, CuSbS₂ is different from Cu₃SbS₃, Cu₃SbS₄, and Cu₁₂Sb₄S₁₃. Using CuSbS₂ as an absorber has been actively studied (Septina et al., 2014; Yang et al., 2014; Choi et al., 2015), and conversion efficiencies have been investigated because it has a relatively optimal band gap and similar cell parameters to the well-known CIGS absorber. Recently, over 3%

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conversion efficiencies have been reported in CuSbS₂ devices created from low-cost and environmental-friendly non-vacuum processes (Banu et al., 2016; Septina et al., 2014). However, most of the research on other Cu-Sb-S systems have only focused on material synthesis and non-performance related characterizations even though their material characters show enough potential to be absorbers.

Until now, nanoparticles of Cu-Sb-S phases have been mainly synthesized as materials for characterization (van Embden et al., 2013; Ikeda et al., 2014; Ramasamy et al., 2014); the thin film fabrication of these materials with a non-vacuum process has rarely been studied. Therefore, the fabrication of Cu-Sb-S thin films using non-vacuum hybrid ink can lead to possible applications in thin film solar cell devices. Previously, we have set up the concept of hybrid ink and showed its ability to form dense thin layers (Cho et al., 2012; Cho et al., 2013; Cho et al., 2014). In the hybrid ink, the chelating agent plays a key role to form a layer. Therefore, the complex formation of a metal precursor and the chelating agent decides whether the ink is a hybrid ink or not, to generate dense layers.

In this work, Cu and Sb precursors were used with a chelating agent to prepare a hybrid ink, and the Cu/Sb ratio was controlled in preparing each Cu-Sb-S phase (CuSbS₂ vs. Cu₃SbS₃, Cu₃SbS₄, Cu₁₂Sb₄S₁₃). After coating, these phases were sulfurized using a rapid thermal annealing (RTA) process with different reaction temperatures, reaction times, and chamber pressures to form thin films of each Cu-Sb-S phase. As a result, each phase was characterized and compared to determine the optimal conditions for thin film formation.

2. Experimental section

2.1. Reagents

For preparing the hybrid ink, copper(I) acetate (Cu(CH₃COO) or Cu(Ac), 99.97%, Aldrich), antimony acetate (Sb(CH₃COO)₃ or Sb(Ac)₃, 99.99%, Aldrich), methanol (CH₃OH or MeOH, 99.6%, Junsei), and monoethanolamine (NH₂CH₂CH₂OH, MEA, 99.0%, Aldrich) were used as the analytical reagents. All chemicals were used as received without further purification and stored in a nitrogen-filled glove box to prevent air or humidity from inducing degradation. The sulfur (S) powder (99.98%) for sulfurization was purchased from Aldrich. The Mo-coated soda lime glass was fabricated using a lab-made DC sputtering system with a thickness of approximately 1 μm.

2.2. Preparation of hybrid ink

The hybrid ink was prepared with Cu(Ac), Sb(Ac)₃, MeOH, and MEA as a chelating agent and a binder. In a glove box, Cu(Ac) and Sb(Ac)₃ were each mixed with MEA and MeOH in separate 10 ml vials and closed lids. In this case, the Cu(Ac) to Sb(Ac)₃ molar ratio was approximately 1:1 or 3:1 to control the Cu/Sb ratio, and each precursor to MEA molar ratio was 1:6 due to an adequate coordination between MEA and the precursors. Both precursor to MeOH ratio was 1:6 by weight; however, to adjust the viscosity of the precursor ink for the spin-coating step, the quantity of MeOH was controlled by using an individual coating procedure. Then, both vials were taken out of the glove box, and the contents were dissolved thoroughly by ultra-sonication without opening the lids. After dissolving, both vials were placed in the glove box again and mixed together. All preparation processes were performed at room temperature in the glove box except for the ultra-sonication step.

2.3. Thin film deposition and sulfurization

Precursor films were deposited on a 1 μm-thick Mo-coated soda lime glass using a spin-coater (ACE-200, Dong Ah Tech., Korea) at 2000 rpm for 20 sec. The samples were then dried at 80 °C, 120 °C, and 200 °C for 5 min in air on a hot plate to evaporate the MeOH and MEA. This process was repeated four times to obtain the desired thickness. The RTA sulfurization was performed at various temperatures and times with 0.2–0.5 g of S powder under different conditions. The samples and the S powder were placed in a graphite box which was placed in the chamber. The chamber was initially evacuated to a low vacuum pressure (1×10^{-3} torr) with a simple rotary pump and filled up with N₂ gas. Then, it was evacuated again for at least 10 min. Before starting the reaction, the chamber was filled with N₂ gas until the pressure gauge showed 1 atm or 1.68 atm (1 atm + 10 psi) using a check valve which was connected to the chamber. The typical time for reaching the target temperature of the chamber (450–520 °C) was 5 min using a halogen heater, and reaction times were 3–30 min, depending on the reaction condition. During sulfurization, S vapor from the S powder was contained in the closed chamber and pressurized the reaction to maintain a sufficient S atmosphere. After the reaction, the S vapor was removed at approximately 200 °C by evacuating using a rotary pump connected to the scrubber.

2.4. Solar cell fabrication

Solar cells were fabricated according to the conventional Mo/CIS/CdS/i-ZnO/n-ZnO/Al structure. A 60 nm-thick CdS buffer layer was deposited on the fabricated thin films using a chemical bath deposition (CBD) method, and i-ZnO(50 nm)/Al-doped n-ZnO (500 nm) was deposited by radio-frequency (rf) magnetron sputtering on the CdS layer. An Al grid with a thickness of 500 nm was deposited as a current collector using thermal evaporation. The active area of the completed cells was 0.4848 cm².

2.5. Characterization and analysis

The morphologies and compositions of the sulfurized films were analyzed using high-resolution scanning electron microscopy at 10 kV (HRSEM, XL30SFEG Phillips Co., Holland) and energy dispersive spectroscopy (EDS, EDAX Genesis apex; acceleration voltage of 30 kV and collection time of 100 s). For measuring the smoothness of the surface, atomic force microscopy (AFM, Park System XE-100, 0.6 Hz scan rate) was also performed. The optical transmittance and reflectance were measured using a UV spectrophotometer (UV-Vis, Shimadzu Japan, UV-2600). The data were recorded in the wavelength (λ) range of 300–1400 nm with an uncoated soda lime glass as a reference.

The crystalline structure of the films was identified using X-ray diffraction (XRD, Rigaku Japan, D/MAX-2500) with a CuKα line. Device performance, i.e., the conversion efficiency and the EQE (external quantum efficiency), was characterized using a class AAA solar simulator (WXS-155S-L2, WACOM, Japan) and an IPCE (Incident Photon Conversion Efficiency) measurement unit (PV measurement, Inc., USA), respectively.

3. Results and discussion

According to our previous work (Cho et al., 2012; Cho et al., 2013; Cho et al., 2014), the metal-chelate complex in the ink was what made the hybrid ink unique because it can control the reaction rate to make dense thin layers. To be used as a chelating agent, it should be able to not only hold precursors but should also be

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