Effect of H₂S Concentration and Sulfurization Temperature on the Properties of Cu₂ZnSnS₄ Thin Films

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Abstract This study reports the effects of H₂S gas concentration on the properties of Cu₂ZnSnS₄(CZTS) thin films. Specifically, sulfurization process with low H₂S concentrations of 0.05 % and 0.1 %, along with 5 % H₂S gas, was studied. CZTS films were directly synthesized on Mo/Si substrates by chemical bath deposition method using copper sulfate, zinc sulfate heptahydrate, tin chloride dihydrate, and sodium thiosulfate pentahydrate. Smooth CZTS films were grown on substrates at optimized chemical bath deposition condition. The CZTS films sulfurized at low H₂S concentrations of 0.05 % and 0.1 % showed very rough and porous film morphology, whereas the film sulfurized at 5 % H₂S yielded a very smooth and dense film morphology. The CZTS films were fully crystallized in kesterite crystal form when they were sulfurized at 500 °C for 1 h. The kesterite CZTS film showed a reasonably good room-temperature photoluminescence spectrum that peaked in a range of 1.4 eV to 1.5 eV, consistent with the optimal bandgap for CZTS solar cell applications.

Key words Cu₂ZnSnS₄, CZTS, CBD, sulfurization.

1. Introduction

Cu₂ZnSnS₄(CZTS), p-type semiconductor, has been widely researched for a potential absorber material for thin film solar cells because of its inexpensive and earth abundant elements. CZTS has large absorption coefficient (−10⁴ cm⁻¹) with near-optimum band gap of about 1.45 eV.¹ Several vacuum based methods, such as electron beam evaporation,² sputtering deposition,³ and pulsed laser deposition,⁴ have been utilized to synthesize CZTS thin films. However, recently wet chemical approaches, such as chemical bath deposition(CBD),⁵ spray pyrolysis,⁶ electro deposition,⁷ and sol-gel deposition methods,⁸ have emerged well because of their low cost and mass-production capability. The highest conversion efficiency for CZTS solar cell prepared by solution approach is 12.6 %.⁹

CZTS properties, including structural, electrical, and optical properties, should be improved to achieve higher conversion efficiency. These properties are majorly dependent on the synthesis techniques and post-sulfurization step. The sulfur source for the sulfurization process can be either H₂S gas or elemental sulfur (S) powders.¹¹

Recent sulfurization studies have mostly focused on optimization of sulfurization parameters, such as temperature, time, and pressure.¹¹ However, limited information is available on the effect of H₂S gas concentration on CZTS properties. Recently, Maeda et al.¹³ reported that sulfurized CZTS with 3 % H₂S had larger grains and higher solar-cell conversion efficiency than those with higher H₂S gas concentration(5 %, 10 %, and 20 %). Moreover, H₂S concentration must be minimized during sulfurization process for safety and precaution. The present paper reports on the effect of H₂S gas concentration on properties of sulfurized CZTS films synthesized by CBD. In particular, the sulfurization process at low H₂S gas concentrations of 0.05 and 0.1 % H₂S, along with typically used H₂S gas concentration of 5 %, was systematically studied. In addition, the sulfurization temperature and time are optimized to achieve fully kesterite-crystallized CZTS films.

2. Experimentals

CZTS thin films were grown on Mo/Si substrates at 90 °C through the chemical bath method. All reaction
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chemicals, such as copper sulfate (CuSO$_4$), zinc sulfate heptahydrate (ZnSO$_4$·7H$_2$O), tin chloride dihydrate (SnCl$_2$·2H$_2$O), sodium thiosulfate pentahydrate (Na$_2$S$_2$O$_5$·5H$_2$O), 99 % triethanol amine (TEA), and 28 % NH$_4$OH, were of pure analytical grade and purchased from Sigma-Aldrich. In this procedure, a chemical bath containing copper, zinc, and tin metal ion precursors was mixed well with complexing agents TEA and NH$_3$ for 20 min. Sodium thiosulfate was then added as precipitating agent at room temperature, while pH was maintained at approximately 10.5. Bath composition was maintained at molar concentrations of 2:1:1:5 ratio for Cu$^{2+}$, Zn$^{2+}$, Sn$^{2+}$, and S$^{2-}$. Pre-cleaned substrates were vertically inserted into the reaction mixture; after completion of deposition, films were cleaned with double-distilled water for 5 min and dried with N$_2$ gas. The as-synthesized CZTS thin films were sulfurized in 0.05 %, 0.1 %, and 5 % H$_2$S concentrations of gas mixture H$_2$S and N$_2$ at 270°C to 500°C for 30 min to 2 h. The resulting films were characterized using scanning electron microscopy (SEM: Hitachi S-4800), X-ray diffraction (XRD; Rigaku Ru200B), micro-Raman spectroscopy (Uninanotech UR1207J), room-temperature photoluminescence (PL) spectroscopy (532 nm DPSS laser), and UV-visible spectrophotometry (Scinco S-3100).

3. Results and Discussion

Fig. 1 shows the SEM images of the microstructure evolution of the as-synthesized CZTS films annealed under N$_2$ + H$_2$S (0.05 %, 0.1 %, and 5 %) atmosphere in a tubular furnace at 500°C for 2 h. The particle size in the as-synthesized granular film was smaller than 200 nm (Fig. 1(a)). As the film was sulfurized at 0.05 % and 0.1 % of H$_2$S concentrations, the films were porous with non-uniform grains (Figs. 1(b) and 1(c)). When H$_2$S concentration was increased to 5 %, the surface became significantly smooth and uniform with increased grain sizes (> 300 nm) because of adequate amount of sulfur (Fig. 1(d)). At a low H$_2$S concentration, kesterite-crystallized grains can be formed locally in the early stage of annealing due to insufficient supply of sulfur ions. Such early-formed grains can be grown predominantly, resulting in non-uniform rough morphology with big size grains. By contrast, at 5 % H$_2$S concentration, kesterite-crystallized grains can be formed uniformly on overall film and be developed to uniform grains.

Fig. 2 shows SEM images of the microstructure evolution of CZTS films sulfurized under N$_2$ + H$_2$S (5 %) atmosphere at temperatures that range from 270°C to 500°C for 1 h. Grain size was increased with uniform smooth film with the increase in temperature from 270°C to 420°C (Figs. 2(a) and 2(b)). Upon sulfurization at 500°C for 30 min, uniform fine grains with compact morphology were formed (Fig. 2(c)). When sulfurized time was increased to 1 h at 500°C, the CZTS grain size increased and became well-faceted with densely packed granular film morphology (Fig. 2(d)).

Fig. 3 shows XRD patterns of as-synthesized and
sulfurized samples at various H$_2$S concentrations from 0.05 % to 5 % annealed at 500 °C for 2 h. A major peak at 28.5° was observed for all sulfurized CZTS films, which is related to the (112) diffraction plane of CZTS kesterite phase. However, (200) peak was barely observed at the sample sulfurized at 0.05 % H$_2$S. With increasing H$_2$S concentration, the intensity of (200) peak was increased. This suggests that 0.05 % H$_2$S concentration is too low to develop CZTS phase fully. Finally, at 5 % H$_2$S, films showed a polycrystalline kesterite CZTS crystal structure with sharp major reflections along the (112), (220), and (312) planes(JCPDS #00-026-0575). No secondary phases were observed in the sulfurized CZTS film. This finding was confirmed by Raman spectra (Fig. 4), wherein, characteristic CZTS peaks at 287, 339, and 368 cm$^{-1}$ were obtained.$^{[14]}$ The CZTS film sulfurized at 0.1 % showed a main peak at 331 cm$^{-1}$, indicating cation
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...sub-lattice disordering such as non-stoichiometric Cu-poor and Zn-rich CZTS. Meanwhile, the Mo XRD peaks of sulfurized samples were slightly shifted with respect to that of as-synthesized sample due to interdiffusion of Mo and CZTS.

Fig. 5 shows XRD patterns of sulfurized CZTS thin films at various temperatures from 270 $^\circ$C to 500 $^\circ$C under 5% H$_2$S concentration.

...undesired phases, which is in good agreement with (112), (220) and (312) planes (JCPDS #00-026-0575). This finding was confirmed by Raman spectra (Fig. 6), wherein, characteristic CZTS peaks at 287, 338, and 368 cm$^{-1}$ were obtained.

Fig. 7 shows room-temperature PL spectra of sulfurized CZTS films annealed at 500 $^\circ$C for 1 h under 0.1% and 5% H$_2$S concentrations. Both samples yielded considerable PL intensity even at room temperature. Moreover, the PL peaks were around 1.45 eV, which is consistent with the bandgap energy of CZTS. This suggests that the PL peaks are mainly attributed to band-to-band transitions, implying high quality CZTS formation.

4. Conclusion

The effects of H$_2$S concentration (0.05%, 0.1%, and 5%) on the structural and optical properties of CZTS thin films deposited by CBD method were systematically studied. The 5% H$_2$S concentration was found to be optimal for sulfurization of chemical bath deposited CZTS films. CZTS films sulfurized at lower H$_2$S concentrations of 0.05% and 0.1% showed inhomogeneous and rough surface, whereas those sulfurized at 5% H$_2$S yielded very smooth and uniform morphology. These results can be attributed to uniform formation of kesterite-crystallized grains in the early stage of annealing, significantly affected by optimal H$_2$S gas concentration. The grain size, crystallinity, and smoothness of CZTS films were also enhanced with increasing annealing temperature and time. The CZTS films seemed to become fully crystallized kesterite after sulfurization under 5% H$_2$S gas environment at 500 $^\circ$C for 1 h. Kesterite CZTS films are...
useful for solar cell device fabrication with optimal bandgap of approximately 1.4 eV to 1.5 eV.

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