Characterization of Ag-incorporation Cu_2ZnSnS_4 thin films as phoabsrobers for photovoltaic and photoelectrochemical water reduction

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Abstract: Silver (Ag)-incorporated kesterite Cu_2ZnSnS_4 (ACZTS) thin films were fabricated by a facile spray pyrolysis method. When these films are applied to solar cells and photoelectrochemcal (PEC) water reduction, they exhibited better properties in both systems though a difference in optimum contents of Ag in the films were different. Electrostructural analyses of the thus-obtained films suggested that these films achieved reduction in the amounts of unfavorable copper on zinc antisite defects compared to the bare CZTS film. Moreover, these films improved band alignment at the CdS(buffer)-CZTS interface. These alterations contributed improvements of photovoltaic properties as well as photoelectrochemcal (PEC) functions for water reduction.

Keywords: Cu_2ZnSnS_4 thin films, Ag incorporation, PEC water reduction.

1. Introduction

Cu_2ZnSnS_4 (CZTS) is a promising photoabsorber material for photovoltaic (PV) solar cells as well as a photocathode for PEC water splitting and carbon oxide fixation.[1-4] We have recently demonstrated successful fabrication of CZTS film with sufficient qualities for PV and PEC applications by using a facile spray pyrolysis method.[5-7] In the present study, we investigated impacts of controlled addition of various amounts of Ag to the CZTS thin films on their solar cell[8] and PEC properties in relation to their structural, electrical, and morphological characteristics. The spray pyrolysis method was used for fabrication of these chalcopyrite films due to its low cost and easiness of compositional controls.

2. Experimental

Four precursor films with different amounts of Ag were fabricated by varying the molar ratio of Ag/(Cu + Zn + Sn) in aqueous precursor solutions (Ag/(Cu + Zn + Sn) = 0, 0.02, 0.05, 0.1). Sources of metallic elements were copper nitrate ($Cu(NO_3)_2$), zinc nitrate ($Zn(NO_3)_2$), tin methanesulfonate ($Sn(CH_3SO_3)_2$), and silver nitrate ($AgNO_3$); thiourea ($SC(NH_2)_2$) was used as the sulfur source. Deposition was carried out by spraying aqueous solutions containing these sources with pH adjusted to 1.5 on Mo-coated glass substrates heated at 380 °C. The thus-obtained films were sulfurized in the presence of 5 mg elemental sulfur powder in an evacuated Pyrex ampoule at 600 °C for 10 min. To complete the solar cell device, a CdS buffer layer was deposited on CZTS and ACZTS films by chemical bath deposition (CBD).15,16 Then, intrinsic ZnO (*i*ZnO) and indium tin oxide (ITO) layers were sequentially deposited by radio frequency magnetron sputtering on CdS-covered CZTS and ACZTS films. Finally, an Al top contact was deposited by thermal evaporation. For the PEC water splitting, CZTS and ACZTS by a CdS and In_2S_3 double layer (In_2S_3/CdS) by CBD. Then Pt as a hydrogen evolution promoter was photoelectrochemically deposited on the top of the In_2S_3/CdS-covered CZTS and ACZTS films. The PEC H_2 generation from the Pt-CdS/CIS and Pt-CdS/CIGS was examined from 0.1 M Na_2SO_4 (pH = 9) as an electrolyte by using the three-electrode system with a Pt wire as a counter electrode and an Ag/AgCl as a reference electrode.

3. Results and discussion

Crystallographic analyses indicated successful incorporation of various amounts of Ag up to a Ag/(Ag + Cu) ratio of ca. 0.1 into the crystal lattice of CZTS in a homogeneous manner without formation of other impurity compounds. From the results of morphological investigations, ACZTS films had larger crystal grains than the CZTS film. Moreover, the sample with a relatively low Ag content (Ag/(Ag + Cu) of ca. 0.02) had a compact morphology without appreciable voids and pinholes. However, an increase in the Ag content in the CZTS film (Ag/(Ag + Cu) ca. 0.10) induced the formation of a large number of pinholes. As can be expected from these morphological properties, the best sunlight conversion efficiency (η) was obtained by the solar cell based on the film with Ag/(Ag + Cu) of ca. 0.02 (Table 1). On the other hand, the properties of PEC water reduction showed somewhat different trend: relatively high rate of H_2 evolution through the PEC water reduction (R_{H2}) was achieved on the photocathode based on ACZTS film with relatively higher Ag content (i.e., Ag/(Ag + Cu) of ca. 0.05). Since the photocathode for PEC water reduction does not require the front contact, the system would be relatively insensitive against shunts when compared to the photovoltaic system. In addition, the TRPL measurements of CZTS and ACZTS films indicated that lifetimes of photoexcited carriers in these films tended to increase with increase in the Ag content. This should be one of the important reasons of better PEC performances observed on the ACZTS films with relatively high Ag contents.

Tabel 1. Solar cell and PEC H_2 evolution properties of CZTS and ACZTS

	CZTS	ACZTS (0.02)	ACZTS (0.05)	ACZTS (0.1)
η (solar cell) /%	5.6	**7.7**	6.8	5.8
R_{H2} (PEC) /μmol h^{-1}	5.9	23.1	**39.0**	13.5

Analyses of the solar cell devices performed by the capacitance-voltage (C-V) measurement suggested that the ACZTS films in the devices achieved reduction in the amounts of unfavorable copper on zinc antisite defects compared to the bare CZTS film. Moreover, band alignments of at the CdS(buffer)—CZTS (or ACZTS) interfaces determined by analyses of core and valence band energy levels by using XP spectra and band gaps by using EQE spectra were confirmed to be improved by the uses of ACZTS films. These electrostructural alterations induced by the Ag-incorporation should also contribute to enhancement of solace cell properties as well as PEC functions for water reduction.

4. Conclusions

We have demonstrated fabrication of Ag-incorporated CZTS thin films applicable for photovoltaics and PEC water reduction. Various analyses suggested that these properties in the present system depend strongly on defect disparities, and band alignments toward the CdS layer. Hence, the strategy for Ag incorporation is promising for further improvements. In addition, we also found that influences of film morphologies (e.g., presence of voids and pinholes) were different between photovoltaics and PEC properties. These results suggest that the optimum structure of the CZTS film is different depending on the applied systems. Based on this idea, further designs and modifications of CZTS films to achieve more better photovoltaic or PEC water reduction performances are now in progress.

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