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Photoelectrochemical performances of the cubic $AgSnSe_2$ thin film electrodes created using the selenization of thermal evaporated Ag-Sn metal precursors

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ABSTRACT

In this study, we prepared the cubic $AgSnSe_2$ thin film photoelectrodes on substrates using the selenization of Ag–Sn metal precursors and examined the influence of silver content in samples on their photoelectrochemical properties in the aqueous solution. With the selenization temperature kept at 410 °C for 1 h in the selenization apparatus, the cubic $AgSnSe_2$ samples can be obtained. The results of phase characterization show that the phase change from the cubic $AgSnSe_2$ to the cubic Ag_8SnSe_6 phase takes place at the selenization temperature between 425 to 440 °C. The optical energy band gaps, carrier concentrations, and mobilities of samples are in the range of 1.24–1.30 eV, 1.75×10^{18}–4.68×10^{19} cm^{-3}, and 43–253 $cm^2/V/s$, respectively. It was found that the sample with the [Ag]/[Ag + Sn] molar ratio of 0.48 had a maximum photo-enhancement current density of 1.26 mA/cm^2 at an external bias of + 1.23 V vs. the reverse hydrogen electrode in the 0.35 M Na_2S + 0.25 M K_2SO_3 aqueous solution. The electrochemical impedance spectra of samples in the aqueous solution containing S^{2-} and SO_3^{2-} ions were also employed to examine the possible reaction mechanisms taking place at the sample surfaces.

1. Introduction

Because of the increase demands for the future global energy requirements, more and more carbon-based fuels have to be converted into the electrical powers for the industrial applications. However, the utilization of carbon-based fuels may result in the global warming effect associated with climate change. The Paris Agreement, which was based on the decrease of the global warming effect caused by the utilization of carbon-based fuels, has been approved in 2015. In order to reach the goal set by Paris Agreement, the developments of the renewable energy technologies such as solar or wind energy is thus necessary. However, the major obstacle for the large-scale applications of these renewable energies is the energy storage system due to the unstable supplement of these renewable energies. Considering the further applications of these renewable energies, it is necessary to develop the suitable energy storage systems that have the abilities to store these unstable renewable energies. Hydrogen gas, which is an energy carrier, has the capacity to store these renewable energies as the chemical form. Industrial steam reforming of the carbon-based organic compounds is the major way to produce the hydrogen gas. In order to decrease the influence of the global warming effect, it is necessary to develop a suitable hydrogen production process without using the steam reforming process [1,2]. In 1972, the photoelectrochemical (PEC) water splitting process using TiO_2 and platinum (Pt) electrodes as the photoelectrode and the counter electrode, respectively, was reported by Fujishima and Honda [3]. The PEC water splitting reported a possible process that can convert the solar energy into the clean energy carriers (ex: hydrogen gas) for the further storage in the chemical form. However, due to the large energy band gap of 3.2 eV for TiO_2, the PEC water splitting performance in an electrolyte using TiO_2 as the photoelectrode was poor. Various new semiconductors with good absorption coefficients in the visible-light region have been reported as the possible photoelectrodes for solar-driven water splitting in order to improve the efficiency of PEC water splitting process [4–10]. Recently, the quaternary I-II-IV-VI semiconductors (I = Cu, Ag, II = Cd, Zn, IV = Sn, VI = S, Se) as the photo-absorbers in the thin film solar cells with the photo-conversion-efficiency of around 12% have been reported [11,12]. Compared with the I-III-VI multi-component semiconductors such as the $Cu(In,Ga)Se_2$, the I-II-IV-VI semiconductors are the earth-abundant materials that may decrease the manufacture costs

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of the thin film solar cells. The quaternary I-II-IV-VI semiconductors are the solid solutions of ternary I-IV-VI (ex. Cu_2SnSe_3) and binary II-VI (ex. ZnSe) semiconductors and their physical properties such as energy band gap or electrical properties can be adjusted by altering the ratios of ternary I-IV-VI and binary II-VI semiconductors. The ternary I-IV-VI semiconductors such as Cu_2SnS_3 [13–15] also have the applications in the solar energy related technology. Many studies about the preparation and applications of Cu-based I-IV-VI semiconductors have been reported [13–15]. Another interesting I-IV-VI semiconductor that may also has the potential for the application of photo-conversion technology is the Ag-based I-IV-VI samples such as Ag_8SnS_6, Ag_8SnSe_6 and $AgSnSe_2$ [16–19]. For the evaluation of PEC response of Ag_8SnS_6 samples in electrolytes, Sasamura et al. [16] prepared Ag_2ZnSnS_4/Ag_6SnS_6 nanoparticles and deposited these nanoparticles onto the substrates using the layer-by-layer deposition [16]. The Ag_2ZnSnS_4/Ag_6SnS_6 photoelectrodes in an electrolyte containing $LiClO_4$ and triethanolamine showed a photo response of around 0.03 mA/cm^2 at an external bias of 0 V vs. Ag/AgCl under light irradiation. Our group prepared the Ag_8SnS_6 photoelectrodes using chemical bath deposition (CBD) [17] and the sulfurization of radio-frequency sputtering Ag-Sn metal alloys [18], respectively. The results showed that the Ag_8SnS_6 photoelectrodes prepared using CBD had a PEC performance of 1.13 mA/cm^2 at an applied voltage of 0 V vs. Ag/AgCl in the $Na_2S + K_2SO_3$ aqueous solution and increased to 2 mA/cm^2 at the same measurement condition using the sulfurizaion of sputtering Ag-Sn metal alloys. We found that the major contribution for the improvement of the PEC performances for Ag_8SnS_6 samples in electrolytes is due to the increase and decrease in the grain size and defects in the samples, respectively. We also prepared the cubic Ag_8SnSe_6 thin films with various [Ag]/[Ag + Sn] molar ratios on substrates. The energy band gap of these samples are in the range of 0.86–1.19 eV [19]. Our previous study reported that the maximum PEC performance of the Ag_8SnSe_6 photoelectrode in aqueous Na_2S (0.35 M) + K_2SO_3 (0.25 M) solution was 1.22 mA/cm^2 at an external bias of 1.23 V vs. reverse hydrogen electrode (*RHE*) [19]. According to the phase diagram of Ag_2Se and $SnSe_2$ [20], there is still one interesting ternary semiconductor ($AgSnSe_2$) that may also have the potential as the photoelectrode in the PEC cell for solar-driven hydrogen production. Cubic $AgSnSe_2$ can be obtained at an annealing temperature in the range of 400–480 °C; it has potential for applications in superconductor, gas sensor and thermoelectric technologies due to natural valence skipping (theoretic ratio of 1: 1 for Sn^{2+}: Sn^{4+} ions in cubic $AgSnSe_2$ sample) [21–23]. Because both two oxidation states for the Sn ions are observed in $AgSnSe_2$ sample, the preparations of the pure $AgSnSe_2$ sample are difficult. Small changes in the composition for sample result in the phase separation taking place in the samples [19,20]. Theoretically, it has low resistivity of around 0.23 mΩ/cm^2 at room temperature [23] and the photo-excited carriers in the $AgSnSe_2$ samples can easily move to the samples surface at a low given voltage in the electrolyte under light irradiation. However, few studies reported the PEC performances of cubic $AgSnSe_2$ photoelectrode in electrolytes under light irradiation. Poor PEC performance of around 0.15 mA/cm^2 at the applied voltage of 1.23 V vs. reverse hydrogen electrode (*RHE*) in the electrolyte containing Na_2S (0.35 M) + K_2SO_3 (0.25 M) under light irradiation was reported in our group [19]. The PEC performances of $AgSnSe_2$ photoelectrode may be improved with suitable adjusting the [Ag]/[Ag + Sn] molar ratio of samples. In this study, we tried to improve the preparation process for the cubic $AgSnSe_2$ samples with adjusting various [Ag]/[Ag + Sn] molar ratios using the selenization of thermally evaporated silver-tin metal precursors and tested their electrochemical properties and PEC activities in the electrolyte in the dark and under light irradiation.

2. Experiments

In this study, we prepared the $AgSnSe_2$ samples on substrates using the selenization of thermal evaporated Ag-Sn metal precursors. Detail deposition process and apparatus are similar with that reported in our previous study [19]. Brief description of experimental procedures is given here. The Ag-Sn bi-layers were directly deposited onto the surface of substrates (soda-lime glass or indium-tin-oxide (ITO) coated-glass substrates, Union-Chemicals Co. Taiwan, sheet resistance of 7 Ω/sq.) using the thermal evaporation. First, the pressure of the camber for thermal evaporation apparatus was evacuated of less than 5×10^{-6} Torr. Then a tin metal layer with the thickness in the range of 441–518 nm was deposited onto the surface of substrates using thermally evaporated tin slug (> 99.99%, Summit Co., Taiwan) in a tungsten boat. A silver metal layer with the thickness of 309–232 nm was then deposited onto the surface of tin layer using thermally evaporated silver slug (> 99.995%, Summit Co., Taiwan) in another tungsten boat. The deposition rate of around 1 nm/s was set by controlling the current applied across the tungsten boat. The thickness of each metal layer was measured using a digital quartz controller (Fil-Tech, SQM-180). Total thickness of Ag-Sn metal precursors was set at 700 nm. After the thermal evaporation, the binary metal layers were annealed at 200 °C for 1 h in the thermal evaporation chamber.

The selenization apparatus was the same with our previous study [19], as shown in Fig. 1. The Se slugs (around 1 g) in an open graphite box was put in the zone 1 as the Se source. The temperature in the zone 1 and 2 was set at 400 °C and 800 °C, respectively, in order to make the formation of Se vapor from the Se slugs in the graphite box (melting point of Se = 220 °C) [19] and avoid the formation of Se clusters in the vapor phase, respectively. The Ag-Sn metal precursors was put in the zone 3 under various selenization parameter tests (temperatures and times) in order to find the optimal selenizaiton parameters for the preparation of the $AgSnSe_2$ samples with high PEC performances. The ultra-pure N_2 gas with a flow rate of 10 SCCM (standard cubic centimeters per minute) was used as the carrier gas and the pressure of 7.6 Torr was kept in the selenization apparatus.

An X-ray diffractometer (D5005, Siemens Co.) was employed to analyze the crystal phases of metal precursors and samples. The X-ray diffraction (XRD) patterns of metal precursors and samples on substrates were recorded in the 2θ range of 20–85°. A scanning electron microscope (Hitachi, S-3000 N) equipped with energy dispersive analysis of X-ray (EDAX, Horiba 7021-H) with the acceleration voltage of 20 kV and working distance of 20 mm was employed to analyze the composition of samples on glass substrates. A surface profile (ET 3000, Surfcofer Co.) with the scanning rate of 50 μm/s and scanning length of 5000 μm was employed to measure the sample thickness. A filed-emission scanning electron microscope (FE-SEM, Hitachi S-4800) with acceleration voltage of 15 kV and an atomic force microscope (AFM, Park system, XE70) with non-contact model were employed to study the surface microstructures and roughness of samples, respectively. The electronic properties of samples on the glass substrate were measured using room-temperature Hall effect measurement (HMS-3000, magnetic flux = 0.57 T). Optical properties of samples such as transmittance and reflectance spectra of samples on glass substrates in the light wavelength range of 500–1200 nm were recorded using an ultraviolet-visible-near-infrared (UV–vis-NIR) spectrophotometer (JASCO V670) with an integrated sphere. Electrochemical properties of samples in an aqueous Na_2S (0.35 M) + K_2SO_3 (0.25 M) solution were analyzed using a tradition cell, as shown in our previous study [24]. The electrochemical impedance spectra (EIS) of samples in the electrolyte were measured using a potentiostat (CHI 600C) equipped with a frequency response analyzer. The EIS data of all samples in the dark with

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