Surface modification of $CuInS_2$ thin films for enhanced energy conversion efficiency

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Currently, improving the energy conversion efficiency of $CuInS_2$ thin films is a challenge. In this study, the energy conversion efficiency of $CuInS_2$ thin films is enhanced by surface modification methods. Either electrodeposition of lead on $CuInS_2$ thin films or deposition of PbS can increase their energy conversion efficiency to some extent, however electrodeposition of lead followed by deposition of PbS can enhance the efficiency dramatically.

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1. Introduction

The photovoltaic devices have attracted considerable attention in the development of clean energy. $CuInS_2$ is a promising candidate for solar device material since it has high absorption coefficient, high electron transfer rate, bandgap that matches the solar spectrum well (about 1.5 eV), uncomplicated manufacturing operation and low cost. However, its energy conversion efficiency is much lower than its theoretical value [1, 2]. So far, its fabrication methods have improved, and low-dimension materials, *e.g.* nanotubes, have been developed; nevertheless, its conversion efficiency has not yet been enhanced significantly [3-6].

The recombination of photo-induced electrons and holes in semiconductors is a major reason for low energy conversion efficiency. In order to inhibit the recombination, strategies to separate charge carriers by means of metal nanoparticles or another semiconductor have been introduced [7-11]. For example, small bandgap semiconductors can serve as sensitisers as they can transfer electrons to large bandgap semiconductors [9-11]. Owing to its small bandgap and favourable energetics, $CuInS_2$ has been used to sensitise wide-gap semiconductors for increasing the response to visible light. However, up to date, there have no reports on metal-loading $CuInS_2$ or sensitised $CuInS_2$ with a smaller bandgap semiconductor for higher energy conversion efficiency.

In this communication, the photoelectrochemical performance of metal-loading and semiconductor-sensitising $CuInS_2$ thin films is studied.

2. Experimental method

$CuInS_2$ thin films were fabricated by electrodeposition of Cu_2In alloy layers followed by sulfurization. A standard three-electrode cell was used; indium tin oxide (ITO) conductive glass ($1\times1.7cm^2$), platinum foil and saturated calomel electrode (SCE) were used as the working electrode, counter electrode and reference electrode, respectively. Before each measurement, the working electrode surface was cleaned by ultrasonic washing in ethanol, acetone, and distilled water in turn for three times. Cu_2In alloy layers on ITO were prepared using an electroplating bath containing 5 mmol L^{-1} $CuCl_2$, 5 mmol L^{-1} $InCl_3$, 0.2 mol L^{-1} triethanolamine and 0.015 mol L^{-1} sodium citrate. The electrodeposition was conducted at -1 V (vs. SCE) for 1800s at 30 ^oC. After electrodeposition, Cu_2In alloy layers were annealed in a tube furnace with sulphur powder for 0.5 h in a N_2 atmosphere at 400 ^oC, thus $CuInS_2$ thin films with chalcopyrite structure were obtained. The thickness of the samples was determined to be about 0.29 μm using an Alpha-Step Instrument (Dektak 150, VEECO).

$CuInS_2$ thin films were modified by electrodeposition of lead, deposition of PbS by successive ionic layer adsorption and reaction (SILAR), and electrodeposition of lead followed by deposition of PbS (the integrated method). In a typical experiment, electrodeposition of lead on $CuInS_2$ thin films was conducted in 0.043 mol L^{-1} $Pb(NO_3)_2$ solution at -170 mV (vs. SCE) for 5 s. PbS particles on $CuInS_2$ thin films were fabricated by four steps: (1) $CuInS_2$ thin films were immersed in 0.426 mol L^{-1} $Pb(NO_3)_2$ solution for 30 s, (2) rinsed in deionized water for 30 s, (3) immersed in 0.3 mol L^{-1} Na_2S solution for 10 s, and (4) rinsed in deionized water for 30 s.

The measurements of the photocurrent density were

carried out in a quartz glass beaker containing 0.1 mol L^{-1} Na_2SO_4 aqueous solution. The unmodified or modified $CuInS_2$ thin film was used as the working electrode, graphite rod and SCE were used as the counter electrode and reference electrode, respectively. The potential was scanned from -100 to -700 mV (vs. SCE) at scanning rate of 50 mV s^{-1}. The xenon lamp was used as the light source, and the calibrated irradiation intensity is 100 mW cm^{-2}.

The UV-Vis-IR spectra of unmodified and modified $CuInS_2$ thins were measured with UV759S spectrophotometer (Shanghai Precision & Scientific Instrument Co. Ltd., P. R. China). The x-ray photoelectron spectra (XPS) were measured by ESCALAB 250 (ThermoFisher Scientific, USA) equipped with x-ray source of twin anode Al Kα 300W. The XPS spectrometer was configured to operate with 200 eV pass energy for survey, and 30 eV for high resolution scans. All binding energies were calibrated to C1s at 284.6 eV.

3. Results and discussion

XPS of $CuInS_2$ thin films modified by electrodeposition and by deposition of PbS are shown in Fig. 1. Pb4f peak locates at 137.7 eV for $CuInS_2$ thin film modified with PbS; in contrast, for the thin film modified by electrodeposition, Pb4f peak is split into two: one is at 137.7 eV, the other is at 137.0 eV, which are corresponding to Pb^{2+} and Pb^0 respectively. Namely, not only metallic lead but also PbS is formed on $CuInS_2$ thin film by electrodeposition. The formation of PbS particles is owing to the existence of sulphur atom on $CuInS_2$ thin film surface.

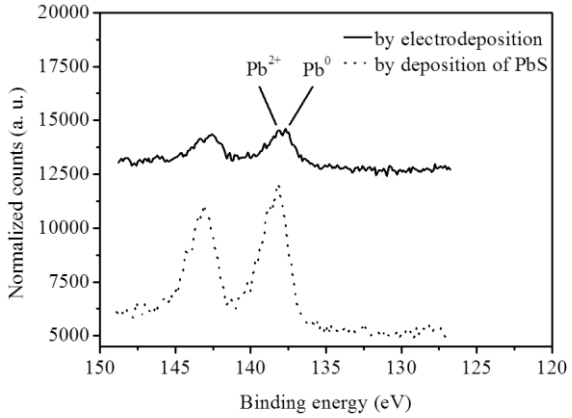

Fig. 1. XPS spectra of $CuInS_2$ thin films modified by electrodeposition and by deposition of PbS.

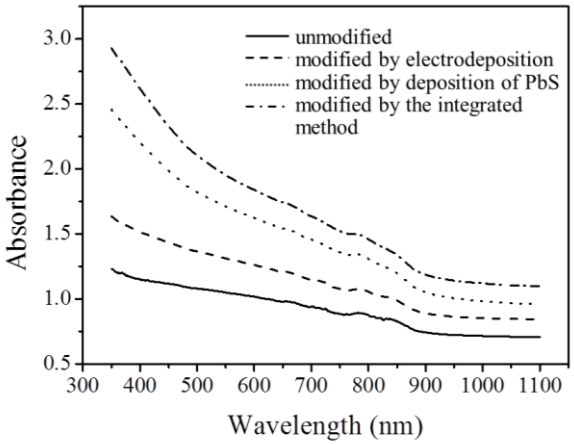

Fig. 2. UV-vis-IR spectra of unmodified and modified $CuInS_2$ thin films.

The absorbance of unmodified and modified thin films is shown in Fig. 2. The modified thin films exhibit better absorption performance than the unmodified in visible and near infrared light regions. Since PbS has a bandgap of 0.37 to 0.41 eV at 300 K [10], it can expand the spectrum range of $CuInS_2$ to near infrared range. Among the modified thin films, thin film modified by the integrate method gives the highest absorbance, and that modified by electroplating gives the lowest absorbance, which is consistent with the amount of PbS on thin films.

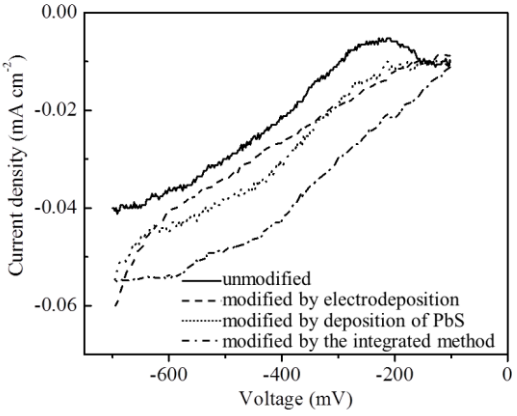

Fig. 3. Photocurrent density of unmodified and modified $CuInS_2$ thin films.

The photocurrent density of unmodified and modified $CuInS_2$ thin films is shown in Fig. 3. When $CuInS_2$ thin films modified with PbS particles are illuminated, not only visible light but also infrared light can be utilised to induce the separation of holes and electrons, therefore the photocurrent density increases, indicating that the energy conversion efficiency is enhanced. For the thin film modified by electrodeposition, since metallic lead particles, as the accumulating centres of photo-induced electrons,

promote the separation of electrons and holes, the energy conversion efficiency is improved. Furthermore, electrodeposition of lead followed by deposition of PbS can enhance the efficiency dramatically. The important reason may be the formation of PbS/Pb/$CuInS_2$ Ohmic heterojunction. Due to a lower resistance of the metal contact of metallic lead, the excited electrons from PbS can be more efficiently transferred to $CuInS_2$. In addition, the metallic lead particles are electron storage centres that benefit to the charge separation.

4. Conclusions

The energy conversion efficiency of $CuInS_2$ thin films is enhanced by electrodeposition of lead, deposition of PbS, and electrodeposition of lead followed by deposition of PbS, and the highest efficiency can be obtained by the integrated method. Not only lead particles but also PbS particles are formed on $CuInS_2$ thin films by electrodeposition of lead. Compared with the pristine $CuInS_2$ thin film, modified films demonstrated remarkably improved absorbance in visible and near infrared light regions, and enhanced energy conversion efficiency.

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