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THE INFLUENCE OF SYNTHESIZING TEMPERATURES ON THE PROPERTIES OF THE Cu/Sn/ZnS PRECURSOR THIN FILMS

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Cu_2ZnSnS_4 thin films were prepared on soda-lime glass by sulfurization of the Cu/Sn/ZnS precursors. The microstructure, morphology and optical properties of the films were investigated by X-ray diffraction (XRD), Raman scattering (Raman), scanning electron microscopy (SEM) and UV-visible spectrophotometer (UV-Vis). The SEM images of the precursor and the thin films annealed at different temperatures are very different due to their different surface products. The absorption spectrum shifts to high-wave band region with increasing annealing temperatures. The precursor thin film annealed at 500°C for 2 h forms a single CZTS phase with kesterite structure and the bandgap is estimated to be 1.54 eV.

Keywords: Cu_2ZnSnS_4; thin film; absorption spectrum.

1. Introduction

At present, the world's energy consumption increases massively and most of the world's energy resources are being produced by burning fossil fuels. However, the fossil fuels are nonrenewable and exhaustible. Burning fossil fuels causes global warming and pollution. Climate change and a sustainable development of energy resources were put into the limelight to a greater extent. Solar energy is a renewable free source of energy that is sustainable and totally inexhaustible, unlike fossil fuels. It is a nonpolluting source of energy and it does not emit any greenhouse gases. So far, three thin film materials have become industrially produced solar cells: Amorphous silicon (a-Si), Cadmium telluride (CdTe) and Copper–Indium–Gallium–Selenide/Sulfide (CIGS), where CIGS

reached the highest efficiency and the commercialization stage. CIGS is composed of rare Indium and toxic Selenium. Since the CZTS thin film is cheap, formed from nontoxic elements, it has a near-optimum bandgap and high absorption coefficient of more than $10^4\,cm^{-1}$. It has become the hotspot of contemporary research, which has emerged as one of the most promising candidates. The best conversion efficiency of solar cell based on $Cu_2ZnSn(SSe)_4$ absorbers has been improved to 12.0%.[1] The fabrications and properties of CZTS thin film have been studied extensively.[2–9]

The influences of synthesizing temperatures on the properties of Cu_2ZnSnS_4 (CZTS) thin films prepared by a solution-based precursor method,[6] Single step electrosynthesis[7] and sol–gel[8] have been reported. Magnetron sputtering is an exceptionally versatile technique, suitable for depositing high-quality, well-adhered films. It has developed rapidly over the last decade and has successfully been applied for the deposition of thin films in industry. In this paper, CZTS thin films were prepared by magnetron sputtering of Cu/Sn/ZnS precursors and by sulfurizing method. The influence of synthesizing temperatures on the properties of the Cu/Sn/ZnS precursor thin films was studied.

2. Experimental Methods

The stacked precursor thin films on soda-lime glass substrates were prepared by sputtering depositing first ZnS, and the next Sn and the last Cu. The sputtering powers of ZnS, Sn and Cu were 80, 14 and 30 W, respectively. The precursor thin films were annealed under sulfur (S) atmosphere at 330°C, 400°C, 450°C and 500°C for 2 h, respectively in a tubular furnace with two zones, where one zone was for laying the precursor thin film and the other was for laying S source. The S source temperature is 500°C.

The microstructures of CZTS films were analyzed by X-ray diffraction (XRD, D/max 2500/PC, CuKα, $\lambda = 1.5406$ Å), scanning electron microscopy (SEM, S-570) and Raman spectroscopy. The Raman spectroscopy measurement was carried out with an Invia Raman spectrometer with excitation wavelength of 514 nm. The crystallite size (D) is calculated by Scherrer formula $D = 0.89\lambda/\beta\cos\theta$ (β is full width at half maximum (FWHM), θ is Bragg angle, λ is X-ray wavelength). The composition of CZTS films was determined by energy dispersive spectroscopy (EDS, Genesis). The optical properties were analyzed by UV-visible spectrophotometer (UV-Vis, UV-5800PC).

3. Results and Discussion

Figure 1 shows the XRD patterns of the precursor and the thin films annealed at different temperatures. Besides ZnS, Cu and Sn phases, Cu_6Sn_5 is observed in the precursor, indicating that Cu atoms diffuse into the Sn film. After annealing at 330°C, Cu_6Sn_5, Cu and Sn phases disappear, and SnS and CuS are observed. At higher temperatures, binary phases disappear. At 500°C, only the CZTS diffraction peaks (112), (200), (220) and (312) are observed. The thin film is preferentially oriented to (112) plane. The corresponding crystallite size of CZTS is 47.8 nm.

As ZnS, Cu_2SnS_3 and Cu_2ZnSnS_4 have very similar d-spacings, it is difficult to distinguish these phase from XRD. The Raman method is taken. The Raman spectra of the precursor thin films annealed at different temperatures are shown in Fig. 2. Only the CuS peak is observed in the Raman spectrum of the film annealed at 330°C. SnS phase is observed in the XRD pattern, but not shown in the Raman spectrum, whose peaks are at 160, 190 and 219 cm^{-1}.[10] It should be due to that SnS phase is in the middle layer of the film. The penetrating depth of the Raman laser (514 nm) is limited, which fails to detect the existence of SnS phase. The $Cu_{2-x}S$ peak at 476 cm^{-1} and Cu_2SnS_3 peaks at 300.7, 335.5 and 351.1 cm^{-1} are observed at 400°C.

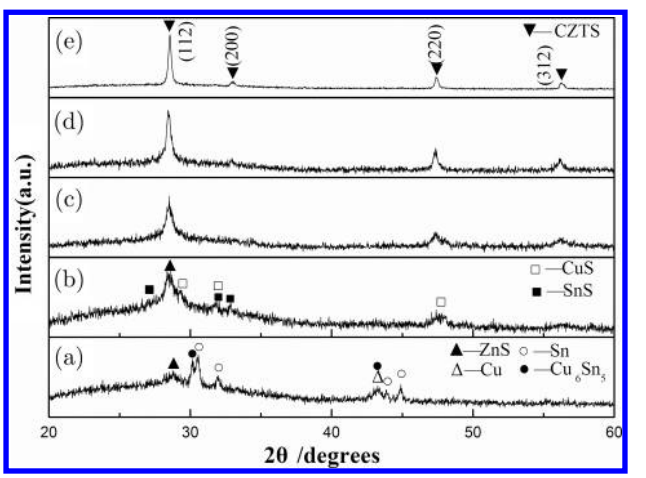

Fig. 1. XRD patterns of the precursor and the thin films annealed at different temperatures (a) precursor, (b) 330°C, (c) 400°C, (d) 450°C and (e) 500°C.

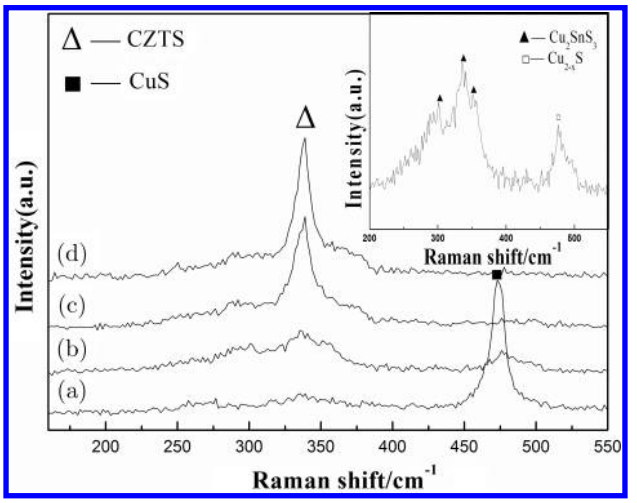

Fig. 2. Raman spectra of the precursor thin films annealed at different temperatures. The inset curve corresponds the Raman spectrum of the precursor annealed at 400°C. (a) 330°C, (b) 400°C, (c) 450°C and (d) 500°C.

It can be seen that CuS is transformed to $Cu_{2-x}S$. The formation of Cu_2SnS_3 is due to the reaction: $Cu_{2-x}S + SnS + S \rightarrow Cu_2SnS_3$. After annealing at 450°C and 500°C, $Cu_{2-x}S$ peak disappears and only the Cu_2ZnSnS_4 peak at 338 cm^{-1} is observed. The reaction is $Cu_2SnS_3 + ZnS \rightarrow Cu_2ZnSnS_4$. The CZTS peak intensity of the film annealed at 500°C is higher and the corresponding FWHM is narrower than those of the film annealed at 450°C, indicating that the crystallinity improves.

Figures 3(a)–3(e) show the SEM images of the precursor and the thin films annealed at different temperatures. The SEM images are very different due to their different surface products. For the precursor thin film, the top is Cu and the corresponding surface presents uniform grain topography. When the precursor is annealed at 330°C, the top is CuS and the corresponding surface was more compact with bigger grain size. When annealed at 400°C, the top is mainly Cu_2SnS_3 and the thin film displayed a flake-like structure. When annealed at 450°C and 500°C, Cu_2ZnSnS_4 forms completely, both the thin films exhibit compact and uniform grain characteristics. The grain size of the thin film annealed at 500°C is bigger and the corresponding cross section SEM image is shown in Fig. 3(f). The thickness is around 0.75 μm. The cross section of the thin film is compact and it is firmly adhered to the glass substrate.

Figure 4 shows the absorption spectra of the precursor and the thin films annealed at different temperatures. For the precursor thin film, there is nearly

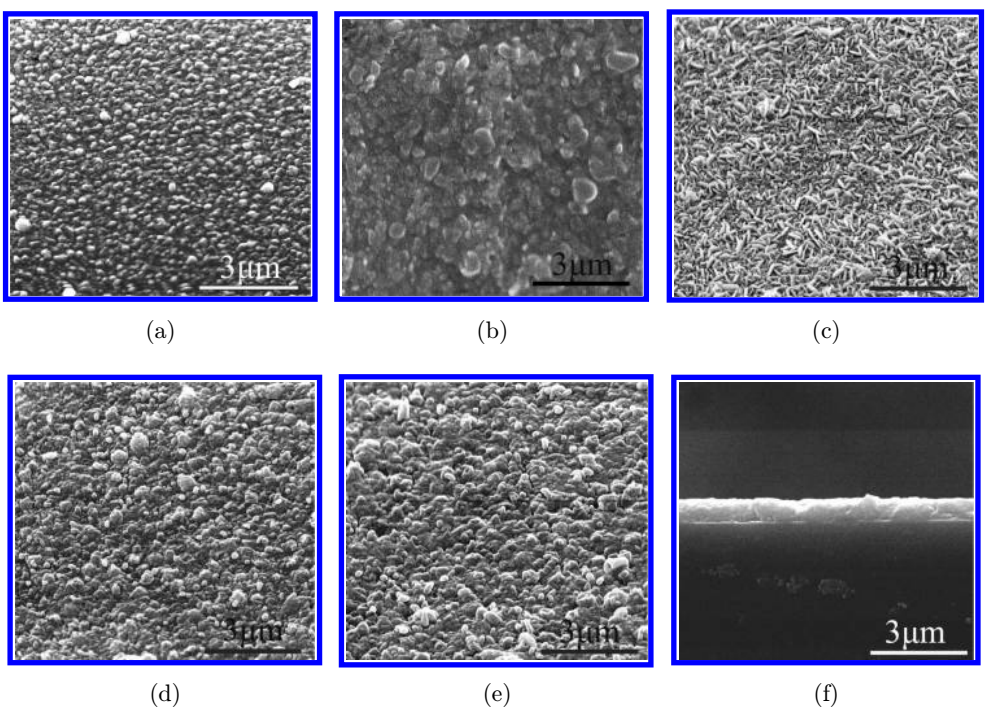

Fig. 3. SEM images of the precursor and the thin films annealed at different temperatures (a)–(e) and the cross section of the thin film annealed at 500°C (f) (a) precursor, (b) 330°C, (c) 400°C, (d) 450°C and (e) 500°C.

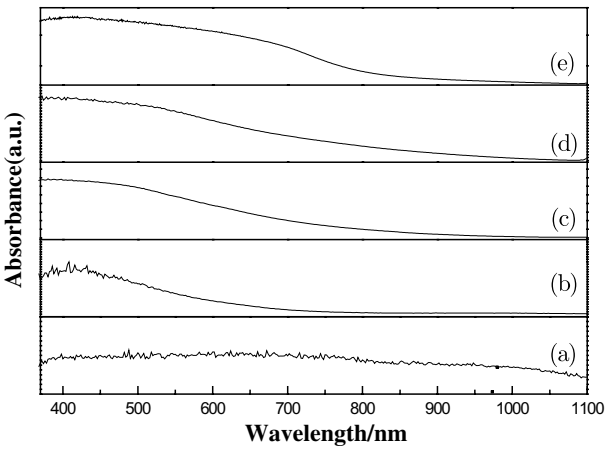

Fig. 4. Absorption spectra of the precursor and the thin films annealed at different temperatures (a) precursor, (b) 330°C, (c) 400°C, (d) 450°C and (e) 500°C.

no change in absorption spectrum. However, the precursor thin film annealed at 330°C exhibits an obvious absorption in the low Visible light band region due to the formation of SnS phase. The absorption spectrum shifts to high-wave band region due to the formation of Cu_2SnS_3 and Cu_2ZnSnS_4 phases. The absorption spectrum of the thin film annealed at 500°C presents broad and enhanced absorption characteristics over the visible and near-infrared region.

Figure 5(a) shows a plot of α vs the photon energy and Fig. 5(b) shows a plot of $(\alpha h\nu)^2$ vs the photon energy of the thin film annealed at 500°C (α is the absorption coefficient and $h\nu$ is photon energy).

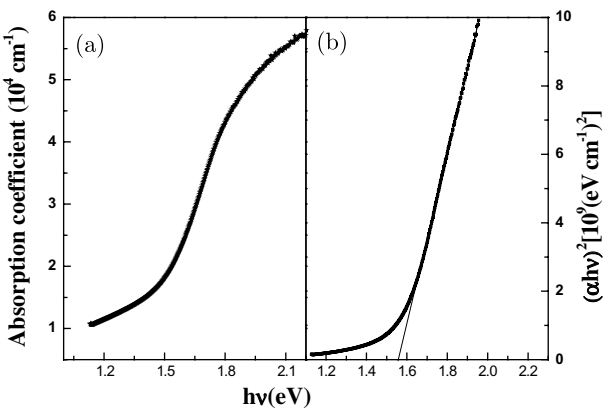

Fig. 5. A plot of α vs the photon energy (a) and a plot of $(\alpha h\nu)^2$ vs the photon energy (b) of the thin film annealed at 500°C.

Figure 5(a) presents a high absorption coefficient larger than $1 \times 10^4\,\mathrm{cm}^{-1}$. The bandgap of the film is estimated by extrapolating the straight line of the $(\alpha h\nu)^2$ to the intercept of the $h\nu$ axis. The bandgap of the film is estimated to be 1.54 eV, which is in good agreement with the reported literature results.[11–13]

4. Conclusions

The influences of synthesizing temperatures on the properties of the thin films were studied in this paper. The SEM images of the precursor and the thin films annealed at different temperatures are very different due to their different surface products. The absorption spectrum shifts to high-wave band region with increasing annealing temperatures. When the precursor is annealed at 500°C, the pure Cu_2ZnSnS_4 thin film was prepared by sulfurization of Cu/Sn/ZnS precursors. The corresponding surface exhibits compact and uniform grain characteristics. The absorption spectrum presents broad and enhanced absorption characteristics over the visible and near-infrared region. The bandgap of the film is estimated to be 1.54 eV.

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