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Cu₂ZnSnSe₄ Thin Films by Selenization of Simultaneously Evaporated Sn-Zn-Cu Metallic Lays for Photovoltaic Applications

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Abstract

Cu₂ZnSnSe₄ (CZTSe) thin films were prepared by selenization of simultaneously evaporated metallic Cu-Zn-Sn on soda lime glass (SLG) substrates. The selenization were performed in elemental selenium vapor ambient at 450 °C for 1.5 h using Argon as the carrier gas. The compositions and structural properties of the films were characterized by using EDS, XRD, and Raman, respectively. The results show that the synthesized CZTSe thin films are nearly stoichiometric and single-phase with a kesterite structure. The measurement for electrical and optical properties indicated that a high absorption coefficient of 10⁴ cm⁻¹ and a low resistivity of 30 Ω·cm are obtained. The optical band-gap energy of the CZTSe thin film can be fitted to be as 1.52eV, which closes to the optimum value for solar cell absorber. The preparation processing for CZTSe developed in this week is more attractive than others reported in the industrialization applications because the atomic ratio of Cu:Sn:Zn in the precursor can be easily controlled by adjusting the ratio of the evaporation sources, meanwhile, it is more suitable for large-scale production.

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1. Introduction

The reported high efficiency CuInGaSe₂ thin film solar cells (up to 19% in the lab) need expensive and rare metals such as indium and gallium, which affects the large-scale production of these modules at low cost. To achieve the goal of cost-effective photovoltaic technology, there is still a need to explore other low cost chalcopryite-like semiconductors such as Cu₂ZnSnS₄, Cu₂CdGeS₄, Cu₂ZnSnSe₄ and Cu₂CdGeSe₄. These quaternary compounds can be used as excellent alternative to CIGS materials, in which the extremely expensive and rare element of Indium has been replaced by the cheap and abundant elements. The Cu₂ZnSnSe₄ (CZTSe) have been considered as one of the most promising absorber layer materials for thin-film solar cells owing to its suitable direct optical band gap of 1.45 eV, high optical absorption coefficient (~ 10⁵ cm⁻¹) and p-type electrical conductivity. The CZTSe thin films were first investigated by Friedlmeier et al., who reported an efficiency of about 2% in a
solar cell with this material. However, the CZTSe films in their case contained secondary phases and the adhesion was poor. Actually, the stoichiometry and crystallization quality of the CZTSe films is the most essential factors affecting the performance of the cells. So, how to control accurately ratio of the atomic ratio of the constituents in the quaternary film, as well as a thorough understanding of the basic structural, optical and electrical properties for the films deposited under various conditions is very important.

The paper addresses the formation of CZTSe thin films in the process of selenization of simultaneously vacuum evaporated Cu/Zn/Sn metallic lays in the vapour of elemental selenium. This preparation method for CZTSe films is more attractive than others in the industrialization applications because it is more suitable for large-scale production, and the atomic ratio of Cu:Sn:Zn in the precursor can be easily controlled accurately by adjusting the ratio of the evaporation sources.

2. Experimental details

The CZTSe thin films were prepared by a two-step approach. The Cu/Sn/Zn precursors were first deposited on soda lime glass substrates by simultaneous evaporation, then the precursors were selenized in the selenium (Se) ambient of the quartz chamber of an electric furnace to obtain CZTSe films. Before depositing the precursors, the substrates were thoroughly cleaned with organic solvents and deionized water. The background pressure of the evaporation chamber was evacuated below $1 \times 10^{-3}$ Pa with a rotary mechanical pump and a diffused pump. The metallic Cu, Sn and Zn (purity 99.99%) were used as the evaporation sources. The pressure was maintained at $2 \times 10^{-3}$ Pa during evaporation. The thicknesses of the precursors could be well adjusted by the weight of evaporation sources. After depositing, the precursors were immediately transferred to the electric furnace for selenization. The background pressure of the quartz chamber of the electric furnace was evacuated below $1 \times 10^{-2}$ Pa with a rotary pump. The Se source for selenization of metallic lays was supplied by the selenium vapour from a molybdenum boat containing high-purity Se powder. The temperature was measured by a thermocouple and maintained at approximately 250 °C. Simultaneously, the growth temperature of the CZTSe samples was monitored by another thermocouple. To void the reevaporation of the elementary metals within the precursors, the growth temperature was maintained at 300 °C for 1 h at first. And then, the temperature was elevated quickly to 450 °C and kept for another 1.5 h. After selenization, the sample was naturally cooled down to room temperature in the furnace.

The compositions, crystallographic structure and surface morphology of samples were studied by energy dispersive spectroscopy (EDS, Hitachi S4800), x-ray diffractometer (XRD, Rigaku D/Max-IIIC), scanning electron microscope (SEM, Hitachi S4800), and Raman spectroscopy (Jobin-Yvon, LabRam, HR80). The electrical and optical properties were analyzed by Hall effect measurements with Van der Pauw method and UV-VIS spectrophotometer (UV-3000), respectively.

3. Results and discussion

| Contents of evaporation sources Chemical composition ratios of CZTSe thin films |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Sample | Cu (at.%) | Zn (at.%) | Sn (at.%) | Cu/Zn+Sn | Zn/Sn | (Cu+Zn+Sn)/Se |
| A | 55 | 22.5 | 22.5 | 1.21 | 1.12 | 0.96 |
| B | 50 | 25 | 25 | 1.03 | 1.13 | 0.98 |
| C | 45 | 27.5 | 27.5 | 0.83 | 1.11 | 0.94 |

Table 1 shows the contents of the evaporation sources and chemical compositions of the synthesized CZTSe thin films, which were determined by EDS measurements. The compositions of the CZTSe samples were determined by EDS. In this study, the predicted composition ratios of Cu/(Zn+Sn) in the evaporation sources were set as 1.22, 1.00 and 0.82, respectively, and the related selenized samples were named as A, B and C. The ratio of Zn/Sn have been set as 1. It can be seen from Table 1 that, high level selenizations (nearly 100 at.%) were occurred in this study, and the compositions of CZTSe thin films changed with the contents of the evaporation sources changing. The composition ratios of Cu/(Zn+Sn) in CZTSe thin films is about same as that in the evaporation sources. so the atomic ratio of Cu:Sn:Zn in CZTSe thin films can be easily controlled by adjusting the ratio of the evaporation...
sources accurately. The low atomic percent of Sn in the CZTSe thin film might be due to reevaporation of Sn in the selenization process, since the melting point of tin are lower than that of Cu and Zn.

Figure 1. The XRD patterns of the CZTSe thin films.  Fig. 2. The Raman scattering spectra of the sample B

The XRD patterns of the synthesized CZTSe thin films are presented in Figure 1. The results reveal that all the CZTSe thin films possess the simple phase, but polycrystalline kesterite structure. The obvious peaks could be attributed to (112), (220) and (312) crystalline planes of kesterite CZTSe. Moreover, the strongest diffraction of all samples occurred in (112) plane. This result is well agreed with the previous literatures.[2] It seems to be predicted from the EDS results in table 1 that the high level of Zn compositions could lead to the presence of ZnSe. However, the XRD peaks of ZnSe cannot be distinguished from that of CZTSe in the spectrum, suggesting no second phase ZnSe present. Actually, the diffraction of CZTSe and ZnSe are nearly at the same angles. Therefore, the identification of the CZTSe samples was further conducted on a Raman spectroscope. All the samples have nearly the same Raman spectra and a typical one from sample B is showed in Fig. 2. The Raman peaks locating at about 173.3 cm$^{-1}$, 196.1 cm$^{-1}$ and 231.2 cm$^{-1}$ can be assigned to the characteristic modes of the Kesterite-structure CZTSe films identified by Altosaar et al.[5]. No evidence of ZnSe was found. It is possible to say that samples B contain CZTSe and not ZnSe. This suggests that the contents of evaporation sources for the sample B are the most suitable to the preparation of CZTSe.

Fig. 3. The typical SEM image of the surface morphology of the CZTSe thin films.

SEM observation found that all the synthesized CZTSe samples show nearly the same surface morphology too and a typical SEM image from sample B is indicated in Fig. 3. The films have a compact structure consisting of about 300 nm crystallites, which is large enough for the use as the absorber application of thin film solar cells. It is well known that the conversion efficiency of polycrystalline solar cells increases with increasing grain size in the absorber materials[6]. So, large grain size is advantageous to improving the performance of photovoltaic devices.
The optical properties of the synthesized CZTSe samples deposited on SLG were further explored by the transmittance spectra. Fig. 4 shows the optical transmittance spectrum and the squared absorption coefficient as a function of the photon energy for the CZTSe thin film B. All of the samples in this study have a large absorption coefficient in the order of $10^4$ cm$^{-1}$ near a fundamental absorption edge. The band gap energy of the CZTSe has been extrapolated to be as 1.52 eV. This value is very close to that of an appropriate energy band gap of the solar cell absorber for high conversion, because this type of thin film can absorb all of the photons with energy from visible to infrared\cite{7}.

The hot-probe measurements indicated that all CSTZe thin films exhibit p-type conductivity. Table 2 lists the results of Hall effect measurements. The resistivity, carrier concentration, and Hall mobility range from 30 to 178 $\Omega$cm, 1.7 to 2.3 cm$^2$/V·sec, and $2.1 \times 10^{17}$ to $6.5 \times 10^{18}$ cm$^{-3}$, respectively. The CZTSe film B has the lowest resistivity and Hall mobility, but the highest carrier concentration.

### Table 2. Results of the Hall effect measurements for the synthesized CZTSe samples.

| Name | Resistivity ($\Omega$cm) | Mobility (cm$^2$/V·sec) | Carrier concentration (cm$^{-3}$) |
|------|------------------------|-------------------------|----------------------------------|
| A    | 76.8                   | 1.7                     | 7.3 E+17                         |
| B    | 30                     | 2.3                     | 6.5 E+18                         |
| C    | 178                    | 1.4                     | 2.1 E+17                         |

C$_{x}$ZnSnSe$_{4}$ thin films with high crystallinity quality were successfully fabricated by selenization of the Cu/Zn/Sn precursors. The experimental results show that the electrical properties of the samples have a strong dependence on the atomic ratio of the constituents in the thin films. When the ratios of the constituents are close to stoichiometric, the single phase of kesterite type structure CZTSe was obtained. Furthermore, by optimizing the precursor preparation conditions a low sheet resistivity as about 30 $\Omega$cm and a high absorption coefficient as 104 cm$^{-1}$ can be achieved in this experiment. The optical band-gap energy of the CZTS sample is about 1.52 eV, which is very close to the optimum value for a solar-cell absorber. These results show that CZTSe samples with well performance could be easily prepared by this approach.
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References

1. M.A. Contreras, K. Ramanathan, J.A. Shama, F. Hasoon, D.L. Young, B. Egass, R. Noufi, Prog. Photovoltaics Appl. 13(2005) 209.
2. H. Matsushita, T. Maeda, A. Katsui, T. Takizawa, J. Cryst. Growth 208 (2000) 416.
3. I.D. Olekseyuk, L.D. Gulay, I.V. Dydchak, L.V. Piskach, O.V. Parasyuk, O.V. Marchuk, J. Alloy. Compds. 340 (2002) 141.
4. T.M. Friedlmeier, H. Dittrich, H.W. Schock, The 11th Conference on Ternary and Multinary Compounds, ICTMC-11, Salford, 8 – 12 September, 1997, p. 345.
5. M. Altosaar, J. Raudoja, K. Timmo, M. Danilson, M. Grossberg, J. Krustok, E. Mellikov, Phys. Status Solidi, A 205 (1) (2008) 167.
6. A. Feltrin, A. Freindlich, Renewable Energy 33 (2008), 180.
7. R. A. Wibowo, E.S. Lee, B. Munir, K. H. Kim, phys. stat. sol. (a) 204 (2007) 3373.