Observation of Cu$_2$ZnSnS$_4$ thin film prepared by RF magnetron sputtering for heterojunction applications

Bo He$^*$, Jing Xu, Hong Zhi Wang, Yao Gang Li, Huai Zhong Xing, Chun Rui Wang, Qing Hong Li and Zhong Quan Ma

$^*$Department of Applied Physics and State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, 2999 Renmin Rd. North, Songjiang District, Shanghai 201620, China

$^1$Instrumental Analysis and Research Center, Shanghai University, Shanghai 200444, China

$^2$Department of Physics, Shanghai University, Shanghai 200444, China

§laserhebo@163.com

Received 8 January 2014
Revised 25 May 2014
Accepted 26 May 2014
Published 24 June 2014

In this paper, copper-zinc-tin-sulfide (Cu$_2$ZnSnS$_4$, CZTS) thin film was successfully fabricated by radio-frequency (RF) magnetron sputtering on glass substrate. The structural, optical and electrical properties of the film were studied by X-ray photoelectron spectroscopy (XPS), laser micro-Raman spectrometer, field emission scanning electron microscope (FESEM), UV-VIS spectrophotometer and Hall effect measurement, respectively. The results show that Cu$_2$ZnSnS$_4$ film is of good quality. A good nonlinear rectifying behavior is obtained for the GZO/Cu$_2$ZnSnS$_4$ heterojunction. Under reverse bias, high photocurrent is obtained.

Keywords: Cu$_2$ZnSnS$_4$ film; RF magnetron sputtering; heterojunction; current–voltage ($I$–$V$) characteristic.

1. Introduction

Copper-zinc-tin-sulfide (Cu$_2$ZnSnS$_4$, CZTS) film is considered as an ideal absorber material for solar cell and visible light photodetector. It has many merits, such as a direct bandgap of about 1.5 eV and an optical absorption coefficient higher than $10^4$ cm$^{-1}$. Therefore, a thickness of 1–2 μm is sufficient for absorbing the solar radiation. The Cu$_2$ZnSnS$_4$ is composed of low-cost, earth-abundant and nontoxic elements. Because of these advantages, it is a promising alternative to semiconductors based on Ga or In as a solar absorber material, for example Cu (In,Ga) Se$_2$ and CuInSe$_2$ film.
Cu₂ZnSnS₄ is a p-type direct bandgap semiconductor with a kesterite structure. It was prepared by various deposition techniques, such as thermal evaporation, e-beam evaporation, pulsed laser deposition, sol–gel process, spray pyrolysis, electrochemical deposition, and so on. Among these techniques, RF magnetron sputtering is convenient and fast.

Zinc oxide (ZnO) is a II–IV compound semiconductor which can be used for photoelectric devices and flat panel displays, because of its wide direct bandgap (about 3.3 eV), large exciton binding energy (about 60 meV) and good thermal stability. The conductivity of ZnO films can be significantly improved by replacing Zn atoms with higher valence elements, such as Al, Ga, In. Among these elements, the atomic radius of Ga is similar to that of Zn. By means of Ga doping, good conductivity as well large range of transparency in the visible can be obtained. Therefore, Ga-doped ZnO (GZO) film has recently gained much attention.

In this paper, Cu₂ZnSnS₄ film prepared by RF magnetron sputtering was deposited on glass substrate to fabricate n-ZnO:Ga/p-Cu₂ZnSnS₄ heterojunction. Then the structural, optical and electrical properties of the sample were studied by X-ray photoelectron spectroscopy (XPS), laser micro-Raman spectrometer, field emission scanning electron microscope (FESEM), UV-VIS spectrophotometer and Hall effect measurement, respectively. The electrical GZO/Cu₂ZnSnS₄ heterojunction properties were investigated by current–voltage (I–V) measurement.

2. Experiment

2.1. Preparation of the Cu₂ZnSnS₄ thin film

The Cu₂ZnSnS₄ film was deposited on the glass substrate in a RF magnetron sputtering system. Cu₂ZnSnS₄ ceramic target was fabricated through hot pressed sintering. Cu₂S, ZnS and SnS₂ powders were used. The purity of the target is 99.99% and the size is Φ 60 mm × 4 mm. The distance between the target and the substrate was 6 cm. The base pressure inside the chamber was pumped down to less than 5 × 10⁻⁴ Pa. Sputtering was carried out at a working gas (pure Ar) pressure of 1 Pa. The Ar gas flow ratio was 40 sccm. The RF power and the temperature on substrate were kept at 100 W and 400°C, respectively. The sputtering was proceeded for 30 min. The thickness of Cu₂ZnSnS₄ film is about 700 nm.

2.2. GZO/Cu₂ZnSnS₄ heterojunction device fabrication

Following the above step, GZO layer was deposited on Cu₂ZnSnS₄ film by direct current (DC) magnetron sputtering. The target was sintered ceramic disk of ZnO doped with 2 wt.% Ga₂O₃ (purity 99.99%). The base pressure inside the chamber was pumped down to less than 5 × 10⁻⁴ Pa. Sputtering was carried out at a working gas (pure Ar) pressure of 1 Pa. The Ar flow ratio was 40 sccm. The DC power and the temperature on substrate were kept at 100 W and 300°C, respectively. The sputtering was proceeded for 20 min. The thickness of GZO film is about 200 nm.
Finally, by sputtering, Ag metal films were deposited with a shadow mask on the GZO and Cu$_2$ZnSnS$_4$ surfaces for the top electrodes, respectively. The area of the Ag electrode is 1 × 1 mm$^2$.

2.3. Characterizations

Microstructure of the Cu$_2$ZnSnS$_4$ film was investigated by XPS, FESEM and laser micro-Raman spectrometer. The optical transmission of the film was measured by UV-VIS spectrophotometer. The electrical properties of Cu$_2$ZnSnS$_4$ film were characterized by Hall effect measurement (Accent HL5500pc) at room temperature. The $I−V$ characteristic of the device was measured by Agilent 4155C semiconductor parameter analyzer.

3. Results and Discussion

3.1. Microstructural, optical and electrical properties of Cu$_2$ZnSnS$_4$ film

The valence states of constituent elements of the film were characterized by X-ray photoelectron spectroscopy (WICALAB) with a monochromatic Al K$\alpha$ (1486.6 eV) radiation source. Figures 1(a)-1(d) show the X-ray photoelectron spectroscopy (XPS) spectra, which were used to confirm the constituent elements in

![XPS spectra of Cu$_2$ZnSnS$_4$ film](image)

Fig. 1. XPS spectra of Cu$_2$ZnSnS$_4$ film (a) core-level spectrum for Cu 2p, (b) core-level spectrum for Zn 2p, (c) core-level spectrum for Sn 3d and (d) core-level spectrum for S 2p.
B. He et al.

Fig. 2. Raman spectra of Cu$_2$ZnSnS$_4$ film.

the Cu$_2$ZnSnS$_4$ film. The sample contains Cu, Zn, Sn and S. Narrow scan XPS spectra of Cu 2$p$ state of the sample is shown in Fig. 1(a). A well-resolved doublet corresponding to Cu 2$p_{3/2}$ and Cu 2$p_{1/2}$ can be observed. The binding energies for Cu 2$p_{3/2}$ and Cu 2$p_{1/2}$ are 932.28 eV and 952.18 eV, respectively, with peak splitting of 19.9 eV, revealing that copper is in the Cu$^{+}$ state. The Zn 2$p_{3/2}$ and Zn 2$p_{1/2}$ peaks shown in Fig. 1(b) are present at 1022.38 eV and 1045.38 eV, respectively, with a separation of 23 eV, which confirms the presence of Zn$^{2+}$ state. The binding energy values for Sn 3$d_{5/2}$ and Sn 3$d_{3/2}$ are 487.28 eV and 495.78 eV in Fig. 1(c), with a peak splitting of 8.5 eV, indicating the formation of Sn$^{4+}$ state. In Fig. 1(d), the S 2$p$ peak located at 162.38 eV shows sulfide phase. Consequently, based on the XPS analysis, the presence of CZTS phase in the RF sputtered film is confirmed.

To further confirm the phase purity of the Cu$_2$ZnSnS$_4$ film, Raman spectroscopy was carried out. The Raman spectra was recorded on a LABRAM-1 Bconfocal laser micro-Raman spectrometer with 532 nm (Nd:YAG laser) radiation at room temperature. Raman spectra of Cu$_2$ZnSnS$_4$ film prepared by RF magnetron sputtering was obtained as seen in Fig. 2. A distinctive peak appears at 332 cm$^{-1}$, in agreement with well-known vibrational characteristic of kesterite Cu$_2$ZnSnS$_4$ film. Thus, Raman study confirmed the kesterite structure of the Cu$_2$ZnSnS$_4$ film prepared by RF magnetron sputtering.

Figure 3 shows the FESEM surface image of the Cu$_2$ZnSnS$_4$ film prepared by RF magnetron sputtering on glass. The result indicates that the film consists of compact structure grains with sub-micron size and low roughness, which is suitable for the absorber of thin film solar cells. The Cu$_2$ZnSnS$_4$ film consists of globular shaped grains. It can be easily seen that the grains are densely packed and the size varies from 20 nm to 100 nm.

Optical transmittance spectra of Cu$_2$ZnSnS$_4$ thin film was measured by a UV-VIS spectrometer, as shown in Fig. 4. The absorber layer shows low transmittance in visible light. The absorption coefficient $\alpha$ was evaluated from the measurement.
Observation of $\text{Cu}_2\text{ZnSnS}_4$ thin film

Fig. 3. FESEM image of $\text{Cu}_2\text{ZnSnS}_4$ film.

Fig. 4. Transmission spectrum of $\text{Cu}_2\text{ZnSnS}_4$ film.

of optical transmittance $T$ according to the following relation:\(^{33}\)

$$\alpha = \frac{1}{d} \ln \frac{1}{T},$$  \hspace{1cm} (1)

where $d$ is the thickness of film. The optical bandgap of film is determined through the extrapolation of linear part of the absorption edge to $\alpha = 0$ in the relationship as

$$(\alpha h\nu)^2 = A(E_g - h\nu).$$  \hspace{1cm} (2)

The inset in Fig. 4 shows the plot of $(\alpha h\nu)^2$ versus $h\nu$ for $\text{Cu}_2\text{ZnSnS}_4$ film prepared on glass. The optical bandgap energy $(E_g)$ value of $\text{Cu}_2\text{ZnSnS}_4$ is about
1.5 eV. The value of bandgap is in good agreement with the bandgaps reported for Cu$_2$ZnSnS$_4$ films. From the perspective of optical properties, the Cu$_2$ZnSnS$_4$ film prepared by RF magnetron sputtering can be considered as a suitable absorber material for solar cell and visible light photodetector.

Electrical properties of the Cu$_2$ZnSnS$_4$ film were measured by Hall effect measurement. It is a p-type semiconductor. The resistivity is as low as 0.88 Ω·cm, the hole concentration and mobility are as high as $1.55 \times 10^{19}$ atom/cm$^3$ and 0.45 cm$^2$/V·s, respectively.

3.2. Device characteristics

The XPS spectra were measured for studying the chemical binding states of the GZO film. The wide-scan XPS spectrum (from 0 eV to 1300 eV) of the film is shown in Fig. 5(a), where binding energy peaks of Ga, Zn, O and C are detected. The carbon is the only major contaminant. The presence of carbon in the GZO film can be attributed to contamination which resulted from the sample being exposed to ambient atmosphere. The binding energy values for Ga 2$p_{3/2}$ and Ga 2$p_{1/2}$ are 1118.71 eV and 1145.71 eV in Fig. 5(b), with a peak splitting of 8.5 eV, indicating the formation of Ga$^{3+}$ state. The intensity of Ga 2$p$ peak is obvious. The Zn 2$p_{3/2}$ and Zn 2$p_{1/2}$ peaks shown in Fig. 5(c) are present at 1022.48 eV and 1045.48 eV, respectively, which confirms the presence of Zn$^{2+}$ state. In Fig. 5(d), the O 1$s$ peak is observed at 531.38 eV.

![XPS spectra of GZO film](image)

Fig. 5. XPS spectra of GZO film (a) survey scan, (b) core-level spectrum for Ga 2$p$, (c) core-level spectrum for Zn 2$p$ and (d) core-level spectrum for O 1$s$. 


Observation of \( \text{Cu}_2\text{ZnSnS}_4 \) thin film

Fig. 6. (Color online) (a) \( I-V \) characteristic of Ag ohmic contacts to \( \text{Cu}_2\text{ZnSnS}_4 \) and (b) \( I-V \) characteristic of Ag ohmic contacts to GZO.

Fig. 7. (Color online) \( I-V \) characteristic of the \( n-ZnO:Ga/p-\text{Cu}_2\text{ZnSnS}_4 \) heterojunction in dark and in light (20 W halogen lamp).

The linear \( I-V \) behaviors between the two Ag electrodes on the surface of the \( \text{Cu}_2\text{ZnSnS}_4 \) and GZO films are shown in Figs. 6(a) and 6(b), respectively. The inset shows the schematic of the test structure. It indicates a good ohmic contact. The distance of the two Ag electrodes on the film is 1 cm. Figure 7 shows a typical \( I-V \) characteristic of the GZO/\( \text{Cu}_2\text{ZnSnS}_4 \) heterojunction device measured at room temperature. The inset in Fig. 7 shows the GZO/\( \text{Cu}_2\text{ZnSnS}_4 \) thin films device structure for electrical characterization. A good nonlinear rectifying behavior is obtained. A small leakage current is observed in the reverse bias region, but the forward current is much higher than the reverse current. And the turn-on voltage spectrum peaked at 531.38 eV shows a high binding energy shoulder due to chemisorbed oxygen. Therefore, it can be found that Ga-doped ZnO phase already formed in the DC sputtered film.
of the GZO/Cu$_2$ZnSnS$_4$ heterojunction is about 5 V. The result indicates that the GZO/Cu$_2$ZnSnS$_4$ heterojunction has good diode characteristic. The rectification in $I-V$ characteristic should come from the $p$–$n$ heterojunction in Cu$_2$ZnSnS$_4$ and GZO. Because Cu$_2$ZnSnS$_4$ film generally shows $p$-type semiconductor property. The $p$–$n$ heterojunction is formed at the interface of $p$-type Cu$_2$ZnSnS$_4$ and $n$-type GZO thin films.

The photo $I-V$ characteristic of the GZO/Cu$_2$ZnSnS$_4$ heterojunction device was measured under illumination by 20 W halogen lamp in Fig. 7. Typical good rectifying and photoelectric behavior are observed for the device. Under reverse bias, photocurrent is obviously much larger than the dark current. For example, when the reverse bias is $-10$ V, the dark current is only $2.97 \times 10^{-6}$ A. While the photocurrent reaches to $5.17 \times 10^{-6}$ A under 20 W halogen lamp illumination. Because the GZO film is highly transparent in the visible region, the visible light passes through GZO film and is absorbed primarily in the underlying $p$-Cu$_2$ZnSnS$_4$, generating electron–hole pairs, responsible for the observed photocurrent under reverse bias conditions (inset Fig. 7), while the UV photons are mainly absorbed in the GZO layer. Consequently, the photocurrent increases as the reverse bias increases.

4. Conclusion

Cu$_2$ZnSnS$_4$ thin film was successfully fabricated by RF magnetron sputtering on glass substrate. Raman spectra prove that the film is of kesterite structure. The film consists of compact structure grains with sub-micron size and low roughness. The optical property was a bandgap energy of 1.5 eV and low transmittance in visible light. The XPS analysis confirmed the presence of all four constituent elements in the Cu$_2$ZnSnS$_4$ film. The film is a $p$-type semiconductor. The values of the resistivity, carrier concentration and mobility of the Cu$_2$ZnSnS$_4$ film are 0.88 $\Omega \cdot$ cm, $1.55 \times 10^{19}$ atom/cm$^3$ and 0.45 cm$^2$/V·s, respectively. The film can be applied as absorber layer in solar cell and visible light photodetector.$^{36}$

A good nonlinear rectifying behavior is obtained for the GZO/Cu$_2$ZnSnS$_4$ heterojunction, which is a typical $p$–$n$ heterojunction. It is formed at the interface of $p$-type Cu$_2$ZnSnS$_4$ and $n$-type GZO thin films. Under reverse bias, photocurrent is obviously much larger than the dark current.

Acknowledgment

The project was supported by the Fundamental Research Funds for the Central Universities, China, Dong Hua University (Grant No. 13D110913), Opening Project of State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Dong Hua University (Grant No. 13M1060102), Innovation Fund of Shanghai University (Grant No. K.10-0110-13-005), National Natural Science Foundation of China (Grant Nos. 61274067 and 11174048).
Observation of Cu$_2$ZnSnS$_4$ thin film

References