

Study of the characteristics of ohmic contact between metal electrodes and $\text{Cu}_2\text{ZnSnS}_4$ thin films

Bo Long¹ ✉, Sile Lin¹, Walter Nsengiyumva¹, Lingyan Lin²

¹College of Mechanical and Electrical Engineering, Fujian Agriculture and Forestry University, Fuzhou, Fujian Province, CN 350002, People's Republic of China

²College of Electronic Information Science, Fujian Jiangxia University, Fuzhou 350108, People's Republic of China

✉ E-mail: longbole@foxmail.com

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Selection of ohmic contacts to $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) films is one of the most crucial tasks involved in the fabrication of efficient CZTS devices. In the present work, the formation of ohmic contact with the p-type CZTS films was studied. The p-type CZTS thin films were fabricated by thermal evaporation, followed by the subsequent sulphurisation in the atmosphere of $\text{N}_2 + \text{H}_2\text{S}$ (5%). Ag, In, Al and Ti were chosen as the metal electrodes of the CZTS-based films. The characteristics of CZTS thin films and the structure of Mo/CZTS/M ($M = \text{Ag, In, Al and Ti}$) were investigated using XRD, Raman, SEM, and EDX, to name but a few. The ohmic contact property of the studied material was tested using an I - V characterisation system. The results showed that Al could form a high-quality ohmic contact with the p-type CZTS films among the metallic electrodes.

1. Introduction: $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is one of the promising absorber materials in thin-film solar cells (TFSCs) [1–3]. The material presents a number of interesting features such as the direct band gap of 1.51 eV which is very close to an optimum band gap of semiconductors used for photovoltaic conversion as well as a high absorption coefficient ($\geq 10^4 \text{ cm}^{-1}$), among others [4–6]. Moreover, CZTS has versatile electrical properties which can suitably be benefitted by the structures of the solar cell device [7, 8].

The formation of metal–semiconductor contact and the subsequent extraction of the contact parameters are of great importance since they are presently the most important research aspects in the TFSCs industry. For the research and fabrication of the CZTS TFSCs, it is important to determine the electronic parameters of the CZTS films and the ohmic contact between the CZTS films and the metal electrodes. A stable back contact is essential for a significantly rectifying performance and a long-term stability of the CZTS TFSCs. In addition, it should be mentioned here that CZTS thin films undergo structural transformation upon sulphurisation and the compositional change is quite common owing to desulphurisation. With the growing interest in the fabricating CZTS photovoltaic devices, the barrier characteristics of the contacts between the CZTS films and different metal electrodes have become more and more important.

Of significance, it is well known that Mo is commonly used as the back electrodes for chalcogenide TFSCs, and there are relatively few reports are available in the literature on both the fabrication and the subsequent extraction of diode parameters of M/p-CZTS Schottky barriers [9–11]. Harmonising with the aforesaid, the literature indicates that the formation of MoS_2 is rapid due to the S atom diffusion from the atmosphere of $\text{N}_2 + \text{H}_2\text{S}$ and CZTS during the sulphurisation [12]. Besides, thick MoS_2 layers can hinder the carriers injection from the CZTS thin films to the Mo back contact electrodes and the series resistances are increased [13, 14]. Therefore, finding appropriate back contact electrode materials would contribute significantly to the overall progress in the area of thin films.

This Letter aims to determine the ohmic contacts characteristics between CZTS thin films with different orders of both the metal precursors and the metal electrodes.

2. Experiment details: The layered structure used to make Schottky or ohmic contact normally consists of MSM sandwich

geometry [15]. In the present study, the samples were fabricated as follows. Firstly, Mo thin films were deposited on cleaned $30 \times 20 \text{ mm}^2$ soda-lime glass (SLG) substrates. In addition, Mo was used as the back contact electrode material. Then, p-type CZTS films of about 1200 nm on the Mo back electrodes were prepared. Finally, upper metal layers were deposited on the CZTS films. Here, Ag, In, Al and Ti (the work functions are 4.64, 4.09, 4.20 and 4.33 eV, respectively) were chosen separately as the upper metal layers since their working functions are close to that of our CZTS samples (4.75 eV). Moreover, these metal materials can establish ohmic contacts with CZTS because of their Fermi level exactly pinning between conduction and valence bands of CZTS. The CZTS thin films were grown by evaporating precursors followed by sulphurisation. The metal precursors of the CZTS thin films were SLG/ZnS/Cu/Sn and SLG/ZnS/Sn/Cu. The evaporation process was carried out in a vacuum of $5 \times 10^{-4} \text{ Pa}$ at an evaporation rate of 2^{-3} Å/s . Then, the metal precursors were sulphurised in the atmosphere of $\text{N}_2 + \text{H}_2\text{S}$ (5%) at 500°C for 1 h [16].

The metal electrodes were deposited on the CZTS films by both the evaporation and the DC sputtering methods. The thickness of each metal electrode film was around 100 nm. Precautionary measurements were taken to avoid sideways diffusion and provide metal contacts for I - V measurements.

The film thicknesses were measured by a stylus profiler (TENCOR D100). The crystallinity of the CZTS thin films was ascertained by an X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ Å}$). The elemental composition of the CZTS films was analysed by EDX profiles. The surface morphology of the CZTS films and the top metal electrodes were observed using a scanning electron microscope (SEM) (HITACHI S-4800). In order to evaluate the electrical and optical properties of the as-grown CZTS films, the Hall-effect measurement system and PerkinElmer Lambda 900 UV/VIS/NIR spectrometer were used. The I - V characteristics of MSM devices were measured using a Model 4200-SCS semi-conductor characterisation system and Interactive Characterization Software.

3. Results and discussions

3.1. The characteristics of CZTS thin films: From the EDX profiles of the CZTS thin films in Fig. 1 and the atomic ratio data in Table 1, it was noticed that both types of CZTS films had the similar

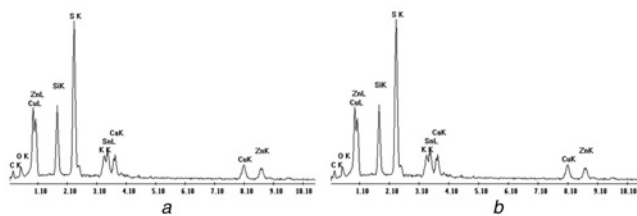


Fig. 1 EDS patterns of the CZTS films with different stacking sequence precursors
a SLG/ZnS/Cu/Sn
b SLG/ZnS/Sn/Cu

Table 1 The atomic ratio of two kinds of CZTS thin films

Sample	$n_{\text{Cu}}/(n_{\text{Sn}} + n_{\text{Zn}})$	$n_{\text{Zn}}/n_{\text{Sn}}$	$n_{\text{S}}/n_{\text{etal}}$
SLG/ZnS/Cu/Sn	0.64	1.63	1.09
SLG/ZnS/Sn/Cu	0.68	1.65	1.13

elemental composition. It was noticed that the as-grown CZTS films were Cu poor and zinc rich. Fig. 2 shows the XRD patterns of the two CZTS films. The two CZTS films were polycrystalline CZTS and had kesterite structure with XRD peaks corresponding to (112), (020), (220) and (132) reflections [17, 18]. From Scherrer's formula, the average grain size of the films was found to be 180 nm. Fig. 3 shows the Raman spectra (532 and 325 nm excitation) of CZTS thin films with different stacking sequence precursors. Three peaks at 285, 335 and 367 cm^{-1} matched with the Raman spectroscopy of CZTS and the peak at 475 cm^{-1} matched with the Raman spectroscopy of Cu_xS in the previous reports in Fig. 3a. The major peak (335 cm^{-1}) was narrow when the stacking sequence was SLG/ZnS/Cu/Sn. This means that the stacking sequence of SLG/ZnS/Cu/Sn improved the formation of the pure CZTS phases. Raman spectroscopy with 325 nm excitation wavelength was also used to further identify the

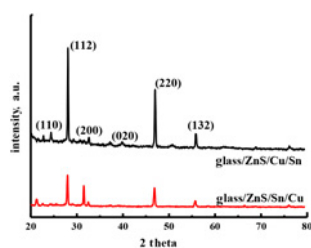


Fig. 2 XRD patterns of the CZTS films with different stacking sequence precursors

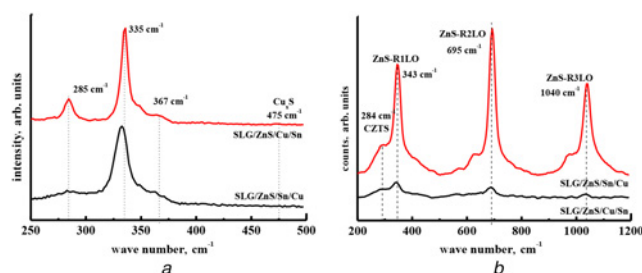


Fig. 3 The Raman spectra of the CZTS thin films with different stacking sequence precursors
a 532 nm excitation
b 325 nm excitation

existence of ZnS, as shown in Fig. 3b. The peaks at 343, 695 and 1040 cm^{-1} can be assigned to the R1LO, R2LO and R3LO vibrational modes of ZnS. XRD and Raman results show that the CZTS samples had the secondary phase ZnS and Cu_xS . From the surface analysis with SEM analysis (Fig. 4), we found that there were large clumpy granules on the surfaces of the CZTS films. These granules were loosely packed together and formed a continuous network. In addition, it also shows that both the samples seem to have analogous surface morphology. Hall-effect measurements show that the as-grown CZTS films were of p-type conduction as shown in Table 2, and the optical band gaps of the films were around 1.51 eV. It shows that the electrical resistivity increased while the hole concentration decreased with the stacking sequence of the precursor of the CZTS thin film before changing from SLG/ZnS/Cu/Sn to SLG/ZnS/Sn/Cu. As there were more ZnS and Cu_xS on the surfaces of the samples in the CZTS thin films with the stacking sequence of SLG/ZnS/Sn/Cu, and ZnS and Cu_xS could increase the electrical resistivity of the CZTS thin films. The increase in ratios of $\text{Cu}/(\text{Zn} + \text{Sn})$ meant the decrease in the Cu vacancies which were the main sources of the hole carriers in the CZTS thin films. Therefore, it would result in the decreasing of the hole concentration of the samples.

3.2. Electrical properties of the Mo/CZTS/metal structures: Fig. 5 shows the I - V characteristics of different MSM devices with the CZTS thin films. When the stacking sequence of the precursor was SLG/ZnS/Cu/Sn, the voltage was varied from -3 to +3 V. However, when the voltage exceeded 2 V, the characteristics of Schottky contacts with the four types of metals became worse. In contrast to the I - V characteristics of the four kinds of devices, it was found that Mo/CZTS/Al structure exhibited good ohmic behaviour. In Fig. 5a, the Mo/CZTS/Ag exhibited quite a good linear behaviour when the voltage was 1 V. However, when the voltage was 2 V, the curve of Mo/CZTS/Ag was not linear and had a bending angle through the data collection besides the other structures performing Schottky contacts. This indicated that Mo/CZTS/Al structure strongly followed the tunnelling transport mechanism in the entire measured voltage range. On the other hand, the peculiar behaviour of Mo/CZTS/M (M=Ag, In and Ti) structures particularly at higher voltages probably due to the presence of bias-dependent interface charges or states controlled the barrier height and hence the current flowed across the junction. Fig. 6

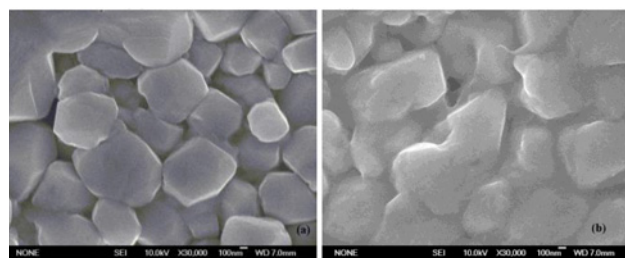


Fig. 4 SEM profiles of the CZTS films with different stacking sequence precursors
a SLG/ZnS/Cu/Sn
b SLG/ZnS/Sn/Cu

Table 2 The electrical characteristics of the two CZTS thin films

Sample	p , cm^{-3}	μ , $\text{cm}^2/(\text{V s})$	ρ , $\Omega \text{ cm}$
SLG/ZnS/Cu/Sn	2.959×10^{17}	9.157	2.303
SLG/ZnS/Sn/Cu	2.784×10^{17}	5.901	3.800

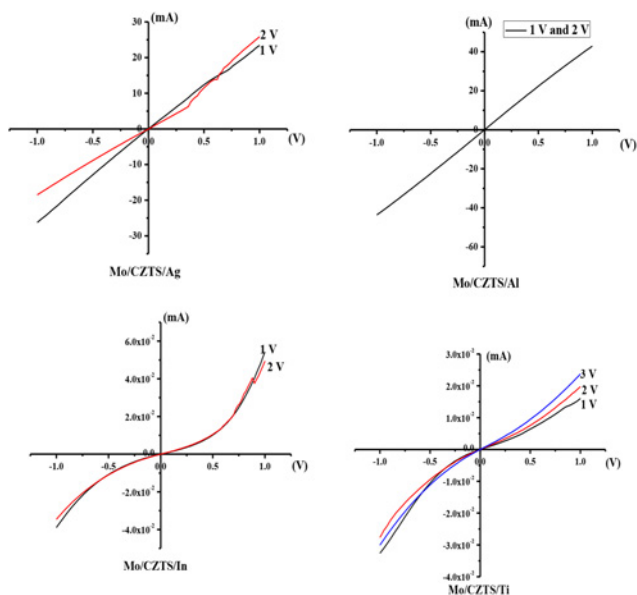


Fig. 5 *I-V* curves of the electrical contacts between the CZTS (SLG/ZnS/Cu/Sn) films and the metals (Ag, Al, In and Ti)

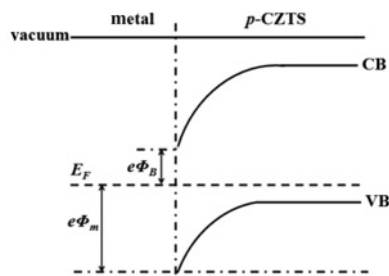


Fig. 6 The band diagram of the Schottky potential barrier about the non-ohmic contact MSM devices

shows the band diagram of the Schottky potential barrier about the non-ohmic contact MSM devices. Therefore, the Mo/CZTS/M structures that followed the two types of transport mechanisms depended on the applied bias voltage. These differences in the behaviour of Mo/CZTS/M structures might be attributed to the diffusion of metal ions into the CZTS crystal lattice and/or the formation of different intermediate binary and/or ternary phases (M–Zn–Sn–Cu–S) between M and CZTS films.

Fig. 7 shows the *I-V* curves of the electrical contacts between the four metal electrodes (Ag, Al, In and Ti) and the CZTS thin films with the SLG/ZnS/Sn/Cu stacking sequence. It was found that all the four metals cannot ohmic contacts with the CZTS thin films and all the diodes had Schottky contacts as shown in Fig. 6. After the sulphurisation, there was the Cu_3S phase on the surface of the sample which had the SLG/ZnS/Sn/Cu stacking sequence of the precursor, and the second phase increased the interface state and the potential barrier on the interface. In contrast to the *I-V* characteristics of metal contacts between the two CZTS thin films, the CZTS thin films with the SLG/ZnS/Cu/Sn stacking sequence of precursors could be found to form a better ohmic contact with Al. This revealed that the diffusion of Al atoms into the CZTS crystal lattice, as an interstitial dopant, improved the crystallinity of the CZTS films by decreasing the defect centres within the CZTS lattice that led the electrical resistivity of the films to lower values. This may be an appropriate reason for the decrease in the resistivity in Mo/CZTS/M structures.

Fig. 8 shows the SEM images of CZTS (SLG/ZnS/Cu/Sn) with different electrode materials. Fig. 8a shows the non-uniform

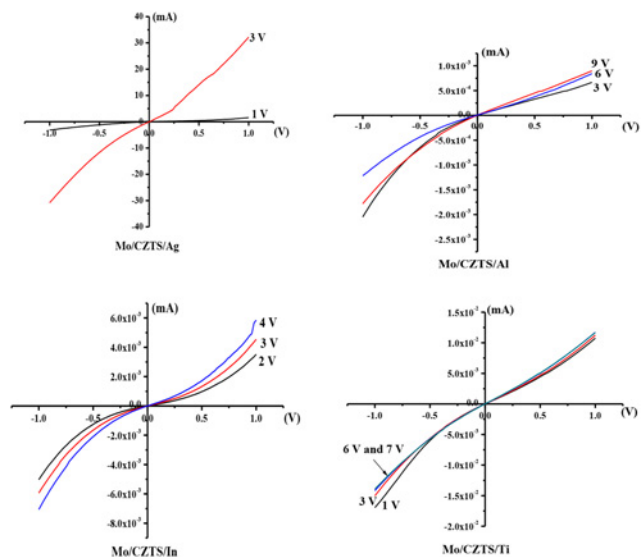


Fig. 7 *I-V* curves of the electrical contact between the CZTS (SLG/ZnS/Sn/Cu) films and the metals (Ag, Al, In and Ti)

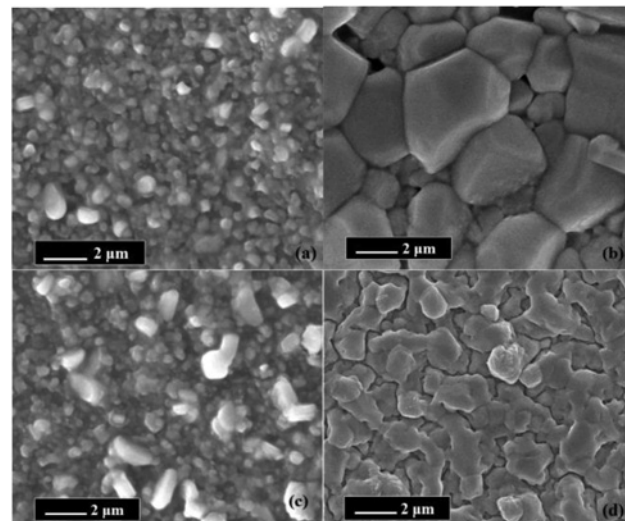


Fig. 8 SEM images of as-deposited CZTS (SLG/ZnS/Cu/Sn) with different metal electrode materials

- a Ag
- b Al
- c In
- d Ti

mixture of the grain size distribution with some sporadic cylindrical crystallites, whereas that of CZTS with the Al electrode depicted dense closely packed spherical crystallites with nearly equal size distribution in Fig. 8b. At the same time, the grain size of the CZTS was increased. With In and Ti electrodes, the segregation of smaller grains had been observed and the crystallites of the CZTS thin films had been broken (Figs. 8c and d).

4. Conclusion: The comparison between CZTS films and the precursors of SLG/ZnS/Sn/Cu revealed that the CZTS films with the precursors of SLG/ZnS/Cu/Sn can form better ohmic contacts with the metal electrodes. It was owing to the Cu_3S phase on the surface of the sample which had the SLG/ZnS/Sn/Cu stacking sequence after the sulphurisation, and the second phase made the interface state and the potential barrier on the interface increased. Among the metal electrodes of Ag, Al, In and Ti,

the Mo/CZTS/Al structure has the best ohmic contact characteristics. The diffusion of Al atoms into CZTS crystal lattice, as an interstitial dopant, improved the crystallinity of the CZTS film by neutralising the defect states within the CZTS lattice that led the electrical resistivity of the films to lower values.

For thin-film solar cells, ohmic contact formation is essential for extraction of maximum power from the device. It was observed that aluminium metal exhibits good ohmic contact with the p-type CZTS film, unlike Ag, In and Ti which showed somewhat poor I - V characteristics.

5 References

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