Effect of Prefabricated Layer Structure on Properties of CZTS Thin Films and Solar Cells

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Abstract. Cu2ZnSnS4 (CZTS) thin films based on single-layer and double-layer prefabricated layer structure were prepared on substrates by two-step method. The influence of prefabricated layer structure on the surface morphology, element composition and photoelectric properties of CZTS thin film was studied. The crystal structure, surface morphology and composition of the films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively. The experimental results showed that the CZTS thin film with double-layer prefabricated structure had larger grain size, better crystallization and uniform distribution of film components than the CZTS thin film with single-layer prefabricated structure. The conversion efficiency of CZTS solar cells based on the double-layer prefabricated structure increased from 0.25% of the single-layer prefabricated structure to 3.05%. Therefore, the double-layer prefabricated structure CZTS thin film was more suitable as the absorption layer of CZTS thin film solar cells.

1. Introduction

Thin film solar cells become the focus of recent development research due to their advantages of mass production, low material consumption and low manufacturing cost[1]. CZTS belongs to the I-II-IV-VI group of p-type quaternary compound semiconductor materials. It has a direct band gap (1.45–1.5eV) and a high absorption coefficient (>10^4 cm⁻¹) which match the solar spectrum very well. CZTS thin film was cheap, almost non-toxic, and rich in elements in the earth's crust, which made CZTS film become one of the most potential new solar cell film absorbing layer materials[2-4]. The theory shows that the CZTS thin film cell has a maximum conversion efficiency of 32.2%[5], but the current maximum efficiency was only 12.6%[6]. One of the main limiting factors was related to the prefabricated structure of CZTS film. W Li et al. studied the influence of prefabricated layer structure on the microstructure and optical properties of CZTS thin film, and compared with the prefabricated layer structure of SnS2/Cu/ZnS and ZnS/SnS2/Cu, the CZTS thin film prepared by the prefabricated layer structure of Cu/ZnS/SnS2 had better crystallization[7]. M Yang et al. studied the influence of Zn/Sn/Cu and ZnS/Sn/Cu prefabricated layers on CZTS thin film solar cells, and found that the cells prepared based on ZnS/Sn/Cu prefabricated layers had higher conversion efficiency[8]. The element distribution in precursors had a high impact on the crystallization and opto-electronic properties of the CZTS thin films. Thus it was an important research topic to study and improve the prefabricated structure of CZTS thin film.
In this paper, CZTS thin films based on single-layer and double-layer precursor structure were prepared on substrates by two-step method. The law of the distribution of elements in CZTS precursors during growth process was studied. And the factors in obtaining CZTS films with high crystal quality and improving the conversion efficiency of CZTS solar cells were discussed by analyzing the properties of CZTS thin films with different precursor structure.

2. Experimental details

2.1. Preparation of CZTS thin film and solar cell
The CZTS precursors were prepared on Mo-coated glass substrates by sputtering method. The single-layer prefabricated precursor was co-sputtered with CZTS target and Cu target, and the deposition thickness was 800nm. The upper layer of the double-layer prefabricated precursor was co-sputtered by CZTS target and Zn target with RF power of 10W for Zn target and deposition thickness of 100nm. The lower layer was co-sputtered by CZTS target and Cu target, and the deposition thickness was 700nm. Then the precursors were transferred to tubular furnace to form CZTS thin films under S atmosphere at 580℃ for 50min. More details could be found in our previous work[9]. The CZTS thin film based on single-layer prefabricated structure was denoted as sample A, while the film based on double-layer prefabricated structure was denoted as sample B. Then the CZTS thin films were fabricated to solar cells with a glass/Mo/CZTS/CdS/i-ZnO/AZO structure under standard process.

2.2. Characterization and testing of CZTS thin film and solar cell
X-ray diffraction (XRD, Rigaku Ultima-IV diffraction-meter with Cu–Kα radiation source) was used to analyze the phase structure of the film. Scanning electron microscope (SEM, Hitachi S4800) and energy spectrometer (EDS) were used to analyze the micromorphology and element composition of the film. The J-V characteristics of CZTS solar cells were achieved by using a digital source meter under standard test conditions using a solar simulator as the light source (Oriel Solar simulator, 91192–1000 W).

3. Results and discussions
The crystallinity and phase structure of the two samples were compared and analyzed by X-ray diffractometry. The results were shown in figure 1. Except for Mo peak, the XRD patterns of the two samples had four obvious peaks at 2θ = 28.5°, 32.9°, 47.3° and 56.8°, which corresponded to the diffraction peaks of (112), (200), (220) and (312) crystal surfaces of CZTS with Kesterite structure (JCPDS 26-0575). The (112) main peak strength was enhanced by introducing double-layer structure. The FWHM of the main peak could be used to explain the crystallinity of the films. The smaller the FWHM is, the better film crystallinity it has. The calculated FWHM of sample A was 0.234° and the FWHM of sample B was 0.211° which indicated that the crystallization quality of sample B was better than that of sample A. It also showed that the crystallinity of the film could be improved by the structure of double-layer prefabricated layer.
Figure 1. XRD pattern of CZTS thin films with different prefabricated layer structures.

Figure 2 showed the SEM images of the surface of CZTS thin films based on different prefabricated layer structures. It could be seen from the figure that the grain size of sample A was small (100~200nm), and the grain size of sample B was significantly increased (>1μm). This indicated that the double-layer prefabricated structure could promote the growth of CZTS grain.

Figure 2. SEM images of CZTS films with different preformed layer structures: (a) sample A; (b) sample B.

The cross-section morphology of the thin films were observed as shown in figure 3, which were in accordance with the planar-view results. No obvious grains were found on sample A prepared by single-layer prefabricated layer, which was more like a thin film stacked by little grains, indicating that the quality of the film was poor. The section of sample B had monolecular large grain morphology, which again proved that the double-layer prefabricated layer structure promoted the grain growth of CZTS thin film. This kind of large grain layer which ran through the top and bottom of the film as the absorption layer could effectively reduce the string resistance and carrier recombination probability of solar cells.

Figure 3. SEM images of CZTS thin film section of different prefabricated layers: (a) sample A; (b) sample B.
In order to study the influence of prefabricated layer structure on the longitudinal distribution of thin film elements, EDS line scanning test was used. The results were shown in figure 4. In order to reduce the interference of the bottom Mo electrode on the detection of S element signal, the EDS line scanning test of the cross-section was to sweep from CZTS thin film surface to a depth of 750nm. The Cu and Zn elements in sample A showed an obvious opposite trend of diffusion. The content of Zn on the surface of the film was much higher than that at the bottom of the film, while the content of Cu on the surface was lower than that at the bottom, which was consistent with the findings of J Zhong[10]. With the introduction of the double-layer prefabricated structure, the outward diffusion of Zn was inhibited due to the excess Zn amount on top. And the longitudinal distribution of other components were more balanced.

![Figure 4. EDS results of Cu, Zn, Sn and S elements in CZTS thin film with different prefabricated layers from surface to depths of 750nm: (a) sample A; (b) sample B.](image)

The formation of CZTS grain could be divided into two steps[11]. At lower temperature, metal elements began to diffuse and form their own binary sulfides. Firstly, Cu and Sn sulfides could react as follows:

$$\text{Cu}_2\text{S} + \text{SnS} \rightarrow \text{Cu}_2\text{SnS}_3$$  \hspace{1cm} (1)

When the temperature exceeded 480°C, the sulfide of Zn participates in the reaction to form CZTS, and the reaction was as follows:

$$\text{Cu}_2\text{SnS}_3 + \text{ZnS} \rightarrow \text{CZTS}$$  \hspace{1cm} (2)

Because the diffusion direction of Zn and Cu in sample A was opposite, and the single-phase stable chemical potential of CZTS was small[12]. The reaction of forming CZTS was difficult and the crystallinity of the film was poor. After the introduction of double-layer prefabricated layer structure, due to the increase of Zn content in the upper layer, the composition gradient of Zn and Cu in CZTS thin film became smooth, and an appropriate element ratio was provided for CZTS grain generation in the longitudinal direction, which facilitated the crystallization of the thin film. On the other hand, the excess Zn in the upper layer could promote reaction 2 and further improve the crystallinity of CZTS thin film. A low Cu-rich prefabricated surface could reduce the amount of Cu$_2$S remaining on CZTS thin film surface after vulcanization and help to reduce carrier recombination in solar cells[13].

Figure 5 showed the current density–voltage (J–V) curves of CZTS solar cells with different prefabricated layers. The specific photovoltaic performance parameters were summarized in table 1. Due to the poor crystallinity and serious recombination of carriers at the grain boundary, the open circuit voltage $V_{OC}$ and short circuit current density $J_{SC}$ of CZTS solar cells prepared by single-layer prefabricated layer are relatively low, resulting in only 0.25% battery conversion efficiency. With the introduction of double-layer prefabricated layer, the photoelectric performance of the solar cells was also improved due to the improvement of the crystallinity of the films. The grain size of sample B was larger than that of sample A, and the smaller grain boundary would help reduce carrier recombination and increase $V_{OC}$ and FF of solar cells. It could be seen from the cross-section (Figure 3(b)) that most of the longitudinal region of the film was a single crystal grain layer structure, which would help to reduce the series resistance of the battery and increase the JSC of the battery. Therefore, the conversion
efficiency $Eff$ of sample B reached 3.05%. In conclusion, the CZTS film with double-layer prefabricated structure had better performance than that with single-layer prefabricated structure.

![Current density–voltage curves of CZTS solar cells with different prefabricated layers.](image)

Table 1. Photoelectric performance parameters of CZTS solar cells with different prefabricated layers.

| Sample | $V_{OC}$ (mV) | $J_{SC}$ (mA·cm$^{-2}$) | $FF$ (%) | $Eff$ (%) |
|--------|---------------|----------------|---------|---------|
| A      | 155           | 7.21           | 22.37   | 0.25    |
| B      | 525           | 11.89          | 48.86   | 3.05    |

4. Conclusion
CZTS thin films based on single-layer and double-layer prefabricated structure were prepared by two-step method. The Cu and Zn elements in CZTS thin film with single-layer prefabricated structure showed an obvious trend of diffusion in opposite direction. With the introduction of the double-layer prefabricated structure with a Zn excess upper layer, the outward diffusion of Zn was inhibited, and the longitudinal distribution of the film components was more balanced. CZTS thin film with double-layer prefabricated structure had large grain size and good crystallization. The conversion efficiency of CZTS solar cell based on double-layer prefabricated structure was 2.80% higher than that of single-layer prefabricated structure. Therefore, the CZTS thin film with double-layer prefabricated structure could be used as the absorption layer to further improve the conversion efficiency of CZTS solar cell.

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