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Improvement in efficiency of solar cell by removing $Cu_{2-x}Se$ from CIGS film surface*

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CIGS thin films are deposited by sputtering and selenization. The synthesis of semiconducting polycrystalline thin films and characteristics of devices based on the CIGS absorbing layers are investigated. Their microstructures are characterized by x-ray diffraction and Raman spectroscopy. The results reveal that there exist metallic $Cu_{2-x}Se$ compounds in CIGS film surfaces and the compounds are thought to be responsible for the degradation of the open circuit voltage of solar cells. The optimization of selenization temperature profile and copper content in the precursor surfaces is studied, concluding that the conversion efficiency may be improved by removing metallic $Cu_{2-x}Se$ compounds from the surfaces of CIGS thin films.

Keywords: $Cu_{2-x}Se$, CIGS thin films, optimization of temperature profile
PACC: 8630J, 4280Y, 8610K

1. Introduction

Copper indium gallium diselenide (CIGS) thin films have shown considerable promise in being used as absorbing layers in high-efficiency solar cells. The highest conversion efficiency of solar cells made by NREL (National Renewable Energy Laboratory) of America is more than 19%. The control of band gap in $Cu(In,Ga)Se_2$ (CIGS) based solar cells is an interesting method to improve the performances of CIGS solar cells, so we adjust gallium concentration in CIGS film surface and its back to optimize the energy band gap grade. This method requires an increase in gallium content in the surfaces of CIGS films, but we find that $Cu_{2-x}Se$ compounds can occur in the surfaces of CIGS films and bring about a negative result, and we think them to be responsible for the degradation of open circuit voltage of solar cells.

In this paper, we report on an improvement in the efficiency of CIGS solar cells by removing $Cu_{2-x}Se$ compounds from the surfaces of CIGS thin films. The optimization of temperature profile and a reduction in copper content in a film surface are the key points. It is known that dipping in KCN solution is effective in removing Cu–Se compounds from CIGS film surfaces, and several researchers have successfully fabricated CIGS-based solar cells without Cu–Se compounds by use of this method.[1] However KCN is highly toxic. In this paper, we present a new method to remove the Cu–Se compounds from CIGS film surfaces. Firstly, the copper content in the precursor surface should be reduced in sputtering process; secondly, the fast heating rate and higher selenization temperature are used to eliminate Cu–Se compounds from the surfaces.

The absorptions of the CIGS layers are determined and compared with corresponding quantum efficiency (QE) measurements in order to obtain the optically related losses. The surface morphologies and crystalline phases are examined by scanning electron microscopy (SEM) and x-ray diffraction (XRD), respectively. The Cu–Se compounds in the surfaces of CIGS thin films are determined by Raman spectra. The composition of CIGS films is confirmed by x-ray fluorescence (XRF) measurements.

2. Experiment

In this study, device-quality $Cu(In,Ga)Se_2$ absorbing films were prepared by a relatively simple two-stage growth technique via various precursor struc-

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tures. First, a Mo back contact with a thickness of 800 nm was deposited on a soda-lime glass substrate by DC magnetron sputtering in Ar atmosphere. The soda-lime glass substrate was not heated during the sputtering deposition. The metallic precursors were deposited sequentially on Mo/glass substrate using Cu–Ga alloy and In targets by DC magnetron sputtering. These metallic precursors were then selenized with solid Se pellets in a vacuum furnace. Selenization was accomplished in a one-step fast heating process. The CIGS films were about 1.85 μm in thickness.

In order to investigate the state of Cu–Se compound in a CIGS film surface, we changed the Cu content in precursor surface in sputtering stage. The ratio of Cu:Ga in the whole precursor film was about 3:1 normally. We reduced the ratio of Cu:Ga down to 3:2 in the film surface. During selenization, a faster heating rate of 40°C/min was used to pass through a critical temperature range of 80–300°C quickly, and then a higher selenization temperature of 550°C and lower selenization temperature of 500°C were applied to study the state of Cu–Se compound in the film surface, because the Cu–Se compound was thought to be decomposed when temperature was over 530°C.

CIGS solar cells with a structure of Al / ZnO / CdS / CIGS / Mo / glass were fabricated. After selenization, a 50-nm-thick CdS film was deposited by chemical bath deposition (CBD) from an aqueous solution containing 0.015-M $CdSO_4$, 1.5-M NH_4OH and 0.75-M thiourea. A bilayer of ZnO films of 50-nm i-ZnO films and 700-nm n-ZnO films doped with Al_2O_3 was deposited by RF magnetron sputtering. Finally, a Ni–Al metal grid was deposited through an aperture mask. A total cell area of 1.2 cm^2 was defined by mechanically scribing. I/V curves of the solar cells were measured under standard AM1.5 global spectrum, 100-mW/cm^2 illumination at 25°C, and there was not any MgF_2 film as an anti-reflection coating on our solar cell surface.

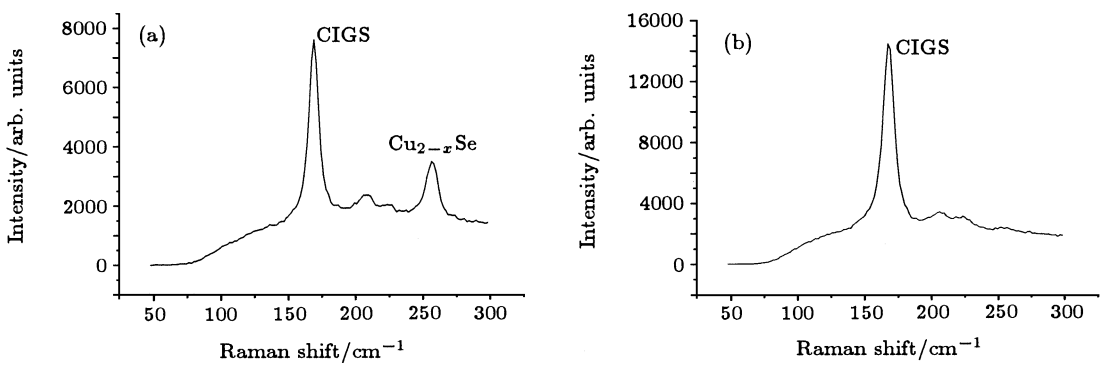


Fig.1. Raman spectra of the films prepared at different selenization temperatures.

3. Results and discussion

Raman spectroscopy has been used for the analysis of CIGS absorbing layers in recent years. Raman spectra of the films prepared at different selenization temperatures are shown in Fig.1. There is a small copper content in each surface of these two samples. Sample *a* was selenized at 500°C; while sample *b* at 550°C. A_1 mode of the lattice vibrations is indicated by a peak at 175cm^{-1} and is commonly observed in the I–III–VI_2 chalcopyrite compounds.[2] Only a sharp peak A_1 (CIGS) is observed for the film selenized at a higher temperature (sample *b*,); there is a $Cu_{2-x}Se$ peak at 265cm^{-1} in sample *a*, which reveals that the formation of $Cu_{2-x}Se$ is favoured over $CuIn_{1-x}Ga_xSe_2$ at a lower temperature. $Cu_{2-x}Se$ compound can deteriorate the performances of solar cells, which is proved by quantum efficiency and conversion efficiency of CIGS cells.

Figure 2 shows the Raman spectra of two $CuIn_{1-x}Ga_xSe_2$ films with the copper content being different in surfaces. These two samples were selenized at 550°C. In the surface of sample *a*, the atom ratio of Cu:Ga was about 3:2; while for sample *b* the atom ratio of Cu:Ga was about 3:1 at the surface. From these two figures, it is clearly seen that a $Cu_{2-x}Se$ peak at 260cm^{-1} is evident in the Raman spectra pattern of sample *b*. In our study, the intensity of the Raman spectrum peak approximately at 265cm^{-1} obviously decreases with the reduction of copper content in the surface of CIGS film. So we think that $Cu_{2-x}Se$ may be removed to a great extent by controlling the copper

atom fraction in CIGS film surface.

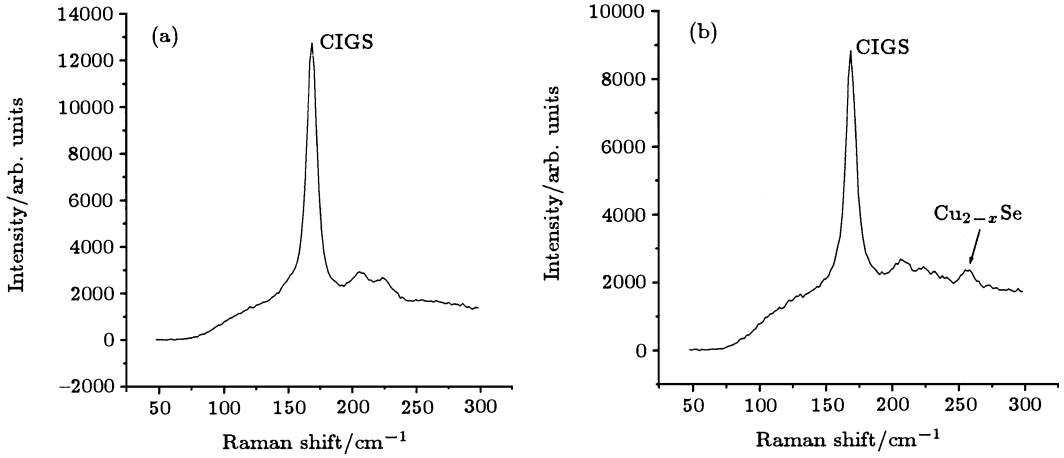


Fig.2. Raman spectra of the films prepared at different copper content in surfaces of CIGS films.

In the selenization, a one-step fast heating process was used. It has been reported that in a temperature range between 100°C and 300°C the formation of $Cu_{2-x}Se$ is favoured over $CuInSe_2$,[3] Once the former is formed, the thermodynamic force towards CIS formation is said to be very small due to high stability of the binary selenide. Subsequently, it seems to be necessary to pass through a critical temperature range of 80–300°C in a time as short as possible. Although the above was in contrast to the thermodynamic data cited earlier.[4] we decided to apply a heating rate of 40°C/min in order to reduce the thermal budget and prevent any possible negative effects.

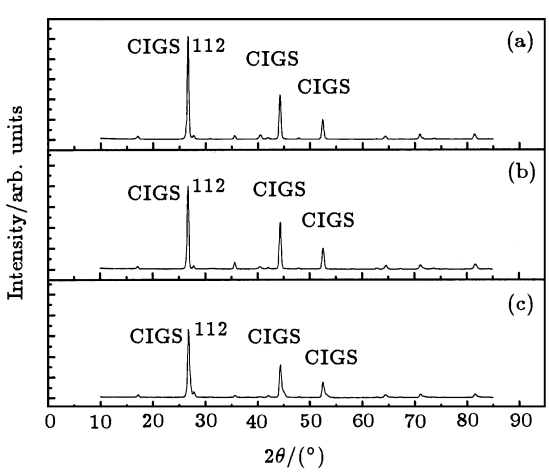


Fig.3. XRD patterns of CIGS thin films at selenization temperatures: 560°C (a), 530°C (b), and 500°C (c), separately.

Figure 3 shows typical patterns of CIGS films selenized at different temperatures. It can be seen that all of the films have the basic chalcopyrite crystal structure and very similar XRD patterns. But the diffraction peak 112 of sample *a* is the strongest among all the films, which means that the crystallization of CIGS thin films is better with $Cu_{2-x}Se$ compounds removed from surface at higher temperatures.

Figure 4 shows the quantum efficiency of CIGS solar cells: sample *a* and sample *b*. Sample *a* has a smaller copper content in surface of CIGS film; while sample *b* has a more copper content in surface of CIGS film. As can be clearly seen from the QE graphs, sample *a* has an improved response not only in the middle wavelengths but also in the short wavelengths, it is just slightly descending in long wavelengths. We know that the intensity responsive to the middle wavelength spectra is significant to the solar cell. The conversion efficiency of solar cell device made of sample *b* is about 8%, but the efficiency of solar cell made of sample *a* is over 9%.

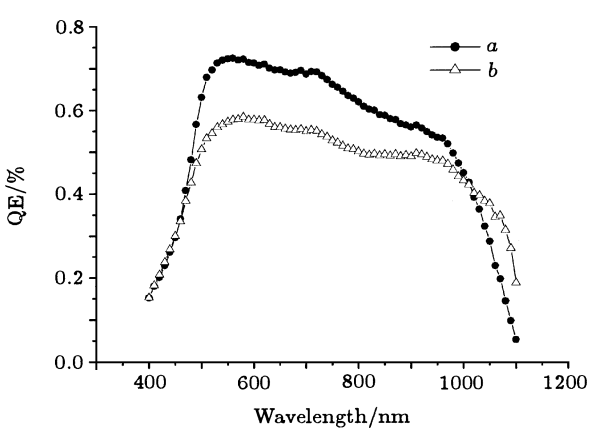


Fig.4. Quantum-efficiency curves for representative cells with different copper content in the surfaces.

The CIGS thin films, fabricated with proper composition precursor by optimizing the selenization process, have very smooth morphologies and single chalcopyrite phases. Figure 5 shows I/V curve of the CIGS solar cell. The best cell fabricated with an active area of 1.2 cm^2 was obtained at a higher selenization temperature of 550°C. Its conversion efficiency measured at AM1.5 was 9.4% in the absence of an anti-reflection coating.

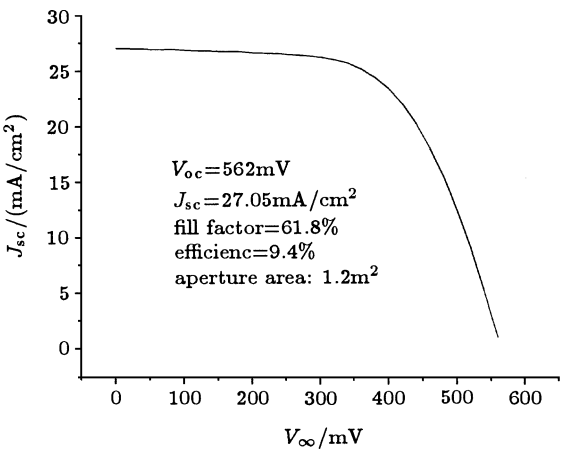


Fig.5. *I-V* characteristic of a 9.4% efficiency CIGS solar cell.

4. Conclusion

Many metallic precursors with different copper content in surfaces have been prepared, and many selenization temperature profiles have been applied. Based on the findings so far, it appears that the $Cu_{2-x}Se$ compounds have a great influence on CIGS solar cells, and they may be removed from the surfaces of CIGS thin films at a higher selenization temperature and fast heating rate before selenization; on the other hand, reducing the copper content in the CIGS film surface is also of considerably benefit to the removal of $Cu_{2-x}Se$ from CIGS films. The best CIGS films are obtained from precursors with the desired elemental concentration, selenized at 550°C for 30 min at a heating rate of 40°C/min, the efficiency of the best cell fabricated by optimizing the selenization process has achieved 9.4%.

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