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# The effects of Na on the growth of $Cu_2ZnSnSe_4$ thin films using low-temperature evaporation process[*]

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$Cu_2ZnSnSe_4$ (CZTSe) absorbers were deposited on borosilicate glass substrate using the low-temperature process, and different Na incorporation methods were applied to investigate the effects of Na on the CZTSe growth. Na was diffused into some of the absorbers after growth, which led to strongly improved device performance compared with Na-free cells. With the post-deposition treatment, the effect of Na on CZTSe growth was excluded, and most of Na was expected to reside at grain boundaries. The conversion efficiency of the completed device was improved due to the enhancement of open circuit voltage and fill factor. The efficiency of 2.85% was achieved at substrate temperature as low as 420 °C.

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In recent years, earth-abundant $Cu_2ZnSnSe_4$ (CZTSe) solar cells have gained a lot of attention within the photovoltaic community[1-4]. This kind of absorber derives from the $Cu(In,Ga)Se_2$, where every two In or Ga atoms are replaced by a Zn or Sn atom[5]. As is well known, CIGS absorbers for high efficiency cells require the incorporation of typically 0.1 at.% Na. The benefits of Na incorporation in CIGS solar cells were observed for enhancement of open circuit voltage ($V_{oc}$) and fill factor ($FF$)[6]. Furthermore, Na incorporation process is usually used in flexible CIGS solar cells on polyimide (PI) substrate. In contrast to rigid soda-lime glass substrates, the growth temperature of CIGS is lower owing to the limited thermal stability of PI. Also the lower-temperature process can reduce the energy consumption and hence decrease the manufacturing costs[7]. However, the effects of Na on the structural and electrical properties of CZTSe films by using a low temperature have not been reported. Thus we investigate different Na incorporation strategies for CZTSe growth at low substrate temperature in this letter.

A molybdenum back contract layer was deposited on borosilicate glass by RF magnetron sputtering method and the typical thickness is around 1 μm. The CZTSe films were deposited on Mo-coated borosilicate glass which was free from Na by co-evaporation process. Four sources of elements Cu, Zn, Sn and Se were evaporated simultaneously at the substrate temperature of 420 °C. The typical thickness of the CZTSe films is 1.5 μm.

Na was incorporated in different stages of the process: (1) ~20-nm-thick NaF precursor was evaporated on the Mo layer prior to the CZTSe deposition (Na_PRE); (2) After the CZTSe growth, ~20-nm-thick NaF was evaporated onto the cooled absorber film, which was followed by an annealing process to obtain Na-contained CZTSe film (Na_PDT).

In addition, a CZTSe thin film without Na (Na_0) was fabricated as a reference. Solar cells were then completed by the chemical bath deposition of a 50-nm-thick CdS buffer layer on the absorber layers, followed by the deposition of 100-nm-thick i-ZnO and 1 000-nm-thick B-doped ZnO layers using metal-organic chemical vapor deposition (MOCVD). The CdS (2.4 eV) buffer layer can moderate the bandgap between CZTSe (1.1 eV) and ZnO (3.3 eV) to reduce the conduction band offset. The role of i-ZnO can be explained by improving the locally non-uniform electronic quality of the CZTSe layer that can be modeled by a parallel diode with higher recombination current. As a result, the influence of these non-uniform regions on the device performance is reduced by the series resistance of i-ZnO. This series resistance has a negligible effect on the performance of the dominant part of the device area[8]. The Al grid was evaporated and the cell area was delineated by mechanical scribing to give an area of 0.34 $cm^2$, resulting in a cell structure of borosilicate glass/Mo/ CZTSe/CdS/ i-ZnO/ZnO:B/Al grid[9]. Structural propertiese

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were determined using the X-ray diffraction (Rigaku, ATX-XRD) with Cu $K_\alpha$ radiation ($\lambda$=1.540 5 Å). The scanning electron microscopy (SEM) images were recorded on a jeol JSM 6700F. Electrical characterizations of the films were performed by Hall effect measurement, where the CZTSe film on borosilicate glass without the Mo back contact was used. The current-voltage (*J-V*) measurements were performed under the standard AM1.5 spectrum with 100 mW/cm$^2$ at 25 °C. The light source of solar simulator was calibrated by a standard single crystal Si solar cell.

Fig.1 shows the XRD patterns of CZTSe films with and without Na-precursor. The two CZTSe films show three peaks related to kesterite compounds, a strong peak of (112) reflection, a weak peak of (220) reflection, and a peak of (312) reflection. The average grain size (*D*) of a given crystal plane can be estimated from the full width at half-maximum (*FWHM*) of the XRD spectra using Scherrer's formula[10]

$$D=\frac{0.9\lambda}{\beta\cos\theta}, \qquad (1)$$

where $\lambda$ is the X-ray wavelength, and $\beta$ is the *FWHM* of the film diffraction peak at $2\theta$, where $\theta$ is the Bragg's diffraction angle. As can be seen from the expanded XRD patterns in Fig.1, the Na-PRE sample has larger *FWHM* value, which means that the CZTSe film grown on Na-free glass exhibits better crystal quality than that on Na-precursor.

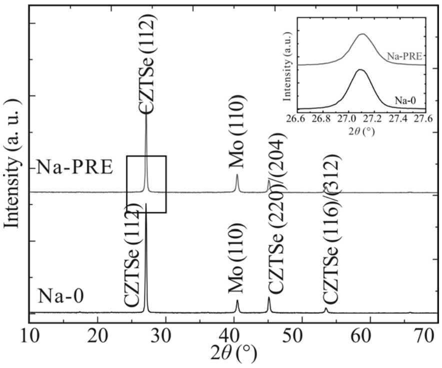


**Fig.1 XRD patterns of CZTSe films with and without Na-precursor**

The SEM images of the samples Na_PRE and Na_0 are shown in Fig.2. The two CZTSe samples were fabricated in one deposition process. An important structural property affected was the grain size in the film. As can be clearly seen, the films grown on borosilicate glass without Na-precursor have larger grain size. These results are consistent with our XRD results. Researches show that Na is found at the surface and grain boundaries (GBs) rather than in the bulk[11,12]. Thus it is proposed that Na-containing compounds reside at the surface and GBs of CZTSe, and act as a diffusion barrier for constitution atoms. The barrier caused by Na at GBs could hinder the exchange of atoms across GBs, which slows down the grain growth.

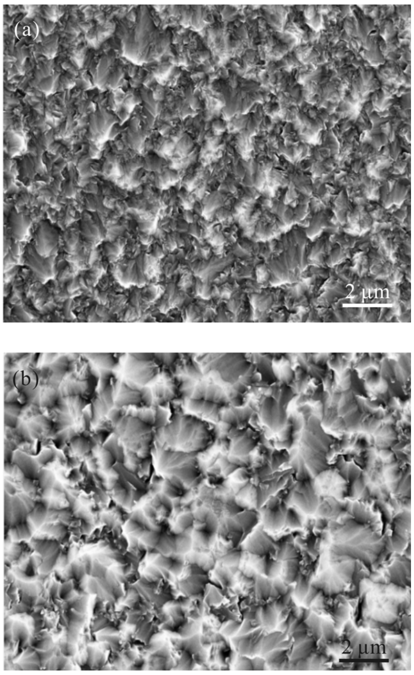
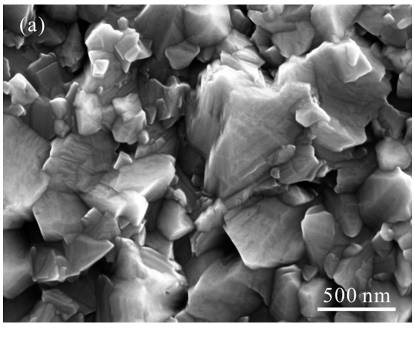


**Fig.2 SEM images of the CZTSe films grown on borosilicate glass: (a) With NaF precursor; (b) Without Na precursor**

To solve the problem mentioned above, post-deposition treatment (PDT) was studied. Fig.3 shows the SEM images of the samples Na_0 and Na_PDT. No obvious difference can be observed for CZTSe films with and without Na incorporation. In the case of the Na_PDT film, no Na was included during the CZTSe growth. Since the diffusion along GBs is generally much faster than that into grains, the absorber growth is not affected by Na. And the final film presents larger grain sizes, which is like the case in the Na_0 film.

The measurements of resistivity ($R_S$) and carrier concentration ($N_P$) were performed by the Van Der Pauw technique[13]. Tab.1 lists the Hall effect results of CZTSe films without Na and with PDT Na incorporation. The Na-free CZTSe films show a very high resistivity, and inversely $R_S$ can be decreased. When the additional Na was supplied, the $N_P$ can be increased by reducing certain deep recombination centers[14]. Similarly, the enhancement of the net carrier concentration and improved conductivity by Na incorporation have been reported by other groups[15]. The mobility increases with Na incorporation, which might be related to the passivation of GBs.



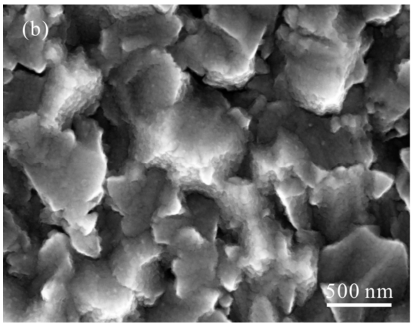


**Fig.3 SEM images of the CZTSe films grown on borosilicate glass: (a) Without Na; (b) With addition of Na by means of PDT**

**Tab.1 The resistivity and carrier concentration for CZTSe films with and without Na by Hall effect measurements**

| Resistivity ($\Omega\cdot$cm) | Mobility (cm$^2$/V$\cdot$s) | Carrier concentration (cm$^{-3}$) | Na |
|---|---|---|---|
| 129.50 | 0.59 | $8.15\times10^{16}$ | Without |
| 19.14 | 2.64 | $1.24\times10^{17}$ | PDT |

Fig.4 shows *J-V* curves of CZTSe solar cells without Na and with PDT Na incorporation. The two CZTSe films were obtained under the same deposition conditions. A conversion efficiency of 2.85% for CZTSe solar cells with Na is demonstrated and the *J-V* parameters are as follows: open circuit voltage is $V_{oc}$=226.0 mV, short circuit current density is $J_{sc}$=23.6 mA/cm$^2$ and fill factor is *FF*=53.6%. Compared with the device with Na, the Na free solar cell shows lower efficiency of 1.47% ($V_{oc}$=169.7 mV, $J_{sc}$=21.8 mA/cm$^2$ and *FF*=39.7%). The enhanced performance by using PDT Na incorporation can be explained by the improvement of electrical properties of CZTSe films, as the results by Hall measurements. The increased hole density leads to higher build-in voltage, and consequently higher $V_{oc}$. The *FF* is dominated by the series resistance and shunt resistance. In this case, the CZTSe cell with Na incorporation has lower bulk resistance from Tab.1, which improves the *FF* by decreasing the series resistance.

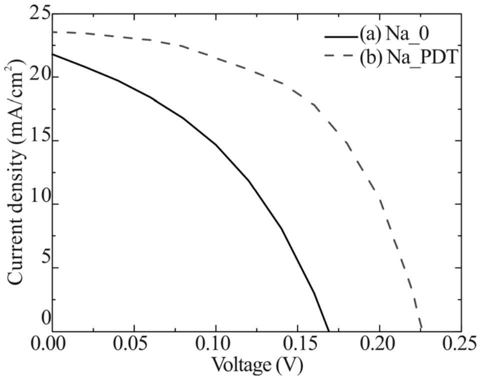


**Fig.4 *J-V* characteristics of CZTSe solar cells with and without Na incorporation**

In summary, Na can decrease the grain size of CZTSe films at low substrate temperature. By in-diffusion of Na into Na-free CZTSe absorbers, we excluded the influence of Na on CZTSe growth. Post-deposition-treated CZTSe films exhibit increased net carrier concentration and conductivity compared with the Na-free CZTSe films, while the microstructural properties of the layers are not affected. A strong improvement of cell efficiency is achieved due to the increased $V_{oc}$ and *FF*. Efficiency of 2.85% can be achieved at substrate temperature of 420 °C with Na incorporation by post-deposition.

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