1. Introduction

Selenide kesterite semiconductor Cu$_2$ZnSnSe$_4$ (CZTSe), sulfide (CZTS) and sulfo-selenide (CZTSSe) counterparts have been considered as potential absorber materials in thin film solar cell [1] owing to their high absorption of solar light [2], to the tunable band-gap energy $E_g$ falling in the optimal range for solar energy conversion [3] and due to the relatively high abundance of Cu, Zn and Sn compared to In and Te used in other thin film photovoltaic conversion [4] and due to the relatively high abundance of Cu, Zn and Sn compared to In and Te used in other thin film photovoltaic conversion [4]. The interstitial incorporation of Na in the kesterite lattice is also favourable substitutional defects [23–25] which are expected not to form deep-defects and should thus be benign for device efficiency. The interstitial incorporation of Na in the kesterite lattice is also likely due to its low formation energy [23]. The possibly detrimental substitutional deep-defects are Sn related and show a high formation energy [24].

The two main strategies to incorporate alkali elements in kesterite is either to supply them during kesterite synthesis [5–7,11,12,16,19,22] or after the growth as a post-deposition treatment (PDT) [11,18]. Here we investigated PDT of CZTSe thin films using NaF and KF at low temperature (100 ◦C). From a theoretical point of view NaCu, NaZn and KCu are the most favourable substitutional defects [23–25] which are expected not to form deep-defects and should thus be benign for device efficiency. The interstitial incorporation of Na in the kesterite lattice is also likely due to its low formation energy [23]. The possibly detrimental substitutional deep-defects are Sn related and show a high formation energy [24].

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2. Experimental details

2.1. CZTSe growth and post-deposition treatment

CZTSe thin films were grown on a Mo-coated soda lime glass (SLG) substrate heated at 470 ◦C in a molecular beam epitaxy system

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by co-evaporation of Cu, Zn, Sn, SnSe and Se. More details about the process can be found in Refs. [26,27].

An optional two step PDT was applied to the CZTSe thin films. The first step consisted of an approximately 5 nm thick alkaline fluoride layer deposition by electron beam evaporation. The second step was an annealing in a tube furnace at atmospheric pressure and 100 °C for 1 h under a N₂ atmosphere. Prior to solar cell processing, the samples, which underwent a PDT, were washed with deionized water.

2.2. Solar cell preparation

After a surface etching of the CZTSe thin films using KCN solution, solar cells were prepared by chemical bath deposition of a 50 nm thick CdS buffer layer [28]; followed by the deposition of an intrinsic ZnO layer (80 nm thickness) and a transparent conductive ZnO layer (380 nm thickness) by non-reactive magnetron sputtering [29]. Metallic contacts were achieved by a Ni/Al grid. 6 to 8 solar cells of about 10 × 5 mm² were tested for each preparation route.

2.3. Characterization

The global composition of the CZTSe films was measured by Energy dispersive X-ray spectroscopy using an accelerating voltage of 20 kV. Secondary ion mass spectrometry (SIMS) depth profiling was used to characterize the solar cells. The samples were bombarded by a 1 keV Cs⁺ beam. With these conditions, the elements of interest were detected as MCs+ clusters (M = Na, K, Zn, O, C, S, Se, Cu, Zn, Sn, Mo and F) to allow a quantitative comparison of Na and K contents between samples. A cold mirror halogen lamp calibrated with a silicon reference solar cell was used to illuminate the cells during current-voltage characteristic measurements (JV) and temperature dependent JV (JVT). Admittance spectroscopy (AS) recorded without bias voltage and capacitance-voltage measurements (CV) were performed with a precision LCR meter using 30 mV modulation amplitude. The solar cells were placed in a closed cycle He cryostat for temperature dependent measurements (JVT, AS or CV). For CV measurements, the temperature (100–130 K) and the frequency (1 kHz) were set according to Ref. [30]. The EQE was measured using lock-in technique using a monochromated light source calibrated with Si and InGaAs photodiodes. The PL was measured at room temperature with an InGaAs detector under a continuous red excitation of 6.6 kW·m⁻².

3. Results and discussion

Untreated absorbers, absorbers treated with NaF and absorbers treated with KF were investigated. Those sets will hereafter be referred to as "Std", "NaF" and "KF" respectively. The absorber film composition prior to any PDT was Cu-poor \( \text{Cu}_{\text{poor}} \), 0.8 and Zn-rich \( \text{Zn}_{\text{rich}} \), 1.27 which is the composition leading to the most efficient CZTSe based solar cell [4,8].

The SIMS profiles of Na and K are shown in Fig. 1 where the solar cells were sputtered from the top (ZnO, CdS) to the SLG substrate. NaF-PDT did not significantly change the Na incorporation into the film which is mainly controlled by Na diffusion from the SLG. Nonetheless Na-PDT could possibly change the Na concentration at the very top of the CZTSe surface and at the grain boundaries without changing the SIMS profile because of the large amount of Na already present in the film. KF–PDT was found to effectively increase K concentration throughout the CZTSe film.

The JV parameters of the solar cells are plotted in Fig. 2. PDT with NaF and KF increased the average conversion efficiency ef from 6.4% to 7.8% and 7.7%, respectively. It is interesting to notice that the PDT without supply of alkaline fluoride (AW) has a detrimental effect on the eff, therefore the improvement seen with NaF-PDT or KF-PDT can be attributed unambiguously to the presence of alkaline fluoride. For both NaF-PDT and KF-PDT the improved eff is resulting from an increase in all solar cell parameters such as fill factor ff, \( V_{\text{oc}} \) and \( J_{\text{sc}} \). The ff rise under Na doping has been attributed to the increase of kesterite conductivity [16]. The \( J_{\text{sc}} \) enhancement is due to better collection of carriers generated by long-wavelength light, as seen in EQE (not shown) which can partly be attributed to a change in the space charge region width (derived from not shown CV) from 145 nm to 206 nm and 213 nm respectively for Std, NaF and KF. The PDT effect on \( J_{\text{sc}} \) is more pronounced for KF, in agreement with the significant increase in \( J_{\text{sc}} \) reported after K doping of CZTS [22]. The \( V_{\text{oc}} \) improvement by both PDT goes together with a drop of the reverse saturation current density, in average \( J_{0} = 1.05 \times 10^{-5}, 3.7 \times 10^{-6} \).
and $3.7 \times 10^{-6} \text{mA} \cdot \text{cm}^{-2}$, and a decrease in diode quality factor in average $A = 1.75$, 1.60 and 1.52 for Std, NaF and KF respectively. In addition, for KF-PDT an increase of the shunt resistance promotes the increase in $V_{oc}$ (in average $R_{sh} = 147, 141$ and 169 $\Omega \cdot \text{cm}^{-2}$ for Std, NaF and KF respectively).

Fig. 3 (a) shows the evolution of the $V_{oc}$ with the temperature under 1 sun illumination. Within the one diode model, assuming that $A$ and the reference current density are temperature independent and neglecting shunt conductance and voltage dependence of the carrier collection, the linear extrapolation of $qV_{oc}$ ($q$ being the elementary charge) to 0 K gives the activation energy of the main recombination path $E_{a}^{\text{rr}}$. For the limiting case of bulk recombination, $E_{a}^{\text{rr}}$ is expected to equal $E_g$. However, for kesterite, due to potential or $E_g$ fluctuations, $E_{a}^{\text{rr}}$ should be compared to the PL signal [26,32] which gives the energy of radiative bulk recombinations. The values of $E_{a}^{\text{rr}}$ of 844 meV, 849 meV and 858 meV for Std, NaF and KF samples, respectively, agree within measurement errors with the energy of the maximum of the PL spectra, plotted in Fig. 3 (b), found at 854 meV, 855 meV and 847 meV respectively, indicating that the main recombination occurs in the bulk. The value of $E_{a}^{\text{rr}} = 858$ meV measured for the KF sample is less accurate due to a slight variation of $\Delta V_{oc}/dT$ (bended curve). It is not possible to conclude on the increase in $E_{a}^{\text{rr}}$ seen after both post-deposition treatments as the variation is within measurement error. If confirmed such increase would have a positive effect on the $V_{oc}$.

Std and NaF samples show the same normalized PL spectrum. Because the PL at room temperature is mainly due to band-tail to band-tail recombination, the nature of the tail seems not to be changed by the Na-PDT, as could be expected from SIMS measurement since there is no incorporation of additional Na in the bulk of the film. The improved radiative efficiency (being the ratio between radiative recombination and radiative recombination plus non-radiative recombination and indicated by a higher PL intensity) seen after NaF-PDT could be attributed to a passivation effect of Na at the CdS/CZTSe interface or at the grain boundaries. The increase in radiative efficiency by factor of 1.2 seen after NaF-PDT cannot account entirely for the 28 mV difference in $V_{oc}$ reported in Fig. 2 (c) since the change in quasi Fermi level splitting due to higher PL intensity is only $\Delta \mu \approx k_{B}T\ln(1.2) \approx 5$ meV. The red-shifted PL and the higher low-energy wing after KF-PDT suggests a higher density of tail or defect states possibly due to the incorporation of K in the bulk of the absorber. Despite this, KF-PDT has a beneficial effect on the radiative efficiency and thus on the $V_{oc}$. The red-shifted PL and the lower radiative efficiency of KF when compared to NaF explains why KF shows lower $V_{oc}$ even though KF devices show improved $J_{0}$, $A$ and $R_{sh}$.

From Fig. 3 (c) (showing the Tauc’s plot derived from IQE data), since all linear extrapolations cross the energy axis at the same position, one can conclude that $E_{g}$ was not modified by the PDT and therefore cannot account for the $V_{oc}$ difference, $E_{a}^{\text{rr}}$ variations or PL shifts.

Capacitance spectra plotted in Fig. 4 show one main drop when decreasing the temperature and increasing the frequency which have been attributed to carrier or mobility freeze-out [26]. The capacitance spectra were fitted using Weiss method according to Ref. [33] and the extracted apparent defect densities are presented in Fig. 4. The higher activation energy of defects measured for the KF sample could possibly be due to a deeper acceptor level, that would increase the hole Fermi level in the band gap [16] thus limiting the $V_{oc}$ improvement. These defects deeper in the band gap could also contribute to the higher defect density observed by PL. On the contrary, for NaF sample we observe shallower defects than in the Std sample; these shallower acceptors would help to further enhance the $V_{oc}$.

4. Conclusion

We applied low temperature (100 ºC) post-deposition treatments with NaF and KF to CZTSe. KF-PDT increased the K concentration in the CZTSe film, whereas the change in Na could not be resolved by SIMS. The changes of Na concentration induced by NaF-PDT are small compared to the Na level already incorporated during the CZTSe growth as those changes might be limited to interfaces and grain boundaries. Both PDT lead to higher solar cell conversion efficiency driven by a simultaneous increase in $J_{sc}$, $V_{oc}$ and $F$. The $V_{oc}$ improvement is attributed to a decrease in $A$ and $J_{0}$ and to a better radiative efficiency. The best $V_{oc}$ improvement was obtained with NaF-PDT which showed the highest radiative efficiency and the lowest activation energy of doping defects, whereas for KF-PDT the $V_{oc}$ improvement was limited by red-shifted PL, larger band-tail state density and deeper defects. The highest $J_{sc}$ was achieved with KF-PDT associated with larger space charge region width.
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