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Effect of ammonium sulfide treatments on the surface properties of $\text{Cu}_2\text{ZnSnSe}_4$ thin films

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ABSTRACT

In this contribution, we report on the impact of ammonium sulfide ($(\text{NH}_4)_2\text{S}_x$) chemical treatments done at room temperature on the surface properties of $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) thin film. The first approach is based on the immersion of the absorber layer in a $(\text{NH}_4)_2\text{S}_x$ solution (20 wt.%). This method results in the preferential etching of Se, Sn and Zn atoms from the absorber surface. After a treatment time of 1 min, the performances of the solar cells are found to be improved. The second approach consists in the exposure of the CZTSe layer to ammonium sulfide vapors. In this case, it was found that the progressive sulfurization of the surface of the absorber leads to the decomposition of the CZTSe phase into $\text{Sn}(\text{S,Se})_x$ and Se^0 secondary phases. As a consequence, the short circuit current of the corresponding solar cells is reduced.

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1. Introduction

$\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTSSe) solar cells have been extensively studied during the last decade to offer a reliable and low-cost alternative to other inorganic thin film photovoltaic technologies such as $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ (CIGSSe) and CdTe based devices. The p-type CZTSSe compounds have a direct band gap that can be tuned between 1 and 1.5 eV depending on the $[\text{S}]/([\text{S}] + [\text{Se}])$ ratio, leading to high absorption coefficients [1,2]. Using a standard CZTSSe/CdS p–n heterojunction, a record efficiency of 12.6% has been achieved [3]. A higher record up to 12.7% has been further reached by using a hybrid CdS/ In_2S_3 emitter [4], indicating that the engineering of the heterojunction properties could be a leverage to achieve higher efficiency. In the meantime, cleaning the CZTSSe surface using etchants such as KCN, HCl or a bromine-methanol solution was also found to considerably improve the efficiency of the devices when using an absorber layer that is covered with secondary phases (such as Se^0 , $\text{Zn}(\text{S,Se})$, $\text{Cu}_x(\text{S,Se})$, $\text{Sn}(\text{S,Se})_x$ or $\text{Cu}_x\text{Sn}(\text{S,Se})_3$) [5–7]. It was also demonstrated that dipping air-exposed CZTSSe samples into a KCN solution reduces the surface

recombination rate of the aged absorber [8]. As for any semiconductor intended to solar cell application, all these studies have shown that the properties of the absorber/buffer layer region and the quality of the CZTSSe surface are key factors for the development of high performance kesterite solar cells.

Applying a chemical treatment step is a simple route to control the surface properties of a semi-conductor. Many specific procedures were implemented in the past to passivate, to etch or/and to modify the composition of photovoltaic absorber such as CIGSSe [9–12], CdTe [13,14], Si [15,16] or III–V compounds [17,18]. Among others, the passivation methods based on ammonium sulfide $(\text{NH}_4)_2\text{S}_x$ developed for III–V semiconductors (i.e., GaAs, InP, etc.) were found to be particularly successful to stabilize the absorber surface [19]. After such treatment, native oxides, together with a few monolayers of the absorber surface, are removed and the fresh III–V surface is covered with a monoatomic layer of sulfur which has no dangling bonds, preventing the surface re-oxidation of the material [20]. This passivation treatment can be applied either by immersing the sample in an ammonium sulfide solution, or by exposing the surface sample to the vapors of the $(\text{NH}_4)_2\text{S}_x$ solution in a closed environment [21]. More recently, ammonium sulfide solution was used as a safe alternative to KCN for etching Cu_xSe secondary phases from the surface of CIGSe absorber [22]. According to Xie et al. [23], this chemical compound can also etch $\text{Sn}(\text{S,Se})$ clusters on the

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surface of CZTSe layer, by dipping the absorber into the $(\text{NH}_4)_2\text{S}_x$ solution for 1 min.

In this work, we report on the impact of both liquid and vapor-based ammonium sulfide treatments on the surface properties of $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) thin films synthesized by a two-step process. A detailed analysis, consisting of chemical, physical and electrical measurements, was carried out on the related solar cells.

2. Experimental details

2.1. Synthesis of CZTSe absorber

The CZTSe absorber layers were synthesized using a sequential DC-sputtering of CuSn, Zn and Cu onto molybdenum-coated soda lime glass substrates. The stack of the metallic layers was then annealed for 15 min at 450 °C under a continuous flow of diluted H_2Se (10%) in N_2 . Further details about the synthesis of the CZTSe layer can be found in [24]. In order to remove most of the secondary phases from the surface of the absorber prior to the ammonium sulfide vapors treatment, the CZTSe thin films were immersed for 30 s in a KCN (5 wt.%)/KOH (0.5 wt.%) solution, rinsed in deionized water (DIW) and then dried using a N_2 flow.

2.2. Ammonium sulfide treatments

Two procedures involving the use of pure ammonium sulfide solution (20 wt.%) at room temperature were investigated. While the first procedure is based on the immersion of the CZTSe sample in the solution (see [22] for further details), the second method uses the vapors of the solution to modify the surface of the samples. In this case, the absorber samples were first mounted on the cover of a 50 mL beaker using a double-face carbon tape, while 25 mL of a fresh $(\text{NH}_4)_2\text{S}_x$ solution was poured into the beaker. To start the surface treatment, the cover was placed over the top of the beaker, in order to orient the surface of the sample downward toward the solution. The beaker was progressively filled by the vapors originating from the $(\text{NH}_4)_2\text{S}_x$ solution. According to selected-ion flow-tube mass spectrometry (SIFT-MS) measurements performed on these vapors, the gas phase consists mainly of NH_3 (190 mg/m³) and H_2S (5.3 mg/m³). To stop the treatment, the cover was simply removed from the beaker.

2.3. Solar cell processing

For the CZTSe absorber layer treated in liquid ammonium sulfide, the solar cells were directly completed after the treatment with a 50 nm thick CdS layers grown by chemical bath deposition using a cadmium sulfate (0.1 M)-ammonia (4 M)-thiourea (0.4 M) aqueous solution. A ZnO (120 nm)/ZnO:Al (AZO) (250 nm) bilayer was then deposited using RF-magnetron sputtering in pure Ar plasma without applying any intentional heating to the substrate. For the CZTSe absorber layer treated in ammonium sulfide vapors, the standard CdS layer could not be deposited since the change at the surface of the absorber induced by the treatment altered the deposition of the buffer (i.e., formation of a yellow-brown precipitate at the surface of the absorber). Therefore, the ZnO/AZO bilayer was directly deposited on the kesterite absorber. Finally, the fabrication of the solar cells was completed by deposition of Ni/Al front contacts on the AZO film by e-beam evaporation. The standard size of the solar cells is 0.5 cm².

2.4. Characterization

To evaluate the etching rate, inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were performed on $(\text{NH}_4)_2\text{S}_x$ solutions (10.0 mL) in which $1.0 \times 1.0 \text{ cm}^2$ CZTSe samples were immersed for different durations. The Se, Cu, Zn and Sn standard solutions used for the calibration were prepared in DIW. The

morphology of the films was characterized using Jeol 7600 scanning electron microscope (SEM) at an accelerating voltage of 5 kV. The surface chemical state was probed using X-ray photoelectron spectroscopy (XPS) (AXIS Nova, Kratos, monochromatic Al K α X-ray source, base pressure in the analysis chamber: 10^{-8} Pa). All the samples were analyzed in the same conditions. The energy scale was calibrated using C 1s peak position (284.6 eV). The quantification carried out by XPS is based on the following elements and RSF: Cu 2p_{3/2} (RSF = 3.55), Sn 3d_{5/2} (RSF = 4.73), Zn 2p_{3/2} (RSF = 3.73), Se 3d (RSF = 0.393) and S 2p (RSF = 0.668). Therefore, one must carefully consider the absolute atomic ratios calculated from the XPS measurements, as the analysis depth differs from one element to another. Finally, the cell performances were compared using current-voltage (I-V) measurements (Wacom Solar Simulator System, with an AM1.5G spectrum with an illumination density of 1000 W/m² and a Keithley 2600 Source meter for curve tracing).

3. Results and discussion

3.1. CZTSe layers treated in liquid phase ammonium sulfide

Fig. 1 shows the evolution of the concentrations of Cu, Zn, Sn and Se species in the aqueous $(\text{NH}_4)_2\text{S}_x$ solutions after immersion of a Cu-poor CZTSe sample ($[\text{Cu}]/([\text{Zn}] + [\text{Sn}]) = 0.85$, $[\text{Zn}]/[\text{Sn}] = 1.12$, as measured

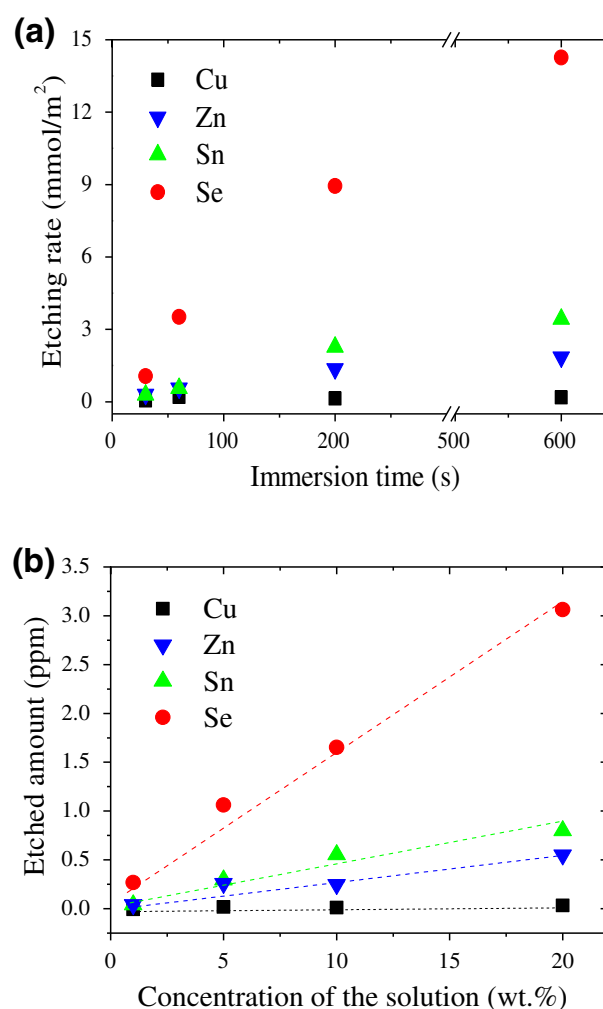


Fig. 1. Evolution of the etching rates of Cu, Zn, Sn and Se atoms from CZTSe samples in $(\text{NH}_4)_2\text{S}_x$ solution as a function of: (a) the immersion duration while fixing the solution concentration to 20 wt.% and (b) the solution concentration while fixing the duration to 60 s.

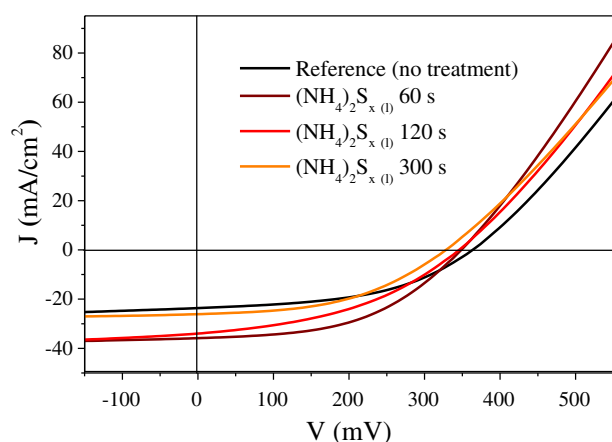


Fig. 2. I-V curves of CZTSe/CdS/ZnO-based solar cells prepared with absorber treated for different times in ammonium sulfide solution in liquid phase.

by ICP-AES). The analysis were recorded for different immersion times (i.e., 30, 60, 200 and 600 s) in a 20 wt.% concentrated solution (Fig. 1(a)), and for different ammonium sulfide concentrations (i.e., 1, 5, 10 and 20 wt.%) after an immersion time of 60 s (Fig. 1(b)). Overall, one can clearly observe that this chemical treatment leads to the removal of Se, Sn and Zn atoms from the CZTSe surface. The proportion in etched Se:Sn:Zn remains relatively constant (atomic ratio close to 6:2:1) for the different immersion durations and $(\text{NH}_4)_2\text{S}_x$ concentrations. Although this observation may confirm the etching of the SnSe secondary phase as described in [23] for CZTSe thin films, the high etched amount of Se as well as the loss in Zn from the absorber surface suggest that other secondary phases such as Se^0 and ZnSe could also be removed after such a treatment. However, in our case, the quasi-linear

evolution of the concentrations of Se, Sn and Zn atoms in the ammonium sulfide solution as a function of the immersion duration and the high amounts of elements removed from the CZTSe surface rather show that the atoms present in the solutions are the products of a preferential etching of the CZTSe. This effect would be comparable (although more pronounced) to the impact of the KCN/KOH solution on the surface properties of CZTSe thin films as described in [6], where a long immersion duration in KOH is found to selectively etch Se, Sn and Zn from the absorber surface, leading to the formation of a Cu-rich shell at the top of the CZTSe grains. Further ICP-AES measurements (not presented here) carried out on ammonia solution (1 M) after immersion of a CZTSe samples also revealed the presence of Se, Sn and Zn elements in the solution, although in lower concentrations than in the case of ammonium sulfide. Therefore, it could be that the degradation of the CZTSe layer obtained in this case is due to its exposure to an alkaline medium.

In Fig. 2, the I-V curves measured on a series of four samples using the same CZTSe absorber immersed for different times (i.e., 0, 60, 120 and 300 s) in a 20 wt.% ammonium sulfide solution are presented. The short circuit (J_{sc}) of the device is first improved after a short treatment time of 60 s while the value of the series resistance (R_s) decreases, likely due to the cleaning of the absorber surface from secondary phases. Consequently, the efficiency of the device increases from 4.0% to 6.0% when using a liquid ammonium sulfide treatment of 1 min on the absorber. For longer immersion durations of the absorber in the ammonium sulfide solution (i.e. 120 s and 300 s), the J_{sc} decreases drastically. Meanwhile, the open circuit voltage (V_{oc}) values progressively decrease from 363 mV to 327 mV when increasing the treatment duration from 0 to 300 s, indicating an overall degradation of an interface. In this case, it can be due to the increase of the Cu content at the CZTSe/CdS junction coming from the preferential etching of Se, Sn and Zn atoms from the CZTSe surface after treatment. Both effects have been also observed after KCN/KOH treatment [6], which tend to confirm that similar

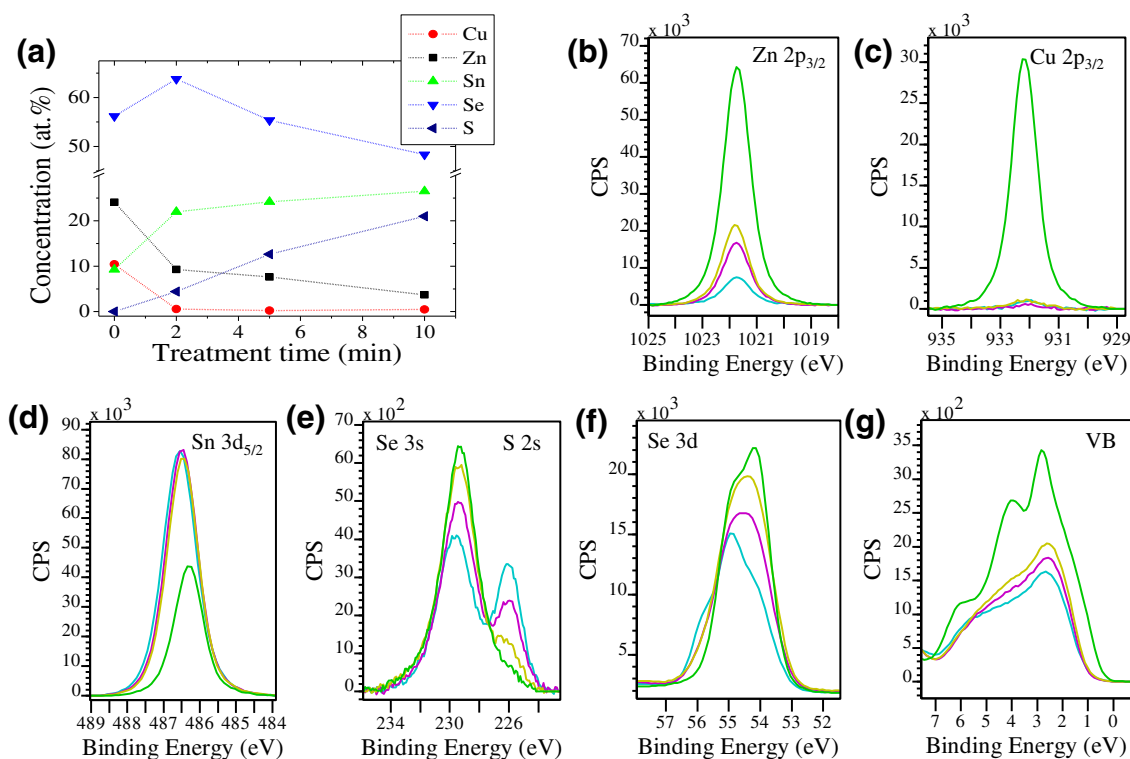


Fig. 3. (a) Evolution of the atomic concentrations (as deduced from XPS measurements) of the elements present at the surface of the CZTSe samples as a function of the exposure time to ammonium sulfide vapors. (b-g) XPS spectra recorded on the CZTSe samples before (green line) and after treatment for 2 min (yellow line), 5 min (pink line) and 10 min (blue line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

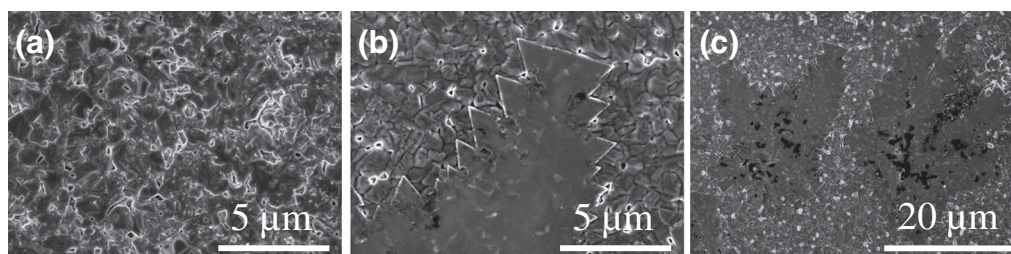


Fig. 4. Top view SEM micrographs of the CZTSe sample before (a) and after (b) 10 min of exposure to the ammonium sulfide vapors. (c) Low magnification top-view SEM image showing the whole size of the features partially shown in panel b.

preferential etching and surface cleaning mechanisms occur at the surface of CZTSe absorbers when using a $(\text{NH}_4)_2\text{S}_x$ solution-based treatment.

3.2. CZTSe layers treated in vapors of ammonium sulfide

Fig. 3(a) shows the atomic concentrations of Cu, Zn, Sn, Se and S detected at the surface of CZTSe samples after exposure to the ammonium sulfide vapor for different durations (i.e., 0, 120, 300 and 600 s); these values were deduced from the XPS Zn 2p_{3/2}, Cu 2p_{3/2}, Sn 3d_{5/2}, Se 3s/2s and Se 3d spectra recorded on the treated samples (Fig. 3(b–f)). The valence band in the XPS spectra is shown in Fig. 3(g). It can be seen that after only 2 min of treatment, the Cu content drops from 10 at.% to less than 1 at.%. Similar evolution was observed for the Zn content which was found to decrease from about 25 at.% (the relatively high initial Zn content being due to the presence of ZnSe secondary phase at the surface of the samples [25]) to 10 at.%. In the meantime, the Sn content drastically increases (from 9 at.% to 22 at.%) accompanied by a shift to higher binding energies of the Sn XPS peak indicating the formation of a Sn-based secondary phase. The shape of the Se XPS spectra is also modified (i.e. an additional contribution to the Se 3d signal was detected), and their intensity decreases as the sulfur content increases at the surface of the CZTSe film. Furthermore, the value of the valence band maximum is shifted from 0.1 to 0.9 eV, confirming the formation of a new compound at the surface of the sample. According to these observations, this Sn-rich compound could be the SnSe_2 phase [26]. When increasing the treatment duration from 2 min to 10 min, the Zn content is further reduced, leading to the increase of the relative Sn content at the surface of the absorber. As the position of the Sn XPS peaks is slightly shifted to the higher binding energies, it might be concluded that a part of the SnSe_2 phase is sulfurized. Meantime, the Se concentration decreases proportionally to the increase of the S content as a function of the exposure time to the chemical vapors. The fit of the Se 3d XPS signal also reveals that the component at the low binding energies attributed to the SnSe_2 phase progressively decreases, while the one at the high binding energies, which can be assigned to elemental Se, increases. Therefore, it seems that Se^0 is progressively formed in addition to the $\text{Sn}(\text{S,Se})_2$ phase. Thus, the ammonium sulfide vapor treatment applied to CZTSe surface leads (1) to the segregation of the Sn and Se atoms toward the CZTSe absorber surface leading to the formation of SnSe_2 secondary phases and (2) to the progressive sulfurization of the secondary phase into $\text{Sn}(\text{S,Se})_2$, and the formation of Se^0 phase due to the segregation of the remaining Se atoms. The segregation mechanisms (1) is also observed by Zhong et al. during standard sulfurization process at high temperature of kesterite thin films [27]. During this sulfurization process, the Sn atoms react with the chalcogen precursor to form SnS molecules in the phase, leading to a Sn loss in the absorber and the redeposition of SnS_2 at the surface of the absorber. In our case, the fast segregation observed at room temperature of Sn and Se atoms at the surface of the absorber might be due to their selective reactivity with the ammonium sulfide vapor (as similarly observed during the liquid phase treatment) resulting in the formation of secondary compounds which condensate on the surface of the absorber. It might also be a

polarization effect, due to the change of charge of Sn atoms when reacting with the vapors; this could weaken the Cu–Se covalent bonds and thus lead to the diffusion of Cu atoms away from the surface, as observed in the case of oxygenation of CIGSe surfaces [28].

To support our results, SEM analyses were carried out on the CZTSe samples before and after 600 s of exposure to the ammonium sulfide vapors (Fig. 4(a) and 4(b,c)). The CZTSe reference sample exhibits relatively small grain size (i.e. less than 1 μm), and several nanovoids are visible at the grain boundaries. After exposure to the vapors, the color of the CZTSe samples progressively turns from grey to dark blue, and large (i.e. up to 50 μm length) features with a very particular shape (i.e. saw tooth edges) are formed at the surface of the absorber. These polycrystalline features are homogeneously distributed on the treated sample and were not observed on the reference sample. Energy dispersive X-ray analyses (not presented here) have revealed that these features contain mainly Se, in larger proportion compared to the other areas on this sample. This observation confirms the formation of Se^0 secondary phase during the treatment as previously revealed by XPS. The surface of the CZTSe grains is also found to be slightly rougher after treatment, likely due to the segregation of $\text{Sn}(\text{S,Se})_2$ at the surface of the absorber. Therefore, we can conclude from the XPS and SEM analyses that the exposure of CZTSe surface to $\text{NH}_3/\text{H}_2\text{S}$ vapors at room temperature leads to the decomposition of the kesterite phase, confirming the low stability of such compound [29–31].

Finally, CZTSe absorbers before and after 10 min of exposure to ammonium sulfide vapors were used to prepare solar cells, in order to assess the impact of modification observed at the CZTSe surface on the electrical properties of the corresponding devices. An overview of the best measured I–V characteristics of CZTSe/ZnO photovoltaic cells with or without treatment is shown in Fig. 5, and a summary of the PV parameters extracted from the I–V curves shown in Fig. 2 and Fig. 5 is available in Table 1. Note that the higher efficiency obtained for the CZTSe/

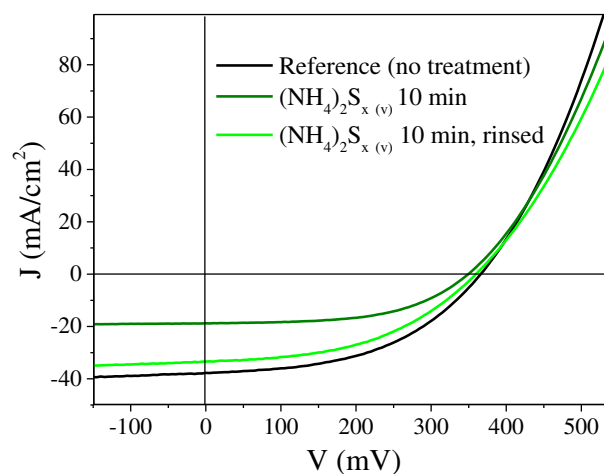


Fig. 5. I–V curves of CZTSe/ZnO-based solar cells prepared with absorber before and after treatment for 10 min in ammonium sulfide vapors.

Table 1

Electrical parameters of the solar cells studied in this work, extracted from the I-V curves shown in Fig. 2 and Fig. 5.

Sample	Voc (mV)	Jsc (mA/cm ²)	FF (%)	PCE (%)	Rsh (Ω·cm ²)	Rs (Ω·cm ²)
CZTSe/CdS/ZnO solar cells, ammonium sulfide liquid treatment (l)						
0 s (reference)	363	23.6	47.7	4.0	160	1.81
60 s (l)	348	35.8	48.4	6.0	195	1.59
120 s (l)	345	33.9	41.3	4.8	82	2.02
300 s (l)	327	26.1	46.4	3.9	214	2.09
CZTSe/ZnO solar cells, ammonium sulfide vapor treatment (v)						
0 s (reference)	366	38.0	49.1	6.8	237	1.10
600 s (v)	349	18.9	47.2	3.1	281	1.21
600 s (v), rinsed	359	33.5	48.4	5.8	233	1.34

ZnO reference compared to the CZTSe/CdS/ZnO reference can be explained by the KCN etch step used for the first sample, while the second one did not received any surface treatment prior to the buffer layer deposition. However, the reasonable efficiency obtained without CdS raise the question of the need a buffer layer to achieve high efficiency kesterite solar cells. The exposure of the absorber to ammonium sulfide vapors for 10 min is found to drastically decrease the J_{sc} value of the solar cell (from 38 mA/cm² to 19 mA/cm²), and consequently leads to the decrease of the efficiency. Interestingly, upon rinsing with DIW, the surface of the CZTSe sample seems to be reverted back to the status before the vapor treatment. This is also reflected into a restored J_{sc} with respect to the reference device. Therefore, it seems that part of the secondary phases blocking the current that are formed at the surface of the CZTSe absorber after treatment are soluble in water, which could be the case of Se⁰ phases (according to ICP-AES measurements performed on the rinsing water) due to their low adhesion to the surface. The drastic decrease of the J_{sc} value in presence of the Sn(S₂Se)₂ and Se⁰ compounds at the surface of the absorber could be explained by the shadowing effect induced by the large Se⁰ capping domain and/or the increase of the Rs value after treatment. It can be noted that the V_{oc} values of the devices are only slightly influenced by the presence of the secondary phases.

4. Conclusions

In summary, we assessed the modifications induced at the CZTSe surface after applying ammonium sulfide-based treatments to the samples, by exposing the samples to a liquid or vapor phase of ammonium sulfide. When using the liquid-based treatment, both ICP-AES and I-V measurements tend to confirm that short treatment time (i.e., below 1 min) can be beneficial to the performance of the device, by removing some extra-Se, Sn and Zn from the absorber surface (likely coming from secondary phases such as SnSe_x and Se⁰). However, as in the case of KCN/KOH treatment, longer treatment durations tend to degrade the performance of the solar cells, due to the preferential etching of Se, Sn and Zn atoms from the surface of the kesterite phase, leading to a modification of the band alignment at the CZTSe/CdS interface. In the case of the vapor phase treatment, the segregation of Sn(S₂Se)₂ and Se⁰ secondary phases was observed at the surface of the CZTSe phase after exposure. Consequently, this treatment was shown to degrade the J_{sc} values of the CZTSe/ZnO devices. Although using an ammonium sulfide vapor-based treatment was found to be inappropriate to enhance the properties of the CZTSe surface, our results demonstrate that the limited stability of the surface of the kesterite compound might be an issue to further control the p/n junction properties of the related devices.

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References

- [1] S. Siebentritt, S. Schorr, Kesterites, a challenging material for solar cells, *Prog. Photovolt. Res. Appl.* 20 (2012) 512–519.
- [2] C. Persson, Electronic and optical properties of Cu₂ZnSnS₄ and Cu₂ZnSnSe₄, *Appl. Phys.* 107 (2010) 53710.
- [3] W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, D.B. Mitzi, Device Characteristics of CZTSe Thin-Film Solar Cells with 12.6% Efficiency, *Adv. Energy Mater.* 4 (7) (2014) 1301465.
- [4] J. Kim, H. Hiroi, T. Todorov, O. Gunawan, M. Kuwahara, T. Gokmen, D. Nair, M. Hopstaken, B. Shin, Y. Lee, W. Wang, H. Sugimoto, D. Mitzi, High Efficiency Cu₂ZnSn(S,Se)₄ Solar Cells by Applying a Double In₂S₃/CdS Emitter, *Adv. Mater.* 26 (2014) 7427–7431.
- [5] A. Fairbrother, E. García-Hemme, V. Izquierdo-Roca, X. Fontané, F. Pulgarín-Agudelo, O. Vigil-Galán, A. Pérez-Rodríguez, E. Saucedo, Development of a selective chemical etch to improve the conversion efficiency of Zn-rich Cu₂ZnSnS₄ solar cells, *J. Am. Chem. Soc.* 134 (2012) 8018–8021.
- [6] M. Buffière, G. Brammertz, S. Sahayaraj, M. Batuk, S. Khelifi, D. Mangin, A.-A. El Mel, L. Arzel, J. Hadermann, M. Meuris, J. Poortmans, KCN chemical etch for Interface engineering in Cu₂ZnSnSe₄ solar cells, *ACS Appl. Mater. Interfaces* 7 (27) (2015) 14690.
- [7] M. Mousel, A. Redinger, R. Djemour, M. Arasimowicz, N. Valle, P. Dale, S. Siebentritt, HCl and Br₂-MeOH etching of Cu₂ZnSnSe₄ polycrystalline absorbers, *Thin Solid Films* 535 (2013) 83–85.
- [8] M. Buffière, G. Brammertz, A.-A. El Mel, N. Lenaers, Y. Ren, A.E. Zaghi, Y. Mols, C. Koeble, J. Vlegels, M. Meuris, J. Poortmans, Recombination Stability in Polycrystalline Cu₂ZnSnSe₄ Thin Films, *Photovoltaic Specialists Conference (PVSC) 2013 IEEE 39th 1941–1944*.
- [9] K. Ramanathan, F.S. Hasoon, S. Smith, D.L. Young, M.A. Contreras, P.K. Johnson, A.O. Pudov, J.R. Sites, Surface treatment of CuInGaSe₂ thin films and its effect on the photovoltaic properties of solar cells, *J. Phys. Chem. Solids* 64 (2003) 1495–1498.
- [10] W. Li, S.R. Cohen, D. Cahen, Effect of chemical treatments on nm-scale electrical characteristics of polycrystalline thin film Cu(In,Ga)Se₂ surfaces, *Sol. Energy Mater. Sol. Cells* 120 (2014) 500–505.
- [11] T. Nakada, K. Matsumoto, M. Okumura, Improved efficiency of Cu(In,Ga)Se₂ thin film solar cells by surface sulfurization using wet process, *Photovoltaic Specialists Conference (PVSC), 29th IEEE 2002*, pp. 527–530.
- [12] S. Luo, C. Eisler, T.-H. Wong, H. Xiao, C.-E. Lin, T.-T. Wu, C.-H. Shen, J.-M. Shieh, C.-C. Tsai, C.-W. Liu, H.A. Atwater, W.A. Goddard, J.-H. Lee, J.R. Greer, Suppression of surface recombination in CuInSe₂ (CIS) thin films via Trioctylphosphine Sulfide (TOP:S) surface passivation, *Acta Mater.* 106 (2016) 171–181.
- [13] I.M. Dharmadasa, J.M. Thornton, R.H. Williams, Effects of surface treatments on Schottky barrier formation at metal/n-type CdTe contacts, *Appl. Phys. Lett.* 54 (1989) 137.
- [14] B.E. McCandless, K.D. Dobson, Processing options for CdTe thin film solar cells, *Sol. Energy* 77 (2004) 839–856.
- [15] K. Tsujino, M. Matsumura, Y. Nishimoto, Texturization of multicrystalline silicon wafers for solar cells by chemical treatment using metallic catalyst, *Sol. Energy Mater. Sol. Cells* 90 (2006) 100–110.
- [16] H. Angermann, L. Korte, J. Rappich, E. Conrad, I. Sieber, M. Schmidt, K. Hübener, J. Hauschild, Optimisation of electronic interface properties of a-Si:H/c-Si heterojunction solar cells by wet-chemical surface pre-treatment, *Thin Solid Films* 516 (2008) 6775–6781.
- [17] R.J. Nelson, J.S. Williams, H.J. Leamy, B. Miller, H.C. Casey Jr., B.A. Parkinson, A. Heller, Reduction of GaAs surface recombination velocity by chemical treatment, *Appl. Phys. Lett.* 36 (1980) 76.
- [18] M.G. Mauk, S. Xu, D.J. Arent, R.P. Mertens, G. Borghs, Study of novel chemical surface passivation techniques on GaAs p/n junction solar cells, *Appl. Phys. Lett.* 54 (1989) 213.
- [19] H. Oigawa, J.-F. Fan, Y. Nannichi, H. Sugahara, M. Oshima, Universal passivation effect of (NH₄)₂S_x treatment on the surface of III-V compound semiconductors, *Jpn. J. Appl. Phys.* 30 (1991) L322–L325.
- [20] Y. Nannichi, J.-F. Fan, H. Oigawa, A. Koma, A model to explain the effective passivation of the GaAs surface by (NH₄)₂S_x treatment, *Jpn. J. Appl. Phys.* 27 (1988) L2367–L2369.
- [21] V.N. Bessolov, M.V. Lebedev, Chalcogenide passivation of III–V semiconductor surfaces, *Semiconductors* 32 (1998) 1141–1154.
- [22] M. Buffière, A.-A. El Mel, N. Lenaers, G. Brammertz, A.E. Zaghi, M. Meuris, J. Poortmans, Surface cleaning and passivation using (NH₄)₂S treatment for Cu(In,Ga)Se₂ solar cells: a safe alternative to KCN, *Adv. Energy Mater.* 5 (2015) 1401689.
- [23] H. Xie, Y. Sánchez, S. López-Marino, M. Espíndola-Rodríguez, M. Neuschitzer, D. Sylla, A. Fairbrother, V. Izquierdo-Roca, A. Pérez-Rodríguez, E. Saucedo, Impact of Sn(S₂Se)₂ secondary phases in Cu₂ZnSn(S,Se)₄ solar cells: a chemical route for their selective removal and absorber surface passivation, *ACS Appl. Mater. Interfaces* 6 (2014) 12744–12751.
- [24] G. Brammertz, M. Buffière, S. Oueslati, H. ElAnzeery, K. Ben Messaoud, S. Sahayaraj, C. Köble, M. Meuris, J. Poortmans, Characterization of defects in 9.7% efficient Cu₂ZnSnSe₄-CdS-ZnO solar cells, *Appl. Phys. Lett.* 103 (2013) 163904.

- [25] M. Buffière, G. Brammertz, M. Batuk, C. Verbist, D. Mangin, C. Koble, J. Hadermann, M. Meuris, J. Poortmans, Microstructural analysis of 9.7% efficient $\text{Cu}_2\text{ZnSnSe}_4$ thin film solar cells, *Appl. Phys. Lett.* 105 (2014) 183903.
- [26] Y. Bertrand, A. Divrechy, C. Raisin, Reflectivity and band structure of SnSe_2 , *J. Phys. C Solid State Phys.* 10 (1977) 4155.
- [27] J. Zhong, Z. Xia, M. Luo, J. Zhao, J. Chen, L. Wang, X. Liu, D.-J. Xue, Y.-B. Cheng, H. Song, J. Tang, Sulfurization induced surface constitution and its correlation to the performance of solution-processed $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ solar cells, *Sci. Report.* 4 (2014) 6288.
- [28] L. Kronik, U. Rau, J.-F. Guillemoles, D. Braunger, H.-W. Schock, D. Cahen, Interface redox engineering of $\text{Cu}(\text{In,Ga})\text{Se}_2$ – based solar cells: oxygen, sodium, and chemical bath effects, *Thin Solid Films* 361–362 (2000) 353–359.
- [29] A. Redinger, D.M. Berg, P.J. Dale, S. Siebentritt, The consequences of kesterite equilibria for efficient solar cells, *J. Am. Chem. Soc.* 133 (10) (2011) 3320–3323.
- [30] J.J. Scragg, P.J. Dale, D. Colombara, L.M. Peter, Thermodynamic aspects of the synthesis of thin-film materials for solar cells, *Chem. Phys. Chem* 13 (2012) 3035–3046.
- [31] S.V. Baryshev, E. Thimsen, Enthalpy of formation for Cu-Zn-Sn-S (CZTS) calculated from surface binding energies experimentally measured by ion sputtering, *Chem. Mater.* 27 (7) (2015) 2294–2298.