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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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Keywords: Solar cells, CZTSe, kesterite, chemical treatment, secondary phases, decomposition.

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 minute, 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 absorber lead to the decomposition of the CZTSe phase into $\text{Sn}(\text{S},\text{Se})_x$ and Se^0 secondary phases. As a consequence, the short circuit current of the corresponding solar cells is reduced.

1. Introduction

$\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (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 $\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se})_2$ (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 or HCl 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 , $\text{Zn}(\text{S},\text{Se})$, $\text{Cu}_x(\text{S},\text{Se})$, $\text{Sn}(\text{S},\text{Se})_x$ or $\text{Cu}_2\text{Sn}(\text{S},\text{Se})_3$).⁵⁻⁶ It was also demonstrated that dipping air-exposed CZTSSe samples into a KCN solution reduces the surface recombination rate of the aged absorber.⁷ 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 solar cells.

Applying a chemical treatment step is a simple route to control the surface properties of a semiconductor. Many specific procedures were implemented in the past to passivate, to etch or/and to modify the composition of photovoltaic absorber such as CIGSSe,⁸⁻¹⁰ CdTe,^{11,12} Si^{13,14} or III-V compounds.^{15,16} 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.¹⁷ 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.¹⁸ 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.¹⁰ 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.²⁰ According to Xie *et al.*,²¹ this chemical compound can also etch $\text{Sn}(\text{S},\text{Se})$ clusters on the surface of CZTSSe layer, by dipping the absorber into the $(\text{NH}_4)_2\text{S}_x$ solution for 1 minute.

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

2.1. Synthesis of CZTSe absorber

The CZTSe absorber layers were synthesized using 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 [22]. 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 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 [20] 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, under a wet bench equipped with an exhaust. 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/m^3) and H_2S (5.3 mg/m^3). 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 (0.1M)-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 cm^2 .

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 x 1.0 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 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

Figure 1 shows the evolution of the concentrations of Cu, Zn, Sn and Se species in the aqueous (NH₄)₂S_x solutions after immersion of a Cu-poor CZTSe sample ([Cu]/([Zn]+[Sn])=0.85, [Zn]/[Sn]= 1.12, as measured 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)**). One can clearly observe that, in overall, 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 (NH₄)₂S_x concentrations. Although this observation may confirm the etching of the SnSe secondary phase as described in [21] for CZTSSe 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 Se⁰ 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 phase. 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 **Figure 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 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. Both effects have been also observed after long KCN/KOH treatment,⁶ which tend to confirm that similar preferential etching mechanisms occurs at the surface of CZTSe absorbers when using a $(NH_4)_2S_x$ solution-based treatment.

3.2. CZTSe layers treated in vapors of ammonium sulfide

Figure 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/S 2s and Se 3d spectra recorded on the treated samples (**Figure 3(b-f)**). The valence band in the XPS spectra

is shown in **Figure 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)²³ to 10 at.%.²³ 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 (VBM) 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 SnSe₂ phase.²⁴ 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 SnSe₂ 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 SnSe₂ phase progressively decreases, while the one at the high binding energies, that can be assigned to elemental Se, increases. Therefore, it seems that Se⁰ is progressively formed in addition to the Sn(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 SnSe₂ secondary phases and (2) to the progressive sulfurization of the secondary phase into Sn(S,Se)₂, and the formation of Se⁰ phase due to the segregation of the remaining Se atoms. The segregation mechanisms (1) was also observed by Zhong *et al.* during standard sulfurization process at high temperature of kesterite thin films.²⁵ During this sulfurization process, the Sn atoms react with the chalcogen precursor to form SnS molecules in the gaz phase, leading to a Sn loss in the absorber and the re-deposition of SnS₂ at the

surface at 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.²⁶

To support our previous results, SEM analyses were carried out on the CZTSe samples before and after 600 s of exposure to the ammonium sulfide vapors (**Figure 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 (EDX) 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 phases 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 $\text{Sn}(\text{S},\text{Se})_2$ 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, pointing out the low stability of such compound.

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 **Figure 5**. 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, if the CZTSe sample is rinsed with deionized water after the treatment, the color of the absorber turns back from blue to grey and the J_{sc} of the corresponding CZTSe solar cells is found to be improved compared to the sample without rinsing. Therefore, it seems that part of the secondary phases that are formed at the surface of the CZTSe absorber after treatment are soluble in water, which is the case of Se⁰ phases (according to ICP-AES measurements performed on the rinsing water). The drastic decrease of the J_{sc} value in presence of the Sn(S,Se)₂ and Se⁰ compounds at the surface of the absorber can be explained by the shadowing effect induced by the large Se⁰ capping domain. 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, either by exposing the samples into a liquid phase or vapor phase of ammonium sulfide. When using the liquid-based treatment, both ICP-AES and I-V measurements tend to confirm that

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Abstract

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1. Introduction

a short treatment time (i.e., below 1 minute) 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 Se^0). 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. In the case of the vapor phase treatment, the segregation of $\text{Sn}(\text{S,Se})_2$ and Se^0 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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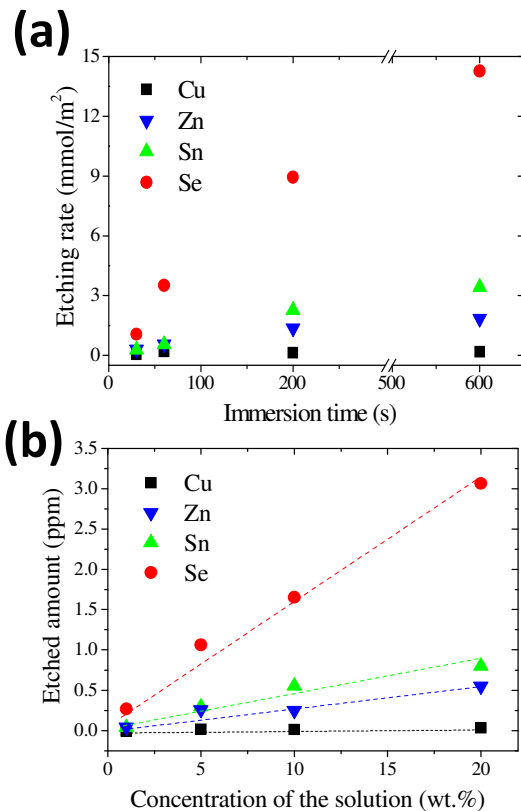


Figure 1. Evolution of the etching rates of Cu, Zn, Sn and Se atoms from CZTSe samples in $(\text{NH}_4)_2\text{S}_x$ solution as a function of: (a) the immersion duration while fixing the solution concentration to 20 wt. % and (b) the solution concentration while fixing the duration to 60 s.

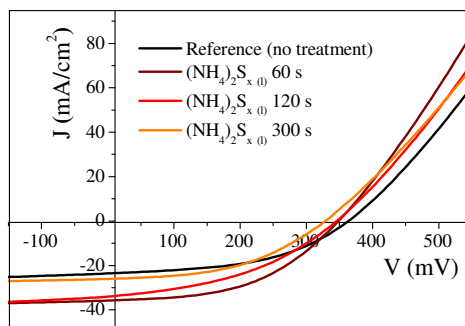


Figure 2. I-V curves of CZTSe/CdS/ZnO-based solar cells prepared with absorber treated for different times in ammonium sulfide solution in liquid phase.

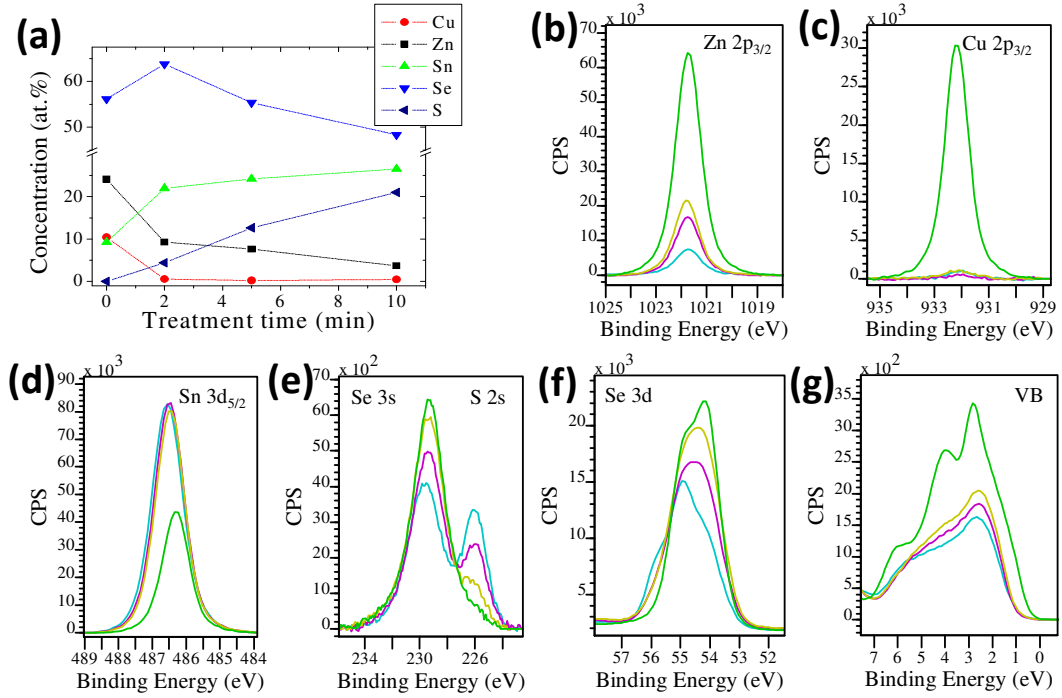


Figure 3. (a) Evolution of the atomic concentrations (as deduced from XPS measurements) of the elements present at the surface of the CZTSe samples as a function of the exposure time to ammonium sulfide vapors. (b-g) XPS spectra recorded on the CZTSe samples before (green line) and after treatment for 2 min (yellow line), 5 min (pink line) and 10 min (blue line).

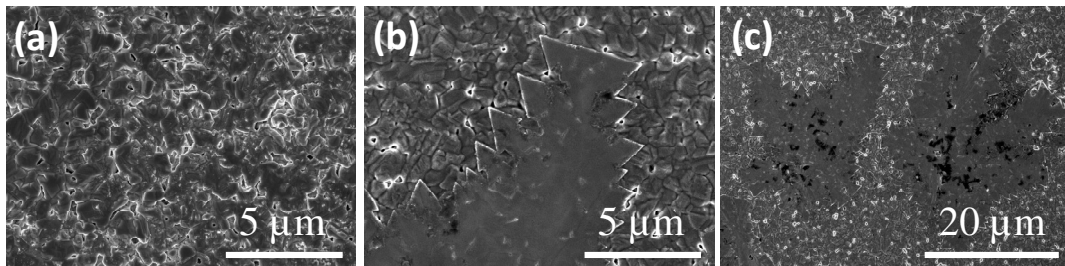


Figure 4. Top view SEM micrographs of the CZTSe sample before (a) and after (b) 10 min of exposure to the ammonium sulfide vapors. (c) Low magnification top-view SEM image showing the whole size of the features partially shown in panel b.

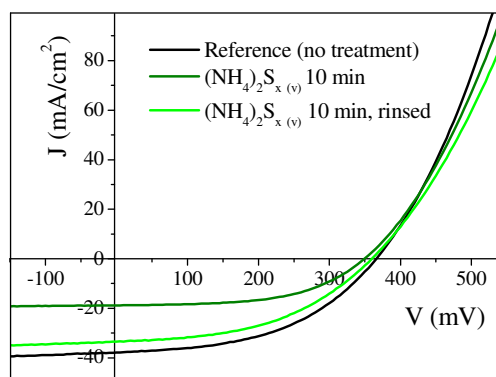


Figure 5. *I-V curves of CZTSe/ZnO-based solar cells prepared with absorber before and after treatment for 10 min in ammonium sulfide vapors.*