



HCl and Br₂-MeOH etching of Cu₂ZnSnSe₄ polycrystalline absorbers

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ABSTRACT

Cu₂ZnSnSe₄ solar cells made from absorbers etched in HCl and Br in methanol (Br₂-MeOH) are studied. The absorbers show surface compositions, different from bulk compositions, as revealed by secondary ion mass spectrometry (SIMS) depth profiles. They indicate the presence of secondary phases where the most prominent are a Zn related phase and a Cu, Sn related phase. The secondary phases can be removed by etching in HCl or Br₂-MeOH. The absorbers are analyzed before and after etching by scanning electron microscopy and SIMS, and solar cells by current–voltage measurements. These results indicate that the Cu, Sn related phase is strongly detrimental to solar cell devices by reducing drastically open-circuit voltage (V_{OC}) and fill factor (FF) and is etched by Br₂-MeOH, but not by HCl. In fact solar cell results improved from about 4% to above 5%. All solar cell parameters improved slightly for HCl etching but for Br₂-MeOH etching we observe a significant increase of V_{OC} and FF. An efficiency of 5% was obtained in both cases and 5.8% efficiency is the best device obtained after Br₂-MeOH etching.

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1. Introduction

Cu₂ZnSn(S,Se)₄ (CZTS(e)) absorbers for photovoltaic applications gain more and more interest in thin film solar cell research and have already achieved 10.1% efficiency [1]. Considering their direct band gap [2], high absorption coefficient and abundance of raw materials, they present a promising alternative to existing thin film solar cell technologies. It is well known that the existence region of pure CZTS(e) is much smaller compared with that of Cu(In,Ga)(S,Se)₂ (CIGS(e)) material [3] and thus the formation of detrimental secondary phases is a challenging issue for Cu₂ZnSn(S,Se)₄ based solar cells. Current knowledge places the more efficient devices in the Cu-poor and in the slightly Zn-rich region [4]. However, even in this region, secondary phases are very likely and probably detrimental, thus limiting solar cell efficiencies. The most prominent secondary phases are the ternary Cu₂SnSe₃ and the ZnSe phases. The presence of secondary phases at the interfaces has already been reported in literature for CZTS [5,6] and CZTSe [7–9] systems. Detrimental ZnSe secondary phase at the back contact has been observed by S. Ahn et al. [7] and by A. Redinger et al. [8] and recently J.T. Wätjen et al. [9] and A. Redinger et al. [10] showed direct evidence of detrimental ZnSe at the interface. In fact, the heterojunction interface is still a limiting factor in CZTSe solar cells since most devices exhibit dominant interface recombination [11]. In order to improve the heterojunction interface chemical etching methods can be used to remove detrimental secondary phases.

In this regard Timmo et al. [12] studied chemical surface treatment on monograin powders using several etchants such as HCl and Br₂-MeOH. Although chemical etching has been less studied for CZTS(e) absorbers compared with CIGS(e) (see for example [13]) it is clear that bromine solutions are efficient etchants. Bromine etching results in a global flattening of the initial surface providing a non-selective thinning of the absorber [13]. Moreover it was shown that surface compositions stay constant during the etching process in the case of CIGSe. In this paper, we studied surface etching with HCl and Br₂-MeOH of CZTSe polycrystalline absorbers with respect to secondary phases and solar cell parameters.

2. Experimental details

The CZTSe polycrystalline absorbers were produced by a precursor-annealing process. First all the elements (Cu, Zn, Sn and Se) were co-evaporated at 320 °C onto a molybdenum coated soda lime glass in a molecular beam epitaxy system as described elsewhere [14]. Precursors with different compositions were obtained by tuning the fluxes of the elements. The precursors were then annealed for 30 min in a tube furnace at 500 °C in an H₂/N₂ atmosphere with 10² Pa total pressure. To avoid decomposition of the CZTSe during the final heat treatment, the films were annealed in an SnSe and Se atmosphere provided in form of powders in the graphite box (for further details see [15]). After the annealing some of the absorbers were etched for 1 min either with concentrated (37 wt.%) HCl or with 0.02 M bromine methanol (Br₂-MeOH). The morphology and the composition before and after etching were analyzed by scanning electron microscopy (SEM) and by 20 keV energy-dispersive X-ray spectroscopy (EDX). The compositions

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of the precursors were varied from $\text{Cu}/(\text{Zn} + \text{Sn}) = 0.8$ to 1.6 and from $\text{Zn}/\text{Sn} = 0.7$ to 1.7. Secondary ion mass spectrometry (SIMS) depth profile measurements were performed on the absorbers with Cs^+ -ions and positively charged Cs-metal clusters have been detected. The element intensities of the SIMS measurements are normalized to the middle of the absorber in order to highlight changes compared with the bulk.

In order to remove a possible Cu_2Se secondary phase, all the annealed samples were etched in 5 wt.% KCN for 30 s as standard procedure. After depositing the CdS buffer layer by chemical bath deposition, the window deposition was performed by magnetron sputtering of i-ZnO and Al-doped ZnO. At last, an Ni-Al grid was deposited by e-beam evaporation for front contacting. The typical size for the solar cells is 0.5 cm^2 total area. The solar cell parameters were determined using a current–voltage (I–V) measurement set-up equipped with a halogen lamp which has been adjusted to 100 mW/cm^2 . Further solar cell parameters have been extracted with J.R. Sites et al.'s [16] method.

3. Results and discussion

Fig. 1 shows the sample compositions as determined by EDX plotted in the phase diagram adapted from I.V. Dudchak and L. Piskach [17] as precursors and after annealing. In order to be able to represent the compositions of the samples in the phase diagram, the Se content was assumed to be stoichiometric. Although a relatively broad region of the phase diagram around the single phase $\text{Cu}_2\text{ZnSnSe}_4$ existence region has been prepared via coevaporation, after the annealing the compositions shift significantly and the final film compositions are always situated on the Cu_2SnSe_3 – $\text{Cu}_2\text{ZnSnSe}_4$ and on the ZnSe – $\text{Cu}_2\text{ZnSnSe}_4$ tie lines. From that figure it is suggested that for this set of samples we have either the ternary Cu_2SnSe_3 , or the binary ZnSe as secondary phases in the absorber.

The best absorber layers gave an efficiency of around 4% when the composition was Cu-poor and Zn-rich. Although the composition of the absorbers changed after annealing there was a clear correlation between solar cell efficiency and precursor composition. The precursor

compositions close to Cu-poor and Zn-rich gave the best results as absorbers whereas Cu-rich and Sn-rich precursors did not lead to working devices. Moreover SIMS depth profile measurements performed on the absorbers indicate a clear trend of two different profiles related to the efficiency of the solar cells. Two typical examples of those SIMS depth profiles are depicted in Fig. 2. The solar cells with an efficiency above 4% (Fig. 2(a)) show a depth profile where the Zn ratio at the surface is higher than in the bulk. The low efficiency or non-working solar cells exhibit SIMS depth profiles similar to the one shown in Fig. 2(b). These depth profiles have in common that the Zn content at the interface decreases compared with that in the bulk. Moreover the Cu and Sn contents are slightly increased in the first few hundred nanometers of the absorber compared with the rest of the film. Finally the Cu-content very close to the heterojunction strongly decreases. Additionally it has to be pointed out that Cu and Sn profiles in all SIMS measurements vary together over almost all the absorber depth. The Zn increase at the back occurring in most of the SIMS profiles is in agreement with a ZnSe phase at the back contact [8].

This shows that we have different compositions at the surface than in the bulk which could not necessarily be determined via integral composition measurements. Moreover the different compositions at the surface can be related to secondary phases. The Cu and Sn related phase strongly inhibits solar cell devices. It is safe to assume that the profiles in Fig. 2(a) indicate a ZnSe phase at the surface, and the profiles in Fig. 2(b) a ternary Cu_2SnSe_3 phase. Although the ternary Cu_2SnSe_3 phase has not been directly measured, this phase presents a lower band gap of 0.84 eV [18] which will result in a strongly reduced open-circuit voltage (V_{OC}). This lower V_{OC} was observed in the set of solar cells in correlation with the Cu, Sn related phases at the surface in the SIMS profiles. Both secondary phases are detrimental to solar cell devices. The ternary due to its lower band gap leads to increased recombination, while the ZnSe phase limits the current, as shown recently [9]. However HCl solutions have successfully been employed by H. Tamura et al. [19] to etch ZnSe crystals. Bromine solutions are known to be efficient etchants and were used to reduce the thickness of CIGSe absorbers

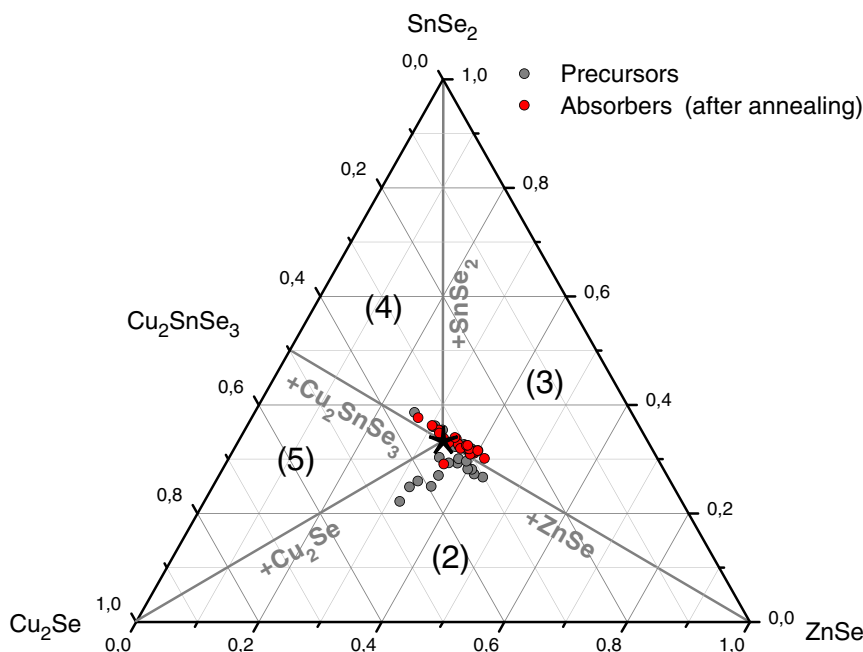


Fig. 1. Sample compositions plotted in the phase diagram adapted from [17] as precursor (gray dots) and after annealing (red dots). The different regions of the phase diagram (★) $\text{Cu}_2\text{ZnSnSe}_4$, (2) $\text{Cu}_2\text{ZnSnSe}_4 + \text{Cu}_2\text{Se} + \text{ZnSe}$, (3) $\text{Cu}_2\text{ZnSnSe}_4 + \text{SnSe}_2 + \text{ZnSe}$, (4) $\text{Cu}_2\text{ZnSnSe}_4 + \text{Cu}_2\text{SnSe}_3 + \text{SnSe}_2$ and (5) $\text{Cu}_2\text{ZnSnSe}_4 + \text{Cu}_2\text{SnSe}_3 + \text{Cu}_2\text{Se}$ represent the existence region of $\text{Cu}_2\text{ZnSnSe}_4$ and secondary phases. The tie lines represent the regions where $\text{Cu}_2\text{ZnSnSe}_4$ and one other secondary phase are present as indicated in the graph.

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