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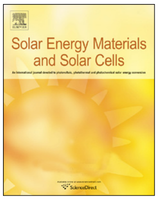

Interplay between surface preparation and device performance in CZTSSe solar cells: Effects of KCN and NH_4OH etching

Mehmet Eray Erkan [a], Vardaan Chawla [1,b], Ingrid Repins [c], Michael A. Scarpulla [a,d,*]

[a] Department of Electrical and Computer Engineering, University of Utah, Salt Lake City, UT 84112, USA
[b] AQT Solar Inc., Sunnyvale, CA 94086, USA
[c] National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401, USA
[d] Department of Materials Science and Engineering, University of Utah, Salt Lake City, UT 84112, USA

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ABSTRACT

Despite the many similarities between $Cu_2ZnSn(S,Se)_4$ (CZTSSe) and $Cu(In,Ga)(S,Se)_2$ materials and device architecture, open questions remain about the optimal surface preparation steps for CZTSSe absorbers, including whether differences exist for absorber layers deposited by different methods. In this work, we investigate KCN etching and NH_4OH treatment as surface preparation methods for the absorber/CdS interface for two-stage processed CZTSSe and co-evaporated CZTSe absorber layers. Ambient-exposed, thus oxidized and contaminated, thin film absorbers are utilized to examine the effectiveness of these surface preparation methods and to elucidate their effects on device performance. Topography and surface potential images simultaneously obtained by Kelvin probe force microscopy (KPFM) show the existence of an overlayer on the ambient-exposed absorbers. Moreover, KPFM results also demonstrate that although NH_4OH treatment removes much of the overlayer from the CZTSSe surface, KCN etching removes the overlayer completely. In addition, differences in the deposited CdS layer and depletion region width result depending on the surface preparation method, with the NH_4OH-treated solar cells having narrower depletion region. This is reflected in device results in which KCN-etched solar cells outperform their NH_4OH-treated counterparts due to increases in external quantum efficiency at long wavelengths and in open circuit voltage. KPFM measurements also demonstrate that grain boundaries (GBs) in the KCN-etched two-stage processed CZTSSe thin films are either negatively charged or neutral. On the other hand, KCN etching makes the surface almost equipotential in the co-evaporated CZTSe thin film by causing disappearance of positively charged GBs that existed before etching.

1. Introduction

Continuous improvement in the power conversion efficiency (PCE) of thin film solar cells made from $Cu_2ZnSn(S,Se)_4$ (CZTSSe)-based absorber layers has been motivating solar cell researchers for pursuing this absorber material further. Experience and mature processes transferred from $Cu(In,Ga)(S,Se)_2$ (CIGSSe)-based thin film solar cell technology have expedited the progress in the CZTSSe solar cell field, and the current highest is 12.6% in laboratory [1], whereas it was 0.66% in 1997 [2]. Two processes that proved themselves for the CIGSSe solar cells and that are now used for the CZTSSe devices are KCN etching and CdS buffer layer deposition by chemical bath deposition (CBD).

KCN etching is primarily used to remove any existing Cu_xSe/S secondary phases from CIGSSe and CZTSSe absorbers, particularly if the absorber is grown in Cu-rich compositional regime [3–6]. Studies have shown that KCN etching also affects surface composition of an absorber [7–9]. Bär et al. [7] have reported the capability of KCN etching in removing oxides from a CIGSe thin film surface regardless of the extent of oxidation. Studies performed on CZTSSe monograin powders [8] and CZTS thin films [9] have shown that KCN preferentially etches Cu, chalcogens and, to a lesser extent, Sn thus resulting in surface Zn enrichment. This KCN-induced change in CZTS surface composition has been reported to result in a larger interface bandgap ($E_{g,i}$) at the CZTS/CdS junction [10], and a larger $E_{g,i}$ is expected to reduce interface recombination and the resulting open circuit voltage (V_{OC}) deficit [10,11] –an important hurdle identified in (particularly sulfur-containing) CZTSSe-based devices [12–14]. The observed dominant interface

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[*] Corresponding author at: Department of Electrical and Computer Engineering, University of Utah, Salt Lake City, UT 84112, USA. Tel.: +1 801 585 1231; fax: +1 801 581 5281.
E-mail address: scarpulla@eng.utah.edu (M.A. Scarpulla).
[1] Current affiliation: SunEdison, Belmont, CA 94002, USA.

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recombination is probably caused by a negative conduction band offset (or "cliff" band alignment) at the CZTS/CdS junction [10,15–18]. Cliff band alignment is known to lower V_{oc} especially in conjunction with high interface defect density at the junction [19,20]. Therefore, it should be noted that absorber/buffer interface preparation and interface quality have significant impact on CZTSSe devices having cliff band alignment. Increases in the characteristics of devices fabricated with KCN-etched absorbers have been reported, with particular increase in V_{OC} that indicates reduced interface recombination [10]. Consequently, all these studies demonstrate that KCN etching of CZTSSe thin film absorbers may have various outcomes depending on details of the absorber preparation, and thus it warrants further investigation.

CdS deposition by CBD has been the preferred junction formation method for CZTSSe thin film solar cells [1,21]. CBD was transferred to the CZTSSe field from CIGSSe technology, because it is an established process of CdS deposition in the CIGSSe field and offers beneficial ancillary effects, such as etching of surface oxides from the absorber surface by the NH_4OH present in the CBD solution [22,23]. Success of NH_4OH in etching native oxides from the CZTSe absorber surface has also been demonstrated [24]. Moreover, research on CZTSSe monograin powders [8] has demonstrated that NH_4OH selectively removes Cu, chalcogen and, to a lesser extent, Zn from CZTSSe; thus, Sn enrichment in surface composition can be expected. This may relate to (but not be the only cause of) the established requirement in co-evaporative CZTSe growth of producing a Zn-rich final surface for devices with the highest PCE [21]. Taking these observations together, it is clear that NH_4OH in the CBD bath has multiple effects on the CZTSSe absorber surface that differ from those encountered for CIGSSe. Thus, efforts towards better understanding of the effects of existing CdS CBD chemistry are warranted.

In this study, we investigate the effects of two surface preparation methods, KCN etching and NH_4OH treatment, on CZTSSe thin film absorbers and solar cell device performance. The effects of storage conditions on CZTSSe absorbers as well as the effects and extensiveness of surface preparation methods on the absorbers are demonstrated by using absorbers that are oxidized and contaminated by exposure to ambient for long times. The surfaces of CZTSSe thin films are evaluated by simultaneously acquired topography and surface potential images by Kelvin probe force microscopy (KPFM) in an atomic force microscope (AFM). Device characteristics of KCN-etched and NH_4OH-treated solar cells fabricated in four batches with two CZTSSe absorbers synthesized in different batches give further insights to the effects of these surface preparation methods and demonstrate the importance of surface preparation in device fabrication. Our results present that CZTSSe surface preparation has a significant importance in device performance, especially when the V_{OC} deficit due to the interface recombination occurring in these devices is considered. Lastly, the effects of KCN etching on grain boundaries (GBs) in both CZTSSe and CZTSe thin films are also presented and discussed.

2. Experimental

CZTSSe thin films were deposited on Mo-coated soda-lime glass (SLG) substrates by a two-stage process at AQT Solar, Inc. (USA). In the first stage, a SLG/Mo/ZnS/Sn/$CuSe_2$ precursor stack was prepared by sputtering, and the second stage consisted of annealing of the prepared stack at 550–600 °C under a SnS and S_2 atmosphere created from a SnS_2 source. Solar cells fabricated with similar CZTSSe absorbers at AQT Solar Inc. demonstrated $>9\%$ PCE [25]. The pure selenide CZTSe thin films were deposited by co-evaporation from elemental sources on SLG/Mo substrates at the National Renewable Energy Laboratory (NREL, USA) (NREL film ID: M3797). Details of the CZTSe deposition process can be found in Ref. [21]. Solar cells fabricated with the same CZTSe absorber at NREL demonstrated $>8\%$ PCE. Throughout this paper, the samples made from AQT Solar Inc.'s two-stage processed CZTSSe thin films are referred to as "A-CZTSSe", whereas the samples made from NREL's co-evaporated CZTSe thin films are referred to as "N-CZTSe".

In this study, two types of surface preparation methods were investigated: KCN etching and NH_4OH treatment. KCN etching was done by immersing a sample in an aqueous KCN solution (5 wt%) for ~1 min, followed by deionized (DI) H_2O rinse and N_2 dry. NH_4OH treatment was incorporated as a part of the CdS deposition process that is detailed below. CdS was deposited by CBD by following a modified version of the recipe explained in Ref. [23]. Our CBD process began with the NH_4OH treatment; 62.5 ml NH_4OH (14.8 M) and 366 ml DI H_2O were poured into a water-jacketed beaker kept at 65 °C with a circulating water bath, when substrates were inside the beaker. After the samples were exposed to the NH_4OH and DI H_2O mixture for ~1 min, i.e. they were NH_4OH-treated, 50 ml $CdSO_4$ (0.015 M) and 25 ml $SC(NH_2)_2$ (1.5 M) were added into the same beaker to start the CdS deposition. The solution was stirred with a magnetic bar starting from the NH_4OH treatment until the end of CBD process. At the end of the deposition, the substrates were rinsed with DI H_2O and dried with N_2. When preparing a sample for investigating the sole effect of the NH_4OH treatment without depositing CdS, only the 1 min NH_4OH treatment part of the CBD process was performed, then the sample was rinsed with DI H_2O and dried with N_2. In addition, effects of NH_4OH treatment and CBD process on KCN-etched A-CZTSSe thin films were also investigated. For this purpose, three samples were prepared from KCN-etched A-CZTSSe absorbers, which were etched by KCN as explained above. The first one (named as "KCN+NH_4OH") underwent the 1 min NH_4OH treatment part of the CBD process only. The second one (named as "CBD-1 min") was taken out of the CBD beaker 1 min after the deposition was started by $CdSO_4$ and $SC(NH_2)_2$ addition into the beaker, i.e. it got exposed to the CBD solution for 1 min only. And, the third one went through the whole CBD process (named as "KCN+CdS"). All of these samples were rinsed with DI H_2O and dried with N_2, once their individual processes were done. CdS layer on the KCN+CdS sample was removed by running dilute HCl over the sample from a pipette to expose the underlying absorber for KPFM measurements, and then it was rinsed with DI H_2O and dried with N_2. Although all processes explained above were investigated on A-CZTSSe thin film, KCN etching was the only surface preparation that was examined on N-CZTSe thin film.

Solar cells were fabricated only by using A-CZTSSe thin film absorbers, and CdS buffer layer was deposited onto both KCN-etched and NH_4OH-treated absorbers in the same batch. After an A-CZTSSe thin film was etched with KCN as explained above, both it and an unetched sample went through the CBD process together to be coated with a 60–70 nm CdS buffer layer. The sample that was non-KCN etched thus became the NH_4OH-treated A-CZTSSe solar cell, because the NH_4OH treatment was a permanent step in our CdS deposition recipe as explained above. According to this process, KCN-etched absorber also went through the NH_4OH treatment naturally during CBD; however, it is referred to as "KCN-etched solar cell". CdS deposition was followed by deposition of a 1.1 μm i-ZnO/ZnO:Al window layer by RF-sputtering (Denton Discovery 18) and a 2.5 μm Ni/Al front contact by e-beam evaporation (Denton SJ20C) onto both KCN-etched and NH_4OH-treated A-CZTSSe/CdS substrates in the same run. Device isolation was done by mechanical scribing. Fabricated solar cells were characterized by dark and illuminated (AM1.5 by solar simulator Oriel Sol3A, Newport) current–voltage measurements at room temperature as well as external quantum efficiency (EQE) measurements (Oriel IQE-200, Newport).

Composition of the A-CZTSSe thin films was measured in a scanning electron microscope (SEM) (FEI Quanta 600 FEG) equipped with an energy dispersive x-ray spectroscope (EDS) (EDAX), and that of the N-CZTSe thin films was measured by x-ray fluorescence (XRF) (Rontgenanalytik Maxxi5pin). The XRF measurements were