Thin Solid Films xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Effect of the duration of a wet KCN etching step and post deposition annealing on the efficiency of $Cu_2ZnSnSe_4$ solar cells

Sylvester Sahayaraj [b,c,d,*], Guy Brammertz [a,b], Bart Vermang [c,d], Samaneh Ranjbar [b,c,e], Marc Meuris [a,b], Jef Vleugels [f], Jef Poortmans [b,c,d]

[a] imec division IMOMEC - partner in Solliance, Wetenschapspark 1, 3590 Diepenbeek, Belgium
[b] Institute for Material Research (IMO) Hasselt University, Wetenschapspark 1, 3590 Diepenbeek, Belgium
[c] imec- partner in Solliance, Kapeldreef 75, 3001 Leuven, Belgium
[d] Department of Electrical Engineering (ESAT), KU Leuven, Kasteelpark Arenberg 10, 3001 Heverlee, Belgium
[e] I3N - Departamento de Física, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
[f] Department of Materials Engineering (MTM), KU Leuven, Kasteelpark Arenberg 44, 3001 Heverlee, Belgium

A R T I C L E I N F O

Article history:
Received 31 May 2016
Received in revised form 23 September 2016
Accepted 27 September 2016
Available online xxxx

Keywords:
KCN solution
Surface degradation
Post deposition annealing
Bulk defect density
Wet etching
Copper zinc tin selenide

A B S T R A C T

The influence of the duration of the KCN etching step on the efficiency of $Cu_2ZnSnSe_4$ (CZTSe) solar cells and Post deposition annealing (PDA) has been explored. CZTSe thin film absorbers prepared by selenization at 450 °C were etched by 5 wt% KCN/KOH from 30s up to 360 s before solar cell processing. KCN etching times above 120 s resulted in poor efficiencies. The fill factor (FF) and short circuit current density (Jsc) of these devices were affected severely. After annealing the solar cells at 200 °C in N_2 atmosphere the best devices degraded and poor devices improved. Combined physical and optoelectronic characterization of the solar cells showed that PDA modifies the bulk defect density and also surface composition which reflects in the solar cell performance.

1. Introduction

Kesterite $Cu_2SnZn(S,Se)_4$ (CZTSSe) solar cells have promising potential to replace the well-known CIGS ($CuInGaSe_2$) and CdTe solar cells in the long-term not only due to their earth abundant and nontoxic constituents (except Se which has low toxicity and also is readily available) but also due an excellent p type conductivity, a high absorption coefficient (10^4 cm^{-1}) and a direct band gap that can be tuned from 1 eV to 3.1 eV by simply adding or substituting the cation (Sn) with other elements (Ge, Si) or the anion (Se) by S [1]. The narrow region of stability [2] of kesterites leads to the formation of different binary selenides of the constituents elements such as $Cu_x(S,Se)$, Zn(S,Se), $Sn(S,Se)_x$ or $Cu_2Sn(S,Se)_3$ during the processing which dent the performance of the solar cells in varying magnitudes [3,4]. Therefore getting rid of these unwanted phases from the active material is paramount to obtaining good devices. The removal of these secondary phases traditionally requires the use of a wet chemical step. The most widely adapted etching technique for obtaining high efficient CZT(SSe) is the KCN based solution [5,6]. In our previous work [7] we have shown that avoiding the KCN etching step results in less efficient solar cells mainly due to the presence of secondary phases thereby re instating the importance of the KCN immersion step. However, due to persistent problems associated in processing as mentioned earlier the duration and the consequences of KCN etching step also needs some revision and understanding. Ever since IBM reported >10% efficiencies for CZTSe solar cells [8] with the introduction of a low temperature annealing step in their processing routine it has been used by many groups processing CZTSe devices as a way to improve the efficiency. The reason for this improvement has a variety of perspectives. Among them, the formation of a Cu poor and Zn rich surface and grain boundaries [9] and change in the concentration of Na in the bulk [10] are widely accepted. Since Post deposition Annealing (PDA) is carried out on our samples after full processing to improve solar cell efficiency and not much has been understood even at a qualitative level certain aspects that help in the understanding of the consequences of PDA have also been discussed in this work. Within this framework a few aspects that will enable better understanding of the influence these two steps in processing pure selenide kesterite CZTSe solar cells have been answered.

* Corresponding author at: IMEC, 75 Kapeldreef, 3001, Heverlee, Belgium.
E-mail address: sahaya@imec.be (S. Sahayaraj).

http://dx.doi.org/10.1016/j.tsf.2016.09.055

2. Experimental methods

2.1. Processing procedure

All solar cells are fabricated on a 3 mm thick, 25 cm^2 soda lime glass substrate covered by 400 nm of Molybdenum (Mo) as electrical back contact. The constituent elements that make up the absorber layer are deposited in the order Sn/Zn/Cu on top of Mo by electron beam evaporation. The precursor films are then selenized at high temperatures (450 °C) to form crystalline CZTSe thin films. During selenization the sample is held on a square shaped graphite plate to which a thermocouple is connected from the side wall. The temperature is measured from the isolating glass substrate and not from the sample surface. Due to difference in the thermal conductivities one can expect the sample surface to be slightly hotter than the glass substrate. The selenization takes place in a rapid thermal annealing system under a Se rich atmosphere created by a constant flow of H_2Se in the chamber. The absorbers are then immersed in KCN solution (5 wt% in aqueous KOH. The concentration of KOH is 0.5 wt% in the KCN solution.) for 30 or 360 s to remove secondary phases, elemental selenium and native oxide from the absorber surface. The CdS buffer layer is deposited by chemical bath deposition at 70° C using $Cd(CH_3CO_2)_2$ and $SC(NH_2)_2$ as precursors in aqueous NH_3 medium. The solar cells were finished by a transparent bi-layer of RF magnetron sputtered i-ZnO (120 nm) and Al:ZnO (280 nm) followed by the deposition of 1 μm thick Al fingers as front contact. Individual cells with an area of 0.5 cm^2 were laterally isolated by mechanical scribing.

2.2. Physical analysis

The cross section and chemical composition of the CZTSe thin films used in this study were evaluated by Scanning electron microscope (SEM) Nova 200 FEI tool, equipped with an energy dispersive X-ray analysis (EDX) system. The accelerating voltage used for the EDX analysis was 20 kV. X-ray Diffraction (XRD) measurements were carried out on a X'Pert Pro MRD X-ray diffractometer in the conventional Bragg-Brentano ω-2θ geometry using the CuKα (1.5418 A°) radiation as the incident beam. X-ray photoelectron spectroscopy (XPS) measurements were performed using a monochromatized AlKα X-ray source (1486.6 eV) and a spot size of 400 μm using a Theta300 system in AR-mode. The XPS measurements were performed on identical CZTSe thin film absorbers and not the solar cells that are discussed in the manuscript. For this purpose the trilayer selenization followed by KCN etching (both described previously) were performed on the same day back to back. This was followed by Post deposition Annealing. The Post deposition Annealing step was carried out for 10 min at 200 °C after which the sample.

was allowed to cool down to <50 °C in roughly 15 min prior to the XPS measurement of the respective sample. After this the samples were vacuum packed and were taken for measurement.

2.3. Electrical and optical analysis

The processed solar cells were analyzed using Current-Voltage (IV) measurements, using a 2401 Keithley Source meter, under standard test conditions for Kesterite solar cells with a solar simulator system using an AM1.5G spectrum with an illumination density of 1000 W/m^2 at 25 °C. The external quantum efficiency (EQE) has been measured at room temperature using a laboratory-built system with a grating monochromator-based dual-beam setup under chopped light from a Xe lamp. The doping profile of the absorbers was measured by capacitance voltage (CV) measurements, which were performed with an Agilent 4980 A LCR-meter with frequencies varying from 10 kHz to 100 kHz. The excitation dependent photoluminescence analysis was performed was measured using a Hamamatsu C12132 near infrared compact fluorescence lifetime measurement system equipped with a cryostat that can be cooled down to liquid N_2 (77 K) temperatures. The tool uses 15 kHz, 1.2 ns pulsed 532 nm laser and the average laser power was varied between 0.08 mW to 56 mW to illuminate an area of 3 mm diameter on the measured solar cell.

3. Results and discussion

3.1. Influence of KCN immersion time on CZTSe absorber and solar cells

Fig. 1a)–e) shows the X-SEM Images of CZTSe thin film absorbers with different KCN immersion times. The CZTSe thin film layers were prepared by the selenization of a Sn/Zn/Cu stack as explained in the previous section. The starting precursor composition is $[Zn]/[Sn] = 1.07 \pm 0.06$ and $[Cu]/[Zn] + [Sn] = 0.69 \pm 0.03$. The absorber thickness is somewhat higher in the case of the sample that had no KCN immersion compared to the others. (The absorber thickness was calculated from the SEM pictures with the micro marker from 5 different places and averaged). The average thickness of the absorber for no KCN immersion is

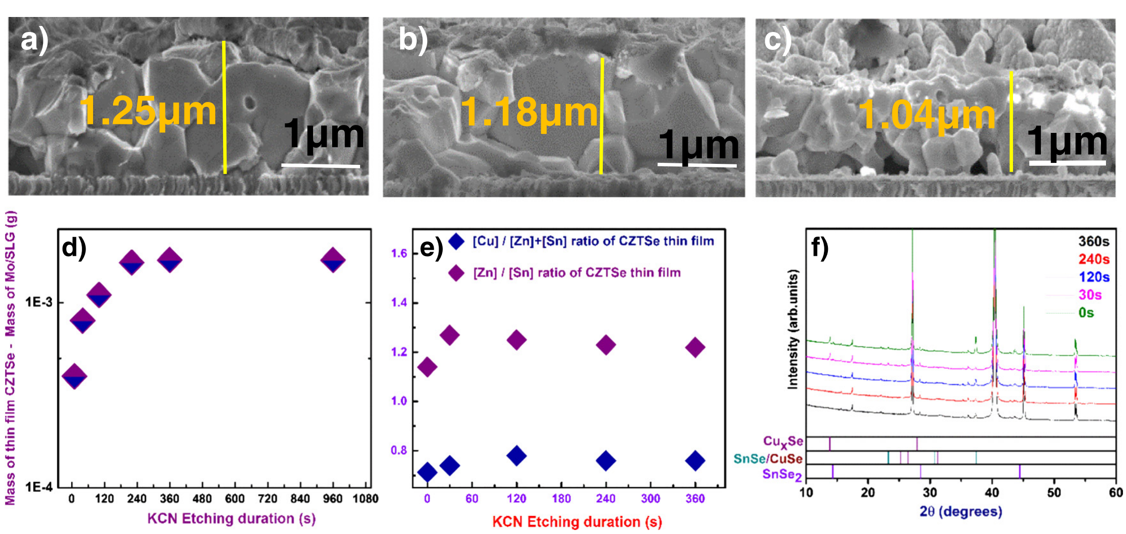

Fig. 1. X-SEM Images of CZTSe thin film with a) no KCN immersion step. b) & c) immersed in KCN for 120 s and 360 s. d) Mass of material removed from CZTSe thin film as a function of KCN immersion time. e) Cation ratios of CZTSe thin films as a function of different KCN immersion times measured by SEM – EDX. f) XRD patterns of CZTSe thin films as a function of KCN immersion time.

Please cite this article as: S. Sahayaraj, et al., Effect of the duration of a wet KCN etching step and post deposition annealing on the efficiency of Cu2ZnSnSe4 solar cells, Thin Solid Films (2016), http://dx.doi.org/10.1016/j.tsf.2016.09.055