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Nanoscale Surface and Interface Characterization of Earth-Abundant Thin-Film Solar Cells

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Nanoscale Surface and Interface Characterization of Earth-Abundant Thin-Film Solar Cells

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy

in

Materials Science and Engineering

by

Kasra Sardashti

Committee in Charge:

Professor Andrew C. Kummel, Chair
Professor Peter Asbeck
Professor Yeshaiahu Fainman
Professor David Fenning
Professor William C. Trogler

2016
The Dissertation of Kasra Sardashti is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California, San Diego

2016
DEDICATION

To my parents, Mahnaz and Sady, whose endless love and support have turned my dream into a reality
Nothing in life is to be feared, it is only to be understood.

*Marie Curie*
# TABLE OF CONTENTS

Signature Page...........................................................................................................iii
Dedication...................................................................................................................iv
Epigraph......................................................................................................................v
Table of Contents.......................................................................................................vi
List of Symbols and Abbreviations...........................................................................ix
List of Figures..............................................................................................................xi
List of Tables.............................................................................................................xiv
Acknowledgments.....................................................................................................xv
Vita............................................................................................................................xviii
Abstract of the Dissertation.....................................................................................xxi

**Chapter 1 Introduction**.........................................................................................1

1.1 Thin film solar cells...............................................................................................1
1.2 Auger Nanoprobe Microscopy.............................................................................2
1.3 Kelvin Probe Force Microscopy.........................................................................2
1.4 References..........................................................................................................8

**Chapter 2 Nano-scale Characterization of Grain Boundaries in High-performance Kesterite Thin Films**.............................................................................9

2.1 Abstract..............................................................................................................9
2.2 Introduction.........................................................................................................9
2.3 Materials and Methods.....................................................................................12
2.4 Results and Discussion.....................................................................................14
Chapter 3 Determining Oxide Composition at Grain Boundaries vs. on Grain Surfaces for CZTSSe Thin Films

3.1 Abstract
3.2 Introduction
3.3 Materials and Methods
3.4 Results and Discussion
3.5 Conclusions
3.6 Acknowledgments
3.7 References

Chapter 4 Cross-sectioning of Thin-film Solar Cells via Grazing Angle of Incidence Cryogenic Focused Ion Beam

4.1 Abstract
4.2 Introduction
4.3 Experimental Details
4.4 Results and Discussion
4.5 Conclusions
4.6 Acknowledgements
4.7 Supporting information........................................................................................................88

4.8 References..........................................................................................................................98
LIST OF SYMBOLS AND ABBREVIATIONS

Å  angstrom
AA  air anneal
AES  auger electron spectroscopy
BE  binding energy
CB  conduction band
CBD  chemical bath deposition
CIGSe  copper-indium-gallium-selenide
CMA  cylindrical mirror analyzer
CPD  contact potential difference
Cryo-FIB  cryogenic focused ion beam
CZTSSe  copper-zinc-tin-sulfide-selenide
DI  deionized
e  electron
E_f  Fermi level
φ  work function
FF  fill factor
fs-UPS  femtosecond-ultraviolet photoelectron spectroscopy
GB  grain boundary
HB  hard bake
ICP-MS  inductively coupled plasma mass spectrometry
J  current density
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J_{SC} )</td>
<td>short circuit current</td>
</tr>
<tr>
<td>KE</td>
<td>kinetic energy</td>
</tr>
<tr>
<td>KPFM</td>
<td>kelvin probe force microscopy</td>
</tr>
<tr>
<td>NanoAuger</td>
<td>auger Nanoprobe Microscopy</td>
</tr>
<tr>
<td>NanoSIMS</td>
<td>nanoscale Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
</tr>
<tr>
<td>PV</td>
<td>photovoltaics</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SP</td>
<td>surface potential</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra-high vacuum</td>
</tr>
<tr>
<td>V</td>
<td>voltage, volts</td>
</tr>
<tr>
<td>VB</td>
<td>valence band</td>
</tr>
<tr>
<td>( V_{OC} )</td>
<td>open circuit voltage</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRF</td>
<td>x-ray fluorescence</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1.1 Global production of elements (in million metric ton) used in thin film solar cell absorbers.................................................................5

Figure 1.2 Schematic diagrams of (a) interaction volume formed as a result of incident electron beam, (b) cylindrical mirror analyzer (CMA) Auger detector used for elemental mapping.................................................................6

Figure 1.3 A block diagram for the dual lock-in amplifier experimental setup ............7

Figure 2.1 Elemental maps for air-annealed CZTSSe..................................................31

Figure 2.2 Elemental maps for NH₄OH-cleaned CZTSSe...........................................32

Figure 2.3 Solar cell device performance........................................................................33

Figure 2.4 Electronic and chemical properties of SnO₂ / CZTSSe and CdS / CZTSSe interfaces....................................................................................34

Figure 2.5 Solar cell device simulation for various CZTSSe thicknesses and back contact work functions........................................................................34

Figure 2.6 Auger survey from 30 to 2200 eV on as-is air-annealed CZTSSe surface..........................................................................................35

Figure 2.7 Elemental composition of the CZTSSe surfaces with no surface clean (black), or NH₄OH (red) and HOOH/NH₄OH (blue) cleans........................................36

Figure 2.8 XPS surface composition of CZTSSe surfaces after cleaning by NH₄OH (a) and HOOH/NH₄OH (b).........................................................................................37

Figure 2.9 Se3d XPS peak for CZTSSe sample cleaned by NH₄OH.................................40

Figure 2.10 Planar elemental maps for CZTSe (pure selenide) measured by Auger Nanoprobe.........................................................................................41

Figure 2.11 Three lines traces extracted from Cu, Zn, Sn and O elemental maps for the NH₄OH-cleaned sample surface.........................................................42

Figure 2.12 Left: Line scans extracted from Sn and O elemental maps for NH4OH-cleaned CZTSSe surface. Right: Grain boundary widths obtained by
measuring the full width at half max (FWHM) of Sn and O spikes at 8 different points.

Figure 2.13 Two typical depth profiles measured in planar and cross-sectional mode on uncleaned air-annealed CZTSSe sample.

Figure 2.14 Planar elemental maps showing the lateral distribution of Cu, Zn, Sn, S, Se and O on the CZTSSe surface after HOOH/NH₄OH cleaning.

Figure 2.15 Atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) images of CZTSSe surface less than 30min after NH₄OH clean.

Figure 2.16 Planar SEM and Cu, Sn and O elemental maps for the CZTSSe samples with and without air anneal.

Figure 2.17 fs-UPS spectra for CZTSSe surfaces after NH₄OH cleaning (a) HOOH / NH₄OH cleaning (b) and 0.3nm Cu deposition followed by anneal at 200 °C (c).

Figure 3.1 Secondary electron micrograph and NanoAuger elemental maps for Cu, Zn, Sn, Se and O measured on as-inserted CZTSSe surface.

Figure 3.2 (a) Secondary electron micrograph and O elemental map for air-annealed CZTSSe surface with the position of the horizontal line trace shown by the dotted lines. (b) Peak-to-peak intensities for Cu, Zn, Sn and O, normalized to the relative sensitivity factors (RSFs), along line traces shown in (a).

Figure 3.3 Secondary electron micrograph and NanoAuger elemental maps for Cu, Zn, Sn, Se and O measured on air-annealed CZTSSe surface 30s of Ar⁺ sputtering.

Figure 3.4 (a) Secondary electron micrograph and Sn elemental map for air-annealed CZTSSe top surface after 30s of Ar⁺ sputtering. (b) Auger survey spectra for area 1 (grain) and point 2 (grain boundary).

Figure 3.5 (a) Secondary electron micrograph of air-annealed CZTSSe surface before Ar⁺ sputtering. The area chosen for spectroscopy is marked by the yellow box. (b) Elemental ratios calculated for Cu, Zn, Sn, S, Se and O in area 1 before (red) and after (blue) Ar⁺ sputtering.

Figure 3.6 Planar secondary electrons and elemental maps for O, S and Se for three different frames measured by NanoSIMS.
Figure 3.7 Planar secondary electrons and elemental maps for O, S and Se measured by NanoSIMS (Cs⁺ source) on (a) hard-baked (HB) and (b) Air-annealed (HB+AA) CZTSSe surfaces.

Figure 4.1 J-V characteristics of two solar cell devices fabricated on the as-deposited CIGSe film.

Figure 4.2 Cryo-FIB cross-sectioning procedure.

Figure 4.3 Topography and surface potential maps for CIGSe thin films in planar and cross-sectional geometries.

Figure 4.4 Nanoauger elemental maps for cigs in planar and cross sectional geometry surfaces.

Figure 4.5 NanoAuger and KPFM measurements on CIGSe/Mo back interface.

Figure 4.6 (a) KPFM surface potential map for sloped cross-section prepared by cryo-FIB. (b) Average grain boundary potential difference (ΔSP_{GB}) as a function of distance from the top of the scan area.

Figure 4.7 NanoAuger elemental maps for Cu, Sn, S, O and Se on CZTSSe sample cleaned by immersion in NH₄OH solution for 5 min.
LIST OF TABLES

Table 2.1 Elemental concentration ratios for cleaned CZTSSe surface calculated from XPS results.................................................................39

Table 2.2 Standard enthalpies of formation at 298.15 K for the oxides of the elements present in CZTSSe.................................................................45

Table 4.1 PV device performance parameters for the CIGSe thin films.........................91
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Sardashti, K.; Chagarov E.; Gershon, T.; Gokmen, T.; Antunez, P.; Ueda S.T.; Haight R.; Kummel A.C. “Potential Control Layer for Back Surface Engineering of Thin-Film Solar Cells” (manuscript in preparation)


Park J.H.; Movva H; Chagarov E; Sardashti K; Chou H; Kwak I; Hu K.T; Fullerton-Shirey S; Choudhury P; Banerjee S; Kummel A.C. “In-Situ Observation of Sub-nanometer Dielectric Growth with Ultrahigh Nucleation Density on Two-Dimensional Surfaces”, Nano Letters 15 (2015).


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Major Field: Materials Science and Engineering

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Professor Andrew C. Kummel
ABSTRACT OF THE DISSERTATION

Nanoscale Surface and Interface Characterization of Earth-Abundant Thin-Film Solar Cells

by

Kasra Sardashti

Doctor of Philosophy in Materials Science and Engineering

University of California, San Diego, 2016

Professor Andrew C. Kummel, Chair

Thin-film kesterites have been explored as promising absorbers in future photovoltaic devices due to their earth-abundant and non-toxic constituents, which do not impose any future production limitations. However, the current record conversion efficiency of polycrystalline kesterite devices is 12.6%—i.e., at least 2.4% short of the efficiency threshold needed to make this material competitive with chalcogenide-based thin film technologies such as Cu(In,Ga)Se₂ and CdTe. This shortage in conversion efficiency has been in part ascribed to the large extent of carrier recombination by defects at the grain boundaries and contact/absorber interfaces.
In this work, methods for nanoscale compositional and electrical characterization of grain boundaries and contact/absorber interfaces in kesterite solar cells have been developed, using a unique combination of advanced nanocharacterization tools including Auger Nanoprobe Microscopy (NanoAuger), Kelvin Probe Force Microscopy (KPFM) and Cryogenic Focused Ion Beam (Cryo-FIB). NanoAuger and KPFM measurements on high-performance CZTSSe thin film PV devices revealed the presence of SnO\textsubscript{x} at the grain boundaries is essential to high $V_{OC}$. This passivation layer needs to be formed by an air-anneal process performed after the film deposition. In contrast to the oxide at the grain boundary, oxide layers on the top surfaces of the grains have been found to be SnZnO\textsubscript{x}. In addition, a cross-sectioning method via grazing angle of incidence Cryo-FIB milling, has been developed where smooth cross-sections with at least 10x scale expansion are prepared. These cross-sections were characterized for CIGSe test films confirming the presence of MoSe\textsubscript{2} interlayer acting as a proper hole contact on the back surface.
Chapter 1

Introduction

1.1 Thin-film solar cells

Among various sources of renewable energy, photovoltaics (PV) are the one of the fastest-growing technologies projected to grain more than 10% of the global electricity market by year 2050. One of the major challenges faced by the PV technology is to be cost efficient relative to the current sources of energy, which requires higher efficiencies and lower materials cost (particularly the absorber), therefore lower cost per generated watt power. Use of thin film PV has been proposed as a viable path to reduce the overall material consumption and as results, the total module cost. For thin film chalcogenide PV technologies such as CdTe and Cu(In,Ga)Se₂ (CIGSe), absorber thickness is no more than 5 µm, and efficiencies beyond 20% have been achieved. In addition, relatively simple growth techniques for these thin films enable large-area monolithic manufacturing of the modules. However, the presence of toxic and non-earth-abundant constituents including Cd, In and Ga could impose potential constraints on the large-scale deployment of the current thin film technologies, preventing them from reaching the goal of a few TW/year power generation levels. As a result, Cu₂ZnSn(S,Se)₄ (CZTSSe) has been introduced as a promising non-toxic and earth-abundant thin film material, where In and Ga replaced with Zn and Sn. Fig. 1.1 displays the annual production rate of the constituents for CZTSSe in comparison with CIGSe. The current record efficiency for CZTSSe is about 12.6%; at least 2.4% short of the
efficiency threshold needed to make this material competitive with chalcogenide-based thin film technologies.\textsuperscript{5,6} Many efforts are being to improve the performance of this material by optimizing the quality of bulk crystals as well as contact / absorber interfaces. The goal of this work is to understand the impact of the nanoscale composition and electronics of the surfaces and grain boundaries in the PV performance of these materials.

\subsection*{1.2 Auger nanoprobe microscopy (NanoAuger)}

Auger nanoprobe microscopy (NanoAuger, also known as scanning Auger microscopy) is a strong tool for nanoscale chemical analysis of surface and interfaces with high lateral resolution (\textasciitilde5 nm) and surface sensitivity (analysis depth < 3 nm). Despite lower resolution than TEM-EDS and TEM-EELS, high surface sensitivity and minimal needs for sample preparation makes NanoAuger a promising nanocharacterization tool. During NanoAuger elemental mapping, an electron beam with typically 10 – 30 kV beam energy and about 1.0 nA beam current is rastered over the sample surface. Fig. 1.2 (a) shows the interaction volume formed as a result of electron beam irradiation of a solid sample. Secondary electrons provide information on the surface topography while Auger electrons provide information on the elemental composition. During the mapping measurements, secondary and Auger electrons are collected simultaneously using scintillation detector and cylindrical mirror analyzer (CMA), respectively. Fig 1.2 (b) displays the generation and collection geometry for the Auger electrons. The CMA geometry enables a 360° azimuthal collection angle around
the electron gun thereby collecting Auger electrons from any sample surface that is in
the line of sight to the incident electron beam. Therefore, Auger signal remains
insensitive to the emission angle and surface topography. The chamber pressure during
the measurements was maintained within $6 \times 10^{-10}$ to $3 \times 10^{-9}$ torr range.

1.3 Kelvin probe force microscopy (KPFM)

KPFM measurements determine the contact potential difference (CPD) (or
surface potential) between a conductive probe and sample with resolutions as low as 1
nm, in ambient conditions. Surface potential ($V_{SP}$) can be derived as a function of tip
and sample work functions:

$$V_{SP} = \frac{\varphi_{tip} - \varphi_{sample}}{-e},$$

(1.1)

, where $\varphi_{tip}$ and $\varphi_{sample}$ are the work functions of the tip and sample, respectively, and $e$
is the elementary charge. By knowing the tip work function and measuring $V_{SP}$, local
work function on the sample surface can be determined. KPFM measurements in air or
under inert atmospheres (i.e. $N_2$ or Ar) with high lateral resolution are typically
performed using dual lock-in amplifier setup, which enables simultaneous
measurements of topography and surface potential. A block diagram of the dual lock-in
amplifier (LIA) configuration is shown in Fig. 1.3. Measurements are performed in
intermittent contact mode (known as tapping mode) where topography is probed at or
close to the resonance frequency of the cantilever. The modulation and detection of surface topography is performed by the first LIA. The second LIA applies an AC bias with frequencies between 5 – 10 KHz (depending on the resonance frequency), therefore modulating the electrostatic force between the tip and the sample surface. A servo is used to apply a DC bias (equivalent to $V_{SP}$) in order to nullify this electrostatic force. Use of dual LIA setup allows minimal crosstalk between topography and surface potential signals. For KPFM measurements, it is necessary to use highly-conductive AFM probes made of heavily-doped n-type Si coated with Pt/Ir (NANOSENSORS™ PPP probes).
Figure 1.1 Global production (in million metric ton per year) for the elements used in thin film solar cell absorbers.
Figure 1.2 Schematic diagrams of (a) interaction volume formed as a result of incident electron beam, (b) cylindrical mirror analyzer (CMA) Auger detector used for elemental mapping.
Figure 1.3 A block diagram for the dual lock-in amplifier experimental setup to implement amplitude-modulated kelvin probe force microscopy (AM-KPFM) measurements.
1.4 References


Chapter 2

Nano-scale Characterization of Grain Boundaries in High-performance Kesterite Thin Films

2.1 Abstract

The effort to develop earth-abundant kesterite solar cells has led to an approximate doubling of the power conversion efficiency over the past five years to 12.6%, primarily due to increases in short-circuit current and fill factor; open-circuit voltage has resisted similar change, limiting further efficiency improvement. In the present investigation, Auger nanoprobe spectroscopy, X-ray/ultraviolet photoelectron spectroscopy and device characterization are employed to provide a comprehensive understanding of the role of grain boundaries and interfaces in limiting performance in kesterite-based devices. High photovoltaic performance is found to correlate with grain boundaries that are Cu-depleted and enriched with SnOx. The formation of this bulk-like oxide at grain boundaries with type I band offset provides a unique effective passivation that limits electron-hole recombination. Building on these new insights, photovoltaic device simulations were performed that show optimized electrostatic designs can compensate for bulk defects, allowing efficiencies closer to the theoretical limit.

2.2 Introduction
Among chalcogenide solar cell absorbers, copper-indium-gallium-sulfide-selenide (CIGSSe) compounds have shown power conversion efficiencies of as high as 20.9%. However, scarcity and rising cost of In and Ga are expected to limit the maximum power production capacity to ~100 GWp yr\(^{-1}\). In kesterites like copper-zinc-tin-sulfide/selenide (Cu\(_2\)ZnSn(S\(_x\)Se\(_{1-x}\))\(_4\) or CZTSSe), In and Ga are replaced with the more earth-abundant and low-cost elements, Zn and Sn; overall production capacity of >100 GWp yr\(^{-1}\) has been foreseen for CZTSSe devices. While power conversion efficiency of polycrystalline CZTSSe solar cells has increased from 0.66% to 12.6%, to compete with CIGSSe technologies, CZTSSe devices need conversion efficiencies in excess of 15%. With short-circuit-current (\(J_{sc}\)) having reached >81% of the Shockley-Queisser (SQ) limit, open-circuit-voltage (\(V_{oc}\)) represents the predominant barrier to further efficiency improvement, currently rising to only 62% of the theoretical limit. Improvement in \(V_{oc}\) directly relies on understanding and controlling defect-mediated recombination mechanisms within the bulk, at the grain boundaries (GBs) and at interfaces between CZTSSe and buffer layers or secondary phases.

Champion devices for both CIGSSe and CZTSSe employ CdS buffers deposited by chemical bath deposition (CBD). CdS/CZTSSe and CdS/CIGSSe junction qualities have been theoretically and experimentally shown to be superior for Cu-poor absorber surfaces. The Cu-poor surfaces can accommodate Cd\(^{2+}\) ions from the chemical bath within the high density of Cu vacancies, forming a sub-surface p-n homojunction a few nanometers below the physical CdS/CIGSSe heterojunction. However, Zn-rich surfaces might give rise to higher recombination rates by formation
of secondary phases such as Zn(S,Se)$^{19, 20}$ and Cu$_2$Sn(S,Se)$_3$$^{21, 22}$ CZTSSe oxides can also form during the growth or post-growth processing. In contrast to Si-based photovoltaics, oxidation by air anneal at 300-400 °C increases CZTSSe cell efficiencies; inspired by the extensive studies on CIGSSe, it is hypothesized that during the air anneal oxygen and sodium (from the soda-lime glass substrate) diffuse through the GBs and passivate the defect sites that cause non-radiative recombination.$^{23-25}$ However, oxide formation at the GBs has not been directly observed, and it is unknown whether this process leads to atomic scale substitution of sodium and oxygen at CZTSSe lattice sites as proposed theoretically$^{26}$ or to formation of a bulk oxide phase selectively at the grain boundaries.

In this chapter, the dependence of the macroscale CZTSSe photovoltaic device performance on the nano-scale elemental distributions on the surface and at the grain boundaries are determined with Auger Nanoprobe Spectroscopy (NanoAuger). This is the first time that Auger Nanoprobe elemental mapping has been employed to determine the nanoscale elemental distribution on the kesterite absorber surfaces, and the 8nm lateral resolution provides an unprecedented view of grain features both at the surface and in cross-section. Device characterization and photoelectron spectroscopy data are consistent with the formation of grain boundaries enriched with tin oxide (SnO$_x$), along with Cu-poor CdS/CZTSSe interfaces, being crucial for high efficiency CZTSSe solar cells. These observations go beyond the models predicting passivation of GBs simply with atomic scale replacement of CZTSSe constituents with Na and O.$^{23, 26, 27}$ Device simulations for the CZTSSe solar cells show that, with effective grain boundary
passivation, current bulk defect densities can be compensated by engineering the electrostatics in the devices (by combination of thinner absorbers with high-reflectivity, high-work-function backside contacts) to raise efficiencies to >16%.

2.3 Materials and Methods

Solution-phase thin film CZTSSe preparation and surface cleaning: 2-μm-thick CZTSSe films were prepared by spin coating of hydrazine-based precursor solutions onto Mo-coated soda lime glass substrates in a nitrogen-filled glove box. Further details of the synthesis have been published. The bulk [Cu]/[Zn] and [Se]/[S]+[Se] measured by X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) analysis were 1.8 and 0.7, respectively. The resulting band gap for the CZTSSe films was 1.13 eV. After spin coating, all samples were subjected to a 15-min hard bake (HB) heat treatment at 600 °C in a nitrogen-filled glove box followed by an air anneal (AA) at temperatures in the range of 300 – 400 °C for several minutes. To remove the surface oxide two surface cleaning recipes were used: 1) 5 min dip in 7% aqueous NH₄OH solution followed by N₂ drying for 20 s; 2) 1 min dip in 30% aqueous H₂O₂ solution followed by 5 min dip in 7% aqueous NH₄OH solution and N₂ dry for 20 s. Sub-surface incorporation of Cu into CZTSSe has been conducted on the samples, cleaned with 5 min NH₄OH dip, by 3-5 Å Cu e-beam evaporation deposition and post deposition annealing in N₂-filled glove box at 200 °C.

Solar cell device fabrication: The typical device structure for champion CIGSSe and CZTSSe was employed throughout the study. 25-nm-thick CdS buffers were
deposited onto CZTSSe films by standard chemical-bath deposition followed by RF magnetron deposition of 10-nm-thick ZnO window and 50-nm-thick ITO top transparent contacts. Patterned 2-µm-thick Ni/Al collector grids were also applied. The total device area defined by mechanical scribing was 0.45 cm².

Solar power conversion efficiency characterization: Current-voltage measurements were performed using a Newport solar simulator with simulated AM1.5G illumination and 6” × 6” beam. A Keithley 2400 sourcemeter was used for bias application and current measurement. The system is equipped with custom-designed software that controls light stabilization and automates data acquisition using a Keithley 2400.

X-ray photoelectron spectroscopy (XPS) and femtosecond-ultraviolet photoelectron spectroscopy (fs-UPS): XPS measurements were carried out using a monochromatic XM 1000 MkII/SPHERA (by Omicron Nanotechnology) XPS system with an Al-Kα source (E=1486.7 eV). For all measurements, a take-off angle of 30° from the sample surface was used. Surface compositional analysis using XPS spectra was performed using CASA XPS v.2.3. Femtosecond UPS (fs-UPS) has been previously described in detail. In the fs-UPS measurement, a regeneratively amplified, 1 kHz repetition rate Ti:Sapphire laser is utilized for pump and probe steps, with probe photon energies of 15 to 40 eV and light pulse widths of 50 fs. For CZTSSe surfaces, 1.55 eV pump pulses were focused on the probe area.
Auger nanoprobe spectroscopy and microscopy (NanoAuger): Auger spectroscopy and compositional mapping has been performed using a Physical Electronics PHI-700 Auger Nanoprobe Microscope at the Stanford Nanocharacterization Laboratory. For spectroscopy and mapping, a 10 KeV and 1.0 nA electron beam was focused on the sample (with 3.75x5 µm$^2$ raster) and secondary and Auger electrons were collected by the two separate detectors, both located above the sample (take off angle of 90°). The base pressure for the measurements was ~ 1-2x10$^{-9}$ torr. Intensities used for single point and line trace composition measurements were normalized to the relative sensitivity factors of the elements’ primary Auger peaks.

Solar Cell Device Simulations: Device simulations were carried out using the WXAMPS software with parameters optimized for hydrazine-processed CZTSSe samples with world record efficiency of 12.6%.

2.4 Results and Discussion

Nanoscale surface compositional variations on CZTSSe films were obtained by highly surface-sensitive Auger Nanoprobe elemental mapping using Auger primary peaks for Cu, Zn, Sn, S, Se and O (for details see supplemental materials Fig 2.6 and 2.7). Fig. 2.1(a) shows the elemental maps in planar mode for the CZTSSe surface after air-anneal at 375 °C for 10min (a typical treatment for high-performance devices). X-ray photoelectron spectroscopy (XPS) results show that the air anneal produces an oxide-covered, Cu-depleted surface with high Zn and Sn concentration ([Cu]/[Zn]+[Sn]=0.32, [Sn]/[Sn]+[Zn]=0.47; supplemental materials Fig 2.8, Table
2.1). On the air-annealed surface, a relatively uniform distribution of S and Zn is observed between the grains and GBs. In stark contrast, both Sn and O appear as bright lines and Cu as dark lines that delineate the boundaries between the grains where grooving also occurs (GBs are denoted by ① and ⑤ in the SEM image). The bright Sn and O lines indicate the formation of SnOₓ enriched layers at the GBs. However, in the compositional map a uniform background subtraction is automatically performed which highlights enrichment at grain boundaries when the elemental composition is uniform across all grains. In contrast, single point measurement presented in table 1 give accurate compositional ratios since a full spectrum is recorded at each point. Based on single point spectroscopy, the amount of Zn at the GBs is comparable to Sn (Sn/(Zn+Sn) = 0.48 -0.51) similar to the oxide on grains top surfaces. In both elemental maps and spectroscopy results, the actual compositional contrast between the grains and GBs can be screened by the presence of oxide on the top surface.

The more exothermic formation reaction for SnO₂ and ZnO relative to SeO₂ and CuO, make them the more thermodynamically favorable native oxides on CZTSSe (see supplementary materials). Despite a smaller enthalpy of formation, both SeO₂ and selenates (as NaSeO₂ or SnSeO₄) have been observed on the CZTSSe surfaces (supplemental materials Fig 2.9).²⁴ The SO₂ enthalpy of formation is as large as Sn and Zn oxide but its high vapor pressure is consistent with its evaporation in UHV. Therefore, although in principle the compositional variations depicted in Fig. 2.1 could be understood in terms of highly oxygen-substituted CZTSSe interfaces, a combination
of zinc, tin and selenium oxides on the surface of air annealed CZTSSe can be expected from thermodynamic considerations.

Cross-sectional elemental maps for the cleaved air-annealed sample are shown in Fig. 2.1(b). Polycrystalline CZTSSe mechanical fracture will occur predominantly along the grain boundaries; therefore, cleavage should expose the surface of oxidized grains at the GBs (called GB faces) instead of the unoxidized grain interior.\textsuperscript{28} Due to a sample stage tilt of 2°, the cross-sectional maps include some view of the top film surface. Compared to the top surface, Cu, S and Se have higher intensities on the cross-sectional GB faces while intensities of Sn, Zn and O are smaller. However, GBs perpendicular to the imaging section (③and ⑤) as well as a fraction of GB faces, are Cu-poor and Sn-/O- rich. When compared with the single points spectroscopy results in planar maps (Table in Fig. 2.1(a)), GBs seen in the cross-sectional images contain more Se (higher [Se]/CZTSSe) and more Sn (higher [Sn]/([Zn]+[Sn])). Se oxidation has been previously reported on CIGSSe\textsuperscript{25} and CZTSSe\textsuperscript{24} surfaces, and it is expected that Se from CZTSSe oxidizes during the air anneal to form Sn(O,Se)\textsubscript{X}. Formation of Sn(O,Se)\textsubscript{X} is consistent with the XPS and SIMS measurements (see supplementary materials).

To replicate the conditions of the CdS chemical bath deposition step used to make devices, samples were treated with dilute ammonium hydroxide (NH\textsubscript{4}OH), which is present in the CdS deposition bath solution and is known for dissolving metal oxides.\textsuperscript{24} XPS measurements showed that NH\textsubscript{4}OH surface cleaning reduced the surface O intensity to 10% of substrate intensity (sum of Cu, Zn, Sn, S and Se intensities) and resulted in a Cu-deficient surface ([Cu]/([Zn]+[Sn])) = 0.67; see supplemental materials
While very low oxygen concentrations were measured by XPS and large area AES, elemental maps in Fig. 2.2 clearly depict the GBs (point ① and ③) as Sn/O-rich and Cu-/Se-poor, consistent with SnO_x enrichment of grain boundaries and grooves even after NH_4OH oxide removal from the top surface. Moreover, small SnO_x-rich patches can be observed in planar maps (point ⑤) consistent with the NH_4OH clean leaving oxide in the all grain boundaries and in a few small regions of the top surface. After oxide removal, single point spectroscopy results for GBs in Fig. 2.2 show higher concentration of Sn (higher [Sn]/([Zn]+[Sn])) consistent with removal of more ZnO from the top surface of the GBs. Similar to air-annealed surfaces prior to NH_4OH cleaning, single point spectroscopy (Table in Fig. 2.2(b)) and line scans of the NH_4OH-cleaned surface extracted from the elemental maps (see supplemental materials Fig 2.11, 2.12) show that GBs are not completely depleted from Cu, Se and S. The width of the SnO_x-rich GBs extracted from line traces in the elemental maps varies between 90 nm and 270 nm implying that the SnO_x layer is bulk-like in character and covers the GBs. However, based on the comparison between depth profiles in planar and cross-sectional NanoAuger, thickness of SnO_x patches at the GB faces was estimated to be at least three times thinner than the native oxide on the grain surfaces of the air-annealed sample (supplemental materials Fig 2.13). Therefore, it is hypothesized that SnO_x is present at the GBs in the form of thin SnO_x crystallites that when probed by NanoAuger, due to large incident electron beam size, cannot be resolved as individual features since a large area of CZTSSe matrix surrounding the crystallites is concurrently probed. Furthermore, Cu, Sn and Se Auger electrons have larger mean escape depths than Sn.
and O increasing the probability of probing the CZTSSe matrix around SnOx crystallites.

Comparison of the top surface with the GB faces shown in the cross-sectional maps of the NH$_4$OH-cleaned CZTSSe (Fig. 2.2(b)) reveals that GBs remain Sn- and O-rich after the oxide removal from the top surface. Furthermore, consistent with the uncleaned air-annealed sample’s cross-section (Fig. 2.1(b)), GB faces (point ②) as well as GBs perpendicular to the cross-section (① and ③) are covered in SnO$_x$ and partly Sn(O,Se)$_x$. More O- and Sn-rich oxide patches can also be observed on the GB surfaces, adjacent to the bottom of the film (point ⑤). This confirms that NH$_4$OH clean influences only the composition of the top surface and leaves the oxides at the GBs within the film.

In order to correlate the compositional variations measured by NanoAuger with PV device characteristics, solar cells were fabricated with the device structure shown in Fig. 2.3(a). CdS buffers were deposited by CBD in NH$_4$OH solution on the top surfaces of polycrystalline CZTSSe films prepared under various conditions. To determine the effect of various surface cleaning elements on the surface composition and solar cell performance, beside NH$_4$OH single dip two additional cleaning recipes were investigated: 1) HOOH followed by NH$_4$OH (HOOH/NH$_4$OH clean); 2) NH$_4$OH clean followed by 0.3nm Cu deposition and UHV anneal at 200 °C. Exposure of the CZTSSe to 30% HOOH generates a surface oxide that is subsequently removed by the NH$_4$OH; this two-step process etches down into the CZTSSe producing an oxygen-free (O intensity as low as 5% of the substrate intensity) surface with slightly higher Cu
concentration than the NH₄OH-cleaned surface ([Cu]/([Zn]+[Sn])=0.71; supplemental materials). Deposition of 0.3 nm of Cu on a NH₄OH-cleaned surface followed by UHV anneal ensures formation of a Cu-rich top surface via Cu incorporation into the top few monolayers of CZTSSe. Prior to all surface preparations, samples were annealed in air at 375 °C for several minutes.

Air-annealed samples cleaned with NH₄OH (resulting in relatively Cu-poor surfaces) showed efficiencies of 11-12% without antireflection coating (Fig. 2.3(b) and (c)). HOOH/NH₄OH-cleaning of CZTSSe devices, as well as Cu deposition and post-deposition annealing, resulted in poor device efficiencies (~ 0.1%). Both cells suffered from low open circuit voltage (V_{oc}), short circuit current (J_{sc}) and fill factor (FF), all giving rise to very low efficiencies. However, the efficiency of CZTSSe solar cells first etched by HOOH/NH₄OH can be restored to 11% by a second air anneal followed by oxide etch in NH₄OH (Fig. 2.3(d)). This confirms that the mechanisms limiting their performance are only limited to the top surface of the film and can be improved by repeating the proper surface treatment.

The difference in device performance results can be explained in the context of the elemental maps for the CZTSSe surface cleaned by HOOH/NH₄OH (Fig. 2.4(a)). A majority of GBs after HOOH/NH₄OH clean are no longer Cu-deficient and Sn- and O-rich (maps for all the elements are available in the supplemental materials Fig 2.14). Since HOOH/NH₄OH affects only the near surface region, only GBs adjacent to, or at the film top surface lose their SnOₓ termination. Conversely, air-annealed devices cleaned only with NH₄OH (Fig. 2.3) performed comparably to the highest efficiency
CZTSSe devices. Therefore, some combination of film surface/grain boundary stoichiometry modification (i.e., especially Cu content) and the passivation of the GBs with thin SnOₓ crystallites spanning the full film thickness and including the regions adjacent to the buffer/absorber interface must be critical to efficient device performance. NH₄OH removes the oxides on the grains at the CZTSSe/CdS interface, which is critical to high Jᵥsc. Fig. 2.4(b) depicts the band bending diagram for CdS/CZTSSe/SnOₓ constructed by femtosecond ultraviolet photoelectron spectroscopy (fs-UPS, see methods) measurements on CdS/CZTSSe combined with UPS results from the literature for SnO₂. There is at least a 1.9-eV barrier for holes between CZTSSe and SnOₓ due to the large valence band offset, and the electron barrier varies between 0.6-0.8eV depending on the concentration of the oxygen vacancies (as donors) and Zn (as acceptors); the UPS data is consistent with the SnOₓ crystallites neither trapping electrons nor holes. Also, note that non-conducting oxide-rich grain boundaries running perpendicular to the film surface should not impede current collection, which is also primarily a vertical process. Since the grains in these films are quite large, there are relatively few horizontal grain boundaries that the current needs to traverse to be collected.

Complimentary Kelvin probe force microscopy at the grain boundaries showed 60 to 100 meV higher work function for GBs relative to the grains on the NH₄OH-cleaned CZTSSe surfaces (supplemental materials Fig 2.15). These KPFM measurements are consistent with internal fields resulting in upward band bending and negative charge at and near the GB that repels electrons and prevent recombination in
the vicinity of GBs. Therefore, upward band bending combined with type I band offset at the grain boundaries prevents the photoexcited electrons or holes from entering the GBs and recombining at the GB defects. This contrasts with the hypothesis of electron collection at the GBs and electron current flow in their vicinity in the absence of CZTSSe grain boundary oxidation.\textsuperscript{34} Removal of the SnO\textsubscript{x}-passivation layer at the GBs at and near HOOH/NH\textsubscript{4}OH-cleaned surface will lead to higher recombination rates near the CdS/CZTSSe junction and a significant decrease in both V\textsubscript{OC} and J\textsubscript{SC}. Similarly, poor PV device performance was observed for CZTSSe without air anneal where Auger Nanoprobe elemental maps show the absence of SnO\textsubscript{x} at the grain boundaries (supplemental materials Fig 2.16).

In order to explain the poor device performance in the sample with 0.3 nm Cu deposition, the effect of Cu concentration on the surface charge and CdS/CZTSSe heterojunction quality was assessed by measuring surface work function, band bending and flat band Fermi level positions (relative to the valence band) using fs-UPS (Fig. 2.4 (c) and supplemental materials Fig 2.17).\textsuperscript{24} Surface band bending is an important indication of charged defects at or near the surface. Particularly, the density of ionized, and hence negatively charged, Cu vacancies (V\textsubscript{Cu}) near the Cu-depleted surface directly corresponds to the magnitude and direction of the band bending, consistent with the mechanisms suggested for CIGS.\textsuperscript{17, 25, 35} As shown in Fig. 2.4(c), for the most Cu-depleted (NH\textsubscript{4}OH-treated) surfaces, an upward band bending of 180 meV was measured indicating substantial negative charge; this value dropped by only 50 meV to 130 meV for the HOOH/NH\textsubscript{4}OH-etched surface possessing a higher Cu concentration. Finally the
surface following 0.3 nm Cu deposition and anneal displayed a switch to downward band bending of 100 meV indicating the full eradication of negative charge at and near the surface.

By linking the spectroscopy and device results, the critical role of \( V_{Cu} \) in solar cell performance can be hypothesized. Angle-resolved XPS and transmission electron microscopy (TEM) studies on Cu-poor CIGSSe samples, suggest that \( Cd^{2+} \) from the CdS bath diffuses up to 30nm into the substrate.\(^{15, 16}\) \( Cd^{2+} \) is believed to occupy vacant Cu sites (\( V_{Cu} \)) forming positively-charged donor states (\( Cd_{Cu}^+ \)) in CIGSSe and resulting in a thin n-doped region a few tens of nanometers away from the CdS/CIGSSe junction.\(^{18, 36-38}\) Cd has been predicted to behave similarly at the CdS/CZTSSe interface, although in this system there is also the likelihood of Cd occupying the Zn site.\(^{13, 39, 40}\) Therefore, poor PV performance after 0.3nm of Cu deposition followed by post deposition anneal can be attributed to removal of the majority of \( V_{Cu} \) at or near the surface. Conversely, since surface negative charge (equivalent to \( V_{Cu} \) concentration) has not been eliminated for HOOH/NH\(_4\)OH, the deterioration in its performance can be attributed to the removal of SnO\(_x\) crystallites at the GBs near the CdS/CZTSSe junction.

Compositional measurements along a line from the CdS top surface to the bottom of the CZTSSe film in Fig. 2.4(d) and (e) show that Cd and S signals do not reach their minimum until 260 nm beyond the point where Cu and Se (representing the CZTSSe substrate) reach their maximum intensity. The data is consistent with CdS depositing conformally on the surfaces as well as within GBs over a distance of 200-300 nm from the surface. Therefore, the CdS/ CZTSSe interface extends to the grain
sidewalls at the GBs, increasing the CdS/CZTSSe junction area and necessitating Cu-poor sidewalls for better device performance.

While a thin SnO$_x$ barrier layer and a Cu-depleted surface can passivate grain boundaries and improve the CdS/CZTSSe junction properties, high densities of anti-site disorder lead to band tailing, thereby providing another pathway for $V_{oc}$ reduction driven by the bulk of the CZTSSe grains. The presence of an internal electric field across the film can overcome the adverse effect of the bulk defects in an absorber and result in substantially higher $V_{oc}$ and power conversion efficiency. Effective internal electric fields can be introduced by modification of the back contact work function in concert with an optimal CZTSSe absorber thickness. Coupling CZTSSe, whose work function (WF) is 5.2 eV, to a back contact material with a greater WF (for instance MoO$_3$, WF=6.5eV) will result in electron transfer and a resulting electric field that will drive the photoexcited electrons to the front contact. Since the sum of the minority carrier diffusion length and depletion width in CZTSSe is less than 1µm, the absorber thickness is an important parameter. In order to model this device architecture, device simulations were performed with WXAMPS, whose parameters were first extracted from detailed modeling of 12.6% efficiency devices. A schematic showing the electronic structure of the device and results of WXAMPS modeling for efficiency, $V_{oc}$ and $J_{sc}$ are shown in Fig. 2.5. The model compares the performance of a CZTSSe device for a standard Mo/glass substrate with that achieved for a high WF back contact such as MoO$_3$, which possesses a 6.5 eV WF. Additional comparisons are made for a reflective (R=1) layer added to the contact. For absorber thicknesses below 1µm, substantial
increases in $V_{OC}$ are observed with decreasing thickness, while $J_{SC}$ peaks near 600nm; below this the CZTSSe is simply too thin to fully absorb the incoming light. With this approach, efficiencies of as high as 15-16% result within the device simulation for a reflective back contact and absorber thicknesses ~0.5 µm.

2.5 Conclusion

It has been shown for the first time that the nanoscale elemental compositions of the grain boundaries and absorber/buffer interface strongly influence performance of polycrystalline CZTSSe photovoltaic devices. In particular, the presence of tin oxide at the grain boundaries, formed after annealing the bare absorber in air, is found to correlate with high device performance and is proposed to passivate GB recombination sites. Observation of a distinct tin-oxide layer suggests that GB passivation by an air anneal may occur due to thin bulk-like crystallite formation rather than simple atomic-scale O and Na defect passivation, thereby providing a new method of grain boundary passivation. NanoAuger and photoelectron spectroscopy experiments are consistent with a Cu-deficient buffer/absorber interface being required for the formation of a proper p-n junction to guide electrons from the CZTSSe top surface into the buffer and subsequent top contacts. PV device modeling shows that, given the effective passivation of the grain boundaries and interfaces using mechanisms described in this study, internal electrostatic fields may be used to reduce the effect of remaining bulk defects and substantially raise both Voc and power conversion efficiency. Utilization of a high work function, reflective back contact coupled with careful selection of absorber thickness
introduces an internal electrostatic field to efficiently drive the separation of photoexcited electrons and holes. This work provides a detailed evaluation of interface properties in high-performance CZTSSe devices and, given an effective pathway to interface passivation, provides a roadmap for fabrication of higher efficiency, earth abundant, kesterite thin-film photovoltaic devices, even in the presence of bulk defects.

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2.7 Supplemental materials

NanoAuger quantitative analysis: Fig. 2.6 shows the Auger survey for the as-is air-annealed CZTSSe surface. The peaks used for single point and line scan spectroscopy as well as elemental mapping are marked by green boxes. Note that for S both high and low kinetic energy peaks are shown. For quantitative Auger analysis and mapping purposes, only the low kinetic energy S peak was used. To obtain the elemental composition of the surface, relative sensitivity factors (RSF) have been applied. RSF accounts for the difference in the sensitivity of Auger spectroscopy in measuring the core levels of various elements—i.e. RSF normalizes the peak intensity to the core level’s photoionization cross-section and mean free path of photoelectrons in the compound. Elemental concentration of element A ([A]) can be calculated by dividing its intensity (I_A) normalized by its RSF by the sum of all normalized intensities for the elements present in the material:
\[ [A] = \frac{I_A}{\sum \frac{I_i}{RSF_i}} \]  

(2.1)

\[ \sum \frac{I_i}{RSF_i} = \frac{I_{Cu}}{RSF_{Cu}} + \frac{I_{Zn}}{RSF_{Zn}} + \frac{I_{Sn}}{RSF_{Sn}} + \frac{I_S}{RSF_S} + \frac{I_{Se}}{RSF_{Se}} \]  

(2.2)

Elemental composition for as-is CZTSSe surfaces as well as NH₄OH- and HOOH/NH₄OH-cleaned surfaces are shown in Fig. 2.7. Elemental compositions are consistent with formation of more Cu-rich surface after HOOH/NH₄OH compared to NH₄OH clean. Elemental maps are showing the variations in absolute intensity for each element on the sample surface. For the elemental maps, compositional ratios such as \([Cu]/[Zn]+[Sn]\) and \([Se]/[S]+[Se]\) were calculated using equations similar to 2.1 and 2.2. However, instead of peak area, signal intensity at the point of interest was normalized by the relevant peak’s RSF. RSF values used in this study were obtained from the Handbook of Auger Electron Spectroscopy.⁴⁹

XPS measurements were carried out on air annealed and cleaned CZTSSe surfaces by measuring the following peaks: Cu3d, Zn3d, Sn4d, S2p, Se3d, C1s and O1s. XPS quantification was performed similar to the Auger measurements, by using RSF values calculated specifically for XPS measurements by Yeh and Lindau.⁵⁰ Atomic concentrations were obtained using Eq. 2.1 and 2.2 with the relevant RSF values. Fig. 2.8 shows the elemental concentrations for air annealed CZTSSe surface before and after NH₄OH and HOOH/NH₄OH cleaning. Some of the critical elemental ratios for the cleaned CZTSSe surfaces including \([Cu]/[Zn]+[Sn]\) are listed in the table S1. As
observed in Auger measurements, HOOH/NH$_4$OH cleaning leads to higher Cu content at the surface with 3x smaller carbon content.

Fig. 2.9 shows the Se3d spectra for the NH$_4$OH-cleaned CZTSSe surface (magenta line). After surface clean, the sample was exposed to air for 7 days and Se3d measurement was repeated (black line). Also for as-is air annealed CZTSSe surfaces, Se3d spectra for the NH$_4$OH-cleaned sample exposed to air has a second peak at ~5eV higher binding energy than the Se peak at 54 eV. This peak can be attributed to the presence of SeO$_2$ or selenates such as NaSeO$_3$ and SnSeO$_4$ on the surface.

Fig. 2.10 shows the Auger Nanoprobe elemental maps for CZTSe (pure selenide) that were grown by thermal evaporation. Unlike CZTSSe planar elemental maps, CZTSe maps show Zn signal enhancement at the grain boundaries and some spots on the grains. Se enhancement can be observed at the same location as Zn, consistent with formation of ZnSe secondary phase. This proves that the Auger Nanoprobe microscope employed in this study is capable of measuring the lateral distribution as well as other elements in CZTSSe and the uniform distribution of Zn in CZTSSe elemental maps (Fig. 2.1 and 2.2) is not because of measurement artifacts.

KPFM combined with atomic force microscopy (AFM) was employed in order to measure the variations in the work function and resulting electric fields on the CZTSSe surface and in between grains and grain boundaries. KPFM measures the contact potential difference or surface potential (CPD or SP) between a metallic or
metal-coated AFM probe and sample surface. The surface potential voltage \( V_{SP} \) directly corresponds to the difference between the tip and sample work functions:

\[
V_{SP} = \frac{\phi_{tip} - \phi_{sample}}{-e},
\]

where \( \phi_{tip} \) and \( \phi_{sample} \) are the work functions of the sample and tip, respectively, and \( e \) is the elementary charge. Knowing the tip work function, variation of surface work function over the sample surface can be determined with resolutions as good as AFM resolution (~1-5 nm). In this study, KPFM measurements were performed using an Agilent 5500 AFM with built-in dual lock-in amplifier (LIA) that enables simultaneous measurement of topography (probed at 65 KHz) and surface potential (probed at 10 KHz). This dual LIA setup ensures minimal crosstalk between KPFM and AFM signals.

KPFM on CZTSSe surfaces cleaned with 5 min of NH\(_4\)OH were performed within 30 min after the cleaning. AFM and KPFM images of the cleaned CZTSSe surface is shown in Fig. 2.15. By correlating the AFM and KPFM images using the line traces (lines 1 and 2), it can be concluded that GBs have smaller surface potentials and hence larger work functions. This is consistent with upward band bending at the grain-boundary grooves (GBs) that prevents the electrons from entering the GBs.

Fig. 2.17 shows the elemental maps for Cu, Zn, Sn and O for CZTSSe samples with and without air anneal at 375 °C. Both samples were undergone the hard bake step after the spin coating. The auger maps before air anneal are showing much smaller enhancement of O at the grain boundaries compared to the sample with air anneal. However, Sn-rich layers do exist at the grain boundaries and could cause inferior device
performance due to improper grain boundary passivation. Air anneal resulted in efficiency improvements as high as 45%. Comparing the performance to air-annealed samples, it can be explained that air anneal improves the device performance by oxidizing the Sn-rich grain boundaries and passivating the GB defects.
Figure 2.1 Elemental maps for air-annealed CZTSSe: a) Planar secondary electrons and elemental maps showing the lateral distribution of Cu, Zn, Sn, S, Se and O on the surface after air anneal. Scan size is 3.75 x 5 µm². Maps reflect the intensity of primary Auger peaks. b) Secondary electrons and cross-sectional elemental maps. 2° tilt of the sample stage was applied in order to detect top surface and compare its composition with the cross-section. Tables present the composition of various points on the surface derived from the ratios between RSF-normalized Auger peak intensities for the comprising elements. [O] / CZTSSe is the ratio of oxygen peak intensity to the sum of Cu, Zn, Sn, S and Se peak intensities. Green columns mark the GBs that have been quantified in the tables.
Figure 2.2 Elemental maps for NH$_4$OH-cleaned CZTSSe: a) Planar elemental maps showing the lateral distribution of Cu, Zn, Sn, S, Se and O on the surface after cleaning by NH$_4$OH. Scan size is 3.75 x 5 µm$^2$. Maps reflect the intensity of primary Auger peaks. b) Cross-sectional elemental maps. 2° tilt of the sample stage was applied in order to detect top surface and compare its composition with the cross-section. Top surface has higher Cu and Se and lower Sn and O compared to the GB surfaces. Tables present the composition of various spots on the surface derived from the ratios between RSF-normalized Auger peak intensities for the comprising elements. [O]/CZTSSe is the ratio of oxygen peak intensity to the sum of Cu, Zn, Sn, S and Se peak intensities. Green columns mark the GBs that have been quantified in the tables.
Figure 2.3 Solar cell device performance: a) Cross-sectional TEM image of a complete CZTSSe device. Different layers of the device are shown with various colors on the right. HAADF refers to high angle annular dark field imaging. b) J-V curves for devices fabricated on CZTSSe surfaces prepared by NH$_4$OH clean and HOOH/NH$_4$OH clean. c. Efficiency, open-circuit voltage ($V_{oc}$), short-circuit current ($J_{sc}$) and fill factor (FF) for samples with surfaces prepared by NH$_4$OH clean, HOOH/NH$_4$OH clean or Cu deposition/anneal. d. Solar cell efficiency as a function of surface preparation process. High efficiency for HOOH/NH$_4$OH cleaned CZTSSe devices can be recovered by second air anneal followed by NH$_4$OH clean.
Figure 2.4 Electronic and chemical properties of SnO$_2$/CZTSSe and CdS/CZTSSe interfaces: a) SEM micrograph and Cu and O elemental maps for CZTSSe surface after HOOH/NH$_4$OH cleaning. Scan size is 3.75 x 5 µm$^2$. b) Band alignment between SnO$_x$, Cu$_2$ZnSn(S$_{0.45}$,Se$_{0.55}$)$_4$ and CdS buffer showing existence of both electron and hole barriers at the SnO$_x$/CZTSSe interface. Band diagram has been constructed by combining the UPS measurements for CdS/CZTSSe with data from the literature for SnO$_2$/CdS junctions.$^{31,32}$ c) Surface Fermi level position and surface band bending of NH$_4$OH-cleaned, HOOH/NH$_4$OH-cleaned and Cu-incorporated CZTSSe surfaces measured by fs-UPS. d) SEM image of CdS/ CZTSSe cross-section with the red dashed line along which the composition was measured. e) Compositional variation for Cd, Cu, S and Se along the CdS/CZTSSe interface.
Figure 2.5 Solar cell device simulation for various CZTSSe thicknesses and back contact work functions: a) Band diagram for the proposed PV device architecture with thin absorber and high work function (HWF) back contact. b,c) Open circuit voltage ($V_{oc}$) and short-circuit current ($J_{sc}$) as a function of CZTSSe thickness for PV devices with film baseline (FB) or high work function (HWF) materials as the back contact. Reflectivities (R) of 0 and 1 were tested. $V_{oc}$ and $J_{sc}$ for thin devices strongly depend on backside contact work function and reflectivity. d) Device efficiency vs. CZTSSe film thickness with variable back contact configuration. Using a high work function backside contact with a large reflectivity, CZTSSe device efficiency may be boosted up to 16% for thinner films.
Figure 2.6 Auger survey from 30 to 2200 eV on as-is air-annealed CZTSSe surface, showing all the peaks for the comprising elements plus oxygen and carbon.
**Figure 2.7** Elemental composition of the CZTSSe surfaces with no surface clean (black), or NH$_4$OH (red) and HOOH/NH$_4$OH (blue) cleans. Data for O and C are not shown here. Both surface cleaning recipes lead to [O] = 8% or lower. The probe area for this measurement was 11.25 x 15 µm$^2$ that included grains and grain boundaries.
**Figure 2.8** XPS surface composition of CZTSSe surfaces after cleaning by NH₄OH (a) and HOOH/NH₄OH (b). All the peak areas have been corrected by their relative sensitivity factors. Elemental concentrations are given by dividing the corrected peak areas by the sum of substrate peaks: Cu3p, Zn3d, Sn4d, S2p and Se3d.
Table 2.1 Elemental concentration ratios for cleaned CZTSSe surface calculated from XPS results.

<table>
<thead>
<tr>
<th></th>
<th>[Cu]/[Zn]</th>
<th>[Cu]/[Sn]</th>
<th>[Cu]/[Zn]+[Sn]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄OH</td>
<td>1.65</td>
<td>1.12</td>
<td>0.67</td>
</tr>
<tr>
<td>HOOH+NH₄OH</td>
<td>1.74</td>
<td>1.21</td>
<td>0.71</td>
</tr>
</tbody>
</table>
Figure 2.9 Se3d XPS peak for CZTSSe sample cleaned by NH$_4$OH for 10 min (magenta line) and exposed to air for 7 days (black line). The peak with higher binding energy indicates the formation of SeO$_2$ and selenates as SnSeO$_4$. 

\[\Delta E = -5 \text{ eV}\]
Figure 2.10 Planar elemental maps for CZTSe (pure selenide) measured by Auger Nanoprobe. Compared to air-annealed CZTS-Se, grain boundaries are mostly Zn- and Se-rich instead of Sn- and O-rich. This confirms that our instrumentation is capable of showing contrast in the elemental distribution of Zn as well as all the other elements. CZTSe samples prepared for this measurement were grown by thermal evaporation which could be the reason for the difference in the grain boundary composition compared to solution-based growth of CZTS-Se.
Figure 2.11 Three lines traces extracted from Cu, Zn, Sn and O elemental maps for the NH$_4$OH-cleaned sample surface. Grain boundaries are marked by arrows along the horizontal axes. The spikes in Sn and O lines occur at the grain boundaries. The width of the spikes (defined by full width at half maximum: FWHM) varies between 90 nm to 160 nm. Single SnO$\text{x}$ layers or crystallites cannot be detected by Auger nanoprobe and a large Cu, Zn, S and Se background is present in these wide regions. In other words, Auger beam size is not small enough to determine the individual SnO$\text{x}$ crystallites.
Figure 2.12 **Left:** Line scans extracted from Sn and O elemental maps for NH4OH-cleaned CZTSSe surface. **Right:** Grain boundary widths obtained by measuring the full width at half max (FWHM) of Sn and O spikes at 8 different points along the three line scans shown in Figure 2.11.
Figure 2.13 Two typical depth profiles measured in planar (left) and cross-sectional (right) mode on uncleaned air-annealed CZTSSe sample. The dotted lines indicate the time at which the intensity of oxygen drops to 25% of its value at the surface. The intensity ratio is defined as the ratio of Cu, Zn, Sn or O auger intensity to the sum of Cu, Zn and Sn intensities (i.e. Intensity ratio of Cu = I_{Cu}/(I_{Cu}+I_{Zn}+I_{Sn})). O drops to 25% of its intensity on the grains' top surfaces three times slower than GB faces. Therefore, the oxide thickness on GB faces can be estimated three times as thin as grains top surfaces.
Table 2.2 Standard enthalpies of formation at 298.15 K for the oxides of the elements present in CZTSSe. Solid phase enthalpies of formation are shown for solid oxides such as CuO, SnO$_2$ etc. Enthalpies of formation for SO$_2$ and SO$_3$ are based on gas phase reactions.

<table>
<thead>
<tr>
<th>Oxide Formula</th>
<th>Enthalpy of formation ($\Delta H^\circ$) at 298.15 K (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>$-156.06$</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>$-170.71$</td>
</tr>
<tr>
<td>ZnO</td>
<td>$-350.46$</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>$-577.63$</td>
</tr>
<tr>
<td>SnO</td>
<td>$-280.71$</td>
</tr>
<tr>
<td>SeO$_2$</td>
<td>$-110.59$</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>$-296.81$</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>$-395.90$</td>
</tr>
</tbody>
</table>
Figure 2.14 Planar elemental maps showing the lateral distribution of Cu, Zn, Sn, S, Se and O on the CZTSSe surface after HOOH/NH₄OH cleaning. Maps reflects the intensity of primary Auger peaks corrected by their relative sensitivity factors. O distribution is almost uniform over the surface. The dark and bright regions in all Cu, Zn, Sn, S and Se maps are correlated. Dark/bright regions correspond to grain top surfaces rather than grain-boundary grooves. Table presents the composition of various spots on the surface derived from the ratios between RSF-normalized Auger peak intensities for the comprising elements. Green columns mark the GBs that have been quantified in the table.
Figure 2.15 a-b) Atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) images of CZTSSe surface less than 30min after NH$_4$OH clean. c-d) Line traces for the AFM and KPFM images obtained from the line traces 1 and 2 on the images, denoting the grain-boundary grooves (GBs). GBs were observed in the KPFM maps as dark regions with higher work function leading to the conclusion that an upward band bending of 60-80 mV exists at the GBs. The scan size for AFM and KPFM images is 5x5 $\mu$m$^2$. 
**Figure 2.16** Planar SEM and Cu, Sn and O elemental maps for the CZTSSe sample without (top) and with (bottom) air anneal at 375 °C in air. Prior to mapping, both samples were cleaned by 5min of NH₄OH dip.
Figure 2.17 fs-UPS spectra for CZTSSe surfaces after NH$_4$OH cleaning (a) HOOH/NH$_4$OH cleaning (b) and 0.3nm Cu deposition followed by anneal at 200 °C (c). 0 eV is the Fermi level. Upward band bending is largest for NH$_4$OH, less for HOOH/NH$_4$OH and reverses to downward bending for the Cu deposited surface. Extrapolated valence edge (solid black line) shifts closer to the Fermi level by increase in the surface Cu content.
2.8 References


Chapter 3

Determining Oxide Composition at Grain Boundaries vs. on Grain Surfaces for CZTSSe Thin Films

3.1 Abstract

Kesterite Cu₂ZnSn(S,Se)₄ (CZTSSe) absorbers are considered promising alternatives to commercial thin film technologies including CdTe and Cu(In,Ga)Se₂ (CIGSe) owing to the earth abundance and non-toxicity of their constituents. However, to be competitive with the existing technologies, the photovoltaic performance of CZTSSe solar cells needs to be improved beyond the current record conversion efficiency of 12.6%. In this study, nanoscale elemental mapping using Auger nanoprobe microscopy (NanoAuger) and Nano secondary ion mass spectrometry (NanoSIMS) are used to provide a clear picture of the compositional variations between the grains and grain boundaries in Cu₂ZnSn(S,Se)₄ kesterite thin films. NanoAuger measurements revealed that the top surfaces of the grains are coated with a Zn-rich (Zn,Sn)Oₓ layer. While thick oxide layers were observed at the grain boundaries, their chemical compositions were found to be closer to SnOₓ. NanoSIMS elemental maps confirmed the presence of excess oxygen deeper within the grain boundary grooves, as a result of air annealing of the CZTSSe films.

3.2 Introduction
The market for thin film photovoltaics (PV) has been expanding over the past decade due to the technological advances in developing low-cost and high-efficiency chalcogenide-based devices with CdTe and Cu(In,Ga)Se$_2$ absorbers. However, the total power generation capacity per year for these chalcogenide-based technologies is projected to saturate at about 100 GW$^p$.\textsuperscript{1,2} This is mainly due to the limited accessible reserves of In and Te in the earth’s crust, as well as the toxicity of Cd.\textsuperscript{3} Alternatively, In and Ga in the CIGSe films can be replaced with more earth-abundant, non-toxic elements such as Zn and Sn forming Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) which has kesterite crystal structure. The current record conversion efficiency of polycrystalline thin film CZTSSe solar cell is 12.6%; 2.4% short of the efficiency threshold needed to make this material competitive with the commercial thin film technologies.\textsuperscript{2,4} This deficit in performance has been mostly ascribed to the limited open-circuit voltage ($V_{oc}$) due in large to the extent of carrier recombination at the defects sites within the bulk of the absorbers or at the interfaces that exist in the PV devices.\textsuperscript{5-8}

One of the critical interfaces in polycrystalline thin films is the one between adjacent grains, called grain boundaries. If not properly passivated, grain boundaries can introduce a large density of carrier recombination sites within the absorber region where the electron-hole pairs are generated. Local surface electronic measurements of high-efficiency CIGSe thin films have shown modest levels of downward band bending (100 – 300 mV) at the grain boundaries.\textsuperscript{9,10} This downward band bending (equivalent to smaller work function of the grain boundaries) has been attributed to a variety of factors including Cu depletion\textsuperscript{11} and Na or O accumulation\textsuperscript{12} at the grain boundaries. In
the case of CZTSSe thin films, both upward and downward band bending were observed at the grain boundaries depending on the growth method.\textsuperscript{13-15} Similar to CIGSe, atomic scale substitutions with alkali metals (such as Na and Li) or O in the crystal structure adjacent to the grain boundaries have been identified as the major grain boundary passivation mechanisms.\textsuperscript{16, 17}

In the champion CZTSSe solar cells with 12.6\% energy conversion efficiency, a critical processing step is the air anneal where the samples are heated up to 300 – 400 °C in ambient air for several minutes. Kelvin probe force microscopy (KPFM) measurements on air-annealed CZTSSe films showed upward band bending of 70 – 100 mV at the grain boundaries correlated with the presence of 100 – 200 nm thick SnO\textsubscript{x} layer within the grain boundary grooves.\textsuperscript{18} This SnO\textsubscript{x} layer is believed to grow during the air anneal process where oxygen is provided from the ambient to oxidize the excess Sn at the grain boundaries. In addition to the grain boundaries, air anneal has been found to assist formation of a Cu-poor top surface that is critical in realizing optimal top junctions between CdS buffers and CZTSSe grains.\textsuperscript{19} Cd from CdS chemical bath deposition can replace Cu within tens of nanometers away from the junction, resulting in a sub-junction doping and improvement of the CdS/absorber junction quality.\textsuperscript{20, 21} However, very limited work has been performed to compare the oxide composition on the top surfaces of the grains with grain boundaries formed during the air anneal process.

In this chapter, nanoscale elemental analysis of CZTSSe grain surfaces and grain boundaries is carried out with Auger Nanoprobe Microscopy (NanoAuger). To compare
the composition of the oxide formed during the air anneal, NanoAuger spectroscopy and elemental mapping were performed before and after oxide removal using in-situ Ar$^+$ sputtering. Elemental maps of the air-annealed surfaces showed formation of Zn-rich (Sn,Zn)O$_x$ on grain surfaces and SnO$_x$ at the grain boundaries. Using nanoscale secondary ion spectrometry (NanoSIMS) elemental mapping on air-annealed CZTSSe films, it was confirmed that excess oxygen exists deep within grain boundaries, consistent with the SnO$_x$ layer covering a large fraction of the grain walls through the films. Comparison of NanoSIMS elemental maps before and after air anneal led to the conclusion that the O accumulation is a result of air annealing process.

3.3 Materials and Methods

CZTSSe films were grown by spin coating of a hydrazine-based precursor slurry onto soda lime glass substrates coated with 100 nm thick Mo layers. Spin coating of slurry onto the substrates was performed in a nitrogen-filled glove box. After the thin film deposition, CZTSSe films underwent two steps of post deposition annealing: i) hard bake (HB): annealing at 600 °C for 15 min in a nitrogen-filled glove box; ii) air anneal (AA): annealing at 350 °C for 10 min in air with average relative humidity of 40 – 50 %. Further details of the CZTSSe growth procedure have been published elsewhere.$^{22-24}$ The bulk [Cu]/[Zn] and [Se]/[S]+[Se] measured by X-ray fluorescence (XRF) were 1.8 and 0.7, respectively.

Auger Nanoprobe measurements were performed using a PHI-710 Auger Nanoprobe Microscope (NanoAuger). The NanoAuger tool provides 1% energy resolution for
spectroscopy and 5 nm spatial resolution for elemental mapping. A 20 kV, 10 nA electron beam was used for both Auger spectroscopy and elemental mapping. Additionally, to remove the native oxide from the thin films’ top surfaces, in-situ Ar+ ion sputtering with 500 eV energy was applied. To minimize the sputtering rate dependence on the surface geometry, the sputter gun was perpendicular to the sample surface.

NanoSIMS elemental mapping was achieved by using a CAMECA NanoSIMS 50L tool with Cs+ as the primary ion beam (2–8 pA) with a nominal spot size of 100–200 nm. The beam was rastered over areas as large as 5 μm x 5 μm on the sample surface. Negative secondary ions for the elements of interest were collected simultaneously on the NanoSIMS multi-collection system.

3.4 Results and Discussion

3.4.1 Auger Nanoprobe Microscopy (NanoAuger)

Fig. 3.1 displays the NanoAuger elemental maps in planar mode for a CZTSSe surface after the air annealing at 350 °C. Since no chemical treatment was performed on the sample after air anneal, the top surface is expected to be covered by an oxide layer. Distributions of all five elements (Cu, Zn, Sn, Se and O) on the grains’ surfaces were relatively uniform. In stark contrast, the grain boundaries appeared to have higher concentrations of Sn and O and smaller concentrations of Cu, Zn and Se relative to grains. This is consistent with the previous report on the observation of a thin SnOx layer at the grain boundaries of air annealed CZTSSe thin films.18
It should be noted that in the elemental maps, a uniform background subtraction is applied; smaller intensity in the elemental map does not necessarily correlate with the full depletion of the corresponding elements. In order to determine the extent of the compositional variation between the grains and grain boundaries, a line trace across the scan region is measured as shown in Fig. 3.2 (a). Each elemental line trace in Fig. 3.2 (b) consists of 128 data points with their intensity corresponding to the peak-to-peak intensity of the element’s derivative Auger spectrum (dN/dE vs. kinetic energy). For the grain boundary on the left, about 30% enhancement in Sn and 40% enhancement in O intensities were observed while only 20% drop in Zn and Cu intensities were estimated. This can be in part due to the larger escape depths of Zn and Cu Auger peaks which make them less surface sensitive.\textsuperscript{25, 26} In addition, the signal enhancement at the grain boundaries seemed to be gradual (not very sharp), consistent with a beam size larger than the width of the grain boundary. Therefore, the rather small drop in the Zn and Cu signal could be a result of the large beam spot size (larger than grain boundary width) and the larger escape depth for the Auger peaks for Zn and Cu vs. Sn and O.

A mild Ar\textsuperscript{+} sputtering at 500 V ion energy (filament current = 600 nA) was applied in-situ for 30 s to remove the oxide layer from the CZTSSe top surface. The sample stage was titled 30° in order to align the ion gun with the sample’s surface normal. Secondary electron images and Auger elemental maps of the sample surface after 30 s of Ar\textsuperscript{+} sputtering are shown in Fig. 3.3. It should be noted that different scan locations were chosen for Fig. 3.1 and Fig. 3.2. After sputtering, the contrast in signal intensity between the grains and grain boundaries for Sn and O has increased relative to
the as-inserted surface. Additionally, lower intensities for Cu, Zn and Se were observed at the grain boundaries relative to the grains, although the contrast between the grains and grain boundaries seems to be smaller than the as-inserted surface. There were few zones on the grain surfaces with O, Zn and Sn signal enhancement (blue arrows). These could be due to non-uniformities in the oxide thickness resulting in incomplete removal of the oxides during the short Ar⁺ sputtering step.

To quantify the chemical composition of the grain and grain boundaries after Ar sputtering, single point Auger spectroscopy was carried out on top surface of a grain (Area 1) and a grain boundary adjacent to it (Point 2), as shown in Fig. 3.4 (a). The Auger survey spectra measured on area 1 and point 2 are shown in derivative format in Fig. 3.4 (b). The elemental composition for each scan location was estimated using the elemental peaks marked with * sign (example: Cu⁺, Zn*, etc). In comparison with the grain surface in area 1, the grain boundary at point 2 has about 2x larger concentration of Sn and O. In addition, the grain boundary oxide has [Sn]/[Zn] = 1.87. Considering the large beam spot size (larger than grain boundary width) and longer escape depth for Zn Auger peak, the majority of the Zn signal in the single point measurements could be detected from the CZTSSe grains adjacent to the grain boundary oxide. Therefore, it is expected that the grain boundary grooves near the top surface are terminated by an oxide with composition close to SnOₓ. This oxide has been found necessary for maintaining low grain boundary recombination rates and high V_{oc} in CZTSSe solar cells.¹⁸

To determine the composition of the oxide formed on the grain surfaces, variations in the Auger spectra of top surfaces of grains were monitored before and after
Ar\(^{+}\) sputtering (Area 1 in Fig. 3.5 (a)). The elemental ratio for each element was calculated by normalizing its Auger peak-to-peak intensity (I\(_{p-p}\)) to its relative sensitivity factor (RSF) (I\(^n\) = I\(_{p-p}\) / RSF) and then dividing by the sum of the normalized intensities of CZTSSe constituents (i.e. [O] = I\(^n\)\(_{O}\) / (I\(^n\)\(_{Cu}\) + I\(^n\)\(_{Zn}\) + I\(^n\)\(_{Sn}\) + I\(^n\)\(_{S}\) + I\(^n\)\(_{Se}\))). Fig. 3.5 (b) displays the elemental ratios for Cu, Zn, Sn, S, Se and O in area 1 before and after sputtering. As a result of sputtering, the [Zn] and [Sn] ratios were reduced by about 60\% while [O] decreased by 12x, from 0.6 to 0.05. Concurrently, [Cu] and [Se] were increased by 60\% and 76\%, respectively. Therefore, it can be concluded that the thin overlayer present on the as-inserted CZTSSe surface contains large amounts of Sn, Zn and O. Considering the short amount of time needed to remove the oxide from the grains’ top surfaces via Ar\(^{+}\) sputtering (~ 30 s), the overlayer thickness can be approximated to < 1.5 nm. Due to their large inelastic mean free path (IMFP), large fractions of the Cu (IMFP ~ 1.6 nm) and Se (IMFP ~ 2.4 nm) Auger signals are expected to be received from the CZTSSe underneath the oxide on air-annealed surfaces.

To confirm this, Zn and Sn Auger peaks in absolute mode before and after sputtering were compared, as shown in Fig. 3.5 (c) and (d). After Ar\(^{+}\) sputtering, Sn and Zn peaks shifted to higher kinetic energies by 1 eV and 3.3 eV. These shifts to higher kinetic energies for Zn and Sn peaks after sputtering is consistent with these elements bonding to O before sputtering and bonding to S or Se after sputtering. It should be noted this difference in the chemical shift is due to the three-electron nature of the Auger process resulting in variations in sensitivity of Auger peaks to the changes in the elements’ chemical bonding state. The difference in chemical shifts observed here for
Zn LMM and Sn MNN peaks are consistent with the previous reports on Auger spectroscopy of Zn and Sn surface oxides.\textsuperscript{27, 28} Considering the quantitative analysis given above, grain surfaces in air annealed CZTSSe are hypothesized to be terminated by a thin layer of (Zn,Sn)O with Sn/Zn $\approx$ 1. This is consistent with previous large area Auger spectroscopy measurements where the native oxide is identified as a Cu-free overlayer with large Zn and Sn concentrations.\textsuperscript{29}

It should be noted that CZTSSe top surface oxide can be removed by NH$_4$OH in the chemical bath solution used for CdS buffer deposition.\textsuperscript{18,19} Therefore, thin surface oxides are expected to have no effect on the quality of the CdS / CZTSSe top junction in eventual photovoltaic devices.

### 3.4.2 Nanoscale Secondary Ion Mass Spectrometry (NanoSIMS)

While NanoAuger measurements determined that grain boundaries are terminated by SnO$_x$, NanoAuger does not provide direct information of the depth of this passivation layer. To clarify the depth distribution of the SnO$_x$ passivation layer, elemental mapping using NanoSIMS was performed with the primary Cs$^+$ was rastered over a 5 $\mu$m x 5 $\mu$m area over the surface of an air-annealed CZTSSe film. NanoSIMS allow simultaneous sputtering with elemental mapping with high chemical sensitivity and depth resolution, but with lower spatial resolution than cyclic sputtering and NanoAuger (best lateral resolution of $\sim$ 50 – 60 nm). For NanoSIMS, the amount of negatively charged secondary ions including O, S and Se were measured simultaneously.
using three detectors in parallel. Maps for secondary electrons as well as O, S and Se were recorded after 1 min long ion sputtering time intervals.

Secondary electron and elemental maps for O, S and Se after 1 min (frame 1), 2 min (frame 2) and 3 min (frame 3) of Cs⁺ sputtering are shown in Fig. 3.6. Similar to the NanoAuger maps, grain boundaries on the starting surfaces were found to be O-rich and depleted from S and Se. As the films are eroded during the milling process, although the O intensity at the grain boundaries decreased, the grain boundaries still appeared to be O-rich. Even after 3 min of ion milling excess O at the grain boundaries can be observed (NOTE: The decrease in the intensity of O signal for longer sputtering times could be due to the smaller width of SnOₓ layer at the grain boundaries deeper within the CZTSSe films. As the width of the O-rich region shrinks below the NanoSIMS elemental mapping resolution (~ 100 – 150 nm), the signal is averaged over grain boundaries and adjacent grains surfaces, resulting in smaller total O intensity.). This is consistent with the (Zn,Sn)O grain boundary passivation layer extending deeper within the grain boundary grooves at least for the thickness equivalent of 3 min long Cs⁺ milling (70 – 100 nm). In addition, by moving from frame 1 to 3, the S and Se intensities increase on the grain surfaces consistent with the removal of the top surface (Zn,Sn)Oₓ.

Fig. 3.7 displays the NanoSIMS elemental maps for O, S and Se elemental maps for hard baked (HB, Fig. 3.7 (a)) and air-annealed (HB+AA, Fig. 3.7 (b)) CZTSSe films. Maps were summed for 7 different imaging frames to enhance the overall signal intensity and contrast. In comparison with the hard-baked CZTSSe film (Fig. 3.7 (a)) grain boundaries in the air-annealed film appeared to have larger O accumulation and
smaller chalcogen (S, Se) depletion. This is consistent with the air anneal process assisting the grain boundary oxidation via oxidants in air or enhanced oxygen diffusion from the soda-lime glass substrate into CZTSSe back surface. Previous NanoAuger work demonstrated the presence of excess Sn at the grain boundaries even for films that underwent hard bake only.\textsuperscript{18} Therefore, the air anneal process oxidizes the Sn-rich grain boundaries forming a charge passivating SnO\textsubscript{x} layer that induces upward band bending in the regions adjacent to the grain boundaries.\textsuperscript{15,18}

### 3.5 Conclusion

Qualitative and quantitative elemental analysis by NanoAuger as well as qualitative elemental mapping as a function of depth by NanoSIMS were used to determine the chemical composition of the top surfaces of grains and grain boundaries in air-annealed CZTSSe thin film absorbers. Grain boundaries appear to have larger concentrations of Sn and O even before any oxide removal. By performing Auger spectroscopy on individual grain surfaces, it was determined that the oxide formed on the grain surface during the air anneal process is composed of (Zn,Sn)O with Zn : Sn of about 1:1. Similar small area spectroscopy measurements revealed that grain boundary oxide composition is closer to pure SnO\textsubscript{x}. NanoSIMS elemental maps showed that O-rich grain boundaries extend deeper within the grain boundary grooves for up to 3 min of ion milling. This O-rich layer was determined to be a direct result of the air annealing treatment since much smaller O accumulation was observed at the grain boundaries of the CZTSSe films with hard bake only.
3.6 Acknowledgments

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Figure 3.1 Secondary electron micrograph and NanoAuger elemental maps for Cu, Zn, Sn, Se and O measured on as-inserted CZTSSe surface after 10 min air anneal at 350 °C. The scan size is 2 x 2 µm². Grain boundaries have higher concentration of Sn and O compared to the top surfaces of the grains. There is a void from which very small Auger signals were detected. Therefore, this void appeared as a region in all the five elemental maps.
Figure 3.2 (a) Secondary electron micrograph and O elemental map for air-annealed CZTSSe surface with the position of the horizontal line trace shown by the dotted lines. (b) Peak-to-peak intensities for Cu, Zn, Sn and O, normalized to the relative sensitivity factors (RSFs), along the line traces shown in (a). The line traces show that the variations in peak-to-peak intensities between the grains and grain boundaries are only 20 – 40%. Therefore, darker or brighter regions in the elemental maps do not correspond to full depletion or accumulation of the elements.
Figure 3.3 Secondary electron micrograph and NanoAuger elemental maps for Cu, Zn, Sn, Se and O measured on air-annealed CZTSSe surface 30 s of Ar\(^+\) sputtering with 0.5 kV ion beam energy and 600 nA filament current. The scan size for these measurements is 3 x 3 \(\mu m^2\). Similar to the as-inserted sample, grain boundaries appear to have larger concentrations of Sn and O.
Figure 3.4 (a) Secondary electron micrograph and Sn elemental map for air-annealed CZTSSe top surface after 30 s of Ar$^+$ sputtering. (b) Auger survey spectra for area1 (grain) and point 2 (grain boundary). Elemental compositions calculated from the Auger spectra are shown in the boxes on the bottom right of the spectra.
Figure 3.5 (a) Secondary electron micrograph of air-annealed CZTSSe surface before Ar⁺ sputtering. The area chosen for spectroscopy is marked by the yellow box. (b) Elemental ratios calculated for Cu, Zn, Sn, S, Se and O in area 1 before (red) and after (blue) Ar⁺ sputtering. (c) Sn MNN Auger peak before and after surface oxide removal by Ar⁺ sputtering. (d) Zn LMM Auger peak before and after surface oxide removal by Ar⁺ sputtering. For both (c) and (d) Auger peaks are in absolute mode and the peak intensities are normalized the maximum intensities. It should be noted the left shoulder for sputtered surface seems to be larger than the as-inserted surface. This background increase could be due to the overlap between Cu1 and Zn1 Auger peaks, particularly considering the increase in [Cu] after sputtering.
Figure 3.6 Planar secondary electrons and elemental maps for O, S and Se for three different frames measured by NanoSIMS (Cs$^+$ source) on air-annealed CZTSSe surfaces at 3 different times during the profiling. Frame 1, 2 and 3 are subsequently showing deeper layers on the sample surface. O is present at the GBs of the air-annealed sample after more 3 min of depth profiling (equivalent to 70 - 100 nm of CZTSSe removal).
Figure 3.7 Planar secondary electrons and elemental maps for O, S and Se measured by NanoSIMS (Cs+ source) on (a) hard-baked (HB) and (b) Air-annealed (HB+AA) CZTSSe surfaces. Data has been integrated over 7 measurement frames. According to the O maps, air annealing the sample resulted in significantly higher O content at the GBs.
3.8 References


Chapter 4

Cross-sectioning of Thin-film Solar Cells via Grazing Angle of Incidence

Cryogenic Focused Ion Beam

4.1 Abstract

$\text{Si}_{0.5}\text{Ge}_{0.5}(110)$ surfaces were passivated and functionalized using atomic H, hydrogen peroxide ($\text{H}_2\text{O}_2$), and either tetrakis(dimethylamino)titanium (TDMAT) or titanium tetrachloride ($\text{TiCl}_4$), and studied in-situ with multiple spectroscopic techniques. Cryogenic Focused Ion beam (Cryo-FIB) milling at near-grazing angles is employed to fabricate cross-sections on thin Cu(In,Ga)Se$_2$ with $>8\times$ expansion in thickness. Kelvin probe force microscopy (KPFM) on sloped cross-sections showed reduction in grain boundaries potential deeper into the film. Cryo FIB-KPFM enabled the first determination of the electronic structure of the Mo/CIGSe back contact, where a sub 100 nm thick MoSe$_2$ assists hole extraction due to 45 meV higher work function. This demonstrates that CryoFIB-KPFM combination can reveal new targets of opportunity for improvement in thin-films photovoltaics such as high-work-function contacts to facilitate hole extraction through the back interface of CIGS.

4.2 Introduction

Photovoltaics (PV) is a fast-growing source of renewable energy and is projected to gain more than 11% of the global electricity market by 2050.$^1$ To become more
competitive with the current sources of electricity, it is crucial to reduce the cost per watt generated power by lowering the manufacturing costs and increasing the conversion efficiencies.\(^2\) This can be achieved by the use of thin film PV technologies such as CdTe and Cu(In,Ga)Se\(_2\) (CIGSe), where the overall materials consumption is lowered by reducing the film thickness to less than 5 \(\mu\)m.\(^3\) In addition, relatively simple growth techniques for thin films enable large-area monolithic manufacturing of the modules. In order to reaching the goal of few TW/year power generation,\(^4\) in addition to CdTe and CIGSe which have achieved record cell efficiencies above 20\%, other earth-abundant thin film alternatives such as Cu\(_2\)ZnSn(S,Se)\(_4\) (CZTSSe) and the perovskite family (MAPbI\(_3\) in particular) are being explored.\(^4\,5\)

The wide majority of thin film absorbers are polycrystalline with a large density of grain boundaries. Grain boundaries, if not properly passivated, could be detrimental to the device performance of solar cells by accommodating a large density of recombination sites.\(^6\) In addition, thin film devices are composed of multiple layers of materials (i.e. absorbers, buffers, contacts, etc) with heterojunctions that are required to have low defect density. Therefore, it is essential to employ low damage techniques to measure the composition and electrical properties of the grain boundaries and interfaces in thin film PV device. Specifically, measurements of composition and charge distribution in the cross-sections of the devices via energy-dispersive x-ray spectroscopy (EDX), Auger nanoprobe microscopy (NanoAuger) and scanning probe microscopy (SPM) can correlate the device performance with the chemistry and physics of the interfaces within the device.\(^7\) However, unlike single crystalline materials (Si,
GaAs, etc), preparation of flat cross-sections by single-step cleaving is challenging for thin films solar devices, since fracture in polycrystalline materials mostly occurs along the grain boundaries.\textsuperscript{7-8} Consequently, smooth cross-sections for polycrystalline absorbers are only achieved after additional processing steps following the cleaving such as chemical-mechanical or mechanical polishing and ion milling.\textsuperscript{9-11} In addition to increase in processing complexity, these additional steps potentially induce mechanical damage in the sample and make the cross-sectional measurements rather unrepresentative.

In the present report, an alternative method is proposed for preparation of smooth cross-sections for thin film solar cell absorbers by using cryogenic focused ion beam (Cryo-FIB) milling with near grazing angles of incidence of the $\text{Ga}^+$ ion beam. Successful application of this technique in characterization of grain boundaries and back contacts in CIGSe absorbers is demonstrated. Grazing incidence ion beam angles are beneficial in reducing the $\text{Ga}^+$ implantation during the milling process by shrinking the ion – surface interaction cascade’s effective volume.\textsuperscript{12-13} Moreover, since the sample is cooled to cryogenic temperatures (80 – 100 K), local ion beam heating and $\text{Ga}^+$ ion diffusion within the bulk of the films are expected to be significantly suppressed.\textsuperscript{14-15} Therefore, this combination ensures minimal beam damage and $\text{Ga}^+$ incorporation during the milling procedure of sloped cross-sections.

\section*{4.3 Experimental Details}
CIGSe growth: CIGSe thin-film absorbers were grown on soda-lime glass (SLG) substrates coated with a 1 μm thick Mo layer deposited by DC magnetron sputtering in Ar gas. CIGSe was deposited by a 3-stage physical vapor deposition process.\textsuperscript{16-19} First, 90% of the total In and Ga was deposited on the Mo/SLG substrate that was heated to 300 °C. At this stage, the flux contained excess of Se such that \([\text{Se}] / ([\text{In}]+[\text{Ga}]) \sim 3\) forming \((\text{In,Ga})_2\text{Se}_3\). In order to convert this layer to CIGSe, the substrate was then exposed to a flux of Cu and Se (with \([\text{Se}]/[\text{Cu}] \sim 0.3\)) at temperatures above 500 °C. This stage resulted in \([\text{Cu}] / ([\text{In}]+[\text{Ga}])\) of 0.95 – 1.1. To make the surface Cu-poor, during the third stage In and Ga were co-deposited with Se at above 500 °C. Finally, the films were cooled in a flux of Se to 350 °C. The average film thickness was about 2 μm. The compositional analysis carried out by x-ray fluorescence (XRF) microscopy showed the CIGSe film contains in average 23.2 at. % Cu, 17.1 at. % In, 8.0 at. % Ga and 51.6 at. % Se.

Photovoltaic devices were fabricated on the resulting CIGSe films by depositing 40 – 50 nm of CdS buffer layer using chemical bath deposition (CBD), followed by RF magnetron sputtering of ZnO bilayer with total thickness of 400 nm. Afterwards, to collect the generated electron from the top surface, a metal grid that consists of 50 nm Ni and 3 μm Al was deposited on top of the ZnO layer by physical vapor deposition. The J-V characteristics of two of the resulting devices (P0502-31 and 32) are displayed in Fig. 4.1. The standard PV performance parameters extracted from the J-V characteristics of these devices are listed in Table 4.1.
Kelvin Probe Force Microscopy (KPFM): KPFM measurements were performed using an Agilent / Keysight 5500 scanning probe microscope equipped with two built-in lock-in amplifiers (LIA) that enable simultaneous measurement of topography and surface potential. Measurements were performed in intermittent contact mode (known as tapping mode) where topography is probed at or close to the resonance frequency of the cantilever (~65 KHz), while surface potential is probed at 10 KHz. Use of dual LIA setup allows minimal crosstalk between topography and surface potential signals. Highly conductive AFM probes used in this study were fabricated from heavily-doped n-type Si coated with Pt/Ir (NANOSENSORS™ PPP probes). Prior to KPFM measurements, CIGSe surfaces were cleaned with 10 – 15 min of 8 vol. % NH₄OH and transferred to the SPM environmental chamber in less than 5 min. During the KPFM measurements the SPM environmental chamber was continuously purged with ultrahigh purity Ar gas, in order to minimize the in situ oxidation throughout the measurements.

Auger Nanoprobe Microscopy (NanoAuger): Auger elemental mapping has been performed using a Physical Electronics PHI-700 Auger Nanoprobe Microscope at the Stanford Nanocharacterization Laboratory. For spectroscopy and mapping, a 20 kV and 1.0 nA electron beam was used. The chamber pressure during the measurements was maintained within 1 x 10⁻⁹ to 3 x 10⁻⁹ torr range. Intensities used for single point and line trace composition measurements were normalized to the relative sensitivity factors of the elements’ primary Auger peaks. The PHI-700 Auger Nanoprobe microscope used in this study employs a cylindrical mirror analyzer (CMA) for Auger
electron detection, which is coaxial with the field emission electron source. This analyzer geometry enables a 360° azimuthal collection angle around the electron gun thereby collecting Auger electrons from any sample surface that is in the line of sight to the incident electron beam. As a result, Auger signals remains insensitive to the emission angle and surface topography.\(^6\)

4.4 Results and Discussion

Fig. 4.2 (a) shows a schematic of the grazing incidence Cryo-FIB cross-sectioning process for a multi-layer solar cell stack. It also outlines another important advantage of milling with grazing incidence angles: scale expansion. The thickness probed from each layer is proportional to the cosecant of \(\theta\) (angle between \(\text{Ga}^+\) ion beam and sample surface, cosec \(\theta = 1/\sin \theta\)). Therefore, considering \(\theta < 10^\circ\), the lateral scale can be expanded between 7.2 and 11.5 times. A SEM micrograph of a sloped cross-section milled with 5° incidence ion beam angle, on a 2 \(\mu\)m thick CIGSe ([Ga]/[In]=[Ga] = 0.3) absorber layer deposited on Mo-coated soda lime glass (SLG) is shown in Fig. 4.2 (b). Milling the sloped cross-section was achieved in two steps: 1) Bulk milling where a 30 kV, 3 nA beam is used for quick removal of the film and back contact layer; 2) Fine milling where a 5 kV, 48-77 pA beam is used to remove the damaged layer formed near the top surface. The total milling time for the two steps is less than 20 min. It should be noted the streaks expanding from the CIGSe top surface to the bottom Mo/glass interface were caused by the “curtaining effect”; an effect known to be caused by orientation induced sputter rate variations due to ion channeling.\(^{20-21}\) However, the
roughness level resulting from the curtaining is less than 10 nm (RMS roughness ~ 6.7 nm) which is much lower than what is typically measured on CIGSe films top surfaces (about 100-200 nm). Therefore, the cross-sections have sufficiently smooth surfaces that are ideal for scanning probe measurements where cross-talk between electrical and topographical signals is a concern.\textsuperscript{22}

Kelvin probe force microscopy (KPFM) was employed to determine the surface potential (or contact potential difference) variations across the grain boundaries on both the top surface and within the sloped cross-sections. KPFM measurements were performed using a dual lock-in amplifier configuration in which topography and surface potential are measured simultaneously with minimal cross-talk. Fig. 4.3 (a) and (b) show the topography and surface potential maps measured simultaneously on top surfaces of bare CIGSe films. To minimize oxidation of clean surfaces during the measurements, the atomic force microscope (AFM) chamber was continuously purged by high purity Ar gas. By correlating the two maps, it becomes evident that the majority of the grain boundaries have more positive charge relative to the grains. These results are consistent with the previous reports on planar KPFM measurements of CIGSe where positive charge (or downward band bending) of about 100 – 200 mV was measured at the grain boundaries.\textsuperscript{23,24} On the top surface, the amount of band bending at the grain boundaries varies between 120 mV and 160 mV, as shown by surface potential line traces in Fig. 4.3 (c). These lines traces were taken from three different locations in the surface potential map, marked by yellow lines, where grain boundaries exist.
Fig. 4.3 (d) and (e) display the topography and surface potential maps, measured under Ar, on CIGSe sloped cross-sections milled using a 5° ion beam incidence angle. This cross-section was prepared under the same condition as the one shown in Fig. 4.2 (b). Similar to planar KPFM measurements, positively-charged grain boundaries are observed from the top to the bottom of the 15 x 15 µm² scan area. The surface potential line traces shown in Fig. 4.3 (f), confirm that the extent of downward band bending varies between 110 and 140 mV. Therefore, grain boundaries maintained the same charge polarity as the top surface after Cryo-FIB milling, consistent with minimal ion beam damage to the electronic structure. There is also 40 – 50 meV reduction in the amount of band bending from the top to the bottom of the scan area (Supporting information, Fig. 4.6) consistent with the 3D models proposed for CIGSe where grain boundary band bending is combined with the upward band bending of individual grains due to Cu-depleted top surfaces.\(^\text{24}\) Smaller band bending at the grain boundaries deeper into the film might increase the overall grain boundary recombination. Therefore, cryo-FIB milling at grazing ion beam incidence angles can be a strong tool for preparing smooth surfaces on which variation of grain boundary potential as a function of depth can be investigated to determine targets of opportunity for PV performance improvement.

The downward band bending at the grain boundaries of low Ga content CIGSe thin films has been attributed to a number of factors including Cu-depletion as well as Na accumulation adjacent to the grain boundaries.\(^\text{25,26}\) Na can either diffuse from the soda lime glass (SLG) substrate into the grain boundaries or be intentionally added as a
layer of NaF. In order to determine the grain boundary composition, planar and cross-sectional NanoAuger measurements were performed on CIGSe films. Fig. 4.4 (a) displays the SEM micrograph and NanoAuger elemental maps for Cu, In, Ga, Se and O in planar mode on CIGSe surfaces. The surface oxide was removed by immersion in NH₄OH for 15 minutes followed by a short rinse in DI water. Grain boundaries in CIGSe appear to vary in composition with some regions being In-poor (blue arrows) and some In-rich (yellow arrows). Moreover, some fraction of grain boundaries appears to be slightly Cu-poor (white arrows). The Ga map is slightly non-uniform, and the majority of Ga depletion occurs on the top surfaces of the grains. Unlike the elemental maps for CZTSSe, where a uniform layer of SnOₓ is observed at grain boundaries (Supporting information Fig. 4.7), for CIGSe films O distribution is quite non-uniform and O-rich regions are divided in between the grain surfaces and grain boundaries. Therefore, the downward band bending cannot be attributed to a distinct grain boundary composition visible within the NanoAuger resolution limit (~ 8 nm).

Fig. 4.4 (b) shows cross-sectional NanoAuger measurements on the vertical cross-sections prepared by cryo-FIB with 90° ion beam incidence angle. The milling parameter for bulk and fine milling were 30 kV, 3 nA and 5 kV, 77 pA, respectively. In this flat cross-section, two vertical grain boundaries are visible near the left hand side of the images. The tops of these grain boundaries are covered with some Cu-rich features (yellow arrow) which could be formed as a result of CIGSe re-sputtering during the milling process. However, near the bottom, these grain boundaries appear to be Cu-poor (blue arrow) consistent with results suggested by atom probe tomography, etc.
Therefore, at least in the few grain boundaries captured by NanoAuger mapping, Cu depletion occurs which could lead to lower work function and downward band bending.

Beside characterization of grain boundaries deeper within the polycrystalline films, FIB cross-sectioning with grazing incidence angle has been used to characterize the interface between Mo and CIGSe near the backside. Fig. 4.5 (a) shows the SEM micrograph and NanoAuger elemental maps for Cu, In, Se and Mo for a 1 x 8 μm² section of CIGSe/Mo back contact interface. These NanoAuger measurements were performed on a sloped cross-section milled with the incidence angle of 8°. The maps and line scans at the bottom of the figure. (Mo, Se, In and Ga lines) demonstrate that there is an overlap region between the Mo and Se signals, highlighted by pale orange, consistent with formation of a thin layer of MoSeₓ between Mo and CIGSe. The Mo/Se ratio determined by single point Auger spectroscopy is about 1 (y ~ 1). This layer is believed to grow during the selenization process of the CIGSe films, where Se gas is introduced into the growth chamber in order to react with metallic components deposited on the Mo film. However, Mo would also react with Se to form a thin layer of MoSeₓ.

Although presence of MoSeₓ between Mo and CIGSe has been previously determined by chemical composition measurements such as TEM-EELS and XPS, little is known about the electrical potential variations across the CIGSe / MoSeₓ / Mo interfaces. To determine the electronic structure of these interfaces, KPFM measurements were performed under Ar environment on a sloped cross-section milled at 5° ion beam incidence angle. A smaller ion beam incidence angle was chosen in order
to further expand the scale since minimum resolution for KPFM measurements (> 20 – 30 nm) is at least three times larger than NanoAuger (~ 8 nm). Topography and surface potential maps measured by cross-sectional KPFM are shown in Fig. 4.5 (b). The KPFM images show a region between Mo and CIGSe with slightly lower potential ($\Delta (SP)_{avg} \sim 45$ mV) than CIGSe. Therefore, based on the KPFM fundamental equation ($SP = \varphi_{tip} - \varphi_{sample} / e$), the MoSe$_y$ layer has a 45 meV higher work function than CIGSe. Due to the larger work function, MoSe$_y$ induces upward band bending within the CIGSe close to the back interface, thereby assisting hole extraction from the film. On the basis of work function difference, as well as theoretical predictions on the back surface band diagram, the band structure shown in the inset of Fig. 4.5 (b) has been proposed. However, the resulting upward band bending near the back surface can be too small for maximal hole extraction, necessitating application of back contacts with higher work functions like MoO$_x$ and WO$_x$. In addition, there is about 350 mV downward band bending within the MoSe$_y$ because of its large difference in work function with Mo. Since the MoSe$_y$ actual thickness is few tens of nanometers, it is predicted that despite downward band bending, holes are able to tunnel from the CIGSe back surface to the Mo contact. It should be noted that the actual work function for Mo is lower than the values measured by KPFM. The reason for this difference is oxidation of Mo after Cryo-FIB and its chemical resistance to NH$_4$OH, which was used to remove the oxide from the CIGSe top surfaces.

4.5 Conclusion
In summary, cryo-FIB milling at grazing incidence angles was employed to prepare smooth cross-sections with scale expansions of 7.5 – 11.5x. KPFM measurements showed little or no change to the grain boundary polarity on these cross-section as a result of ion beam milling. In the cross-sections, positively-charged grain boundaries are observed from the top to the bottom with downward band bending varying from 140 mV to 75 mV from the top to the bottom. Additionally, this cross-sectioning method enabled the first direct determination of the composition and the electronic structure of the Mo/CIGSe back contact, where a thin layer of MoSe$_y$ was detected by both Auger Nanoprobe and KPFM. Due to 45 meV larger work function than CIGSe, MoSe$_y$ formation can be beneficial in hole extraction by inducing upward band bending in the CIGSe back surface. Hole extraction is expected to improve by the application of high-work-function contact materials such as MoO$_x$. This cross-sectioning method with minimal processing steps can be beneficial in characterizing various interfaces in multilayer thin film solar cell stacks particularly for sensitive films such as hybrid inorganic-organic perovskites and organic solar cells as well as other inorganic thin films such as CdTe and CZTSSe; this enables identification of targets of opportunity for improvements of PV beyond bulk defects.

4.6 Acknowledgments

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4.7 Supporting information

To determine the variations in the extent of potential spike at the grain boundaries relative to the grains ($\Delta SP_{GB}$) as a function of depth, grain boundary potentials at 8 – 11 different locations were averaged over four zones shown in Fig. 4.6 (a), on the surface potential map measured for the sloped cross-section milled at the grazing incidence angle of 5°. Each zone is about 3.75 x 15 um² in size. The value $X_i$ shown on the left side of Fig. 4.6 (a) indicates the distance between the center of the box and top of the scan area. Fig. 4.6 (b) displays the average extent of downward band bending as a function of $X_i$. This is consistent with reduction of the downward band bending by moving within the film due to the presence of Cu-poor top surfaces.²³

Fig. 4.7 shows the SEM micrograph as well as the elemental maps for Cu, Sn, S, Se and O measured by NanoAuger on a CZTSSe surface cleaned by 5 min of immersion in 8 vol. % NH₄OH solution. Grain boundaries appear to be Cu-poor, Sn-
rich and O-rich. This is consistent with the formation of a passivating SnO$_x$ layer at the grain boundaries, formed as a result of post deposition annealing in air at 350 °C.$^7$
Figure 4.1 J-V characteristics of two solar cell devices fabricated on the as-deposited CIGSe film.
Table 4.1 PV device performance parameters derived from the J-V measurements on the CIGSe solar cells.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$V_{OC}$</th>
<th>$J_{SC}$</th>
<th>FF</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0502-31</td>
<td>0.69 V</td>
<td>33.4 mA/cm$^2$</td>
<td>0.78</td>
<td>18.1 %</td>
</tr>
<tr>
<td>P0502-32</td>
<td>0.69 V</td>
<td>33.8 mA/cm$^2$</td>
<td>0.74</td>
<td>17.2 %</td>
</tr>
</tbody>
</table>
Figure 4.2 Cryo-FIB Cross-Sectioning Procedure: (a) Schematic showing the process of grazing incidence cross-sectioning of multilayer thin film substrates by focused ion beam (FIB). The parameter $\theta$ is the angle between the incoming beam and sample surface which was varied between 5° and 8° depending on the required amount of scale expansion. The thickness of each layer exposed by grazing incidence milling is proportional to $1/\sin \theta$. (b) SEM micrograph of a cross-section milled using a grazing ion beam incidence angle of 5° on a CIGSe film (bright top surface) grown on Mo-coated soda lime glass (SLG).
Figure 4.3 Topography and Surface Potential Maps in Planar and Cross-sectional Geometries: (a,b) Planar topography and surface potential maps for clean a CIGSe surface recorded simultaneously during the Kelvin probe force microscopy (KPFM) measurements. Scan size is 15 µm x 15 µm. (c) Line traces for surface potential in three different locations shown by yellow lines in (b). The yellow bars specify the locations of the grain boundaries where the line traces were measured. (d,e) Topography and surface potential maps measured on sloped cross-sections milled with the incidence angle of 5°. Measurements were carried out on the upper half of the cross-section to exclude the Mo/CIGSe interface. Scan size is 15 µm x 15 µm. (f) Line traces for topography and surface potential lines shown by yellow lines in (e). The yellow bars specify the locations of the grain boundaries where the line traces were measured.
Figure 4.4 NanoAuger Elemental Maps for CIGS in Planar and Cross Sectional Geometry: (a) Planar SEM micrograph and NanoAuger elemental maps for Cu, In, Ga, Se and O for clean CIGSe surface. The non-uniformity in the elemental maps does not correspond to the grain boundaries but to the grain top surfaces. (b) Cross-sectional SEM micrograph and NanoAuger elemental maps for Cu, In, Ga, Se and O measured on surfaces prepared by normal incidence Cryo-FIB. Two of the vertical grain boundaries appear to be Cu-rich near the top (yellow arrow) and Cu-poor near the bottom (blue arrow) of the CIGSe film.
Figure 4.5 NanoAuger and KPFM Measurements on CIGSe/Mo Back Interface: (a) SEM micrograph and NanoAuger elemental maps for Cu, In, Se and Mo for a CIGSe sloped cross-section prepared by Cryo-FIB milling at 8° ion beam incidence angle. The Mo and Se maps show an area of overlap which is the MoSe$_y$. Line traces confirm the presence of a MoSe$_y$ layer between Mo and Se in CIGSe. (b) Topography and surface potential measurements performed on the CIGSe sample with 5° ion beam incidence angle, showing a small potential drop across the interface between Mo and CIGSe that corroborates the presence of MoSe$_y$. 
Figure 4.6 (a) KPFM surface potential map for sloped cross-section prepared by cryo-FIB. Four different areas were used to calculate the average grain boundary potential difference relative to the grains. (b) Average grain boundary potential difference ($\Delta SP_{\text{GB}}$) as a function of distance from the top of the scan area.
Figure 4.7 Auger nanoprobe elemental maps for Cu, Sn, S, O and Se on CZTSSe sample cleaned by immersion in NH4OH solution for 5 min. Scan area size is 11.25 x 15 µm².
4.8 References


P. R. Munroe, Materials Characterization 60, 2 (2009).


