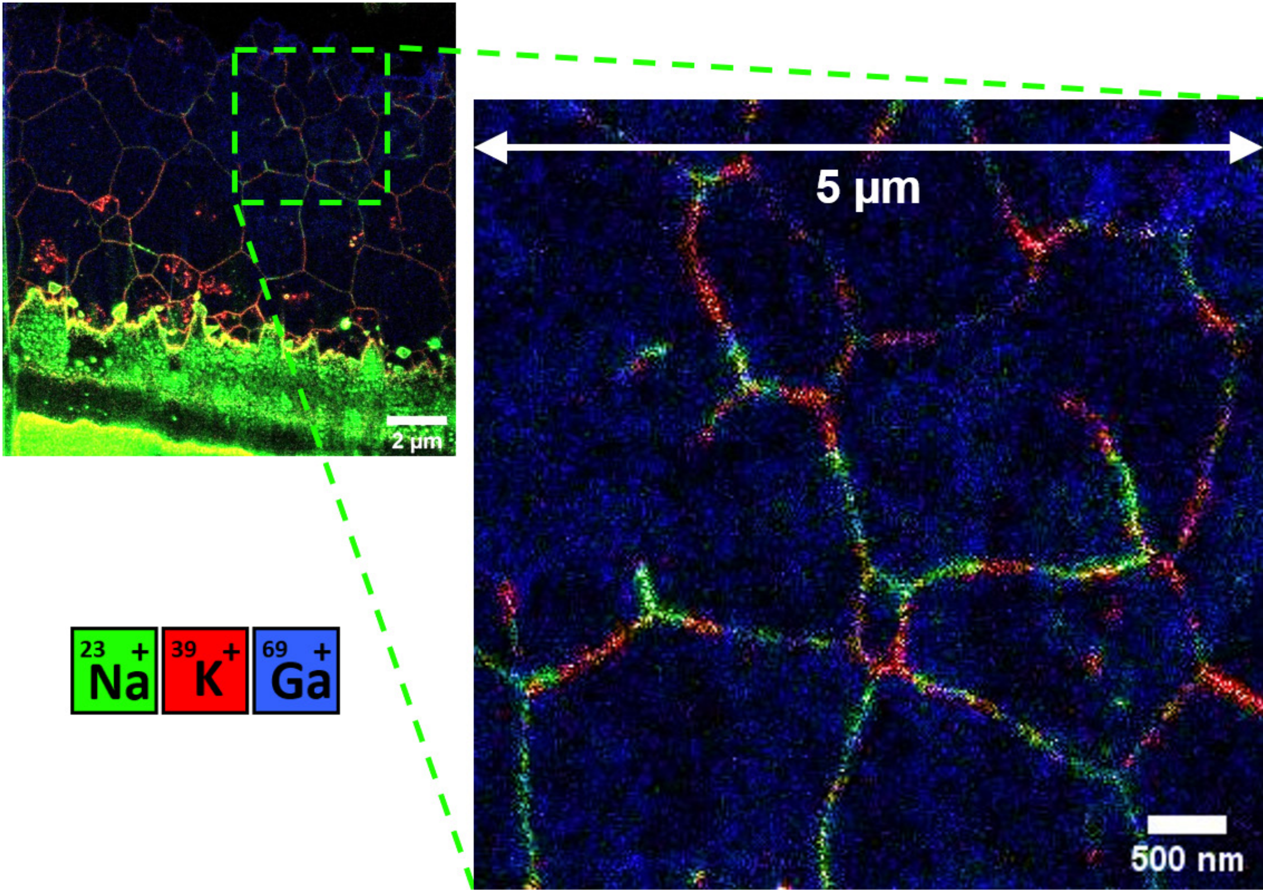

Alkali Diffusion in CIGS Solar Cells Studied by Gallium and Neon SIMS

ZEISS Crossbeam and ZEISS ORION NanoFab

Seeing beyond

Alkali Diffusion in CIGS Solar Cells Studied by Gallium and Neon SIMS

ZEISS Crossbeam and ZEISS ORION NanoFab

Authors: Fabián Pérez-Willard
Carl Zeiss Microscopy GmbH, Oberkochen, Germany
Fouzia Khanom, Chuong Huynh, John Notte
Carl Zeiss Microscopy, LLC, Peabody, MA, United States
Theresa Magorian Friedlmeier
Center for Solar Energy and Hydrogen Research (ZSW), Stuttgart, Germany

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Secondary ion mass spectrometry (SIMS) was used to study alkali element diffusion in high-efficiency copper indium gallium selenide (CIGS) solar cells. Traces of alkali elements in the CIGS active layer are known to have a positive impact on cell efficiency. SIMS depth profiling through the complete layer structure – from front electrode to substrate – was conducted by time of flight SIMS in a gallium FIB-SEM. As expected, Na and K diffusion into the CIGS active layer was present on samples grown on soda lime glass as opposed to reference samples grown on alumina. Furthermore, high resolution neon beam SIMS in a HIM (helium/neon ion microscope) was done on cross sections of the sample revealing the alkali element distribution in the CIGS layer with unprecedented spatial resolution.

Introduction

Thin-film solar cells based on $Cu(In,Ga)Se_2$ (CIGS) are an attractive alternative to silicon solar cells in terms of energy costs in production and aesthetics [1,2]. During the last decade the Center for Solar Energy and Hydrogen Research (ZSW) has held several times the world record in energy conversion efficiency for this type of solar cell. Today, the record stands at impressive 23.35% [3].

In order to achieve such high efficiency levels, different parameters require optimization. For example, the right choice of deposition conditions affects grain size and the diffusion of alkali elements from the substrate or other sources [4]. Another example is post-deposition treatment to integrate alkali elements into the CIGS active material [5]. Visualizing and understanding the effects of these "levers" is key to improve cell performance.

In this context, electron and focused ion beam (FIB) microscopy play crucial roles because they allow the analysis of the microstructure of the solar cell through all relevant length scales and with very high resolution [6,7].

In this note, we used secondary ion mass spectrometry (SIMS) with Ga and Ne FIBs to study alkali element diffusion in CIGS solar cells. SIMS depth profiles and SIMS maps on cross sections were acquired.

SIMS Depth Profiling with ZEISS Crossbeam

The SIMS depth profiling experiments were done using a Ga FIB-SEM, ZEISS Crossbeam, equipped with an orthogonal time of flight (ToF) SIMS spectrometer as described in [8].

In this setup, SIMS depth profiling is done by scanning the Ga FIB over an area of the sample as shown schematically in Figure 1(a). By doing so, different ion species and neutrals are sputtered from the surface. All ions, either positively or negatively charged, are collected and analyzed as a function of their mass-to-charge ratio in the ToF spectrometer.
The average SIMS signal for a given frame and mass/charge value is plotted as a function of the frame number. Assuming a constant sputter rate during the experiment, the frame number would be directly proportional to the FIB milling depth.

Figure 1(b) shows a schematic of the model CIGS solar cell. From bottom to top, the cell comprises a glass substrate, a molybdenum back electrode, the CIGS absorber, a CdS buffer layer, a roughly 50 nm thin layer of non-doped or intrinsic ZnO, and a thicker layer of aluminum-doped ZnO (front electrode). As a reference, a second sample with the same composition and layer arrangement, but on an alumina substrate, was measured as well.

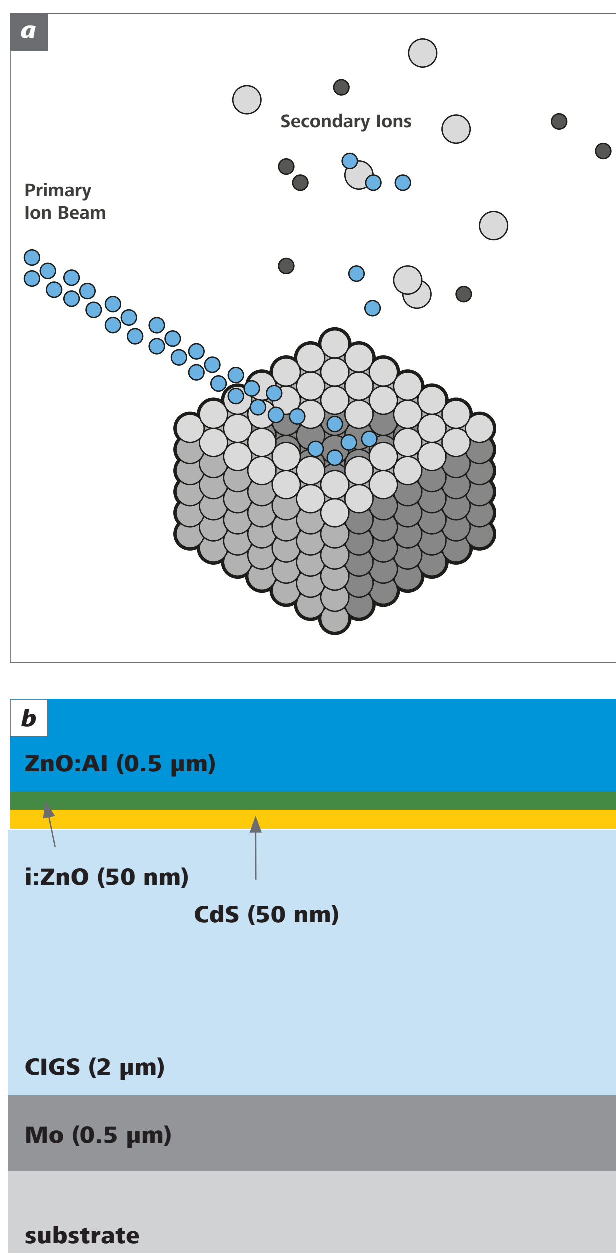


Figure 1: *(a) Working principle of SIMS. (b) Layer structure of a model CIGS solar cell.*

For the SIMS depth profile measurements, areas of 10 × 10 µm² were scanned with a FIB probe of 180 pA current and 20 keV energy.

Figure 2 shows the SIMS depth profiles measured on the glass and alumina sample for mass/charge = 115 Th, 39 Th and 25 Th which correspond to ^{115}In, ^{39}K, and ^{23}Na, respectively. The shape of the In curve is very similar for both substrates. The same applies for Zn, Mo and Cu (not shown), but not for Na and K. For the glass sample, clear Na and K signals are observed between frames 250 and 900, at which the FIB is milling its way through the CIGS active layer. After that both signals continue to increase moderately for roughly 250 more frames to then rise steeply as the glass substrate is approached. For the reference sample, the Na and K curves are relatively flat and close to zero.

While Na and K are present in the soda lime glass, they are not contained in the alumina substrate material. The CIGS cell fabrication process parameters are such that K, and Na coming from the glass can diffuse into the CIGS active layer. Obviously, this cannot happen for the cell on alumina where these elements are not present to start with.

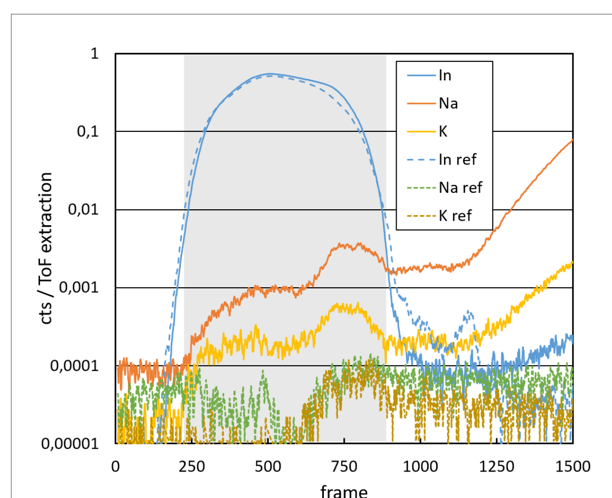


Figure 2: *Elemental depth profile of the CIGS solar cell measured by ToF SIMS for glass and alumina (ref) substrates. The grey shaded area roughly denotes the location of the CIGS layer.*

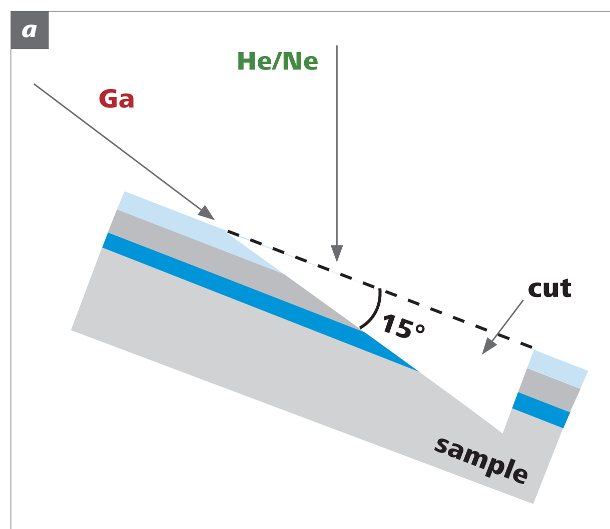
The SIMS depth profile results presented in this section are fully consistent with an earlier experiment in which a quadrupole SIMS was used to analyze samples from the same production batch [7]. As compared to the quadrupole system, the ToF features the advantage of detecting all ions – either positive or negative – in parallel. The disadvantages are a smaller useful dynamic range – about two orders of magnitude less – and a shorter duty cycle [8].

A quantification of the SIMS data to determine the concentration of the alkali elements in the different layers of the solar cell is difficult, because yields of secondary ions vary very strongly depending on their surroundings. This is the so-called matrix effect. For quantitative work, measurements on reference samples would be needed. Such were beyond the scope of this study. From a previous study we know that Na and K concentrations are below the detection limits of EDS [7], i.e. below 1%. Here, as a consistency test, we limit ourselves to compare SIMS data from the glass substrate sample, where alkali diffusion is expected, with the same data acquired on an alumina substrate sample, where no alkali elements are expected.

SIMS on the Cross Section – HIM-SIMS

Cross sections of the samples were characterized with SIMS in ZEISS ORION NanoFab, also known as helium ion microscope (HIM). The HIM provides sub-nanometer focused helium and neon ion beams for surface-sensitive imaging and most precise direct patterning [9]. In combination with a floating magnetic sector spectrometer specifically designed for this instrument, the Ne beam can be used for SIMS analysis, too [10]. High-sensitivity SIMS with spatial resolution well below 15 nm is then possible.

The SIMS spectrometer in the HIM uses a magnetic field to separate the different secondary ions according to their mass/charge ratio physically in space. Four individual detectors (one fixed and three movable) can collect signals from four different ion masses of choice in parallel.



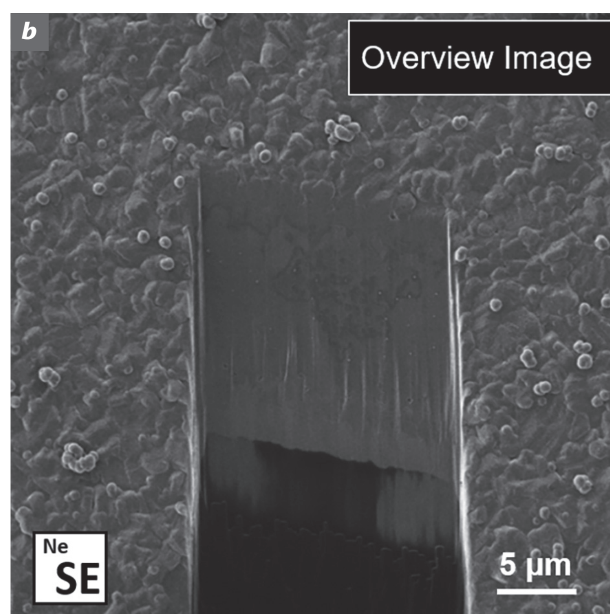


Figure 3: *(a) Preparation of a slanted cross section. The cross section is at an angle of 15° to the sample surface. (b) Overview Ne FIB image. The sample is at 0° tilt.*

Preliminary experiments on cleaved CIGS samples mounted on edge suffered from inefficient SIMS detection because the electrical field of the SIMS collector was disturbed too strongly by the sample geometry. Therefore, slanted cross sections were prepared by gallium FIB milling at 30kV:1.5nA (trenching) and subsequent polishing at 30kV:300pA in a HIM equipped with a Ga FIB. For this purpose, a pre-tilted sample holder was used. The cross sections were cut at an angle of 15° to the sample surfaces as shown in Figure 3(a). The samples were then transferred to a HIM equipped with the magnetic sector SIMS, where the SIMS analysis was done at 0° sample tilt. The collector-sample arrangement is then ideal for an efficient secondary ion collection.

The Ne beam was used for traditional secondary electron (SE) imaging to navigate to the ROI. Note that from the perspective of the Ne beam, the stack of layers appeared stretched by a factor of 3.7. For all SIMS measurements, the Ne beam current was between 8 to 9 pA and maps of 1024 × 1024 pixels were acquired with a pixel dwell time of 1500 µs. Thus, acquisition time for one SIMS map was 26 min. The FOV was 15 µm for the glass and 13 µm for the alumina sample.

With one of the mass selective detectors set for 39 amu (K), the other ones for 23 amu (Na) and 69 (Ga), the same neon beam was used to generate mass-filtered images of the ROI on both the glass and alumina substrates. The results for K are shown in Figure 4. For the alumina reference (on the right), no alkali elements could be detected in the CIGS layer. For the glass sample (on the left) K is present at the grain boundaries of the CIGS active layer.

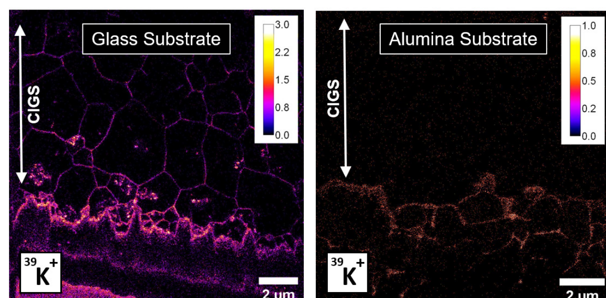


Figure 4: *(a) Ne SIMS maps of the model CIGS solar cell on glass (left) and alumina (right) substrates.*

In Figure 5 K, Na, and Ga SIMS maps are overlaid. An area of 5 x 5 µm² in size out of the map is shown in greater detail to provide a better idea of the achieved Ne SIMS lateral resolution.

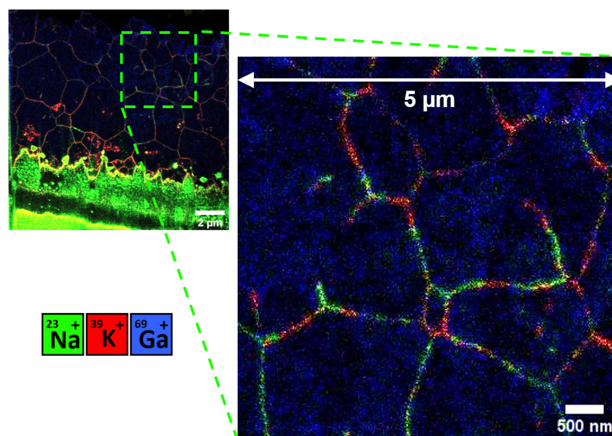


Figure 5: *Composite image of Na, K, and Ga SIMS maps. An area of 5 × 5 µm² has been zoomed in.*

Conclusion

SIMS in the FIB-SEM allowed detection and depth profiling of alkali elements in a model CIGS solar cell. The technically relevant alkali concentrations are below the limits of detection of EDS.

ORION NanoFab with magnetic sector SIMS revealed the distribution of the alkalis in the CIGS layer of fully processed cross sectioned samples. The alkalis were found preferentially at grain boundaries. The presented technique provides unprecedented SIMS spatial resolution and at the same time allows to study a large number of grain boundaries, so that the gained information can be put into context easily.

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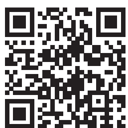

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