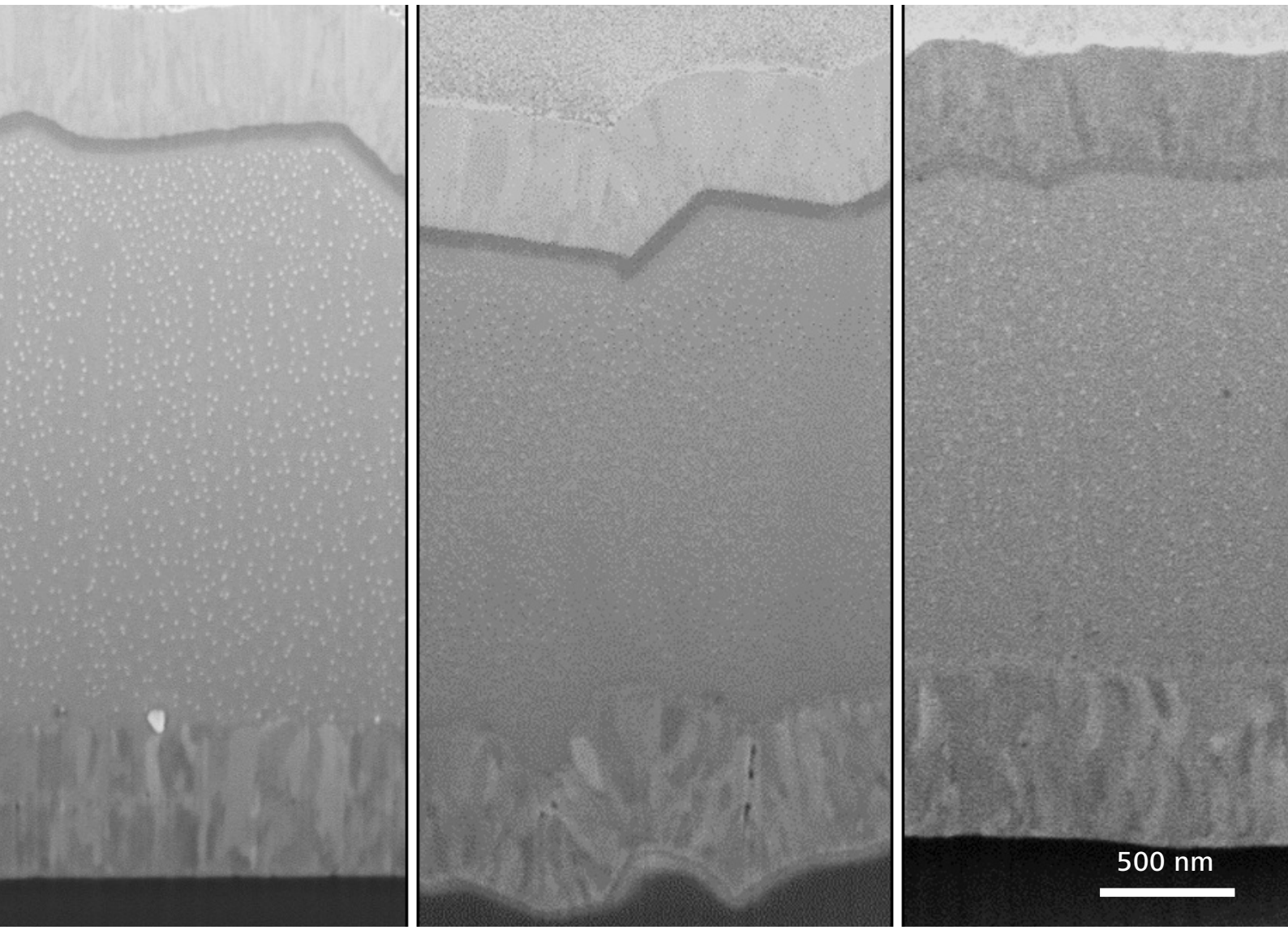
Application Note



FIB-SEM Investigations of the Microstructure of CIGS Solar Cells

ZEISS Crossbeam

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High-efficiency thin-film solar cells based on Cu(In,Ga)Se_2 were studied extensively by focused ion beam – scanning electron microscopy (FIB-SEM). Cross sections of cells on different substrates were prepared by FIB to reveal the internal structure of the cell. This method works well even on ductile or polymer substrates, which are difficult to prepare by traditional means. Scanning transmission electron microscopy (STEM) revealed finer details of front and back electrodes and enables energy dispersive spectroscopy (EDS) measurements with a spatial resolution below 10 nm. Furthermore, secondary ion mass spectroscopy (SIMS) was used to prove alkali diffusion from the substrate into the cell.

Introduction

Solar cells convert sunlight into electricity by the photovoltaic effect. In 2016, around 1.8 percent of the worldwide electricity demand was produced by photovoltaics [1]. In the future, this share is expected to continue its rapid growth as green energies become more and more cost-competitive.

Most commercial solar cells use crystalline silicon as the active material. An alternative to these are thin-film cells. Here, the absorber material is a thin film with a thickness ranging from tens of nanometers to a few micrometers. The advantages of thin-film cells include lower production costs and weight. Additionally, the absorber is so thin that flexible and transparent cells can be manufactured - opening up new application fields.

Today, the efficiency of thin-film copper indium gallium selenide (CIGS) solar cells is above 22 percent [2] reaching the performance levels of modern polycrystalline silicon solar cells. Strong development efforts are ongoing to further increase cell efficiency. In this context, electron microscopy plays a crucial role because it allows the analysis of the microstructure of the solar cell through all relevant length scales and with very high resolution.

In this note, we describe different experiments which allow for an extensive materials characterization of the CIGS solar cell. These experiments were all carried out using ZEISS Crossbeam.

Cross-section Imaging

In order to analyze the different constituent layers of CIGS solar cells, cross sections need to be prepared. One way to do this is by cleaving the sample. An SEM image of a cleaved sample is shown (Figure 1a). In this case the CIGS cell was deposited on a glass substrate. The different layers in the SEM image have been colored for clarity.

A schematic of the layer structure of a typical CIGS cell is shown (Figure 1b). From bottom to top, the cell comprises a substrate (e.g. glass), 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 (the front contact).

While cleaving is suitable for hard substrates like glass or alumina, it does not work well for ductile steel or soft polymer substrates which are interesting choices for new applications. Cross sections of these samples can be

prepared by tearing the specimen. However, tearing of CIGS cells often leads to layer delamination. It is difficult and time consuming to find a good spot along the edge of the fractured specimen where all layers are intact. The latter can also hold true for cleaved samples.

In situ cross section preparation in the FIB-SEM offers a convenient alternative for the analysis of any CIGS cell independent of its substrate. The sample is shown during FIB-SEM cross sectioning work (Figure 2a). The sample is tilted 54° towards the FIB beam. In this position, the FIB beam is perpendicular to the sample surface and is used to cut a trench in front of the chosen site of interest. Due to the sample being located at the intersection point of FIB and SEM beams, SEM analysis can be done after or even during FIB milling. A FIB cross section in a CIGS cell on glass is shown (Figure 2b). The cross section is 20 µm wide and deep enough to expose the complete layer stack. The preparation time was less than ten minutes.

Cross sections were prepared for CIGS cells on four different substrates. The substrates were glass, alumina, steel, and polyimide. The milling parameters were the same for all samples, which demonstrates the universality of the FIB-SEM approach. Detailed images of the four samples show the layer structure of the CIGS cell (Figure 3). For the steel cell, the conducting substrate was covered with a 2.5 µm thick layer of insulating SiO_x.

A speckle pattern can be observed on the CIGS layer of all four samples. The speckles correspond to copper-rich droplets or agglomerates as reported by Abou-Ras et al. [3]. In Abou-Ras´ work they are attributed to segregation of Cu, due to Cu enrichment at the cross section surface combined with strong surface diffusion. The droplet formation can be minimized by the use of reactive gases during milling, or by milling at cryogenic temperatures [3].

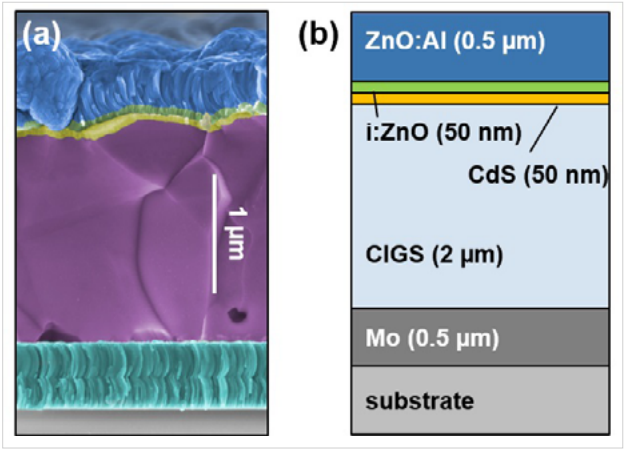

Figure 1 *(a) Colored SEM image of cleaved CIGS sample. (b) Schematic of the standard structure of a CIGS solar cell.*

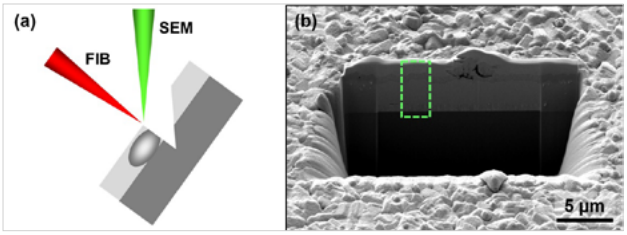

Figure 2 *(a) Schematic showing the arrangement of the sample, and FIB and SEM beams during FIB-SEM cross sectioning work. (b) SEM overview image of a cross section in a CIGS solar cell on glass. The area within the green dashed frame is shown in more detail in Figure 3.*

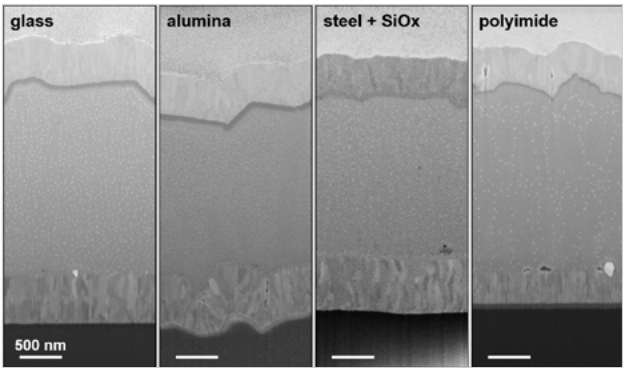

Figure 3 *Cross sections of CIGS solar cells on different substrates. The substrates are, from left to right: glass, alumina, SiOx on steel and polyimide.*

STEM Imaging

For an exemplary STEM study, we prepared a lamella from the CIGS on alumina sample. Electron transparency of the lamella was achieved by a final FIB polishing step at 5 kV energy.

The arrangement of SEM final lens, the sample and the STEM detector are shown (Figure 4a), providing an overview 30 kV brightfield STEM image of the lamella (Figure 4b). Compared to the SE cross section images (Figure 3), the STEM images show different contrasts. Further, a higher imaging resolution can be achieved [4].

Detailed images of the CIGS stack at the Mo and ZnO level are shown (Figure 5). The internal boundary in the Mo layer (dashed line) is caused by a two-step sputtering deposition. The small grains on top of the Mo layer are a very thin layer of $MoSe_2$ formed during the CIGS coating process [5].

Within the ZnO layer the intrinsic ZnO (i:ZnO, between the two dashed lines) can be distinguished from the Al-doped ZnO, because of a different grain morphology. The grains in the Al-doped material are elongated, while the grains in the intrinsic area are much smaller.

High Resolution EDS

EDS mapping was done in a small region of the lamella containing all layers (green frame in Figure 4). The pixel spacing in the map was 2.6 nm in both x and y direction. The measurement was done at 15 kV SEM landing energy using an EDAX Octane Elite Super EDS system and some results are shown (Figure 6). The different colors correspond to the Pt M, Zn K, Cd L, Se L, Mo L and O K lines and are a characteristic signature of the different layers.

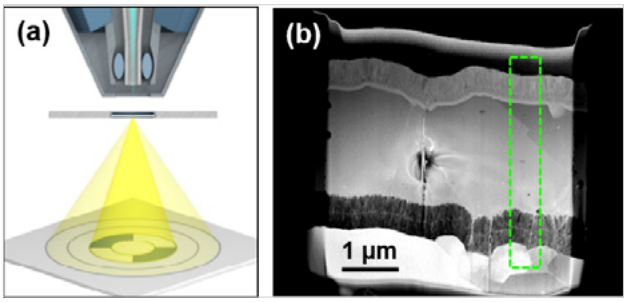

Figure 4 *(a) Schematic showing sample and detector during STEM. (b) Overview STEM image of a CIGS solar cell on alumina.*

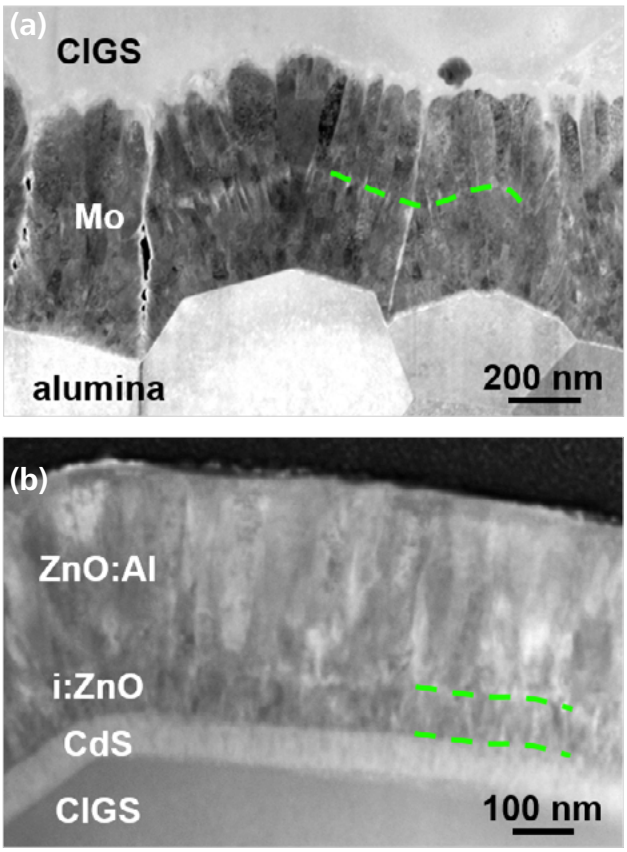

Figure 5 *(a) Detail of Mo back contact. The dashed line shows the internal interface. (b) Detail of ZnO layer. ZnO:Al and i:ZnO show a different grain structure. The dashed lines denote the limits of the i:ZnO layer.*

The CdS layer with 58 nm thickness can be resolved easily in the EDS map. A line scan across this layer was extracted from the spectral data and the Cd L counts plotted as a function of position. This plot was used to estimate the spatial resolution of the EDS measurement, which was found to be well below 10 nm in accordance with a similar earlier experiment in a different material system [6].

Secondary Ion Mass Spectroscopy

Trace concentrations of alkali elements like sodium (Na) and potassium (K) in the CIGS active material are known to improve solar cell efficiency [2]. The alkali elements diffuse from the substrate into the CIGS during growth. Their concentrations are very small and below the detection limits of EDS. Therefore secondary ion mass spectrometry (SIMS, Hiden Analytical EQS 1000) was conducted in the FIB-SEM.

An area of the sample was slowly removed by FIB. During milling, secondary ions are sputtered from the sample. These are fed into a mass spectrometer and analyzed according to their mass to charge ratio m/q. The number of counts for one or more selected m/q values can be measured as a function of the milling cycle. With increasing milling cycle, deeper regions of the sample are probed.

Two such SIMS depth profiles were measured for the CIGS on glass and the CIGS on alumina samples with exactly the same parameters – some results are summarized (Figure 7). Both samples show almost identical elemental depth profiles as exemplarily plotted for In in Figure 7. This is not the case for Na and K signals. For the glass substrate sample, both signals are strong from the substrate up to the ZnO layer in contrast to the reference alumina sample. This is expected because only the glass substrate contains alkali elements.

In this experiment, a quantitative determination of Na and K concentrations was not performed. Such a quantification is difficult, because secondary ion yields depend strongly on the surrounding matrix (matrix effect). Therefore, it is necessary to work with standards, i.e. CIGS samples with well-defined alkali concentrations. This was not done in this work, where only a proof of principle was intended.

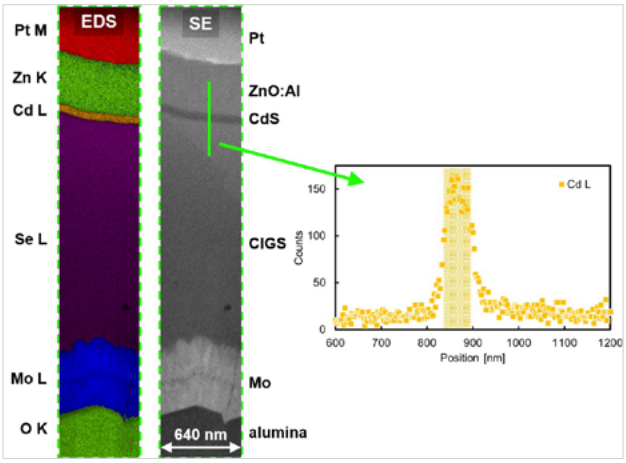

Figure 6 *EDS mapping of an area of a CIGS on alumina lamella. The inset shows the Cd L EDS signal as a function of position for the line shown in green.*

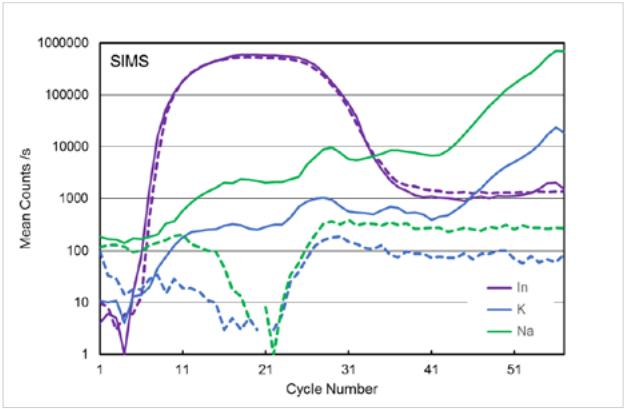

Figure 7 *SIMS depth profiles for In, K, and Na for two CIGS solar cells with different substrates: glass (solid lines) and alumina (dashed lines).*

Conclusion

FIB-SEMs are extremely useful tools for the analysis of microstructure in materials research. This has been illustrated in this note using the CIGS solar cell as a model system.

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