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Assessment of elemental distributions at line and planar defects in $Cu(In,Ga)Se_2$ thin films by atom probe tomography

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ABSTRACT

$Cu(In,Ga)Se_2$ thin-film solar cells exhibit record power-conversion efficiencies of currently 22.6%. Such performance is impressive in view of the rather small average grain sizes of the $Cu(In,Ga)Se_2$ absorber. This work gives insight to the chemistry at linear and planar defects in $Cu(In,Ga)Se_2$ absorber at the nanometer scale by means of atom-probe tomography. Moreover, the tip sample is investigated by transmission electron microscopy prior to the atom-probe tomography experiments to determine the structure of the planar defects. These experimental results are compared with those from theoretical predictions, and consequences for the energy-band diagrams around these planar defects are proposed.

1. Introduction

Nowadays, enhanced understanding of the chemistry and structure for extended structural defects in solar cells is needed. Indeed, in these devices, various line and planar defects, i.e., (partial) dislocations, stacking faults (SFs), twin boundaries (TBs) as special cases of SFs, and random grain boundaries (GBs), can be considered in general electrically active, exerting substantial influence on the electrical properties of the entire device [1].

Out of the various solar cell technologies, those using $Cu(In,Ga)Se_2$ (CIGS) absorber layer exhibit the highest conversion efficiencies of up to 22.6% [2]. Regarding the polycrystalline nature of the CIGS thin-film, enhanced understanding of how the microstructure influences the device performance is of particular importance for the further improvement of the CIGS technology. Part of the related investigations concerns the analysis of structure and composition at and around line and planar defects in CIGS thin-films, which needs to be performed at the nanometer or even subnanometer scale.

For these investigations, it is crucial to link the detected chemical changes to the structures of line and planar defects. Therefore, correlative studies at identical specimen positions are required. One possibility is to apply high-resolution imaging in (scanning) transmission electron microscopy ((S)TEM) and its related techniques such as electron energy-loss spectroscopy (EELS) as well as energy-dispersive X-ray spectroscopy (EDX), which are able to characterize both, chemical and structural properties [3]. However, since EELS and EDX can detect impurities only down to concentrations of about 0.1 at.%, the corresponding compositional information is limited.

As an alternative, the current work will give details on a combinatory approach, comprising first diffraction-contrast imaging and electron diffraction in TEM, and secondly atom-probe tomography (APT). The principle of the latter one is based on the field-evaporation of a tip-shaped specimen and detection of the evaporated atoms employing mass spectroscopy. For the investigation of the structure of extended defects, diffraction techniques in TEM are excellent tools, e.g., when interested in crystallographic grain orientations [4] or in the misorientation angle for a specific GB [5]. In some cases, it is even possible to determine the boundary plane when utilizing the trace of the interface [6].

In the present work, we provide details on how to apply the approach of correlative APT-TEM studies on polycrystalline CIGS as a model system. We will provide an overview of compositional data obtained by APT at various line and planar defects in different CIGS thin-films. Finally, the structure and composition of the extended defects will be linked to the device performance of the CIGS solar cells, providing a possible reason for the limitation of the open-circuit voltage in these devices.

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2. Experimental procedure

2.1. Solar cell production and performance

Various CIGS absorbers had been studied in this paper as described in Table 1 by sample A, B, and C. All the CIGS absorbers were prepared using a three-stage co-evaporation process or interrupted three-stage co-evaporation process either at Helmholtz Zentrum Berlin (HZB) [7, 8] and at Zentrum für Sonnenenergie- und Wasserstoffforschung (ZSW) Stuttgart [9]. The solar cells consisted of a ZnO/CdS/CIGSe/Mo stack on a soda-lime glass substrate.

For the study of SFs (see sample B in Table 1), the CIGS absorber was prepared using a SiN diffusion barrier between Mo and the CIGS substrate to prevent uncontrolled Na diffusion from the glass in the film. Moreover, for this specific sample the CIGS second step in the three-stage process (Cu-Se deposition at 430 °C) was interrupted before the film composition became Cu-rich ([Cu]/([In] + [Ga]) > 1) [7]. The aim is to understand why the Cu-poor CIGS absorber obtained without experiencing a Cu-rich step has a poorer quality than the standard CIGS absorber. It turns out that this is mainly due to the high density of planar defects present in the absorber, defects which enhances the recombination activity inside the cell.

2.2. Analysis conditions of APT

APT tips were prepared utilizing a dual-focused ion beam (FIB) (FEI Helios Nanolab 600i) using the lift-out procedure described in Ref. [11]. TEM studies on the APT tips were carried out in a JEOL JEM-2200FS microscope operated at an acceleration voltage of 200 kV.

APT experiments were performed with a local electrode atom probe (LEAP 3000X HR, Cameca Instruments), applying laser pulses of 532 nm wavelength, 12 ps pulse length, and an energy of 0.1 nJ per pulse at a repetition rate of 100 kHz. The specimen base temperature was about 60 K. Under these conditions, most of the detected events are single events (~80%). However, the mass spectrum from Fig. 1 show the presence of numerous molecular ions such as $CuSe^+$, Cu_2Se^+, $CuSe_2^+$, Se_2^+, Se_2^{2+}, Se_3^+. No molecular ions were detected for In or Na, O, and K impurities.

2.3. Limitations of APT studies on CIGS thin-films

The first limitation of the APT studies when dealing with CIGS material is the peak overlap of elements having the same mass-to-charge ratio in the mass spectrum. For example, the isotopes $^{39}K^+$ and $^{41}K^+$ overlap with $^{78}Se^{2+}$ and $^{82}Se^{2+}$ at 39 a.m.u. and 41 a.m.u., respectively. The excess of K at GBs can be still determined if the Se concentration does not change [12]. To overcome this issue, single atom detectors with kinetic energy discrimination are required [13] to reduce noise and, hence, increase the sensitivity with respect to impurities. Other peak overlaps detected in the mass spectrum of the CIGS compound from Fig. 1 are $^{16}O^+$ and $^{32}O_2^{2+}$ and $^{76,77,78,80,82}Se^+$ and $^{152,154,156,160,164}Se_2^{2+}$. Here, only peak decomposition of overlapping peaks by using the natural isotopic abundancies, which is referred to collective discrimination, can help to determine the correct composition.

The second main limitation of APT is the detection efficiency of the single atom detector. The detection efficiency, which is equal for each element, is limited to ~40–60% in commercially used APT instruments due to geometrical constraints of the microchannel plate (MCP) [14]. Since 2015, APT facilities with 80% detection efficiency [14,15] are available at Cameca Instruments However, a new detector design is needed to achieve 100% detection efficiency.

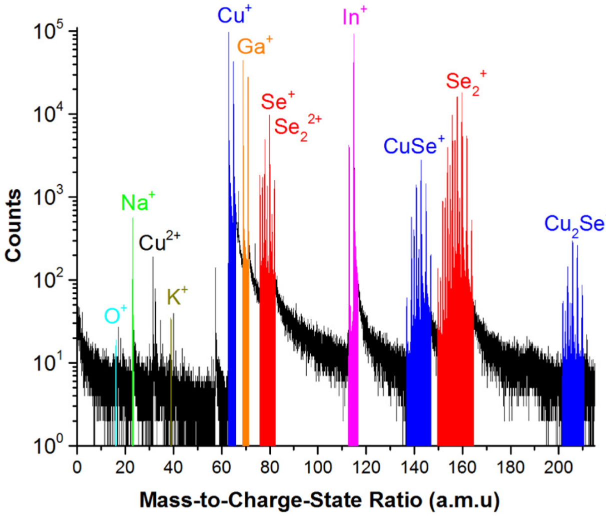

Fig. 1. Mass spectrum of a CIGS absorber.

The third limitation of the APT technique is the impossibility to determine with an accuracy better than 1–2 nm the widths of GBs or other extended defects. This spatial limitation is due to the so-called 'local-magnification effect', which leads to aberrations of ion trajectories due to a difference in the electric field strengths required for field-evaporation of atoms in the grain interior and at e.g. the GB [16]. This effect leads to lateral displacements of atoms and subsequently to density fluctuations and, hence, to a broadening of GB width. This effect is most striking at GB planes being parallel to the analysis direction [16]. Therefore, comparison of absolute impurity concentration at various GBs based only on the 1D concentration profile is not accurate [17]. In order to correctly quantify the amount of impurities segregated at GBs or other defects, one needs to use the so called 'Gibbsian interfacial excess', which represents the number of excess impurity atoms at an interface normalized to its area [18].

3. Results

3.1. TEM-APT correlative approach

A very important issue when dealing with correlative TEM-APT is the quality of the APT tips prepared by FIB milling. Ion-beam-induced amorphisation and Ga, C contamination [19] are indeed very often observed. The ion-beam-induced amorphisation at various acceleration voltages had been studied for CIGS material as depicted in Fig. 2. We observed that a 30 kV acceleration voltage will create a 30 nm amorphous layer at the apex of the tip. It is thus expected that this amorphous layer will drastically decrease the quality of diffraction pattern (DP) and transmission Kikuchi pattern (TKP) quality.

Table 1

General overview of the CIGS solar cells used in the present study. CGI is the ratio $\frac{[Cu]}{[In]+[Ga]}$, whereas GGI is the ratio $\frac{[Ga]}{[In]+[Ga]}$. HZB is the abbreviation of Helmholtz Zentrum Berlin and ZSW of Zentrum für Sonnenenergie- und Wasserstoffforschung.

Sample	Studied defects	Fabrication procedure	Barrier layer at Mo/CIGS	CGI/GGI	Efficiency	Manufacturing place
A	Linear defects (dislocations)	3-stage coevaporation process [8]	No	~0.96/~0.28	~19%	HZB, Germany
B (a)	Planar defects (SFs)	Interrupted 3-stage coevaporation process [7]	Yes (SiN diffusion barrier layer)	~0.71/~0.24	–	HZB, Germany
B (b)	Planar defects (SFs)	interrupted 3-stage coevaporation process [7]	Yes (SiN) NaF treatment of CIGS [10]	~0.71/~0.24	–	HZB, Germany
C	Planar defects (GBs)	3-stage coevaporation process [9]	No	~0.75/~0.3	~15%	ZSW, Germany

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