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Na distribution in $Cu(In,Ga)Se_2$ thin films: Investigation by atom probe tomography

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Atom probe tomography (APT) has been used to study the distribution of Na atoms in polycrystalline $Cu(In,Ga)Se_2$ (CIGSe) thin films. APT, which allows separate investigations of grain boundaries and grain interiors chemistry, shows the presence of inter- and intra-granular Na segregations. It is highlighted that these segregations are found associated to Cu-depletion and In-enrichment. The segregation of Na to crystalline point defects and extended ones is finally discussed regarding its impact on the electrical properties of CIGSe layers.

Keywords: Solar cells; $Cu(In,Ga)Se_2$; Atom probe tomography; Sodium

$Cu(In,Ga)Se_2$ (CIGSe)-based thin film solar cells have reached conversion efficiency of 21.7% for laboratory cells [1] and 16.6% for large modules [2]. Since 1993 and the contribution of Hedström and co-workers [3], most of the best devices are achieved using Mo-coated soda lime glass substrates. It has been confirmed later that the efficiency increase, mainly due to gain in V_{oc}, they observed is related to the presence of Na diffusing from the glass substrate into the CIGSe absorber layer [4]. Since then, a variety of structural and electronic effects of Na on the properties of CIGSe material and thin films has been highlighted and extensively studied by numerous research groups [5–7]. In particular, it is now well established that the efficiency improvement in the presence of Na is due to the increase of net acceptor density of the CIGSe [8,9]. Further electrical characterizations also revealed that Na does not create new doping level, but rather annihilates compensating (i.e., donor) defects [10]; the understanding of the chemical mechanisms behind is still not fully completed. Today, the discussions and models proposed are mainly based on the interpretation of macroscopic observations [9], *ab initio* calculations [11] and electrical characterizations [10]. In order to further evaluate the validity of these theories, access to actual locations of Na within the polycrystalline CIGSe layers is still missing. Up until very recently, the lack of available analysis techniques combining both accurate spatial resolution and high elemental detection limits was restraining such investigations. Since 2010 and the first atom probe tomography (APT) analysis on CIGSe layers reported by Cadel et al. [12], many information concerning grain boundaries (GBs) [13–16] and interface [17,18] compositions has been revealed by APT which confirms the relevance of this technique for the nanoscale characterization of polycrystalline CIGSe thin films.

In this work, the chemistry of co-evaporated CIGSe layers has been investigated by APT and 3D atom distributions reconstructed with the aim of solving interrogations about Na distribution; a particular attention is paid on the composition of the absorbers at the vicinity of Na segregations.

The investigated CIGSe layers were co-evaporated on Mo-coated soda-lime glass (SLG) substrates following the so-called "3-stage process". The nominal composition of the films, determined by Scanning Electron Microscope Electron Dispersive Spectroscopy (SEM-EDS), results in [Cu]/([In] + [Ga]) ratio (i.e., CGI) around 0.85 and [Ga]/([In] + [Ga]) (i.e., GGI) of 0.22. Standard SLG/Mo/CIGSe/CdS/ZnO/ZnO:Al solar cells prepared with these absorber layers achieve energy conversion efficiency of 15% ($V_{oc} = 615$ mV, $J_{sc} = 33$ mA/cm^2, FF = 74.5%, without anti-reflective coating).

APT samples were prepared directly from the CIGSe thin films in a Zeiss NVision 40 CrossBeam FIB using a lift out method [19]. For the analysis of GBs, electron backscattering scanning diffraction (EBSD) has been

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carried out on the surface of each atom probe sample in order to ensure the presence of at least one GB in the volume investigated by APT. A detailed description of the procedure can be found in Ref. [13]. The APT investigations were carried out at 50 K using a CAMECA laser assisted wide angle tomography atom probe (LaWaTAP). An amplified Ytterbium-doped laser operating at a wavelength of 515 nm, with 10 nJ/350 fs pulse focused onto a 0.1 mm^2 spot and a 100 kHz repetition rate was used.

The mass spectra obtained are very similar to those already shown in previous works (see for instance Ref. [13]). Na is clearly identified as a single charged ion. In the mass range around 23 amu, the background noise level is very low (60 < ppm/amu), therefore small dilute Na concentrations, typically a few tens of ppm, can be investigated; note that no peak corresponding to K ions appears in the chart. In contrast to Na, the presence of O is more difficult to assess since peaks from O^{2+} (32 amu) or those from OH^+, H_2O^+ and H_3O^+ (16–19 amu range) can originate from residual gas in the vacuum system. Besides, as already observed in Ref. [16], peaks corresponding to complex ions consisting of N and H, such as N_2H^+ and $(NH)_2^+$, that most likely originate from the residual gas molecules inside the analysis chamber also come out in the mass spectrum. As a consequence of these observations, the composition in O will not be quantitatively discussed in this paper although information on its eventual presence at the vicinity of the Na segregations will be obtained through comparison with the composition measured in the bulk.

In this study, numerous CIGSe volumes have been investigated and reconstructed using APT. Through this large number of analyses, Na atoms have been detected:

(i) segregated at the GBs,
(ii) inside the grain as linear agglomerates and small clusters,
(iii) randomly distributed in grains matrix.

The 3D distribution map presented in Figure 1 shows typical example of these different shapes of Na segregations (each dot corresponds to one detected atom). In the following, each of them is closely studied in order to discuss eventual change of composition at the vicinity of the segregations.

APT distribution map containing a 2 nm-thick planar segregation of Na is presented in Figure 2(a). EBSD has been performed on sidewalls of the CIGSe tip before the APT analysis in order to confirm the presence of a GB in the investigated volume. It can therefore be assumed that the planar distribution of Na highlights the GB interface and corresponds to an inter-granular segregation of Na atoms. Figure 2(b) and (c) also shows the concentration profiles drawn by moving a 0.2 nm-thick sampling slice by steps of 0.2 nm along a direction perpendicular to the segregation. This plot underlines the enrichment in Na at the GB plane where the concentration reaches a maximum of 1.1 at.%; the associated Gibbsian interfacial excess is close to 1.7 atom/nm^2. In addition to Na segregation, composition changes across the GB interface are also observed: the Cu content decreases from 24 to 17 at.% while that of In increases from 21% to 26%; in contrast, no noticeable change on Ga, Se and O compositions is measured. Note that the error bars added to the charts, here and in the following of the paper, are calculated only from statistical sampling error inherent from the APT technique; standard deviation 2σ with $\sigma = (C(1-C)/N)^{1/2}$, N being the number of detected ions contained in the sampling box and C the solute concentration. The width of the zone where the changes are observed appears to be spread over 1 nm on both sides of the boundary plane; nevertheless, one should be cautious because this observed interface width could be due to local magnification effect. Indeed, during the field evaporation of the sample, protrusion of segregated atoms from the tip surface leads to higher local magnification and the enriched zone can, as a result, be artificially enlarged on APT reconstructed volume [20]. The selenium content appears under-estimated suggesting that some Se ions are not detected during the field evaporation of the tip; according to calibration measurements, this issue seems to be caused by Se desorption under laser pulsing.

As can be seen in Figure 1, different shapes of Na segregations have been observed within the CIGSe grains. A

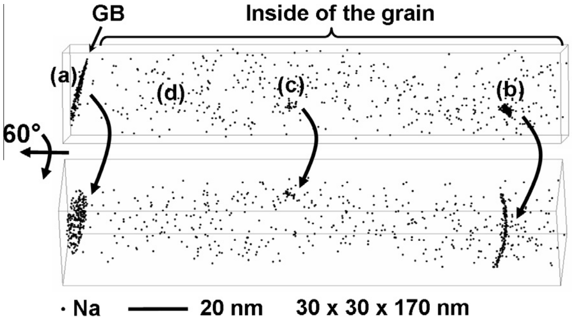

Figure 1. Typical 3D distribution map of Na atoms showing: (a) planar segregation of Na atoms at GB (b) linear and (c) cluster segregations inside the grain and (d) Na atoms randomly distributed in the grain matrix. View of the same 3D atom map turn from 60° around the z-axis is also presented.

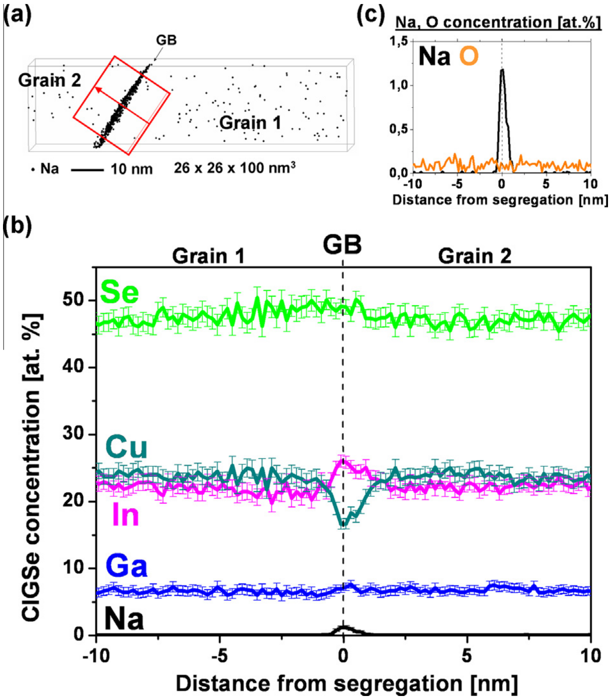

Figure 2. (a) APT reconstructed volumes of Na atoms (black dots) containing a GB planar segregation. (b and c) Cu, In, Ga, Se, O and Na concentration profiles perpendicularly to the sodium segregation in the box represented in the distribution maps of Figure 2(a).