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Atom probe study of sodium distribution in polycrystalline $Cu(In,Ga)Se_2$ thin film

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This article reports the first investigations of $CuIn_{1-x}Ga_xSe_2$ (CIGSe) polycrystalline thin films by means of atom probe tomography. Attention is focused on the distribution of Na atoms within the films. Both Na-containing and Na-free CIGSe thin films have been investigated. When Na is available during the CIGSe coevaporation, it is observed to be mainly segregated at the grain boundaries of the films; however, it is also detected within the grains of CIGSe at very low concentration.

Keywords: Thin film solar cell; Atom probe; Sodium; Grain boundary

1. Introduction

Laboratory-scale solar cells based on $CuIn_{1-x}Ga_xSe_2$ (CIGSe) chalcopyrite absorber thin films can reach conversion efficiency close to 20% [1]. However, due to the polycrystalline nature of the CIGSe layers, such high performances could appear unexpected. Although the influence of the grain boundaries on the device operation is still under debate [2–9], several studies suggest that this issue cannot be considered regardless the presence of sodium within the layers [4,6,7]. Indeed, independently of the CIGSe deposition process, the presence of sodium within the CIGSe films is found to improve the solar cells [7,10]. The gain in efficiency (mainly V_{oc}) is imputed to the increased acceptor density in Na-containing CIGSe [10–12]. Further electrical characterizations also reveal that rather than acting as a dopant, sodium passivates compensating defects [12]. However, the chemical mechanisms leading to the defect passivation are still the seeds for many assumptions. Basically, in bulk CIGSe two crystal point defects are recognized to generate donor states [13]: (i) indium in copper antisite, In_{Cu} and (ii) selenium vacancies V_{Se}. The presence of sodium could hinder the formation of these defects by (i) occupying the copper antisites instead of indium, $Na_{In_{Cu}}$ and (ii) enhancing the chemisorption of oxygen atoms in the selenium vacancies, O_{Se}. In order to evaluate these hypotheses, the first requirement is the location of the sodium within the CIGSe layers. This issue has been addressed by several studies [11,14,15] which all suggest that there is sodium at the grain boundaries. Nevertheless, no evidence has been shown on whether the grains contain sodium or not. A reason for this is the lack of available analysis techniques combining both accurate spatial resolution and high elemental detection limits.

Amongst the nano-scale-sensitive analytical techniques (electron holography, electron energy loss spectroscopy), atom probe tomography (APT) is one of the most promising tools thanks to its unique capability to combine atomic scale resolution in three dimensions with quantitative chemical analysis [16,17]. For a long time limited to the investigation of conductive materials, mainly metallic alloys, the laser pulsed version of the APT technique is nowadays open to semiconductor materials as shown in the fields of nanoelectronic or photovoltaic devices for instance [18–23]. The successful use of APT for the analysis

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of thin film reactions and segregation to linear and planar defects, the aim of the present work in the case of coevaporated CIGSe thin films, has already been demonstrated [24–26]. The possibility of sampling all kinds of material configurations (layers, multilayers, thin films, bulks, etc.) using a dual-beam SEM allows new perspectives of selected area atomic scale characterizations. In the present paper, we report for the first time a direct observation of intra- and inter-granular distribution of sodium within CIGSe thin films.

2. Experimental

$CuIn_{0.75}Ga_{0.25}Se_2$ polycrystalline thin films have been grown with Na precursor (NaF) on p-doped Si(1 0 0) substrates by the three-stage process at constant substrate temperature (575 °C); note that the investigated CIGSe grown on standard SLG/Mo yielded a 14.2% cell efficiency. One should note that a reference sample has also been prepared without Na precursor. Because of the low density of grain boundaries in CIGSe thin films and the small volume investigated with APT (typically 100^3 nm^3), the films have been analyzed perpendicular to the grain growth direction in order to increase the probability of probing grain boundaries. With this aim, as illustrated in Fig. 1, the films have been removed from their silicon substrates using a lift off method, then mounted and glued on a truncated tungsten support-tip using Pt-ion-beam-induced deposition. The whole sample is finally aligned along a Ga-30 kV focused ion beam and successive annular pattern millings transformed it to a very sharp atom probe tip (see Fig. 1). One should note that in order to minimize beam damage, lower energy Ga-2 kV beam was used with low incidence angles at the end of the milling process. Further details on this procedure can be found in Ref. [27]. Atom probe investigations were carried out at 80 K using a CAMECA laser assisted tomography atom probe (LaWaTAP) [28]. The laser system is an amplified ytterbium-doped laser (AMPLITUDE SYSTEM s-pulse, $\lambda = 515$ nm) used in the following conditions: ~100 nJ/350 fs pulse focused onto a ~0.1 mm^2 spot. The base pressure within the analysis chamber is 3×10^{-10} mbar.

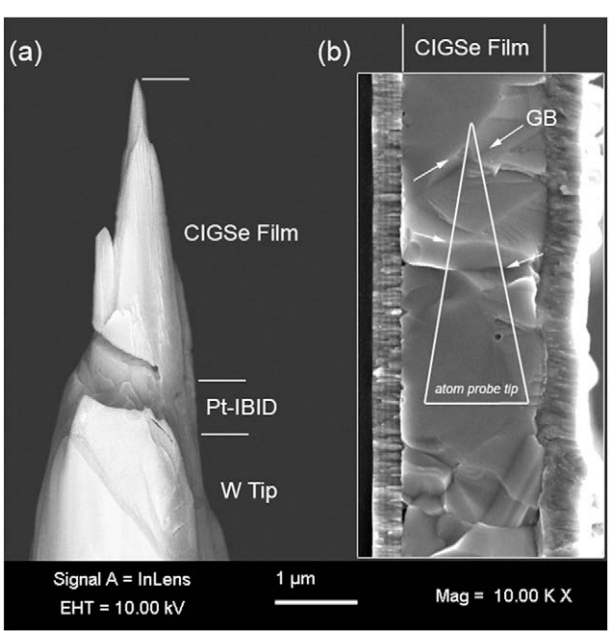

Fig. 1. SEM images of the CIGSe thin film and an atom probe sample (tip) extracted by the "lift off" method from the thin film.

3. Results and discussion

A typical mass spectrum related to a Na-rich region shown in Fig. 2 illustrates that Na is clearly identified as a single charged ion. For this particular atom probe data set, the noise floor in the region close to the ^{23}Na peak is estimated at 20 atomic ppm per atom mass unit (a.m.u.). One should note that no signal relative to ^{23}Na has been detected on the mass spectrum corresponding to the Na-free CIGSe reference sample. The presence of Al^+ (<0.1 at.%) observable on the mass spectrum could originate from the use of alumina crucibles as metal evaporation sources.

The Na distribution within the reconstructed volume resulting from the APT analysis of the Na-containing CIGSe thin film is presented in Fig. 3; each black dot corresponds to one detected Na atom. The Na atoms are randomly distributed (typically 85 ± 20 atomic ppm) within the investigated volume at the exception of 2D-like areas where its density is much higher. This observation confirms that, as already suggested in the literature, Na atoms are present within the CIGSe grains. In the present article the attention is focused on the upper Na-enriched zone, referred to as interface in Fig. 3, which extends throughout the whole reconstructed cylinder. The width of this interface has been evaluated to be close to 1.3 nm; however, the actual value is likely to be lower taking into account that a solute enriched zone may be artificially enlarged on APT images because of a local magnification effect. Indeed, the atom probe is a projection microscope

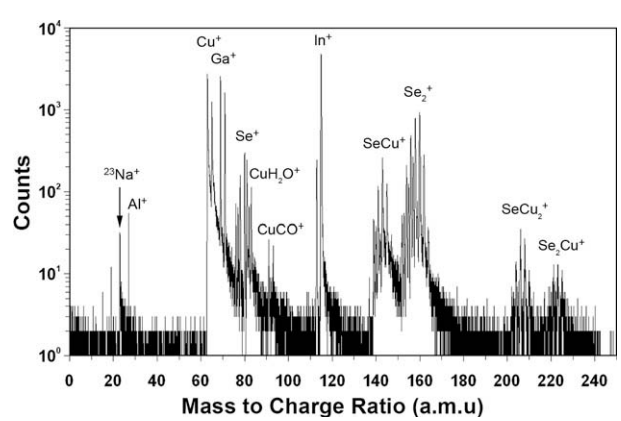

Fig. 2. Mass spectrum related to ions detected in the region named (A) from Fig. 3.

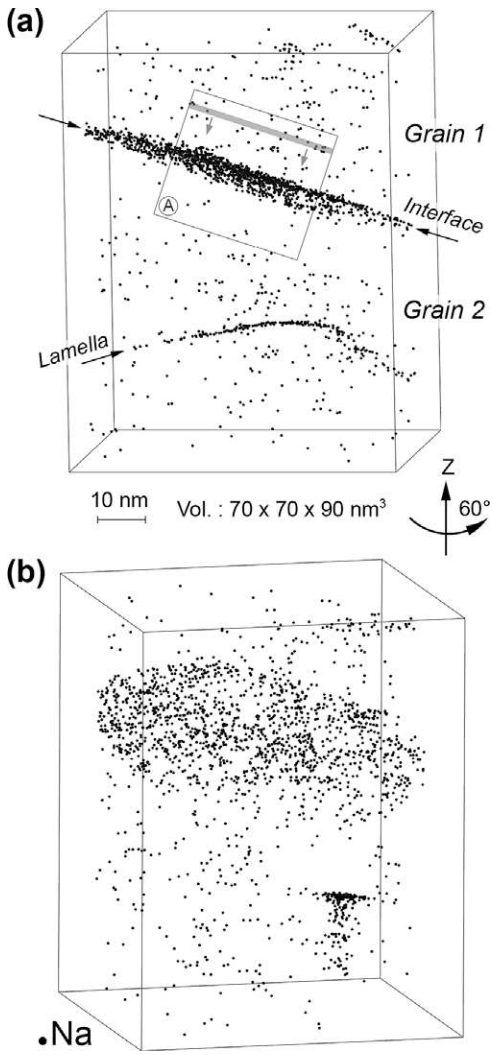

Fig. 3. (a) Spatial distribution of Na atoms (black dots) within CIGSe thin film. (b) View of the same three-dimensional atom probe map of Na atoms with a 60° rotation around the z-axis.

and the presence of a structural defect (such as an interface) emerging at the surface of the sample may produce a slight deviation of atom trajectories [25]. Fig. 4a shows the Na concentration profile measured by moving a 1 nm thick sampling slice by steps of 0.1 nm within the box (A) shown in Fig. 3a. Sampling errors in Na-APT profile (see error bars in Fig. 4a) are given by the standard deviation 2σ with $\sigma = (C(1-C)/N)^{1/2}$ with N the number of detected ions contained in the sampling slice and C the solute concentration. This profile illustrates the abrupt increase of the Na density at the interface. Within this interface, the Na concentration reaches 0.89 ± 0.12 at.% and the Gibbsian interfacial excess Γ_{Na}, defined as the number of segregated Na per unit area, is close to 8×10^{13} at. cm^{-2}. Although no CIGSe atomic planes can be observed in the 3D-APT map (i.e. the existence of a misorientation between the two grains cannot be demonstrated), this interface is assumed to be a grain boundary separating two grains, namely grain 1 and grain 2.

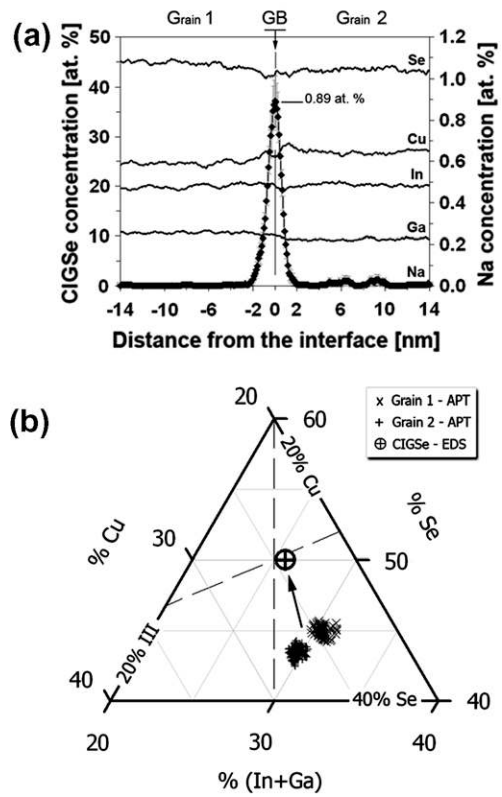

Fig. 4. (a) Cu, In, Ga, Se and Na concentration profiles through the region (A) of Fig. 3. (b) APT and EDS measurements of CIGSe grains composition. The dashed lines represent the Cu_2Se–In_2Se_3 pseudobinary and the Cu-rich/III-rich dividing line (vertical).

In Fig. 4a are also shown the composition profiles of Cu, In, Ga and Se. This plot suggests that the Cu, Ga and Se contents are different in grain 1 and grain 2, whereas that of In appears similar in both grains. No significant enrichment or depletion of Cu, In, Ga and Se is detected through the grain boundary. One should nevertheless be cautious before drawing conclusions from these latter observations. Indeed, this film has also been investigated by energy dispersive X-ray spectroscopy (EDS) and its composition is 24.3 at.% Cu, 21.5% In, 4.2% Ga, 50.0% Se, which is, as expected, near the pseudo binary Cu_2Se–In_2Se_3 tie line. The compositions deduced from APT and EDS are compared on a ternary phase diagram (Cu, group III, Se) in Fig. 4b. This graph clearly shows that selenium is under-estimated in our APT measurement, suggesting that some Se ions are not detected during the field evaporation of the specimen by laser pulses. This effect is known as preferential field evaporation: ions can sometimes be evaporated between two laser pulses and therefore not be detected, which results in differences between the expected and the measured compositions [17]. Preferential field evaporation is mainly observed for alloys containing elements with high evaporation field differences, which is actually the case in CIGSe; it is reported for singly charged ions the following field values: $F_{Cu} = 30$ V nm^{-1}, $F_{In} = 12$ V nm^{-1}, $F_{Ga} = 15$ V nm^{-1} whereas Se is not tabu-

lated [17]. Instrumentation parameters such as pulse laser energy (i.e. pulse fraction) and specimen base temperature must therefore be further optimized in order to ensure accurate quantitative measurements. However, such an artifact only slightly affects the qualitative evolution of the profiles throughout the investigated volume. Therefore, the difference observed in the adjacent grain composition is most probably effective. Moreover, the conclusions concerning the presence of Na within the grains and its accumulation at the grain boundary remain valid. Unfortunately, the present investigations do not allow the determination of the crystal sites occupied by the Na neither within the CIGSe grain structure nor at the grain boundary. Nevertheless, within the grain, the Na concentration being very low, the calculations reported by Wei et al. [13] predict that these atoms most probably occupy the Cu antisites. Such a location could minimize the density of In_{Cu} donor defects, thus effectively improving the acceptor density as experimentally observed.

4. Conclusions

In the present article the first results of APT investigations on CIGSe polycrystalline layers are presented. Both the presence of Na within the grains and its accumulation at the grain boundaries are demonstrated, which confirms many of the conclusions suggested in the literature. This study shows that the use of APT can be a powerful tool for the analysis of the CIGSe.

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