Puzzling diffusion behavior in Na-doped Cu(In,Ga)Se_2 thin films revealed by APT, STEM, SIMS, and nano-AES analysis

Schwarz, T.[1], Colombara, D.[2], Garzón Manjón, A.[1], Werner, F.[2], Valle, N.[3], El Adib, B.[3], Bouttemy, M.[4], Gault, B.[1], Siebentritt, S.[2] and Raabe, D.[1]

[1] Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany, Germany, [2] Laboratory for Photovoltaics, University of Luxembourg, Belvaux, Luxembourg, Luxembourg, [3] Luxembourg Institute of Science and Technology, Luxembourg, Luxembourg, [4] Institut Lavoisier de Versailles, Université de Versailles Saint-Quentin-en-Yvelines, France, France

Cu(In,Ga)Se_2 (CIGSe) thin-films as absorber material provide the most efficient solar energy conversion among all thin-film solar cells. This is achieved by tailored Cu and Ga depth gradients, i.e. band gap engineering, and extrinsic alkali doping in order to increase the collection of photogenerated electrons and to reduce their recombination with holes. Na is well known to impede the In-Ga interdiffusion in polycrystalline CIGSe thin-films and, hence, it affects the Ga depth distribution. Furthermore, doping with Na and K atoms leads to a decrease in recombination of electrons at grain boundaries, where alkali metals tend to segregate. However, due to this segregation, it is difficult to separate the effect induced by alkali atoms on the In-Ga interdiffusion in the grain interior from that at grain boundaries.

Here however, we show that Na, which is incorporated from the gas phase, has the opposite effect in epitaxial Ga free $CuInSe_2$ films on GaAs substrates [1]. Fig. 1 shows that Na incorporation enhances the Ga in-diffusion from GaAs into the film compared to Na-free samples as measured by secondary ion mass spectrometry (SIMS), nano-Auger electron spectroscopy (nano-AES) and atom probe tomography (APT). Furthermore, APT data in Fig. 2 reveals that the Ga in-diffusion leads to the formation of CIGSe and even Cu(In,Ga)$_3$Se$_5$. Moreover, we detect Na segregation at two-dimensionally confined defects, which may consist of dense dislocations arrays as indicated by scanning transmission electron microscopy (STEM). Interestingly, we observe a significantly higher Na solubility in Ga-richer Cu(In,Ga)$_3$Se$_5$ phases (~1 at% Na) than in more Ga-poor Cu(In,Ga)$_3$Se$_5$ and CIGSe (~0.05 at% Na) phases.

Our results show that Na does not decrease per se In-Ga interdiffusion in CIGSe. We suggest that Na promotes In-Ga intragrain diffusion, while it hinders intergrain diffusion due to segregation at grain boundaries in polycrystalline films. The new insights help to develop more effective chemical and electrical passivation strategies in order to increase the cell efficiency. We also present correlated TEM-APT measurements on K treated samples to further gain a better understanding of the effects.

References:

[1] D. Colombara, et al., Na enhances In-Ga interdiffusion in Cu(In,Ga)Se_2 photovoltaic absorber, Nature Communications (2018), accepted.

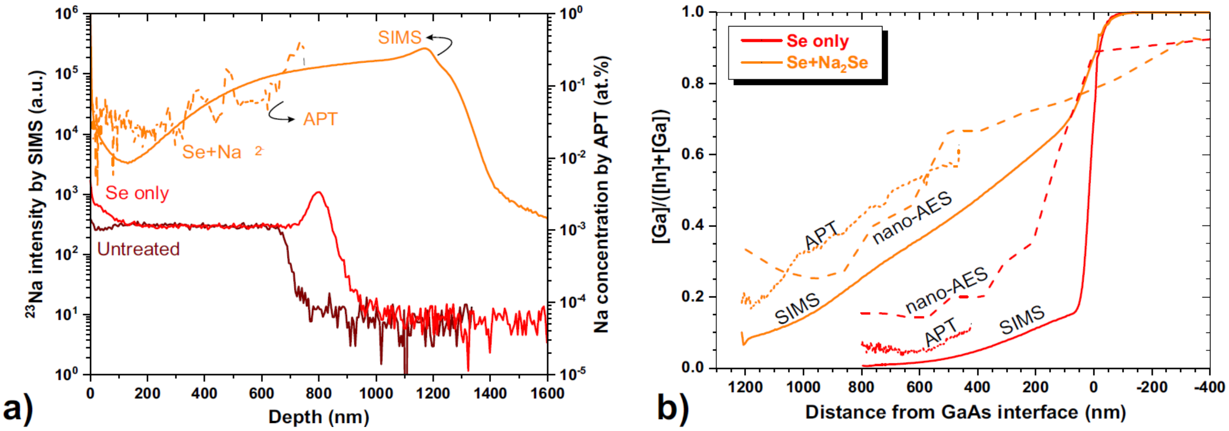
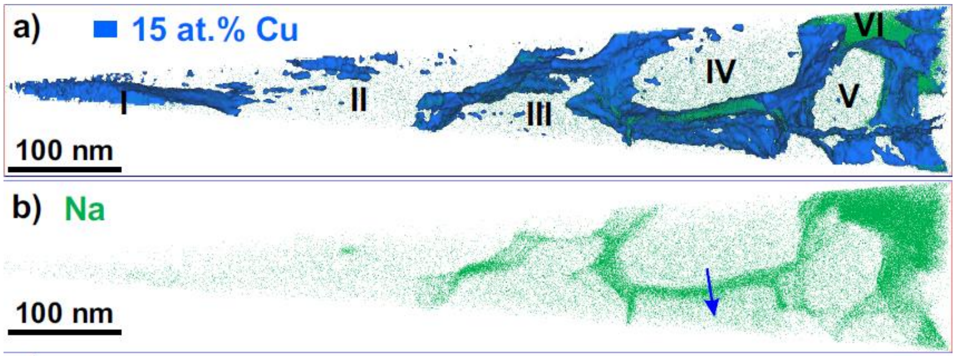


Fig. 1 a) ^{23}Na SIMS concentration profiles (left axis) for Na-treated and Na-free samples and absolute Na concentration from APT (right axis) for Na-treated sample as a function of depth from the CIS surface. **b)** Ga/Ga+In ratio depth profiles measured by SIMS, by nano-AES, and APT for Na-treated and Na-free sample.



c)

Region	Cu (at.%)	In (at.%)	Ga (at.%)	Se (at.%)	Na (at.%)	CGI	GGI
I	12.6	27.3	9.0	51.0	0.05	0.35	0.25
II	22.0	18.9	11.3	47.9	0.02	0.73	0.37
III	21.3	16.0	13.8	48.8	0.03	0.71	0.46
IV	20.4	13.9	16.1	49.6	0.03	0.68	0.54
V	11.5	17.5	17.7	52.3	0.99	0.33	0.50
VI	21.2	12.2	16.8	49.7	0.03	0.73	0.58

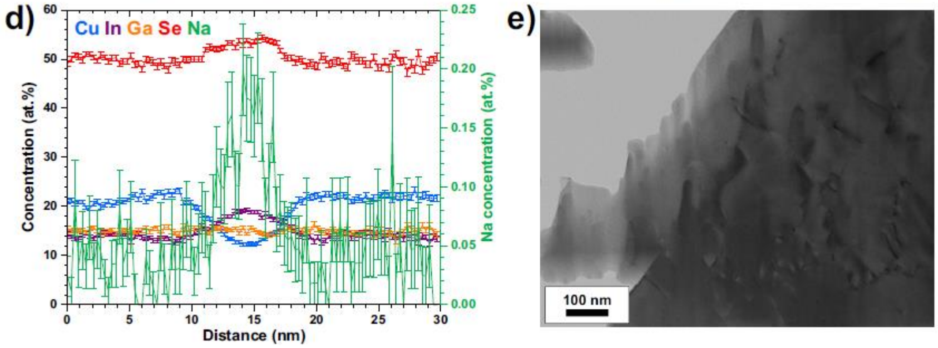


Fig. 2 a)-b) APT analysis of the Na-treated sample showing 15 at. % isosurfaces of Cu (blue) and the Na distribution (green). **c)** Compositions of the regions I-VI shown in a). Region I and VI are related to the $Cu(In,Ga)_3Se_5$ phase. CGI and GGI are the [Cu]/([Ga]+[In]) and [Ga]/([Ga]+[In]) ratio, respectively. **d)** Concentration profile along the blue arrow shown in b). **e)** STEM bright field image showing a dislocation-rich area from the Na-treated sample.