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Quantitative ToF-SIMS analysis of matrix elements and sodium in $Cu(In, Ga)Se_2$ thin films

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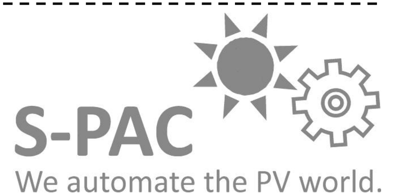
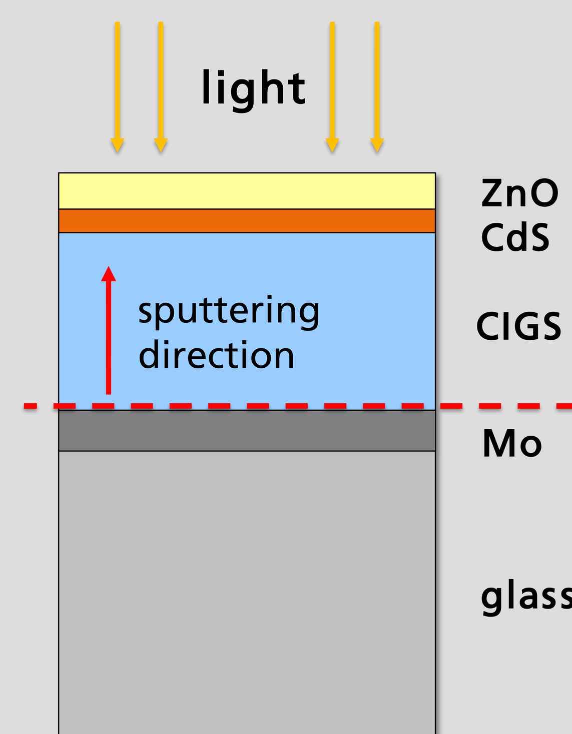


Motivation

In the process of optimizing solar cells the accurate quantitative elemental analysis of photovoltaic thin films is highly desirable.
The depth dependent ratio of Ga and In and the spatial distribution of Na are of particularly great interest because both the In/Ga ratio and the Na concentration have large effect on solar cell efficiencies. However, quantitative analysis by SIMS is limited by matrix effects and interface effects.
We use a combination ToF-SIMS and ICP-MS for quantification of matrix elements and sodium in CIGS and discuss the remaining uncertainties.

Samples and preparation

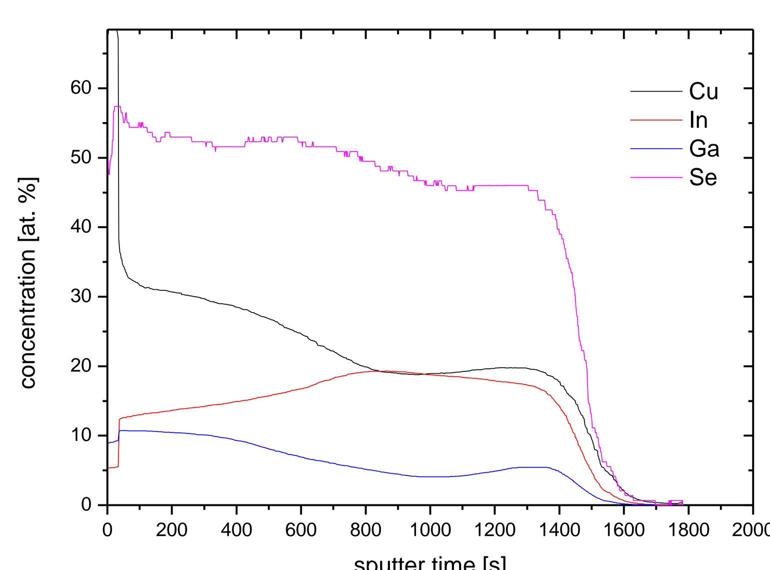


[Fig. 1] CIGS solar cell

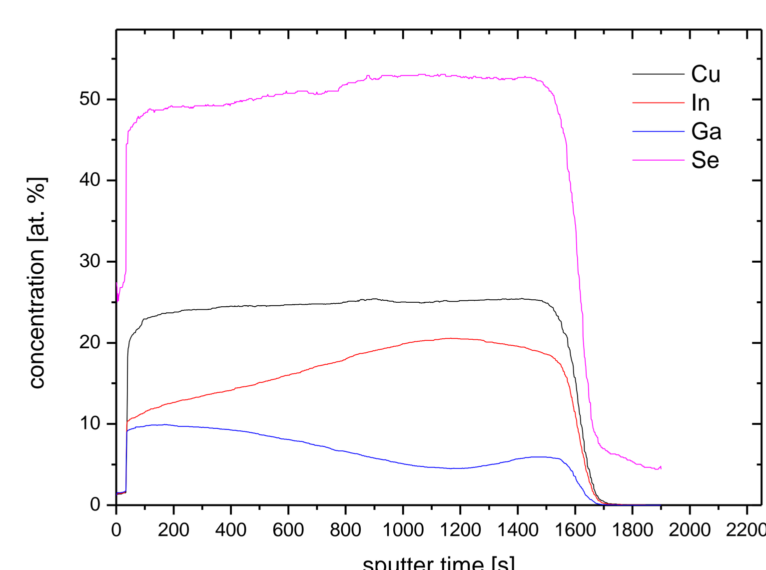
- The samples used were CIGS solar cells containing the layers Mo/CIGS/CdS/ZnO on a glass substrate.
- For ToF-SIMS analysis the CIGS/CdS/ZnO layers is removed from the underlying Mo as shown by the red line in figure [1].
- This provides a clean surface with a very low roughness.
- The thickness of the CIGS layer was about 1,5µm.

Results — Quantitative ToF-SIMS of CIGS matrix elements

- Depth profiles acquired using O_2^+ sputtering show a Ga correlated variation in Cu intensity (see example in fig 2).
- Since experimental conditions and sample preparation is the same this effect is possibly due to matrix effects caused by stoichiometry changes in the CIGS layer [I].
- The use of MCs^+-Clusters reduces this effect greatly .
- Quantification of matrix elements is done with additional ICP-MS measurements to determine the overall CIGS layer composition after dissolution: (Cu:In:Ga:Se = 0,25 : 0,17 : 0,07 : 0,51)



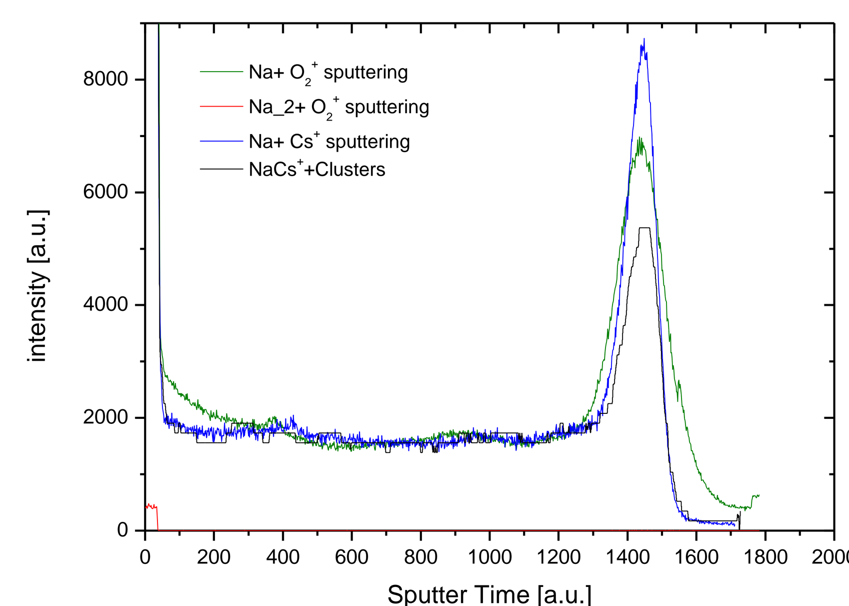
[Fig. 2] depth profile O_2^+ sputtering.



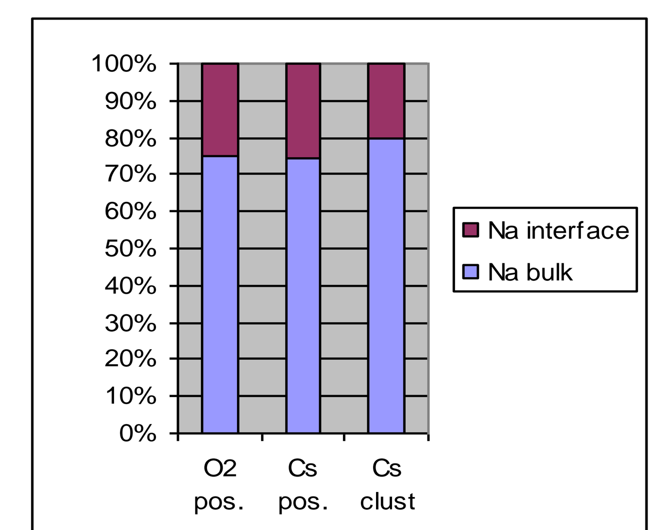
[Fig. 3] quantitative depth profile MCs^+ clusters

Results — Distribution of Sodium

- The sodium depth profiles acquired with two different sputter ions and by detection of $NaCs^+$ clusters were normalized to the mean bulk intensity.
- The Na intensity drops rapidly after the CIGS/CdS interface.
- There is only little depth dependent variation across the CIGS layer for both O_2^+ and Cs^+ sputtering.
- Matrix effects caused by stoichiometry changes in the CIGS should be weak, the RSF changes less than 5% [II].
- Therefore Na intensity correlates strongly with Na concentration.
- Reasons of uncertainties are accumulation of Na at the CIGS/Mo interface, Na drift caused by the sputter beam or the chaning matrix itself.



[Fig. 4] Na distribution normalized to mean bulk intensity of Na



[Fig. 5] comparisson of Na bulk and interface intensites

	O2 pos.	Cs pos.	Cs clust
Na_bulk [cts.]	3,00E+06	1,10E+06	1,40E+04
Na _interface [cts.]	1,00E+06	3,80E+05	3,58E+03
$Na_{bulk}/Na_{bulk+interface}$	0,75	0,74	0,80

- The variation of the $\mathbf{Na_{bulk}/Na_{bulk+interface}}$ ratio is below 10% of the total concentration
- Using ICP-MS data allows quantification of bulk Na with uncertainties in order of 25% absolute.

Summary

- The combination of ToF-SIMS and ICP-MS is suitable to do quantitative depth profiling of CIGS thin films.
- Interface related uncertainties can be estimated to a maximum value of 20% of total Na intensity

References:
[I] D. Bremaud, D. Rudmann, G. Bilger, H. Zogg and A. N. Tiwaril, Towards the development of flexible CIGS solar cells on polymer films with efficiency exceeding 15%, Photovoltaic Specialists Conference, 2005. Conference Record of the Thirty-first IEEE
[II] Larry Wang1, Alice Wang and R.S. Hockett, SIMS study of Na in CIGS and impurities in CdTe/CdS, Photovoltaic Specialists Conference (PVSC), 2009 34th IEEE