Chemical Imaging of Thin-Film Solar Cell Materials using Raman Microscopy

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Introduction

Wide band-gap copper-containing chalcopyrites, such as $CuInS_2$ (CIS) and $CuGaSe_2$ have attracted considerable interest as absorber materials in thin-film solar cells. $CuInS_2$ exhibits an optical band gap (1.5 eV) ideally matching the solar spectrum, whilst $CuGaSe_2$ is a candidate for the top layer in tandem solar cells. The efficiency of such solar cells is greatly dependent on the composition as well as on crystal structure and purity of the compounds involved.

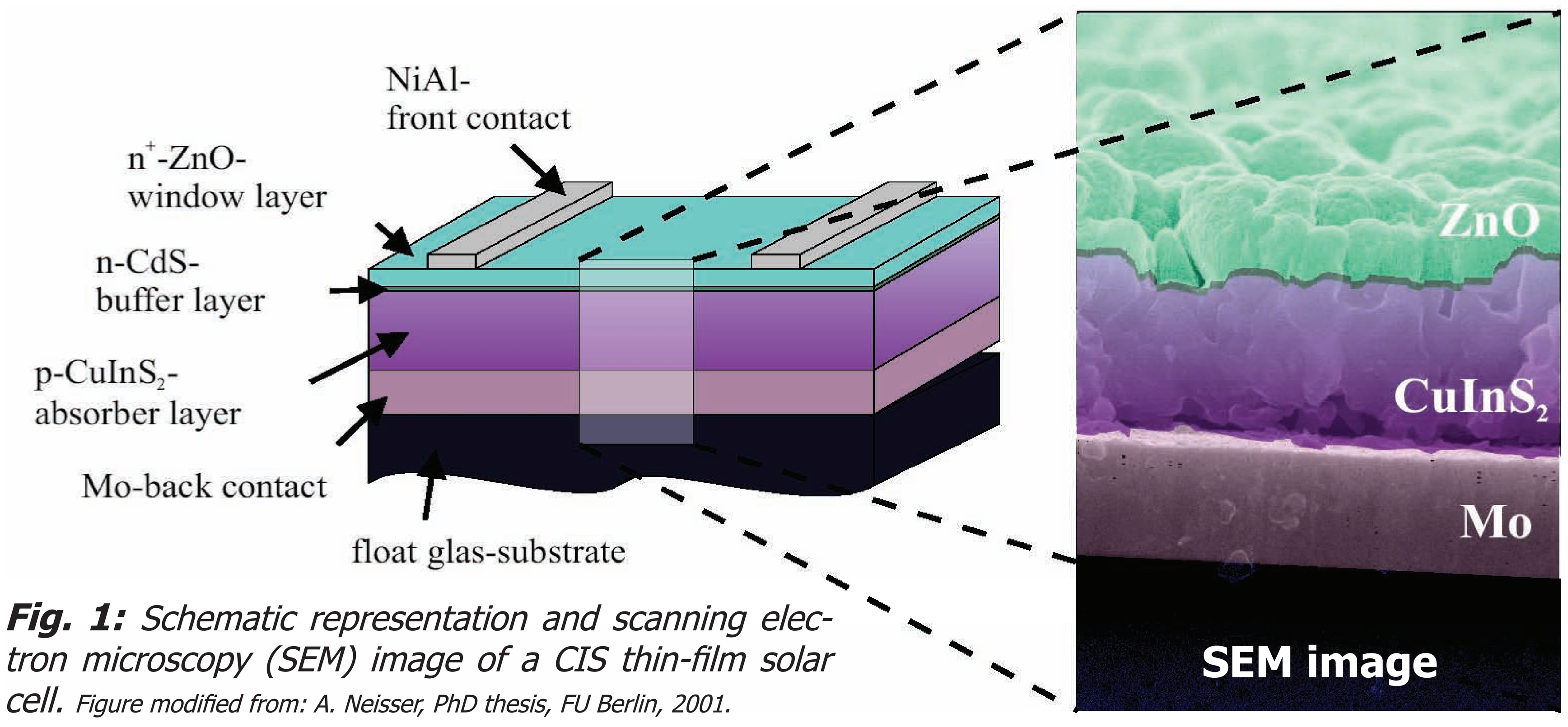


Fig. 1: *Schematic representation and scanning electron microscopy (SEM) image of a CIS thin-film solar cell.* Figure modified from: A. Neisser, PhD thesis, FU Berlin, 2001.

Cross-sectional TEM samples of thin-film solar cell materials were analyzed by Raman microscopy. Based on Raman spectra, not only different chemical species, but even different crystal structures of the same compound can be distinguished.

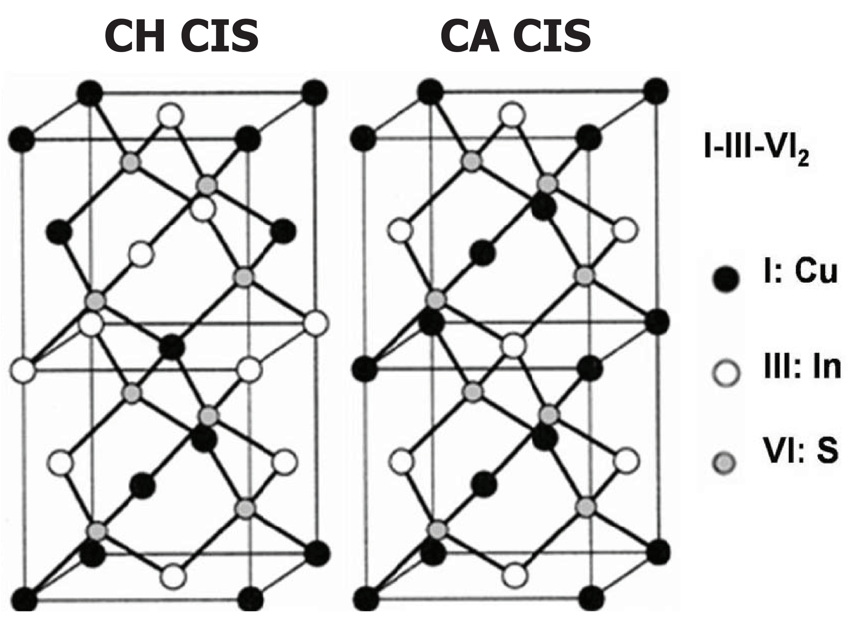


Fig. 2: *Crystal structures of $CuInS_2$ (CIS): chalcopyrite-type CIS (CH CIS) and CuAu I-type CIS (CA CIS). CH CIS is the desired modification of CIS as absorber material in thin-film solar cells, whereas the presence of secondary phases, such as CA CIS, is known to be detrimental for the solar cell efficiency.*

Knowdledge about presence and distribution of chemical species, crystal structures, segregates, and contaminants is crucial for the improvement of the production process of solar cells.

Experimental Setup

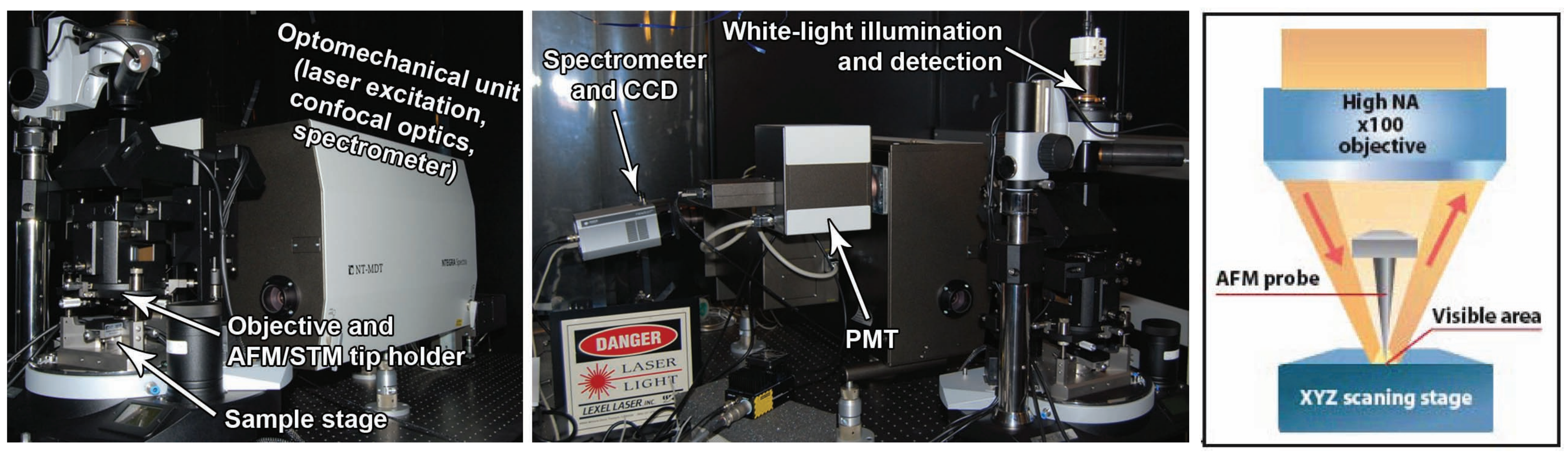


Fig. 2: *The measurements in this study were performed using a NTEGRA Spectra upright system from NT-MDT. The system provides AFM/STM scanning and confocal laser microscopy on the same part of a sample (left). The system is equipped with a photomultiplier tube (PMT) detector for confocal imaging and a Raman spectrograph with both, CCD and photon-counting PMT detection (middle). A long working distance objective with high numerical aperture (NA = 0.7) allows AFM/STM and optical experiments at the same time with transparent and opaque samples (right, Figure from NT-MDT).* NT-MDT

Results: $CuGa_xSe_y$

By Raman microscopy the spatial distribution of chemical compounds can be determined. Even different stochiometries can be discriminated based on their Raman signature.

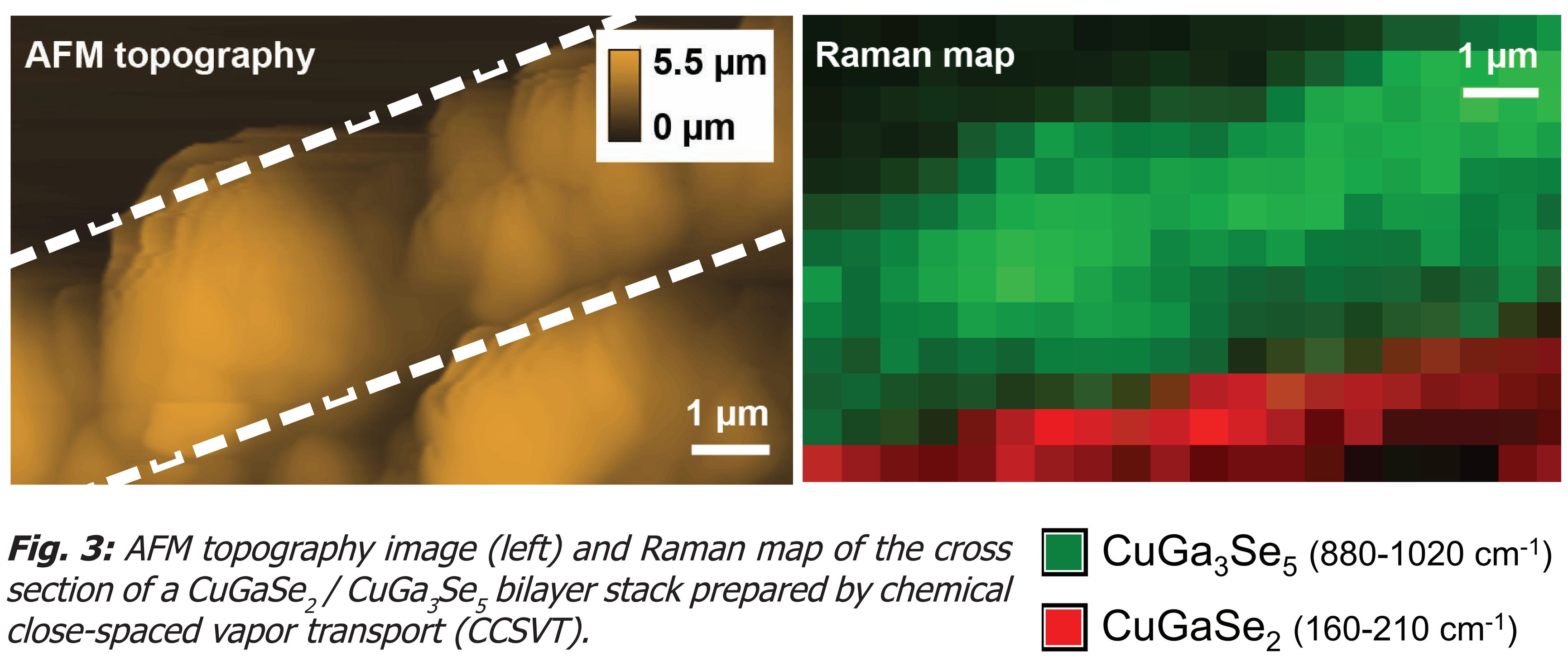
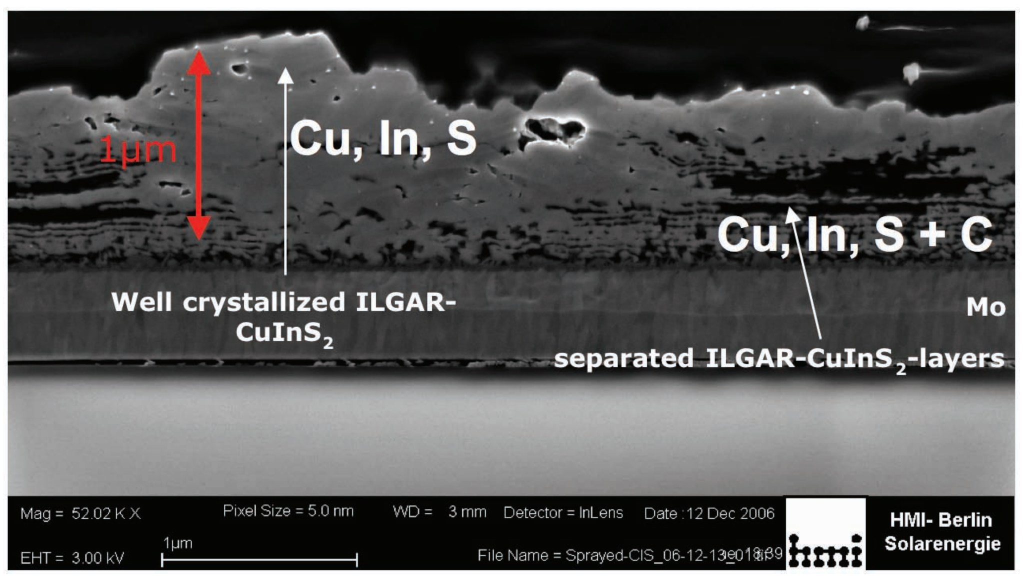


Fig. 3: *AFM topography image (left) and Raman map of the cross section of a $CuGaSe_2$ / $CuGa_3Se_5$ bilayer stack prepared by chemical close-spaced vapor transport (CCSVT).*

Results: $CuInS_2$ (CIS)

The spray ion layer gas reaction (ILGAR) process provides a cost-efficient way to produce thin films of CIS and of other relevant materials for solar cells at atmospheric pressure. Electron microscopy studies have revealed the heterogeneity of spray ILGAR thin films at the sub-micrometer scale. CIS was found to appear in a crystalline and a nano-layered form. Additionally, contaminants (e.g. carbon) and segragates (e.g. copper sulfide species) have been identified. Knowledge about the chemical heterogeneity of the samples was limited, since conventional combinations of electron microscopy and energy dispersive X-ray (EDX) analysis only provide the distribution of chemical elements, but no information on stoichiometry and crystal structure of the chemical compounds.



Open questions:

- Chemical species
- Stoichiometry
- Chemical composition of segregates and contaminants
- Crystal structures / modifications

Fig. 4: *SEM image of an ILGAR CIS thin-film sample on a molybdenum-coated glass substrate. The element symbols represent information obtained by EDX analysis. Open questions mainly concern chemical species and crystal structures formed by these elements.*

By Raman microscopy the distribution of different chemical species and crystal structures can be determined with a lateral resolution of approx. 400 nm.

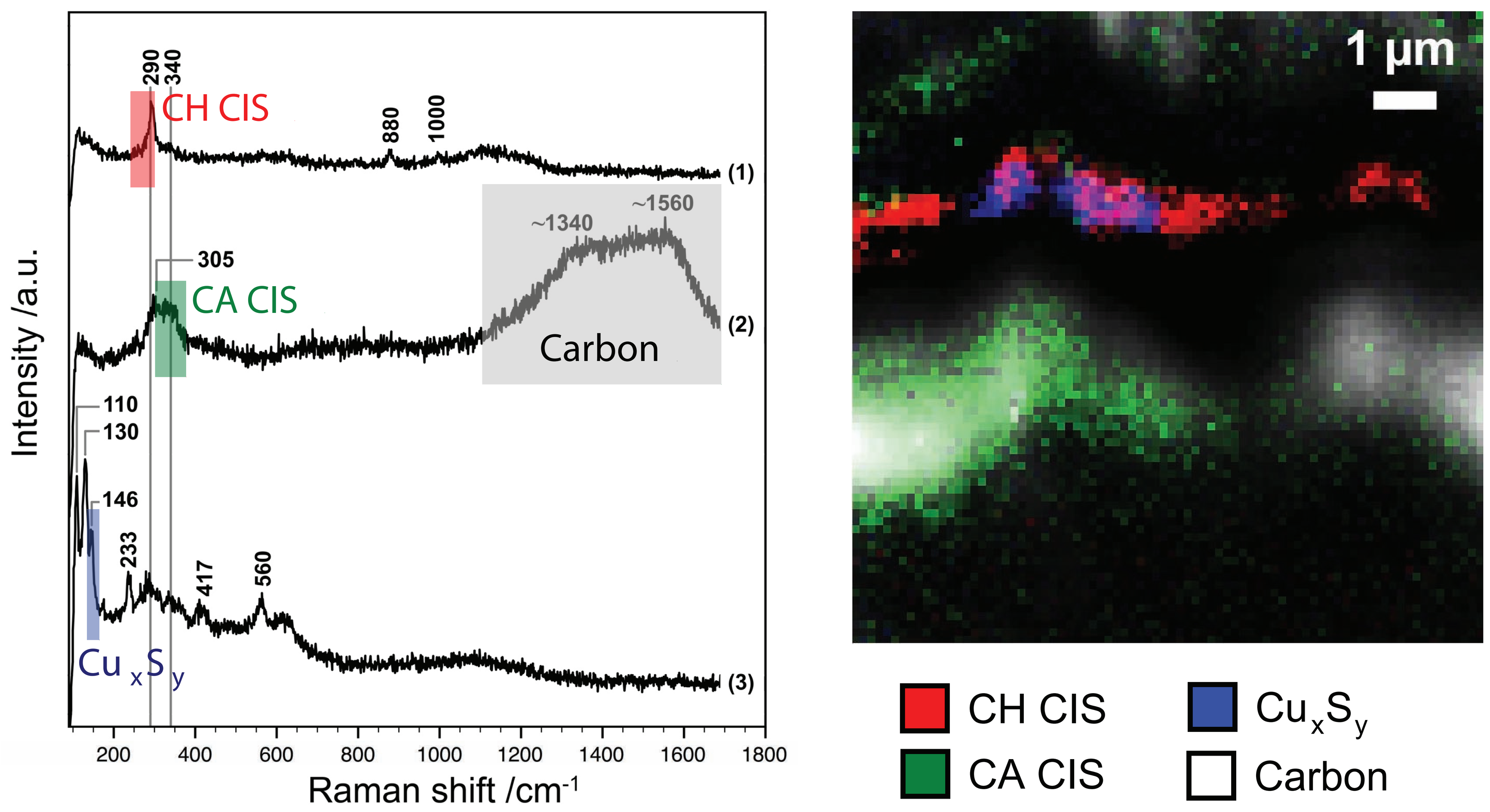


Fig. 5: *Left: Raman spectra collected on different parts of an ILGAR CIS sample representing mainly chalcopyrite-type CIS (CH CIS) (1), CuAu I-type CIS (CA CIS) and amorphous/nanocrystalline carbon (2), and copper sulfide (3). Right: In a mapping experiment with 632.8-nm HeNe-laser excitation, the entire Raman spectrum was collected on every pixel. The intensity of four characteristic spectral ranges is plotted in different colors and represents the distributions of CH CIS, CA CIS, Cu_xS_y and carbon on this ILGAR CIS thin-film cross-section.*
Mapping parameters: 10 x 10 µm², 80 x 80 pixels, 125 nm/pixel, optical resolution: 375 ± 125 nm.

Comparison of Raman and SEM/EDX data has shown that the well-crystallized CIS consists of CH CIS, whereas the layered form contains significant amounts of disordered/CA CIS. The interlayers are mainly amorphous/nanocrystalline carbon.

Conclusions

This study has demonstrated the potential of Raman microscopy in the characterization of thin film solar cell materials. Raman spectroscopy allows the identification/determination of

- Chemical species (e.g. $CuInS_2$, Cu_xS_y)
- Stoichiometries (e.g. $CuGaSe_2$, $CuGa_3Se_5$)
- Crystal structures (e.g. CH CIS, CA CIS)
- Modifications (e.g. graphite, diamond, amorphous/nanocrystalline carbon)
- Chemical identity of segregates and contaminants (e.g. Cu_xS_y, carbon)

By Raman mapping experiments the lateral distribution of chemical compounds and crystal structures can be determined with a resolution of approx. 400 nm. The combination with AFM allows imaging of the same part of the sample with nanometer resolution. Thus, Raman microscopy provides information that is complementary to conventional SEM/EDX analysis.

Literature

T. Schmid, Ch. Camus, S. Lehmann, D. Abou-Ras, Ch.-H. Fischer, M. Ch. Lux-Steiner, R. Zenobi. *Physica Status Solidi* (2009) accepted.

Acknowledgements

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