ESRF	**Experiment title:** **Elucidating the structural nature of pyrite-marcasite phase boundaries in high performance earth-abundant FeS_2 photoabsorbers**	**Experiment number**: MA-3574
Beamline: ID01	**Date of experiment**: from: 1 September 2017 to: 4 September 2017	**Date of report**: March 21, 2018 *Received at ESRF:*
Shifts: 12	**Local contact(s)**: Dr. Marie-Ingrid Richard and Dr. Gilbert Chahine	
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Report:

With nanofocused X-ray diffraction imaging (μXRD) and ptychographic imaging, we planned to obtain information about the structure of the crystalline films and specifically about the phase boundaries between the two FeS_2 polymorphs.[1] This structural information are expected to complement data from high-energy photoelectron spectroscopy, time-resolved electric (μ-wave) conductivity measurements as well as high-resolution TEM imaging.

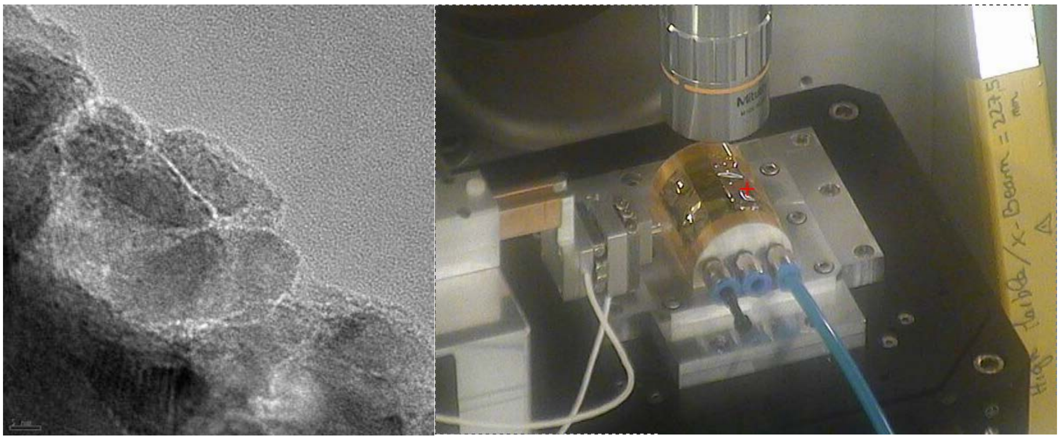

Fig. 1 *Left: Transmission electron microscopy (TEM) image of mixed phase marcasite-pyrite FeS_2. Right: Photograph of the experimental setup at ID01 to do X-ray diffraction in inert atmosphere.*

Both pure phase (pyrite) and mixed phase marcasite-pyrite FeS_2 films were prepared at TU Eindhoven via thermal sulfurization of sputtered metallic Fe on highly n-doped Si. The thickness of the FeS_2 films is in the range of ~350 nm. The FeS_2 films were investigated by coherent x-ray diffraction in Bragg condition using the nano-focused x-ray beam at the ID01 beamline. The measurements were conducted in an N_2 filled sample holder cell (as shown in Figure 1) to prevent possible oxidation of the FeS_2 during the tests. The beam size has been approximately 100×400 nm^2.

The nano-diffraction experiment was carried out at a beam energy of 8 keV. Figure 2 shows the rocking curve of mixed phase marcasite-pyrite film at 2 theta=57°. Pyrite and marcasite have diffraction peaks in close proximity, which allows for simultaneous analysis of both phases (e.g. pyr(311) and mar(031) at 56.3°

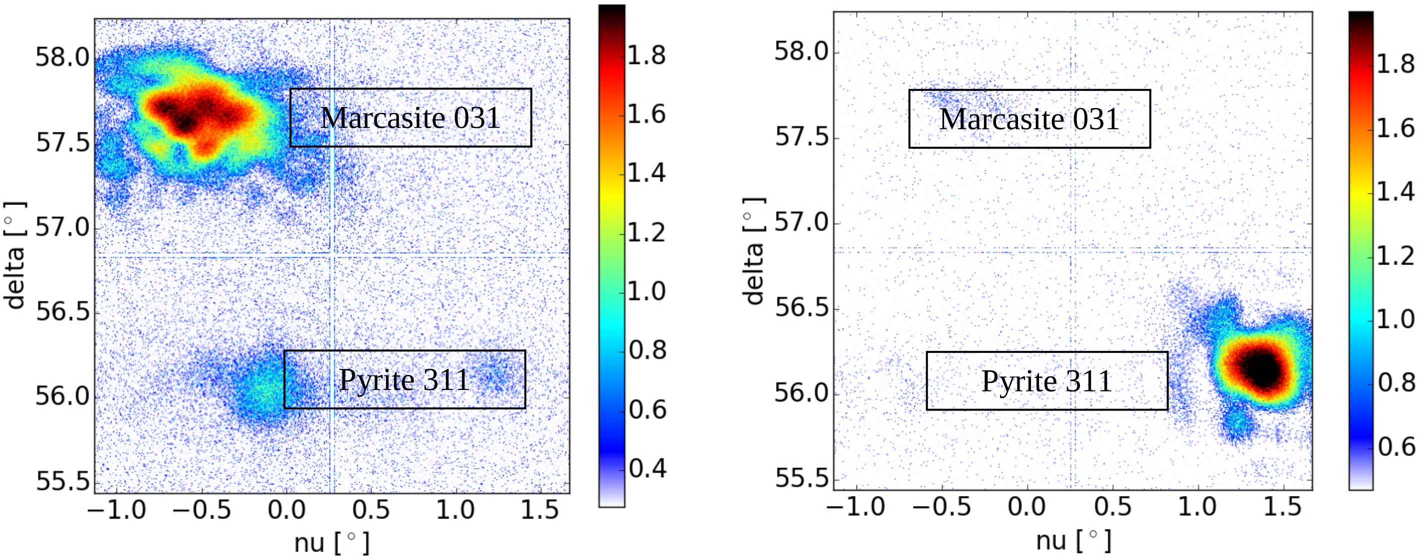

Fig. 2 *Detector images at the maximum of the rocking-curve for the mixed phase marcasite-pyrite film prepared at 380 °C for 5 h for two different locations in the same sample .*

and 57.7° 2θ, respectively. Sub-micrometer resolved phase distribution as well as crystallite size and orientation shown in Figure 2 contribute to a better understanding of the structure of the mixed phase film and help to form a more comprehensive picture of the reasons for the high photocurrents we observed for the marcasite-pyrite phase junctions [1]. Figure 3 shows a K-map taken at 2θ=47.5° (pyrite 220) for phase pure pyrite film, from which we conclude that pyrite nanoparticles are distributed all across the film. The obvious comparison in sub-micrometer phase composition is consistent with results obtained from other techniques such as HRTEM and Raman spectroscopy/imaging. With this knowledge, we expect to be able to tailor materials design for functional materials to be used in earth abundant solar water splitting devices. A manuscript comprising these results is currently in preparation.

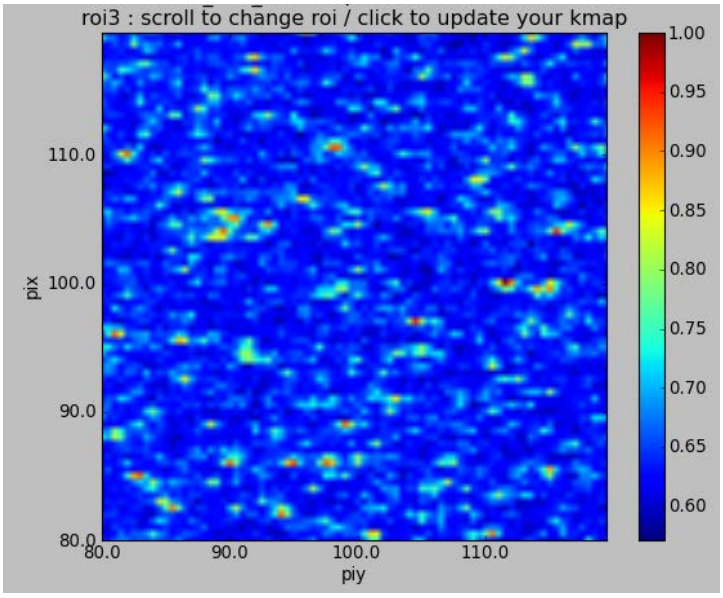

Fig. 3 *K-map at 2 theta=47.5°at grazing incidence geometry to look at the pyrite particles for phase pure pyrite FeS_2 film prepared at 500 °C for 5 h .*

References:

[1] L. Wu, N. Y. Dzade, L. Gao, D. O. Scanlon, Z. Öztürk, N. Hollingsworth, B. M. Weckhuysen, E. J. M. Hensen, N. H. de Leeuw, J. P. Hofmann, Adv. Mater. **28**, 9602 (2016).