Nucleation and growth kinetics of CZTS nanocrystals studied by millisecond time resolved quick scanning X-ray absorption spectroscopy

Oliver Mueller*[1], Justus Just[2], and Pascal Becker[3,4]

[1]*Stanford Synchrotron Radiation Lightsource (SSRL), Menlo Park, CA 94025, USA*

[2]*Division of Chemical Physics, Lund University, Box 124, SE-22100 Lund, Sweden*

[3]*Institute of Energy Materials, Helmholtz-Zentrum Berlin, 14109 Berlin, Germany*

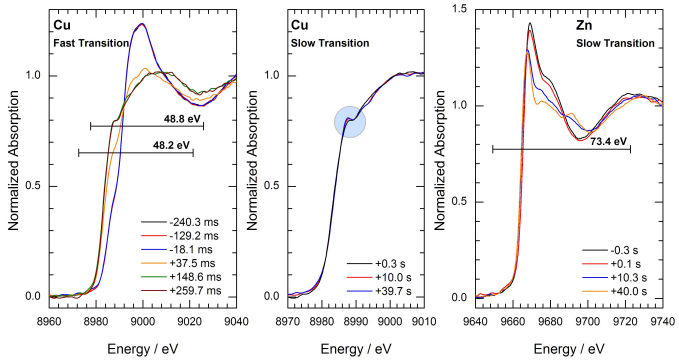
[4]*University of Wuppertal, Faculty 4 - Physics, 42097 Wuppertal, Germany*

**omueller@slac.stanford.edu*

Multicomponent copper based quaternary semiconductors such as CZTS (Cu_2ZnSnS_4) are promising candidates for photon absorber layers in thin film solar cells.[1] These materials can be synthesized in nano-crystalline form by hot-injection one-pot synthesis. During formation of CZTS nanocrystals, the incorporation kinetics of the different atomic species are of particular interest.[2] Using the newly installed dedicated Quick scanning EXAFS (QEXAFS) setup at the SuperXAS beamline (SLS, Switzerland), early stage nucleation and subsequent growth have been studied in-situ with millisecond time resolution.[3,4]

The nanocrystal formation from solved metal salts of copper, zinc and tin was investigated using a specialized in-situ liquid chemical reactor which enables QEXAFS measurements in transmission geometry. The nucleation was remotely triggered by a rapid combustion driven injection of a sulfur source to oversaturate the solution.Injection and complete mixing of the liquids were achieved within a few milliseconds. Enabled by the direct drive driven QEXAFS monochromator, and especially by the microsecond fast gridded ionization chambers and current amplifiers, X-ray absorption spectra of the Cu and Zn K-edges have been recorded simultaneously in real-time with a repetition rate of 36 spectra per second (see fig.). Due to rigorous optimization of the QEXAFS setup and data acquisition system, the collected 'up-' and 'down-' spectra exhibit excellent data quality and both scan directions could be used for data evaluation.

Following the subsequent growth of CZTS nanocrystals multiple reaction stages were found. These findings help to establish and to refine reaction models of CZTS nanocrystal growth. To our knowledge, the conducted experiments were the first in-situ QEXAFS investigations on nanoparticle nucleation and growth with an achieved time resolution of 28 ms.



Cu and Zn K-edge XANES spectra extracted at different times during the reaction.

References

[1] A. Polizzotti et al., Energy Environ. Sci. 6, 3171-3182 (2013).

[2] C. Coughlan and K. M. Ryan, CrystEngComm 17, 6914-6922 (2015).

[3] O. Mueller et al., *J. Synchrotron Rad.* **23**, 260-266 (2016).

[4] O. Mueller et al., *Rev. Sci. Instrum.* **86**, 093905 (2015).