Correlative electron microscopy applied on perovskite-type solar cells

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Helmholtz-Zentrum Berlin

Workshop on Advanced Characterization Possibilities in the Corelab Facilities of HZB for Metal-Halide Perovskite Characterization

Berlin, October 12, 2017

Outline

Overview of CoreLab for Corelative Microscopy & Spectroscopy (CCMS) @ HZB

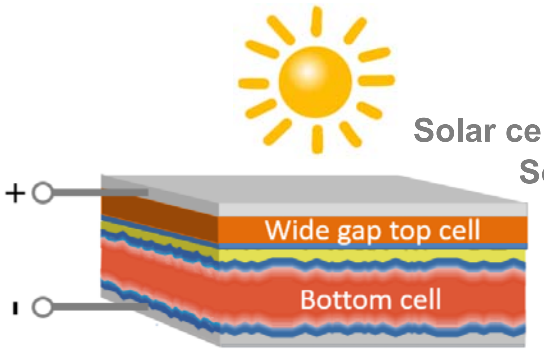
Scanning electron microscopy techniques

Transmission electron microscopy techniques

New Research School from 2018

HI-SCORE

Hybrid Integrated Systems for Conversion of Solar Energy



Solar cell

Solar fuel generator

efficient, stable, and affordable
wide-bandgap semiconductors
as top absorbers

Acknowledgements

Ph.D. and diploma / master / bachelor students

Hannah Funk

Sebastián Caicedo Dávila

Norbert Schäfer

Melanie Nichterwitz

Jens Dietrich

Jürgen Bundesmann (technician)

Jaison Kavalakkatt

Sebastian Schmidt

Aleksandra Nikolaeva

Maximilian Krause

Further colleagues assisting in microscope work

Numerous collaborations in academics and industry

Specimen preparation

Ulrike Bloeck

Christiane Förster

Honorary preparator
Peter Schubert-Bischoff

CCMS: Ion Beam Instruments

Zeiss Orion NanoFab

He/Ne ion sources
Nanostructuring

Zeiss CrossBeam 340

Ga ion source
Tomography
Nanofabrication

Responsible: Dr. Katja Höflich

CCMS: Transmission electron microscopes

Zeiss LIBRA 200FE

TEM/STEM
EELS
EDX (Thermo)
Tomography

Philips CM12

TEM/STEM
EDX (EDAX)

Responsible: Dr. Markus Wollgarten

CCMS: Scanning electron microscopes

Zeiss Merlin

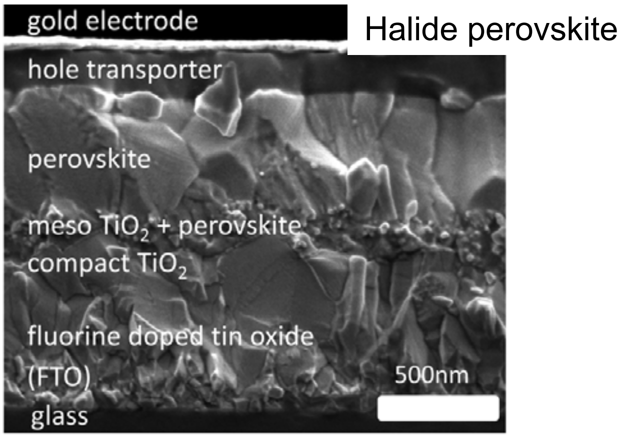
Cathodoluminescence (DELMIC)
AFM setup (SemiLab)
Beam blanker (for lock-in amplification)

Zeiss UltraPlus

EBSD/EDX (Oxford Instr.)
EBIC (point electronic)
Beam blanker
Gas injection system

The issue of surface optimization

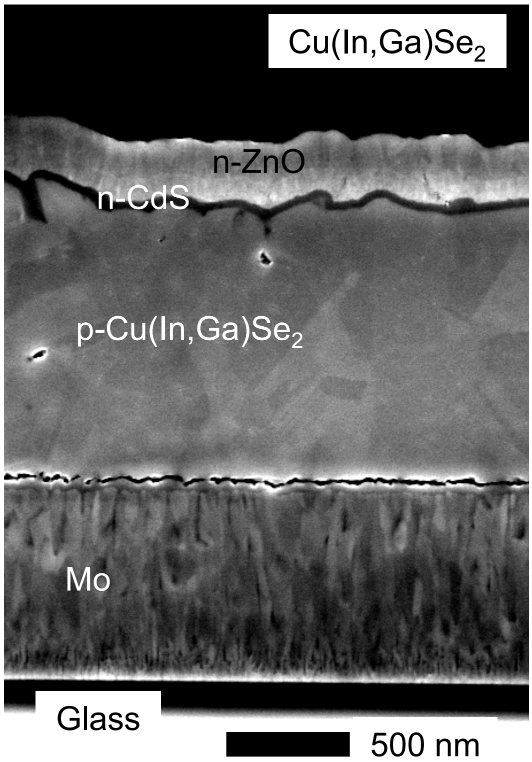
Fractured cross-section



Saliba et al., Energy Environ. Sci. (2016)

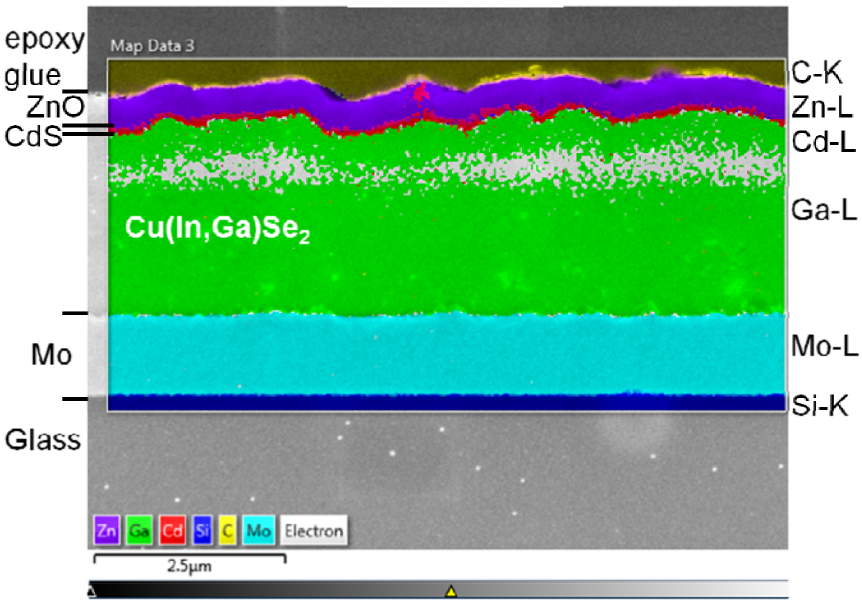
Polishing of halide-perovskite devices difficult due to sensitivity to solvents

Polished cross-section

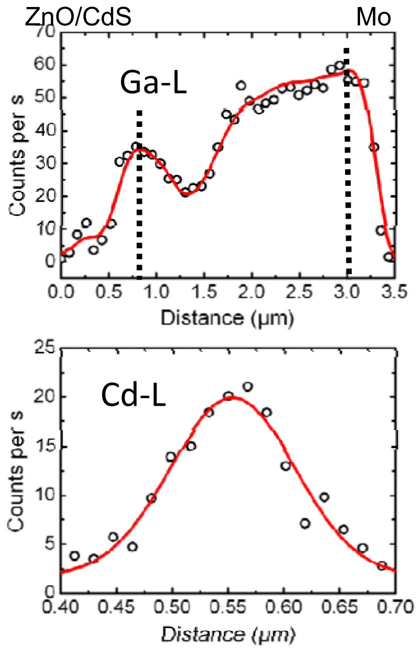


EDX analysis of cross-section specimen

$Cu(In,Ga)Se_2$ solar cell



FWHM of well below 100 nm

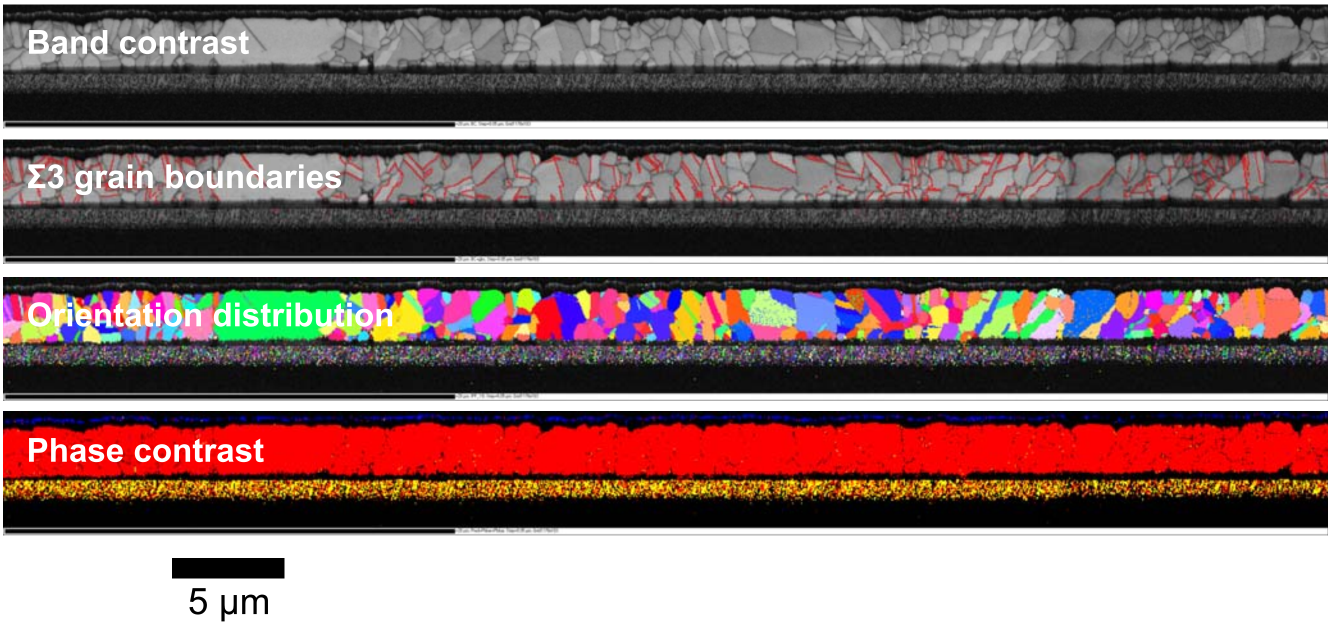


FWHM of 110 nm

See also: Application Note Oxford Instruments

Data from EBSD analysis

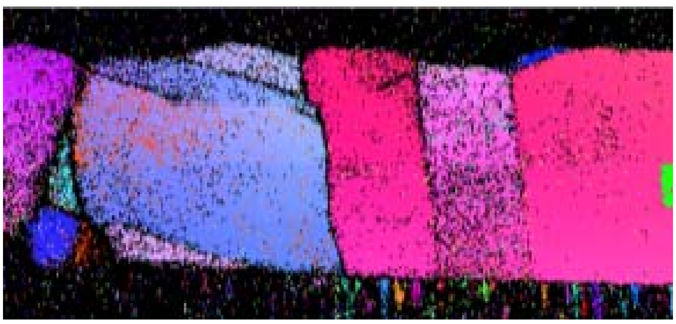
EBSD: electron backscatter diffraction

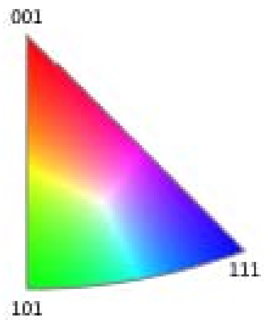


Transmission Kikuchi diffraction on $Cu(In,Ga)Se_2$

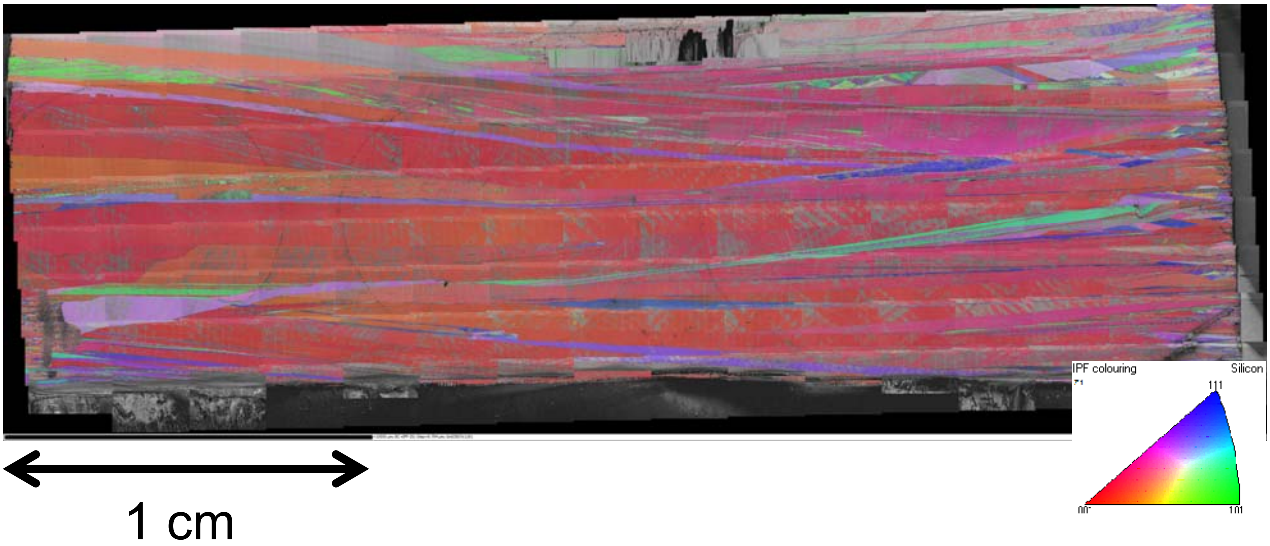
Step size: 10 nm

Transparent (TEM) lamella



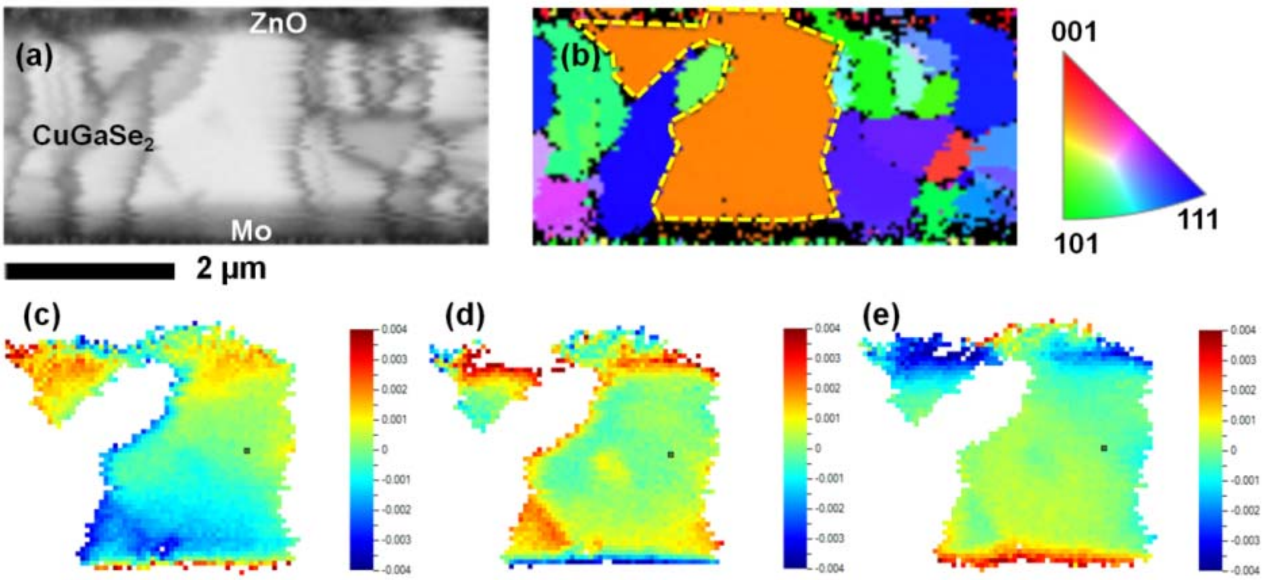


EBSD map of liquid-phase crystallized Si film



Kühnapfel, Abou-Ras, et al., phys. stat. solidi (RRL) (2015)

Strain distributions from EBSD data (CrossCourt3)



Ph.D. thesis Norbert Schäfer, HZB

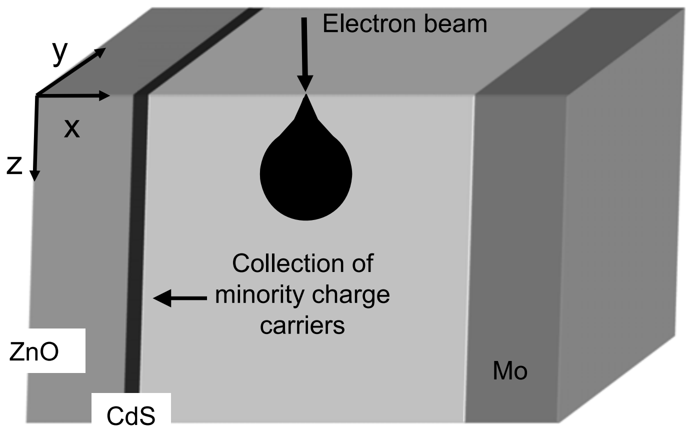
Microstrain within grains about 10^{-4}

Comparison with other techniques: XRD ($\sin^2\psi$, microdiffraction, grazing-incidence), Raman mapping

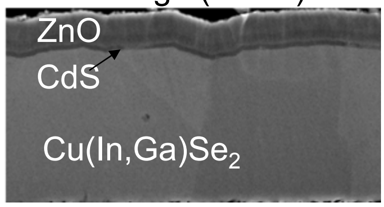
Schäfer, Abou-Ras, et al., Ultramicroscopy (2016)

Electron-beam-induced current measurements on cross-sections

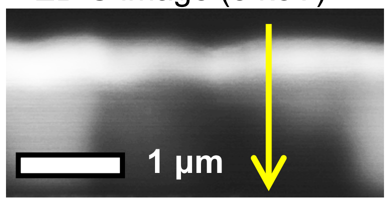
Junction/cross-section configuration

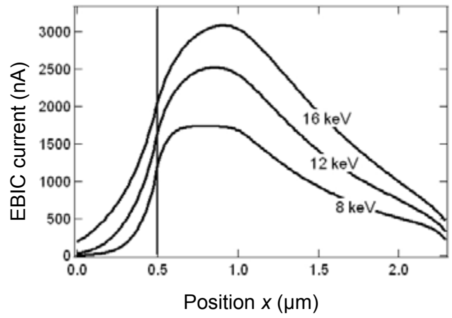


SEM image (3 keV)



EBIC image (8 keV)

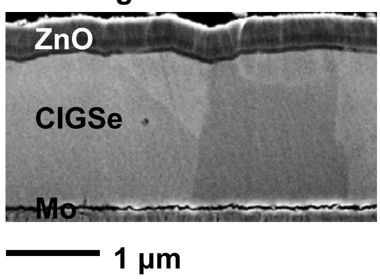


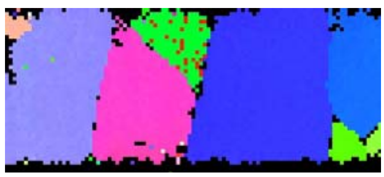


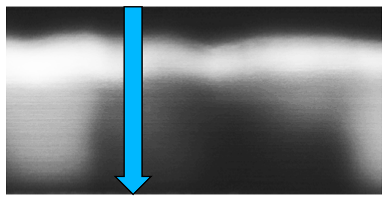
M. Nichterwitz, D. Abou-Ras, et al., Thin Solid Films (2009)

Different EBIC signals between neighboring grains

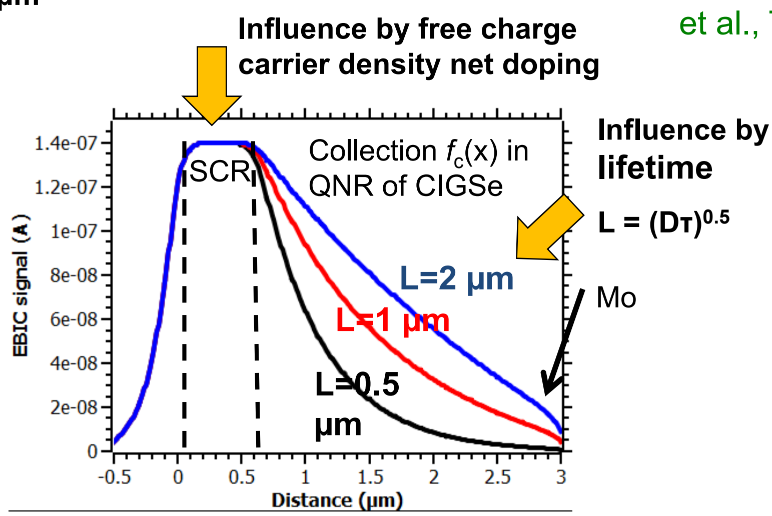
SE image **EBSD map** **EBIC image**







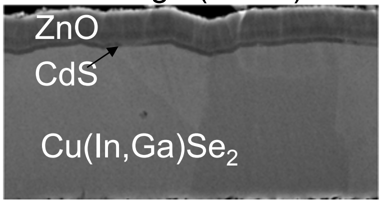
M. Nichterwitz, D. Abou-Ras, et al., TSF (2009)



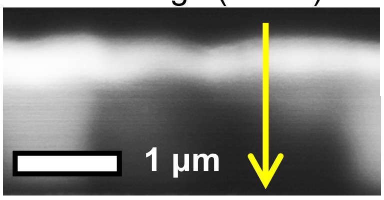
Donolato, APL 1983; JAP 1989

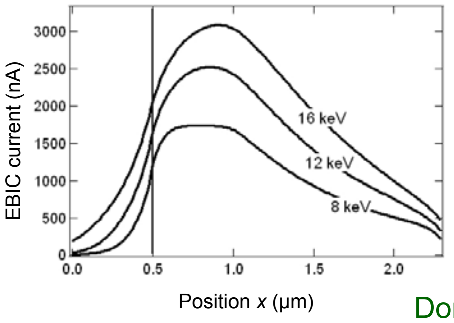
Modeling EBIC profiles

SEM image (3 keV)



EBIC image (8 keV)

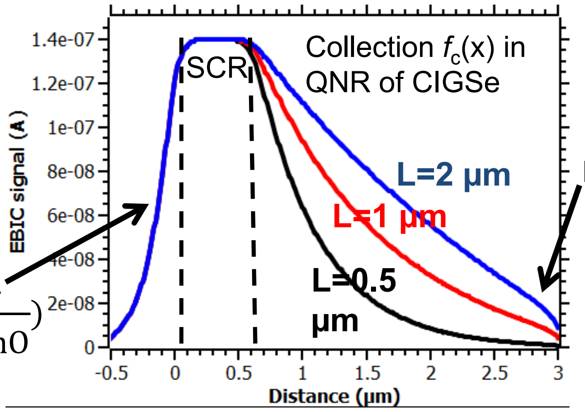




$$I_{\mathrm{EBIC}}(a) = \int_0^\infty g(x,a) f_c(x)\,\mathrm{d}x$$

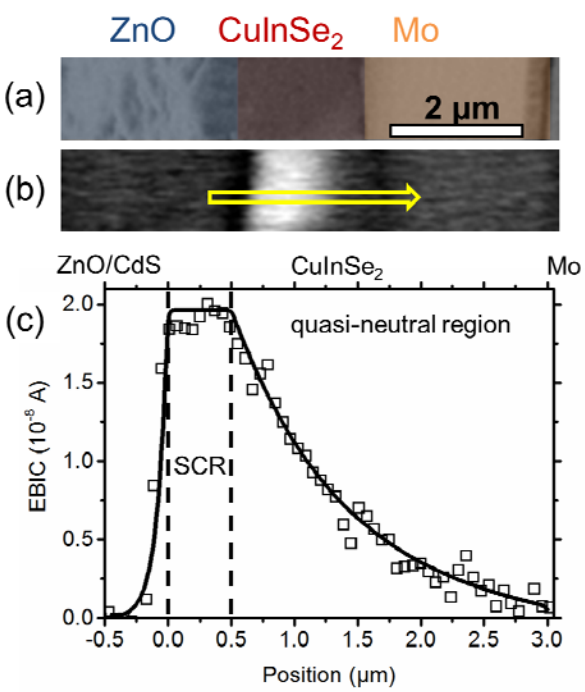
Generation profile: $g(x,a)$ — Collection function: $f_c(x)$

$$f_c(x) = \frac{\frac{1}{L_e}\cosh\left(\frac{x-x_C}{L_e}\right) - \frac{S_C}{D_e}\sinh\left(\frac{x-x_C}{L_e}\right)}{\frac{S_C}{D_e}\sinh\left(\frac{x_C-x_{SCR}}{L_e}\right) + \frac{1}{L_e}\cosh\left(\frac{x_C-x_{SCR}}{L_e}\right)}$$



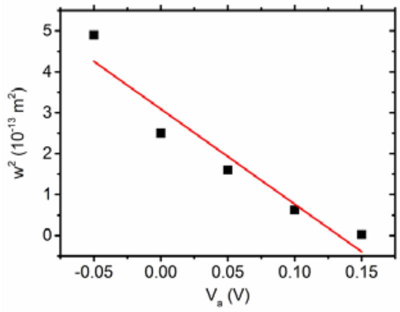
Donolato, APL 1983; JAP 1989

EBIC at applied bias on $CuInSe_2$ solar cell



SEM Zeiss UltraPlus with beam blanker
EBIC system: point electronic GmbH

Variation of SCR width with applied voltage V_a:



$w = (2\varepsilon_r\varepsilon_0(V_b-V_a)/e\,N_A)^{0.5}$

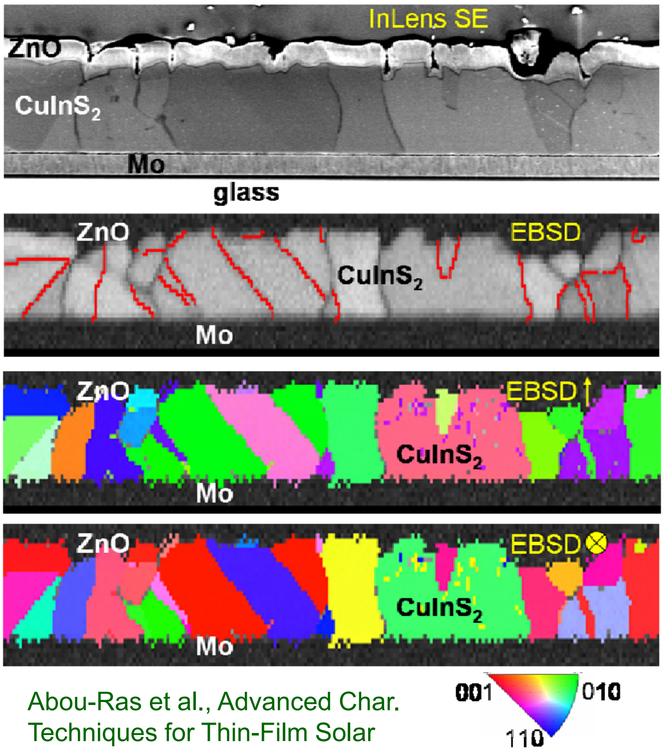
Calculation of acceptor density (net doping)
⇒ Good agreement with capacitance-voltage measurements

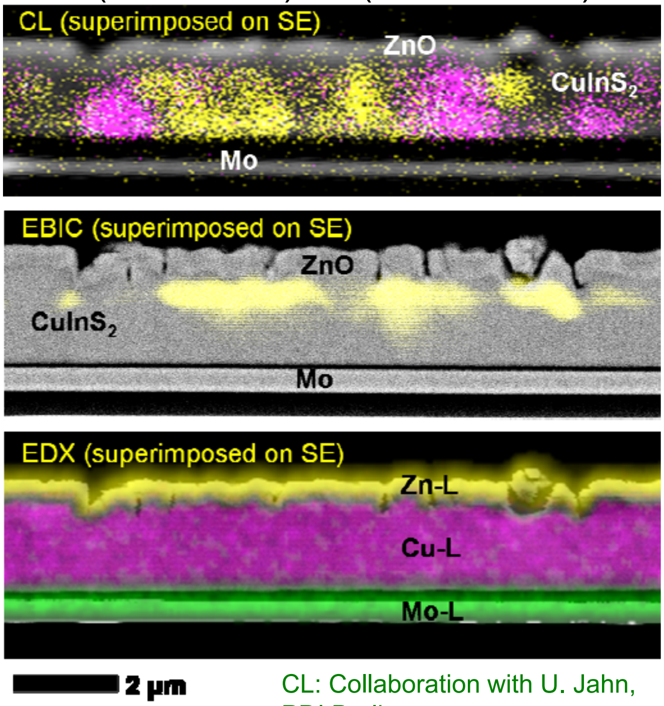
D. Abou-Ras et al., AIP Advances (2015)

Combination of electron microscopy techniques

... on the **identical** position!

yellow: 820 nm, red: 1150 nm
(band-band) (defect states)



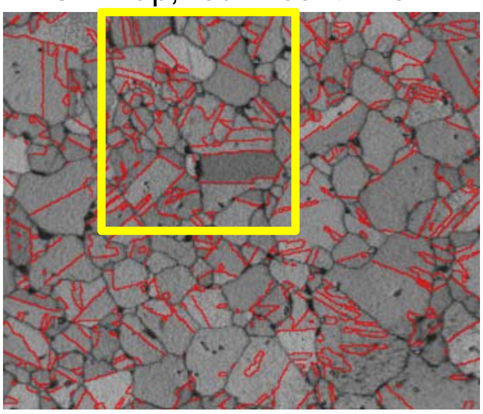


Abou-Ras et al., Advanced Char. Techniques for Thin-Film Solar Cells, Wiley VCH (2016), ch. 12

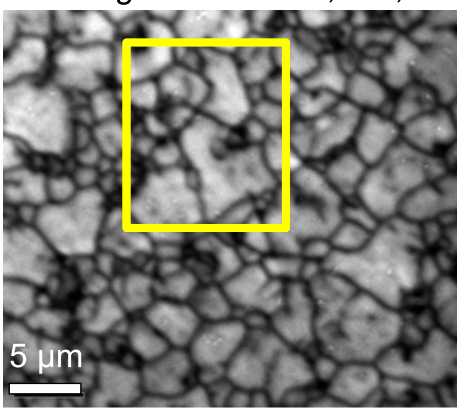
CL: Collaboration with U. Jahn, PDI Berlin

EBSD, CL, EBIC from identical specimen position

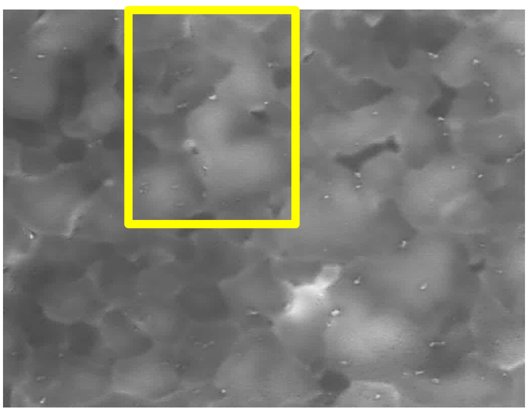
EBSD map, red lines: twins



CL image at 1280 nm, 5 K, 8 kV



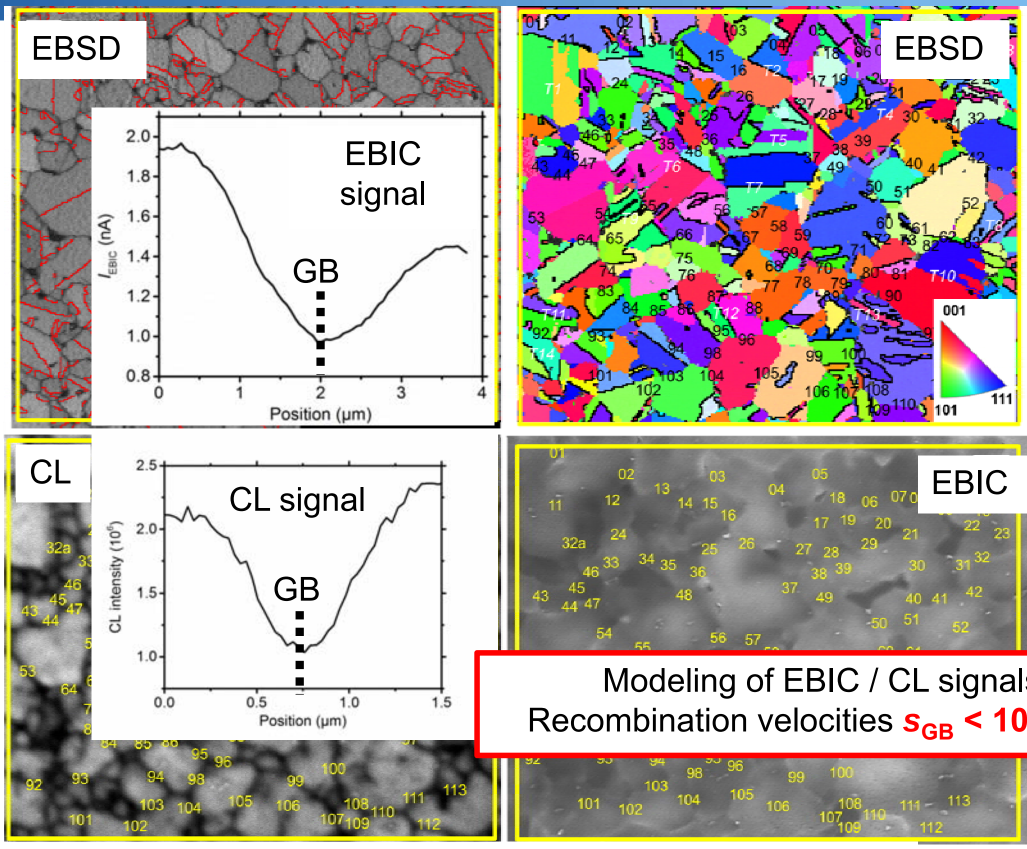
EBIC image at room temp. (8 kV)



CL measurements in collaboration with Univ. Jena, Germany

J. Kavalakkatt, D. Abou-Ras, et al., J. Appl. Phys. (2014)

Statistics on EBIC / CL signals from identical GBs

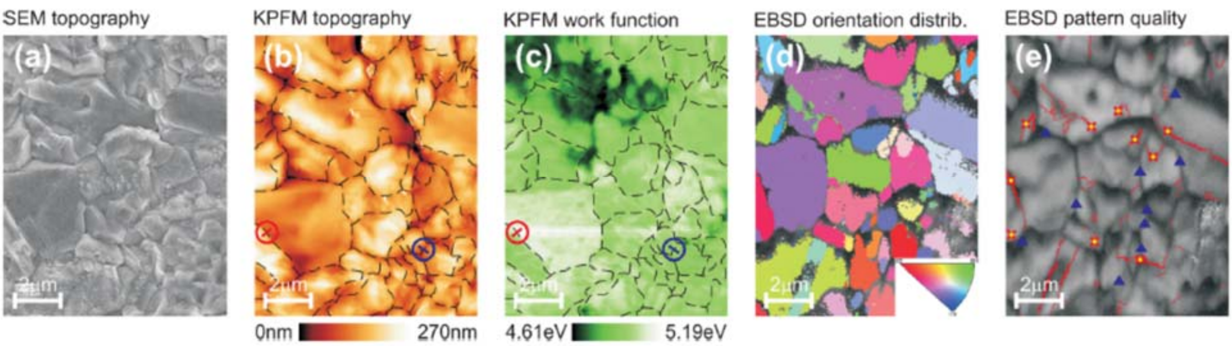


Modeling of EBIC / CL signals:
Recombination velocities $s_{GB} < 10^4$ cm/s

D. Abou-Ras, A.D. Rollett, G.S. Rohrer, et al., Acta Mater. (2016)

Correlation of scanning probe microscopy with EBSD

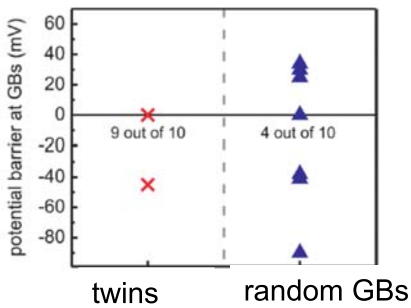
KPFM: Kelvin probe force microscopy: Probing work function distributions



From differences in work function at grain boundaries:
Potential barriers for charge carriers

Together with recombination velocities: important input for 2D device modeling

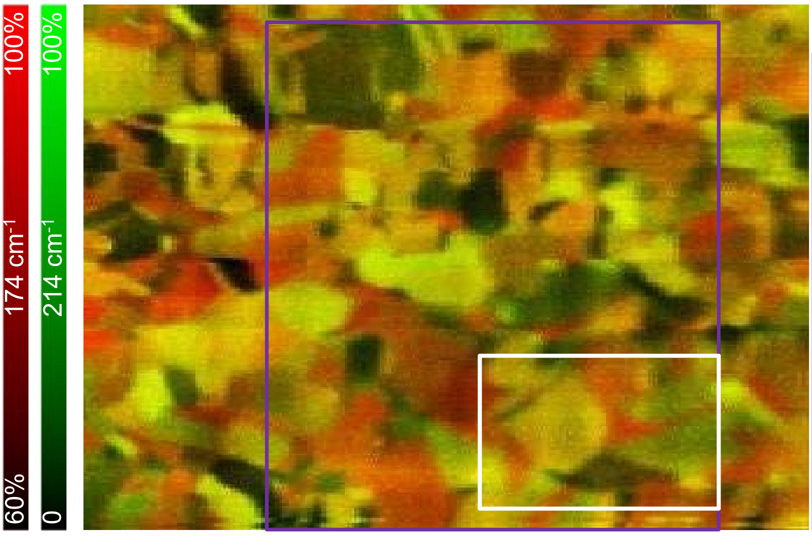
D. Abou-Ras, et al., pss (RRL) (2016)



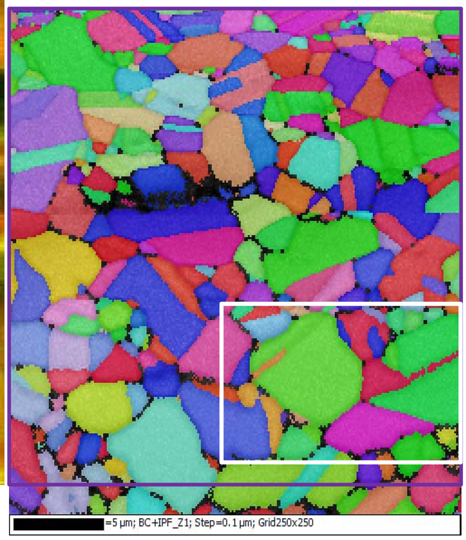
R. Baier, D. Abou-Ras, et al., Appl. Phys. Lett. (2011)

Correlation Raman – EBSD

Raman microscopy



Electron backscatter diffraction (EBSD)

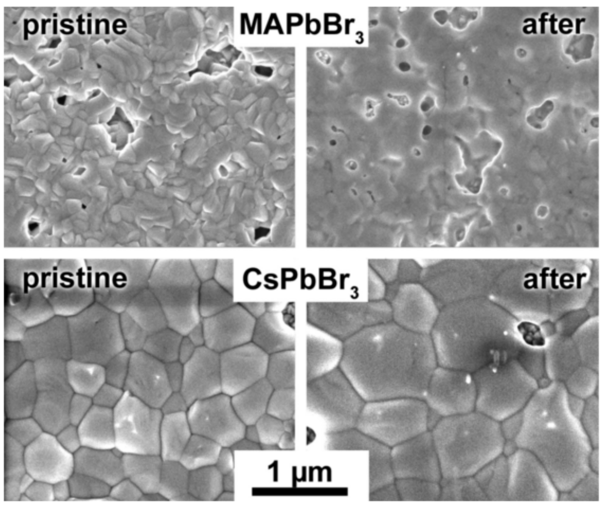


5 µm

T. Schmid, D. Abou-Ras, et al., Nature Sci. Rep. 5 (2015) 18410

Sensitivity of organic-containing halide perovskites

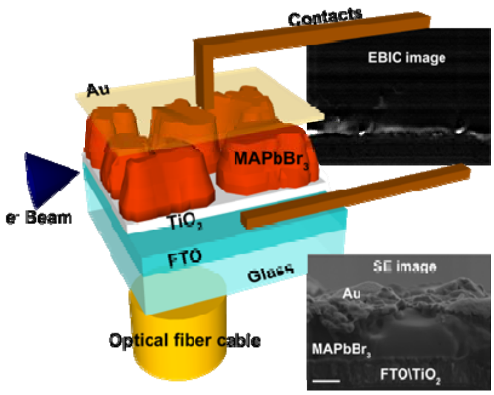
SEM images



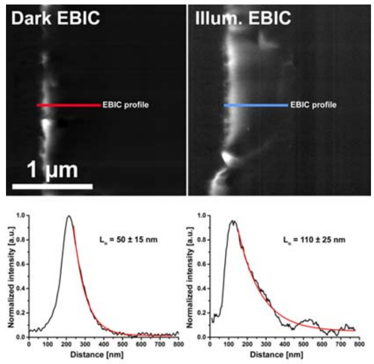
Klein-Kedem, et al. Acc. Chem. Res. 49, 2 (2016)

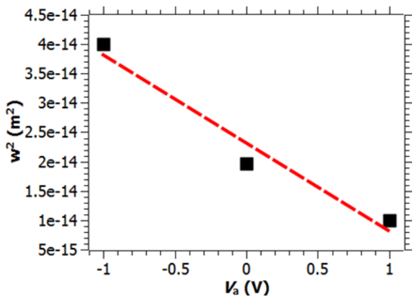
Focus rather on inorganic halide perovskites with wide band gaps

EBIC on $CH_3NH_3PbBr_3$ Perovskite Solar Cell



Variation of applied voltage V_a &
illumination conditions





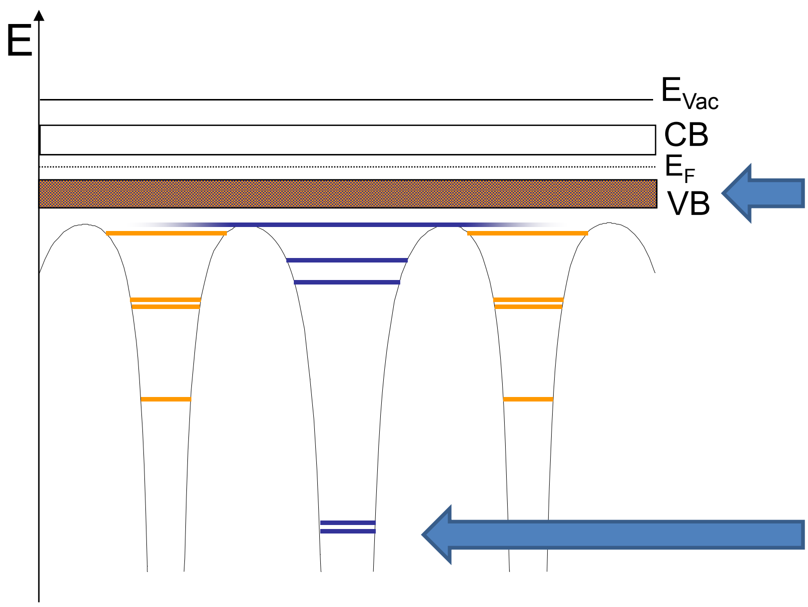
Diffusion length increases when illuminating solar cell

Calculated doping density about 10^{17} cm^{-3}, as confirmed by capacitance analysis

N. Kedem, D. Abou-Ras et al., J. Phys. Chem. Lett. (2015)

Electron energy-loss spectroscopy in TEM

Various losses of impinging e- when scattering with electrons in materials



Loss at phonons (meV)
Structural information (vibrational spectrosc.)

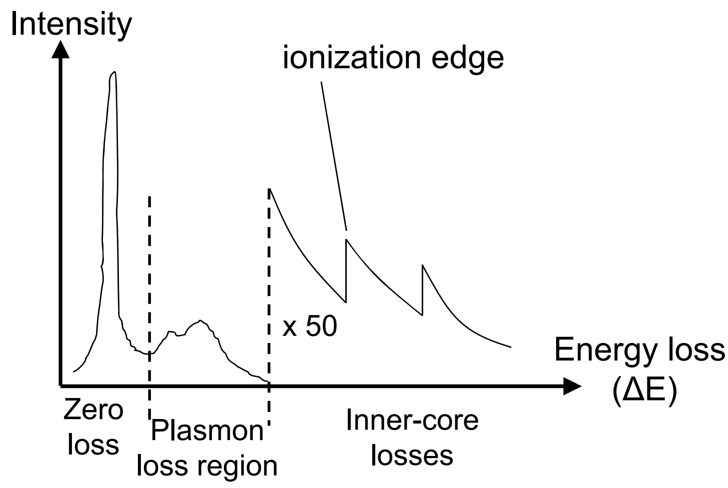
Loss at valence electrons (1-3 eV)
Band-gap energies

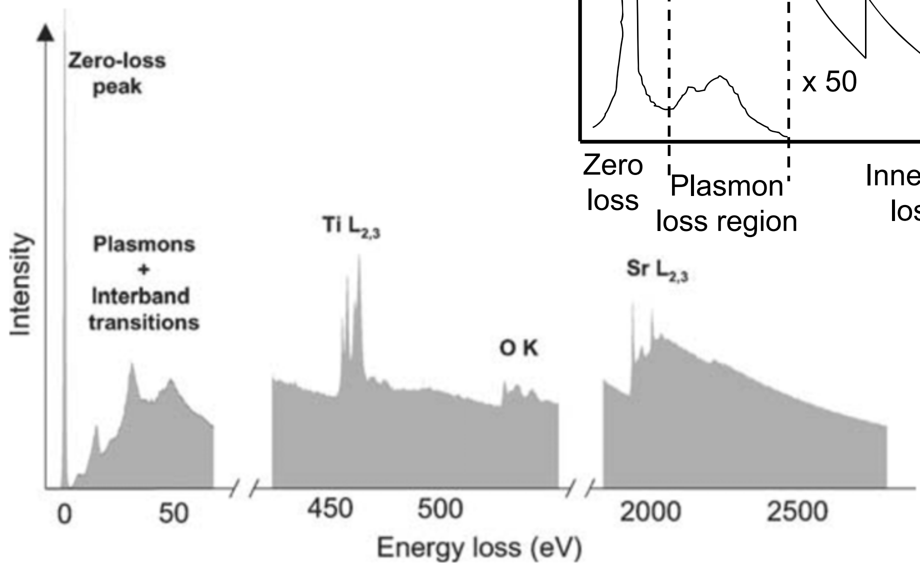
Loss at plasmons (collective vibrations of e- in CB, 5-50 eV)
Phase identification

Loss at core electrons (100-1000 eV)
Compositional analysis

L. Weinhardt, M. Bär, Young Scientist Tutorial,
MRS 2007 Spring Meeting

EEL spectrum – details and example

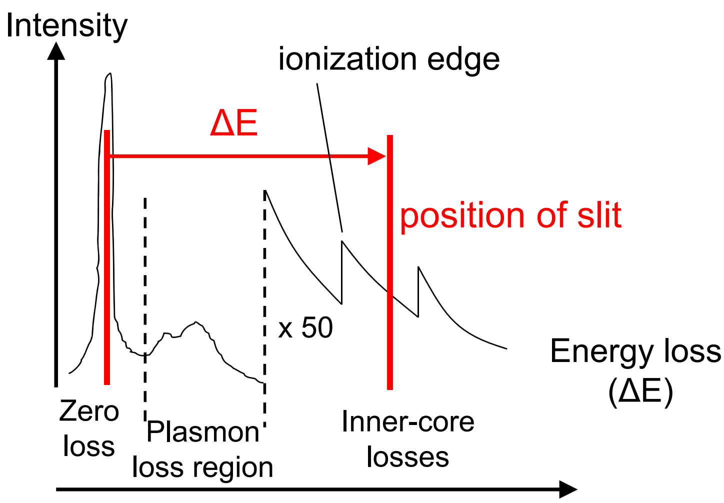




W. Sigle, Ann.Rev.Mat.Res. (2005)

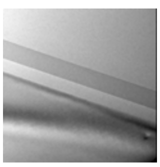
SrTiO3

Energy-filtered TEM (EFTEM)

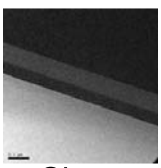


energy-filtered TEM images from $Si/SiO_2/SiN/SiO_2$ stack

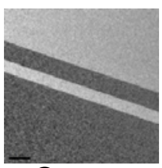
(by courtesy of E. Müller, ETH Zurich, Switzerland)



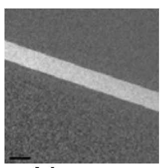
unfiltered



Si map



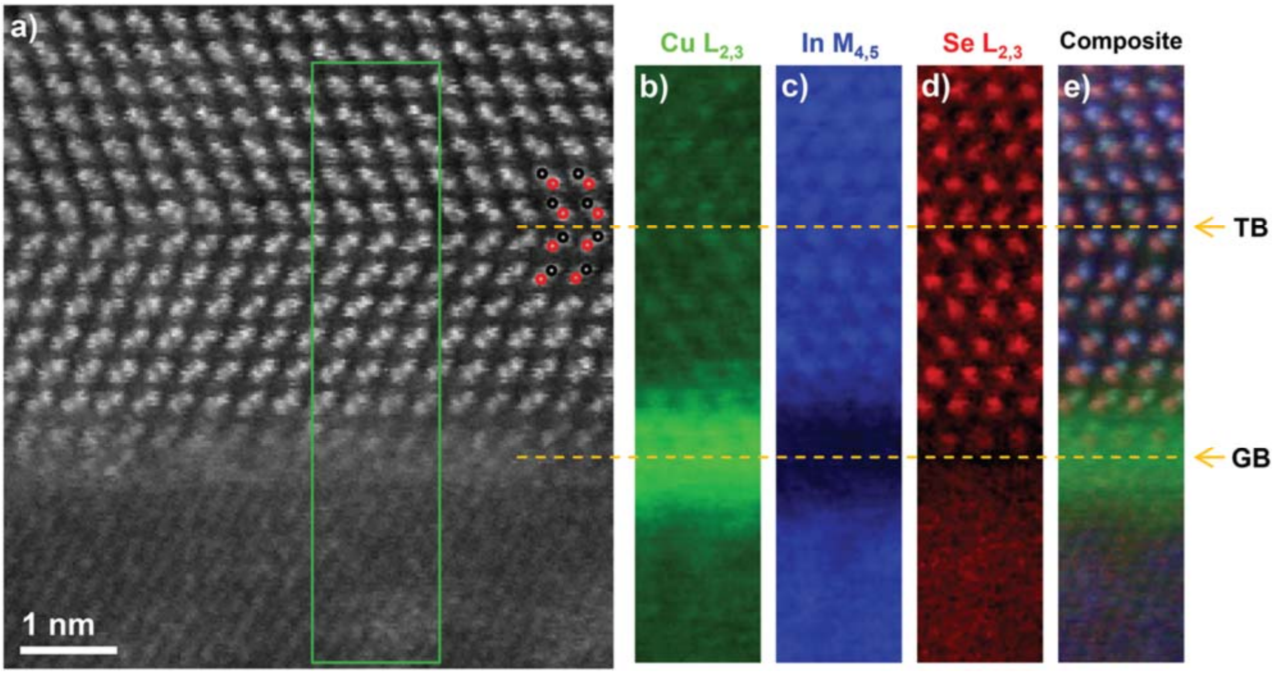
O map



N map

Energy-filtered TEM (EFTEM): High resolution imaging

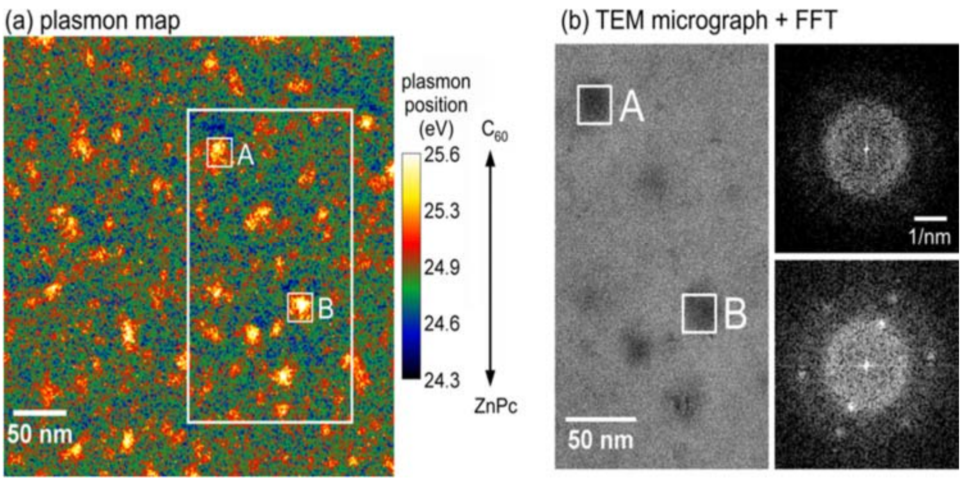
Twin boundary (TB) and random grain boundary (GB) in Cu(In,Ga)Se_2 thin film



E. Simsek-Sanli, D. Abou-Ras, et al., J. Appl. Phys. (2016)

EELS: Plasmon mapping of organic blends

ZnPc/C60 blends used in bulk heterojunction solar cells

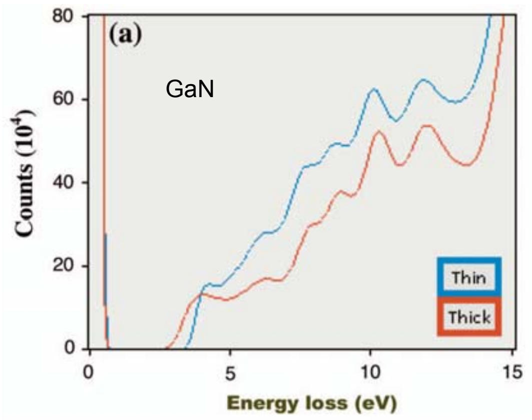


Phase separation of ZnPc and C60 detected by plasmon mapping

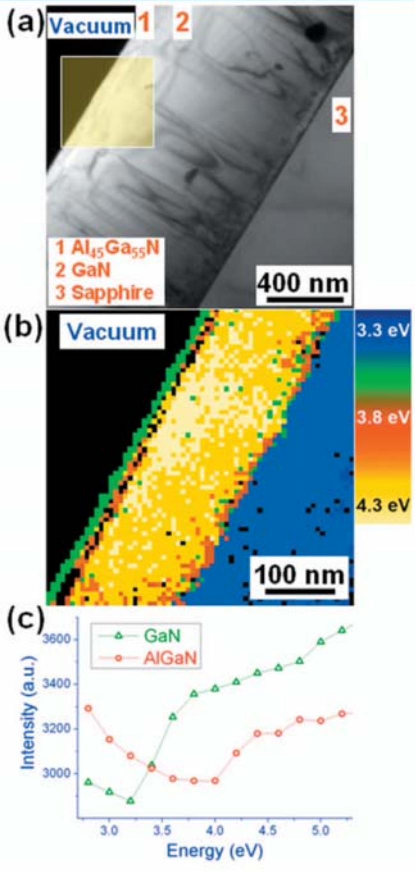
W. Schindler et al., Org. Electron. (2012)

Valence EELS – Mapping of band-gap energies

Energy loss by scattering at valence electrons (1-10 eV)
⇒ Transition VB -> CB
⇒ Energy position of signal en



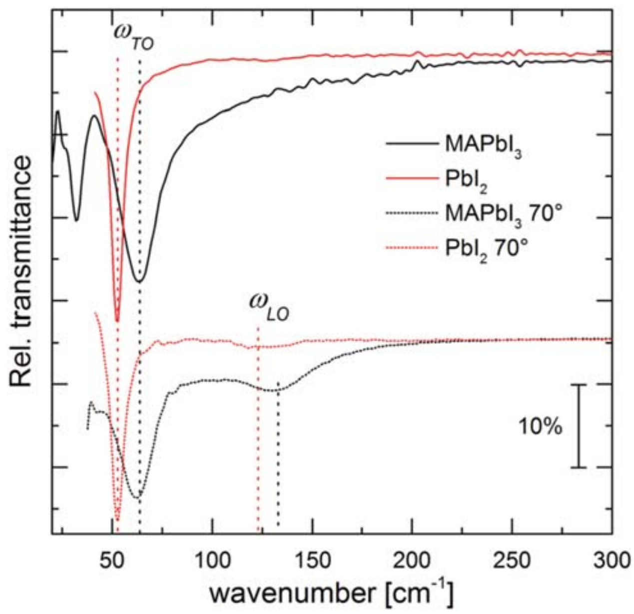
Gu et al., Phys. Rev. B (2007)



Gu et al., J. Appl. Phys. (2010)

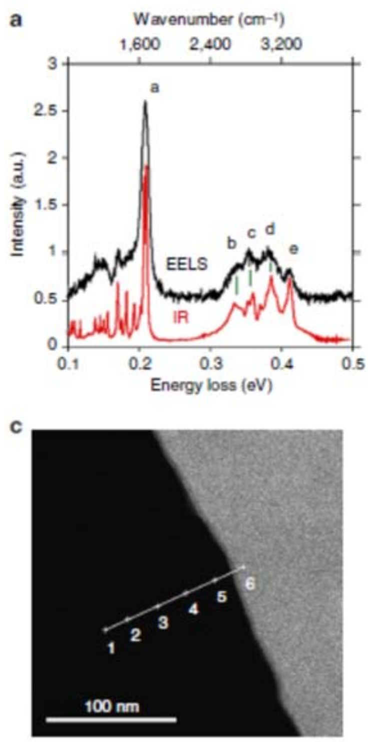
Combination of vibrational spectroscopies

(Macroscopic) IR spectroscopy
Collaboration with R. Lovrincic, Univ. Heidelberg



Sendner *et al*. Optical phonons in methylammonium lead halide perovskites and implications for charge transport. Mater. Horiz., 2016, 3, 613

(Microscopic) STEM-EELS
Collaboration with C.T. Koch, HU Berlin



Rez, P. *et al*. Damage-free vibrational spectroscopy of biological materials in the electron microscope. *Nat. Commun.* 7:10945 doi: 10.1038/ncomms10945 (2016)

Conclusions

Electron microscopy and its related techniques provide insight to

- (Micro)structure, composition, electrical/optoelectronic properties
- Scales from subnanometer to centimeters

Correlative microscopy: combined electron/scanning probe/light microscopy on identical positions
$\Rightarrow$ Enhanced information on materials & devices

Thank you very much!