Ilka Hermes

Impact of Interfaces on Charge Carriers in Semiconductors

Surfaces, interfaces, and microstructure of semiconductors can act as source of defect states, accumulate dopants and locally change the electronic structure and are thus affecting the charge carrier behavior in semiconductor-based (opto)electronic devices. In my group at the Leibniz Institute of Polymer Research Dresden e.V., we are aiming at investigating the impact of surfaces, interfaces and microstructure on charge carrier behavior on the nanoscale by establishing a combination of advanced electrical and electromechanical scanning probe microscopy (SPM) techniques with optical microscopy or spectroscopy and macroscopic current-voltage measurements for low-dimensional and thin film semiconductors as well as full devices. For these investigations, we want to go beyond resolving the static equilibrium state and include dynamic measurements upon in-situ application of electrical, optical and mechanical stimuli or in-operando conditions.

The majority of (opto)electronic devices including diodes, transistors, and solar cells relies on semiconductor materials: Semiconductors feature an energetic gap of up to 3 eV between their occupied valance band and unoccupied conduction band, which electrons can overcome upon thermal, electrical or optical excitation. Due to the band gap, the excited electrons in the conduction band and the remaining holes in the valance band exhibit a relatively long lifetime and facilitate an electrical conduction that can be tuned via doping. Diodes combine n- and p-doped semiconductor regions to a pn-junction, which allows a unidirectional current flow; field effect transistors utilize an additional gate electrode to switch the conductivity of a doped semiconductor; solar cells use optical excitation from the solar irradiance to excite electrons across the band gap, which stabilizes holes and electrons sufficiently long to be extracted via (hetero-)junctions [1].

However, surfaces and interfaces of semiconductors can locally change the electronic properties significantly and, consequently, affect the performance of semiconductor devices. Structural disorder, dangling bonds, and adsorbates can induce band bending via defects or unwanted doping, contaminations or recombination centers [2, 3]. Particularly, grain and domain boundaries in polycrystalline semiconductors are often detrimental to overall device performance since they pose as energetic barriers or lead to recombinative losses of excited charge carriers [4, 5].

Dr. Ilka Hermes
Institute of Physical Chemistry and Polymer Physics
Leibniz Institute of Polymer Research
Hohe Str. 6, D-01069 Dresden
hermes@ipfdd.de

DOI-Nr.: 10.26125/ghh2-8m42

To resolve the impact of the microstructure on the charge carrier transport in semiconductor devices, we are using electrical and electromechanical scanning-probe microscopy (SPM) combined with luminescence measurements. The inherently correlative character of functional SPM allows to map microstructural features in the topography channel simultaneous to the electrical surface potential in the case of Kelvin probe force microscopy (KPFM) [6] or the sample's conductivity (Figure 1a and b) [7]. Electromechanical SPM on the other hand can be employed to resolve features that can be invisible in the sample topography such as ferroelastic domain walls [8].

By combining these measurements with in-situ external optical or electrical excitation, we are able to resolve local electronic changes such as surface band bending visible as positive or negative photo-charging under illumination in n-doped and p-doped semiconductors, respectively [9]. Or we can resolve the local increase in conductivity at the position of ferroelectric domain walls, where the structural disorder at the boundaries results in energetically unfavorable polarization orientations, compensated by a local increase in electrically injected charge carriers [10]. Currently, we are investigating how the electronic properties of the semiconductor microstructure is impacted by mechanical strain by incorporating an in-situ stretching stage into our SPM setups (Figure 1c).

Since KPFM is unable to resolve the distribution of excitonic charge carriers, we are extending our functional SPM capabilities with spatially resolved luminescence measurements. Correlated to the microstructure resolved in SPM, luminescence microscopy allows us to detect whether certain microstructural features are acting as non-radiative recombination centers or energetic barriers (Figure 1d).

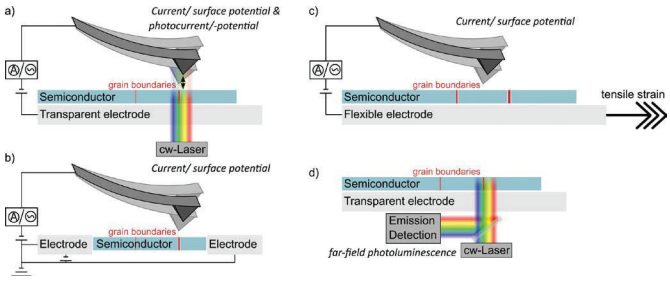

Fig. 1: a) Conductive and Kelvin probe scanning probe microscopy (SPM) to resolve the electronic properties of microstructural features such as grain boundaries with optical excitation, b) in external electric field, c) under mechanical strain, d) correlative far-field luminescence measurements to capture excitonic carriers.

Anisotropic charge carrier transport due to domain walls

In the past, we applied this combinatory SPM and luminescence microscopy approach to resolve the impact of ferroelastic twin domain walls on the charge carrier transport in the hybrid organic-inorganic perovskite semiconductor methylammonium lead iodide $MAPbI_3$, which has been successfully implemented as active layer in perovskite solar cells [11]. For this study, we were able to resolve the topographically invisible domain structure on several µm-large single crystals of $MAPbI_3$ using electromechanical SPM, also called piezoresponse force microscopy (PFM). PFM measurements revealed domains of a few hundred nanometer width that spanned over the whole diameter of the grain. Using time-resolved photoluminescence (tr-PL) with a spatially decoupled excitation and detection, we were able to measure the charge carrier diffusion in dependence of the domain orientation and observed a significant increase of the diffusion times for those charges moving perpendicular to the domain walls as compared to those charges that moved parallel to the domain walls (Figure 2).

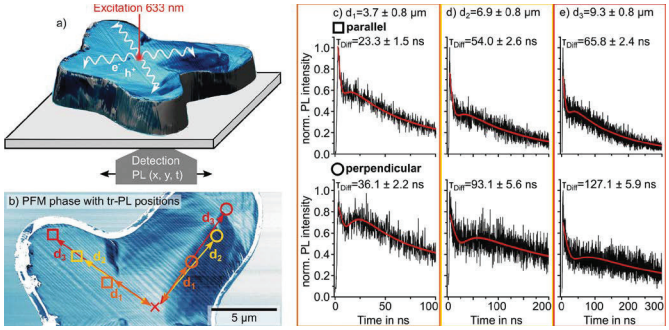

Fig. 2: a) Schematic of photoluminescence setup. b) PFM phase signal showing the periodic ferroelastic domain structure with tr-PL detection positions marked as circles (perpendicular diffusion) and squares (parallel diffusion) in distances d_{1-3} from excitation marked by the red cross, c-e) corresponding tr-PL signals fitted with a monoexponential decay and a peak function to determine the diffusion time τ_{Diff}. Reproduced from [11] with permission from the Royal Society of Chemistry.

Currently, we are focusing on optimizing our experimental toolbox for flexible polymer semiconductors as well as for low-dimensional synthetic semiconductors.

Referenzen

[1] Wolfgang Demtröder: Experimentalphysik 3 - Atome, Moleküle und Festkörper, *Springer* 2016 445 – 464.

[2] P. A. Cox: The Electronic Structure and Chemistry of Solids, *Oxford University Press* 1986 229 – 240.

[3] Ilka Hermes, Yi Hou, Victor Bergmann, Christoph Brabec, Stefan A. L. Weber: The interplay of contact layers: How the electron transport layer influences interfacial recombination and hole extraction in perovskite solar cells, *J. Phys. Chem. Lett*. 2018 **9**, 6249 – 6256.

[4] Dane W. deQuilettes, Sarah M. Vorpahl, Samuel D Stranks, Hirokazu Nagaoka, Giles E. Eperon, Mark E. Ziffer, H. J. Snaith, David S. Ginger: Impact of Microstructure on Local Carrier Lifetime in Perovskite Solar Cells, *Science* 2015 **348**, 683 – 686.

[5] Richard Ciesielski, Frank Schäfer, Nicolai F. Hartmann, Nadja Giesbrecht, Thomas Bein, Pablo Docampo, Achim Hartschuh: Grain Boundaries Act as Solid Walls for Charge Carrier Diffusion in Large Crystal MAPI Thin Films, *ACS Appl. Mater. Interfaces* 2018 **10**, 7974 - 7981.

[6] Amelie Axt, Ilka Hermes, Victor Bergmann, Niklas Tausendpfund, Stefan A. L. Weber: Know your full potential: Quantitative Kelvin probe force microscopy on nanoscale electrical devices, *Beilstein J. Nanotechnol.* 2018 **9**, 1809 – 1819.

[7] Ningwei Sun, Shivam Singh, Haoran Zhang, Ilka Hermes, Ziwei Zhou, Hendrik Schlicke, Yana Vaynzof, Franziska Lissel, Andreas Fery: Gold Nanoparticles with N-Heterocyclic Carbene/Triphenylamine Surface Ligands: Stable and Electrochromically Active Hybrid Materials for Optoelectronics, *Adv. Sci*. 2024, 2400752.

[8] Ilka Hermes, Simon Bretschneider, Victor Bergmann, Dan Li, Alexander Klasen, Julian Mars, Wolfgang Tremel, Frédéric Laquai, Hans-Jürgen Butt, Markus Mezger, Rüdiger Berger, Brian Rodriguez, Stefan A. L. Weber: Ferroelastic fingerprints in methylammonium lead iodide perovskite, *J. Phys. Chem. C* 2016 **120**, 5724 – 5731.

[9] Andrei Mitrofanov, Khrystyna Rymsha, Dmitrii Sychev, Karina Zakirova, Petr Formanek, Darius Pohl, Eva Bittrich, Ilka Hermes, Quinn Besford, Brigitte Voit: Surface-assisted synthesis of perovskite nanosheets with bivalent aromatic cations, *J. Mater. Chem. C* 2024, **12**, 1440 – 1445.

[10] Ilka Hermes, Andrea Cerrata: Capturing conductive ferroelectric domain walls, *Park Atomic Force Microscopy Application Note* **#75**, 2021.

[11] Ilka Hermes, Andreas Best, Leonard Winkelmann, Julian Mars, Sarah Vorpahl, Markus Mezger, Liam Collins, Hans-Jürgen Butt, David Ginger, Kaloian Koynov, Stefan A. L. Weber: Anisotropic carrier diffusion in single $MAPbI_3$ grains correlates to their twin domains, *Energy Environ. Sci.* 2020, **13**, 4168 – 4177.

Dr. Ilka Hermes

Ilka Hermes studied chemistry at the Johannes Gutenberg University in Mainz and began her work on scanning probe microscopy (SPM) in 2013 to resolve the arrangement of water molecules on mineral surfaces. For her dissertation, she moved to the Max Planck Institute for Polymer Research, where she used electrical and electromechanical SPM to understand the impact of different structural interfaces on charge carriers in perovskite solar cells. After a three-year stint in industry at the SPM manufacturer Park Systems Europe GmbH, Ilka started a junior research group for advanced correlative SPM at the Leibniz Institute of Polymer Research in Dresden in 2022.