SFB 595
Synthese
Elektrische Ermüdung
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Phenomenological modelling of field, charge and polarization distributions in ferroelectrics and organic semiconductors

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Project C5

Motivation

Organic semiconductors

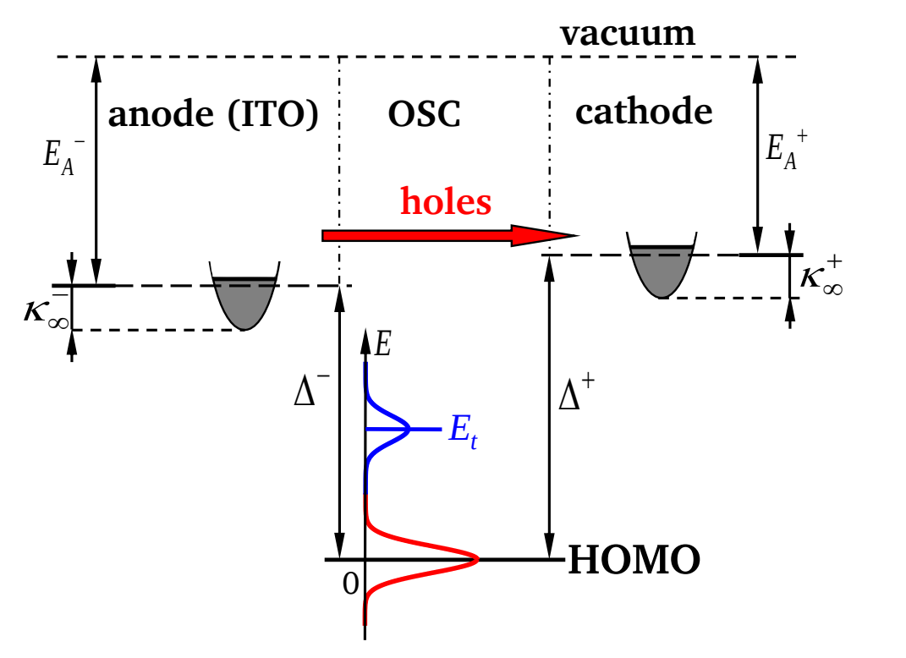
The self-consistent mean-field model of charge-carrier injection into organic semiconductors (OSCs) accounting for discreteness of the injected carriers, which has been developed previously [Y.A. Genenko *et al.*, *Phys. Rev. B* 81, 125310 (2010)], has to be applied to measured current-voltage (I-V) characteristics of single-layer diodes based on polymer and small molecule organic constituents establishing the device operating parameters and tracing their evolution during fatigue. Also, the above approach has to be extended to the case of large densities of injected carriers being applicable for arbitrary values of carrier densities in an OSC.

Ferroelectrics

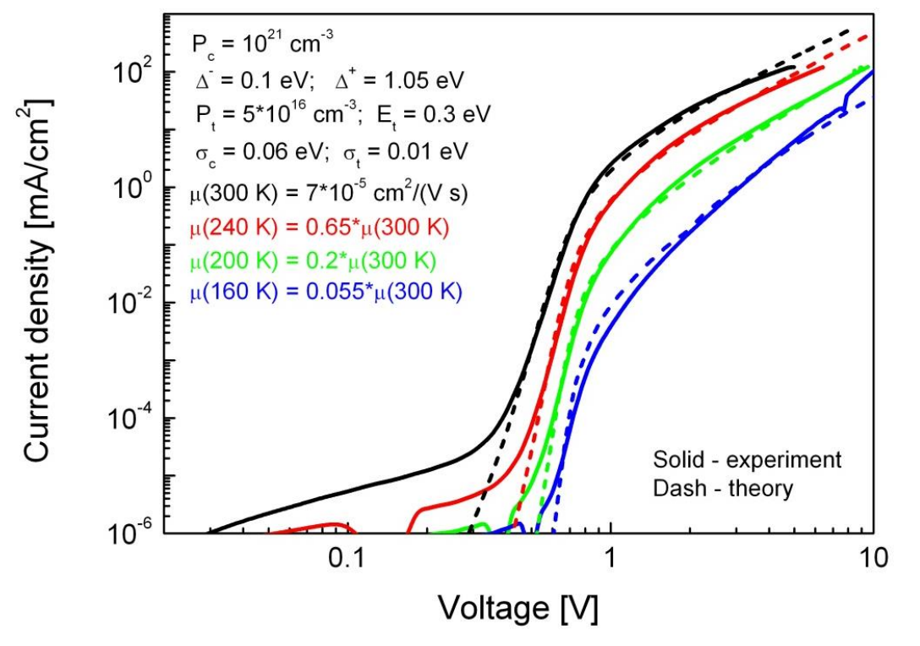
Depolarization fields play important role in aging and fatigue of ferroelectric ceramics. Since the magnitude of these fields is very large, an account of energy band bending and formation of space charges becomes necessary. Nonuniform distribution of electric fields in ceramics has also a great impact on polarization switching resulting in a wide spectrum of switching times, particularly in heavily fatigued ceramics. Inhomogeneous field mechanism (IFM) model allows extraction of statistical distributions of the local fields and local switching times which is now tested on a wide class of disordered ferroelectrics including different bulk ceramics, relaxors and organic ferroelectrics.

Results

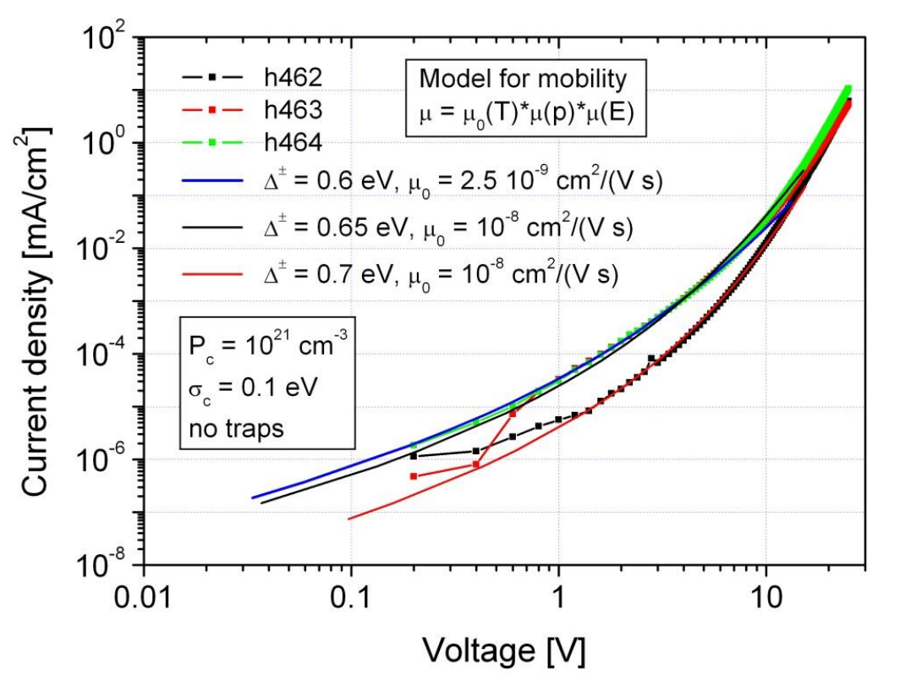
Simulations of measured unipolar I-V characteristics of polymer- and small molecule-based OSC diodes



ITO/P3HT(125nm)/Al diode
(from Nikitenko, et al. JAP 94, 2480 (2003))

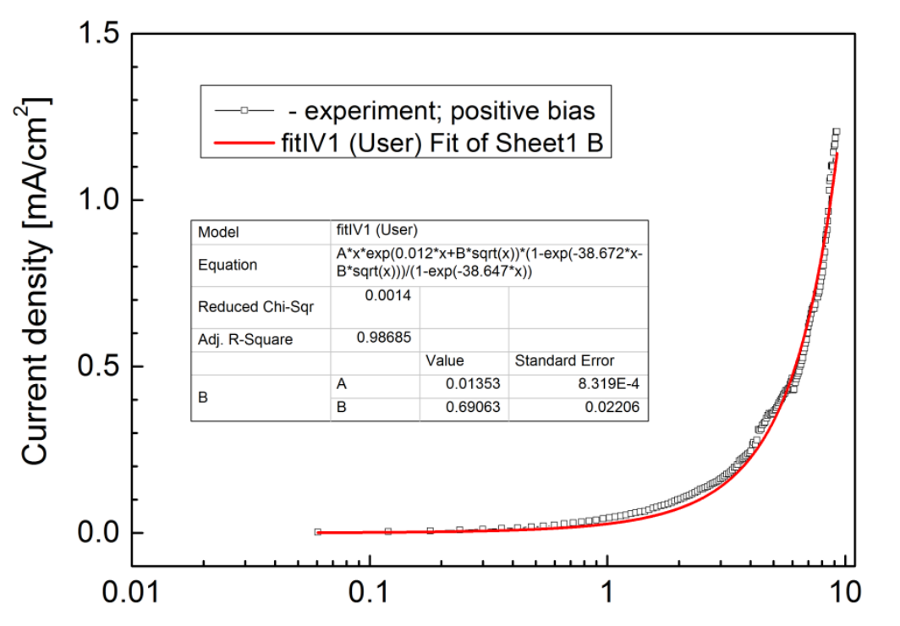


ITO/OC$_1$C$_{10}$-PPV(130nm)/Au diode



(together with D4, submitted to Mater. Sci. Eng. B (2014)(SFB review))

ITO/α-NPD(600nm)/ITO diode



$$A=\frac{e\mu P_{eff}}{L}\exp\left[-\frac{\Delta-E_1}{kT}+\frac{\sigma_1^2}{2(kT)^2}\right]$$

$P_{\mathrm{eff}}=1.4*10^{21}$ cm^{-3}; $\Delta^- - E_t=1.5$ eV
$\mu=4.8*10^{-4}$ cm^2/(V s); $\sigma_1=0.23$ eV

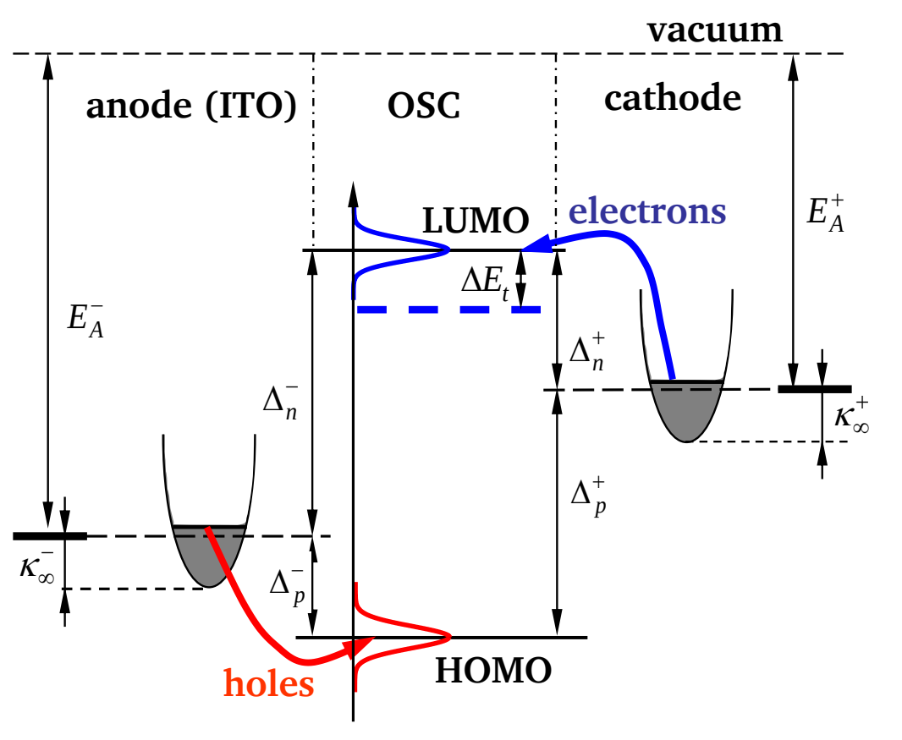
(together with D3, in preparation)

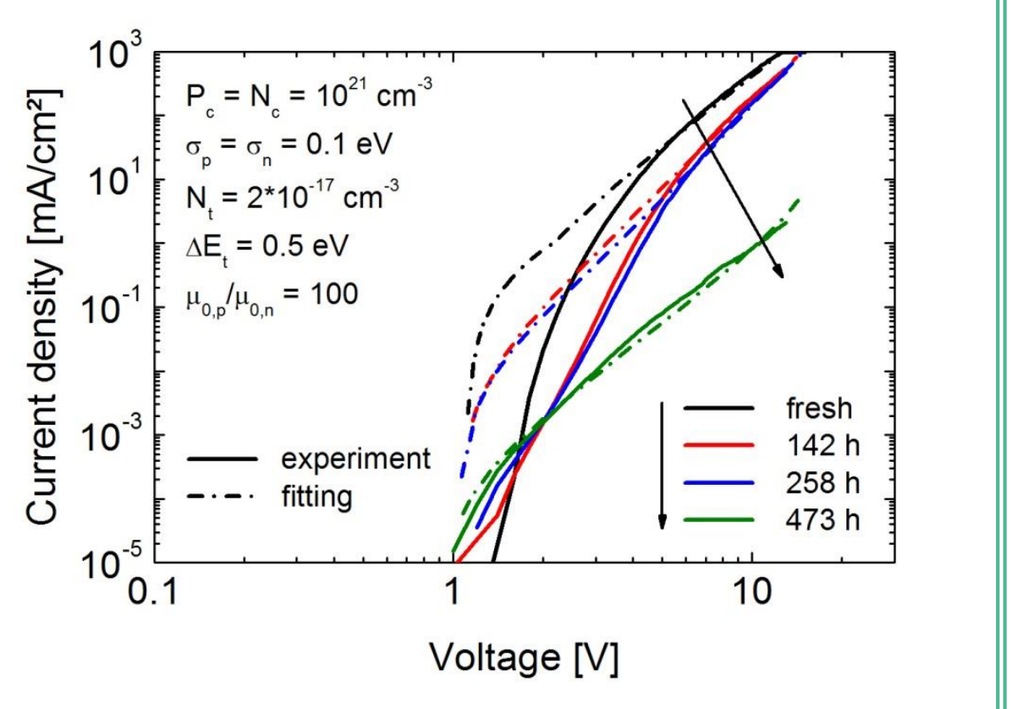
a) both HOMO and trap levels have Gaussian shapes of DOS
b) concentration- and field-dependent carrier mobility is assumed

$\mu_p(x)=\mu_0(T)g_1(p(x))g_2(F(x))$ (from Pasweer et al. PRL **94**, 206601 (2005))

Simulations of fatigued I-V characteristics in a bipolar diode

ITO/PEDOT:PSS/OC$_3$C$_8$-PPV(130nm)/Ca/Al diode





- Direct recombination between HOMO and LUMO
- Electron traps single level

(together with D4, submitted to Mater. Sci. Eng. B (2014)(SFB review))

Fatigued parameters

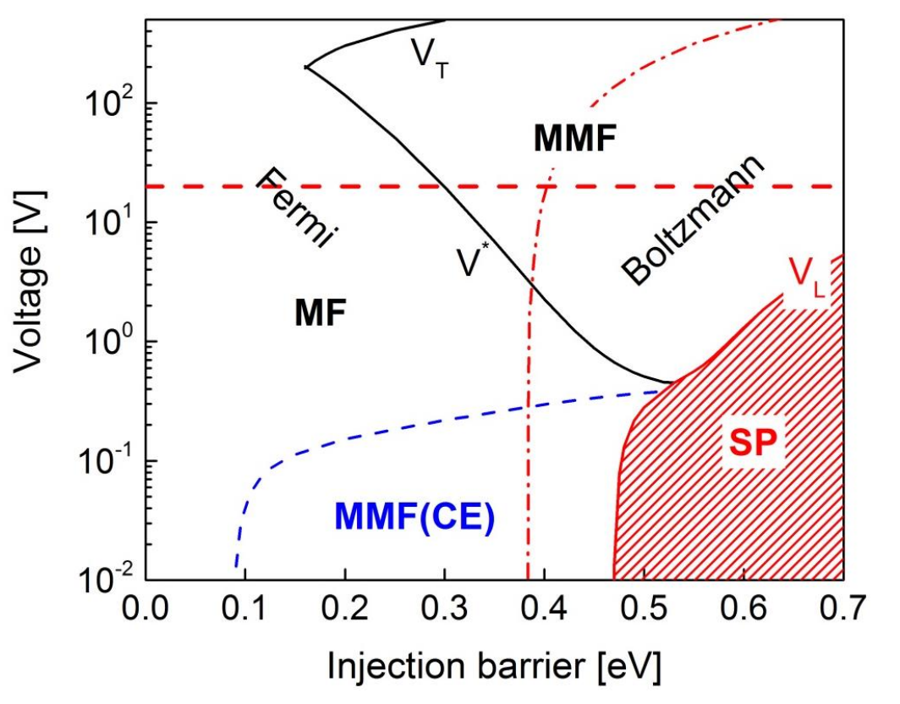
fatigue time	Δ_p [eV]	Δ_n [eV]	$\mu_{0,p}$ [cm^2 V^{-1} s^{-1}]
0 h (fresh)	0.55	0.55	$2.20\cdot10^{-6}$
142 h	0.60	0.60	$1.65\cdot10^{-6}$
258 h	0.60	0.60	$1.30\cdot10^{-6}$
473 h	0.60	0.80	$5.90\cdot10^{-8}$

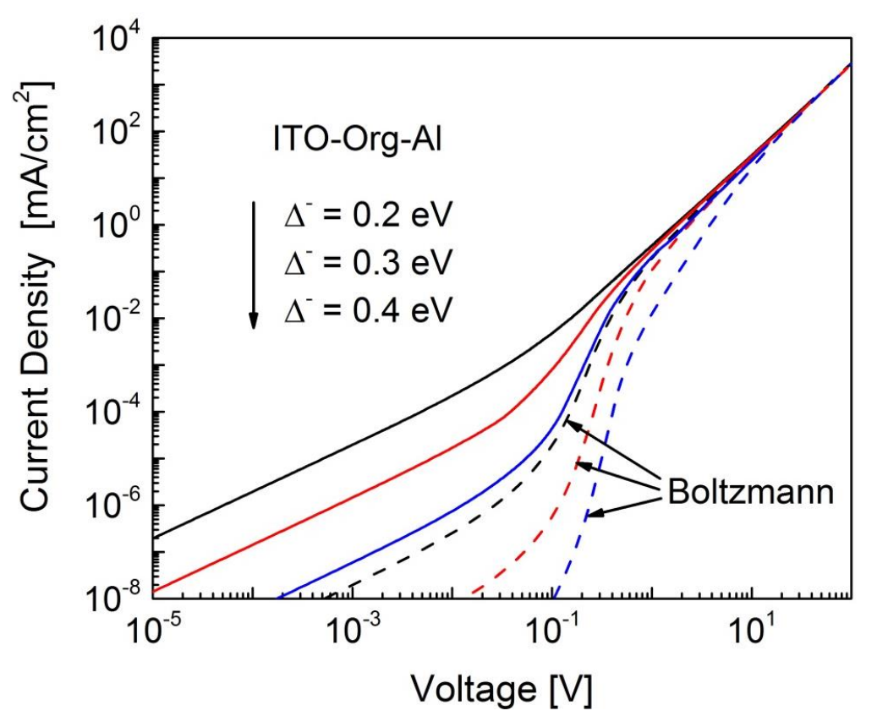
MMF model in the case of large densities of injected carriers

At the electrode/OSC interfaces:

$$p_i\left(\mp\frac{L}{2}\right)=\frac{P_c}{\sqrt{2\pi\sigma_c}}\int dE\exp\left(-\frac{E^2}{2\sigma_c^2}\right)g(E)\left[\exp\left(\frac{\Delta_{eff}^{\mp}-E}{k_BT}\right)+1\right]^{-1}$$

The density of carriers is expressed by adapting of an analytical approximation for the Gauss-Fermi integral for arbitrary value of the Fermi energy
(from Paasch & Scheinert, JAP **107**, 104501 (2010))





Voltage-injection barrier chart (**left**) shows the validity regions of pure mean-field (MF) and mean-field with accounting for discreteness of the injected carriers (MMF) approaches for charge-carrier injection. In the SP region the continuous drift-diffusion description of transport fails. **Right:** simulated IV characteristics using the extended MMF model (solid curves) and the Boltzmann approximation (dashed curves) for injected carrier density

Semiconductor model of ferroelectrics

Due to nonlinear screening of depolarization fields, a stripe domain array creates an effective dipole layer at the interface with a dielectric. The reason for this is the difference in extensions of the negative and positive space-charge regions in front of the differently charged domain boundaries (Fig. 1). The strength of this dipole layer and the consequent surface potential (Fig. 2) at a ferroelectric grain depend on the kinds and amounts of the available defects, particularly, on doping [11]. Effect of space charges on domain wall stability and conductivity was studied by phase-field approach [10,12].

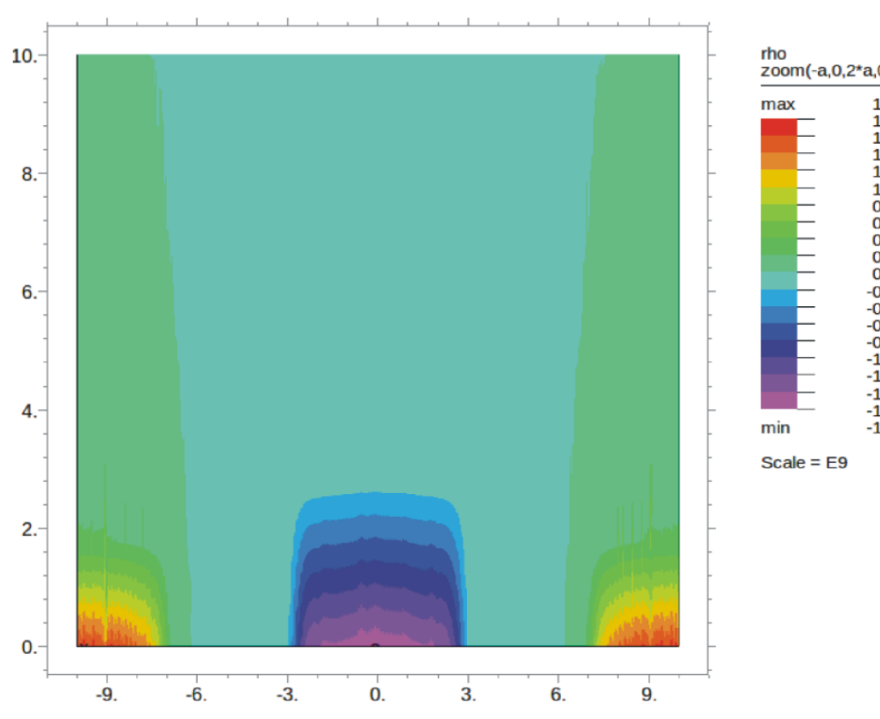


Fig. 1. Space charge density

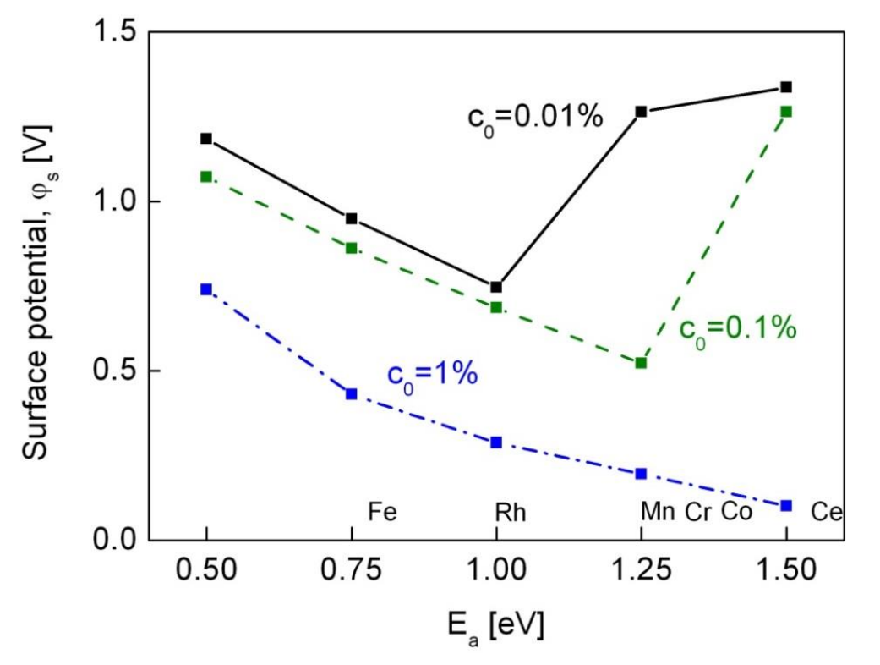


Fig. 2. Surface potential depending on the dopant energy E_a with respect to the valence band in BaTiO$_3$ and the dopant concentration

Statistical models of polarization switching in disordered ferroelectrics

Different classes of disordered ferroelectrics – bulk ceramics, relaxors, and thick organic layers – exhibit scaling properties of polarization response (Fig. 3) which allow for good description of polarization switching data by means of Inhomogeneous Field Mechanism (IFM) model (Fig. 4) [4,5,8].

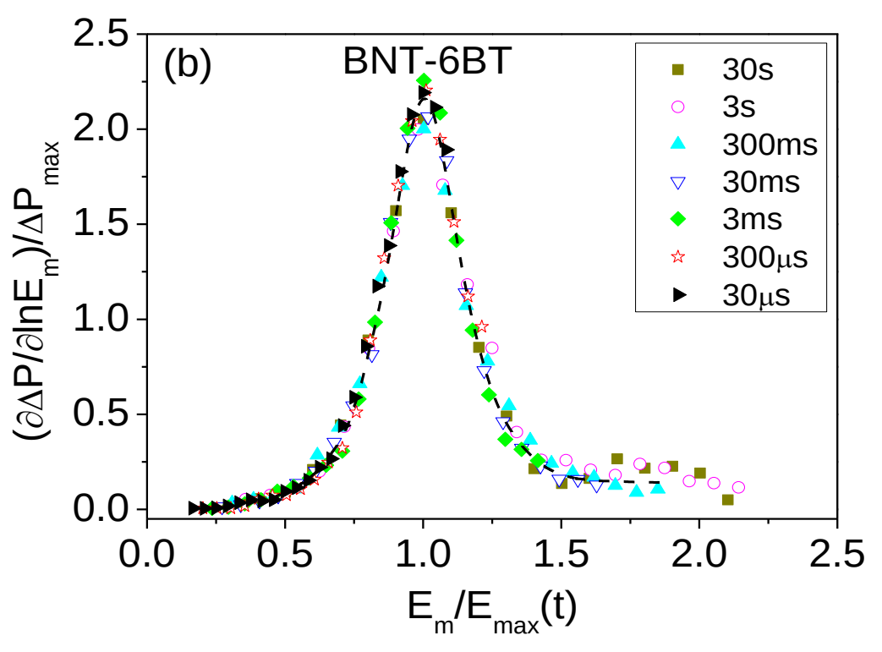


Fig. 3. Logarithmic derivatives for different times fall on the same master curve

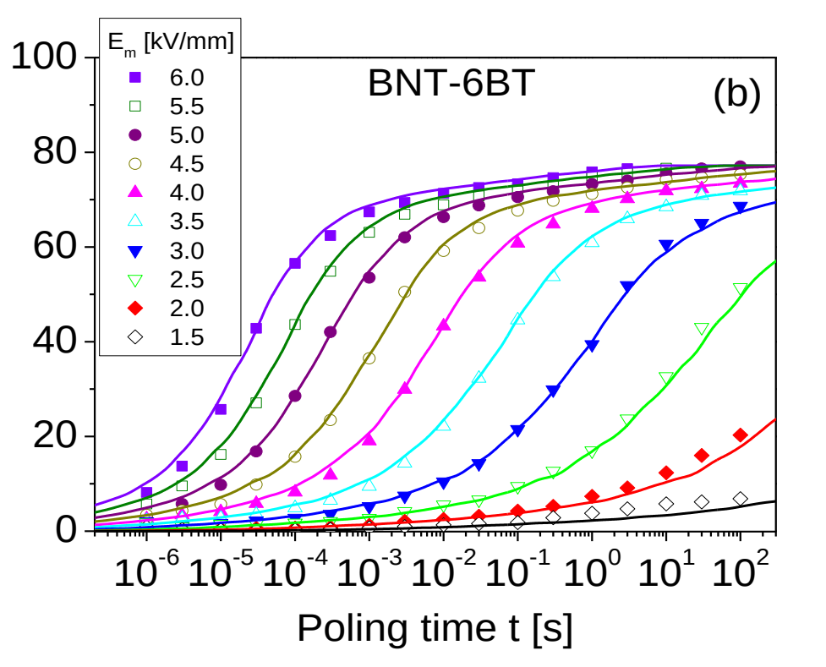
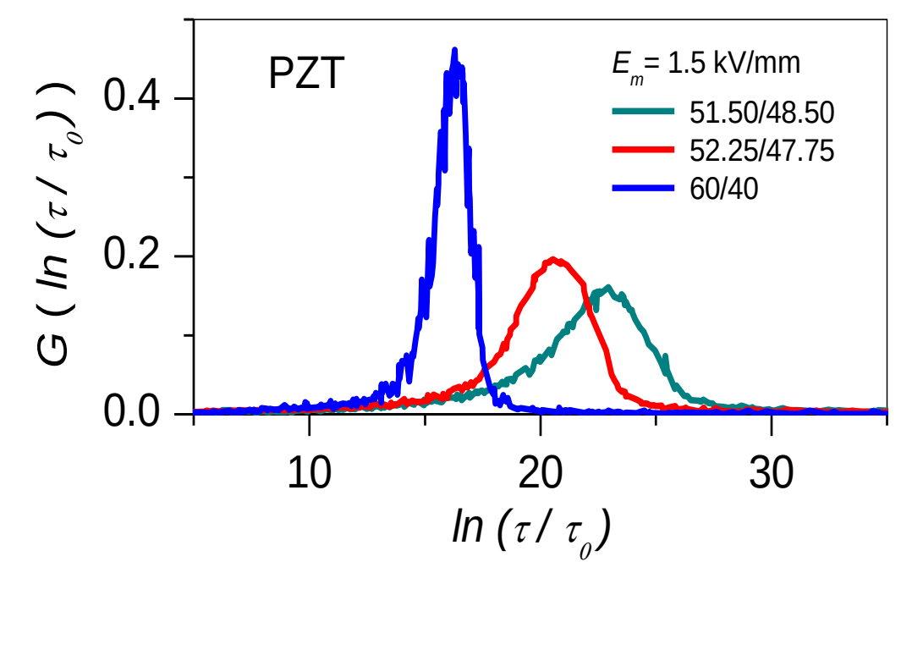
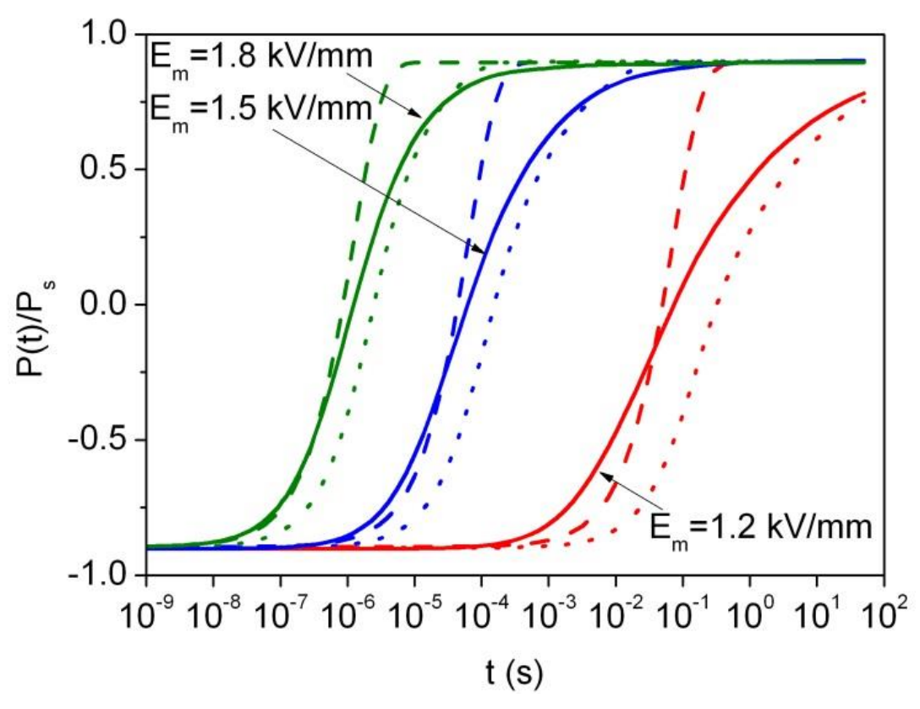


Fig.4. Dynamic polarization curves symbols and they description by IFM model (solid lines).

Polarization switching dynamics in ferroelectrics represented by distributions of polarization switching times exhibits strong dependence on the phase symmetry as revealed by IFM analysis (Fig. 5). Rhombohedral PZT compound (60/40) demonstrates polarization switching which is two orders of the magnitude faster than by the tetragonal one (51.50/48.80)[9]



The role of spatial disorder of the dielectric tensor and evolution of depolarization fields were studied numerically using FEM (Fig. 6)[7]. Polarization switching according to the KAI-law (dashed lines) compared to the response of systems with spatially disordered polarization directions and either isotropic (dotted lines) or anisotropic (solid lines) dielectric tensor for three different values of the applied field is shown.



Publications from the last funding period (2011-2014)

1) S.V. Yampolskii, Y.A. Genenko, C. Melzer, and H. von Seggern, “Self-consistent model of unipolar transport in organic semiconductor diodes: accounting for a realistic density-of-states distribution”, *J. Appl. Phys.* **109**, 073722/1-5 (2011).
2) C. Melzer, Y.A. Genenko, S.V. Yampolskii, K. Stegmaier, O. Ottinger, and H. von Seggern, “Charge carrier injection and transport in OLEDs: single-particle versus mean-field approach”, *J. Photonics for Energy* **1**, 011014/1-9 (2011).
3) K. Stegmaier, A. Fleissner, H. Janning, S.V. Yampolskii, C. Melzer, and H. von Seggern, “Influence of electrical fatigue on hole transport in poly(*p*-phenylenevinylene)-based organic light-emitting diodes”, *J. Appl. Phys.* **110**, 034507/1-9 (2011).
4) J. Schütrumpf, S. Zhukov, Y.A. Genenko, and H. von Seggern, “Polarization switching dynamics by inhomogeneous field mechanism in ferroelectric polymers”, *J. Phys. D: Appl. Phys.* **45**, 165301/1-6 (2012).
5) Y.A. Genenko, S. Zhukov, S.V. Yampolskii, J. Schütrumpf, R. Dittmer, W. Jo, H. Kungl , M.J. Hoffmann, and H. von Seggern, “Universal polarization switching behavior of disordered ferroelectrics”, *Adv. Func. Mat.* **22**, 2058-2066 (2012).
6) J. Glaum, Y.A. Genenko, H. Kungl, L.A. Schmitt, and T. Granzow, “De-aging of Fe-doped lead-zirconate-titanate ceramics by electric field cycling: 180°- vs. non-180° domain wall processes”, *J. Appl. Phys.* **112**, 034103/1-9 (2012).
7) Y.A. Genenko, J. Wehner, and H. von Seggern, “Self-consistent model of polarization switching kinetics in disordered ferroelectrics”, *J. Appl. Phys.* **114**, 084101/1-6 (2013).
8) S. Zhukov, Y.A. Genenko, M. Acosta, H. Humburg, W. Jo, J. Rödel, and H. von Seggern, “Polarization dynamics across the morphotropic phase boundary in Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$-x(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ ferroelectrics”, *Appl. Phys. Lett.* **103**, 152904/1-5 (2013).
9) S. Zhukov, H. Kungl, Y.A. Genenko, and H. von Seggern, “Statistical electric field and switching time distributions in PZT1Nb2Sr ceramics: crystal- and microstructure effects”, *J. Appl. Phys.* **115**, 014103 (2014).
10) Y. Zuo, Y.A. Genenko, A. Klein, P. Stein, and B.X. Xu, “Domain wall stability in ferroelectrics with space charges”, *J. Appl. Phys.* **115**, 084110 (2014).
11) Y.A. Genenko, O. Hirsch, and P. Erhart, “Surface potential at a ferroelectric grain boundary due to asymmetric screening of depolarization fields”, *J. Appl. Phys.* **115**, 104102 (2014).
12) Y. Zuo, Y.A. Genenko, and B.X. Xu, “Charge compensation of head-to-head and tail-to-tail domain walls in barium titanate and its influence on conductivity”, *J. Appl. Phys.* **116**, 044109 (2014).
13) Y.M. Nikolaenko, Y.E. Kuzovlev, Y.V. Medvedev, N.I. Mezin, C. Fasel, A. Gurlo, L. Schlicker, T.J.M. Bayer, and Y.A. Genenko, “Macro- and microscopic properties of strontium doped indium oxide”, *J. Appl. Phys.* **116**, 043704 (2014).

5 Key Publications (2003-2014)

1) F. Neumann, Y.A. Genenko, C. Melzer, S.V. Yampolskii, and H. von Seggern, “Self-consistent analytical solution of a problem of charge-carrier injection at a conductor/ insulator interface”, *Phys. Rev. B* **75**, 205322/1-10 (2007).
2) Y.A. Genenko, “Space-charge mechanism of aging in ferroelectrics: an analytically solvable two-dimensional model”, *Phys. Rev. B* **78**, 214103/1-7 (2008).
3) Y.A. Genenko, S.V. Yampolskii, C. Melzer, K. Stegmeier, and H. von Seggern, “Charge carrier injection into the insulating media: single particle versus mean-field approach”, *Phys. Rev. B* **81**, 125310/1-15 (2010) .
4) S. Zhukov, Y.A. Genenko, O. Hirsch, J. Glaum, T. Granzow, and H. von Seggern, “Dynamics of polarization reversal in virgin and fatigued ferroelectric ceramics by inhomogeneous field mechanism”, *Phys. Rev. B* **82**, 014109/1-8 (2010).
5) Y.A. Genenko, S. Zhukov, S.V. Yampolskii, J. Schütrumpf, R. Dittmer, W. Jo, H. Kungl , M.J. Hoffmann, and H. von Seggern, “Universal polarization switching behavior of disordered ferroelectrics”, *Adv. Func. Mat.* **22**, 2058-2066 (2012).