Phase-field modeling of coupled diffusion in ionic crystals

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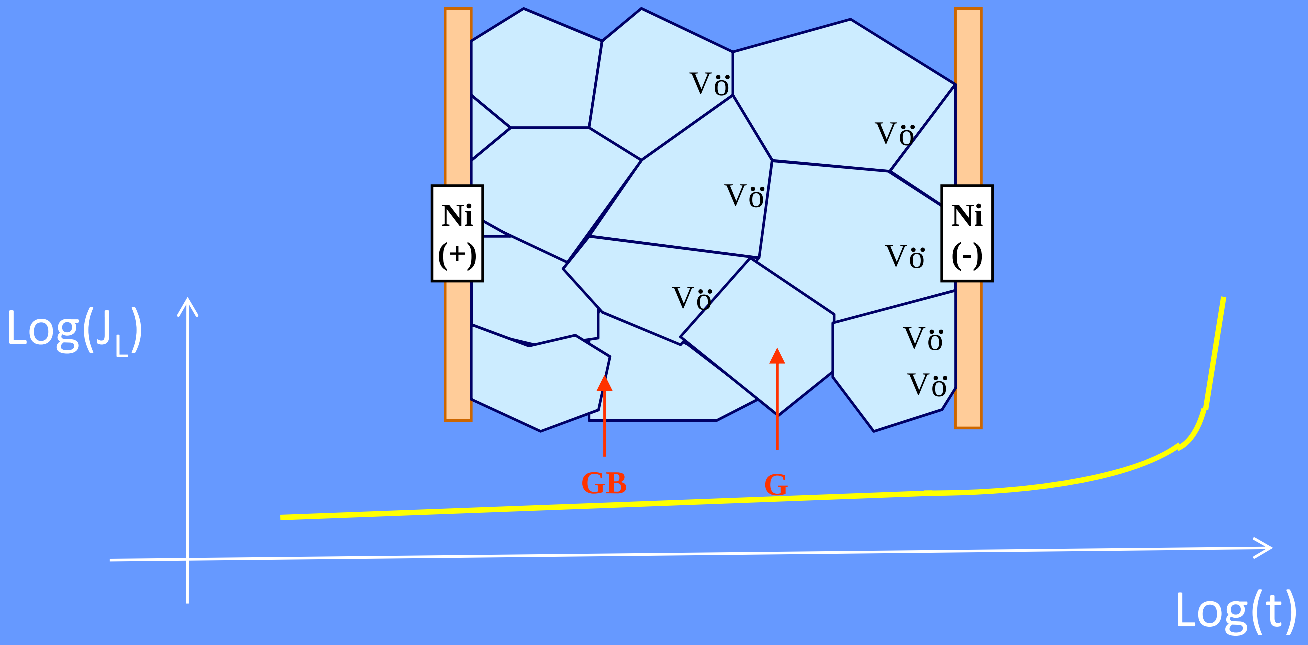
Outline

- Introduction to ionic/electronic transport in oxides – dielectric degradation, resistive switching, conductive-insulator transition, etc.
- Phase-field description of ionic/electronic transport, domain structures, and grain structures in the presence of inhomogeneous electric and stress fields
- Preliminary results on degradation modeling of $SrTiO_3$ and conductive-insulator transition in $BiFeO_3$
- Summary and future work

Ionic/electronic transport in oxides and dielectric degradation

Limiting factors for the improvement of life time for ceramics capacitors

--- ***Long-term resistance degradation***

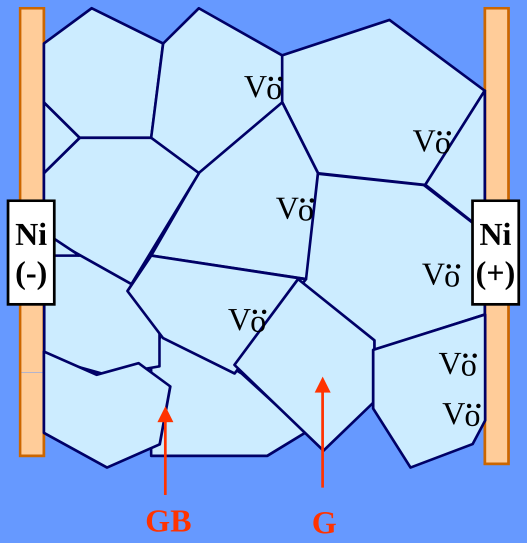


--- Currents increases slowly under an applied voltage stress below the critical breakdown voltage;

--- After a long time, the current increases dramatically, leading to the failure of the dielectrics.

Motivation for Modeling Dielectric Degradation

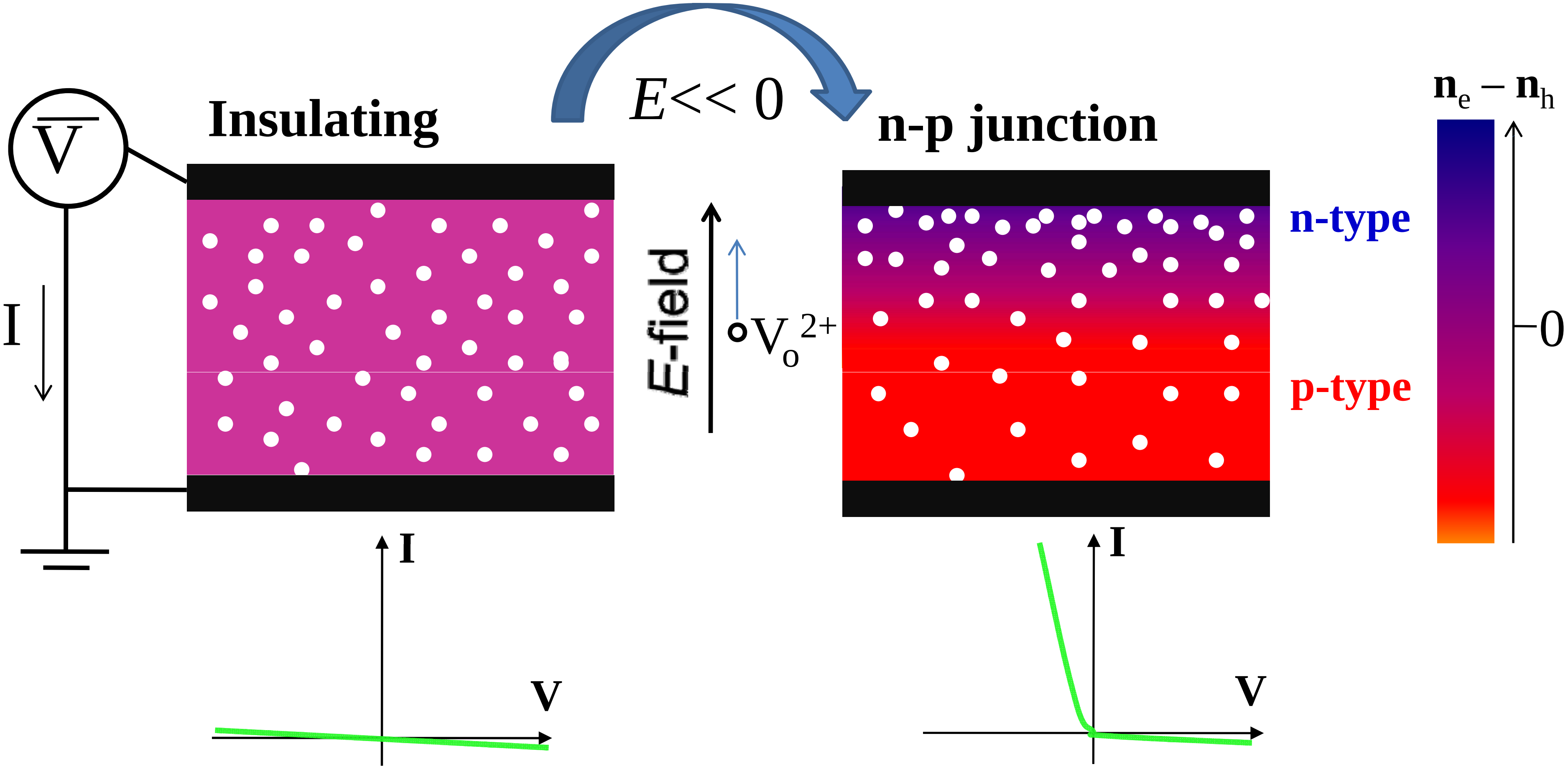
- Many factors influence the dielectric degradation, and experimentally it is almost impossible to isolate one particular parameter to study its effect on degradation:
    - dielectric microstructure
    - domain structure
    - temperature
    - composition
    - electrode microstructure
    - etc.



- Capacitor lifetimes are typically determined by highly accelerated tests (HALTS) in the paraelectric state. On the other hand, for the capacitors in-service, the polarization and the associated electrostrictive/piezoelectric strains may significantly affect local oxygen vacancy concentration and migration, and thus degradation

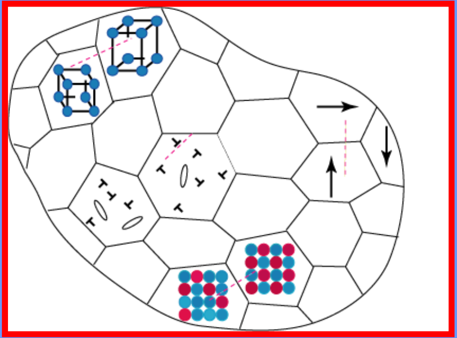
Mobile oxygen vacancies in a electric field

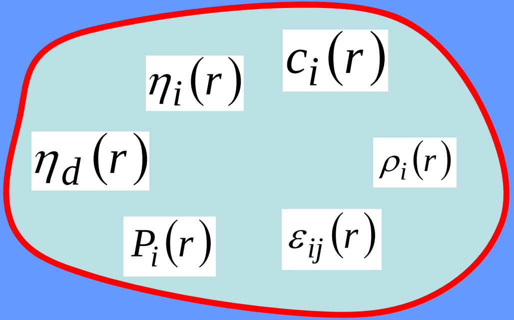
→ *Resistive switching or insulator-conductor transition*

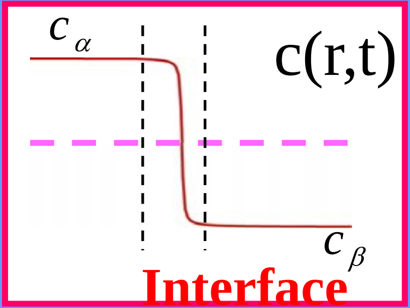


(J. Seidel and R. Ramesh, 2009)

Phase-field model of microstructures, domains, and ionic/electronic transport







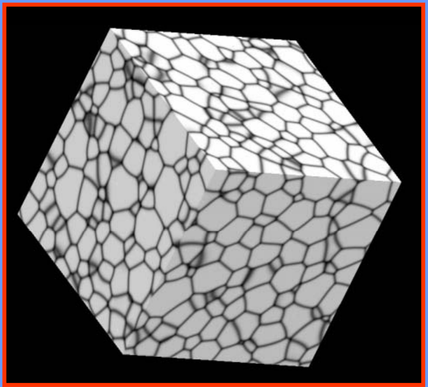
$$F = \int_V \left[f_b(c_i, \eta_i, \ldots) + f_g(\nabla c_i, \nabla \eta_i, \ldots) + f_{el}(c_i, \eta_i, \ldots) + \ldots \right] dV$$

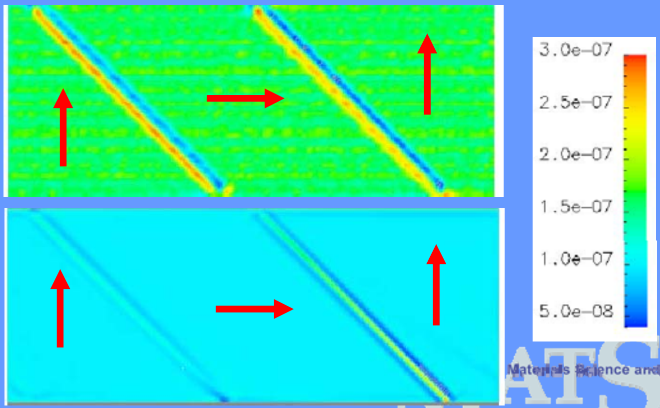
$$\frac{\partial P_i(r,t)}{\partial t} = -L \frac{\delta F_{total}}{\delta P_i(r,t)}$$

$$div\left[\boldsymbol{\kappa_o} \cdot \boldsymbol{E} + \boldsymbol{P}\right] = \sum_i \rho_i$$

$$div\left[\boldsymbol{c} \cdot \left(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon^o}\right)\right] = 0$$

$$\frac{\partial c_i(r,t)}{\partial t} = \nabla M_{ij} \nabla \frac{\delta F}{\delta c_j(r,t)}$$

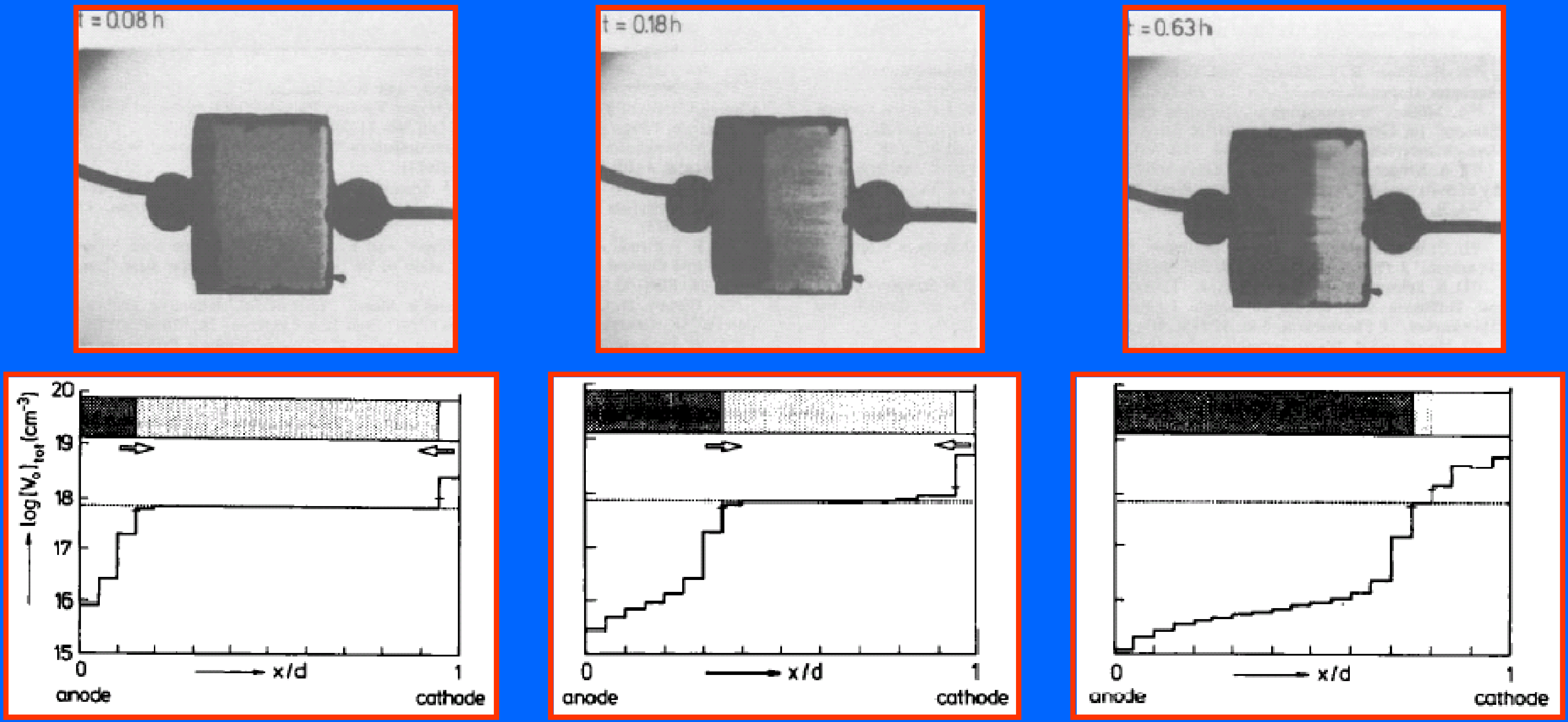




Complications of modeling ionic and electronic transport

- Many defect reactions are potentially operative
- The same defect can have several charge states
- Defect states at extended defects
- The mobility of different transporting species can be many orders of magnitude different
- The nature of the electrode/dielectric contacts
- Highly nonlinear equations

Evolution of Oxygen Vacancies in $SrTiO_3$ Single Crystal



The Fe-doped $SrTiO_3$ crystals appear almost colorless. During electrocoloration, deep red coloration front grows from the anode as (Fe^{3+} oxidized to Fe^{4+}), and bright region emerges at the cathode (small amount Fe^{4+} reduced to Fe^{3+}). Local oxidation or reduction are caused by electromigration of oxygen vacancies from anode to cathode.

R. Waser, T. Baiatu' and K.-H. Hardtl, *J. Am. Ceram. Soc.*, 73 [6], 1654-62, (1990)

Acceptor Doped Single-Crystal $SrTiO_3$

- The total concentration of Sr vacancies is assumed to be small compared to the concentration of foreign acceptor. Therefore, Sr vacancies are essentially ignored in the transport/degradation study.
- The oxidation/reduction reactions (gas-solid reactions) are only operative at high temperatures, e.g., above 700K.
- The foreign acceptors are assumed to be immobile
- The only mobile species are then oxygen vacancies, electrons and holes

$$O_o \rightarrow \frac{1}{2} O_2 + V_o^{\bullet\bullet} + 2e'$$

$$M^{\times} \rightarrow M' + h^{\bullet}$$

$$Null \rightarrow e' + h^{\bullet}$$

T. Baiatu, R. Waser, and K.-H. Hardtl, ***J. Am. Ceram. Soc.*****, 73, 1663, (1990)**

Couple Ionic Electronic Transport Model

$$-\nabla \bullet \left(eD_e \nabla n - en\mu_e \nabla \varphi\right) = 0$$

$$-\nabla \bullet \left(-eD_h \nabla p - ep\mu_h \nabla \varphi\right) = 0$$

$$-\nabla \bullet \left(-eD_i \nabla N_d - eN_d \mu_i \nabla \varphi\right) = e\,\partial N_d / \partial t$$

$$-\varepsilon\varepsilon_o \nabla^2 \varphi = e\left(-n + p + N_d - N_a\right)$$

Boundary Conditions

Ohmic interfaces for electrons and holes

Blocking interfaces for ions:

$$\varphi(x=0) = 0 \qquad \varphi(x=L) = V_a$$

Couple Ionic Electronic Transport Model

$$-\nabla \bullet \left(-eD_i \nabla N_d - eN_d \mu_i \nabla \varphi\right) = e\,\partial N_d / \partial t$$

$$-n + p + N_d - N_a = 0$$

$$-\nabla^2 \varphi = 0$$

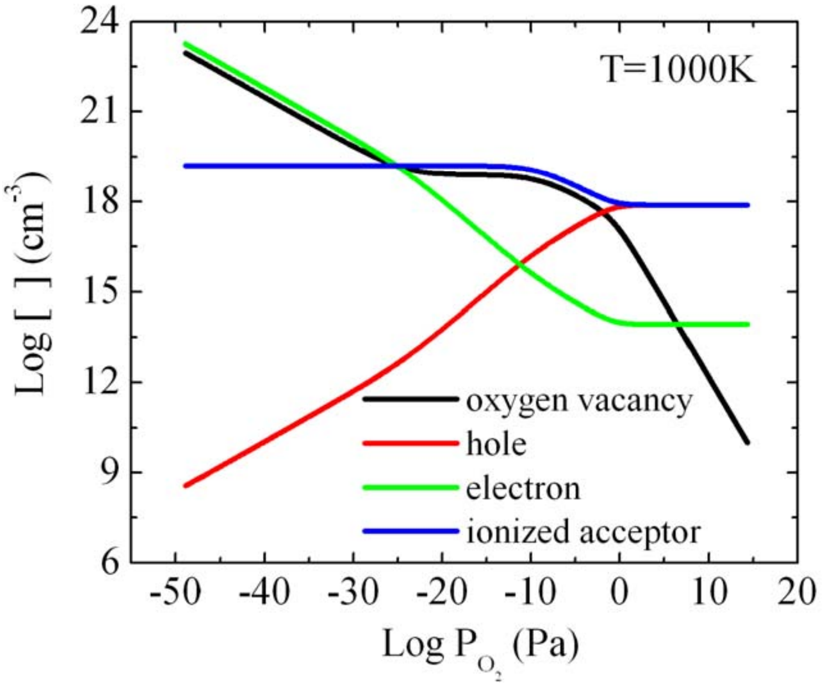
$$np = n_i^2$$

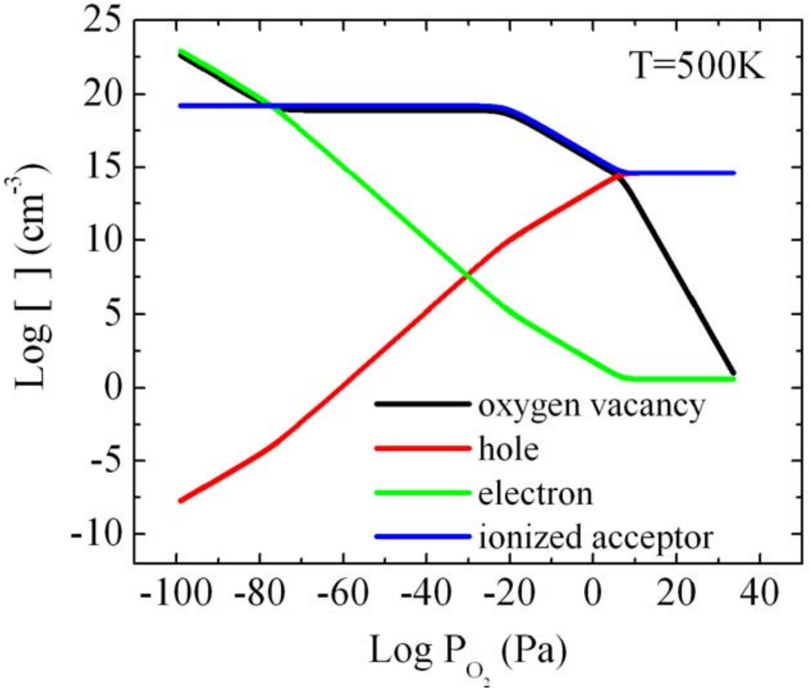
Blocking interfaces for ions

$$\varphi(x=0) = 0 \qquad \varphi(x=L) = V_a$$

Acceptor Doped Single-Crystal $SrTiO_3$

- Initial concentration of oxygen vacancy ~ 1.6×10^{18} cm^3
- Total acceptor concentration $[M]_{tot} = 1.6 \times 10^{19}$ cm^3
- Annealed at 1000 K and then degrade $T = 500$ K

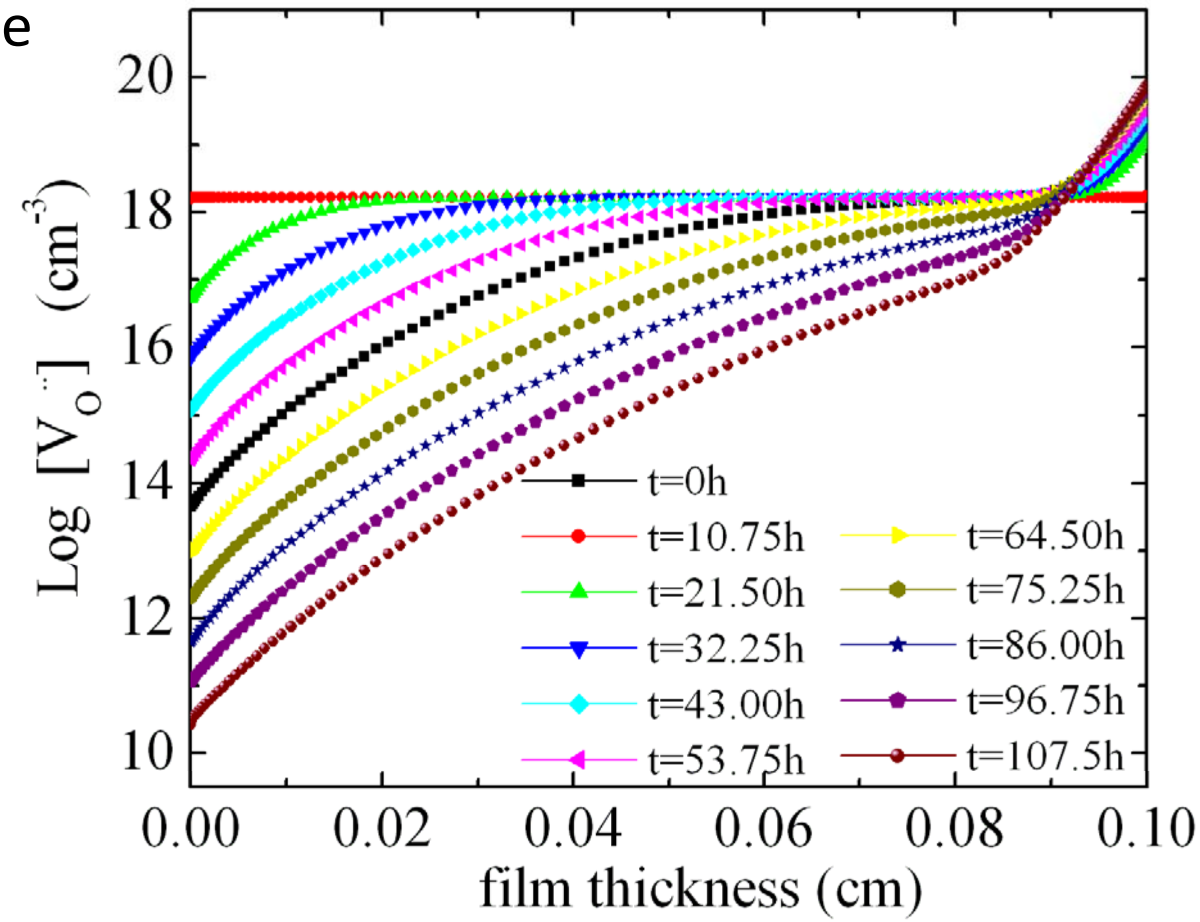




Temporal evolution of oxygen vacancy concentration

Anode

Cathode

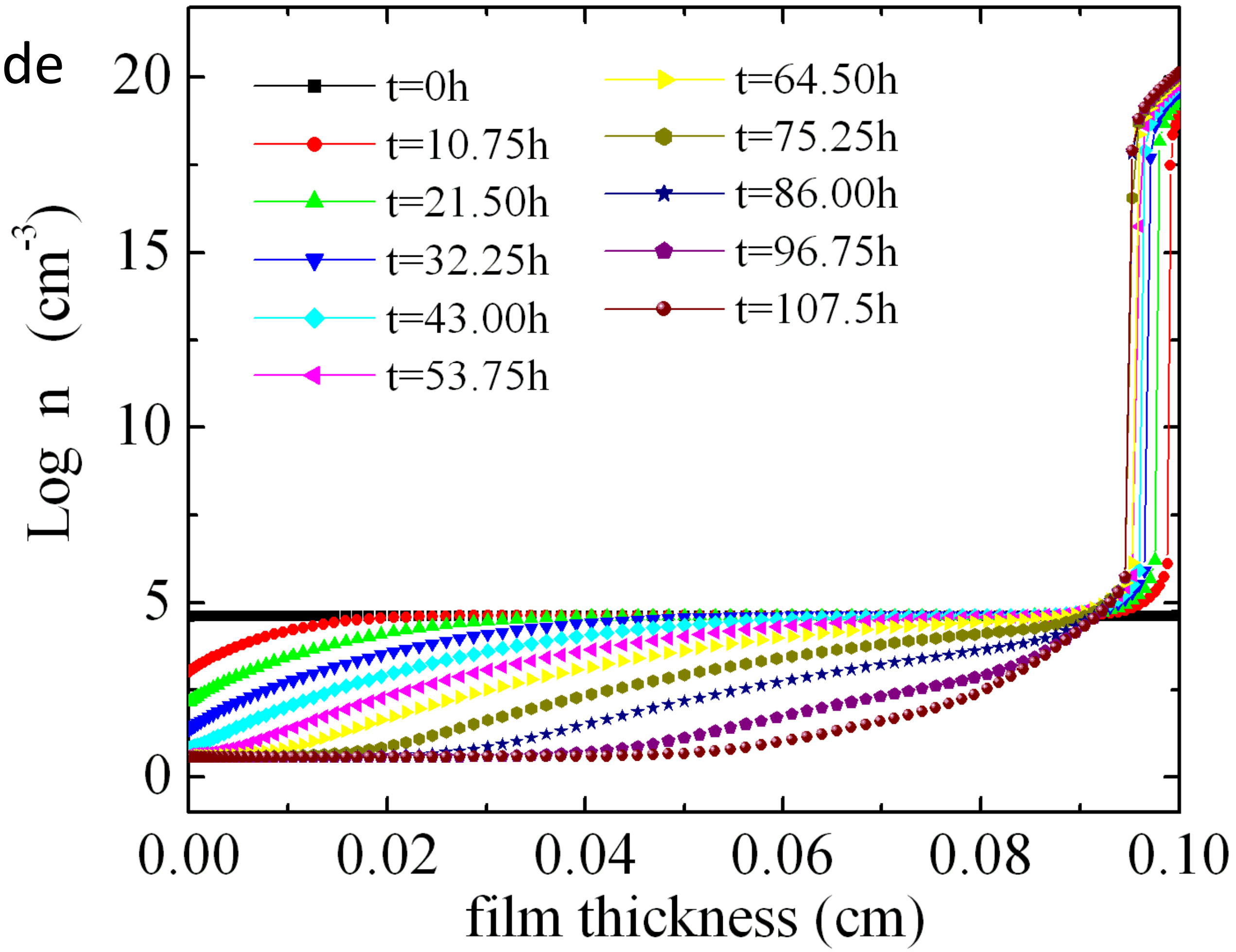


Under an applied field, the oxygen vacancies flow towards the cathode side, leading to higher concentration near the cathode and a depletion near the anode.

Temporal evolution of electron concentration

Anode

Cathode

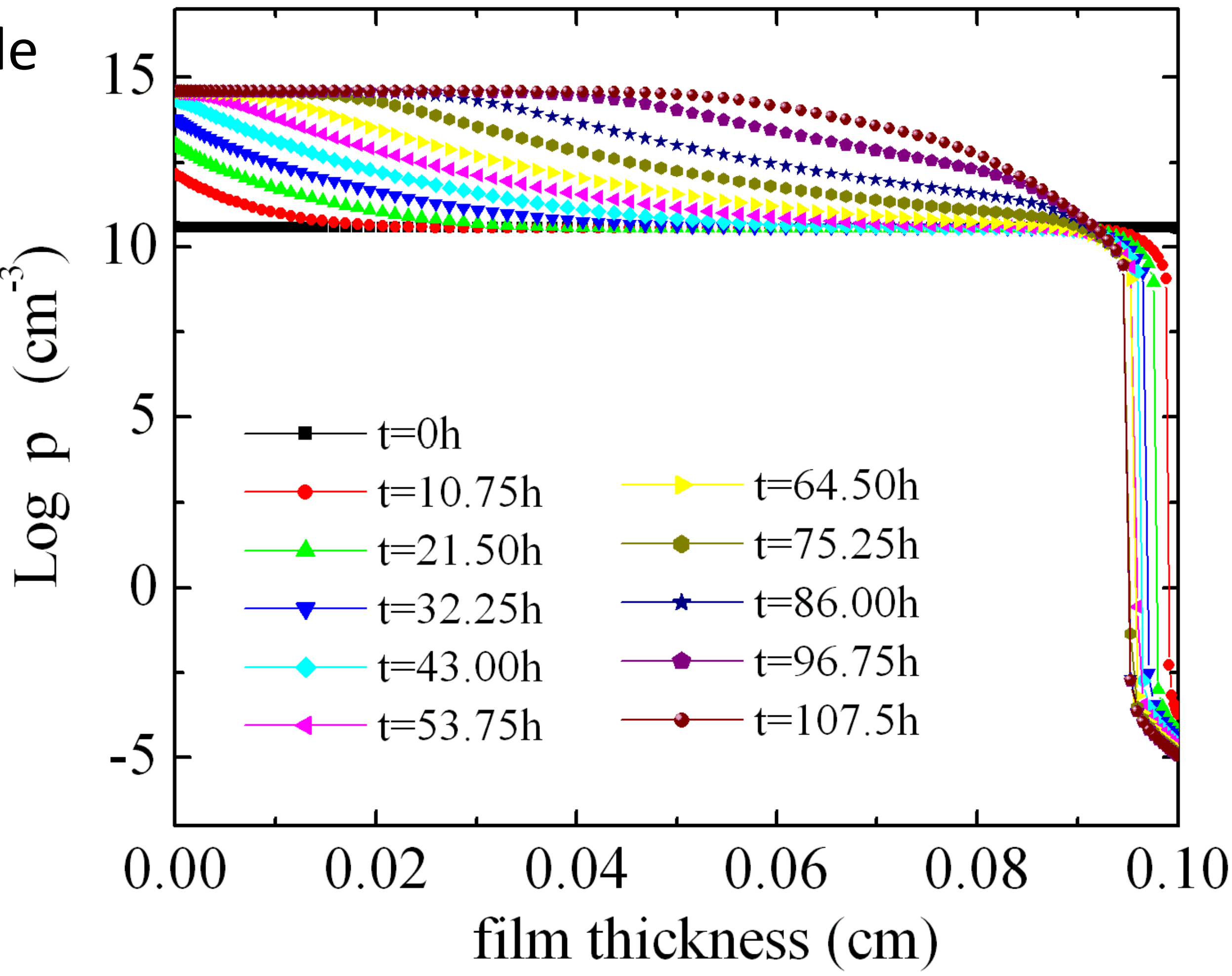


Electrons are accumulated near the cathode for charge compensation

Temporal evolution of hole concentration

Anode

Cathode

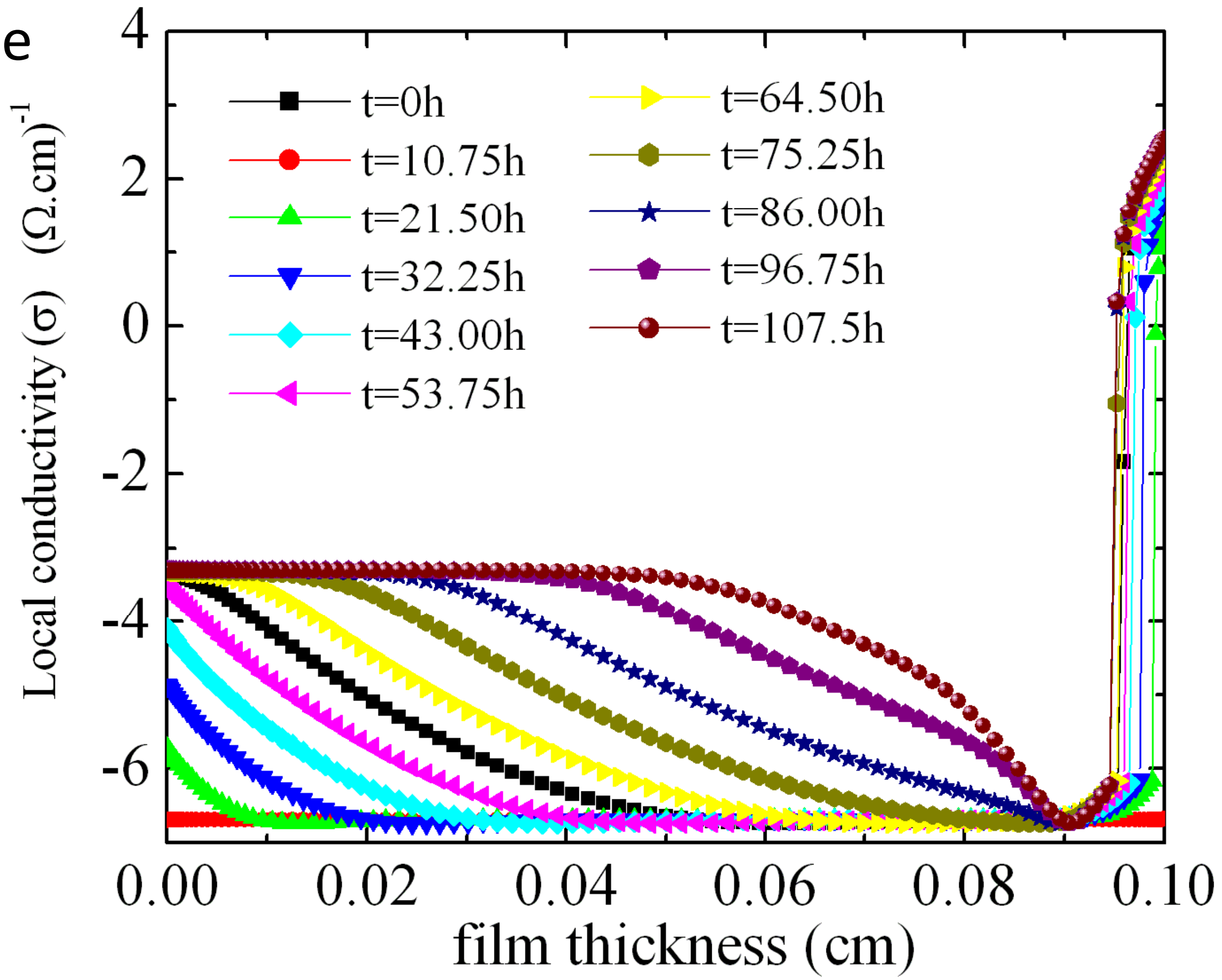


Holes are migrated to the anode for charge compensation

Local Conductivity Distribution

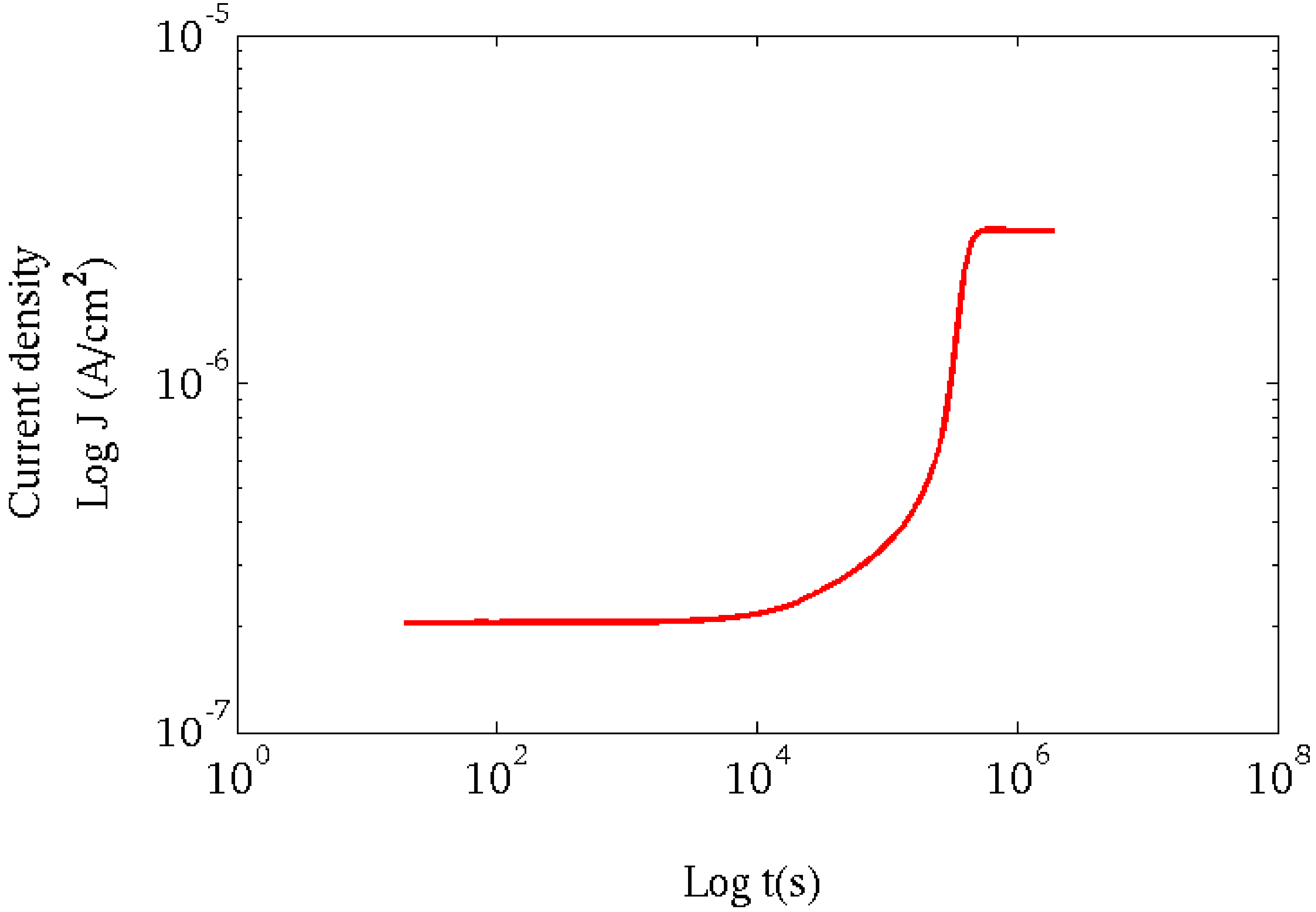
Anode

Cathode



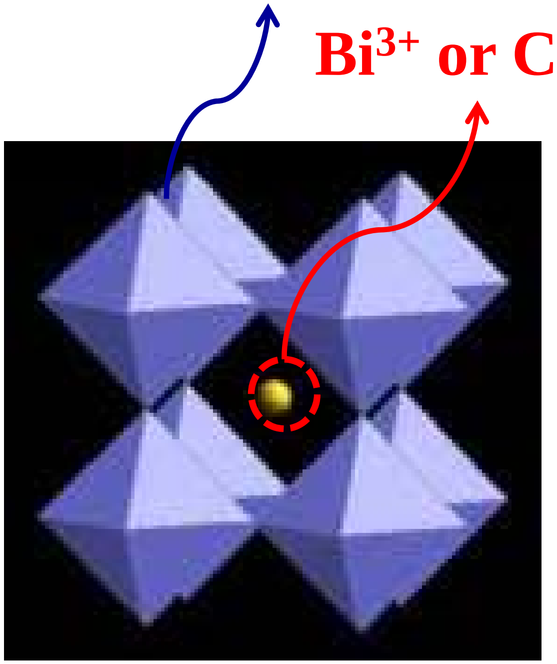
The increase of conductivity near the anode is due to the accumulation of holes near anode, while the increase in conductivity near the cathode side is caused by the significant increase of electron concentration

Current Density as a Function of Time



The slow increase of current density with time, followed by a significant increase of current density more than one order of magnitude

Insulator/Conductor Transition in Ca-doped Multiferroic $BiFeO_3$



FeO_6 octahedron

Bi^{3+} or Ca^{2+}

Oxygen vacancies produced

$Bi_{1-x}\underline{Ca}_xFeO_{3-\underline{\delta}}$

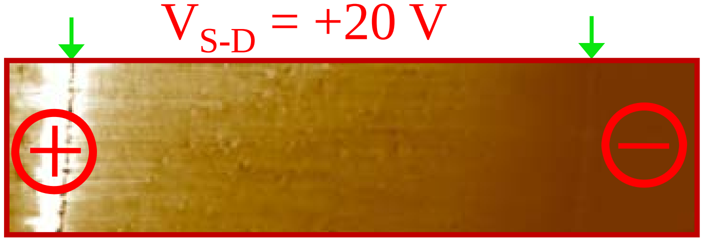
Acceptor **Donor**

$$CaO \rightarrow Ca_{Bi}^{'} + O_o^{\times} + \frac{1}{2}V_O^{\bullet\bullet}$$

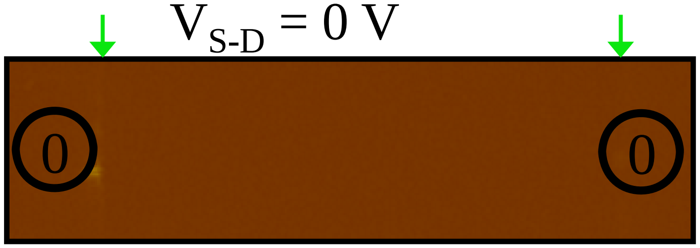
C. H. Yang et al, Nature Materials, Vol. 8, 485 (2009)

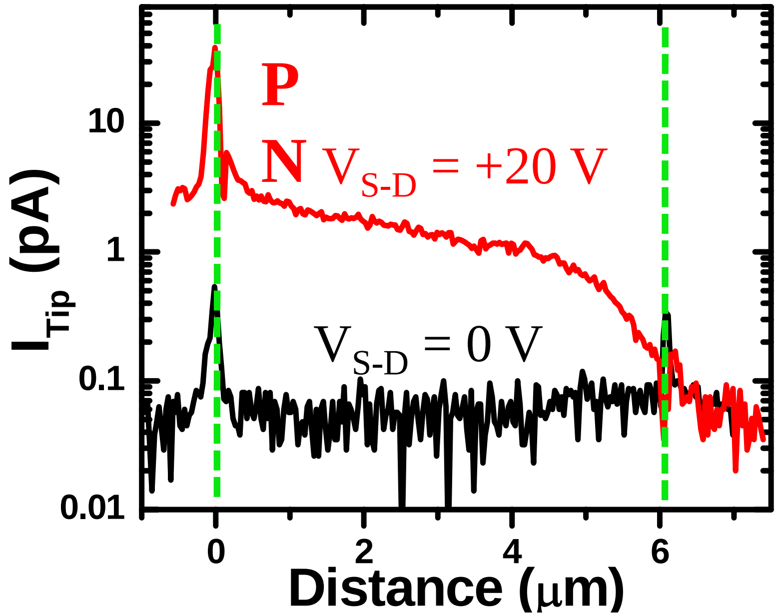
Local conductivity

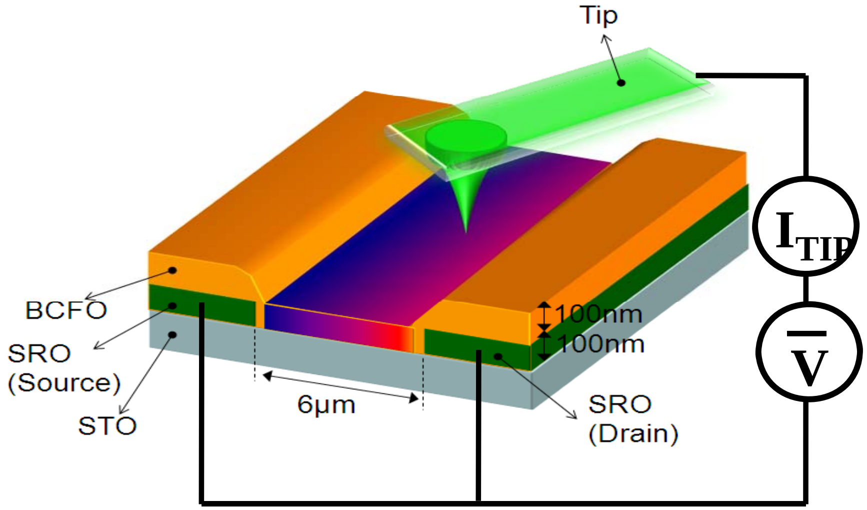
$V_{S\text{-}D}$ = +20 V



$V_{S\text{-}D}$ = 0 V







- **Measuring conductivity at -1.5 V**
- **p-type region → more conductive**

(J. Seidel and R. Ramesh, 2009)

Preliminary Computer Simulations

(In collaboration with R. Ramesh's group at UC Berkeley)

10%Ca-doped $BiFeO_3$ – $Bi_{0.9}Ca_{0.1}FeO_{2.95}$

Assuming initial, ionized solute and vacancy concentrations:

$$\left\lfloor V_O^{\bullet\bullet} \right\rfloor \sim 8 \times 10^{18}\, cm^{-3}$$

$$\left\lfloor Ca'_{Al} \right\rfloor \sim 1.6 \times 10^{19}\, cm^{-3}$$

Estimated mobility at T= 200°C (473K):

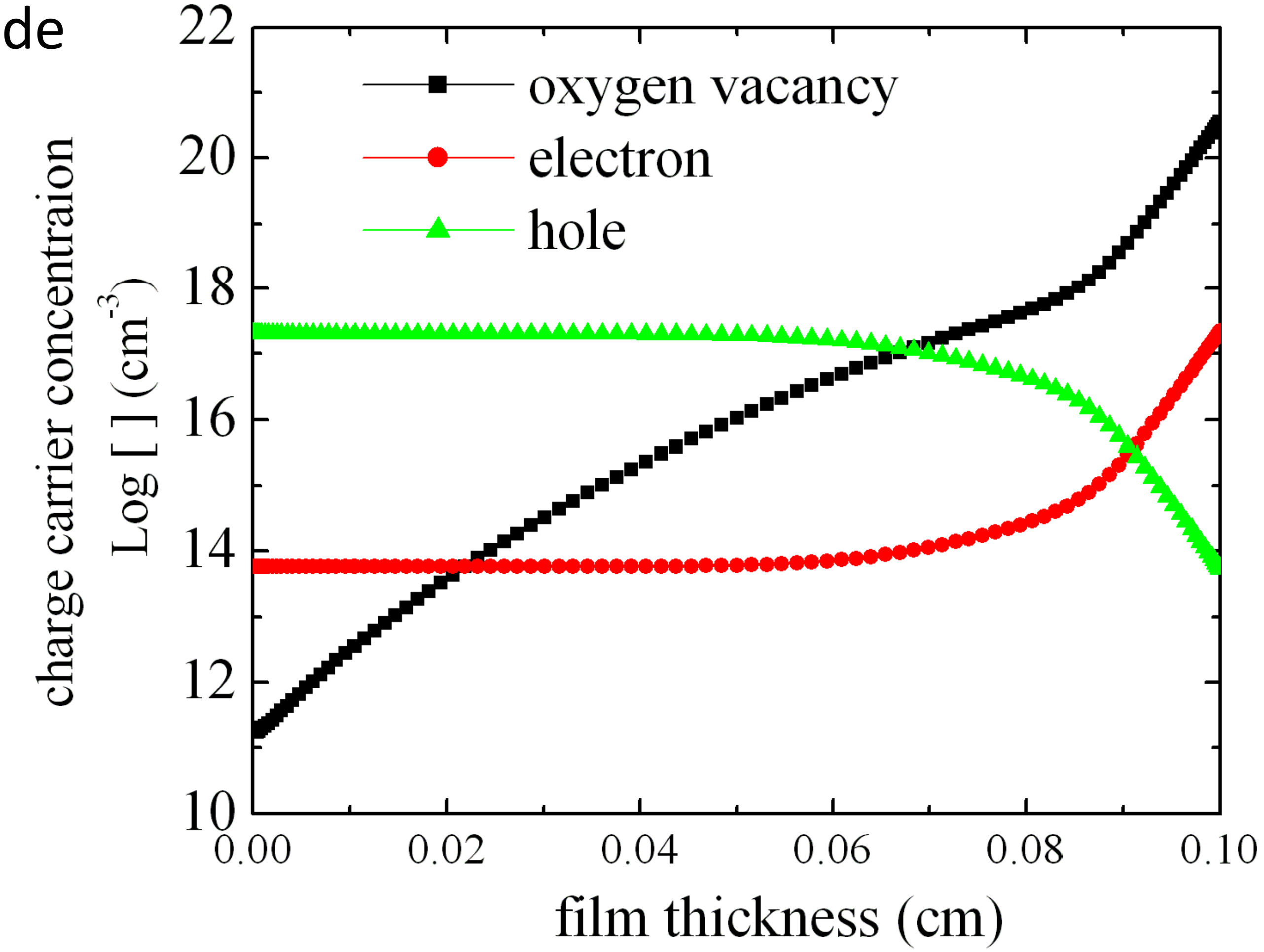
$$\mu_{V_O^{\bullet\bullet}} \sim 8 \times 10^{-11}\, cm^2 / (V \cdot s)$$

$$\mu_{h^{\bullet}} \sim 8 \times 10^{-4}\, cm^2 / (V \cdot s)$$

$$\mu_{e'} \sim 8 \times 10^{-5}\, cm^2 / (V \cdot s)$$

Charge Carrier Concentrations

Anode

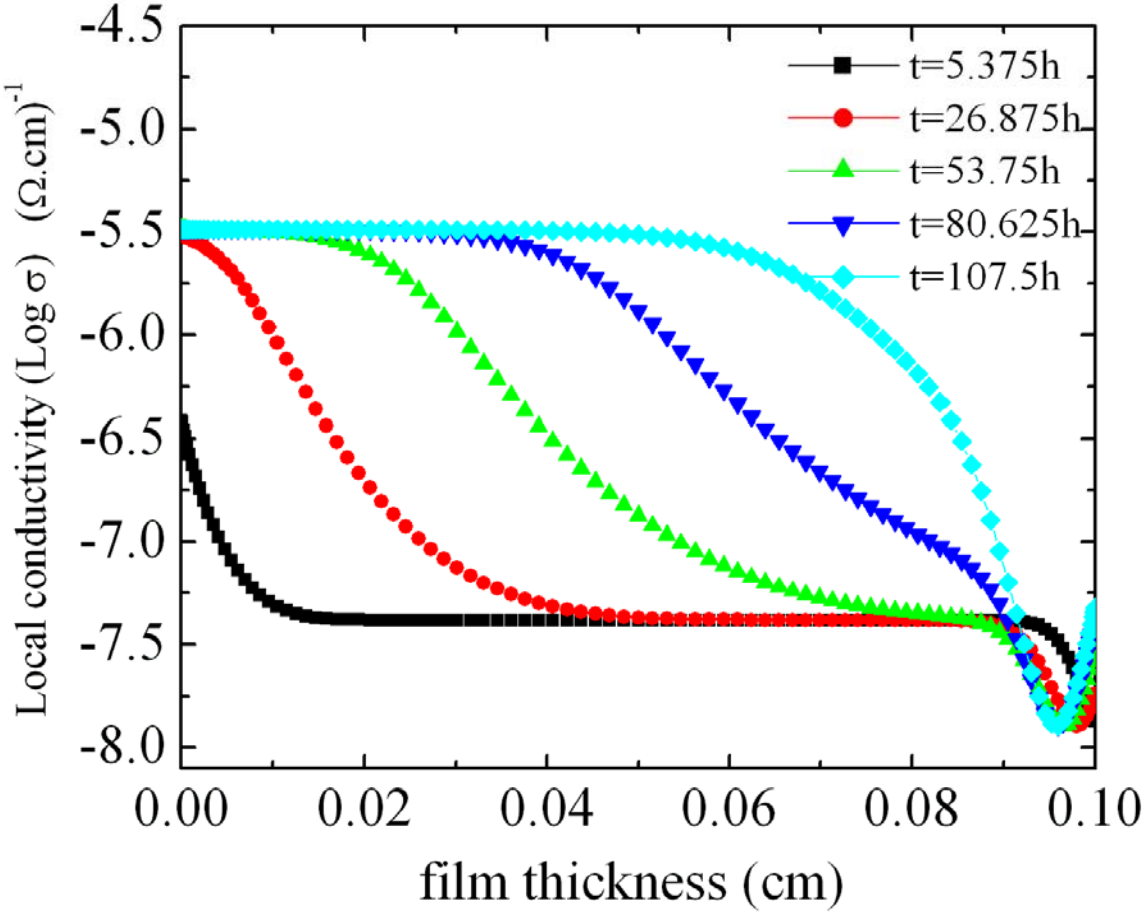


Cathode

Local Conductivity Distribution

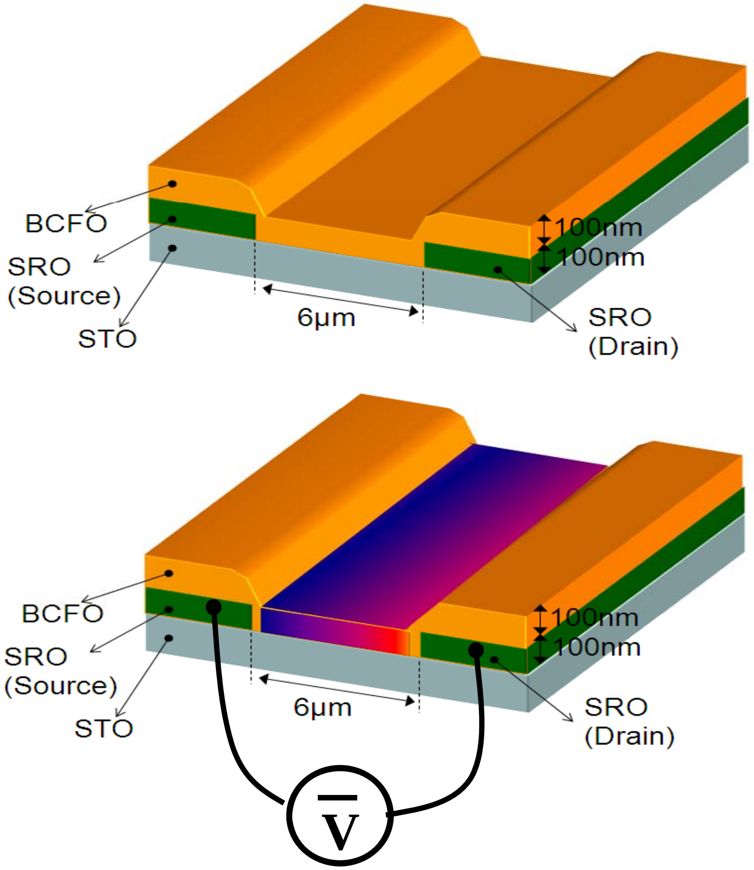
Anode

Cathode

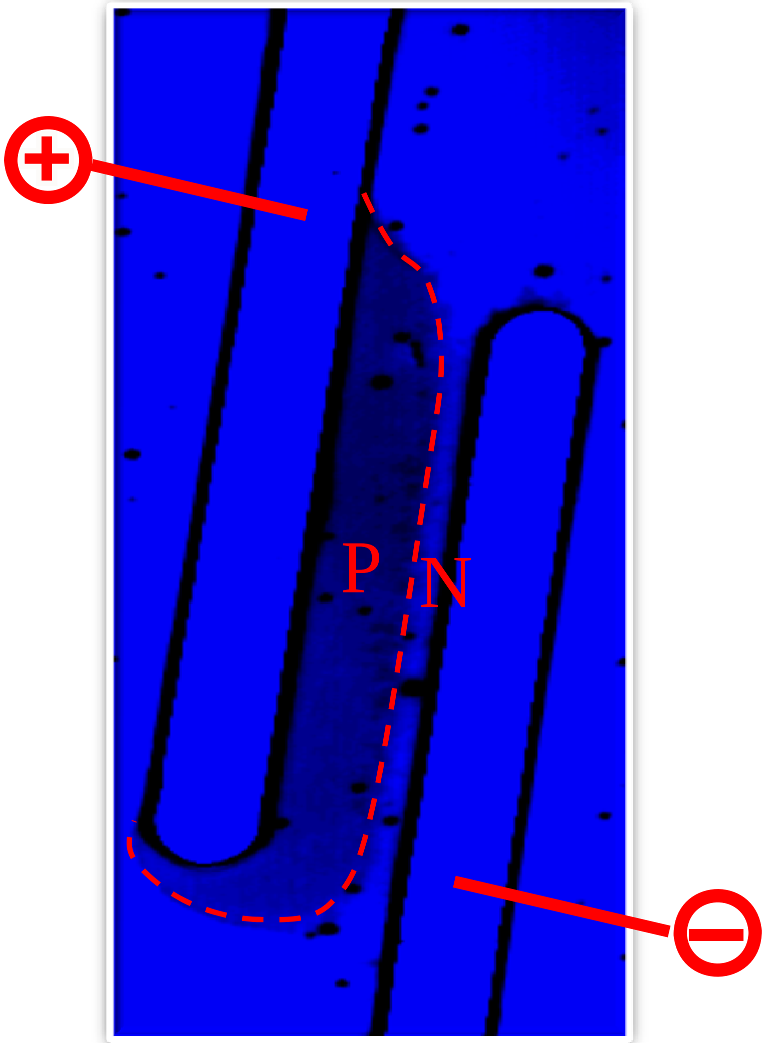


The increase of conductivity near the anode is due to the accumulation of holes near anode which has higher mobility than electrons in $BiFeO_3$

Optical contrast



- Applying voltage(~20V) at elevated temperature 200℃
- The sample is quenched to make the distribution frozen.



p-type region→ shade

Summary

- Based on the phase-field approach as well as basic thermodynamic and transport theories, we developed a preliminary computational model for investigating the effect of defects, space charges, domains, stress on ionic/electronic transport and thus dielectric degradation. The same set of computer codes , with slight modification, will be also applicable to resistive switching, conductor/insulator transition, electrochemical transport in oxide batteries, solid fuel cells, etc.
- Preliminary testing of the model and computer codes on degradation in acceptor-doped $SrTiO_3$ and insulator/conductor transition in Ca-doped $BiFeO_3$ shows very encouraging results
- Future works will include studying the effect of grain boundaries, ferroelectric domains, and stress on ionic/electronic transport on dielectric degradation