Self-consistent modelling of electrochemical strain microscopy in mixed ionic-electronic conductors: nonlinear and dynamic regimes

O.V. Varenyk[1], M.V Silibin[2], D.A Kiselev[3], E.A. Eliseev[4], S.V. Kalinin[5*], A.N. Morozovska[1†]

[1] *Institute of Physics, National Academy of Sciences of Ukraine, 46, pr. Nauki, 03028 Kyiv, Ukraine*

[2] *National Research University of Electronic Technology "MIET", 124498 Moscow, Russia*

[3] *National University of Science and Technology "MISiS", 119049 Moscow, Leninskiy pr. 4, Russia*

[4] *Institute for Problems of Materials Science, NAS of Ukraine,*
Krjijanovskogo 3, 03142 Kyiv, Ukraine

[5] *The Center for Nanophase Materials Sciences, Oak Ridge National Laboratory,*
Oak Ridge, TN 37831

Abstract

The frequency dependent Electrochemical Strain Microscopy (ESM) response of mixed ionic-electronic conductors is analyzed within the framework of Fermi-Dirac statistics and the Vegard law, accounting for steric effects from mobile donors. The emergence of dynamic charge waves and nonlinear deformation of the surface in response to bias applied to the tip-surface junction is numerically explored. The 2D maps of the strain and concentration distributions across the mixed ionic-electronic conductor and bias-induced surface displacements are calculated. The obtained numerical results can be applied to quantify the ESM response of Li-based solid electrolytes, materials with resistive switching and electroactive ferroelectric polymers, which are of potential interest for flexible and high-density non-volatile memory devices.

---

[*] Corresponding author: e-mail sergei2@ornl.gov

[†] Corresponding author: e-mail anna.n.morozovska@gmail.com

1. Introduction

The nanoscale properties of mixed conductors such as Li-based cathodes with mobile ions and electrons as free carriers, memristive materials such as titanates and manganites with mobile oxygen vacancies, and ionically-conductive ferroelectrics are intriguing and very important for fundamental research and numerous applications [1, 2, 3, 4, 5]. Energy storage and conversion now underpin multiple aspects of modern civilization, whereas non-volatile resistive memories hold the promise of beyond CMOS technologies. Beyond these applications, synthetic electroactive polymers are of great importance for a number of research fields including biocompatible tissue engineering and organic electronics [6, 7, 8].

Beyond the energy applications, electromechanical properties of mixed conductors are of particular interest. The coupling between electrical and mechanical phenomena is one of the fundamental processes manifested in physical objects ranging from ferroelectrics to biometric and biological systems [9]. Electromechanics refers to a broad class of phenomena in which mechanical deformation is induced by an external electric field, or, conversely, electric charge separation is generated by the application of an external force. In most materials, electromechanical activity is directly related to the structure and functionality which is important not only for applications, but also for material characterization. In polar compounds, local piezoelectric properties are strongly affected by polarizability, structural defects and mechanical properties. The progress in fundamental studies and technological applications of these materials depends on the ability to test their structural and functional properties at the nanoscale.

Progress in understanding nanoscale electromechanical phenomena has been achieved with the emergence of voltage-modulated scanning probe microscopy (SPM) techniques such as

Piezoresponse Force Microscopy [10, 11, 12, 13, 14, 15, 16 17, 18, 19, 20, 21] (PFM) and Electrochemical Strain Microscopy (ESM) [22, 23, 24, 25, 26, 27]. In PFM, the biased scanning probe microscopy tip creates an electric field in the small volume of material and further detects bias-induced piezoelectric surface deformation [10-21]. In ESM, the biased tip acts as a moving, electrocatalytically active probe exploring local electrochemical activity. Similarly to PFM, the probe concentrates an electric field in a nanometer-scale volume of material. The electric field alters the local electrochemical potential of the mobile (e.g. lithium) ions on the surface. This changes the local concentration of mobile ions by migration (field-driven) and diffusion (concentration gradient-driven) mechanisms. The associated changes in molar volume [28, 29] results in local electrochemical strains, and the resultant dynamic surface deformation is detected by SPM at the 2–5 pm level. For lithium-based materials, ESM can detect volume changes corresponding to complete the lithiation and delithiation on a single atomic layer, or ~5-10% changes in the lithium concentration within the ~20-nm region [22-27]. Experimentally, ESM was shown to resolve electrochemical activity in complex battery, fuel cell, and electroresistive materials with sub – 10 nm resolution, resulting in intense interest to this technique from scanning probe and electrochemical communities. However, applications of ESM necessitate quantitative understanding of local electromechanical responses as a necessary step to its emergence as quantitative local electrochemical probe.

The ESM signal formation mechanisms were extensively studied in linear approximation [30, 31, 32, 33]. The linear models explored the strain response due to Vegard strain and flexoelectric [30] effects and describe adequately its frequency spectrum. To explain the formation of the ESM hysteresis loops, one-dimensional [31] and two-dimensional analytical models [32] of linearized diffusion kinetics, and 2D analytical models that consider linearized drift-diffusion kinetics [33], were developed and were shown to yield the elliptic loop shapes with the "coercive" voltage (defined from the condition of zero response) determined by the applied bias. However, the origins of experimentally-observed ferroelectric-like hysteresis loops remain largely unexplained.

Here, we report self-consistent 2D-modeling of the local mechano-electro-chemical response of solid electrolytes utilizing kinetic theory and taking into account the steric effects for ions (or vacancies) [34, 35], thus including the most common form of the nonlinearity inherent to the system. To obtain further insight into the mechanisms of ESM image formation, we have developed a 2D analytical model of nonlinear drift-diffusion kinetics in ESM. Numerical finite element (FE) modeling for different frequencies and bias voltage amplitudes was performed in a 2D axially symmetric geometry. The obtained 2D maps provide the concentration and strain distributions with an account of the steric effects for the donor Vegard mechanism and electrostriction. These studies provide first insight into the role of non-linear mechanisms and exclusion effects play in ESM, opening pathway for realistic quantitative models.

2. The problem statement and basic equations

Here, we assume the decoupling approximation and ignore contributions of the strain to the ionic transport. The surface of the sample is assumed to be perfectly smooth without any irregularities or roughness. Note, that the aforementioned approximation works adequately for the calculations of solid electrolytes ESM responses, but for the extension of theory to electroactive polymers more nonlinear effects (such as a nonlinear electrostriction), the high order electro-mechanical couplings should be included.

In the case of a tip axial symmetry and homogeneous mixed ionic-electronic conductor all physical quantities depend only on the distance z from the tip-surface interface and polar radius *r* (**Fig.1**). Mobile positively charged point defects, and oxygen vacancies or cations, are further considered as *donors* for the free electrons.

The redistribution of mobile charge carriers creates the internal electric field **E**, where components $E_z = -\partial\varphi/\partial z$ and $E_r = -\partial\varphi/\partial r$ are defined by the electric potential, φ. The potential can be determined self-consistently from the Poisson equation in cylindrical coordinates:

$$\varepsilon_0\varepsilon\left(\frac{\partial^2\varphi}{\partial r^2}+\frac{1}{r}\frac{\partial\varphi}{\partial r}+\frac{\partial^2\varphi}{\partial z^2}\right)=-e\left(Z_d N_d^+(\varphi)-n(\varphi)\right) \qquad (1)$$

Here $\varepsilon_0=8.85\times10^{-12}$ F/m the dielectric permittivity of vacuum; ε is a dielectric permittivity of the mixed ionic-electronic conductor (MIEC), that is regarded as isotropic, electron density is *n*, donor concentrations N_d^+, $e=1.6\times10^{-19}$ C which is the electron charge, and Z_d is the donor charge which is equal to zero for the uncharged vacancies or isovalent impurities. The electric potential satisfies the fixed boundary conditions at the electrodes, $\left.\varphi\right|_{z=h}=U(r,t)$, $\left.\varphi\right|_{z=0}=0$, $\left.\varphi\right|_{r=R}=0$, which corresponds to the MIEC film of thickness *h*.

A periodic voltage *U* is applied to the top electrode. Here, we adopt the Gaussian form , $U(r,t)=U_0\exp\left(-r^2/r_0^2\right)\sin(\omega t)$ to model the localized field and assume that the tip's lateral size r_0 is much smaller than the size of the computation cell *R*, i.e. $r_0 << R$. We carefully checked to see if our numerical results are similar for different radially-symmetric well-localized potential distributions at the MIEC surface z=h, but only the surface area of the potential drop is the same and equal to $r_0 << R$ as used in the manuscript (e.g. for Gaussian, stretched exponential and shielded disk-surface contact). The choice Gaussian distribution is chosen both for simplicity, and for close matching to experimental situation where the tip potential is screened by surface electrochemical charges. Note that more realistic cases including sphere geometry for the probe will necessitate the surface screening phenomena be taken into account as well. Also the potential drops, and its fixing at the surface cannot be directly related with a realistic tip shape in an arbitrary case -to do this, a self-consistent modeling of the three-layer problem is required. But even in this case much is dependant on the surface screening by the sluggish charges. The Gaussian function gives results close to the model situation of a disk radius r_0 in a perfect contact with a "shielded" surface under zero electric potential.

The continuity equation for the donor concentration N_d^+ is:

$$\frac{\partial N_d^+}{\partial t}+\frac{1}{eZ_d}\left(\frac{1}{r}\frac{\partial(rJ_r^d)}{\partial r}+\frac{\partial J_z^d}{\partial z}\right)=0, \tag{2}$$

The donor current J_d has radial and normal components which are proportional to the gradients of the carrier electrochemical potentials levels ζ_d as $J_r^d=-eZ_d\eta_d N_d^+\left(\partial\zeta_d/\partial r\right)$ and $J_z^d=-eZ_d\eta_d N_d^+\left(\partial\zeta_d/\partial z\right)$, where η_d is the ion's/vacancy's mobility coefficient which is regarded as constant. The boundary conditions for the donors are ion-blocking $J_d\big|_{z=0}=0$, $J_d\big|_{z=h}=0$, $J_d\big|_{r=R}=0$.

The electrochemical potential level ζ_d is given by [36]:

$$\zeta_d=-E_d-W_{ij}^d\sigma_{ij}+eZ_d\varphi+k_BT\ln\left(\frac{N_d^+}{N_d^0-N_d^+}\right). \tag{3}$$

Here E_d is the donor level, elastic stress tensor is σ_{ij}, T is the absolute temperature, k_B is the Boltzmann constant, W_{ij}^d is the Vegard strain tensor (another name for elastic dipole). Hereafter, the Vegard tensor is assumed to be diagonal, i.e. $W_{ij}^{d}=W\delta_{ij}$ (δ_{ij} is delta Kroneker symbol). The absolute values of W for ABO$_3$ compounds can be estimated as $|W|\propto$ (1 – 50) Å^3 [37, 38]. The maximum possible concentration of donors is N_d^0 defines the steric effects in the system and limits the donor accumulation in the vicinity of film surfaces [34, 35]. For numerical estimates $N_k^0\equiv a^{-3}$, where a^3 is the maximum volume allowed per donor centre.

The continuity equation for electrons is:

$$\frac{\partial n}{\partial t}-\frac{1}{e}\left(\frac{1}{r}\frac{\partial(rJ_r^e)}{\partial r}+\frac{\partial J_z^e}{\partial z}\right)=0 \tag{4}$$

The electron current has radial and normal components which are $J_r^e=e\eta_e n\left(\partial\zeta_e/\partial r\right)$ and $J_z^e=e\eta_e n\left(\partial\zeta_e/\partial z\right)$ respectively, η_e is the electron mobility coefficient, ζ_e is the electro-chemical potential. The boundary conditions for electrons are taken in the linearized Chang-Jaffe (CJ) [39] form, $\left.\left(J_z^e-\xi_0(n-n_b)\right)\right|_{z=0}=0$, $\left.\left(J_z^e+\xi_h(n-n_b)\right)\right|_{z=h}=0$, $\left.J_e\right|_{r=R}=0$, where $\xi_{0,h}$ is the positive rate constant related with the surface recombination velocity. The CJ condition contains the continuous transition from the “open” electrode ($\xi_{0,h}\to\infty\Rightarrow n=n_0$) to the interface limited kinetics ($0<\xi_{0,h}<\infty$). “Completely blocking” electrodes are defined by the condition $\xi_{0,h}=0$.

The continuous approximation for the electron concentration in the conduction band can be described by the following expression for electro-chemical potential [36]:

$$\zeta_e\approx E_C+k_BT\,F_{1/2}^{-1}\left(\frac{n(\varphi)}{N_C}\right)-e\varphi, \tag{5}$$

valid for parabolic band model. The electro-chemical potential ζ_e tends to the Fermi energy level E_F in equilibrium, E_C is the bottom of the conduction band, $F_{1/2}^{-1}$ is the function inverse to the Fermi integral $F_{1/2}(\xi)=\frac{2}{\sqrt{\pi}}\int_0^{\infty}\frac{\sqrt{\zeta}d\zeta}{1+\exp(\zeta-\xi)}$; effective density of states in the conduction band $N_C=\left(\frac{m_n k_B T}{2\pi\hbar^2}\right)^{3/2}$, and the electron effective mass is m_n. Electron density can be calculated from Eq. (5) as $n=N_C F_{1/2}\left((e\varphi+\zeta_e-E_C)/k_B T\right)$. Note, that the deformation potential effect, (analog of the Vegard effect for electrons), is neglected in Eq. (5) for the sake of simplicity.

Using the electrochemical potential $\zeta_{d,e}$, dependent concentration of donors, $N_d^+=N_d^0 f\left(-E_d-W\sigma+eZ_d\varphi-\zeta_d\right)$, and electrons, $n=N_C F_{1/2}\left((e\varphi+\zeta_e-E_C)/k_B T\right)$, one can express the potentials as the functions of donor and electron chemical potentials $\mu_d=eZ_d\varphi-\zeta_d-W\sigma$ and $\mu_e=e\varphi+\zeta_e$ as $N_d^+=N_d^0 f\left(\mu_d-E_d\right)$and $n=N_C F_{1/2}\left((\mu_e-E_C)/k_B T\right)$. Here $f(x)=\left(1+\exp(x/k_B T)\right)^{-1}$ is the Fermi-Dirac distribution function. The spur of the stress tensor (that is invariant) is introduced as $\sigma=\sigma_{zz}+\sigma_{rr}+\sigma_{\varphi\varphi}$.

Coupled Eqs. (2) and (4) have the following form:

$$\frac{\partial f\left(\mu_d-E_d\right)}{\partial t}-\frac{1}{r}\frac{\partial}{\partial r}\left(r\eta_d f\left(\mu_d-E_d\right)\frac{\partial\left(eZ_d\varphi-\mu_d-W\sigma\right)}{\partial r}\right)-\frac{\partial}{\partial z}\left(\eta_d f\left(\mu_d-E_d\right)\frac{\partial\left(eZ_d\varphi-\mu_d-W\sigma\right)}{\partial z}\right)=0 \quad (6)$$

$$\frac{\partial}{\partial t}F_{1/2}\left(\frac{\mu_e-E_C}{k_B T}\right)-\frac{1}{r}\frac{\partial}{\partial r}\left(r\eta_e F_{1/2}\left(\frac{\mu_e-E_C}{k_B T}\right)\frac{\partial\left(\mu_e-e\varphi\right)}{\partial r}\right)-\frac{\partial}{\partial z}\left(\eta_e F_{1/2}\left(\frac{\mu_e-E_C}{k_B T}\right)\frac{\partial\left(\mu_e-e\varphi\right)}{\partial z}\right)=0 \quad (7)$$

The electrochemical strain can be further introduced via the Hooke's law for a chemically active elastic solid media, which relates the concentration deviation from the average $\delta N_d^+(\mathbf{r},t)=\left(N_d^+(\mathbf{r},t)-\overline{N}_d^+\right)$, mechanical stress tensor σ_{ij}, and elastic strain u_{ij} through the equation

$$u_{ij}=W_{ij}\,\delta N_d^+ + s_{ijkl}\sigma_{kl}+\varepsilon_0\chi_{mq}F_{ijmn}\frac{\partial E_q}{\partial x_n}+\varepsilon_0^2 Q_{ijkl}\chi_{km}\chi_{lp}E_m E_p. \quad (8)$$

Here s$_{ijkl}$ is the tensor of elastic compliances, F_{klmn} is a flexoelectric effect tensor, Q_{ijkl} is electrostriction tensor, electric polarization $P_k = \varepsilon_0 \chi_{km} E_m$ for the considered linear dielectrics, and W_{ij} is the Vegard expansion tensor.

The typical intrinsic resonance frequencies of a material are in the GHz range, which is well above the practically important limits of ion dynamics and the AFM-based detection of localized mechanical vibrations. This allows the use of quasi-static approximation for modeling of mechanical phenomena, namely we solve the general equation of mechanical equilibrium $\partial\sigma_{ij} / \partial x_j = 0$ in the quasi-static case. This leads to the equation for mechanical displacement vector u_i inside the film:

$$c_{ijkl}\left(\frac{\partial^2 u_k}{\partial x_j \partial x_l} - W_{kl}\,\frac{\partial \delta N_d^+}{\partial x_j} - \varepsilon_0 \chi_{mq} F_{klmn}\,\frac{\partial^2 E_q}{\partial x_j \partial x_n} - \varepsilon_0^2 Q_{klst} \chi_{sm} \chi_{tp}\,\frac{\partial\left(E_m E_p\right)}{\partial x_j}\right) = 0 . \tag{9}$$

Here c$_{ijkl}$ is the tensor of elastic stiffness. The boundary condition on the free surface of the film ($z = 0$) is the absence of normal stresses, $\sigma_{3j}(z = 0, t) = 0$. The surface $z=h$ is clamped to a rigid substrate and the displacement components are zero, $u_k\big|_{z=h} = 0$.

3. Electrostriction contribution to the ESM response in 1D case

Below we estimate the electrostriction contribution to the ESM response in the one-dimensional (1D) approximation, for bulk polarization only. The 2D case will be explored separately. To estimate, we consider several important components of the ESM response in the 1D case: the Vegard one, electrostriction and their superposition. The 1D approximation can be justified for the case when Debye length h_d of the MIEC is much smaller then the tip-surface contact radius r_0; however, these estimates can be expected to hold in general case when characteristic length is the tip radius. For the case of the mixed ionic-semiconductor film of thickness h placed in a planar capacitor under the application of *ac* and *dc* voltages superposition, $V_{dc}+V_{ac}\sin(\omega t)$, we calculated all the above mentioned contributions to the displacement of the film surface as explained in **Appendix A** of **Suppl. Mat.**[40] Vegard contribution is proportional to the integral, $W\int_0^h \delta N_d^+ dz$, that is identically zero for the case of ion-blocking electrodes. Electrostriction contribution is proportional to the integral of polarization squire, $u_3^Q(t)=Q_{33}\int_0^h P_3^2(z,t)dz$, flexoelectric effect contribution is $u_3^F(t)=F_{33}\left(P_3\,(h,t)-P_3\,(0,t)\right)$, and the polarization is approximated as $P(z,t)\approx P_W(z,t)+\varepsilon_0\chi\left(E_3^{dc}(z)+E_3^{ac}\sin(\omega t)\right)$. Here $P_W(z,t)=eh_d\delta N_d(z,t)$ is the electric analog of the Vegard elastic dipole, χ is a static relative susceptibility. E_{dc} is the slowly changing component of the electric field induced by tip bias, whereas E_{ac} is the fast component. We note that for typical ionic systems the mobilities are sufficiently lower so that at excitation frequencies ω of about 100 kHz the E_{ac} component can be evaluated as for a dielectric, neglecting ionic motion. For the cases of linear Debye screening (or no screening) of the *ac* component and the abrupt junction approximation for space-charge density induced by the *dc* component, the total mechanical displacement becomes:

$$u_3^Q(t)=u_3^0+u_3^{\omega}\sin(\omega t)+u_3^{2\omega}\cos(2\omega t) \tag{10}$$

The "linear" coefficient is $u_3^{\omega}=2Q_{33}\varepsilon_0\chi P_W V_{ac}+Q_{33}(\varepsilon_0\chi)^2(V_{dc}V_{ac})/h$ for the case of no screening for ac component. In this limit, namely when the screening length $h_d\to\infty$, the *ac* component of flexoelectric contribution tends to zero, because the electric field becomes z-independent,

$E_{ac} = V_{ac}/h$, i.e. $\left(u_3^F\right)_{ac} = \varepsilon_0 F_{33}\chi\left(E_3^{ac}(h) - E_3^{ac}(0)\right) = \varepsilon_0 F_{33}\chi \dfrac{V_{ac}}{h_d}\left(\dfrac{1-\cosh(h/h_d)}{\sinh(h/h_d)}\right)\sin(\omega_0 t)\Big|_{h_d\to\infty} \to 0$.

So we can neglect the flexo-term of *ac* ESM response in the dielectric limit. Numerical estimates proved that for typical flexoelectric coefficient $F_{33} \sim 1$V the term appeared relatively small for $\chi\sim4$, 2D ESM geometry at voltages noticeably smaller than 1V (considered here); the case of higher voltages will be explored elsewhere.

The relative contributions of electrostriction and Vegard effect to the linear dynamic piezoelectric coefficient are $d_{33}^{\omega} = du_3^{\omega}/dV_{ac} = 2Q_{33}\varepsilon_0\chi P_W + Q_{33}(\varepsilon_0\chi)^2(V_{dc}/h)$. For typical values of parameters Q_{33}=0.05 m^4/C^2, P_W=8×10^{-3} C/m^2 (e=1.6×10^{-19} C, h_d=5×10^{-9}m, δN_d =10^{25}m^{-3}), $\chi\sim4$, ε_0=8.85×10^{-12} F/m, V_{dc}=5 V, $h\sim10$ nm. The estimation gives $2Q_{33}\varepsilon_0\chi P_W$ ~ 0.03 pm/V and $Q_{33}(\varepsilon_0\chi)^2(V_{dc}/h)$~0.03 pm/V. Note that rather high electrostrictive response calculated earlier at 1 – 4 V [33] corresponds to $\chi\sim300$.

So in a 1D-approximation both contributions are proportional to the electrostriction coefficient and appear much smaller than typical experimental detection limits ~1 pm/V. This allows us to concentrate further attention on the Vegard strains contribution into the ESM response at low voltages less than 1 V.

4. Results and discussion

All calculations were performed in the COMSOL multiphysics package using the “PDE” and “Solid Mechanics” modules with parameters listed in the Tables B1-B2 of **Appendix B** in **Suppl. Mat** []. Numerical solution of Eqs.(6)-(7) was performed in the dimensionless variables listed in the appendix. For brevity we introduce only the main dimensionless variables and parameters in the main text, namely dimensionless cylindrical coordinates, depth $\tilde{z} = z/L_D$ and polar radius $\tilde{r} = r/L_D$, film thickness $\tilde{h} = h/L_D$ and computation cell size $\tilde{R} = R/L_D$, time $\tilde{t} = t/t_e$; where L_D is a characteristic screening length.

Strong accumulation for both donors and electrons occurs in the corresponding regions adjacent to electrodes. However, we can see from the comparison of **Figs 2a** and **2b** the maximal concentration of electrons are several times more than the maximal concentration of donors, despite the fact that initial concentration for both types of charge carriers was the same. This asymmetry arises due to steric interactions for donors, while electrons are regarded as size-less. In the case of donor-blocking and electron-blocking electrodes, the total concentration of charge carriers in the domain remains constant, while only the local redistribution of carrier concentration occurs. This corresponds to the periodic successive generation and annihilation of dynamic ionic-electron quasi-dipoles and also the formation and reorientation of the corresponding polarization. For the case of the low voltage local extrema of the donor concentration, it always appears in the same regions regardless of the sign of applied voltage; however this differs for the case of electrons, where the number of local extrema are different for different time moments.

The redistribution of donors and electrons leads to the emergence of stress and strain fields. The obtained elastic strains originate from a donor's motion. Radial (σ_{rr}) and azimuthal ($\sigma_{\varphi\varphi}$) components have a similar distribution, which in turn are highly correlated with the donor concentration distribution (compare **Figs 2a,b** and 3a,**b**). The normal stress component σ_{zz}, displays a more uniform distribution compared to σ_{rr} and $\sigma_{\varphi\varphi}$. Generally, the strongest strain appears in the regions with the largest donor concentration gradients (directly under the probe).

Comparison of the surface deformation in **Fig.3a** and **3b, 3c** and **3d** for two different time moments $\tilde{t} = 10$, 20 illustrate the nonlinearity of the ESM response; indeed the absolute values of the local extrema are different during the first and second half of the applied voltage. The first extremum (directly under the probe) does not change its absolute value and position; however the second extremum changes not only the absolute value, but also its position.

The electric potential increases monotonically with $\tilde{z}$, however for a few moments ($\tilde{t} = 10$) local redistribution of the charge carriers cause relatively small extrema (see **Fig. 4a**). The changes in t_d / t_e ratio do not impact the potential depth distribution.

The $\tilde{z}-$distribution of donor concentration is illustrated in **Figure 4b**. Naturally, by applying voltage to the top electrode the donors move to the grounded electrode (see donor concentration in the **Fig. 4a)**. By increasing the applied voltage amplitude, the concentration of donors near the corresponding electrodes increases, reaching the values numerous times larger than the initial one. More interestingly, local extrema of concentration appear, which can be interpreted as dynamic charge waves. As it can be seen from **Figure 4b** the donor charge wave in the $\tilde{z}$-direction consists of two local extrema: one is a local maximum and the other one is the local minimum with several times higher absolute value. Note, that the charge waves for the donors and electrons (shown in the **Appendix B, Suppl. Mat.** [40]) have a different scale. The electron charge waves are more flattened, and their amplitude stays almost constant with changing of applied voltage.

Figure 5 shows that the structure of charge waves can be more complicated in the radial direction. In particular, it demonstrates the appearance of several local extrema. In general, the donor concentration dependence with radius is quite complicated, while for electrons such dependence has no more than one local extremum that moves toward the opposite electrode with a constant amplitude. The dependence of concentration on the radial coordinate changes drastically in the region adjacent to the bottom electrode. Here, the concentration dependence from the radius for electrons have no local extrema, while the donor concentration have only one extremum.

All figures are plotted for the ratio $t_d/t_e \equiv 10$. The same dependencies are calculated for the $t_d/t_e = 10^2$ and $t_d/t_e = 10^3$ and are shown in the **Appendix B, Suppl. Mat.** [40] The general trend is that by decreasing the t_d/t_e parameter one leads to a more pronounced local extrema for donors and do not impact the extrema for electron's dependencies. The crests become wider and have larger amplitude, and are shifted more from the electrode. By increasing the t_d/t_e one will lead to an opposite change.

4. Summary

The self-consistent modeling of dynamic Electrochemical Strain Microscopy for axially symmetric 2D mixed ionic-electronic conductors was performed in the COMSOL Multiphysics package. The 2D map of strain and concentration distributions across a sample and bias-induced surface displacements were obtained. Results show significant impact of nonlinear effects on the ESM image formation mechanisms (i.e. appearance of the charge waves and nonlinear deformation of the surface). It was found that Vegard mechanism plays a key role in the mechanisms of the ESM image formation at low voltages ≤1V, but electrostriction contribution should dominate with a voltage increase.

Acknowledgements

M.V S. acknowledges the grant of the President of the Russian Federation for state support of young Russian scientists-PhD (№14.125.13.3784) the project part of the State tasks in the field of scientific activity № 11.2551.2014/K. O.V.V., E.A.E. and A.N.M. acknowledge Center for Nanophase Materials Sciences, user projects CNMS 2013-293, CNMS 2014-270 and National Academy of Sciences of Ukraine (grant 35-02-14). Authors are very grateful to Dr. Rama K. Vasudevan and Lisa A. Goins for help in the manuscript preparation.

References

---

[1] Sergei V. Kalinin, Nava Setter, and Andrei L. Kholkin. *MRS bulletin* **34**, no. 09: 634-642 (2009).

[2] Alexander K. Tagantsev, Vincent Meunier, and Pradeep Sharma. MRS bulletin **34**, no. 09: 643-647 (2009).

[3] Dawn A. Bonnell, Sergei V. Kalinin, A. L. Kholkin, and A. Gruverman. MRS bulletin **34**, no. 09: 648-657 (2009).

[4] P. Muralt, R. G. Polcawich, and S. Trolier-McKinstry. MRS bulletin **34**, no. 09: 658-664 (2009)

[5] Neeraj Panwar, I. K. Bdikin, A.N. Morozovska, and A. L. Kholkin. J. Appl. Phys. **112**, 052019 (2012).

[6] F. Sachs, W. E. Brownell, and A. G. Petrov. MRS bulletin **34**, no. 09: 665-670 (2009).

[7] S. Ducharme, T. J. Reece, C. M. Othon, and R. K. Rannow, *IEEE Trans. Device Mater. Reliab.* **5**, 720 (2005).

[8] K. Kimura and H. Ohigashi, *Jpn. J. Appl. Phys.* **25**, 383 (1986).

[9] S. V. Kalinin, B. J. Rodriguez, S. Jesse, P. Maksymovych, K. Seal, M. Nikiforov, A. P. Baddorf, A. L. Kholkin, R. Proksch, *Materials Today* **11**, 16 (2008).

[10] Gruverman A, Kolosov O, Hatano J, Takahashi K and Tokumoto H *J. Vac. Sci. & Technol. B* **13,** 1095 (1995)

[11] Gruverman A, Auciello O, Tokumoto H. *Appl. Phys. Lett.* **69,** 3191 (1996)

[12] Gruverman A, Auciello O, Ramesh R, Tokumoto H. *Nanotechnology* **8,** 38 (1997)

[13] Gruverman A, Auciello O, and Tokumoto H. *Annu. Rev. Mater. Sci*. **28,** 101 (1998)

[14] Harnagea C, Pignolet A, Alexe M, Hesse D, and Gösele U *Appl. Phys. A* **70** 261 (2000)

---

[15] Alexe M, Harnagea C, Hesse D and Gösele U. Appl. Phys. Lett. **79**, 242 (2001)

[16] Halperin C, Mutchnik S, Agronin A, Molotskii M, Urenski P, Salai M, Rosenman G. *Nano Lett*. **4** 1253 (2004)

[17]. Shvartsman V V, Pertsev N A, Herrero J M, Zaldo C, Kholkin A L. *J. Appl. Phys*. **97**, 104105 (2005)

[18] A. Gruverman, A. Kholkin. Rep. Prog. Phys. **69**, 2443–2474 (2006).

[19] V V Shvartsman, A L Kholkin. J. Appl. Phys. **101,** 064108 (2007)

[20] Kholkin A L, Bdikin I. K, Shvartsman VV, Pertsev NA. Nanotechnology **18,** 095502 (2007)

[21] S. V. Kalinin, Anna N. Morozovska, Long Qing Chen, and Brian J. Rodriguez. *Reports on Progress in Physics* **73**, no. 5: 056502 (2010).

[22] N. Balke, S. Jesse, A.N. Morozovska, E. Eliseev, D.W. Chung, Y. Kim, L. Adamczyk, R.E. Garcıa, N. Dudney and S.V. Kalinin. Nature Nanotechnology **5**, 749–754. (2010).

[23] Amit Kumar, Francesco Ciucci, A.N. Morozovska, Sergei Kalinin, and Stephen Jesse. Nature Chemistry **3**, 707-713 (2011)

[24] Stephen Jesse, Nina Balke, Eugene Eliseev, Alexander Tselev, Nancy J. Dudney, Anna N. Morozovska, and Sergei V. Kalinin. *ACS Nano*. **5** (12), 9682–9695 (2011)

[25] N. Balke, E. A. Eliseev, S. Jesse, S. Kalnaus, C. Daniel, N. J. Dudney, A. N. Morozovska, and S. V. Kalinin. J. Appl. Phys. **112**, 052020 (2012)

[26] Balke, Nina, Stephen Jesse, Yoongu Kim, Leslie Adamczyk, Ilia N. Ivanov, Nancy J. Dudney, and Sergei V. Kalinin. *ACS Nano* **4**, no. 12: 7349-7357 (2010).

[27] Nina Balke, Stephen Jesse, Yoongu Kim, Leslie Adamczyk, Alexander Tselev, Ilia N. Ivanov, Nancy J. Dudney, and Sergei V. Kalinin. *Nano letters* **10**, no. 9: 3420-3425 (2010).

---

[28] S. R. Bishop, K. L. Duncan, and E. D. Wachsman. *Electrochimica Acta* **54**, no. 5: 1436-1443(2009).

[29] G. G. Botte, V. R. Subramanian, and R. E. White, *Electrochimica Acta*, **45**, 2595-2609 (2000).

[30] A.N. Morozovska, E.A. Eliseev, A.K. Tagantsev, S.L. Bravina, Long-Qing Chen, and S.V. Kalinin. Phys. Rev. **B 83**, 195313 (2011).

[31] A.N. Morozovska, E.A. Eliseev, S.V. Kalinin. Appl. Phys. Lett. **96**, 222906 (2010).

[32] A.N. Morozovska, E.A. Eliseev, N. Balke, S.V. Kalinin. J. Appl. Phys. **108**, 053712 (2010).

[33] A.N. Morozovska, E.A. Eliseev, S.L. Bravina, Francesco Ciucci, G.S. Svechnikov, Long-Qing Chen and S.V. Kalinin. J. Appl. Phys. **111**, 014107 (2012)

[34] Mustafa Sabri Kilic, Martin Z. Bazant, and Armand Ajdari. *Physical Review* **E 75**, 021502 (2007)

[35] Mustafa Sabri Kilic, Martin Z. Bazant, and Armand Ajdari. *Physical Review* **E 75**, 021503 (2007)

[36] Anna N. Morozovska, Eugene A. Eliseev, P.S.Sankara Rama Krishnan, Alexander Tselev, Evgheny Strelkov, Albina Borisevich, Olexander V. Varenyk, Nicola V. Morozovsky, Paul Munroe, Sergei V. Kalinin and Valanoor Nagarajan. Phys.Rev.**B 89**, 054102 (2014).

[37] Daniel A. Freedman, D. Roundy, and T. A. Arias, Phys. Rev. **B 80**, 064108 (2009).

[38] X. Zhang, A. M. Sastry, W. Shyy, J. Electrochem. Soc. **155**, A542 (2008).

[39] H.-Ch. Chang and G. Jaffe, J. Chem. Phys. **20**, 1071 (1952).

[40] See supplementary material as [URL will be inserted by AIP] for mathematical details

---

Captions to Figures

Figure 1. (a) Typical geometry for ESM study of mixed ionic-electronic conductor (MIEC). Electrical and mechanical boundary conditions are labeled. **(b)** The time dependence of the applied voltage.

Figure 2. Dimensionless donor **(a)** and electron **(b)** concentrations, and the stress invariant $\sigma=\sigma_{zz}+\sigma_{rr}+\sigma_{\varphi\varphi}$ **(c)** for time moments $\tilde{t}=10,20$. Due to the axial symmetry only the semi-slice of the cylinder is shown. Ratio $t_d/t_e\equiv 10$. Electrodes are donor- and electron-blocking. Applied voltage is 1V, $L_D=2.8\cdot 10^{-9}m$, $t_e=8\cdot 10^{-5}s$.

Figure 3. Dimensionless stress tensor $\tilde{\sigma}_{\varphi\varphi}\approx\tilde{\sigma}_{rr}$ **(a)** and $\tilde{\sigma}_{zz}$ **(b)** components for time moments $\tilde{t}=10,20$. The shape profile deviation from the empty rectangle shows its deformation, scaled with factor 4×10^3. Other parameters are the same as in figure 2.

Figure 4. (a) Depth distributions of dimensionless potential, $\tilde{\varphi}=e\varphi/k_BT$, along the axes $\tilde{r}=0$ and **(b)** donor concentration, $\tilde{N}=N_d^+/N_d^0$, calculated for donor-blocking and electron-blocking electrodes at different moments of time $\tilde{t}=$0, 5, 10, 15, 18 (curves 1, 2, 3, 4 and 5) and $\tilde{r}=0$.

Figure 5. Radial distributions of dimensionless electron and donor concentrations, $\tilde{n} = n / N_d^0$ and $\tilde{N} = N_d^+ / N_d^0$, at different moments of time $\tilde{t}$ =0, 5,10,15,18 (curves 1, 2, 3, 4 and 5). Ratio $t_d / t_e \equiv 10$, $\tilde{z} = 0$ **(a, b)** and $\tilde{z} = \tilde{h}$ **(c, d)**.