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Frequency dependent dynamical electromechanical response of mixed ionic-electronic conductors

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Frequency dependent dynamic electromechanical response of the mixed ionic-electronic conductor film to a periodic electric bias is analyzed for different electronic and ionic boundary conditions. Dynamic effects of mobile ions concentration (stoichiometry contribution), charge state of acceptors (donors), electron concentration (electron-phonon coupling via the deformation potential), and flexoelectric effect contribution are discussed. A variety of possible nonlinear dynamic electromechanical responses of mixed electronic ionic conductors (MIEC) films including quasi-elliptic curves, asymmetric hysteresis-like loops with pronounced memory window, and butterfly-like curves are calculated. The electromechanical response of ionic semiconductor is predicted to be a powerful descriptor of local valence states, band structure and electron-phonon correlations that can be readily measured in the nanoscale volumes and in the presence of strong electronic conductivity. © 2012 American Institute of Physics. [doi:10.1063/1.3673868]

I. INTRODUCTION

Materials with dual electronic and ionic conductivity, referred to as mixed electronic ionic conductors (MIECs) are broadly used in energy related applications such as batteries,^{1,2} sensors,^{3,4} and fuel cells,^{5,6} as well as electronic device applications including memristive, and electroresistive memory and logic devices.^{7,8} Beyond these applications, ionic and electrochemical effects can heavily contribute to the operation of ferroelectric devices^{9,10} and capacitors, including ferroelectric fatigue,^{9,10} ferroelectric resistive switching,¹¹ ferroelectric gate devices,¹² or spurious observations of ferroelectricity in centrosymmetric materials in bulk¹³ or SPM geometries,^{14–16} piezoresistive phenomena,¹⁷ and exotic memory and transport effects in nano- and molecular electronic devices.¹⁸ Recently, ionic phenomena are considered as an origin of unique properties of LaAlO₃-SrTiO₃ interfaces.¹⁹ Many oxides such as manganites, cobaltite, and ferrites, are both extensively studied in the condensed matter physics community^{20,21} and are used in energy applications, pointing at the possible role of ionic phenomena in classical physical studies. The multitude of ionic phenomena in nanoscale systems necessitates the development of comprehensive

measurement strategies applicable for nanoscale materials in the form of capacitor-like device structure and scanning probe microscopy (SPM).

Understanding of physical and electrochemical phenomena in these materials necessitates development of measurement techniques addressing local valence states and electrochemical functionality and their response to external bias and chemical stimuli on the local scale. Significant progress in this direction has been achieved with the advent of electron-microscopy based electron energy loss spectroscopy (EELS) imaging²² and synchrotron based X-ray measurements. However, the understanding of these systems can be considerably extended if these studies can be extended to local probing of functionality on a single grain, defect, or domain wall level, combining the broad spectrum of capabilities of conventional electrochemical characterization techniques and high spatial resolution of electron and scanning probe microscopies.

The applicability of traditional electrochemical measurements based on the Faradaic current detection is necessarily restricted to the 1–50 micron length scale due to the electronic current detection limits.^{23,24} The comprehensive analysis²⁵ of recent efforts in extending the electrochemical charge-discharge^{26–29} or impedance spectroscopy^{30–32} methods to SPM environment suggests that these studies are possible only when the process is catalyzed at and around the tip surface junction.³³ At the same time, when tip or surface

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material are active part of the ionic or electrochemical process, corresponding current cannot be probed directly and the progression of reaction can be ascertained only through static changes in surface topography, Raman signature, etc. (e.g., for tip-induced nanooxidation,^{34,35} or deposition of carbon,³⁶ semiconductors³⁷ or metals^{38,39}). This limitation stems both from the smallness of Faradaic currents and presence of surface leakage currents (dc detection) and stray capacitances of the measurement circuits (ac detection).

An alternative approach for probing ionic and electrochemical processes in solids is based on electromechanical and chemo-mechanical coupling. The latter corresponds to chemical expansivity measurements of volume versus chemical potential of volatile component using macroscopic dilatometric test systems or scattering methods, and is now broadly used in solid state ionic community. In electromechanical methods, potential induced by mechanical stimuli applied to MIEC (direct effect) or mechanical response induced by electrical stimuli (inverse effect) is detected. In particular, this approach offers the advantage of direct implementation in capacitor-like structures with interferometric or vibrometric detection of associated surface displacements, or implementation in the SPM setup. An example of this approach is electrochemical strain microscopy (ESM),^{40,41} in which the periodically biased conductive SPM tip concentrates electric field in a small volume of the material, resulting in redistribution of mobile ions through diffusion and electromigration mechanisms. The associated changes in molar volume and strains result into periodic surface displacement detected by a SPM tip, somewhat similar to the piezoresponse force microscopy (PFM) of piezoelectric and ferroelectric materials.^{42–46}

In systems with large background conductivity, the bias-induced electromechanical process can be separated into the interfacial reaction process and subsequent diffusion of the chemical species through the lattice. This problem then reduces to the solution of linear diffusion or coupled diffusion-strain equations, and is well developed in the context of electrochemical storage and metallurgical systems.^{47–52} However, in MIEC systems, the response will be determined by coupled ionic and electronic motion, giving rise to significantly more complex coupled diffusion-migration problem.

To the best of our knowledge the **dynamical local electromechanical properties** of MIECs is poorly studied theoretically,^{23,24,40,53,54} in contrast to the theory of their dynamical current-voltage response, that is well elaborated (see, e.g., classical papers of Riess *et al.*^{7,8} and Strukov *et al.*⁵⁵ and references therein). The basis of theory of **static local electromechanical properties** of MIECs is presented in Ref. 56.

The paper is organized as follows: The electromechanical and transport phenomena in MIECs are summarized in Sec. II. Section III contains basic equations and boundary conditions for dynamic local electromechanical response calculations. Results of the dynamic response calculations are presented and analyzed in Sec. IV. The linear response is analyzed in Sec. IV A. Nonlinearity effect on the response is analyzed in Secs. IV B 3. These sections are followed by the brief discussion and summary remarks in Sec. V.

II. ELECTROMECHANICAL AND TRANSPORT PHENOMENA IN MIECs

A. Electromechanical coupling in MIECs

Electromechanical coupling in MIECs is controlled by relationships between molar volume and local field, carrier concentration, and ionic concentration. Well-known effect of the stoichiometry on the local strain is the (often linear) dependence of lattice constants on the composition of solid solution (Vegard law of chemical expansion). The deviations from Vegard law are typically indicative of non-trivial physical phenomena including phase separation, metal insulator transitions, and thus are intrinsically linked to the fundamental physics of the material. Recent experimental studies of correlated oxides including ceria, titanates, ferrites, cobaltites, nikelates analyze chemical expansion effects as related to the oxygen vacancies appearance and migration. Adler *et al.*^{57–59} analyzed the temperature and oxidation-state dependence of lattice volume in $\text{La}_{1-x}\text{Sr}_x\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ ceramics in terms of thermal and chemical expansion. A similar effect of lattice expansion due to the oxygen non-stoichiometry was observed earlier by the different authors (see, e.g., Refs. 60–62). Bishop *et al.*⁶³ studied the chemical expansion and oxygen non-stoichiometry of undoped and Gd-doped cerium oxide exposed to different partial pressures of oxygen and found that the contribution to a chemical expansion could be attributed to the larger crystal radius of cerium Ce^{3+} compared to the cerium Ce^{4+} . Phenomenological models accounting for the difference in the dopant cation radius and charge as well as the formation of oxygen vacancies have been used to explain experimental results for fluorite-structure oxides^{64,65} assuming linear relations resembling Vegard law. Lankhorst *et al.*⁶⁶ established the relationship between defect chemistry, oxygen nonstoichiometry, and electronic properties (i.e., Fermi level position) in MIEC $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$.

The second effect leading to electromechanical coupling in oxides are the *electron-phonon coupling* via deformation potential.^{56,67} Strong *electron-phonon coupling* associated with the *local Jahn-Teller distortion* was proposed as a possible origin of this very unusual behavior of materials with transition-metal ions.²⁰ Coupling between orbital occupancy and the Jahn-Teller distortion can play a major role as a driving force of symmetry breaking, because the orbital occupation may strongly couple to the lattice (anion distortion) in some cases.²⁰ Jahn-Teller distortions are typical for correlated oxides with partially filled d-orbitals (e.g., t_{2g} and e_g for octahedral and tetrahedral coordinates) such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$,⁶⁸ $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ and even $\text{SrFe}_x\text{Ti}_{1-x}\text{O}_{3-\delta}$.⁶⁹ The bandgap of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (~ 1 eV) is mainly determined by the collective Jahn-Teller distortion.⁷⁰ Since the deformation potential is directly related with the bandgap in the narrow gap semiconductors, Fermi level in (half) metals as well as with the charge gap in correlated metal-insulators,^{71,72} the electromechanical response of correlated oxides like p- $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ could provide the important information about the local band structure and Jahn-Teller distortions.

Using paraelectric SrTiO_3 film as a model material with well-known electromechanical, electronic and electrochemical

properties, we have previously evaluated the contributions of electrostriction, Maxwell stress, flexoelectric effect, deformation potential, and compositional Vegard strains caused by mobile vacancies (or ions) and electrons to the *static* electromechanical response.⁶⁷ Furthermore, in Ref. 56 we developed a *thermodynamic* approach that allows evolving theoretical description of linear mechanical phenomena induced by the electric fields (electro-mechanical response) in solid state ionics toward analytical theory and phase-field modeling of the MIECs in different geometries and under varying electrical, chemical, and mechanical boundary conditions. These results motivate to continue our theoretical study on *dynamic effects* in the present manuscript.

B. Transport in MIECs

To explore the *dynamic electromechanical response*, the knowledge of the changes in electrochemical potentials of electrons and ions induced by bias are required. This coupling was extensively explored in the context of transport modeling in MIECs in the *dc* and *ac* regimes in the framework of the Boltzmann-Planck-Nernst (BPN) approximation for chemical potential and/or Debye linear screening theory assuming constant conductivity. Below, we provide a *brief overview of recent theoretical studies* of coupled diffusion-migration transport in MIECs and factors contribution to the mechanical effects in MIECs.

Gil *et al.*^{7,8} analyzed current-voltage characteristics of metal/semiconductor film/metal structures assuming small variations of holes (electrons) and mobile acceptor (donors) concentrations, and a valid analytical solution was derived in the linear BPN approximation. Svoboda and Fischer⁷³ considered the internal stress relaxation in thin films due to the vacancies diffusion only. Tanagera *et al.* analyzed⁷⁴ the distribution of one type space charge in oxide film between blocking electrodes, but the current was regarded as absent. Using boundary conditions involving the discharge rate for conductance currents at the interfaces, as proposed by Chang and Jaffe,⁷⁵ Macdonald⁷⁶ considered mobile electrons and holes, while supposing the charged ions uniformly distributed independently on applied voltage, supposed small in comparison with thermal energy. Chen⁷⁷ compared two approximate models (local electro neutrality and constant electric field) with numerical solution of BPN equations for fluxes of electrons and oxygen vacancies. Jamnik and Maier⁷⁸ proposed an equivalent circuit for the model system

with constant ionic conductivity. Franceschetti and Macdonald⁷⁹ considered an exact solution of the BPN equation for steady state of the system with holes, electrons, and immobile charged defects. Also they numerically simulated transient currents as system response to step changes of applied bias.

Recently Riess and Maier⁸⁰ proposed an extension of linear irreversible thermodynamics to the case of large driving forces expressing the current via nonlinear function of the drop of electrochemical potential over the “local” hopping distance.

Ciucci *et al.*⁸¹ developed a numerical and analytical framework for the study of small bias response and electrochemical impedance of MIECs. These authors linearized the Poisson Nernst-Planck equations and analyzed 10 μm samples of heavily doped MIEC. Therefore those results (impedance equations) were derived in the assumptions of local electroneutrality. The use of the neutral approximation is questionable when the MIECs’ length scale falls in the nanometer range.

III. BASIC EQUATIONS AND BOUNDARY CONDITIONS FOR DYNAMIC ELECTROMECHANICAL RESPONSE

Here we consider planar configuration, corresponding to the top electrode on the MIEC film. These structures are now actively fabricated for impedance based studies,^{82,83} and can also be used for focused X-ray (e.g. Ref. 84 for ferroelectric materials and Ref. 85 for semiconductor nanostructures) interferometric and vibrometric detection. We further note that the fully 1 D case implies no lateral current and ionic transport from the edges (or completely blocking lateral walls), whereas the deposited electrode can allow for lateral transport at the edges. This affects conservation laws for electrons and ionic species. The SPM experiment with localized tip corresponds to the limiting case of a very small electrode.

Geometry of the considered asymmetric heterostructure electrode/possible gap/ionic semiconductor film/substrate electrode is shown in Fig. 1(a). Electric potential V is applied to the top planar microelectrode. The substrate electrode located at $z = h$ is grounded, $V = 0$. The semiconductor film of thickness h is regarded thick enough to have a continuous band structure [Fig. 1(b)]. The existence of vacuum or air dielectric gap of thickness H between the charged top microelectrode and the MIEC film is also possible, mirroring

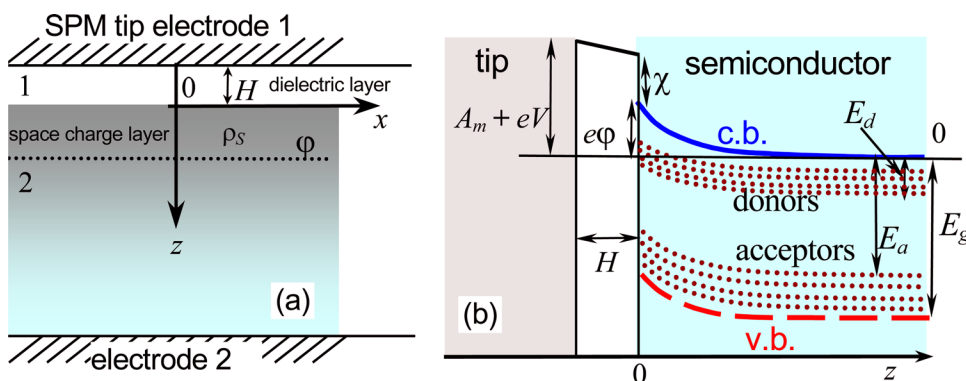


FIG. 1. (Color online) (a) Geometry of the considered asymmetric heterostructure “tip electrode/gap/ionic semiconductor film/substrate electrode.” (b) Schematic band structure at $z=0$: $U = A_m/e + V$, where A_m is the work function difference, $V(t) = V_0 \sin(\omega t)$ is the voltage difference applied to the tip electrode at $z = -H$, ϕ is the electric potential, χ is the electron affinity in the semiconductor.

models for imperfect contact or dead layer in ferroelectric materials.^{86,87}

Here, free electrons in the conductive band (n) and holes (p) in the valence band consider which quasi-levels can be different and coordinate dependent in the dynamic case. The acceptors (donors) are neutral or singly ionized. The neutral acceptors (donors) are *immobile*, and the charged ones could be *mobile or almost immobile*.⁸

A. Dynamic electromechanical response in decoupling approximation: Flexoelectric, Vegard, and electron-phonon contributions

Decoupling approximation has been recently used for MIECs (Refs. 56 and 67) and much earlier for the local electromechanical response calculations of ferroelectrics.⁸⁸⁻⁹⁴ As the sort of perturbation approach, it consists of two successive stages. On the first stage one neglects the elastic stresses originated from electrostriction, piezoelectric effect (for ferroelectrics) and flexoelectric effects and Vegard expansion, in order to calculate the electric potential and mobile charges distribution. On the second stage all these effects are taken into account when the system strain is calculated using the electric potential and mobile charges distribution calculated on the first stage. The accuracy of the decoupling approximation is surprisingly high even for ferroelectrics (error is proportional to the square of the electromechanical coupling coefficient) and approved by other numerical methods like phase-field and FEM.⁹⁵ Earlier we studied the accuracy of the decoupling approximation for paraelectric SrTiO₃ and proved that it is valid with several % accuracy at film thicknesses more than several screening radius and moderate applied voltages. Moreover, the decoupling approximation is valid with very high accuracy at arbitrary thicknesses and voltages after the substitution of the LGD-expansion coefficient $\alpha(T)$ with $\alpha_P = \alpha(T) + 3\tilde{\alpha}_{11}\langle P \rangle^2$ in the electrostriction contribution term (see designations and Fig. 2 in Ref. 67).

We suppose that the total stress tensor $\sigma_{ij}(\mathbf{r})$ is linearly proportional to the Vegard contribution, electron-phonon contribution, flexoelectric and electrostriction contributions,

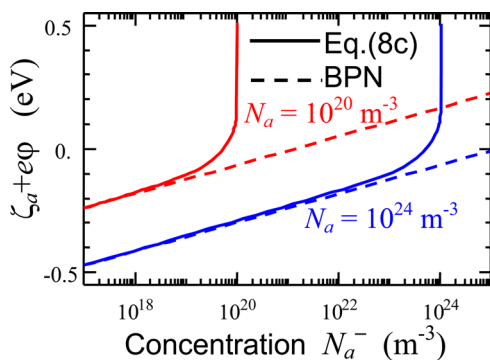


FIG. 2. (Color online) Concentration dependencies of ionized acceptor electrochemical potential levels calculated for $N_a = 10^{20} \text{ m}^{-3}$ and 10^{24} m^{-3} ; $T = 293 \text{ K}$, $u_{jk} = 0$. Solid and dashed curves represent the levels calculated from expressions (8c) and Boltzmann-Planck-Nernst approximation (BPN) correspondingly.

$$\sigma_{ij}(\mathbf{r}) = c_{ijkl}u_{kl}(\mathbf{r}) + \left(\begin{aligned} &\Xi_{ij}^C(n(\mathbf{r}) - n_0) + \Xi_{ij}^V(p(\mathbf{r}) - p_0) + \\ &-\beta_{ij}^a(N_a^-(\mathbf{r}) - N_{a0}^-) - \beta_{ij}^d(N_d^+(\mathbf{r}) - N_{d0}^+) \end{aligned} \right) - \gamma_{ijkl} \frac{\partial^2 \varphi}{\partial x_k \partial x_l} + \tilde{q}_{ijkl} \frac{\partial \varphi}{\partial x_k} \frac{\partial \varphi}{\partial x_l}. \quad (1)$$

Here c_{ijkl} is the tensor of elastic stiffness, $u_{kl}(\mathbf{r})$ is the strain tensor, $\Xi_{ij}^{C,V}$ is a tensor deformation potential of electrons in the conduction (C) and valence bands (V), $\beta_{ij}^{a,d}$ are the Vegard expansion tensors for acceptors (donors). $N_d^+(\mathbf{r})$ is the instant concentration of mobile ionized donors, $N_a^-(\mathbf{r})$ is the instant concentration of mobile ionized acceptors, N_{d0}^+ and N_{a0}^- are their stoichiometric equilibrium concentrations; $n(\mathbf{r})$ is the concentration of electrons in the conduction band, $p(\mathbf{r})$ is the concentration of holes in the valence band, n_0 and p_0 are their equilibrium concentrations, $\varphi(\mathbf{r})$ is the electric potential. Flexoelectric strain tensor γ_{ijkl} has been measured experimentally for several substances and it was found to vary by several orders of magnitude from 10^{-11} C/m to 10^{-6} C/m .⁹⁶⁻⁹⁸

\tilde{q}_{ijkl} is the electrostriction tensor that couples stress and electric field. It is related to the electrostriction tensor q_{ijkl} , that couples strain and polarization, via the dielectric susceptibility $\chi_{ij} = \epsilon_0(\epsilon_{ij} - \delta_{ij})$ as $\tilde{q}_{ijkl} = \chi_{ip}\chi_{jq}q_{pqkl}$ (ϵ_{ij} is the dielectric permittivity). In fact the electrostriction coefficients for typical *semiconductors with low dielectric permittivity (smaller than several tens)* are such that the electrostriction contribution becomes essential only at high electric fields (see, e.g., Refs. 99 and 100). However for paraelectrics with high dielectric permittivity ϵ_{ij} , e.g., for SrTiO₃, electrostriction contribution can be dominant even at moderate electric fields.⁶⁷

Note, that Eq. (1) requires the reference crystallographic lattice to be defined, as analyzed for pure diffusion-stress coupling by Larche and Cahn.¹⁰¹ The reference lattice is regarded strain-free for the case of zero electric potential: $\varphi = 0$ and therefore $n(\mathbf{r}) = n_0$, $p(\mathbf{r}) = p_0$, $N_a^-(\mathbf{r}) = N_{a0}^-$, $N_d^+(\mathbf{r}) = N_{d0}^+$.

Lame-type equation for the electromechanical displacement u_i can be obtained from the equation of mechanical equilibrium $\partial \sigma_{ij}(\mathbf{r}) / \partial x_j = 0$, where the stress tensor $\sigma_{ij}(\mathbf{r})$ is given by Eq. (1). Mechanical boundary conditions¹⁰² corresponding to the ESM experiments²³ are defined on the mechanically free interface, $z = 0$, where the normal stress σ_{3i} is absent, and on clamped interface $z = h$, where the displacement u_i is fixed,

$$\sigma_{3i}(x_1, x_2, z = 0) = 0, \quad u_i(x_1, x_2, z = h) = 0. \quad (2)$$

Using the decoupling approximation in the 1D-Poisson equation for the electric potential, mechanical displacement of the MIEC surface caused by the flexoelectric, electronic, and ionic contributions was calculated as⁵⁶

$$u_3(z = 0) \approx \int_0^h \frac{dz'}{c_{33}} \left(\begin{aligned} &\xi^C(n(z') - n_0) + \xi^V(p(z') - p_0) \\ &-\mu^a(N_a^-(z') - N_{a0}^-) \\ &+\mu^d(N_d^+(z') - N_{d0}^+) + \tilde{q}_{33} \left(\frac{\partial \varphi(z')}{\partial z'} \right)^2 \end{aligned} \right). \quad (3)$$

Here e is the electron charge absolute value, constants $\xi^C \equiv (\Xi_{33}^C - \frac{\gamma_{3333}^C}{\epsilon_{33}^S \epsilon_0})$, $\xi^V \equiv (\Xi_{33}^V + \frac{\gamma_{3333}^V}{\epsilon_{33}^S \epsilon_0})$, $\mu^a \equiv (\beta_{33}^a + \frac{\gamma_{3333}^a}{\epsilon_{33}^S \epsilon_0})$, and $\mu^d \equiv (-\beta_{33}^d + \frac{\gamma_{3333}^d}{\epsilon_{33}^S \epsilon_0})$, ϵ_{33}^S is the universal dielectric constant.

From Eq. (3) the MIEC surface displacement is proportional to the total charge of each species. Note, that the relation between the total charge and electrostatic potential on the semiconductor surface is well established.¹⁰³ Note, that the first terms in material constants $\xi^{C,V}$ originated from the deformation potential or Vegard tensors, while the last ones originated from the flexoelectric coupling. Remarkably, that the strength of tensorial deformation potential $\Xi_{33}^{C,V}$ appeared comparable to the Vegard tensor $\beta_{33}^{a,d}$ or even higher.

Note, that for ion-blocking electrodes the total number of ions remains the same, i.e., $\int_0^h (N_a^-(z) - N_{a0}^-) dz = 0$ and $\int_0^h (N_d^+(z) - N_{d0}^+) dz = 0$ when neglecting generation recombination effects. No such constrains exist for the case when one or two electrodes are ion conducting.

Note, that in principle, the impedance spectroscopy formalism^{78,105,106} can be used to derive the *linear* electro-mechanical response. However, for MIECs this approach requires the distributed models (e.g., see Ref. 107 for a detailed review), since lumped element models generally fail to reproduce the coupled electronic-ionic transport. This approach is then mathematically equivalent to the direct solution of coupled transport equations. Typically distributed circuit models also impose the electroneutrality condition, which is not the case at least near interfaces of MIEC thin films. However, in order to calculate the *nonlinear* electro-mechanical response in MIECs the impedance spectroscopy formalism should be modified to account for nonlinearity,¹⁰⁸ since the impedance relations $V(t) \sim I(t) \cdot R(t)$ for I-V curves and mechanical displacement, as proportional to the total charge $Q(t)$ of each species, $u_3(t) \sim Q(t) \sim \int^t I(y) dy \sim \int^t V(y) \cdot R^{-1}(y) dy$, are valid in the time domain only. The convolution theorem for $u_3(\omega)$ should be applied in the spectral frequency domain, which breaks the proportionality $u_3(\omega) \sim 1/i\omega R$ allowing for the complex nonlinear temporal dependence of the impedance $R(t)$.

B. Poisson equations and electro-dynamics boundary conditions

For frequencies less than 1 MHz, which is a typical operating limit for these experiments, the quasi-static approximation for the electric field $E_z = -\partial\phi(\mathbf{r})/\partial z$ works with high accuracy. Neglecting the flexoelectric term (decoupling approximation), the 1 D-Laplace equation in the dielectric gap (if any) and the 1 D-Poisson equation in MIEC film have the form,

$$\frac{d^2\phi}{dz^2} = 0, \quad -H < z < 0 \quad (\text{gap}) \quad (4a)$$

$$\frac{d^2\phi}{dz^2} = -\frac{\rho(\phi)}{\epsilon_{33}^S \epsilon_0}, \quad 0 < z < h \quad (\text{MIEC film}). \quad (4b)$$

Here $\phi(z)$ is the electric potential and ϵ_{33}^S is MIEC dielectric permittivity. The charge density in the MIEC film has the form,

$$\rho(z) = e(p(z) - n(z) - N_a^-(z) + N_d^+(z)). \quad (5)$$

The boundary conditions for the electrostatic potential $\phi(z)$ are $\phi(z=h) = 0$ on the grounded substrate electrode, $\phi(z=-H) = A_m/e + V$ on the tip electrode-dielectric gap-film, $\phi(z=+0) - \phi(z=-0) \approx V_b$ on the tip electrode-dielectric gap-film, and

$$D_{2n} - D_{1n} = -\epsilon_0 \left(\epsilon_{33}^S \frac{\partial\phi(z=+0)}{\partial z} - \epsilon_{33}^g \frac{\partial\phi(z=-0)}{\partial z} \right) = 0 \quad (6)$$

on the film-dielectric gap boundary. Here, A_m is the work function from the conducting tip electrode that typically determines the contact built-in potential V_b , $V(t) = V_0 \sin(\omega t)$ is the periodic voltage difference applied to the tip electrode at $z = -H$, ϵ_{33}^g is the dielectric constant of the dielectric layer. The normal vector \mathbf{n} is pointed from media 1 to media 2. The free surface charge is regarded absent at $z=0$ in the dynamic case. Note, that the potential can be always set zero at the contact $z=h$, while the contact itself may either have contact barrier or barrierless (ohmic).

C. Kinetic equations and boundary conditions

The total electric current of the MIEC film is $J_f = J_{D_s} + J_c$, where $J_{D_s}(z, t) = \epsilon_0 \epsilon_{33}^{S,g} (\partial E_z / \partial t)$ is the displacement current (existing both in the dielectric and in the MIEC), and $J_c(z, t)$ is the conductivity current that exists in the MIEC only. The continuity equation $(\partial\rho/\partial t) + (\partial J_c/\partial z) = 0$ should be solved along with all electro-dynamics equations.

The conductivity current $J_c(z, t) = \sum_{m=a,p,d,n} J_c^m$ consists of the acceptor (J_c^a), hole (J_c^p), donor (J_c^d), and electron (J_c^n) currents. Under negligibly small impact of the electron-hole recombination-generation process charges conservation equations are

$$-\frac{\partial N_a^-}{\partial t} + \frac{1}{e} \frac{\partial J_c^a}{\partial z} = 0, \quad (7a)$$

$$\frac{\partial p}{\partial t} + \frac{1}{e} \frac{\partial J_c^p}{\partial z} = 0, \quad (7b)$$

$$\frac{\partial N_d^+}{\partial t} + \frac{1}{e} \frac{\partial J_c^d}{\partial z} = 0, \quad (7c)$$

$$-\frac{\partial n}{\partial t} + \frac{1}{e} \frac{\partial J_c^n}{\partial z} = 0. \quad (7d)$$

The electron and hole conductivity currents are proportional to the gradients of the carrier electrochemical potentials levels as $J_c^p = -e\eta_p p (\partial\zeta_p/\partial z)$, and $J_c^n = e\eta_n n (\partial\zeta_n/\partial z)$, where $\eta_{n,p}$ is the constant mobility of electrons (holes) and

$$-\zeta_p(z) \approx \Xi_{ij}^V u_{ij}(z) + e\phi(z) + k_B T \ln \left(\frac{p(z)}{p_0} \right). \quad (8a)$$

Note that holes in the quasi-Fermi levels Eq. (8a) are typically defined in the BPN approximation, since they are mostly not degenerated in the MIECs.

At the same time, the electrons in the correlated oxides are well-localized. Using the rectangular density of states

(DOS) with constant DOS, $g_n = N_n/(\delta E_n)$ over the range $[E_n, E_n + \delta E_n]$, electrochemical potential was derived as¹⁰⁹

$$\zeta_n \approx E_C + \Xi_{ij}^c u_{ij}(z) - e\varphi(z) - k_B T \ln \left(\frac{\exp(-\varepsilon n(z)/N_n) - \exp(-\varepsilon)}{1 - \exp(-\varepsilon n(z)/N_n)} \right). \quad (8b)$$

Here dimensionless energy $\varepsilon = \delta E_n/k_B T$, $k_B = 1.3807 \times 10^{-23}$ J/K, and T is the absolute temperature. In the case $\varepsilon n(z)/N_n \ll 1$, Eq. (8b) gives the BPN approximation $\zeta_n \approx E_C + \Xi_{ij}^c u_{ij} - e\varphi + k_B T \ln(n/n_0)$, where the equilibrium concentration $n_0 = (N_n/\varepsilon)(1 - \exp(-\varepsilon))$.

Then, we substitute the acceptor and donor conductivity currents in Eq. (7) as proportional to the gradients of the corresponding electrochemical potentials,¹⁰³

$$J_c^a = e\eta_a N_a^- \frac{\partial \zeta_a}{\partial z},$$

$$\zeta_a(z) = -E_a + \beta_{jk}^a u_{jk}(z) - e\varphi(z) - k_B T \ln \left(\frac{N_a - N_a^-(z)}{N_a^-(z)} \right), \quad (8c)$$

$$J_c^d = -e\eta_d N_d^+ \frac{\partial \zeta_d}{\partial z},$$

$$-\zeta_d(z) = E_d + \beta_{jk}^d u_{jk}(z) + e\varphi(z) - k_B T \ln \left(\frac{N_d - N_d^+(z)}{N_d^+(z)} \right). \quad (8d)$$

Here $\eta_{d,a}$ is the constant mobility of donors (acceptors), $E_{d,a}$ are their levels position calculated from the bottom of conductive band. Approximate equalities $\ln \left(\frac{N_a - N_a^-(z)}{N_a^-(z)} \right) \approx \ln \left(\frac{N_a}{N_a^-(z)} \right)$ and $\ln \left(\frac{N_d - N_d^+(z)}{N_d^+(z)} \right) \approx \ln \left(\frac{N_d}{N_d^+(z)} \right)$ correspond to the BPN approximation.¹¹⁰ From Eqs. (8c) and (8d) one derives $N_{a0}^- = N_a \left(1 + \exp(-\frac{E_F + E_a}{k_B T}) \right)^{-1}$ and $N_{d0}^+ = N_d \left(1 + \exp(\frac{E_F + E_d}{k_B T}) \right)^{-1}$ in the case $\varphi = 0$, when $\zeta_a = \zeta_d = E_F$.

Note that the dynamics described by Eq. (8) should be valid for local thermal equilibrium conditions and in the presence of small local gradients, i.e., $J_c^m \sim \eta_m \partial \zeta_m / \partial z$ even when the system is not in global equilibrium. For the high values of driving force, $\partial \zeta_m / \partial z$, one should use the expression for currents derived by Riess and Maier.⁸⁰

Concentration dependencies of ionized acceptors electrochemical potential are shown in Fig. 2. From the data in the plots, the BPN approximation in Eq. (8c) works well for concentrations $N_a^- < (N_a^-)_{cr}$, where $(N_a^-)_{cr} = N_a$ is anticipated (see dashed lines). The condition $(N_a^-)_{cr} \approx N_a$ can be readily achieved in the vicinity of the film interfaces, where the space charge accumulation takes place. Exactly in these regions the BPN approximation for acceptor electrochemical potential (and consequently the linear drift-diffusion model for their conductivity currents) become inapplicable.

The material boundary conditions relevant for the considered problem correspond to the limiting cases of the general Chang-Jaffe conditions,^{75,76} namely

$$(J_c^p - w_{p0}(p - p_{s0}))|_{z=0} = 0, \quad (J_c^p + w_{ph}(p - p_{sh}))|_{z=h} = 0, \quad (9a)$$

$$(J_c^n + w_{n0}(n - n_{s0}))|_{z=0} = 0, \quad (J_c^n - w_{nh}(n - n_{sh}))|_{z=h} = 0, \quad (9b)$$

$$(J_c^a + w_{a0}(N_a^- - N_{a0}^-))|_{z=0} = 0, \quad (J_c^a - w_{ah}(N_a^- - N_{ah}^-))|_{z=0,h} = 0, \quad (9c)$$

$$(J_c^d - w_{d0}(N_d^+ - N_{d0}^+))|_{z=0} = 0, \quad (J_c^d + w_{dh}(N_d^+ - N_{dh}^+))|_{z=h} = 0. \quad (9d)$$

Upper and lower signs correspond to boundaries $z = h$ and $z = 0$, respectively. Here $w_{p0,h}$, $w_{n0,h}$, $w_{a0,h}$, and $w_{d0,h}$ are positive rate constants of surface discharge^{7,75,111} corresponding to boundaries $z = h$ and $z = 0$, respectively; frequency-independent constants $p_{s0,h}$, $n_{s0,h}$, $N_{a0,h}^-$, $N_{d0,h}^+$ are equilibrium surface concentrations of holes, electrons, acceptors, and donors at the film interfaces $z = h$ and $z = 0$, respectively (in the absence of any currents). The conditions (9) contain the continuous transition from the **open conducting contacts** $w_n \rightarrow \infty \Rightarrow n(\rho, 0, t) = n_S$ and/or $w_d \rightarrow \infty \Rightarrow N_{d,a}^\pm(\rho, h, t) = N_{d0,h}^\pm$ to the **interface limited kinetics** ($w_{n,d} > 0$) and **blocking contacts** ($w_{n,d} = 0$).¹¹¹

Equations (3)–(8) form the closed nonlinear mixed boundary value problem, while the boundary conditions (9) are linear. The solutions for the case of periodic external voltage change $V(t) = V_0 \sin(\omega t)$ will be analyzed below in the linear approximation analytically and for the nonlinear case numerically.

IV. DYNAMIC ELECTROMECHANICAL RESPONSE

A. Linear electromechanical response of the MIEC film

Here we analyze the linear strain response caused by the periodic tip voltage for the *one prevailing type of carriers*, e.g., when acceptor mobility is absent or much smaller than the holes one, donors are almost absent and thus the concentration of the free electrons is also negligible in comparison with the holes concentration. Analytical expressions for the linear strain response caused by the periodic tip voltage was derived in decoupling approximation [Supplementary Materials,¹⁰⁴ Appendix B]. Mobile donors and electrons are not considered, but this can be done in a similar way.

Substituting in Eq. (3) the expressions for charges variation $\delta Q_p(\omega) = \int_0^h (p(z) - p_0) dz$ (see Supplementary Materials,¹⁰⁴ Appendix B), we obtained an approximate analytical expression for the surface displacement of the MIEC film,

$$u_3(z=0, \omega) \approx -\xi^V \frac{\varepsilon_0 \varepsilon_{33}^S}{c_{33}} \frac{V_0 (1 - \exp(k(\omega)h))^2}{h + \tilde{H} (1 + \exp(2k(\omega)h))} \times \left(i\omega \tau_M + \frac{\tanh(hk(\omega)) + k(\omega)\tilde{H}}{(h + \tilde{H})k(\omega)} \right)^{-1} \quad (10a)$$

Here $\tilde{H} = \varepsilon_{33}^S / \varepsilon_{33}^g H$ and relaxation time $\tau_M = \varepsilon_0 \varepsilon_{33}^S / e p_0 \eta_p$, ω is the frequency of the voltage $V(t) = V_0 \exp(i\omega t)$ applied to the SPM probe. The spatial scale

$$k(\omega) = \sqrt{\frac{i\omega}{D} + \frac{1}{R_S^2}} \equiv \frac{1}{R_S} \sqrt{i\tau_M \omega + 1} \quad (10b)$$

is defined by the diffusion coefficient $D = \eta_p(k_B T/e)$ and Debye screening radius $R_S = \sqrt{\epsilon_{33}^S \epsilon_0 k_B T / e^2 p_0}$.

In the approximate expression (10a) we should neglect electrostriction, because in the linear approximation and under the absence of built-in static electric field, the electrostriction response will be manifested at frequencies doubled in comparison with the frequency of the excitation electric field. In the linear regime the double-frequency signal can be excluded experimentally. Analytical results obtained from Eqs. (10) are justified, if the hole conductivity is constant proportional to the mobility and average concentration of holes, while the acceptor conductivity is negligibly small in comparison with the hole one. Otherwise numerical modeling of the nonlinear problem should be performed.

Note, that Eqs. (10) are derived for the case $J_\omega^c(0) = 0, \rho_S(h) = 0$, where the space charge density $\rho_S(h) = e(-N_a^-(h) + p(h))$. Other types of the boundary conditions, e.g., $\rho_S(0) = \rho_S(h) = 0$ and $J_\omega^c(0) = J_\omega^c(h) = 0$, lead to the total charge absence and consequently to zero surface displacement $u_3(\omega) = 0$ in the linear decoupling approximation (see Table C1 in Supplementary Materials¹⁰⁴).

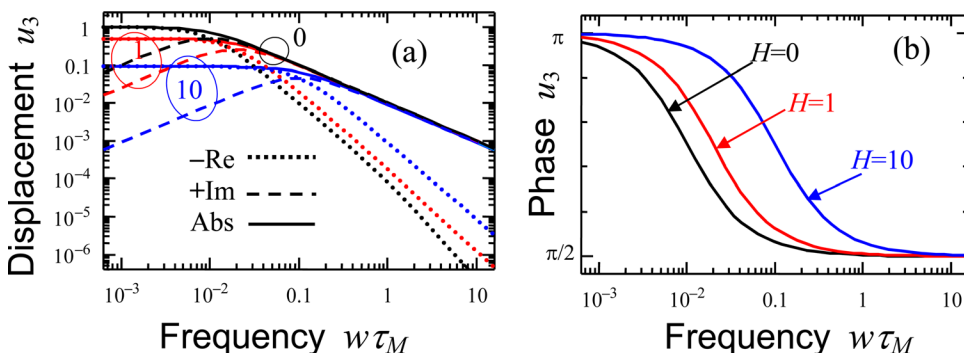
Figures 3 represent the frequency spectra of the surface displacement (10) for several gap thicknesses and mixed-type boundary conditions $J_\omega^c(0) = 0, \rho_S(h) = 0$. The displacement $u_3(z=0, \omega)$ is proportional to the total space charge $\delta Q_p(\omega) = \int_0^h (p(z) - p_0) dz$, since the total acceptor charge $\delta N_a^-(\omega) = \int_0^h (N_a^-(z) - N_{a0}^-) dz \equiv 0$ is zero for the ion-blocking boundary conditions (9a). In the limiting case of zero gap ($H \rightarrow 0$) the displacement is maximal; it decreases with the gap thickness increase. The total displacement absolute value monotonically decreases with frequency increase; while its imaginary part has a maximum.

B. Nonlinear dynamic strain-voltage response of MIEC

Below we analyze the dynamic electromechanical response caused by the mobile ionized donors and electrons in the ionic semiconductor film. Note, that the dynamic electromechanical response caused by the mobile ionized acceptors and holes can be analyzed in a similar way.

For numerical modeling we introduce the Debye screening radius

$$R_S = \sqrt{\frac{\epsilon_{33}^S \epsilon_0 k_B T}{e^2 n_0}}. \quad (11a)$$



The Maxwellian relaxation time that determines the time scale of the considered problem is

$$\tau_M = \frac{R_S^2 e}{\eta_n k_B T}. \quad (11b)$$

Thus below we operate with dimensionless frequency $\tau_M f$, where linear frequency $f = \omega/2\pi$.

Dimensionless rate constants

$$\tilde{w}_{n0,h} = \frac{\tau_M}{R_S e} w_{n0,h}, \quad \tilde{w}_{d0,h} = \frac{\tau_M}{R_S e} w_{d0,h}, \quad (11c)$$

and dimensionless electromechanical response of electrons or donors

$$u_3(z=0) \approx \frac{1}{2} \int_0^h \frac{d\tilde{z}}{c_{33}} \left(\zeta^C \left(\frac{n(\tilde{z}) - n_0}{n_0} \right) + \mu^d \left(\frac{N_d^+(\tilde{z}) - N_{d0}^+}{n_0} \right) + \frac{\tilde{q}_{33} k_B T}{\epsilon_{33}^S \epsilon_0} \left(\frac{\partial \tilde{\varphi}(\tilde{z})}{\partial \tilde{z}} \right)^2 \right). \quad (11d)$$

Here $\tilde{z} = z/R_S$. Electron and donor contributions in Eq. (11d) are divided by the factors c_{33}/ζ^C and c_{33}/μ^d correspondingly, as compared with Eq. (3). The dimensionless parameters $\tilde{q}_{33} k_B T / (2\epsilon_{33}^S \epsilon_0 \zeta^C)$ and $\tilde{q}_{33} k_B T / (2\epsilon_{33}^S \epsilon_0 \mu^d)$ determine the relative strength of the electrostriction contribution. Other dimensionless variables used in Eqs. (3)–(9) under the simulations are introduced in Supplementary Materials,¹⁰⁴ Appendix C1. Also there we analyzed some typical I-V curves in Appendix C2.¹⁰⁴

Dimensionless electromechanical response (11d) was calculated numerically with the help of Matlab (Ref. 112) for the external voltage frequency range $\tau_M f = 0.001 - 0.1$ and different types of boundary conditions (9). The *pdepe* function was used, the latter solved the nonlinear problem via second order finite difference in space and up to fifth order numerical differentiation formula in time. The mesh was nonuniform with up to 1000 elements and the solution time steps were chosen adaptively according to the *ode15s* algorithm. Dimensionless electrochemical potentials (Slootbloom formulation¹¹³) were used as variables for the solution to ensure the stability of the numerical problem.

Typical response curves $\tilde{u}_3(V, f)$ are shown in Figs. 4–9. Different loops (from inner to outer ones) in each plot correspond to the increasing voltage amplitude V_0 (in volts). All plots are generated using expressions (8) for the chemical

FIG. 3. (Color online) (a) Real, imaginary parts, absolute value (dotted, dashed, and solid curves) and phase (b) of the normalized surface displacement $u_3(0, \omega)$ vs dimensionless frequency $w = \omega/2\pi$ calculated for several gap thickness $\tilde{H}/R_S = 0, 1, 10$ (figures near the curves). Film thickness $h/R_S = 100$, mixed boundary conditions $J_\omega^c(0) = \rho_S(h) = 0$ are imposed.

potential of carriers. The differences in loop shape mainly originate from the type of boundary conditions, external voltage frequency, and film thickness as discussed in Secs. IV B 1–IV B 3.

In Figs. 4, 5, 7, and 8 we neglect the electrostriction impact into the electromechanical response (possible case of dielectrically linear materials, like yttria-stabilized zirconia, LiCoO₂, LiMn₂O₄, LiC₆). Electrostriction contribution is included in Figs. 6, 9 and 10 for material parameters $\xi^C = 10$ eV, $\mu^d = 10$ eV (recalculated from known flexoelectric coefficients and the data of Ref. 114), $q_{33} = -13.7 \cdot 10^9$ m J/C² and $\varepsilon_{33} = 300$ corresponding to SrTiO₃ with oxygen vacancies. Since the oxygen vacancy concentration (and corresponding conductivity) can be tuned in the wide range for SrTiO₃,^{115,116} we cannot define τ_M for all cases, but rather consider the range $\tau_M f = 0.001 - 0.1$.

1. Ion-blocking and electron-conducting interfaces

The hysteresis-like loops, shown in Figs. 4, are calculated for the case of asymmetric mixed-type electronic boundary conditions (9): interface $z = 0$ is **almost** electron blocking (“almost” means that results remained the same when we put $\tilde{w}_{n0} \leq 10^{-2}$ in Eq. (9b)), interface $z = h$ is almost electron conducting (we put $\tilde{w}_{nh} \geq 10^2$); both interfaces are ion blocking: we put $w_{d0,h} = 0$ to reach $J_c^d(0) = J_c^d(h) = 0$. Different loops (from inner to outer ones) correspond to the different values of maximal voltage V_0 . Plots (a, b, c) are generated for thin film ($h = 2R_S$) and

plots (d, e, f) for thicker ones ($h = 20R_S$). The loop shape is quasi-ellipsoidal only at small voltage amplitudes $V_0 < k_B T/e$ and becomes asymmetric hysteresis-like with V_0 increase for $f\tau_M \leq 0.01$. The loops become noticeably open (or even circle-like) with the frequency increase $f\tau_M \geq 0.01$. The loop opening becomes much stronger with the thicknesses increase. Note, that the response curves are strongly asymmetric with respect to the voltage sign $V \rightarrow -V$, as can be expected from the asymmetry of the interface electronic conductivity. We further emphasize that the donor blocking boundary conditions ($J_c^d(0) = J_c^d(h) = 0$) and negligible generation-recombination effects, the continuity equation rules that $(d/dt) \int_0^h N_d^+(z) dz = 0$ and ionized donors contribute nothing to the response $u_3(V, f)$. Thus, only the total changes of the electron amount contribute into the MIEC film surface displacement.

The response curves $u_3(V, f)$, shown in Fig. 5, are symmetric with respect to the voltage sign $V \rightarrow -V$, since the curves are calculated for the case of symmetric electron conducting and ion-blocking interfaces at $z = 0$ and $z = h$. Note, that for this case the gaps should be absent. Different loops (black, red, green, and blue ones) correspond to the different values of maximal voltage V_0 . Plots (a, b, c) are generated for thin film ($h = 2R_S$) and plots (d, e, f) for thicker ones ($h = 20R_S$). The curves calculated for low frequencies $\tau_M f = 0.001-0.01$ are symmetric with respect to the voltage sign even after the first cycling. The curves generated at higher frequencies $\tau_M f = 0.1$ become symmetric with respect to the voltage sign only after relatively long relaxation of the initial

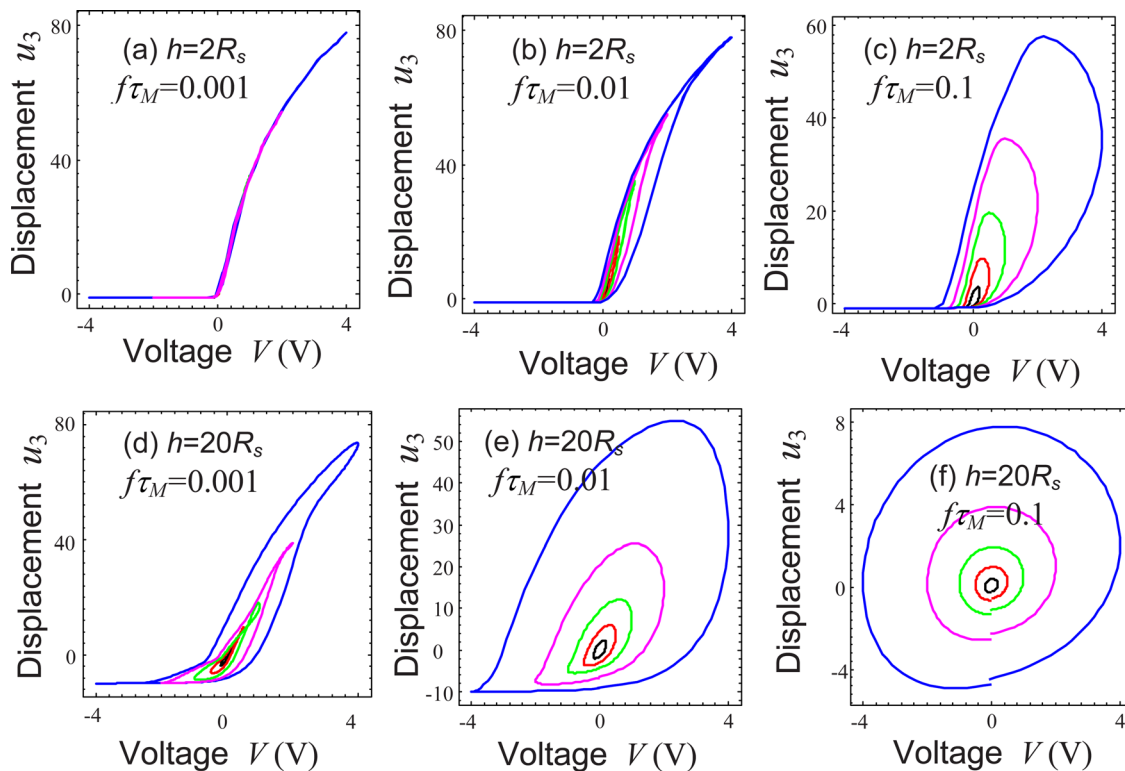


FIG. 4. (Color online) Electromechanical response $\bar{u}_3(V, f)$ calculated for different frequencies: $\tau_M f = 0.001$ (a, d), $\tau_M f = 0.01$ (b, e), and $\tau_M f = 0.1$ (c, f). Film thickness $h/R_S = 2$ (a, b, c) and $h/R_S = 20$ (d, e, f). Interface $z = 0$ is almost electron blocking, $J_c^d(0) = 0$ (we put $\tilde{w}_{n0} \leq 10^{-2}$), interface $z = h$ is almost electron conducting (we put $\tilde{w}_{nh} \geq 10^2$). Both interfaces are ion blocking: we put $w_{d0,h} = 0$ to reach $J_c^d(0) = J_c^d(h) = 0$. Band structure parameters: $E_n = 0$ eV, $\delta E_n = 0.5$ eV for electrons and $E_d = 0.1$ eV for donors. Equilibrium surface concentrations are assumed to be equal to the bulk ones, full amounts ratio $N_d/N_n = 0.1$, mobilities ratio $\eta_d/\eta_n = 0.1$. Also we neglected electrostriction contribution, $\bar{q}_{33} = 0$.

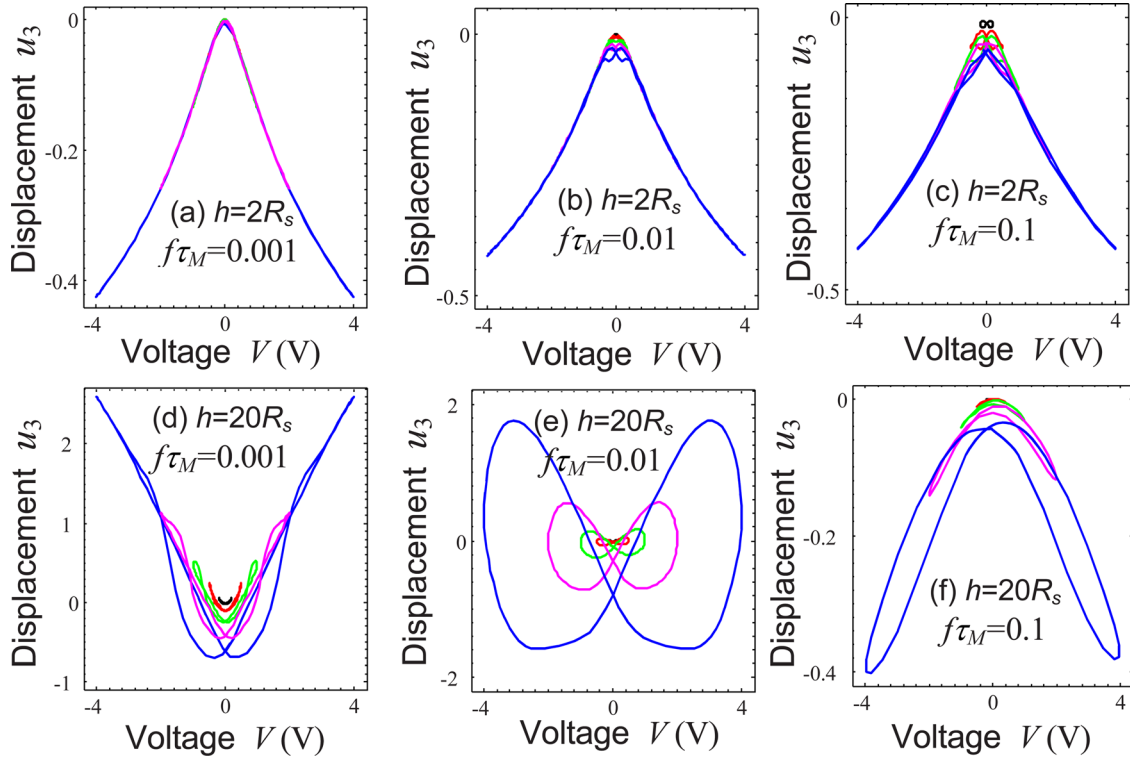


FIG. 5. (Color online) Electromechanical response $\tilde{u}_3(V, f)$ calculated for different frequencies: $\tau_M f = 0.001$ (a, d), $\tau_M f = 0.01$ (b, e), and $\tau_M f = 0.1$ (c, f). Film thickness $h/R_s = 2$ (a, b, c) and $h/R_s = 20$ (d, e, f). Interfaces $z = 0$ and $z = h$ are almost electron conducting (we put $\tilde{w}_{n0,h} \geq 10^2$). Both interfaces are ion blocking: we put $w_{d0,h} = 0$ to reach $J_c^d(0) = J_c^d(h) = 0$. Other parameters are listed in the caption to Fig. 4.

conditions. The curves calculated for thick films are more overblown in comparison with the ones calculated for thin films (compare plots a, b, c with d, e, f). Finally, note that the nonlinear electromechanical response is absent for the

completely blocking conditions $J_c^n(0) = J_c^n(h) = J_c^d(0) = J_c^d(h) = 0$.

Electrostriction is chosen negligibly small in Figs. 4 and 5, that corresponds to the case $|\tilde{q}_{33} k_B T / (2\epsilon_{33}^S \epsilon_0 \xi^C)| \ll 10^{-3}$.

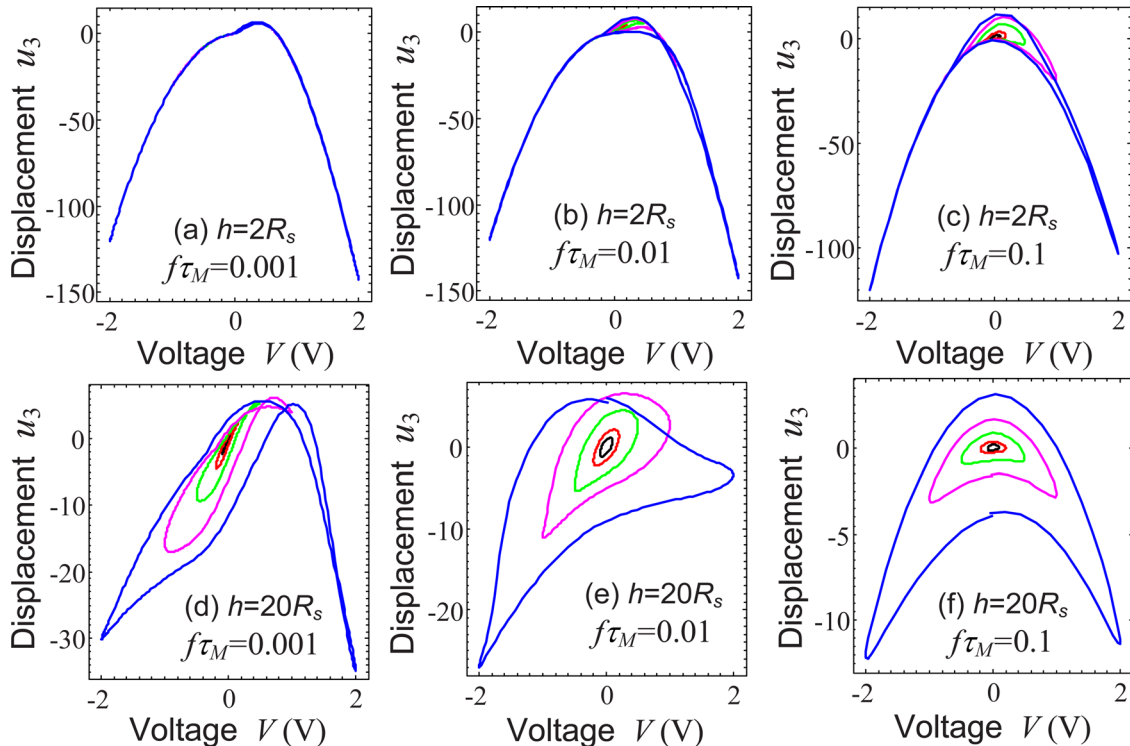


FIG. 6. (Color online) Electromechanical response $\tilde{u}_3(V, f)$ calculated for nonzero electrostriction coefficient $\tilde{q}_{33} k_B T / (2\epsilon_{33}^S \epsilon_0 \xi^C) = -0.04$ at different frequencies: $\tau_M f = 0.001$ (a, d), $\tau_M f = 0.01$ (b, e), and $\tau_M f = 0.1$ (c, f). Boundary conditions and other parameters are listed in the caption to Fig. 4.

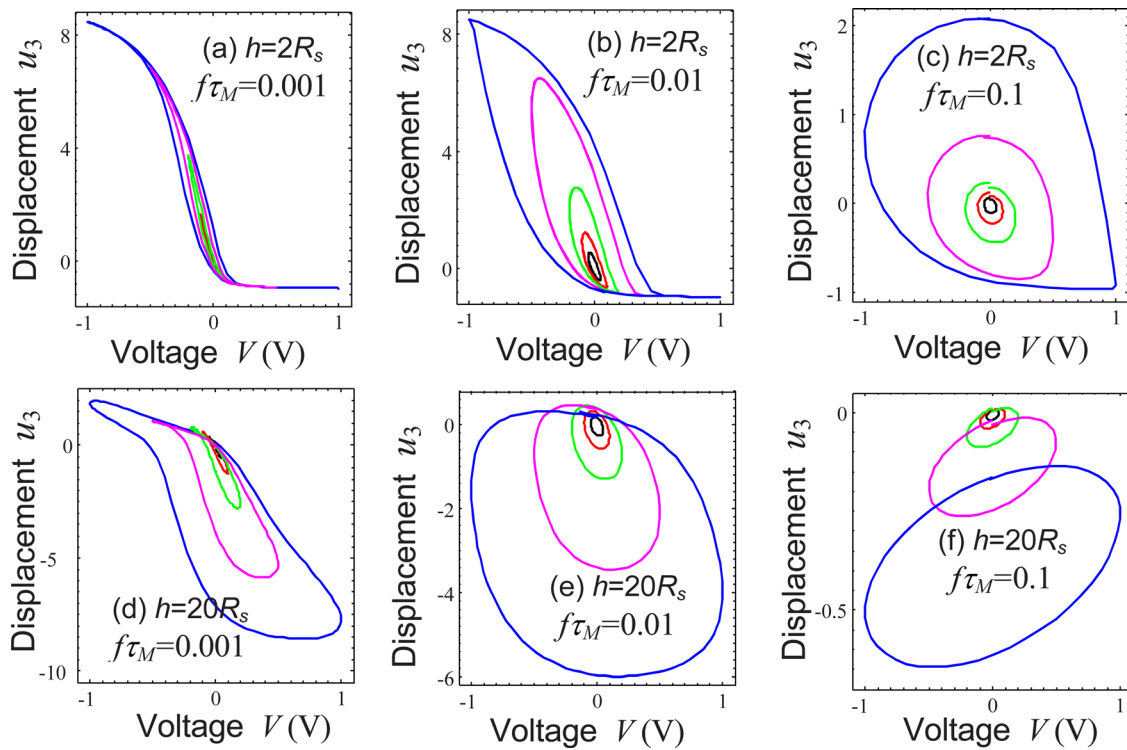


FIG. 7. (Color online) Electromechanical response $\bar{u}_3(V, f)$ calculated for different frequencies: $\tau_M f = 0.001$ (a, d), $\tau_M f = 0.01$ (b, e), and $\tau_M f = 0.1$ (c, f). Film thickness $h/R_s = 2$ (a, b, c) and $h/R_s = 20$ (d, e, f). Interface $z = 0$ is almost donor blocking (we put $\bar{w}_{d0} \leq 10^{-2}$ to reach $J_c^d(0) \approx 0$), interface $z = h$ is almost donor conducting (we put $\bar{w}_{dh} \geq 10^2$). Both interfaces are electron blocking: we put $w_{n0} = w_{nh} = 0$ to reach $J_c^n(0) = J_c^n(h) = 0$. Other parameters are listed in the caption to Fig. 4.

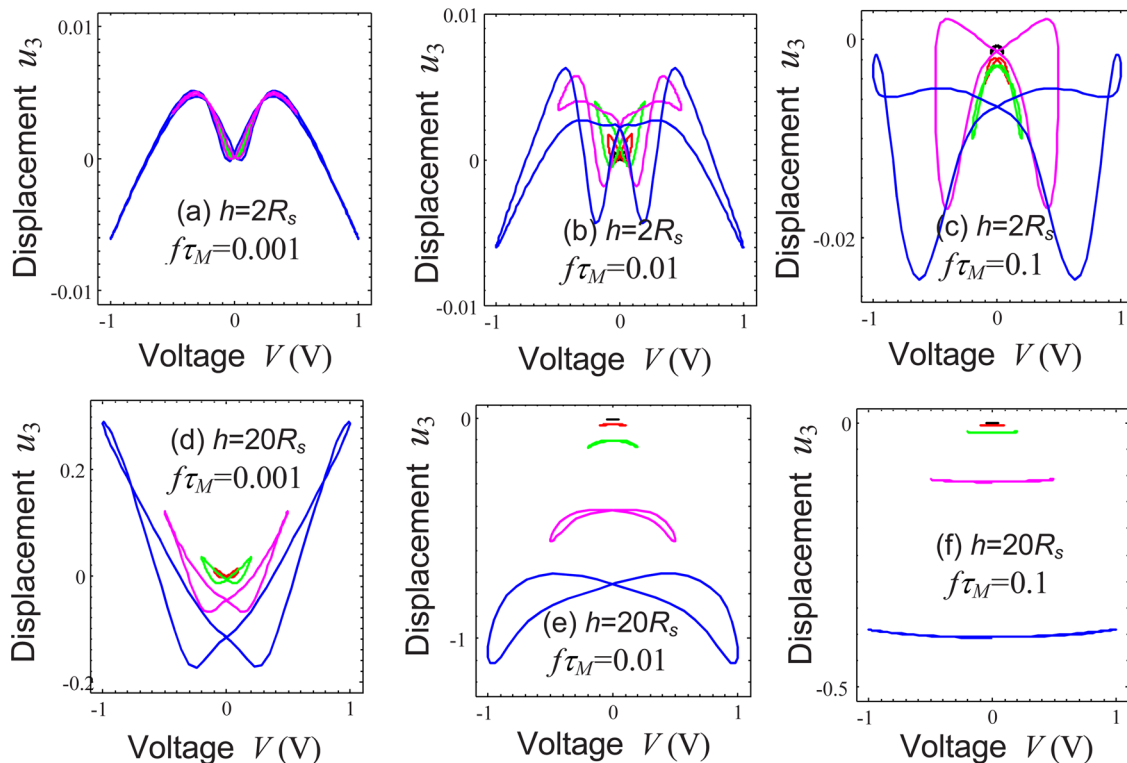


FIG. 8. (Color online) Electromechanical response $\bar{u}_3(V, f)$ calculated for different frequencies: $\tau_M f = 0.001$ (a, d), $\tau_M f = 0.01$ (b, e), and $\tau_M f = 0.1$ (c, f). Film thickness $h/R_s = 2$ (a, b, c) and $h/R_s = 20$ (d, e, f). Interfaces $z = 0$ and $z = h$ are almost donor conducting (we put $\bar{w}_{dh} \geq 10^2$). Both interfaces are electron blocking: we put $w_{n0} = w_{nh} = 0$ to reach $J_c^n(0) = J_c^n(h) = 0$. Other parameters are listed in the caption to Fig. 4.

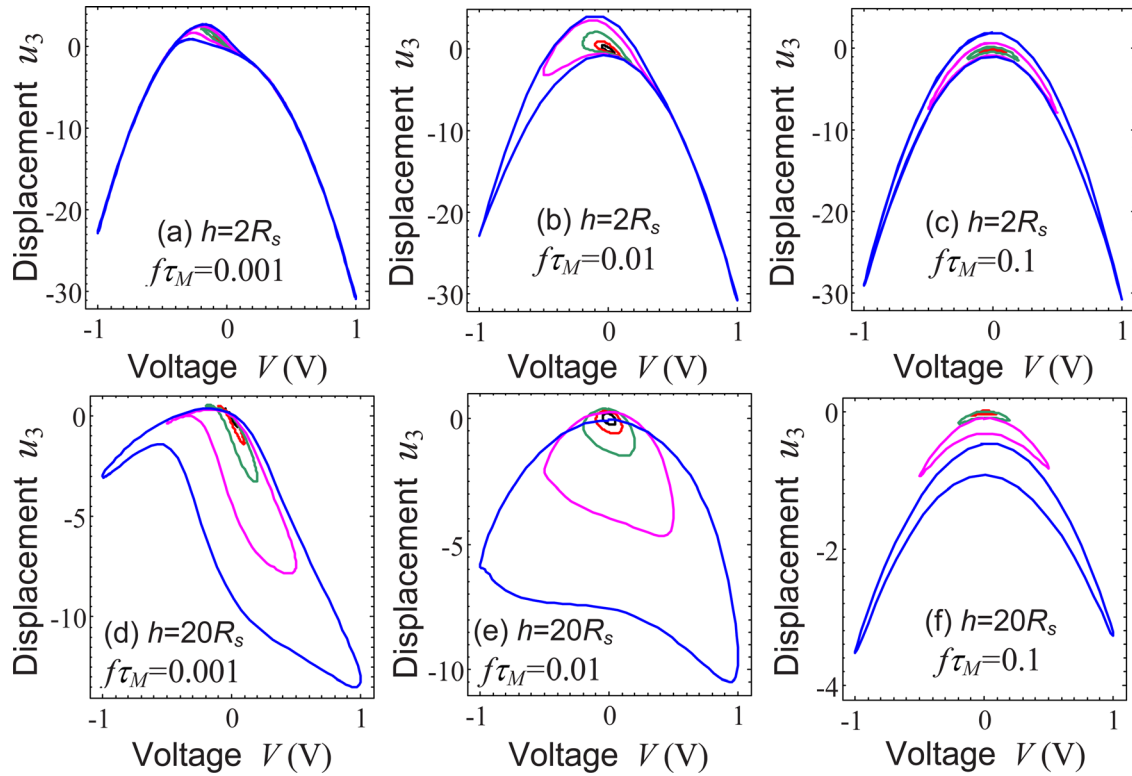


FIG. 9. (Color online) Electromechanical response $\tilde{u}_3(V, f)$ calculated for nonzero electrostriction coefficient $\tilde{q}_{33}k_B T / (2\epsilon_{33}^S \epsilon_0 \mu^d) = -0.04$ at different frequencies: $\tau_M f = 0.001$ (a, d), $\tau_M f = 0.01$ (b, e), and $\tau_M f = 0.1$ (c, f). Film thickness $h/R_s = 2$ (a, b, c) and $h/R_s = 20$ (d, e, f). Boundary conditions and other parameters are listed in the caption to Fig. 7.

Electromechanical response $\tilde{u}_3(V, f)$ calculated for the same parameters as in Fig. 4 and SrTiO₃ electrostriction coefficient \tilde{q}_{33} is shown in Figs. 6. It is seen from Figs. 6 that electrostriction contribution to dynamical electromechanical response is of the same order or essentially higher than the Vegard contribution for paraelectrics and incipient ferroelectrics like SrTiO₃ due to high dielectric permittivity. Corresponding responses acquire “parabolic-like” and “moon-like” shape. Since the “parabolic-like” curves were calculated analytically for the static local electromechanical response of SrTiO₃,⁶⁷ the dynamical response calculated numerically tends to the static limit with the frequency decrease as anticipated. The hysteresis loop opens under the frequency increase (compare Figs. 6(a), 6(b), 6(c)). The film

thickness increase leads to the electric field decrease and thus electrostriction contribution decreases (compare Figs. 6(a)–6(c) with 6(d)–6(f)). Dependencies in Fig. 6 are asymmetric with respect to the voltage sign due to the imposed symmetric mixed-type electronic boundary conditions.

2. Ion-conducting and electron-blocking interfaces

Here, we compare asymmetric and symmetric ion-conducting boundary conditions (9d). Both interfaces are electron blocking: we put $w_{n0} = w_{nh} = 0$ to reach $J_c^n(0) = J_c^n(h) = 0$. The hysteresis-like loops, shown in Figs. 7, are calculated for the case of asymmetric mixed-type ionic boundary conditions: interface $z=0$ is almost donor

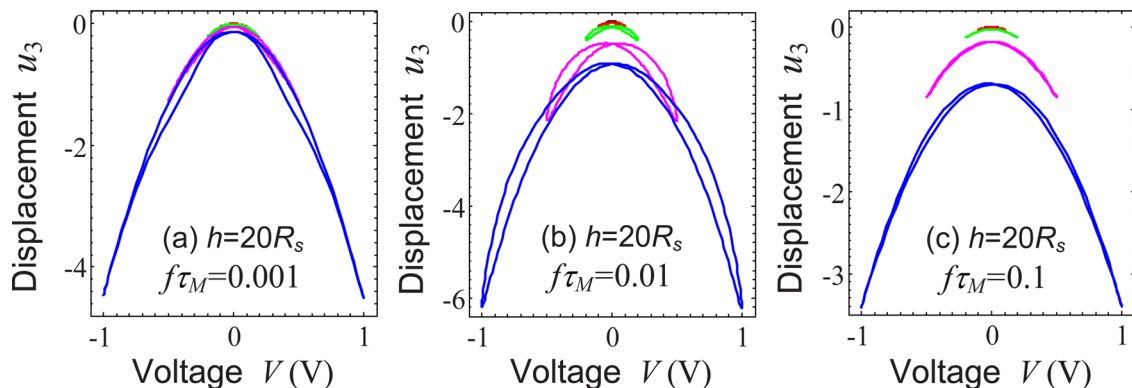


FIG. 10. (Color online) Electromechanical response $\tilde{u}_3(V, f)$ calculated for nonzero electrostriction coefficient $\tilde{q}_{33}k_B T / (2\epsilon_{33}^S \epsilon_0 \mu^d) = -0.04$ at different frequencies: $\tau_M f = 0.001$ (a), $\tau_M f = 0.01$ (b), and $\tau_M f = 0.1$ (c). Film thickness $h/R_s = 20$. Boundary conditions and other parameters are listed in the caption to Fig. 8.

blocking, interface $z=h$ is almost donor conducting; both interfaces are electron blocking. Different loops (from inner to outer ones) correspond to the different values of maximal voltage V_0 . Plots (a, b, c) are generated for thin film ($h=2R_S$) and plots (d, e, f) for thicker ones ($h=20R_S$). At low frequencies $f\tau_M \leq 0.01$ the response curves are strongly asymmetric with respect to the voltage sign $V \rightarrow -V$ as anticipated from the asymmetry of the interfaces ionic conductivity. For this case only the total changes of the ionized donor amount contribute into the MIEC film surface displacement. The loops become noticeably open and almost symmetric with the frequency increase $f\tau_M \geq 0.01$. The inflation becomes much stronger with the thickness increase. From Figs. 7 the loop shape is elliptic for small voltages $V_0 < k_B T/e$, and the corresponding parameters depend on the film thickness and boundary conditions, which is consistent with analytical results of Sec. IV A. For high maximal voltage V_0 the loop shapes demonstrate a pronounced size effect: the transition from the slim hysteresis to ellipse appears with the film thickness increase. The transition most probably originates from the acting electric field decrease with the film thickness increase: the thicker is the film the more close to linear is its response.

The response curves $u_3(V, f)$, shown in Figs. 9, are symmetric with respect to the voltage sign $V \rightarrow -V$, since the curves are calculated for the case of symmetric ion conducting and electron blocking interfaces at $z=0$ and $z=h$. Note, that for this case the gaps should be absent. Different loops (from inner to outer ones) correspond to the different values of maximal voltage V_0 . Plots (a, b, c) are generated for thin film ($h=5R_S$) and plots (d, e, f) for thicker ones ($h=20R_S$). The curves calculated for low frequencies $\tau_M f = 0.001-0.01$ are symmetric with respect to the voltage sign even after the first cycling. The butterfly-like curves generated at higher frequencies $\tau_M f = 0.1$ become symmetric with respect to the voltage sign only after relatively long relaxation of the initial conditions (compare plots a, b, c with d, e, f).

Electrostriction contribution is chosen to be negligibly small in Figs. 7 and 8, namely we regard $|\tilde{q}_{33} k_B T / (2e_{33}^S \epsilon_0 \mu^d)| \ll 10^{-3}$ when we calculate the plots. Dynamical response $\tilde{u}_3(V, f)$ calculated for SrTiO₃ electrostriction coefficient \tilde{q}_{33} , asymmetric and symmetric ion-conducting boundary conditions are shown in Figs. 9 and 10 correspondingly. Figs. 9 and 10 demonstrate that electrostriction contribution is of the same order or even 1-2 orders higher than the ionic and electronic contributions. Corresponding responses acquire “parabolic-like” shape at low frequencies in thin films. The moon-like or asymmetric hysteresis loop opens under the frequency increase. The film thickness increase leads to the electric field decrease and thus electrostriction contribution decreases (compare with Fig. 6).

Quantitatively, the difference in the boundary conditions leads to asymmetry of the discrepancies and asymmetry of the loops shape, which correlates with results of Secs. IV B 1. The main difference between the case of ion-blocking boundary conditions considered in Secs. IV B 1 and the ion-conducting top electrode considered in the subsection is the inverse loop orientation as anticipated from the substitution

of the carrier charge electrons \rightarrow donors. Similar effects can be expected for holes \rightarrow acceptors.

We expect that observable dynamical electromechanical response of MIECs should strongly depend on the relative strength of ionic, electronic, and electrostriction contributions and boundary conditions type (carriers-blocking, carriers-conducting or mixed). In principle all regimes considered in the paper can be realized for proper electrodes (carriers-blocking, carriers-conducting or mixed). However, it is worth noting that parabolic-like or moon-like shape is typical for the majority of loops in Figs. 6, 9 and 10 calculated for SrTiO₃. So, we may conclude that that dynamic electromechanical response of paraelectrics and incipient ferroelectrics like SrTiO₃ with oxygen vacancies or other mobile charge defects is primarily determined by the strong electrostriction contribution and secondary by the electrode type.

V. SUMMARY REMARKS

We performed analytical and numerical calculations of the *dynamic* electromechanical response of the MIEC film caused by the local changes of ions (acceptors or donors) concentration (*conventional stoichiometry contribution*); free electrons (holes) concentration (*electron-phonon coupling via the deformation potential*) and *flexoelectric effect*. Dynamic electromechanical response was not calculated previously, while our estimations performed for correlated oxides show that strength of all three contributions appeared comparable. Moreover, the coupling contribution proportional to the deformation potential may be stimulated by the local Jahn-Teller distortion existing in correlated oxides like La_{1-x}Sr_xMnO₃ and La_{1-x}Sr_xCoO₃. This allows relating the calculated electromechanical response with the local deformation potential of correlated oxides.

A great variety of possible nonlinear dynamic electro-mechanical response of MIEC films is predicted. Electromechanical responses mimic hysteresis loops with pronounced memory window and butterfly-like loops for partially and completely on-conducting boundary conditions correspondingly. Predicted strain-voltage hysteresis of piezoelectric-like, parabolic-like, moon-like, and butterfly-like shape requires experimental justification in ionic semiconductors like correlated oxides, strontium titanate, and resistive switching materials. Consequently, the SPM measurements of the MIEC film surface displacement could provide important information about the local oxidation level, electron-phonon interactions via the deformation potential, and even Jahn-Teller distortions in the films.

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