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Dielectric properties of $\text{NaNbO}_3\text{:SrTiO}_3$ interface nanolayer

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$\text{NaNbO}_3\text{:SrTiO}_3$ interface nanolayers are studied by combining first-principles modeling and experimental approach. The nature of $\text{NaNbO}_3\text{:SrTiO}_3$ interface is investigated using density-functional theory calculations. Interface parameters are experimentally estimated using analysis of the dielectric response of SrTiO_3 and NaNbO_3 epitaxial films and $\text{NaNbO}_3\text{:SrTiO}_3$ superlattices. It is shown that $\text{NaNbO}_3\text{:SrTiO}_3$ interfaces can be approximated by dielectric nanolayers with thickness 1–2 nm and with temperature independent permittivity 25–55. Mechanism responsible for the nanolayer formation is the ionic charge mismatch between constituents. © 2011 American Institute of Physics. [doi:10.1063/1.3527900]

I. INTRODUCTION

Novel ferroics and multiferroics desirable for modern miniature devices can be engineered using size, strain, and interface effects in perovskite-structure oxides.¹ Due to large fraction of the near-interface material in nanostructured ceramic-type composites, thin-film multilayers, and superlattices (SLs), the dielectric, ferroelectric, and other properties of the nanostructures can be especially strongly influenced by peculiar properties of interfaces between constituents. Despite experimental studies of chemical composition, local crystal, and electronic structure of interfaces, the dielectric properties of interfacial layers are mostly unknown. This makes it difficult to evaluate interfacial contribution to the response of nanostructures, important for applications.

Recently, peculiar interfacial phenomena have been detected in short-period multilayers and SLs of paraelectric SrTiO_3 (STO) and NaNbO_3 (NNO),^{2,3} where effects of misfit strain and ferroelectric polarization are negligible. In Ref. 2, the lattice expansion and decrease in the dielectric permittivity observed with decreasing SL period have been ascribed to specific NNO:STO interfaces, with ionic charge mismatch between constituents on both A- and B-sites of the perovskite cell. It has been shown by first-principles analysis that the interfacial charge imbalance can really lead to an expansion of the unit cell (u.c.) volume.³ In the present work, the role of NNO:STO interface in the dielectric response is investigated. The effective thickness and dielectric permittivity of the near-interface layer are determined by combining first-principles calculations and experimental studies.

II. METHOD

The atomic-level properties of the (100) interface between NNO and STO were investigated by density-functional theory (DFT) calculations. The calculations were performed using the VIENNA AB INITIO SIMULATION PACKAGE. The core states were represented using the projector aug-

mented wave method, and the semicore states of Na, Ti, Sr, and Nb were treated as valence electrons. The plane-wave cutoff energy throughout was 700 eV. For structural optimization, the exchange and correlation energies were described using the local-density approximation. No in-plane strain (as imposed by a substrate) was considered. Ionic and cell shape relaxation were performed to determine the minimum energy configuration. The tetrahedron method with Blöchl corrections, the Methfessel–Paxton method, and the frozen phonon method were employed. More details can be found in Ref. 3.

Epitaxial STO and NNO films, and NNO:STO SLs were grown by *in situ* pulsed laser deposition on (001) MgO and (001) LaAlO_3 (LAO) substrates using an oxide $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (LSCO) bottom electrode layer. For all NNO and STO layers, the plane orientation relationship was *layer* (001) || *LSCO*(001) || *substrate* (001). The SL period Λ was varied between 6 and 460 u.c. by varying the number of NNO:STO pairs and keeping the total thickness constant. For electrical characterization, the vertical capacitor structures were formed by pulsed laser deposition of the top Pt electrodes using shadow mask. The dielectric response was measured in the direction normal to substrate surface using an HP 4284A LCR meter at frequencies $f=10^2\text{--}10^6$ Hz, amplitude of ac electric field $E_{ac}<50$ kV/m, and magnitude of dc electric field $E_{dc}=0\text{--}12$ MV/m. The real part of the dielectric permittivity, ϵ , was determined using leaky-parallel-plate-capacitor model.⁴ More details on growth, crystal structure, and electrical characterization of the heterostructures can be found elsewhere.^{2,5}

III. RESULTS AND DISCUSSION

A. Atomic view of NNO:STO interface

To reveal a possible role of interfaces in the dielectric response, a stack of thin NNO layer and thin STO layer is investigated. The (001) crystal planes of the layers and interfaces between the layers are considered to be parallel to the substrate surface. Between the layers, two types of charge-imbalanced NNO:STO interfaces are present. STO has nomi-

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FIG. 1. (Color online) Schematic presentation of (a) and (b) ionic positions in perovskite-type cells of NNO and STO at (a) n -type and (b) p -type interfaces, and of (c) distances between ions.

nally neutral planes of $(\text{SrO})^0$ and $(\text{TiO}_2)^0$, while the NNO planes have alternating nominal charges $(\text{NaO})^-$ and $(\text{NbO}_2)^+$, as illustrated in Figs. 1(a) and 1(b). To retain charge neutrality and prevent the “polar catastrophe,” i.e., a divergent electric field due to an uncompensated dipole, the $(\text{NbO}_2)^+ / (\text{SrO})^0$ interface has an extra half an electron per u.c. compared to nominal charges and it is denoted as an n -type interface, while the $(\text{NaO})^- / (\text{TiO}_2)^0$ interface has half a hole and is denoted p -type. The electronic and structural properties of different charge-imbalanced NNO:STO SLs have been investigated and the detailed results can be found in Ref. 3. In order to estimate the dielectric properties of NNO:STO interfaces, here we focus on ionic positions at interfaces. The NNO:STO stacks containing 12 u.c. (6.5 u.c. of NNO and 5.5 u.c. of STO), with a central interface cell (cell number 0) are selected as an example.

FIG. 2. (Color online) Distance r_A between A-site ions and relative displacement Δr_B of B-site ions as a function of number of u.c. in the vicinity of (a) n -type $\text{NbO}_2\text{:SrO}$ interface and (b) p -type NaO:TiO_2 interface.

Schematic two-dimensional presentation of ionic positions in perovskite-type cells is shown in Fig. 1(c), where A- and B-sites and oxygen O are marked. The distance r_A between A-site ions and the relative displacement Δr_B of B-site ions (with respect to the oxygen octahedron) are selected in the direction normal to substrate surface (i.e., central interface cells are placed parallel to substrate surface). In the constituent layers, the distance r_A is between two similar A-ions (Na in NNO and Sr in STO). In the central interface cell, it is between Na and Sr ions.

The calculated parameters r_A and Δr_B are plotted as a function of distance from the interface cell for two types of interfaces: n -type $\text{NbO}_2\text{--SrO}$ interface [Fig. 2(a)] and p -type NaO--TiO_2 interface [Fig. 2(b)]. At the n -interface, the distance between Na and Sr ions in the interface cell considerably exceeds r_A of the constituent materials. Presence of such cells explains the experimentally detected lattice expansion.² With decreasing SL period, number of interfaces and relative fraction of the enlarged cells increase. This leads to overall increase in u.c. volume of SLs, as has been really observed [Fig. 3]. In three cells near the interface, large off-

FIG. 3. (Color online) u.c. volume V as a function of number n of NNO:STO interfaces in the grown SLs.

center displacement Δr_B of Nb is found. Such a displacement suggests polarization in these cells being different from that inside constituent layers, further away from the interface. This considerable polar distortion can limit the ionic displacements under applied electric field, leading to smaller and field independent dielectric permittivity.

Although the permittivity near the interface is strictly a function of cell's number, the NNO:STO interface can be described as a layer with thickness d_{INS} of at least 3 u.c. and some effective permittivity ϵ_{INS} , smaller than in the constituents. An important feature of the interface nanolayer is its temperature independent mechanism of formation suggesting no or weak temperature dependence of d_{INS} and ϵ_{INS} . At the p -interface, the distance r_B is less affected by the interface. However, the polar distortion connected with Ti displacement is clearly seen [Fig. 2(b)]. Also for the p -interface, the interface nanolayer approximation can be applied.

It must be noted that in NNO:STO interface nanolayers, besides polar distortions related to off-center displacements of B-site ions, also rotations of oxygen octahedra are found (not illustrated here). Both the B-site displacements and the octahedral rotations contribute to the permittivity ϵ_{INS} , smaller than in constituents.

B. Dielectric response

To experimentally determine d_{INS} and ϵ_{INS} , the dielectric response of thin-film NNO:STO stacks with various numbers n of NNO:STO interfaces was measured and analyzed. Growth of stacks with only one selected type of interface, which extends continuously in-plane across a macroscopic sample, is very difficult. Although x-ray diffraction analysis evidenced formation of SLs,² this could not prove existence of a single type of interface. In the deposited SLs, different interfaces are randomly distributed. This prevents experimental studies of the n - or p -type interfaces separately. In the SL stack, the effective interface parameters d_{INS} and ϵ_{INS} result from both types of interfaces.

To correctly extract d_{INS} and ϵ_{INS} from the measurements results, effects of design of the Pt/(NNO:STO)/LSCO capacitors on the measured response should be known.⁴ To avoid uncertainty related to possible onset of spontaneous polarization in the constituents,⁵ the nonferroelectric state of Pt/(NNO:STO)/LSCO should be confirmed too.

First, the contributions from capacitor design are estimated. In the vertical thin-film capacitor heterostructures, the measured capacitance C is usually presented as a series connection of the film and near-electrode interface layers (Fig. 4) (Ref. 6)

$$\frac{1}{C} = \frac{1}{C_F} + \frac{1}{C_I} \quad \text{or} \quad \frac{1}{\epsilon} \cong \frac{1}{\epsilon_F} + \frac{d_I}{d\epsilon_I}, \quad (1)$$

where C and ϵ are the measured capacitance and permittivity, C_F and ϵ_F are the capacitance and the permittivity of the film, C_I and ϵ_I are the total near-electrode interface capacitance (determined mainly by LSCO with a minor effect of Pt)⁷ and the corresponding permittivity, d is the film thickness, and d_I is the thickness of the near-electrode layer ($d_I \ll d$). To find the parameters (d_I, ϵ_I) of the near-electrode

FIG. 4. (Color online) Schematic presentation of the vertical capacitor heterostructure and the total capacitance.

interface, an approach suggested in Ref. 8 is applied. Assuming temperature independent near-electrode interface parameters (d_I, ϵ_I) and the high-temperature paraelectric state of the film, the experimentally measured derivative of inverse permittivity ξ is equal to

$$\begin{aligned} \xi &= \frac{\partial}{\partial T} \left(\frac{1}{\epsilon} \right) = \frac{\partial}{\partial T} \left(\frac{1}{\epsilon_{\text{FE}}} \right) = \frac{\partial}{\partial T} \left(\frac{1}{\epsilon_L + c/(T - \theta)} \right) \\ &= \frac{c}{[\epsilon_L(T - \theta) + c]^2}, \end{aligned} \quad (2)$$

where c and Θ are the Curie constant and the Curie temperature in the modified Curie–Weiss law for the paraelectric state. From the fits of $\xi(T)$ to Eq. (2), the parameters ϵ_L , c , and Θ can be found, and the film permittivity ϵ_F can be reconstructed. The normalized interface permittivity (ϵ_I/d_I) can be then estimated using Eq. (1), the reconstructed ϵ_F and the measured ϵ .

In the grown NNO:STO SLs with the first STO layer near the LSCO electrode, the near-electrode capacitance is similar to that in Pt/STO/LSCO with epitaxial STO film. In the Pt/STO/LSCO heterostructure, the dielectric permittivity was measured as a function of temperature [Fig. 5(a)]. From the fits of the obtained derivative $\xi(T)$ to Eq. (2) [Fig. 5(b)] the fitting parameters are determined: $c \approx 7.4 \times 10^4$ K, $\Theta \approx 38$ K, and $\epsilon_L \approx 55$, all being close to bulk STO values. As seen from [Fig. 5(c)], the difference between $1/\epsilon$ measured in the capacitor and $1/\epsilon_F$ reconstructed in the film is constant in the broad temperature range, evidencing the temperature independent near-electrode capacitance. The normalized permittivity of the near-electrode interface is found to be about $(\epsilon_I/d_I) \approx 2.5 \text{ nm}^{-1}$.

As previously shown in Ref. 4, in thin-film capacitor heterostructures, relatively large resistance of thin-film electrode layers leads to frequency dispersion of the measured permittivity ϵ and loss factor $\tan D$. Such dispersion is not connected to thin-film properties. For correct analysis of the NNO:STO interfaces, a reliable interval of measurement frequencies should be established. In the NNO:STO SLs at different temperatures, the electrode-related decrease in ϵ and increase in $\tan D$ are most noticeable at $f > 300$ kHz (Fig. 6). The low-frequency variations in $\tan D$ and ϵ are connected to the conductance of the SL stack,⁴ which increases on heating. This makes the measurements at $f < 20$ kHz un-

FIG. 5. (Color online) (a) The dielectric permittivity measured at $f = 100$ kHz in capacitor heterostructure of 250 nm thick STO film on LSCO/LAO. (b) The derivative ξ in STO film extracted from data in (a). Excellent fit to the modified Curie-Weiss law is also shown (dashed line). (c) The inverse permittivity reconstructed in STO film and measured in STO thin-film capacitor.

suitable for the analysis. The frequency $f = 100$ kHz is selected for the further analysis (similar to $f = 100$ kHz in Fig. 5).

Our recent studies of epitaxial NNO films have revealed that thermal strain generated by mismatch of the thermal expansion coefficients in NNO film and MgO substrate might lead to an onset of the ferroelectric state.⁵ Presence of strain and spontaneous polarization in the NNO layers of SLs is unwanted for the interface analysis. Studies of ε under applied dc electric field [Fig. 7(a)] reveal a weak sign of ferroelectricity in some SLs on MgO, in agreement with Ref. 5. In SLs on LAO, the shape of $\varepsilon(E_{dc})$ is hysteresis-free and almost flat, evidencing the absence of ferroelectric phase. In

FIG. 6. (Color online) The [(a) and (b)] dielectric permittivity and [(c) and (d)] loss factor as a function of frequency measured at $T = 297$ and 550 K in Pt/(NNO:STO)/LSCO ($\Lambda = 16$ u.c.) capacitor heterostructures on MgO [(a) and (c)] and LAO [(b) and (d)] substrates.

FIG. 7. (Color online) (a) The normalized permittivity $\varepsilon/\varepsilon(0)$ as a function of dc electric field E_{dc} in Pt/NNO/LSCO/MgO (marked with NNO), Pt/(NNO:STO)/LSCO/MgO with $\Lambda = 32$ u.c. (marked with SL/MgO), and Pt/(NNO:STO)/LSCO/LAO with $\Lambda = 32$ u.c. (marked with SL/LAO). (b) The dielectric permittivity ε as a function of decreasing temperature T in Pt/(NNO:STO)/LSCO/LAO. Arrows show direction of decreasing period from 460 to 12 u.c.

the nonferroelectric SLs on LAO, the permittivity was measured as a function of temperature [Fig. 7(b)]. With decreasing SL period, the character of $\varepsilon(T)$ remains practically unaltered, especially at $T = 200$ –400 K.

Based on the results in Figs. 5–7, the permittivity ε measured in the Pt/(NNO:STO)/LSCO/LAO stacks at $f = 100$ kHz and at $T = 200, 300$, and 400 K is selected for the analysis of the NNO:STO interface contribution. Under these conditions, the measured permittivity is not considerably affected by resistance of thin-film electrodes and/or presence of ferroelectric polarization.

The measured capacitance C of SLs can be presented as a series connection of capacitors C_{Ni} and C_{Si} formed by constituent NNO and STO layers, n interface layers between constituents, and near-electrode interface layers (Fig. 8)

FIG. 8. (Color online) Schematic presentation of the capacitance resulting from the constituent layers and the interfaces between them in NNO:STO SL.

FIG. 9. (Color online) (a) The dielectric permittivity ϵ as a function of period Λ in SLs on LAO measured at $f=100$ kHz at temperatures $T=200$, 300, and 400 K. Arrow shows direction of temperature increase. (b) The inverse permittivity as a function of number n of NNO:STO interfaces obtained from data in (a). Straight lines show fit $1/\epsilon \propto n$.

$$\frac{1}{C} \approx \sum_{i=1}^{(n+1)/2} \left(\frac{1}{C_{Ni}} + \frac{1}{C_{Si}} \right) + \sum_{i=1}^n \frac{1}{C_{INS}} + \frac{1}{C_1} = \frac{1}{C_{NS}} + \frac{n}{C_{INS}} + \frac{1}{C_1}. \quad (3)$$

Here C_{NS} is the total capacitance resulting from the constituent layers connected in series, and C_{INS} is the capacitance of the NNO:STO interface layer. Since the permittivity of STO and NNO constituents does not considerably change with decreasing SL period (Figs. 2 and 7), the expression (3) can be rewritten in the form

$$\frac{1}{\epsilon} \approx \frac{1}{\epsilon_{NS}} + n \frac{d_{INS}}{d} \left(\frac{1}{\epsilon_{INS}} - \frac{1}{\epsilon_{NS}} \right) + \frac{d_1}{d\epsilon_1}, \quad (4)$$

where ϵ_{NS} and d_{NS} are the permittivity and thickness of $(n+1)/2$ pairs of alternating NNO and STO layers, and d is the total stack thickness ($d=d_{NS}+nd_{INS}$).

In Fig. 9(a), the measured permittivity ϵ is plotted as a function of SL period Λ . The measured permittivity ϵ drops by approximately a factor of two with decreasing period from 460 to 6 u.c. This agrees with presence of the NNO:STO interface nanolayers possessing small permittivity.

For the revealed temperature independent near-electrode interface (ϵ_1/d_1) and the predicted temperature independent NNO:STO interfaces (ϵ_{INS}, d_{INS}), the inverse permittivity $1/\epsilon$ is expected to be a linear function of number n of NNO:STO interfaces [Eq. (4)]. This linear relationship ($1/\epsilon \propto n$) is experimentally found for $\Lambda \geq 12$ u.c. [Fig. 9(b)]. From the obtained linear fits, the effective permittivity ϵ_{INS}

of the NNO:STO interface layer is estimated using ($\epsilon_1/d_1 \approx 2.5 \text{ nm}^{-1}$ [Fig. 5(c)] and $d_{INS}=1-2 \text{ nm}$ [Figs. 2(a) and 2(b)]. The obtained $\epsilon_{INS} \approx 25-55$ is large compared to many dielectric materials. However, it is noticeably smaller than the permittivity of constituents. For instance, at $T=200-400 \text{ K}$, the permittivity ϵ_F extracted for STO and NNO films using Eq. (1) is about 200–500 (STO) and 350–600 (NNO). It must be noted that intermixing of NNO and STO would lead to $\epsilon_{INS} \approx 200-700$ depending on constituent fractions.⁹ The obtained relatively small ϵ_{INS} agrees with the results of DFT calculations.

The origin of the NNO:STO interface nanolayer with the dielectric permittivity different from NNO, STO, or their solid solutions, is the ionic charge mismatch. Similar effect can exist at interfaces between many perovskites. Being combined with effects of strain on magnitude and direction of polarization, it may principally contribute to permittivity enhancement. The dielectric response of perovskite nanocomposites of two or more constituents can be controlled to a large extent by interface nanolayers with the permittivity different from constituents. In bulk solid solutions with chemically ordered nanoregions, the interface nanolayers can form locally and affect the total response too. Further investigations of nanoscale interfacial phenomena in a broader range of nanostructures and materials will enable design of novel ferroic systems.

IV. CONCLUSIONS

In summary, we have studied the atomistic nature and the effective parameters of the NNO:STO interface nanolayers. In at least 3 cells near the interface, charge mismatch existing between ions of constituents on both A- and B-sites of perovskite cell leads to increase in distance between A-site ions, off-center displacement of B-site ions, and rotation of oxygen octahedral. This is approximated by nanolayers with effective permittivity and thickness. The experimentally estimated nanolayer parameters (thickness 1–2 nm and permittivity 25–55) agree with the first-principles analysis.

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- ¹N. A. Pertsev, A. K. Tagantsev, and N. Setter, *Phys. Rev. B* **61**, R825 (2000); K. Johnston, X. Huang, J. B. Neaton, and K. M. Rabe, *ibid.* **71**, 100103(R) (2005); N. A. Pertsev, *ibid.* **78**, 212102 (2008); S. Okamoto, A. J. Millis, and N. A. Spaldin, *Phys. Rev. Lett.* **97**, 056802 (2006); M. Tyunina, J. Narkilahti, M. Plekh, R. Oja, R. M. Nieminen, A. Dejneka, and V. Trepakov, *ibid.* **104**, 227601 (2010).
- ²J. Narkilahti, M. Plekh, J. Levoska, and M. Tyunina, *Phys. Rev. B* **79**, 014106 (2009).
- ³R. Oja and R. M. Nieminen, *Phys. Rev. B* **80**, 205420 (2009).
- ⁴M. Tyunina, *J. Phys.: Condens. Matter* **18**, 5725 (2006).
- ⁵M. Tyunina and J. Levoska, *Appl. Phys. Lett.* **95**, 102903 (2009).
- ⁶S. L. Miller, R. D. Nasby, J. R. Schwank, M. S. Rodgers, and P. V. Dressendorfer, *J. Appl. Phys.* **68**, 6463 (1990).
- ⁷M. Stengel, D. Vanderbilt, and N. A. Spaldin, *Nature Mater.* **8**, 392 (2009).
- ⁸M. Tyunina and J. Levoska, *J. Appl. Phys.* **101**, 084119 (2007).
- ⁹T. Hungria, M. Alguero, and A. Castro, *Chem. Mater.* **18**, 5370 (2006).