Designing functional ferroelectric interfaces from first-principles: dipoles and band bending at oxide heterojunctions

Rusu Dorin 1, Lucian Dragos Filip 2,3,4, Lucian Pintilie 5, Keith Tobias Butler 1 and Neculai Plugaru 2

1 University of Warwick, Dept. Phys, Coventry CV4 7AL, W Midlands, United Kingdom
2 National Institute of Materials Physics, Atomistilor Str. 405A, Magurele, 077125 Ilfov, Romania
3 Rutherford Appleton Lab, Sci Comp Div, SciML, Didcot OX11 0QX, Oxon, United Kingdom
4 Author to whom any correspondence should be addressed.

E-mail: lucian.filip@infn.it and plug@infn.it

Supplementary material for this article is available online

Abstract

The fundamental phenomena at ferroelectric interfaces have been the subject of thorough theoretical and computational studies due to their usefulness in a large variety of emergent electronic devices, solar cells and catalysts. Ferroelectricity determines interface band-bending and shifts in electron energies, which can be beneficial or detrimental to device performance. However, the underlying mechanisms are still the subject of debate and investigation, as a deeper understanding of the electrochemistry is required to develop bona fide design principles for functional ferroelectric surfaces and interfaces. Here, using first principles calculations within the GGA + U formalism, we investigate the problem of band alignment in non-defective, asymmetric SrRuO3/PbTiO3/SrRuO3 capacitors with ultra-thin ferroelectric layers. The effects of the dielectric size on the polar distortion stability and interface-specific properties are analyzed. It is shown that the critical size of the dielectric for polarization switching is ≈2 nm (5 PbTiO3 u.c.). Below this limit there is no bulk-like region in the dielectric, the space charge accumulated at interfaces leads to the presence of gap states in the whole PbTiO3 layer and ferroelectricity vanishes. We draw the band alignment diagrams as given by the band line-up and band structure terms, as well as by taking Ti 3s semi-core states as reference. In the ferroelectric structures, both approaches predict a strong effect of band-bending on the type of contact, Schottky or Ohmic, at the asymmetric interfaces. The effect of interface states on the interface dipole amplitude and band alignment is discussed.

1. Introduction

Multilayered structures incorporating ferroelectric perovskites and metal/oxide electrodes have extensively been investigated for their use in a wide range of advanced applications, including but not limited to (multiple state) ferroelectric memories [1–5], quantum tunneling junctions [6–14], photo-ferroic solar cells [15–24], and various multilevel architectures with coupled ferroic modes [25–34]. Also, new experimental methods have been envisaged for acquiring an accurate control of polarization when the ferroelectric layer is situated deep into these structures [35–38]. Ferroelectric interfaces are key elements for the functionality of these heterostructures. Their underlying phenomenology is determined by the chemistry of the specific materials, their thickness, as well as the design and quality of interfaces [39–43]. At the interface with a ferroelectric the polar distortions are perturbed, the local strain, bonding across the interface and the built-in electric field promote charge transfers and space charge build-up. In turn, these effects impact on the electronic structure, inducing relative shifts of the energy levels, modifications of band gap values, metal-induced band gap states (MIGS) and interfacial band bending effects [7, 44–48]. The band alignment scheme results as an effect of entangled microscopic mechanisms and plays a major role in setting the operating conditions of practical junctions [49, 50]. Theory and computational methods, particularly those based on first principles calculations, have proven their usefulness in...
exploring the fundamental mechanisms at the interface with a ferroelectric, as well as by revealing practical routes for the device design based on predictive behavior; for a review in the field see [51].

Based on their previous work [52, 53], Stengel et al have developed a new formalism, referred to as the constrained electric displacement method, for the description of the microscopic phenomena in ferroelectric multilayered systems [54, 55]. It was shown that expressing the internal energy of a periodic crystal in a uniform external field in terms of the electric displacement as the fundamental variable—equivalent to fixing the free charge on the plates of a capacitor—enables one to explain the factors determining the depolarizing field, to model the polarization and response of complex super-lattices, capacitors and interfaces in terms of the electrical properties of the elementary building blocks [10], and also provides a convenient route for the treatment of the couplings between different order parameters [54, 55].

A comprehensive study of the band alignment problem in ferroelectric capacitors is presented in [45]. The authors highlight the possible consequences in the interpretation of the LDA/GGA band offsets at interfaces due to band gap under-estimation. In such a situation, denoted as a ‘pathological’ case, a spill-out of charge from the metal to the insulator leads to the appearance of conduction band states at the Fermi level and brings about a degree of arbitrariness in assessing the band edges and hence the band alignment scheme, which no longer is a well-defined interface property [45]. It is also rationalized that the errors in establishing accurate realistic Schottky barrier heights (SBHs) from standard (LDA, GGA) first principles calculations affect the amount of transferred charge and induced metallicity in the dielectric. As a result, these will determine errors in the ground state charge density, which in turn may propagate to alter the predicted electronic and structural properties of the system, as well. The authors elaborate a refined strategy, consisting in a sequence of calculations on bulk and supercell systems, in order to detect the pathological cases, and to derive reliable band edge positions relative to Ti 3s semi-core states, in the non-pathological cases. Their approach also allows the evaluation of the effects of the interface states on band edge positions when MIGS are present [45].

Here it is worth highlighting that an insightful analysis of the MIGS and their effect on the interface dipole and formation of SBHs in ferroelectric/metal junctions has also been presented in [47]. These authors demonstrate that although the most penetrating bands are located at high symmetry points, for the study of tunneling conductance across ultra-thin layers or integrated quantities (where many k parallel points contribute) it is important to consider complex bands in the whole two dimensional Brillouin Zone (BZ). Also, a general recipe is outlined to estimate from the complex band structure of the bulk insulator the effective decay factor (and its dependence with the energy within the gap) of the MIGS in realistic interfaces [47].

Ferroelectric capacitors with asymmetric interfaces have been investigated with the expectation that asymmetry may furnish an enhanced device functionality comparing to the symmetric realizations (see [48] and the references cited therein). The degeneracy of polarization states in symmetric geometries is broken in asymmetric configurations and hence size effects may determine distinct states for forward–backward polarization. Following this line of research, Chen et al [48], carried out a detailed study within LDA on the size effect in ferroelectric BaTiO₃, tunnel junctions with metal Pt and/or oxide SrRuO₃ electrodes, considering the four possible types of electrode/ferroelectric interfaces. They found a significant dependence of the ferroelectric stability of a tunnel junction on the type and combination of the two interfaces. Also, an abnormal enhancement of ferroelectricity due to bonding at the Pt_{2}/BaO interface has been predicted. However, on the grounds of the analysis and results presented in [45], the findings reported in [48] may be affected by the shortcomings inherent to LDA.

Umeno et al [2] investigated the influence of electrode materials and PTO size on the ferroelectric stability and SBHs in ultra-thin perovskite capacitors, with symmetric SrRuO₃/PbTiO₃/SrRuO₃ (SRO/PTO/SRO) or Pt/PbTiO₃/Pt and asymmetric Pt/PbTiO₃/SrRuO₃ configurations. The SBHs were obtained by using a macroscopic averaging of the electrostatic potential, with the p-type SBH calculated from the relation $\phi_p = \Delta V + \Delta E_{bulk}$, where $\Delta V$ is the difference between the macroscopic averages of the electrostatic potentials in the two materials ‘far’ from the interface and $\Delta E_{bulk}$ is the difference between the Fermi energy of the electrode and the valence-band maximum (VBM) of the dielectric material, with the Fermi and VBM energies obtained from independent bulk calculations at the same structural parameters as in the capacitor calculations. Another approximation in this work is the usage of the experimental PTO bandgap for the estimation of the SBHs for electrons. The authors conclude that the influence of polarization on the Schottky barrier is larger in SRO/PTO/SRO than in Pt/PTO/Pt, and also the contribution of the electrical field generated by the asymmetric electrodes influences the Schottky barriers significantly. Also, a considerable change (about 1.0 eV) in the SBH has been predicted in the Pt/PTO/SRO capacitor when switching polarization [2].

As the thickness of the ferroelectric layer decreases, it may become comparable with the spatial extent of the interface-induced phenomena. Ultra-thin layers (only a few nanometers thick) reach a limit where a bulk-like region, with structural regularity and characteristic potential and charge distributions, may not exist any more, to be taken as a reference for resolving the interface contribution. Actually, one has to make a trade-off between...
using elaborate and accurate models, e.g. [45, 47, 55] and a practical approach which encompasses as much as possible the characteristics of the real system. To our knowledge, a proper explanation of size effects and interface specific properties in ferroelectric capacitors with ultra-thin layers is still an open issue.

Therefore, here we have investigated by first principles calculations SrRuO$_3$/PbTiO$_3$/SrRuO$_3$ ferroelectric capacitors with asymmetric interfaces. We discuss the effects of size, asymmetry and polarization on the ferroelectric instability and interface-specific properties, including local structure, potential and charge density distributions, interface dipole extension and amplitude, band bending and band alignment.

The paper is organized as follows: in section 2 we present the computational details and describe the models used in this work. The structural results and their imprint on the electrical properties of the systems under study are presented in section 3. The electronic structure, including partial and local density of states, the potential and charge density variation, as well as the size effect on polarization are discussed in section 4. In section 5, starting from a corrected band gap for the dielectric, we derive the band alignment diagrams both by using the band line-up and band structure terms, as well as by taking Ti 3s semi-core states as reference. The contrasting features predicted by the two different approaches are discussed by considering both the effect of interface states as well as the limitations due to our assumptions. The main conclusions of the work are summarized in section 6 of the paper.

2. Computational details and model structures

2.1. Method

The calculations were performed within the generalized gradient approximation (GGA) using the quantum ESPRESSO plane-wave code [56, 57], and the exchange and correlations functional in the parametrization for solids (PBESol) [58, 59]. We used Vanderbilt ultrasoft pseudopotentials [60] from the QE library [61], with Pb 5d10 6s2 6p2, Sr 4s2 4p6 5s2 5p0, Ti 3s2 3p6 4s2 3d2, Ru 4d7 5s1 5p0 and O 2s2 2p4 states in the valence band. The kinetic-energy cut-off for the plane waves was set at 100 Ry and for the charge density at 800 Ry. The BZ integration was performed on an automatically generated Monkhorst-Pack [62] 4 × 4 × 1 k-mesh, for all slabs, with Gaussian energy level smearing of 0.02 Ry. The total energy per atom was converged to less than 1 × 10$^{-3}$ eV. A dipole correction was applied in order to remove the electrostatic interaction between the electric dipoles in neighboring slabs along the z-axis of broken symmetry [52, 63].

The DFT + U rotationally invariant method, in the atomic projection [64–66], was used to treat orbital-dependent correlations for Ti 3d and O 2p orbitals, and thus to correct their effect on the PbTiO$_3$ band gap. An effective Hubbard term, $U_{\text{eff}} = U - J$, was applied to the correlated orbitals, with $U$ being the screened on-site Coulomb interaction and $J$ the Stoner exchange parameter. The corrective $U_{\text{eff}}$ values used in this study are 7 eV for the Ti 3d orbitals and 6 eV for the O 2p orbitals, as determined empirically on bulk tetragonal PbTiO$_3$, leading to a band gap of 2.98 eV. This value is still a little underestimated with respect to experiment (giving values in the range 3.45–3.6 eV [see 67 and references cited therein]), but significantly improved relative to the GGA result (1.68 eV). Applying the correction also on Ru 4d states had no noticeable effect on the present results and therefore was discarded.

We evaluated the layer-by-layer spontaneous polarization of the PbTiO$_3$ using the following equation [68]:

$$P_k(z) \simeq \sum_i \frac{\partial P}{\partial u_{ki}^0}(u_{ki} - u_{ki}^0) = \frac{1}{V_k} \sum_i Z_{ki}^* \Delta u_{ki},$$  \hspace{1cm} (1)

where $Z_{ki}^*$ and $\Delta u_{ki}$ are the dynamical charge and displacement of ion $i$ in cell $k$, respectively, and $V_k$ is the volume of the cell. The superscript zero refers to a non-polar equivalent of the relaxed PbTiO$_3$ sub-structure. This was constructed by keeping the Pb sublattice fixed and moving the rest of the atoms to equivalent centrosymmetric positions within each PbTiO$_3$ unit cell. $Z_{ki}^*$ were calculated using the linear response to an atomic perturbation [69] at the gamma point, within the Density Functional Perturbation Theory framework, implemented in the PHonon package. Equation (1) can be used with either A or B cation-centered cells.

The spontaneous polarization of the PTO layer was also calculated within the Berry’s phase approach [70] as implemented in the Quantum ESPRESSO package [71]. In order to minimize the number of calculation steps for deriving unambiguous polarization values we applied the method described in [72].

2.2. Model structures

The ferroelectric capacitors were modeled as slabs, schematically depicted in figure 1, with the atomic layers in the sequence (3(SrO − RuO$_2$) − SrO)/m(TiO$_2$ − PbO)/4(RuO$_2$ − SrO), where $m = 3, 5, 7$ and 9. The asymmetry of the structures emerges from the two different interfaces. The thickness of the SRO layers is close to the experimentally detected limit for metallic conduction [73]. We also carried out calculations on 9-PTO models with double numbers of SRO unit cells, both in the slab as well as supercell geometry. This enables a
comparison between data for open and short-circuit conditions, as well as of the interface specific properties and effects in both type of systems [74].

The slabs are separated by $\approx 15 \text{ Å}$ vacuum along z-axis, see figure 1. In all model structures the atomic positions were relaxed until the Hellmann–Feynman forces were less than 0.01 eVÅ$^{-1}$ on each atom. In the initial state, before relaxation, both $\pm z$ ferroelectric distortions, denoted as $P^+$ and $P^−$, were considered.

We implicitly assumed that the structures were grown coherently on a cubic SrTiO$_3$ (001) substrate, with the bulk lattice constant, $a = 3.905$ Å [75], which is slightly less (by 0.64%) than that of pseudocubic SrRuO$_3$ with $a = 3.93$ Å [35], and matches the in-plane lattice constant of tetragonal PTO [76]. Thus, the experimental lattice constants were used in the present study, as suggested in [77]. Also, it has previously been shown that such a geometry determines the direction of PTO layer polarization perpendicular to the capacitor plane [78].

The band structure of interfaces between different materials is a complex interplay of symmetry, strain and chemistry. We have chosen in this work to consider the effects of chemistry and strain at the interface, by choosing to impose the substrate perovskite structure (Pm-3m) on the SRO layers. Previously it has been shown that very thin layers of SRO constrained by a substrate symmetry has octahedral tilt angles determined by the substrate, rather than bulk SRO, up to 3 or 4 layers deep [79]. Moreover experimental characterization of SRO grown epitaxially on PZT up to 25 nm, displays a pseudo-cubic symmetry [80]. In future work it will be interesting to consider also how symmetry effects can influence the interface band structure, but in the interests of clarity and motivated by these previous studies, herein we use a model without the bulk aac-tilting of bulk SRO.

Recently, the magnetism of SrRuO$_3$ thin films has thoroughly been discussed in relationship with size, lattice distortions and electronic correlations [81]. It has been shown that the application of standard methods (LDA and GGA) to describe the magnetic ground state leads to contrasting solutions in complex oxide thin films or their heterostructures. Since in this work our primary goal is to describe the role of bonding, space charge and polarization on band alignment in the studied systems, we have assumed non-magnetic SrRuO$_3$, thus neglecting the effects of interfacial magnetism.

### 3. Structural results

The layer-by-layer cation-oxygen (M–O) relative z-displacements, $Z_{M/Z}$, where $Z_{M/Z} = Z_{M/Z}^{(0)} - Z_{M/Z}^{(0)}$, stand for the cation and anion positions in the relaxed layers relative to their positions in the centro-symmetric layers, are plotted in figure 2 and the corresponding data for the 9-PTO slab with thick electrodes are shown in figure S1 (supporting information is available online at stacks.iop.org/NJP/21/113005/mmedia). The positions of the geometric interfaces (GI1/2) are marked by vertical dashed lines at half distance between adjoining SRO and PTO monolayers. In the case of the 9- and 7-PTO slabs the initial $\pm z$ polar distortions are preserved in the relaxed structures: the Pb–O and Ti–O relative shifts are larger at interfaces and gradually decrease towards inside the layer, where a regular, bulk-like behavior may be observed. However, their values are smaller than in bulk PbTiO$_3$. In the relaxed 5- and 3-PTO structures, the negative values of the relative ionic displacements show that the $P^-$ state is favored. A similar behavior was previously reported for the SrRuO$_3$/BaTiO$_3$/SrRuO$_3$ capacitors [82, 83]. These results are consistent with the unit cell tetragonality, $c/a$, in the relaxed state, shown in figure 3. The PTO tetragonality decreases with the layer thickness, from 1.064 in the bulk (marked by the blue dashed line) to $\approx 1.03$ for 9-PTO, to $\approx 1.02$ for 7-PTO, to 1.01 $\pm$ 1.02 for 5-PTO and to $\approx 1.00$ for 3-PTO.

In figures 2 and S1 one should also remark the presence of cation-oxygen relative z-displacements in the SRO electrodes, for the 9- and 7-PTO structures, which are driven by the ionic relaxations in the dielectric at interfaces. These ionic displacements, larger at interfaces and decreasing inside the electrode, as well as the cubic
to tetragonal distortion of the SRO unit cell show that a polar state may onset in the metallic phase at the interface with a ferroelectric, in agreement with previous results, \([7, 84]\). The phenomenon has been explained by the softness of the metallic oxide lattice, which allows the ferroelectric displacements in PTO to penetrate into the metal electrode, acting toward the stabilization of a ferroelectric phase in a narrow region at the interface \([7]\).

More recently, Filippetti et al reported that Bi$_5$Ti$_5$O$_{17}$ complies with the sufficient symmetry requirements for a switchable polarization to exist and the material can sustain a sizeable potential drop along the polar direction, in spite of being a metal \([84]\). However, in the present case the results do not reveal the presence of a ferroelectric polarization in the SRO electrodes, as discussed further.

The values of the bond lengths across the SRO–PTO interfaces, collected in table S1, show that Ru–O, Pb–O and Pb–Ru bonds are larger than the Ti–O, Sr–O and Sr–Ti, respectively, due to the larger Shannon–Prewitt radii of Ru (0.760) and Pb (1.63) than the radii of Ti (0.745) and Sr (1.58) \([85]\). In the case of the 9- and 7-PTO slabs, the M–O bonds show variations of the order of the M–O displacements, when switching polarization along ±z. Increasing the electrode thickness does not effect the bond lengths at interfaces, as evidenced by a

\[\text{Figure 2. Cation-oxygen displacements, } (z_M - z_O), \text{ as a result of structure relaxation, for } P^+ \text{ distortion, right, and } P^- \text{ distortion, left.}\]
comparison between the values for the 9-PTO slabs with thin and thick SRO layers. The relaxation of the 5-PTO slab determines only very small differences between the corresponding bond lengths in the two polar states. In the case of the 3-PTO slabs one obtains identical bond lengths after relaxation, consistent with only a slight difference in the total energy between the two states (less than 5 meV).

These structural results indicate that the ferroelectric states along ±z are not equivalent, as expected for asymmetric interfaces, and that a switchable polarization can exist only in the 9 and 7-PTO slabs, albeit with smaller values than calculated in bulk PTO (0.88 C m⁻¹). In the case of the 5-PTO slab, only one stable polarization state is revealed, while the polar distortion in the 3-PTO slab is suppressed.

4. Electronic structure results

4.1. Partial and local density of states

The total and partial densities of states of the thin electrode structures, plotted in figure S2, reveal the following features: (i) the Fermi level is pinned in the PTO band gap by Ru 4d and (SRO) O 2p states; (ii) a significant dependence on the polarization direction in the 9- and 7-PTO slabs, only slight differences for the 5-PTO slabs, and no difference for the 3-PTO slabs; (iii) the PTO band gap is smaller than the value in the bulk material; (iv) the presence of PTO band gap states.

More insight is brought by inspecting the PTO local DOS, (LDOS), displayed in figure 4 for the 9-PTO system and figure S3(a)–(c) for the 7-, 5- and 3-PTO ones. These data show a layer dependence of the position of the VBM and CBM in the 9, 7 and 5 layer systems, but not in the 3 layer system. The reason for this is discussed in more detail in the next section on electrostatic potential. Band gap states are visible in the LDOS of the first PTO unit cell (one or two monolayers) at an interface. They form bands at certain energy values, a feature which is associated with the formation of chemical bonds across the interface.

4.2. Electrostatic potential and charge density

We calculated the electrostatic potential, $V(r) = V_b + V_{\text{el}}$, where $V_b$ is the inter-ionic term, and $V_{\text{el}}$ is the electron–electron term given by:

$$V_{\text{el}} = \int \! \! \! \! \! dr' \rho(r') \frac{1}{r-r'},$$

(2)
with \( \rho(r') \) being the electron density. Then, the planar average \( \nabla \bar{V}(z) \) and the nanoscale smoothed electrostatic potential, \( \bar{V}_z(z) \), were obtained \[86\]. Their profiles along \( z \)-axis are plotted in figure 5 for the slabs with thin electrodes and in figures S4 and S5 for the 9-PTO slab and 9-PTO supercell, respectively.

Figure 5 shows that in the 9- and 7-PTO thin electrode structures, the nano-smoothed potential varies linearly with \( z \) in the PTO layers, with the sign of the slope dependent on the polarization direction. This explains the observations in the previous section on the layer dependence of the local density of states. In the case of the 5-PTO system, the stable polarization state is that for \( P^+ \) direction. In the 3-PTO slab the potential shows no slope along \( z \) axis, supporting its non ferroelectric state, in agreement with the ionic displacements and LDOS data. The potential gradient is the source of the built-in electric field, which is responsible for the energy level shift in the LDOS diagrams of figures 5 and S3(a), (b). Because the thickness of the thin electrodes is comparable with the penetration length of the ionic distortions from the PTO into the SRO layers, the nano-smoothed potential is not flat within these electrodes. The different vacuum levels on the left and right-hand sides of the slabs are due to the electrostatic dipolar interaction between surface charges in the neighboring slabs along \( z \) axis. By doubling the size of the SRO layers, e.g. the case of the 9-PTO capacitors, see figures S4 and S5, the potential recovers its flat profile within the electrodes. Also, it acquires the same value in the vacuum regions on each side of the slab, due to a better screening of the interface charges by the thicker SRO electrodes.

In the case of the thick electrode 9-PTO capacitor, at the SrO/TiO\(_2\) interface, the observable flat portion of the macroscopic potential suggests a better \textit{in situ} compensation of the polarization charges in the dielectric by the transferred charge from the electrode, than in the case of the PbO/RuO\(_2\) interface. This implies that the amount of charge transferred at interface \( I \) is larger than that at interface \( II \). Therefore, a larger interface dipole may be expected at the SrO/TiO\(_2\) interface than at the PbO/RuO\(_2\) interface.

In order to reveal the build-up of interface charge from the calculated charge density data we calculated the charge density difference, \( \delta(\rho) \), by subtracting the charge densities calculated individually for each component of the capacitor from the slab total density, \[87\]. As a result, one obtains the charge density at interfaces due to bonding and charge transfer, i.e. the microscopic dipole \[88\], all other effects being removed. These results are displayed in figure 6 for the thin electrode slabs and in figure 7 for the 9-PTO slabs with thick electrodes. Referring to the nano-smoothed data, these plots indicate the formation of distinct interface dipoles in all slabs, with larger amplitude at the SrO/TiO\(_2\) interface than at the PbO/RuO\(_2\) one in the 9 and 7-PTO capacitors. Also, the interface dipoles are larger for the \( P^+ \) than for the \( P^- \) direction. It is interesting to note that in the metallic SRO layer the effects of charge redistribution can penetrate beyond the interface as shown in figure 7 where there is an additional sub-surface redistribution of charge in SRO when polarization is \( P^+ \).
We have also analyzed the charge transfer at interfaces using an alternative approach and found the same effects (see figures S6–S8 in supporting information for details).

4.3. Polarization

The values of the layer-by-layer polarization calculated using equation (1) are plotted in figure 8. The relaxed ionic displacements in the SRO–PTO–SRO capacitors uphold a stable, switchable polarization, of about 0.6 C m$^{-2}$ and 0.5 C m$^{-2}$ in the 9- and 7-PTO capacitors, respectively. When the thickness of the dielectric is...
Figure 6. Charge density difference plots obtained by subtracting the partial charge densities calculated individually for each component of the slab from the total quantity: the macroscopic averaged data, black line, and the corresponding nano-smoothed data, red–blue line.

Figure 7. Charge density difference plots for the thick electrodes slab: the macroscopic averaged data, black line, and the corresponding nano-smoothed data, red–blue line.
down-sized to 5 unit cells, (~2 nm) a critical limit of polarization bi-stability is reached and only one energy minimum is effective in setting the spontaneous polarization direction, along $-z$. A further decrease of the PTO layer thickness to three PTO u.c. (about 1.2 nm) leads to space charge build-up throughout the whole structure, see figure S6, and the material loses ferroelectricity although it still experiences a finite polarization value.

A similar trend in the size effect on the ferroelectric state was also reported for ultrathin SrRuO$_3$/BaTiO$_3$/SrRuO$_3$ epitaxial heterostructures and was ascribed to a fixed, unfavorable interface dipole at the BaO/RuO$_2$ interface [82].

The ionic and electronic contributions to polarization were also calculated on supercells of the PTO layers at the structural parameters in the slab geometry, by employing the Berry's phase formalism [70]. This approach avoids the potential error due to metallic state in PTO unit cells at interfaces [51]. The results are plotted in the inset in figure 8 and show a fair agreement with the values of the layer-by-layer polarization calculated by using the Born charges.

5. Discussion

Based on the LDOS and electrostatic potential data shown in figures 4, S3(a)–(c) and figure 4, we have drawn the energy level schemes for the systems with thin electrodes in figure 9. The segments that mark the valence and conduction band edges of the individual PTO unit cells extend over the length of a lattice constant along $z$, and their colors, black and red, correspond to TiO$_2$ and PbO monolayers.

While most of the SBHs have positive values, (here we adhere to the sign convention on SBHs as also adopted in [45], at the SrO/TiO$_2$ interface in the case of 9- and 7-PTO capacitors we note negative SBHs (Ohmic contact, possible ‘pathological’ situation) for electrons and $P^+$, and negative SBHs for holes and $P^+$. At the PbO/RuO$_2$ interface, negative SBHs for holes are predicted for the 7- and 5-PTO slabs, for $P^+$. One may observe a relative large shift in energy, of about 2 eV, for the VBM and CBM when switching the orientation of polarization in the 9- and 7-PTO capacitors. This is about twice the value previously reported for symmetric SRO–PTO–SRO capacitors, 1 eV [2]. The SBHs and $\Delta V_H$ values referring to the band alignment diagrams in figure 9 are also collected in table 1.

We suggest that at the SrO/TiO$_2$ interface, for $P^+$, the 9- and 7-PTO systems show blocking contacts for holes, considering that the PTO layer is an (undoped) insulator [89]. A similar behavior is predicted at the PbO/RuO$_2$ interface, for $P^-$, in the case of the 7- and 5-PTO systems. Actually, the systems under study show a transition of the Schottky barrier type for holes between the interfaces when changing the dielectric size and polarization direction.

The SBHs values derived from the energy level scheme drawn in figure 9 are affected by the presence of interface states due to bonding across interfaces and charge transfer from the metallic SRO to the dielectric PTO. An estimation of the effect of the interface states on the band alignment may be obtained by taking the Ti3s semi-core states as reference for the VBM energy. These states are situated deep, at about $-58$ eV below the Fermi level, and hence their energy is barely sensitive to valence charge redistribution. Therefore, we have followed a

Figure 8. Layer-by-layer polarization calculated within DFPT. Solid symbols, $P^+$, hollow symbols, $P^-$. Color code: red, blue, green and magenta stand for the 9-PTO, 7-PTO, 5-PTO and 3-PTO slabs, respectively. Inset: PTO layer polarization obtained from Berry phase calculations. Solid symbols, $P^+$, hollow symbols, $P^-$. 

New J. Phys. 21 (2019) 113005 R Dorin et al
route as basically described in [17, 45] in order to align the band edges in the slabs with reference to Ti 3s states. First, we performed a bulk self-consistent calculation at the PTO structural parameters before the relaxation of the atomic positions in the slabs, to determine the Ti 3s energy level in the bulk, $E_{\text{sc b}} = -57.95 \text{ eV}$, with $E_{\text{VBM b}} = 0 \text{ eV}$ (the VBM energy in the bulk calculation). Then, we performed self consistent calculations on slabs in order to obtain the energy of the Ti 3s states, $E_{\text{sc s}}$, with $E_{\text{VBM s}}$ set at 0 eV. The VBM position with the Ti 3s level in the slab aligned to that in the bulk is given by:

$$E_{\text{VBM s}} = E_{\text{sc s}} + \Delta E_b$$  \hspace{1cm} (3)
Table 1. Schottky barrier heights (SBHs) for electrons (holes) $\Phi_n (\Phi_p)$ and $\Delta V_{H}$ in eV.

|   | $\Phi_n$ | $\Phi_p$ | $\Phi_n$ | $\Phi_p$ | $\Delta V_{H}$ |
|---|---------|---------|---------|---------|---------------|
| 9 | P+      | 2.690   | —       | 1.297   | 1.103         | 1.38         |
|   | P– Ohmic| 2.110   | 0.135   | 2.125   | 1.81          |
| 7 | P+      | 2.477   | —       | 1.476   | 0.824         | 1.10         |
|   | P– Ohmic| 1.776   | 2.486   | —       | 1.6           |
| 5 | P+      | 1.007   | 1.304   | 2.040   | 0.659         | 0.46         |
|   | P–      | 0.687   | 1.369   | 1.731   | —             | 0.86         |

Figure 10. LDOS (in states/eV/u.c.) for the 9-PTO system with reference to Ti 3s semi-core states (the red line). For comparison, the LDOS from figures 5 and S3(a)–(c) are also plotted as the hatched area with black contour. Note that the TiO2 and PbO DOS contributions were summed up for each unit cell. In the case of the 7-PTO and (P+), the LDOS with the VBM aligned relative to Ti 3s and the bulk calculation performed using the structural data from the bulk-like region, are also plotted (the blue curve). See text for details.
where $\Delta E_h = E_{VBM,h} - E_{c,h}$. The LDOS plots calculated according to this approach are shown as red curves in figure 10 and S9(a)–(c), superposed on the LDOS in figures 5 and S3(a)–(c), to enable a comparison between the results.

The approximation to use an unique Ti $3s$ energy value from bulk calculation for all the slabs is made in order to allow a straight comparison of the results, having in view the lack of bulk-like regions in the 5 and 3-PTO slabs, see figure 2). As an error check, we have made an evaluation of the variation in the Ti $3s$ energy level when the structural parameters of a PTO cell in the bulk-like region of the slab were used for the SCF bulk calculation, as proposed in [45], instead of an unique reference as described herein. For example, bulk calculations for the 9- and 7-PTO slabs, were performed at the structural parameters of the bulk-like cells in these slabs. We found that the term $\Delta E_h = E_{VBM,h} - E_{c,h}$ varies by 76 meV for 9-PTO and 81 meV for 7-PTO with respect to the initial value calculated for the bulk PTO before relaxation. Based on these results, we suggest that such small shifts in the LDOS, shown in figure S9(a) for the 7-PTO slab $P^+$ (in blue), as an example, can not determine qualitative changes in the predicted positions of the band edges. The LDOS plots in figures 10 and S9(a)–(c) reveal significant differences between the positions of the valence and conduction band edges in the two data sets, particularly for the 9- and 7-PTO capacitors. Referring to the LDOS results in the alignment

**Figure 11.** The interface dipole as a function of the VBM shift due to the presence of interface states. The potential drop at each interface was calculated as $\delta \delta_{dip} = V_{PTO} - V_{SRO}$ where $V_{PTO}$ and $V_{SRO}$ denote the potential values on the PTO and SRO sides of the interface, respectively.
relative to the Ti 3s semi-core states, the presence of MIGS and the Fermi level location relative to the conduction band edge points to a ‘pathological’ regime at the PbO/RuO2 interface, according to [45], for the 9 and 7-PTO slabs, for P\(^+\), and at the SrO/TiO2 interface for P\(^-\). In the case of the 5-PTO slab, a ‘pathological’ regime may be invoked at the SrO/TiO2 interfaces for both directions of polarization. Nevertheless, taking into account that the present results have been obtained using a band gap corrective approach, with a calculated band gap of about 3 eV in the bulk PTO, we suggest that the predicted behaviors are not artefacts of the DFT calculations, but real Ohmic contacts. We emphasize that in such cases, the experimental verification of the calculation results is highly recommended.

Information on the charge re-arrangement and formation of interface dipoles may provide useful hints for understanding the factors contributing to the interface properties, such as bonding across interface, interface states and effect of the built-in electric field. Therefore, we evaluated the magnitude of the interface dipoles in the systems under investigation, starting from the charge density difference data in figure 6 and solving the 1D Poisson equation for the electrostatic potential. Then, the microscopic interface dipole, \(\delta_{\text{dip}}\), was evaluated as the potential drop at each interface [88, 90]. Figure 11 displays the \(\delta_{\text{dip}}\) values for the thin electrode capacitors as a function of the VBM shift when the Ti 3s semi-core states are used as reference with respect to the band line-up scheme (see figure 9). This difference reflects the effect of the interface states on the VBM (CBM) positions. In the case of the 9- and 7-PTO capacitors, figure 11 shows the following: (i) the dipoles change sign according to the polarization direction, at both interfaces; (ii) also, for a given interface, the dipoles are bigger, in absolute value, for P\(^+\) than for P\(^-\) orientation. (iii) The dipoles are bigger at the SrO/TiO2 interface than at the PbO/RuO2 interface, for \(\pm z\) polarization. (iv) In the case of the 5- and 3-PTO slabs, the dipoles do not change sign with the polarization direction, in accordance with polar displacement and polarization results.

We also note a direct correlation between the magnitude of \(\delta_{\text{dip}}\) and the VBM shift at the PbO/RuO2 interface, for the 9-, 7- and 5-PTO slabs. However, at the SrO/TiO2 interface we note a direct correlation for P\(^+\), and a reciprocal correlation for P\(^-\). In the open-circuit condition of the capacitors under investigation, we suggest that the bonding at the SrO/TiO2 interface favors local charge build-up and therefore the creation of a larger dipole than that at the PbO/RuO2 interface.

### 6. Conclusions

We performed first principles calculations of the polar distortions and electronic properties in SrRuO3/PbTiO3/SrRuO3 ferroelectric capacitors with asymmetric interfaces, in order to examine the band bending, band alignment and interface dipoles in their dependence on the dielectric size. The main results of this work are summarized as follows.

- It is shown that a switchable polarization, of about 0.5 C m\(^{-2}\) is preserved in capacitors with dielectric size larger than 2 nm.
- A monostable polarization state is evidenced in capacitors with PTO layer of about 2 nm.
- No band bending and a loss of ferroelectricity is predicted below this limit.
- The band alignment scheme drawn from the local density of states calculated within the GGA + U framework shows possible Ohmic contact at an interface and Schottky barrier at the other interface in the 9- and 7-PTO structures, for a given polarization direction. If experimentally proven realistic, such characteristics may be of interest to achieve tunneling electro-resistive junctions.
- The LDOS plots with the VBM aligned relative to Ti 3s semi-core states clearly evidence Ohmic contacts at the PbO/RuO2 interface for P\(^+\), and at the SrO/TiO2 interface for P\(^+\), in the case of the 9 and 7-PTO slabs. Possible Ohmic contact is predicted at the SrO/TiO2 interface for the 5-PTO slab.
- The interface dipoles re-orient themselves with the forward–backward polarization only in the 9- and 7-PTO capacitors. They are significantly bigger at the SrO/TiO2 interfaces than at the PbO/RuO2 ones. It is found that at the PbO/RuO2 interface, the larger is the VBM shift, the larger is the interface dipole. Contrasting correlations for forward–backward polarization are predicted at the SrO/TiO2 interfaces. These results suggest intricate effects of bonding across interfaces, internal electrostatic field and dielectric size on local charge transfers.
- The size of the barrier and the switching effect can be changed by changing the thickness of the PTO layer.
Finally, it is worth highlighting the significant polar displacements induced by the ferroelectric dielectric into the SRO electrodes. However, taking into account the high density of states at the Fermi level in the SRO layer, we rule out a possible onset of a ferroelectric metallic state at the SRO–PTO interfaces.

Acknowledgments

The authors LDF, LP and NP thank the financial support of the Romanian Ministry of Research and Innovation through the Core Program of NIMP (contract PN18-110101), PFE-CDI-339 (contract PFE nr. 12 din 2018) and the FCCF project nr. PN-III-P4-ID-PCCF-2016-0047 (contract PCCF nr. 16 din 2018) funded by the Ministry of Research and Innovation through UEFISCDI.

ORCID iDs

Lucian Dragos Filip  https://orcid.org/0000-0001-7319-1758

References

[1] Junquera J and Ghosez P 2003 Critical thickness for ferroelectricity in perovskite ultrathin films Nature 422 506–9
[2] Umeno Y, Albinia J M, Meyer B and Elssasser C 2009 Ab initio calculations of ferroelectric instability in PbTiO3 capacitors with symmetric and asymmetric electrode layers Phys. Rev. B 80 205312
[3] Garcia V and Bipes M 2014 Ferroelectric tunnel junctions for information storage and processing Nat. Commun. 5 4289
[4] Boni A-G, Filip L, Chirila C, Pasuk I, Negrea R, Pintilie I and Pintilie L 2017 Multiple polarization states in symmetric ferroelectric heterostructures for multi-bit non-volatile memories Nanoscale 9 19271
[5] Yin L, Wang X and Mi W 2018 Ferromagnetic, ferroelectric, and optical modulated multiple resistance states in multiferroic tunnel junctions ACS Appl. Mater. Interfaces 11 1057–64
[6] Davber M, Rabé K M and Scott J F 2005 Physics of thin-film ferroelectric oxides Rev. Mod. Phys. 77 1085–130
[7] Gerra G, Tagantsev A K, Setzer N and Parlinski K 2006 Ionic polarizability of conductive metal oxides and critical thickness for ferroelectricity in Rutio, Phys. Rev. Lett. 96 107603
[8] Duan C-G, Sabirianov R F, Mei W-N, Jaswal S S and Tsybalm E Y 2006 Interface effect on ferroelectricity at the nanoscale Nano Lett. 6 483–7
[9] Velev J P, Duan C-G, Belaschenko K D, Jaswal S S and Tsybalm E Y 2007 Effect of ferroelectricity on electron transport in Pt/BaTiO3/Pt tunnel junctions Phys. Rev. Lett. 98 137201
[10] Wu X, Stengel M, Rabé K M and Vanderbilt D 2008 Predicting polarization and nonlinear dielectric response of arbitrary perovskite superlattice sequences Phys. Rev. Lett. 101 187601
[11] Velev J P, Duan C-G, Burton J D, Smogunov A, Ninamaj J K, Tosatti E, Jaswal S S and Tsybal E Y 2008 Magnetic tunnel junctions with ferroelectric barriers: prediction of four resistance states from first principles Nano Lett. 9 427–32
[12] Zhuaravlev M Y, Sabirianov R F, Jaswal S S and Tsybalm E Y 2005 Giant electroresistance in ferroelectric tunnel junctions Phys. Rev. Lett. 94 246802
[13] Lorenz M et al 2016 The 2016 oxide electronic materials and oxide interfaces roadmap J. Phys: D: Appl. Phys. 49 433001
[14] Tornos J et al 2019 Ferroelectric control of interface spin filtering in multiferroic tunnel junctions Phys. Rev. Lett. 122 037601
[15] Walsh A and Butler K T 2013 Prediction of electron energies in metal oxides Acs. Chem. Res. 47 364–72
[16] Butler K T, Buckeridge J, Catlow C R A and Walsh A 2014 Crystal electron binding energy and surface work function control of tin dioxide Phys. Rev. B 89 115320
[17] Butler K T, Frost J M and Walsh A 2015 Ferroelectric materials for solar energy conversion: photoferroics revisited Energy Environ. Sci. 8 858–48
[18] Liu Y et al 2018 Chemical nature of ferroelastic twin domains in CH3NH3Pbl3 perovskite Nat. Mater. 17 1013
[19] Plugaru N, Nennes G A, Filip L, Pintilie I, Pintilie L, Butler K T and Manolescu A 2017 Atomistic simulations of methylammonium lead halide layers on PbTiO3 (001) surfaces J. Phys. Chem. C 121 9096–109
[20] Yang Y et al 2019 An ultrathin ferroelectric perovskite oxide layer for high-performance hole transport material free carbon based halide perovskite solar cells Adv. Funct. Mater. 29 1806506
[21] Wilson J N, Frost J M, Wallace S K and Walsh A 2019 Dielectric and ferroic properties of metal halide perovskites APL Mater. 7 010901
[22] Cui C, Liu S, Han S, Tao K, Sun Z and Luo J 2018 Towards a spatially customized photophorese from an organic–inorganic hybrid ferroelectric Angew. Chem. Int. Ed. 57 16764–7
[23] Cordero F, Cracian F, Trequattrini F, Imperatori P, Paolotti A M and Penesi G 2018 Competition between polar and antiferrodistortive modes and correlated dynamics of the methylammonium molecules in Mapbi3, from anelastic and dielectric measurements J. Phys. Chem. Lett. 9 4401–6
[24] Young J and Rondinelli J M 2018 Inducing spontaneous electronic polarizations in double perovskite iodide superlattices for ferroelectric photovoltaic materials Phys. Rev. Mater. 2 065406
[25] Fiebig M, Lottermoser T, Meier D and Trassin M 2016 The evolution of multiferroics Nat. Rev. Mater. 1 16046
[26] Eerenstein W, Mathur N D and Scott J F 2006 Multiferroic and magnetoelectric materials Nature 442 759
[27] Gajek M, Ribes M, Fusi S, Bouzehouane K, Fontcuberta J, Barthelemy A and Fert A 2007 Tunnel junctions with multiferroic barriers Nat. Mater. 6 296
[28] Ramesh R and Spaldin N A 2007 Multiferroics: progress and prospects in thin films Nat. Mater. 6 21
[29] Velev J P, Jaswal S S and Tsybalm E Y 2011 Multi-ferroic and magnetoelectric materials and interfaces Phil. Trans. R. Soc. A 369 3069–97
[30] Jaim M, Stoic N and Binggril N 2017 Ferroelectric switching of band alignments in ISMO/PZT/Co multiferroic tunnel junctions: an ab initio study Nanotechnology 28 315202
[31] Hausmann S et al 2017 Atomic-scale engineering of ferroelectric-ferromagnetic interfaces of epitaxial perovskite films for functional properties Sci. Rep. 7 10734
Narayan A, Cano A, Balatsky A V and Spaldin N A 2019 Multiferroic quantum criticality Nat. Mater. 18 223
Spaldin N A and Fiebig M 2005 The renaissance of magnetoelectric multiferroics Science 309 591–2
Spaldin N A and Ramesh R 2019 Advances in magnetoelectric multiferroics Nat. Mater. 18 203
Callori S J, Gabel J, Su D, Sinsheimer J, Fernandez-Serra M V and Dawber M 2012 Ferroelectric PbTiO3/SrRuO3 superlattices with broken inversion symmetry Phys. Rev. Lett. 109 076601
De Luca G, Strikalj N, Manz S, Boulliet C, Fiebig M and Trassin M 2017 Nanoscale design of polarization in ultrathin ferroelectric heterostructures Nat. Commun. 8 1419
Kwon O et al 2018 Direct probing of polarization charge at nanoscale level Adv. Mater. 30 1703675
Tănase L. et al 2018 Polarization orientation in lead zirconate titanate (001) thin films driven by the interface with the substrate Phys. Rev. Appl. 10 034020
Granizo F M, Koster G and Rijnders G 2013 Functional oxide interfaces MRS Bull. 38 1017–23
Pintille et al 2015 Polarization induced self-doping in epitaxial Pb(Zr1-xTix)O3 thin films Sci. Rep. 5 14974
Nguyen M D, Houwman E P and Rijnders G 2018 Energy storage performance and electric breakdown field of thin relaxor ferroelectric β"-ZrTiO4 films using microstructure and growth orientation control J. Phys. Chem. C 122 15171–9
Liao Z et al 2017 Thickness dependent properties in oxide heterostructures driven by structurally induced metal–oxygen hybridization variations Adv. Funct. Mater. 27 1606717
Li et al 2018 Epitaxial stress-free growth of high crystallinity ferroelectric Pb(Zr1-xTix)O3/SrO on GaN/ALGaN/Si (111) substrate Adv. Mater. Interfaces 5 1700921
Morozovska A N, Eliseev E A, Svechnikov S V, Krotov A D, Shur V Y, Borisevich A Y, Maksymovych P and Kalinin S V 2010 Finite size and intrinsic field effect on the polar-active properties of ferroelectric–semiconductor heterostructures Phys. Rev. B 81 205308
Stengel M, Aguado-Puente P, Spaldin N A and Junquera J 2011 Band alignment at metal/ferroelectric interfaces: insights and artifacts from first principles Phys. Rev. B 83 235312
Zubko P, Gariglio S, Ghosez P and Triscone J-M 2011 Interface physics in complex oxide heterostructures Amus. Rev. Condens. Matter Phys. 2 141–68
Aguado-Puente P and Junquera J 2013 First-principles study of metal-induced gap states in metal/oxide interfaces and their relation with the complex band structure MRS Commun. 3 191–7
Chen W J, Zhang Y, Luo X, Wang B and Woo C H 2013 Ab initio study on the size effect of symmetric and asymmetric ferroelectric tunnel junctions: a comprehensive picture with regard to the details of electrode/ferroelectric interfaces J. Appl. Phys. 114 0564105
Burton J D and Tsymbal E Y 2010 Evolution of the band alignment at polar oxide interfaces Phys. Rev. B 82 161407
Margaritondo G 2012 Electronic Structure of Semiconductor Heterojunctions vol 1 (Berlin: Springer)
Hong S, Nakhmanson S M and Feng D D 2016 Screening mechanisms at polar oxide heterointerfaces Rep. Prog. Phys. 79 076501
Meyer B and Vanderbilt D 2001 Ab initio study of BaTiO3 and PbTiO3 surfaces in external electric fields Phys. Rev. B 63 205426
Stengel M and Spaldin N A 2007 Ab initio theory of metal–insulator transition in a ferroelectric interface Phys. Rev. B 75 205121
Stengel M, Spaldin N A and Vanderbilt D 2009 Electric displacement as the fundamental variable in electronic-structure calculations Nat. Phys. 5 304
Stengel M, Vanderbilt D and Spaldin N A 2009 First-principles modeling of ferroelectric capacitors via constrained displacement field calculations Phys. Rev. B 80 224110
Giannozzi P et al 2009 Quantum espresso: a modular and open-source software project for quantum simulations of materials J. Phys.: Condens. Matter 21 395502 (19pp)
Giannozzi P et al 2017 Advanced capabilities for materials modelling with quantum espresso J. Phys.: Condens. Matter 29 465901
Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865
Perdew J P, Ruzsinszky A, Csonka G L, Vydrov O A, Scuseria G E, Constantin L A, Zhou X and Burke K 2008 Restoring the density-gradient expansion for exchange in solids and surfaces Phys. Rev. Lett. 100 136406
Vanderbilt D 1990 Soft self-consistent pseudopotentials in a generalized eigenvalue formalism Phys. Rev. B 41 7892
Dal Corso A 2014 Pseudopotentials periodic table: From H to Pu Comp. Mat. Sci. 95 337–50
Morkhorst H J and Pack J D 1976 Special points for brillouin-zone integrations Phys. Rev. B 13 5188
Bengtsson I 1999 Dipole correction for surface supercell calculations Phys. Rev. B 59 12301
Antisov M L, Zaanen J and Andersen O K 1991 Band theory and mott insulators: Hubbard U instead of stoner I Phys. Rev. B 44 943–54
Dudarev S L, Botton G A, Savrasov S Y, Humphreys C J and Sutton A P 1998 Electron–energy-loss spectra and the structural stability of nickel oxide: an lda + u study Phys. Rev. B 57 13505
Cococcioni M and De Gironcoli S 2005 Linear response approach to the calculation of the effective interaction parameters in the LDA +U method Phys. Rev. B 71 035105
Brehm J A, Takenaka H, Lee C W, Grinberg I, Bennett J W, Schoenberg M R and Rapp A M 2014 Density functional theory study of hypothetical phtio 3-based oxysulfides Phys. Rev. B 89 195202
Nakhmanson S M, Rabe K M and Vanderbilt D 2005 Polarization enhancement in two- and three–component ferroelectric superlattices Appl. Phys. Lett. 87 162906
Baroni S, De Gironcoli S, Corso A D and Giannozzi P 2001 Phonons and related crystal properties from density-functional perturbation theory Rev. Mod. Phys. 73 515
King-Smith R D and Vanderbilt D 1993 Theory of polarization of crystalline solids Phys. Rev. B 47 1651
Giannozzi P et al 2009 QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials J. Phys.: Condens. Matter 21 395502
Filip L D, Plugaru N and Pintilie I 2019 Polarization branches and optimization calculation strategy applied to Abo1, ferroelectrics Modell. Simul. Mater. Sci. Eng. 27 045008
Shen X, Qiu X, Su D, Zhou S, Li A and Wu D 2015 Thickness-dependent metal–insulator transition in epitaxial SrRuO3 ultrathin films J. Appl. Phys. 117 015307
Kolpak A M, Sai N and Rappé A M 2006 Short-circuit boundary conditions in ferroelectric Phtio3 thin films Phys. Rev. B 74 054112
Madelung O, Rössler U and Schulz M 2000 Landolt–börnstein new series, group: iii. Condensed matter, ternary compounds, organic semiconductors
Glazer A M and Mahbud S A 1978 Powder profile refinement of lead zirconate titanate at several temperatures: II. pure Phtio3 Acta Crystallogr. B 34 865–70
Rabe K M 2010 First-principles calculations of complex metal-oxide materials Amus. Rev. Condens. Matter Phys. 1 211–35
Pertsev N A, Zembilotov A G and Tagantsev A K 1998 Effect of mechanical boundary conditions on phase diagrams of epitaxial ferroelectric thin films Phys. Rev. Lett. 80 1988–91
[79] He J, Borisevich A, Kalinin S V, Pennycook S J and Pantelides S T 2010 Control of octahedral tilts and magnetic properties of perovskite oxide heterostructures by substrate symmetry Phys. Rev. Lett. 105 227203
[80] Chirila C, Ibanescu G, Hrib L, Negrea R, Pasuk I, Kuncser V, Pintilie I and Pintilie I 2013 Structural, electric and magnetic properties of Pb(Zn$_{0.2}$Ti$_{0.8}$)O$_3$ — CoFe$_2$O$_4$ heterostructures Thin Solid Films 545 2–7
[81] Ryee S and Han M J 2017 Magnetic ground state of SrRuO$_3$ thin film and applicability of standard first-principles approximations to metallic magnetism Sci. Rep. 7 4635
[82] Liu X, Wang Y, Lukashev P V, Burton J D and Tsymbal E Y 2012 Interface dipole effect on thin film ferroelectric stability: first-principles and phenomenological modeling Phys. Rev. B 85 125407
[83] Lu H et al 2012 Enhancement of ferroelectric polarization stability by interface engineering Adv. Mater. 24 1209–16
[84] Filippetti A, Fiorrentinini V, Ricci F, Delugas P and Íñiguez J 2016 Prediction of a native ferroelectric metal Nat. Commun. 7 11211
[85] Shannon R D 1976 Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides Acta Crystallogr. A 32 751–67
[86] Junquera J, Cohen M H and Rabe K M 2007 Nanoscale smoothing and the analysis of interfacial charge and dipolar densities J. Phys.: Condens. Matter 19 215203
[87] Jung Y-K, Butler K T and Walsh A 2017 Halide perovskite heteroepitaxy: bond formation and carrier confinement at the PbS–CaPbBr$_3$ interface J. Phys. Chem. C 121 27351–6
[88] Wagner J F 2008 Transparent electronics: Schottky barrier and heterojunction considerations Thin Solid Films 516 1755–64
[89] Kao K C 2004 Charge carrier injection from electrical contacts Dielectric Phenomena in Solids ed K C Kao (New York: Academic) pp 327–80
[90] Yajima T, Hikita Y, Minohara M, Bell C, Mundy J A, Kourkoutis I F, Muller D A, Kumigashira H, Oshima M and Hwang H Y 2015 Controlling band alignments by artificial interface dipoles at perovskite heterointerfaces Nat. Commun. 6 6739