Polar metals as electrodes to suppress the critical-thickness limit in ferroelectric nanocapacitors

Danilo Puggioni,1 Gianluca Giovannetti,2 and James M. Rondinelli1,*

1Department of Materials Science and Engineering, Northwestern University, IL 60208-3108, USA
2CNR-IOM-Democritos National Simulation Centre and International School for Advanced Studies (SISSA), Trieste, Italy

(Dated: July 24, 2017)

Enhancing the performance of nanoscale ferroelectric (FE) field-effect transistors and FE capacitors for memory devices and logic relies on miniaturizing the metal electrode/ferroelectric area and reducing the thickness of the insulator. Although size reductions improve data retention, deliver lower voltage threshold switching, and increase areal density, they also degrade the functional electric polarization. There is a critical, nanometer length \( t^*_{\text{FE}} \) below which the polarization disappears owing to depolarizing field effects. Here we show how to overcome the critical thickness limit imposed on ferroelectricity by utilizing electrodes formed from a novel class of materials known as polar metals. Electronic structure calculations on symmetric polar-metal electrode/FE capacitor structures demonstrate that electric polarizations can persist to the sub-nanometer scale with \( t^*_{\text{FE}} \rightarrow 0 \) when a component of the polar axis in the electrode is perpendicular to the electrode/insulator interface. Our results reveal the importance of interfacial dipolar coherency in sustaining the polarization, which provides a platform for atomic scale structure-based design of functions that deteriorate in reduced dimensions.

I. INTRODUCTION

When ferroelectric oxides are utilized in metal/oxide heterostructures and nanocapacitors, scaling of the active FE is required to improve performance [1–3]. Nonetheless, deleterious nanoscale effects are amplified in these geometries [4–6] and act to eliminate the functional electric polarization [7–9]. The loss of ferroelectricity in nanoscale capacitors frequently occurs when the polarization is perpendicular to the film surface [4, 10–12], i.e., the desired polarization direction for field-tunable devices [13]. Bound charges are only partially screened at the interface, resulting in a strong depolarizing field that suppresses the polarization. Indeed, numerous reports suggest a critical thickness, \( t^*_{\text{FE}} \) below which the electric polarization disappears. Experimental studies on PbTiO\(_3\) find \( t^*_{\text{FE}} \approx 20 \, \text{Å} \) at 300 K [14] whereas \( t^*_{\text{FE}} \sim 4.0 \, \text{nm} \), in Pb(Zr\(_{0.2}\)Ti\(_{0.8}\))O\(_3\) films [8]. Furthermore, first-principles density functional theory (DFT) calculations predict \( t^*_{\text{FE}} \approx 2.4 \, \text{nm} \) in single-domain BaTiO\(_3\) films between SrRuO\(_3\) electrodes [4], which reduces to \( t^*_{\text{FE}} \sim 1.0 \, \text{nm} \) after accounting for ionic relaxation in the electrodes [5, 6]. With this limitation, ferroelectric based devices are unable to meet the continuous scaling changes demanded by higher density data storage technologies.

Although proposals to overcome the problem exist, a general solution remains elusive. Most approaches focus on tuning the stability of the FE state. Epitaxial strain engineering has been proposed; nonetheless, this strategy extends to a limited number of oxides, requires complex processing steps, and is limited by available commercial substrates. For example, although it is predicted that \( t^*_{\text{FE}} \rightarrow 0 \) in thin films of the incipient ferroelectric BaZrO\(_3\), a large epitaxial compressive strain of 4.25% is required [15], which would produce deleterious misfit dislocations. Integration with silicon is likely to also lead to uncontrolled interface states [16]. Furthermore, at this level of strain \( t^*_{\text{FE}} \) is still finite for BaTiO\(_3\) (Ref. 15).

Alternative solutions change the type of ferroelectric and the active inversion symmetry lifting mechanism. Ab-initio calculations find that \( t^*_{\text{FE}} \rightarrow 0 \) using so-called hyperferroelectrics [17], which have a persistent polarization different from proper FE oxides, or improper ferroelectrics [18, 19]. However, hyperferroelectric bulk materials (and thin films) remain to be synthesized [20]. Another route relies on creating an enhanced interfacial FE state by controlling the covalency of the metal-oxygen bond at the heterointerface [21–24].

Here we examine the critical thickness for ferroelectricity in nanocapacitors consisting of polar-metal electrodes and conventional ferroelectric oxides under short-circuit boundary conditions using DFT calculations. Recently, polar metals have garnered considerable interest [25, 26] because they exhibit simultaneously inversion-lifting displacements and metallicity. In these compounds, the polar displacements are weakly coupled to the states at the Fermi level, which makes possible the coexistence of a polar structure and metallicity [27]. Our main finding is that polar-metal electrodes suppress the critical thickness limit through interfacial polar displacements, which stabilize the ferroelectric (polarized) state; this geometric effect does not rely on interfacial bond chemistry or ‘perfect’ screening of the depolarizing field, but rather results from the intrinsic broken parity present in the electrode.

II. METHODS

We perform first-principles DFT calculations within the local-density approximation (LDA) and hybrid functional (HSE06, Ref. 28 and 29) as implemented in the Vienna \textit{Ab initio} Simulation Package (VASP) [30] with the projector augmented wave (PAW) approach [31] to treat the core and valence electrons using the following electronic
FIG. 1. Symmetric nanocapacitor consisting of polar-metal electrodes and a ferroelectric oxide. a, The centrosymmetric nanocapacitor with insulating NaNbO₃ (m=2) between LiOsO₃ electrodes (n=6). b, The equilibrium structure of the ferroelectric capacitor [LiO-(OsO₂-LiO)ₙ/NbO₂-(NaO-NbO₂)_m]. The direction of the polar displacements in the electrodes and the ferroelectric film (ANNO) are indicated with arrows. Magnification of the LiO/NbO₂ interface of the c, paraelectric aristotype and d, the ground state structure. The FE behavior at the interface is due to the Li, Nb, and O displacements. The direction of the polar displacements at the interfaces for the paraelectric and the ground state structure is indicated with red arrows.

configurations: 1s²2s²2p⁶6s²5d³ (Li), 5p⁶6s²5d³ (Os), 2s²2p⁴ (O), 5s²5p⁶6s² (Ba), 3d²4s² (Ti), 4s²4p⁶5s² (Sr), 4d⁷5s³ (Ru), 2p⁶3s¹ (Na), 4p⁶4d⁷5s³ (Nb). The Brillouin zone integrations are performed with a 13 × 13 × 1 Monkhorst-Pack k-point mesh [32] and a 600 eV plane wave cutoff for the LiOsO₃/NaNbO₃/LiOsO₃ and SrRuO₃/BaTiO₃/SrRuO₃ capacitor structures. We relax the atomic positions (force tolerance less than 0.1 meV Å⁻¹) using Gaussian smearing (20 meV width).

Below 150 K NaNbO₃ and LiOsO₃ are isostructural with rhombohedral space group R₃c and pseudocubic lattice parameters of 3.907 Å (Ref. 33) and 3.650 Å (Ref. 25), respectively. Owing to the large lattice mismatch between the two compounds, we simulate a symmetric ferroelectric capacitor structure with an LiO/NbO₂ interfacial termination, shown in Fig. 1a, under an epitaxial constraint that would be imposed by a (La₀.₃Sr₀.₇)(Al₀.₆₅Ta₀.₃₅)O₃ substrate[34] and we relax the out-of-plane lattice parameter. This results in a compressive strain of ~1% for NaNbO₃ and a tensile strain of ~6% for LiOsO₃. Note that at the bulk level, we find that a tensile strain >6% suppresses the polar instability along the [001]-pseudocubic direction of LiOsO₃. Moreover, we selected NaNbO₃ for the capacitor structures because to eliminate any charge transfer due to ‘polar catastrophe/charge mismatch’ physics as the interface: [LiO]⁻¹⁻, [NaO]⁻¹⁻, [NbO₂]⁺⁺, and [OsO₂]⁺⁺.

For the two ferroelectric capacitors, we adopt the layered-oxide notation used in Ref. 4, that is

- [LiO-(OsO₂-LiO)ₙ/NbO₂-(NaO-NbO₂)_m] and
- [SrO-(RuO₂-SrO)ₙ/TiO₂-(BaO-TiO₂)_m]

to clearly demarcate the interface composition in the LiOsO₃/NaNbO₃/LiOsO₃ and SrRuO₃/BaTiO₃/SrRuO₃ capacitors, respectively. We use a LiO/NbO₂ electrode/ferroelectric interface for the LiOsO₃/NaNbO₃/LiOsO₃ capacitor and a SrO/TiO₂ interface termination for the SrRuO₃/BaTiO₃/SrRuO₃ capacitor. For both ferroelectric capacitors, we constrained the number of 5-atom perovskite units of the electrode at n = 6 to ensure a thickness large enough to avoid interaction between the two interfaces, and m ranged from 1 to 3. The periodic boundary conditions naturally impose the required short-circuit condition between the electrodes. Note that for SrRuO₃/BaTiO₃/SrRuO₃ capacitors, our geometry differs only slightly from that used by Junquera and Ghosez [4], whereby the thickness of our electrode is greater.

The group theoretical analysis was aided by the ISODISTORT software [35]. It is used to evaluate the geometric-induced inversion symmetry-breaking displacements of the P₄mm structure with respect the P₄/mmm phase, reducing the polar structure into a set of symmetry-adapted modes associated with different irreducible representations of the P₄/mmm phase. The “robust” algorithm was used to match an atom in the undistorted structure to every atom in the distorted structure separated by a threshold distance less than 3 Å.

III. RESULTS AND DISCUSSION

The first ferroelectric nanocapacitor we focus on consists of ferroelectric NaNbO₃ of varying thickness m confined between electrodes of the experimentally known polar metal LiOsO₃ (see Fig. 1, m = 2) [25, 36]. We adopt the layered-oxide notation used in Ref. 4, that is [LiO-(OsO₂-LiO)ₙ/NbO₂-(NaO-NbO₂)_m] to clearly demarcate the interface composition (see Methods). We create two symmetric nanocapacitors with a polar and paraelectric configuration for both LiOsO₃ and NaNbO₃, respectively. We then relax the out-of-plane lattice parameter and the moment positions of the nanocapacitors for m=1, 2, and 3. The lowest energy heterostructures are polar with space group P₄mm and exhibit large Li ions displacements along the [001]-pseudocubic direction (Fig. 1b). No zone-center dynamical instabilities are found in these heterostructures. Note that structures with an initial paraelectric configuration relax into a centrosymmetric structure (space group P₄/mmm) with Li atoms displaying large antipolar displacements in LiOsO₃ (Supplementary Fig. 1) that decrease towards the interface (Fig. 1c).

We use representation theory analysis to examine the inversion lifting distortions (see Methods), and find that the distortion vector corresponds to the irreps Γ₁⁺ and Γ₃. The irreps Γ₁⁺ reduces the antipolar displacements...
in LiOsO$_3$ resulting in the centrosymmetric $P4/mmm$ structure depicted in Fig. 1a. Differently, the irreps $\Gamma_3$ and $\Gamma_5$ are both polar modes which involve mainly Li ion displacements—the maximum amplitudes being $\sim$1.3 Å in LiOsO$_3$ with decreasing amplitude towards the LiO/NbO$_2$ interface (Fig. 1b). It also consists of polar displacements of all ions in the dielectric NaNbO$_3$ layers with the Nb ions off-centering the most (Fig. 1d)

For all thicknesses, the NaNbO$_3$ thin film maintains a ferroelectric ground state characterized by both Nb and Na displacements (Fig. 1b). A linear polarization-displacement model using the Born effective charge from Ref. 37 results in a $0.86$ C m$^{-2}$ polarization for NaNbO$_3$ in $m=2$. An analysis of the differential ionic relaxations in the heterostructure reveals polar displacements at the LiO/NbO$_2$ interfaces—an interfacial ferroelectricity—which are a consequence of the polar metal used as an electrode. This produces an enhanced polarization in the ferroelectric compared to that calculated using the aforementioned procedure in the experimental R3c structure (0.59 C m$^{-2}$) [38]. In particular, although the two interfaces of the paraelectric structures exhibit antiparallel polar displacements (Fig. 1c and Supplementary Fig. 1), the interfaces of the polar ground state structures have parallel polar displacements as shown in Fig. 1d.

Fig. 2 shows the electronic properties for the NaNbO$_3$ layer in the LiOsO$_3$/NaNbO$_3$/LiOsO$_3$ ($m=1$) nanocapacitor. The LDA functional predicts that the NaNbO$_3$ film is metallic, rendering the ferroelectric capacitor unusable (Fig. 2a). This behavior is artificial and due to the tendency of the LDA functional to underestimate the band gap in insulating compound [39, 40]. We solve this pathological problem for DFT by using a more sophisticated functional which includes a fraction of exact exchange (HSE06). Fig. 2b shows that the hybrid functional fully opens the gap between the O 2p and Nb 4d states. Moreover, we find that the HSE06-relaxed structures exhibit displacements similar to those obtained from the LDA functional; importantly, polar displacements at the LiO/NbO$_2$ interfaces. This result supports the conclusion that the interfacial ferroelectricity is induced by the polar crystal structure of the metallic electrode and not due to spurious shorting of the capacitor. In the remainder of this paper, we report results obtained using LDA owing to the similar crystal structure obtained with HSE06 functional.

Fig. 3 shows the evolution of the total energy of each capacitor with mode amplitude $A_{NNO}$, which describes the atomic displacements involved in the soft mode of the NaNbO$_3$ film. As expected the largest energy gain occurs when the thickness of the ferroelectric film increases. Note that the shape of the energy surface does not exhibit the characteristic double well behavior, because in our calculations we fix the polar displacements in the metallic electrodes and only change the amplitude of the polar displacements in NaNbO$_3$. Independent of the NaNbO$_3$ film thickness, the energy is minimized for the ferroelectric ground state ($A_{NNO} \neq 0$), indicating that an ideal ferroelectric capacitor can be reduced to an ultrathin (single unit cell) size, i.e., $t_{FE} \rightarrow 0$.

The disappearance of the critical-thickness limit to ferroelectricity is the result of the parallel polar displacements present at the electrode/dielectric interfaces (Fig. 1b). As proposed in Ref. 22, the ferroelectric state in ultrathin-film devices depends crucially on the nature of the chemical bonds at the metal/oxide interface. Here, this interfacial bonding occurs and is an immediate consequence of the structure of the polar-metal electrodes. The enhanced and parallel interfacial polar displacements...
“imprint” and lead to an overall enhancement of the ferroelectric instability of the film, which we assess further below. We stress that differently from Ref. 22, the interfacial dipole distortions are due to a geometrical mechanism driven by the polar structure of the metallic electrode and not due to the stiffness of the electrode-oxide bonds.

We next examine a SrRuO$_3$/BaTiO$_3$/SrRuO$_3$ capacitor (Fig. 4a), which as before may be written as [SrO-(RuO$_2$-SrO)$_m$/TiO$_2$-(BaO-TiO$_2$)$_n$] to reveal the layered monoxide planes in the structures. We focus on the SrO/TiO$_2$ interface geometry to demonstrate the generality of this solution to the critical thickness problem. We constrain the in-plane lattice parameters to that of SrTiO$_3$ (3.905 Å) and we relax the out-of-plane lattice parameter and the atomic positions (see Methods), examining capacitors with $m$=1, 2, and 3 that are well below the reported $m$=7 critical thickness [4]. With nonpolar SrRuO$_3$ electrodes the paraelectric configuration is energetically more stable than the ferroelectric configuration for all BaTiO$_3$ film thicknesses studied. This is confirmed by the increase in total energy as a function of the polar mode amplitude $A_{BTO}$ (Fig. 4b). Indeed, the use of a centrosymmetric metal for the thinnest ferroelectric film results in an antisymmetric poling effect of the two interfaces, which forbids the possibility of a ferroelectric displacement [5].

Now we perform a computational experiment whereby we transmute central SrRuO$_3$ into a hypothetical polar metal by following the design rules for noncentrosymmetric metals introduced in Ref. 27. We do this by imposing a polar distortion in SrRuO$_3$, which involves only the Sr atoms, as the orbital character at the Fermi level has a negligible contribution from these atoms, with parallel polar displacements at the SrO/TiO$_2$ interfaces as suggested by our LiOsO$_3$/NaNbO$_3$/LiOsO$_3$ capacitor results. We point out that bulk SrRuO$_3$ does not exhibit polar distortions and here we make it artificially polar to isolate the interfacial geometric effect independent of chemistry with respect to the model with centrosymmetric electrodes.

In Fig. 5a we show the energy evolution of this hypothetical capacitor as a function of the mode amplitude $A_{BTO}$, with parallel polar Sr displacements imposed uniformly at 0.07 Å with respect to the centrosymmetric structure (see inset). In contrast to Fig. 4a, the ferroelectric state of BaTiO$_3$ is more stable than the paraelectric geometry for all thicknesses $m$=1, 2, and 3 as indicated by the energy gain for $A_{BTO}$ ≠ 0. These results indicate that $t^*_{FE} \rightarrow 0$ in the BaTiO$_3$ film between the polar-metal SrRuO$_3$.

The energy gain is strongly influenced by the polar displacements of the Sr atoms. In particular, by doubling the amplitude of the polar displacements of the Sr atoms, from 0.07 Å to 0.14 Å for the case $m$=1, we find that the energy gain increases from ~3 meV to ~10 meV (Fig. 5b). Comparing Fig. 5a and Fig. 5b, we find a shift in the critical mode amplitude to larger values, which suggests that the device containing a polar-metal electrode with larger Sr displacements displays a larger ferroelectric polarization. Indeed, when we consider the other limit by fully removing the polar displacements at the SrO/TiO$_2$ interface (setting them to 0 Å), the energy landscape presented in Fig. 4b is restored. Note that for the disappearance of the critical thickness, it is necessary that the polar direction (or a component of it) in the electrodes, and therefore that of the interfacial dipole, coincides with the direction of

![FIG. 4](image-url) Typical behavior of a nanoscale ferroelectric capacitor below the critical thickness. a, Nanocapacitor consisting of a BaTiO$_3$ film ($m$=2) between centrosymmetric SrRuO$_3$ ($n$=6) electrodes. The arrow indicates the direction of the polar displacements in BaTiO$_3$. b, Energy as a function of the polar mode amplitude $A_{BTO}$ in BaTiO$_3$. The energy increases for all thicknesses $m$ analyzed.

![FIG. 5](image-url) Energetic landscape of a BaTiO$_3$ nanocapacitor with “polar” SrRuO$_3$ electrodes. Energetic gain for different dielectric thicknesses: $m$=1 (circles), $m$=2 (squares) and $m$=3 (diamonds). The Sr displacements given with respect to the centrosymmetric ground state are fixed to a, 0.07 Å (see inset) and b, 0.14 Å. The energy of the polar structure with $A_{BTO}$=0 Å is taken as reference for each $m$. 

...
polarization of the ferroelectric film (Fig. 5b, inset).

One could argue that the findings here are a result of the polar metals better screening the ferroelectrics polarization; however, this is not the case. Indeed the electrostatic for the BaTiO$_3$ nanocapacitor with “polar” and nonpolar SrRuO$_3$ electrodes are almost the same (Fig. 6). Moreover, polar metals typically have longer screening lengths than conventional metals [41]. This result further confirms the role of interfacial geometric effects induced by the polar structure of the metallic electrode in controlling the critical thickness.

Lastly, we discuss how the proposed device can be switched. Polar metals are not ferroelectrics. Indeed, the application of an electric field cannot switch the polar distortion in the metal because the free electrons will screen the electric field. However, it has been show that the polar distortion in the metal can be switched by applying an electric field to a superlattice composed of an insulating ferroelectric material and a polar metal by coupling to the ferroelectric polarization [42]. Similarly, when an electric field is applied to the aforementioned nanocapacitors, the polar distortion in the ferroelectric thin film should align along the direction of the electric field; then because of the interfacial coupling between the polar metallic electrode and the ferroelectric film [42], the polar displacements in the polar metal and the interfacial polar displacements should follow. Note that the geometric configuration required to sustain ferroelectricity, i.e., $T^\ast_{FE} \rightarrow 0$, is preserved in the switching mechanism. Alternative approaches have also been applied to degenerately doped ferroelectrics.[43]

IV. CONCLUSION

In summary, we proposed a ferroelectric capacitor where the conventional metallic electrodes are replaced by noncentrosymmetric metallic electrodes. We showed that the polar displacements in the noncentrosymmetric metallic electrodes induce interfacial ferroelectricity, which supports a polar instability in the ferroelectric film regardless of the dielectric thickness. Although we utilized LiOsO$_3$ herein for simplicity, we point out that our result is completely general and the same conclusions may be achieved using other noncentrosymmetric metals as electrodes with our described geometric constraints (see Ref. 44 for a list of materials). These polar-metal based nanoscale capacitors maintain the functionality of the ferroelectric film independent of the degree of miniaturization and could lead to device architectures with improved scalability.

ACKNOWLEDGMENTS

D.P. and J.M.R. acknowledge the Army Research Office under Grant No. W911NF-15-1-0017 for financial support and the DOD-HPCMP for computational resources.

* jrondinielli@northwestern.edu

[1] H. Ishiwara, M. Okuyama, and Y. Arimoto, Ferroelectric Random Access Memories: Fundamentals and Applications (Springer, Berlin, Germany, 2004).
[2] G. Muller, N. Nagel, C. U. Pinnnow, and T. Rohr, “Emerging non-volatile memory technologies,” in Solid-State Circuits Conference, 2003. ESSCIRC ’03. Proceedings of the 29th European (2003) pp. 37–44.
[3] J. F. Scott, “Future issues in ferroelectric miniaturization,” Ferroelectrics 206, 365–379 (1998), http://dx.doi.org/10.1080/00150199808009170.
[4] Javier Junquera and Philippe Ghosez, “Critical thickness for ferroelectricity in perovskite ultrathin films,” Nature 422, 506–509 (2003).
[5] G. Gerra, A. K. Tagantsev, N. Setter, and K. Parlinski, “Ionic polarizability of conductive metal oxides and critical thickness for ferroelectricity in batio3,” Phys. Rev. Lett. 96, 107603 (2006).
[6] G. Gerra, A. K. Tagantsev, N. Setter, and K. Parlinski, “Erratum: Ionic polarizability of conductive metal oxides and critical thickness for ferroelectricity in batio3 [phys. rev. lett. 96 , 107603 (2006)],” Phys. Rev. Lett. , 169904 (2007).
[7] Kenji Ishikawa, Takashi Nomura, Nagaya Okada, and Kazumasa Takada, “Size effect on the phase transition in p b t i o 3 fine particles,” Japanese Journal of Applied Physics 35, 5196 (1996).
[8] T. Tybell, C. H. Ahn, and J.-M. Triscone, “Ferroelectricity in thin perovskite films,” Applied Physics Letters 75, 856–858 (1999).
[9] B. Jiang, J. L. Peng, L. A. Bursill, and W. L. Zhong, “Size effects on ferroelectricity of ultrafine particles of pbtio3,” Journal of Applied Physics 87, 3462–3467 (2000).
[10] Ph. Ghosez and K. M. Rabe, “Microscopic model of ferroelectricity in stress-free pbtio3 ultrathin films,” Applied Physics Letters 76, 2767–2769 (2000).
[11] B. Meyer and David Vanderbilt, “Ab initio study of batio$_3$ and phtio$_3$ surfaces in external electric fields,” Phys. Rev. B 63, 205426 (2001).

[12] Igor Korobein, Huaxiang Fu, and L. Bellaiche, “Ultra-thin films of ferroelectric solid solutions under a residual depolarizing field,” Phys. Rev. Lett. 93, 196104 (2004).

[13] R. Ramesh and D. G. Schlom, “MATERIALS SCIENCE: Orienting Ferroelectric Films,” Science 296, 1975–1976 (2002).

[14] L. Despont, C. Koitzsch, F. Clerc, M. G. Garnier, P. Aebi, C. Lichtensteiger, J.-M. Triscone, F. J. Garcia de Abajo, E. Bousquet, and Ph. Gheoz, “Direct evidence for ferroelectric polar distortion in ultrathin lead titanate perovskite films,” Phys. Rev. B 73, 094110 (2006).

[15] Yajun Zhang, Gui-Ping Li, Takahiro Shimada, Jie Wang, and Takayuki Kitamura, “Disappearance of ferroelectric critical thickness in epitaxial ultrathin BaZro$_3$ films,” Phys. Rev. B 90, 184107 (2014).

[16] John Hirth, Dislocations in Solids (Elsevier, 2008).

[17] Kevin F. Garrity, Karin M. Rabe, and David Vanderbilt, “Hyperferroelectrics: Proper ferroelectrics with persistent polarization,” Phys. Rev. Lett. 112, 127601 (2014).

[18] Massimiliano Stengel, Craig J. Fennie, and Philippe Ghosez, “Electrical properties of improper ferroelectrics from first principles,” Phys. Rev. B 86, 094112 (2012).

[19] Na Sai, Craig J. Fennie, and Alexander A. Demkov, “Absence of critical thickness in an ultrathin improper ferroelectric film,” Phys. Rev. Lett. 102, 107601 (2009).

[20] Joseph W. Bennett, Kevin F. Garrity, Karin M. Rabe, and David Vanderbilt, “Hexagonal abc semiconductors as ferroelectrics,” Phys. Rev. Lett. 109, 167602 (2012).

[21] M. Stengel and N. A. Spaldin, “Origin of the dielectric dead layer in nanoscale capacitors,” Nature 443, 679–682 (2006).

[22] Massimiliano Stengel, David Vanderbilt, and Nicola A. Spaldin, “Enhancement of ferroelectricity at metal-oxide interfaces,” Nature Materials 8, 392–397 (2009).

[23] Meng-Qiu Cai, Yue Zheng, Pui-Wai Ma, and C. H. Woo, “Vanishing critical thickness in asymmetric ferroelectric tunnel junctions: First principle simulations,” Journal of Applied Physics 109, 024103 (2011).

[24] Hiroyuki Yamada, Atsushi Tsurumaki-Fukuchi, Masaki Akaogi, Nanlin Wang, Kazunari Yamaura, and Hiroshi Kobayashi, Takuro Nagai, Yoshikiyo Toyama, C. J. Boothroyd, and Akihito Sawa, “Strong Surface-Termination Effect on Electroresistance in Ferroelectric Termination Tunnel Junctions,” Advanced Functional Materials 25, 2708–2714 (2015).

[25] Youguo Shi, Yanfeng Guo, Xia Wang, Andrew J. Princep, Dmitry Khalyavin, Pascal Manuel, Yuichi Michiu, Akira Sato, Kenji Tsuda, Shan Yu, Masao Ara, Yuichi Shirako, Masaki Sakoai, Nanlin Wang, Kazunari Yamaura, and Andrew T. Boothroyd, “A ferroelectric-like structural transition in a metal,” Nature Materials 12, 1024 (2013).

[26] T. H. Kim, D. Puggioni, Y. Yuan, H. Zhou L. Xie, N. Campbell, P. J. Ryan, Y. Choi, J.-W. Kim, J. R. Patzner, S. Ryu, J. P. Podkaminer, J. Irwin, Y. Ma, C. J. Fennie, M. S. Rzchowski, V. Gopalan X. Q. Pan, J. M. Rondinelli, and C. B. Eom, “Polar metals by geometric design,” Nature 533, 68–72 (2016).

[27] Danilo Puggioni and James M. Rondinelli, “Designing a robustly metallic noncentrosymmetric ruthenate oxide with large thermopower anisotropy,” Nat. Commun. 5, 3432 (2013).

[28] Jochen Heyd, Gustavo E. Scuseria, and Matthias Ernzerhof, “Hybrid functionals based on a screened coulomb potential,” J. Chem. Phys. 118, 8207–8215 (2003).

[29] Jochen Heyd, Gustavo E. Scuseria, and Matthias Ernzerhof, “Erratum: hybrid functionals based on a screened coulomb potential [j. chem. phys.118, 8207 (2003)],” J. Chem. Phys. 124, 219906 (2006).

[30] G. Kresse and J. Furthmüller, “Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set,” Computational Materials Science 6, 15–50 (1996).

[31] Peter E. Blöchl, O. Jepsen, and O. K. Andersen, “Improved tetrahedron method for brillouin-zone integrations,” Physical Review B 49, 16223–16233 (1994).

[32] Hendrik J. Monkhorst and James D. Pack, “Special points for Brillouin-zone integrations,” Physical Review B 13, 5188–5192 (1976).

[33] Seidel P. and Hoffmann W., “Verfeinerung der kristallstruktur von NaNbO$_3$,” Zeitschrift fur Kristallographie 143, 444–459 (1976).

[34] J. Liu, M. Kargarian, M. Kareev, B. Gray, Phil J. Ryan, A. Cruz, N. Tahir, Yi-De Chuang, J. Guo, James M. Rondinelli, John W. Freeland, Gregory A. Fiete, and J. Chakhalian, “Heterointerface engineered electronic and magnetic phases of NdNiO$_3$ thin films,” Nat. Commun. 4, 3714 (2013).

[35] Branton J. Campbell, Harold T. Stokes, David E. Tanner, and Dorian M. Hatch, “ISODISPLACE: a web-based tool for exploring structural distortions,” Journal of Applied Crystallography 39, 607–614 (2006).

[36] Gianluca Giovannetti and Massimo Capone, “Dual nature of the ferroelectric and metallic state in liso$_3$,” Phys. Rev. B 90, 195113 (2014).

[37] W. Zhong, R. D. King-Smith, and David Vanderbilt, “Giant lo-to splittings in perovskite ferroelectrics,” Phys. Rev. Lett. 72, 3618–3621 (1994).

[38] S. K. Mishra, N. Choudhury, S. L. Chaplot, P. S. R. Krishna, and R. Mittal, “Competing antiferroelectric and ferroelectric interactions in NaNbO$_3$: Neutron diffraction and theoretical studies,” Phys. Rev. B 76, 024110 (2007).

[39] John P. Perdew, “Density functional theory and the band gap problem,” International Journal of Quantum Chemistry 28, 497–523 (1985).

[40] Massimiliano Stengel, Pablo Aguado-Puente, Nicola A. Spaldin, and Javier Junquera, “Band alignment at metal/ferroelectric interfaces: Insights and artifacts from first principles,” Phys. Rev. B 83, 235112 (2011).

[41] Gianluca Giovannetti, Danilo Puggioni, James M. Rondinelli, and Massimo Capone, “Interplay between electron correlations and polar displacements in metallic SrEuMo$_3$O$_9$,” Phys. Rev. B 93, 115147 (2016).

[42] H. J. Xiang, “Origin of polar distortion in LiNbO$_3$-type “ferroelectric” metals:Role of A-site instability and short-range interactions,” Phys. Rev. B 90, 094108 (2014).

[43] Pavan Nukala, Mingliang Ren, Rahul Agarwal, Jacob J. Exelby, Gerui Liu, A. T. Charlie Johnson, and Ritesh Agarwal, “Inverting polar domains via electrical pulsing in metallic germanium telluride,” Nat. Commun. 7, 15033 (2016).

[44] Nicole A. Benedek and Turan Birol, “‘ferroelectric’ metals reexamined: fundamental mechanisms and design considerations for new materials,” J. Mater. Chem. C 4, 4000–4015 (2016).