***In situ* hard x-ray photoemission spectroscopy of barrier-height control at metal/PMN-PT interfaces**

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Metal-ferroelectric interfaces form the basis of novel electronic devices. A key effect determining the device functionality is the bias-dependent change of the electronic energy-level alignment at the interface. Here, hard x-ray photoelectron spectroscopy (HAXPES) is used to determine the energy-level alignment at two metal-ferroelectric interfaces—Au versus SrRuO₃ on the relaxor ferroelectric Pb(Mg_{1/3}Nb_{2/3})_{0.72}Ti_{0.28}O₃ (PMN-PT)—directly *in situ* as a function of electrical bias. The bias-dependent average shifts of the PMN-PT core levels are found to have two dominant contributions on the 0.1–1-eV energy scale: one depending on the metal electrode and the remanent electric polarization and the other correlated with electric-field-induced strain. Element-specific deviations from the average shifts are smaller than 0.1 eV and appear to be related to predicted dynamical charge variations in PMN-PT. In addition, the efficiency of ferroelectric polarization switching is shown to be reduced near the coercive field under x-ray irradiation. The results establish HAXPES as a tool for the *in operando* investigation of metal-ferroelectric interfaces and suggest electric-field-induced modifications of the polarization distribution as a novel way to control the barrier height at such interfaces.

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I. INTRODUCTION

Ferroelectric materials exhibit spontaneous electric polarization that can be reversed by application of an external electric field greater than the coercive field. This property can be used to encode Boolean algebra and thus can form the basis for nonvolatile memory devices [1,2] such as ferroelectric capacitors, diodes [3], tunnel junctions [4,5], and field-effect transistors [6]. In most of these devices, the ferroelectric material is in direct contact with a metal electrode, and the device physics is determined by the metal-ferroelectric interface.

The most important property of a metal-ferroelectric interface related to its electrical characteristics is the Schottky barrier height, i.e., the energy offset between the Fermi level of the metal and the valence or conduction band edge of the (wide-gap semiconducting) ferroelectric [3]. This internal potential barrier for carrier transport generally depends on the bulk band structures of the materials forming the interface and the interfacial dipole determined by the atomic interface structure and the total charge distribution in the system [7]. Intriguingly, in the case of metal-ferroelectric interfaces, the interfacial dipole becomes explicitly dependent on the magnitude and direction of the polarization [8]. This is due to imperfect screening of the bound polarization charges at the surface of the ferroelectric [Fig. 1(a)] [9–11].

The Schottky barrier height change upon polarization reversal is predicted to be

$$e\Delta V = \frac{e}{\epsilon_0} 2\lambda_{\text{eff}} P_S, \quad (1)$$

where λ_{eff} is an effective screening length, P_S the spontaneous polarization, ϵ_0 the vacuum permittivity, and e the elementary charge [8]. The key parameter here is λ_{eff} ; it quantifies the

overall effect of all mechanisms responsible for the imperfect screening of polarization charges including electronic and chemical bonding effects [12]. In simple electrostatic models, λ_{eff} is regarded either as an effective width of the screening charge distribution in the metal electrode [inset of Fig. 1(a)] or as the effective thickness of an interfacial “dead layer” with reduced permittivity [12].

The microscopic physics of λ_{eff} has been extensively investigated by *ab initio* theory [8–11]. Experimental information can in principle be extracted from transport measurements, but only indirectly [5,13]. By contrast, x-ray photoelectron spectroscopy (XPS) has recently been shown to be able to provide direct quantitative information on ΔV and thus λ_{eff} [14–17]. This ability stems from the interface sensitivity of the technique, particularly when hard x rays ($h\nu > 2$ keV) are used to enhance the photoelectron escape depth, and the intrinsic sensitivity of photoelectrons to local internal electric fields: the atomic-site-specific core-level shift is a fine sensor for electrostatic potential differences, and it is highly correlated with the shift of the valence-band edge [18,19].

Previous electric-polarization-dependent photoemission experiments have been performed on interfaces of BaTiO₃ and Pb(Zr_{0.2}Ti_{0.8})O₃ with metals [14–17] (with [15,17] and without [14,16] *in situ* control of the polarization state) using soft [15–17] as well as hard [16] x rays. The obtained $e\Delta V$ values were in the range of 0.42–1.1 eV in some studies [16,17], in good agreement with the results of transport measurements. Element-specific polarization-induced core-level shifts were observed and tentatively attributed to dynamical charge variations at the interface [17], and x-ray radiation effects were investigated to some extent [14,17].

Here, we use hard x-ray photoelectron spectroscopy (HAXPES) with *in situ* electrical biasing to determine Schottky barrier height changes at interfaces of the relaxor ferroelectric [20,21] Pb(Mg_{1/3}Nb_{2/3})_{0.72}Ti_{0.28}O₃ (PMN-PT) with Au

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FIG. 1. (a) Schematic depiction of a short-circuited asymmetric ferroelectric (FE) capacitor with different metal electrodes (M1, M2). The solid (dashed) line represents the electrostatic potential for the P_+ (P_-) polarization state. In the inset, the potential change at the interface upon polarization reversal, ΔV , and a typical information depth for hard x-ray photoemission spectroscopy, L_{PES} , are indicated. (b) Schematic representation of sample structures and bias-dependent interface-sensitive x-ray photoemission spectroscopy. (c) Representative polarization hysteresis loop of the PMN-PT substrate. (d) Pb 4*f* and Sr 3*d* core-level photoemission spectra of SrRuO₃/PMN-PT for different temperatures T (above and below the Curie temperature $T_C = 401 \pm 3$ K) and applied bias fields E (top: $T = 425$ K, $E = \pm 10$ kV/cm; bottom: $T = 300$ K, $E = \pm 15$ kV/cm; $h\nu = 1.6$ keV). The potential change ΔV is reflected in the bias-dependent shift of the Pb 4*f* emissions for $T < T_C$.

and SrRuO₃ metal electrodes. In addition to the expected electrode dependence of ΔV , our core-level spectroscopy results reveal three important effects: first, an x-ray-radiation-induced suppression of the amount of switchable polarization for biases near the coercive field; second, systematic element-specific deviations from the average polarization-dependent core-level shift related to predicted dynamical charge variations; and third, a sizable field-dependent contribution to the core-level shift correlated with field-induced lattice strain. This latter effect is explained by an analytical model assuming a nonuniformly polarized ferroelectric layer and represents a novel mechanism for enhancing Schottky barrier height changes at metal-ferroelectric interfaces.

II. EXPERIMENT

The samples used in this study consist of ~ 200 - μm -thick PMN-PT single crystals with polished (001) and (00 $\bar{1}$)

faces [22], sandwiched between a 3-nm-thin Au electrode or a 6-nm-thin SrRuO₃ electrode at the top and a 50-nm-thick Au electrode at the bottom [Fig. 1(b)]. Polishing of the PMN-PT substrate surfaces was done chemomechanically (Crystec GmbH, Berlin) with a resulting surface roughness of about 7 Å (root mean square), as determined by atomic force microscopy. Au films were deposited by dc magnetron sputtering and SrRuO₃ films were grown by pulsed laser deposition. During SrRuO₃ deposition, the substrate temperature was held at 630° C and the oxygen pressure was 7×10^{-2} mbar. The remanent polarization, coercive field, and Curie temperature of the samples were measured to be $22.9 \pm 1.0 \mu\text{C}/\text{cm}^2$, 2.0 ± 0.2 kV/cm, and 401 ± 3 K, respectively. A typical polarization hysteresis loop of the PMN-PT substrate is shown in Fig. 1(c).

In the photoemission experiments, the top electrode is connected to ground, and bias potentials of up to ± 300 V are applied to the bottom electrode, positive bias corresponding to an electric polarization pointing to the top electrode (P_+ state) [Fig. 1(b)]. Photoemission measurements were performed at beamlines P04 [23] and P09 [24,25] of PETRA III (Hamburg) using photon energies of 1.6 and 6.0 keV, respectively. In both cases, a grazing-incidence geometry was used and the total energy resolution was 300 meV. For the high-energy experiments, the photon flux and spot size on the sample were $\sim 4 \times 10^{12}$ ph/s and $400 \times 100 \mu\text{m}^2$, respectively [25]. Typical acquisition times for core-level spectra were 5–20 min, and the information depth [denoted L_{PES} in Figs. 1(a), 1(b), and 2(c), corresponding to three times the electron inelastic mean free path] was about 21 nm [26].

III. RESULTS AND DISCUSSION

A. Repoling behavior

The bias- and temperature-dependent spectra shown in Fig. 1(d) validate our experimental approach. The Sr 3*d* peaks associated with emissions from the metallic top electrode provide a constant energy reference. The Pb 4*f* emissions from PMN-PT near the interface, on the other hand, display a bias-dependent energy shift consistent with the polarization-direction-dependent potential drop at the interface, as depicted in Fig. 1(a), and they display this effect only when PMN-PT is in the ferroelectric phase. However, polarization switching may not be complete, as the Pb 4*f* spectrum corresponding to the P_+ state exhibits a residual signal at the positions of the P_- peaks [see red spectrum at the bottom of Fig. 1(d)]. The origin of this effect is now explored.

Figure 2(a) shows how the Pb 4*f* and Sr 3*d* spectra taken from the SrRuO₃/PMN-PT system evolve as a function of repoling time. The experimental protocol for these measurements was as follows. First, the sample was poled by an electric field of +15 kV/cm. The electric field was then turned off and the remanent P_+ state was (partially) switched to P_- under x-ray illumination by gradually changing the applied electric field from zero to −2.5 kV/cm in a given time span. After that, the electric field was set to −15 kV/cm, which did not change the polarization state, and photoemission spectra were recorded under this condition.

In Fig. 2(a), again no changes are observed in the Sr 3*d* emissions, whereas the evolution of the Pb 4*f* spectra shows an

FIG. 2. Pb 4*f* and Sr 3*d* core-level photoemission spectra of SrRuO₃/PMN-PT as a function of (a) repoling time, (b) lateral beam position on the sample surface, and (c) photoelectron emission angle with respect to normal emission. All spectra were measured at $T = 294$ K, $E = -15$ kV/cm, and $h\nu = 6$ keV after switching from the P_+ to the P_- state at $E \geq -2.5$ kV/cm under x-ray illumination (see text). The dashed line in (b) indicates the position at which the spectra in (a) and (c) were recorded. Spectra in (c) are normalized to the intensity of the Sr 3*d* emission. The spectrum recorded at an angle of 5° in (c) corresponds to the top spectrum in (a).

exponential increase of the unswitched P_+ spectral component with repoling time [with a time constant of 35 ± 10 min] as well as a continuous shift of all Pb 4*f* components of up to 0.20 ± 0.02 eV toward lower energies. The linear position scan on the sample surface shown in Fig. 2(b) identifies the incomplete switching as a radiation effect; the residual P_+ component can only be observed at the spot hit by the x-ray beam during polarization reversal. The emission-angle-dependent variation of the relative intensities of the P_+ and P_- components at the longest repoling time, which is shown in Fig. 2(c), finally indicates a characteristic depth dependence. Near normal emission, where photoemission is more bulk sensitive and deeper layers beneath the top interface are probed, the P_+ component dominates, whereas the P_- component becomes the predominant one at larger emission angles corresponding to increased interface sensitivity. This is consistent with the common switching process [1,2], in which cone-shaped P_- domains will grow from the top interface of the ferroelectric into the bulk, if a negative bias is applied to the bottom electrode [27]. We emphasize that the residual P_+ state can in principle be completely erased by subjecting the sample to an electric field of +15 kV/cm, followed by fast (< 1 s) poling at a strong enough negative field ($|E| \gg 2.5$ kV/cm). However, we also note that, depending on the sample, there

may be an asymmetric persistence of a residual P_+ [Fig. 2(a)] or P_- [Fig. 1(d)] component.

The suppression of the amount of switchable polarization by above-band-gap radiation, as demonstrated by the results in Fig. 2, has previously been explained by trapping of photo-generated charge carriers at domain walls inclined to the polarization direction [28,29]. The presence of trapped charge carriers compensating the polarization charges of misaligned domain walls strongly diminishes the electric-field-induced driving force acting on these walls, which hinders the growth of antiparallel domains [30]. Our results are consistent with the implications of this model. The number of locked P_+ domains beneath the top interface should increase at longer repoling times because of the increasing number of trapped carriers at longer illumination, and the evolution of the sub-surface polydomain state of PMN-PT should be accompanied by an increase in the P_+ spectral component and a reduction of the P_- one, as observed experimentally. In addition, the dependence of the electrostatic potential in the probed PMN-PT layer on the mean polarization [see Eq. (3) below] could explain the observed time-dependent shift of both the P_+ and P_- Pb 4*f* component toward lower energies. Further, the charge carrier trapping should predominantly occur at misaligned domain boundaries that indeed are more likely to exist at bias fields near the switching threshold [28,29]. And finally, complete erasure of the locked polarization state should be possible under illumination and large bias fields, as the trapped charge carriers can now recombine with free carriers [29]. Since we find no evidence for the presence of radiation-induced defects or oxygen vacancies [31] in the spectroscopic data, domain-wall pinning by these types of defects seems unlikely.

B. Core-level-shift systematics

The bistable behavior of the Pb 4*f* emissions from the SrRuO₃/PMN-PT interface indicates a switchable Schottky barrier height, i.e., an interpretation based on Eq. (1). We therefore now turn to a systematic investigation of the field, polarization, element, and interface dependence of the core-level shift in PMN-PT.

Figure 3 displays “spectroscopic hysteresis loops” covering representative PMN-PT core levels for two different interfaces: Au/PMN-PT versus SrRuO₃/PMN-PT. The sequence of applied electric fields was +15, 0, −15, 0, and +15 kV/cm, where at each step a complete set of core-level spectra was measured. The beam position on the sample was not varied while the loops were recorded. Core-level peak positions were determined by line-shape analysis using Lorentzian (Pb 4*f*, Nb 3*d*, O 1*s*) and Doniach-Šunjić (Ti 2*p*, Mg 1*s*) profiles convoluted with a Gaussian. The Doniach-Šunjić line shape was chosen for practical reasons, as it could reproduce a slight asymmetry in the measured Ti 2*p* and Mg 1*s* lines. A background and residual peaks were added where necessary. The best fits are overplotted on the experimental data in Fig. 3. Remarkably, each bias-dependent series of spectra for a given core level can be fit with a constant line width, and the line positions at the start and end of the hysteresis loop match within 30 ± 30 meV. This, together with the overall sharpness of the photoemission peaks, demonstrates a high

FIG. 3. Bias-dependent core-level photoemission spectra of PMN-PT for two different top electrodes: (a) Au and (b) SrRuO₃. Best fits to the experimental spectra and spectral decompositions are indicated by solid lines. Vertical dashed lines mark the peak positions at $E = +15$ kV/cm (red line) and $E = -15$ kV/cm (blue line), respectively. Gray-filled boxes indicate peak shifts upon reversal of the remanent polarization. In both panels, the measurement sequence is from bottom to top ($T = 294$ K and $h\nu = 6$ keV).

degree of lateral interface homogeneity (on the length scale of the beam spot on the sample) as well as hardness against x-ray-radiation-induced polarization losses and defect creation on the time scale of hours.

Our central result is that the line-shape analysis reveals three distinct contributions to the bias-dependent PMN-PT core-level shifts: (i) an interface-dependent average shift upon reversal of the remanent polarization of 0.40 ± 0.04 eV and 0.84 ± 0.04 eV for Au/PMN-PT and SrRuO₃/PMN-PT, respectively (gray-filled boxes in Fig. 3), (ii) systematic element-specific deviations from this shift in the range of -70 to $+50$ meV as listed in Table I, and (iii) an additional electric-field-induced shift with a magnitude of 0.19 ± 0.04 eV (at ± 15 kV/cm), independent of the interface (vertical dashed lines in Fig. 3). We now discuss these three contributions in turn.

As to the average energy-level changes upon polarization reversal, we note that the $e\Delta V$ values measured for the two interfaces fall in the range of values previously obtained from metal-ferroelectric interfaces by XPS [14–17]. Plugging the value for the bulk remanent polarization of our PMN-PT

crystals into Eq. (1) gives λ_{eff} values of 0.077 Å and 0.162 Å for Au/PMN-PT and SrRuO₃/PMN-PT, respectively. These values are close to the effective screening lengths calculated for Pt/PbTiO₃ and SrRuO₃/PbTiO₃ interfaces, respectively, and they confirm the predicted more efficient screening at the elemental metal electrode [11]. Unfortunately, metal/PMN-PT interfaces, to our knowledge, have not yet been studied by *ab initio* theory.

TABLE I. Element-specific deviations from measured average $e\Delta V$ values in meV (top rows; error bar: 10 meV), compared to calculated dynamical effective charges (in elementary charge) for the respective atoms in PMN-PT from Ref. [36] (bottom row).

	Mg 1s	O 1s	Ti 2p	Nb 3d	Pb 4f
Au/PMN-PT	-10	-60	0	50	10
SrRuO ₃ /PMN-PT	-10	-70	20	40	30
PMN-PT	1.9	-2.1, -5.1	5.8	7.4	3.6

Nevertheless, to gain deeper insight into the factors influencing the barrier-height change upon polarization reversal, we calculated the spatial distribution of the electrostatic potential inside a nonuniformly polarized ferroelectric layer of thickness t_f sandwiched between two dissimilar electrodes. Since the proper physical characteristic of a metal-dielectric interface is the interfacial capacitance density c_i [11,32] rather than the effective screening length, the capacitances c_{i1} and c_{i2} per unit area of the top and bottom interfaces were used in our electrostatic calculations. Taking into account the presence of a voltage V_a applied to the bottom electrode and the condition $\text{div } \mathbf{D} = \rho$, which is imposed on the electric displacement $\mathbf{D}$ inside the ferroelectric layer containing a density $\rho(z)$ of charge carriers, we derived the following relation for the electrostatic potential $V(z)$ in a ferroelectric layer at a distance $z > 0$ from the interface with the grounded top electrode:

$$V(z) = \frac{z + \epsilon_0 \epsilon_b / c_{i1}}{t_f + \epsilon_0 \epsilon_b / c_{i\Sigma}} \times \left(V_a - \frac{P_m t_f}{\epsilon_0 \epsilon_b} + \frac{Q_f}{c_{i2}} + \frac{1}{\epsilon_0 \epsilon_b} \int_0^{t_f} Q(\zeta) d\zeta \right) + \frac{1}{\epsilon_0 \epsilon_b} \left(P_{mz} z - \int_0^z Q(\zeta) d\zeta \right), \quad (2)$$

where ϵ_b is the background permittivity of the ferroelectric material [33], $c_{i\Sigma} = (c_{i1}^{-1} + c_{i2}^{-1})^{-1}$ the total interfacial capacitance, $Q(z) = \int_0^z \rho(\zeta) d\zeta$, $Q_f = Q(z = t_f)$, and P_m and $P_{mz}(z)$ denote the mean values of the voltage-dependent polarization $P(V_a)$ in the whole ferroelectric layer and the slab of thickness z adjacent to the top interface, respectively. At $\rho = 0$ and $t_f \gg \epsilon_0 \epsilon_b / c_{i\Sigma}$, Eq. (2) reduces to

$$V(z) \cong \left(\frac{z}{t_f} + \frac{\epsilon_0 \epsilon_b}{c_{i1} t_f} \right) V_a + \frac{P_{mz} - P_m}{\epsilon_0 \epsilon_b} z - \frac{P_m}{c_{i1}}. \quad (3)$$

In our case of $t_f = 200 \text{ } \mu\text{m}$ and $z \leq L_{\text{PES}} \approx 20 \text{ nm}$, the first term in Eq. (3) appears to be rather small ($\leq 0.03 \text{ V}$) even at the maximum applied voltage $V_a = 300 \text{ V}$. Neglecting this term in the first approximation, we obtain $V(z) \approx -P_m / c_{i1}$ for a homogeneously polarized ferroelectric, which yields $\Delta V \approx 2P_m(V_a) / c_{i1}$ in similarity to Eq. (1). Setting P_m equal to the remanent polarization of PMN-PT, we get, from the measured values of ΔV , capacitance densities c_{i1} of about 1.1 and 0.5 F/m^2 for the Au/PMN-PT and SrRuO₃/PMN-PT interfaces, respectively. We note that these values are of the order of the capacitance $c_{i1} \approx 0.9 \text{ F/m}^2$ expected for the SrRuO₃/BaTiO₃ interface [34]. However, even a small inhomogeneity in the polarization distribution near the interface could significantly affect ΔV via the second term in Eq. (3). This renders the interpretation of the above value of c_{i1} as a quantitative measure of the screening ability of SrRuO₃ premature. It should be emphasized here that capacitances of ferroelectric-electrode interfaces represent important physical quantities, as they strongly affect the equilibrium polarization in nanoscale ferroelectric capacitors [34] and the tunneling electroresistance of asymmetric ferroelectric tunnel junctions caused by the depolarizing-field effect [35].

The measured element-specific contributions to the core-level shift for the two interfaces are compared with corresponding calculated dynamical charges for bulk PMN-PT [36] in

Table I. Dynamical charges are a measure for the polarization change or charge transfer induced by the displacement of specific ions in the unit cell [37]. There is some correlation between the two quantities in that the overall trends are similar, with Nb and O displaying the largest positive and negative values, respectively, and the values for Mg, Ti, and Pb lying in between. Yet, the correlation is not perfect, as, e.g., the measured Ti 2*p* core-level shifts appear to be smaller than the Pb 4*f* ones, whereas the calculated dynamical charge for Ti is larger than the one for Pb.

Such a semiquantitative connection between measured element-specific core-level shifts and calculated dynamical charges has been observed before in a less systematic photoemission study of the Pt/BaTiO₃ interface [17]. It is an intuitive connection at first because of XPS's capability to probe atomic-site-specific *static* charge differences. However, for polarization-direction-dependent *dynamical* charge variations to be observable, asymmetric atomic displacements at the interface are actually required, and these have so far only rarely been investigated [38]. The possibility to measure dynamical charges by core-level photoemission spectroscopy, as suggested by the results shown in Fig. 3, is intriguing, but there remains the need to understand the underlying mechanism of the dynamical-charge-induced core-level shift.

Finally, as to the electric-field-induced contribution to $e\Delta V$, it is tempting to associate the enhancement of $e\Delta V$ at large electric fields with the saturated polarization being probed rather than the (lower) remanent polarization [15]. In that case, however, the magnitude of the additional shift should also depend on the interface properties, i.e., it should scale with the effective screening length [Eq. (1)] or the inverse interface capacitance [third term in Eq. (3)], respectively, which is not observed.

To elucidate the origin of this effect, we show in Fig. 4(a) a complete spectroscopic hysteresis loop for the Pb 4*f*_{7/2} emission from the SrRuO₃/PMN-PT interface. Here, we specifically make use of the radiation-induced presence of the P_+ spectral component even at negative fields. Remarkably, the P_+ component shifts toward lower energies with increasing field strength, independent of the field direction. Figure 4(b) shows the extracted P_+ energy shift as a function of the applied electric field for both the SrRuO₃/PMN-PT and the Au/PMN-PT interfaces. The magnitude and field dependence of the energy shift are the same within $\pm 40 \text{ meV}$, and the observed field dependence is strongly reminiscent of typical butterfly-shaped PMN-PT strain loops [22]. Figures 4(b) and 4(c) corroborate this correlation by comparing the spectroscopic hysteresis loops to the variation of the out-of-plane lattice constant that was measured for the SrRuO₃/PMN-PT system by x-ray diffraction.

What is the origin of this core-level shift whose absolute value is a function of the magnitude of the bias voltage and whose direction is determined by the direction of the P_+ component of the polarization at the interface (see dashed lines in Fig. 3) and not by the sign of the bias voltage [see Figs. 4(a) and 4(b)], a shift that depends on bulk rather than interface properties and that seems to be correlated with lattice strain?

Bulk band-structure modifications due to changes of the lattice constants or atomic displacements within the unit

FIG. 4. (a) Bias-dependent Pb $4f_{7/2}$ core-level photoemission spectra of SrRuO₃/PMN-PT. Solid lines with circles indicate the energy positions of spectral components corresponding to P_+ and P_- states. Vertical dashed lines and gray-hatched box are the same as in Fig. 3(b). The measurement sequence is from bottom to top ($T = 294$ K and $h\nu = 6$ keV). (b) Bias-dependent energy position of the Pb $4f_{7/2}$ P_+ component for SrRuO₃/PMN-PT (top) and Au/PMN-PT (bottom). (c) Out-of-plane lattice constant c of PMN-PT as a function of electric field strength, as measured for the SrRuO₃/PMN-PT system by x-ray diffraction.

cell can be ruled out because the core-level shift resulting from such modifications would have to be unidirectional, independent of the polarization direction [8]. Moreover, for typical deformation potentials of a few eV and a strain of 0.15% at 15 kV/cm [39,40], the expected energy shift is ≤ 10 meV, approximately one order of magnitude lower than the measured shift. However, we note that a unidirectional strain and/or polarization [8] effect may in fact give rise to the slight asymmetry between the positions of the core-level emissions on the 20 meV scale at $E = \pm 15$ kV/cm in Fig. 3 (cf. positions of the red and blue dashed lines relative to the gray-filled boxes).

To explain the field-induced energy shift of the P_+ component, we can apply the electrostatic model described by Eq. (2) to the discussed case of the ferroelectric crystal containing residual P_+ domains at the interface. As already noted in Sec. III A, these domains are locked due to the presence of photogenerated charge carriers compensating the

polarization charges at their boundaries. Assuming that this compensation is complete ($\rho = \text{div } \mathbf{P}$), we calculated the electrostatic potential $V(z)$ inside the P_+ domains and found that, at $t_f \gg \epsilon_0 \epsilon_b / c_{i\Sigma}$, it is described by the modified Eq. (3), where P_m now denotes the mean polarization in the P_+ domains. Remarkably, the direction of the energy shift induced by such a potential distribution is determined by the polarization direction at the interface, but not by the mean polarization in the sample poled in the opposite direction, which agrees with the experimental data shown in Fig. 4. Moreover, Eq. (3) in all cases contains the term $(P_{mz} - P_m)z/(\epsilon_0 \epsilon_b)$, which is practically independent of the electrode material because the measured macroscopic polarization is sensitive to the interfacial capacitance only in ultrathin ferroelectric films. Since this term changes sign after the polarization switching at the interface, it is a good candidate for the explanation of the observed electric-field-induced core-level shifts.

Furthermore, an increase in the absolute value of this term with increasing positive and negative bias voltages may be attributed to the strain effect on the polarization inhomogeneity near the ferroelectric-electrode interface. Indeed, the polarization in the unit cells adjacent to the electrode is expected to be suppressed and less sensitive to lattice strains than inside the ferroelectric crystal. Therefore the absolute value of $(P_{mz} - P_m)z/(\epsilon_0 \epsilon_b)$ should grow in the presence of a bias voltage increasing the out-of-plane lattice constant c . (Note that, since the residual P_+ domains are clamped by the oppositely polarized surrounding material, the lattice constant c in these domains should increase as well despite the fact that their polarization is directed against the electric field.) Importantly, even very small changes in the difference $P_{mz} - P_m$ can affect $V(z = L_{\text{PES}})$ significantly because the factor $L_{\text{PES}}/(\epsilon_0 \epsilon_b) \approx 100 \text{ m}^2/\text{F}$ is much larger than $1/c_{i1} \approx 1 \text{ m}^2/\text{F}$. We are thus led to conclude that the field-induced contribution to $e\Delta V$ is due to the presence of an interfacial ferroelectric layer with suppressed polarization and the strain-induced change in the polarization inhomogeneity near the interface.

IV. CONCLUSION

In summary, our *in operando* HAXPES results provide a comprehensive view on polarization- and electric-field-induced effects on the electronic structure at metal/PMN-PT interfaces. In particular, the results reveal a polarization-dependent Schottky barrier height for Au and SrRuO₃ electrodes. The measured interfacial capacitances are 1.1 and 0.5 F/m², respectively. Moreover, we find direct evidence for element-specific dynamical-charge-induced core-level shifts as well as a sizable field-dependent overall core-level shift correlated with strain. The latter observation suggests electric-field-induced modifications of the polarization distribution at interfaces as a novel approach to control Schottky barrier heights. Our study establishes HAXPES with *in situ* electrical biasing as a tool for probing electronic properties at metal-ferroelectric interfaces, and we hope that our experimental results will motivate theoretical efforts in understanding interfaces between metals and PMN-PT.

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