Ferroelectric Diodes with Charge Injection and Trapping

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Ferroelectric diodes with polarization-modulated Schottky barriers are promising for applications in resistive switching (RS) memories. However, they have not achieved satisfactory performance reliability as originally hoped. The physical origins underlying this issue have not been well studied, although they deserve much attention. Here, by means of scanning Kelvin probe microscopy we show that the electrical poling of ferroelectric diodes can cause significant charge injection and trapping besides polarization switching. We further show that the reproducibility and stability of switchable diode-type RS behavior are significantly affected by the interfacial traps. A theoretical model is then proposed to quantitatively describe the modifications of Schottky barriers by charge injection and trapping. This model is able to reproduce various types of hysteretic current-voltage characteristics as experimentally observed. It is further revealed that the charge injection and trapping can significantly modify the electroresistance ratio, RS polarity, and high- or low-resistance states initially defined by the polarization direction. Several approaches are suggested to suppress the effect of charge injection and trapping so as to realize high-performance polarization-reversal-induced RS. This study, therefore, reveals the microscopic mechanisms for the RS behavior comodulated by polarization reversal and charge trapping in ferroelectric diodes, and also provides useful suggestions for developing reliable ferroelectric RS memories.

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1. INTRODUCTION

Ferroelectric resistive memories have emerged as an attractive candidate for next-generation nonvolatile memory technology, owing to the promise of subnano-second switching speed, high read-write endurance cycles, low power consumption, and nondestructive readout [1–5]. They can be further categorized into two types according to the mechanism variance. One is the ferroelectric tunnel junctions, in which an ultrathin ferroelectric layer acts as a tunneling barrier and the tunneling resistance can be modulated by the polarization. The other is the ferroelectric diodes utilizing the polarization to tune the interface Schottky barriers. Because ferroelectric resistive memories are based on polarization-reversal-induced resistive switching (RS), high reliability seems to be taken for granted. Unfortunately, ferroelectric resistive memories often show poor reproducibility and device-to-device variability [6–9], severely hindering the practical applications. To address these issues, a thorough understanding of the origin underlying the huge diversity of RS phenomena is urgently needed [10]. This paper, therefore, aims to investigate the fundamentals of ferroelectric RS effects and will mainly deal with the physics of ferroelectric diodes.

Ferroelectric diodes were first developed in Au/PbTiO$_3$/La$_{0.5}$Sr$_{0.5}$CoO$_3$ heterostructures by Blom et al. [11] in 1994. It was observed that the polarization-induced band bending could change the Au/PbTiO$_3$ contact from the Schottky type to the Ohmic type, thus giving rise to a resistance change of 2 orders of magnitude. Pintilie et al. [12,13] developed a theoretical model for ferroelectric diodes. Their model adapted classic theories of Schottky diodes. Their model adapted classic theories of Schottky contacts for ferroelectric diodes by treating the polarization as a charge sheet [12]. This model fairly described the experimentally observed current-voltage (I-V) and capacitance-voltage (C-V) characteristics of ferroelectric diodes [13]. Recently, switchable diode effects coupled with tunable photovoltaic responses were discovered in BiFeO$_3$ single crystals [4,14] and thin films [5,15], and since then there has been a boost in the number of studies on ferroelectric diodes.

While previous studies were largely concerned with the effect of polarization reversal on RS, much less attention was paid to other possible effects, e.g., those caused by defects. Indeed, according to the theories of ferroelectric diodes [12,13], ionic defects are indispensable, as they
could render the ferroelectric layer semiconducting. This is the prerequisite for forming a Schottky barrier. The charges at ionic defects (either donors or acceptors) in the space-charge region (SCR) are compensated by the polarization charges. Hence, the width of SCR could be modulated by the polarization, resulting in tunable Schottky barriers and a switchable diode effect. Without these defects, the ferroelectric layer will be insulating and the switchable diode-type RS behavior could be weak in spite of good ferroelectricity [9]. Given the presence of the charged defects, however, common defect-mediated RS mechanisms, like migration of oxygen vacancies and charge trapping and detrapping, may also exist [16,17]. The overall RS behavior is therefore a consequence of the competition between polarization-modulated RS and defect-mediated RS. For example, it was recently found that BiFeO$_3$ with $p$-type semiconducting characteristics arising from Bi deficiencies could exhibit the polarization-controlled switchable diode effect [18–20], whereas oxygen vacancy-rich $n$-type BiFeO$_3$ shows only the conventional bipolar RS behavior irrelevant to polarization [20]. Along this line, it is of great importance to figure out the roles of polarization and defects in ferroelectric diodes and their respective impacts on the RS behavior. In this regard, most previous studies still remain at a qualitative level, while a quantitative model on ferroelectric diodes taking into account the defect-mediated RS mechanisms is still lacking. Such a quantitative model may be helpful for guiding a delicate control of defects so as to achieve high reliability and reproducibility in ferroelectric diodes.

Among various defect-mediated RS mechanisms, the charge injection and trapping effect will be mainly focused in this study. The charge injection and trapping are likely to occur because the ionic defects in the SCR of ferroelectric diodes may create deep trap states, which can capture the charge carriers injected from the electrodes. The charge trapping has a great impact on RS and this has been widely reported in transitional metal oxides [21]; however, it has not received due attention in ferroelectric diodes, although it may be closely related to the aforementioned issues of reliability and reproducibility [22]. Herein, we report a systematic study of polarization reversal and chargetrapping comodulated RS behavior in ferroelectric diodes. We first demonstrate by using scanning Kelvin probe microscopy (SKPM) that upon an electrical poling, the charge injection and trapping do occur concurrently with the domain switching. Then, we present evidence that the reproducibility and stability of switchable diode-type RS behavior are significantly influenced by the interfacial traps. Based on the experimental observations and previous theories [12,13], we develop a model of ferroelectric diodes involving the effect of charge injection and trapping. This model quantitatively reveals how both polarization and trapped charges modify the Schottky barriers and, consequently, influence the RS behavior.

II. EXPERIMENTAL METHODS AND RESULTS

In our experiments, ferroelectric BiFeO$_3$ (BFO) thin films with the thickness of ~40 nm are deposited on La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO)-buffered SrTiO$_3$ (001) substrates by pulsed laser deposition at a temperature of 680 °C and an oxygen pressure of 15 Pa. The crystal structures of the deposited films are characterized by x-ray diffraction (XRD) and reciprocal space mappings (RSMs). The XRD $\theta$-20 diffraction patterns in combination with the (103) and (113) RSMs demonstrate that both the BFO and LSMO films are fully strained (see Fig. S1 in the Supplemental Material [23]). In addition, the BFO unit cell exhibits a $c/a$ ratio of ~1.04 and a monoclinic tiling angle of ~1.3°.

For the electrical measurements, the top Au electrodes with different sizes are tested. The large-area Au electrodes (200 $\mu$m in diameter) are deposited by conventional sputtering using a shadow mask, while nanoelectrodes with an area of ~0.05 $\mu$m$^2$ each are prepared using a polystyrene spheres template [24]. It is found that the large-area Au electrodes are not suitable for electrical measurements, because of the leakage issues caused by the conductive filaments (although the BFO bulk matrix could still have a good quality; see Fig. S2 in the Supplemental Material [23]). Electrical conduction through the filaments also makes the switchable diode-type RS behavior unobservable since the conduction mechanism in this case is no longer the interface-controlled Schottky emission. Therefore, to avoid the effect of the conductive filaments, nanoelectrodes are used in this study.

The SKPM and piezoresponse force microscopy (PFM) are conducted using a scanning probe microscope (Cypher, Asylum Research). The PFM characterizes the domain structures and the local domain switching behavior. The SKPM measures the surface potential, which depends on the relative amounts of polarization charges and screening charges [25]. It is known that there are mainly three types of screening charges: (i) charged species (either electronic or ionic) within the film that are migrated towards the surface region, (ii) surface adsorbates, and (iii) injected charges that are trapped at the surface. Upon an electrical poling, the injected charges often become the dominating part of the screening charges [26].

In our experiments, two adjacent areas are electrically poled with ±5 V, respectively, for subsequent observations. After the poling, the topography, PFM phase, and SKPM surface-potential images are recorded. Figure 1(a) shows almost no morphological changes in the poled regions, thus denying the occurrence of electrochemical reactions. The PFM phase image in Fig. 1(b) shows that the BFO domains are switched into two opposite orientations after the ±5 V poling. Meanwhile, the +5 V (−5 V) poled region shows increased (decreased) surface potential compared with the as-grown region [Fig. 1(c)]. Here, it should be mentioned that in the absence of screening charges, the
negative (positive) polarization charges attracted to the surface by the $+5 \, \text{V}$ ($-5 \, \text{V}$) poling will lead to the surface-potential variations opposite to what have been observed. This suggests that the polarization charges are overcompensated by the screening charges, and more specifically, the injected charges (confirmed by the poling voltage-dependent SKPM and PFM results; see Fig. S3 in the Supplemental Material [23]). After the film is poled with $+5 \, \text{V}$ ($-5 \, \text{V}$), holes (electrons) are injected from the tip and trapped at the surface, and they can even overcompensate the negative (positive) polarization charges. This will cause the surface-potential variations, consistent with the SKPM results. The SKPM image taken after the grounded-tip scanning [Fig. 1(d)] shows that the contrasts between the poled and as-grown regions still remain in spite of a certain degree of decay. The persisted surface-potential differences suggest that some of the injected charges are captured by deep traps and are thus difficult to remove. Therefore, it has been demonstrated that the electrical poling induces not only polarization switching but also charge injection and trapping. Similar observations have been reported in a wide variety of ferroelectrics [27,28].

To qualitatively show the influence of charge injection and trapping on the transport properties, the $I-V$ characteristics are measured for two different samples. One is the as-grown sample while the other one is treated by the $\text{O}_2$ plasma with a power of 15 W and a pressure of $\sim 10 \, \text{mtorr}$ for 20 min. The $\text{O}_2$ plasma treatment causes almost no changes in the sample surface morphology (see Fig. S4 in the Supplemental Material [23]). However, more defects are generated in the surface regions (see Fig. S5 in the Supplemental Material [23]), perhaps due to the ion bombardment during the plasma treatment [29,30]. These defects can also induce an increased density of surface states (also acting as the interfacial traps), and therefore the effect of charge injection and trapping in the plasma-treated sample is more significant. This has been confirmed by the SKPM results. As seen from Figs. 2(a) and 2(b), the surface-potential changes induced by $\pm 5 \, \text{V}$ poling in the plasma-treated sample are much larger than those in the as-grown sample, indicating that more charges are trapped in the surface regions of the plasma-treated sample. Then, $I-V$ curves are swept within $\pm 3 \, \text{V}$ on the Au nanoelectrodes of the two different samples. Figure 2(c) presents the $I-V$ curves measured on different electrodes of the as-grown sample, and they all exhibit similar switchable diode-type RS behaviors. However, for the plasma-treated sample, the $I-V$ curves with various shapes are observed and the representative results are shown in Fig. 2(d). These $I-V$ curves may be classified into four types: (i) a conventional switchable diode, (ii) hysteresis only in the positive branch, (iii) hysteresis only in the negative branch, and (iv) negligible hysteresis. In addition, for a specific device with the plasma-treated sample, the $I-V$ curves vary irregularly in the cycling tests (results not shown here), indicating a poor RS stability. It is noted that the domains in both samples can be fully switched at $\pm 3 \, \text{V}$ [Figs. 2(e) and 2(f)], thus excluding the incomplete domain switching as one possible origin of the great diversity of $I-V$ hysteresis in the
plasma-treated sample. It may therefore be deducible that the charge injection and trapping greatly influence the RS behavior of the plasma-treated sample which is confirmed to have a high density of interfacial traps.

III. THEORETICAL MODEL

Given the experimental confirmation of the existence of charge injection and trapping and its influence on the transport properties of ferroelectric diodes, we then develop a theoretical model of polarization reversal and charge-trapping comodulated ferroelectric diodes. Several assumptions which set the basis for the present model will be made as follows, and most of them were already employed in the model of Pintilie et al. [12].

(1) A ferroelectric layer is either a p-type or an n-type semiconductor depending on the defect chemistry. Taking the p-type ferroelectric layer as an example, it can form a Schottky barrier with a low-work-function metal. The effective charge density \( N_{Q\ eff} \) in the SCR of a Schottky barrier consists of both shallow- and deep-level acceptors. Note these deep-level acceptors need to be distinguished from the deep traps that will be introduced later, because the deep-level acceptors can still be ionized once the quasi-Fermi-level is above the deep acceptor level.

(2) A metal-ferroelectric-metal (MFM) structure may be regarded as two back-to-back Schottky diodes [Fig. 3(a)] or a single diode plus an Ohmic contact [Fig. 3(b)]. The ferroelectric layer is thick enough to avoid the overlapping of two SCRs in the back-to-back diode model (or larger than the SCR width in the single-diode model). The neutral regions outside SCRs are assumed to have negligible resistances.

(3) The polarization is treated as a charge sheet located in the ferroelectric layer, which is separated from the metal-ferroelectric interface by a so-called dead layer. This dead layer may have a large number of deep traps besides the shallow- and deep-level acceptors. These traps can be assumed to be uniformly distributed in the dead layer with a density of \( N_\gamma \). They are able to capture both electrons and holes, according to previous theories [31] and our experimental observations. It may be conveniently assumed that the empty traps are neutral but they become negatively (positively) charged if electrons (holes) are trapped [31]. The charge-trapping effect at the interface of an Ohmic contact can be safely neglected because the charge carriers are rather free to move from electrodes to the ferroelectric layer or vice versa. Thus, we consider only the charge-trapping effect in the Schottky contacts.

(4) Polarization switching as well as charge injection and trapping are assumed to occur instantly under the same switching field (i.e., coercive field \( E_c \)), and there will be no changes of polarization and trapped charges except at \( E_c \). To be more specific, upon the application of \( +E_c \) ("+") denotes the direction from top to bottom), negative (positive) polarization charges are attracted to the top (bottom) interface (i.e., \( P^\downarrow \)), and holes (electrons) are also trapped at the top (bottom) dead layer. Both the polarization and trapped charges remain unchanged unless the electric field changes to \(-E_c \). At \(-E_c \), the polarization will be reversed (i.e., \( P^\uparrow \)), and originally trapped holes (electrons) will be detrapped and subsequently those traps will be refilled with electrons (holes). This “ideal switching” assumption is made because it is very difficult to simulate the electric field-dependent behaviors of polarization switching and charge injection and trapping. In addition, the time-dependent characteristics of charge injection and trapping are not considered because they are quite elusive. In the equilibrium state, the total amount of charges induced by polarization and dielectric response is

\[
\sigma_{tot} = \varepsilon_0 \varepsilon_st E_c + P, \tag{1}
\]

where \( \varepsilon_0 \) and \( \varepsilon_st \) are the vacuum permittivity and static dielectric constant, respectively. If all of these charges are assumed to be injected from the electrodes to the ferroelectric layer, the amount of charges trapped at the dead layer may be

\[
Q_{\text{trapped}} = qN_{\text{trapped}}\delta = \min(\sigma_{tot}, qN_\gamma \delta), \tag{2}
\]

where \( q \) is the electron charge, \( N_{\text{trapped}} \) is the number of trapped charge carriers, and \( \delta \) is the dead-layer thickness.

(5) The measured I-V characteristics are assumed to be quasistatic. The transient currents at \( \pm E_c \) arising from the polarization switching and charge injection are not taken
into account. The $I$-$V$ characteristics may be conveniently
described by the thermionic emission model [12]. However,
in a realistic MFM structure, the mean free paths of the
injected charge carriers are often smaller than the film
thickness. The conduction mechanism is therefore no
longer a pure thermionic emission. The overall conduction
process consists of an interface-controlled injection, fol-
lowed by a low-mobility drift through the film volume.
This may be adequately described by the Schottky-Simmon
model [32]. The difference between the Schottky-Simmons
equation and the thermionic emission equation lies in the
preexponential term [32]. In the Schottky-Simmons equa-
tion, the preexponential term depends on the electric field $E$
and carrier mobility $\mu$ [see Eq. (14) in Ref. [32]]. However,
it is revealed that the dependence of the preexponential
term on $E$ is rather weak [32]. Therefore, the Schottky-
Simmons equation is similar in form to the thermionic
emission equation. The thermionic emission equation may
be applicable to simulate the $I$-$V$ characteristics, but one
has to bear in mind that the Richardson constant $A^*$ being
used is a factor related to the drift-diffusion process.
Nevertheless, the values of $A^*$ will not affect the most
concerned resistive switching properties, e.g., electroresis-
tance (ER) ratios.

We first introduce the concept of apparent built-in
potential ($V_{\text{bi}}^\text{app}$) in the present model [12]. Because of
the presence of polarization and trapped charges, the built-in
potential as employed in the conventional Schottky barrier
($V_{\text{bi}}$) should be replaced with the apparent built-in potential
$V_{\text{bi}}'$ [Figs. 3(c)–3(e)]. By further using the Gauss’s law and
Poisson’s equation, $V_{\text{bi}}'$ can be derived from $V_{\text{bi}}$ as

$$V_{\text{bi}}' = V_{\text{bi}} \mp \frac{P}{\varepsilon_0 \varepsilon_{\text{st}}} \delta \pm \frac{q N_{\text{trapped}}}{2 \varepsilon_0 \varepsilon_{\text{st}}} \delta^2. \quad (3)$$

In Eq. (3), the lower signs apply to the case of the
negatively poled Schottky barrier, where the $P^\uparrow$ state is
established and electrons are injected from the electrode and
subsequently trapped in the dead layer [Fig. 3(d)]. In
contrast, the upper signs in Eq. (3) apply to the reverse case,
i.e., the positively poled Schottky barrier [Fig. 3(e)]. The
$V_{\text{bi}}'$ in Eq. (3) is linked with the Schottky barrier height at
zero field ($\Phi_B^0$) by

$$V_{\text{bi}}' = \Phi_B^0 - \frac{k T}{q} \ln \left[ \frac{N_V}{p(T)} \right]. \quad (4)$$

where $k$ is the Boltzmann’s constant, $T$ is the temperature,
$N_V$ is the effective density of states for holes in the valence
band, and $p(T)$ is the hole concentration at the temperature $T$. $N_V$ is determined by the hole effective mass ($m_h^*_{\text{eff}}$)
and temperature $T$ as

$$N_V = 2 \left[ \frac{2 \pi m_h^*_{\text{eff}} k T}{\hbar^2} \right]. \quad (5)$$

where $h$ is the Planck constant.

The SCR width $\omega$ can be derived from the apparent built-
in potential $V_{\text{bi}}'$ as

$$\omega = \sqrt{\frac{2 \varepsilon_0 \varepsilon_{\text{st}} (V + V_{\text{bi}}')}{q N_{\text{eff}}}}. \quad (6)$$

where $V$ is the applied bias. According to assumption (2),
the SCR width is narrower than half of the film thickness $d/2$
in the back-to-back diode model ($d$ in the single-diode
model). On the other hand, the SCR width could not be too
small; otherwise, conduction mechanisms other than therm-
ionic emission, such as tunneling, will be involved. We,
therefore, set the lower limit of $\omega$ as $\delta$. Hence, the boundary
conditions of $\omega$ are

$$\delta \leq \omega \leq \frac{d}{2} \quad \text{(or } d \text{ in the single-diode model)}. \quad (7)$$

The maximum field at the interface ($E_{\text{m}}$) is then given by

$$E_{\text{m}} = \frac{q N_{\text{eff}}}{\varepsilon_0 \varepsilon_{\text{st}}} \omega \pm \frac{P}{\varepsilon_0 \varepsilon_{\text{st}}} \mp \frac{q N_{\text{trapped}}}{\varepsilon_0 \varepsilon_{\text{st}} \delta}. \quad (8)$$

Again, the upper signs apply to the positively poled
Schottky barrier while the lower signs apply to the
negatively poled one.

The current density arising from thermionic emission of
a reverse-biased Schottky barrier is expressed as

$$J = A^* T^2 \exp \left[ -\frac{q}{k T} \left( \Phi_B^0 - \sqrt{\frac{q E_{\text{m}}}{4 \pi \varepsilon_0 \varepsilon_{\text{op}}}} \right) \right]. \quad (9)$$

where $A^*$ is the Richardson’s constant and $\varepsilon_{\text{op}}$ is the optical
dielectric constant. An apparent Schottky barrier height
($\Phi_{\text{app}}$) can be defined as [32]

$$\Phi_{\text{app}} = \Phi_B^0 - \sqrt{\frac{q E_{\text{m}}}{4 \pi \varepsilon_0 \varepsilon_{\text{op}}}}. \quad (10)$$

Hereinafter, the barrier height as mentioned refers to
$\Phi_{\text{app}}$. The current density of a forward-biased Schottky
barrier is given by

$$J = A^* T^2 \exp \left( -\frac{q \Phi_{\text{app}}}{k T} \right) \exp \left( \frac{q V}{n k T} \right). \quad (11)$$

where $n$ is the ideality factor and it reflects the barrier-
height variation induced by the applied voltage $V$ [33].
Therefore, $V$ may not need to be included in the expression
of $\Phi_{\text{app}}$ for a forward-biased Schottky barrier.
The effective charge density because some parameters of BFO are absent. For example, parameters for calculations [13]. BFO will be less focused due to the convenience of accessing all the relevant parameters for calculations. Therefore, using PZT rather than BFO as an example will not affect the general applicability of our model.

The simulated I-V characteristics of a PZT back-to-back diode model with different \( N_{\text{trapped}} \) are shown in Fig. 4. In the simulation, besides the basic parameters of PZT listed in Table 1, \( d = 200 \) nm, \( \delta = 3 \) nm, \( A^* = 520 \) A cm\(^{-2}\), and \( p \) \((T = 300 \text{ K}) = 5 \times 10^{18} \) cm\(^{-3}\) are used [13]. \( N_{\text{eff}} = 9.92 \times 10^{20} \) cm\(^{-3}\), the maximum value allowed by the constraint of Eq. (7), is also used. As seen from Fig. 4(a), conventional switchable diode behavior is observed if the influence of charge injection and trapping is not considered [4,5,15]. This can be understood by the fact that the top Schottky barrier will be higher when the MFM structure is in the \( P \uparrow \) state and thus the hole transport will be more difficult under positive bias. As the electric field reaches \(+2 \) V (corresponding to \(+E_C\)), the polarization switching occurs, leading to the \( P \downarrow \) state. The top Schottky barrier height will be reduced and thus the hole transport will be facilitated under the positive bias. Therefore, a transition from the high-resistance state (HRS) to the low-resistance state (LRS) is observed at \(+2 \) V in the positive branch of the I-V curve [Fig. 4(a)]. The I-V hysteresis in the negative branch can be analyzed in the same way. In the presence of \( N_{\text{trapped}} = 4.5 \times 10^{20} \) cm\(^{-3}\), however, the I-V hysteresis almost disappears [Fig. 4(b)]. When \( N_{\text{trapped}} \) further increases to \( 9 \times 10^{20} \) cm\(^{-3}\), the I-V hysteresis reappears, but its RS polarity becomes the opposite [LRS \( \rightarrow \) HRS at \( \pm 2 \) V; see Fig. 4(c)]. This type of RS polarity reversal is an indicator that the RS is caused by the charge injection and trapping at both interfaces [43]. These results, therefore, show that as \( N_{\text{trapped}} \) increases, the trapped charges will suppress and further dominate over the polarization charges in inducing RS. The reason is that the trapped charges modify the key parameters of a Schottky barrier, such as \( V_{\text{bi}} \) and \( E_m \), in a way opposite to polarization charges [see Eqs. (3) and (8)]. Note that in real ferroelectric perovskite thin films, the trap density \( N_T \) could reach \( \sim 10^{21} \) cm\(^{-3}\) [44]. In addition, the charge injection is able to supply a carrier density of \( \sim 10^{21} \) cm\(^{-3}\) according to Eq. (1). Therefore, the values of \( N_{\text{trapped}} \) used in our calculations may be reasonable.

Figure 5 shows the I-V characteristics of the PZT single-diode model, which are simulated using the same parameters adopted in the back-to-back diode model. Unlike the back-to-back diode model, there is only one Schottky barrier (the top one is assumed) limiting the conduction in the single-diode model. Therefore, the current rectifying direction remains unchanged, although the barrier height may vary. In addition, the imprint effect (i.e., the shift of \( E_C \)) caused by the asymmetric interface barriers is neglected. As shown in Fig. 5(a), at \( N_{\text{trapped}} = 0 \), the RS behavior with a “countereightwise” polarity is observed. To be more specific, \( P \uparrow (P \downarrow) \) results in a HRS (LRS) in both positive and negative voltage regimes, because \( P \uparrow (P \downarrow) \) induces a higher (lower) top Schottky barrier for the hole transport under both reverse and forward bias conditions. This observation is consistent with that reported in Ref. [45]. As \( N_{\text{trapped}} \) increases to \( 4.5 \times 10^{20} \) cm\(^{-3}\), however, the I-V hysteresis becomes almost negligible [Fig. 5(b)]. At \( N_{\text{trapped}} = 9 \times 10^{20} \) cm\(^{-3}\), the RS behavior with an “eighthwise” polarity appears [Fig. 5(c)]. This is a
typical feature of charge trapping at one of the interfaces in a MFM structure [46–48]. Therefore, the charge-trapping-induced RS gradually masks the polarization-induced RS as $N_{\text{trapped}}$ increases, which is similar to what has been observed in the back-to-back diode model.

The above results may help explain the poor reproducibility and stability of RS behavior observed in our plasma-treated sample which has a high density of interfacial traps. Because the amount and location (either or both interfaces) of trapped charges can vary in different devices and even in different switching cycles, the resultant $I$-$V$ curves may have a wide variety of shapes [Fig. 2(d)].

We then focus our attention on the ER ratio of ferroelectric diodes under the influence of charge injection and trapping. The ER ratio is defined as the ratio of $J(P_\uparrow; V_{\text{read}} = 1 \text{ V})$ versus $J(P_\downarrow; V_{\text{read}} = 1 \text{ V})$. The PZT back-to-back diode model is used as an example. Figure 6(a) reveals that the initial ER ratio higher than 1 can be continuously tuned to be even lower than 1 as $N_{\text{trapped}}$ increases. This means that the HRS and LRS initially defined by the polarization state can be reversed when the charge injection and trapping occur. Next, one may be interested in how to engineer the effective charge density ($N_{\text{eff}}$) and the deep trap density ($N_T$) to achieve the best performance of polarization-reversal-induced RS. Figure 6(b) shows the ER ratio as a function of $N_{\text{eff}}$ at different $N_T$. Here, all traps are assumed to be filled, i.e., $N_{\text{trapped}} = N_T$. At $N_T = 0$, the ER ratio increases with decreasing $N_{\text{eff}}$. This may be interpreted by the fact that the polarization-induced variation in the SCR width will be larger when $N_{\text{eff}}$ becomes smaller [see Eq. (6)]. The resultant variation in the apparent barrier height ($\Phi_{\text{app}}$) will also be larger. However, when $N_T$ is large, e.g., $1.35 \times 10^{24} \text{ cm}^{-3}$, smaller $N_{\text{eff}}$ will lead to a more significant ER ratio reduction caused by charge injection and trapping. At a moderate $N_T$, e.g., $7.2 \times 10^{20} \text{ cm}^{-3}$, there is

<table>
<thead>
<tr>
<th>Material</th>
<th>$P$ (μC/cm$^2$)</th>
<th>$E_c$ (kV/cm)</th>
<th>$\varepsilon_{\text{st}}$</th>
<th>$\varepsilon_{\text{op}}$</th>
<th>$\Phi_0^0$ (eV)/electrode</th>
</tr>
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<tr>
<td>PZT$^a$</td>
<td>40</td>
<td>400</td>
<td>180</td>
<td>6.5</td>
<td>1.3/SrRuO$_3$</td>
</tr>
<tr>
<td>PTO</td>
<td>80$^b$</td>
<td>280$^b$</td>
<td>130$^b$</td>
<td>6.25$^c$</td>
<td>1.5/Pt</td>
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<tr>
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<td>~30$^d$</td>
<td>150$^d$</td>
<td>500$^d$</td>
<td>6.1$^c$</td>
<td>~1.5/Au and LSMO</td>
</tr>
<tr>
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<td>40$^f$</td>
<td>400$^g$</td>
<td>5.3$^c$</td>
<td>1.2/Pt</td>
</tr>
<tr>
<td>BFO</td>
<td>~60$^h$</td>
<td>200$^h$</td>
<td>100$^i$</td>
<td>6.25$^j$</td>
<td>~0.9/Pt and SrRuO$_3$</td>
</tr>
</tbody>
</table>

$^a$See Ref. [13]. $^b$See Ref. [34]. $^c$See Ref. [35]. $^d$See Ref. [36]. $^e$See Ref. [37]. $^f$See Ref. [9]. $^g$See Ref. [38]. $^h$See Ref. [39]. $^i$See Ref. [40]. $^j$See Ref. [41]. $^k$See Ref. [42].

TABLE I. Basic parameters of different ferroelectric materials used for calculations.
not much change in the ER ratio as $N_{\text{eff}}$ varies. Therefore, to achieve a high ER ratio of polarization-reversal-induced RS, the deep traps need to be minimized to the greatest extent first, and then $N_{\text{eff}}$ is also reduced under the constraint of Eq. (7). Figure 6(c) shows that the critical $N_T$ at ER ratio = 1 increases as $N_{\text{eff}}$ decreases. This implies that decreasing $N_{\text{eff}}$ can tolerate more deep traps to be present without changing the HRS and LRS defined by the polarization state.

It is also of great interest to study how the properties of the dead layer influence the RS behavior. The dead-layer thicknesses ($\delta$) often vary in different metal-ferroelectric interfaces, e.g., Pt/BFO, and this has been proposed to be one of the major origins of different RS behaviors observed in Pt/BFO/SrRuO$_3$ heterostructures [18]. As shown in Fig. 7(a), the polarization-reversal-induced RS behavior becomes more significant as the dead-layer thickness $\delta$ decreases. For all $\delta$ being investigated, the ER ratios modified by the full-charge injection and trapping ($qN_{\text{trapped}}\delta = \sigma_{\text{tot}}$) are all below 1 and they decrease as $\delta$ increases. This suggests that the charge-trapping-induced RS could be suppressed by decreasing $\delta$, which was experimentally demonstrated in Pt/Nb:SrTiO$_3$ heterostructures [49,50]. Therefore, keeping $\delta$ as small as possible is beneficial not only for achieving large ER ratios of polarization-reversal-induced RS, but also for suppressing the interference from charge injection and trapping.

Because the static dielectric constant of the dead layer ($\varepsilon_{\text{st, d}}$) is often lower than that of the bulk region ($\varepsilon_{\text{bi}}$) [51], the dependence of ER ratio on $\varepsilon_{\text{st, d}}$ needs to be investigated. In this case, Eqs. (3) and (8) need to be modified as

$$\frac{qN_{\text{eff}}}{2\varepsilon_{\text{0}}\varepsilon_{\text{st, d}}}\omega_b^2 + \frac{qN_{\text{eff}}^2}{2\varepsilon_{\text{0}}\varepsilon_{\text{st, d}}}\omega_b\delta = V'_{\text{bi}} = V_{\text{bi}}$$

$$+ \frac{P}{\varepsilon_{\text{0}}\varepsilon_{\text{st, d}}}\delta \pm \frac{qN_{\text{trapped}}}{2\varepsilon_{\text{0}}\varepsilon_{\text{st, d}}},$$  \hspace{1cm} (12)

and

$$E_m = \frac{qN_{\text{eff}}}{\varepsilon_{\text{0}}\varepsilon_{\text{st, d}}}\omega_b + \frac{qN_{\text{eff}}}{\varepsilon_{\text{0}}\varepsilon_{\text{st, d}}}\delta \pm \frac{P}{\varepsilon_{\text{0}}\varepsilon_{\text{st, d}}} + \frac{qN_{\text{trapped}}}{\varepsilon_{\text{0}}\varepsilon_{\text{st, d}}}\delta,$$  \hspace{1cm} (13)

respectively. Here, $\omega_b$ is the width of SCR in the bulk region. As shown in Fig. 7(b), smaller $\varepsilon_{\text{st, d}}$ leads to a larger ER ratio for polarization-reversal-induced RS. However, smaller $\varepsilon_{\text{st, d}}$ also makes the interference from charge injection and trapping more severe. The reduction of $\varepsilon_{\text{st, d}}$ leading to more significant charge-trapping-induced RS has been observed in metal-Nb:SrTiO$_3$ junctions [52]. Therefore, an appropriate $\varepsilon_{\text{st, d}}$ is needed to optimize the RS behavior that is simultaneously influenced by polarization and trapped charges.

We finally investigate the material dependence of polarization reversal and charge-trapping comodulated RS behavior. As can be seen from Fig. 7(c), PTO and BFO, which have the largest polarizations (see Table I), show the highest ER ratios when $N_{\text{trapped}} = 0$. However, their ER ratios are most significantly reduced under the condition of full-charge injection and trapping. This is because a large polarization gives a large $\sigma_{\text{tot}}$ according to Eq. (1), thus leading to a large $N_{\text{trapped}}$ if the full-charge injection and trapping occur ($qN_{\text{trapped}}\delta = \sigma_{\text{tot}}$).

Based on the above results, some effective approaches are suggested to suppress the effect of charge injection and trapping and thus realize high-performance polarization-reversal-induced RS:

(i) Using materials with large polarization to achieve large modulation of Schottky barriers by polarization

(ii) Minimizing the deep trap density ($N_T$), which is a straightforward way to reduce the amount of trapped charges

(iii) Keeping the effective charge density ($N_{\text{eff}}$) small, which can amplify the variation of SCR width
induced by polarization reversal and also can tolerate more deep traps to be present without changing the HRS and LRS defined by the polarization state

(iv) Reducing the dead-layer thickness (δ)

(v) Attaining an appropriate dielectric constant of the dead layer (ε_{st,d}).

The last two approaches emphasize the importance of the properties of the dead layer, because they are crucial in determining the magnitudes of Schottky barrier modulations induced by both polarization reversal and charge injection and trapping [see Eqs. (3), (6), (8), (12) and (13)].

V. CONCLUSIONS

In summary, the effects of charge injection and trapping on the switchable diode-type RS behavior in ferroelectric diodes have been investigated both experimentally and theoretically. By using the SKPM technique, we have shown that the charge injection and trapping occur simultaneously with polarizations switching in the electrical poling process. In addition, the sample with high density of interfacial traps exhibits poor reproducibility and stability of hysteretic I-V characteristics, indicating that the RS behavior is significantly influenced by charge injection and trapping. A theoretical model has been proposed to describe the coeffect of polarization reversal and charge injection and trapping on ferroelectric diodes. It has been demonstrated that the trapped charges could modify the Schottky barrier in a way opposite to the polarization. As a result, various types of hysteretic I-V characteristics could be observed. In addition, the ER ratio, RS polarity, and the HRS and LRS initially defined by the polarization state could all be modified by the trapped charges. Our model, therefore, successfully extends the model of Pintilie et al. to explain the commonly observed RS phenomena in realistic ferroelectric diodes. Finally, several approaches that are useful to suppress the effect of charge injection and trapping and to further realize high-performance polarization-reversal-induced RS, have been proposed. The present work therefore sheds light on the microscopic mechanisms of polarization reversal and charge-trapping comodulated RS behavior in ferroelectric diodes, and also provides guidance for developing reliable ferroelectric RS memories.

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