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Ferroelectric Schottky diode behavior from a $SrRuO_3$-$Pb(Zr_{0.2}Ti_{0.8})O_3$-Ta structure

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A single ferroelectric Schottky diode was obtained on a $SrRuO_3$-$Pb(Zr_{0.2}Ti_{0.8})O_3$-Ta (SRO-PZT20/80-Ta) structure in which the SRO-PZT20/80 interface is the rectifying contact and the PZT20/80-Ta interface behaves as a quasiohmic contact. Both the capacitance-voltage (*C*-*V*) and the current-voltage (*I*-*V*) characteristics show the memory effect due to the ferroelectric polarization. However, retention studies had revealed that only the "down" orientation of ferroelectric polarization is stable in time (polarization oriented from top to bottom contact). The analysis of the experimental results suggests that the PZT20/80 is *n* type and that the stable orientation of polarization is related to the presence of a depletion region at the SRO-PZT20/80 Schottky interface.

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I. INTRODUCTION

Among functional materials the ferroelectric compounds with perovskite structure are subject of intensive study due to their wide range of properties (dielectric, ferroelectric, piezoelectric, pyroelectric, and nonlinear optical properties) which makes them very attractive for numerous applications such as nonvolatile memories, microwave devices, infrared detectors, piezoelectric transducers, microactuators and nanoactuators, displays, etc.[1–3] For many years these materials were used mainly in form of bulk ceramics or polycrystalline films making difficult their integration in microelectronics.[4,5] Attempts were made to use ferroelectric films as gate oxide on silicon (Si) in order to develop ferroelectric field-effect transistors for memory applications but the poor quality of the ferroelectric-Si interface prevented the large scale production of these devices.[6,7] The coexistence of semiconductor and ferroelectric properties in some perovskite compounds together with the recent advance of chemical-physical deposition techniques, such as pulsed laser deposition (PLD) or metal-organic chemical-vapor deposition, had offered the possibility to grow high-quality epitaxial ferroelectric films and opened the gate toward the manufacturing of "ferroelectronic" components.[8–11] These are electronic components, such as diodes or transistors, in which the active material is a semiconductor with ferroelectric properties. In this context, a first step would be the manufacturing of a true ferroelectric Schottky diode. In a paper from 1994 Bloom *et al.*[12] claimed that they have realized and characterized such a diode, consisting of a 200 nm $PbTiO_3$ epitaxial layer with an Au Schottky contact on one side and a $La_{0.5}Sr_{0.5}CoO_3$ ohmic contact on the other side. However, the current-voltage (*I*-*V*) characteristic based on which they have concluded that the structure is a ferroelectric Schottky diode does not show the expected rectifying behavior. Also, the presence of a surprisingly symmetric hysteresis loop does not support the existence of a Schottky diode which is known to be a highly asymmetric device. Much more recently, Choi *et al.*[13] reported on a switchable ferroelectric diode made of $BiFeO_3$ crystal with symmetric Au electrode. Although the shape of the *I*-*V* characteristic is very similar to a diode, the conclusion that the observed rectifyinglike behavior is a bulk effect raises serious question marks whether the structure can be considered a diode, in the true sense of the concept, or not. Both in the case of *p*-*n* junctions and metal-semiconductor Schottky diodes, the characteristic features are the presence of an interface and the presence of a depleted region near this interface. The unique phenomenon in a diode is that the width of the depletion region can be controlled through the applied voltage. This is visible both in the *I*-*V* and capacitance-voltage (*C*-*V*) characteristics, giving the rectifying behavior of the current flowing through the interface, and the voltage dependence of the capacitance. Therefore, the structure presented by Choi *et al.* is not a diode and the rectifyinglike *I*-*V* characteristic may be the effect of a nonhomogeneous distribution of traps correlated with different densities of interface states at the two $BiFeO_3$-Au interfaces. At best it can be considered a back-to-back connection of two Schottky $BiFeO_3$-Au diodes, with asymmetric *I*-*V* characteristics, which are significantly affected by the properties of the bulk if there are important amounts of structural defects affecting the mobility of the injected charge carriers.

In this paper, a ferroelectric Schottky diode is presented. The single ferroelectric Schottky diode was obtained using high-quality epitaxial PZT films grown on $SrRuO_3/SrTiO_3$ (SRO/STO) substrates. Both the *I*-*V* and *C*-*V* characteristics are specific for a diode, presenting also the characteristic hysteresis due to polarization switching.

II. EXPERIMENTS AND RESULTS

A. Film deposition and characterization methods

The $Pb(Zr_{0.2}Ti_{0.8})O_3$ (PZT20/80) layer was grown by PLD on single-crystal (001)-oriented STO substrates. First, a bottom SRO electrode was epitaxially grown by PLD, then PZT20/80 films with thickness in the 100–200 nm range were deposited.[11,14] The top tantalum (Ta) electrodes of 70×70 μm^2 were deposited by radio-frequency sputtering through a shadow mask. The Ta contact was preferred because, according to recent reports, has the potential to form ohmic contacts with tetragonal PZT.[15]

The electrical characterization comprises hysteresis, *I*-*V*, and *C*-*V* measurements at various temperatures between 200

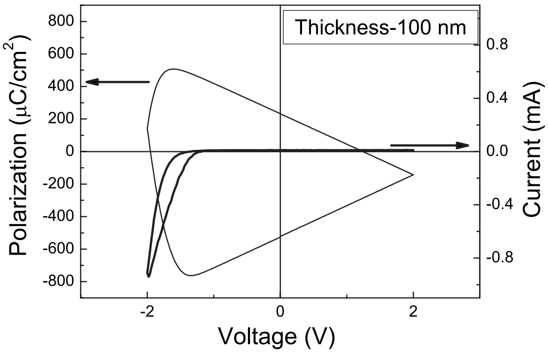

FIG. 1. Hysteresis loops for SRO-PZT-Ta structures with 100 nm thickness of the PZT layer.

and 450 K. The measurements were performed in a cryostat with liquid-He circulation by using a Keithley 6517 electrometer and a HP 4194A impedance/gain analyzer. Hysteresis loops were also recorded using a TF2000 ferroelectric analyzer (AixAcct). The short-circuit current of the photovoltaic effect was measured using the same Keithley electrometer, in conjunction with a grating monochromator operating in the 200–1100 nm wavelength range.

B. Electrical measurements

Typical hysteresis loops at room temperature (RT), for polarization and current, are presented in Fig. 1. The both loops were obtained by using a triangular voltage with a frequency of 1 kHz. The *I-V* loop recorded during hysteresis measurement does not show the expected current peaks associated with polarization reversal. It might be that the switching peaks are hidden by the large leakage current obtained for the negative bias polarity. However, an indication for the polarization switching is the hysteresis observed on the negative side of the *I-V* characteristic. The *I-V* characteristic presents a strong rectifying behavior very similar to a Schottky diode.

The *C-V* characteristic shown in Fig. 2 just confirms the Schottky-type behavior of the SRO-PZT-Ta structure. The *C-V* measurement was performed at 100 kHz. It appears that for positive polarity the diode is reverse biased, as the capacitance decreases with increasing the voltage. For negative polarity, the capacitance increases up to a certain voltage then, quite abruptly, becomes negative when the neutral volume reaches the electrode. This is equivalent to the situation when the depletion region is no longer present. Therefore, the structure is no longer a capacitor with capacitance value controlled by the applied voltage but transforms into a resistor. This explains both, the negative capacitance of the *C-V* characteristic and the high currents in the *I-V* hysteresis when negative voltages are applied (see Fig. 1). Furthermore, the capacitance values are affected by the presence of the polarization charges in the depleted region and are different for the two orientations of the ferroelectric polarization.

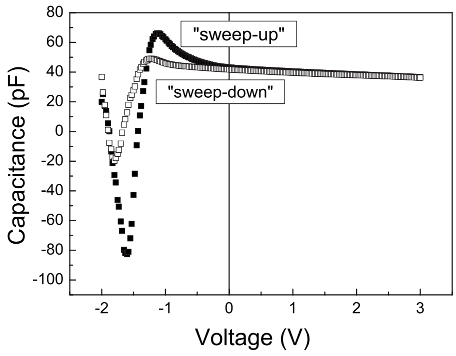

FIG. 2. Typical *C-V* characteristic for SRO-PZT-Ta structure.

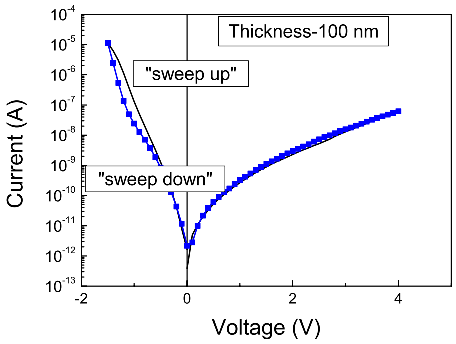

FIG. 3. (Color online) *I-V* characteristics for SRO-PZT-Ta structures with 100 nm thickness of the PZT layer.

The dc *I-V* characteristics are shown in Fig. 3. These were measured with a delay time of 10 s, which proved to be long enough for a stable reading of the current. Again, these are typical characteristics for a single Schottky diode. For the positive polarity the diode is reverse biased while for negative polarity is forward biased. The rectification factor at room temperature, taken as the ratio between current at −1 V forward bias and +1 V reverse bias is about 410.

The presence of a photovoltaic effect was evidenced in this SRO-PZT-Ta heterostructure with Schottky diodelike behavior. The spectral distribution of the short-circuit current was recorded after setting the polarization orientation “up” or “down” by the application of a suitable dc poling field. The results are shown in Fig. 4. It can be observed that the spectral distributions for the two directions of the polarization are identical, contrary to the results reported in the case of a normal ferroelectric capacitor.[16,17] This behavior suggests

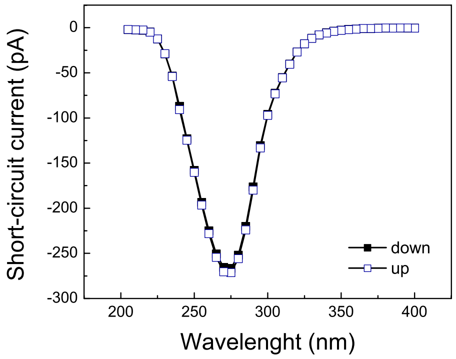

FIG. 4. (Color online) Spectral distributions for the short-circuit current of the photovoltaic effect in the case of the SRO-PZT ferroelectric Schottky diode.

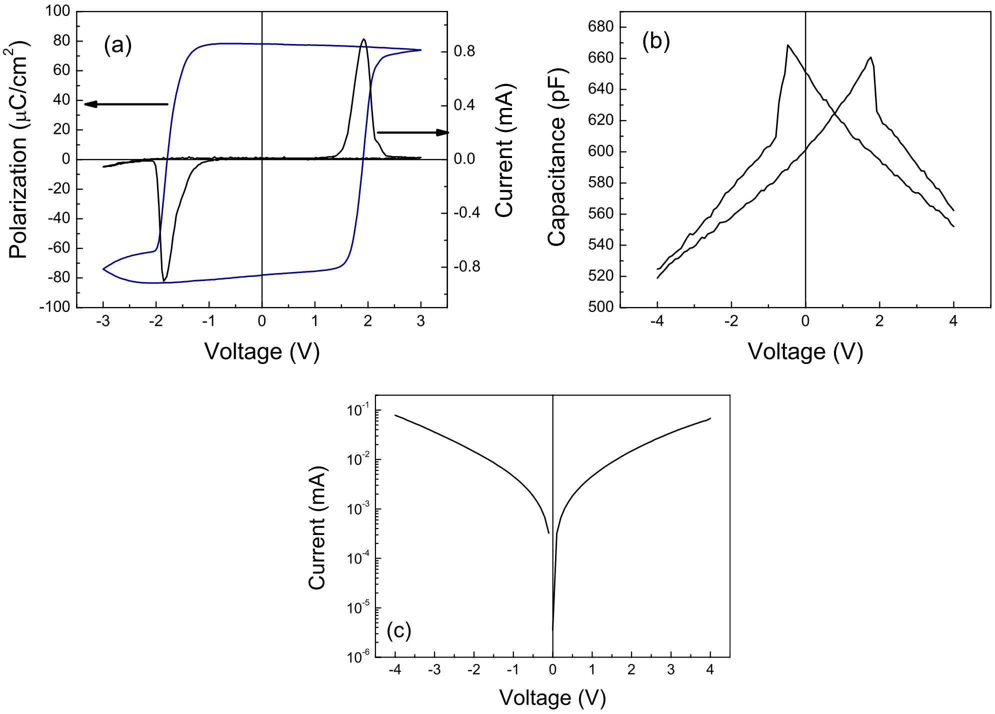

FIG. 5. (Color online) (a) Hysteresis; (b) *C-V* characteristic; and (c) *I-V* characteristic in the case of a symmetric epitaxial SRO-PZT-SRO structure with a thickness of the PZT film of about 200 nm.

that only one direction of the polarization is stable in the SRO-PZT-Ta structure. This aspect will be discussed in more detail later. It is worth to mention that the short-circuit photocurrent was recorded from the top Ta contact. According to Ref. 16, the sign of the photocurrent should be positive for down orientation. However, the sign is negative, which is possible if the current is, in fact, generated not at the top PZT-Ta interface but at the bottom PZT-SRO interface. Thus, the ferroelectric Schottky diode is located at the SRO-PZT interface. These results support the hypothesis that the origin of the photovoltaic effect in ferroelectric thin films is related to the presence of Schottky contacts and not to the bulk photovoltaic effect observed in ferroelectric ceramics and crystals.[16]

According to the results presented above one can conclude that the SRO-PZT-Ta structure behaves like a single Schottky diode. Although there are hints that the Schottky diode behavior is related to the SRO-PZT interface, this fact is not straightforward. Therefore we have performed a comparison with a symmetric SRO-PZT-SRO structure grown in the same conditions and of the same structural quality. The results of the electrical measurements (hysteresis, *C-V*, and *I-V* characteristics) are presented in Fig. 5. As can be observed in Fig. 5(a), the polarization and current hysteresis loops are symmetric, and the *C-V* characteristic shown in Fig. 5(b) has the usual butterfly shape, specific for ferroelectric capacitors. The dc *I-V* characteristic is also symmetric [see Fig. 5(c)].

Comparing the results of the symmetric SRO-PZT-SRO structure with those of the asymmetric SRO-PZT-Ta structure, we can clearly conclude that the asymmetry is due to the replacement of the top SRO electrode with Ta. Furthermore, in order to show that the PZT-Ta contact is ohmic, we have performed some *I-V* measurements in coplanar configuration between to neighboring top Ta contacts. The result is shown in Fig. 6. The obtained characteristic is linear with a confidence factor higher than 99%. The very small nonlinearities and hysteresis observed in the characteristic are related to the ferroelectric polarization. Without further details, we can conclude that the Ta-PZT contact behaves as ohmic and that the Schottky diodelike behavior is related to the bottom SRO-PZT interface. Considering the magnitude of the current in Fig. 6, one can conclude that the PZT layer is behaving more as a semiconductor than as a dielectric. Thus, in the particular case of epitaxial PZT layers, the ferroelectric polarization cannot be measured when the contacts are ohmic, due to the high leakage currents. The polarization is however, measurable when Schottky contacts are used. A

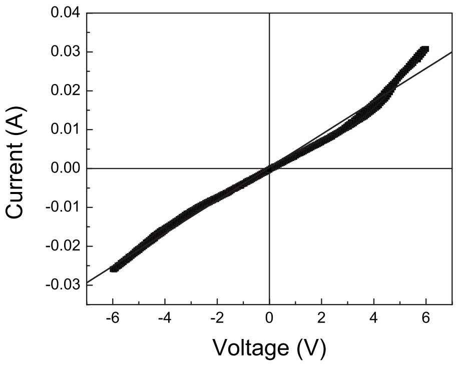

FIG. 6. The *I-V* characteristic obtained by performing *I-V* measurement in coplanar configuration between two neighboring top Ta contacts. The straight line is the linear fit with a confidence factor of 0.99397.

symmetric SRO-PZT-SRO structure behaves as a back-to-back connection of two Schottky diodes with a leaky ferroelectric in between. If the Schottky contacts are of very good quality we can obtain a nice, rectangular hysteresis, as shown in Fig. 5(a). If one of the Schottky contacts is replaced with an ohmic one, then the hysteresis is inflated by the leakage current and the polarization switching, although present in the PZT layer, is no longer visible (see Fig. 1) These results are a strong support for Vanderbilt's interface theorem stating that insulating interfaces are needed in order to measure the polarization.[18]

III. DISCUSSIONS

The results presented in the previous section lead us to conclude that the PZT-Ta contact is ohmic and that the observed Schottky diodelike behavior is related to the PZT-SRO interface. This finding is in agreement with previous reports regarding the presence of a potential barrier of about 0.8–0.9 eV at the SRO-PZT contact.[19,20]Assuming that there is a Schottky diode formed at the SRO-PZT interface, then the results of the *C*-*V* and *I*-*V* measurements suggests that the PZT is of *n* type. We remind that the voltage polarity was applied on the top contact. Thus, when the bias polarity on top contact is positive, then the bottom Schottky diode is reverse biased only if the PZT acts as *n*-type semiconductor.

The fact that the epitaxial PZT film behaves like *n*-type semiconductor is somehow surprising, considering that the defect chemistry support the idea of a *p*-type doping.[1,21,22] According to the literature there could be two possible explanations for the *n*-type conductivity. One was suggested by Scott[1] as being the high mobility of the electrons in the PZT compared with the holes mobility. The second could be related to the fact that the epitaxial films are grown by PLD method at high temperature and relatively low oxygen pressure (100–200 mTorr), very different growth conditions compared to polycrystalline films deposited by spin coating in air and crystallized by thermal annealing in air or oxygen atmosphere. There are reports claiming *n*-type conductivity in PZT films grown in low oxygen pressure,[23] due to a higher probability for the formation of oxygen vacancies acting as donors. When the amount of oxygen vacancies overcompensate the initial *p*-type doping, due to acceptor impurities coming from the target employed for PLD (Mn, Fe), the conduction will change to *n* type.

The magnitude of the potential barrier can be obtained from the temperature dependence of the dc *I*-*V* characteristics in the reverse bias range. There are two equations that can be used for calculating the reverse current density in the case of the thermionic emission. If the electron mean-free path is equal or higher than the film thickness then the Richardson-Schottky equation applies for the current density. If the mean-free path is smaller than the film thickness, then the Simmons equation applies as the drift diffusion controls the current density.[1,24–26] The electron mean-free path was estimated to be around 20 nm for our epitaxial PZT films, therefore the Simmons equation[26] was further used for the extraction of the potential barrier's height at the SRO-PZT interface. Following the same procedure as in Ref. 20 a value of about 0.8 eV was obtained for the potential barrier at zero bias, comparable to the value of 0.83 eV reported by Stolichnov *et al.*[19] for the SRO-PZT interface.

Regarding the *C*-*V* measurements presented in Fig. 2, the observed hysteresis can be explained based on the following equation:[9]

$$C=\sqrt{\frac{q\varepsilon_0\varepsilon_{st}N_{eff}}{2\left(V+V_{bi}\pm\dfrac{P}{\varepsilon_0\varepsilon_{st}}\delta\right)}}. \tag{1}$$

C is the capacitance per unit area (specific capacitance), q is the electron charge, ε_0 is the permittivity of vacuum, ε_{st} is the static dielectric constant, N_{eff} is the effective density of charge in the space charge region of the Schottky diode, V_{bi} is the built-in potential in the absence of polarization, P is the ferroelectric polarization, and δ is the distance between the polarization sheet of charge and the physical metal-ferroelectric interface. The $+/-$ sign correspond to the two orientations of polarization. It can be seen that, depending on the polarization orientation, the capacitance can have different values, especially at low voltages. As the voltage increases the polarization term becomes negligible and the capacitance values become similar, as shown in Fig. 2 for the positive part.

As known, the *C*-*V* characteristic for a Schottky diode can be used to extract some information about the free carrier concentration.[27] Equation (1) can be represented as

$$\frac{1}{C^2}=\frac{2}{q\varepsilon_0\varepsilon_{st}n(T)}\left[V-\left(V_{bi}\pm\frac{P}{\varepsilon_0\varepsilon_{st}}\delta\right)\right]. \tag{2}$$

The free carrier concentration $n(T)$ at temperature T can be extracted from the slope of $1/C^2$-V representation if the static dielectric constant at the same temperature is known. The $1/C^2$-V results for three temperatures (200, 300, and 450 K) are given in Fig. 7.

A first observation is that the sweep up and sweep down are not identical as should be for a nonferroelectric Schottky diode. We can presume that this is the effect of the ferroelectric polarization, which change orientation during the *C*-*V* measurement. The numbers on the graphs are the slopes and they can be used to estimate the product $\varepsilon_{st}n(T)$. We prefer to estimate this product as we do not have reliable information regarding the temperature variation in the true static dielectric constant of the epitaxial PZT film. The temperature dependence of the $\varepsilon_{st}n(T)$ product is presented in Fig. 8 and the values for the three temperatures mentioned in relation with Fig. 7 are shown in Table I.

Some comments can be made, concerning the results shown in Fig. 7 and Table I: (1) when the positive voltage on top Ta contact is large the Schottky diode is reverse biased and the depletion region extends far from the SRO-PZT interface. In this case we can consider the numbers for the sweep up (small slope) and sweep down as proportional with the free carrier concentration in what it is usually named "the neutral volume" of the Schottky diode.[28] It can be seen that this concentration does not vary too much with the temperature. Considering for the static dielectric constant a value around 100 between 200 and 450 K, it results that the free

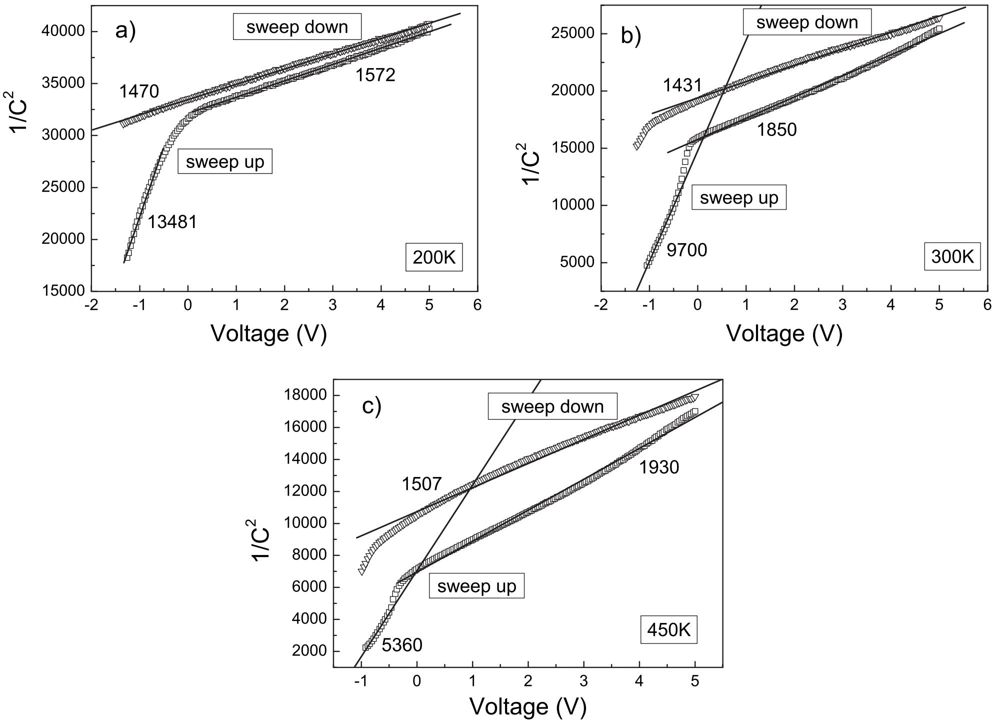

FIG. 7. The $1/C^2$-V representation for three different temperatures: (a) 200 K; (b) 300 K; and (c) 450 K. The $\varepsilon_{st}n(T)$ product was calculated from the slopes of these representations.

carrier concentration in the bulk of the PZT film is around 10^{18} cm^{-3}. (2) An increased "hysteresis" between the sweep up and sweep down can be observed in the voltage range where the Schottky diode is reverse biased. This hysteresis can be attributed to the presence of some deep traps. The defect centers are inactive at low temperatures, when the hysteresis is negligible and the $\varepsilon_{st}n(T)$ product is about the same for the sweep up and sweep down. It means that the trapped carriers are frozen and they cannot affect the density of the free carriers $n(T)$. The deep traps become active at higher temperatures, when they start to release the trapped carriers in the conduction band of PZT. This will lead to a larger density of free carriers for sweep down. This can be explained by the sequence of the C-V measurements starting always with sweep up from the maximum negative voltage. This means that the Schottky diode is forward biased at the beginning and electrons are injected in the depletion region, some of them being trapped. When the diode becomes reverse biased the trapped electrons starts to be released. However, this is possible only at high temperature and/or after long waiting time,[27] The sweep down starts then from the maximum positive voltage when the diode is reverse biased. In this case no electrons are injected into the depleted region and the density of the free carriers does not vary much with the temperature. The values given in Table I support these explanations. (3) The numbers obtained for sweep up (high slope) are significantly lower than the others. We remind that in this case the diode starts as forward biased and the polarization charge near the bottom SRO-PZT interface is negative. This means that the free electrons will be rejected from the interface, which will lead to a lower density of free carriers near the interface with SRO contact. Therefore, the concentration of the free carriers in the interface region is about one order of magnitude lower than in the bulk of the PZT film.

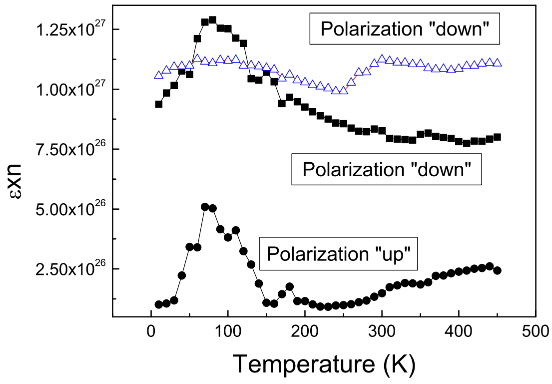

FIG. 8. (Color online) The temperature dependence of the $\varepsilon_{st}n(T)$ product.

TABLE I. The values of the $\varepsilon_{st}n(T)$ product extracted from the slope of the C-V characteristic and the built-in potential V_{bi} at different temperatures.

	$\varepsilon_{st}n(T)$ ($\times 10^{26}$ m^{-3})			V_{bi} (V)
Temperature (K)	Sweep up (high slope)	Sweep up (small slope)	Sweep down	Sweep up (high slope)
200	1.04	8.9	9.5	2.6
300	1.44	7.6	9.8	1.6
450	2.61	7.3	9.4	1.3

As mentioned above, the *C*-*V* measurement was always performed starting with the diode in forward bias and the ferroelectric polarization in up direction (oriented toward the top contact). The applied field preserves the polarization orientation and the forward biasing during sweep up until the applied voltage becomes comparable with the built-in potential (~ -1 V) of the Schottky SRO-PZT diode. At this voltage the diode will turn from forward to reverse biased.

When the diode becomes reverse biased a depletion region starts to form and a finite capacitance can be measured. The capacitance decreases as the voltage increases and the depletion region widens. The fact that the slope changes abruptly just around 0 V during the sweep up could be related to the polarization reversal, which leads to a change in the concentration of free carriers near the interface. Before the switching the polarization is up and the corresponding charge near the SRO-PZT interface is negative. This charge will reject the electrons from the interface region leading to a lower density of free carriers. After the switching, the polarization is down and the corresponding charge at the SRO-PZT interface becomes positive. It will attract electrons for compensation, increasing the free electron density in the interface region. This state will last for almost all the sweep down, until the polarization switches up again at negative voltages.

Returning to Fig. 8, it can be seen that the $\varepsilon_{st}n(T)$ product has a maximum around 100 K. This is visible for the sweep-up part of the *C*-*V* characteristics, both for the high-slope part (when the polarization is up and the electrons are repelled from the SRO-PZT interface) and for the small-slope part (when the polarization is down and the electrons are attracted to the SRO-PZT interface). For the sweep-down part of the *C*-*V* characteristic, the $\varepsilon_{st}n(T)$ product is practically independent of temperature. This behavior needs some comments: (1) assuming that the dielectric constant ε_{st} has a monotonically increase with temperature it appears that the concentration of the free carriers is decreasing as the temperature is increased, which would be uncommon for a semiconductor. On the other hand, the ferroelectric polarization decreases with temperature, requesting thus less charge for compensation, including a lower concentration of free carriers into the PZT film. Apparently, the polarization is governing the electronic properties of the PZT. In any case, the intimate link between polarization, leakage, and electronic properties cannot be neglected and needs further studies. (2) The maxim of the $\varepsilon_{st}n$ product is present only for sweep-up part of the *C*-*V* characteristic, without influence from polarization orientation. This fact suggests that the maximum is related to some trapping-detrapping phenomena at one of the interfaces, most probably at the SRO-PZT interface. When sweep up starts the SRO-PZT Schottky contact is forward biased, thus a high current is injected into the PZT film, filling all the traps. When the SRO-PZT interface turns to reverse bias, the band bending in the interface region changes. Therefore, some of the filled traps are brought above the Fermi level and have to be emptied of the trapped carriers. The emission from the traps is temperature dependent, thus a maximum may occur at some temperature, similar to the ones observed in the thermally stimulated currents method.[29] During the sweep-down part of the *C*-*V* characteristic, the SRO-PZT interface is already reverse biased, thus the filling pulse is missing and the emission from the traps is no longer visible.

As for the standard metal-semiconductor Schottky contacts, an apparent built-in potential $V'_{bi}=V_{bi}\pm\frac{P}{\varepsilon_0\varepsilon_{st}}\delta$ can be extracted from Eq. (2). The obtained values are also given in Table I. At RT the V'_{bi} is well above the usual values for semiconductors. As recently shown, the built-in potential is reduced when the polarization charge has the same sign as the fixed charge in the depletion region and is increased when the two charges are of opposite sign.[9] The last case is valid up to the voltage when the SRO-PZT contact goes from forward to reverse bias. In this case the polarization charge at the interface is still negative (polarization still up) while the charge in the depleted region of a *n*-type semiconductor is always positive. Therefore, the built-in potential is higher than normal.

For the sweep down, the polarization is down up to the negative coercive voltage. The polarization charge at the SRO-PZT interface will be positive, as it is the normal charge in the depletion region of a *n*-type semiconductor. This can lead to a significant decrease in the apparent-built-in potential and even to an apparent change in the sign. This is equivalent with an accumulation of electrons at the SRO-PZT interface, due to the positive polarization charge, although the contact is reverse biased. At some negative voltage the contact becomes forward biased, the depletion region disappears and the current increases dramatically, masking the polarization switching.

An estimation of the depletion region at zero voltage can be also made, as in the case of semiconductors.[27] In our case, a value of about 45 nm is obtained by using the intrinsic dielectric constant of PZT.[30]

Figure 2 shows that the ferroelectric Schottky diode has different values of capacitance for the two orientations of the ferroelectric polarization. For example, at a voltage of −1 V applied on the top contact the diode capacitance is about 45 pF for the down direction of polarization and about 61 pF for the up direction. Such a behavior would be extremely advantageous for memory applications because it would be much easier to have capacitors of different values for different orientations of polarization, for example, high capacitance (corresponding to bit 1) for one orientation and low capacitance (corresponding to bit 0) for the opposite one. The problem is to evaluate how stable is the information written in this way. Some experiments were performed in order to assess the retention characteristic for ferroelectric Schottky diode considered as the simplest memory cell. First, the polarization was set for down direction by applying a dc voltage of +2 V on the top Ta contact, then the poling voltage was removed and the capacitance at −1 V was measured at different time intervals up to 30 min. It was found that the measured value is stable around 45 pF. Second, the polarization was set up by applying −2 V on the top contact and the capacitance at −1 V was measured at the same time intervals as for opposite orientation. It was found that in approximately 5 min the capacitance value drop from about 60 pF to about 45 pF and then remains stable. This result suggests that the up orientation of polarization is not stable in time, the polarization preferring the down orientation. Even though it was set up by

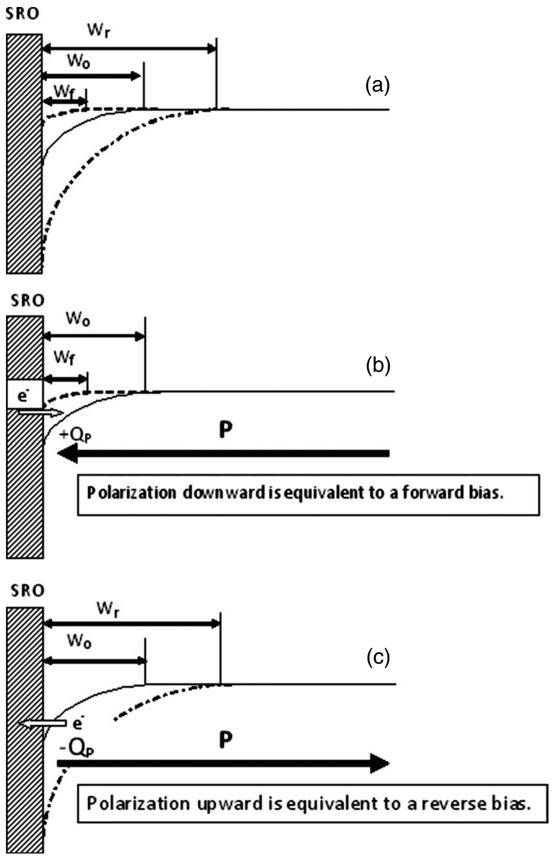

FIG. 9. Schematic band diagrams for: (a) Schottky diode with no ferroelectric polarization; (b) Schottky diode with down polarization; and (c) Schottky diode with up polarization.

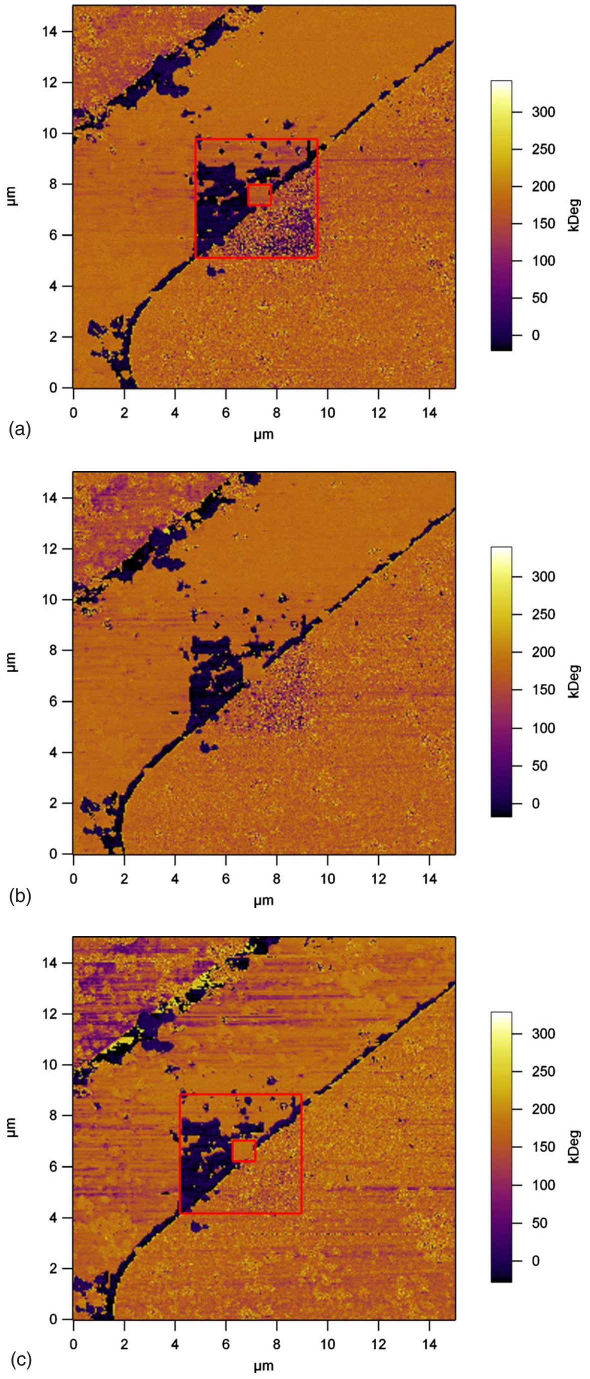

FIG. 10. (Color online) (a) Area poled up, including part of Ta contact and part of bare surface, just after poling with a dc voltage of 13 V applied on the bottom SRO electrode; (b) same area scanned after approximately 30 min; (c) same area scanned after 70 min from poling. In the (c) photo it can be observed that on the Ta electrode the polarization is no longer oriented up while on the bare surface is no significant change.

an external field, the polarization reversed its orientation after the field was removed. This behavior can be explained based on the schematic band diagrams presented in Fig. 9. The first diagram, Fig. 9(a), shows the situation of a normal Schottky diode, in the absence of ferroelectric polarization. W_0 stands for the width of the depleted region in the case of zero voltage applied on the diode. W_f and W_r are the width of the depleted region for forward bias and reverse bias, respectively. Figure 9(b) presents the situation of the Schottky diode when the ferroelectric polarization is present and it is down oriented. As mentioned above, this means that a positive polarization sheet of charge $+Q_\mathrm{P}$ is located near the interface, in the depleted region. Electrons are attracted to compensate the polarization charge, which is similar to the forward biasing. Therefore, although no external voltage is applied on the Schottky diode, the band bending will change upward due to the presence of the ferroelectric polarization oriented down. This orientation is stable because, for compensation, electrons are injected from the electrode, an abundant reservoir of electrons, into the PZT film. Figure 9(c) shows what it is happening with the band bending when the polarization is up. In this case the polarization charge is negative and will reject the electrons from the interface region leading to a larger depleted volume, similar to the reverse biasing. Therefore, the band bending will increase downward due to up oriented polarization. However, this orientation is not stable because the electrons needed for compensation are injected from the PZT film into the electrode. This means to inject more negative charge in a metal film already full of negative charge. This is not possible in the absence of an external applied voltage. Moreover, injection of electrons from PZT into the SRO film will make the bottom electrode more negatively charged than the top Ta contact. An electric field will buildup, of opposite orientation to the up polarization. In conclusion, the up orientation is not stable and the polarization will start to turn down as soon as the poling voltage is removed.

We have checked this interpretation for the polarization behavior by performing some piezoelectric force microscopy (PFM) measurements on the bare surface and on the Ta electrode. The PFM scanning has revealed that the as-grown sample is with polarization down. To monitor the time stability of the opposite orientation we have poled up an area including part of a Ta electrode as well as bare surface near the electrode. After removing the poling voltage we have scanned the same area from time to time. We have found that on the bare surface nothing changed after 70 min from poling while on the Ta electrode most of the up polarization switched down after only few minutes from poling (see Fig. 10). The performed PFM measurements are thus supporting the interpretation of an unstable up orientation for the polarization in the SRO-PZT-Ta diodelike structure. The fact that on the bare surface the up polarization is stable could be due to the fact that the PZT-air interface is insulating due to the presence of some potential barrier[18] while in the case of the PZT-Ta contact no potential barrier is present and the contact is ohmic.

IV. CONCLUSIONS

In summary, we have realized and characterized a ferroelectric Schottky diode. This allowed us to extract information about the properties of the SRO-PZT interface, as well as about the properties of the PZT film itself. It can be a first step toward further electronic devices made of ferroelectric materials and opens new perspectives regarding memory devices.

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