Ferroelectric Schottky Diode

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A Schottky contact consisting of a semiconducting ferroelectric material and a high work function metal shows a bistable conduction characteristic. An on/off ratio of about 2 orders of magnitude was obtained in a structure consisting of a 0.2 μm ferroelectric $PbTiO_3$ film, a Au Schottky contact, and a $La_{0.5}Sr_{0.5}CoO_3$ Ohmic bottom electrode. The observations are explained by a model in which the depletion width of the ferroelectric Schottky diode is determined by the polarization dependence of the internal electric field at the metal-ferroelectric interface.

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When a metal is brought into contact with a semiconductor, a barrier is formed at the metal-semiconductor interface [1]. The height of the barrier can be estimated from the difference of the work function of the metal and the electron affinity of the semiconductor, which is the famous Schottky-Mott rule [2,3]. Experimentally obtained barrier heights deviate from this rule and the basic mechanisms of the Schottky barrier formation are still a field of intensive research [4]. It is by now well accepted that interfacial states as defect- and metal-induced gap states play an important role in the Schottky barrier formation process. In the present work a fundamentally different mechanism causing a change in the Schottky barrier is demonstrated: The interface charge and thus the band diagram of a single ferroelectric Schottky diode is shown to be continuously and remanently variable by applying an external electric field. Experimentally, the polarization dependence of the Schottky barrier formed at a Au-$PbTiO_3$ interface gives rise to a bistable behavior of the current-voltage characteristics. The diode can be brought into a conducting state when exceeding a threshold voltage which is related to the coercive field of the ferroelectric layer. From our calculations we obtain that the change of the depletion width of a ferroelectric Schottky diode after a polarization reversal is governed by the altered field dependent permittivity of the ferroelectric. The transport properties of the ferroelectric Schottky diode are shown to be dominated by the polarization dependence of the depletion width.

To study the effect of polarization on metal-ferroelectric contacts experimentally, we have fabricated a metal-ferroelectric-metal (M-FE-M′) stack with two different metallic electrodes. Ferroelectric $PbTiO_3$ thin films and $La_{0.5}Sr_{0.5}CoO_3$ (LSC) bottom electrodes were epitaxially deposited on lattice-matched $LaAlO_3$ substrates using the pulsed laser deposition technique [5]. Because of the presence of lattice vacancies, $PbTiO_3$ is a p-type semiconductor. From studies on the conductance of lead-titanate related thin films it is known that the current is limited by barriers formed between the p-type ferroelectric and the electrodes [6], however, the intrinsic effect of ferroelectric polarization on the properties of a metal-ferroelectric contact has not been addressed. The LSC bottom electrodes are heavily p-type doped conductors and thus function as efficient hole-injection contacts. The top contacts consist of sputtered Au dots with diameters of 100, 200, and 500 μm. The Au forms a Schottky contact on the $PbTiO_3$ due to the difference in metal work function and semiconductor electron affinity [7], which amounts to about 1 eV. Measurements of polarization hysteresis loops are made with a Sawyer-Tower circuit. In Fig. 1(a) a typical hysteresis loop of a 0.2 μm $PbTiO_3$ thin film is shown for a maximum applied voltage of 20 V_{pp} at a frequency of 1 kHz. For a bias of 20 V_{pp}, the hysteresis loop is not saturated and the remanent polarization P_r of the 0.2 μm film only amounts to 10 $\mu C/cm^2$. For larger bias P_r increases to a maximum value of 52 $\mu C/cm^2$, but in dc current-voltage experiments, the samples break down for voltages exceeding 20 V_{pp}. Furthermore, we observe that the hysteresis loop is shifted towards positive bias and the polarization changes occur between -2 and -3 V and between $+4$ and $+6$ V. This asymmetry results from the use of electrodes with different work functions.

The bistable conduction properties of the ferroelectric Schottky diode are most easily demonstrated by applying voltage pulses with alternating polarity and a peak value less than the switching voltage. The response of the M-FE-M′ stack to these voltage pulses was monitored with an oscilloscope, which measures the voltage drop across a series resistance of 100 kΩ. Before the measurement was started, a dc poling voltage of $+10$ or -10 V was applied in order to set the polarization to $+P_r$ or $-P_r$, respectively. In Fig. 1(b) the response of the ferroelectric Schottky diode to 3 V_{pp} voltage pulses with a width of 10 ms is shown for the two orientations of the polarization, using a 200 μm Au electrode. We observe that the current through the ferroelectric increases by more than an order of magnitude upon changing the polarization from $+P_r$ to $-P_r$. The stability of the switching characteristics is dependent on the peak voltage and frequency of the applied pulses. For pulses with a peak to peak amplitude close to the switching voltage (6 V_{pp}) and a frequency of a few kHz, the fer-

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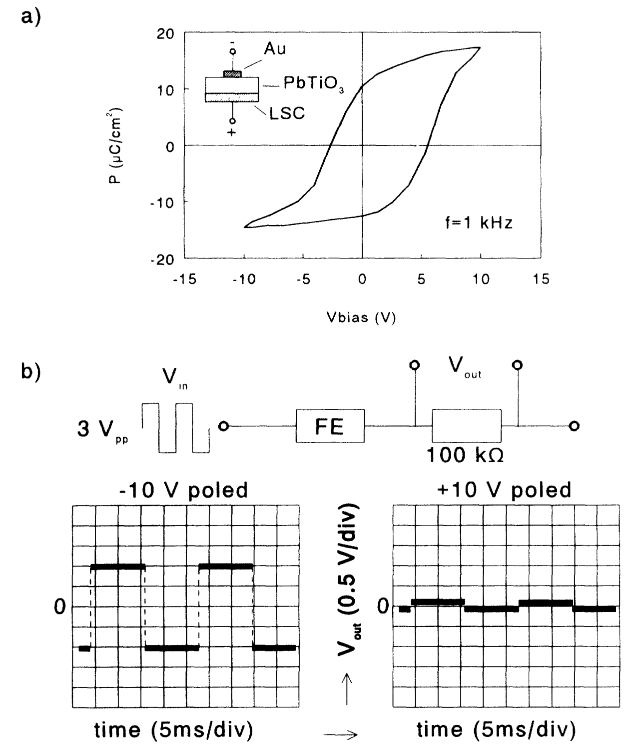

FIG. 1. Hysteresis loop (a) and pulsed current-voltage measurements (b) of a 0.2 μm ferroelectric $PbTiO_3$ film sandwiched between a $La_{0.5}Sr_{0.5}CoO_3$ (LSC) bottom electrode and a gold (Au) top electrode. For a bias voltage of 20 V_{pp}, a remanent polarization of 16 $\mu C/cm^2$ has been obtained, and the switching voltages of the polarization amount to -2–-3 V and 4–6 V. In (b) a schematic of the pulsed current-voltage measurements is shown. The LSC contact is positively biased with regard to the Au electrode. The input signal consists of alternating positive and negative pulses with a width of 10 ms and a total height V_{pp} of 3 V. The response of the structure demonstrates a bistable behavior of the conductivity with an on/off ratio of more than an order of magnitude for the two different polarization directions.

roelectric film switches from the "closed" state to the "open" state within a few seconds. For lower voltages (3 V_{pp}), however, the retention of a switched state at room temperature is stable over the measuring period amounting to several days. For a further investigation of the switching characteristics we performed dc current-voltage measurements. In Fig. 2(a) the current-voltage (I-V) characteristics are shown for a dc voltage loop ranging from $0 \rightarrow 4 \rightarrow -4 \rightarrow 0$ V on a 200 μm Au electrode. The voltage loop is labeled as *ABCDEF* in the inset of Fig. 2(a), where the current is plotted on a logarithmic scale. Before the measurement, a voltage of -10 V was applied in order to set the ferroelectric-metal contact in the open state, and a negative polarization charge is induced at the Au-$PbTiO_3$ interface. After applying a positive bias (*AB*), which gives rise to a decrease of the negative polarization charge at the interface, the conduction of the ferroelectric at zero bias (*C*) is reduced *by 2 orders of magnitude*. In this closed state the current-voltage characteristics (*BCD*) exhibit a rectifying behavior. At the switching voltage of -3 V (*D*), the current drastically increases by 2 orders of magnitude and the open state is reached. In this open state the current-voltage characteristic is symmetric for positive and negative bias (*EFAB*).

In order to determine the conduction mechanism in our films, the slope of the $\log(I)$ vs $\log(V)$ curve, which provides information about the conduction mechanism, is plotted in Fig. 2(b). For small positive bias (<1 V), we observe an Ohmic behavior [$d\log(I)/d\log(V) = 1$]. With decreasing positive bias (*BC*) the current is dominated by space-charge-limited (SCL) conduction, which is characterized by a quadratic current-voltage dependence [$d\log(I)/d\log(V) = 2$]. For negative bias (*CD*) the slope of the $\log(I)$-$\log(V)$ curve increases, pointing to Schottky barrier controlled conduction. Finally, after exceeding the coercive field (*EF*) the conduction is again characterized by Ohm's law. Thus we observe both bulk-limited (Ohmic, SCL) and electrode-limited (Schottky barrier con-

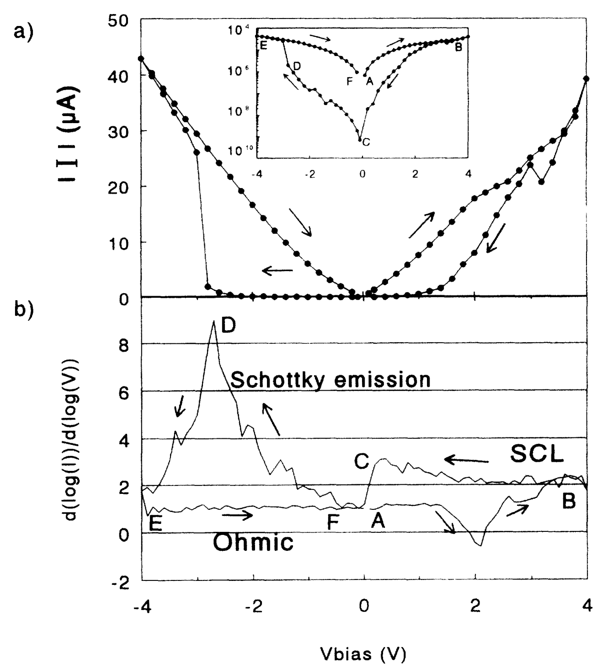

FIG. 2. dc current-voltage (I-V) characteristics (a) and slope of the $\log(I)$-$\log(V)$ curve (b), indicating the conduction mechanism through the 0.2 μm $PbTiO_3$ film for a voltage sweep from $0 \rightarrow 4 \rightarrow -4 \rightarrow 0$ V. The inset (a) shows the I-V characteristics on a logarithmic scale. Before the measurement was started the polarization was set to $-P_r$ by applying a dc bias of -10 V and the structure was switched into the open state, characterized by Ohmic conduction. With increasing positive bias (*AB*) the conductivity decreases and the structure exhibits an asymmetric Schottky-like I-V behavior (*BCD*). In the closed state (*BC*) the current for positive bias is dominated by space-charge-limited conduction, due to the increased depletion of the film. For negative bias (*CD*) the large reverse-biased barrier of the Au contact gives rise to Schottky barrier controlled conduction. After exceeding the switching voltage (*D*) the conduction increases with 2 orders of magnitude and the I-V characteristic of this open state (*EF*) is symmetric and again Ohmic.

trolled) conduction. We model our structure assuming ideal metal-ferroelectric interfaces as a back-to-back double Schottky system. This assumption, as exemplified by Norde [8], allows us to determine from the Schottky-like part of the I-V curve (BCD) effective barrier heights of $\phi_{\mathrm{LSC}} \approx 0.5$ eV and $\phi_{\mathrm{Au}} \approx 2.0$ eV. From the work function difference we expect for the gold electrode an electron barrier height of about 1 eV, which in combination with the band gap of 3 eV of the $PbTiO_3$ gives rise to a hole barrier height of 2 eV. Furthermore, the difference of 1.5 eV between the barrier heights of the LSC and Au electrode also accounts for the observed shift of the hysteresis loop in the positive direction. Thus we conclude that, with increasing negative polarization charge at the interface, the Au-ferroelectric contact changes from a rectifying Schottky-like contact into a more Ohmic-like contact.

In order to understand the observed switching behavior, we will now discuss the relevance of polarization charge for the properties of a metal-ferroelectric semiconductor Schottky contact. In a conventional metal-semiconductor contact, a space-charge region in the semiconductor builds up in order to line up the Fermi levels, and an exactly equal and opposite charge exists on the metal surface. The electric field in the space-charge region of the semiconductor decreases linearly from its maximum value at the interface toward zero at the end of the depletion region, the slope of this decrease being determined by the inverse of the dielectric constant of the semiconductor. This standard textbook result [9] is obtained by assuming that the dielectric constant of the semiconductor does not depend on the electric field. In ferroelectric materials, however, the ionic part of the dielectric constant drastically decreases with increasing electric field due to the increasing stiffness of the perovskite lattice [10]. Therefore, the positional dependence of the internal electric field in the space-charge region of a Schottky diode automatically implies that the dielectric constant of the ferroelectric semiconductor is also a function of the position. We will now describe the relevance of the ferroelectric polarization for the barrier width of the Schottky diode and assume the barrier height to be constant. We consider a p-type semiconductor with acceptor density N_A and assume (abrupt approximation) that $\rho_{\mathrm{free}} = qN_A$ inside the space-charge region of the diode and $\rho_{\mathrm{free}} = 0$ outside. Then the band bending of the ferroelectric Schottky diode is calculated using Gauss' law

$$\nabla \cdot \mathbf{D} = \rho_{\mathrm{free}}\,, \tag{1}$$

with D the dielectric displacement given by

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}\,. \tag{2}$$

Since in a ferroelectric semiconductor the polarization is not proportional to the electric field, the dielectric permittivity of the semiconductor is defined as

$$\epsilon_0 \epsilon_r \equiv \partial D / \partial E\,. \tag{3}$$

From Eqs. (1) and (3) it follows directly that the gradient of the electric field is given by

$$\nabla \cdot \mathbf{E} = \rho_{\mathrm{free}} / \epsilon_0 \epsilon_r\,, \tag{4}$$

with

$$\epsilon_r = 1 + \epsilon_0^{-1} \partial P / \partial E\,. \tag{5}$$

From Eqs. (2) and (4) we obtain for the polarization charge ρ_{pol} in the space-charge region

$$\rho_{\mathrm{pol}} = -\delta P / \delta x = -[(\epsilon_r - 1)/\epsilon_r] \rho_{\mathrm{free}}\,. \tag{6}$$

Thus the polarization charge ρ_{pol} is of opposite sign and nearly equal to the space charge, $\rho_{\mathrm{free}} = qN_A$, since the dielectric constant ϵ_r of a ferroelectric is much larger than 1. The resulting net charge $\rho_{\mathrm{free}} + \rho_{\mathrm{pol}}$, which was not taken into account in a theoretical analysis of the properties of a ferroelectric p-n homojunction [11], is responsible for the divergence of the electric field in the space-charge region. In Eq. (5) the field dependence of ϵ_r arises from the derivative of the polarization on the electric field. Finally, we model the hysteresis loop analytically using [12]

$$P(E) = \epsilon_0(\epsilon_{r\infty} - 1)E + P_r \frac{\tanh(E + E_c)}{\tanh(E_c)}\,, \tag{7}$$

with $\epsilon_{r\infty}$ equal to 10, a coercive field E_c of 100 kV/cm, and a remanent polarization P_r of 10 μC/cm^2.

Equations (1)–(7) are solved self-consistently and the experimental barrier heights of 0.5 (LSC) and 2 eV (Au), determined using the Norde method, are substituted together with an acceptor density [6] of 1×10^{18} cm^{-3}. The calculated energy-band diagram (a) and polarization (b) are shown in Fig. 3 as a function of the distance in a 0.2 μm ferroelectric film. At the LSC contact, where the built-in electric field is small, the polarization is parallel ($P < 0$) or antiparallel ($P > 0$) to the built-in (negative) electric field inside the space-charge region of the Au electrode, depending on the history of the applied external electric field. For the polarization parallel to the built-in field ($P < 0$), the magnitude of the polarization inside the space-charge region of the Au electrode is increased. For polarizations larger than P_r the derivative of the P-E hysteresis loop and thus the permittivity of the ferroelectric is relatively low, resulting in a small depletion width. In the antiparallel situation the magnitude of the polarization is reduced and even changes sign in the space-charge region. A small polarization gives rise to a large dielectric constant, especially at the coercive field ($P = 0$) and thus to a large depletion region. As a result, the barrier width of the Au electrode is strongly reduced when the polarization is parallel to the space-charge field at the Au-$PbTiO_3$ interface. Furthermore, in Fig. 3(b) it is shown that the polarization in the space-charge regions varies almost linearly with distance [viz. Eq. (6)]. At the LSC electrode the interface field changes sign after a polarization switch, but the electric fields and thus the band bending effects are small. The transport properties are therefore dominated mainly by the switching properties of the Au electrode. The calculated energy bands also demonstrate that, for the antiparallel situation, the ferroelectric film is strongly depleted. In this case, the calculated band bending shows close resemblance to the band bending of an insulator, where the electric field is constant through the film and is governed by the work

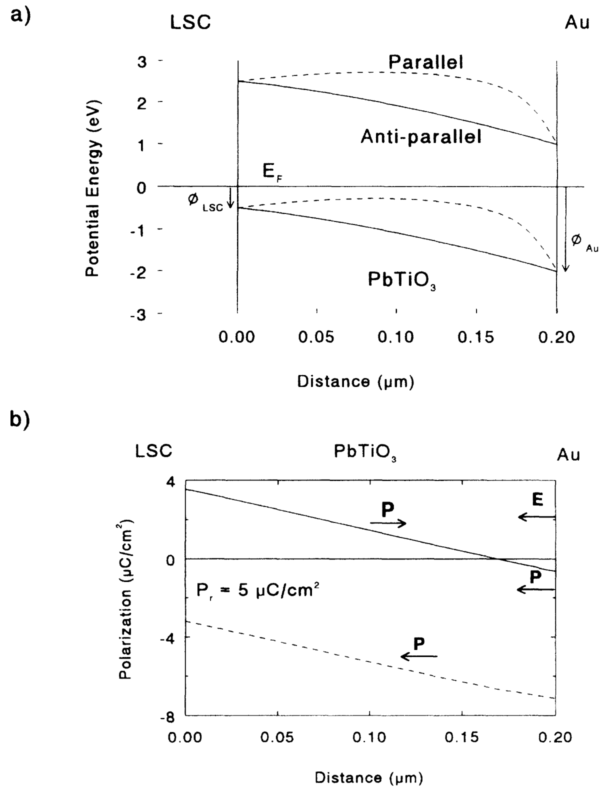

FIG. 3. Calculated band diagram (a) and polarization (b) as a function of position for a ferroelectric semiconductor with an acceptor density of 1×10^{18} cm^{-3} contacted with electrodes which form Schottky barriers of 0.5 eV (LSC) and 2.0 eV (Au). When the polarization is antiparallel to the built-in field of the Au-$PbTiO_3$ Schottky diode, the semiconductor is depleted. For the parallel case the barrier width of the Schottky barrier is strongly reduced and the energy distance between the maximum of the valence band and the Fermi level amounts to 0.3 eV.

function difference of the electrodes. For the polarization parallel to the space-charge field the valence band reaches a maximum, which is 0.3 eV below the Fermi level. The resulting difference in free-carrier density after a polarization switch will also have a large effect on the transport properties of the structure.

The observed switching (Fig. 1) and conduction behavior (Fig. 2) can now be interpreted by using the results of our band-structure calculations. After applying a poling voltage of -10 V, the polarization is parallel to the electric field of the Au electrode, which according to Fig. 3(a) means that the Au-electrode barrier is relatively thin. In this case an Ohmic behavior is observed which demonstrates that the current is not limited by the current transport across the Au electrode. With increasing (positive) voltage the negative polarization at the Au contact is reduced which, according to our physical model, gives rise to an increase of the barrier width. An increase of the Au Schottky barrier width also increases the depletion of the film and the Ohmic conduction changes into SCL conduction. With decreasing positive bias (BC) the polarization and thus also the Au diode changes only slightly, and due to the depletion the current is dominated by space-charge-limited conduction even at small voltages. For negative bias (CD), the carriers have to be injected over the increased barrier of the reverse biased Au contact, giving rise to Schottky barrier controlled conduction. Then the current increases exponentially with the square root of the applied voltage, and the slope of the $\log(I)$-$\log(V)$ curve increases. When the coercive field is reached (D) the magnitude of the (negative) polarization abruptly increases, giving rise to a decrease of the barrier width and to an increase of 2 orders of magnitude in the current. Finally, when returning to zero bias (EF) the conduction is again characterized by Ohm's law.

In conclusion, our experimental results show hysteretic diode characteristics of a ferroelectric Schottky diode. The conduction state of the diode is set by a bias exceeding a threshold voltage which is related to the coercive field of the ferroelectric. The state of the diode can be continuously monitored keeping the applied voltage in between the thresholds. Experimentally, a difference of 2 orders of magnitude in the current through a ferroelectric $PbTiO_3$ film between a $La_{0.5}Sr_{0.5}CoO_3$ bottom and Au top electrode is obtained at a bias of 1 V. Theoretically, we have demonstrated the effect of remanent polarization on the properties of a ferroelectric Schottky diode. The polarization dependence of the band bending of a Schottky diode arises from the local field-dependent permittivity. The Schottky barrier width is reduced whenever the polarization in the space-charge region of the diode is parallel to the internal electric field.

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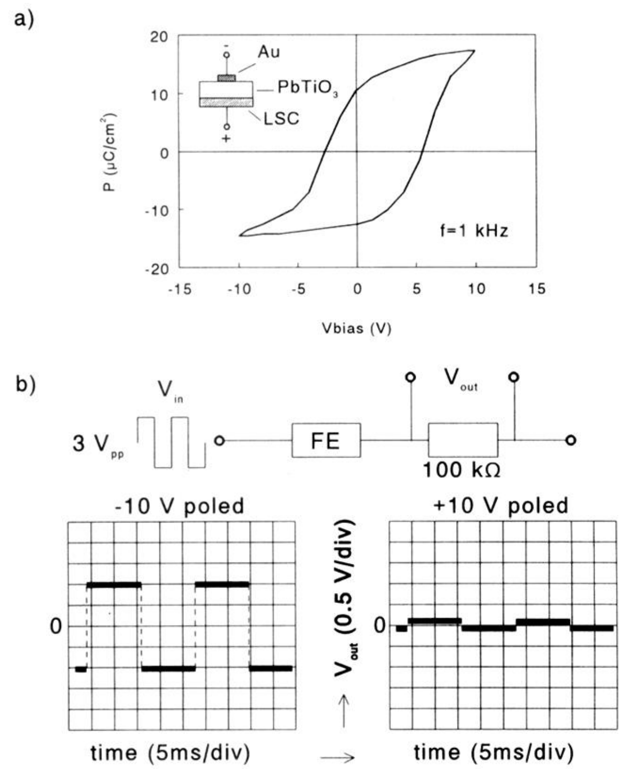

FIG. 1. Hysteresis loop (a) and pulsed current-voltage measurements (b) of a 0.2 μm ferroelectric $PbTiO_3$ film sandwiched between a $La_{0.5}Sr_{0.5}CoO_3$ (LSC) bottom electrode and a gold (Au) top electrode. For a bias voltage of 20 V_{pp}, a remanent polarization of 16 $\mu C/cm^2$ has been obtained, and the switching voltages of the polarization amount to $-2--3$ V and 4–6 V. In (b) a schematic of the pulsed current-voltage measurements is shown. The LSC contact is positively biased with regard to the Au electrode. The input signal consists of alternating positive and negative pulses with a width of 10 ms and a total height V_{pp} of 3 V. The response of the structure demonstrates a bistable behavior of the conductivity with an on/off ratio of more than an order of magnitude for the two different polarization directions.