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Orientation-dependent potential barriers in case of epitaxial Pt–$BiFeO_3$–$SrRuO_3$ capacitors

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The leakage current in epitaxial $BiFeO_3$ capacitors with bottom $SrRuO_3$ and top Pt electrodes, grown by pulsed laser deposition on $SrTiO_3$ (100), $SrTiO_3$ (110), and $SrTiO_3$ (111) substrates, is investigated by current-voltage (*I-V*) measurements in the 100–300 K temperature range. It is found that the leakage current is interface-limited and strongly dependent on the orientation of the substrate. The potential barriers at the electrode interfaces are estimated to about 0.6, 0.77, and 0.93 eV for the (100), (110), and (111) orientations, respectively.
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$BiFeO_3$ (BFO) is a unique multiferroic material which simultaneously possesses ferroelectric and magnetic properties at room temperature. Due to the coupling between polarization and magnetization, BFO is very interesting for memory devices with multiple states or in which the information can be magnetically written and electrically read or vice versa.[1–5] Due to this large application potential a significant effort has been paid in the past years to grow high quality films on various substrates and to investigate their electrical properties, especially polarization and leakage current in BFO capacitors. Among the preparation techniques, pulsed laser deposition (PLD) proved to be one of the most suitable methods to obtain thin films of epitaxial quality on single-crystal substrates such as $DyScO_3$ (DyScO) and $SrTiO_3$ (STO) showing large polarization values up to 100 $\mu C/cm^2$ for the BFO films with (111) orientation.[6,7] Good results can be obtained by radio-frequency (rf) sputtering also.[7,8]

One of the main problems in the case of BFO films is the high leakage current, though the conduction mechanism responsible for this behavior is not yet clarified. In a previous report Poole–Frenkel emission was assumed as the dominant conduction mechanism in BFO films with symmetric $SrRuO_3$ (SRO) electrodes deposited on DyScO (110) substrates.[9] A mixed, i.e., Poole–Frenkel emission and Fowler–Nordheim tunneling for negative and positive biases, respectively, was assumed in the case of BFO films deposited on $SrTiO_3$ (001) substrate with bottom SRO and top Pt contacts.[10] Also, space charge limited current (SCLC) was considered in the case of doped BFO films, doping being a useful option to reduce the leakage current.[11,12] Apparently, the conduction mechanism in BFO films is bulk limited, irrespective of electrodes, doping, or crystalline quality (polycrystalline or epitaxial). However, a recent study shows that the effect of the BFO-electrode interface on the dielectric properties of the film cannot be neglected.[13] It is thus expected that the same interface will affect the leakage current also.

In the present letter we report on the leakage current behavior in epitaxial BFO thin films grown by PLD on $SrTiO_3$ substrates with different orientations. The bottom electrode was in all cases SRO epitaxially grown on STO, and the top electrode was Pt. It is shown that the magnitude of the leakage current is dependent on the substrate orientation. The results are discussed assuming interface-controlled injection of charge into the BFO film, which leads to orientation-dependent potential barriers at the electrode interfaces.

BFO films were grown by PLD on STO substrates with (100), (110), and (111) orientations, respectively. Details about growth and structure can be found in previous papers.[11,14,15] Capacitance-voltage (*C-V*) and current-voltage (*I-V*) measurements were performed at various temperatures in the 100–300 K range. The applied voltage was stepwise swept from zero to the desired value in the case of *I-V* measurements and, in order to reach a steady state, a delay time of 3 s up to 10 s was used between the voltage setting and the current reading. The ferroelectric polarization was saturated before recording the *I-V* characteristic by applying a dc electric field higher than the coercive field and with the same polarity as the one used for current measurements. In this way the polarization orientation, as well as its value, are set and the contribution of the current due to polarization reversal is minimized. This contribution is negligible in the case of materials with rectangular hysteresis loops.

The voltage dependence of the dielectric constant, calculated from the capacitance measured at 100 kHz and 260 K, is shown in Fig. 1 for the three crystalline orientations. A significant asymmetry can be observed, suggesting important influence of the electrode interfaces on the measured capacitance. Quite the opposite, *I-V* characteristics shown in Fig. 2 are relatively symmetric and this may suggest that the leakage current is bulk limited and the electrode interfaces would

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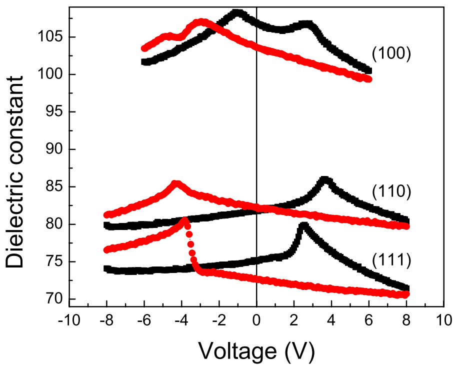

FIG. 1. (Color online) The voltage dependence of the dielectric constant for epitaxial BFO films deposited on STO substrates with different orientations.

have less influence. However, the requirement to explain both *C-V* and *I-V* characteristics within the frame of the same model requires considering both interface-controlled charge injection into the BFO film and volume-limited charge transport across the BFO film through bulk-related parameters such as carrier mobility.[16,17] The SRO–BFO–Pt structure can be modeled as a back-to-back connection of two Schottky diodes. Unfortunately, due to the unknown conduction type in BFO films it is difficult to establish which of the two interfaces (bottom SRO–BFO or top BFO–Pt) is reverse biased for a certain polarity. A recent study claims that BFO should be *p*-type due to the Bi loss,[18] whereas the oxygen vacancies introduce conduction electrons, which should lead to a *n*-type conductivity.[19] In any case, the relative symmetry of the experimental results suggests that both electrode interfaces, bottom SRO–BFO and top BFO–Pt, are affected in a similar way by the orientation of the BFO film.

The magnitude of the potential barrier can be estimated by applying the model for the leakage current in ferroelectric

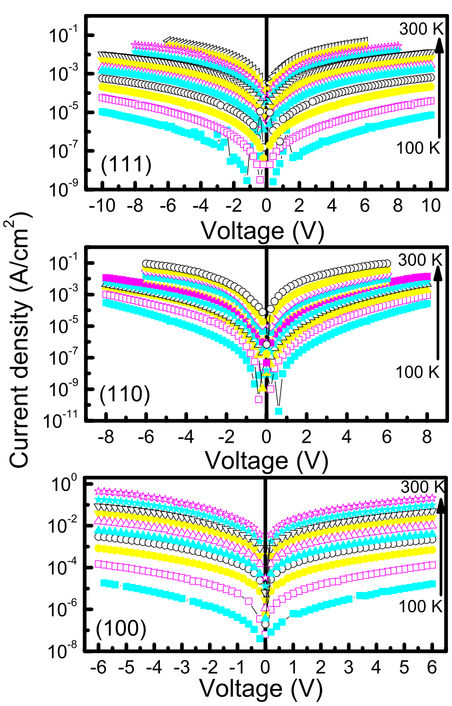

FIG. 2. (Color online) *I-V* characteristics for epitaxial BFO films deposited on STO substrates with different orientations. The characteristics were recorded in the 100–300 K temperature range. In all cases the bottom electrode was SRO and the top one was Pt.

TABLE I. The orientation dependence of spontaneous polarization P_S, static dielectric constant ε_{st}, apparent potential barrier at zero field $\Phi_{B,\text{app}}{}^0$, and true potential barrier at zero field $\Phi_B{}^0$, in case of BFO films deposited on STO substrates.

Orientation	P_S (μC/cm^2)	ε_{st}	$\Phi_{B,\text{app}}{}^0$ (eV)	$\Phi_B{}^0$ (eV)
(100)	73	102	0.16	0.62
(110)	102	83	0.17	0.77
(111)	115	73	0.26	0.92

capacitors.[17,20,21] The discussion will be presented for the positive part of the *I-V* characteristic, similar results are being obtained for the negative part. The current density is given by the following equation:[17]

$$J \sim \exp\left(-\frac{q}{kT}\left[\left(\Phi_B{}^0 - \sqrt{\frac{qP}{4\pi\varepsilon_0^2\varepsilon_{op}\varepsilon_{st}}}\right) - \sqrt{\frac{2q^2N_{\text{eff}}V}{8\pi\varepsilon_0\varepsilon_{op}P}}\right]\right), \tag{1}$$

where $\Phi_B{}^0$ is the potential barrier height at zero applied field, P is the polarization, V is the applied voltage, N_{eff} is the effective charge density in the space charge region near the electrode, T is the temperature, ε_{st} is the static dielectric constant, ε_{op} is the dynamic (high frequency) dielectric constant, ε_0 is the permittivity of the free space, q is the electron charge, and k is Boltzmann's constant. This equation is valid in both cases, i.e., pure thermionic (Schottky) or bulk-limited (Schottky–Simmons) injection, and it was deduced in the hypothesis that $\sqrt{2qN_{\text{eff}}V/\varepsilon_0\varepsilon_{st}} \ll P/\varepsilon_0\varepsilon_{st}$. This condition may be well fulfilled considering the measured values of polarization presented in Table I. The dielectric constant extracted from capacitance measurements for the voltage range where polarization is saturated are also presented in Table I.

According to Eq. (1) the apparent potential barrier is

$$\Phi_{\text{app}} = \left(\Phi_B{}^0 - \sqrt{\frac{qP}{4\pi\varepsilon_0^2\varepsilon_{op}\varepsilon_{st}}}\right) - \sqrt{\frac{2q^2N_{\text{eff}}V}{8\pi\varepsilon_0\varepsilon_{op}P}}. \tag{2}$$

Assuming the dominance of the Schottky thermionic emission, the apparent potential barrier given by Eq. (2) can be estimated from the slope of the representation of $\ln(J/T^2)$ as a function of $1000/T$. Similar results are obtained for the Schottky–Simmons case, although the temperature dependence is slightly different ($J-T^{3/2}$ instead of $J-T^2$). Further on, representing the obtained Φ_{app} values as a function of $V^{1/2}$ from the intercept one can extract the apparent potential barrier at zero bias $\Phi_{B,\text{app}}{}^0$. $\Phi_{B,\text{app}}{}^0$ depends on the true potential barrier $\Phi_B{}^0$ and the polarization and is given by

$$\Phi_{B,\text{app}}{}^0 = \Phi_B{}^0 - \sqrt{\frac{qP}{4\pi\varepsilon_0^2\varepsilon_{op}\varepsilon_{st}}}. \tag{3}$$

Knowing the polarization and the dielectric constants, one can estimate the true potential barrier at the SRO–BFO interface for films grown on different substrates.

The Φ_{app} versus $V^{1/2}$ representations for all three film orientations are shown in Fig. 3, and the $\Phi_{B,\text{app}}{}^0$ values are presented in Table I. Using Eq. (3) and the given values of polarization and static dielectric constants, and considering a value of 5.6 for the optical dielectric constant, results in a

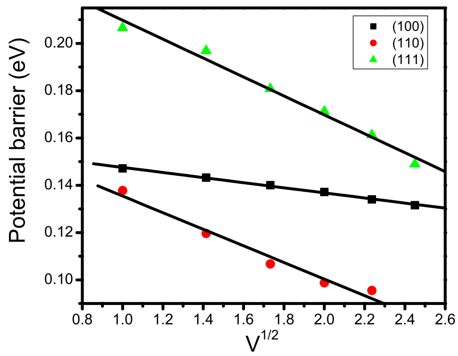

FIG. 3. (Color online) $V^{1/2}$ dependence of the apparent potential barrier given by Eq. (2) in the text, for BFO films deposited on STO substrates with different orientations.

potential barrier at zero bias $\Phi_B{}^0$ of about 0.6, 0.77, and 0.93 eV for the (100), (110), and (111) orientations, respectively (see Table I). It can be clearly observed that the height of the potential barrier at both interfaces is dependent on the substrate orientation and consequently on the orientation of the BFO film. This difference may well explain the low leakage current usually occurring in case of (111) orientation compared to the (100) orientation, since a difference of 0.2 eV in $\Phi_B{}^0$ might induce an order of magnitude increase in the leakage current. It remains to be established whether this variation in the potential barrier is intrinsic or extrinsic respectively related to a different band alignment at the metal-BFO interfaces for different orientations, or whether it is given by a different pinning of the Fermi level due to a different density of interface defects.

In summary, current-voltage measurements performed on epitaxial BFO films deposited on single-crystal STO substrates with different orientations and with SRO and Pt electrodes revealed that the potential barriers at the electrode interfaces are affected by the substrate orientation. It appears that the leakage current in epitaxial BFO capacitors is interface-limited and not dominated by the volume-controlled conduction mechanisms, such as Poole–Frenkel emission or SCLC, as was assumed in previous studies. The change in substrate orientation could be a method to tune the height of the potential barrier and thus the leakage in epitaxial ferroelectric films.

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