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Mechanism of polarization fatigue in BiFeO₃: The role of Schottky barrier

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By using piezoelectric force microscopy and scanning Kelvin probe microscopy, we have investigated the domain evolution and space charge distribution in planar BiFeO₃ capacitors with different electrodes. It is observed that charge injection at the film/electrode interface leads to domain pinning and polarization fatigue in BiFeO₃. Furthermore, the Schottky barrier at the interface is crucial for the charge injection/accumulation process. Lowering the Schottky barrier by using low work function metals as the electrodes can also improve the fatigue property of the device, similar to what oxide electrodes can achieve. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4861231>]

Ferroelectric fatigue refers to the decrease of switchable polarization in a ferroelectric material after repetitive electrical cycling.¹ It is detrimental to ferroelectric based devices and should be minimized. There have been a large number of reports on the mechanism of the polarization fatigue.^{2–5} Different models have been proposed, including electrode delamination,⁶ charge injection,^{7–10} defects, i.e., oxygen vacancies, redistribution,^{11–15} and local phase decomposition.^{16–18}

In our previous report, we have demonstrated that charge injection is likely the cause of fatigue in BiFeO₃.¹⁹ By using a planar capacitor (inset of Fig. 1(a)), we have conducted piezoelectric force microscopy (PFM) and scanning Kelvin probe microscopy (SKPM) studies to investigate the domain evolution and space charge activities in BiFeO₃ during fatigue measurement. SKPM is one of the atomic force microscope (AFM)-based techniques. The potential difference between the sample and the tip can be obtained and reflects the space charge distribution in the film. In our setup, dark and bright contrast indicates negative and positive charges, respectively. Figure 1(a) shows the in-plane (IP) PFM image of a BiFeO₃ thin film on SrTiO₃ substrate after 10¹⁰ cycles of switching using in-plane Pt electrodes. The color code is shown in the insets of Figs. 1(d) and 1(e). Upon reversing the electric field, some domains are clearly unswitchable as shown in Fig. 1(b). SKPM measurement at the same location indicates negative charge, i.e., electrons, accumulation at the Pt/BiFeO₃ interfaces, as shown in Fig. 1(c). Detailed study on the time evolution of pinned domains and injected electrons has clearly demonstrated the correlation between the two, and with the macroscopic fatigue of the BiFeO₃ film. (For details, please refer to Supplementary material²⁰ or Ref. 19). However, this is not to say that defects are irrelevant to polarization fatigue. On the contrary, these injected electrons must be trapped in gap states which can be associated with existing defects or created by the high energy injected electrons. We emphasize that it is not the redistribution/accumulation of defects, but

rather the charging/discharging of defects, leads to polarization fatigue eventually.

After establishing the correlation between charge injection and fatigue,¹⁹ one naturally wonders what controls the charge injection process. Previous studies have shown that oxide electrodes improve the fatigue performance of ferroelectric devices dramatically,²¹ so how is charge injection affected when different electrodes are used? We try to clarify this issue by investigating planar BiFeO₃ capacitors with different electrodes. It was observed that the Schottky barrier at the electrode/BiFeO₃ interface plays a significant role in the charge injection/accumulation process. By reducing the barrier height, metal electrodes with low work functions can also improve the fatigue performance of BiFeO₃.

All the films and electrodes in this work are deposited by pulsed laser deposition (PLD). For the planar devices, 40 nm BiFeO₃ thin films are grown at 650 °C under 100 mTorr oxygen partial pressure. During the BiFeO₃ growth, the laser frequency is fixed at 5 Hz and energy density at ~1 J/cm². The electrodes are prepared using standard photolithography process and the channel width is 5 μm. Conventional vertical capacitors have also been prepared to further support our conclusion. For this purpose, bottom (La_{0.7}Sr_{0.3})MnO₃ electrodes are grown on (001)-oriented SrTiO₃ substrate at 800 °C under oxygen partial pressure of 200 mTorr followed by BiFeO₃ films (~100 nm) deposited at 675 °C and under 50 mTorr oxygen partial pressure. Precision LC Ferroelectric tester (Radiant Technologies) is used to measure the polarization and apply bipolar electrical pulses for the fatigue measurement. A commercial AFM (Asylum Research MFP3D) is used to conduct the PFM and SKPM scanning and MikroMasch DPE 14 tips (Pt-coated, 160 kHz, and 5.7 N/m) are used.

To clarify the difference between metal and oxide electrodes, we have prepared and investigated BiFeO₃ planar capacitors using (La_{0.7}Sr_{0.3})MnO₃ as electrodes. All the parameters for BiFeO₃ films deposition are the same as reported in our previous study.¹⁹ Since (La_{0.7}Sr_{0.3})MnO₃ requires higher deposition temperature than BiFeO₃, the electrodes are prepared (by standard lithography and

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FIG. 1. IP PFM ((a), (b), (d), and (e)) and SKPM ((c) and (f)) images of planar (a)–(c) Pt-BiFeO₃-Pt and (d)–(f) (La_{0.7}Sr_{0.3})MnO₃-BiFeO₃-(La_{0.7}Sr_{0.3})MnO₃ devices after 10¹⁰ cycles of switching. (a) and (b) Domain pinning (outlined) across the whole Pt-BiFeO₃-Pt channel can be observed in the IP-PFM images. (c) Considerable charge injection (dark region) is observed at the Pt/BiFeO₃ interfaces from the SKPM image. (d)–(f) Negligible domain pinning and charge injection are observed when (La_{0.7}Sr_{0.3})MnO₃ electrodes are used. Inset of (a) shows the planar device structure. The AFM cantilever is placed along the pseudo cubic [110] direction to effectively identify the IP polarization directions in BiFeO₃ films. The insets of (d) and (e) show the color code of IP-PFM images (IP components represented by the dash arrows), in which brown color means IP polarization parallel to the AFM cantilever, while purple and yellow represent IP polarization perpendicular to the cantilever.

etching) first followed by BiFeO₃ (40 nm) deposition. Macroscopic polarization-electric field measurement reveals no fatigue after 10¹⁰ cycles (data not shown). In the IP PFM images taken after opposite electric field is applied to the film, no domain pinning is observed up to 10¹⁰ cycles (Figs. 1(d) and 1(e)). Furthermore, SKPM image reveals negligible electron injection at the (La_{0.7}Sr_{0.3})MnO₃/BiFeO₃ interfaces (Fig. 1(f)), whereas significant domain pinning and electron injection are found at the Pt/BiFeO₃ interface after the same number of switching cycles (Figs. 1(a)–1(c)). The microscopic observation is consistent with previous reports that oxide electrodes can improve the fatigue performance of ferroelectric materials.

Why is there negligible charge injection occurring at the (La_{0.7}Sr_{0.3})MnO₃/BiFeO₃ interface? To answer this question, we have to turn to the differences between Pt/BiFeO₃ and (La_{0.7}Sr_{0.3})MnO₃/BiFeO₃ interfaces. From electronic structure point of view, Pt forms a Schottky barrier with BiFeO₃ (Ref. 22) while (La_{0.7}Sr_{0.3})MnO₃/BiFeO₃ interface is Ohmic. Our detailed temperature dependent *I*-*V* study has indeed confirmed this conclusion.²⁰ By measuring the current vs. temperature behavior, we can calculate the Schottky barrier at the Pt/BiFeO₃ interface to be ~1.1 eV (Fig. 2(b)), while the (La_{0.7}Sr_{0.3})MnO₃/BiFeO₃ interface shows no barrier. One possible scenario is that the Schottky barrier helps to retain the injected charges at the interface region while an Ohmic contact allows them to move across the interface freely during fatigue measurement. For the Pt-BiFeO₃-Pt planar capacitor, a large voltage drop arises at the reversely biased Schottky interface and external electric field drives electrons to overcome the barrier and inject into the BiFeO₃ film during the fatigue measurement (Fig. 2(c)). Once injected, electrons are accelerated by the high local electric

field and gain high energy.⁷ They can thus be trapped at deep gap states and immobilized to form charged defects.⁵ Once immobilized, they can hardly be removed when opposite field is applied which mainly drops across the other interface (reversely biased). Instead, they accumulate at the interface after repetitive switching (Fig. 1(c)), pin the domains and give rise to macroscopic fatigue in ferroelectric films. On the other hand, (La_{0.7}Sr_{0.3})MnO₃ forms Ohmic contact with BiFeO₃, and a flat band with negligible barrier is expected at the interface (Fig. 2(d)). In this case, external field drops uniformly across the whole film and high energy of injected electrons is unlikely to occur owing to the absence of localized high electric field. Even though the electrons may still be injected, associated with higher leakage current, they can easily jump back to the electrode under opposite field. In other words, there is no (or negligible) accumulation of the injected electrons at (La_{0.7}Sr_{0.3})MnO₃/BiFeO₃ interface under repetitive cycling because of the high detrapping rate.^{5,8} Without accumulation of the injected charges, the fatigue performance will be improved. Furthermore, the Schottky barrier at forward biased Pt/BiFeO₃ interface is not completely removed (though reduced) by the external field. This barrier, by preventing injected electrons from moving across the interface freely, also contributes to the accumulation of injected electrons at the Pt/BiFeO₃ interface.

If the above model is correct and the Schottky barrier at the electrode/film interface helps the charge injection process which eventually leads to polarization fatigue, then the low work function metals should improve the fatigue performance of BiFeO₃ by reducing the Schottky barrier. We have tested this prediction using Fe, which has a work function of ~4.5 eV, comparable to that of BiFeO₃ (~4.7 eV). Fe-BiFeO₃-Fe planar capacitors are prepared following the

FIG. 2. Leakage current density and energy band diagrams of planar BiFeO₃ devices. (a) The I - V curves show higher leakage current density when $(La_{0.7},Sr_{0.3})MnO_3$ electrodes are used, indicating a lower energy barrier at the $(La_{0.7},Sr_{0.3})MnO_3$ /BiFeO₃ interface. (b) Fitting of I - T curve leads to a barrier height of ~ 1.1 eV for the Pt-BiFeO₃-Pt device. (c) A large Schottky barrier is expected at the Pt/BiFeO₃ interface. A large voltage drop arises at the reversely biased interface under external electric field, which drives electrons into the BiFeO₃ film. And the injected electrons can be accelerated by localized high electrical field to gain high energy and trapped at deep levels. (d) A flat band with negligible barrier is expected at the $(La_{0.7},Sr_{0.3})MnO_3$ /BiFeO₃ interface, and external field drops uniformly across the film. Even though electron injection still occurs, they can easily be detrapped under reversed field, giving rise to negligible electron accumulation at the interface.

same procedure. Much higher leakage current is observed, reflecting the lower interface barriers as expected. After the device is subjected to electrical switching (100 kV/cm square pulse at 0.1 ms) for 10^{10} cycles, we observe no fatigue in the polarization-electric field (P - E) loops (Fig. 3(a)). More importantly, the PFM images indicate a very small amount of domain pinning (Figs. 3(c) and 3(d)) and SKPM image shows negligible injected electrons at the interfaces (Fig. 3(b)). This observation confirms that the Schottky barrier does play a role

in the charge injection/accumulation process, and low work function metals, such as Fe, should improve the fatigue performance of BiFeO₃.

In order to further support our claim, we have conducted fatigue measurements using conventional vertical capacitors. 100 nm BiFeO₃ films are deposited on (001)-oriented single crystal SrTiO₃ substrates with 20 nm $(La_{0.7},Sr_{0.3})MnO_3$ as the bottom electrode. The schematic structure of the devices is given in Fig. 4(a). Pt, Fe, and $(La_{0.7},Sr_{0.3})MnO_3$, are

FIG. 3. Fatigue performance of planar Fe-BiFeO₃-Fe device. (a) Switchable polarization vs. cycling number indicates no macroscopic fatigue up to 10^{10} cycles. Inset shows the remanent hysteresis loops before and after electrical switching. SKPM image indicates negligible charge injection (b) and IP-PFM images show a very small amount of domain pinning (c)-(d) at the Fe/BiFeO₃ interface after 10^{10} switching cycles. Inset of (b) shows the same SKPM image with reduced scale, and a small number of injected electrons (dark region) are observed, which explain the small number of pinned domains at the interface.

FIG. 4. Fatigue performance of vertical BiFeO₃ capacitors. (a) Schematic illustration of the device structure. (b) Comparison of fatigue behaviors using three different top electrodes. Fatigue appears after 10⁴ cycles when Pt is used as top electrode, whereas both Fe and (La_{0.7}Sr_{0.3})MnO₃ top electrodes significantly improve the BiFeO₃ fatigue performance.

deposited as the top electrodes. They all have the same size of $\sim 100 \mu\text{m}^2$. When high work function metal electrode Pt is used, fatigue appears relatively soon. Considerable reduction of switchable polarization is observed after only 10⁴ electrical cycles (Fig. 4(b)). For low work function metal electrode (Fe), on the other hand, no fatigue is observed up to 10⁷ cycles, though further cycling leads to break down of the device due to the larger leakage current associated with the low interface barrier. For (La_{0.7}Sr_{0.3})MnO₃, no fatigue occurs up to 10⁸ cycles. We thus conclude that Schottky barrier at the electrode/ferroelectric interface indeed plays a role in polarization fatigue and low work function electrodes, metal or oxide, can improve the fatigue performance. However, the fact that why Fe electrode makes the device more prone to breakdown is still under investigation.

In summary, following our previous study, where charge injection/accumulation at the electrode/ferroelectric film interface was identified as the cause of fatigue in BiFeO₃, we have conducted further experiments and demonstrated that the Schottky barrier at the interface plays a significant role. By reducing the barrier height, even metal electrodes can significantly improve the fatigue performance of ferroelectric devices. This conclusion is corroborated by investigation using conventional vertical capacitors, and is valuable for better understanding and application of ferroelectric materials.

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