An Epitaxial Ferroelectric Tunnel Junction on Silicon

Zhipeng Li, Xiao Guo, Hui-Bin Lu,* Zaoli Zhang, Dongsheng Song, Shaobo Cheng, Michel Bosman,* Jing Zhu, Zhili Dong, and Weiguang Zhu*

The pursuit of non-volatile memory devices on silicon with high storage density, high speed and low power consumption has been an important driving force for the study of new materials and designs of nanoscale architectures. Flash memory is currently the main commercialized non-volatile memory in embedded chips. However, flash has some drawbacks, such as long programming times, limited cycle endurance and high programming voltages (around 10 V). A number of alternative memory technologies, namely magnetic random access memory (MRAM) and ferroelectric RAM (FeRAM) have achieved higher programming performance than flash, but scaling-down these technologies remains challenging. Recently, ferroelectric tunnel junction (FTJ) devices emerged as an alternative memory technology, attracting much attention of solid-state physicists and materials scientists. Conceptualized in the 1970s by Esaki et al., it has been experimentally demonstrated that when an ultrathin ferroelectric film serves as barrier layer in tunnel junction devices, the quantum-mechanical tunneling current and resistance can be manipulated non-destructively via the polarization direction of the ferroelectric barrier, an effect known as the tunneling electroresistance (TER) effect. An FTJ device can achieve two conductance states with a ratio as high as two orders of magnitude, as well as memory programming with a short voltage pulse (10 ns) and at modest current densities (∼1 × 10^4 A cm⁻²). In addition, FTJ devices have the potential to function as nanometer-scale non-volatile memory devices, operating with low power consumption. Nonetheless, FTJ devices with nearly ideal characteristics have only been demonstrated on perovskite heterostructures that were deposited on closely lattice-matched, non-silicon substrates such as SrTiO₃ (STO) and NdGaO₃. Although these substrates can provide compressive strain to the ferroelectric BaTiO₃ (BTO), achieving room temperature ferroelectricity and possibly the TER effect in layers only a few nanometer thick, they are not compatible with the ubiquitous microfabrication technologies based on the silicon platform. This has so far limited the application of FTJs as memory technology.

In this work, we demonstrate epitaxial FTJ devices with the TER effect on Si(001) wafers, fabricated by pulsed laser deposition (PLD). This is accomplished by including a thin layer of STO as an epitaxial template on silicon. Using transmission electron microscopy (TEM), scanning TEM (STEM) high angle angular dark field (HAADF) imaging, and electron energy loss spectroscopy (EELS), we demonstrate near-atomically sharp chemical interfaces with c-axis orientation in the perovskite heterostructures. Enhanced tetragonality (c/a) and room temperature ferroelectricity in ultrathin BTO are revealed by aberration-corrected high resolution TEM (HRTEM) and piezoelectric force microscopy (PFM), respectively. Using conductive AFM, the polarization switching-induced change in tunneling resistance is measured to be two orders of magnitude. This resistive switching behavior is further verified using a model based on tunneling currents through a trapezoidal potential barrier whose profile can be modulated by polarization switching.

The epitaxial La₀.₇Sr₀.₃MnO₃ (LSMO) and 3.2 nm thick BTO films used in this work were grown by pulsed laser deposition on silicon wafer using an STO buffer layer. Figure 1a presents the LSMO/BTO heterostructure and corresponding atomic-resolution STEM-HAADF image of the cross-sectional sample. As the HAADF intensity is proportional to the local atomic number (~Z^1.7), the different chemical layers can be identified. The BTO barrier layer is confirmed to be 8 unit cell thick. The HAADF image and intensity profile in Figure 1b demonstrate near-atomically sharp interfaces in the STO/LSMO/BTO stack, suggesting that cationic mixing at the interfaces is minimal. In addition, the conventional HRTEM image in Figure 1c presents the c-axis oriented epitaxial perovskite stacks with BTO and LSMO thickness of ~3.2 nm and 13.3 nm, respectively.
Figure 1c also shows that the layer between the silicon and the STO is amorphous. As was shown earlier in experiments that used molecular beam epitaxy (MBE, instead of our PLD) as growth technique,[11] such an amorphous layer forms when silicon reacts with the oxygen from the epitaxially grown STO; in the Supporting Information (Figure S3c), we demonstrate that this amorphous layer consists of SiO$_2$. The X-ray diffraction (XRD) $\theta$–$2\theta$ scan of the Si/STO/LSMO/BTO stack confirms the TEM results, indicating monocrystallinity and $c$-axis orientation of the perovskite films on (001) silicon (Supporting Figure S1). From selected area electron diffraction (SAED), the crystal orientation is determined as perovskite (100) // parallel to silicon (110), which shows that the perovskite orientation is rotated in-plane by 45$^\circ$ with respect to the silicon crystal (Supporting Figure S2). These results are similar to the epitaxial perovskite films on silicon grown by MBE.[12,13] The average in-plane lattice parameter of perovskite films measured by SAED is 0.391 ± 0.005 nm which is smaller than that of bulk BTO (0.399 nm), suggesting possible strain enhancement of ferroelectricity in ultrathin BTO.

Typically, the epitaxial strain and polarization in ferroelectric materials are coupled, leading to a direct relationship between polarization and tetragonality ($c/a$).[14,15] To quantitatively study the degree of tetragonality in the BTO barrier layer, spherical aberration-corrected HRTEM with sub-Angstrom resolution is used. A HRTEM image of ultrathin BTO on the [010] zone axis with multislice-simulated atom positions is shown in Figure 2a. The accurate positions (coordination) of cation columns are determined by means of a least-squares fit of the individual contrast minima by Gaussian intensity profiles, and the positions of contrast minima are regarded as the peak centroids. The lattice parameters $a$ and $c$ can then be extracted from the coordination of the cation columns.[16] Figure 2b presents a unit-cell scale mapping of tetragonality $c/a$ values in the BTO film from an area of 21 unit cells along the in-plane direction by 8 unit cells along the out-of-plane direction. It can be seen that the spatial distribution of tetragonality values is quite uniform in BTO. The tetragonality as a function of distance along the $c$-axis, shown in Figure 2c, plots the average values for each of the 8 rows of BTO unit cells, with the error bars indicating the 95% confidence interval. The tetragonality remains nearly constant around 1.045 from the LSMO/BTO interface to the BTO surface. Compared with the $c/a$ value of bulk BTO (1.010), the tetragonality of this ultrathin BTO on LSMO grown on silicon is enhanced. The lattice constants of BTO are measured as $a = 0.395 \pm 0.005$ nm and $c = 0.413 \pm 0.005$ nm, with the corresponding compressive strain level +1.0% along the in-plane direction compared with the bulk BTO. The tetragonality value of BTO on our silicon platform is similar to the earlier published $c/a = 1.051$ obtained from 2 nm BTO grown on a NdGaO$_3$ substrate with an LSMO buffer, and larger than the $c/a = 1.038$ from BTO grown on DyScO$_3$ for $T_C > 900$ K.[14,17] As epitaxial strain can also modify the crystal field-sensitive EELS fine structure,[18,19] we confirm from the BTO EELS Ti $L_2$ edge energy splitting in Figure S3 that the BTO lattice is strained. In addition, the EELS fine structure of the BTO Ti $L_2,3$ edge is typical of Ti$^{4+}$ cations, excluding the possibility of oxygen vacancies-driven formation of Ti$^{3+}$ cations in BTO.[20]

The surface topography of the Si/STO/LSMO/BTO is shown in Figure 3a. The roughness is ~300 nm, indicating an atomically smooth surface. Ferroelectric characterization is performed by PFM; Figures 3b and 3c show the out-of-plane PFM phase and amplitude images, respectively, of ferroelectric
domains written on the 3.2 nm thick BTO. The antiparallel polarization is revealed by 180° domains written on the 3.2 nm thick BTO. The antiparallel conductive AFM tip on the BTO film surface, measuring the bottom electrode, and contact is made through contacting a possibility of FTJs made on silicon: the voltage is applied to the BTO layer. The coercive voltages are found to be –1.4 V and 4.63 × 10⁻¹¹ A at the polarization down (ON) state and the up (OFF) state, respectively when the $V_{\text{Read}}$ is 250 mV, giving a TER ratio of 212. The Hertz model is used here to estimate the area of AFM tip-sample contact, giving an approximate value of 105 nm² [24]. Then the measured tunneling currents in Figure 3e imply a current density $j$ of $9 \times 10^3$ A/cm² and a sheet resistance of $2 \times 10^3 \ \Omega \cdot \mu$m² when $V_{\text{Read}} = 250$ mV in the ON state. These values are comparable with the experimental data of FTJ with a BTO barrier layer grown on perovskite substrates. [7,25] A similar ON/OFF phenomenon induced by polarization reversal was also reported in a ferroelectric Schottky diode, however, the thickness of the ferroelectric layer was hundreds of nanometers and the current density around $10^{-3}$ A/cm²; [26] That value is several orders of magnitude smaller than what we obtained in this work, therefore, the ferroelectric Schottky diode mechanism can be excluded here. In addition, we performed a fatigue and endurance test of the resistive switching in this FTJ, the results are shown in Figure 3f. It is demonstrated that the ON/OFF ratio of about 200 in the FTJ on silicon can be maintained for up to at least 10 000 cycles.

Theoretically, the polarization reversal can change the density of states at BTO/electrodes interfaces and the electronic band structure of the barrier. To simulate the measured $I–V_{\text{Read}}$ curves and verify the mechanism of the observed resistive switching associated with polarization reversal, a model based on the TER effect is employed, involving a tunneling current through a trapezoidal potential barrier whose profile depends on polarization direction [6,27] (details can be found in the Supporting Information). In the configuration of transport measurement, the LSMO bottom electrode and Pt-Ir top electrode (the AFM tip is coated with Pt-Ir alloy, so it is regarded as the top electrode of the BTO here) have different screening lengths, which leads to an asymmetry in the potential profiles of the junction. The barrier has a width of $d$ and amplitudes of electrostatic potential at the LSMO/BTO and BTO/Pt-Ir interfaces of $\phi_1$ and $\phi_2$, respectively. Figure 3e shows a fit of the experimental $I–V_{\text{Read}}$ curves for 3.2 nm thick BTO using the following parameters: $\phi_1 = 0.21$ eV and $\phi_2 = 0.71$ eV for polarization down (ON state), and $\phi_1 = 0.15$ eV and $\phi_2 = 1.43$ eV for polarization up (OFF state). The respective change in the potential energy profiles of the junction is schematized in Figure 5a in the Supporting Information. The potential energy difference $\phi_2–\phi_1$ is adjusted from 0.5 eV to 1.28 eV due to polarization reversal in the down-to-up direction. The 0.78 eV change of $\phi_2–\phi_1$ value in our experiments is close to that reported by Gruverman et al. [6] This energy difference controls the asymmetry of the potential energy difference...
profile and plays a decisive role in the resistance change due to the polarization reversal. Meanwhile, the average potential barrier height $U_{\text{Up}}$ (0.79 eV) for the polarization up-state is larger than $U_{\text{Down}}$ (0.46 eV) for polarization-down. This fact makes the conductance for polarization-down much larger than that for polarization-up, resulting in the observed TER effect.

Although the above results are measured from a non-optimized device, nanoscale ferroelectricity and the giant TER effect have been readily observed in our FTJ on silicon. Some key parameters of the junction, including the tetragonality and ferroelectricity of BTO, the TER ratio, current density and the modified potential barrier height are comparable with junctions grown on perovskite substrates. With this device built on silicon, the FTJ memory can be integrated with other microelectronic components to form integrated circuits. Furthermore, our design is expected to lead to nonvolatile memory units on silicon wafers, opening a door to greatly miniaturized silicon-based, non-volatile memory devices.

**Experimental Section**

The silicon substrates were first dipped into a ~5% HF solution for 20–30 s to remove the native silicon oxide on the surface and to form a hydrogen-terminated surface, followed by an immediate transfer into the PLD chamber. The deposition process of the perovskite films was performed using a KrF laser ($\lambda = 248$ nm) with a fluence of 2 J/cm$^2$ and repetition rate of 1 Hz. STO with a thickness of 3 nm was deposited on silicon substrates as buffer layers at room temperature under an oxygen pressure of $\sim 1 \times 10^{-4}$ Pa. The substrate temperature was then raised to 620 °C for the annealing process. An in-situ reflected high energy electron diffraction (RHEED) system and CCD camera were used to monitor the crystallization process of the STO layer. The RHEED streak pattern was observed when the STO was well-crystallized from amorphous to a $c$-axis oriented single crystal. Afterwards, LSMO, which worked as an electrode to facilitate electrical measurements, was subsequently deposited at a temperature of 780 ºC under an oxygen pressure of 26 Pa, avoiding oxygen vacancies and cation non-stoichiometry during growth. The BTO was grown at 650 ºC under an oxygen pressure of 7 Pa. The samples were annealed for 0.5 h at 650 °C and then cooled to room temperature, all under an oxygen pressure of 1000 Pa. A Rigaku Smartlab high-resolution diffractometer with copper X-ray generator tube was used for XRD measurements. Before TEM sample preparation, a Cr/Au layer was deposited on BTO, to protect the perovskite film from beam damage during ion milling. TEM specimens were prepared to electron transparency by grinding, dimpling, and ion milling in a Catan.
Precision Ion Polishing System. The specimens were cleaned briefly in an oxygen plasma, and then transferred directly into the microscopes for observation. An FEI Titan 80-300 TEM with Schottky emitter, operated at 200 kV was employed for Z-contrast imaging and EELS line scans with a probe diameter of 1 nm, in STEM mode. The TEM images of BTO for tetragonality analysis were taken by a conventional JEOL 2100F TEM and a JEOL 2100F TEM equipped with an imaging spherical aberration corrector.[32] Scanning probe microscope experiments were conducted on a Cypher AFM from Asylum Research. Conductive Pt-Ir-coated silicon cantilevers (from NanoWorld Company) were used for piezoelectric force microscope (PFM) imaging and polarization switching studies. The ferroelectric hysteresis loops collected during polarization switching were measured in DART (dual a.c. resonance tracking) mode. Both phase and amplitude images were recorded in single-frequency PFM mode. The I–V characteristics of the tunnel junction were performed in conductive AFM (C-AFM) mode using a Keithley 6430 Source Meter connected with the sample holder. The bias voltage was applied to the LSOM bottom electrode and the AFM tip was grounded for all C-AFM measurements. In the fatigue and endurance test of the resistive phase and amplitude images were recorded in single-frequency PFM mode. The bias voltage was applied to the BTO with a square wave form of ±3 V during cycling. After every 1000 cycles, the ON (polarization down)/OFF (polarization up) state was set by applying a 100 μs voltage pulse of –3 V/+3 V for the corresponding tunneling current measurements (with $V_{\text{fixed}} = 250 \text{ mV}$).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors would like to thank the Science and Engineering Research Council (SERC) of Singapore Agency for Science, Technology and Research (A*STAR) for their financial support (Grant Number 102 101 0019) and the Office of China Postdoctoral Council for the scholarship under the International Postdoctoral Exchange Fellowship Program.

Received: June 6, 2014
Revised: July 11, 2014
Published online: