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Effects of ferroelectricity and magnetism on electron and spin transport in $Fe/BaTiO_3/Fe$ multiferroic tunnel junctions

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First principles electronic structure and transport calculations are used to demonstrate the impact of the electric polarization on electron and spin transport in $Fe/BaTiO_3/Fe$ multiferroic tunnel junctions (MFTJs). We find that the polarization of $BaTiO_3$ reduces the tunneling conductance, as compared to a nonpolarized barrier, due to the change in the electronic structure driven by ferroelectric displacements, similar to that found previously for $Pt/BaTiO_3/Pt$. For the MFTJ, however, this effect has different magnitudes for majority- and minority-spin channels and for parallel and antiparallel orientations of the magnetization of the electrodes. As a result, we find a substantial drop in the spin polarization of the tunneling current in the parallel configuration and an inversion of the magnetoresistance as polarization of the barrier is turned on. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2828512]

In the past decade, the phenomena of electron tunneling and ferroelectricity have attracted significant interest due to their potential applications in thin-film electronic devices such as magnetic tunnel junctions[1] and nonvolatile ferroelectric memories.[2] There has been a number of experimental[3–5] and theoretical[6–8] studies of perovskite ferroelectric oxides demonstrating that ferroelectricity persists down to a nanometer scale, which makes it possible to use ferroelectrics as tunnel barriers in ferroelectric tunnel junctions (FTJs).[9] If a FTJ is made of ferromagnetic metal electrodes, the junction becomes multiferroic (that is, simultaneously ferromagnetic and ferroelectric). The interplay between ferroelectric and ferromagnetic properties in a multiferroic tunnel junction (MFTJ) may affect the electric polarization of the ferroelectric barrier, the electronic and magnetic properties of the interface, and the spin polarization of the tunneling current.[10]

Recent theoretical work demonstrated that electric polarization can have significant effect on the properties of MFTJs. Based on a simple model it was predicted that the reversal of the electric polarization of the ferroelectric barrier can produce a sizable change of the resistance of FTJs (Ref. 11) and a change of the spin polarization of the tunneling current in MFTJs.[12] Using first principles calculation, it was shown that in $Pt/BaTiO_3/Pt$ FTJs ferroelectricity has a pronounced influence on tunneling mediated by coupling between the electric polarization of the barrier and the electronic structure of the electrodes at the interfaces.[13] Similarly, polarization dependent bonding between the Fe and Ti atoms at the interface was predicted to produce a magnetoelectric effect in $Fe/BaTiO_3/Fe$ MFTJs.[14] An analogous effect was recently found at the interface between half-metallic Co_2MnSi and perovskite $BaTiO_3$.[15]

In this paper, we investigate electron tunneling in $Fe/BaTiO_3/Fe(001)$ MFTJs from first principles. Our calculations predict ferroelectric instability for $BaTiO_3$ thickness as small as 1.8 nm. By comparing the polarized with the unpolarized case we find that ferroelectricity strongly suppresses tunneling, similar to what was found previously for the $Pt/BaTiO_3/Pt$. For the MFTJ, however, this effect has different magnitude for majority- and minority-spin channels and for parallel and antiparallel orientations of the magnetization of the electrodes. These results indicate the possibility of electrical control of the spin polarization (SP) and the tunneling magnetoresistance (TMR) in MFTJs.

First principles calculations, based on density functional theory, of the electronic and atomic structures of $Fe/BaTiO_3$ are performed within supercell geometry using the projector augmented wave method implemented in the Vienna *ab initio* simulation package[16,17] (VASP) and a tight-binding linear muffin-tin orbital (TB-LMTO) method.[18,19] We consider a TiO_2-terminated interface with interfacial O atoms occupying sites atop Fe. The $BaTiO_3$ lattice fits epitaxially on the bcc Fe lattice rotated by 45°. The in-plane lattice constant is fixed to be the experimental value of bulk $BaTiO_3$ (3.991 Å), which is smaller than the theoretical lattice constant for the cubic phase of $BaTiO_3$ (4.033 Å). This produces a tetragonal distortion of both $BaTiO_3$ ($c/a=1.02$) and bcc Fe ($c/a=1.01/\sqrt{2}$) structures. Thus, supercells in our calculations are $(Fe_2)_9-TiO_2-(BaO-TiO_2)_m$, where $m=1-8$. Figure 1 shows the atomic structure of the $m=4$ MFTJ.

First, we assume that $BaTiO_3$ is in paraelectric (PE) state. For this purpose, we enforce reflection symmetry with respect to the central TiO_2 monolayer and relax the atomic structure of the whole system. We find that, although the net polarization of the $BaTiO_3$ film is zero, bonding at the interface induces displacements of the interface Ti atoms [Fig. 1(a)]. The interface displacements are about half the size of

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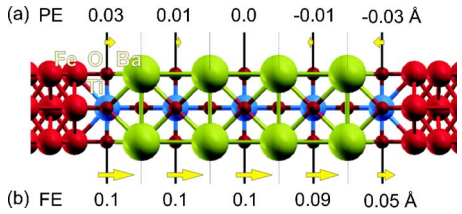

FIG. 1. (Color online) Atomic structure of a $Fe/BaTiO_3/Fe(001)$ tunnel junction. Arrows show displacements of Ti atoms with respect to O atoms within each TiO_2 monolayer for (a) paraelectric (PE) and (b) ferroelectric (FE) $BaTiO_3$.

those found in $Pt/BaTiO_3/Pt$ and in the opposite direction.[13] Next, we allow for the ferroelectric (FE) state to develop by removing the constraint of reflection symmetry and minimize the total energy with respect to atomic coordinates of all atoms in the supercell. We find the critical thickness for ferroelectricity to be $t=1.8$ nm ($m=4$) [Fig. 1(b)]. For $m=4$ the displacements of Ti atoms at the central TiO_2 monolayer are about 0.1 Å, which is close to displacements in bulk $BaTiO_3$ (0.123 Å) and twice as large as those in $Pt/BaTiO_3/Pt$. This is caused by the smaller magnitude of the interface polarization dipole.

The electronic structure of the paraelectric $Fe/BaTiO_3$ interface is characterized by large charge transfer between the Ti and Fe atoms, which results in a magnetic moment on the Ti atom of about $0.3\mu_B$ opposite to that of the Fe.[14] Ferroelectric displacements produce notable changes in the electronic structure of a $Fe/BaTiO_3/Fe$ MFTJ. It is seen from Fig. 2 that the local density of states (DOS) for the Ti atoms at the left and right interfaces [distinguished by the polarization orientation, as in Fig. 1(b)] are different. The displacement of the Ti atoms toward/away from the plane of Fe atoms is about 0.08 Å, which strengthens/weakens the Fe–Ti bond. This is responsible for the changes in the magnetic moments of the interface atoms and the origin of the magnetoelectric effect.[14]

The strength of the Fe–Ti bond at the interface also affects the interface transmission function and therefore should influence the tunneling conductance.[13] The conductance is calculated by considering a $BaTiO_3$ ($m=4$) layer placed between two semi-infinite Fe electrodes, using the TB-LMTO method and principal-layer Green's function technique.[20]

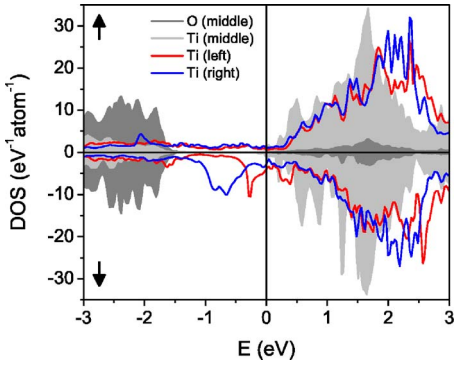

FIG. 2. (Color online) Local DOS in a $Fe/BaTiO_3/Fe$ ($m=4$) tunnel junction as a function of energy. The O_2 and Ti DOS in the middle TiO_2 monolayer are shown by the shaded area. The polarization is assumed to be pointing to the right, as in Fig. 1(b).

TABLE I. Calculated conductance (G in units of $\times 10^{-5}\ e^2/h$), spin polarization (SP), change in conductance (ΔG), and tunneling magnetoresistance (TMR) in $Fe/BaTiO_3/Fe$ ($m=4$) MFTJ for $BaTiO_3$ is in a paraelectric (PE) and a ferroelectric (FE) state. Quantities are defined as follows: $\Delta G=(G_{PE}-G_{FE})/(G_{PE}+G_{FE})$, $SP=(G_{\uparrow\uparrow}-G_{\downarrow\downarrow})/(G_{\uparrow\uparrow}+G_{\downarrow\downarrow})$, and $TMR=(G_P-G_{AP})/G_{AP}$.

	PE	FE	ΔG (%)
$G_{\uparrow\uparrow}$	14.3	2.0	−75
$G_{\downarrow\downarrow}$	53.0	3.9	−86
G_P	67.3	5.9	−84
SP (%)	−58	−31	
$G_{\uparrow\downarrow}$	5.4	7.1	14
$G_{\downarrow\uparrow}$	5.4	0.6	−80
G_{AP}	10.8	7.8	−17
TMR (%)	520	−24	

Again, we first assume that $BaTiO_3$ is in the paraelectric state. The conductance for the majority- and minority-spin channels ($G_{\uparrow\uparrow}, G_{\downarrow\downarrow}$) in the parallel configuration and either spin channel ($G_{\uparrow\downarrow}, G_{\uparrow\downarrow}$) in the antiparallel configuration is shown in the first column of Table I. The current in the parallel configuration displays large negative spin polarization due to the complex band structure of $BaTiO_3$ which allows tunneling of the d electrons, which is similar to the origin of the negative SP in $Co/SrTiO_3/Co$ MTJs.[21] Conductance in the antiparallel configuration is much smaller due to band mismatch between majority and minority states in the leads. As a result, we obtain large TMR of 520%.

The conductance per unit cell area when $BaTiO_3$ alters its state from paraelectric to ferroelectric is shown in the second column of Table I. In the parallel configuration the conductance decreases substantially when the polarization in the ferroelectric is turned on. This is due to the change in the electrostatic potential and the bonding at the interface and the change in the decay rates of the evanescent states in the barrier as in the case of $Pt/BaTiO_3/Pt$.[13] However, here the minority conductance is affected more by the polarization which is reflected in the twofold decrease in the spin polarization of the current, compared to the PE case. In the antiparallel configuration the overall conductance also decreases but by a much smaller amount. As a result, the antiparallel conductance becomes larger than the parallel conductance, and an *inverse* TMR of 24% is obtained.

Some insight into the influence of ferroelectric displacements on the transport can be gained by looking into the transmission of the different propagating states in the Fe leads through the interface at $\mathbf{k}_\parallel=0$. There are four Fe propagating states in both majority (Δ_1, Δ_5, and $\Delta_{2'}$) and minority (Δ_5, Δ_2, and $\Delta_{2'}$) Fe bands[22] of which only Δ_5 and Δ_1 have low decay rates in $BaTiO_3$.[13] The propagation of probability density of the Δ_5 state through the interface is shown in Fig. 3. In the parallel configuration the dominant tunneling processes are $\Delta_5^{\uparrow}-\Delta_5^{\uparrow}$ in the majority and $\Delta_5^{\downarrow}-\Delta_5^{\downarrow}$ in the minority states. The minority-spin tunneling is facilitated due to strong hybridization of the Ti and the minority Fe interface states.[23] Evidence for this is the local DOS of the interface Ti (Fig. 2) and Fe (not shown) atoms, as well as the interface

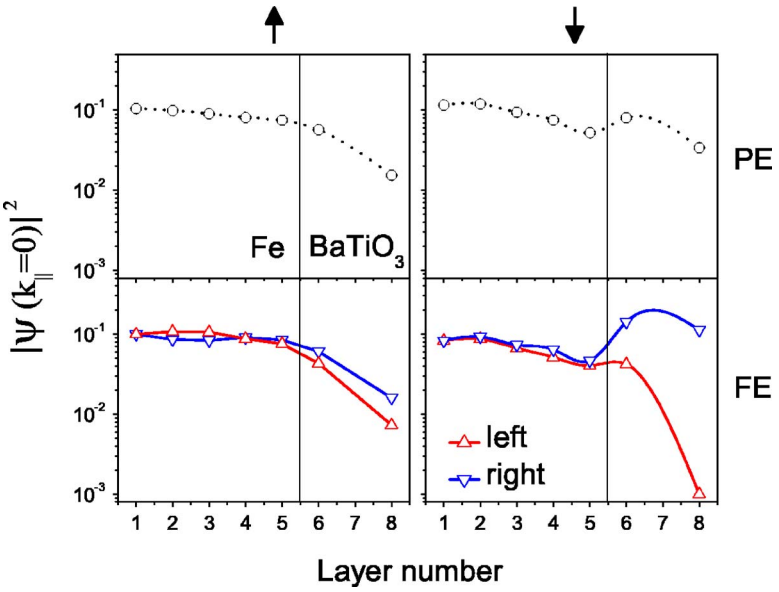

FIG. 3. (Color online) Majority-(left) and minority-spin (right) probability densities $|\psi|^2$ for the state at $\mathbf{k}_\parallel=0$ with the lowest decay rate (Δ_5) for paraelectric (top) and ferroelectric (bottom) states of a $Fe/BaTiO_3/Fe$ MFTJ at the Fermi energy. The results are obtained using VASP for a $m=4$ $BaTiO_3$ barrier layer. Within $BaTiO_3$ $|\psi|^2$ is displayed on Ti atoms.

dipole is clearly visible in the minority-spin probability density (Fig. 3). In the antiparallel configuration the dominant tunneling processes are $\Delta_5^{\uparrow}-\Delta_5^{\downarrow}$ and $\Delta_5^{\downarrow}-\Delta_5^{\uparrow}$ which are made inequivalent by the ferroelectric polarization. Ferroelectric displacements cause smaller changes in the interface transmission probability of the majority-spin electrons than that of the minority-spin electrons. This allows the $\Delta_5^{\uparrow}-\Delta_5^{\downarrow}$ process to have very high tunneling probability, comparable to that of the paraelectric case.

In conclusion, we predict that electric polarization of ferroelectric insulators used as barriers in tunnel junctions will generally lower the tunneling probability due to the reduction of the symmetry of the junction. However, the reduction affects differently the two spin channels in the parallel and antiparallel magnetization configurations. As a result, we find that polarization can significantly change the spin polarization of the current and invert the tunneling magnetoresistance. In addition, different spin transmission functions across interfaces with locally opposite ferroelectric polarization orientations indicate the possibility to use such a multiferroic tunnel junction as a four-state resistance device where the resistance depends both on magnetic and electric polarization orientations. These observations open interesting opportunities for electrically controlled spin polarization and magnetoresistance.

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