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Electric modulation of magnetization at the BaTiO$_3$/La$_{0.67}$Sr$_{0.33}$MnO$_3$ interfaces

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We report large (>10%) magnetization modulation by ferroelectric polarization reversal in the ferroelectric-ferromagnetic BaTiO$_3$/La$_{0.67}$Sr$_{0.33}$MnO$_3$ (BTO/LSMO) heterostructures. We find that the electrically induced change in magnetization is limited to the BTO/LSMO interface but extends about 3 nm deep into the LSMO layer—far beyond the expected screening length of metallic LSMO. It is suggested that this effect is due to a metal-insulator transition occurring at the BTO/LSMO interface as a result of electrostatic doping. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4726427]

While the possibility of a magnetoelectric effect was first mentioned by Pierre Curie in 1894 (Ref. 1) and predicted to exist in Cr$_2$O$_3$ in 1960, 2 until recently it was assumed that the external electric fields cannot significantly alter the properties of magnetic materials. The effect was considered simply too small for any practical applications. The experimental observation of electrical modulation of magnetization in III-V magnetic semiconductors 3 sparked a surge of activity in search of other materials exhibiting magnetoelectric coupling. Breakthrough possibilities have been offered with the recent advances in fundamental understanding and experimental studies of coexistence of ferroelectric and ferromagnetic ordering in multiferroic materials. 4, 5 As single-phase room-temperature multiferroics are rare in nature (with Cr$_2$O$_3$ as a noticeable exception 6), artificial multiferroic heterostructures made of ferroelectric and ferromagnetic phases have been extensively engineered and studied in search for large magnetoelectric coupling. 7–10 Among the most attractive materials for practical implementation of multiferroic heterostructures and fundamental studies of magnetoelectric coupling are the doped lanthanum manganites La$_{1-x}$A$_x$MnO$_3$, (A = Ca, Sr, or Ba). 11 These materials are characterized by a strong interplay between electron transport, magnetism, and crystal lattice distortions and a rich carrier-density-temperature phase diagram. A possibility of effective electrical modulation of carrier concentration and magnetic properties makes these materials extremely attractive for numerous applications in field-effect devices. 12 Modulation of carrier density in metallic manganite films can be realized by employing polarization ferroelectric materials as the gate electrodes. 13 The sensitivity of the magnetic state of manganites to electrical charge was predicted for BaTiO$_3$/La$_{1-x}$Sr$_x$MnO$_3$ (BTO/LSMO) interfaces 14 and experimentally explored using spin-dependent tunneling. 15 A number of theoretical and experimental studies 16–21 attributed magnetoelectric coupling to the interplay between changes in magnetization and accumulation/depletion states at the ferroelectric-ferromagnetic interfaces, which is fundamentally different from the coupling mechanism in single phase materials. 2

In this paper, we investigate modulation of magnetization by ferroelectric polarization reversal in ferroelectric-ferromagnetic BaTiO$_3$/La$_{0.67}$Sr$_{0.33}$MnO$_3$/SrTiO$_3$ (BTO/LSMO/STO) heterostructures as a function of the ferromagnetic layer thickness. We find that the effect is limited to the BTO/LSMO interface but extends up to about 3 nm into the LSMO layer beyond the expected screening length of metallic LSMO. It is suggested that the latter effect is due to a metal-insulator transition occurring at the BTO/LSMO interface as a result of electrostatic doping.

Pulsed laser deposition was used to grow atomically flat single-crystalline epitaxial BaTiO$_3$ films on TiO$_2$-terminated SrTiO$_3$ substrates with the La$_{0.67}$Sr$_{0.33}$MnO$_3$ films of variable thickness as bottom electrodes. It has been shown previously 22 that growing compressively strained BaTiO$_3$ films on SrTiO$_3$ substrates enhances the resulting polarization and aligns it normal to the surface. In our studies, thickness of BaTiO$_3$ was chosen to be 48 unit cells (~19 nm) to ensure stable and switchable polarization, and LSMO thickness varied in the range from 10 to 50 nm. Structural quality and ferroelectric properties of the grown heterostructures are very similar to those reported in our earlier studies. 23 The atomic force microscopy (AFM) topographic image of the surface morphology in Fig. 1(a) shows atomically flat terraces with one unit-cell high (~4 Å) steps indicating epitaxial structure of the BaTiO$_3$ films. Details on sample preparation can be found elsewhere. 22

A commercial AFM system (MFP-3D, Asylum Research) was used for piezoresponse force microscopy (PFM) testing of polarization state in the BaTiO$_3$ layers. Pt-coated conductive cantilevers (DPER18/Pt, Mikromasch) were employed for polarization imaging at a frequency of about 300 kHz in the resonance-enhanced PFM mode. Superconductivity quantum interference device (SQUID) magnetometer (MPMS, Quantum Design) and Kerr microscope based on longitudinal magneto-optical Kerr effect (MOKE) have been used to measure magnetization of LSMO films.
MOKE measurements have been performed by focusing the green ($\lambda = 532$ nm) laser beam to the spot of less than 100 $\mu$m indiameter on the BaTiO$_3$ surface.

Investigation of magnetic response by means of SQUID requires large-scale sample area poling (about several mm$^2$), which is difficult to accomplish if the ferroelectric film does not have a top electrode (for comparison, an AFM with a conductive probe can only pole an area of up to 150 $\times$ 150 $\mu$m$^2$ which might also take up to an hour of scanning). To overcome this problem, we have employed macroscopic non-contact probe poling technique. A Pt needle with the 20-$\mu$m-apex-curvature-radius held at a distance of about 100 $\mu$m above the BTO film surface and electrically biased at $\pm$800 V scanned the whole sample area in high vacuum conditions. The step increment during scanning was 50 $\mu$m. (c) PFM phase image of the polydomain structure of the as-grown BTO film. (d) PFM phase image of the uniformly polarized BTO film after noncontact poling. (e), (f) PFM amplitude (e) and phase (f) images showing comparison between the macroscopic non-contact poling and poling by PFM. Central 2 $\times$ 2 $\mu$m$^2$ and 0.5 $\times$ 0.5 $\mu$m$^2$ squares have been produced by scanning with an AFM tip under $\pm$4 V/$\pm$4 V dc bias in contact mode, while an outer region shows the result of macroscopic non-contact poling. Saturated polarization has been obtained for both poling methods. Scan size is the same for all AFM/PFM images.

Figures 1(c) and 1(d) show 3 $\times$ 3 $\mu$m$^2$ PFM phase images of the BTO film before and after noncontact poling demonstrating that the polarization had been effectively switched from as-grown polydomain state to a single domain state. Figures 1(e) and 1(f) show a comparison of the poling results by the macroscopic non-contact method and by PFM (in PFM, the BTO film has been poled by scanning the surface in contact with the PFM probe under a $\pm$4 V dc bias). It can be seen that both poling methods result in fully switched single-domain polarization states.

SQUID measurements of the BTO/LSMO/STO heterostructures have been performed for both BTO polarization directions after verification of the results of large-scale non-contact poling by PFM. Cycles of the BTO films poling followed by the SQUID measurement have been carried out several times to ensure that magnetic response of the LSMO layer is reproducible and not affected by possible artifacts, such as sample misalignment. Typical in-plane magnetization curves of LSMO acquired at room temperature for two antiparallel polarization states of the BTO film are shown in Fig. 2(a). It is seen that polarization reversal in BTO leads to a sizable change in the magnetic moment of the adjacent LSMO layer. For all studied samples, the magnetic moment of LSMO decreases as the BTO film is electrically switched from the upward (away from the substrate) to downward (toward the substrate) polarization state.

To substantiate the results obtained by SQUID, additional measurements by local MOKE measurements have been performed using the same samples. Ferroelectric poling of two regions of approximately 100 $\times$ 100 $\mu$m$^2$ of the BTO film have been carried out using a conductive PFM probe in contact with the surface by applying a dc bias of $\pm$5 V, followed by MOKE measurements of in-plane magnetization (using surface topographic markers the laser spot was focused on exactly the same regions where polarization reversal had been performed). The results in Fig. 2(b) indicate the same trend as those in Fig. 2(a): LSMO magnetization decreases when the polarization in the BTO layer is switched from the upward to downward direction.

Further, we studied the relative change in saturated magnetization, $\Delta M = (M(P_{up}) - M(P_{down}))/M(P_{down})$, as a function of LSMO thickness (Fig. 2(c)). It should be mentioned that both upward and downward polarization states in the BTO film were found to be stable for the 25- and 50-nm-thick LSMO layers, while for the 10-nm-thick LSMO layer, only upward polarization was found to be stable. Attempts to switch the BTO film downward in this case resulted in formation of the polydomain structure with the $P_{down}/P_{up}$ ratio of approximately 1/2 (most likely due to spontaneous back-switching). This effectively means that only 1/3 of the total downward polarization state had contributed to the
magnetization change. By taking into account this correction, which reflects non-complete downward poling, the resulting relative magnetization change $\Delta M$ was estimated to be about 27% (without this correction the measured $\Delta M$ value was $\sim$9%).

Figure 2(d) shows a temperature dependence of saturated magnetization in the BTO/LSMO(25 nm)/STO heterostructure measured at a constant magnetic field 2500 Oe. No noticeable change in the Curie temperature with polarization reversal has been observed. The temperature dependence of $\Delta M$ (see the inset in Fig. 2(d)) shows that the polarization-induced change in magnetization peaks in the vicinity of the Curie temperature and decreases as temperature decreases.

Data in Fig. 2(c) show that the relative change in magnetization $\Delta M$ becomes more pronounced as the LSMO thickness decreases. The thickness dependence of $\Delta M$ can be fitted well to the $t_m/t$ function, where $t$ is the LSMO layer thickness and $t_m$ is the fitting parameter. This suggests an interface mechanism behind the observed magnetization modulation by polarization reversal, i.e., that the magnetization change in LSMO is limited to a thin layer at the BTO/LSMO interface. The fit allows us to estimate the effective layer thickness at the BTO/LSMO interface where the magnetization change occurs. Assuming that within this layer the reversal of ferroelectric polarization completely destroys magnetism, we can interpret $t_m$ as the thickness of this layer. From the fit we find that $t_m$ is approximately 2.9 nm.

The observed effect is in qualitative agreement with our first-principles calculations performed using the plane-wave pseudopotential method. Reversal of the ferroelectric polarization leads to a change in the accumulation/depletion charge built up on the LSMO side of the interface. We find that all of the electronic screening is limited to an accumulation/depletion of majority spin electrons, which leads to a significant change in magnetic moment near the interface. In bulk, $La_{0.67}Sr_{0.33}MnO_3$ has a magnetization of $3.67 \mu_B$/Mn, whereas the average Mn moment varies significantly in the first 2–3 unit-cells near the interface with BTO, depending on the polarization orientation. For the BTO polarization pointing towards the BTO/LSMO the interface, for example, the magnetic moments on the Mn sites are essentially the same as they are in the bulk, leading to a near complete absence of electronic screening. On the other hand, for the BTO polarization pointing away from this interface, the negative surface polarization charge from the BTO leads to a significant depletion of majority spin electrons in the first 2–3 unit-cells of LSMO: the first Mn layer at the interface is reduced by $\sim$0.45 $\mu_B$, the second is reduced by $\sim$0.2 $\mu_B$, and the third is reduced by $\sim$0.05 $\mu_B$. This corresponds to an effective penetration depth of the magnetoelectric response on the order of 0.8–1.2 nm in our zero temperature calculations, which in qualitative agreement with our experimental results.

Quantitatively, however, the experimentally observed magnetoelectric effect is significantly larger in magnitude than that predicted theoretically. Also, the thickness of the ferroelectrically modulated magnetic layer estimated from the experimental data is much larger than theoretically predicted ($\sim$3 nm versus $\sim$1 nm, respectively), which cannot be explained solely within the model assuming uniform and constant metallicity of LSMO at the BTO/LSMO interface. Below, we propose a qualitative model, which explains our experimental data based on the metal-insulator transition at the LSMO interface induced by the ferroelectric polarization.
The screening charge at the ferroelectric-manganite interface produces carrier depletion or accumulation in LSMO near the interface, analogous with chemical doping. Since $x$ in the La$_{1-x}$Sr$_x$MnO$_3$ chemical formula reflects the substitution of trivalent La with divalent Sr and is an effective measure of holes concentration, we can consider the effect of electric field as a corresponding shift in the LSMO phase diagram\(^1\) (Fig. 3(a)) to the right, if a negative polarization charge is to be screened, or to the left, if positive polarization charge is to be screened, relative to the starting point of $x = 0.33$. It can be seen from the diagram that while the rightward shift keeps the LSMO layer in the metallic state, the leftward shift can lead to a metal-insulator transition. The presence of the metal-insulator transition occurring locally, within the screening length at the LSMO interface, would inevitably move the screening region deeper into the bulk LSMO (Fig. 3(b)). For example, assuming that the strained BTO has the polarization of 48 $\mu C/cm^2$, and all the screening charge is accumulated within 2.5 unit cells of LSMO (as in our theoretical calculations), the total doping (both chemical and electrostatic) within the screening region becomes $x \approx 0.13$, which lies deep in the paramagnetic insulator region at room temperature in the phase diagram of LSMO (Fig. 3(a)). This suggests that the screening region expands beyond that found for the metallic phase of LSMO (Fig. 3(b)). This effect is expected to be more pronounced in the vicinity of $T_C$, where the difference in free energy between the metal and insulating states for the LSMO film is minimal.

In order to correlate our experimental results with the phase diagram of LSMO, we have calculated the occurrence of the metal-insulator phase transition based on our experimental data for the polarization-induced change in magnetization shown in the inset of Fig. 2(d). Assuming as before that within the layer of thickness $t_m$ ferroelectric polarization reversal completely destroys magnetism, we can calculate $t_m$ as a function of temperature (Fig. 3(c)). Using this temperature dependence and known values of the polarization charge for BTO we can find the phase boundary between the metal and insulator regions in the phase diagram simply by estimating the amount of doping level in the layer of thickness $t_m$ as a function of temperature. The estimated equivalent changes in the holes concentrations (change in $x$) that are required to accommodate all the polarization charge are shown in Fig. 3(a) for two BaTiO$_3$ polarization values: experimentally measured\(^2\) value of 35 $\mu C/cm^2$ and predicted in our first-principles calculations value of 48 $\mu C/cm^2$. There is a clear correlation between the bulk phase diagram of LSMO and the predicted metal-insulator phase boundaries.

In summary, we have observed large (>10%) room-temperature electrical modulation of magnetization in ferroelectric/ferromagnetic BaTiO$_3$/La$_{0.67}$Sr$_{0.33}$MnO$_3$/SrTiO$_3$ heterostructures induced by polarization reversal in BaTiO$_3$. The relative magnetization change is inversely proportional to the LSMO layer thickness, indicating that the effect is limited to a thin (~3 nm) LSMO layer at the BTO/LSMO interface. The thickness of this layer and the magnitude of magnetization change are significantly larger than those predicted by first-principle calculations at zero temperature. The experimental data can be qualitatively explained using a model based on a polarization-induced metal-insulator transition in the LSMO layer near the interface.

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