Electric Field Effect in Diluted Magnetic Insulator Anatase Co: TiO$_2$

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An external electric field induced reversible modulation of a room temperature magnetic moment and coercive field is achieved in an epitaxial and insulating thin film of dilutely cobalt-doped anatase TiO$_2$. This first demonstration of an electric field effect in any oxide-based diluted ferromagnet is realized in a high quality epitaxial heterostructure of PbZr$_{0.2}$Ti$_{0.8}$O$_3$/Co: TiO$_2$/SrRuO$_3$ grown on (001) LaAlO$_3$. The observed effect, which is about 15% in strength in a given heterostructure, can be modulated over several cycles. Possible mechanisms for electric field induced modulation of insulating ferromagnetism are discussed.

The rapidly developing field of spin electronics embodies the notion of the synergetic and multifunctional use of charge and spin dynamics of electrons, aiming to transcend the traditional dichotomy of semiconductor electronics and magnetic storage technology [1]. Such new functionalities require new materials encompassing both semiconducting and magnetic properties. An important approach to the development of such materials is to examine the possibility of magnetizing a functional nonmagnetic host by dilute magnetic-impurity doping which allows the host to retain its other desirable properties [2]. Such materials, classified as diluted magnetic semiconductors (DMS), have been reported in III-V and group IV semiconductors [3–5], and in oxide hosts [6–11]. Unfortunately, possibilities of extrinsic effects such as dopant clustering, impurity magnetic phases, etc. have been noted in some cases under certain growth conditions [7,11–14].

It is generally suggested that any new material must satisfy three specific tests to qualify as an intrinsic (carrier-induced, uniformly dispersed dopants) diluted ferromagnetic system: observation of (a) the anomalous Hall effect (AHE) [15,16], (b) optical magnetic circular dichroism (O-MCD) [17,18], and (c) electric field induced modulation of magnetization [19,20]. We have recently shown that observation of AHE, although desirable, is not really a strict test and can be realized even in a sample with non-percolating magnetic clusters [14,21]. The O-MCD test has been demonstrated in different systems including some oxide-based materials [17,18,22]. The electric field modulation, which in some sense is the most stringent test of intrinsic ferromagnetism, has, however, been demonstrated only in III-V DMS systems [19,20], but not yet in any oxide-DMS materials. In this Letter we report the first successful implementation of an external electric field modulation of ferromagnetism in DMS anatase Co: TiO$_2$, grown under conditions suggested to yield uniform matrix incorporation of cobalt. We should, however, like to point out that the corresponding material is insulating in nature.

The sample structure employed in this study is shown in the inset in Fig. 1. The basic methods of growing and testing such heterostructure devices are similar to those used in our previous studies on manganites [23–26]. A bottom electrode layer SrRuO$_3$ (SRO), a DMS anatase Co: TiO$_2$ (CTO) layer (7 at. % Co), and a ferroelectric PbZr$_{0.2}$Ti$_{0.8}$O$_3$ (PZT) layer were grown on LaAlO$_3$ (LAO) substrate by pulsed laser deposition (PLD). The temperature and oxygen pressure during growth were 650 °C and 10^{-1} Torr for SRO and PZT, and 875 °C and 3 × 10^{-5} Torr for CTO , respectively. The choice of high temperature for growth of the CTO layer was guided by the work of Shinde *et al.* [7] in which it was found that a 900 °C annealing of a 700 °C-grown sample led to a cluster free lattice incorporation of cobalt, as confirmed by several techniques [27]. A top Pt layer was deposited by PLD as well. A 200 μm × 200 μm electrode size and a 50% coverage of the surface were achieved by standard photolithography and lift-off process.
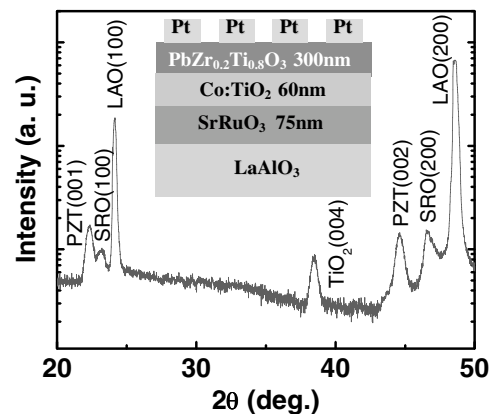

FIG. 1. X-ray diffraction θ-2θ scan of the deposited PZT/CTO/SRO/LAO multilayers. The inset is the schematic structure of the sample.

From the x-ray diffraction (XRD) θ-2θ scan shown in Fig. 1, all the SRO, CTO, and PZT films are (00l) oriented without any impurity phases. The in-plane epitaxy of all these layers was confirmed by four 90 °-separated peaks in a XRD Φ scan measurement. TEM images in Fig. 2 show good crystallinity, no interdiffusion between the PZT and CTO, and between the CTO and SRO layers, and no obvious signature of Co clustering in the CTO layer. A Rutherford backscattering (RBS) measurement further confirmed the composition for every layer and the clean interfaces between them. We note that magnetic force microscopy images for the films were mostly featureless with weak domainlike contrast, possibly due to net weak magnetization. Occasional nanometer scale local dipole signatures could be seen, which could arise due to surface topology defects or a local $CoTiO_3$ type magnetic phase [28]. If we liberally calculate the concentration of such defects and attribute them entirely to such magnetic complexes [27], it still leads to $\sim 4\%$ cobalt dispersed uniformly in the matrix.

Ferroelectricity in the PZT layer was characterized using a Radiant Technology RT-6000 system. Low frequency (16 kHz) ferroelectric hysteresis measurements show a clear hysteresis loop as shown in the upper panel of the inset in Fig. 3(a) indicating the high quality of the PZT film. To measure the ferroelectric field effect on the CTO magnetization, an electric voltage pulse (1 ms) was applied to the PZT layer through the top and bottom electrodes. The magnetization of the CTO layer was measured by SQUID magnetometry at room temperature after the electrical poling of all the top electrodes. During the magnetization measurement, the electrical voltage was turned off.

Figure 3(a) shows the magnetic hysteresis loops of the CTO layer measured after PZT poling. After poling of the PZT with a positive voltage, the loop showed a saturation magnetization (M_S) of about 100 μemu [squares in Fig. 3(a)]. Then the PZT was negatively poled and M_S was measured again. It was seen to drop to about 85 μemu [up triangles in Fig. 3(a)]. After the PZT was plus poled again, M_S went back to its initial value of $\sim$100 μemu [down triangles in Fig. 3(a)]. After a second negative poling, M_S dropped again to $\sim$87 μemu [circles in
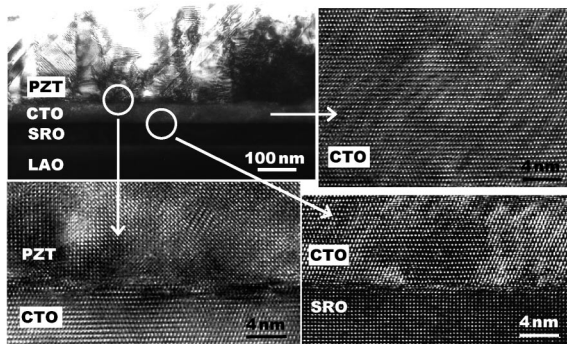
Fig. 3(a)]. The M_S value as a function of applied voltage is plotted in the lower inset in Fig. 3(a). It is very clear that the M_S of CTO can be switched with a difference of about 15% by switching the polarization states of PZT. In Fig. 3(b) we show the data of Fig. 3(a) on an expanded H scale to bring out two significant points: (a) the loops are ferromagnetic with well-defined coercivity (H_C) and remanence values, and (b) the H_C is also modulated reversibly with positive and negative poling. In fact, the modulation is as large as 40%. A similar magnetization modulation behavior was also measured on a PZT/CTO sample on a conducting Nb: $SrTiO_3$ substrate, indicating that the observed effect is robust and reproducible.

The magnetization of the CTO film was also measured as a function of temperature as shown in Fig. 4. The circles and up triangles represent the data measured after a positive and a negative poling, respectively. On the right axis (the squares) we show the percent modulation. The modulation is seen to be $\sim$13.5% at $H = 1300$ Oe (consistent with room temperature data) and is seen to drop gradually with temperature down to $\sim$9% at 170 K, as expected due to stiffening of the magnetic order. As ferromagnetism sets in the SRO layer ($T_c \sim 160$ K), the modulation shows a sudden drop to $\sim$4.5% followed by a gradual decrease as the temperature is lowered further. The drop near 160 K can be attributed to the ferromagnetic coupling between
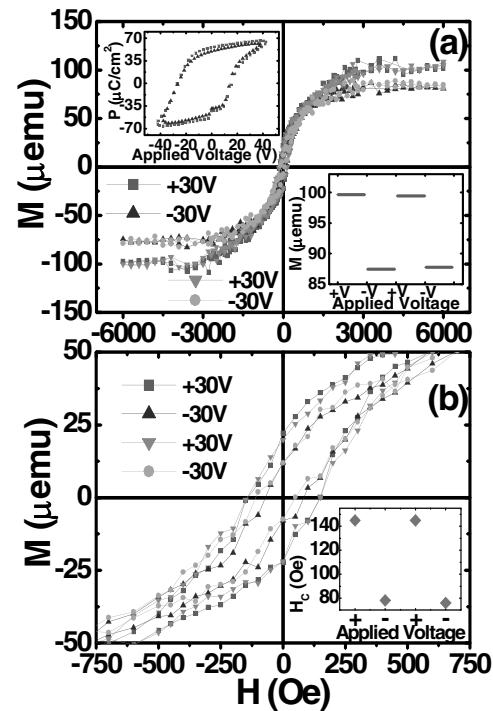
FIG. 2.　Transmission electron microscopy images of the PZT/CTO/SRO/LAO sample.

FIG. 3.　Magnetic hysteresis loops of the CTO layer after several electric voltage poling on the PZT layer in a smaller (a) and a larger (b) H scale. The upper panel of the inset in (a) shows the ferroelectric hysteresis loops of the PZT layer, while the lower panel is the saturation magnetization of CTO as a function of the applied voltage on PZT. The inset in (b) is the coercive field of CTO as a function of the applied voltage on PZT.
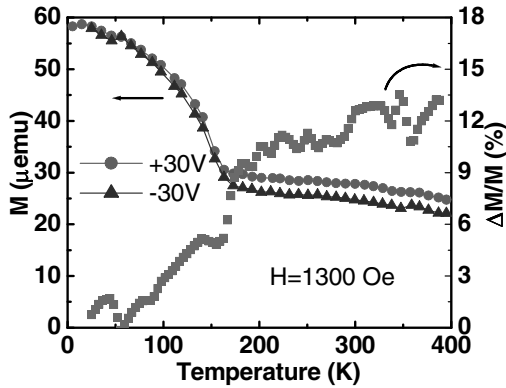
FIG. 4.   Temperature dependence of magnetization of the CTO layer measured under a magnetic field of 1300 Oe after positive and negative poling on PZT (left axis) and the percentage difference between them (right axis).

the CTO and SRO layers through their interface, decreasing the ease of electric field modulation of the CTO magnetization.

When the PZT is positively poled, its polarization points down, inducing electron accumulation in the CTO layer towards the interface, while negative poling has an opposite effect on the distribution. In the presence of two interfaces for the CTO channel (PZT/CTO and CTO/SRO) and a long electric field penetration depth in insulating CTO, the quantitative aspects of the effective degree of charge modulation/injection/depletion will be controlled by the corresponding band offsets. Also, within the possible polaronic picture of ferromagnetism discussed later, factors such as polaronic redistribution and ionization under the applied electric field may be relevant. It is important to recognize here that although the CTO/SRO interface is in play here electronically, at room temperature SRO is not ferromagnetic, and hence the observed room temperature magnetic modulation effects originate in CTO. Our *experimental finding* of a direct influence of the electric field modulation on M_S as well as H_C strongly favors an intrinsic nature of this DMS system.

Given the lattice parameters of anatase TiO_2 of $a = b = 3.782$ Å and $c = 9.514$ Å (2 molecules/cell), one has $\sim 8.8 \times 10^{16}$ TiO_2 molecules in the 600 Å $\times$ 1 cm $\times$ 1 cm volume of the film. This yields $\sim 6 \times 10^{15}$ Co atoms in this volume. Replacing Ti^{4+} with Co^{2+} will accommodate one oxygen vacancy in the proximity for local charge neutrality. This impurity-defect complex could serve as a weakly attractive site for the carriers, presumably facilitating an exchange mechanism of ferromagnetism as discussed later. The polarization charge obtained from the inset of Fig. 3 is ~ 60 $\mu C/cm^2$, which corresponds to a surface density of $\sim 3.5 \times 10^{14}$ charges/cm^2. Given the insulating nature of the sample and assuming that none of these charges are compensated by interface states or traps, this represents an upper limit on the areal density of the induced or depleted number of carriers in the film. In order to make a quantitative estimate of the expected

modulation of ferromagnetism, one needs information such as the density of localized carriers, the precise fraction of uniformly dispersed and ionized cobalt, the valence state(s) of cobalt ions, oxygen vacancy concentration, etc., which is unavailable at this time. A typical value of carrier density of $\sim 10^{20}/cm^3$ corresponds to an areal density of $\sim 6 \times 10^{14}/cm^2$ in our 600 Å film. Clearly, an induced or depleted density of $\sim 10^{14}$ charges/cm^2 can lead to a significant modulation of ferromagnetism, as observed, especially in a percolative ferromagnet as discussed below. Large electric field modulation has been demonstrated in percolative manganite systems [25,26,29].

Given the highly insulating nature of the samples, no itinerant electron based picture is feasible, and therefore the RKKY-type scenario discussed extensively in the context of GaMnAs magnetization [19,20] simply does not apply here. Other physical pictures which could conform naturally to the attendant insulating magnetic state may thus be relevant. These include the bound magnetic polaron (BMP) percolation picture [30] discussed in the context of strongly insulating DMS materials, and the defect (*F*-center) state percolation model discussed by Coey *et al.* [31]. We suggest that the two mechanisms come together in giving rise to the ferromagnetic ordering in Co: TiO_2. In particular, the *F*-center defects may very well be the bound magnetic polarons, which eventually form a percolating cluster producing global ferromagnetism as discussed in Ref. [30]. The local ferromagnetism (i.e., the BMP) here is envisioned to be due to the *F*-center exchange (FCE) facilitated by the electron trapped in an oxygen vacancy. The diameter of the *F*-center carrier wave function is dependent upon the dielectric constant of the host and is between 1–2 nm for high dielectric constant materials such as TiO_2 or SnO_2. Overlap of the *d*-shell orbitals of the magnetic dopant with the perturbation orbital is then suggested to lead to a *cooperative percolative ordering* of such magnetic ions even in the absence of (mediating) itinerant carriers. It is useful to point out here that the vacancy defects may themselves be susceptible to electric field induced reorganization [32].

In the polaron percolation picture [30], each local magnetic moment (the local moment bound to carriers) is the effective magnetic polaron (here, it is just the FCE) and the whole system is a collection of a random distribution of these polarons. At T_c, the bound magnetic polarons form a percolating path leading to global ferromagnetism. (The magnetic percolation does not imply transport percolation since each polaron is strongly localized.) Subjecting such a system to strong external electric field could lead to electric dipolar distortion of the magnetic polaron with attendant distortion of the shape of the corresponding wave function and field driven redistribution effects. The corresponding changes in the local exchange energy and the global geometry of the percolation network should then influence the magnetic moment and coercivity of such a system. A complete theory, taking into account the actual FCE size as the BMP and their eventual coalescence

through percolation is beyond the scope of this experimental Letter.

In conclusion, we have demonstrated for the first time a reversible external electric field induced modulation of room temperature magnetic moment as well as a coercive field in an oxide-based diluted magnetic semiconductor. A strong modulation of $\sim 15\%$ is realized in a high quality epitaxial heterostructure of $PbZr_{0.2}Ti_{0.8}O_3/$ Co: $TiO_2/SrRuO_3$ grown on (001) $LaAlO_3$. Observation of electric field effect strongly favors the intrinsic (i.e., carrier-induced) nature of ferromagnetism in the high temperature grown insulating Co: TiO_2 films. Our finding is also the first report of field effect on ferromagnetism in an *insulating* diluted magnetic system.

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