Room-temperature ferromagnetism in the Co-doped Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ thin films

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The authors report the room-temperature ferromagnetism in the epitaxial thin films of 3% Co-doped Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (CBSTO) grown by pulsed laser deposition. These films show the single phase character with Co dopants in the +2 state. More interestingly, ferromagnetic and ferroelectric transitions were observed at 570 and 150 K, respectively. The CBSTO films also show the exchange bias effect manifested by the negative shift and training effect of the hysteresis loops at 5 K. This work demonstrates that ferromagnetism can be induced in the ferroelectric materials, which is significant for shedding light on the mechanism of dopant induced ferromagnetism in insulators and applications. © 2008 American Institute of Physics. [DOI: 10.1063/1.2945282]

Multiferroic materials that exhibit simultaneous ferroelectric and ferromagnetic ordering are of great interest, both in the fundamental concepts and potential applications.\(^1\) However, the coexistence of strong ferromagnetism (FM) and ferroelectrics is rarely satisfied in a single phase compound, which has been a great challenge in this field. Recently, the researches of dilute magnetic semiconductor (DMS) have demonstrated that substitution of magnetic ions can dramatically alter the electronic and magnetic properties of the semiconductors.\(^2\) Especially, room-temperature FM was reported in several oxides doped with magnetic ions,\(^3–6\) indicating the possibility of FM in the magnetic ion doped ferroelectric materials. In this letter, we have fabricated epitaxial thin films of Co-doped Ba$_{0.5}$Sr$_{0.5}$Ti$_{0.97}$Co$_{0.03}$O$_3$ (CBSTO) and performed investigations on their structure, magnetic properties, and ferroelectric properties. The selection of ferroelectric BSTO is guided by its important applications in the tunable microwave devices and dynamic random access memories.\(^7,8\)

A target with a nominal composition of Ba$_{0.5}$Sr$_{0.5}$Ti$_{0.97}$Co$_{0.03}$O$_3$ was prepared by the solid-state reaction method from BaCO$_3$, SrCO$_3$, TiO$_2$, and Co$_3$O$_4$ with 99.999% purity. The CBSTO films with about 155 nm thickness were grown on the (001)-oriented SrTiO$_3$ (STO) substrates by pulsed laser deposition using a KrF excimer laser (\(\lambda=248\) nm). The deposition temperature was 770 °C and the oxygen partial pressure was 35 Pa for deposition and 0.8 atm for cooling down. A Rigaku x-ray diffractometer and a Tecnai-F20 (200 kV) transmission electron microscope (TEM) were used for the structure analysis. X-ray-absorption near-edge spectrum (XANES) of the Co K-edge was measured at the U7C (XAFS) end station of NSRL to determine the oxidation state of the Co dopants in the BSTO lattice. Magnetic measurements were carried out on a Quantum Design MPMS XL7. For the permittivity measurement using a LCR meter, the CBSTO films with thickness about 300 nm were grown on 1 wt % Nb-doped STO substrates (bottom electrode). Au was used as the top electrode. Ferroelectric hysteresis of CBSTO film was also measured by using a Radiant Premier II. For comparisons, the undoped BSTO films were also grown under the same conditions.

Figure 1(a) is the XRD pattern of a typical CBSTO film, indicating a single phase character and (001)-oriented growth of the film. In order to directly reveal the microstructure...
features of the CBSTO films, we have performed a TEM observation on a well-characterized sample. Figure 1(b) shows the TEM images obtained from a cross-sectional CBSTO/STO specimen. The lattice mismatch between CBSTO and STO is relatively small (~1.4%). Therefore, no visible spot splitting is observed in the diffraction pattern. The interface between the film and substrate is clean without visible interdiffusion between CBSTO and STO. The high quality of the epitaxially grown CBSTO film and sharp interface are also recognizable in the high-resolution TEM image. Our careful examinations in both the CBSTO film and the interfacial region demonstrate that no second-phase particles or Co nanoclusters exist in our sample.

As the oxidation state and local environment of the Co dopants play a crucial role in the magnetism of DMS, we performed the XANES investigations on the CBSTO films and referenced samples containing Co. Figure 2 shows that the Co K-edge absorption of CBSTO has a close match to that of CoO, in which Co has an oxidation state of +2. In contrast, the onset and the shape of the absorption spectra for CBSTO are quite different from that of Co metal. So the Co dopants are expected to be in the +2 state in CBSTO, and the local environments of the dopants are similar to that of CoO.

Figure 3(a) is the $M(H)$ curve of the CBSTO film on STO at 300 K, which shows a remarkable hysteresis suggesting the room-temperature FM. In contrast, the undoped BSTO film on STO [Fig. 3(b)] exhibits only diamagnetism at 300 K. So Co doping should be responsible for the observed FM in the CBSTO film. Figure 3(c) displays $M(H)$ curves of the CBSTO film at 300 and 10 K, respectively, after subtracting the background contribution. The saturation moment per Co ion ($\mu_s$) increases from 1.07 $\mu_B$ at 300 K to 1.27 $\mu_B$ at 10 K, while the coercivity ($H_c$) increases from 140 Oe at 300 K to 270 Oe at 10 K. The magnetization [Fig. 3(d)] decreases with increasing temperature, and shows a sharp drop at about 570 K, indicating a ferromagnetic transition. In order to investigate the possible magnetic coupling within the CBSTO film, we measured the magnetic loops after zero-field cooled (ZFC) and field cooled (FC) processes. Figure 3(e) shows the loops of the CBSTO film at 5 K after cooling under a 400 Oe and ZF, respectively. The FC loop displays a negative shift with respect to the cooling field, while the ZFC loop does not. In addition, the magnitude of the negative shift decreases when the measurements of magnetic loop are repeated. Such a negative shift is the hallmark of exchange bias (EB) effect, and the corresponding decrease in the shift through consecutive field cycling is the training effect. The EB field of the CBSTO film, defined as the shift of the gravity center along the field axis, is 29 Oe at 5 K. It is noted that EB was found in the Cr-doped GaN thin film (FM) with an antiferromagnetic (AFM) MnO overlay, but not within a single-phase diluted magnetic compound. The EB effect in CBSTO film suggests that FM regions coexist with AFM regions or spin glass regions.

To study the change in ferroelectric transition temperature ($T_{FE}$) of CBSTO films due to Co doping, we performed the permittivity measurement, which has been widely used in determining the $T_{FE}$. Figure 4(a) is the permittivity ($\varepsilon_r$-$T$) for the CBSTO and BSTO thin film capacitors respectively. For the BSTO film, $\varepsilon_r$ (100 kHz) shows a maximum at about 200 K, indicating a ferroelectric transition around it. In contrast, the $\varepsilon_r$ peak of the CBSTO film with 100 kHz is 50 K lower, indicating a decrease in $T_{FE}$ due to Co doping. The ferroelectric hysteresis loops of the CBSTO film are

![Figure 2](Color online) Co K-edge XANES spectra for CBSTO film with reference samples: Co metal and CoO.

![Figure 3](Color online) A comparison of $M(H)$ curves of the CBSTO/STO sample (a) and BSTO/STO sample (b) measured at 300 K. (c) $M(H)$ curves of the CBSTO film at 300 and 10 K, respectively. (d) Magnetization ($M$-$T$) measured at 20 Oe. (e) Hysteresis loops of the CBSTO film at 5 K after ZFC and FC processes. The enlarged view of loops for ZFC and FC processes (upper inset) and the first and the fifth field cycles after FC process (lower inset) were also shown.
shown in Fig. 4(b), indicating ferroelectricity of the film. As the ferroelectric transition of Ba$_{1-x}$Sr$_x$TiO$_3$ system accompanies a cubic-to-tetragonal structure transition, the decrease in $T_{FE}$ reveals that Co doping increases the stability of the cubic structure. Ihrig systematically studied $T_{FE}$ of polycrystalline BaTiO$_3$ doped with the 3$d$ elements, and demonstrated the important role of the oxygen vacancies in determining the phase stability. In CBSTO film, the Co ions substituted at Ti$^{4+}$ site are in the Co$^{2+}$ state, which tends to generate oxygen vacancies and internal dipole required by charge neutrality. Such oxygen vacancies are expected to make the cubic structure favorable in energy. Thus $T_{FE}$ shifts to lower temperatures.

It can be concluded that the CBSTO film exhibits ferromagnetic and ferroelectric transitions at about 570 and 150 K, respectively. Careful TEM and XANES investigations have ruled out the possibility of Co metal nanocluster formations, suggesting the intrinsic FM of the film. As $\mu_s$ of the CBSTO film is obviously smaller than 1.72 $\mu_B$ ($S=1/2$) even at 10 K, only some proportions of the doped Co ions make direct contributions. Recently, Coey et al. proposed that the bound magnetic polarons (BMP) formed by shallow donor electrons are expected to overlap to generate FM in DMS. In this model, the magnetism of DMS depends on the cation and donor polaron concentration, and the local magnetic structure is related to the distributions of the magnetic polarons. In the CBSTO film, the oxygen vacancies tend to appear in proximity to Co ions to keep charge neutrality, leading to the formation of BMP. With a proper polaron concentration, the neighboring BMPs are likely to overlap and interact to create global FM. Meanwhile, other regions containing Co ions may be AFM, spin glass, or paramagnetic in certain conditions. Thus, EB in CBSTO film can be interpreted as the consequences of the interactions of FM regions with the AFM (or spin glass) regions. Recently, it was reported that FM of (Zn,Cr)Te is dominated by the formations of Cr-rich metallic nanocrystals. However, such dopant-rich nanocrystal was not observed in the CBSTO film during the TEM study. Very recently, Lin et al. reported the ferromagnetic behavior of 5% cobalt doped BaTiO$_3$ thin film with Co$_{17}^{15}$ oxidation state, but no study on the ferroelectricity or the EB effect was performed.

In summary, high quality epitaxial CBSTO thin films have been fabricated by pulsed laser deposition. The films exhibit ferromagnetic transition at 570 K and ferroelectric transition at about 150 K. The mechanisms of Co doping induced FM and the EB are discussed in terms of the bound magnetic polarons and magnetic inhomogeneity. This work could be helpful for shedding light on the mechanism of dopant induced ferromagnetism in insulators and exploring multiferroics via doping of ferroelectric compounds.

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