Rectifying property and magnetocapacitance in multiferroic *p-n* junction

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Multiferroic *p-n* junctions were fabricated by growing $La_{0.1}Bi_{0.9}MnO_3$ films on Nb–$SrTiO_3$ using pulsed laser deposition. The current-voltage curves of the junction show good rectifying property. Both the ferroelectric transition and ferromagnetic transition of $La_{0.1}Bi_{0.9}MnO_3$ have remarkable influence on the transport properties of the junction. A large positive magnetocapacitance was also observed in this junction. Analysis suggests that the property of $La_{0.1}Bi_{0.9}MnO_3$/Nb–$SrTiO_3$ is dominated by the property of $La_{0.1}Bi_{0.9}MnO_3$. This work demonstrates that multiferroic *p-n* junctions possess some interesting properties that may be useful for future applications. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2883942]

Multiferroic materials, which possess two or three of the ferroic orders, ferroelectric, (anti)ferromagnetic, and ferroelastic, in a single phase[1–3] have attracted much attention in recent years because of their intriguing physics and potential applications.[2,3] Although a lot of work has been done on multiferroic materials, the research of *p-n* junctions consisting of multiferroic materials was rather limited until now. *p-n* junctions have been widely used as the basic elements in various semiconductor devices. The study of transition metal oxide based *p-n* junctions is also a hot topic in recent years due to their interesting physics and remarkable tunability by different means.[4] Multiferroic materials are very unique, considering their multiferroic nature and the coupling among different orders. Thus, it is interesting to explore the fabrication of *p-n* junctions composed of multiferroic materials and the behavior of the junctions that originates from the multiferrocity. This will give some input to the physics of *p-n* junctions as well as the potential applications.

As an interesting multiferroic material, $BiMnO_3$ (BMO) exhibits both ferroelectricity and ferromagnetism, which is rare in multiferroic materials.[5,6] There have been some reports on the properties of BMO thin films, such as ferroelectricity,[6] magnetism,[7] and nonlinear optical response.[8] It has been shown that La-doped BMO films are more easily fabricated than the parent BMO,[9] and that La doping reduces the ferroelectric transition temperature of BMO from 750–770 K to around 150 K.[10] A large positive magnetodielectric effect was also observed in $La_{0.2}Bi_{0.8}MnO_3$ thin films.[10] It was reported that Bi is easily volatile,[11] leading to Bi deficiency in the samples. Because Bi vacancies act as acceptors,[12] La-doped BMO films are more likely to be treated as a *p*-type material.

In this letter, we report the fabrication of $La_{0.1}Bi_{0.9}MnO_3$ (LBMO) based *p-n* junction by growing LBMO on the *n*-type Nb-doped $SrTiO_3$ (NSTO) substrate. This junction shows good rectifying property and a remarkable positive magnetocapacitance (MC). Both the ferroelectric and ferromagnetic transitions have a dramatic influence on the properties of the junction.

Considering the volatility of Bi, a bismuth-rich $La_{0.1}BiMnO_3$ target was prepared by the solid state reaction method using La_2O_3, Bi_2O_3, and MnO_2 as the starting materials. LBMO/NSTO *p-n* junctions were prepared by growing LBMO on a 0.7 wt % NSTO (001) single crystal substrate by pulsed laser deposition using a KrF excimer laser ($\lambda = 248$ nm) with a pulse energy density of 2 J/cm^2 at a repetition rate of 2 Hz. During the deposition, the substrate temperature is 625 °C and the oxygen pressure is 10 Pa. After the deposition, the sample was cooled down to room temperature in an oxygen pressure of 0.9 atm. In order to estimate the contact between Au and LBMO, LBMO thin films were also grown on $SrTiO_3$ (001) substrates with the same conditions. A step was made on the LBMO films of LBMO/NSTO junction by the chemical etching method. The height of the step (film thickness) was measured using Ambios XP-1, which showed that the film thickness is 75 nm. X-ray diffraction (XRD) data shown in the upper inset of Fig. 1 indicate that the LBMO films are (010) oriented.[8] The magnetization of the films was measured with an in-plane field of 2 kOe (field cooled) employing a Quantum Design MPMS-XL7. As shown in the right bottom inset of Fig. 1, LBMO films display a ferromagnetic transition at $T_{CM} \approx 90$ K. The configuration of electrodes is shown in the left bottom inset of Fig. 1. Au was deposited on the LBMO films by magnetron sputtering. Indium was pressed on the back of the NSTO substrate. The area of both electrodes is approximately 3 mm^2. Current-voltage (*I-V*) curves of the junctions were measured by a Keithley 2400 source meter. The polarization-

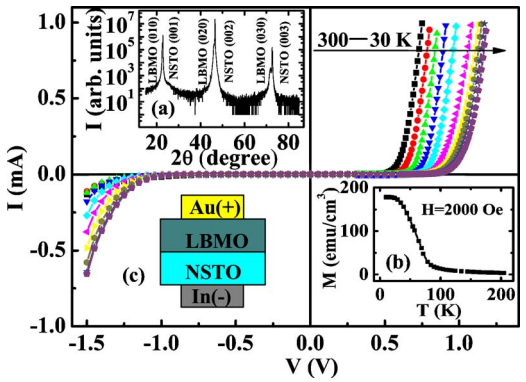

FIG. 1. (Color online) *I-V* curves at different temperatures for LBMO/NSTO. The upper inset shows the XRD pattern for LBMO/NSTO. The right bottom inset is the temperature dependence of magnetization of 75 nm LBMO films. The left bottom inset is the layout of the device for measurement.

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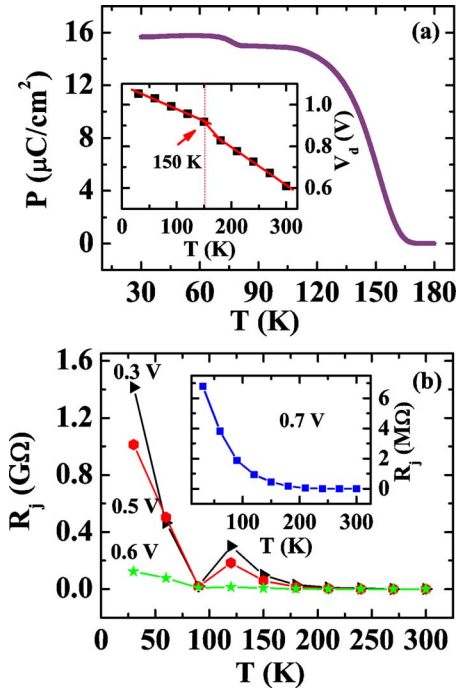

FIG. 2. (Color online) (a) *P-T* curves of LBMO films. The inset is the temperature dependence of V_d. (b) R_j-T curve for different forward bias voltages (0.3, 0.5, and 0.6 V) derived from the *I-V* curves with different temperatures. The inset is the R_j-T curve for 0.7 V.

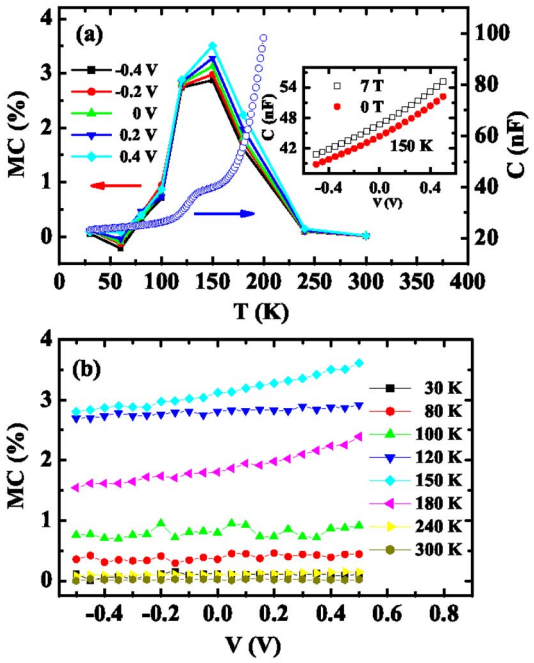

FIG. 3. (Color online) (a) Temperature dependence of the capacitance and MC. The inset is the *C-V* curves measured at 150 K with and without a magnetic field. (b) MC-*V* curves for samples at different temperatures.

temperature (*P-T*) curve was measured by a Keithley 6517A electrometer. The capacitance-temperature (*C-T*) curve and capacitance-voltage (*C-V*) curves were measured by a ZM2353 *LCR* meter. To decrease the possible influence of the relaxation of the space charge at low frequencies,[13] the capacitance was measured at a high frequency of 10 kHz, and the measuring level is 50 mV.

I-V curves of LBMO/NSTO *p-n* junction from 30 to 300 K with an interval of 30 K are shown in Fig. 1. They show good rectifying properties. In order to estimate the contribution from Au/LBMO, two Au electrodes were deposited on LBMO grown on $SrTiO_3$ with a distance of 50 μm. The *I-V* curve of Au/LBMO/Au is linear and the current is much larger than that of the Au/LBMO/NSTO. The In/NSTO contact is Ohmic.[14] Therefore, the contribution of the electrode contacts can be neglected and the rectifying properties of the junction originate from the LBMO/NSTO interface. With increasing positive voltage, the current increases dramatically at the threshold voltage (diffusion potential V_d). The temperature dependence of V_d is shown in the inset of Fig. 2(a), which indicates that V_d increases with decreasing temperature and shows a step near 150 K. This temperature is consistent with the ferroelectric transition temperature of LBMO, as shown by the *P-T* curve in Fig. 2(a). The step of V_d near 150 K is expected to be caused by the ferroelectric transition of LBMO. The diffusion potential V_d is equal to the workfunction difference between LBMO and NSTO in the paraelectric phase. In the ferroelectric phase, the barrier of the junction increases due to the depolarization field of LBMO. The modification of ferroelectric polarization on the barrier of the *p-n* junction has been reported in other oxide *p-n* junctions that contain ferroelectric materials.[15] Therefore, the additional barrier that originated from the depolarization field of the LBMO increases the V_d in the ferroelectric phase. This can account for the step of V_d near the ferroelectric transition temperature (150 K).

The temperature dependence of the junction resistance, defined by $R_j = V/I$, is obtained from the *I-V* curves and the results for different bias voltages (below V_d) are shown in Fig. 2(b). A minimum of R_j is observed around 90 K. This minimum was confirmed by directly measuring the R_j-T curve at 0.3 V, and thus indicates that this minimum is intrinsic. As shown in the inset of Fig. 1, there is a ferromagnetic transition near 90 K for LBMO. Interestingly, the polarization also shows a remarkable increase near this temperature [see Fig. 2(a)]. Recently, Montanari *et al.* observed a large magnetoelastic strain at the ferromagnetic transition in BMO by neutron powder diffraction.[16] It is likely that LBMO also possesses the magnetoelastic strain property of its parent BMO near the ferromagnetic transition, and this magnetoelastic strain results in the increase of polarization of LBMO, as well as the decrease of R_j. The decrease of R_j due to the magnetoelastic strain, combined with the main trend of increase for R_j with decreasing temperature, results in the R_j minimum near 90 K. It is noteworthy that the R_j minimum disappears under a higher voltage [0.7 V, see the inset of Fig. 2(b)], indicating that the magnetoelastic strain only affects R_j in the low voltage regime ($V < V_d$). *I-V* curves of the sample with different electrode areas were also measured. They show similar phenomena of the V_d step near 150 K and the R_j minimum near 90 K.

Capacitance is another important property of the *p-n* junction. Figure 3(a) shows the *C-T* curve of the junction. It can be seen that the capacitance of the junction decreases with decreasing temperature, which is due to the decrease of the dielectric constant of LBMO with decreasing temperature[10] since the junction capacitance is proportional to the dielectric constant of LBMO. It also displays a capacitance peak around 150 K, which is consistent with the ferroelectric transition shown in the *P-T* curve in Fig. 2(a). The inset of Fig. 3(a) shows the *C-V* curves measured at 150 K

with and without a magnetic field. A remarkable positive MC can be seen. The C^{-2}-V curves derived from the inset of Fig. 3(a) show linear behavior (not shown), indicating their characteristic of junction capacitance. The temperature dependence of MC, defined as $\mathrm{MC}=[(C_{7\ \mathrm{T}}-C_{0\ \mathrm{T}})/C_{0\ \mathrm{T}}]\times 100\%$, at different bias voltages is shown in Fig. 3(a), which is obtained from the C-V curves measured at different temperatures with and without a magnetic field. They all show peaks near 150 K, which corresponds to the ferroelectric transition of LBMO. It has been reported that the dielectric constant of $La_{0.2}Bi_{0.8}MnO_3$ films increases when a magnetic field is applied.[10] Since the junction capacitance is proportional to the dielectric constant of LBMO, the temperature dependence of MC and the presence of a peak near 150 K can be understood by considering the increase of the dielectric constant of LBMO with the magnetic field. Figure 3(b) shows the MC-V curves at different temperatures. MC increases slowly with increasing voltage. Since the carrier density of NSTO is much larger than that of LBMO, the depletion layer is dominated by LBMO. Based on the theory of p-n junction,[17] the C-V formula is $1/C^2 \propto (V_d - V)/q\varepsilon N$, where ε is the dielectric constant of LBMO, q is the carrier charge and N is the carrier density of LBMO.[17] Then, we can deduce that $\mathrm{MC} \propto (\varepsilon_{7\ \mathrm{T}}^{1/2} - \varepsilon_{0\ \mathrm{T}}^{1/2})$, which suggests that MC is independent of V, consistent with the experimental results. The small increase of MC with increasing voltage is likely due to the change of ε under bias voltage.

In summary, a multiferroic LBMO/NSTO p-n junction was fabricated by pulsed laser deposition. This junction shows good rectifying property. Both ferroelectric and ferromagnetic transitions have remarkable influence on the current-voltage behavior of the junction. A large positive magnetocapacitance with a peak near 150 K was observed. The results were discussed by considering the change of LBMO with both electric field and magnetic field. This work demonstrates that p-n junctions composed of multiferroic materials and other oxides can show some interesting properties, which may have potential applications.

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