Giant Electric Field Modulation of Double Exchange Ferromagnetism at Room Temperature in the Perovskite Manganite/Titanate *p-n* Junction

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We report on the electrical modulation of double exchange ferromagnetism at room temperature in hole-doped manganites of a metal oxide *p-n* junction. In this $(La_{0.9}Ba_{0.1})MnO_3$/Nb doped $SrTiO_3$ *p-n* junction, the temperature dependence of the junction resistance shows a metal-insulator transition whose temperature, corresponding to that of ferromagnetic transition, is hugely modulated from 290 to 340 K by a bias voltage increasing from +1.0 to +1.8 V. The magnetoresistance can also be modulated electrically.

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Transition metal oxides, having strongly correlated electron systems, show unusually drastic phase transitions (Mott transitions) under external perturbation, including ferromagnetism, superconductivity, and others. Because of the strong coupling between spin, charge, and orbital degrees of freedom [1], colossal magnetoresistive (CMR) perovskite manganites [2,3] typically exhibit a rich variety of electronic and magnetic properties, such as ferromagnetism with metallic conduction, and charge/orbital ordering, depending on carrier concentration. The parent compound, $LaMnO_3$, is an antiferromagnetic insulator, whereas the hole-doped (*p*-type) $(La_{1-x}Sr_x)MnO_3$ are ferromagnetic metals with a metal-insulator transition at a wide range of Curie temperatures, (T_C), from 250 K to over room temperature [1]. If it were possible to effectively control carrier concentration by electric field or light, novel functional devices could be created, such as electrical and light tunable (at room temperature) magnets. The *p-n* junction has been so widely used in semiconductor technology that control of carrier concentration is easily achieved by designing specific interfacial electronic band structures. However, it was believed that the band theory for *p-n* junctions would be difficult to apply to transition metal oxides, including manganites, due to the strong Coulomb repulsion among electrons. Beyond this difficulty, to unify the "Mott transition" in the strongly correlated electron and band gap engineering field would be invaluable, leading to new ways of controlling the physical properties of transition metal oxides.

In this paper we report the fabrication of a (La, Ba)-MnO_3/Sr(Ti, Nb)O_3 functional oxide *p-n* junction and the demonstration for the first time of "giant electric field modulation" of double exchange ferromagnetism at room temperature. To date, a field-effect-transistor(FET)-type magnetic heterostructure using a dielectric insulating layer has been applied to an (In, Mn)As magnetic semiconductor, one of the candidates for this novel device. Ferromagnetism was subsequently controlled by forced carrier modulation at the very low temperature of 25 K [4] from a very large electric field of 125 V. Furthermore, in a (La, Ca)MnO_3/insulative-Pb(Zr, Ti)O_3 oxide FET, the resistivity change was found to be relatively small [5]. Our new system, taking advantage of "band gap engineering" can offer large changes in both electrical and magnetic properties resulting from an electric field of a few volts or exposure to light [6], which is an advanced concept when compared with the insulative-gate FET.

We selected Ba-doped manganites, (La, Ba)MnO_3 (LBMO), as the *p*-type conductor with ferromagnetism and Nb-doped strontium titanate, Sr(Ti, Nb)O_3, as the *n*-type conductor. This is considered one of the best combinations since perovskite $SrTiO_3$ is the standard substrate for the deposition of functional perovskite compounds, whose semiconductive property is easily controlled by La or Nb doping [7]. We found that a thinner $(La_{1-x}Ba_x)MnO_3$ thin film deposited on the $SrTiO_3$ resulted in a higher T_C [8]. Figure 1 shows the typical temperature dependency of magnetization and resistivity, for lightly doped $(La_{0.9}Ba_{0.1})MnO_3$ on the $SrTiO_3$ substrate, having film thicknesses (t_{LBMO}) of 15 and 30 nm, respectively. The insulator-to-metal transition occurs, accompanied by paramagnetic-to-ferromagnetic transition, at $T_P = 250$ K for $t_{LBMO} = 30$ nm and 323 K for $t_{LBMO} = 15$ nm. Because of tensile strain, the thinner LBMO films are expanded more along the in-plane direction by the $SrTiO_3$

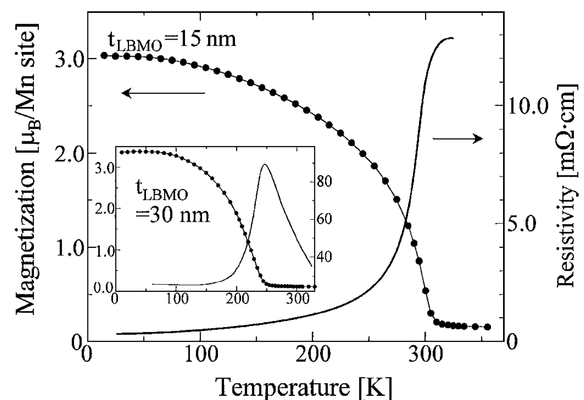

FIG. 1. Temperature dependence of magnetization and resistivity of $(La_{0.9}Ba_{0.1})MnO_3$ epitaxial thin film (15 nm thickness) on a $SrTiO_3$ (001) single crystal substrate. The inset shows that of 30 nm thickness.

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substrate, so that the energy level of the $d_{x^2-y^2}$ orbital along the in-plane direction becomes more stable than that of the $d_{3z^2-r^2}$ orbital, inducing the increase of conductive electrons having larger transfer integrals which leads to the increase of T_C and the reduction of resistively keeping the low La/Ba ratio [9]. From the standpoint of carrier modulation, a lower hole-doping ratio of x is effective for controlling their physical properties [10]. The resulting $(La, Ba)MnO_3$ thin film exhibits room temperature ferromagnetism at a low doping ratio of $x = 0.1$ [11]. This is the characteristic feature of the $(La, Ba)MnO_3$ system, which is different from other well-investigated (La, Sr)-MnO_3 and $(La, Ca)MnO_3$.

To form p-n junctions, we deposited the $(La_{0.9}Ba_{0.1})$-MnO_3 epitaxial thin films (in thicknesses of 30 and 15 nm) on Nb-0.01 wt% doped $SrTiO_3$ (001) single crystal substrates using the laser molecular-beam epitaxy technique at a substrate temperature of 750 °C and then annealed them at the same temperature in O_2 under 1 atm. X-ray diffraction and reflection high-energy electron diffraction measurements confirmed that the films had c-axis orientations with flat surfaces [8], and cross-sectional high-resolution transmission microscopy showed a very clear interface, indicating that we could neglect interdiffusion problems at the interface [11]. To obtain Ohmic contact, Au and In electrodes were placed on the $(La, Ba)MnO_3$ and Nb-doped $SrTiO_3$ (Nb-STO), respectively. The electrode area (S) was 1.0 mm^2.

The current density ($J_{\mathrm{interface}}$) to voltage (V_{bias}) curves of the p-LBMO/n-Nb-STO heterojunction, measured by voltage source, showed suitable rectifier properties at various temperatures, as shown in Fig. 2. The electron concentration for Nb-STO was 6.6×10^{-5}/Ti site (1.1×10^{18} cm^{-3}) at room temperature, confirmed by the Hall coefficient measurement, and hole concentration for LBMO was estimated from the chemical formula as 0.1 per Mn site (an order of 10^{21} cm^{-3}). Judging from the $J_{\mathrm{interface}}$-V_{bias} curves, the band picture was basically applicable to also modulate the carrier concentration in the hole-doped manganites. The diffusion potential (V_D) was 0.5 V (at 320 K) to 1.2 V (at 20 K) for the junction of $t_{\mathrm{LBMO}} = 15$ nm, at which point $J_{\mathrm{interface}}$ started to increase as a result of the application of a positive bias voltage, as shown in Fig. 2. Kudo *et al.* also proposed a band diagram for oxide heterostructure including $(La, Sr)MnO_3$ as a degenerate semiconductor [12]. Our junction is precisely the type of degenerate p^+-n junction below T_P, and a p-n one above T_P, considering the temperature dependence of resistivity and the carrier concentrations. However, conductive electrons should still be correlated by electron repulsion and dynamic Jahn-Teller effects [13].

The most fascinating characteristic of the manganites is their ability to control both magnetic and electrical properties drastically at high temperatures. In the double exchange mechanism [14–16], ferromagnetism appears at almost the same temperature as when the insulator-to-metal transition occurs, as shown in Fig. 1. Therefore

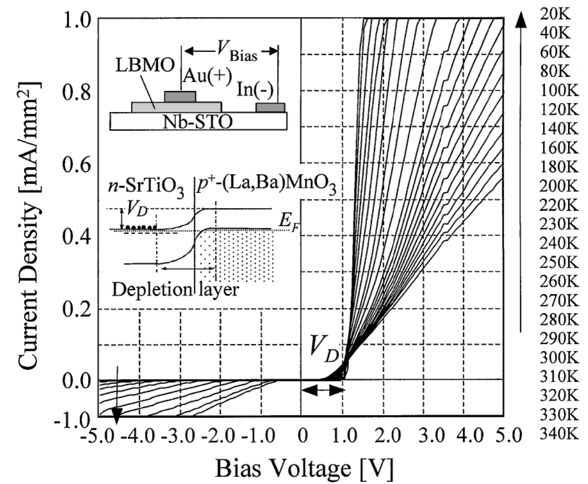

FIG. 2. Current density–voltage characteristic curves for a $(La_{0.9}Ba_{0.1})MnO_3$/Nb-doped $SrTiO_3$ p-n heterojunction perpendicular to the interface at various temperatures ($t_{\mathrm{LBMO}} = 15$ nm). The insets show a schematic illustration of the heterojunction sample and an energy diagram for the p^+-$(La, Ba)MnO_3$/n-$Sr(Ti, Nb)O_3$ heterojunction.

its insulator-to-metal transition temperature (T_P) is a good index to check the emergence of ferromagnetism.

Figure 3 shows the temperature dependence of the junction resistance, defined as $R_{\mathrm{junction}}(V_{\mathrm{bias}}) = V_{\mathrm{bias}}/J_{\mathrm{interface}}$. At a low V_{bias} of +0.6 to +0.8 V, it shows semiconductive property (negative dR/dT). With increasing V_{bias}, R_{junction} is drastically reduced from 3×10^3 to 8×10^1 Ω, even within bias voltages from +0.6 to +1.8 V. At $V_{\mathrm{bias}} = +1.0$ V, a semiconductor-to-metal transition appears in R_{junction}-T curves, which is a characteristic feature of double exchange ferromagnetism. Furthermore, with increasing V_{bias} from +1.0 to +1.8 V, T_P increased gradually from 290 to over 340 K. This transition temperature, T_P, also corresponds to T_C. The change of resistance observed here includes both the manganite and titanate parts at the interface, but the temperature range of electrical modulation of T_P strongly depends on the intrinsic T_P ($T_P^{\mathrm{intrinsic}}$) of the strained LBMO film, that is, from 280 to 340 K for $T_P^{\mathrm{intrinsic}}$ of 323 K ($t_{\mathrm{LBMO}} = 15$ nm) and from 180 to 270 K for $T_P^{\mathrm{intrinsic}}$ of 250 K ($t_{\mathrm{LBMO}} = 30$ nm). Therefore, we can conclude that the physical properties of the manganite itself were controlled through carrier modulation by the electric field near the interface. This reduction of resistance in ferromagnetic manganites is exceptionally huge due to the use of the potential difference between p-type and n-type materials. The estimated depth of the depletion layer in LBMO is less than 1 unit cell as a simple semiconductor, and it is very difficult to explain the experimental change of T_P. The metal-insulator transition in the transition metal oxides is quite anomalous. Near the insulator region, most carriers are localized by strong Coulomb repulsion, so that the number of conductive carriers is greatly reduced even if formal carrier concentration is of the order of 10^{21} cm^{-3}. Furthermore, electron-lattice (Jahn-Teller) interaction enhances

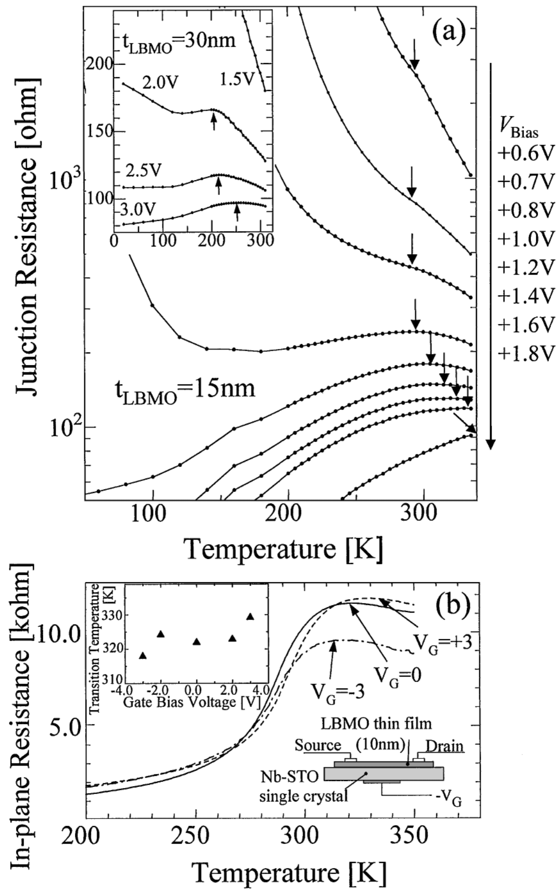

FIG. 3. (a) Temperature dependence of junction resistance (R_{junction}) of a p-(La, Ba)MnO_3 (15 nm)/n-Nb-doped $SrTiO_3$ heterojunction measured under various bias voltages. The arrows indicate metal-insulator transition temperatures. The inset shows that of $t_{\text{LBMO}} = 30$ nm. (b) Temperature dependence of in-plane resistance of (La, Ba)MnO_3 layer ($t_{\text{LBMO}} = 10$ nm) in the transistor-type structure under the gate bias voltage (V_G) of -3.0, 0, and $+3.0$ V, respectively, as shown in the inset illustration. The inset figure shows gate bias voltage dependence of metal-insulator transition temperature.

this localization tendency. In fact, $(La_{1-x}Sr_x)MnO_3$ ($0 < x < 0.175$) is an insulator with a formal carrier of the order of 10^{21} cm^{-3}. Therefore the depletion layer of LBMO appears to become much deeper than that of an ordinal semiconductor, due to electron localization by strong electron correlation (Coulomb repulsion, Jahn-Teller effect).

According to the phase diagram of hole-doped manganites [1], enhancement of the hole concentration enhances ferromagnetic double exchange interaction, leading to the decrease of resistivity and the increase of T_P. The change of electromagnetic properties in the LBMO layer caused by applying an electric field is explained by the reduction or enhancement of the concentration of effective holes. At the p-n junction interface, a depletion layer of hole-type carriers within the LBMO layer should be formed at $V_{\text{bias}} = 0$ V, leading to the large resistivity shown in the inset of Fig. 2. By increasing the bias voltage from 0 V to approximately 1.0 V, the depletion layer is suppressed by reducing the potential barrier, so that T_P approaches the intrinsic $T_P(T_P^{\text{intrinsic}})$ of the strained LBMO film. Furthermore, at larger V_{bias} than V_D ($\sim$1.0 V), hole concentration near the interface is enhanced, leading to enhancement of T_P. The hole concentration within the LBMO layer of $n(l)$, as a function of depth (l) from the interface, is increased from almost zero at interface ($l = 0$) (or decreased from enhanced carrier concentration at $l = 0$) to its intrinsic concentration at the end of the depletion layer ($l = l_{\text{depletion}}$). Therefore, the observed R_{junction} can be expressed as an integration of resistivity $[\rho(l)]$ at each depth,

$$R_{\text{junction}}(T, V) = \int_0^{l_{\text{depletion}}} \{\rho[n(l, V), T]/S\} dl$$
$$= \int_{n_{(\text{interface})}}^{n_{(\text{intrinsic})}} \rho[n, T] \frac{dl}{dn} dn/S . \quad (1)$$

We observe as a result (shown in Fig. 3) an R_{junction}-T curve with a relatively broad peak when compared with the intrinsic R-T curve shown in Fig. 1.

As another possibility for the reduction of resistance caused by an electric field, we should consider a disruption of the insulative layer, such as the charge-ordered state or Jahn-Teller polarons, which may exist at the interface as a dead layer [17]. Asamitsu *et al.* [18] reported electrical current switching of the resistive state in a (Pr, Ca)MnO_3 single crystal with a narrow band due to the sudden collapse of the charge-ordered insulative state at 700 V. In our junction using a wide bandwidth LBMO, transition temperature and conductivity are gradually increased with increasing V_{bias} in the positive region. Importantly, below $V_{\text{bias}} < 0$, the junction resistance maintains a very high value (more than several $M\Omega$) down to -5 V even at room temperature without any metallic phase. If the reduction of resistance were caused by disruption of the insulative state at the interface by the electric field, it should also occur symmetrically over the $V_{\text{bias}} < 0$ region. As further evidence for carrier injection, we measured in-plane resistance and the change of T_P of the (La, Ba)MnO_3 layer itself ($t_{\text{LBMO}} = 10$ nm, constant current of 1 μA) in the semiconductive gate FET structure against various gate biases (V_G), as shown in Fig. 3(b). T_P is enhanced with increasing positive V_G, whereas it is reduced by applying negative V_G. In this structure, current can flow in the greater part of the film layer (not limited to the interface layer) so that, at least, we cannot attribute the change of T_P to only the disruption of the possible insulative layer at interface. On the basis of these results, we consider that the measured effect can be significantly attributed to the carrier injection effect through the p-n interface.

We have summarized the electrical-magnetic phase diagram of the heterojunctions against V_{bias} in Fig. 4. T_P is systematically decreased by a smaller bias and increased by a larger bias than V_D from each $T_P^{\text{intrinsic}}$. Especially in the case of $t_{\text{LBMO}} = 15$ nm, the tuning range of T_P appeared across room temperature as a result of very small changes in the electric field, in fact less than 1 V. Furthermore, since this control mechanism is based on carrier

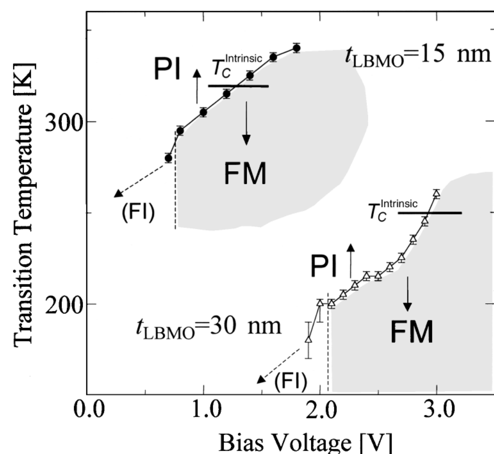

FIG. 4. Phase diagram of the $(La_{0.9}Ba_{0.1})MnO_3$ layers, having 15 and 30 nm thicknesses in the p-n heterojunction, against bias voltage. FM: metallic conduction with ferromagnetism; PI: insulative conduction with paramagnetism; (FI): insulative (negative $d\rho/dT$) conduction (with a possibility of ferromagnetism) such as the FI region in $(La_{1-x}Sr_x)MnO_3$ $(0.1 < x < 0.175)$ (Ref. [1]). The solid lines indicate the intrinsic transition temperature for each strained $(La, Ba)MnO_3$ thin film on $SrTiO_3$ ($T_P^{\text{intrinsic}}$).

injection by the potential difference between p-type and n-type materials, light control of ferromagnetism will also be possible via photocarrier injection. In fact, at low temperatures of less than 105 K, we have also demonstrated photocontrol of ferromagnetism in the $(La, Sr)MnO_3$/band-insulating $SrTiO_3$ heterostructure [6].

Finally, there now follows a brief discussion of the magnetoresistance in the heterojunction. By applying a magnetic field of 5 T, R_{junction} was reduced in all temperature ranges from 300 to 10 K ($t_{\text{LBMO}} = 30$ nm), as shown in Fig. 5. With decreasing temperature, this magnetoresistance effect increased monotonically. This MR effect was enhanced from 5% to 30% at 10 K, while decreasing V_{bias} from 3.0 to 1.0 V. The magnetoresistance of semiconductive Nb-STO is much smaller than that of magnetoresistive LBMO, so the change of junction resistance is mainly dominated by LBMO. The magnitude of CMR (~MR of junction) is express in the relatively low magnetization region as follows [1]:

$$-\Delta\rho(H)/\rho(0) = C(x)(M/M_S)^2 \qquad (2)$$

where M/M_S is normalized magnetization. While decreasing x from 0.4 to 0.175, $C(x)$ increases from 1 to approximately 4 [1]. The lower hole concentration gives a larger MR. Therefore, lower V_{bias} will give a larger MR ratio at low temperature. This observed MR behavior is also expressed as the convolution of the modulated MR ratio on the basis of Eqs. (1) and (2). It would appear that an electric field can also modulate the CMR of the manganites.

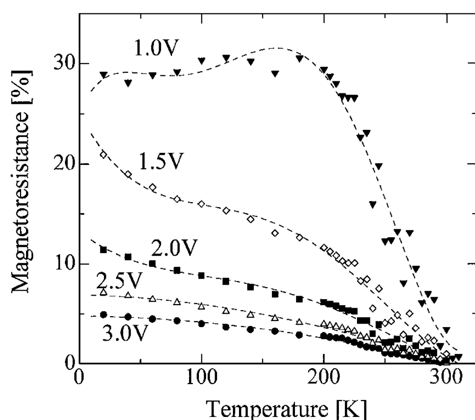

FIG. 5. Temperature dependence of magnetoresistance at the magnetic field (H) of 5 T measured under various bias voltages of the LBMO/Nb-STO heterojunction ($t_{\text{LBMO}} = 30$ nm). The MR ratio is defined as $[R_{\text{junction}}(H = 0\ \text{T}) - R_{\text{junction}}(H = 5\ \text{T})]/R_{\text{junction}}(H = 0\ \text{T}) \times 100[\%]$.

Our results demonstrate that the double exchange ferromagnetism in manganites can be switched at "room temperature" by an electric field of a "few volts" on the basis of a p-n junction. We believe that these results will open up a "strongly correlated electron engineering" discipline, unifying "band gap engineering" and "Mott transition" which includes switching of rich functionality such as ferromagnetism, superconductivity, and more. This will lead to new control methods for electric/magnetic phases in the transition metal oxides and in novel functional optical, magnetic, and electrical devices.

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[1] A. Urashiba *et al.,* Phys. Rev. B **51**, 14 103 (1995).
[2] R. von Helmolt *et al.,* Phys. Rev. Lett. **71**, 2331 (1993).
[3] S. Jin *et al.,* Science **264**, 413 (1994).
[4] H. Ohno *et al.,* Nature (London) **408**, 944 (2000).
[5] S. Mathews *et al.,* Science **276**, 238 (1997).
[6] H. Katsu, H. Tanaka, and T. Kawai, Appl. Phys. Lett. **76**, 3245 (2000).
[7] Y. L. Soo *et al.,* Phys. Rev. B **53**, 4905 (1996).
[8] T. Kanki, H. Tanaka, and T. Kawai, Solid State Commun. **114**, 267 (2000).
[9] T. Kanki, H. Tanaka, and T. Kawai, Phys. Rev. B **64**, 224418 (2001).
[10] H. Katsu, H. Tanaka, and T. Kawai, J. Appl. Phys. **90**, 4578 (2001).
[11] J. Zhang, H. Tanaka, T. Kanki, J. Choi, and T. Kawai, Phys. Rev. B **64**, 184404 (2001).
[12] T. Kudo *et al.,* Jpn. J. Appl. Phys. **37**, L999 (1998).
[13] A. J. Millis *et al.,* Phys. Rev. Lett. **77**, 175 (1996).
[14] C. Zener, Phys. Rev. **82**, 403 (1951).
[15] P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).
[16] P. G. de Gennes, Phys. Rev. **118**, 145 (1960).
[17] J. Z. Sun *et al.,* Appl. Phys. Lett. **74**, 3017 (1999).
[18] A. Asamitsu *et al.,* Nature (London) **388**, 50 (1997).