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# Fabrication and Characteristic Investigation of Multifunctional Oxide p-n Heterojunctions

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**Abstract.** A series of all-perovskite oxide p-n heterojunctions (PNHs) as well as perovskite oxide and Si PNHs have been fabricated by a laser molecular-beam epitaxy. The good nonlinear and rectifying I-V characteristics in the PNHs, unusual and high sensitivity of positive magnetoresistance in low magnetic field in $SrNb_xTi_{1-x}O_3/La_{1-y}Sr_yMnO_3$ and $La_{1-x}Sr_xMnO_3$/Si PNHs, ps orders ultrafast photoelectric effect in $La_{1-x}Sr_xMnO_3$/Si PNHs, as well as ferroelectric property due to the interface enhancement in $BaNb_{0.3}Ti_{0.7}O_3$/Si PNHs have been observed. It is expected that the further investigation on the PNHs could not only stimulate theoretical study on the mechanisms but also would open up new possibilities in the development and application of electrical devices.

## Introduction

Perovskite oxide materials have attracted much attention because of their various properties: insulating, ferroelectric, ferromagnetic, superconducting, having colossal magnetoresistance, and others. The fabrication of artificial crystalline materials through layer-by-layer epitaxial growth with full control over the composition and structure at the atomic level has become one of the most exciting areas of research in condensed matter physics and materials sciences. Some research works have been devoted recently to explore quantum functional properties and verify new device concepts based on perovskite oxide. The electrical modulation of double exchange ferromagnetism in $La_{0.9}Ba_{0.1}MnO_3$/Nb-doped $SrTiO_3$ p-n junction [1], the large positive magnetoresistance (MR) in $La_{0.7}Ca_{0.3}MnO_3/SrTiO_3/La_{0.7}Ce_{0.3}MnO_3$ tunnel junction [2], and the photovoltaic effect in a $La_{0.29}Pr_{0.38}Ca_{0.33}MnO_3/SrNb_{0.05}Ti_{0.95}O_3$ p-n heterojunction (PNH) [3] have been reported. Several groups have tried to combine perovskite oxides such as $SrTiO_3$, $BaTiO_3$ and $Bi_{3.25}La_{0.75}TiO_{12}$ with Si wafer, which is the most basic technique in fabricating electronic devices [4-6]. We have reported the high sensitivity of positive MR in low magnetic field in all-perovskite oxide p-n heterojunctions (PNHs) [7] and the nanosecond (ns) and picosecond (ps) photoelectric effects in perovskite oxide PNHs [8]. In this letter, we report the fabrication and characteristic cnvestigation of multifunctional oxide PNHs.

## Fabrication of all-oxide PNHs and oxide and Si PNHs

We have developed the technology in atomically controlled fabricating oxide films on other oxides and on Si substrates [9]. A series of all-perovskite oxide p-n heterojunctions (PNHs) as well as perovskite oxide and Si PNHs, such as $SrNb_xTi_{1-x}O_3/SrIn_yTi_{1-y}O_3$, $SrNb_xTi_{1-x}O_3/BaIn_yTi_{1-y}O_3$, $BaNb_xTi_{1-x}O_3/BaIn_yTi_{1-y}O_3$, $SrNb_xTi_{1-x}O_3/La_{1-y}Sr_yMnO_3$, $La_xSr_{1-x}MnO_3$/Si, $SrTiO_{3-\delta}$/Si, and $Ba_{1-x}Nb_xTiO_3$/Si, have been fabricated by a laser molecular-beam epitaxy [7-10]. A *in-situ* reflection high-energy electron diffraction (RHEED) and charge coupled device (CCD) camera can provide us

with useful information on the crystal structure and morphology of a growing film surface. The RHEED intensity oscillation enables us to control the exact number of grown molecular layers. We can observe more than 1000 cycles of RHEED intensity oscillation during the epitaxial growth of oxide thin films. Fig. 1 (a) shows a cross-sectional high-resolution transmission electron microscopic (HRTEM) image of $SrNb_{0.01}Ti_{0.99}O_3/La_{0.9}Sr_{0.1}MnO_3$ PNH. Fig. 1 (b) shows a cross-sectional transmission electron microscopic (TEM) image of $SrNb_{0.1}Ti_{0.9}O_3/La_{0.9}Sr_{0.1}MnO_3$ multilayer PNH. The measurements of atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM) reveal that the surfaces and interfaces of the PNHs are atomically smooth.

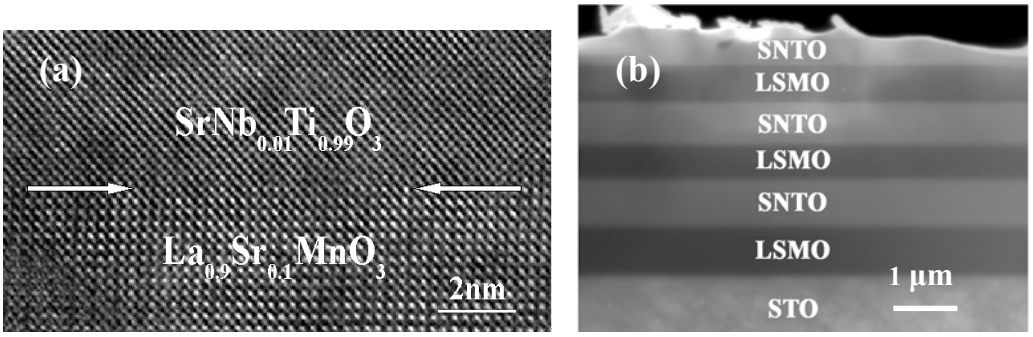


Fig.1 (a) The cross-sectional high-resolution transmission electron microscopic image of $SrNb_{0.01}Ti_{0.99}O_3/La_{0.9}Sr_{0.1}MnO_3$ p-n heterojunction interface; (b) The cross-sectional transmission electron microscopic image of $SrNb_{0.1}Ti_{0.9}O_3/La_{0.9}Sr_{0.1}MnO_3$ multilayer p-n heterojunction

**I-V characteristics in all-oxide PNHs and oxide and Si PNHs**

The current and voltage (I-V) characteristics of the all-perovskite oxide PNHs as well as perovskite oxide and Si PNHs were measured with a pulse-modulated current source at various temperatures. Fig. 2 (a) and (b) show the I-V curves of $La_{0.9}Sr_{0.1}MnO_3/SrNb_{0.01}Ti_{0.99}O_3$ and $SrTiO_{3-\delta}$/Si PNHs [11], respectively. The schematic illustration of the PNH sample is shown in the inset of Fig. 2 (a). Most of PNHs exhibit good nonlinear and rectifying I-V characteristics.

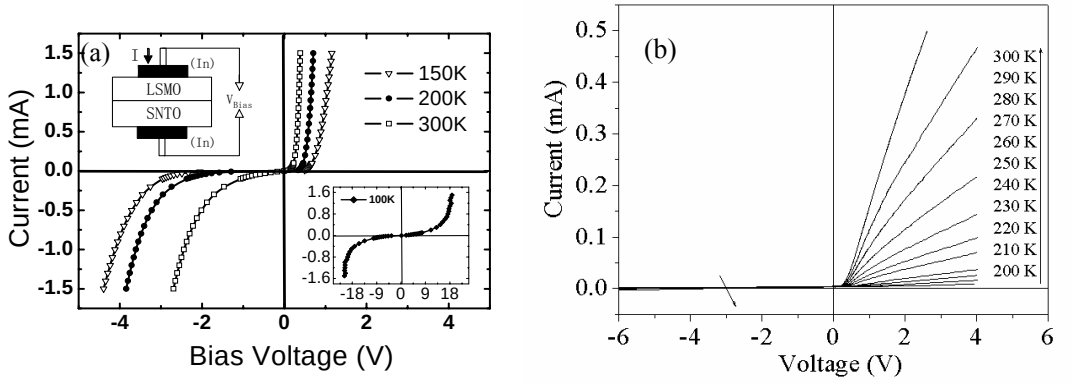


Fig. 2 (a) The I-V curves of $La_{0.9}Sr_{0.1}MnO_3/SrNb_{0.01}Ti_{0.99}O_3$ p-n heterojunction at different temperature; (b) The I-V curves of SrTiO3-δ/Si p-n heterojunction at different temperature

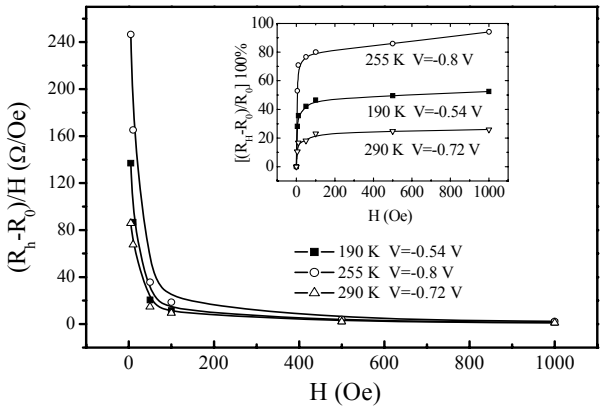


Fig. 3 The sensitivity of MR/H as a function of magnetic field at optimal bias voltage for $SrNb_{0.01}Ti_{0.99}O_3/La_{0.9}Sr_{0.1}MnO_3$ p-n heterojunction. Inset: the MR ratios of the p-n junction as a function of the magnetic field at 290 K and $V_{bias}$=-0.73 V, 255 K and $V_{bias}$=-0.80 V, 190 K and $V_{bias}$=-0.54 V

**Positive MR in all-oxide PNHs and oxide and Si PNHs**

In order to fabricate MR PNHs, we chose Sr-doped manganites, $La_{1-x}Sr_xMnO_3$, as p-type material, and Nb-doped strontium titanate, $SrNb_xTi_{1-x}O_3$ or Si, as n-type material. We fabricated $SrNb_xTi_{1-x}O_3/La_{1-y}Sr_yMnO_3$ and $La_{1-x}Sr_xMnO_3$/Si (x=0.1, 0.2, 0.3; y=0.1, 0.01) PNHs. The magnetic properties of the PNHs are measured at various temperatures by a superconductive quantum interference device (SQUID, Quantum Design MPMS 5.5T). We define the MR ratio as $\triangle R/R_0=(R_H-R_0)/R_0$, where $R_H$ is the resistance in the applied magnetic field and $R_0$ is the resistance in zero field.

The MR ratios of a $SrNb_{0.01}Ti_{0.99}O_3/La_{0.9}Sr_{0.1}MnO_3$ PNH are plotted as a function of applied magnetic field, the magnetic field paralleled the junction interface, as inset in Fig. 3 for -0.73 V bias at 290 K, -0.80 V bias at 255 K, and -0.54 V bias at 190 K. The MR is always positive and increases abruptly with the applied magnetic field. For example, the MR ratios are 11 % in 5 Oe, 23 % in 100 Oe, and 26 % in 1000 Oe at 290 K, 53 % in 5 Oe, 80 % in 100 Oe and 94 % in 1000 Oe at 255 K, 24% in 5 Oe, 47% in 100 Oe and 53% in 1000 Oe at 190 K. The sensitivity of resistance variation under applied magnetic field is another prime important factor for potential application. Then, the MR variation versus magnetic field, defined as $(R_H-R_0)/H$, is calculated at optimal bias voltage and shown in Fig. 3. With a small change from 0 to 5 Oe of the applied magnetic field, the MR sensitivities are 85 Ω/Oe at 290 K, 246 Ω/Oe at 255 K and 136 Ω/Oe at 190 K. Correspondingly, the maximum change of the bias voltage can be deduced as 45 mV/ 5 Oe in the current of -0.7 mA at 290 K, 164 mV/5 Oe in

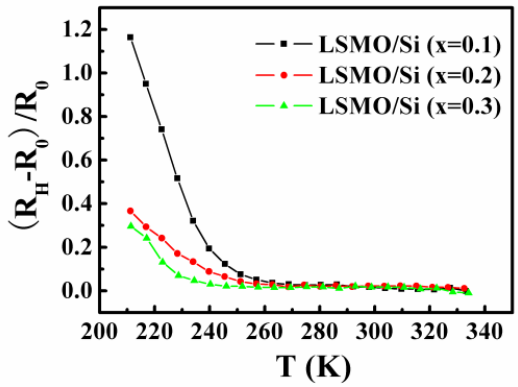


Fig. 4 The MR ratios of $La_{1-x}Sr_xMnO_3$/Si (x=0.1, 0.2, 0.3) p-n heterojunctions as a function of temperature

-0.6 mA at 255 K, and 50 mV/5 Oe in -0.5 mA at 190 K.

Similar to $SrNb_{0.01}Ti_{0.99}O_3/La_{0.9}Sr_{0.1}MnO_3$ PNHs, the MR ratios of $La_{1-x}Sr_xMnO_3/Si$ (the thicknesses of $La_{1-x}Sr_xMnO_3$ being 400 nm) PNHs as a function of temperature are plotted in Fig. 4. The positive MR ratio as large as 116%, 38% and 30% in applied magnetic field as low as 100 Oe at the temperature of 210 K for the doping $La_{1-x}Sr_xMnO_3$, $x$ =0.1, 0.2, 0.3, in the LSMO/Si PNHs, respectively.

The positive MR properties of PNHs are quite different from that of the $LaMnO_3$ compound family in that the latter has negative MR. A mechanism based on the different density of states for electrons with spins in the interface region from that in the region far from the interface has been proposed by us recently to explain the unusual positive MR property of the PNHs [12].

**Picosecond photoelectric effects in $La_{0.7}Sr_{0.3}MnO_3$/Si PNH**

The photoelectric behaviors of the $La_{0.7}Sr_{0.3}MnO_3$/Si PNH were investigated using 1.064 μm (pulse width 25 ps), and 1. 34 μm as well as 10.6 μm pulsed laser and measured by an oscilloscope of 130 ps rise time (Tektronix TDS7254B) at room temperature. Fig. 5 shows a typical photovoltaic pulse as a function of time when the $La_{0.7}Sr_{0.3}MnO_3$ film in a $La_{0.7}Sr_{0.3}MnO_3$/Si PNH was irradiated with a 1.064 μm laser pulse. The rise time is 330 ps and the FWHM is 580 ps for the open-circuit photovoltaic pulse when a 0.2 Ω resistance was connected in parallel with the PNH as shown in the inset. The FWHM in Fig. 5 is about seven orders of magnitude narrower than that of ~8 ms observed in a $La_{0.29}Pr_{0.38}Ca_{0.33}MnO_3/SrNb_{0.05}Ti_{0.95}O_3$ PNH. [3]

We did not observe the photoelectric effect when the $La_{0.7}Sr_{0.3}MnO_3$ film in the $La_{0.7}Sr_{0.3}MnO_3$/Si PNH was irradiated by 1.34 μm or 10.6 μm laser pulse. As the photon energy of 1.064 μm laser is slightly higher than the band gaps of $La_{0.7}Sr_{0.3}MnO_3$ (1.0~ 1.3 eV) and Si ( ≈ 1.12 eV), the electrons and holes in $La_{0.7}Sr_{0.3}MnO_3$ and Si can be created in the system. For 1.34 μm and 10.6 μm laser, the photon energies are lower than the band gaps of either the $La_{0.7}Sr_{0.3}MnO_3$ or Si. This result clearly demonstrates that the photovoltaic pulse is a photoelectric effect instead of a thermoelectric effect.

In order to understand the mechanism of the photoelectric effect in the $La_{0.7}Sr_{0.3}MnO_3$/Si PNH, the photoelectric behaviors of $La_{0.7}Sr_{0.3}MnO_3$ thin films were further investigated under the same experimental condition with Fig.4. Similar to the $La_{0.7}Sr_{0.3}MnO_3$/Si PNH, a ps order open-circuit photovoltage pulse was observed. The FWHM of the photovoltage pulse for $La_{0.7}Sr_{0.3}MnO_3$ thin film is about three orders of magnitude narrower than that of ~200 ns observed in the doped $LaMnO_3$ films

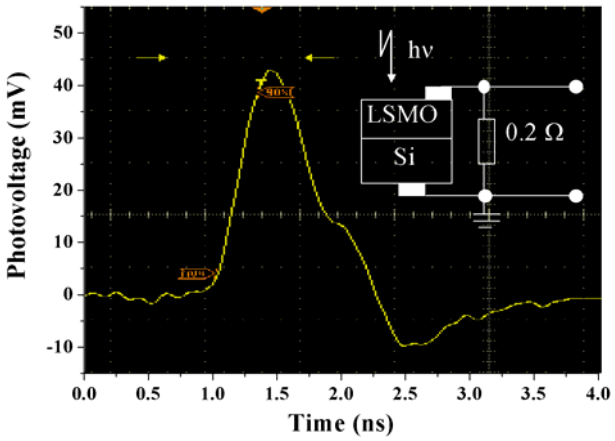


Fig. 5 The photovoltaic pulse as a function of time when the $La_{0.7}Sr_{0.3}MnO_3$ film in $La_{0.7}Sr_{0.3}MnO_3$/Si p-n heterojunction was irradiated with a 1.064 μm laser pulse. Inset: a 0.2 Ω resistance was connected in parallel with the p-n heterojunction

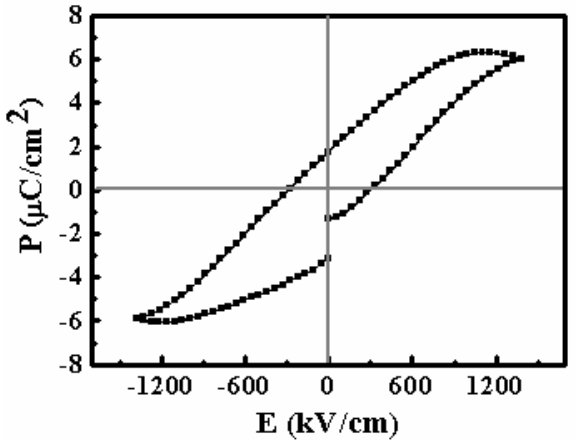


Fig. 6 Ferroelectric hysteresis loop of the $BaNb_{0.3}Ti_{0.7}O_3$/Si *p*-*n* heterojunction

[13].

**Ferroelectricity in BaNb0.3Ti0.7O3/Si PNH**

For the $BaNb_{0.3}Ti_{0.7}O_3$/Si PNH, the most interesting property is the ferroelectricity [14]. The polarization versus electric field (P-E) hysteresis loops were measured with RT6000S ferroelectric test system in virtual ground model at ambient temperature. Fig. 6 shows the P-E hysteresis of $BaNb_{0.3}Ti_{0.7}O_3$/Si PNH, in which an increased reverse field was applied at the beginning of the measurement. The remnant polarization ($P_r$) and coercive field ($E_c$) for the PNH are 1.78 μC/cm$^2$ and 278 kV/cm, respectively. It is worth to note that we have not observed the P-E loop in the $BaNb_{0.3}Ti_{0.7}O_3$ thin film due to the higher Nb-doped (30%) and very large leakage current. This fact gives a support for the enhanced ferroelectricity originating from the junction interface. The detailed mechanism needs further investigation. It is noteworthy that the interface of the PNH can enhance the ferroelectric property even if the ferroelectric property is not good enough because the ferroelectric property do not present in the higher Nb-doped BNTO film. Further investigation on the improvement of the ferroelectricity by changing Nb-doped concentration and growth conditions, and the mechanism behind the interesting phenomena are under going.

We have studied the PNH consist of *n*-type amorphous $LaAlO_{3-\delta}$ and p-type Si. The good I-V rectifying property, the ferroelectricity of interface enhancement and the fast photovoltaic effect have been observed in $LaAlO_{3-\delta}$/Si PNH. The results shows that the PNH consist of *n*-type amorphous provskite oxide of oxygen-deficient and *p*-type Si also are possessed of the better multifunctional properties of rectification, ferroelectricity and photoelectric effect.

**Summary**

In today's most advanced electronics research much attention is paid to the fabrication of artificially designed structures to verify new device concepts based on quantum effects. A key structure of the electronics devices is the P-N junction. A series of all-perovskite oxide PNHs as well as perovskite oxide and Si PNHs have been fabricated by a laser molecular-beam epitaxy. We observed, besides their multifunctional properties of rectification, MR and ultrafast photoelectric effect, some unusual properties which neither Sr-doped $LaMnO_3$ nor Si has. While both the bulk and thin-film of doped $LaMnO_3$ show negative MR, the PNHs consisting of Sr-doped $SrMnO_3$ and Nb-doped $SrTiO_3$ or Si we fabricated shows a high sensitivity of positive MR in low magnetic field. It is also noteworthy that the ferroelectric property due to interface enhancement was observed experimentally in $BaNb_{0.3}Ti_{0.7}O_3$/Si PNHs even if the ferroelectric property is not good enough because the ferroelectric property do not present in the higher Nb-doped $BaNb_{0.3}Ti_{0.7}O_3$ film. Our

experimental results show that the PNHs properties of the low doping are better than that of the higher doping not only for electrical property but also for magnetic property. We have to emphasize that most of the properties in the PNHS depend on the doped concentration and growth conditions. However, it is expected that the further investigation on the all-perovskite oxide PNHs as well as perovskite oxide and Si PNHs could not only stimulate theoretical study on the mechanisms but also would open up new possibilities in device developments.

**Acknowlegements**

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