Many efforts have been devoted recently to explore quantum functional properties and verify new device concepts based on manganese oxide. Tanaka et al. reported the electrical modulation of double-exchange ferromagnetism in La$_{0.9}$Ba$_{0.1}$MnO$_3$ in the junction of a $p$-$n$ $p$-$n$ junction. Mitra et al. observed a large positive magnetoresistance (MR) effect in systems of Sr-doped LaMnO$_3$ and Nb-doped SrTiO$_3$-$p$-$n$ junctions as well as multilayer $p$-$n$ heterostructure. We have investigated the fabrication technology of atomically controlled oxide films on other oxides and discovered the modulation effect of current and voltage as well as a large positive MR effect in systems of Sr-doped LaMnO$_3$ and Nb-doped SrTiO$_3$-$p$-$n$ junctions, as well as multilayer $p$-$n$ heterostructure. With regard to optical effects on manganese oxides, Zhang et al. reported the experimental laser-induced thermoelectric voltages in La$_{1-x}$Ca$_x$MnO$_3$ films with a photovoltaic pulse of $\sim 2$ $\mu$s full width at half-maximum (FWHM) when the film was irradiated by a 1064 nm laser pulse of 15 ns duration. Sun et al. observed a positive photovoltaic effect in La$_{0.9}$Pr$_{0.38}$Ca$_{0.33}$MnO$_3$ films with a photovoltaic pulse of $\sim 8$ ms FWHM when the La$_{0.9}$Pr$_{0.38}$Ca$_{0.33}$MnO$_3$ film was irradiated by a 532 nm laser pulse of 10 ns duration. In order to control the functional properties of oxide with Si electronics, several insulating oxide films, such as SrTiO$_3$, BaTiO$_3$, and ferroelectric Bi$_{12}$TiO$_{20}$ films, were reported to be epitaxially deposited on Si substrates. In this letter, we present the laser molecular-beam epitaxy (laser MBE) and ultrafast photoelectric effect of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO)/Si-$p$-$n$ junctions. The rise time was $\sim 210$ ps and FWHM was $\sim 650$ ps of the photovoltaic pulse when the LSMO film in the junction was irradiated by a 1064 nm laser pulse of 25 ps duration.

To form a $p$-$n$ junction with functional properties by using an oxide and Si semiconductor, we chose LSMO as a $p$-type material, and 2 in. $n$-type Si (001) wafers with resistivity of 4 $\Omega$ cm as the substrates. The lattice mismatch between LSMO ($\sim 3.86$ Å) and Si (5.43 Å) is fairly small ($\sim 0.55\% = (3.86/5.43)$) with the LSMO unit cell rotated 45$^\circ$ around the Si surface normal [100] axis. The LSMO films were fabricated by a computer-controlled (laser MBE). Before depositing the LSMO film, Si substrates were carefully cleaned sequentially using alcohol, acetone, and deionized water. The substrates were then dipped into a $\sim 5\%$ HF solution for 20–30 s to remove the native silicon oxide on the surfaces and to form a hydrogen-terminated surface at the same time. Subsequently, the Si substrates were transferred into the epitaxial chamber immediately. When the base pressure of epitaxial chamber was pumped to $5 \times 10^{-6}$ Pa, a focused pulsed XeCl excimer laser beam ($\sim 20$ ns, 2 Hz, $\sim 1.5$ J/cm$^2$) was irradiated onto a hot-pressed LSMO target. The initial about 12 Å ($\sim 3$ unit cells) LSMO film was deposited onto the Si substrate surface at room temperature to prevent the formation of the amorphous SiO$_2$ layer. The Si substrate was then raised to $620$ °C in the base pressure of $\sim 1 \times 10^{-5}$ Pa before the deposition of the LSMO film started again. An in situ reflection high-energy electron diffraction (RHEED) system and CCD camera was used to monitor the growth process of the LSMO thin films. The RHEED streak pattern of the LSMO film with the thickness of 12 Å appeared when the initial 12 Å LSMO film was crystallized by increasing the substrate temperature up to $620$ °C and the thermal annealing process. The LSMO was continuously deposited and meanwhile an active oxygen source ($\sim 10\%$ O) was introduced into the chamber and a pressure of 3 $\times 10^{-2}$ Pa was kept during the deposition. The thickness of the LSMO films of samples deposited for the measurement were in the range of 300–600 nm. The crystallization of the LSMO film was examined in situ by RHEED, and also characterized ex situ using x-ray diffraction (XRD) analysis.

The RHEED pattern of 400 nm LSMO film is shown in the inset of Fig. 1. The sharp streak pattern indicates that the LSMO film has a good crystallized structure and smooth surface. Figure 1 shows a typical XRD pattern of 400 nm LSMO film on Si substrate. Except for LSMO (001) and (002) and Si (002) diffraction peaks, there is no diffraction peak from impurity phases or randomly oriented grains, which implies that the LSMO film is $c$-axis oriented; that is, LSMO [110]$_{\parallel}$[Si[001]]

To determine the electrical and photoelectric behaviors of the $p$-$n$ junction, the 2 in. sample of LSMO/Si was cut into $5 \times 6$ mm$^2$ and $2 \times 2$ mm$^2$ for the photovoltaic and electrical measurements. The indium (In) electrodes were placed on the surfaces of the LSMO thin films and Si substrates, as shown in the insets of Figs. 2, 3, and 4. For the
photoelectric measurement, the In electrode was placed on a corner of the LSMO film surface.

The $I-V$ characteristic of the LSMO/Si $p-n$ junctions (2 $\times$ 2 mm$^2$) was measured with a pulse-modulated current source. Figure 2 shows an $I-V$ curve of a LSMO/Si $p-n$ junction at room temperature. The junction exhibits good nonlinear and rectifying $I-V$ characteristics.

The photoelectric behaviors of LSMO/Si $p-n$ junctions (5 mm $\times$ 6 mm) were further investigated using a 1064 nm Nd:YAG laser (pulse width 25 ps) as well as a 10.6 $\mu$m CO$_2$ pulse laser and measured by an oscilloscope of 130 ps rise time (Tektronix® TDS7254B) at ambient temperature. An open-circuit photovoltage to the $p-n$ junction was observed between the two electrodes when the LSMO film surface was irradiated by a laser pulse. One of the most striking observations of the present work is the picosecond ultrafast photoelectric effect. Figure 3 shows the typical photovoltaic pulse as a function of time when the LSMO/Si $p-n$ junction is irradiated with a 1064 nm laser pulse. The rise time is about 10 ns and the FWHM is about 12 $\mu$s when the photovoltage is directly measured. It should be noted that there is a sharp rise of the pulse at the very beginning, but then the photovoltage signal gradually decreases. When a 0.2 $V$ resistance is connected in parallel across the $p-n$ junction, as shown in Fig. 4, the rise time dramatically reduces to $\sim$210 ps and the FWHM also reduces to $\sim$650 ps. Evidently, the rise time and FWHM in Fig. 4 are much shorter than those in Fig. 3. The FWHM in Fig. 4 is about four orders of magnitude narrower than that of $\sim$2 $\mu$s observed in Ref. 8, and about seven orders of magnitude narrower than that of $\sim$8 ms observed in Ref. 9.

There are two main factors that influence the rise time and FWHM of the photovoltaic effect in Fig. 3. First, the interface of the $p-n$ junction must be of good quality, as well as the LSMO film, because either defect at the interface or in the material would influence the production and lifetime of nonequilibrium carriers, which are of the same order as the decay time of the photovoltaic pulse in Fig. 3. Second, there is a junction capacitance in the LSMO/Si $p-n$ junction as well as the impedance of the measurement system. In our case, the junction capacitance is about 30 pF at 500 MHz for the LSMO/Si sample of 5 $\times$ 6 mm$^2$, and the input impedance of the oscilloscope is 1 M$\Omega$. In other words, the discharge time constant is about 30 $\mu$s, which is comparable to the FWHM of the photovoltaic pulse in Fig. 3, so it seems that the photovoltaic decay time in Fig. 3 is closely related to the $p-n$ junction capacitance and the impedance in the measurement system. Therefore, the ultrafast photovoltaic pulse observed after connecting a 0.2 $\Omega$ resistance in parallel across the junction, as shown in Fig. 4, reveals a more realistic process of photoelectric emission in the $p-n$ junction.

Our experimental results show that the photoelectric effect in the $p-n$ junctions is not only an ultrafast effect, but is also highly sensitive to the laser pulse. The maximum photovoltaic sensitivity was 435 mV/mJ, and the maximum cur-
We did not observe any photoelectric effect when the LSMO film in the junction was irradiated by a 10.6 μm CO₂ laser pulse for which the photon energy is much smaller than either of the band gap of the LSMO or Si. This result clearly demonstrates that the ultrafast photovoltaic is a photoelectric effect instead of a thermoelectric effect.

In conclusion, we have fabricated the LSMO/Si p-n junctions and observed the ultrafast photoelectric effects in the junctions. It is noteworthy that the p-n junction of LSMO and Si combine the functional properties of oxide with Si electronics. The key advantages of LSMO/Si is that the new structure consisting of a manganite as a MR material (LSMO) and a conventional semiconductor (Si) combines multifunction of MR,11 rectification, and ultrafast photoelectric characteristic, which is with potential of new applications. The interesting properties of such a new structure related to spin ordering, charge carrying, and electron-photon interaction in the system are stimulating a widely study. Further investigation, both experimental and theoretical, on the mechanism of the multifunctional properties of electricity and optics and magnetics in such systems are under going.

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