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Pico-second photoelectric characteristic in manganite oxide $La_{0.67}Ca_{0.33}MnO_3$ films*

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Ultrafast photoelectric characteristic has been observed in $La_{0.67}Ca_{0.33}MnO_3$ films on tilted $SrTiO_3$ substrates. A pico-second (ps) open-circuit photovoltage of the perovskite manganese oxide films has been obtained when the films were irradiated by a 1.064 μm laser pulse of 25 ps duration. The rise time and full width at half-maximum of the photovoltage pulse are ~300 ps and ~700 ps, respectively. The photovoltaic sensitivity was as large as ~500 mV/mJ.

Keywords: manganese oxide, thin film, photoelectric characteristic
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$REMnO_3$ (RE = trivalent rare earth element) with the structure of perovskite type are usually an antiferromagnetic semiconductor or insulator. If the trivalent rare earth element is partially doped with the divalent alkaline earth element, the doped manganese oxides $RE_{1-x}A_xMnO_3$ are formed and show colossal magnetoresistance (CMR) effect.[1] In the past ten years, due to its potential application in high-density magnetic head, sensor, and photoswitching etc, researches on CMR thin films with the application of external fields, such as magnetic field, temperature, electric field, and on the transport properties of the carriers have attracted much attention.[2−5]

In order to investigate the photoelectric characteristic, a low-frequency optical response was studied in the epitaxial thin films of the CMR oxide La–Ca–Mn–O and a bolometric optical response was observed by Rajeswai *et al.*[6] They suggested that the optical response is thermal in nature. Recently, Habermeier *et al*[7] and Zhang *et al*[8] found larger laser-induced thermoelectric voltages in the CMR films deposited on vicinal cut $SrTiO_3$ (STO) substrates. They think that it is compatible with the predictions given by a thermopile model based on the existence of off-diagonal elements of a Seebeck tensor. Up to now, few reports about the photoelectric characteristic in perovskite manganese oxide films have been presented.[9]

In this short note, we report the ultrafast photoelectric characteristic in $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) films on tilted STO substrates. We have observed the open-circuit photovoltaic pulse with a rise time of about 300 pico-second (ps) and full width at half-maximum (FWHM) of about 700 ps when the LCMO films were irradiated by a laser pulse of 25 ps duration and 1.064 μm wavelength.

To fabricate high-quality LCMO thin films on STO substrates, a computer-controlled laser molecular beam epitaxy (laser MBE) system was used to deposit the LCMO films with laser energy density ~1 J/cm^2, wavelength λ=308 nm, repetition rate 2 Hz and pulse duration ~20ns.[10] In order to obtain a large photoelectric effect, we deposited the LCMO film on the 10° tilted to [001] STO substrate. The thickness of the LCMO film was 200–400 nm. Examination of the *in situ* reflection high-energy electron diffraction and *ex situ* x-ray diffraction shows that the LCMO

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films are single phase and epitaxially grown on the STO substrates.

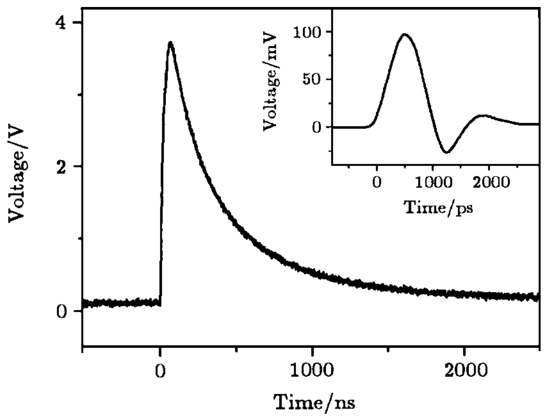

Fig.1. Variation of the open-circuit photovoltage with time after excitation with a 1.064 μm laser pulse on the LCMO film. The inset is the variation of the open-circuit photovoltage with time after a 0.5 Ω resistance was connected in parallel with the LCMO film.

Two indium (In) electrodes were attached on the two ends of the LCMO film surface (5mm$\times$10mm). The photoelectric characteristic of the LCMO films was studied with a mode-locked Nd-YAG pulsed laser (λ=1.064 μm, energy: 0.85 mJ, FWHM=25 ps) as well as a 10.6 μm CO_2 pulse laser, and measured by an oscilloscope of 130 ps rise time (Tektronix TDS7254B) at ambient temperature. Figure 1 shows the typical photovoltage pulse as a function of time when the LCMO film (250 nm thick) is irradiated with a 1.064 μm laser pulse. The photovoltaic sensitivity is as large as ~500 mV/mJ. The rise time is about 45 ns and the FWHM is about 280 ns when the photovoltage is directly measured. The influence of measurement circuit should be noted, especially, for the response time, because there are capacitance and impedance in the measurement circuit. When a 0.5 Ω resistance is connected in parallel with the LCMO film, under the same experimental condition mentioned above, the rise time dramatically reduces to ~300 ps and the FWHM also reduces to ~700 ps, as shown in the inset of Fig.1. Evidently, the rise time and FWHM in the inset of Fig.1 are much shorter than that in Fig.1. The FWHM in the inset of Fig.1 is three orders of magnitude narrower than that of ~2μs reported in Ref.[8]. The experimental results reveal a more realistic process of photoelectric emission in the film, and show that the photovoltaic effect is an ultrafast process.

We have not observed any photovoltaic signal when the LCMO films were irradiated by a 10.6 μm CO_2 laser pulse. As the photon energy of 1.064 μm wavelength is larger, and the photon energy of 10.6 μm wavelength is much smaller than the band gaps of LCMO (1–1.3 eV), so the results above clearly demonstrate that the nonequilibrium charge carriers, i.e., electrons and holes, are created in the LCMO film when the surface of LCMO film is irradiated by photons with an energy larger than the band gap of the system. In other words, the creative process of nonequilibrium charge carriers is a photoelectric process.

In conclusion, a photoelectric characteristic of ps response has been observed in manganese oxide LCMO films to the best of our knowledge for the first time. We believe that the photovoltaic characteristic we observed is an intrinsic characteristic in the perovskite manganese oxide films, and the study on physical mechanisms of directional movement of the nonequilibrium charge carriers is underway.

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