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Laser-induced ultrafast photovoltaic effect in $La_{0.67}Ca_{0.33}MnO_3$ films at room temperature

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Abstract

Pulsed laser-induced ultrafast photovoltaic effects have been investigated in $La_{0.67}Ca_{0.33}MnO_3$ films on tilted $SrTiO_3$ substrates fabricated by laser molecular beam epitaxy. A picosecond (ps) photovoltaic pulse without any applied bias to the film has been observed at room temperature. The rise time and full-width at half-maximum of the photovoltaic pulse are as short as 300 and 700 ps, respectively when the film has been irradiated by a laser pulse of 25 ps duration and 1.064 μm wavelength. The photovoltage sensitivity is as large as 0.45 V/mJ, and the photocurrent sensitivity is more than 0.25 A/mJ. The mechanism is proposed as the combination of a photoelectron and a Seebeck processes, and the Seebeck coefficient we obtained, ~4.04 μV/K, is one order larger than previous report.

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Keywords: Colossal magnetoresistance; Photovoltaic effect; Thin film

1. Introduction

Interest in the constant search and exploration of new materials is simulated by the scientific significance of phenomenon and its practical applicability. The effect of colossal magnetoresistance (CMR), observed in hole-doped manganites with the basic formula of $RE_{1-x}A_xMnO_3$ (RE = trivalent rare earth element, A = Ca, Sr, Pb, Ba), triggered keen interest to this particular class of manganites since it shows no saturation, even in very strong magnetic fields [1]. It is more attractive to study the optical response in these materials towards understanding the nature of electrical transport. Since the material has a high optical absorption coefficient over a broad wavelength range, the CMR materials offer promise as potential uncooled or moderately infrared detectors [2,3]. The photon-induced change of the transport characteristic in (La,Ca)MnO thin films was observed under illumination with visible light [4], suggesting that a novel photon-doping effect may exist in doped manganites. The transient resistance change induced by modulated laser pulse was reported in the double-doped perovskite $La_{0.67}(Ca_{0.33}Sr_{0.67})_{0.33}MnO_3$ thin film and explained them by the double exchange model and the small polaron theory [5]. The results mentioned above were observed with an applied bias on the system. Recently, laser-induced thermoelectric voltages were found in $La_{1-x}Ca_xMnO_3$ thin films grown on vicinal cut substrates, which is compatible with the predictions given by a thermopile model based on the existence of off-diagonal elements of the Seebeck tensor [6,7], in which both the rise time and full-width at half-maximum (FWHM) are as long as several hundreds nanoseconds or even in the order of microseconds.

In this paper, we report the observation of ultrafast photovoltaic effects in epitaxial $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) films on a degree varying from 1° to 20° tilted to [0 0 1] direction of $SrTiO_3$ (STO) substrates induced by pulsed laser irradiation at room temperature. Under laser

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pulse irradiation of 25 ps in duration, the FWHM of photovoltaic pulse is 700 ps and the rise time is 300 ps. Especially, the photovoltaic signals were generated without an applied bias to the films in our experiments.

2. Experimental details

LCMO films with thickness of about 250 nm were deposited on STO substrates vicinal cut with the surface at an angle varying from 1° to 20° to the (0 0 1) plane by the laser molecular beam epitaxy [8]. An in situ reflection high-energy electron diffraction (RHEED) system and charge-coupled device (CCD) camera were used to monitor the growth process of the LCMO thin films. The fine RHEED intensity oscillation and sharp RHEED streak patterns showed that the films had smooth surface and were grown two-dimension epitaxially on the substrates. For the photovoltaic measurement, the In electrodes were placed on the surface of the LCMO films as shown in the inset of Fig. 2, and were always kept in the dark to prevent the generation of any electrical contact photovoltage. The irradiation area was about 20 mm^2. The signal was monitored with an oscilloscope of 130 ps rise time (Tektronix TDS7254B) at room temperature.

3. Results and discussion

Taking the *c*-axis diffraction peak of the substrate as an internal standard, the X-ray diffraction (XRD) $\theta-2\theta$ pattern of LCMO (250 nm) film is given in Fig. 1(a), indicating a single phase structure. Specially, the XRD pattern of LCMO can only be observed with the sample being carefully aligned with the [0 0 1] direction of substrate and the offset point being set as α, which indicates the coherently titled LCMO film with the *c*-axis exactly along the *c*-axis of STO and also inclined by α to the surface normal.

The resistance was measured by the standard linear-four-probe technique with current-in-plane (CIP) geometry using Physical Properties Measurement System (PPMS) made by Quantum Design Inc., USA. Fig. 1(b) shows the temperature dependence of the resistance of LCMO films on 10° tilted and untilted STO substrates. The film is metallic at low temperature and insulating above T_{MI}, where T_{MI} is a temperature corresponding to the maximum of the resistance. Compared with that of untilted one, the higher resistivity of tilted film is resulted from the conductive anisotropy due to the change of Mn–O bond length, which can be simulated by using the random network model based on the phase separation scenario [9].

Fig. 2 presents a typical open-circuit photovoltage transient of LCMO (250 nm) on 10° tilted STO substrate to a pulsed laser irradiation of 1.064 μm and 25 ps in duration. The pulsed laser energy density was ~0.04 mJ/mm^2. The peak voltage U_P is 0.36 V. The *RC* constant in the circuit should be responsible for the slow decay component in Fig. 2. The rate of laser induced carriers in

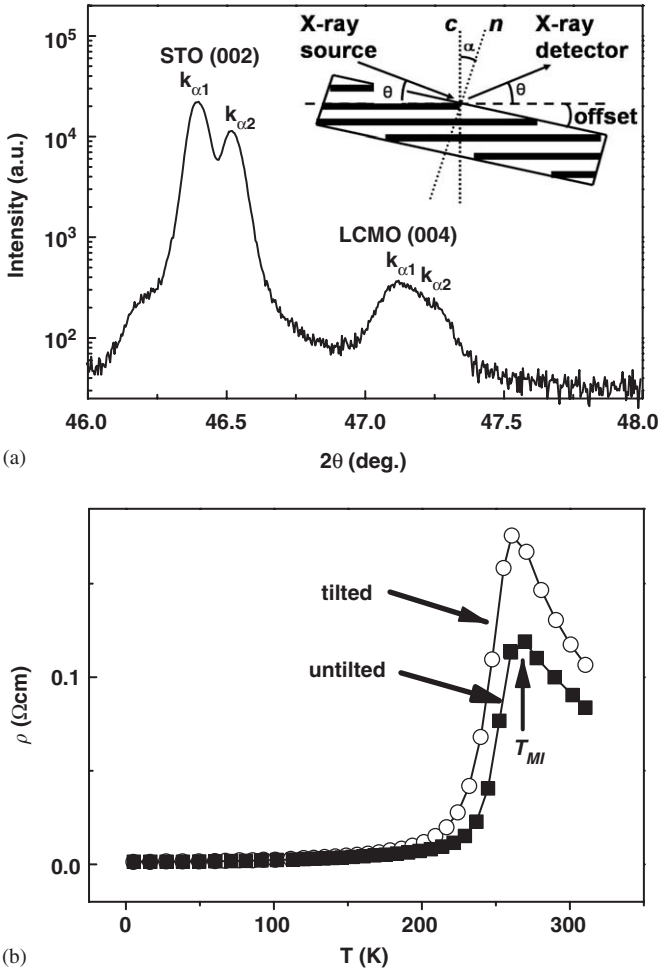

Fig. 1. (a) XRD pattern of LCMO (250 nm) thin film on 10° tilted to [0 0 1] direction of STO substrate. The inset shows the configuration of $\theta-2\theta$ scan for the vicinal film, where, offset $=\alpha=10°$. (b) The resistivity of LCMO (250 nm) thin films on tilted and untilted STO substrates as a function of temperature. T_{MI} marks the temperature for the metal–insulator transition.

LCMO can be presented as $\cosh^{-2}(t/\tau_1)$ where τ_1 denotes the duration of laser pulse, thus the laser induced voltage with τ_2, here τ_2 being equivalent to the recharging time *RC* of the circuit, can be obtained by the equation as follows, $U(t) \propto e^{-t/\tau_2}\int_{-\infty}^{t}\cosh^{-2}(t'/\tau_1)e^{t'/\tau_2}\,dt'$. The numerical results are plotted by the solid line in Fig. 2, which are in excellent agreement with the experimental data shown by circle points. The τ_2, as a parameter, is taken as 330 ns, and τ_1 is taken the same as the laser pulse duration, 25 ps, in the calculation. The good agreement of the calculation with the experimental result demonstrates that the long-time decay of the laser-induced voltage in the system is indeed caused by the *RC* effect in the circuit.

To obtain a fast response of the laser-induced voltage in LCMO, the influence of circuit in the measurement and the long tail of the decay time due to *RC* in the signal has to be reduced. For this purpose, a 0.5 Ω resistance was connected in parallel with the LCMO film. As shown in Fig. 3, the rise time is dramatically reduced to be about 300 ps and the

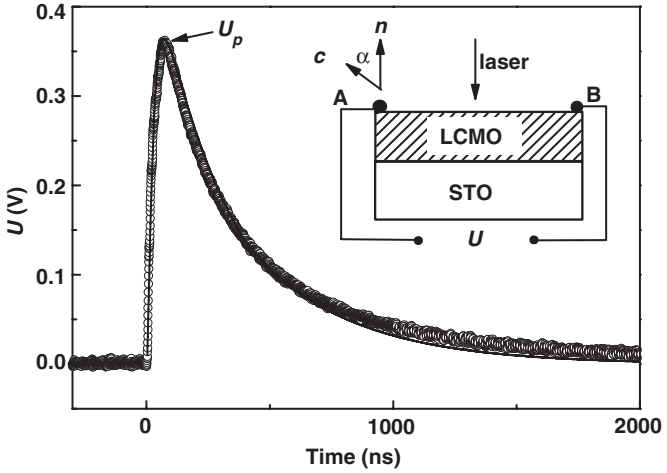

Fig. 2. The open-circuit photovoltaic pulse (circles) of LCMO (250 nm)/STO sample irradiated by a 1.064 μm laser pulse of 25 ps duration. The solid line shows the calculated result. Schematic cross section (see the inset) indicates that the *c*-axis is tilted by an angle α with respect to the surface normal *n*, here $\alpha = 10^\circ$. *A* and *B* denote the electrodes, and the voltage *U* is observed under a laser irradiation normal to the LCMO layer.

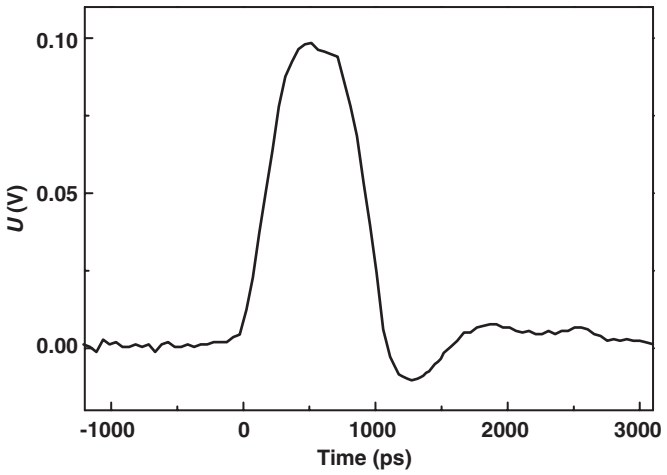

Fig. 3. Variation of the photovoltage with time after a 0.5 Ω resistance was connected in parallel with the LCMO film ($\alpha = 10^\circ$) under an excitation with a 1.064 μm laser pulse.

FWHM is also reduced to be about 700 ps for the photovoltaic pulse. The dip of the signal and the slightly oscillation behavior may come from an impedance mismatching in the circuit. The FWHM in Fig. 3 is about three orders of magnitude narrower than that of ~1.5 μs reported in Ref. [7].

Our experimental results show that the photovoltaic effect in the LCMO films is not only an ultrafast process but also highly sensitive to the laser pulse. The maximum photovoltaic sensitivity was 0.45 V/mJ, and the maximum photocurrent sensitivity was more than 0.25 A/mJ when a resistance $\leqslant 0.5\,\Omega$ was connected in parallel with the film.

STO single crystal we used exhibits a sharp absorption edge at 0.388 μm, which is in agreement with its band gap of ~3.2 eV. Thus photo-carriers in STO can be only generated under ultraviolet light with the wavelength less than 0.4 μm [10]. Furthermore, the photovoltaic pulse in LCMO/STO cannot be observed with a laser wavelength of 1.34 or 10.6 μm. This can be easily understood by the comparison of the photon energy and the band gap of the sample we measured. The photon energies, both 0.925 and 0.117 eV corresponding to the light with the wavelength of 1.34 and 10.6 μm, respectively, are smaller than both the band gap of LCMO (~1 eV) films and that of STO (~3.2 eV) substrate, so that it is impossible for the photons to excite the electron–hole pairs in either the LCMO film or the STO substrate. The experimental results demonstrate that the production of the photon-induced carries in the system play a crucial role in the photovoltaic process.

In particular, the signal polarity is reversed when the samples are irradiated from the sides of the STO substrates comparing to being irradiated from the sides of the LCMO films. This phenomenon can be understood by the reversal of temperature gradients in the film thickness direction based on the atomic layer thermopile model [11]. By irradiating the film surface with a short laser pulse, a time-dependent temperature gradient $\nabla T(t)$ within the film and perpendicular to the film surface is obtained. A thermoelectric field, $\mathbf{E}(t) = \boldsymbol{S}\nabla T(t)$, is generated due to the Seebeck effect, where $\boldsymbol{S}$ is the Seebeck tensor. The off-diagonal element in $\boldsymbol{S}$ gives rise to an electric field perpendicular to the temperature gradient resulting in a directional movement of the non-equilibrium photo-generated carriers in LCMO film and leading to a lateral voltage given by $U = l(S_{ab} - S_c)\sin(2\alpha)\nabla_n T/2$. Here l is the laser spot diameter, S_{ab} and S_c are the Seebeck coefficients of the crystalline *ab*-plane and along the *c*-axis [12].

The voltage is induced by the combination of a photoelectron and a Seebeck processes. In photoelectron process, electrons and holes were created by photons, and then the thermal gradient caused the carrier moving in the system resulting in the voltage in the system. It has been well known that each element of Seebeck tensor is proportional to the corresponding electrical resistivity of the system, and the electrical resistivity is reverse proportional to carrier density of the system. In this way, Seebeck tensor strongly depends on the carrier density in the system [12], as well as the voltage. In the system we studied, most of carriers are induced by photons by photoelectric effect, and Seebeck effect caused the carrier moving, so the combination of these two effects resulted in the voltage we observed.

LCMO (250 nm) films on STO substrates with different tilted degree α have been deposited, and the peak values of open-circuit photovoltage, U_P, as a function of $\sin(2\alpha)$ are shown in Fig. 4. We can see that the U_P increases linearly with $\sin(2\alpha)$ and the slope β is ~1.05 V, which is in consistent with Seebeck theory. From the heat flow equation $Q = \kappa\nabla_n T \approx E_{laser}/\tau_2$, where Q is the heat current density, the temperature gradient $\nabla_n T$ can be

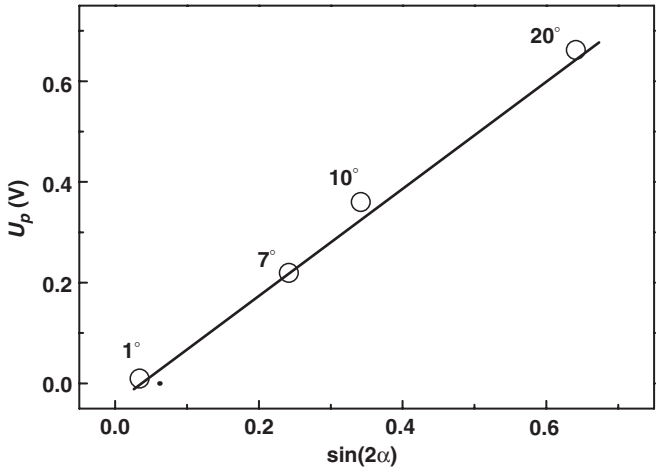

Fig. 4. U_P of LCMO (250 nm) films on STO substrates with different tilted degree α as a function of $\sin(2\alpha)$. The solid lines are guides for the eye.

estimated. E_{laser} is the absorbed 1.064 μm laser energy density and is assumed as 0.04 mJ/mm^2 since LCMO films were found to have high absorption coefficient over a broad wavelength range [13]. $\kappa = 14\,\text{mW/cmK}$ is the thermal conductivity [14]. With these values, $\nabla_n T \approx 1.73 \times 10^5\,\text{K/mm}$, and we obtain $S_{ab} - S_c = 2\beta/l\nabla_n T = 4.04\,\mu\text{V/K}$, inserting $l = 6\,\text{mm}$. This result is one order larger than that of 0.22 μV/K reported in Ref. [7].

4. Conclusion

In conclusion, ultrafast photovoltaic effects have been studied in epitaxial LCMO films. A ps photovoltaic pulse has been observed under the excited laser pulse of 25 ps duration and 1.064 μm wavelength. The rise time and FWHM is 300 and 700 ps, respectively. Based on our observation, a new mechanism combining photoelectron Seebeck effect has been proposed and the Seebeck coefficient we obtained is one order larger than previous reports. The high sensitivity of photovoltage and photocurrent suggests the promising potential of Manganite Oxide thin film as a new type of optical detector for application.

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