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Reversal transient laser-induced voltages in $La_{2/3}Ca_{1/3}MnO_3$ films*

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This paper reports that the transient laser-induced voltages have been observed in $La_{2/3}Ca_{1/3}MnO_3$ thin films on MgO (001) in the absence of an applied current. A peak voltage of $\sim$ 0.15 V was detected in response to 0.015 J pulse of 308 nm laser. It is demonstrated that the signal polarity is reversed when the films are irradiated through the substrate rather than at the air/film interface. Off-diagonal thermoelectricity may support the inversion of the signal when the irradiation direction is reversed.

Keywords: manganite oxide, thin film, photovoltaic effect
PACC: 7570, 7847, 7865

1. Introduction

The perovskite oxides have been investigated because of their interesting properties, including ferromagnetism, antiferromagnetism, metal–insulator transition, superconductivity, colossal magnetoresistance, optical properties and so on, depending on the carrier concentration due to strong coupling among the spin, charge, and orbital degrees of freedom.[1−7] During the past few years there has been active study of the photoresponse of manganite thin films. Technological interest has centred on bolometers,[8] while more basic issues have involved quasi-particle generation and carrier relaxation times.[9−11]

In our previous experiments, ultrafast photoelectric effect has been observed at room temperature in manganite oxide films in response to pulsed laser irradiation.[12−14] It is noted that no photovoltage has been found when the photon energy is larger than the band gap of these manganites (1–1.3 eV),[12] demonstrating that the production of the photon induced carriers plays a crucial role in the photovoltaic process. In this paper, we report the transient photovoltaic effect in $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) films on MgO (001) substrates at room temperature. It is emphasized that the polarity of the signal was reversed if the film was irradiated through the substrate rather than the film surface.

2. Experimental details

LCMO (800 nm) films on MgO (001) substrates were prepared by using a facing target sputtering technique.[15,16] X-ray analyses have shown that the films are oriented with the crystal c-axis perpendicular to the surface of the substrate. The sample was irradiated with 308 nm laser in duration of 20 ns, and the pulse energy density was 1 mJ/mm^2. The contacts were made by using the indium electrodes on the film surface, and the irradiated area is 5×3 mm^2. The photovoltage signal was recorded with a 500 MHz oscilloscope terminated into 1 MΩ.

3. Results and discussion

The band gap of LCMO is $\sim$ 1 eV, suggesting that the nonequilibrium charge carriers can be created in the LCMO film irradiated by 308 nm photons ($\sim$ 4 eV). Figure 1 shows a typical photovoltage together with the orientation of the laser beam with respect to the sample. When the film surface was irradiated directly (front-side), the response has a 10–90% rise time of 20 ns, a 10%–90% fall time of 800 ns, and

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a full width at half maximum (FWHM) of 120 ns.

The polarity reversal is obvious and intriguing if the film is irradiated through the transparent MgO substrate (back-side irradiation), rather than at the air/LCMO interface, the side to which the leads are attached. The peak voltage of the transient induced by the back-side irradiation is slightly lower than that by the front-side mode because of the $\sim$ 7% transmission losses associated with the two surfaces of the MgO substrate.

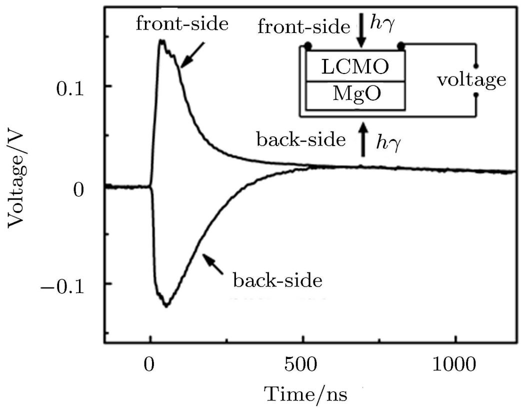

Fig.1. Photovoltaic response of LCMO film to 308 nm laser pulse in duration of 20 ns when the film was irradiated at the air/LCMO interface (front-side) and through the MgO substrate (back-side). The inset shows the schematic circuit of the sample measurement.

The average absorbance for LCMO film is over 90% in the region of 300–500 nm, as shown in Fig.2. The peak absorption for MgO substrate is found at 255 nm, which is in agreement with the band gap energy of MgO, $\sim$ 5 eV, suggested that it is impossible for the 308 nm photons to excite the electron–hole pairs in the MgO substrate and the photovoltage is mainly resulted from the nonequilibrium charge carriers created in the LCMO film.

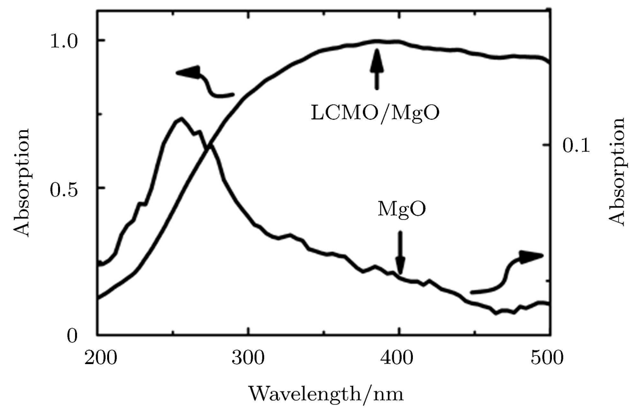

Fig.2. The absorption spectra of LCMO thin film and MgO substrate.

Off-diagonal thermoelectricity, an uncommon phenomenon which only occurs in low symmetry environments, has been suggested to the large anomalous laser-induced voltages observed in $YBa_2Cu_3O_{7-\delta}$ film on untilted substrate.[17] The theory may support the inversion of the signal when the direction of irradiation is reversed. As shown in Fig.3, by irradiating the film surface with a short laser pulse, a time-dependent temperature gradient $\nabla T(t)$ perpendicular to the film surface is obtained. A thermoelectric field, $\boldsymbol{E}(t) = \boldsymbol{S}\nabla T(t)$, is generated due to the Seebeck effect, where $\boldsymbol{S}$ is the Seebeck tensor and is of the form

$$\boldsymbol{S} = \begin{pmatrix} S_{ab}\cos^2\alpha + S_c\sin^2\alpha & 0 & (S_{ab}-S_c)\sin(2\alpha)/2 \\ 0 & S_{ab} & 0 \\ (S_{ab}-S_c)\sin(2\alpha)/2 & 0 & S_{ab}\sin^2\alpha + S_c\cos^2\alpha \end{pmatrix}. \tag{1}$$

Here S_{ab} and S_c are the Seebeck coefficients of the crystalline ab-plane and along c-axis respectively, and α is the tilt angle between the surface and surface normal.

In this study, the small angles between surface normal and c-axis may be induced by imprecisely cutting substrates, or the film deposition process. So the off-diagonal element in $\boldsymbol{S}$ is generated, and gives rise to an electric field perpendicular to the temperature gradient resulting in a directional movement of the non-equilibrium carriers in LCMO film and leading to a lateral voltage

$$U = \frac{l}{2d}(S_{ab} - S_c)\sin(2\alpha)\Delta T, \tag{2}$$

where ΔT is the temperature difference between film surface and film bottom, l the diameter of the irradiated spot, d the film thickness.

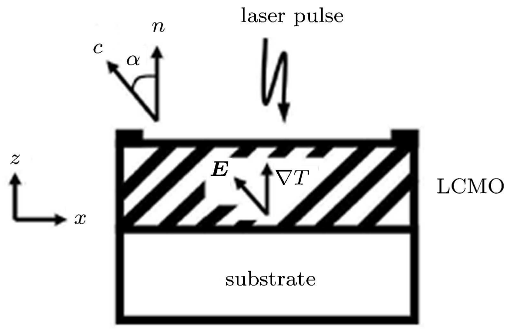

Fig.3. Schematic cross section of a LCMO film with the c axis tilted by an angle α with respect to the macroscopic surface normal n. The laser induced temperature gradient leads to a thermoelectric $\boldsymbol{E}$ which has a component in the plane of the film.

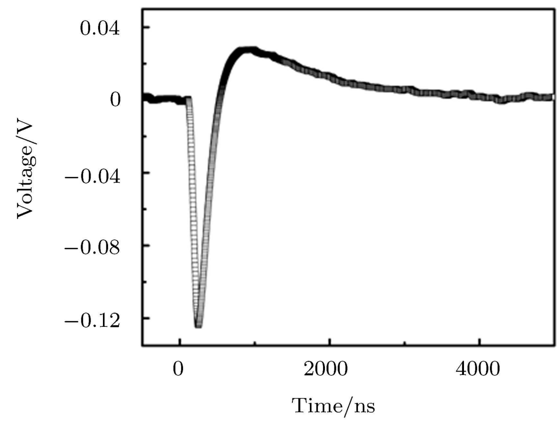

Fig.4. Photovoltaic response of LCMO film to 308 nm laser pulse in duration of 20 ns when the film was irradiated through the MgO substrate (back-side).

In particular, at 300 ns after completion of the laser pulse, the polarity of the signal changes again as shown in Fig.4, and is the same as irradiating the free surface of the film. This observation proves the interpretation that the voltage signal is caused by a temperature gradient normal to the film. When heating of the film under back-side irradiation of laser is terminated, as the heat flow from the film to the substrate is larger than that from the free film surface to the ambient air, the temperature gradient in the freely cooling film gets reversed and, therefore, the induced voltage changes sign.

4. Conclusions

In conclusion, transient laser-induced voltages have been observed in LCMO thin films epitaxially grown on MgO (001) in the absence of an applied current. The 308 nm photon energy ($\sim$ 4 eV) is larger than the band gap of LCMO ($\sim$ 1 eV), so that it is possible for the photon to excite the electron–hole pairs in the LCMO film. In particular, the signal polarity is reversed when the films are irradiated through the substrate rather than at the air/film interface. Further investigations of this phenomenon are underway to elucidate the mechanism of the effect.

References

[1] Barner J B, Rogers C T, Inam A, Ramesh R and Bersey S 1991 *Appl. Phys. Lett.* **59** 742

[2] Grishin A M, Khartsev S L and Johnsson P 1999 *Appl. Phys. Lett.* **74** 1015

[3] Xi L, Yang X L, Li C X and Ge S H 2006 *Acta Phys. Sin.* **55** 854 (in Chinese)

[4] Tang W H, Li P G, Lei M, Guo Y F, Chen L M, Li L H, Song P Y and Chen C P 2006 *Chin. Phys.* **15** 767

[5] Si J W, Cao Q Q, Gu B X and Du Y W 2005 *Chin. Phys.* **14** 2117

[6] Zhao K, Huang Y H, Zhou Q L, Jin K J, Lü H B, He M, Cheng B L, Zhou Y L, Chen Z H and Yang G Z 2005 *Appl. Phys. Lett.* **86** 221917

[7] Zhao K, Jin K J, Lü H B, Huang Y H, Zhou Q L, He M, Chen Z H, Zhou Y L and Yang G Z 2006 *Appl. Phys. Lett.* **88** 141914

[8] Rajeswai M, Chen C H, Goyal A, Kwon C, Robson M C, Ramesh R, Venkatesan T and Lakeou S 1996 *Appl. Phys. Lett.* **68** 3555

[9] Zhao Y G, Li J J, Shreekala R, Drew H D, Chen C L, Cao W L and Lee C H 1998 *Phys. Rev. Lett.* **81** 1310

[10] Averitt R D, Lobad A I, Kwon C, Trugman S A, Thorsmlle V K and Taylor A J 2001 *Phys. Rev. Lett.* **87** 017401

[11] Zhang R L, Dai J M, Song W H, Ma Y Q, Yang J, Du J J and Sun Y P 2004 *J. Phys. Condens. Matter* **16** 2245

[12] Zhao K, Huang Y H, Lü H B, He M, Jin K J, Chen Z H, Zhou Y L, Cheng B L, Dai S Y and Yang G Z 2005 *Chin. Phys.* **14** 420

[13] Lü H B, Jin K J, Huang Y H, He M, Zhao K, Zhou Y L, Cheng B L, Chen Z H, Dai S Y and Yang G Z 2004 *Chin. Phys. Lett.* **21** 2308

[14] Lü H B, Jin K J, Huang Y H, He M, Zhao K, Zhou Y L, Cheng B L, Chen Z H, Dai S Y and Yang G Z 2005 *Appl. Phys. Lett.* **86** 241915

[15] Zhao K, Zhou L Z, Leung C H, Yeung C F, Fung C K and Wong H K 2002 *J. Cryst. Growth* **237-239** 608

[16] Zhao K and Wong H K 2003 *J. Cryst. Growth* **256** 283

[17] Lengfellner H, Kremb G, Schnellbogl A, Betz J, Renk K F and Prettl W 1992 *Appl. Phys. Lett.* **60** 501