

Research Article

Polarity Switchable Photovoltages in Miscut $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ Films

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We report the transient laser-induced anomalous photovoltaic effect in the $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film grown on miscut LaSrAlO_4 (001) substrate under 248 nm pulsed laser irradiation at ambient temperature without any applied bias. A photovoltaic pulse signal was observed when the $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film was irradiated directly, and the signal polarity was reversed when the sample was irradiated through the LaSrAlO_4 substrate, while the signal recorded between the two electrodes on the surface of LaSrAlO_4 was not reversed when the sample was irradiated through $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film rather than at the surface of LaSrAlO_4 . The switchable signal polarity provides a potential application of miscut manganite films as optical components. A possible mechanism is introduced to explain the experiment results.

1. Introduction

Up to now, investigations of manganites have been focused on their interesting properties, including ferroelectric, ferromagnetic, giant magnetoresistance, and superconducting and electrooptic properties [1–6]. Several researches about photovoltaic effect and thermoelectric response were carried out for exploring their potential applications in detector [7–10]. Anomalous photovoltaic effect has been observed in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ films grown on SrTiO_3 (001) substrates. The research results provided the anisotropy of the thermoelectric power [11].

It is known that heating the surface of a thin film grown on miscut substrate by the absorption of radiation establishes a temperature gradient ∇T perpendicular to the film surface. Due to the Seebeck effect, a thermoelectric field, $E = S \nabla T$, is generated with the Seebeck tensor S [12]. The lateral voltage can be written as

$$U_l = \frac{l(S_{ab} - S_c) \sin(2\theta) \Delta T}{2d}, \quad (1)$$

where l is the irradiated length by the laser beam between two electrodes, S_{ab} and S_c are the Seebeck coefficients of the

crystalline ab plane and along the c axis, respectively, θ is the tilting angle between the c axis and the direction of laser irradiation, ΔT is the temperature difference between film surface and film bottom, and d is the film thickness.

In this paper, we focus on the polarity-switchable signal which arose in the $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film (LCMO) grown on miscut LaSrAlO_4 (LSAO) (001) substrate under 248 nm pulsed laser irradiation at ambient temperature without any applied bias. We not only observed a photovoltaic signal produced in LCMO film that was reversed when the sample was irradiated through the substrate rather than at LCMO film, but also found a tiny signal generated in LSAO substrate, which was not reversed when the incident light irradiated the substrate in the opposite direction. The possible mechanism introduced to explain the experiment results provides a potential application of manganite films in optical components.

2. Experimental

Epitaxial LCMO film with a thickness d_1 of about 120 nm was deposited on the LSAO substrate with a thickness d_2 of 0.5 mm and an intentional 10° vicinal cut toward the [010] direction by facing-target sputtering technique. The

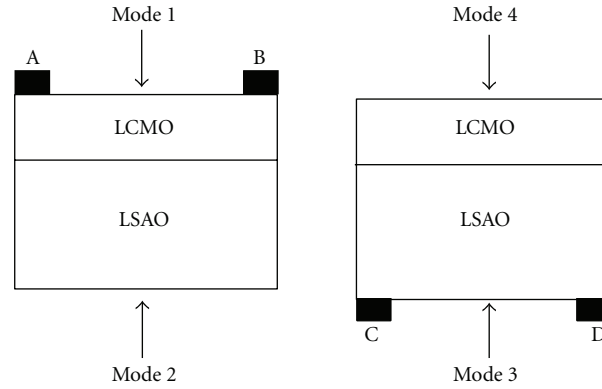


FIGURE 1: Schematic illustration of photoelectrical experiment on LCMO/LSAO sample.

substrate was kept at 680°C with the oxygen pressure of 30 mTorr during deposition. After the deposition, the vacuum chamber was immediately back-filled with 1 atm oxygen gas. The LCMO film was then cooled to room temperature with the substrate heater power cut-off. The structure of the sample was characterized by X-ray diffraction (XRD).

Figure 1 shows the schematic illustrations of photovoltaic response measurement. LCMO/LSAO sample of $5 \times 2.5 \text{ mm}^2$ geometry was used with two in-plane colloidal silver electrodes separated by 3 mm being individually placed on the surface of the LCMO film and LSAO substrate as displayed in Figure 1. Modes 1 and 4 (Modes 2 and 3) stand for irradiating the sample through LCMO film (LSAO substrate) with electrodes on LCMO film and LSAO substrate, respectively. The anode was connected with A (and C), and the cathode was connected with B (and D). The electrodes were always kept in the dark to prevent the generation of any electrical contact photovoltaic effect. The 248 nm KrF excimer laser (pulse duration of 20 ns, repetition rate of 1 Hz) was used as the light source at ambient temperature in air with a pulse energy of 2.88 mJ. The waveform was recorded by a sampling oscilloscope terminated into 1 M Ω .

3. Results and Discussion

The XRD θ - 2θ scan curve of the LCMO/LSAO is presented in Figure 2, where the [001] axis was aligned carefully. Except for the diffraction peaks of LSAO (00 l) and LCMO ($h0h$), there are no diffraction peaks from impurity phases or randomly oriented grains, indicating that the LCMO film is a single phase and [202] oriented.

Figure 3 displays the photovoltaic responses of LCMO/LSAO under the 248 nm pulsed laser irradiation without any applied bias. Two significant characteristics of the photovoltaic signals were observed: (i) the polarity of the signal gotten from LCMO film switched when the sample was irradiated through the substrate rather than at the film surface (Figure 3(a)). While no reversed signal polarity arose for modes 3 and 4 (Figure 3(b)). (ii) The order of the peak photovoltage (U_p) according to intensity is $U_1 > U_2 > U_3 >$

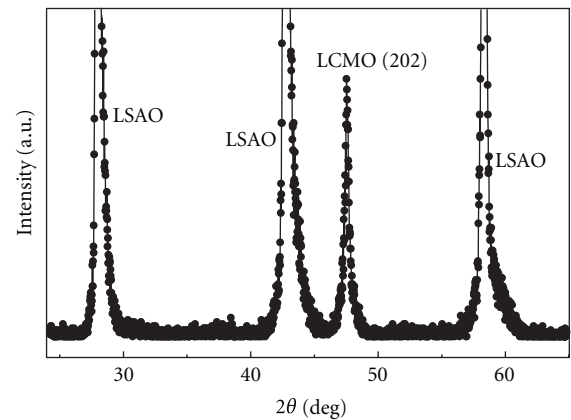


FIGURE 2: XRD pattern of LCMO/LSAO sample.

U_4 , where U_1 , U_2 , U_3 , and U_4 correspond to the peak photovoltage for modes 1, 2, 3, and 4. The maximum U_p of 0.476 V was observed with a rising time of 140 μs and a full width at half maximum (FWHM) of 29 μs in mode 1. While the smallest U_p of 0.013 V was observed in mode 4, almost 40 times lower than that of mode 1.

To investigate the anomalous photovoltaic effect, we measured the absorption spectra of LCMO/LSAO and LSAO single crystal as presented in Figure 4. The absorption edge of LSAO crystal is located at 253 nm in agreement with its band gap of 5.3 eV, indicating that nonequilibrium charge carries in LSAO crystal can be created under 248 nm ultraviolet irradiation. However, the substrate thickness (0.5 mm) is much longer than the diffusion length of the charge carries in the LSAO side. In addition, due to the strong absorption in LSAO substrate, few photons can inject into the LCMO layer. As a result, a smaller photovoltage presents for mode 2 compared with that for mode 1.

Concerning to illustrate the generation of polarity switchable photovoltages, several researches focused on changing film thickness and regulating the incident angle were carried out [13–16]. These researches involve both tilted films and single crystals where the Seebeck effect is widely used. The reversal signal generated in LCMO film under working

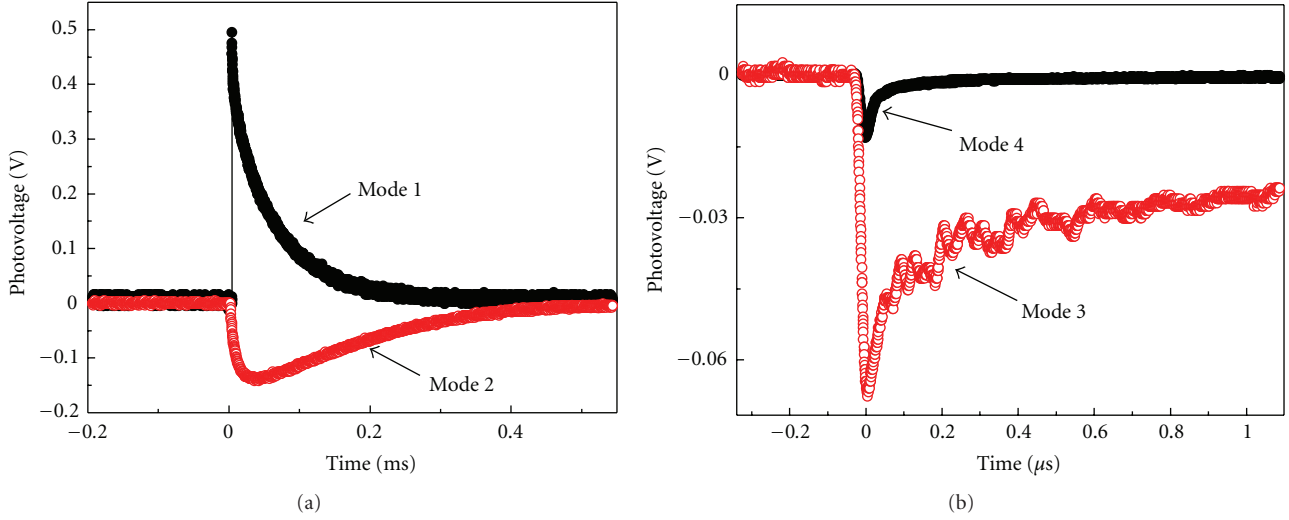


FIGURE 3: Typical photovoltaic pulses as functions of time for LCMO/LSAO sample.

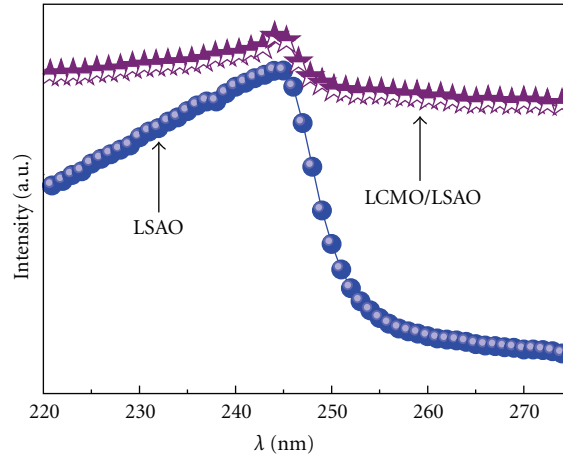


FIGURE 4: The absorption spectra of the LCMO/LSAO sample and LSAO single crystal.

mode 2 is in accordance with our previous study [11], which was attributed mainly to the ∇T reversal between the front and back end of LCMO film. In order to explain the experiment results shown in Figure 3, the schematic model of the procedure of induced charge and Seebeck processes is built in Figure 5. Due to the Seebeck effect, a positive potential difference U_{+AB}^1 along the LCMO film arises when the laser irradiates the sample in the air/LCMO-direction (mode 1). The photo-induced charge carries distribution in LCMO film induces a reversed charge carries distribution along the back-face of LSAO owing to the capacity effect of dielectric, which leads to a negative potential difference U_{-CD}^4 (mode 4).

Irradiating the LSAO substrate directly leads to a negative U_{-CD}^3 along their surface (mode 3), which induced reversed charge distribution on the LCMO/LSAO interface due to the capacity effect and resulted into a positive U_{+AB} in LSMO film. However, a negative lateral voltage U_{-AB} along the LCMO is generated due to reversal of the ∇T in the thickness direction for mode 3. Thus there exist two opposite photovoltages in LCMO. U_{+AB} is much smaller than U_{-AB}

because the induced charge on the interface produced by LSAO dielectrics is an extremely small amount compared to that from the reversed ∇T in LCMO. In sum, a negative U_{-AB}^2 , equal to $U_{-AB} + U_{+AB}$, is generated along the surface of LCMO film (mode 2).

Generally speaking, the polarity of signal generated in LCMO film (modes 1 and 2) is reversed mainly owing to the ∇T reversal between the front and back end of LCMO film according to Seebeck effect. And two different physical mechanisms, capacity effect of dielectric and Seebeck effect, determine the conformity of photovoltaic polarity under working modes 3 and 4. In addition, the polarity of photovoltage generated under working mode 3 is reversed, comparing with that under mode 1, due to the supplementary tilting angle θ and connection pattern of electrodes.

It is easy to understand that the absolute value of U_{+AB}^1 is larger than U_{-AB}^2 because U_{+AB} did much to offset U_{-AB}^2 . Since the thermoelectric field leading to U_{-CD}^3 is much larger than the electric field generated by induced charge of LSAO dielectrics, U_{-CD}^3 is larger than U_{-CD}^4 . The potential

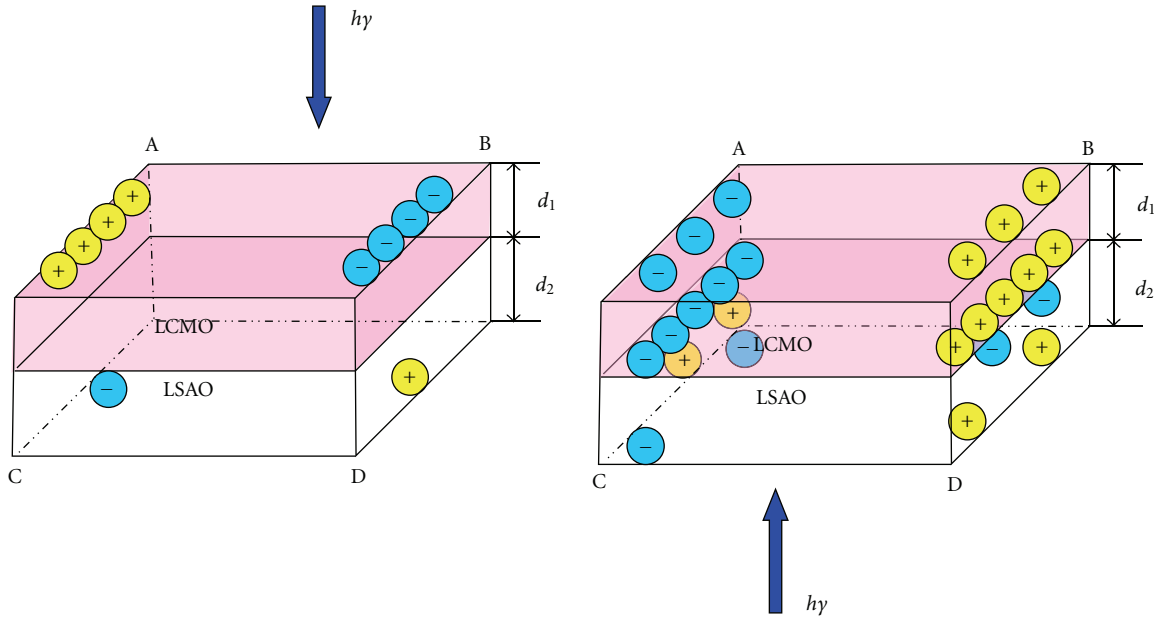


FIGURE 5: The schematic drawing explaining carriers distribution under opposite irradiation directions.

difference produced between A and B on LCMO surface is much larger than that between C and D on LSAO surface because of the significant difference of thicknesses between LCMO and LSAO ($d_1 \ll d_2$) according to (1).

4. Conclusions

In summary, we have observed the lateral photovoltaic effects in the LCMO thin film and LSAO substrate under the 248 nm pulse laser irradiation. The signal polarity inversion shows dependency of irradiation direction and electrode positions. That provides a potential application of the manganite film for photodetector.

Acknowledgments

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