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EPL, **97** (2012) 46005

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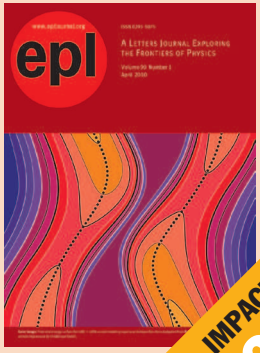

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A Letters Journal Exploring the Frontiers of Physics

February 2012

EPL, **97** (2012) 46005
doi: 10.1209/0295-5075/97/46005

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Nano-domain orientation modulation of photoresponse based on anisotropic transport in manganite films

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received 26 November 2011; accepted in final form 20 January 2012
published online 20 February 2012

PACS 68.37.-d – Microscopy of surfaces, interfaces, and thin films
PACS 68.55.-a – Thin film structure and morphology
PACS 78.67.-n – Optical properties of low-dimensional, mesoscopic, and nanoscale materials and structures

Abstract – Anisotropic carrier transports have been observed in $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.4}Ca_{0.6}MnO_3$ films grown on miscut MgO (001) substrates under pulsed-laser irradiations without external bias. We discussed the mechanism of the transport process under ultrafast laser irradiation in tilted manganite films. A model of anisotropic diffusion in transient photoresponse is presented. From the microstructure of $La_{0.4}Ca_{0.6}MnO_3$ and its photoresponse property in different directions, we can see that the nanometer size domain orientation can modulate the photoresponse signals, indicating a new-type nanometer scale photosensitive source.

Recently, many researchers have been devoted to exploring photoresponse characteristics and verifying device concepts based on perovskite materials [1–10]. Technological interest has centered on solar cells, light-emitting diodes, and photoelectric detectors [5,6], while more basic issues have involved the nature of carrier transport in the photoelectric process [7–10]. Especially, ultrafast and high-sensitivity photovoltaic response has been found in perovskite oxide with tilted structure (the tilted structure means that the crystallographic axis of the single crystal or the thin film tilt with respect to the surface normal) without external bias [11–15]. These research results indicated that the tilted perovskite thin films should be very useful for the design of photoelectric devices as light-sensitive material. However, in a tilted structure, the mechanism of the photoresponse without any bias and of carriers transport is not very clear. The mechanism of the photoresponse was attributed to the thermoelectric effect at first [11–14]. Afterwards, based on the new experimental results about photoresponse observed in the tilted insulator perovskite oxide, a theory combining the photoelectric effect and the Seebeck effect was presented which states that charge carriers are generated by laser irradiation and separated in the thermal electric field [15]. However, all these theories did not consider the transport process in the ultrafast photoresponse directly. Discussing the motion behavior of the photoinduced carrier in ultrashort response time could help to understand the inner mechanism of photoresponse. Moreover, all the studies are focused on bulk single crystals and thin films, which limited the application of device integration in the micrometer and nanometer scale.

In the present study, we deposited $La_{0.67}Ca_{0.33}MnO_3$ (LCMO1) and $La_{0.4}Ca_{0.6}MnO_3$ (LCMO2) thin films on miscut MgO substrates, and observed anisotropic photoresponse signals under pulsed-laser irradiations without external bias. We discuss the mechanism of the transport process under ultrafast laser irradiation in these tilted manganite films. Based on the anisotropy, a model of anisotropic diffusion in transient photoresponse is presented. In tilted-film systems, because of the ultrashort

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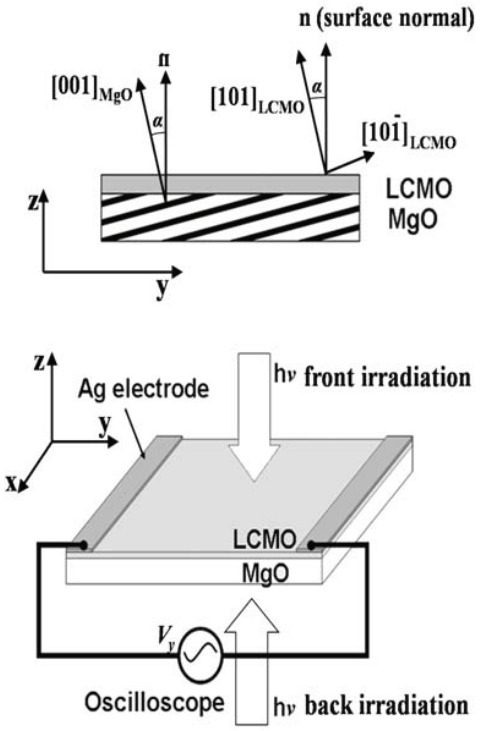

Fig. 1: Schematic illustration of the samples, electrodes structure and the circuit of the measurements. α is the tilt angle and y is the "tilt direction" of the film.

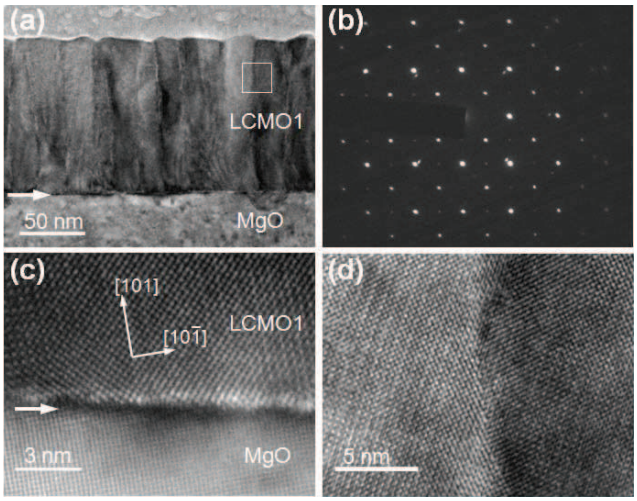

Fig. 2: (a) A low-magnification cross-sectional image of the LCMO1 film on tilted (001) MgO. (b) Corresponding selected-area electron diffraction pattern taken along the [010] zone axis. (c) Cross-sectional high-resolution images taken along the [010] zone axis of the interface region. (d) The domain boundary marked with a white box in fig. 2(a).

response time, diffusion behaviors of photoinduced carriers in a short period of time before recombination make the main contribution to the photoresponse signals and should be along the crystal axis with smaller resistance. The lateral photovoltage varies sinusoidally with the tilt angle of the oriented domains, and other influences are discussed. Moreover, by the analysis of the microstructure of LCMO2 and its photoresponse property in different directions, we can see that the nanometer size domain orientation can modulate the photoresponse signals, indicating a new-type nanometer scale photosensitive source.

The 100 nm thick $La_{1-x}Ca_xMnO_3$ (LCMO) thin films were deposited on miscut MgO substrates with the $(001)_{MgO}$ plane tilted to the surface wafer at an angle α of 10° by the facing-target sputtering technique [16]. During the deposition, the substrates were kept at 680 °C in an oxygen atmosphere of 30 mtorr. The film thickness is ∼100 nm, controlled by sputtering time with the deposition rate (∼0.03 nm/s). After the deposition, the vacuum chamber was immediately back-filled with 1 atm oxygen gas to improve the oxygen stoichiometry. A high-resolution transmission electron microscopy (HRTEM) was adopted to characterize the structure of the as-deposited products.

Figure 1 shows a schematic illustration of the samples, electrodes structure and the measurement circuit. The MgO (001) plane and the LCMO (101) plane are tilted to the surface wafer at an angle of 10°. The sample was cut into 5 mm × 5 mm and two colloidal silver electrodes of 1 mm × 5 mm area, separated by 3 mm, were prepared on the film surface. An actively-passively mode-locked Nd: YAG (yttrium aluminum garnet) laser, operated at 355 nm with a pulse width of 25 ps and a repetition rate of 2 Hz was used as the light source. Photovoltaic signals between two silver electrodes were recorded by a 2.5 GHz bandwidth sampling digital oscilloscope (Tektronix® TDS7254B) terminated into 50 Ω. The LCMO films were always kept in the dark and an aperture of 3 mm × 5 mm area was chosen to keep the laser from irradiating the electrodes.

Figure 2 shows the microstructure characteristics of LCMO1/MgO. A low-magnification cross-sectional image (fig. 2(a)) shows that the film thickness is fairly uniform and the interface is quite flat and sharp without any visible secondary phases and appreciable interdiffused areas. The selected area electron diffraction (SAED) pattern corresponding to fig. 2(a) is shown in fig. 2(b), which is indexed as a single [010] zone axis of the orthorhombic LCMO1 structure and a [010] zone axis of the face-centered cubic MgO single crystal. Such an analysis indicates that the LCMO1 film grows with its (101) plane parallel to the MgO (001) surface, which shows an in-plane orientation relationship with respect to the MgO substrate of LCMO1[010]//MgO[010] and LCMO1[10$\bar{1}$]//MgO[100]. The cross-sectional HRTEM image (fig. 2(c)) taken with the incident beam parallel to the $[010]_{MgO}$ direction shows atomic scale information on the [101]-oriented epitaxial growth across the LCMO1/MgO interface. The HRTEM image of domain boundary marked with a white box in fig. 2(a) is shown in fig. 2(d), indicating that the domain on either side presents the same oriented growth. Such a

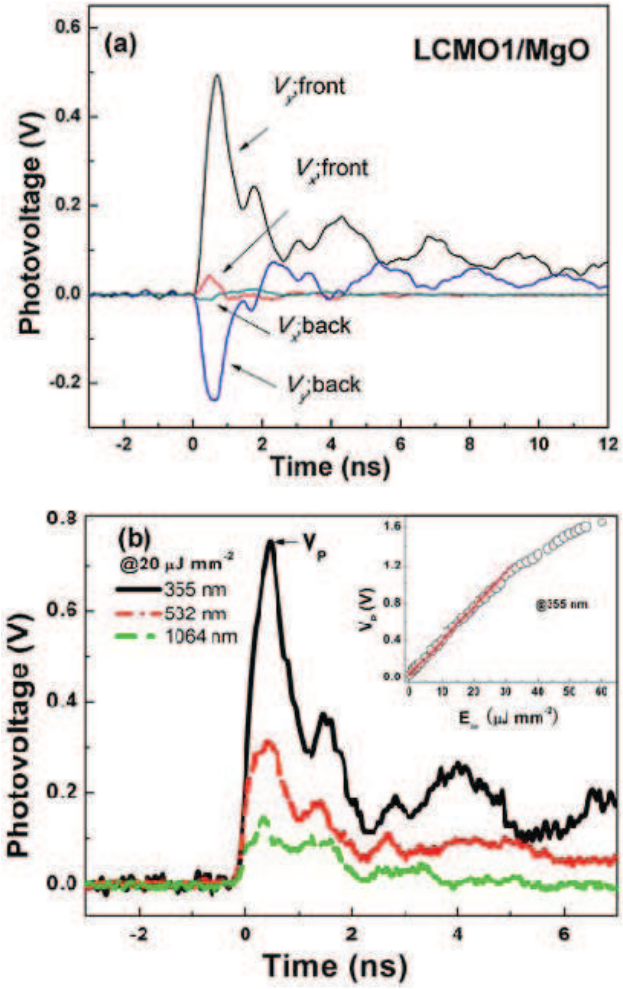

Fig. 3: (Colour on-line) (a) The photovoltaic pulses for the LCMO1 film along the x-axis (V_y) and the y-axis (V_x) from the LCMO1 side (front irradiation) and the MgO side (back irradiation) with 355 nm laser pulses. (b) Photoresponse waveforms under the illumination of 355, 532 and 1064 nm laser pulses. The inset shows the photovoltage amplitude V_P as a function of E_{in}.

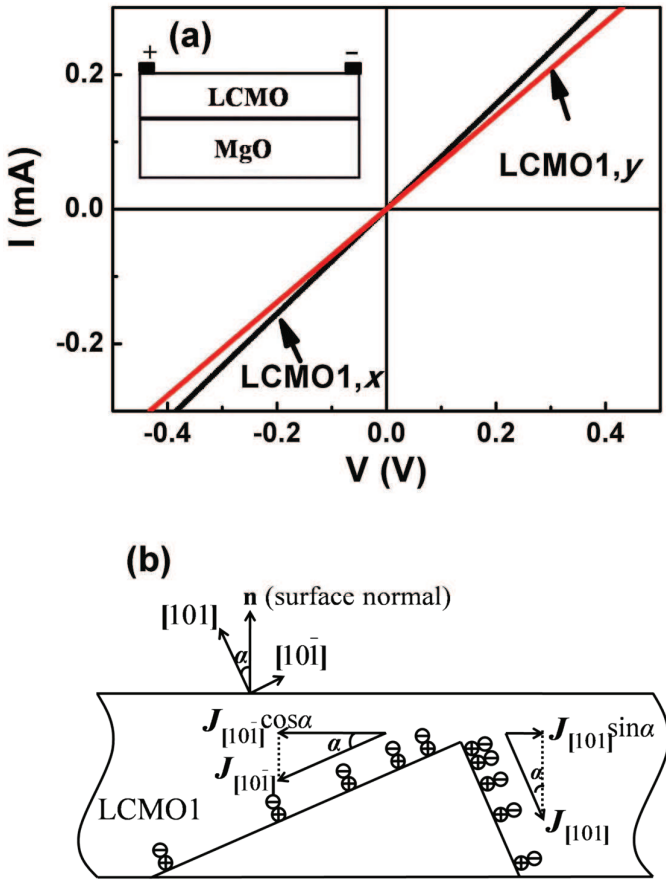

Fig. 4: (Colour on-line) (a) I-V characteristics of the LCMO1 films along x and y directions at room temperature. (b) Schematic drawing of the photovoltaic response mechanism.

configuration is believed to balance the lattice mismatch between the LCMO1 film and the MgO substrate.

In order to study the influence on the photovoltaic and transport properties by the tilt structure, we measured the photovoltages along the x and y axes. The photovoltaic signals of LCMO1 films, as a function of time, are shown in fig. 3(a) when the 355 nm laser pulse irradiated the LCMO1-side (front irradiation) and MgO-side (back irradiation). V_y and V_x denote the photovoltages along the x and y axes, respectively. It should be noted that there is almost no photovoltaic signal along the x-axis, meaning that the in-plane component of nonequilibrium charge carriers' transport is along the y-axis in the transient photoresponse process. In addition, photovoltages reversed in polarity when the film was under laser radiation from the MgO-side. Since the band gap of LCMO1 is lower than 1064 nm photon energy, the laser pulses irradiating the LCMO1 film surface can generate photoinduced charge carriers and result in the photovoltaic responses (fig. 3(b)). In our case, we only chose 355 nm pulse laser as the light source, and the irradiated energy density E_{in} was fixed at 12.7 μJ mm^{-2} to prevent the photovoltaic signal saturation as shown in the inset of fig. 3(b).

The linear current-voltage (I-V) characteristics, shown in fig. 4(a), of the LCMO1 film indicate ohmic contacts between the films and Ag electrodes. And the resistivity of the LCMO1 film along the tilting direction (y-axis) is larger than that perpendicular to the tilting direction (x-axis), indicating anisotropic carrier mobilities. The anisotropic resistivity can be understood on the basis of the Mn–O–Mn bond distance and angle. The tilted crystal structure increases the spin scattering in conduction carriers and decreases the electron hopping probability due to the change of Mn–O bond in the plane, which can be simulated by using the random network model based on the phase separation scenario [17]. From the rotation of the resistivity tensor, we get

$$R_x = \frac{l}{wd}\rho_{ab}$$

and

$$R_y = \frac{l}{wd}\left(\rho_{ab}\cos^2\,\alpha + \rho_c \sin^2\alpha\right),$$

where l, w, and d denote the length, width, and thickness of the film ($l = 3\,\mathrm{mm}$, $w = 5\,\mathrm{mm}$, $d = 100\,\mathrm{nm}$) [18]. Thus from the measurements of R_x and R_y in LCMO1 the principal components of in-plane as well as the out-of-plane resistivities, $\rho_{(101)}$ and $\rho_{[101]}$ can be calculated and $\rho_{[101]}/\rho_{(101)}$ is $\sim$37.

Therefore, based on the observations, the mechanism of the transient photovoltaic effect in tilted LCMO1 can be explained by the anisotropic diffusion effect. The ultrafast laser pulses irradiated the LCMO1 film surface uniformly and generated the photoinduced charge carriers (electron and hole pairs) with gradient distribution ($\mathrm{d}n_i/\mathrm{d}z$) perpendicular to the film surface and, at the same time, a temperature gradient ($\mathrm{d}T/\mathrm{d}z$) within the film and perpendicular to the film surface. In the carriers' diffusion process, because of the much larger mobility of electrons than that of holes ($\mu_n - \mu_p > 0$), electron-hole pairs were separated and the diffusion current density $\boldsymbol{J}$ was generated, which can be presented as $\boldsymbol{J} = \boldsymbol{J}_n + \boldsymbol{J}_p = k_0 T \Delta\boldsymbol{\mu}\,(\mathrm{d}n_i/\mathrm{d}z)$ based on the diffusion law and Einstein relation. Here $\boldsymbol{J}_p$ and $\boldsymbol{J}_n$ are the current density of hole and electron, k_0 is the Boltzmann constant and $\Delta\boldsymbol{\mu} = \boldsymbol{\mu}_n - \boldsymbol{\mu}_p$ is the difference of the diffusion coefficient of electron and hole. Accordingly, in LCMO1 with the [101] axis inclined with respect to the surface normal by an angle α, a surface-parallel component $\boldsymbol{J}_y$ consists of two components $-\boldsymbol{J}_{[10\bar{1}]}\cos\,\alpha$ and $\boldsymbol{J}_{[101]}\sin\alpha$, as shown in fig. 4(b). Furthermore, due to the anisotropy and the large ratio $\rho_{[101]}/\rho_{(101)}$ in LCMO1, the diffusion current along the $[10\bar{1}]$ axis is much larger than that along the [101] axis, and consequently lateral diffusion current densities are obtained and can be presented as

$$\begin{aligned} J_y &= J_{[10\bar{1}]}\cos\,\alpha - J_{[101]}\sin\alpha \\ &= k_0 T \Delta\mu_{[10\bar{1}]}\left(\mathrm{d}n_i/\,\mathrm{d}[10\bar{1}]\right)\cos\alpha \\ &\quad -k_0 T \Delta\mu_{[101]}(\mathrm{d}n_i/\,\mathrm{d}[101])\sin\alpha \\ &= k_0 T(\Delta\mu_{[10\bar{1}]} - \Delta\mu_{[101]})\sin 2\alpha(\mathrm{d}n_i/\,\mathrm{d}z)/\,2 \\ &\approx k_0 T \Delta\mu_{[10\bar{1}]}\sin 2\alpha(\mathrm{d}n_i/\,\mathrm{d}z)/\,2 \end{aligned} \quad (1)$$

and

$$\begin{aligned} &J_x = J_{[010]}\cos\,\beta - J_{[101]}\sin\,\beta = J_{[010]} = \\ &k_0 T \Delta\mu_{[010]}\left(\mathrm{d}n_i/\,\mathrm{d}[010]\right)\sin 0 = 0, \end{aligned} \quad (2)$$

where α ($=10^\circ$) and β ($=0^\circ$) are the tilt angles between the [101] axis and the normal $\mathbf{n}$ of the wafer surface on the projection of the (010) plane and the $(10\bar{1})$ plane. Through eqs. (1), (2), we can clearly see the relationship between the tilted structure and photovoltage and some other parameters which have time factors in ultrafast photoresponse and their influences on photoresponse. Moreover, a transient temperature gradient tilts the Fermi level within the film from high to low temperature and affects the gradient distribution of the charge carrier concentration, which results in a transient thermoelectric field [19]. Furthermore, 355 nm laser pulses (a photon energy of $\sim$3.5eV) can transmit through the MgO substrate (a bandgap of $\sim$5.0 eV) and be absorbed in the LCMO1 layer. Therefore, the sign of photovoltages for front (V_{front}) and back (V_{back}) irradiations should be reversed and there should be no photovoltaic signal along the x-direction.

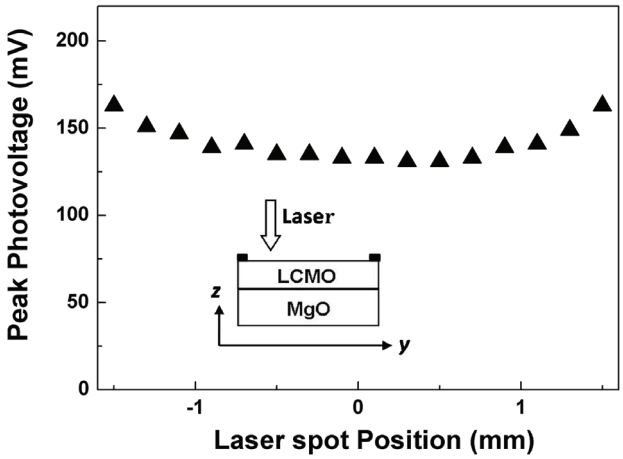

Fig. 5: The peak photovoltage as a function of irradiated laser spot position along the tilted direction (y-axis) for the LCMO1 film.

For further study the diffusion process of photoinduced carriers after ultrafast pulse laser irradiation, we measured the laser spot position dependence of the peak photovoltage in LCMO1 film, as shown in fig. 5. A pulse laser with 248 nm in wavelength was used to scan the sample along the tilted direction and a 1 mm diameter circular aperture was placed to narrow the laser spot. The peak photovoltages are nearly invariable at different position along the tilted direction. The experiment results, different from the conventional Dember effect, further demonstrated that the ultrafast process of the photoinduced carriers diffusion is quite different from conventional diffusion process and should be the same no matter what the laser spots is. In the ultrafast photoresponse in LCMO1, the diffusion process of photoinduced carriers lasts only hundreds of piseconds before recombination (see fig. 3(a)). Thus, the photoinduced carriers do not have enough time to get the state of equilibrium in the whole sample before recombination. In other words, the photoinduced carriers can diffuse only through a very small area in the sample in a very short time (hundreds of piseconds) before recombination, which means that the diffusion behavior of carriers in a very short period of time at the beginning is crucial for the ultrafast photoresponse. Due to the anisotropy, no matter the laser spot is at different position, the diffusion of the carriers, at first, will be along the direction which has

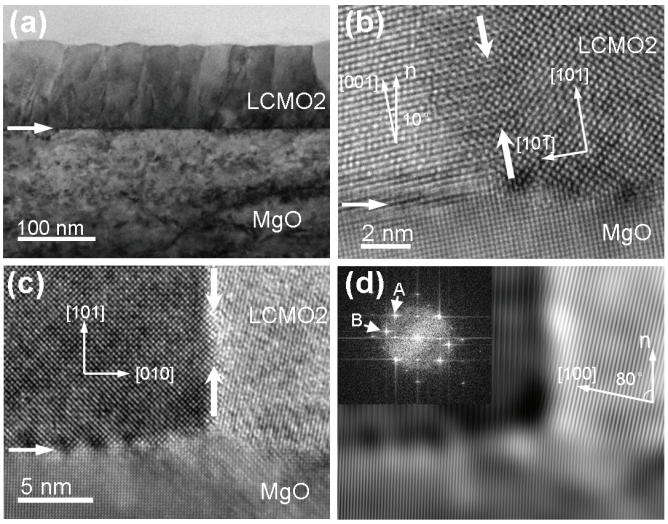

Fig. 6: (a) A low-magnification cross-sectional image of LCMO2 films on tilted (001) MgO. (b) and (c) Cross-sectional HRTEM images taken with the incident beam parallel to the $[010]_{\mathrm{MgO}}$ and $[100]_{\mathrm{MgO}}$ directions near the interface region. (d) Corresponding Fourier-transform patterns of (c).

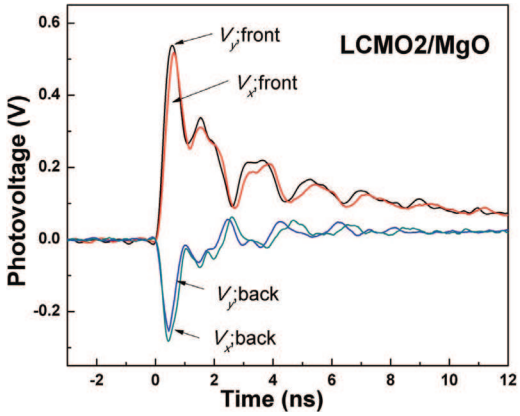

Fig. 7: (Colour on-line) The photovoltaic pulses for the LCMO2 film along the x-axis (V_y) and the y-axis (V_x) from the LCMO1 side (front irradiation) and the MgO side (back irradiation) with 355 nm laser pulses.

the smallest resistivity in the material, resulting in nearly invariable photovoltages. When the laser spot is near the electrodes, the larger peak photovoltage is obtained due to the greater number of carriers collected by the electrodes.

Differently from LCMO1, the LCMO2 film exhibited a less uniform structure. Figure 6(a) shows a sharp and flat interface and a columnar structure originating from the interface between the film and the substrate. HRTEM images show atomic scale information of the columnar structure with different oriented domains (fig. 6(b) and 6(c)). Not only the [101]-oriented domains but other oriented domains are observed and their boundaries are marked with two thick white arrowheads. Fourier-transform is adopted to analyze the different oriented domains structure shown in fig. 6(d). The existence of two types of diffraction spots and the lattice fringe image indicates the two-oriented domains in the LCMO2 film. It was confirmed that the right domain in fig. 6(b) is [001]-oriented and the right domain in fig. 6(c) grows with its (100) plane tilted to the film surface at an angle of 80°. The above HRTEM experiments indicate that the doping level has a strong influence on perovskite-derived crystal structures and on the lattice parameters of the LCMO, leading to different multi-oriented domains intergrowth in the epitaxial films.

Based on HRTEM experiments and the above analyses, the unusual photovoltaic effect in LCMO2 films shown in fig. 7 can be easily understood. The [101]-oriented and [001]-oriented domains in fig. 6(b) lead to the lateral diffusion current density along the y-axis, and the irradiation in the other oriented growth domains tilted to the surface plane along the x-axis (fig. 6(c)) generate the lateral photovoltage along the x-axis. Due to the oriented growth domains with a tilted structure along the x-axis in fig. 6(c), V_y and V_x have almost the same value in LCMO2 films under uniform laser irradiation. The polarity reversal of photovoltage for back irradiation also proved the above mechanism. The results indicate that the photocurrent can be modulated through the nanometer domain orientation. This modulation of the photovoltaic effect by microstructure should be useful for the integrated and miniature design of photoelectric devices.

In conclusion, the anisotropic carrier photoresponse signals have been observed in LCMO1 and LCMO2 films grown on miscut MgO (001) substrates under pulsed-laser irradiations without external bias. We have discussed the intrinsic relationship between the tilted structure of the film and the transient transport process of photoinduced charge carriers without external bias. By reason of the anisotropy, photoinduced carriers diffuse along the crystal axis with smaller resistance at the beginning which makes the main contribution for the photocurrent and gives rise to a lateral photovoltaic effect. According to the equations presented above, the lateral current density varies sinusoidally with the tilt angle. The invariable photovoltages at the different laser spot position along the tilted direction demonstrate the transient anisotropic diffusion process which is irrelevant to the spot position. Furthermore, from the HRTEM and photoelectric experiments of LCMO2 films, it can be seen that the photocurrent can be modulated through the nanometer domain orientation.

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This work has been supported by NCET, NSFC, RFDP, Direct Grant from the Research Grants Council of the Hong Kong Special Administrative Region (Grant No. C001-2060295) and Foresight Fund Program from China University of Petroleum (Beijing).

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