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Ultrafast transverse thermoelectric response in *c*-axis inclined epitaxial $La_{0.5}Sr_{0.5}CoO_3$ thin films

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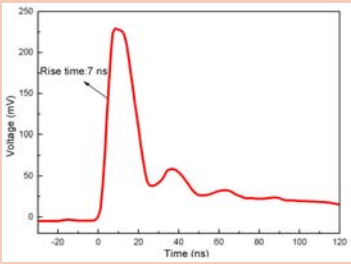
Ultrafast transverse thermoelectric voltage response has been observed in *c*-axis inclined epitaxial $La_{0.5}Sr_{0.5}CoO_3$ thin films. Voltage signals with the rise time of 7 ns have been detected under the irradiation of pulse laser with duration of 28 ns. A concept, named response rate ratio, has been proposed to evaluate the intrinsic response rate, and this ratio in $La_{0.5}Sr_{0.5}CoO_3$ is smaller than that in other reported materials. The low resistivity is thought to be responsible for the ultrafast response, as low resistivity induces small optical penetration depth, and response time has a monotonous increasing relationship with this depth.



Transverse thermoelectric voltage with the rise time of 7 ns in $La_{0.5}Sr_{0.5}CoO_3$ thin film.

1 Introduction Recently, the transverse thermoelectric (TTE) effect (also called atomic layer thermopile, ALTP) has attracted more and more attention due to its great potential applications in photoelectric or thermoelectric detecting [1–4], infinite-staged cooling [5, 6] and clean energy conversion of heat to electricity [7]. This effect is based on the anisotropic Seebeck coefficient of materials and it also requires to fulfil certain geometric conditions, such as the tilted angle θ between the orientation of *c*-axis and the surface normal (see Fig. 1(b)) [1, 2, 8, 9]. When $\theta \neq 0°$ or 90°, the off-diagonal terms of the Seebeck tensor will be non-zero and then contribute to the thermoelectric effect. The unique property of this effect is that the electrical and thermal flows are perpendicular to each other, while these two flows have the same directions in conventional thermoelectric effect. In other words, the introduction of a temperature gradient along the longitudinal direction can give rise to a transverse electric field in TTE effect, which means the capability of managing particular heat flux by adjusting the dimensions of the specimens [1]. For example, we can realize a fast response time in heat flux or laser measurements by sacrificing the thickness and maintain the signal magnitude by extending the length [1, 3].

Till now, the TTE effect has been carried out in several kinds of thin films, such as $YBa_2Cu_3O_{7-\delta}$ [8, 9], $Bi_2Sr_2CaCu_2O_8$ [10], $La_{2-x}Sr_xCuO_4$ [11], $La_{1-x}Ca_xMnO_3$ [12–14], Ca_xCoO_2 [15–17], $Bi_2Sr_2Co_2O_y$ [18], Al-doped ZnO [19], when these films have inclined *c*-axis orientation. Generally, a pulse laser is used as thermal source to heat the top surface of thin film. The laser irradiation can establish a temperature gradient along the out-of-plane direction (on the *z*-axis) of the film, and then generate a thermoelectric voltage signal in the in-plane direction (on the *x*-axis) (see Fig. 1(b)). The in-plane voltage induced by the TTE effect

in the film surface can be described in the form of

$$U = \frac{l}{2d}\sin(2\theta)\,\Delta S\,\Delta T = \frac{l}{2}\sin(2\theta)\,\Delta S\,\nabla_z T\,, \qquad (1)$$

where U is the thermal voltage, l and d are the illumination length and the thickness of film, respectively, θ is the c-axis tilted angle of film, $\Delta S = |S_{ab} - S_c|$ is the difference of Seebeck coefficient between S_{ab} (Seebeck coefficient in the ab-plane of the material) and S_c (Seebeck coefficient along the c-axis of the material), ΔT is the temperature difference between top and bottom of the film, and $\Delta T/d = \nabla_z T$ represents the temperature gradient along the direction of film thickness [8, 9].

However, most research about TTE effect just focuses on the increase of voltage responsivity, and less attention has been paid to the response rate. In this Letter, we investigate the TTE effect in highly conducting $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) thin films and the ultrafast TTE voltage response has been observed. A concept to evaluate the response rate has been proposed and the mechanism about the response rate modification has been discussed.

2 Experiment LSCO thin films with thickness of 200 nm were deposited on commercial 5° vicinal cut $LaAlO_3$ (LAO) (100) substrates by pulse laser deposition (PLD). The PLD system had a KrF-excimer laser with wavelength of 248 nm and pulse laser duration (τ_p) of 28 ns. Laser fluence and pulse frequency were fixed at 1.8 J/cm^2 and 5 Hz, respectively. A homogeneous LSCO ceramic target with disc-shape was used and detailed information concerning target preparing can be found in Ref. [20]. During the deposition process, the temperature of substrates and the pressure of oxygen were precisely kept at 750 °C and 60 Pa, respectively. Afterwards, the films were *in situ* annealed (temperature: 750 °C, oxygen pressure: 50000 Pa, time: 1 h) and *post* annealed (temperature: 500 °C, oxygen pressure: 100000 Pa, time: 1 h).

X-ray diffraction (XRD, Rigaku TTR III) with Cu $K_{\alpha 1}$ radiation has been used to characterize the epitaxial relationship between vicinal cut substrates and inclined thin films. The details of the method can be found in Ref. [2]. For the TTE voltage measurement, an optical setup was used, shown in Fig. 1(a). It consisted of a 248 nm KrF pulse laser with duration of 28 ns, an attenuator to reduce the laser power, a light homogenized system to make laser beam distribute homogeneously as the primal laser beam is Gaussian shape, a mask to control the size of the laser beam, and a split lens exporting two beams with fixed energy ratio. Figure 1(b) shows the magnified schematic cross-section of a tilted LSCO thin film with c-axis inclined by an angle θ with respect to surface normal N. Cr/Au electrodes for the voltage measurement are evaporated through metal masks. The distance between the two electrodes (corresponding to the illumination length l) is 3 mm and the voltage signals were monitored by an oscilloscope (HP 54522A, 500 MHz bandwidth) with the terminations of 50 Ω and 1 MΩ impedance. It must be pointed out that this work shows some differences compares with our previous results in Ref. [21]: (1) A higher oxygen pressure annealing for film growth has been employed in this Letter, which reduces the oxygen deficiency and leads to lower resistivity; (2) Cr/Au evaporated electrodes have been used, instead of in-plane indium electrodes, ensuring the Ohmic contact; (3) a much more advanced optical setup with precise control of energy density and laser beam size has been utilized; (4) an oscilloscope with larger bandwidth and two terminations has been employed to record voltage signals accurately. These changes should be responsible for the new results in this Letter.

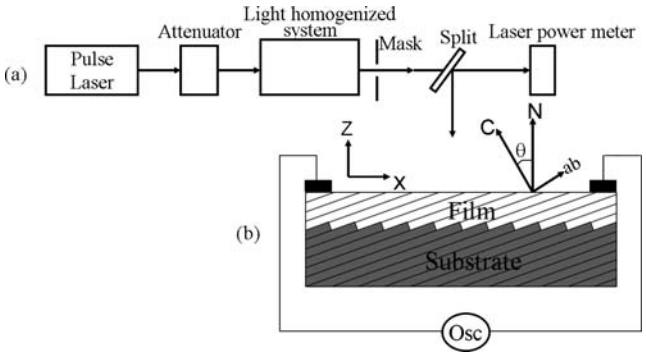


Figure 1 (a) Optical setup for measuring the TTE voltage signal. (b) Magnified schematic cross-section of epitaxial LSCO thin film with tilted c-axis by an angle θ with respect to surface normal N. ab represents the ab-plane of the thin film and C represents the c-axis, while x and z represent the spatial axes.

3 Results and discussion In Fig. 2, voltage signals of the tilted LSCO thin film recorded by 50 Ω and 1 MΩ terminations under the same irradiation condition are depicted. Films are irradiated at room temperature by the optical setup as shown in Fig. 1(a), where the energy density on the film surface is 3 mJ/cm^2. As displayed in Fig. 2, the peak voltage (U_p) is 114 mV when using the 50 Ω impedance termination of the oscilloscope. Changing to the 1 MΩ termination, U_p rises to 229 mV. As the tilted LSCO film has a resistance of about 2 Ω, the U_p measured by the

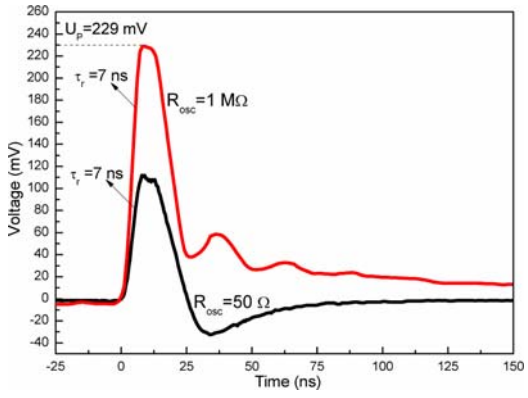


Figure 2 (online colour at: www.pss-rapid.com) Voltage signals of tilted LSCO thin film measured by the 50 Ω and 1 MΩ terminations of the oscilloscope.

1 MΩ termination is much more credible than the voltage recorded by the 50 Ω termination because there is a voltage division when using the 50 Ω termination. The origin of these voltage signals induced by the laser irradiation in this kind of materials has been discussed in our previous results [2, 12, 13, 21], which concludes that the transverse Seebeck effect should be responsible for these signals. Considering an irradiation area of $3 \times 2.7 = 8.1\ mm^2$ and the tilted angle of 4.855°, the responsivity of LSCO film is as large as 0.194 $V(mJ)^{-1}$ $(degree)^{-1}$, which is higher than that in $La_{1-x}Ca_xMnO_3$ (0.02 ~ 0.07 $V(mJ)^{-1}$ $(degree)^{-1}$) [12–14], $Bi_2Sr_2Co_2O_y$ (0.03 $V(mJ)^{-1}$ $(degree)^{-1}$) [18], and Al doping ZnO (0.0011 $V(mJ)^{-1}$ $(degree)^{-1}$) [19] thin films.

Voltage signals of tilted LSCO thin films under irradiation of pulse laser with duration of 28 ns have a rise time (τ_r) (0–100% of peak value) of 7 ns (see Fig. 2) when using both 50 Ω and 1 MΩ terminations. The absolute values of the TTE response time under the radiation of pulse lasers with different durations cannot be compared simply as pulse laser with narrower duration generally leads to a faster response, and vice versa. From this viewpoint, we propose a concept to evaluate the response rate of the TTE voltage signal, named response rate ratio (A_r), and which can be represented in the form of

$$A_r = \frac{\tau_r}{\tau_p}, \tag{2}$$

where τ_p is the duration of pulse laser. A_r is dimensionless, and its value indicates the relative response rate. Smaller A_r corresponds to faster response rate, and vice versa. To compare the response rate between different materials, the film thickness also cannot be neglected, mainly because the thermal relaxation time in the film/substrate heterostructure decreases monotonically with decreasing film thickness [16, 22, 23], naturally resulting in a faster response rate of thinner film. The A_r of our LSCO thin films is 0.25 and we have summarized the response rate ratio taken from various experiments in different materials, as shown in Table 1, which indicates that the response rate ratio in LSCO is smaller than that in any other reported thin films with thickness less than or equal to 200 nm. It needs to be emphasized that the ultrafast thermoelectric response in this work is an intrinsic behavior in LSCO thin film, which is different from other reports about reducing rise time by applying a low-value resistance parallel to the film, when measuring the TTE voltage [29].

Table 1 Summary of experimental response rate ratio and resistivity (at 300 K) in different materials.

material	d (nm)	τ_r (ns)	τ_p (ns)	A_r	ρ (mΩ cm)	Ref.
$La_{0.9}Ca_{0.1}MnO_3$	100	51	28	1.82	1000	[14]
$La_{1.85}Sr_{0.15}CuO_4$	200	46	28	1.64	1.25	[11, 24]
Ca_xCoO_2	150	10	8	1.25	4.8	[16, 25]
$La_{0.67}Ca_{0.33}MnO_3$	180	28	28	1	26	[12]
$YBa_2Cu_3O_{7-\delta}$	80	25	30	0.83	1	[26, 27]
$Bi_2Sr_2Co_2O_y$	130	15	25	0.6	2	[18, 28]
Al-doped ZnO	150	8	20	0.4	0.487	[19]
$La_{0.5}Sr_{0.5}CoO_3$	200	7	28	0.25	0.66	this work

The ultrafast transverse thermoelectric response in LSCO thin film is probably due to its low resistivity (ρ). The time dependence of laser-induced thermoelectric voltage model based on the one-dimensional heat conduction equation has been employed to explain this. In this model, the temperature difference between top and bottom of the film can be given by $\Delta T = Q(e^{-\frac{\delta^2}{4Dt}} - e^{-\frac{d^2}{4Dt}})/(ac\sqrt{4\pi Dt})$, where Q is the absorption energy, a is density, c is heat capacity, D is thermal diffusivity, and δ is optical penetration depth [13]. At the peak voltage, there is the equation $\partial(\Delta T)/\partial t = 0$, and then the expression to describe the relations among D, δ, d, and τ_r can be written in the form

$$\left(\frac{\delta^2}{2D} - \tau_r\right) e^{-\frac{\delta^2}{4D\tau_r}} + \left(\tau_r - \frac{d^2}{2D}\right) e^{-\frac{d^2}{4D\tau_r}} = 0. \tag{3}$$

Using $d = 200$ nm and $D = 2.17 \times 10^{-3}\ cm^2/s$ [30], we can attain the numerical relation between rise time τ_r and optical penetration depth δ, as shown in Fig. 3. It is clearly shown in Fig. 3 that rise time increases monotonously with increasing optical penetration depth, which agrees quite well with a previous report by Lengfellner et al. [26]. The smaller optical penetration depth means that the effective thickness of the film for absorbing heat is smaller and then it is much more easier to establish heat saturation. The increasing rate of τ_r is not the same during different regions of δ: the rise time has a power function of $\tau_r = 0.00283\delta^{1.94}$ for small δ (see the inset of Fig. 3); while the rise time has a linear function of $\tau_r = 0.16\delta - 1.113$ in the region of large δ. Based on the measured rise time of 7 ns (shown in Fig. 2) and theoretical relationship between rise time and optical penetration depth (shown in Fig. 3), the optical penetration depth of LSCO thin film under 248 nm irradiation is estimated to be about 50 nm, which is in the same magnitude as the experimental result of about 41.7 nm [31].

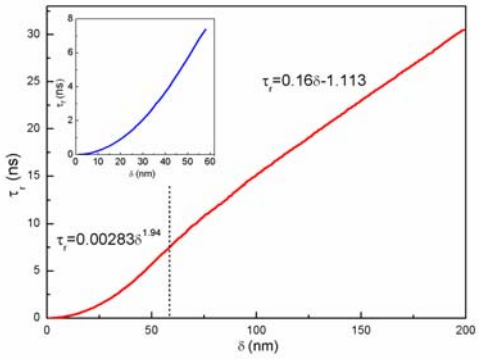


Figure 3 (online colour at: www.pss-rapid.com) Rise time versus optical penetration depth curve of LSCO thin film. The inset is the magnified curve for small optical penetration depth region.

Generally, the optical penetration depth is given by

$$\delta = \sqrt{\frac{\varepsilon_0 \lambda_0 c_0}{4\pi\sigma}}, \quad (4)$$

where ε_0 is vacuum permittivity, λ_0 the wavelength of laser, c_0 is velocity of light, and $\sigma = \sigma_\infty \left[1 - \left(\frac{1}{2} + \frac{3}{4}\frac{\lambda}{t}\right)\left(1 - p\, e^{-\frac{\xi}{\lambda}t}\right) e^{-\frac{t}{\lambda}}\right]$ (σ_∞ is the conductivity of films with infinite thickness, λ is the mean free path of electron, t the film thickness, p the specular reflection coefficient of surface scattering, and ξ is the penetration parameter for film surfaces parallel to grain boundary scattering) is the conductivity in dependence on optical parameters of thin films [32]. As we lack this kind of conductivity of LSCO thin film, it is hard to calculate its optical penetration depth and rise time exactly. But we can attain the qualitative conclusion that low resistivity (high conductivity) will result in small δ (see Eq. (4)) and then induce fast response rate. The resistivity of our sample is about 0.66 mΩ cm at 300 K, which is smaller than that in most other materials mentioned above (see Table 1). From Table 1, we can observe a tendency that material with low resistivity will have fast response rate, although the Al-doped ZnO thin film seems to be a little out of the frame. These theories are effective to explain the experimental result of Lengfellner et al., that infrared (IR) radiation has slower response rate than ultraviolet (UV) radiation [26]. IR radiation will have the larger optical penetration depth than UV because of its larger wavelength (see Eq. (4)), consequently the response rate of IR will be slow. The oscillation of voltage signals in LSCO thin films may originate from the reflections due to the impedance mismatch in the transmission process.

In summary, the ultrafast transverse thermoelectric voltage of 7 ns rise time has been detected in *c*-axis inclined epitaxial $La_{0.5}Sr_{0.5}CoO_3$ thin films under the irradiation of a pulse laser with duration of 28 ns at room temperature. Response rate ratio has been introduced to evaluate the intrinsic response rate, and $La_{0.5}Sr_{0.5}CoO_3$ thin film has the faster response rate compared with other reported materials. This ultrafast response rate is due to its low resistivity, as the low resistivity will bring the small optical penetration depth and then leads to the small response time.

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