Laser-induced voltage effects in $Ca_3Co_4O_9$ thin films on tilted $LaAlO_3(001)$ substrates grown by chemical solution deposition*

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Laser-induced voltage effects in *c*-axis oriented $Ca_3Co_4O_9$ thin films have been studied with samples fabricated on 10° tilted $LaAlO_3$ (001) substrates by a simple chemical solution deposition method. An open-circuit voltage with a rise time of about 10 ns and full width at half maximum of about 28 ns is detected when the film surface is irradiated by a 308-nm laser pulse with a duration of 25 ns. Besides, open-circuit voltage signals are also observed when the film surface is irradiated separately by the laser pulses of 532 nm and 1064 nm. The results indicate that $Ca_3Co_4O_9$ thin films have a great potential application in the wide range photodetctor from the ultraviolet to near infrared regions.

Keywords: laser-induced voltage, $Ca_3Co_4O_9$ thin films, chemical solution deposition
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1. Introduction

Laser-induced voltage (LIV) effects in thin films of strongly correlated oxides such as $YBa_2Cu_3O_{7-\delta}$ and $La_{1-x}Ca(Sr)_xMnO_3$ have been widely studied due to their great potential applications in photodetectors.[1−3] It was considered that the LIV signals in these oxides originated from the anisotropy of Seebeck coefficient (S) in these oxides: heating the surface of a film by the absorption of the incident pulsed laser radiation establishes a temperature gradient perpendicular to the film surface. This temperature gradient can generate an electric voltage through the Seebeck effect, and the voltage can be quantitatively described by the equation $U = (l/2d)\sin(2\alpha)\Delta S\Delta T$, where U is the induced voltage, l and d are the illumination length and the thickness of the film respectively, α is the tilt angle of the substrate, $\Delta S = S_{ab} - S_c$ is the difference in Seebeck coefficient between in the *ab*-plane and along the *c*-axis of the film, and ΔT is the temperature difference between the top and the bottom of the film.[4]

Recently, strongly correlated layered cobalt oxides have attracted great attention as a promising thermoelectric material due to their good thermoelectric performance and high stability in air at high temperature. Many layered cobalt oxides such as Na–Co–O, Bi(Pb, Ti)–Sr–Co–O, Ca–Co–O, and Sr–Co–O were synthesized.[5−11] Among the above various layered cobalt oxides, $Ca_3Co_4O_9$ has been extensively studied and a large anisotropic Seebeck coefficient with $S_{ab} - S_c \sim 70$ μV/K was obtained in epitaxial thin film, which indicates that this material is also a very promising candidate for high sensitive photodetectors.[12] However, so far very few studies on LIV effects in $Ca_3Co_4O_9$ thin films are available in the literature.[13] In the present paper, we report the LIV effects in $Ca_3Co_4O_9$ thin films fabricated by a simple chemical solution deposition (CSD) method. Compared with the widely used vacuum deposition techniques for $Ca_3Co_4O_9$ thin films such as pulsed laser deposition (PLD) and radio frequency (rf) mag-

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netron sputtering,[7,8,12,13] the CSD method does not require a vacuum system and a complex apparatus, so that we can grow thin films at low cost. The resulting CSD-derived film on 10° tilting $LaAlO_3$ shows an open-circuit voltage with a rise time of about 10 ns and a full width at half-maximum (FWHM) of about 28 ns under an 308-nm irradiation with a pulse duration of 25 ns. Open-circuit voltage signals are also observed when the film surface is irradiated separately by the laser pulses of 532 nm and 1064 nm. The results indicate that $Ca_3Co_4O_9$ thin films have a great potential application in the wide range photodetctor from the ultraviolet to near infrared regions.

2. Experimental details

$Ca_3Co_4O_9$ thin films were prepared through a CSD method. Briefly, the precursor solution for $Ca_3Co_4O_9$ was prepared by dissolving the calcium and cobalt acetates into propionic acid with the cation ratio of Ca:Co=3:4. The solution with the concentration of 0.1 mol/l was then spin-coated on (001) $LaAlO_3$ single crystal substrates with different tilt angles (0°, 3°, 5° and 10°) at 3600–4000 rpm for 40 s to form single-layer $Ca_3Co_4O_9$ thin films. Each coated layer was heat-treated at about 100 °C for 2 min and then at 400 °C for 30 min in air. The spin coating was repeated to obtain the desired film thickness. The films were then post-annealed at a temperature of about 820 °C for 2 h under flowing high-purity oxygen at a pressure higher than 1 atm (1 atm=1.01325×10^5 Pa). Energy-dispersive x-ray spectroscopic analyses performed on the whole surfaces of the films with a Ca:Co ratio inside are very close to that of the nominal chemical composition of this material. Resistivity and Seebeck coefficient of the film on a 0° tilting $LaAlO_3$ substrate, measured by using the Physical Property Measurement Systems (PPMS), show that the ρ_{ab} and S_{ab} values in *ab*-plane at room temperature are about 12 mΩ·cm and 127 μV/K respectively, as shown in Fig. 1. Both are comparable to those reported for $Ca_3Co_4O_9$ single crystals (ρ_{ab} ∼10–40 mΩ·cm, $S_{ab}\sim125$ μV/K)[14] as well as the best film samples fabricated by vacuum techniques such as rf magnetron sputtering ($\rho_{ab}\sim8$ mΩ·cm, $S_{ab}\sim110$ μV/K)[12] and PLD ($\rho_{ab}\sim4$ mΩ·cm, $S_{ab}\sim130$ μV/K),[7,8] revealing high quality of our CSD-derived film samples.

For the LIV measurements, two silver electrodes were deposited on the films separated by 4 mm. To prevent the generation of any electric contact photovoltage, the electrodes were always kept in the dark. The induced voltage signals were recorded with a 500-MHz bandwidth oscilloscope (Tektronix, TDS 3052).

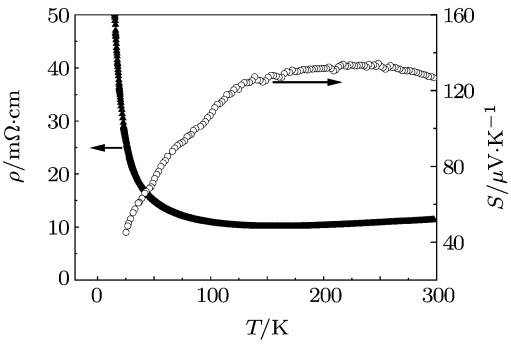


Fig. 1. Temperature dependences of *ab*-plane resistivity and Seebeck coefficient for the $Ca_3Co_4O_9$ thin film on untilted $LaAlO_3$ (001) substrate.

3. Results and discussion

Figure 2 shows the x-ray diffraction (XRD) θ–2θ scan of a 300-nm thick $Ca_3Co_4O_9$ thin film on a 10° tilting $LaAlO_3$(001) substrate, measured using a Philips X'Pert 4-circle diffractometer. Here, the offset angle ω was set as 10°, where ω is the angle between the *c*-axis direction and the surface-normal direction of the substrate. In Fig. 2, only peaks from diffraction of (0 0 *l*) $Ca_3Co_4O_9$ planes are observed besides the substrate peaks, indicating that a very pure $Ca_3Co_4O_9$ thin film with *c*-axis oriented growth is obtained on a 10° tilting (0 0 1) $LaAlO_3$ substrate.

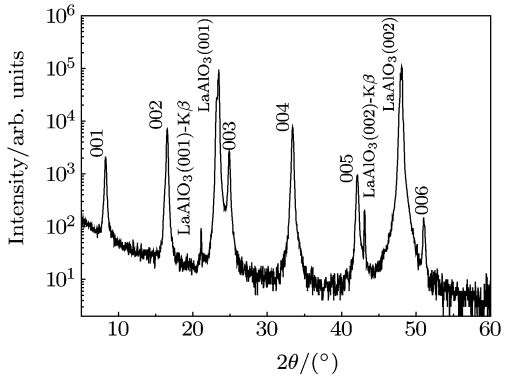


Fig. 2. The x-ray diffraction θ–2θ scan for a $Ca_3Co_4O_9$ thin film on 10° tilting $LaAlO_3$ (001) substrate.

Figure 3 presents the laser-induced open-circuit voltage signal of the film on a 10° tilting $LaAlO_3$(001) substrate under the 308-nm laser irradiation with a

pulse duration of 25 ns. The laser energy on the film surface is about 1 mJ and the input impedance of the oscilloscope is 1 MΩ. The induced voltage shows a peak value (V_p) of about 230 mV, and its photovoltaic sensitivity is calculated to be as large as 230 mV/mJ. The rise time (the time interval spanned between 10% and 90% of the peak voltage) and the full width at half maximum (FWHM) of the induced voltage signal are about 60 ns and 700 ns, respectively. In addition to the film on the 10° tilting substrate, we also measured the LIV signals of other $Ca_3Co_4O_9$ film samples on $LaAlO_3(001)$ substrates with the tilt angles of 0°, 3° and 5° separately. We find that the V_p value increases with the title angle α and is approximately proportional to $\sin 2\alpha$.

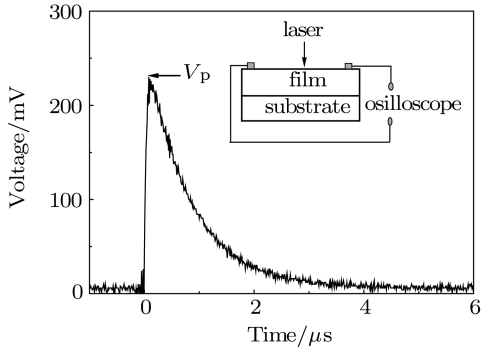


Fig. 3. Laser induced voltage signal of $Ca_3Co_4O_9$ film on 10° tilting $LaAlO_3(001)$ substrate, with an energy on-sample being 1 mJ and an input impedance of the oscilloscope 1 MΩ. The inset shows the schematic circuit of the sample measurement.

To reduce the influence of the RC measurement circuit on the response time, we changed the input impedance of the oscilloscope from 1 MΩ to 50 Ω while keeping other experimental conditions the same as those of Fig. 3. As shown in Fig. 4, the rise time is reduced to 10 ns and the FWHM drops off to 28 ns, which is close to the limitation of the duration of the laser pulse (25 ns). Besides the 308-nm radiation, we also performed the LIV measurements on the 10° tilted sample by using the laser pulses of 532 nm and 1064 nm respectively, and the open-circuit voltage signals were observed for both cases. This fact indicates that the $Ca_3Co_4O_9$ thin films have a great potential application in the wide range photodetector from ultraviolet to near infrared regions.

The physical origin of LIV signals in the $Ca_3Co_4O_9$ films on tilted substrates can be explained as follows: on the one hand, $Ca_3Co_4O_9$ films (with bandgap about 1.0 eV) absorb the incident laser radiation and generate the photoinduced carriers. On the other hand, as described in the Introduction of this paper, heating the $Ca_3Co_4O_9$ film surface by the absorption of the laser radiation can induce a temperature gradient perpendicular to the film surface. This temperature gradient gives rise to a lateral thermoelectric field through the Seebeck effect. This thermoelectric field leads to the separation of photoinduced carriers in the lateral direction and results in a photovoltage between the two electrodes.[15] Therefore, the LIV signal observed in $Ca_3Co_4O_9$ films on tilted substrates should be a process combined by photoelectric effect and thermoelectric effect. Further work needs to be done in future to confirm this explanation as well as which effect would play a dominant role in the LIV process.

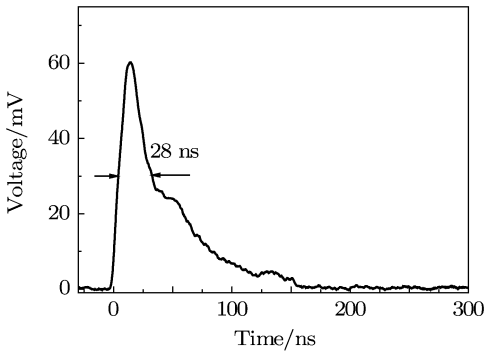


Fig. 4. Laser induced voltage signal of a $Ca_3Co_4O_9$ film on 10° tilting $LaAlO_3(001)$ substrate, measured by using an oscilloscope with input impedance 50 Ω.

4. Conclusion

We have investigated the LIV effects in $Ca_3Co_4O_9$ thin films fabricated on tilted $LaAlO_3(001)$ substrates by using a simple chemical deposition solution method. The resulting film on a 10° tilting substrate shows an open-circuit voltage with a rise time of about 10 ns and an FWHM of about 28 ns when the film surface is irradiated by a 308-nm laser pulse with a duration of 25 ns. Open-circuit voltage signals are also observed when the sample was irradiated separately by 532 and 1064 nm laser pulses. The results suggest that the CSD-derived $Ca_3Co_4O_9$ thin films have a potential application for wide range photodetector from the ultraviolet to near infrared regions.

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