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Ultraviolet photovoltaic effect in tilted orientation $LaAlO_3$ single crystals

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Abstract

Pulsed laser-induced photovoltaic effects were observed in the tilted orientation $LaAlO_3$ (LAO) single crystal wafers without any bias at ambient temperature when the LAO wafers were irradiated by the laser pulses of 246 nm ultraviolet (UV) wavelength. The rise time is 13 ns, and the full-width at half-maximum (FWHM) is 25 ns for the open-circuit photovoltage. The sensitivities of the photovoltage and the photocurrent are 270 mV/mJ and 0.91 mA/mJ for the tilting 20° LAO wafer, respectively. The mechanism of the photo-induced photovoltage in LAO wafers is proposed as the combination of a photoelectric process and a Seebeck one.

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Keyword: Photovoltaic effect; $LaAlO_3$ single crystal

1. Introduction

Perovskite oxide materials attracted many interests in recent years for their remarkable dielectric, piezoelectric, ferroelectric, optical, electro-optic, ferromagnetic, superconducting and catalytic properties [1,2]. $LaAlO_3$ (LAO) is one of the perovskite oxide materials and itself is an insulator with a band gap of ~5.6 eV [3]. LAO single-crystal wafer has been widely used as the substrate for growing perovskite oxides thin films, especially, for superconductors. In addition, LAO attracted much attention as one of the most promising alternative gate dielectrics due to many advantages such as a high dielectric constant of ~26, wide band gap, as well as chemically and compositionally stability [3–7]. The optical properties of the perovskite oxide materials and heterojunctions were investigated by some research groups [8–10]. We observed the ultrafast photoelectric effects in the p–n heterojunctions of $La_{0.7}Sr_{0.3}MnO_3$/Si, $SrTiO_{3-\delta}$/Si and $LaAlO_{2.73}$/Si, as well as in the $La_{0.67}Ca_{0.33}MnO_3$ films on tilted $SrTiO_3$ substrates [11–15]. However, the optical properties about LAO single crystal have not been widely examined.

In this letter, we will report the ultraviolet (UV) photovoltaic effects in the tilted orientation LAO single-crystal wafers. As far as we know, it is the first time to observe the nanosecond (ns) photovoltaic effect in LAO wafer at ambient temperature without any applied bias. The mechanism is proposed as the combination of a photoelectric process and a Seebeck process.

2. Experimental details

The LAO (0 0 1) single-crystal wafers used in this study are the as-supplied LAO substrates with the purity of 99.99% and mirror single polished. The size of the samples is 3 mm × 5 mm with the thickness of 0.5 mm. The (0 0 1) plane is tilted to the surface of the wafers with an angle α. We measured the samples with α equal to 10° and 20° in this study. The tilting of the c axis was further confirmed by an X-ray diffraction measurement with the usual θ–2θ scan.

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For the measuring of the optic behaviors, two indium electrodes separated about 1 mm were painted on the polished surface of the LAO wafers. The surface of the LAO wafers was irradiated by laser pulses of 248 nm and 532 nm at ambient temperature. During the experiments, two indium electrodes were always kept in the dark to prevent the influence of any electrical contact photovoltage. The photovoltaic signals were measured with an oscilloscope with 500 MHz bandwidth.

3. Results and discussion

The open-circuit photovoltaic pulses between the two electrodes painted on the surface of the LAO wafers were observed without any applied bias when the LAO wafers' surfaces were irradiated by a KrF laser with a wavelength of 248 nm and an energy density $E_d = 0.3\,mJ\,mm^{-2}$. Fig. 1 shows the typical open-circuit transient photo-induced voltages for 10° and 20° tilting LAO single-crystal wafers. The peak voltages V^P are 90 mV for the 20° tilting LAO, and 51 mV for the 10° tilting LAO, respectively. The rise time (10–90% of the peak value) is ~6 μs and the full-width at half-maximum (FWHM) is 260 μs for both LAO samples of the 20° and 10° tilting when the photovoltaic pulses were directly measured with 1 MΩ import impedance of the oscilloscope. To reduce the influence of the RC effect in the measurement circuit, we changed the import impedance of the oscilloscope from 1 MΩ to 50 Ω. As shown in Fig. 2, the photovoltaic pulses are almost symmetrical, and the rise time reduced to about 13 ns and the FWHM reduced to about 25 ns, which is in good agreement with the duration of the KrF laser pulse. Obviously, the response time of the LAO wafers may be faster than 13 ns because the rise time is limited by the excitation laser pulse in this case, and the photovoltaic pulses shown in Fig. 2 reflect the realistic process of photo-induced voltage.

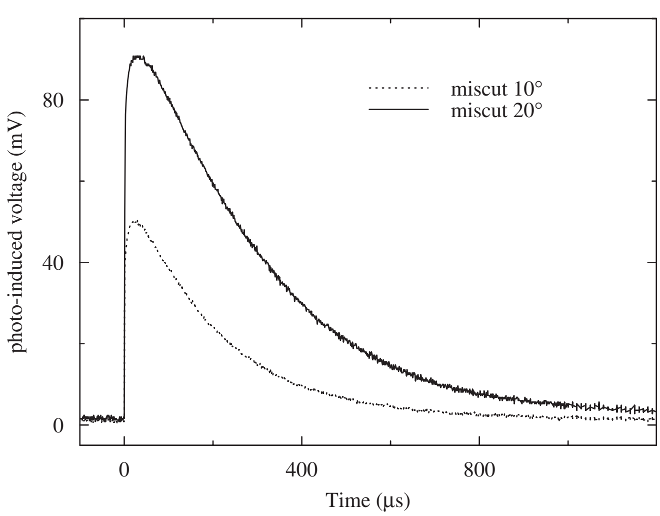

Fig. 1. The open-circuit photovoltaic pulses for tilting 20° and 10° LAO wafers under the excitation of a 248 nm laser pulse and measured by a oscilloscope with 1 MΩ import impedance. The inset shows the schematic circuit of the measurement.

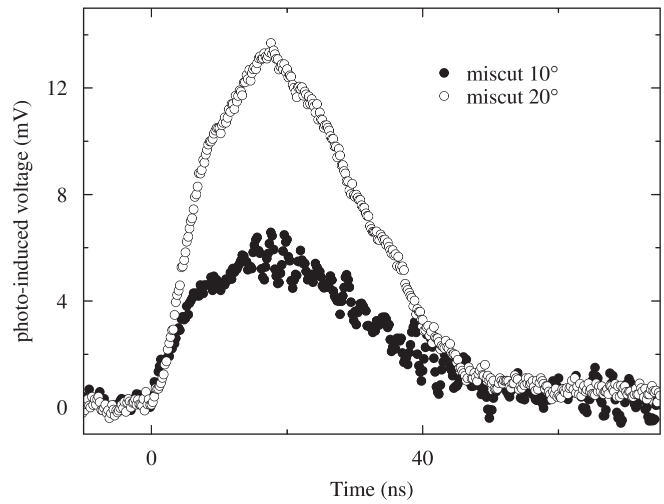

Fig. 2. The open-circuit photovoltaic pulses for tilting 20° and 10° LAO wafers under the excitation of a 248 nm laser pulse and measured by an oscilloscope with 50 Ω import impedance.

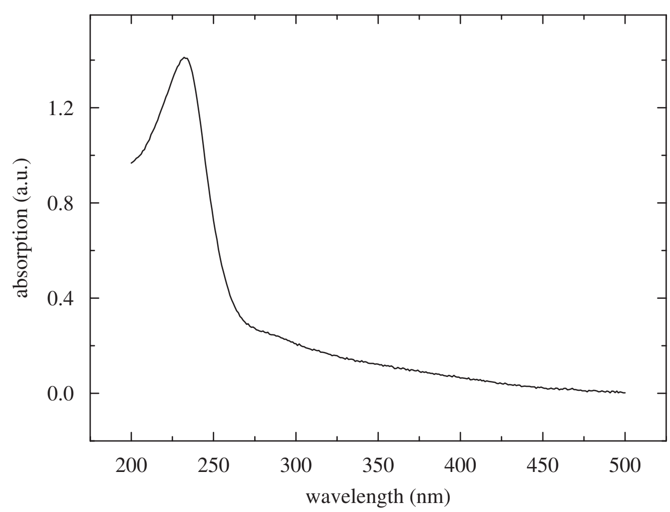

Fig. 3. The absorption spectrum of $LaAlO_3$ single-crystal wafers used in this study at ambient temperature.

From Fig. 1, we can deduce that the voltage sensitivities are $270\,mV\,mJ^{-1}$ for tilting 20° LAO and $132\,mV\,mJ^{-1}$ for tilting 10° LAO. Similarly, from Fig. 2, we can get the current sensitivities of $0.91\,mA\,mJ^{-1}$ for tilting 20° and $0.44\,mA\,mJ^{-1}$ for tilting 10°. The experimental results show that the photo-induced voltage effect in the tilted LAO single-crystal wafers is not only an ultrafast process but also highly sensitive to the ultraviolet laser pulse.

We have not observed the photovoltaic signal when the LAO wafers were irradiated by the laser pulses of 532 nm. For better understanding of the photo-induced voltage effects, we measured the UV–visible absorption spectrum of LAO single-crystal wafers. An absorption band with an edge at about 255 nm was observed as shown in Fig. 3. The optical band gap of the LAO wafers used in our study is about 4.9 eV. The absorption spectrum indicates that the photo-induced carriers in LAO wafers can be only generated under UV light with the wavelength less than 255 nm and the peak of the absorption spectrum is at 232 nm (5.345 eV). The optical band gap of 4.9 eV is smaller than usual 5.6 eV [3]. The reason for causing the difference of band gaps may be that the LAO single crystals were grown with different preparation processes.

It can be easily understood that we can observe the photovoltaic pulse with the laser pulse of 248 nm wavelength and cannot observe the photovoltaic pulse with the laser pulse of 532 nm wavelength because the photon energy of 248 nm (5.0 eV) wavelength is larger than the absorption edge of LAO single crystal (4.9 eV) and the photon energy of 532 nm wavelength is smaller than the absorption edge of LAO single crystal. The experimental results demonstrate that the production of the photo-induced carriers in the system plays a crucial role in the photovoltaic process. In addition, higher sensitivities of photovoltage and photocurrent would be expected if we select 232 nm light because the absorption peak of LAO single crystal is at 232 nm and the 248 nm used in this study is not the optimum wavelength.

As mentioned above, the sensitivity of photo-induced voltage is higher for the tiling 20° LAO wafer than that for the tilting 10° LAO wafer. In addition, no photo-induced voltage was observed along the non-tilting [0 1 0] direction of the LAO wafers. The experimental results can be considered to support the suggestion that the photovoltage is due to the combination of a photoelectric and a Seebeck process.

The intrinsic absorption including direct and indirect transitions in LAO will be occurred when the LAO surface is irradiated by the laser pulse of 248 nm wavelength. It is known that the direct transitions will induce a lot of the photo-generated carriers and the phonon generation is accompanied by the indirect transition. Meanwhile, the other absorptions such as exciton absorption and impurity absorption can generate heat. The temperature gradient in the LAO surface will cause the Seebeck effect. The Seebeck process provides a built-in field to separate the photo-induced carriers.

In this case, the photo-induced voltage can be represented by

$$V(\alpha) = l(S_{ab} - S_c)\, sin(2\alpha)(\mathrm{d}T/\mathrm{d}z)/2, \tag{1}$$

where the l is the irradiation length of the laser spot, S_{ab} and S_c are the Seebeck coefficients of the LAO crystalline ab plane and along the c-axis, and $\mathrm{d}T/\mathrm{d}z$ denotes the temperature gradient in the direction of the irradiation (perpendicular to LAO surface) [15–18]. Suppose $S_{ab}-S_c$ and other parameters are stable with angle α, then we can get $V(\alpha) \propto \sin(2\alpha)$, $V(20^\circ)/V(10^\circ) = \sin(40^\circ)/\sin(20^\circ) \approx 1.88$. In our case, we can obtain $V(20^\circ)/V(10^\circ) = 1.765$ from Fig. 1 and $V(20^\circ)/V(10^\circ) = 2.08$ from Fig. 2. The results are in good agreement with the theory.

4. Conclusion

In summary, we observed the photovoltaic effects in commercial tilting LAO single-crystal wafers without any bias at ambient temperature when the $LaAlO_3$ wafers were irradiated by the laser pulses of 246 nm ultraviolet wavelength. The rise time is 13 ns and the FWHM is 25 ns for the open-circuit photovoltaic pulse. The mechanism of the photo-induced voltage in $LaAlO_3$ wafers can be explained by the combination of a photoelectric and a Seebeck process. It is noteworthy that the absorption spectrum of LAO wafer and our experimental results manifest that the LAO single-crystal wafer has the potential application in UV photodetectors because the LAO single-crystal wafer has many advantages of not only chemical and compositional stability as well as low cost, but also visible-blindness.

Acknowledgments

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