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Ultraviolet photoresponse properties of $SrTiO_3$ single crystals

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Abstract. We have observed ultraviolet photosensitive properties of $SrTiO_3$ single crystals. The photoresponse signal reaches 7.6 mV under a bias voltage of 110 V and an on-sample energy of 250 nJ for a 15-ps-duration 355 nm laser pulse. A linear relationship is obtained to the peak signal as a function of bias without any saturation trend from 1 to 110 V. Ultrafast characteristic as a function of time was also presented with the rise time as short as 750 ps. Furthermore, a weak photoresponse was detected with a large bias of 2.5 kV under a 420-nm-wavelength laser pulse due to band edge tilting, and drop three orders of magnitude than that under the 355 nm laser pulse, indicating the setup consisting of $SrTiO_3$ single crystal is suitable for detecting ultraviolet radiation.

PACS. 78.20.-e Optical properties of bulk materials and thin films – 72.40.+w Photoconduction and photovoltaic effects

1 Introduction

At present, there is an increasing demand for an ultraviolet (UV) selective and sensitive photodetector which offers potential applications in environmental monitoring such as ozone-hole sensing, flame detection for a fire alarm, and secure communication using the solarblind region [1,2]. The selectivity of lights depends on the band gap of an absorbing material, while the sensitivity does on the efficiency of generating and collecting photoinduced carriers. These applications utilize photomultiplier tubes with high internal gain and low noise but having the disadvantages of being large and requiring a complicated fabrication process.

Strontium titanate oxide, $SrTiO_3$, is an interesting perovskite compound both from a fundamental and a practical application point of view, showing a band gap of ∼3.2 eV and exhibiting a marked absorption in UV region [3–5]. Over the years, $SrTiO_3$ has been mainly used for dielectric devices whereas very little work has been devoted to optical applications.

Laser irradiation is known to modifying the electrical properties of the surfaces of ceramic materials. Previously, several groups have reported on the existence of photoconduction in $SrTiO_3$, and found that $SrTiO_3$ surface exhibited semiconductivity and even conductivity under laser irradiation [6–9]. Yasunaga has measured the photoconductivity and the Hall mobility of photo-electrons in pure $SrTiO_3$ single crystals over the temperature range from 10-230 K [6,7]. Yoon and coworkers have investigated the effect of excimer laser irradiation on electrical properties for insulating $SrTiO_3$ single crystals, and observed a drastic drop of surface resistance from $>10^{13}$ Ω/cm^2 to about 10^4 Ω/cm^2 [9].

In this paper, following our recent work on UV fast-response photoelectric effect in tilted orientation $SrTiO_3$ single crystals [10], we focused on the photoresponse characteristics of $SrTiO_3$ single crystals as photosensitive resistors under the irradiation of UV laser at room temperature.

2 Experimental technique

The $SrTiO_3$ single-crystal wafers in the present study are the as-supplied $SrTiO_3$ substrates with the purity of 99.99% and mirror single polished. The sample geometry is 5 mm × 5 mm with the thickness of 0.5 mm. The samples were carefully treated by mechano-chemical processing and vacuum annealing for photoresponse measurements.

Figure 1 shows the schematic circuit of the photoresponse measurement. The third harmonic of an

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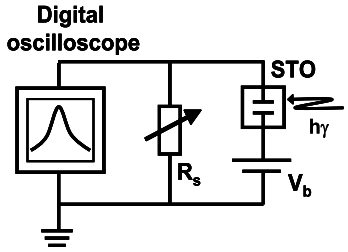

Fig. 1. The schematic circuit of the sample measurement. R_s is the load resistor and V_b is the bias voltage.

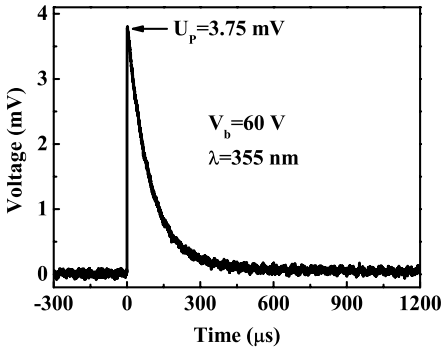

Fig. 2. Photoresponse signal of $SrTiO_3$ crystal as a function of time under the irradiation of a 355 nm laser pulse in duration of 15 ps with an on-sample energy intensity of 250 nJ.

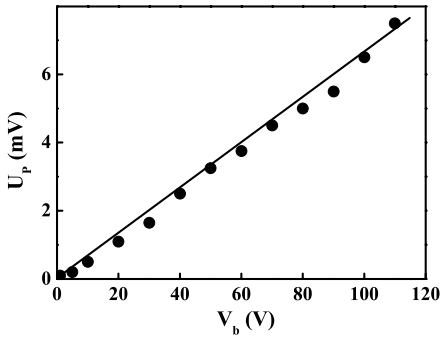

Fig. 3. The dependence of peak voltage signal U_P on bias voltage V_b under the irradiation of a 355 nm laser pulse of 15 ps duration with an on-sample energy intensity of 250 nJ.

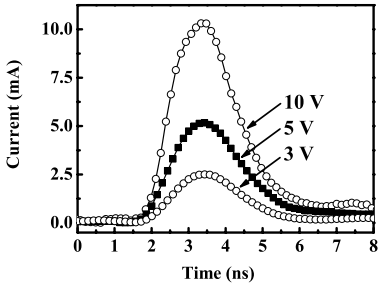

Fig. 4. Photocurrent as a function of time with $R_s = 0.1\ \Omega$ under 355 nm laser pulses in duration of 15 ps at different bias of 3, 5 and 10 V.

actively-passively mode-locked Nd:YAG laser was used as the source at room temperature in air, operating at a wavelength of 355 nm (3.49 eV photon energy) with 15 ps duration at a 1 Hz repetition rate and an single pulse energy density of 5 mJ/cm^2. To prevent signal saturation, the laser beam was weakened by an optical attenuator and the on-sample energy is about 250 nJ for single laser pulse. Two indium strips of ohmic contacts were separated by a 10 μm gap on the $SrTiO_3$ surface. Thus, the irradiated area is 0.05 mm^2. A programmable dc power supply was used as external voltage source. In order to eliminate the external interference, the sample was mounted in a chamber with an exit slit in front. For comparison, a 420 nm (2.95 eV photon energy) laser pulse of 15 ps duration was also used to irradiate the surfaces of the $SrTiO_3$ single crystals at ambient environment. The photoresponse signal was recorded using a digital oscilloscope of 400 ps resolution with an input impedance of 1 MΩ.

3 Results and discussion

Figure 2 shows a typical voltage transient of $SrTiO_3$ single crystal under the irradiation of a pulsed 355 nm laser of 15 ps in duration. Here, load resistor R_s is 1 MΩ, and bias voltage V_b is 60 V. The peak voltage signal U_P is 3.75 mV. As reviewed in Figure 3, the U_P has a linear relationship to the V_b from 1 to 110 V. In particular, U_P is as large as 7.6 mV at $V_b = 110$ V.

To reduce the influence of the circuit in the measurement and the long tail of the decay time due to the RC effect in the photoresponse signal, a 0.1 Ω load resistance was connected in the two electrodes and parallel with the surface of $SrTiO_3$ crystal. As reported in the perovskite oxide p-n junctions of $La_{0.7}Sr_{0.3}MnO_3$/Si, $SrTiO_{3-\delta}$/Si, $BaNb_{0.3}Ti_{0.7}O_3$/Si and $LaAlO_{2.73}$/Si [10–13], as well as in the $La_{0.67}Ca_{0.33}MnO_3$ films on tilted $SrTiO_3$ substrates [14], ultrafast photoresponse characteristic was also observed in the present untilted single crystals under bias voltages applied. As shown in Figure 4, the full width at half maximum is about 2 ns, and the 10–90% rise and fall times are 750 ps and 900 ps, respectively. The current, defined as Voltage/R_s, is very sensitive to the bias, and the peak value is about 2.5 mA, 5.1 mA and 11 mA at $V_b = 3$ V, 5 V and 10 V, respectively.

It is well known that the photothermal and the photoexcitation effects occurred at the same time under the irradiating laser. The laser energy could be instantaneously converted to thermal energy in the surface region and a local molten layer of the $SrTiO_3$ surface is formed [15,16]. Based on the oxygen vacancy model as following

$$O_O^* \Leftrightarrow \frac{1}{2}O_2(g) + V_{\ddot{O}} + 2e', \qquad (1)$$

oxygen atoms are thermally vaporized and accompanied by the formation of the two electrons. Due to the laser photon energy (3.5 eV) above the optical band gap of $SrTiO_3$ (3.2 eV), the two extra electrons coming from the

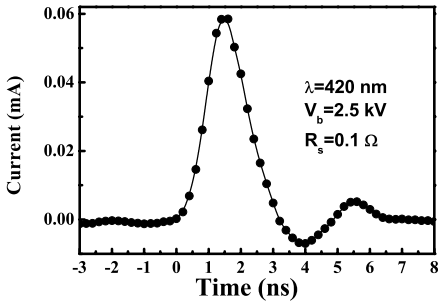

Fig. 5. Transient photoresponse under the irradiation of a 420 nm pulsed laser of 15 ps duration.

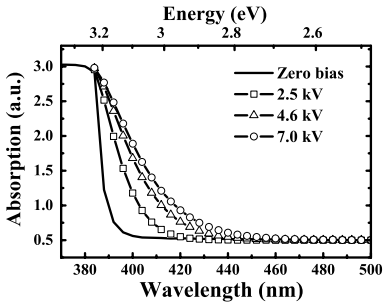

Fig. 6. The absorption spectra of $SrTiO_3$ crystal under the bias of 0, 2.5, 4.6 and 7.0 kV.

surface are excited from the valance band (O $2p$) to the conduction (T $3d$) band, leading to the appearance of the laser-irradiated photocurrent. Under the external bias, the carriers are speeded up and the photoresponse is enhanced consequently.

Furthermore, we investigate the photoresponse on the 420 nm laser pulse irradiation with an on-sample energy of 250 nJ and a duration of 15 ps. When a 0.1 Ω resistance is applied, a pulsed current signal with a peak of about 0.06 mA is detected under a very large bias $V_b = 2.5$ kV as shown in Figure 5. There is no measurable signal above noise if no bias or only small bias is applied because of the energy of the visible light (2.95 eV) lower than the band gap of $SrTiO_3$.

The photoresponse signal in Figure 5 can be determined by the Franz-Keldysh effect in the presence of an electric field [17], which is a change in optical absorption by a semiconductor when an electric field is applied. The tilted band edge makes acoustic phonon-assisted indirect transitions much easier. Figure 6 shows the absorption spectra, one for zero bias, and the others for applied bias derived from the photon absorption as a function of the external field:

$$\alpha(\hbar\omega) \propto \exp\left[-\frac{4\sqrt{2m^*}(E_g - \hbar c/\lambda)^{3/2}}{3|e|E\hbar}\right] \qquad (2)$$

where m^* is the effective electron mass, $\hbar$ Plank constant divided by 2π, and E the electric field strength. By calculation, the bias between the two electrodes should not create an effective photoresponse in the region of 420 nm wavelength until above 2 kV.

4 Conclusion

In summary, we have developed a photosensive resistor based on $SrTiO_3$ bulk material with high-speed characteristic. The origin of the laser-irradiated response has an important relationship with the dissociation of surface oxygen and the electronic excitation under the applied bias. It is worth to note that the photoresponse shows an UV/visible rejection ratio of about three orders of magnitude, suggesting the promising potential of $SrTiO_3$ as a new type of ultrafast UV detectors with high sensitivity for application.

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