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Ultraviolet fast-response photoelectric effect in tilted orientation $SrTiO_3$ single crystals

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Ultraviolet photoelectricity based on the vicinal cut as-supplied $SrTiO_3$ single crystals has been experimentally studied in the absence of an applied bias at room temperature. An open-circuit photovoltage of 130 ps rise time and 230 ps full width at half maximum was observed under the irradiation of a 355 nm pulsed laser of 25 ps in duration. The dependence of the photoelectric effect on the tilting angles was studied, and the optimum angle is 20.9°. Seebeck effect is proposed to elucidate the tilting angle dependence of laser-induced photovoltage. This work demonstrates the potential of $SrTiO_3$ single crystals in ultraviolet detection. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2367658]

In recent years, there has been an increasing demand for an ultraviolet (UV) selective and sensitive photodetector which offers potential applications in environmental monitoring such as solar UV radiation monitoring, ozone-hole sensing, flame detection for a fire alarm, and secure space-to-space communication. Main efforts are currently directed to wide band gap semiconductors, such as III-V nitrides,[1] silicon carbide,[2] zinc oxide,[3] and diamond,[4] which are a much more attractive choice for selective UV detection. A response of 8 ns rise time and 1.4 μs fall time has been achieved in UV photoconductive detector based on epitaxial $Mg_{0.34}Zn_{0.66}O$ thin films.[5] Highly quality GaN devices exhibit 1.4-ps-wide electrical transients under illumination by 100 fs duration and 360 nm wavelength laser pulses.[6] However, these devices require a complicated fabrication process and high-cost manufacturing.

Strontium titanate oxide ($SrTiO_3$) is a promising wide band gap material and appears to be excellent in the field of electronic industry. Over the years, $SrTiO_3$ has been mainly used for dielectric devices,[7–9] whereas very little work has been devoted to optical applications.[10,11] In agreement with its band gap of 3.2 eV, $SrTiO_3$ absorbs lights with a wavelength of less than 390 nm, presenting a high transparency in the visible and infrared wavelength range and selectively sensitive to a UV light.

Our previous work considered mainly a functional heterojunction consisting of oxygen-deficient $SrTiO_{3-\delta}$ and Si, and their UV photovoltage characteristics resulted from the optical excitation of the nonequilibrium charge carriers and their separation due to the built-in field near the n-$SrTiO_{3-\delta}/p$-Si interface.[12] However, this device also shows the response of visible and near infrared since the Si has a band gap of ~1.12 eV, which must be corrected with filters in UV detection. Although the photoconductivity of insulative $SrTiO_3$ single crystal under an UV light irradiation has been reported for more than 40 years,[13–16] as far as we know, no open-circuit photovoltage and UV photodetector based on $SrTiO_3$ single crystals were reported. In this letter, we report the UV laser-induced photovoltaic effect in commercial vicinal cut $SrTiO_3$ single crystals without an applied bias, which has ultrafast response time at room temperature.

As-supplied $SrTiO_3$ (001) single crystals with the purity of 99.99% are mirror double polished in the present study. The geometry of the sample we used is 3 mm × 10 mm with the thickness of 0.5 mm. The (001) plane is tilted as an angle of α with respect to the surface. The angles α ranged from 0 to 45 ° in our measurement. As shown in Fig. 1, the tilting of the c axis was confirmed by x-ray diffraction measurement with the usual θ-2θ scan. To satisfy the Bragg's diffraction geometry, the [001] axis was aligned carefully and the offset point was set as ω. Here, ω was α or α-45 ° to detect (00ℓ) or $(\ell 0\ell)$ peaks, respectively.

For the photovoltaic measurements, two indium electrodes separated by 1 mm were painted on the laser-irradiated surface of the $SrTiO_3$, and always kept in the dark to prevent the generation of any electrical contact photovoltage. The third harmonic of an actively passively mode-locked Nd:yttrium–aluminum–garnet laser was used as the source at room temperature in air, operating at a wavelength of 355 nm (3.49 eV photon energy) with 25 ps duration at a 1 Hz repetition rate and an energy density of 0.05 mJ mm^{-2}. Thus the on-sample energy is 0.15 mJ. The photovoltaic signals were monitored with a Tektronix sampling oscilloscope (2.5 GHz bandwidth) terminated into 1 MΩ.

The pulsed photovoltage occurred when the $SrTiO_3$ surface was irradiated directly by a laser pulse. Figure 2 presents a typical open-circuit photovoltage transient of a 15° tilting $SrTiO_3$ single crystal. The peak photovoltage V_L^P is

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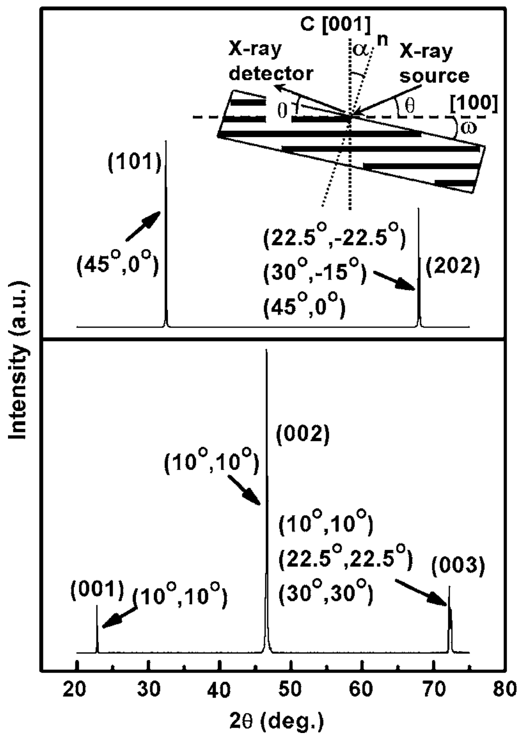

FIG. 1. X-ray diffraction patterns of tilted $SrTiO_3$ crystals. The inset shows the configuration of θ-2θ scan. To get different diffraction peaks, (00ℓ), (101) and (202), ω was adjusted as shown in the angle arrays (α,ω) for different α.

52 mV, the rise rime is 80 ns, and the full width at half maximum (FWHM) 2.8 μs.

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 photovoltaic signal, a 0.5 Ω load resistance was connected in the two electrodes and parallel with the $SrTiO_3$ crystal. As shown in Fig. 3, the rise time is dramatically reduced to about 130 ps, which is limited by the oscilloscope, and the FWHM is also reduced to be about 230 ps. The peak photocurrent I_L^P is 4.7 mA, here, $I_L = V_L/0.5\ \Omega$.

We did not observe the photovoltaic signal when the $SrTiO_3$ crystal was irradiated by the 532 or 632.8 nm lasers. To characterize the photogenerated carriers of the samples

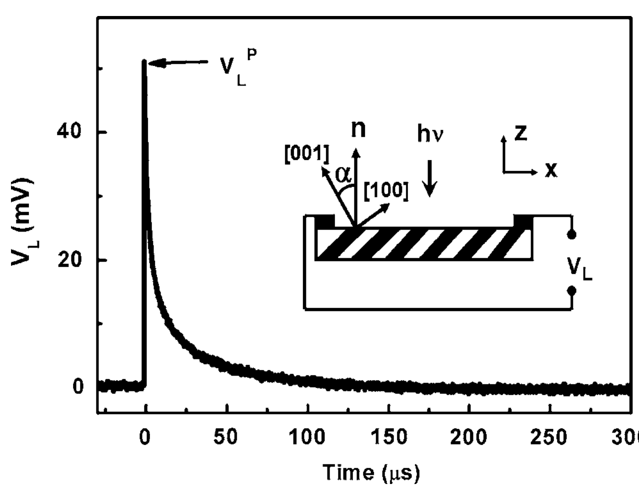

FIG. 2. A typical open-circuit photovoltage under an excitation of a 355 nm laser pulse. The tilted degree α is 15°. The inset displays the schematic circuit of the measurement. V_L^P denotes the peak value of the transient photovoltage.

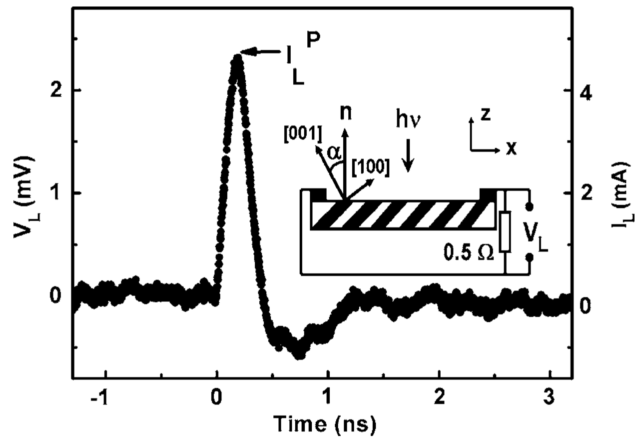

FIG. 3. A typical photovoltage with a 0.5 Ω resistance in parallel with the $SrTiO_3$ single crystal under an excitation of a 355 nm laser pulse. The tilted degree α is 15°. The inset displays the schematic circuit of the measurement. I_L^P denotes the peak value of the transient photocurrent.

used in present study, we determined the optical absorption spectrum from the optical transmission measurement using a SpectraPro500i spectrophometer. Figure 4 shows the UV-visible absorption spectrum of $SrTiO_3$ samples as a function of the wavelength. The sharp absorption edge is at ~385 nm, which is in agreement with the optical band gap of $SrTiO_3$ and the experimental results, indicating that photovoltaic signals cannot have been observed when the samples are irradiated by lasers with the photon energies smaller than the band gap of $SrTiO_3$. This property demonstrates that the production of the photongenerated carriers plays a crucial role in the process of laser-induced voltage in this system.

To understand the mechanism of the photoelectric effect, we illuminate the $SrTiO_3$ crystal through the reverse face which is opposite to the side where leads are attached. The signal polarity reversal is obvious, and the response is essentially mirror images of each other. In addition, no photovoltage was generated along the nontilting [010] direction. These facts can be considered to support the suggestion that this phenomenon is due to a transverse thermoelectric effect.[17] In this case, the voltage can be represented by

$$V_x = \ell\,(S_{[100]} - S_{[001]})\sin(2\alpha)(dT/dz)/2. \quad (1)$$

Here ℓ is the illumination length, $S_{[100]}$ and $S_{[001]}$ are the Seebeck coefficients along the [100] and [001] axis, and

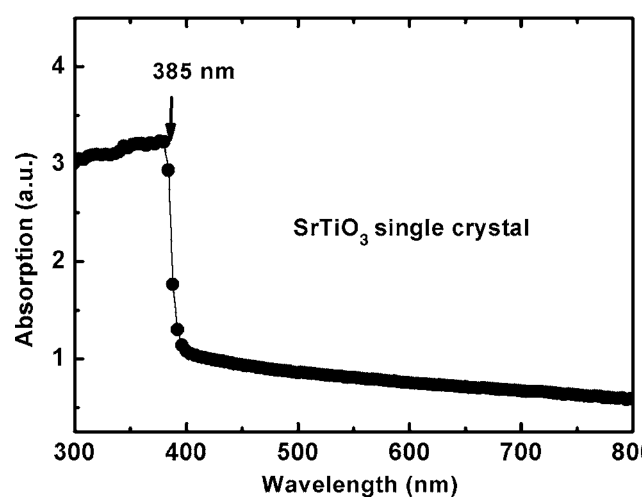

FIG. 4. Spectral absorption of $SrTiO_3$ single crystal with a thickness of 0.5 mm.

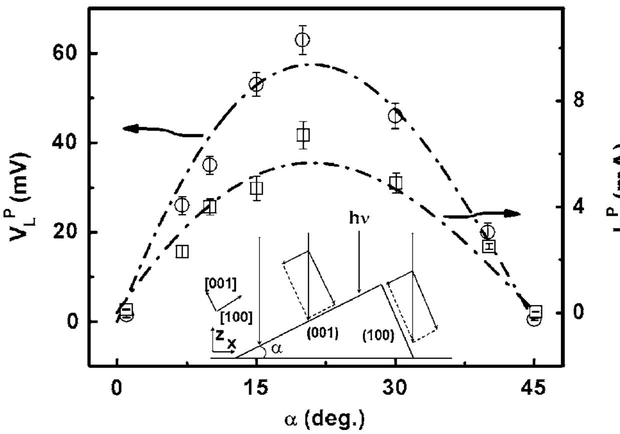

FIG. 5. Peak photovoltage (open circle) and peak photocurrent (open square) dependence of the tilting angle. The dashed lines show the fitting results using Eq. (2).

dT/dz is the temperature gradient in the direction of irradiation (the surface normal direction of $SrTiO_3$ crystal).

Furthermore, we chose several $SrTiO_3$ samples with different tilting angles (1°, 7°, 10°, 15°, 20°, 30°, 40°, 45°) and measured V_L^P and I_L^P as the function of α. The experimental procedures are the same as shown in Figs. 2 and 3. Results are plotted in Fig. 5. The signal amplitude increases with α until 20°, and then decreases. At $\alpha=45°$, the detected signal, similar to that at $\alpha=0°$, is basically a random noise due to the electrical-magnetical emission by the operation of the excimer laser. The maximum of the signal height, a photovoltage of 63 mV and a photocurrent of 67 mA, appears at $\alpha=20°$.

It has been well known that each element of Seebeck tensor is proportional to the corresponding electrical resistivity of the system, and the electrical resistivity along each axis is reverse proportional to the transient carrier density correspondingly. In this way, Seebeck tensor strongly depends on the transient carrier density along each axis. The inset of Fig. 5 shows the schematic drawing under the irradiation of a UV pulsed laser. If we divided the laser into two components of being parallel and being perpendicular to the tilting direction, the transient carrier density along each axis is proportional to the illuminated power perpendicular to the tilting direction, leading to $S_{[100]}-S_{[001]} \propto (\cos\alpha - \sin\alpha)$. So, we can get

$$V_x \propto \ell (\cos\alpha - \sin\alpha)\sin(2\alpha)(dT/dz)/2, \qquad (2)$$

where the maximum occurs at $\alpha=20.9°$. From Fig. 5, we can see that the calculated results (dashed lines in Fig. 5) from Eq. (2) are in very good agreement with the measured points, which indicates that the present model of the mechanism for laser-induced voltage becomes convincing. This result also suggests the importance of the anisotropic thermoelectricity. Our further studies will be aimed at higher sensitivity and faster response of this system.

In summary, we observed UV photovoltage in as-received tilting $SrTiO_3$ single crystals. High-speed performance of a 130 ps rise time and 230 ps FWHM was achieved. The tilting angle dependence of laser-induced photoelectric effect can be described by the Seebeck effect, and the optimum angle is 20.9°. The experimental results can be considered to support the suggestion that the photovoltage is due to the combination of a photoelectron and a Seebeck process. It is worth noting that the present ultrafast UV photovoltaic effect is based on commercial $SrTiO_3$ crystals and no external bias is required for the operation, which is suggestive of the advantage of simple process and low cost. The present work manifests the potential application of $SrTiO_3$ single crystals in UV photodetectors.

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