Ultraviolet Photoelectric Effect in ZrO_2 Single Crystals *

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Nanosecond photoelectric effect is observed in a ZrO_2 single crystal at ambient temperature for the first time. The rise time is 20 ns and the full width at half maximum is about 30 ns for the photovoltaic pulse when the wafer surface of the ZrO_2 single crystal is irradiated by 248 nm KrF laser pulses. The experimental results show that ZrO_2 single crystals may be a potential candidate in UV photodetectors.

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Zirconium oxide (ZrO_2) is a technologically important material.[1,2] It has many excellent qualities, such as high melting point (2860°C), large resistance against oxidation, good thermal and chemical stabilities, and high refractive index. These properties make it be widely used in many fields including high-reflectivity laser mirrors, broadband interference filters, and waveguides with small losses.[3−6] In addition, zirconium oxide is a promising candidate to replace silicon oxide as the gate dielectric in complementary metal-oxide-semiconductor technology.[7] Due to its wide range of interesting applications, great efforts have been devoted to synthesize zirconium oxide by different methods.[8−11] Some research groups have reported that the optical properties of zirconium oxide, such as reflective indices, optical conductivity and energy band transition, are closely related to its structures and preparation condition.[12−15] However, to date, to our knowledge, there have been few works on the photoelectric effect of zirconium oxide single crystal. In this Letter, we report the photoelectric effect of zirconium oxide single crystal, which has short response time and high sensitivity with laser pulse irradiation under an external bias at ambient temperature.

The ZrO_2 (001) single crystal wafers used in the present study are the as-supplied ZrO_2 substrates and double-polished. The geometry of the sample is 5 mm × 10 mm in thickness 0.5 mm. The absorption spectrum of ZrO_2 was measured as shown in Fig. 1. The absorption peak and the absorption edge are located at 248 nm and 260 nm, respectively. The optical band gap of ZrO_2 can be determined by the absorption spectrum to be about 4.7 eV.

In order to study the photoelectric effect, two indium electrodes separated by 1 mm were painted on the ZrO_2 surface. The ZrO_2 surface was irradiated by a 248 nm (5.0 eV, 25–30 ns duration) KrF laser beam at ambient temperature. The photoelectric signal was measured by a 500 MHz Tektronix sampling oscilloscope. The laser energy density was $0.3\,mJ\cdot mm^{-2}$. The applied voltage source was a tunable dc power supply. The load resistance R was 68 MΩ. The schematic circuit of sample measurement is shown in the inset of Fig. 2.

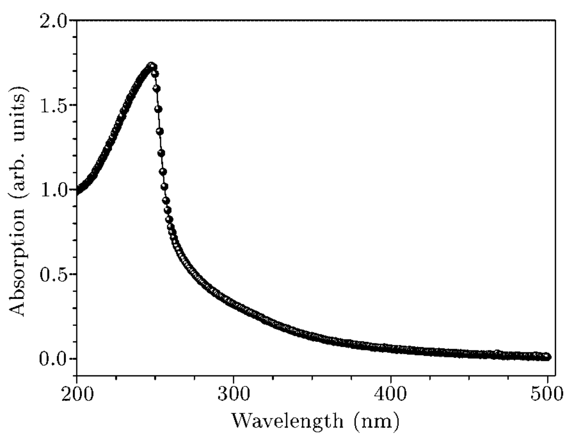

Fig. 1. Absorption spectrum of ZrO_2 single crystal.

Figure 2 shows a typical photovoltaic pulse as a function of time when the ZrO_2 surface was irradiated directly with a 248 nm KrF laser pulse and measured by using 1 MΩ input impedance of the oscilloscope under 20 V biased voltage. The peak value V^P of photovoltaic pulse is 1300 mV and its photovoltaic sensitivity is $867\,mV\cdot mJ^{-1}$. The rise time (10–90%) is $2\,\mu s$ and the full width at half maximum (FWHM)

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is 168 μs for the photovoltaic pulse. It should be noted that there is a sharp rise at the very beginning of the photovoltaic pulse and then the signal gradually decreases.

For reducing the influence of the measurement system, we measured the photovoltaic pulse using 50 Ω input impedance of the oscilloscope. Under the same experimental conditions, the trace of the photovoltaic pulse is nearly symmetrical as shown in Fig. 3. The rise time is dramatically reduced to about 20 ns, and the FWHM is also reduced to about 30 ns, which is very close to the FWHM of the laser pulse.

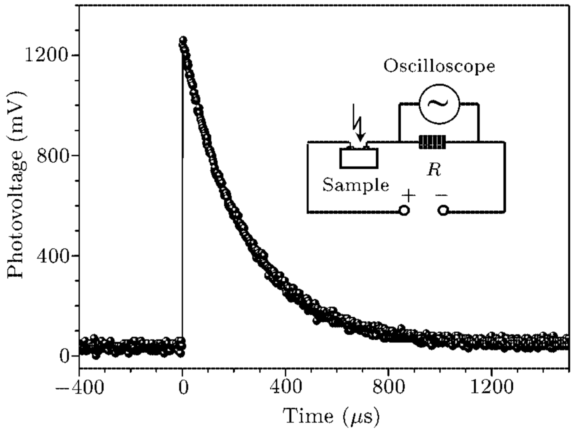

Fig. 2. Typical photovoltaic pulse as a function of time for the ZrO_2 surface irradiated directly with a 248 nm KrF laser pulse and measured by using 1 MΩ input impedance of the oscilloscope under 20 V biased voltage. The inset is the schematic circuit of the photoelectric measurement system.

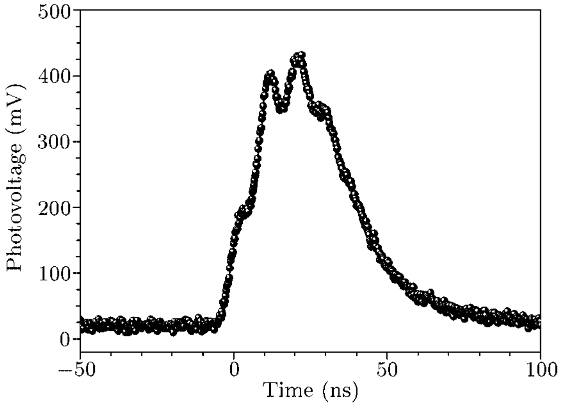

Fig. 3. Photovoltaic pulse as a function of time for the ZrO_2 surface irradiated directly with a 248 nm KrF laser pulse and measured by using 50 Ω input impedance of the oscilloscope.

We also measured the photovoltaic effects with a 308 nm XeCl laser and a 632.8 nm He-Ne laser. No photovoltaic signal was observed because both the phonon energies of the 308 nm and 632.8 nm lasers are smaller than the band gap of ZrO_2. The experimental results demonstrate that the photon-induced carriers play a crucial role in the process of laser-induced voltage. When the ZrO_2 surface is irradiated by photons with energy larger than the bandgap of ZrO_2, the nonequilibrium charge carriers can be created. As the nonequilibrium charge carriers are promptly parted by the electric field supplied by applied voltage, the photovoltage appears. The experimental results demonstrate that the photo-induced voltage effect in the ZrO_2 single crystal is a photoelectric effect and it is not only a highly sensitive to the laser pulse irradiation process but also a nanosecond order fast photoelectric process.

In summary, we have observed the high sensitivity and nanosecond order ultraviolet photoelectric response in ZrO_2 single crystals at ambient temperature for the first time. It is worth noting that the photoelectric effect we observed is based on commercial ZrO_2 single crystal wafers and no complicate power supply connection is employed, which is suggestive of the advantage of simple process and low cost. From the practical application point of view, our experimental results manifest that ZrO_2 single crystals have potential applications in visible–blind UV photodetectors.

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