Ultraviolet photovoltage characteristics of $SrTiO_{3-\delta}$/Si heterojunction

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A photovoltaic effect is observed in the heterostructure of *p*-Si/*n*-$SrTiO_{3-\delta}$ (*p*: hole carrier type, *n*: electron carrier type). The current–voltage curve exhibits a good rectifying characteristic similar to that of the traditional diode. The junction shows the open circuit voltage of 126 mV/mJ, the short circuit current of 1.78 mA/mJ, and the response time faster than 10 ns for ultraviolet pulsed laser of 25 ns in duration at room temperature, suggesting the promising potential of this junction as a new type of ultrafast ultraviolet detectors with high sensitivity for application. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1943495]

Crystalline metal oxides have attracted much attention for a wide variety of device applications. Perovskite-type metal oxides (ABO_3), in particular, have become an important class of materials due to their unusual dielectric, piezoelectric, ferroelectric, ferromagnetic, optical, electro-optic, and catalytic properties.[1,2] $SrTiO_3$ as a member of perovskite family is an incipient ferroelectric material with a relatively high dielectric constant with possible applications in dynamic random access memories (DRAMs)[3,4] and in high value or tunable capacitors.[5–7] The driving force of the semiconductor industry to integrate the transition-metal oxides with Si has led to the development of $SrTiO_3$ thin film growth on Si (001).[8,9] These STO films have served as the gate-oxide layer for metal-oxide field-effect transistors and as the buffer layer for III–V on Si semiconductor technology.

Stoichiometric $SrTiO_3$ with Ti^{4+} ions has a d^0 electron configuration, and consequently is an insulator with a band gap of ~3.2 eV.[10] The electrical properties of $SrTiO_3$ can be changed from insulator to *n*-type semiconductor by reducing it to $SrTiO_{3-\delta}$[11–13] or doping impurity ions.[14,15] $SrTiO_3$ thin films prepared by vacuum processes usually contain oxygen vacancies and these oxygen vacancies can form positive space charge under high electric fields by detrapping electrons. Then the $SrTiO_3$ films will possess some characteristics of the *n*-type semiconductors. Compared to the traditional semiconductor *p*-*n* junctions, these oxide junctions could be expected to exhibit characteristics, such as magnetic,[16,17] electric,[18] or light-controlled behavior.[19]

In this letter, we present a functional *p*-*n* heterojunction consisting of a *p*-type B-doped Si and *n*-type oxygen-deficient $SrTiO_{3-\delta}$ we fabricated and its photovoltaic effect under the pulsed ultraviolet (UV) irradiation. Results of this study revealed that the present heterojunction, based on perovskite oxide thin film on conventional semiconductor material, had the potential for using as sensitive UV detectors with ultrafast response time, high open circuit voltages and short circuit currents.

$SrTiO_{3-\delta}$ thin film was deposited directly on a *p*-type silicon substrate (resistivity is 12.95 Ω cm) by the laser molecular-beam epitaxy (LMBE) technique.[20] First, after wet-chemical cleaning, the Si substrate was dipped into a buffered solution with 4% HF for 60 s to remove the amorphous SiO_2 layer from the surface of the silicon, leaving a hydrogen-terminated surface. Then the Si substrate was immediately put into an epitaxial chamber. The initial deposition of about two atomic layers of SrO film was under the base pressure of 5×10^{-6} Pa at the substrate temperature of 300 °C to prevent the formation of the SiO_2 interface layer. After that, the substrate temperature was raised to 620 °C, and the oxygen pressure was raised to 2×10^{-4} Pa. Then, a $SrTiO_{3-\delta}$ layer with a thickness of 200 nm was deposited. The crystallization of the film was *in situ* monitored by reflective high-energy electron diffraction (RHEED). The bright RHEED pattern clearly indicates the smooth STO surface and high degree of crystallinity of the film. For measurement, indium (In) electrodes of 0.5 mm^2 were used on $SrTiO_{3-\delta}$ and Si, respectively.

Figure 1 displays the typical *I*–*V* behavior of the *p*-Si/*n*-$SrTiO_{3-\delta}$ junction by tuning the applied voltage in a wide range at room temperature. The well-rectified *I*-*V* characteristic of a *p*-*n* diode is prominent similar to that of conventional semiconductor *p*-*n* junctions. The structure appears to be reverse biased when the negative polarity of the dc voltage source is applied on the Si side. The leakage current is as low as 16 μA even when −20 V is applied to the junction. When the polarity changes (positive polarity on the Si side), the current increases rapidly with the enhancement of the applied voltage and the structure can be considered as forward biased.

An energy band profile of the *p*-Si/*n*-$SrTiO_{3-\delta}$ heterojunction in the equilibrium state is obtained by using an iterative method to solve the Poisson equation and Boltzmann formulas self-consistently, as shown in Fig. 2. The inset is

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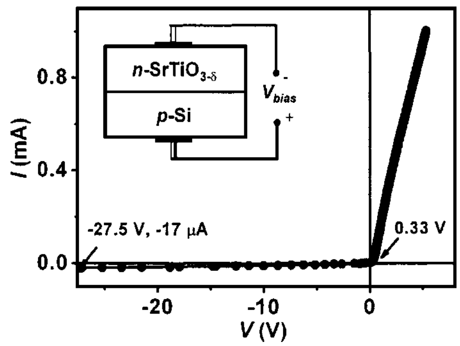

FIG. 1. $I-V$ characteristic of a p-Si/n-$SrTiO_{3-\delta}$ junction diode at 300 K. The voltage polarity is defined at the electrode on Si side. The schematic circuit of the sample measurement is shown in the inset.

the amplified part near the spike of the interface. Carriers concentrations used as the parameters can be directly taken from our results of Hall measurement, being about 1.45×10^{15} cm^{-3} for Si and 4.83×10^{19} cm^{-3} for $SrTiO_{3-\delta}$. Furthermore, the energy gaps of Si and $SrTiO_{3-\delta}$ are 1.12 and 3.2 eV, respectively. And the work functions without doping in these two materials are regarded as 4.6 and 5.2 eV.[21] The offset of valence band and that of the conduction band (E_V and E_C) for $SrTiO_3$ on p-Si are about −1.43 and 0.65 eV, respectively, at the interface. According to the band diagram, it can be seen clearly that the barrier height of the spike is about 0.4 eV. And this can be comparable to the threshold voltage that is about 0.33 V under the forward bias voltage, as presented in Fig. 1.

A typical voltage transient of unbiased p-Si/n-$SrTiO_{3-\delta}$ junction under the pulsed 308 nm laser irradiation of 25 ns in duration is presented in Fig. 3. The energy density is $0.5\ mJ/mm^2$ and the irradiated area is $2\ mm^2$. The pulse response was monitored with a sampling oscilloscope which has a response speed of 2 ns and an input impedance of 1 MΩ. We note that the response is composed of a fast rise time and much slower decay. The *RC* constant in the circuit should be responsible for the slow decay phenomenon. The rate of laser induced carriers in the junction can be presented as $\mathrm{sech}^2(t/\tau_1)$ where τ_1 denotes the duration of laser pulse, thus the laser induced voltage with τ_2, here τ_2 being equivalent to the recharging time *RC* of the circuit, can be obtained by the following equation:

$$U(t) \propto e^{-t/\tau_2} \int_{-\infty}^{t} \mathrm{sech}^2\left(\frac{t'}{\tau_1}\right) e^{t'/\tau_2} dt'. \quad (1)$$

The calculated results from the above equation as shown in Fig. 3 by solid line are in excellent agreement with the experimental data. The τ_2, as a parameter, is taken as 40 μs, and τ_1, as the laser pulse duration, is 25 ns in the calculation. When a 0.5 Ω resistance is connected in parallel with the junction as shown in Fig. 3, the trace is almost triangular and symmetrical (see the inset of Fig. 3). The fast response has a 10%–90% rise time of 8 ns, a 10%–90% fall time of 9 ns, and a full width at half maximum (FWHM) of 11 ns, which are limited by the excitation laser.

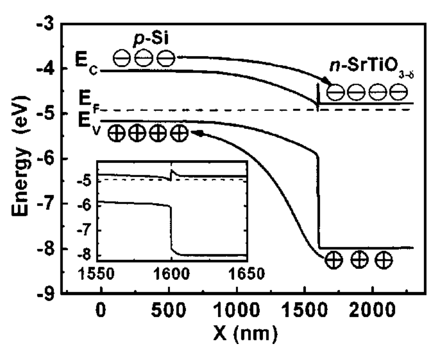

FIG. 2. Schematic band structure for p-Si/n-$SrTiO_{3-\delta}$ junction. The inset is the amplified part near the spike of the interface.

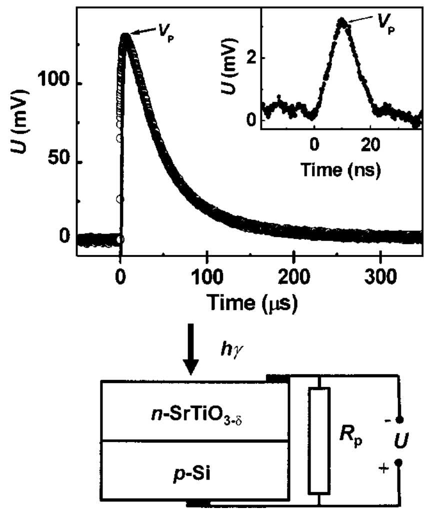

FIG. 3. Typical voltage response of p-Si/n-$SrTiO_{3-\delta}$ junction to 308 nm pulsed laser irradiation. The solid line shows the fitting result using Eq. (1). The inset displays the fast response to laser pulse with a 0.5 Ω resistance connected in parallel across the p-n junction. V_P denotes the peak value of the transient voltage. The sketch shows the schematic circuit of the sample measurement.

The peak values of short-circuit current I_{SC} and open-circuit voltage V_{OC}, generated by the heterojunction under UV pulse irradiation, were measured using the circuit presented in Fig. 3 with smaller and larger impedances R_P, respectively. We can get I_{SC} ($R_P=0$) and open-circuit voltage V_{OC} ($R_P=\infty$) by fitting the data carefully, $V_P \sim R_P$ and $I_P(=V_P/R_P) \sim R_P$, in Fig. 4. The insets in Figs. 4(a) and 4(b) indicate that the I_{SC} and V_{OC} are both linear with the irradiated area S, and with a sensitivity of 1.78 mA/mJ and 126 mV/mJ, respectively.

From the band structure shown in Fig. 2, we can obtain the origin causing the laser induced voltage in the system. Under UV laser irradiation, electrons in the valence bands of $SrTiO_{3-\delta}$ and Si absorb the UV photons and make the transition into the conduction bands, thus holes in the valence bands and electrons in the conduction bands are created, respectively. Holes in the valence bands of $SrTiO_{3-\delta}$ will be drifted into the valence band of Si, and meanwhile, electrons in the conduction band of Si will be drifted into $SrTiO_{3-\delta}$ due to the built-in electric field in the system as shown in Fig. 2. Then the nonequilibrium carriers are partially separated by the built-in electric field near the interface of the junction. Eventually, the Fermi level in Si is lowered and that of $SrTiO_{3-\delta}$ is raised, leading to the appearance of an instant photovoltage.

The photovoltage is decreased by 20 times when the junction is irradiated through the p-Si substrate rather than through the $SrTiO_{3-\delta}$ film. This can be understood in the following way. The substrate thickness is much longer than the diffusion length of the photogenerated carriers in the Si side, so only very few photons can be injected into the deple-

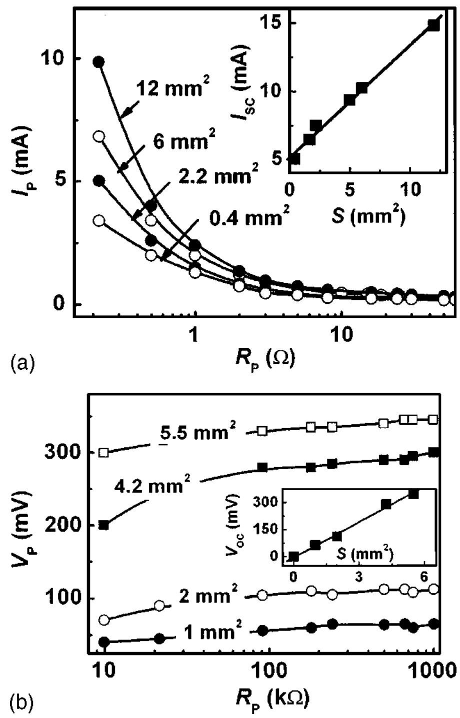

FIG. 4. (a) Peak values of transient current $I_P(I_P=V_P/R_P)$ and (b) V_P as functions of the input impedance R_P connected in parallel across the p-n junction. The insets summary the short-circuit current I_{SC} and open-circuit voltage V_{OC} as functions of the irradiated area S. Numbers in the figure denote the S values. The solid lines are guides for the eye.

tion layer due to the strong absorption in Si substrate, resulting in a small photovoltage. Here, it should be noticed that the $SrTiO_{3-\delta}/n$-Si, an n^+-n junction we prepared, exhibits only a very small photovoltaic current and a small open circuit voltage. These facts give a support for the photovoltaic effect originating from the p-Si/n-$SrTiO_{3-\delta}$ interface.

In conclusion, a new heterostructure is proposed in this letter. The $I-V$ characteristic of the structure shows a diode-type behavior. Under UV laser irradiation, the junction shows high performance such as open circuit voltage of 126 mV/mJ, short circuit current of 1.78 mA/mJ, and response time faster than 10 ns, suggesting the potential for optoelectronic detection applications.

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