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Photoinduced phase transition and relaxation in bare $SrTiO_3$ single crystals

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The photoinduced insulator-metal phase transition and relaxation characteristics have been investigated in bare $SrTiO_3$ single crystals. The photoinduced relaxation time constant after the irradiation shows an increase with increasing temperatures. The $SrTiO_3$ single crystal has a cutoff wavelength and an absorption edge of spectrum at about 385 nm, which agrees well with the band gap. The photocurrent responsivity is 1.36×10^{-5} A/W at 300 nm wavelength. The relative change in resistance is more than above six orders at room temperature, possessing potential applications in ultraviolet sensitive and detecting devices. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4815950]

I. INTRODUCTION

As one of the most important oxide substrates for use in devices owing to matching with other perovskite oxides, strontium titanate $SrTiO_3$ (STO) has attracted much attention since the discovery of its incipient ferroelectricity and first polar soft mode behavior.[1] In fact, STO is a typical nonpolar band insulator with an indirect band gap of ~3.3 eV. Moreover, STO itself has rich and interesting properties, such as an insulator-metal transition and superconductivity at low temperatures by electron doping,[2,3] Shubnikov-de Haas (SDH) oscillations,[4] blue light emission in Ar-irradiated, electron-doped and O-deficient STO,[5–7] ferroelectricity without any intentional doping,[8] two dimensional electron gas at the bare STO surface,[9,10] resistive switching phenomena,[11] photocarrier-doped effect,[12,13] and photovoltages.[14,15] On the other hand, the photoinduced process, being an external perturbation, offers a convenient method to change the phase configuration between metastable states and induce an insulator-metal transition. A photoinduced phase transition is used to photogenerate a hidden electronic phase or a state of the matter.[16] Some photoinduced-phase-transition's phenomena have been discovered in the magnetization of cobalt-iron cyanides and manganites with multiphase coexistence.[17–19] The persistent and reversible phases have been observed in charge-ordering thin films, which is promising for photonic device applications.[20,21] Furthermore, considering a marked absorption in the ultraviolet region of less than 390 nm wavelength, STO has a high transparency in a visible-infrared wavelength range and selectively sensitivity to an ultraviolet light.[22] Therefore, STO is a potential ultraviolet sensitive photodetector, possessing practical applications. The present work aims at studying the photoinduced phase transition and the resistance relaxation process in bare STO single crystals under the irradiation of ultraviolet light.

II. EXPERIMENT

The one-side-polished commercial STO (100) single crystals were supplied by Hefei Kejing Materials Technology Co. Ltd. The Pt/Al square-shaped electrodes with the size of 0.5 mm × 0.5 mm were deposited on the as-received STO single crystals using a conventional spin coater. The Pt layers were covered on Al electrodes to prevent Al oxidations. The distance between two electrodes is about 0.5 mm. Steady-state photoconductivity measurements were carried out with the conventional lock-in technique. The light source was a Xenon lamp and coupled into a monochromator. The monochromatic light was modulated by a mechanical chopper with the frequency of 140 Hz and then was focused down to samples by using a pair of parabolic mirrors. The data obtained were normalized by the incident light spectrum after each run with a calibrated Si photodiode. The Keithley multimeter (model 2635A) was used for the current-voltage measurements. The ultraviolet light with the wavelength of about 365 nm and the power density of 2.6 W/cm^2 typically illuminated the sample.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the normalized steady-state photo responsivity spectra as a function of wavelength for STO single crystals between Pt/Al electrodes. The photo responsivity values are defined by the photocurrent per watt of incident radiation at zero bias field. The photocurrent responsivity is 1.36×10^{-5} A/W at 300 nm wavelength and increases with bias voltages shown in inset of Fig. 1(a). The ultraviolet/visible (300 versus 400 nm) contrast ratio is more than three orders of magnitude and the cutoff wavelength appears at about 385 nm. Considering the ultraviolet-visible absorption spectrum of STO single crystals shown in Fig. 1(b), we found that the sharp absorption edge is at 385 nm, which is consistent with the cutoff wavelength of photo responsivity results (see Fig. 1(a)). Therefore, when it is irradiated by the lights with the photon energy larger than the band gap, STO single crystals will demonstrate a band gap excitation

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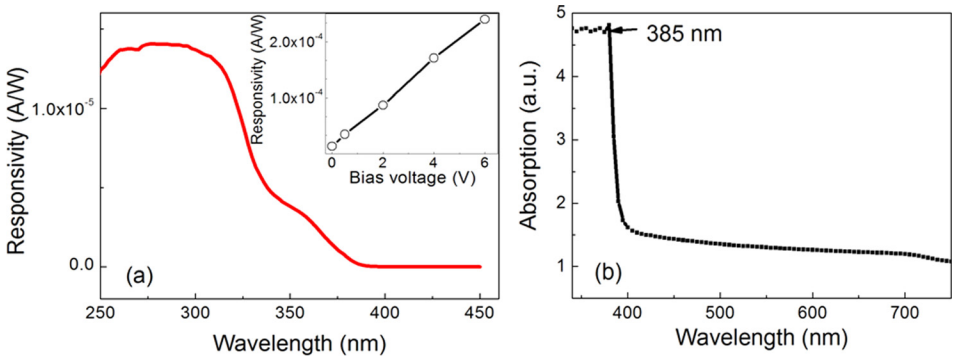

FIG. 1. (a) The normalized steady-state photo responsivity spectra as a function of wavelength for the as-received STO single crystals. The inset is the bias dependence of the photocurrent responsivities. (b) The ultraviolet-visible absorption spectrum of STO single crystals as a function of wavelength.

process.[15] As a result, we measured the photoinduced effect of STO single crystals under the irradiation of light with the photon energy of about 3.39 eV (365 nm). Figure 2 presents the current-voltage curves in log scale of STO single crystals under the irradiation at different temperatures. The inset reveals the simplified schematic diagram of the electrode assembly. The STO single crystal exhibits a linear current-voltage relationship, indicating that an Ohmic contact forms between Pt/Al electrodes. The temperature dependence of the resistance of STO single crystals with and without the light irradiations is shown in Fig. 3(a). The STO single crystal originally is an insulator and the resistance almost cannot be measured in the temperature range. When it is irradiated by the light, STO single crystal shows a metallic conduction and the resistance increases with increasing the temperature. The photoinduced insulator-metal phase transition is observed. The inset of Fig. 3(b) shows that resistance versus temperature fitting curve of STO single crystals under the light irradiation. The R vs. T curve of STO single crystals under the light irradiation can be fitted by the formula[23]

$$R = R_0 + R_1 \times T^2 + R_2 \times T^5, \tag{1}$$

where R_0 is the residual resistance, R_1 and R_2 are the coefficient and T is the temperature in Kelvin. The second term originates from electron-electron interactions and the third term is the contribution from electron-phonon processes. The solid line is the best fit to the data with three fitting parameters, $R_0 = 63268\ \Omega$, $R_1 = 3.22\ \Omega/\mathrm{K}^2$, and $R_2 = 1.27 \times 10^{-7}\ \Omega/\mathrm{K}^5$. It is noted that the resistance has a dominant T^2 temperature dependence with evidence of a small T^5 contribution. It is

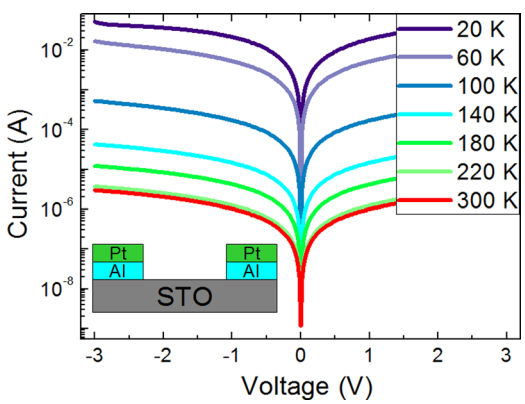

FIG. 2. The current-voltage curves in log scale of STO single crystals under the irradiation of light at different temperatures.

likely, then, that the metallic conduction arises from electron-electron interactions and the acoustic phonon scattering.[24] Meevasana *et al.* have discovered that the two-dimensional electron gas at the surface and considered the density can be controlled by the exposure of surface to intense ultraviolet light.[10] The extrinsic states, such as donor-like defects or absorbates, induce the two-dimensional electron gas. In particular, oxygen vacancies localized at the surface would be expected to lead to a surface electron accumulation with charge neutrality requiring the creation of an electron gas to screen the positive surface charge of such ionized defect centers. In addition, the migration of photogenerated carriers at the conduction band plays an important role in the transport process. The photoinduced relative change in the resistance of STO single crystals is defined as $\Delta R/R_L = (R_0 - R_L)/R_L \times 100\%$, where R_0 is the resistance without any external field and R_L is the resistance of STO single crystals irradiated by the light. The photoinduced relative change in resistance as a function of temperature is shown in Fig. 3(b). The relative change is more than eleven orders of magnitude at $T = 20\ \mathrm{K}$ and above six orders at room temperature. The relative change decreases with increasing the temperature and this is ascribed to the thermal fluctuation.

To gain a deeper insight into the photoinduced insulator-metal transition, we performed the dependence of the resistance on time at different temperatures under the same photoexcitation condition. The time dependence of the resistance of STO single crystals is shown in Fig. 4(a). When STO single crystal is irradiated by the light beam, the resistance is quickly decreased to the minimum values. And then the resistance shows a decay to its original value after the irradiation. The recovery of the resistance after the irradiation is the relaxation process of carriers, indicating the carrier's dynamics of recombination. Usually the band-band excitation is very fast. A longer generation lifetime is mostly due to a more complex process, which involves the trapping and thermal activation processes and forms shallow energy levels in the band gap. The resistance vs. time curves of STO single crystals after the irradiation can be fitted by the following exponential formula:

$$R = A \times \exp(t/\tau_1) + B \times \exp(t/\tau_2) + C, \tag{2}$$

where A and B are the magnitude, t is the time, τ_1 and τ_2 are the time constant of relaxation process. The time impendent term C is presumably due to the heating effect lasting for

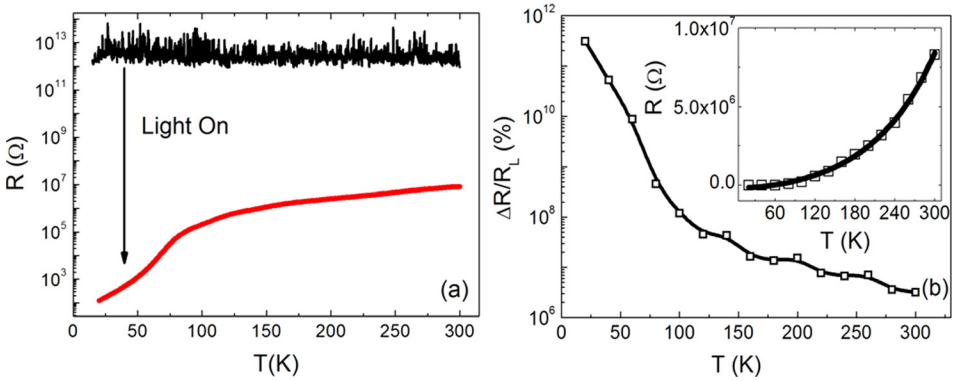

FIG. 3. (a) The temperature dependence of the resistance of bare STO single crystals with and without the light irradiations. (b) The photoinduced relative change in resistance as a function of temperature. The inset shows that resistance vs. temperature curve of STO single crystals under the light irradiation. The solid line is the best fit to the data.

longer time than time range concerned here. The fitted results are not shown. Good agreement between the fitted and experimental data is obtained. There are two distinct recombination lifetimes due to a more complicated recombination process with independent Shockly-Read-Hall centers at different recombination rates.[25] Here, two kinds of additional sources for carriers after the removal of light must be considered: photogenerated carriers and those associated with oxygen vacancies or other defects in the bulk created by the addition of light irradiation. The first process corresponding to τ_1 is purely electronic and should be fast compared with others. Thereby, there obviously exists a much faster change with τ_1 less than 1 s at the very beginning, which is too short to estimate in the present experiment. The second constant τ_2 shows a slow process. The temperature dependence of the time constant (τ_2) is shown in Fig. 4(b). It is shown that the time constants decrease with decreasing the temperature. The thermal activation process plays an important in the resistance recovery of STO single crystals after the ultraviolet irradiation. In a thermally activated process, the time constant of relaxation process follows Arrhenius-law,[26] which is expressed by $\tau_2 = \tau_0 \times e^{-E/kT}$, where τ_0 is the pre-exponential factor, E is the thermally activated energy, the essential energy after the removal of illumination, and k is Boltzmann constant. As shown in the inset of Fig. 4, the logarithm of the time constant yields a straight line as a function of reciprocal temperature. The time constant is well fitted by the formula. From the slope (about −85.3) of the line, the activated energy of the process has been evaluated and the calculation of E is about 69.7 meV for STO single crystals after the irradiation. Similar relaxation phenomena have been observed in the polarization of dielectric mode and the sheet resistance of irradiated sample.[27,28] In high quality STO single crystals, low concentration defects/impurities may be present. In this work, the existence of oxygen vacancies is quite possible in STO single crystals. Thereby, it is reasonable to assume that the slow relaxation originates from the reorientation of oxygen vacancy dipoles and the interaction with soft phonon modes in the host lattice.[29]

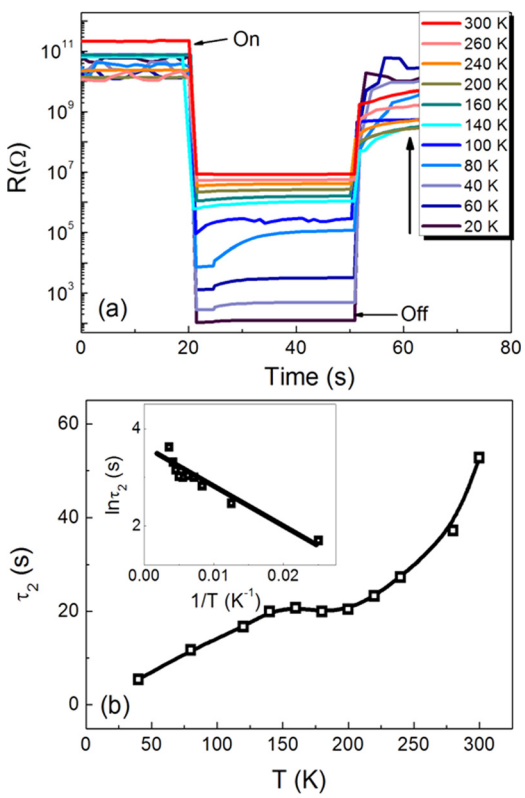

FIG. 4. (a) The time dependence of the resistance of STO single crystals under the irradiation of 365 nm. (b) The time constants as a function of temperature. The inset shows the ln τ_2 vs. T^{-1} curve.

IV. SUMMARY AND CONCLUSIONS

In summary, the photoinduced insulator-metal phase transition and the relaxation after the irradiation have been investigated in the bare STO single crystals. Our observation is attributed to the further understanding of the optic-electric effect in STO single crystals and offers the possibility of developments and applications of STO single crystals ultraviolet detecting and response devices.

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