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Kyoto University
Spatial distribution of carriers in SrTiO₃ revealed by photoluminescense dynamics measurements

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We report on the optical determination of the carrier-density profiles near surfaces in SrTiO₃ crystals by means of photoluminescence (PL) dynamics measurements. The PL dynamics under band-to-band excitation depends strongly on the excitation photon energy for different optical penetration depths. In nondoped and Ar⁺-irradiated SrTiO₃ crystals, we evaluate the depth profile of carriers near the surface based on the lifetime of the Auger recombination of electrons originating from oxygen vacancies with photocarriers. Our PL spectroscopy clarifies that in nondoped SrTiO₃, the near-surface oxygen-deficient region is a few tens of nanometers in depth.

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Perovskite oxides and their heterostructures have attracted a great deal of attention as new device materials because of their multifunctional properties.¹ With its unique electrical and optical properties, SrTiO₃ is a key oxide material, both from a fundamental physics viewpoint and because of its potential for device applications. On the basis of electron doping, SrTiO₃ shows multifunctional electrical properties ranging from insulating to semiconducting, metallic, and superconducting.²–⁵ The interest in SrTiO₃ is further increased by the unique electronic and magnetic properties of the two-dimensional electron-gas system formed at the interfaces between SrTiO₃ and other oxides.⁶–⁹ The mechanism of metallic-interface formation is currently under discussion, and two models have been proposed: charge transfer from a fundamental physics viewpoint and because of its high photoexcited SrTiO₃ samples show blue photoluminescence

with photocarriers determines the PL lifetime and that the combination of electrons originating from oxygen vacancies in the SrTiO₃ substrate.¹⁰–¹⁴ The development of noncontact probes of the carrier and oxygen-vacancy densities in the microscale region is required, and a quantitative evaluation of the spatial carrier- and defect-density profiles will provide further insights into the physics behind SrTiO₃ bulk crystals and heterostructures.

We have reported that Ar⁺-irradiated, electron-doped, and highly photoexcited SrTiO₃ samples show blue photoluminescence (PL) at room temperature.¹⁵,¹⁶ The PL dynamics of SrTiO₃ can be explained on the basis of a simple model that includes nonradiative Auger recombination.¹⁵ Because we quantitatively evaluated the Auger recombination rate, whereby the carrier dynamics depends on the carrier density, the analysis of the PL dynamics provides the required information on the carrier density. In addition, the optically monitored region of the sample surface can be controlled by changing the photon energy of the excitation light. Therefore, PL spectroscopy becomes a powerful experimental technique for studying the carrier-density profiles in SrTiO₃.

In this Brief Report, we demonstrate that the PL-decay dynamics in nondoped SrTiO₃ (STO) and Ar⁺-irradiated SrTiO₃ (Ar-STO) depends strongly on the excitation photon energy. With an increase in the photon energy, the PL decay time decreases and the PL profile becomes nonexponential. This behavior can be explained by assuming that Auger recombination of electrons originating from oxygen vacancies with photocarriers determines the PL lifetime and that the electron densities near the surface are much higher than those in the bulk crystal. We successfully demonstrate the optical measurement of the depth profile of carriers in the near-surface region of the SrTiO₃ samples on the basis of PL dynamics.

We used nondoped SrTiO₃ crystals and two types of electron-doped SrTiO₃ crystals: Sr₀.99La₀.01TiO₃ and Ar⁺-irradiated SrTiO₃ (using 300 V accelerated voltage and 3 ml min⁻¹ Argon-gas flow for 10 min). Nondoped samples were annealed under oxygen flow for 24 h at 700 K to reduce oxygen vacancies. In the electron-doped samples, electrons were doped by cation substitution (i.e., chemical doping of La ions) and oxygen deficiency (Ar-ion irradiation). All samples were 0.5 mm thick. Time-resolved PL spectra were measured with a time resolution of 40 ps using a streak camera and a monochromator. The excitation light source was an optical parametric amplifier system based on a regenerative amplified mode-locked Ti:sapphire laser with a pulse duration of 150 fs and a repetition rate of 1 kHz. The laser spot size on the sample surface was carefully measured using the knife-edge method. All spectroscopic measurements were carried out at room temperature. The samples used in this work showed broad blue PL peaks at around 2.9 eV. The excitation density $n$ was fixed at $1 \times 10^{18}$ cm⁻³, which is low enough to neglect the Auger recombination process of photocarriers, by considering the penetration depth at the photon-excitation energy. We confirmed that the PL dynamics is independent of the excitation intensity under these low-density excitation conditions.

Figure 1(a) shows the PL dynamics monitored at 2.9 eV for STO, La-doped SrTiO₃ crystal (La-STO), and Ar-STO samples under 3.26 eV excitation. The excitation energy is close to the band-gap energy of nondoped SrTiO₃ of $\sim$3.2 eV and the optical penetration depth at 3.26 eV is large and is about 10 μm. The PL dynamics of nondoped SrTiO₃ shows a single exponential decay profile with a lifetime of 50 ns. La-doped SrTiO₃ also shows a single exponential decay profile, but the lifetime (2 ns) is much shorter than that of nondoped SrTiO₃. In Ar⁺-irradiated SrTiO₃, we observe two decay components. The first is a fast decay component with a decay time of a few nanoseconds and the second is a slow decay with a decay profile that is quite similar to that of nondoped SrTiO₃. It is notable that the fast PL-decay component appears clearly in both electron-doped samples (La-doped and Ar⁺-irradiated SrTiO₃) under weak laser excitation.
The PL decay time becomes shorter as the doped electron density is increased. In the chemically doped Sr$_{0.99}$La$_{0.01}$TiO$_3$ crystals, doped electrons are distributed homogeneously throughout the sample. In this case, the PL decay is a single exponential curve. In contrast, in Ar$^+$-irradiated SrTiO$_3$, we observe two distinct decay components. Ar$^+$ irradiation introduces oxygen vacancies near the surface, and the density profile of electrons originating from oxygen vacancies is inhomogeneous in depth. We argue that the fast decay component comes from the near-surface metallic layer where Auger recombination of doped electrons with photocarriers is dominant. The slow component comes from the nondoped SrTiO$_3$ substrate. Therefore, the two decay components in the Ar$^+$-irradiated SrTiO$_3$ crystal originate from two different electron-density regions: the oxygen-deficient metallic layer near the surface and the nondoped insulating substrate. The fast PL-decay component provides quantitative information about the density and spatial profile of carriers in the sample.

Figure 1(b) shows the PL dynamics in three samples under an excitation of 3.87 eV. The excitation energy is well above the band-gap energy of the nondoped samples, and the penetration depth at 3.87 eV is very small and is about 40 nm. Thus, the photocarriers are generated in the near-surface region, and the PL dynamics is strongly affected by oxygen vacancies in the near-surface region. Nondoped SrTiO$_3$ shows nonexponential decay that is faster than that under an excitation of 3.26 eV. Even in the nominally nondoped sample, defects producing electron carriers are inevitably introduced, especially very close to the surface. In contrast, in La-doped SrTiO$_3$, the absence of any significant dependence of the PL decay time on the excitation energy also clearly supports the spatially homogeneous distribution of doped electrons. Moreover, Ar$^+$-irradiated SrTiO$_3$ shows only the fast decay component; the slow decay component disappears. This implies that the PL dynamics is determined by the near-surface oxygen-deficient metallic layer under high-energy excitation. Our findings show that the spatial distributions of electron carriers in SrTiO$_3$ crystals can be estimated from the photon-energy dependence of the PL dynamics.

First, we discuss the spatial distribution of electron carriers originating from oxygen vacancies in Ar$^+$-irradiated SrTiO$_3$ composed of the metallic near-surface layer and insulating nondoped substrate. In Fig. 2(a) we show the excitation photon-energy dependence of the intensity ratio of the fast decay components. The optical penetration depth, estimated from the reflection spectra from Ref. 20, is also shown. Here, we approximately describe the PL-decay curves shown in Fig. 1 using two exponential functions and fix the decay time of the slow decay component to 50 ns. With an increase in the excitation energy, the optical penetration depth decreases and the photocarriers are generated in the near-surface region. Therefore, the PL from the near-surface metallic layer increases and that from the insulating substrate decreases.

To evaluate the electron-carrier distribution near the surface quantitatively, we focus on the fast PL dynamics. Figure 2(b) shows the PL-decay curves in Ar$^+$-irradiated SrTiO$_3$ samples under excitation of 3.76, 3.87, and 4.00 eV. To study the spatial distribution of the carrier density, we assumed

\[
\frac{dn}{dt} = -An - Bn^2 - Cn^3, \tag{1}
\]

where $n$ is the photocarrier density and $A$, $B$, and $C$ represent the nonradiative single-carrier-trapping rate, the radiative bimolecular-recombination coefficient, and the nonradiative Auger recombination coefficient, respectively. The bimolecular radiative recombination $Bn^2$ is negligibly small at room temperature because the PL efficiency is quite low. Previously, we evaluated the Auger coefficient $C$ = $1.3 \times 10^{-32}$ cm$^6$ s$^{-1}$ under high-density photoexcitation. Because the Auger recombination rate is low enough in the low-density excitation condition, the PL dynamics shows a single exponential decay profile [Fig. 1(a)], from which we obtained $A = 7.9 \times 10^6$ s$^{-1}$ for the experimental result using the nondoped SrTiO$_3$ samples.

In La-doped and Ar$^+$-irradiated SrTiO$_3$ samples, the rapid PL decay is caused by the Auger recombination of electrons originating from oxygen vacancies with photocarriers. When the doped electron density $N_e$ is higher, i.e., $N_e > (A/C)^{1/2}$ ($=2 \times 10^{19}$ cm$^{-3}$), Auger nonradiative recombination dominates the photocarrier dynamics. In highly doped SrTiO$_3$ such as in Sr$_{0.99}$La$_{0.01}$TiO$_3$ crystals, Eq. (1) no longer describes the photocarrier dynamics and should be modified as

\[
\frac{dn}{dt} = -An - CN_e^2n \quad (N_e \gg n). \tag{2}
\]
transmission electron microscopy observations in Ref. 15. The metallic near-surface layer is estimated to be about 10 nm, which is determined by the penetration depth in an exponential decay profile from the surface. In the electron carriers doped by oxygen deficiencies are distributed and form a metallic layer formed at the surface of Ar+-irradiated SrTiO3 crystals.

The inset illustrates the exponential distribution of the carriers. The fitting parameters are $N_0 = 10^{20} \text{ cm}^{-3}$. Therefore, to evaluate the density of electrons from the oxygen vacancies in the near-surface region and the Auger recombination rate of photocarriers, it is necessary to measure the PL decay time as a function of the excitation intensity. Figure 4 shows the photocarrier-density dependence of the decay time at different excitation photon energies. At high densities $n > 10^{19} \text{ cm}^{-3}$, the decay time shows a rapid decrease proportional to $1/n^2$, indicating the appearance of the Auger recombination of the photocarriers. Under low-density excitation, below the solid line in Fig. 4, the decay time remains almost constant for each excitation photon energy. Thus, the electron-density profile in the near-surface region, $N_e(z)$, is determined by the photon-energy dependence of the
PL-decay profile at the low photocarrier density of \( n = 1 \times 10^{18} \text{ cm}^{-3} \).

By comparing Figs. 2(b) and 3(a), we assume that the oxygen-deficient layer is formed near the surface of nondoped SrTiO\(_3\) and that the electron-density profile is exponential in depth similar to that for Ar\(^{+}\)-irradiated SrTiO\(_3\). Using Eq. (3), we obtain the exponential carrier profile \( N_e(z) = N_0 \exp(-\beta z) \), where \( N_0 = 8 \times 10^{19} \text{ cm}^{-3} \) and \( 1/\beta = 16 \text{ nm} \). The fitting results reproduce the experimental results fairly well, as shown by the solid lines in Fig. 3(a). This means that very thin and electron-rich layers are formed near the surface, even in nondoped SrTiO\(_3\). The electron density is low and the thickness of the layer is very thin compared to the insulator.

In conclusion, the PL dynamics under band-to-band excitation depends strongly on the excitation photon energy. The excitation-energy-dependent PL dynamics can be explained by the Auger recombination process of electrons originating from oxygen vacancies with photexcitons. We have clarified that in nondoped SrTiO\(_3\), an oxygen-deficient near-surface layer exists with a depth of a few tens of nanometers.

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