Photogenerated Carriers in SrTiO$_3$ Probed by Mid-Infrared Absorption

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Infrared absorption spectra of SrTiO$_3$ have been measured under above-band-gap photoexcitations to study the properties of photogenerated carriers, which should play important roles in previously reported photoinduced phenomena in SrTiO$_3$. A broad absorption band appears over the entire mid-infrared region under photoexcitation. Detailed energy, temperature, and excitation power dependences of the photoinduced absorption are reported. This photo-induced absorption is attributed to the intragap excitations of the photogenerated carriers. The data show the existence of a high density of in-gap states for the photocarriers, which extends over a wide energy range starting from the conduction and valence band edges.

KEYWORDS: SrTiO$_3$ (strontium titanate), quantum paraelectric, photocarriers, infrared spectroscopy

Structural, electronic, and magnetic changes in solids induced by photoexcitations have attracted much interest recently, since a photoexcitation technique allows one to control these properties in unique manners that cannot be achieved by varying other external parameters such as temperature, pressure, electric and magnetic fields. One of such photoinduced phenomena is an enhancement of dielectric properties under photoexcitation in a range of dielectrics called “quantum paraelectrics”, a well-known example of which is SrTiO$_3$ (STO).

STO is an insulator with a band gap of about 3.2 eV. Upon a photoexcitation above the band gap energy, it gives a broad photoluminescence (PL) band between 1.6 and 3.0 eV. The Stokes shift between the absorption edge and the center of PL band is about 0.8 eV, showing that the photogenerated electron-hole pairs experience large energy relaxations before recombination. Time-resolved PL and spectral hole burning (SHB) experiments of STO have shown that the photogenerated carriers (photocarriers) reach a localized state before recombination, which has been discussed in terms of self-trapped excitons, polarons and strong electron-lattice coupling. Figure 1 illustrates the situation in STO expected from these optical results. STO is also well known for a high photoconductivity. According to photo-Hall studies, the majority photocarriers are negatively charged, with a mobility as high as $10^5$ cm$^2$/Vsec at 5 K. Regarding the photocarriers in STO, it has been debated how their high mobility shown by transport experiments and their localized characters shown by optical experiments can be understood in a consistent manner.

STO has a large static dielectric constant of $\varepsilon_r \sim 200$ at 300 K, which further increases upon cooling, reaching $\sim 20000$ at 4 K. In spite of the extremely large $\varepsilon_r$, STO remains paraelectric down to 0.3 K due to a quantum paraelectricity. Recently, it has been found that the static dielectric constant of STO remarkably increases under photoexcitations above the band gap energy. It is likely that the photocarriers also play an important role in this phenomenon, but its microscopic mechanism is not clear yet.

In this work, we study the infrared absorption in STO under photoexcitation, to probe the properties of photocarriers. A broad absorption band has been observed over the entire mid-infrared under a photoexcitation at 3.4 eV. This photo-induced infrared absorption is attributed to intragap excitations of carriers by the infrared photons, rather than to their Drude response. The present results demonstrate that there are a high density of in-gap states for the photocarriers, and that the in-gap states are distributed over a wide energy range reaching the band edges.

The single crystal sample of STO, purchased from Earth Chemical Co., Ltd., was initially a plate of 0.5 mm thickness, with polished (110) faces. To avoid detecting internally reflected light beam, one of the two faces was further polished to create a wedge of about 3° between them. The IR transmission of STO under photoexcitation were measured at the beam line BL43IR of SPring-8, using a Fourier-transform infrared interferometer and a HgCdTe detector. The UV photoexcitation was provided by a frequency-doubled, mode-locked Ti:sapphire laser operating at 84.7 MHz. The photon energy (wavelength) of the laser was set to 3.4 eV (365 nm), which was well above the band gap energy (3.2 eV) of STO. Special care was taken so that the IR beam arising from the reflection off the rear surface of the sample was rejected, and that the excitation laser beam covered the entire (2 mm diameter) area of the sample through which the IR beam transmitted. The PL of the same sample was measured using the same laser source. Furthermore, the reflectivity spectrum $R(\omega)$ of the same sample was measured at photon energies 0.01 - 30 eV (without photoexcitation).
Figure 2(a) shows the infrared transmittivity spectrum $T(\omega)$ of STO at 8 K without photoexcitation. Here, $T(\omega)$ is defined simply as the transmitted IR spectrum with the sample divided by that without the sample. The strong absorption below $\sim 0.15$ eV is due to optical phonons. The dips observed at 0.22 and 0.27 eV were previously discussed in terms of defect-related absorption. When a UV photoexcitation was made on the sample, $T(\omega)$ was observed to decrease slightly, i.e., a photoexcitation induced an additional IR absorption in STO. Figure 2(b) plots the measured photoinduced IR absorption (PIA) spectrum $A(\omega)$ at various temperatures. Here, $A(\omega)$ has been defined as

$$A(\omega) = -\frac{T_{\text{on}}(\omega) - T_{\text{off}}(\omega)}{T_{\text{off}}(\omega)} = 1 - \frac{T_{\text{on}}(\omega)}{T_{\text{off}}(\omega)},$$

where $T_{\text{on}}(\omega)$ and $T_{\text{off}}(\omega)$ are $T(\omega)$ spectra measured with the excitation laser on and off, respectively. It is seen that a broad absorption band has been induced by the photoexcitation over a wide energy range. Although not shown here, the absorption persisted up to 2 eV (the high-energy limit of our measurement), in agreement with a previous report. In addition to a broad component rising toward lower energy, a shoulder is observed at 0.23 eV [indicated by the arrow in Fig. 1(b)]. This shoulder becomes clear only below 100 K. When the laser was turned off, the absorption disappeared immediately. The temperature below which the PIA appeared, about 130 K, well coincided with that below which the PL was strong enough to be observed by the naked eye. Figure 2(c) shows $A(\omega)$ at 8 K recorded under different laser powers ($P_{\text{laser}}$). The appearance and growth of PIA with increasing $P_{\text{laser}}$ is very similar to that with decreasing temperature in Fig. 1(b). Figure 2(d) compares $A(\omega)$ at 8 K with the temperature-induced absorption without photoexcitation, $1-T(T(20 \text{K})/T(8 \text{K}))$. The photon- and temperature-induced absorption spectra are apparently very different; i.e., the PIA is not due to a sample heating by the laser. Similar measurements were also made at various laser powers ($P_{\text{laser}}$) between 0.18 and 0.55 eV, and use of the same laser source with the same (3.4 eV) photon energy. A Si photodiode detector was used without a spectrometer, so that the total PL intensity in the 1.1-3.2 eV range was recorded. Figure 3 summarizes the results, where the intensities have been normalized to the maximum value in each graph. The PL intensity is almost constant below 35 K, but it decreases rapidly above 35 K, in agreement with previous report. Then the PL intensity shows a plateau at 70-90 K range. In contrast, the PIA decreases more gradually with increasing temperature, with two plateaus at 30-50 K and 70-90 K ranges. Above 70 K, the PL intensity is only $\sim 5\%$ of the maximum intensity, while the PIA is still 30% of the maximum. Note that both PIA and PL have a plateau at almost the same temperature range of 70-90 K. Regarding the $P_{\text{laser}}$ dependence, the PL shows almost linear dependence, although the slope is slightly larger at low-power region below 0.2 W/cm$^2$. On the other hand, the PIA increases much more rapidly with $P_{\text{laser}}$ below 0.1 W/cm$^2$ than above. Namely, the dependences of PIA and PL on the temperature and $P_{\text{laser}}$ share some common features, but they are quantitatively very different.

Now we shall consider possible mechanisms by which the photocarriers give rise to the observed PIA. Since STO shows high photoconductivity with a mobility reaching $10^4$ cm$^2$/Vs,$^8,^9$ an apparent possibility is a free-carrier absorption. Below, we use the Drude model to calculate the absorption coefficient $\alpha_0(\omega)$ due to free carriers having a density $n$ and an effective mass $m^*$. The real ($\epsilon_1$) and imaginary ($\epsilon_2$) dielectric functions are expressed as:

$$\epsilon_1(\omega) = \epsilon\infty - \frac{\omega_p^2}{\omega^2 + \tau^{-2}}, \quad \epsilon_2(\omega) = \frac{\tau^{-1}}{\omega} \cdot \frac{\omega_p^2}{\omega^2 + \tau^{-2}}$$

where $\epsilon\infty$ is the contribution from higher-energy interband transitions, $\omega_p = 4\pi n e^2/m^*$ the plasma energy, $\tau$ the average relaxation time of the carriers, and $\omega$ the photon energy. $\epsilon\infty = 6.9$ was obtained from the $\epsilon_1(\omega)$ given by the K-K analysis of the measured $R(\omega)$. $\tau$ was estimated from the previously reported value of $\mu=10^4$ cm$^2$/Vs at 5 K,$^9$ assuming the free carrier relation $\mu = \sigma \tau/m^*$. Then $\epsilon_1$ and $\epsilon_2$ can be evaluated through Eq. (2) for given values of $m^*$ and $n$. The imaginary refractive index is given as $\kappa = \frac{1}{\sqrt{\epsilon}} [\epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2}]^{1/2}$, and the absorption coefficient due to free carriers is finally obtained as $\alpha_D = (4\pi/\epsilon) \omega \kappa$. In a photo-Hall experiment,$^9$ $n \sim 5 \times 10^{14}$ cm$^{-3}$ has been obtained under a photon flux density of $2 \times 10^{16}$ cm$^{-2}$sec$^{-1}$, assuming that the photocarriers are uniformly distributed within a plate of thickness $t=10$ $\mu$m. Our maximum photon flux density is $\sim 5 \times 10^{18}$ cm$^{-2}$sec$^{-1}$, hence the corresponding $n$ could be $\sim 10^2$ times larger than the above value for the same value of $t$. The penetration depth at the laser photon energy (3.4 eV) was $\sim 0.2$ $\mu$m from the absorption coefficient of STO at 3.4 eV ($\sim 5 \times 10^4$ cm$^{-1}$), obtained from the K-K analysis of measured $R(\omega)$. Since the photocarriers have a high mobility, $t$ may be larger than the penetration depth of the laser, but $t=10$ $\mu$m might be an overestimation. If a value of $t=1$ $\mu$m is used instead, $n$ becomes 10 times larger than that in Ref. 9. Taking into account these effects of $P_{\text{laser}}$ and $t$, we estimate $n$ to be $10^{17} - 10^{18}$ cm$^{-3}$ for the maximum laser power in this study. Figure 4(a) shows $\alpha_D(\omega)$ calculated
for $m^* = m_0$ and $n = 10^{17}$, $10^{18}$, and $10^{19} \text{ cm}^{-3}$. Regarding $m^*$, no data are available for photocarriers in STO, but $m^* = 5 - 20 m_0$ have been reported for chemically carrier-doped STO.$^{15}$ Using these values instead of $m_0$ would further reduce $\alpha_{\text{D}}$ compared with those in Fig. 4(a).

Next, we will estimate the absorption coefficient due to the photocarriers, $\alpha_{\text{ph}}(\omega)$, using the present PIA data. We again assume that the PIA occurs within a plate of thickness $t$. Then one may express the experimental data in terms of $\alpha_{\text{ph}}$ as:

$$T_{\text{on}} = T_{\text{off}} \exp(-\alpha_{\text{ph}} t) \quad (3)$$

Figure 4(b) plots $\alpha_{\text{ph}}(\omega)$ obtained using Eq. (3) and the $A(\omega)$ spectrum at 8 K under $P_{\text{laser}} = 1.3 \text{ W/cm}^2$ for $t = 1 \mu\text{m}$. $[\alpha_{\text{ph}}(\omega) = 10 \mu\text{m is, for example, simply 0.1 times that in Fig. 4(b).] Comparing Figs. 4(a) and 4(b), it is clear that the free-carrier absorption for the values of $n$ and $t$ expected for the current study is too small to account for the observed PIA.

Having seen that a Drude response of photocarriers cannot account for the PIA, the most likely mechanism for the PIA should be excitations of photocarriers to above (below) the conduction (valence) band edge, as schematically shown by the process (4) in Fig. 1. In this case, apparently the intensities of PL ($I_{\text{PL}}$) and PIA ($I_{\text{PIA}}$) should be proportional to the time-averaged photocarrier density $\bar{n}$. However, there should be other factors affecting $I_{\text{PL}}$ and $I_{\text{PIA}}$, since they have different dependences on the temperature and $P_{\text{laser}}$ as observed in Fig. 3. Suppose that a laser pulse initially creates $n_p$ photocarriers, which subsequently decay with a mean lifetime of $\tau$. Here, $\tau$ includes both radiative ($\tau_r$) and non-radiative ($\tau_{\text{nr}}$) decays, $\tau^{-1} = \tau_r^{-1} + \tau_{\text{nr}}^{-1}$.

Then

$$\bar{n} = (1/T) \int_0^T n_0 e^{-t/\tau} dt = n_0 \tau/T,$$

where $T$ is the pulse interval, and one obtains the following relations:

$$I_{\text{PL}} = (1/\tau_r) \bar{n} \propto n_0 \tau/\tau_r, \quad (4)$$

$$I_{\text{PIA}} = (1/\tau_{\text{nr}}) \bar{n} \propto n_0 \tau/\tau_{\text{nr}}. \quad (5)$$

Here $1/\tau_r$ and $1/\tau_{\text{nr}}$ are the probabilities (oscillator strengths) of the radiative (PL) recombination and the IR absorption, respectively. Hence, the different temperature and $P_{\text{laser}}$ dependences of $I_{\text{PL}}$ and $I_{\text{PIA}}$, observed in Fig. 3, are probably due to different dependences of $\tau_r$ and $\tau_{\text{nr}}$ on these parameters. Below 35 K, both the time-averaged intensity and the mean lifetime of the PL was found almost constant, hence $\bar{n}$ in STO should be independent of temperature below 35 K. Then the observed increase of $I_{\text{PIA}}$ with decreasing temperature even below 35 K should be due to a change in $1/\tau_{\text{nr}}$. On the other hand, the common feature in $I_{\text{PL}}$ and $I_{\text{PIA}}$ in Fig. 3, i.e., the presence of a plateau at 70-90 K, probably results from the temperature dependence of $\bar{n}$, which is commonly contained in both $I_{\text{PL}}$ and $I_{\text{PIA}}$.

The present PIA data show two important results: (i) The density of in-gap states occupied by the photocarriers is high, as shown by the large magnitude of $\alpha_{\text{ph}}$ [Fig. 4(b)]. (ii) The distribution of the in-gap states extends continuously to the conduction and valence band edges, as shown by the increasing PIA toward $\omega = 0$. The situation is illustrated in Fig. 5. Of course, the observation of strong PL well below the absorption edge had previously shown a presence of in-gap states, and its broad bandwidth had also shown thier distribution over a wide energy range.$^{2-4}$ However, it is well known in semiconductor physics$^{19}$ that even a very low density of impurities or defects may give rise to a strong PL below the band gap energy. In such a case, the impurities or defects would show only a weak or negligible absorption, in striking contrast to the present observation of large $\alpha_{\text{ph}}$ in SrTiO$_3$. It is also well known that the PL recombination tends to occur at a lower-energy part of the DOS spectrum, so that an observed PL spectral shape does not necessarily show the true spectral shape of the PL-emitting DOS. Since $A(\omega)$ increases with decreasing $\omega$ down to the lowest measured energy, it is likely to keep increasing as $\omega$ approaches zero. Namely, the in-gap DOS should extend to the band edges as shown by the thin solid curves in Fig. 5, in contrast to what would be suggested by the PL spectrum alone (dotted curves).

The present results do not explicitly show whether or not the photocarriers giving rise to the PIA are localized. However, previous results of time-resolved PL experiments$^{3-6}$ strongly suggest that, after a photoexcitation, the photocarriers quickly relax in energy to localized in-gap states, from which the PL recombinations take place. As shown by the present study, the density of these in-gap states is quite high. Therefore, it is very likely that the photocarriers are mobile only for a short time period right after their generation, and that they occupy the in-gap, localized states for the rest of their lifetime. This is equivalent to stating that only a small fraction of the photocarriers are mobile at a given time.

To actually study how the photocarriers relax in energy as a function of time, it would be necessary to perform a time-resolved PIA experiment. Note also that one cannot distinguish contributions by the electrons from those by the holes in the present PIA study. Although the spectra in Fig. 2 show two distinct spectral components, namely a broad component rising toward lower energy and a narrower one peaked at 0.23 eV, it is unclear whether or not they correspond to electrons and holes. A time-resolved PIA experiment might reveal different temporal dynamics corresponding to electrons and holes, since the conduction electrons in STO, having a strong Ti 3d character,$^{20}$ are expected to experience a stronger electron correlation and a stronger electron-phonon coupling than the holes having an O 2p character.

In conclusion, SrTiO$_3$ has shown a broad photoinduced absorption band over the entire mid-IR region under an above-band-gap photoexcitation. Their detailed energy, temperature, and excitation power dependences have been reported. The photoinduced absorption has been interpreted as arising from excitations of photocarriers to the conduction and valence bands. The present result shows that there is a high density of in-gap states available for the photocarriers, and that they are distributed over a wide energy range extending to the conduction and valence band edges. In considering the properties of photocarriers in SrTiO$_3$, these results should be taken into account in addition to the previous photo-
luminescence results. A time-resolved photoinduced IR absorption experiment is proposed as a future study to further clarify the temporal relaxation of photocarriers.

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1) See, for example, K. Nasu ed., Photoinduced Phase Transitions (World Scientific, Singapore, 2004).
2) L. Grabner: Phys. Rev. B 177 (1969) 1315.
3) T. Feng: Phys. Rev. B 25 (1982) 627.
4) R. Leonelli and J.L. Brebner: Phys. Rev. B 33 (1986) 8649.
5) T. Hasegawa, M. Shirai and K. Tanaka: J. Lumines. 87-89 (2000) 1217.
6) T. Hasegawa and K. Tanaka: J. Lumines. 94-95 (2001) 15.
7) H. Katsu, H. Tanaka and T. Kawai: Jpn. J. Appl. Phys. 39 (2000) 2467.
8) H. Tokunaga: J. Phys. Soc. Jpn. 24 (1968) 1035.
9) T. Ishikawa, M. Kurita, H. Shimoda, Y. Sakano, S. Koshihara, M. Itoh and M. Takesada: J. Phys. Soc. Jpn. 73 (2004) 1635.
10) K. Nasu: Phys. Rev. B 67 (2003) 174111.
11) K.A. Muller and Berkard: Phys. Rev. B 19 (1979) 3593.
12) M. Takesada, T. Yagi, M. Itoh and S. Koshihara: J. Phys. Soc. Jpn. 72 (2003) 37.
13) T. Hasegawa, S. Mouri, Y. Yamada and K. Tanaka: J. Phys. Soc. Jpn. 72 (2003) 41.
14) J. L. Brebner, S. Jandl and Y. Lepine: Phys. Rev. B 23 (1981) 3816.
15) H. P. R. Frederikse, W. R. Thurber and W. R. Hosler: Phys. Rev. 134 (1964) A442.
16) H. Okamura, K. Fukui, M. Matsunami, T. Terakami, M. Koyanagi, T. Koretsumi, T. Moriwaki, H. Kimura, H. Nakagawa, Y. Kondo, and T. Nanba: Nucl. Instr. Methods Phys. Res. A 467-468 (2001) 1465.
17) F. Wooten: Optical Properties of Solids (Academic Press, 1966).
18) H. Okamura, T. Michizawa, T. Nanba and T. Ebihara: J. Phys. Soc. Jpn. 73 (2004) 2045.
19) P.Y. Yu and M. Cardona: Fundamentals of Semiconductors (Springer, Berlin, 2001) 3rd ed., Chapter 7.1.
20) L. F. Mattheiss: Phys. Rev. B 6 (1972) 4718.
$P_{\text{laser}} = 1.3 \text{ W/cm}^2$ 

$P_{\text{laser}} (\text{mW/cm}^2) = 1.0 \times 10^3, 5.0 \times 10^2, 2.5 \times 10^2, 25, 13, 2.5$ 

SrTiO$_3$

8 K
Normalized Intensity

Temperature (K)

Laser Power (W/cm²)

$P_{\text{laser}} = 1.0 \text{ W/cm}^2$

$P_{\text{laser}} = 80 \text{ mW/cm}^2$

$8 \text{ K}$

$80 \text{ K}$
(a) Drude ($\varepsilon_\infty=6.9, m^* = m_0$)

$n=10^{17}$ cm$^{-3}$
$n=10^{18}$ cm$^{-3}$
$n=10^{19}$ cm$^{-3}$

(b) PIA data
(8 K, 1.3 W/cm$^2$)

$\alpha_{ph}$ (cm$^{-1}$)

$\alpha_D$ (cm$^{-1}$)

Photon Energy (eV)
Absorption edge (~3.2 eV)

PL (1.6 ~ 3.0 eV)

PIA

DOS

VB

CB

E

Absorption edge (~3.2 eV)