Dynamics of photo-excited carriers in anatase TiO$_2$ thin film investigated by pump-probe method

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Abstract. We measured transient absorption spectra with pump-probe technique to investigate the dynamics of photo-excited carriers at 300 K and 12 K in anatase TiO$_2$ epitaxial film. Although the photoluminescence (PL) originated from self-trapped excitons (STEs) vanished at 300 K, we observed the change in probe signal. On the other hand, the intensity of the transient absorption signal at 12 K was much weaker than that at 300K. Therefore the carriers at 300 K become trapped at the surface, leading to a pump-probe signal, while at 12 K, the remained carriers inside the bulk arise from STE recombination. These results suggest that the pump-probe signal is derived from the trap state(s) near the surface.

1. Introduction
Anatase TiO$_2$ is well known to show high photocatalytic activity, and numerous studies have taken place [1] [2]. It is thought that photo-excited carriers create activated species by reacting with water and oxygen at the crystal surface, and such activated species decompose pollution (organic) substance. However, it is not known that why photo-excited carriers in anatase TiO$_2$ have long life time (a few hours) [3], and how both electrons and holes reach the surface. To understand the dynamics of photo-excited carriers, pump-probe [4] and PL measurement[5] have been done. However, the former were performed only at room temperature, and no study has compared pump-probe and PL results. In this study, we investigated the dynamics of photo-excited carriers by pump-probe technique at 12 and 300 K, and observed the changes in transient absorption and PL spectra before and after annealing in oxygen atmosphere.

2. Experiment
2.1. Sample
Anatase TiO$_2$ thin film was grown on LaSrAlO$_4$ (LSAO; a = 0.3755 nm) substrates by pulsed laser deposition (PLD) method using TiO$_2$ ceramic targets and a KrF excimer laser (248 nm wavelength) in the presence of oxygen. The growth temperature was 700°C. The film thickness was ~200 nm. The sample was cut into two pieces, and one of them was annealed 10 hours at 600°C in oxygen atmosphere to investigate the effect of oxygen vacancies and the change of crystalline.

2.2. Experimental setup
The schematic setup of the pump-probe system is shown Figure 1. We used a regenerative amplified Ti:sapphire laser with a repetition rate of 100 kHz. The laser output (800 nm) was divided into two beams. The pump beam was the third harmonic (266 nm), and the probe beam was a white light continuum generated by focused on a sapphire crystal. The signal of probe beam was filtered by a spectrometer and detected by a Si:photodiode using a lock-in technique. The time resolution of our setup is about 1 ps. Measurements were performed at 12 K (cooled by cryostat) and 300 K (in air).

For PL measurements, samples were mounted on the cryostat and excited at 3.7eV using the second harmonic of the output from an optical parametric amplifier pumped by a regenerative amplifier. The time-resolved PL was measured using a streak camera.

![Fig.1 Pump-probe system](image)

### 3. Results and Discussion

![Fig. 2](image)

**Fig. 2** TiO$_2$ thin films at 12 K: (a) PL spectra; (b) Time-resolved PL decay curve, where the time constants $t_1$ and $t_2$ are for direct and indirect formation STE, respectively. The spike at 1.85eV of PL spectra is the second diffraction of the excitation light.

Figure 2 shows the PL spectra (a) and time-resolved PL decay curves (b) at 12 K before and after annealing. The PL of anatase TiO$_2$ is originated from the recombination of self-trapped excitons (STEs) [6]. It is known that the relaxation processes to the STE state proceeds in two ways: the fast component ($< 1 \mu$s) of the PL decay curves is due to the direct formation of STEs by free electrons; the slow component ($> 1 \mu$s) of the curves is due to indirect formation of STEs by electrons hopping between oxygen vacancies [7]. If the number of oxygen vacancies decreases because of annealing in oxygen atmosphere, the decay time for indirect formation of STEs should increase. If the crystalline improves, STEs should form more effectively and PL intensity should increase. In our experiment only the fast component became slower and the total luminescence intensity increased after annealing. These results indicate that with annealing, the quantity of oxygen vacancies inside the sample remains
constant while the crystalline improves. PL intensity decreases as temperature increases, and PL is not observed at 300 K in our system, consistent with the report by Tang et al. for a single crystal [5].

**Figure 3** TiO$_2$ thin films at 300 K: (a) Transient absorption spectra, where “as” is the as-grown sample and “an600” is the annealed sample; (b) Decay curve of annealed sample at 670 nm.

Figure 3 shows transient absorption spectra at 300 K and the decay profile at 670 nm. The presence of induced absorption indicates that photo-excited carriers exist at 300 K. Therefore, this absorption change is not derived from STEs. The peak positions of the as-grown and annealed sample are at 620 nm and 670 nm, respectively. Rothenberger et al. and Colombo et al. observed a similar broad transient absorption spectrum centered at 620 nm in TiO$_2$ particles, and they assigned the absorption to trapped electrons at the surface [8][9][10]. Thus, we can conclude that the signal in this study is strongly influenced by the surface condition. The signal at 670 nm is increased after annealing, leading to peak shift of the signal. To our knowledge, there is no previous report of such observation. This observation of peak shift and/or signal enhancement at 670 nm suggests that the oxygen vacancies at the surface are significantly affected by annealing in oxygen atmosphere as well as by improvement in crystalline.

**Figure 4.** TiO$_2$ thin films: (a) Transient absorption spectra of TiO$_2$ films at 12 K in vacuum; (b) Normalized decay curves of annealed sample at 670 nm at 12 and 300 K.

Figure 4 shows transient absorption spectra at 12 K and the decay profile at 670 nm. The signal intensity is almost one order of magnitude weaker than at 300 K. In general, the diffusion rate of photo-excited carriers decreases as temperature decreases. Thus, at 12 K, many carriers are expected to remain in the bulk. Our observation of a long-lived PL signal, on the order of up to microseconds (Figure 2b), supports this model.
As shown in Figure 3a and 4a, the shift in peak position to lower energy is greater at 12K than at 300 K. To explain this result, we must consider differences in both temperature and atmosphere. Furube et al. also observed that for TiO$_2$ powders, the peak positions measured at room temperature in air and vacuum differ [11], but shifts of their study is opposite to our results.

We can reproduce the decay curves of the pump-probe signal (Figure. 4b) by fitting with double exponential decays; and the fast component shows the same decay time, ~15 ps, at both temperatures, but the slow component shows different decay times, ~600 and ~150 ps, at 12 and 300 K, respectively. This difference can also be attributed to differences in both measurement temperature and atmosphere (air/vacuum).

The peak position at 12 K is the same for both as-grown and annealed samples. We are planning further investigations to understand this result.

4. Conclusion
We measured transient absorption spectra at 12 K in vacuum and at 300 K in air by pump-probe method, for both as-grown and annealed samples. We confirmed that photo-excited carriers exist at 300 K. We believe the signal come under the influence of near the sample surface. The signal intensity is much weaker at 12 K than at 300 K, presumably because the diffusion rate is much lower at 12 K than at 300 K. At 12 K, many photo-excited carriers remain in the bulk. After hopping between internal oxygen vacancies for a long time (on the order of nanoseconds to microseconds), they finally undergo STE recombination. On the other hand, at 300 K, photo-excited carriers are more diffusive and become trapped at the surface state.

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