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Time-resolved luminescence spectra in colorless anatase TiO_2 single crystal

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Abstract

Time-resolved luminescence was measured on a colorless anatase single crystal under pulsed-laser excitation. The time evolution of luminescence is composed of fast and slow components with time constants of 10^{-6} and 10^{-5} s, respectively. The fast component corresponds to a direct formation of STE. Some traps near the conduction band give a retardation effect on the slow component. The traps are occupied by conduction electrons at low temperatures and the trapped electron can be excited thermally at temperatures higher than 100 K. They compete with non-radiative recombination process. A possible model for the relaxation process is proposed.

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Keywords: Self-trapped exciton; Luminescence; Relaxation process

Titanium dioxide (TiO_2) has been studied and utilized for a material for photo-catalyst [1], solar cells [2], bio-compatible elements [3], gas sensor [4] and pigments [5]. It is well-known that TiO_2 occurs in three crystalline modifications, rutile (stable phase), anatase (low-temperature phase) and brookite (metastable phase). Among them, the anatase modification has attracted much attention for its high technological potentials. In contrast to extensive studies on rutile, fundamental properties of anatase modification have not been well understood because of the difficulty to synthesize single crystal of good quality. Some years ago, we succeeded in growing anatase single crystals by the chemical vapor transport method [6,7]. Moreover, we reported that a defective state can be controlled by heat treating under oxygen or hydrogen atmosphere [8]. The resultant crystals can be classified by optical absorption and ESR spectroscopy into five types: colorless, pale blue, dark blue, dark green and yellow crystals. The colorless crystal is considered to be stoichiometric with few defects [8]. On uv-light irradiation to colorless anatase, a broad luminescence is

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observed at about 2.2–2.3 eV [9–11]. This emission is known to originate from the recombination of self-trapped exciton (STE) [12]. In this study, we report the results of time-resolved luminescence measured for a colorless anatase single crystal.

Anatase single crystals were grown by the chemical vapor transport method [6,7]. The single crystal used in this study was a fresh one, different from the previous study [11]. The colorless anatase crystal was obtained by heating as-grown crystal at 800 °C for more than 48 h under oxygen pressure of 1.0 MPa. Optical absorption measurement of the resultant crystal revealed no absorption band in the visible region. The luminescence of the crystal was measured in the way previously used [11].

The colorless anatase single crystal gives a broad photoluminescence spectrum at about 2.2 eV with 0.7 eV band width, in accordance with the previous report [11]. Fig. 1 shows time evolution of photoluminescence for the single crystal observed at 2.35 eV depending on the excitation energy at 80 K, which is independent from observation energy [11]. The luminescence starts just after the laser light irradiation. The luminescence decays faster with increase in the excitation energy, as seen in Fig. 1. All the decay curves seem to be well described by two components of simple exponential functions, $f_i(t) = A_i \exp(-t/\tau_i)$ $(i = 1, 2)$. The response of the laser pulse, that is instrumental function, is assumed to be a Gaussian-type function, $r(t)$. Then the observed curve can be fit using a convoluted function obtained by $F(t) = \sum_{i=1}^{2} \int_{-\infty}^{\infty} r(t') f_i(t - t')\,dt'$. The result of the curve-fitting between the observed and calculated curves is listed in Table 1. The lifetimes of fast and slow components decrease with increase in the excitation energy. The lifetimes of the fast and slow components at 80 K in this study are estimated to be about 10^{-6} and 10^{-5} s, respectively. We reported in the previous study [11] that they have an order of 10^{-7} and 10^{-6} s, respectively. These suggest that the decay time of luminescence depends on the sample and that some crystalline defects have an influence on the decay process.

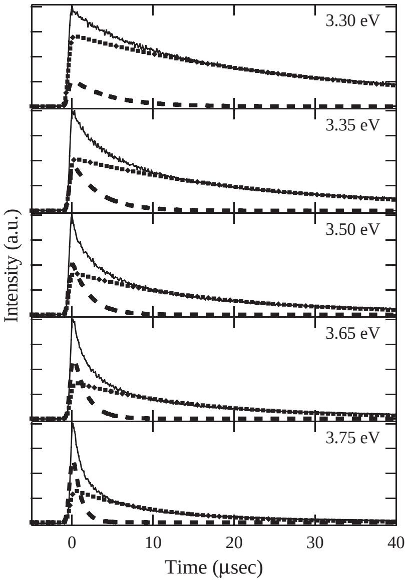

Fig. 1. Time-resolved luminescence of colorless anatase at 80 K as a function of excitation energy. The broken and dotted lines are fast and slow decay components, respectively.

Temperature dependence of the time-resolved luminescence on exciting at 3.30 eV was shown in Fig. 2. The intensity of the luminescence becomes large with decrease in temperature. In Fig. 2, each decay curve was normalized at peak intensity for clarity and is deconvoluted into two components with time constants of 10^{-6} and 10^{-5} s by above-mentioned way. In Fig. 3, the resultant lifetime parameters τ_i and relative integrated intensities $A_i\tau_i/(A_F\tau_F + A_S\tau_S)$ $(i = F, S)$ of the two components are plotted against temperatures. The lifetime parameters of the two components elongate with increase in temperature from 4 to 100 K and decrease above 100 K. On the other hand, the

Table 1
Result for curve-fitting of the decay curves measured at 80 K by the excitation at the desired energies

Excitation energy (eV)	80 K	
	Fast component (μs)	Slow component (μs)
3.30	4.6	33
3.35	3.3	25
3.50	2.1	18
3.65	1.6	16
3.75	0.93	11