TIME-RESOLVED LUMINESCENCE SPECTRA IN COLORLESS ANATASE TiO₂ 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} sec and 10^{-5} sec, 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 the higher temperatures than 100 K. They compete with non-radiative recombination process. Possible model for the relaxation process is proposed.

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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 technological high 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 chemical vapor transport method [6, 7]. Moreover, we reported that a defect 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 observed at about 2.2-2.3 eV [9-11]. This emission is known to be originated from 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 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 more than 48 hrs 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 previous report [11]. Figure 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

$$F(t) = \sum_{i=1}^2 \int_{-\infty}^{\infty} r(t') f_i(t-t') dt'. \text{ The result of the curve-fitting between the observed and}$$

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} sec and 10^{-5} sec, respectively. We reported in previous study [11] that they have an order of 10^{-7} sec and 10^{-6} sec, respectively. These suggest that the decay time of luminescence depends on sample and that some crystalline defects have an influence on the decay process.

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} sec and 10^{-5} sec 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 whole luminescence intensity decreases with increasing temperature from 4 K. This temperature quenching in lifetime and luminescence intensity above 100 K indicate that the radiative recombination of STE competes with non-radiative one in high temperatures. In order to explain these changes depending on temperature, we propose a possible model shown in Fig. 4. The final state of exciton in relaxation process is considered to be STE state and the luminescence is due to recombination of STE. The decay curve starts without delay after the photoexcitation. This suggests that the recombination of STE should occur in much short time and that the relaxation path from the photoexcited state (channel A in Fig.4) to STE formation (channel F) will dominates the whole relaxation time. The result of the decay curve analysis suggests the existence of two paths up to the STE state with different time constants. Some of the electrons promoted to the conduction band by uv-light absorption (channel A) and relaxed immediately to the bottom of the conduction band (channel B) result in the formation of polarons (channel C). Such polarons localized by a strong interaction with holes result in the formation of STE (channel F). This process on direct formation of STE will correspond to the fast component of the luminescence. The temperature quenching on the fast component above 100 K seems to be due mainly to the non-radiative process

and can be evaluated by $\frac{1}{L + s \exp(-E_N/kT)}$, where L , s and E_N are transition

probability of Luminescence, frequency factor and activation energy, respectively. The curve-fit analysis reveals that the activation energy E_N is 72 meV and resultant curve also shown in Fig. 3(a) by a solid line. For the slow component, we assume the presence of some traps near the conduction band (channel D). The trapped electron can be thermally re-excited to the conduction band (channel E) and be relaxed to the STE state. Such traps have a retardation effect depending on temperature. At the lower temperatures than 80 K, many electrons occupy the traps without thermal excitation, so that the direct relaxation to STE becomes dominant. Therefore, the relative intensity of

the fast component increases with decrease in temperature below 80 K, as seen in Fig. 3(b). The decrease in life time of the slow component above 100 K can be analyzed by Arrhenius' equation with an activation energy of 25 meV. The result is plotted in Fig. 3(a) by a dotted line. This suggests that, with increases in temperature, the trapped electrons will be excited thermally to the conduction band and have a contribution on the formation of STE. In many cases, such retarded process related to the traps gives rise to a power-law decay [10, 13]. In the experimental results measured by the streak-camera in 50 μ sec range, it is uncertain of the existence of power-law components.

The fact that the lifetimes of the fast and slow components decrease with increase in the excitation energy (Table. 1) can be also explained by this model. The electrons excited by large excitation energy relax to the bottom on the conduction band with emission of excess energy. Such emitted energy accelerates not only the thermal activation of the trapped electrons to the conduction band following STE formation but also the activation to the non-radiative process.

Time-resolved photoluminescence was investigated on a colorless anatase single crystal at desired excitation energies and temperatures. The analysis on the decay curve reveals the existence of three relaxation channels; (a) the direct formation of STE which is remarkable at low temperatures or high energy excitation corresponds to fast decay component with time constant of 10^{-6} s. (b) electron trapping and thermal re-excitation channel has time constant of 10^{-5} s. (c) recombination of exciton with non-radiative process. Possible model for these relaxation processes is proposed.

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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.

Fig. 2 Time resolved luminescence of colorless anatase depending on temperature. The excitation energy was 3.30 eV. The broken and dotted lines are fast and slow decay components, respectively.

Fig. 3 (a) Temperature dependence of the lifetimes of fast and slow components, τ_F and τ_S , respectively. (b) Temperature dependence of relative integrated intensities of the lifetimes of fast and slow components, $A_i \tau_i / (A_F \tau_F + A_S \tau_S)$ ($i = F, S$).

Fig. 4 Possible model for the excitation-relaxation process. The luminescence is due only to the recombination of STE. A: photoexcited electron, B: quench to the bottom of the conduction band, C: formation of small polaron, D: electron capture into traps, E: thermal excitation from traps, F: formation of STE, G: non-radiative recombination process.

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 (μ s)	slow component (μ s)
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