RELAXATION PROCESS IN ANATASE TiO₂ SINGLE CRYSTALS WITH DIFFERENT COLORS

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Abstract

Photoluminescence and excitation spectra were measured on anatase single crystals with different colors; colorless, pale blue, dark blue, dark green and yellow. Time evolution of the emission in relation to the crystalline color, observed energy and excitation energy was investigated. A possible model for the relaxation process is proposed.

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1. Introduction

Titanium dioxide TiO_2 has been extensively studied for its interesting electric, optical and electrochemical properties. It is well-known that TiO_2 occurs in three crystalline modifications, rutile (stable phase), anatase (low temperature phase) and brookite (metastable phase). Anatase has attracted much attention in many years because of its high photocatalytic properties, but it is very difficult to synthesize anatase single crystals large enough to measure the electric or optical properties. There have been a few reports of investigations of the luminescence, and its time dependence, for anatase single crystals [1-5]. Some years ago, we have grown anatase single crystals by a chemical vapor-transport method [6]. As-grown crystals have generally octahedral shape and a transparent pale-blue color. Recently, we succeeded in controlling the crystal color by heat-treatment under oxygen pressure or in a hydrogen atmosphere. The resultant crystals can be classified by optical-absorption and ESR spectroscopy into 5 types; colorless, pale blue, dark blue, dark green and yellow crystals [7, 8]. The crystal color reflects the difference in defect states present. In this study, we report the effect of defects on the photoexcited state and its relaxation process.

2. Experimental

Photoluminescence and its associated excitation spectra were measured for anatase single crystals. A single crystal mounted in a cryostat was irradiated by monochromatic light between 4.50 and 3.10 eV at intervals of 0.05 eV and the emission was observed over the range 3.5 to 1.4 eV by a single polychromator with a liquid-nitrogen cooled CCD device. Time-resolved luminescence was measured either with a pulsed Nd:YAG laser system with an optical parametric oscillator (Spectraphysics, MOPO-SL) operated at 3.35 and 3.65 eV or with third-harmonic generation output from a pulsed Nd:YAG laser (Continuum, Minilight) as alternative exciting-light sources. The pulse width (FWHM) of these two laser light sources was less than 10 nsec. The emission from the crystal was recorded in two-dimensional digital-data form using a streak camera system (Hamamatsu, C4334) equipped with a 250 mm spectroscope. It is possible to measure variations of the light emission with respect to both time and wavelength. A decay curve of the emission intensity was obtained over a small energy region of about 0.05 eV by the collection of the wavelength-dispersed light. All the measurement was done at 77 K.

3. Results and discussion

Figure 1 shows polarized optical-absorption curves of the crystals which have five different colors: colorless, pale-blue, dark-blue, dark-green and yellow. All of the curves indicate the existence of a sharp absorption edge at about 3.3 eV, which is ascribed as intrinsic to anatase. Tang, et al. [9] analyzed the temperature dependence of the absorption edge with an Urbach tail and concluded that the exciton would be relaxed to a selftrapped exciton (STE) state through exciton-lattice interaction. Then the luminescence of anatase would be expected to be a single broad band with a large Stoke's shift, which originates from recombination of the STE.

The luminescence spectra of the five crystals are shown in Fig. 2. All the crystals have a broad emission band at around 2.2 eV, which is independent of the excitation photon energy except for the yellow crystal irradiated by uv-light higher than 3.50 eV. A slight difference due to the crystalline color is observed in this band feature. On irradiating the yellow crystal with uv-light higher than 3.50 eV, the emission band showed a small red-shift with increase in excitation energy. These observations suggest

that the emission band at about 2.2 eV has a close relation to the STE state which is an intrinsic property of anatase. The slight difference in the band feature and the peak energy depending on the crystalline color may be due to defects in the crystals.

The excitation spectra of the emission band observed at 2.2 eV are shown by open circles in Fig. 3. The emission intensity for all the crystals rises at 3.3 eV corresponding to the intrinsic-absorption edge. The higher-energy side of the spectra exhibit a large difference depending on the crystalline color. The spectrum of the colorless crystal has a maximum at about 3.4 eV and its FWHM is about 0.2 eV. For the colored crystals, the maximum of the excitation band shifts to higher energy and the bandwidth becomes larger.

Some information about the relaxation process can be obtained by time-resolved luminescence. First, we discuss the time evolution of luminescence depending on the observed energy. Decay curves of the luminescence intensities at 2.60, 2.35 and 2.25 eV were measured for excitation at 3.50 eV for each crystal. Because of differences in the luminescence intensity, each decay curve was normalized to its peak intensity. In the colorless, pale blue, dark green and pale blue crystals, the normalized decay curves observed at 2.60 eV completely agree with those at 2.35 and 2.25 eV. **On the other hand, the time evolution of luminescence has a dependence on the crystalline color, as shown in Fig.4.** These facts indicate that, in these crystals, the photoexcited states relax to a common state which seems to be the intrinsic STE state. A large fraction of such excitons directly relax to the ground state with emission. The slight difference of the emission band feature suggests that a small fraction of them relax by way of defect states. Figure 5 is a scheme of possible relaxation processes for those crystals. In the yellow crystal, the normalized decay curve observed at 2.35 eV is the same as at 2.60 eV, but different from that at 2.25 eV. This indicates that the relaxation process of the yellow crystal is different from that of the other four crystals. The existence of the absorption band near the absorption edge characteristic of the yellow crystal has some influence on the relaxation process.

The crystalline color dependence of the decay curves suggests that the final relaxation process with emission is not the rate-determining step in the relaxation sequence. So, we investigated the time variation dependence on excitation energy. The normalized decay curves of the luminescence intensities for the crystals were measured for excitation energies of 3.65, 3.50 and 3.35 eV. It was obvious that the decay curves depend on the excitation energy as well as crystalline color. This indicates that the defect states have a close relation to the initial stage of the relaxation process. All the decay curves seem to be well described by two components of simple exponential functions $f_i(t)$ ($i = 1, 2$). The response of the laser pulse, which is instrumental, is assumed to be a Gaussian-type function $r(t)$. Then the observed curve can be fitted using a convolution function

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

observed and calculated curves revealed that the fast and slow components have time constants of about 10^{-8} and 10^{-7} sec, respectively. These are inconsistent with our previous report [3] in which irradiation of a strong laser pulse seemed to induce a phase transition from anatase to rutile. In this present work, the crystals keep their phase because of the low excitation density.

The contribution to the excitation spectrum was estimated by time-integration of the components of the decay curve. The estimated values for the fast and slow components

in the spectra are shown in Fig. 3 by open and closed squares, respectively. It is revealed that the excitation spectrum of the colorless crystal is composed mainly of the slow component. The colorless crystal has no absorption in the visible region. An electron spin resonance (EPR) measurement revealed an absence of paramagnetic spin species [8]. It is reasonable to conclude that the colorless crystal contains few defects. Then, we can conclude that the slow component is intrinsic to anatase. In the pale blue, dark blue and dark green crystals, the slow component has a relatively large contribution in the energy region lower than 3.6 eV, while the contribution of the fast component tends to increase with increase in the excitation-photon energy. This suggests that the fast component has a close relation to defects.

4. Summary

The final relaxation process is mainly due to recombination of STEs with emission at 2.2 eV and the influence of defects is very small. The relaxation process from the photoexcited state to the STE dominates the decay time of the relaxation sequence. The slow decay time of 10^{-7} sec is related with the intrinsic excitation band of luminescence, which is located near the band gap. The defects have relatively large influence for excitation energies higher than 3.6 eV, which gives the fast decay time of 10^{-8} sec.

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Fig.1 Polarized optical-absorption spectra of anatase single crystals with five different colors.

Fig.2 Photoluminescence spectra of anatase single crystals with five different colors.

Fig.3 Excitation spectra of anatase single crystals with five different colors (Open circles). The open and closed squares represent the fast and slow components of the time variation of the emission.

Fig.4 Crystalline-color dependence of the normalized decay curve of the luminescence for excitation at 3.50 eV.

Fig.5 Possible relaxation processes in colorless, pale blue, dark blue and dark green anatase.