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Time-resolved study of self-trapped exciton luminescence in anatase TiO_2 under two-photon excitation

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Abstract

We have studied the dynamics of photocarriers in anatase phase of TiO_2 with time-resolved spectroscopy of self-trapped exciton (STE) luminescence. It is found that the decay curve of luminescence under one-photon excitation well above the band gap energy shows power-law behavior, suggesting that spatial separation of an electron–hole pair occurs under interband excitation. A similar result is obtained under two-photon excitation. We conclude that the carrier separation is ascribed to intrinsic dynamical properties of photocarriers in anatase. It is inferred that the carrier separation occurs during energy relaxation towards the band bottom. Temperature dependence of the decay curve is also discussed in terms of thermal dissociation of STEs.

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The anatase phase of titanium dioxide, TiO_2, is a wide band-gap semiconductor and is widely applied in various fields such as photoelectrochemistry. A study of the dynamical properties of photocarriers in anatase is important in terms of the clarification of the photoelectrochemical process in this material. Moreover, the study provides information as to the nature of photocarriers in insulating transition metal oxides. Under interband excitation, anatase exhibits a broad luminescence band with a large Stokes shift [1,2]. The luminescence band is assigned to radiative recombination of self-trapped excitons (STEs). The STE is supposed to be localized on a TiO_6 octahedron which is the unit structure of anatase. Time-resolved study of the luminescence under one-photon excitation revealed that the decay curve consists of two components obeying exponential decay and power-law one, reflecting two formation

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processes of STEs from photocarriers [3]. The efficiency of the two components was found to depend significantly on excitation photon energy [4]. For excitation energies well above the band gap, the power-law component dominates the decay curve, indicating that spatial separation of a photoexcited electron–hole pair occurs efficiently. In the present work, in order to clarify the mechanism of the carrier separation, we study the time response of the STE luminescence under two-photon excitation and discuss the dynamics of photocarriers by comparing the result with that of one-photon excitation. We also report the temperature dependence of the two decay components.

Single crystals of anatase TiO_2 were grown by chemical transport reactions. They were kept in a continuous flow helium cryostat. For the measurements of luminescence decay curves, the samples were excited with either a dye laser (6 Hz repetition rate, 5 ns pulse width, BPBD-365 in *p*-dioxane as the active medium) pumped by a N_2 laser or the N_2 laser itself for one-photon excitation and with the second harmonic of an optical parametric amplifier (10 Hz, 2 ns) for two-photon excitation. Luminescence was detected through a monochromator equipped with a photomultiplier and the signal was analyzed by an oscilloscope.

A dotted curve in Fig. 1 shows the luminescence spectrum of anatase TiO_2 measured at 2 K under interband excitation. There is a broad luminescence band with the peak near 2.3 eV. This band is assigned to radiative recombination of STEs [1,2]. One-photon excitation spectrum of the luminescence detected at 2.3 eV is shown by a solid line in Fig. 1. The spectrum shows a sharp rise at 3.2 eV, which corresponds to the absorption edge of anatase [5], and has a maximum at 3.3 eV followed by a gradual decrease with higher excitation energy.

So far we have investigated the time response of STE luminescence under one-photon excitation [3,4]. Fig. 2 shows the decay curves of the luminescence intensity measured with various excitation photon energies. The excitation energies are indicated by arrows in Fig. 1. All data were taken at low temperatures below 6 K. Under one-photon excitation at 3.22 eV close to the absorption edge, the decay curve can be described by a single exponential function with a time constant of 1.5 μs as shown by a dotted curve. For higher excitation energy (b), a slow decaying component, which obeys a power law, $1/t^m$, appears in addition to the exponential one. It is found that the decay curve can be reproduced well by a sum of the above exponential function and an empirical expression:

$$\frac{I_0}{(1 + t/\tau_p)^m}. \tag{1}$$

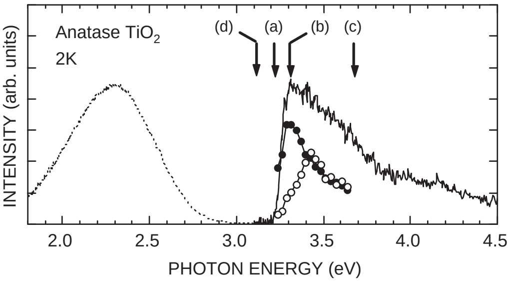

Fig. 1. Luminescence (dotted line) and excitation (solid line) spectra of anatase TiO_2. Closed and open circles represent time-resolved excitation spectra for the exponential and power-law components, respectively.

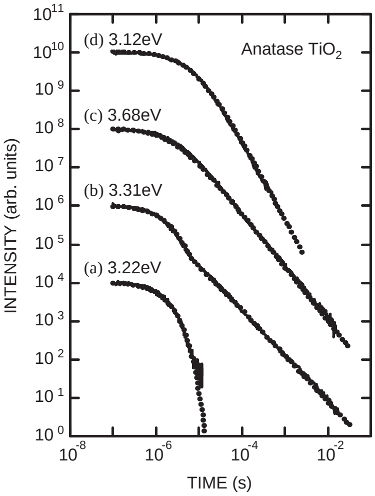

Fig. 2. Log–log plot of luminescence decay curves measured with various excitation photon energies. The signal is detected at the peak energy of the luminescence. Each decay curve is normalized at the peak intensity and is offset by two decades for clarity. Dotted lines represent fits to the data as described in the text.

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