

Carrier lifetime measurements on various crystal faces of rutile TiO₂ single crystals

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Abstract

Carrier lifetimes in rutile TiO₂ single crystals were measured by the microwave photoconductivity decay method. The measurement results showed that carrier lifetimes in rutile TiO₂ single crystals were dominated by the surfaces recombination but not recombination centers in the bulk. The surface recombination at the (110) face is the slowest among the crystal faces, and thus photocatalytic activity would be relatively high for a crystal with the (110) face.

1. Introduction

TiO₂ is a common oxide material for photocatalyst application [1]. Rutile and anatase are two important polymorphs of TiO₂ for photocatalyst, and single crystals of rutile can be artificially grown with low impurity concentration [2]. By characterizing high purity single crystals, we can elucidate properties of the material. Among the properties, carrier lifetime, which is time of survival for electrons and holes excited in materials, is important for photocatalyst. In the photocatalyst operation, electrons and holes are generated by light and either the electrons or holes move to the material surface and cause chemical reactions, and the efficiency of photocatalysts is the ratio of the energy transferred from light to the chemical reactions. Therefore, if the carrier lifetime is longer, more electrons or holes reach the surface, resulting in the high efficiency [3,4]. It has also been reported that surface defects, which trap and recombine carriers at the surface, have drastic influences on the photocatalytic activity of rutile TiO₂ powders [5,6]. Density of such the surface defects will depend on crystal faces (orientation) because of their different atomic arrangements. Although carrier lifetimes in rutile TiO₂ single crystals have been reported, its dependence on the crystal faces and measurement temperature is merely reported [7-10]. Therefore, in this work, we measured carrier lifetimes in rutile TiO₂ single crystals for various crystal faces at various temperatures by the microwave photoconductivity decay (μ -PCD) method, which is a common technique for carrier lifetime measurements for single crystal semiconductors [11-15].

2. Experimental Details

The samples were commercially available undoped rutile TiO₂ single crystals grown by the Verneuil method. Their size was 10 × 10 × 0.5 mm and they are polished on the (001), (101), (100), (110), and (111) faces. Only for the (001) polished samples, we bought two crystals from different vendors (Vendor A and B). In μ -PCD, the sample was irradiated by a pulsed light and the conductivity was probed by reflection of 10 GHz microwave in the atmosphere. Light excitation was carried out using 266 and 355 nm lasers, which have photon densities per pulse of $2\text{-}3 \times 10^{15} \text{ cm}^{-2}$ and a pulse width of 1-3 ns. Measurement temperatures were controlled by hot-air heater with thermocouple detection near to the sample.

3. Results and Discussion

Figure 1 shows normalized μ -PCD signals for the samples with the (001) face measured with two excitation sources at room temperature. As shown in this figure, the decays of all the signals were similar and carrier lifetimes estimated from slopes of exponential parts are ~ 28 ns; this value is similar to the reported carrier lifetime (24 ns) in single crystal rutile TiO_2 observed by photoconductivity [7]. In general, the carrier lifetime strongly depends on the concentration of defects. Even though crystals from different vendors possibly have different defect concentrations, they showed almost the same lifetimes. Furthermore, absorption coefficients for 266 and 355 nm in rutile TiO_2 would be very high considering those for ~ 400 nm reported in Ref. 16, and thus carriers were excited and decay within ~ 10 nm from the sample surfaces. Therefore, most carriers would recombine near the surfaces. The μ -PCD signals for two excitation wavelengths also suggest information of the carrier mobility. Excitation with the shorter wavelength induces more carrier near the surface. If excited carriers suffer the electron-hole scattering [12], the decays of the μ -PCD signals for 266 nm excitation will be slower than those for 355 nm. However, as shown in Fig. 1, the μ -PCD signals were independent on the excitation wavelength, and thus the carrier mobility is independent on excited carrier concentrations in our measurement condition.

Figure 2 shows μ -PCD signals for the samples with various crystal faces from Vendor A at room temperature. The decays of the signals were different for the crystal faces, and the slowest decay is observed from the sample polished on the (110) face. The estimated carrier lifetime for the (110) polished sample is 120 ns, which is four times longer than that observed from the (001) polished sample. Therefore the carrier lifetimes strongly depend on the crystal faces.

Considering the results obtained from Figs. 1 and 2, the surface recombination is the dominant carrier recombination mechanism in rutile TiO_2 , and the carrier lifetime would not be sensitive to concentrations of recombination centers in the crystal bulk. There has been reported that the density of states at the surface revealed by the density functional theory depend on the crystal faces [17], and difference in photoluminescence (PL) spectra and photocurrents in aqueous solutions has also been observed for the (110) and (100) faces [18-20]. According to these reported works, concentrations of the surface recombination centers depend on the crystal faces, and this dependence induces difference in surface recombination velocities among the crystal faces. Furthermore, as shown in Fig. 2, the surface recombination velocity is slower on the (110) face than on the other crystal faces. It has been reported that the (110) face has a relatively low surface energy and is the

most stable surface among the crystal faces of rutile [17,21]. The stable (110) surface would have small microscopic roughness. The flat surface induces a relatively small number of exposed atoms within a unit surface resulting in low concentration of surface defects and recombination centers. The slow recombination at the (110) face will contribute high photocatalytic activity of this surface.

Figure 3 shows μ -PCD signals for the (110) polished sample from Vendor A measured with 355 nm excitation and at various temperatures. Even though the signals were noisy at high temperature, the decays of all the signals are similar, indicating a temperature independent carrier lifetime. Also for the other samples, carrier lifetimes were temperature independent up to $\sim 250^\circ\text{C}$. Such temperature independence has been observed for carrier lifetimes in nanocrystalline TiO_2 [22]. The temperature independence implies that the recombination centers at the surface have levels deep enough not to emit carriers from the center to the conduction or valence band. Considering the reported gap states [17] and 800 nm PL emission for the (110) and (100) faces [19,20], presence of the deep level recombination center is reasonable.

4. Summary

We found that carrier lifetime in rutile TiO_2 single crystal is dominated by the surface recombination. The surface recombination is the slowest on the (110) face among five different crystal faces and is temperature independent. These results suggest that if we use rutile TiO_2 crystals with large surface areas of the (110) face, we will obtain high photocatalytic activity.

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Figure captions

Fig. 1 μ -PCD signals for the (001) polished samples from two vendors at room temperature.

Fig. 2 μ -PCD signals for the samples polished on the various crystal faces from Vendor A with 355 nm excitation at room temperature.

Fig. 3 Temperature dependence of μ -PCD signals for the (110) polished sample from Vendor A with 355 nm excitation.

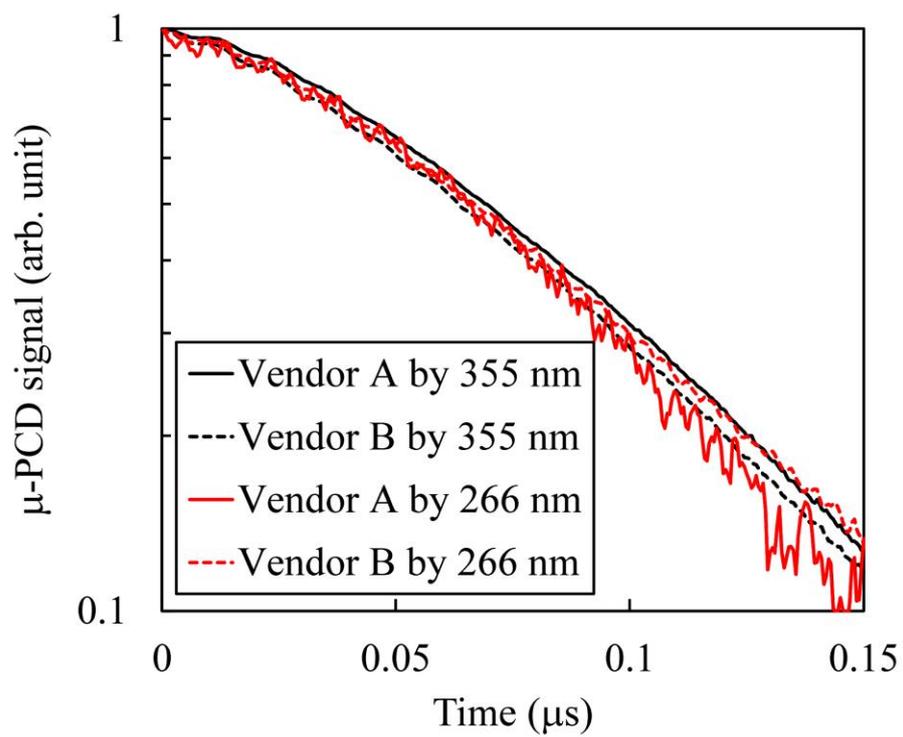


Fig. 1

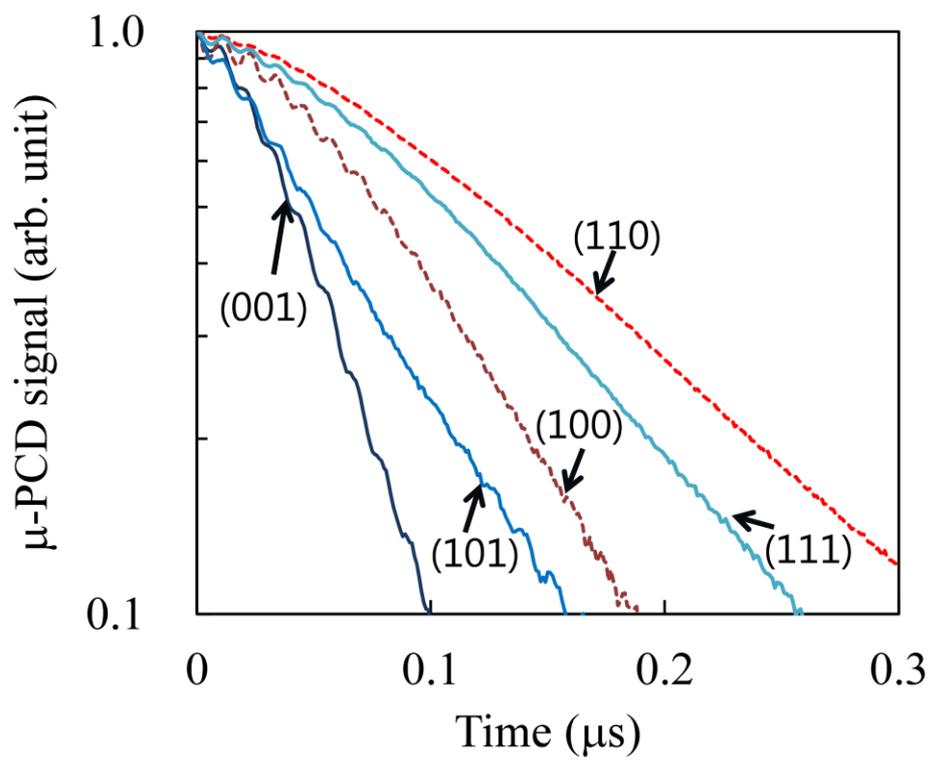


Fig.2

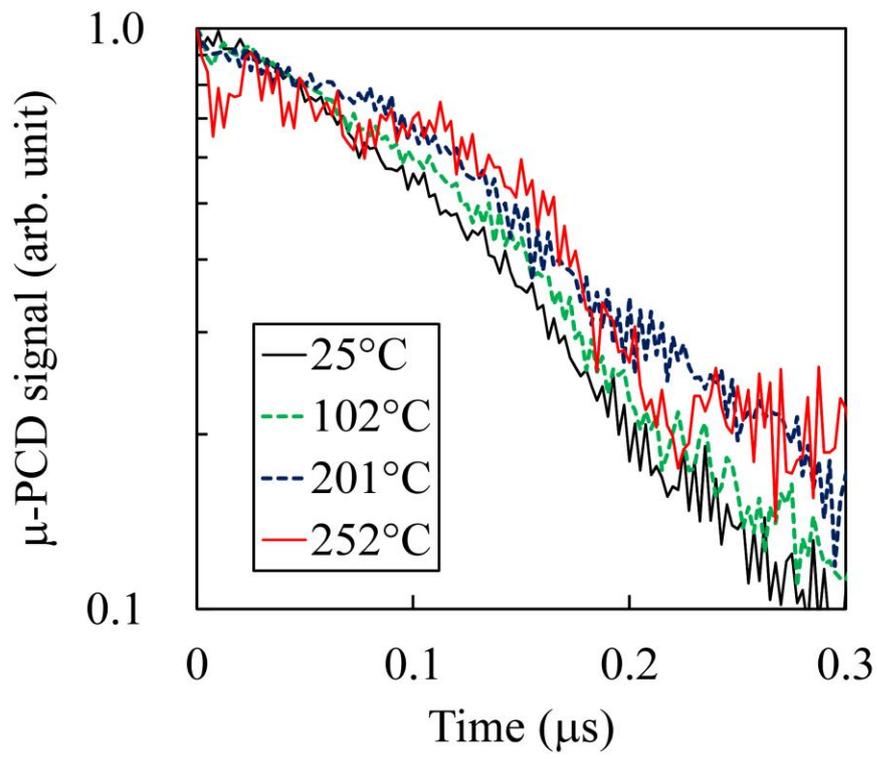


Fig.3