

Dynamics of Photoexcited Carriers at Titania Photocatalyst Surfaces: Time-Resolved Photoelectron Spectroscopy Study

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Titanium dioxide (TiO₂) has been attracted much attention as a photocatalyst because of its promising properties such as high photocatalytic activity and nontoxicity.^[1] When a semiconductor is irradiated with a light having photon energies larger than a band gap, electrons are excited to the conduction band and holes are left in the valence band. The photogenerated electrons and holes are diffused to the catalyst surface and initiate redox reactions. This process competes with electron-hole recombination. Photochemical efficiency is, therefore, determined by the charge carrier dynamics.

Anatase TiO₂ is known to exhibit higher photocatalytic activities than rutile TiO₂.^[2] Since the structure-dependent photocatalytic activity is considered to be originated from the difference of the carrier dynamics, various time-resolved techniques such as photoconductance measurements, transient absorption spectroscopy and photoluminescence spectroscopy have been applied to evaluate the carrier lifetime.^[3] The carrier lifetimes reported in the previous studies, however, range from picoseconds to microseconds. One of the hypotheses that explain this complicated situation is the existence of a space charge layer (SCL) at the TiO₂ surface. Despite the importance of the SCL for the carrier transport from the bulk to the surface, carrier dynamics have not been discussed in relation with the SCL in the previous studies. For the proper comprehension of the photocatalytic activity, it is crucial to access the effect of the SCL on the carrier dynamics. In the present study, a recombination time of the photoexcited electrons and holes on single-crystal anatase TiO₂(001) and rutile TiO₂(110) surfaces have been investigated using time-resolved photoelectron spectroscopy (TRPES) with a laser-pump/synchrotron-radiation-(SR)-probe method.

An anatase TiO₂(001) single-crystal film deposited on a LaAlO₃(100) substrate by pulsed laser deposition and a rutile TiO₂(110) single-crystal were inserted into the ultrahigh vacuum chamber and were cleaned *in situ* by cycles of Ar⁺ sputtering and annealing in O₂ atmosphere. The clean surfaces exhibited a double-domain (4×1) low energy electron diffraction (LEED) pattern for the anatase(001) surface and a (1×1) pattern for the rutile(110) surface, respectively [Fig. 1(a)]. The TRPES measurements were conducted at the beam line BL07LSU in SPring-8. The time evolution of the carrier relaxation was evaluated by measuring the surface photo-voltage (SPV) effect. The photon energy of the pump-laser and SR light were set at 3.06 and 600 eV, respectively. Details of the sample preparations and the TRPES measurements are given elsewhere.^[4]

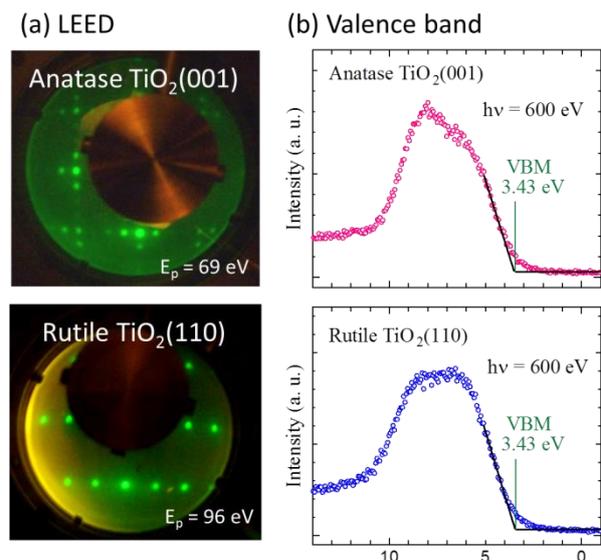


FIG. 1. (a) LEED images for anatase and rutile TiO₂. (b) Valence band spectra of anatase and rutile surfaces.

As shown in Fig. 1(b), the valence bands are observed between 3 and 12 eV with the valence band maximum (VBM) at 3.43 eV on both surfaces. Since the band-gap energies of anatase and rutile TiO₂ are 3.2 and 3.0 eV, respectively, conduction band minima should be located at 0.2 and 0.4 eV below the Fermi level on the anatase and rutile surfaces, respectively. The TiO₂ bands, therefore, bend downwardly to form charge accumulation layers on the surfaces. Figure 2(a) shows Ti 2p_{3/2} core-level photoelectron spectra of the anatase(001) surface acquired before and after laser pulse irradiation. A laser-induced shift toward lower-binding-energy side is clearly observed. In Fig. 2(b), the peak shifts are plotted as a function of the time after pump laser irradiation (the delay time t). When the valence electrons within the SCL are excited to the conduction band, the electrons and holes are separated by the electric field in the SCL. This charge separation diminishes the intrinsic band bending. Since the bands bend downwardly at the initial surfaces, the observed shifts are ascribed to the SPV-induced shifts. The SPV shifts decrease gradually with t because the densities of the photogenerated carriers are reduced by the surface recombination. Solid lines represent fitting results of the SPV decay by an equation of the thermionic emission model, in which the photogenerated carriers overcome the surface potential and migrate to the semiconductor surface. In this process, the time dependence of the SPV shift is described as

$$V_{SPV}(t) = \left| -\eta kT \ln \left[1 - \left\{ 1 - \exp \left(-\frac{V_{SPV}(0)}{\eta kT} \right) \right\} e^{-t/\tau_s} \right] \right|, \quad (\text{Eq. 1})$$

where τ_s is a relaxation time in the absence of the SPV. Definitions of the other parameters in this equation are described elsewhere.^[4] The best fitted values of τ_s are 50 ns for anatase and 180 ns for rutile, respectively. τ_s is shorter on the anatase surface than the rutile surface in the dark condition. This is because the surface potential of the anatase is smaller than that of the rutile so that the holes in the anatase easily diffuse to the surface and recombine with the surface trapped electrons. The barrier-height dependence of the carrier lifetime τ is expressed as: $\tau = \tau_0 \exp\{(V_s - V_{SPV})/(\eta kT)\}$, where τ_0 is the lifetime under the flat-band condition calculated by $\tau_0 = \tau_s \exp\{-V_s/(\eta kT)\}$ and V_s is the initial barrier height of the surface potential.^[4] This equation indicates that τ is exponentially increased with the barrier height. The barrier height of the surface potential depends sensitively on the size of the system, surface conditions like the defect concentrations, and the surrounding environments. Accordingly, to make a comparison of the lifetimes with different barrier heights possible, it is crucial to deduce surface-potential-independent parameters such as τ_0 . τ_0 , the intrinsic carrier lifetime, is estimated to 0.25 and 0.02 ns for anatase and rutile, respectively.

Since the carrier lifetime is closely related to the photocatalytic activity, the higher photocatalytic activity of the anatase TiO₂ should be originated from the longer lifetime on anatase TiO₂ than rutile TiO₂. Even when the crystal is reduced to the nanometer size and the flat-band condition is realized, the carrier lifetime is sufficiently longer on anatase than rutile.

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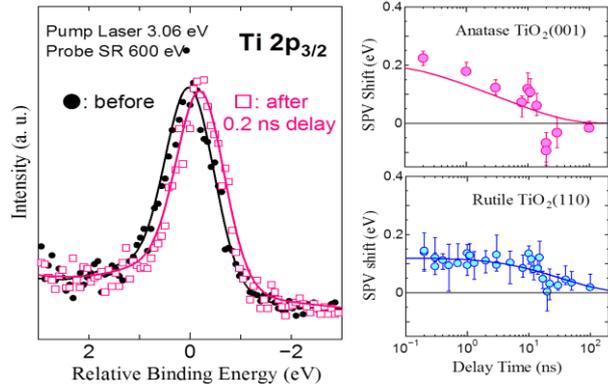


FIG. 2. (a) Ti2p_{3/2} spectra of anatase TiO₂(001) before and after laser irradiation. (b) Peak shifts plotted as a function of the time after pump laser irradiation.