Carrier Dynamics at the Anatase TiO₂(001) Surface Studied by Time-Resolved Photoelectron Spectroscopy

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Titanium dioxide (TiO₂) is the most useful oxide as a photocatalyst, and great scientific and technological efforts have been devoted to elucidate the mechanism of photocatalysis as well as to enhance the photocatalytic efficiency. It has been known that anatase, one of the polymorphs of TiO₂, has higher photocatalytic activity than rutile, thermodynamically the most stable form of TiO₂. A number of hypotheses have been raised to explain the difference in the photocatalytic efficiency between these two polymorphs; a difference in the density of active sites (steps, kinks, defects, etc.) on the surfaces, a difference in the band gap energy between anatase (3.2 eV) and rutile (3.0 eV), a difference in the lifetime of photoexcited carriers, which originates from the different band-gap types between anatase (an indirect band gap material) and rutile (a direct band gap material) [1]. Recent time-resolved transient photoconductance [1], photoluminescence, photoconductance and transient absorption measurements [2] of single crystal anatase and rutile TiO₂ have indicated a longer lifetime of photoexcited carriers in anatase than in rutile. Thus, the difference in the carrier dynamics in the crystals must be largely responsible for the difference in the polymorph-dependent photocatalytic activity.

Although the importance of carrier dynamics has been indicated, little is known about the elemental steps of the carrier behavior from photoinduced generation to recombinative extinction and to charge transfer into reactants. The present study aims to elucidate the

extinction and to charge transfer into reactants. dynamical behavior of photoexcited carriers and its timescale at the (001) surface of single crystal anatase TiO_2 utilising time-resolved photoelectron spectroscopy (TRPES). Information on charge dynamics can be obtained through the observation of the time-resolved energy shift of the photoemission spectra caused by the surface photovoltage (SPV) effect.

The TRPES experiment was done at beam line BL07LSU in SPring-8. The time-resolved measurements were made by a pump-probe method using laser as a pump light and synchrotron radiation as a probe light, which was injected onto the sample after a laser pulse injection with certain delay times. Details of the TRPES system is described elsewhere [3, 4]. Single-crystal anatase TiO₂ were grown as a thin film (1 µm thickness) with (001) orientation on $LaAlO_3(100)$ by pulsed laser deposition. The sample surface was cleaned by cycles of Ar⁺ sputtering (2 kV) and annealing at 950 K in O₂ atmosphere (1 x 10^{-4} Pa). The clean surface was terminated with (4×1) double domains



Fig. 1 Photoemission spectra of the valence band and Ti 3p core-level regions.





Fig. 2 Ti $2p_{3/2}$ core-level spectra before and after laser irradiation. The lower density of the pump laser is 23 mJ/cm². Solid lines are the best fitted results using Gaussian functions as a peak and a linear background

Fig. 3 SPV induced shift of the Ti $2p_{3/2}$ spectra as a function of (a) the laser power density (1 ns delay time) and (b) the delay time (the power density of 23 mJ/cm²).

which were rotated by 90° , as proved by low-energy electron diffraction measurements. The density of the surface O vacancy was kept so low that no structures associated with the Ti³⁺ species were observed in the photoemission spectra of the in-gap region and the Ti 3p core-level region as shown in Fig. 1. The TRPES measurements were carried out under the ultrahigh vacuum condition and at room temperature.

Although anatase TiO₂ has a band gap of 3.2 eV, the SPV shift is induced by irradiation of the laser at 3.06 eV (405 nm). Fig. 2 shows Ti $2p_{3/2}$ core-level spectra (hv = 600 eV) before and after laser irradiation (0.2-ns delay time). The energy shift by 0.22 eV toward the lower binding energy side is caused by the SPV effect. Thus, multiple photon absorption is operative when the laser at 3.06 eV is illuminated. The magnitude of the shift depends on both the laser power and the delay time as indicated in Fig. 3. Fig. 3a shows the change in the SPV shift as a function of the power density of the pump laser. The SPV shift is not induced at the power density lower than 5 mJ/cm², and the shift becomes larger at the higher The threshold behavior supports the multiple photon absorption mechanism. density. At the constant power density of 23 mJ/cm², where the SPV shift is induced, the magnitude of the shift is diminished as the delay time is increased (Fig. 3b). No shift is already observed at the delay times longer than 20 ns. Thus, all the photoexcited carriers, electrons and holes, are quenched by recombination within 20 ns on anatase $TiO_2(001)$. The solid line in Fig. 3b is an exponential decay curve with the decay time, i.e., the lifetime of the carriers, of 9 ns. This is in good agreement of the carrier lifetime on anatase $TiO_2(101)$ (> 10 ns) [1] but is rather shorter than that on anatase $TiO_2(100)$ (31 ns) [2]. Interestingly, as the surface is roughened by Ar⁺ sputtering, the carrier lifetime is diminished (results not shown). This implies that the electron-hole recombination should mainly occur at the surface and, on the rough surface, the density of the recombination centers is increased so that the photogenerated charge carriers are promptly quenched.

References

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