

## Electronic structure of epitaxial anatase TiO<sub>2</sub> film

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### Introduction

Titanium dioxide (TiO<sub>2</sub>) has been widely used for the past two decades owing to its technologically promising properties such as a large refractive index, a high dielectric constant and a high photochemical activity. Among different polymorphs of TiO<sub>2</sub>, anatase is the most commonly used for photocatalysis. However, fundamental properties of anatase are less known than those of rutile despite of the higher photocatalytic activity of anatase than rutile. In particular, it still remains open whether the optical interband transition is direct or not.

Many theoretical studies have been carried out to elucidate the band structure of anatase. However, the position of the valence band maximum (VBM) depends on calculation techniques employed<sup>[1,2]</sup>. In order to understand the mechanism and the superiority of the photocatalytic activity of anatase TiO<sub>2</sub>, it is necessary to experimentally determine the band structure of anatase. In the present study, we fabricated high-quality single-crystal anatase thin films, and examined the valence electronic structures by angle-resolved photoelectron spectroscopy (ARPES).

### Experimental

TiO<sub>2</sub>(001) thin films were grown using pulsed laser deposition with a KrF excimer laser ( $\lambda = 248$  nm) on LaAlO<sub>3</sub>(100), whose in-plane lattice constants are matched to those of anatase. The *in situ* preparation to remove surface contamination involved cycles of Ar<sup>+</sup> sputtering (2.5 kV, 0.5  $\mu$ A) and annealing at 900 K for several times. The sample was, then, annealed at 700 K in O<sub>2</sub> atmosphere ( $1.0 \times 10^{-6}$  Torr) for 5 min to restore the surface stoichiometry.

The ARPES measurements were performed at beamline 3B of the Photon Factory. A hemispherical electron energy analyzer (HA45, VSW) was used to acquire the spectra with a typical overall energy resolution of c.a. 0.2 eV. The electronic structures along high symmetry axes of the bulk Brillouin zone, i.e., the  $\Gamma$ -M,  $\Gamma$ -X, Z-A and Z-R axes, were determined by off-normal emission measurements.

### Results and discussion

Figure 1 shows the band structures of anatase determined by ARPES measurement. The P <sub>$\pi$</sub>  state is observed as an almost flat band at 4.3 eV on  $\Gamma$ -X and Z-R, while the state moves to the shallower energies from 4.3 eV ( $\Gamma$ ) to 3.8 eV (M) and from 4.3 eV (Z) to 4.1 eV (A). No other states with binding energies smaller than 3.8 eV are found in any other points. Thus, it is confirmed that

the P <sub>$\pi$</sub>  state at the M point correspond to the VBM. On the other hand, the theoretical band-structure calculations conducted so far for anatase TiO<sub>2</sub> have all indicated the conduction band minimum (CBM) at  $\Gamma$ <sup>[1,2]</sup>. Therefore, we draw the conclusion that anatase TiO<sub>2</sub> is an indirect band gap material.

The indirect band gap in anatase should affect the behavior of photoexcited electrons and holes. Photoexcited electrons and holes in bulk TiO<sub>2</sub> suffer from direct recombination immediately after their relaxation to the CBM and VBM. However, the direct recombination requires the absorption or emission of phonons in anatase, whereas it is not necessary in rutile. Therefore, the lifetimes of photoexcited electrons and holes should be longer in anatase than in rutile. The lifetime of photogenerated carriers is closely related to the photocatalytic activity; the longer the lifetime is, the higher the chemical reaction on the surface involving the excited carriers. Therefore, the superiority of the photocatalytic activity of the anatase over the rutile can be explained partly by the valence band structure with the indirect band gap.

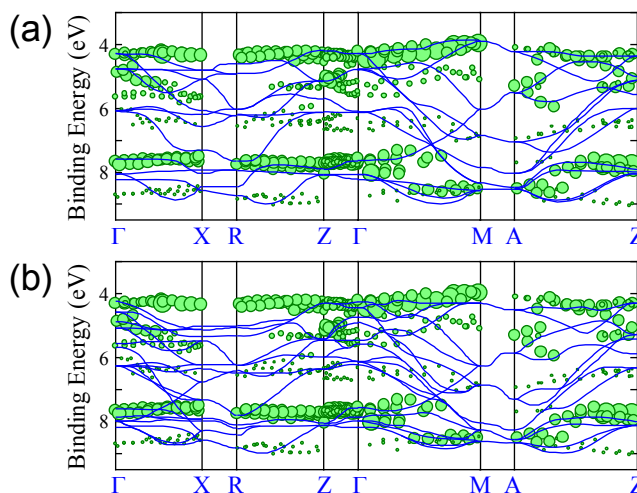


Fig.1 Comparison of the experimental band with the theoretical bands. Theoretical bands are obtained by (a) the hybrid DFT calculation<sup>[1]</sup>, and (b) the FLAPW calculation<sup>[2]</sup>.

### References

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