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# ARPES study on bulk electronic structures of anatase $TiO_2$

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## Introduction

Titanium dioxide ($TiO_2$) 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 the prototypes of $TiO_2$, anatase is one of the most commonly used materials for photocatalysis. A large number of studies of the photocatalytic activities of anatase have been performed thus so far. However, in spite of the importance of anatase from the viewpoint of photocatalytic applications, the fundamental properties of anatase are less known than those of rutile. Anatase is commercially available in powder form. In general, powder materials contain a considerable amount of impurities and many types of defect such as grain boundaries, dislocations and point defects, which markedly influence the properties of these materials. Thus, their quantitative analysis is difficult. The difficulty in obtaining single-crystal anatase arises from the fact that anatase is a low-temperature phase. Instead, we successfully fabricated high-quality single-crystal anatase thin films for the investigation of the fundamental properties of anatase crystal [1].

## Experimental

$TiO_2$ thin films were grown using pulsed laser deposition (PLD) with a KrF excimer laser ($\lambda$= 248nm ) on $LaAlO_3$(100). Highly oriented anatase films (thickness: 1μm) with a c-axis normal to the substrate surface were epitaxially grown with the in-plane epitaxial relationship of [100]anatase//[010]$LaAlO_3$ between films and substrate.

The ARPES measurements were performed at beam line 1C. Prior to the measurements, the surface of thin film was cleaned by an $Ar^+$ bombardment followed by annealing at 400°C under $O_2$ atmosphere of $10^{-4}$Pa.

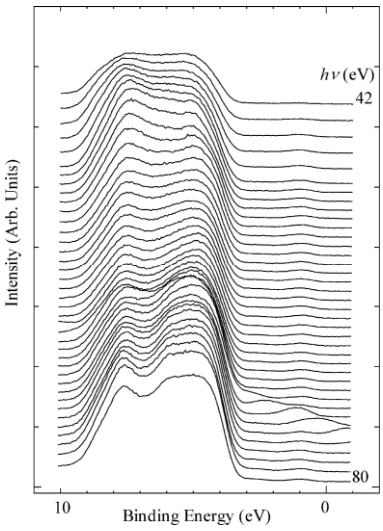


Fig.1 Photoemission spectra

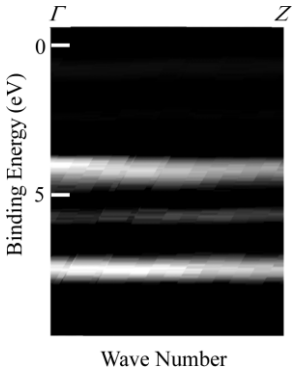


Fig.2 Valence band electronic structures of anatase along $\Gamma$–$Z$ direction of incident photon energy

## Results and discussion

Figure 1 shows the normal-emission spectra along $\Gamma$–$Z$ direction for anatase valence band as a function of incident photon energy. The valence band electronic structures of anatase along $\Gamma$–$Z$ are presented in Fig. 2, where the second derivatives of photoemission intensities are mapped as an grey scale image. Three almost dispersionless valence bands are clearly shown. According to a molecular-orbital bonding diagram for anatase, the upper, middle and lower bands can be attributed to $p_\pi$, , $\pi$ and $\sigma$ sates derived mainly from O 2$p$ orbitals, respectively [2]. They are in good agreement with the calculated band structures of anatase, although much more structures are obtained theoretically [2-4].

## References

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