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Electronic structure of anatase TiO_2 film epitaxially grown on $LaAlO_3$(100): Angle-resolved photoelectron spectroscopy study

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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 three different polymorphs of TiO_2, i.e., anatase, rutile and brookite, the former two polymorphs (anatase and rutile) are commonly used for industry purposes. However, fundamental properties of anatase are less known than those of rutile. In particular, because there are a few theoretical and experimental investigations carried out so far on the electronic structure of anatase, it still remains open whether the optical interband transition is direct or not [1,2] in spite of the importance of anatase as a photocatalyst, which is known to superior to rutile. In order to understand the mechanism and the superiority of the photocatalytic activity of anatase TiO_2, 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 resolution photoelectron spectroscopy (ARPES).

Experimental

TiO_2(001) thin films were grown using pulsed laser deposition with a KrF excimer laser (λ= 248 nm) on $LaAlO_3$(100), whose in-plane lattice constants are matched to those of anatase TiO_2. Oriented anatase films were epitaxially grown with a relationship of [100] anatase//[010] $LaAlO_3$[3]. The *in situ* preparation to remove surface contamination involved cycles of Ar^+ sputtering (2.5kV, 0.5μA) and annealing at 900 K for several times. The sample was, then, annealed at 700 K in O_2 atmosphere (1.0×10^{-6} Torr) for 5 min to restore the surface stoichiometry.

The ARPES measurements were performed utilizing synchrotron radiation at Beam Line 3B of the Photon Factory, High Energy Accelerator Research Organization (KEK). A hemispherical electron energy analyzer (HA45, VSW) was used to acquire the spectra with a typical overall energy resolution of c.a. 0.25 eV. The electronic structures along high symmetry axes of the bulk Brillouin zone, i.e., the Γ-M, Γ-X, Z-A and Z-R axes, were determined by off-normal emission measurements. The binding energy of the spectra was referenced to the Fermi energy, which was determined from the spectra of the Ta sample holder.

Results and discussion

Fig.1 (a) shows ARPES spectra along the Γ-M axis. Several emission peaks are observed in the valence band region between 3 and 9 eV. The plots of the peak positions against the wave-number vector (k) are shown in Fig.1 (b). Of the five branches resolved, the shallowest band is associated with the O 2p nonbonding state ($P\pi$)[1]. Other branches in a deeper energy region are assigned to the Ti 3d-O 2p bonding states (π and σ)[1]. The $P\pi$ band shows upward dispersion from 4.1 eV at Γ to 3.8 eV at M. No other states with binding energies smaller than 3.8 eV are found in any other high symmetry points. Thus, the $P\pi$ state at the M point is the valence band maximum (VBM).

The theoretical band-structure calculations conducted so far for anatase TiO_2 have all indicated the conduction band minimum at Γ [1,2]. On the other hand, the VBM should coincide with Γ [1] or M [2] depending on the calculation methods employed in the studies. The present study shows experimentally that the VBM is located at M. Therefore, we draw the conclusion that anatase TiO_2 is an indirect band gap material.
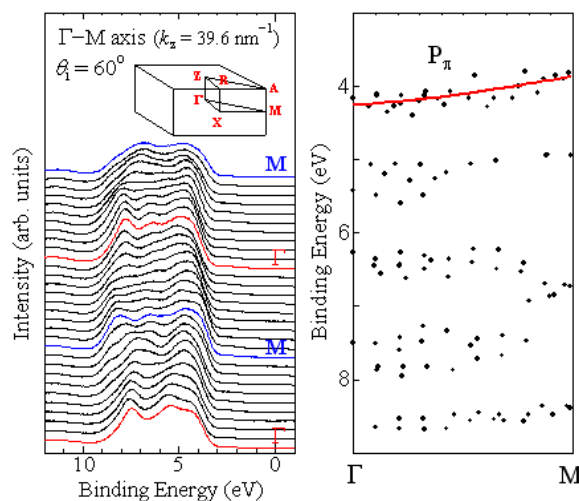

Fig. 1 (left) ARPES spectra along the Γ-M axis. The inset show the bulk Brillouin zone of anatase TiO_2. (right) The plots of the peak positions against k on the Γ-M axis.

References

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