Electronic Structure of $InTaO_4$ with Monoclinic Structure

Shigenori Matsushima,* Hiroyuki Nakamura,† Masao Arai,†† and Kenkichiro Kobayashi†††
Department of Materials Science and Chemical Engineering, Kitakyushu National College of Technology,
5-20-1 Shii, Kokuraminami-ku, Kitakyushu 802-0985
†*Integrated Arts and Science, Kitakyushu National College of Technology,*
5-20-1 Shii, Kokuraminami-ku, Kitakyushu 802-0985
††*Advanced Materials Laboratory (AML), National Institute of Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044*
†††*Department of Materials Science, Shizuoka University, 3-5-1 Jyohoku, Hamamatsu 432-8011*

(Received September 30, 2002; CL-020837)

From a first-principles band calculation, $InTaO_4$ is predicted to be an indirect-gap material, because the valence band maximum (VBM) is located in the middle point on the ZD line and the conduction band minimum (CBM) in the middle point on the DX line. The valence band with the width ca. 6.0 eV is mainly constructed from O 2p orbitals hybridized with In4d5s5p and Ta5d orbitals, whereas the lower conduction band is constructed from Ta5d orbitals.

Photocatalysis of TiO_2 (anatase) has been investigated from viewpoints of utilization of solar energy. Anatase TiO_2 exhibited several advantages of stability, low cost, and nontoxic, but a disadvantage of no photocatalysis in visible region. Many attempts were made to find new photocatalysts, e.g., $K_4Nb_6O_{17}$,[1] $K_2La_2Ti_3O_{10}$,[1] $Sr_2Nb_2O_7$,[1] $SrIn_2O_4$,[1] and $RbNdTa_2O_7$.[2] Nevertheless, these oxides exhibited no photocatalysis in the visible region, because of the large band-gap energy. In contrast, Arakawa et al.[3] reported that $InNbO_4$ and $InTaO_4$ could evolve H_2 from pure water even in the visible region, although the mechanism is not clear. To reveal the mechanism of photocatalysis of these oxides in the visible region, we need information on electronic structures of these oxides such as the band-gap energy and types of the optical transition. Unfortunately, there are few reports on the electronic structure of these oxides because of many atoms in the unit-cell and the complex crystal structure. In this letter, we calculate the electronic structure of $InTaO_4$ using a first-principles band calculation based on the density-functional theory (DFT), and discuss the mechanism of photocatalysis of $InTaO_4$.

$InTaO_4$ has layered wolframite-type structure (the space group is $P2/a$), and In, Ta and O atoms occupy the Wyckoff positions 2f, 2e and 4g, respectively.[4] The lattice constants and atomic positions are taken from Reference 4. For the first-principles energy-band calculation, the full-potential linearized augmented plane-wave (FLAPW) method has been applied.[5] Exchange and correlation are treated within the framework of the generalized gradient approximation (GGA).[6] The space in a unit cell was divided into two types of regions: the muffin-tin (MT) region inside the MT spheres associated with each atom, and the interstitial region defined as the space other than the MT region. Therefore, we employed two types of the basis functions; a linear combination of (1) radial functions multiplied by spherical harmonics inside the MT spheres and (2) plane wave in the interstitial region. In the calculation of the electronic structure, the MT spheres radii (R_{MT}) of the In, Ta and O atoms were 2.0, 2.0 and 1.6 a.u., respectively, and approximately 1500 plane waves were adopted. The plane wave cutoff was $R_{MT} \cdot K_{max} = 7.0$ and the k-point sampling was chosen to be 45 irreducible points within the first Brillouin zone (Figure 1).

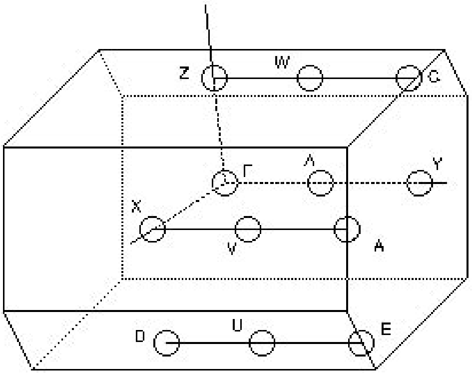

Figure 1. First Brillouin zone of the primitive monoclinic structure.

The calculated self-consistent band structure is shown in Figure 2. In order to clarify their dispersion relation, the energy levels are plotted along the high-symmetry directions (Z–C, Γ–Y, X–A, and D–E) of the irreducible BZ and other directions. The Fermi energy, defined as the highest occupied energy level, has been taken as the valence band maximum (VBM). The VBM is located near the middle point on the ZD line and the conduction band minimum (CBM) near the middle point on the DX line. This means that $InTaO_4$ is an indirect-gap material. A minimum forbidden gap between VBM and CBM is ca. 3.7 eV, which agrees with the calculations by Oshikiri et al.[7] but is larger than experimental optical band gap (ca. 2.6 eV) as reported by Arakawa.[3] It is empirically well known that theoretical values of the energy gap between unoccupied and occupied orbitals in semiconductors and insulators are underestimated compared with experimental ones, because the discontinuity in the exchange-correlation potential is not taken into account within the framework of density functional theory. In fact, calculated values of the band-gap energy of metal oxides are smaller than experimental values without exception. Therefore, it is considered that the optical band gap reported by Arakawa et al. is not originated from bulk, but from surface and defects.

To confirm the band-gap energy of $InTaO_4$, we have also measured diffuse reflectance spectra in the range of 200 to 800 nm of $InTaO_4$ powders, which were prepared from In_2O_3 and Ta_2O_5 powders by solid-state reaction. The diffuse reflectance spectra suggest that the onset of absorption was observed at 4.3 and 2.6 eV. The former is strong, indicating that the absorption is originated from the optical transition from the valence band and the conduction band. The latter is too weak to be attributed to the band-gap

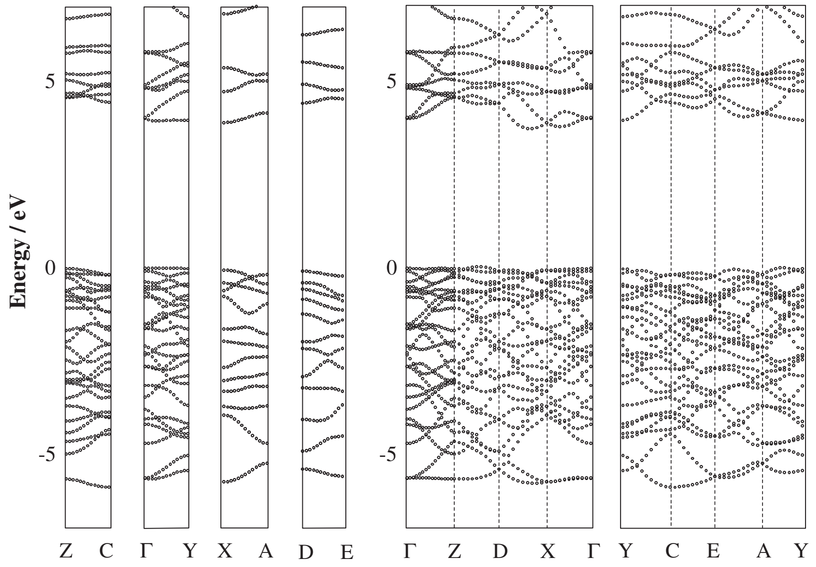

Figure 2. Energy band structure of $InTaO_4$ along the symmetry lines of the first Brillouin zone.

excitation. The absorption in the visible region is probably attributable to the gap states such as impurities and defects. The presence of such gap states was reported in luminescence studies by Brixner et al.[8] In exciation and emission spectra of $InNb_{0.05}Ta_{0.95}O_4$, excitation at 260 nm (4.77 eV) gave rise to emission at 404 nm. The emission at 404 nm occurs via gap states. Accordingly, it is considered that the absorption in the visible region results from the optical excitation via the gap states, rather than the band-gap excitation. On the basis of the band-gap energy of $InTaO_4$, we propose a possible mechanism of photocatalysis in the visible region: The visible light excitation results in the electron transfer from the valence band to the vacant gap-states, and subsequently transferred electrons in the gap states are optically excited to the conduction band.[9] In the two-step processes, both electrons and holes can be generated by the excitation of sub-band gap. Of course, the sub-band gap energy is at least larger than one-half the band-gap energy.

Figure 3 shows the total density of states (TDOS) and partial density of states (PDOS), corresponding to the energy region in Figure 2. The valence band in the range from −6.0 to 0 eV mainly consists of O 2p orbitals, where In 4d5s5p and Ta5d orbitals hybridize with O 2p orbitals. The DOS peaks at the top of the valence band are constructed from only O 2p orbitals and the contribution of In and Ta orbitals is negligible small. This implies that the mobility of holes generated by band-gap excitation is expected to be fairly low. The electronic structure of the valence band is not preferable for photocatalysis. There are two different oxygen sites, O1 and O2, and each bond length of In–O and Ta–O ranges from 0.21208 to 0.21994 nm and from 0.19107 to 0.21219 nm, respectively. The PDOS of two types of oxygen sites distributes similarly because they have similar interatomic distances and coordination environment of In–O and Ta–O bonds. On the other hand, the conduction band below 5.5 eV is mainly composed of the Ta 5d orbitals and the contributions of In and O orbitals are small. Ta 5d orbitals are divided into two peaks in the range of 3.6 to 4.6 eV and of 4.6 to 6.4 eV as a result of the crystal field splitting in the octahedral TaO_6 environment.

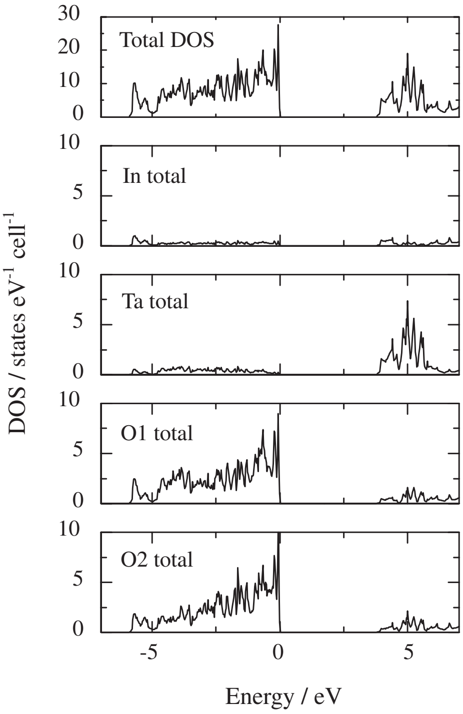

Figure 3. Calculated density of states (DOS) of $InTaO_4$.

References

1 A. Kudo, *Shokubai*, **44**, 308 (2002) and references therein.
2 M. Mochida, J. Yabunaka, and T. Kijima, *Chem. Mater.*, **12**, 812 (2000).
3 Z. Zou, J. Ye, and H. Arakawa, *Chem. Phys. Lett.*, **332**, 271 (2000).
4 O. Harneit and Hk. Muller-Buschbaum, *J. Alloys Compd.*, **194**, 101 (1993).
5 P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Techn. Universitat Wien, Austria), (2001), ISBN 3-9501031-1-2.
6 J. P. Perdew, S. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, **77**, 3865 (1996).
7 M. Oshikiri, M. Boero, J. Ye, Z. Zou, and G. Kido, *J. Chem. Phys.*, to be published.
8 L. H. Brixner and H.-y. Chen, *Mater. Res. Bull.*, **15**, 607 (1980).
9 K. Kobayashi, T. Maeda, S. Matsushima, and G. Okada, *Jpn. J. Appl. Phys.*, **31**, L1079 (1992).