## Direct band bending observation by angular-resolved HAXPES for semiconductor films in contact with metal nanoparticles

Systematic combinations of metals and semiconductors are widely applied and important for devices such as sensors, power devices, solar cells, and photocatalysts for solar energy conversion and environmental purification. In photocatalysis, photocatalytic activity is improved by the surface adsorption of metal or metal oxide co-catalysts. For example, volatile organic compounds (VOCs) are decomposed by photoexcited TiO<sub>2</sub>. This decomposition is accelerated by surface loading with nanoscale Pt (Pt/TiO<sub>2</sub>). For solar energy conversion, Pt/TiO<sub>2</sub> is used to split water for the stoichiometric production of hydrogen and oxygen under ultraviolet light irradiation, in which a nanoscale Pt co-catalyst attached to TiO<sub>2</sub> plays a significant role in improving chemical reaction rates [1]. Although the nanoscale Pt functions as an effective co-catalyst for TiO<sub>2</sub>, it cannot be universally applied to all semiconductors. For example, a Pt co-catalyst does not enhance photocatalytic H<sub>2</sub> production in water splitting over semiconductor photocatalysts such as TaON and Ta<sub>3</sub>N<sub>5</sub> [2]. This suggests that the difference in photocatalytic activity is responsible for the difference in the electronic states of both nanoscale co-catalysts and semiconductors after the formation of metal-semiconductor junctions. However, this phenomenon has not been clarified experimentally.

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The position of the energy band can be directly measured by photoelectron spectroscopy. In hard X-ray photoemission spectroscopy (HAXPES), raising the X-ray photon energy for excitation extends the analysis depth compared with the case of XPS measurements. Thus, band bending in semiconductors from the bulk to the surface can be measured dynamically by angular distribution of HAXPES peak (angle-resolved HAXPES), which reflects depth profile of the electronic structures [3].

In this paper, we describe the direct observations of band bending near the surfaces of films of bare TiO<sub>2</sub>, nanoscale metal-adsorbed TiO<sub>2</sub>, bare N-doped Ta<sub>2</sub>O<sub>5</sub> (N-Ta<sub>2</sub>O<sub>5</sub>), and nanoscale metal-adsorbed N-Ta<sub>2</sub>O<sub>5</sub> by angular-resolved HAXPES, which was conducted at SPring-8 **BL47XU** using a photon energy of 7940 eV. Our results clearly showed that the Mott-Schottky rule for metal-semiconductor junctions was not applicable to semiconductors with adsorbed nanoscale metals, because the electrostatic potentials between them are mainly dominated by the electric dipole in the ground state. The data presented in this report provides new insights into electrostatic interactions at the junctions in the ground state [4].

Figure 1 shows HAXPES spectra for Ti  $2p_{3/2}$  and Ta  $3d_{5/2}$  core state photoemissions. The bare TiO<sub>2</sub> films at take-off-angles of 65° (bulk phase; maximum analysis

depth of ca. 31 nm) and 10° (surface; maximum analysis depth of ca. 6 nm) produced similar spectra without any significant shifts. On the other hand, the peak for N-Ta<sub>2</sub>O<sub>5</sub> at take-off-angles of 10° (surface; maximum analysis depth of ca. 5 nm) shifted by 0.4 eV to a higher binding energy than that at a take-off-angle of 65° (bulk phase; maximum analysis depth of ca. 24 nm). However, upon deposition with nanoscale Pt, markedly different spectra were observed. For example, the film (Pt/TiO<sub>2</sub>) exhibited upward band bending by 0.07 eV with the binding energy peak for a nearby surface (take-off-angle of 10°) positioned higher than that for the bulk (angle of 65°). In addition, the peak position of Ti  $2p_{3/2}$  bulk (65°) of bare TiO<sub>2</sub> was shifted negatively by 0.25 eV by the deposition of Pt (Pt/TiO<sub>2</sub>) as shown in Fig. 1(a). A strong electrostatic interaction was also obtained for a N-Ta2O5 film deposited with Pt (Pt/ N-Ta<sub>2</sub>O<sub>5</sub>). The large downward band bending observed in a bare N-Ta<sub>2</sub>O<sub>5</sub> film (0.40 eV) was also greatly reduced to 0.05 eV by the surface deposition of nanoscale Pt. Almost the same phenomenon was observed using other metal nanoparticles such as Au and Rh. In general, the degree



Fig. 1. Series of Ti  $2p_{3/2}$  spectra measured on (a) TiO<sub>2</sub> and (b) Pt/TiO<sub>2</sub> using angular-resolved HAXPES [take-off angles 10° (red line) and 65° (black line)]. The upper panel shows a single shot of Ti  $2p_{3/2}$  peaks from a 2D image for take-off angles from 10° to 65°. Series of Ta  $3d_{5/2}$  spectra measured on (c) N-Ta<sub>2</sub>O<sub>5</sub> and (d) Pt/N-Ta<sub>2</sub>O<sub>5</sub> by angular-resolved HAXPES (take-off angles of 10° and 65°). The upper panel shows a single shot of Ta  $3d_{5/2}$  peaks from a 2D image of take-off angles from 10° to 65°. Adapted from Ref. 4 with permission from the PCCP Owner Societies.



Fig. 2. (a) Binding energy of the Ti  $2p_{3/2}$  peak for metal particles or thin films on TiO<sub>2</sub> calculated using DFT [red circles: Pt particles on TiO<sub>2</sub>; blue circles: Au particles on TiO<sub>2</sub>; purple circles: Rh particles on TiO<sub>2</sub>; red squares: thin Pt film on TiO<sub>2</sub>; blue squares: thin Au film on TiO<sub>2</sub>; purple squares: thin Rh film on TiO<sub>2</sub> (b) Relation between calculated binding energy of Ti  $2p_{3/2}$  peak and intensity of charge transfer ( $\Delta Q$ ) between metal particles and TiO<sub>2</sub>; film [red circles: Pt particles on TiO<sub>2</sub>; purple circles: Au particles on TiO<sub>2</sub>; purple circles: Pt particles on TiO<sub>2</sub> [4]

and direction of band bending in metal-semiconductor junctions can be explained by the difference in their work functions using the Mott-Schottky model [5]. The work functions of Pt, Au, and Rh are 5.65 eV, 5.1 eV, and 4.9 eV, respectively, which are greater than that of TiO<sub>2</sub> (4.5 eV). Therefore, the upward band bending in the metal/TiO<sub>2</sub> films observed by HAXPES was consistent with the Mott-Schottky rule. However, the peak shift cannot be explained by the Mott-Schottky rule. This result indicated that there is a strong interaction between the metal nanoparticles and the semiconductor in the ground state.

To clarify the reason for the peak shift upon the adsorption of metal nanoparticles, we attempted to simulate the phenomenon by density function theory (DFT) calculation. Results of the DFT calculation are shown in Fig. 2. It was found that all of the Ti  $2p_{3/2}$  peaks of TiO<sub>2</sub> films with metals were shifted negatively from that for the bare TiO<sub>2</sub> film (Fig. 2(a)). Figure 2(b) shows the calculated binding energies of the Ti  $2p_{3/2}$  peak as a function of the intensity of the charge transfer between TiO<sub>2</sub> and the metals. This result indicated that the negative peak shift of Ti  $2p_{3/2}$  is determined by the amount of charge transfer from the nanoscale metal to TiO<sub>2</sub>. This charge transfer forms the dipole moment at the interface and thus results in a shift of the electrostatic potential.

Figure 3 is a schematic drawing of the summarized results, which can be conducted by angle-resolved HAXPES. As a result of charge migration from the nanoscale metal to the semiconductor, the electric dipole

formed at the surface modifies the electrostatic potential in the ground state, resulting in band bending and a band shift (Fermi level shift) as shown in Fig. 3(b). This illustrates a major difference from the Mott-Schottky rule normally observed in a solid-state junction composed of a bulk metal and a semiconductor as shown in Fig. 3(a). Although we usually use a co-catalyst such as nanoparticle metals to improve the catalytic activity of a semiconductor photocatalyst, the semiconductor band potentials can be affected by them. Therefore, if we use metal nanoparticles as photocatalysts, devices, and so forth, we will have to consider the electric dipole from the nanoparticles.

In conclusion, angle-resolved HAXPES measurements can simultaneously evaluate the electronic states of both the surface and bulk of a semiconductor film. From the HAXPES and DFT results, it was revealed that the dipole moment from metal nanoparticles strongly affects semiconductor properties such as the band position and bending.



Fig. 3. Schematic illustration of metal and n-type semiconductor  $(TiO_2)$  contact: (a) between the bulk metal and  $TiO_2$  (ideal state according to Mott-Schottky rule); (b) between nanoscale metal and  $TiO_2$  (charge migration from metal to semiconductor with dipole moment). Black solid line shows CB and VB after contact between the bulk metal and semiconductor; black dashed line shows CB and VB before contact between the metal and semiconductor; red solid line shows CB and VB after contact between the nanoscale metal and semiconductor.  $\delta$  shows polarization of materials.

Shunsuke Sato\* and Takeshi Morikawa

Toyota Central R&D Labs., Inc.

\*Email: ssato@mosk.tytlabs.co.jp

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