High-Resolution Hard-X-ray Photoemission Spectroscopy

Photoemission spectroscopy (PES) is a method of measuring the kinetic energy distribution of photoelectrons emitted from materials excited by monochromatic light. It gives information on bound electron states in materials; thus, it has been used extensively to study electronic structures as well as chemical bonding states [1]. Synchrotron radiation (SR) has extended the applicability of PES widely, owing to its high brilliance and energy tunability. However, conventional SR-PES, in which the excitation photon energy is usually less than 1 keV, has a fatal deficiency in detecting bulk electronic structure information. That is, because probing depth is too small, and surface sensitivity is too high due to the short inelastic-mean-free-paths (IMFPs) of the photoelectrons [2]. It is obvious that soft X-ray (SX) PES is still surface sensitive because the IMFPs of the electrons for Au and Si are only 1.3 and 2 nm at a kinetic energy of 1 keV, respectively [2]. As for chemical state analysis, nondestructive measurements of layered materials are becoming more important for the current and future technologies of nanoscience and engineering. The extension of the probing depth up to, for example, 10 nm will greatly widen the applicability to various materials with nanolayered structures and nanoparticles.

Here, we report that core level and valence band (VB)-PES at hard X-ray (HX) excitation of 5.95 keV was realized for the first time with high throughput and resolution. Unprecedentedly, high photon flux density from an undulator compensates for the decrease in cross section, which prevented high resolution measurements in Lindau *et al.*'s preceding trial [3]. Due to the large IMFPs of 5 ~ 15 nm, we do not need to prepare an ideal clean surface.

Experiments were performed at the undulator beamline **BL29XU** [3-5]. A schematic of the experimental setup including optics is shown in Fig. 1. The Si 333 channel cut monochromator reduces photon bandwidth down to 50-70 meV. A Gammadata Scienta SES2002 electron analyzer was modified to measure high-kinetic-energy photoelectrons up to 6 keV.

The performance of the detection system was tested [4,5] by measuring Au $4f$ spectra with an analyzer pass energy (E_p) of 200 eV. To confirm surface insensitivity, no surface treatment was made on the Au sample plate before or after introducing it into the analyzer chamber. Figure 2 shows the observed spectra with accumulation times of 10 min at 80 mA ring current. The full width at half maximum (FWHM) of the Au $4f_{7/2}$ peak is 470 meV. The VB spectrum was obtained with an accumulation time of 30 min and the Fermi-edge of Au is clearly observed at 20 K as shown in the inset of Fig. 2. The instrumental energy resolution including the X-ray bandwidth is determined to be 240 meV from the Fermi-edge profile.

To confirm the capability of the present method to probe the bulk states of reactive surfaces, the VB spectrum of a thin SiO_2 layer (0.58 nm) on Si(100) was measured. Figure 3 shows the spectrum obtained at 5.95 keV with an accumulation period of 30 min at room temperature. The spectrum measured with SX excitation at 0.85 keV using SR is also shown as a reference. The reference SX spectrum is evidently
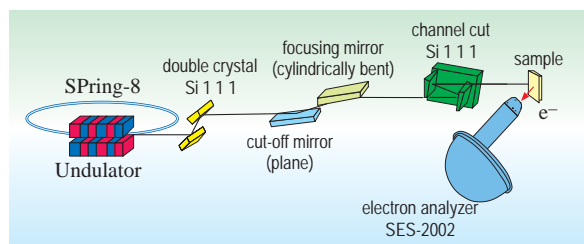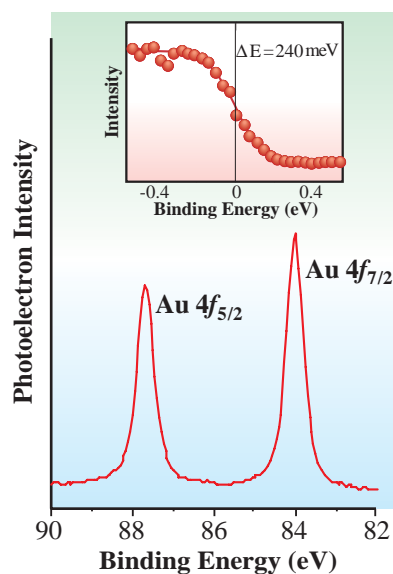

Fig. 1. Schematic of experimental setup including optics. A channel-cut monochromator with Si 333 reflection placed downstream of the mirror made it possible to reduce the energy bandwidth down to 70 meV. At the sample position, photon flux in a focal spot of 0.12 mm (vertical) × 0.7 mm (horizontal) was measured to be 2×10^{11} counts/sec.

Fig. 2. Au $4f$ core level spectra of a Au plate measured at 5950 eV excitation with $E_p = 200$ eV. The inset shows the Fermi-edge spectrum at 20 K with $E_p = 200$ eV. The total energy resolution was estimated to be 240 meV for $E_p = 200$ eV from the Fermi-edge broadening.

dominated by the peaks of structures originated from surface SiO_2. These peaks vanish in the hard X-ray spectrum, indicating the negligible contribution of the surface oxide layer of 0.58 nm thickness. From this result, we can expect to obtain "surface insensitive" spectra for most materials without resorting to surface treatment procedures. The total curve (red line) obtained by summing the weighted *s*-like (blue: multiplied by 1) and the *p*-like (green: multiplied by 0.07) partial density of states reproduces the experimental spectra at 5.95 keV.

We also successfully applied this method to detect the chemical reaction in the buried interface of high-k gate dielectrics in Si-LSI. Figure 4 shows the Si 1*s* spectra of this $HfO_2/SiO_2/Si(100)$ structure [5]. The Si 1*s* spectra of a sample with 1.32 nm SiO_2 on Si(100) are shown as a reference. After the deposition of the HfO_2 film, the Si 1*s* peak for the intermediate layer shifts to the lower-binding-energy side by 0.6 eV and is broader than the SiO_2 peak. This is an indication of an interface reaction. Annealing the sample at 1000°C in dry nitrogen gas for 5 sec enhanced the intensity of the Hf silicate peak. This result suggests that silicate formation is related to the diffusion of Si atoms into the deposited layers from the Si substrate. A detectable increase in spectral intensity appearing on the low-binding-energy side of the substrate peak indicates the formation of Hf-Si bonds by the annealing. The present hard X-ray photoemission (HX-PES) is inevitably necessary for the investigation of nanolayers and their buried interfaces in most of real devices, because the thicknesses are far beyond the probe depths of the conventional PES.
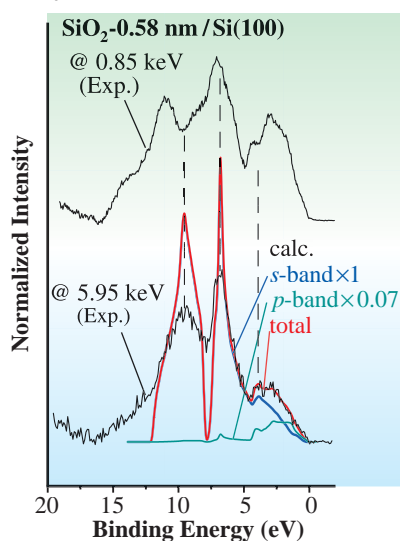

Fig. 3. VB-PES spectra of a thin SiO_2 layer (0.58 nm) on Si(100) measured at 5.95 (lower) and 0.85 keV (upper) with the same E_p = 200 eV. The red curve shows the weighted sum of the *s*-like (blue) and *p*-like (green) partial DOS obtained from first principles calculations.

We have tested the feasibility of this HX-PES to various classes of materials. All the results verify that HX-PES is successfully applied to the investigation of bulk electronic structures and chemical bonding states and can thus contribute to a wide range of basic science and technologies. It should be mentioned that this method has been developed by the collaboration between the X-ray optics group at SPring-8/RIKEN and solid state spectroscopy groups (SPring-8/JASRI, SPring-8/RIKEN, and Hi-SOR).
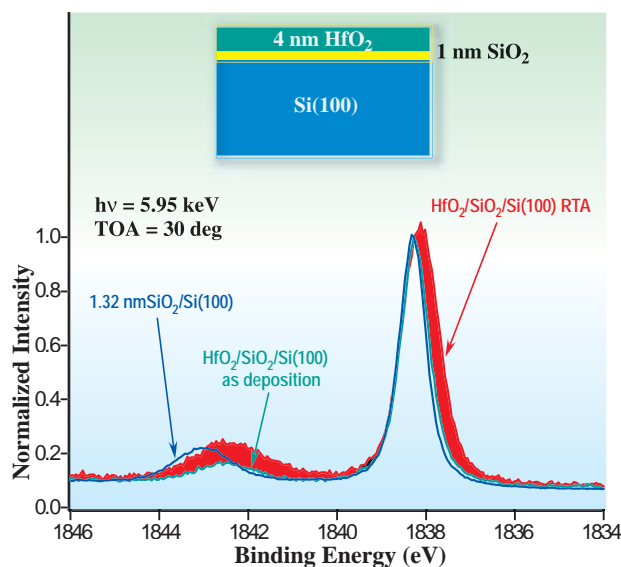

Fig. 4. Si 1*s* spectra measured for as-deposited (green) and treated by (red) rapid thermal annealing (RTA, 5 sec 1000°C) $HfO_2/SiO_2/Si(100)$ are compared with that measured for 1.32 nm $SiO_2/Si(100)$ (blue). The shift of the oxide peak in the as-deposited spectrum from that of the SiO_2 spectrum evidences interface reaction. The RTA spectrum shows a further shift of the oxide peak and an increase in intensity at the lower-binding side of the substrate Si peak. This is attributed to silicide-like Si-Hf bond formation by RTA.

Keisuke Kobayashi[a] and Yasutaka Takata[b]

(a) SPring-8 / JASRI
(b) SPring-8 / RIKEN

E-mail: koba_kei@spring8.or.jp

References
[1] S. Hüfner: Photoelectron Spectroscopy (Springer-Verlag, Berlin-Hidelberg, 1995).
[2] NIST Standard Ref. Database 71, "NIST Electron Inelastic-Mean-Free-Path Database: Ver. 1.1", http://www.nist.gov/srd/nist71.htm, and references therein.
[3] P. Lindau *et al.*: Nature **250** (1974) 214.
[4] K. Kobayashi *et al.*: Appl. Phys. Lett. **83** (2003) 1005.
[5] Y. Takata, K. Tamasaku, T. Tokushima, D. Miwa, S. Shin, T. Ishikawa, M. Yabashi, K. Kobayashi, J.J. Kim, T. Yao, T. Yamamoto, M. Arita, H. Namatame and M. Taniguchi: Appl. Phys. Lett. **84** (2004) 4310.