

BL23SU

JAEA Actinide Science II

1. Abstract

BL23SU is the JAEA actinide science beamline mainly designed for actinide material science. The beamline is also utilized for surface chemistry and biophysical spectroscopy. There are three end stations in the beamline: a real-time photoelectron spectroscopy station and a biophysical spectroscopy station in the experimental hall and actinide science stations in the RI laboratory building.

2. Real-time photoelectron spectroscopy station for surface and interface research

Research on the surfaces and interfaces of solids based on chemical analysis using soft X-ray synchrotron radiation photoelectron spectroscopy (SR-XPS) is conducted at the real-time photoelectron spectroscopy station of BL23SU. This station has also been employed to promote the nanotechnology platform of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan as a member of the advanced characterization nanotechnology platform to establish shared use of advanced characterization equipment. The apparatus is widely used for research on the physicochemical properties, functionalities of surface/interface, and mechanisms of surface reactions.

To develop ultralarge-scaled integrated (ULSI) circuits, it is crucial to elucidate the mechanisms of oxide formation/decomposition on Si surfaces. Oxidation reactions for various crystal faces have been clarified by real-time observations using *in situ* SR-XPS under O₂ gas-surface reactions. A novel reaction model mediated by point defect

generation due to oxidation-induced strain and thermal strain was constructed, which provided a basic understanding of O₂ dissociative adsorption [1]. Initial oxidation of the Si(113) surface was also investigated by combining *in situ* SR-XPS with a supersonic molecular beam (SSMB) to elucidate nonthermal processes due to kinetic energies (Et) of O₂ molecules. Et largely altered the oxide quality and oxidation kinetics [2].

The initial oxidation of ultrathin Hf films deposited on Si(100)-2×1 [Hf/Si(100)] and on Si(111)-7×7 [Hf/Si(111)] was studied by *in situ* SR-XPS due to its importance in high-k dielectric material applications for future electronic devices. The metallic Hf component plays a vital role in the initial oxidation. Annealing at ~1073 K induced oxygen removal and Hf disilicide island (i-HfSi₂) formation on a bare Si(100)-2×1 surface. i-HfSi₂ exhibited slightly reactive properties for O₂ at room temperature. The dangling bonds on a bare Si(100)-2×1 surface among i-HfSi₂ were oxidized preferentially due to the oxidation of back bonds of the Si dimers on bare Si(100)-2×1 [3]. The surface and interface of Hf/Si(111) contained three components (metallic Hf, HfSi, and Si-rich Hf silicide). Annealing changed the Hf layers into HfSi₂ islands. Both the size and shape strongly depended on the Hf coverage. The growth direction was related to the DAS model structure of a clean Si(111)-7×7 surface [4].

Germanium (Ge) and its oxides are important materials for future electronic devices. SR-XPS was applied to analyze the chemical states of Ge oxides formed on the Ge(100)2×1 surface in a standard

atmosphere at room temperature. Oxidation forming oxides with 4+ Ge oxidation states at a maximum proceeded slowly even in a standard atmosphere. The O 1s spectra clearly exhibited –OH component, indicating that water molecules from ambient humidity likely promote oxidation [5].

AlGaIn/GaN metal–oxide–semiconductor (MOS) structures are important for power electric device applications. Low-power inductively coupled plasma reactive ion etching (ICP-RIE) and chemical vapor deposition of SiO₂ dielectrics on the etched surfaces were used. This research demonstrated the significant advantages of the proposed low-damage recessed gate process for fabricating next-generation materials [6].

Carbon materials such as graphite and carbon black (CB) are important materials as catalysts for H₂ production from CH₄. The catalytic behavior and associated mechanisms of fullerenes with 6-membered rings and those comprising 5- and 7-membered rings with *sp*² bonds were investigated. *In situ*–heating SR-XPS analysis and TEM observations indicated that ring structures without six-membered rings in carbon materials with *sp*² bonding should contribute to this catalytic behavior for CH₄ decomposition at a low temperature of 400 °C [7].

As described above, studies on the reactions and chemical analysis of surfaces and interfaces of various functional materials have been conducted at the real-time photoelectron spectroscopy station.

3. Biophysical spectroscopy station

The biophysical spectroscopy station focuses on various photochemical processes in biomolecules caused by soft X-ray excitation from the viewpoint of radiation damage to DNA. The station consists of

three experimental apparatuses: an X-band EPR (SLEEPRS: Synchrotron Light Excited EPR Spectrometer), a quadrupole mass spectrometer (QMS), and an apparatus for a liquid microjet for photoelectron spectroscopy. SLEEPRS is the first method to allow transient radical species at a DNA damage site to be investigated *in situ*. The photon-stimulated desorbing ions from the irradiated DNA are observed with QMS. The photoelectron spectrometer was installed as a collaboration between the National Institutes for Quantum and Radiological Science and Technology (QST) and Tokyo University of Agriculture and Technology. These unique spectrometers should identify the physicochemical pathways to DNA nucleobase lesions and strand breakages, which are thought to induce genetic effects such as mutations and cancer.

To identify the precise early radiation process of DNA lesions, we measured the electron kinetic energy spectra emitted from uridine-5'-monophosphate (UMP) in an aqueous solution jet for the photoionization of the nitrogen 1s orbital electron and the following Auger effect using a monochromatic soft X-ray at energies above the nitrogen K-shell ionization threshold [8]. The change in the photoelectron spectra for UMP in aqueous solution at different proton concentrations (pH=7.5 and 11.3) was ascribed to the chemical shift of the nitrogen atom in uracil moiety of canonical and deprotonation forms. The lowest double ionization potentials for aqueous UMP at different pH values obtained from the Auger electron spectra following the nitrogen 1s photoionization values showed the electrostatic aqueous interaction of the canonical (neutral) and deprotonated (negatively charged) uracil moiety with hydrated water molecules.

Adenosine triphosphate (ATP), which is a ribonucleic acid, acts as intra-cellular energy transfer. ATP is also used as a substrate to synthesize messenger RNA and as a ligand of upregulation of these biological functions. The relation between molecular activity, genetic information transfer, and intercellular signaling activity was examined [9]. The altered ATP molecule may contribute to the induction of a change in the radiation sensitivity of cancer cells.

4. Actinide science stations

In the RI laboratory building, there are photoelectron spectroscopy and soft X-ray magnetic circular dichroism (MCD) stations. In addition, the commissioning of a newly developed scanning transmission X-ray microscopy (STXM) station is underway.

In the photoelectron spectroscopy station, photoelectron-spectroscopy studies for strongly

correlated materials such as actinide and rare-earth compounds have been conducted. For example, the electronic structure of UTe_2 , which is a newly discovered unconventional superconductor, was studied by resonant photoelectron spectroscopy (RPES) and angle-resolved photoelectron spectroscopy (ARPES) with soft X-ray synchrotron radiation [10]. The partial U $5f$ density of states of UTe_2 was imaged by the U $4d$ – $5f$ RPES, and the U $5f$ state had an itinerant character, but an incoherent peak existed due to the strong electron correlation effects. On the other hand, the band structure of UTe_2 was obtained by ARPES, and its overall band structure was mostly explained by band structure calculations (Fig. 1). These results suggest that the U $5f$ states of UTe_2 have an itinerant but strongly correlated nature. ARPES experiments for Eu-based compound were also conducted, and the basic electronic structures of typical Eu^{2+} and Eu^{3+} compounds were revealed [11].

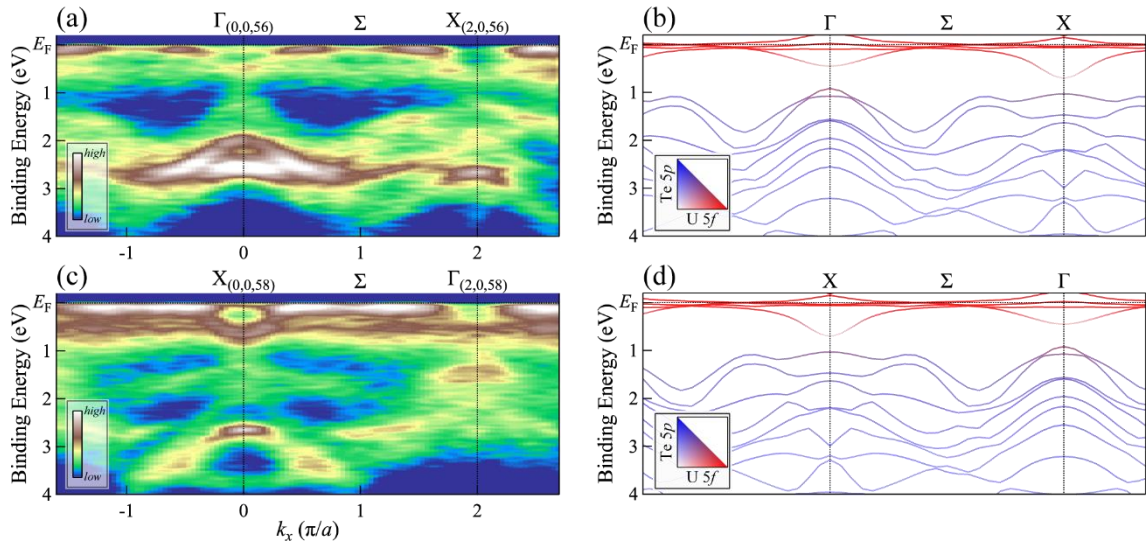


Fig. 1. ARPES spectra of UTe_2 along with the corresponding results of the band structure calculations. (a) ARPES spectra measured along the $\Gamma_{(0,0,56)}$ – (Σ) – $X_{(2,0,56)}$ high-symmetry line. (b) Corresponding calculated band structure. Color coding represents the contribution from the U $5f$ states. (c) ARPES spectra measured along the $X_{(0,0,58)}$ – (Σ) – $\Gamma_{(2,0,58)}$ high-symmetry line. (d) Corresponding calculated band structure and the simulated ARPES spectra.

In 2019A, the soft X-ray magnetic circular dichroism (XMCD) in the RI laboratory was out of service due to the commissioning of the scanning transmission X-ray microscope, which was installed in the end of FY2018. At the XMCD experimental station, a wide range of research was conducted on magnetic properties of uranium compounds, as well as topological insulators and functional magnetic materials [12-18]. One study found that in topological insulators (TIs) in vanadium-doped (Sb, Bi)₂Te₃, antiparallel magnetic moments on the Te sites with respect to the Sb and V sites are crucial for the formation of long-range magnetic ordering in the system [12]. In addition, the magnetic properties in TI Sb_{2-x}V_xTe₃ were investigated on V, Sb, and Te [14]. The advantage of XMCD, which is an element-specific magnetic probe, is that it can capture crucial evidence of the emergence of the intrinsic ferromagnetism in V₅Se₈ epitaxial thin films. The study demonstrated a new class of two-dimensional (2D) magnets as an itinerant 2D Heisenberg ferromagnet [15]. Furthermore, the origin of ferromagnetism in ferromagnetic semiconductors, which are key materials for spintronics, were discussed based on XMCD investigations [16, 17]. In microscopic magnetic investigations for new and novel materials such as topological insulators and ferromagnetic semiconductors, XMCD has become an indispensable experimental tool.

Akitaka Yoshigoe*¹, Kentaro Fujii*², Shin-ichi Fujimori*¹, and Yukiharu Takeda*¹

*¹. Japan Atomic Energy Agency, Materials Sciences Research Center

*². Institutes for Quantum and Radiological Science and Technology, Quantum Beam Science Research Directorate

References:

- [1] S. Ogawa, A. Yoshigoe, J. Tang, Y. Sekihata, and Y. Takakuwa, *Jpn. J. Appl. Phys.* **59**, SM0801 (2020).
- [2] S. Ohno, K. Tanaka, H. Kodama, M. Tanaka, A. Yoshigoe, and Y. Teraoka, *Surf. Sci.* **697**, 121600 (2020).
- [3] T. Kakiuchi, H. Yamasaki, C. Tsukada, and A. Yoshigoe, *Surf. Sci.* **693**, 121551 (2020).
- [4] T. Kakiuchi, T. Matoba, D. Koyama, Y. Yamamoto, K. Kato, and A. Yoshigoe, *Surf. Sci.* **701**, 121691 (2020).
- [5] A. Yoshigoe, *Jpn. J. Appl. Phys.* **59**, SMMB05 (2020).
- [6] M. Nozaki, D. Terashima, A. Yoshigoe, T. Hosoi, T. Shimura, and H. Watanabe, *Jpn. J. Appl. Phys.* **59**, SMMA07 (2020).
- [7] T. Tokunaga, K. Kuno, T. Kawakami, T. Yamamoto, and A. Yoshigoe, *Int. J. Hydrog. Energy* **45**, 14347 (2020).
- [8] Y. Takeda, et al., *Quantum Beam Sci.* **4** (2020) 10.
- [9] K. Fujii, et al., *Adv. X-Ray. Chem. Anal., Japan* **51** (2020) 251-259.
- [10] S. Fujimori, I. Kawasaki, Y. Takeda, H. Yamagami, A. Nakamura, Y. Homma, D. Aoki, *J. Phys. Soc. Jpn.* **88**, 103701 (2019).
- [11] I. Kawasaki, S. Fujimori, Y. Takeda, H. Yamagami, W. Iha, M. Hedo, T. Nakama, Y. Ōnuki, *Phys. Rev. B* **100**, 035111 (2019).
- [12] M. Ye, T. Xu, G. Li, S. Qiao, Y. Takeda, Y. Saitoh, S.-Y. Zhu, M. Nurmamat, K. Sumida, Y. Ishida, S. Shin, and A. Kimura, *Phys. Rev. B*

- 99, 144413 (2019).
- [13] K. Yoshimatsu, J. Ishimaru, K. Watarai, K. Yamamoto, Y. Hirata, H. Wadati, Y. Takeda, K. Horiba, H. Kumigashira, O. Sakata, and A. Ohtomo, *Phys. Rev. B* **99**, 235129 (2019).
- [14] K. Sumida, M. Kakoki, J. Reimann, M. Nurmamat, S. Goto, Y. Takeda, Y. Saitoh, K. A. Kokh, O. E. Tereshchenko, J. Gdde, U. Hfer and A. Kimura, *New J. Phys.* **21**, 093006 (2019).
- [15] M. Nakano, Y. Wang, S. Yoshida, H. Matsuoka, Y. Majima, K. Ikeda, Y. Hirata, Y. Takeda, H. Wadati, Y. Kohama, Y. Ohigashi, M. Sakano, K. Ishizaka, and Y. Iwasa, *Nano Letters* **19**, 8806 (2019).
- [16] S. Sakamoto, N. T. Tu, Y. Takeda, S.-i. Fujimori, P. N. Hai, L. D. Anh, Y. K. Wakabayashi, G. Shibata, M. Horio, K. Ikeda, Y. Saitoh, H. Yamagami, M. Tanaka, and A. Fujimori, *Phys. Rev. B* **100**, 035204 (2019).
- [17] S. Sakamoto, L. D. Anh, P. N. Hai, Y. Takeda, M. Kobayashi, Y. K. Wakabayashi, Y. Nonaka, K. Ikeda, Z. Chi, Y. Wan, M. Suzuki, Y. Saitoh, H. Yamagami, M. Tanaka, and A. Fujimori, *Phys. Rev. B* **101**, 075204 (2020).
- [18] K. Ito, Y. Yasutomi, S. Zhu, M. Nurmamat, M. Tahara, K. Toko, R. Akiyama, Y. Takeda, Y. Saitoh, T. Oguchi, A. Kimura, and T. Suemasu, *Phys. Rev. B* **101**, 104401 (2020).