

BL23SU (JAEA Actinide Science II)

1. Abstract

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

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

Research on reactions at surfaces and interfaces based on chemical analysis using soft X-ray synchrotron radiation photoelectron spectroscopy (SR-XPS) is conducted at the real-time photoelectron spectroscopy end-station of BL23SU. As a member of the advanced characterization nanotechnology platform, JAEA promotes the nanotechnology platform in Japan with support from the Ministry of Education, Culture, Sports, Science and Technology (MEXT). Specifically, JAEA established shared-use of advanced characterization equipment. This experimental end-station is widely used for research on physical properties, functions of material surfaces, and mechanisms of surface reactions.

The difference between the bcc phase and fcc/bcc phase for hydrogen adsorption/absorption was investigated by *in situ* SR-XPS for a PdCu alloy, which is a potential catalyst and hydrogen storage material [1]. Although the initial hydrogen adsorption does not impact the structure, the bcc phase exceeds the hydrogen diffusion rate

compared to the bulk. The reaction site and hydrogen adsorption/absorption mechanism for the temperature dependence of surface segregation are related.

Gallium nitride (GaN) is an important material for the development of future power electronic devices. Several studies on the insulating properties of AlGaN/GaN, physical and electrical properties of AlGaN/GaN with AlON, and AlGaN/GaN with the oxidized AlGaN were conducted by SR-XPS [2-4].

To realize ultralarge-scaled integrated circuits, it is important to elucidate the mechanisms of oxide formation/decomposition on Si crystal surfaces. SR-XPS and scanning tunneling microscopy were applied to study the thermal stability and decomposition processes of SiO₂ films formed on Si(110) surfaces [5,6].

Nanoparticles (NPs) are interesting materials because they exhibit different properties from the bulk such as a catalytic function. The chemical states of NP surfaces were studied by SR-XPS. Gold nanoparticles (AuNPs) prepared by plasma methods using 5 mM CsCl aqueous solution have Cs–Au, Cl–Au, and Cs–Cl–Au bonds near the surface at a depth of approximately 1.2 nm, whereas Cs–Cl–Au bonds occur in the deeper region below 2.5 nm [7].

Two kinds of organosilica NPs fabricated from thiol-containing precursors, (3-mercaptopropyl) trimethoxysilane (MPMS) and (3-mercaptopropyl) methyltrimethoxysilane (MPDMS), are promising as drug delivery vehicles. However, there is little information about their biodegradation properties based on chemical analysis. Therefore, the chemical states after the reaction between organosilica and

glutathione (GSH) were analyzed by SR-XPS. The disulfide bond on the surface layer of MPDMS NP decomposes (is reduced) by GSH, indicating that it has a biodegradable function for nanomedicines [8]. As described above, studies on the reactions and chemical analysis of the surfaces and interfaces of various functional materials have been carried out at the real-time photoelectron spectroscopy end-station.

3. Biophysical spectroscopy station

The biophysical spectroscopy station at the BL23SU focuses on various photochemical processes on biomolecules caused by soft X-ray excitation from the viewpoint of radiation damage to DNA. The station consists of two experimental apparatuses, an X-band EPR (SLEEPRS: Synchrotron Light Excited EPR Spectrometer) and a quadruple mass spectrometer (QMS). SLEEPRS allows transient radical species to be investigated at a DNA damage site *in situ* for the first time [9]. The photon stimulated desorbed ions from the irradiated DNA are pursued by QMS. In addition to these apparatuses, we installed an apparatus for liquid microjet for photoelectron spectroscopy during the beamtime as a collaboration between QST and the Tokyo University of Agriculture and Technology [10]. These unique spectrometers will identify the physicochemical pathways to DNA base damage and strand breaks, which are thought to induce genetic effects such as mutations and cancer.

To reveal the role of hydration in the physicochemical process of DNA strand breakage, we investigated the decomposition of deoxyribose (dR) induced by *K*-ionization of oxygen utilizing photon-stimulated ion desorption during the irradiation of synchrotron soft X-rays to hydrated

dR films. Water molecules surrounding a dR suppress the Coulomb repulsion. Hence, dR undergoes extensive molecular decomposition [11]. Although we obtained insight into the ultrafast (~10 fs) proton transfer after *K*-ionization from a molecular dynamics simulation, little is known about the molecular structure produced as a result of *K*-ionization.

To analyze the molecular structure of the products, we observed the oxygen *K*-edge XANES spectra before and after *K*-ionization. Hydrated dR films were prepared by exposing water vapor to the cooled dR film surface. XANES spectra were obtained by measuring the sample drain current. The XANES spectrum obtained after the ionization shows an increment of $\pi^*(C=O)$ peak (around 532 eV) intensity and a decrement of $\sigma^*(C-O)$ (around 538 eV). In addition to these spectral changes, characteristic peak structures occur in 534–536 eV. These peaks, which are assigned to a production of carboxyl group by the ionizations, are not observed by the ionizations of dry dR film. The aldehyde group should be produced by hydrolysis with hydration water, while the carbonyl group should be produced after the fragmentation of dR. The aldehyde can then react with a nearby water molecule to afford a carboxyl group. This structure might be formed at the strand-break termini of DNA due to radiation damage. When this structure is produced in a DNA molecule, a hydroxyl group remains at the strand-break terminus.

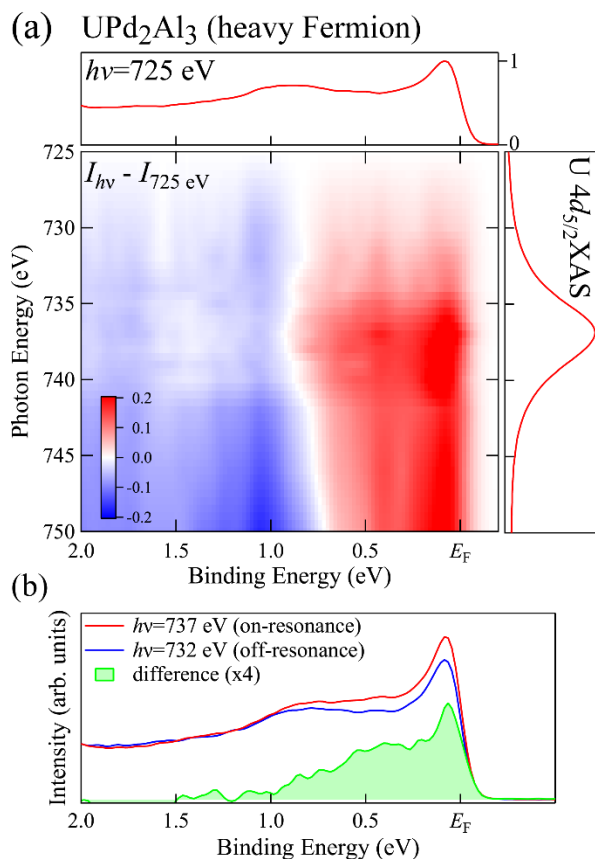


Fig. 1. RPES spectra of UPd_2Al_3 . (a) Density plot of RPES spectra together with the U $4d_{5/2}$ XAS spectrum. (b) On- and off-resonance spectra measured at $h\nu = 737$ and 732 eV, respectively, and the corresponding U $5f$ difference spectrum.

This hydroxyl group can easily be repaired by a glycosylase enzyme. By contrast, the direct effect of ionizing radiation on dry films can produce a β - δ -SSB terminal structure. This structure is irreparable when an 8-oxo-7,8-dihydroguanine moiety is in the vicinity of the strand breakage. Consequently, hydration water may play a role in generating a repairable structure at the strand-break terminus rather than an irreparable structure upon K -shell ionization of oxygen [12].

4. Actinide science stations

The RI laboratory building has a photoelectron spectroscopy station and a soft X-ray magnetic circular dichroism (MCD) station. Additionally, a newly developed scanning transmission X-ray microscopy (STXM) station has been commissioned.

In the photoelectron spectroscopy station, photoelectron spectroscopy studies for strongly correlated materials such as actinide and rare-earth compounds are conducted. We discovered that there is a finite resonant enhancement of the U $5f$ signals in the U $4d$ - $5f$ resonant photoelectron spectroscopy (RPES) [13]. For more than 20 years, its existence has not been confirmed. We utilized the RPES to image the U $5f$ electronic structure of uranium (U) compounds and revealed the nature of the electron correlation effect in the U compounds for the first time (Fig. 1) [13]. The angle-resolved photoelectron spectroscopy (ARPES) experiments for an Eu-based compound were also conducted, and the changes in its electronic structure due to the antiferromagnetic transition were observed [14]. The result is a peculiar case where the antiferromagnetic transition is clearly detected by the ARPES experiment as the folding of the Brillouin zone in the momentum space.

At the soft X-ray magnetic circular dichroism (XMCD) experimental station, we promote a wide range of research on the magnetic properties of U compounds, strongly correlated electron systems, functional magnetic materials, etc. [15-17]. To investigate the complicated magnetism of U compounds, we have recently focused not only on magnetic properties of the U atom but also on those of other elements, including non-magnetic ones [15, 16]. For example, in the case of UCoAl , which shows

a metamagnetic transition at low temperatures, distinct differences in the temperature and magnetic field dependence of the magnetic properties are observed between the U 5*f* and Co 3*d* electrons, suggesting that the Co 3*d* electrons play an important role in the magnetism of this compound [15].

We also introduced a remarkable study in the field of spintronics. A group at The University of Tokyo investigated the thickness dependence of the magnetic properties on the (Ni_{1-x}Co_x)Fe₂O₄ film. They revealed that a spinel ferrite film on a Si substrate with only a few nm thickness possesses ferrimagnetism [17]. It is expected to exhibit a strong spin-filter effect, which can be used for efficient spin injection into Si.

The XMCD apparatus in the RI laboratory was relocated toward upstream of the beamline in January 2019 to make room for STXM. STXM will investigate materials generated through the Fukushima-Daiichi Nuclear Power Plant accident on Mar. 11, 2011. The STXM apparatus was newly equipped at the terminal position of the beamline in March 2019. There are two apparatuses, XMCD and STXM, being commissioned.

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