BL07LSU
The University-of-Tokyo Outstation Beamline for Materials Science

The soft X-ray undulator beamline BL07LSU was constructed by the Synchrotron Radiation Research Organization [1], The University of Tokyo, at the long-straight section of SPring-8 and devoted to joint research with domestic and international researchers since 2009B. In this article, we report the status of the beamline and introduce selected achievements at the experimental stations.

1. Undulator beamline

The high-brilliant soft X-ray undulator beamline, SPring-8 BL07LSU, generates the synchrotron radiation beam of (1) hv: 250-2000eV, (2) E/ΔE: > 10,000, (3) spot-size: < 10μm（zone-plate: 70nm）, (4) flux: 10^{12}photons/s, and (5) variable light polarization. Since 2012B, the beamline offers continuous polarization switching at a frequency of 13 Hz for user experiments at the end-stations.

2. Experimental stations

In 2021, there were five different end stations at the beamline: (1) time-resolved soft X-ray (TR-SX) spectroscopy, (2) ambient-pressure X-ray photoelectron spectroscopy (AP-XPS), (3) 3D nano-ESCA, (4) ultrahigh-resolution soft X-ray emission spectroscopy (HORNET), and (5) free port. All the stations are opened for users. Innovative developments of novel soft X-ray experiments, such as imaging or magneto-optical spectroscopy, were conducted at the free-port station. Here, we introduce our achievements with users [2,3].

2-1 TR-SX station: *Operando* X-ray photoelectron spectroscopy during oxygen permeation at a surface

Oxygen permeability is a significant functionality of a material for wide applications, such as cathodes in solid oxide fuel cells, solid oxide electrolysis cells, and oxygen separators. Recently, ionic-electronic mixed conductive oxides, such as $La_{0.65}Ca_{0.35}FeO_{3-\delta}$ (LCF), have attracted interest owing to their high oxygen permeability and high generation rate of pure oxygen gas. However, the applications have commonly been required to overcome the issue of slow surface exchange reactions at moderate temperatures (< 600 ºC). Thus, it has been demanded to examine the microscopic picture directly by observing the chemical state at the surface during oxygen permeation.

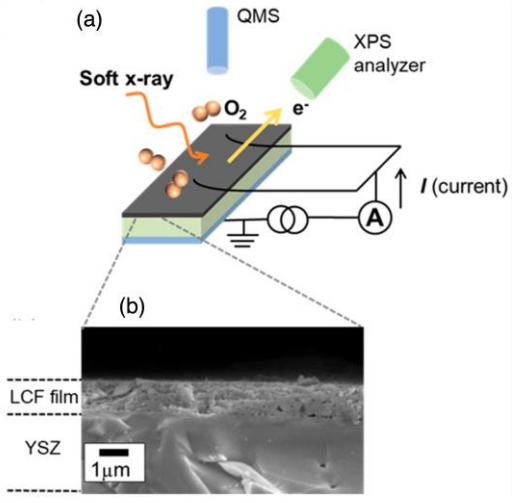

Fig. 1. (a) Schematic illustration of the *operando* XPS setup, where the applied positive current desorbs oxygen from the LCF film surface. (b) Cross-sectional scanning electron microscopy image of the prepared LCF film on yttrium-stabilized zirconia (YSZ).

In the present research, we carried out *operando* X-ray photoelectron spectroscopy (XPS) measurements to quantitatively specify the oxygen species that developed on the LCF film surface during oxygen incorporation and release [1]. The *operando* XPS experiment, as shown in Fig. 1, was carried out with the applied current at 600 °C while monitoring the product gas molecules by mass spectroscopy. The experiment was conducted with the XPS system at the TR-SX station with the Kagomiya group [2].

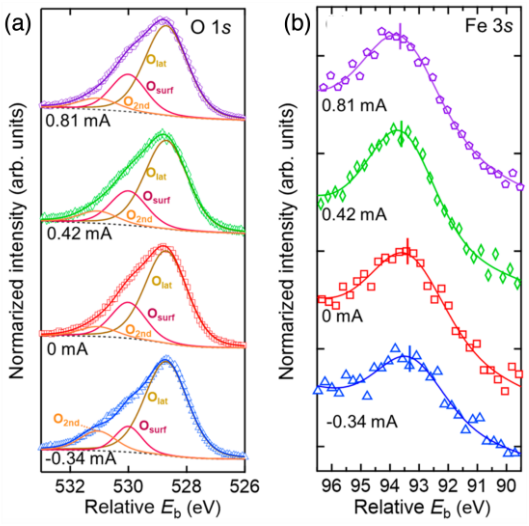

Fig. 2. *Operando* XPS spectra of (a) O 1*s* and (b) Fe 3*s* core levels in the LCF film on YSZ at 600 °C with applied currents. The photon energy was 700 eV. In (a), curve fittings of the peaks were made to decompose components of the chemical species, O_{lat}, O_{surf}, and O_{2nd}.

Figure 2 shows the dependence of the applied current on the *operando* XPS spectra of O 1*s* and Fe 3s core levels at 600 °C. Individual O 1*s* profiles were curve-fitted by the three O 1*s* components of O_{lat}, O_{surf}, and O_{2nd} that are assigned to the atoms in the bulk lattice, surface oxides, and surface secondary phases of impurity, respectively. One can observe systematic variations with current. The peak positions of the Fe 3*s* XPS spectra also shift systematically. These results indicate that, by applying the current from a negative to a positive value, there are significant increases in the numbers of surface oxide species and ligand holes near Fe^{3+} ions on the surface. One can infer that ligand holes in the Fe 3*d*–O 2*p* hybrid orbitals correspond to active reaction sites at which surface oxide species change to oxygen molecules, providing a clue to improve the performance of the oxygen permeability of mixed conductive oxides.

2-2 HORNET station: Resonant inelastic soft X-ray scattering of Heusler alloys in magnetic fields

Half-metallic ferromagnets have been intensively investigated in the field of spintronics since half-metallic electronic structures were theoretically predicted in some half-Heusler and full-Heusler alloys in the 1980s. When the electrons around the Fermi level (E_F) are completely spin-polarized, they are very useful as a ferromagnetic electrode for spin injection and tunnel magnetoresistance as well as in various spin-utilizable devices. Recently, the electronic structures of the Mn_2VAl Heusler alloy of bulk single crystal and its magnetic circular dichroism (RIXS-MCD) have been successfully detected by resonant inelastic X-ray scattering in an external magnetic field [4,5]. Systematic studies of RIXS-MCD have also been performed on Co_2MnSi [6], Co_2FeSi, and Co_2MnGa Heusler alloys.

The RIXS measurements were performed at room temperature at the HORNET station using left and right circularly polarized light. An external

magnetic field of 0.25 T was applied by a magnetic circuit with a permanent magnet (Fig. 3). The total energy resolution was set to ~200 meV.

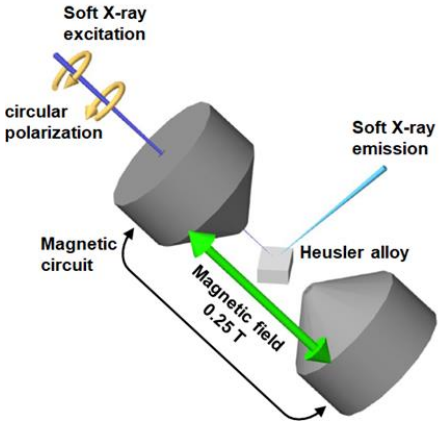

Fig. 3. Geometry of RIXS experiments under a magnetic field.

Figure 4 shows the intensity plots of the RIXS-MCD spectra given by $\mu^+-\mu^-$ at the Mn $2p_{3/2}$ edge for the ferrimagnet Mn_2VAl and ferromagnet Co_2MnSi [5,6], where μ+ and μ− represent RIXS spectra in parallel and antiparallel configurations between the light helicity and the direction of the magnetic field (Fig. 3). Significantly different features of RIXS-MCD are observed between the two alloys. Since the half-metallic gap of Mn_2VAl opens on the up-spin side, the negative RIXS-MCD signals of Mn_2VAl can branch off from the elastic line due to the spin-polarized electronic structures for the spin-down sub-band around E_F. Moreover, the antiparallel spin coupling between Mn and V in ferrimagnetic Mn_2VAl induces the opposite order of the core-level Zeeman splitting for Mn and V $2p_{3/2}$ (not shown) states. This is attributed to the reversed RIXS-MCD contrast between the Mn and V edges of Mn_2VAl, and the gap of the m_j = +3/2 components at the V $2p_{3/2}$ edge (not shown) reflects the up-spin band gap of the V 3*d* PDOS of Mn_2VAl.

It is practically important that RIXS-MCD directly probes which spin sub-bands open the half-metallic gap as observed in the difference between Co_2MnSi and Mn_2VAl, giving important information to design spintronic devices.

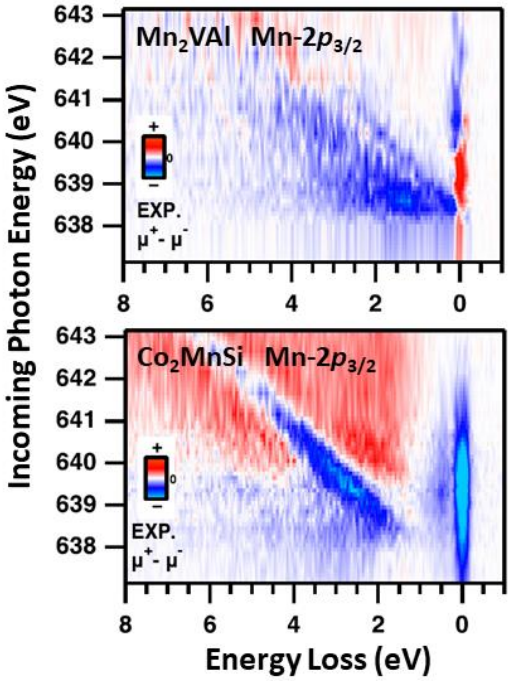

Fig. 4. Intensity plots of RIXS-MCD spectra for Mn $2p_{3/2}$ edge in (a) Mn_2VAl and (b) Co_2MnSi Heusler alloys [5,6].

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