

ISSP

**ACTIVITY
REPORT
OF
SYNCHROTRON
RADIATION
LABORATORY**

2014

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Preface

The Synchrotron Radiation Laboratory (SRL) in Institute for Solid State Physics (ISSP) has been taking part in the Synchrotron Radiation Research Organization (SRRO) of the University of Tokyo since 2005 and operating a new beamline (BL07LSU) at the SPring-8 and experimental apparatuses in soft X-ray region. The beamline has a 27m-long polarization-controlled undulator and a monochromator covering the photon energy range from 250 eV to 2 keV, which was fully opened to users since 2009. The members of solid state spectroscopy group of SRL play an essential role to promote advanced materials sciences utilizing high brilliance SR from the new undulator. In FY 2010, they have succeeded to measure time-resolved photoelectron spectroscopy of the surface photo-voltage in Si surface with the time-resolution of 30 ps by utilizing the time-structure of synchrotron radiation and an ultra-fast laser. In FYs 2011 and 2012, energy resolution of soft X-ray emission spectroscopy becomes 10,000 and the spatial resolution of the scanning photoelectron microscope (3D nano-ESCA) is better than 70 nm. In 2014, they succeeded to operate the undulator to use the circular and parallel polarization light. The first aims of BL07LSU have been achieved already. The SRL-ISSP and SRRO contribute the cutting-edge basic sciences and the applied sciences using synchrotron radiation.

August, 2015

Shik Shin
Director of SRL-ISSP

Activity Report2014

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Publication List

1. Status of Beamline BL07LSU at SPring-8

The University-of-Tokyo high-brilliance synchrotron soft X-ray outstation beamline BL07LSU at SPring-8 has been maintained by the permanent staff members with adjuncts for user operations. A scientific aim of the beamline is to promote advanced spectroscopy for solid state and soft materials. There are currently three regular endstations: time-resolved soft X-ray spectroscopy (TR-SX spectroscopy), 3D-scanning photoelectron microscope (3D nano-ESCA) and ultrahigh resolution soft X-ray emission spectroscopy (HORNET), along with a free port station for users who bring their own experimental apparatus.

In 2014, permanent magnet and electromagnet phase shifters were commissioned, to offer circular polarization mode over the whole photon energy range of 250–2000 eV and for fast polarization switching, respectively. The gaps of the permanent magnet phase shifters for the circular polarization mode were determined using an ellipsometer and the circular polarization mode was released to users since November 2014. Air core coils for orbit correction to the electromagnet phase shifters were installed into the both end of the ID section in the SPring-8 storage ring at the spring of 2014. After several machine studies, the orbit corrections for both DC and AC pattern operations of the electromagnet phase shifters have become available since June 2015. Finally experiments using fast polarization switching are ready to be conducted.

At the beamline endstations, various scientific researches were carried out by both the laboratory staff and general users (G-type application). Below are brief introduction of recent activities at each station.

(1) Time-Resolved soft X-ray spectroscopy station (TR-SX spectroscopy)

The station is to perform time-resolved photoemission spectroscopy experiments by synchronizing the high-brilliant soft x-ray and the ultra-short laser pulses. A new type of the electron spectrometer, the two-dimensional angle-resolved time-of-flight (ARTOF) analyzer, has been used for the efficient time-resolved measurements and a low temperature manipulator (15 K) is installed for extensive experiments for users. In 2014, we further developed a time-resolved measurement system for samples at temperature as high as 900°C and a pumping laser system for repetition frequency of the MHz-range. Users have performed time-resolved photoemission measurements especially on optical functional materials, such as for solar cells and for photocatalysts. The temperature dependence of the surface photovoltage effect was revealed for a silicon crystal. For experiments on the adsorbed surfaces, chemical selectivity of core-level photoemission spectroscopy allows one to trace carrier dynamics in adsorbates and in substrate separately. In a case of fullerene molecules on a titanium dioxide surface, for example, optical response and the subsequent relaxation was found to be different from each other. While understanding of carrier dynamics have been one of the challenging issues in condensed matter physics, a series of the time-resolved data, accumulated by users, has captured the universal trends and the theoretical models have also been developing at the station.

(2) 3D-scanning photoelectron microscope (3D nano-ESCA)

The endstation is for three-dimensional (3D) spatially resolved electron spectroscopy for chemical analysis (ESCA). In order to enable operando nano photoemission spectroscopy of green nano-devices, we have installed a semiconductor parameter analyzer for electrical properties measurements during SR nano analysis. The first example is graphene FETs where hole doping by negative biasing to the back gate was clearly observed and C 1s binding energy shift corresponding to Fermi level shift depending on gate voltage was well correlated with the theoretical calculation based on gate insulator capacitance and linear density of states of graphene. The second example is organic FETs with C10-DNBDT 3ML ultrathin film with back gate where hole doping was also observed during device operation, and measured drain current proportional to hole concentration doped by field effect was well explained by the Boltzmann distribution using chemical potential as a function of gate voltage. Furthermore, unique line profiles of potential across the channel region (5 micron) from source to drain were observed depending on the micro-domain in the channel. Thus, operando nano-spectroscopy is opening up new prospects which would provide useful information in development of nano-devices.

(3) Ultra high-resolution soft X-ray emission spectroscopy (HORNET)

The station is for soft X-ray emission spectroscopy measurements with ultra high-resolution ($E/\Delta E > 10^4$) and under various environmental conditions (gas, liquid and solid). In 2014, a differential pumping system for windowless atmospheric pressure experiments has been developed. The system was successfully aligned to fully transmit incident soft X-rays. For the XES spectrometer, a thin film window was installed to realize differential pumping while keeping wide acceptance angle of the X-ray emission. Finally XES measurement under 10^4 Pa (0.1 atm) was performed. For the XES study of magnetic materials a set of permanent magnets (~ 0.23 T) were installed and spin polarized electronic structures of VO_2 , CrO_2 and Fe_2O_3 were demonstrated. Using the ultrahigh resolution XES spectrometer, an anisotropic vibrational mode around 100 meV was observed in anatase TiO_2 , which is the direct consequence of the anisotropic polaronic screening mechanism in the dielectric environment of anatase TiO_2 . Another important progress was made on the reduction of radiation damage in XES: Mn 3d states of highly charged Mn atoms in the model system of photosystem II Mn cluster were successfully obtained without radiation damage using an originally developed sample auto-scanning system. Other experiments performed using the HORNET station, also fully utilized the privilege of ultrahigh resolution and in situ/operando spectroscopy.

(4) Free-port station

The station is equipped with a focusing mirror chamber, and users can connect their own experimental chambers. In 2014, the following four experiments were performed at this station: resonant soft x-ray scattering, resonant magneto-optical Kerr effects,

ambient-pressure x-ray photoemission spectroscopy, and two-dimensional photoemission spectroscopy with a display-type ellipsoidal mesh analyzer. Moreover, laser beams from the time-resolved soft x-ray spectroscopy station are available for users and the time-resolved measurements were started for experiments of the resonant soft x-ray scattering and the resonant magneto-optical Kerr effects.

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2. Status of spin- and angle-resolved photoelectron spectroscopy with laser light at LASOR

Spin- and angle-resolved photoelectron spectroscopy (SARPES) is a powerful technique to investigate the spin-dependent electronic states in solids. The Synchrotron Radiation Laboratory (SRL) had developed SARPES systems with synchrotron radiation and had provided opportunities of SARPES experiments at BL19A in KEK-PF until FY 2013. SARPES at this beamline attracted much attention of many users. There was however a lowering of international competitiveness throughout recent years because the performance became outdated. From FY 2014, SRL started a project to construct new SARPES apparatus using laser light instead of the synchrotron radiation in Institute for Solid State Physics.

The new system is designed to provide high-energy and -angular resolution and high efficiency of spin detection for SARPES. Figure 1 represents a schematic drawing of an analysis chamber. The apparatus is equipped a high-energy resolution photoelectron analyzer (VG Scienta, D80 analyzer) with deflectors (VG Scienta, DA30L) that enable us to collect photoelectrons in the $(\theta_x \times \theta_y) = (30^\circ \times 20^\circ)$ cone acceptance without sample rotation. The apparatus is also equipped two high efficient spin detectors associating very low energy electron diffraction (VLEED), which allows us to analyze the three-dimensional spin polarization of electrons. The electrons are excited with 6.994 eV photons, yielded by 6th harmonic of a Nd:YVO₄ quasi-continuous wave laser with repetition rate of 80 MHz. A He discharge lamp (VG Scienta, VUV5000) is also available as a photon source. Samples are cooled

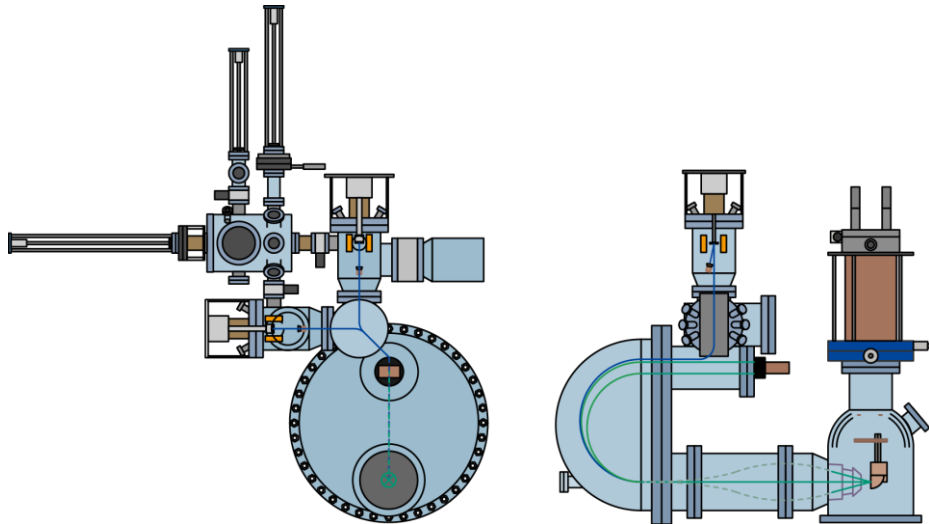


Fig. 1. Schematic drawing of the SARPES apparatus at LASOR in ISSP. Green and blue curves represent the trajectory of the photoelectrons to MCP for normal ARPES and to the VLEED spin polarimeter for SARPES, respectively.

by the liquid He cryostat below 9 K.

The normal ARPES can be performed with imaging-type detection with the energy resolution of 700 μeV . For SARPES mode, the energy resolution of 1 meV is achieved, which is the best performance in the world. The users can select suitable energy resolutions between 1 and 20 meV.

The experiment station also consists of an MBE chamber and a carousel chamber connected to a load-lock chamber. At the MBE chamber, samples can be heated by a direct current heating or electron bombardment, and cooled by a liquid N₂ cryostat below 120 K. The surface evaluating and preparing instruments, such as evaporators, LEED, RHEED, Sputter-gun, quartz microbalance can be installed. At the carousel chamber, 16 samples can be stocked in the ultra-high vacuum environment.

The new SARPES system is utilized to obtain precise information on spin-dependent electronic structures near the Fermi level in solids. Joint research at this station has been started from FY 2015.

3. Workshops & Meetings

ISSP workshop “Toward a paradigm shift of synchrotron radiation based materials science in the VUV-SX region”

Date: 2014/9/20(Sat)-2014/9/21(Sun)

Place: Lecture Room (A632), 6th Floor, ISSP, the University of Tokyo

In order to encourage a motivation and discussions that demand an internationally competitive vacuum ultra-violet - soft X-ray (VUV-SX) light source in Japan in addition to the present synchrotron light sources, it is now necessary to accelerate mutual communications not only within the present VUV-SX community but also with broad scientific community. This workshop was held aiming to boost a paradigm shift of synchrotron radiation based materials science and further of all the scientific community in Japan by broad-ranging discussions beyond the concept of community such as ultra-violet, soft X-ray, hard X-ray and even inside/outside synchrotron radiation. The program was categorized into four sessions by “catalyst/battery”, “soft matter/biomaterial”, “solid and surface physics” and “materials science” and representative or energetic and pioneering young researchers in each field were selected as speakers of review-talks. In all sessions there were a lot of questions and comments, regarding such as new scientific directions by a combination of different synchrotron techniques, actual scientific requests for the energy/spatial resolution that much exceed the ability of the present synchrotron techniques, possible collaborative synchrotron and neutron studies and so on. The workshop dealt with issues mostly aiming at real applications, thus it was unique among workshops held in ISSP and will contribute to establish a new scientific trends in ISSP.

Program

2014/9/20(Sat)

13:00- **Opening Address**

Hitoshi Takigawa (ISSP, The University of Tokyo)

13:10- **Materials design and characterization for next generation rechargeable batteries**

Atsuo Yamada (The University of Tokyo)

13:45- **Size-distribution analysis and electron density mapping of functional particles by coherent X-ray diffraction**

Yukio Takahashi (Osaka University)

14:20- **Materials for rechargeable Li and Na batteries**

Shinichi Komaba, Kei Kubota (Tokyo Univ. of Science, Kyoto Univ.)

14:55- **Photocatalytic Hydrogen Production from Water**

Kazunari Domen (The University of Tokyo)

15:30- Coffee Break

15:45- **Structure and Properties of High-performance Polymer Networks**

Mitsuhiro Shibayama (ISSP, The University of Tokyo)

16:20- **Many-electron wave function of the photosynthetic Mn₄CaO₅ cluster computed from density matrix renormalization group theory**

Takeshi Yanai (Institute for Molecular Science)

16:55- **Nano-devices using Macromolecular Metal Complexes**

Mutsumi Kimura (Shinshu University)

17:30- **Liquid Structure and Hierarchy**

Hajime Tanaka (The University of Tokyo)

2014/9/21(Sun)

9:40- **Role of Synchrotron Radiation on the Study of Strongly Correlated Electron Systems**

Takami Tohyama (Tokyo University of Science)

10:15- **Exploration for novel multiferroics and magnetoelectric phenomena**

Tsuyoshi Kimura (Osaka University)

10:50- New 2D electron systems created at interfaces and their functions

Yoshihiro Iwasa (Univ. Tokyo & RIKEN CEMS)

13:00- Cutting Edge Electronic Devices by Novel Oxide Materials

Hideo Hosono (Tokyo Institute of Technology)

13:35- Overview of development of spintronic devices

Teruo Ono (Institute for Chemical Research, Kyoto University)

14:10- Molecular Design of 5f elements selective ligands, and challenge for disposal of radioactive wastes

Tsuyoshi Yaita (JAEA)

14:45- Applications of first principles calculations for fundamental issues of structure materials

Isao Tanaka (Kyoto University)

15:20- Recent Development Plasma Nano-processes and Expectations for Radiation Light Experiments

Hiroki Kondo, Masaru Hori (Plasma nanotechnology research center, Graduate school of engineering,

16:00- Closing Address

Hiroshi Kondo (Keio University, VSX Users' Organization)



ISSP workshop “Status of SPring-8 BL07LSU and prospects for the next generation synchrotron light sources”

Date: 2015/3/5(Thu)

Place: Lecture Room (A632), 6th Floor, ISSP, the University of Tokyo

Synchrotron radiation laboratory has a Harima branch to maintain and develop a high-brilliance soft X-ray beamline BL07LSU at SPring-8. There we are performing time-resolved, spatial-resolved and energy-resolved soft X-ray spectroscopy to study electronic states and their dynamics of new materials. In this workshop, recent research activities at our beamline were reported and our future prospects toward the next generation synchrotron light sources were discussed. The speakers talked about their recent results from each end station (time-resolved spectroscopy, 3D nano-ESCA, emission spectroscopy, and so on).

There were two invited talks; one is about synthesizing new materials and the advantage of using synchrotron x-rays for this synthesis process, and the other is about the upgrade plan of the light source to SPring-8 II. There were a lot of discussions for each talk, and we successfully started to obtain a clear vision about how we can utilize the next generation synchrotron light sources for the condensed-matter research. We also encouraged the young generation in this research field by awarding the best poster prizes to two graduate students.

Program

- 10:00- **Opening Address** Hiroshi Kondo (Keio University, VSX Users' Organization)
10:05- **Guest Address** Yoshiharu Doi (JASRI)
10:10- **Introduction** Yoshiyuki Amemiya (The University of Tokyo)
10:20- **Development of Polarization-Controlled Undulator and Frontier Experiments at SPring-8 BL07LSU** Iwao Matsuda (ISSP, the University of Tokyo)
10:45- **Systematic charge distribution changes in Bi and Pb perovskites** Masaki Azuma (MSL, Tokyo Tech)
11:25- **Poster short Presentation**
11:50- **lunch**
13:00- **Poster session**
14:00- **Local electronic structure analysis of nano-devices: towards *operando* nano-analysis** Masaharu OSHIMA (SRRO, The University of Tokyo)
14:30- **Application of external fields and *operando* condition: novel soft X-ray emission spectroscopy** Yoshihisa HARADA (ISSP & SRRO, The University of Tokyo)
15:00- **Studying magnetism by using polarization of x-rays** Hiroki Wadati and Iwao Matsuda (ISSP & SRRO, Univ. of Tokyo)
15:30- **SPring-8 Upgrade Plan**
- **Practical Approach towards High Coherence Ring-based Light Source -** Takahiro Watanabe (Japan Synchrotron Radiation Research Institute (JASRI))
16:30- **Carrier dynamics on surfaces studied by time-resolved soft x-ray photoelectron spectroscopy: Present status and future prospect** Susumu Yamamoto (ISSP, University of Tokyo)
16:50- **Operando Spectromicroscopy on 2D Electron Devices by Using 3D nano-ESCA** Hirokazu Fukidome (Research Institute of Electrical Communication, Tohoku University)
17:10- **Electronic-Structure Analyses for Secondary-Battery Electrodes by Electrochemical Operando Soft X-ray Emission Spectroscopy** Daisuke Asakura (AIST)
17:30- **Creating Novel Functional Materials by Clarifying Local Electronic States and 3-Dimensional Atomic Structures at the Active Sites** Hiroshi Daimon (NAIST)
17:50- **The construction of ambient pressure photoelectron spectroscopy at SPring-8 BL07LSU** Jun Yoshinobu (ISSP, The University of Tokyo)
18:10- **Closing address** Shik Shin (ISSP, the University of Tokyo)

4. Seminar

Date: April 4, 2014

Title: Modulation of bond density between ligand and transition-metal ions in Stripe-like order of IrTe_2 revealed by resonant soft x-ray scattering

Speaker: Dr. Dr. Kou Takubo (ISSP, the University of Tokyo)

Date: April 25, 2014

Title: Analysis of the topmost structure of crystal surfaces by using TRHEPD

Speaker: Dr. Izumi Mochizuki (KEK-PF)

(ISSP Colloquium)

Date: July 17, 2014

Title: Novel magnetic structures revealed by resonant soft x-ray diffraction

Speaker: Dr. Hiroki Wadati (ISSP, the University of Tokyo)

(ISSP Lectures by Visiting Professors)

Date: October 16, 2014

Title: Dynamics of Structure and Electronic States of Two-dimensional Phases on Solid Surfaces

Speaker: Dr. Tadashi Abukawa (IMRAM, Tohoku University)

Date: November 12, 2014

Title: Electronic States and Carrier Dynamics of Titania Photocatalyst

Speaker: Masato Emori (Sophia University)

Date: November 20, 2014

Title: Electronic properties of ladder-type iron-based compound AFe_2X_3 ($\text{A}=\text{Ba}, \text{Cs}$;

Speaker: Dr. Yasuyuki Hirata (ISSP, the University of Tokyo)

(LASOR Seminar)

Date: November 26, 2014

Title: Ab-initio Many-Electron Calculations for Transition Metal $\text{L}_{2,3}$ X-ray Absorption and Resonant Inelastic X-ray Scattering

Speaker: Dr. Hidekazu Ikeno (Osaka Prefecture University Nanoscience and Nanotechnology research centre)

(LASOR Seminar)

Date: December 19, 2014

Title: Surface Structure Analysis by the Electron Diffraction Patterson Map Method

Speaker: Dr. Tadashi Abukawa (IMRAM, Tohoku University, ISSP Visiting Associate Professor)

Date: January 13, 2015

Title: Anion doping into oxide thin films by topotactic synthesis

Speaker: Dr. Akira Chikamatsu (Faculty of Science, the University of Tokyo)

Date: January 16, 2015

Title: Carrier dynamics in metal oxides: bulk, surface, and nanocell

1, Wendy R Flavell(School of Physics & Astronomy and Photon Science Institute, The University of Manchester).

Title:Unravelling the mysteries of solar nanocells using synchrotron radiation and laser techniques

2, Ryu Yukawa(School of Science, the University of Tokyo)

Title:Electronic Structures and Carrier Dynamics at Metal Oxide Surfaces

3, R. Arita(Institute of Laser Engineering, Osaka University)

Title: ZnO luminescence research for potential in-situ EUV imaging device and fast-response time scintillator applications

OPERANDO NANO-SPECTROSCOPY FOR ENERGY EFFICIENT, POWER GENERATION AND ENERGY STORAGE DEVICES

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In order to investigate pin-point electronic structure in green nano-devices such as energy efficient devices like ReRAM and graphene FET, power generation devices like fuel cells and photocatalysts for hydrogen generation and energy storage devices like Li/Na ion batteries during device operation, we have developed soft X-ray scanning photoelectron emission microscopy with an angle-resolved electron analyzer (3D-nano-EASCA) where different voltages can be independently applied to five electrodes for gate, source, drain and ground in a sample holder connected to a semiconductor parameter analyzer. The spatial resolution was determined to be 70 nm [1].

The first example for energy efficient devices is graphene FET with a back gate structure for nano-spectroscopy in collaboration with Prof. H. Fukidome and Prof. K. Nagashio. The line profile analysis of the C 1s peak (sp^2) in the channel across the graphene-Ni electrode interface clearly demonstrates the existence of the charge transfer region [2]. Furthermore, we discovered the linear band dispersion in graphene FET for the first time by direct observation of p-type doping feature under back gate biasing [3].

The second example for energy efficient devices is organic FET which has attracted great attention because of their unique properties such as light weight, flexible electronics and low cost. Prof. J. Takeya's group succeeded in developing good performance OFETs using single-crystalline C10-DNBDT-NW films on SiO₂ (200 nm)/Si substrates [4]. In this study, OFETs for *operando* nano-spectroscopy were fabricated using ultrathin (3ML or 12 nm) single-crystalline C10-DNBDT-NW films on SiO₂ (200 nm)/Si substrates, with a backgate electrode and top source/drain Au electrodes. C 1s line profiles under biasing at the backgate and drain electrodes were measured. Figure 1 shows schematic of SPEM measurements, (b) Sample holder with five individual electrodes, optical microscope image of OFET, and Au 4f SPEM of OFET. As shown in Fig. 2, this ultrathin OFET exhibits good electrical properties. *Operando* measurements of line profiles of C 1s binding energy across the OFET channel from drain to source, and gate bias voltage dependence of C 1s binding energy and drain current are shown in Fig. 3, suggesting that drain current proportional to hole concentration in the channel generated by the back gate biasing is well correlated by the simple Boltzmann equation with the chemical potential [5]. Furthermore, potential profiles in the channel from source to drain are in good agreement with potential profiles calculated by gradual channel approximation (GCA) [6].

As for power generation devices, we have investigated pin-point electronic structure of photocatalysts for water splitting. Prof. K. Domen's group succeeded in developing a novel water splitting photocatalysts La₂Ti₅CuS₅O₇ (LTC) as a p-type semiconductor electrode with Sc doping, as shown in Fig. 4 [7]. We have analysed each photocatalyst with the size of 350 nm to 1000 nm in diameter and several μ m in length by 3D-nano-ESCA. It is revealed that pin-point valence band spectra shift towards lower binding energy, suggesting successful hole doping probably into Cu 3d band by substituting Ti sites by Sc ions. Investigation on catalyst size dependence of doping efficiency and *operando* valence band analysis are on-going.

Thus, *operando* nano-spectroscopy can provide us with useful information for improving performances of green nano-devices.

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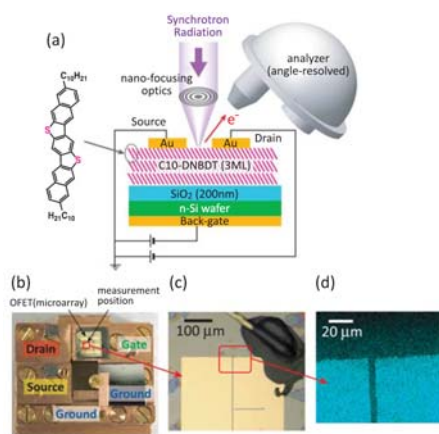


Fig. 1. (a) Schematic of SPEM measurements, (b) Sample holder with five individual electrodes, (c) Optical microscope image of OFET, (d) Au 4fSPEM of OFET.

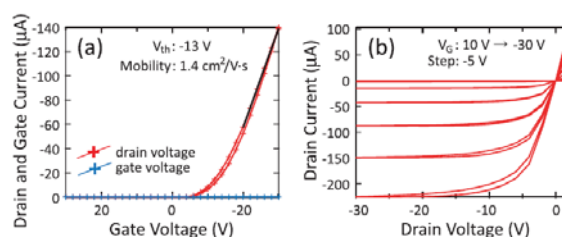


Fig.2. (a) Typical drain and gate current as a function of gate voltage for OFET and (b) Typical drain current as a function of drain voltage at different gate voltage.

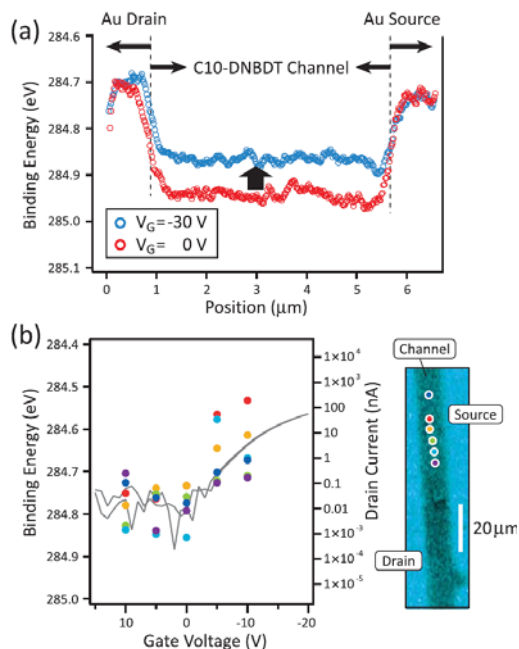


Fig. 3. (a) Operando measurements of line profiles of C 1s binding energy across the OFET channel from drain to source, (b) gate bias voltage dependence of C 1s binding energy and drain current.

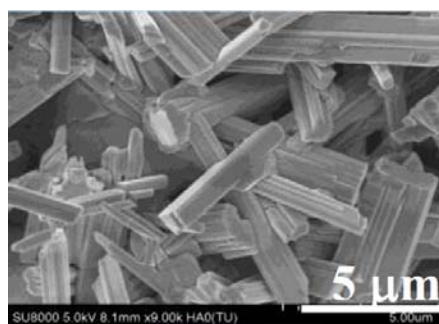


Fig. 4. SEM image of Sc-doped LTC photocatalysts.

DEVELOPMENT OF AMBIENT PRESSURE ANGLE RESOLVED ULTRA-HIGH RESOLUTION RIXS SYSTEM

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We have constructed and developed an ultra-high resolution soft X-ray emission spectrometer with its energy resolution $E/\Delta E > 8000$ optimized in the energy range from 350 eV to 750 eV. We also have developed sample holders not only for solids but also for liquids and gases, enabling both ultra-high vacuum and ambient pressure experiments.

In the FY 2013 we developed a differential pumping system for the incident beam in order to facilitate the use of soft X-ray emission spectroscopy for those who are interested in solution chemistry or chemical reactions under ambient pressure. In the off-line test (Fig. 1) we estimated the optimum vacuum levels for each chamber and determined the aperture size and vacuum pumps. We found the minimum length from the sample to the mirror center required to insert the differential pumping system is 500 mm, and simulated the optical parameters for the vertical post-focusing mirror. Eventually slope error of the mirror less than 0.1" was requested in order to realize the spot size less than 2 μm , which is the requisite to keep the energy resolution $E/\Delta E > 8000$ of the soft X-ray emission spectrometer. We also have started a design study of a rotation stage for momentum dependent soft X-ray emission spectroscopy.



Fig. 1 Off-line test of the differential pumping system for the incident beam.

Using the liquid cell system we performed high resolution resonant inelastic X-ray scattering experiments of liquid water and observed multiple OH stretching vibrational excitation profiles for several excitation energies. Depending on the intermediate species selected by the excitation energy, we found a slight shift of the OH stretching mode energy. As shown in Fig. 2, the energy of the first vibrational excitation for the pre-edge excitation (A) well coincides with that for the gas phase water, strongly suggesting the hydrogen-bond broken picture of the pre-edge peak in the O 1s X-ray absorption, while at post edge excitation the energy is going down from 0.453 eV to 0.426 eV, which again well coincides with that for the ice-like or tetrahedrally coordinated water, in accordance with the ordered hydrogen bond picture of the post-edge feature in the O 1s X-ray absorption. This method is very original and promising because we can directly compare the local structural information from the vibrational profile to the local electronic structure information from the

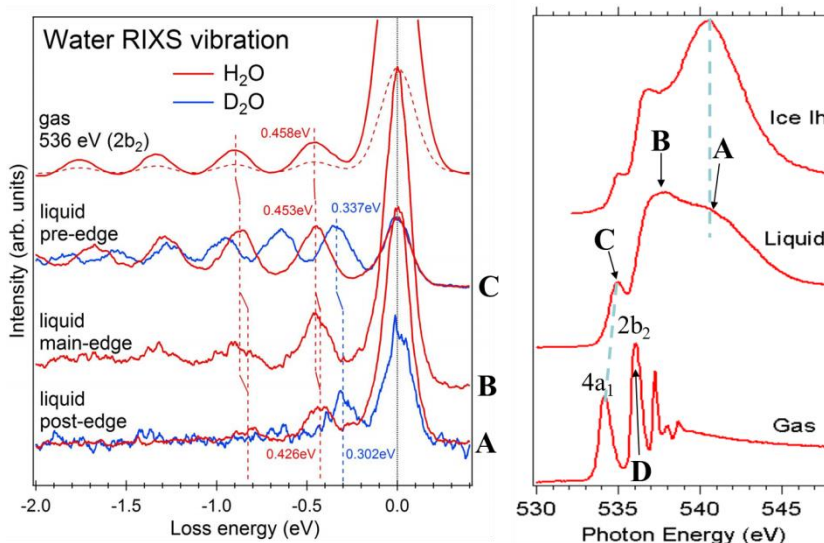


Fig.2 Multiple vibrational excitation in the resonant soft X-ray emission of pure liquid H₂O water obtained at different excitation energies as selected from the peak structures in the X-ray absorption taken by Myneni *et al.*, J. Phys. 14, 213 (2002).

valence band profile in one spectrum. This can easily be extended to the applications like the study on the hydration of solutes and ions in the solution.

Another good example of the application using our system was demonstrated on a series of tetraalkylammonium solutions. Tetraalkylammonium ions have positively charged N ion in the center surrounded by four alkyl chains. The hydrophobic alkyl chains will interact with water by hydrophobic interaction while the central charge will polarize the surrounding water, thereby demonstrating a unique hydration structure. Fig. 3 shows the comparison of the O 1s X-ray emission spectra for pure liquid H₂O water, 0.08 M tetrabutylammonium solution, and 0.5M, 1.0M, 2.0M NaCl solutions. The dense NaCl solutions show a slight decrease of the relative peak height at around 526 eV compared to 527 eV, which is consistent with the hydrogen bond broken picture of the hydrated water around the sodium ions. However, the 526 eV peak of the tetrabutylammonium solution significantly decreases even below the peak intensity at 527 eV. This is surprising considering one orders of magnitude small density of the solute to the sodium ions. The strong distortion of the hydrogen bond in the tetrabutylammonium solution should be related to the multiple function of this ion as a phase transfer catalyst.

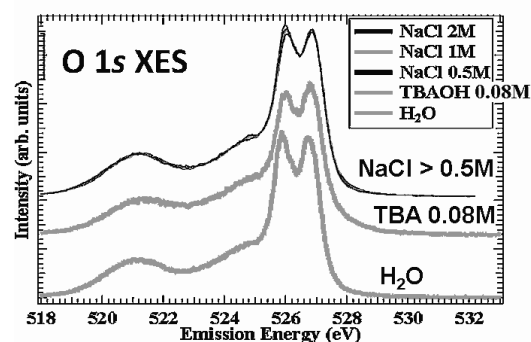


Fig. 3 O 1s X-ray emission of pure liquid H₂O water, 0.08 M tetrabutylammonium (TBA) solution and NaCl solutions at three densities.

DEMONSTRATION OF A L-EDGE RESONANT MAGNETO-OPTICAL KERR EFFECT MEASUREMENT IN AN IRON THIN FILM WITH SUPERCONDUCTING MAGNETS AND A ROTATING-ANALYZER ELLIPSOMETRY

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[Introduction]

Magneto Optical Kerr effect (MOKE) is one of the central issues in the condensed matter physics as well as an elemental technology in a modern society. Traditionally, MOKE using a visible light has been utilized as a magnetic probe and the magnitude of the Kerr angle in visible region for typical transition metals is much less than 1 degree. In contrast, we have discovered a giant magnetic response, which the magnitude of Kerr rotation angle reaches to 50 times larger than that in visible MOKE in a typical 3d transition metal by *M*-edge resonant MOKE measurements [1]. There is a preceding study in which measurement of an *L*-edge MOKE in a longitudinal configuration [2] had been conducted. In this article, we report the result of measurement of *L*-edge resonant MOKE in the longitudinal geometry in an iron thin film for the demonstration using a superconducting magnet and our own detection system called rotating-analyzer ellipsometry (RAE).

[Experiment and Results]

Figure 1a) shows the schematic view of the sample composition. The Ta (2 nm)/Cu(2 nm) capping layer prevents oxidation of the Fe layer. Figure 1b) depicts the geometry for RAE to measure the longitudinal MOKE in which the external magnetic field (± 0.3 T) is applied parallel to the sample surface using superconducting magnet. The magnitude of the applied field is larger than that of the saturation field of the iron thin film. The grazing angle of synchrotron radiation (SR) to the sample is ~ 10 degree. The light reflected from the sample is transferred to the multilayer used as an analyzer and then arrives at the detector, micro-channel plate (MCP). The Kerr rotation angle, θ_K can be experimentally determined with RAE composed of the multilayer and the detector. The intensity of light reflected by the analyzer is monitored at the detector as a function of χ .

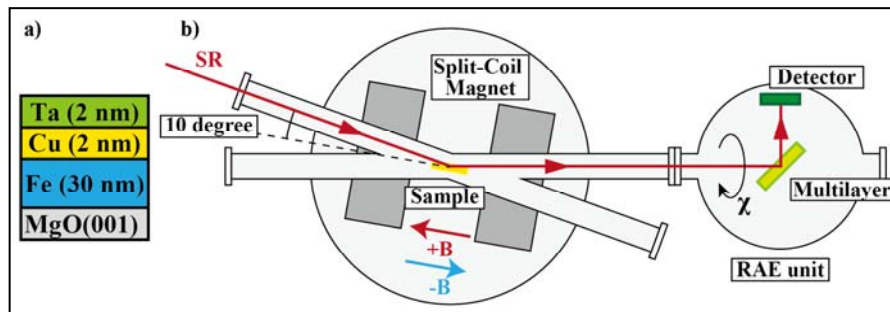


Figure 1: a) A schematic view of a 30-nm-thick Fe film b) Geometry for rotating-analyzer ellipsometry (RAE) to measure the longitudinal MOKE. The magnetic field (± 0.3 T) is applied along the surface.

In Fig. 2 the intensity curves obtained using RAE are shown taken at $h\nu = 709$ eV. The Kerr rotational angle is determined from the difference of the phase shift shown in Fig. 2. The measurement was conducted at room temperature.

In Fig. 2 a), X-ray absorption spectra (XAS) around Fe $L_{3,2}$ -edge is shown for the iron thin film using total electron yield (TEY). The energy range used for the measurement of the Kerr rotation angle is marked by red-coloured area. In Fig. 2 b) the result of the Kerr spectra is shown. The maximum of the Kerr angle is 11.75 degree taken at $h\nu = 710$ eV and the minimum of that is 0.6 degree obtained at $h\nu = 707$ eV, which corresponds to the leading edge of the L_3 absorption edge according to the XAS shown in Fig. 2 a). The error bars come from the each step of rotation angle χ when the curves such as ones in Fig. 2 c) were obtained.

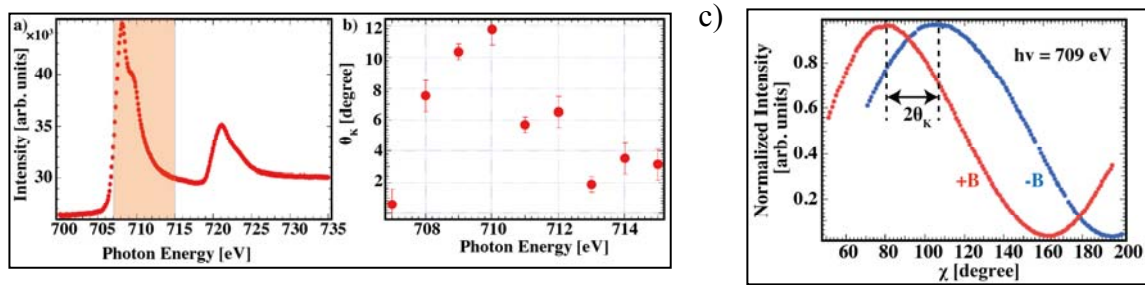


Figure 2: a) X-ray absorption spectra of the Fe film at the $L_{3,2}$ edge. The two resonant L_3 and L_2 peaks originate from the $2p_{3/2}$ and $2p_{1/2}$ core excitations, respectively. b) Photon energy dependence of the Kerr rotation angle, θ_K , of the Fe film. c) Typical results of the intensity variation with rotation angle, χ , taken at $h\nu = 709$ eV.

[Discussion]

Compared XAS with Kerr spectra shown, the Kerr rotation angle is enhanced around the post- L_3 -edge. This tendency is different from the Kerr spectra obtained from the measurement for M -absorption edge of nickel, which the finite Kerr rotation angle exists around the pre-edge because of the effect of quantum interference effect known as Fano effect [1]. The result obtained from our measurement of L -edge resonant MOKE is consistent with the preceding studies in terms of the magnitude of the Kerr angle and the Kerr spectra shape [2].

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ELECTRONIC-LEVEL STRUCTURAL MATERIALS SCIENCE BY ARBITRALLY-POLARIZED-LIGHT HIGH-ENERGY-RESOLUTION TWO-DIMENSIONAL MICROSCOPIC PHOTOELECTRON SPECTROSCOPY

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The main purpose of this study is to develop and establish the experimental methods for structural and electronic states by using two-dimensional microscopic photoelectron spectroscopy so-called DELMA[1,3]. In this beam-time, we have measured the valence band structure of the parent compound of iron-based superconductors BaFe₂As₂ in order to elucidate the orbital character of each bands near Fermi level.

Unlike the high-T_c cuprates, the Fermi surfaces of the iron-based superconductors exhibit a three-dimensional dispersion with multiple bands and orbitals, which are believed to be crucial for the superconductivity. Therefore, it is very important to resolve the atomic-orbital characters of the Fermi surfaces. Since a two-dimensional photoelectron intensity angular distribution (2D-PIAD) obtained by using a polarized synchrotron radiation light allows us to obtain the atomic-orbital characters of the each bands, we have performed the two-dimensional photoelectron spectroscopy (2D-PES) measurements on the parent compound of BaFe₂As₂.

2D-PES measurements were performed at the free port of BL07LSU in SPring-8. The Display-type Ellipsoidal Mesh Analyser (DELMA) combined with an energy analyser (VG SCIENTA R4000) was used to obtain 2D-PIAD patterns.

Figure 1 shows the 2D-PIAD patterns from BaFe₂As₂. A Fe *LMM* Auger PIAD pattern around $E_{kin} = 700$ eV was taken with Fe 2p $\rightarrow$ 3d resonant photon energy of $h\nu = 707$ eV [Fig. 1(a)]. The pattern shows 4-fold symmetry, consistent with the tetragonal crystal structure of BaFe₂As₂. As shown in Fig. 1(b), the PIAD pattern from Ba 4p ($E_{kin} \sim 700$ eV) taken with $h\nu = 900$ eV are different with that from Fe *LMM* Auger, due to the different surrounding atomic-arrangements between Ba and Fe sites. Thus, site-specific photoelectron diffraction (PED) patterns were successfully obtained by DELMA screen.

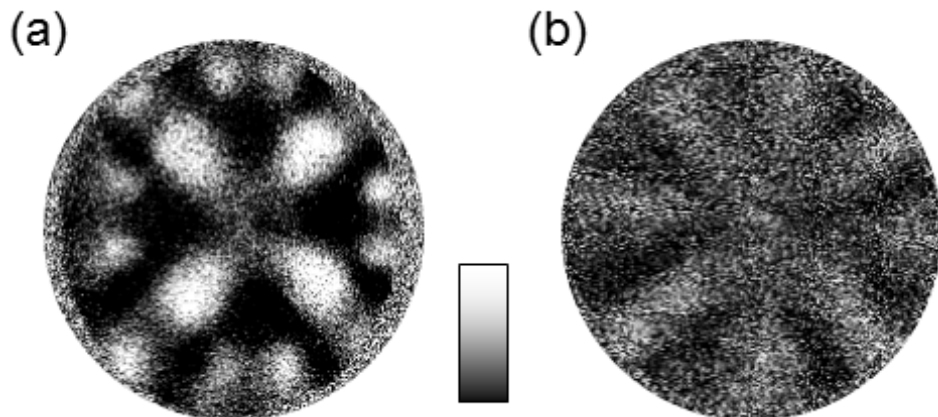


Fig. 1: 2D-PIAD patterns obtained by DELMA screen. (a) PED pattern from Fe sites.

(b) PED pattern from Ba site.

As shown in Fig. 2, energy-dependent 2D-PIAD patterns are obtained by utilizing the combined energy analyser. The 2D-PIAD pattern at $E_{kin} = 702.5$ eV [Fig. 2(b)] is similar to the central part of Fig. 1(a). The patterns change with increasing the kinetic energy [Fig. 2(b-d)]. The pattern at $E_{kin} = 706.5$ eV (near Fermi level) is different from the PED pattern [Fig. 2(b)], indicating the Fermi surface of BaFe_2As_2 . Thus, energy-dependent 2D-PIAD patterns were successfully obtained by the combined energy analyser.

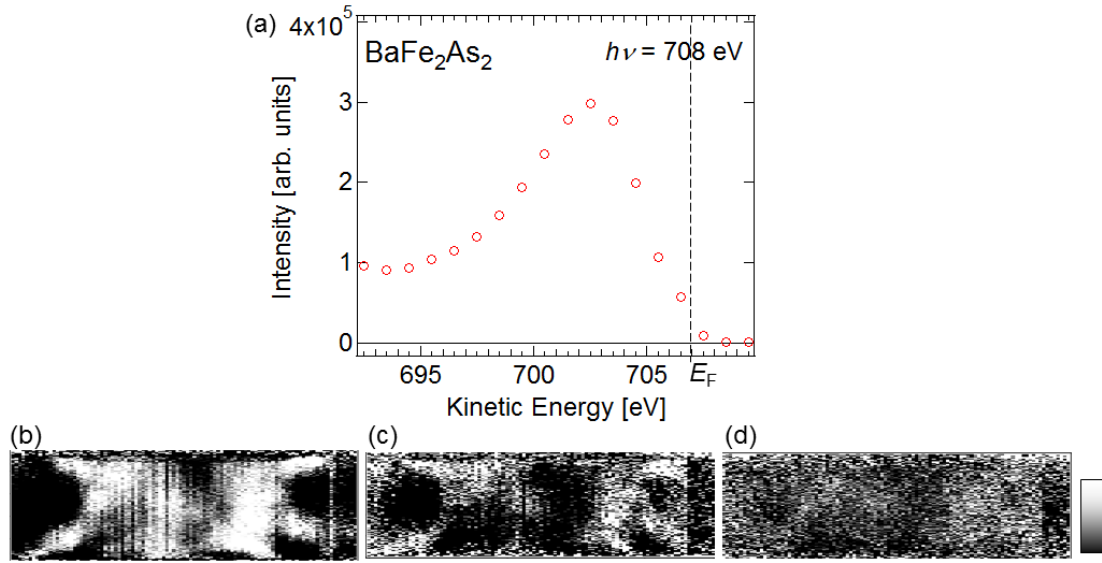


Fig. 2: 2D-PES result obtained by the combined energy analyzer. (a) Angle-integrated PES spectrum. The 2D-PIAD patterns at $E_{kin} = 702.5$ eV (b), 705.5 eV (c), and 706.5 eV (near Fermi level) (d).

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PHOTOINDUCED CARRIER BEHAVIOUR AT THE C₆₀/TITANIA INTERFACE STUDIED BY TIME-RESOLVED PHOTOELECTRON SPECTROSCOPY

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INTRODUCTION

One of key technologies for realizing sustainable society is an efficient conversion of the sunlight into chemical and electrical energies. Titanium dioxide (TiO₂) exhibits a high photocatalytic activity, owing to a high separation rate of electron-hole pairs generated upon light absorption. This property is also ideal for solar cells, whose efficiency is defined by the electrical-power output divided by the irradiance of the incident light and the surface area of the solar cell. One of strategies to enhance the photocatalytic activity and the solar cell efficiency is sensitization of TiO₂ by coating the surface with visible-light sensitive dye molecules [1]. Suppression of the electron-hole recombination rate by capturing the electrons or holes by adsorbed layers is another often employed technique [2]. For adsorbate-decorated composite materials, the charge transfer across the overlayer-substrate interface is an important elemental step to define the performance of the materials. Thus, many theoretical and experimental studies have been devoted to elucidate the interface electronic structure, from which one can predict the charge transfer mechanism by assessing electron- and hole-injection barriers. On the other hand, real-time observations of the carrier dynamics at the interface have been scarce, unfortunately, so that the relation between the interface electronic structure and the charge transfer time has not been established yet. In the present study, we have examined the photogenerated carriers at the rutile TiO₂(110) surface covered with a C₆₀ layer by time-resolved photoelectron spectroscopy (TRPES) and have elucidated how the carriers behave at the C₆₀/TiO₂ interface.

EXPERIMENTAL

The TRPES measurements were carried out at SPring-8 BL07LSU employing a laser-pump/synchrotron-radiation-probe method. For the pump laser, a second harmonic of an amplified Ti:sapphire laser with a 3.06-eV energy was used. The pulse duration and a repetition rate were 35 fs and 1 kHz, respectively. The probe light was provided by a single bunch in an H-mode operation. The pulse width was 50 ps, and a time interval between the pulses was 4.79 μ s. Single crystalline rutile TiO₂ with (110) orientation was used as a substrate. The sample surface was cleaned by annealing and Ar⁺ sputtering until a sharp (1 $\times$ 1) low energy electron diffraction pattern was obtained. C₆₀ (99.5% purity) was deposited on the surface at the sublimation temperature of 680 K while keeping the substrate at room temperature. The thickness of the C₆₀ overlayer was estimated to be 0.9 nm, which is nearly equivalent to a monolayer thickness.

RESULTS AND DISCUSSION

The behaviour of the photoexcited electrons and holes on a semiconductor surface is strongly influenced by a space charge layer. Regarding the clean TiO₂(110) surface prepared in the present study, valence PES spectra show that a valence-band maximum (VBM) lies at 3.35 eV. Taking the band-gap energy of 3.0 eV into account, a strong charge accumulation layer is formed with the magnitude of downward band bending of at least 0.35 eV. As the

surface is being covered with C_{60} , the VBM position is not affected, indicating a weak C_{60} - TiO_2 interaction and an absence of charge transfer across the interface. The highest occupied molecular orbital (HOMO) level of C_{60} is observed at a lower portion of the TiO_2 band gap with a leading edge at 1.80 eV. From the experimentally evaluated VBM of TiO_2 and the HOMO position of C_{60} , together with the band gap energies of TiO_2 and C_{60} (2.2–2.7 eV [3]), an energy level diagram of the band structure of $C_{60}/TiO_2(110)$ is depicted as shown in Fig. 1a. The conduction band minimum (CBM) of TiO_2 is expected at 0.35 eV below the Fermi level, whereas the lowest unoccupied molecular orbital (LUMO) level of C_{60} lies well above the Fermi level.

Fig. 1b shows $Ti\ 2p_{3/2}$ and $C\ 1s$ core-level spectra measured without pump laser irradiation and at 1 ns after laser-pulse irradiation. Although laser irradiation affects the $Ti\ 2p_{3/2}$ peak only slightly, a large shift towards the higher-binding-energy side by 0.25 eV is induced in the $C\ 1s$ peak. Both C_{60} and TiO_2 can absorb the pump laser because the photon energy exceeds the band-gap energies of C_{60} and TiO_2 . The electron-hole pairs generated upon laser absorption are either quenched by a recombination process or spatially separated by drift along the potential gradient in the space charge layer within the TiO_2 substrate or by transfer across the C_{60} - TiO_2 interface. The valence electrons promoted to the LUMO or higher levels of C_{60} can be resonantly transferred to the substrate because these levels overlap the conduction band of TiO_2 . Usually, this type of charge transfer occurs in a femtosecond order [4]. Transfer of the holes in the HOMO level of C_{60} to the valence band of TiO_2 is, on the other hand, not expected because the HOMO lies within the band gap of TiO_2 . Thus, C_{60} can be temporarily in an oxidized state. The observed shift of the $C\ 1s$ peak is probably caused by this charging effect of C_{60} .

Regarding the excited carries in the space charge layer of TiO_2 , the charge separation and a resultant decrease in the magnitude of downward bending are expected (a photovoltage effect). A temporal peak shift should, then, be towards the lower-binding energy side, which is an opposite direction of the actually observed shift. Slightly enhanced downward bending may be caused by C_{60} cations on top of the $TiO_2(110)$ surface.

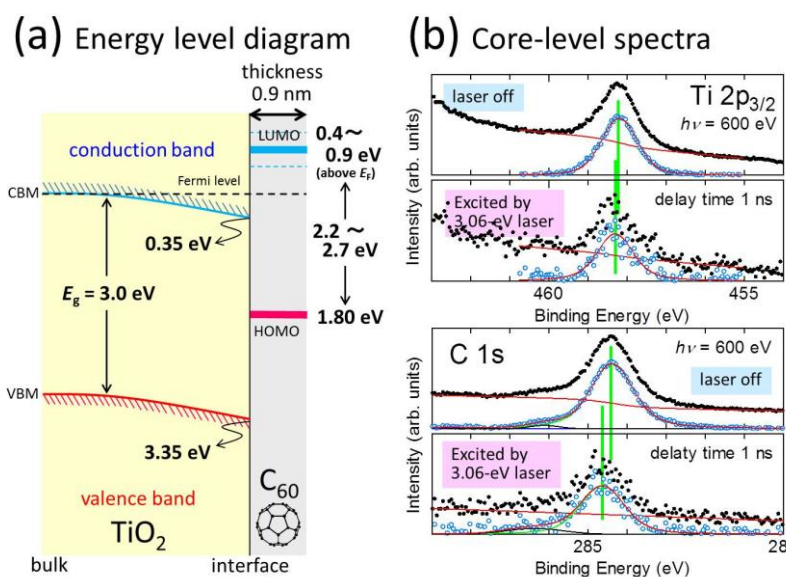


Fig. 1 (a) A schematic energy level diagram of $C_{60}/TiO_2(110)$. (b) $Ti\ 2p_{3/2}$ and $C\ 1s$ core-level spectra measured without laser irradiation and at 1 ns after laser pulse irradiation.

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Operando Mn L_3 soft x-ray emission spectroscopy of LiMn_2O_4 with charge-discharge reactions

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Improving the energy density and power density of electrode materials for Li-ion batteries (LIBs) is highly important for further development of electric and hybrid-electric vehicles. In order to realize the improvements, understanding the charge-discharge mechanisms of the electrode materials from a viewpoint of the electronic structure is indispensable. Recently, electronic-structure analyses for the electrode materials using soft x-ray spectroscopy, which directly reveals the 3d orbital of transition metals, have been of particular importance.

In this study we demonstrate *operando* soft x-ray emission spectroscopy (XES) for LiMn_2O_4 which is a typical cathode material for LIB. We developed an *in situ* cell consisting of the LiMn_2O_4 thin-film cathode, a Li-metal counter electrode and an organic electrolyte solution by modifying the *in situ* cell for fuel cell catalysts¹. The *operando* XES experiments were carried out using ultrahigh-resolution x-ray emission spectrometer, HORNET² at BL07LSU of SPring-8. The charge-discharge experiments were performed by cyclic voltammetry. The XES spectra were analyzed by theoretical analyses using the configuration-interaction full-multiplet (CIFM) calculation³⁻⁵.

Figure 1 shows the *operando* Mn L_3 XES spectra and spectrum for the initial state for excitation energy $E_{\text{in}} = 642.4$ eV⁶. We revealed that the open-circuit voltage (OCV) state is almost the same as the initial state consisting of the Mn^{3+} and Mn^{4+} states. For the charged state, the Mn L_3 XES spectrum largely changed corresponding to the oxidation of Mn^{3+} to Mn^{4+} state at the Mn^{3+} site for the OCV state. The spectrum for the charged state has a large charge-transfer (CT) excitation relative to the *dd*-excitation peaks. The Mn^{4+} state should have a large CT effect. The spectrum for the discharged state almost returned to the spectrum for the OCV state, while the small difference indicates that the Mn^{3+} state is slightly enhanced for the discharged state. Thus, the Mn 3d electronic states were reversibly changed for the charge-discharge process⁶. The enhancement of Mn^{3+} state for the

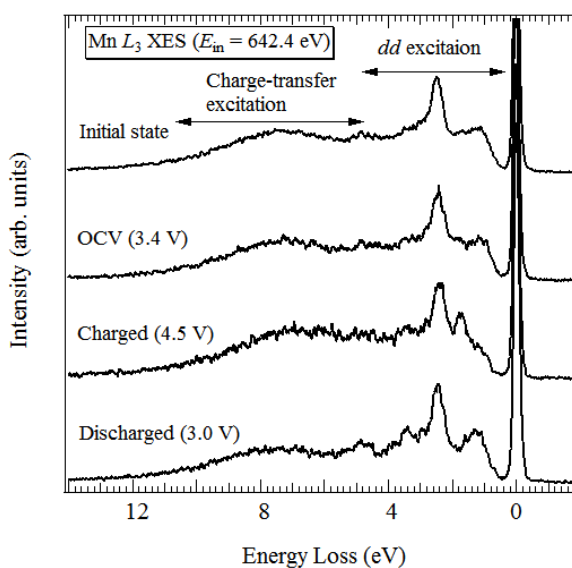


Fig. 1. *Operando* Mn L_3 XES spectra for LiMn_2O_4 ⁶. The XES spectrum for the initial state (as-fabricated LiMn_2O_4) is also shown.

discharged state is consistent with that the voltage of 3.0 V is lower than that of 3.4 V for the OCV state. We found a Jahn-Teller effect on the Mn^{3+} site for the OCV and discharged states by using the CIFM calculation. Moreover, CT effects between the Mn 3*d* and O 2*p* orbitals for each valence state were clarified. For the Mn^{4+} state, a negative CT energy was determined by the CIFM calculation, suggesting a very strong CT effect from the O 2*p* to Mn 3*d* orbitals.

In summary, *operando* XES measurements for LiMn_2O_4 with an organic electrolyte solution were performed to reveal the Mn 3*d* electronic-structure change during the charge-discharge process. A reversible redox reaction of $\text{Mn}^{3+} \rightleftharpoons \text{Mn}^{4+}$ was confirmed. We also found a large CT effect for the Mn^{4+} state.

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VALENCE FLUCTUATING STATE IN QUANTUM CRITICAL Yb(Al,Fe)B₄ STUDIED USING SOFT X-RAY TIME RESOLVED PHOTOEMISSION SPECTROSCOPY

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Introduction

In some heavy-fermion systems, the quantum critical point (QCP), which is the second-order phase transition point or first-order transition end point at absolute zero, can be induced by non-thermal parameters, i.e., magnetic field, pressure, and chemical doping. QCP is strongly attractive in the condensed matter studies because, around QCP, quantum fluctuations induce exotic phenomena such as non-Fermi liquid metallic state and unconventional superconductivity [1]. β -YbAlB₄ is the first-discovered heavy-fermion superconductor ($T_c = 80$ mK) in Yb-based systems [2], and is just at the QCP (or the quantum critical phase) without any external parameters [3]. In addition, the Fermi-liquid metal α -YbAlB₄, which is another polymorph of β -YbAlB₄, shows the same quantum criticality with β -phase with slight doping ($\sim 1.4\%$) of Fe to the Al site [4]. According to a hard x-ray photoemission study [4], this QCP coexists with the unprecedented strong valence fluctuation (the Yb valence of $<2.8+$), which cannot be explained by the conventional Doniach phase diagram, suggesting the role of the valence instability for the quantum critical phenomena. Furthermore, a recent Mössbauer spectroscopy study [6] reported that the valence fluctuation in the YbAlB₄ system shows the very slow time scale of a few nanosecond, which may be a manifestation of the valence quantum criticality. To investigate the dynamics of the valence fluctuating phenomena in α -YbAlB₄, we performed soft x-ray time-resolved photoemission spectroscopy (SX-TRPES) of the whole valence band in which both Yb²⁺ and Yb³⁺ components of the Yb 4f state are included.

Experiment

Single crystals of α -YbAlB₄ were grown by the Al-flux method. SX-TRPES experiments were carried out at BL07LSU of SPring-8 using a VG Scienta ARTOF 10k analyser. The repetition rate of pump laser pulses (1.5 eV) was 1 kHz. The photon energy of probe synchrotron pulses was set to 253 eV. To obtain clean crystal surfaces, we fractured samples *in situ*. All data were acquired at the sample temperature of ~ 30 K. The Fermi level (E_F) was aligned with E_F of the valence band spectrum in α -YbAlB₄ recorded using hard x-ray photoemission spectroscopy at BL47XU.

Results and Discussion

Figure 1 shows SX-TRPES spectra at delay times (t) of 300 ps and 1 ns. For comparison, the valence-band spectrum without pump pulses is also shown as grey curves. The two peaks just below E_F and at 1.8 eV are $J = 7/2$ and $5/2$ states of the Yb 4f^{d3} final state (corresponding to divalent Yb component), respectively, while the peak structures at the region of 5-12 eV are

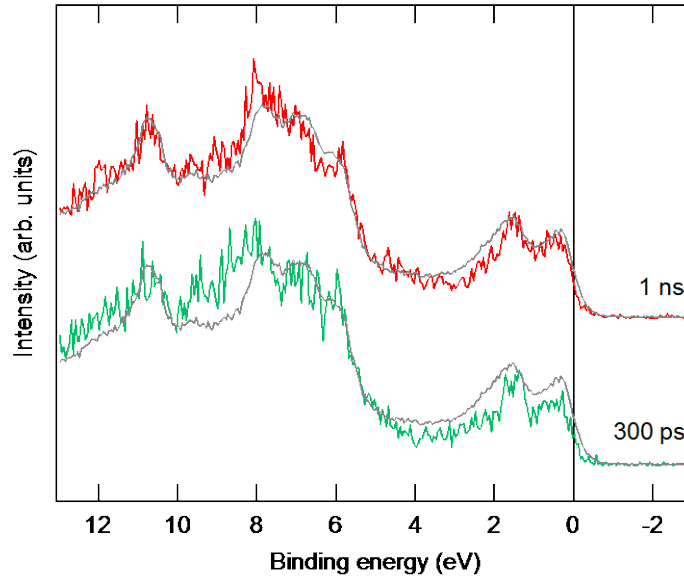


Fig. 1: SX-TRPES results of the valence band in α -YbAlB₄ at delay times of 300 ps and 1 ns. The grey spectra correspond to the no-pump observation.

the Yb $4f^{12}$ final state (corresponding to the trivalent Yb component). In the $t = 300$ ps spectrum, the reduction of the Yb $4f^{13}$ final state intensity and the enhancement of the Yb $4f^{12}$ final state intensity were observed, indicating that the Yb valence increases by the pump pulse excitation. This feature can be found even in the $t = 1$ ns spectrum, though the Yb valence seems to be smaller than the 300-ps spectrum. This suggests that the recovery dynamics of the Yb valence has the time scale of nanosecond, which is consistent with the Mössbauer spectroscopy study [6]. To clarify the dynamics of the valence fluctuation and its relation to the quantum critical phenomena in the YbAlB₄ system, further experiments of SX-TRPES (i.e., more detailed delay-time and Fe-doping dependent measurements) are highly desired.

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PUMP-PULSE INDUCED SPACE CHARGE EFFECTS ON THE TIME-RESOLVED PES SPECTRA OF AN OXIDE SURFACE

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Introduction

Photocatalytic reactions on oxide surfaces can be regarded as an energy conversion process from light energy to chemical energy. Photo-excited carriers, formed upon light absorption in oxides, are the key intermediate in this energy conversion process. The efficiency of photocatalysts thus depends on the efficiency of the formation and transport of electron-hole pairs. Although the oxide surface is the place where the photocatalytic chemical reactions proceed, little is known about dynamics of photo-excited carriers at oxide surfaces. X-ray photoelectron spectroscopy (PES) has been quite successful in providing direct access to electronic structures of materials with surface sensitivity. For example, the change in surface potentials at semiconductor surfaces due to photo-excited carriers, called as surface photovoltage (SPV) effect, can be monitored as an energy shift of PES spectra. The extension of PES to time-domain, or time-resolved PES, thus allows one to study the dynamics of photo-excited carriers at semiconductor surfaces. In the present study, we aimed to study the carrier dynamics on the SrTiO₃(001) surface using time-resolved PES (tr-PES).

Experimental

The tr-PES experiments were carried out at SPring-8 BL07LSU [1] by a laser-pump and synchrotron-radiation (SR)-probe method. The pump laser had an energy of 3.06 eV, pulse duration of 35 fs, and a repetition rate of 1 kHz. The probe SR had an energy of 253 eV, pulse duration of 50 ps. The SrTiO₃(001) surface (0.5 wt% Nb, *n*-type) was cleaned by annealing at 900 K in 1×10^{-3} Pa O₂ gas. On the clean SrTiO₃(001) surface, a charge accumulation layer was formed with a downward band bending of 0.46 eV. All the experiments were performed at 300 K.

Results and discussion

Fig. 1(a) shows Sr 3*d* PES spectra of the SrTiO₃(001) surface with and without pump laser. Upon laser irradiation, the Sr 3*d* core-level shows a peak shift to lower binding energy. The direction of the peak shift is expected for the SPV shift of the downward band bending system as for the SrTiO₃(001) surface studied here.

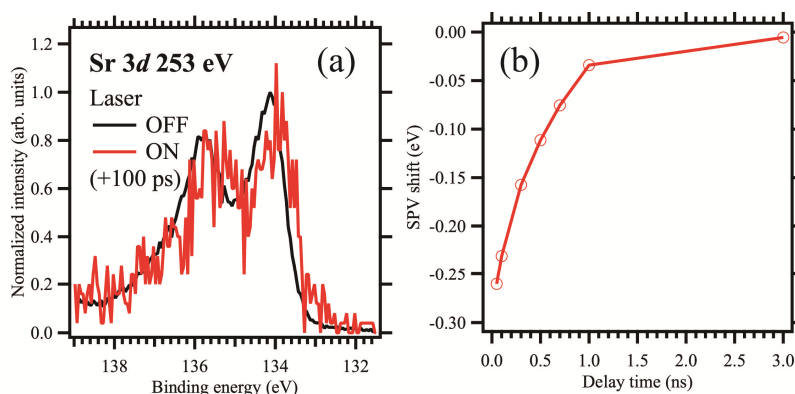


Fig. 1 (a) Sr 3*d* PES spectra ($h\nu = 253$ eV) of the SrTiO₃(001) surface with and without pump laser (3.06 eV, ~ 35 fs, 7.8 mJ/cm²). Pump-probe delay time was set at +100 ps. The peak shift to lower binding energy by 0.23 eV was observed. (b) The SPV peak shift as a function of pump-probe delay time.

As shown in Fig. 1(b), the SPV peak shift is plotted as a function of pump-probe delay time. The SPV relaxation is completed as fast as 1 ns. The time scale of the SPV relaxation on SrTiO₃(001) is much shorter than those on the other oxide surfaces such as TiO₂ [2] and ZnO [3] where the SPV relaxation takes 30-100 ns.

To confirm that the observed peak shift on SrTiO₃(001) originates from SPV, a control experiment was performed. The pump laser with the identical parameters was irradiated on an Au foil, for which SPV does not occur. As shown in Fig. 2, the Au 4*f* core level shows a peak shift to lower binding energy. Therefore, the peak shift observed on SrTiO₃(001) does not originate from SPV, but is interpreted as a space charge effect by intense pump laser pulses [4]. In the pump-probe time-resolved PES, the intense pump laser pulse results in the emission of photoelectrons from the sample surface. After a certain delay time, the probe SR pulse arrives at the surface and emits the photoelectrons with larger kinetic energies. The photoelectrons from probe SR interact with the photoelectrons from pump laser before their detection by an electron analyzer; Coulomb repulsion changes the kinetic energy of photoelectrons.

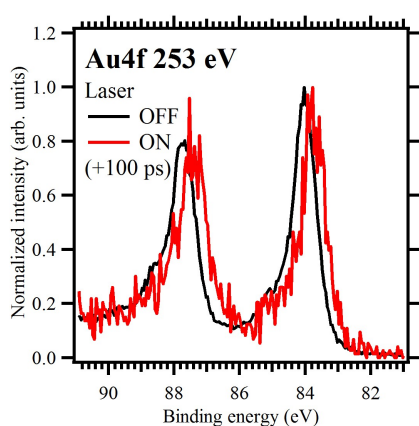


Fig. 2 (a) Au 4*f* PES spectra ($h\nu = 253$ eV) of an Au foil with and without pump laser (3.06 eV, ~ 35 fs, 7.8 mJ/cm²). Pump-probe delay time was set at +100 ps. The peak shift to lower binding energy by 0.28 eV was observed.

Conclusion

The photoexcited SrTiO₃(001) surface showed the spectral shift of Sr 3*d* core-level. The control experiment on the Au foil confirmed that the observed peak shift was not due to the SPV effect, but the space charge effect by intense pump laser pulses. The space charge effect is very common phenomena under strong excitation fields. It is not trivial to distinguish the space charge effect from the SPV effect when the expected direction of peak shift is identical. It is suggested that changing the kinetic energy of photoelectrons by probe pulses (either to measure O 1*s* with the same photon energy or measure Sr 3*d* with different photon energies) can discriminate the space charge effect from the SPV effect; the space charge effect is only affected by changing kinetic energies.

Acknowledgement

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LIGHTING UP THE ROLE OF THE REDOX-INACTIVE METAL M IN [Mn₃M(μ₄-O)(μ₂-O)] MIMICS OF NATURE'S Mn₄O₅Ca OXYGEN-EVOLVING COMPLEX

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A) Purpose

Our initial goal was “to probe by the application of 2p3d resonant X-ray inelastic scattering (RIXS) whether the electron density of the manganese d-states, and the relative intensity of the charge transfer (CT) selective RIXS channels, correlate with reported results that redox-inactive metals modulate the reduction potential of heterometallic manganese-oxido clusters.”

B) Samples, experiment method, equipment used, experiment/measurement conditions

In our previous beamtime (#2013B7457) we had established a methodology for measuring Mn 2p3d RIXS of molecular compounds that contain Mn in high oxidation states, with minimal or no beam damage. During this beamtime we have reaped the benefits of our previous efforts. We have been able to measure RIXS spectra of over 15 radiation sensitive manganese-containing compounds. We mainly used the RIXS spectrometer and the fluorescence yield (FY) SDD detector for XAS. The measurement chamber and load lock were baked out prior to our measurements, which allowed a base pressure well below the detection limit at the beamline of 5×10^{-9} mbar. We used a liquid helium cryostat to perform all our measurements at 30 K. In addition, we managed to measure a large number of air-sensitive measurements by using strict inert environments for preparation and sample transfer.

C) Summary of experiment/measurement results

As an example of the results we were able to obtain at the HORNET endstation of beamline BL07SLU we refer to Figure 1. During our previous run (#2013B7457) we had managed to measure the Mn 2p3d RIXS spectra of undamaged Mn²⁺/Mn²⁺ and Mn²⁺/Mn³⁺ molecular dimers, but we were however not able to measure Mn³⁺/Mn³⁺ and higher manganese oxidation states without damage. This was shown in the original proposal for the currently discussed beamtime. Figure 1 shows the previously obtained RIXS spectra on Mn²⁺/Mn²⁺ and Mn²⁺/Mn³⁺ at HORNET. In addition, it shows two new spectra, obtained at the same excitation energy, that we measured at the SEXTANTS RIXS beamline in SOLEIL and at the HORNET endstation in the current run. The blue spectrum of the Mn³⁺/Mn³⁺ molecular dimer has a much more intense first d-transition around 1 eV as compared to our previous attempt at HORNET. It also shows no signs of Mn²⁺ transitions as previously still present around 3.5 eV. This result is logically explained since no Mn²⁺ should be present in a non-photoreduced Mn³⁺/Mn³⁺ compound. The strongly increased relative intensity of the low energy d-d transition at 1 eV also confirms an increase in the amount of Mn³⁺ content, since this peak originates from a lowering of the manganese site symmetry by the Jahn-Teller distortion of the d⁴ ion. Instead of focusing on the repetition of

this SEXTANTS experiment at HORNET, we aimed for new data and managed to extend the series with the RIXS spectrum of a $\text{Mn}^{4+}/\text{Mn}^{4+}$ compound. The green curve shows almost no sign of the d-d transition at 1 eV implying the total absence of Mn^{3+} ions in this compound and *confirming the successful first measurement of a Mn^{4+} molecular compound known to us*. Also the general broadness of all features in this spectrum confirms the assignment to the Mn^{4+} oxidation state. This great success is only a small part of the many interesting observations we were able to make during this beamtime and several publications are expected to result in due time.

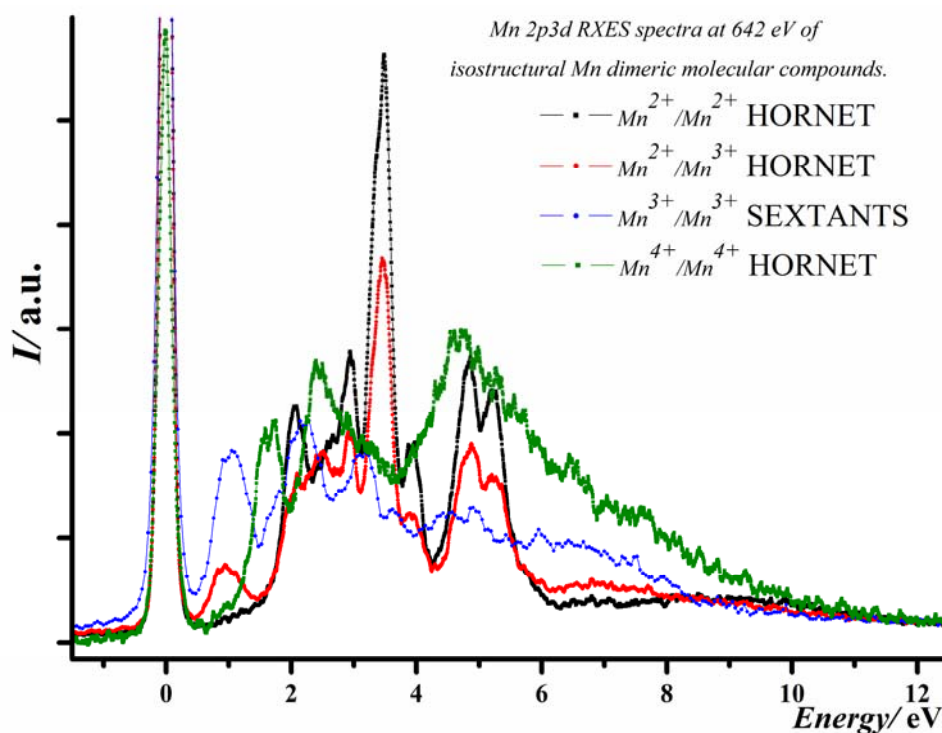


Figure 1. Mn 2p3d RXES spectra acquired at 642 eV and plotted on an energy transfer axis.

PROBING BY RIXS THE NATURE OF LOW-ENERGY EXCITATIONS IN CUPRATES ACROSS THE INSULATOR-TO-SUPERCONDUCTOR PHASE BOUNDARY

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High- T_C superconductivity in cuprates remains an unsolved problem of modern condensed matter physics despite the worldwide effort made from both theoretical and experimental sides.

Resonant Inelastic X-ray Scattering (RIXS) is a novel probe of electronic and magnetic excitations in solids and it has already established its powerful capabilities when applied on cuprates. Most RIXS experiments on cuprates have been performed at the Cu L_3 -edge, which is especially suited for probing the Cu d states, as well as the spin wave excitations. Nevertheless, O K-edge RIXS is becoming an efficient alternative to Cu L_3 -edge, since it provides a complementary perspective on bimagnon excitations, and is predicted to be sensitive to the crucial Zhang-Rice singlet state.

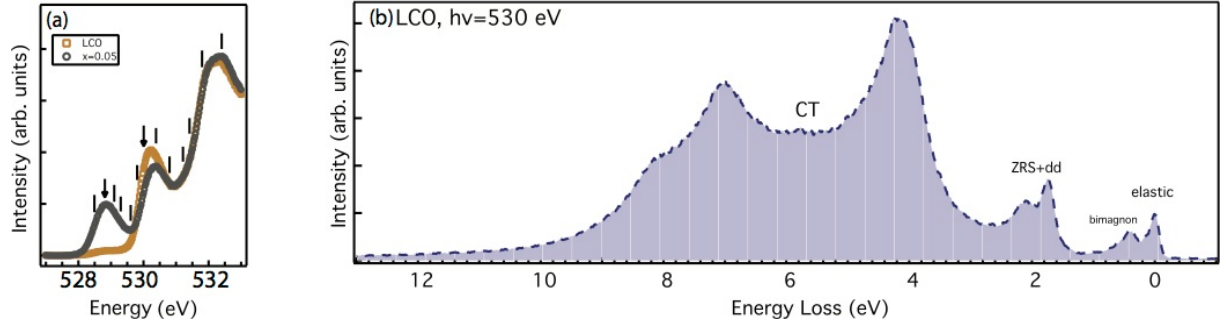


Fig. 1 (a) Comparison of XAS spectra taken with σ polarization in the fluorescence yield mode. Ticks mark the excitation-energies used for the RIXS measurements. (b) O K-edge RIXS spectrum of the undoped compound (LCO, $x=0$). All the possible channels activated by the RIXS process are indicated in the figure.

In the present study carried out at beamline BL07LSU of SPring8 we were able to measure the incident photon energy dependence, around the O K-edge, of the low-energy excitations in the underdoped regime of the $\text{La}_{(2-x)}\text{Sr}_x\text{CuO}_4$, a paradigmatic material of the cuprate family. Namely, we could establish the fluorescent (non-Raman) behaviour of a previously unexplored double peak feature.

The incoming photon-energy was set at the O $1s \rightarrow 2p$ edge, and the achieved energy resolution for the RIXS data was ~ 140 meV. All spectra were recorded at $T = 40$ K in σ polarization and with an incident angle of 20 degrees along the $(\pi,0)$ direction. According to the XAS data, several incoming photon energies have been selected to proceed with the RIXS excitation energy dependence: the values of $h\nu$ are marked by straight lines in Fig.(1.a).

Fig.(1.b) shows a typical O K-edge RIXS spectrum collected from the undoped insulating compound. Among all the excitation features that can be probed by O K-edge RIXS, remarkably, we resolved an excitation feature, which shows a double-peak shape. The incoming-energy evolution of this structure is of significant interest showing a dual nature. Whereas the lower-energy part exhibits a Raman behavior, the higher-energy part shows a “fluorescent” behavior as it moves in energy (dashed lines in Fig.2).

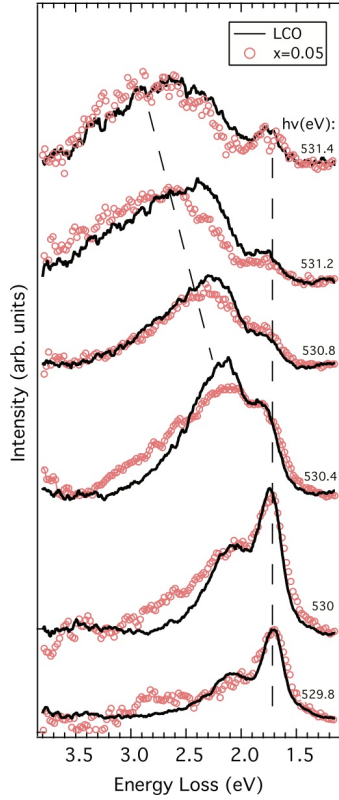


Fig. 2 Excitation-energy evolution of double-peak structure captured by the RIXS measurements.

The dual nature of this feature is shown:

- The lower-energy part can be attributed to the dd excitations (Raman behavior);
- The higher-energy part shows a “fluorescent-like” behavior suggesting a different nature;

Even if this double peak structure has the same energy position as the dd excitations that dominate the Cu L_3 -edge, the measured fluorescent behavior is not compatible with the assignment to dd excitations. Previous theoretical multi-band Hubbard calculations by K. Okada and A. Kotani [1-2] have related these excitations to ZRS- superimposed to dd excitations, an assignment compatible with the fluorescent behavior.

In conclusion, we resolved for the first time a double-peak excitation located around 2 eV energy loss indicating the Zhang-Rice singlet derived excitations.

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Investigation of carrier generation processes of organic solar cells using time resolved X-ray photoelectron spectroscopy

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Organic thin film solar cells have attracted considerable attentions due to their low cost and flexible usages. The mechanism of the device operation, however, has not completely understood yet. The energy loss accompanying the exciton decay, which occurs at the donor/acceptor (D-A) interfaces, is regarded as an important research subject in order to compete with the carrier generation and to enhance the energy conversion efficiency. In this manuscript, we report our study of transient photovoltage generated at D-A interfaces under pulsed laser irradiation using time resolved X-ray photoelectron spectroscopy (TRPES).

Sample preparation was done using the thermal evaporation method. C₆₀ and zinc phthalocyanine (ZnPc) were chosen as acceptor and donor molecules, respectively. A buffer layer of 3 nm-thick copper iodine (CuI) was formed on an Indium Tin Oxide (ITO) substrate for controlling the molecular orientation of ZnPc (face on orientation). C₆₀ thin films were formed on ZnPc/CuI/ITO to make a D-A bilayer heterojunction. TRPES, utilizing the laser-pump synchrotron-radiation (SR)-probe method, was taken at BL07LSU at SPring-8 [1]. Pump laser (pulse duration ~35 fs; photon energy 3.06 eV) and probe SR light (pulse duration ~50 ps; photon energy 400 and 600 eV) were used during the measurements. The absorption coefficient of ZnPc and C₆₀ at 3.06 eV are 4×10^4 and 8×10^4 cm⁻¹, respectively. Therefore, the decay length of the photon is fairly long as compared with the thickness of the specimen, and the pump laser was absorbed for both layers. Amount of the surface photovoltage (SPV) at organic layers was evaluated from the core-level energy shift in the photoelectron spectra.

Fig.1 shows C1s spectra of C₆₀(3 nm)/ZnPc(20 nm) heterostructure formed on CuI buffer layer measured at the probe delay times of 100, 300, 500 ps, and 1 ns. Since mean free path of the C1s photoelectron, under the present measurement condition, is estimated to be below 1 nm, the peak corresponded to the signal of C₆₀. Upon laser pulse irradiation, the C1s peaks were shifted towards the lower binding energy, and the shift was diminished with the delay time evolution. The relaxation time of the spectral shift of the C1s photoelectron is roughly estimated as ~1 ns.

To understand the nature of the spectral shift after irradiation of the pump laser, we investigated TRPES spectra using different probe SR light. In these measurements, the 3.06 eV pump laser with a power density of 50 mJ/cm²/pulse was used, and the probe delay time was fixed to 100 ps. The change in the spectral shift of the C1s photoelectron upon the laser irradiation was found when changing the photon energy of the SR light from 400 to 600 eV, as shown in Fig. 2. If the spectral shift upon the laser irradiation

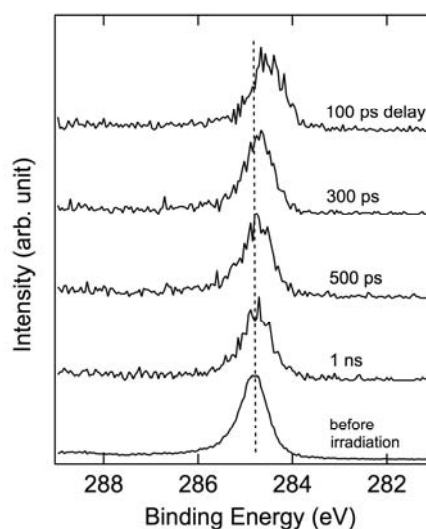


Fig.1 Change in C1s spectra of C₆₀(3 nm)/ZnPc (20 nm) heterostructure formed on CuI buffer layer as a function of delay times. The 3.06 eV laser with a power density of 6.7 mJ/cm²/pulse and the 400 eV SR light were used.

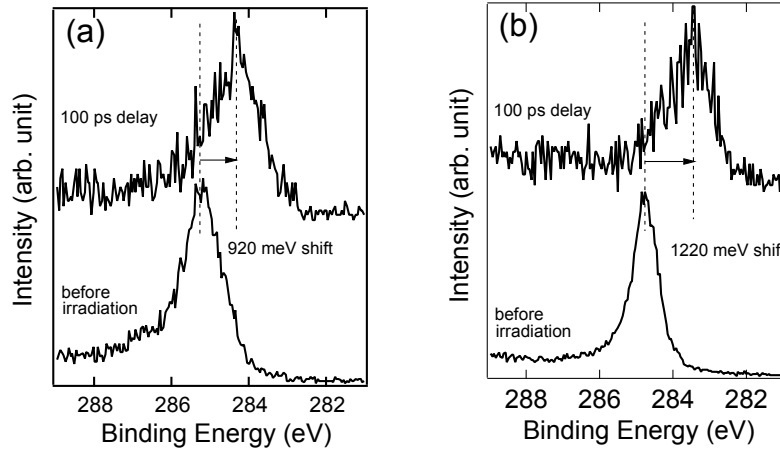


Fig. 2 C1s photoelectron spectra taken with (a) 600 eV and (b) 400 eV probe SR light. The 3.06 eV pump laser with a power density of 50 mJ/cm²/pulse was used. The delay time was fixed to 100 ps. was originated from SPV, the shift of the C1s peak must be constant regardless of the probe SR light. Thus, the spectral shift was not mainly caused by SPV and the other reason has to be considered.

Fig. 3 shows spectral shift of C1s photoelectron as a function of the intensity of the excitation laser in double logarithmic plot. The carrier generation at organic D-A interfaces is known to be proportional to the incident light power. In contrast, the energy shift with TRPES increased in proportion to the square of the excitation laser intensity, as illustrated by slope of the fitted line in Fig. 3. Such a nonlinear increase in the energy shift was commonly observed in case that space charges were induced at the surface by pump laser [2]. Multi-photon electron emission, in which an electron absorbs multiple photons simultaneously, takes place when intense ultrashort laser pulses are irradiated to specimens. Since the ionization energies of ZnPc and C₆₀ are 5.2 and 6.2 eV respectively, two-photon emission, of which probability depends on the square of the excitation light intensity, was probably induced before probe SR light irradiation. The electron cloud emitted along the normal direction by the pump laser influences the distribution of the electric potential on the specimen surface, causing the spectral shift of C1s photoelectrons. The power dependency and the relaxation time of the spectral shift correspond to the trend in the previous report [2].

The injection level of photons by the pump laser is several orders of magnitude higher than that of the sunlight [1]. The absence of the SPV upon pump laser irradiation is likely due to the flat potential in organic layers. Namely, spatial separation of the photo-generated electron-hole pairs hardly occurs due to the lack of the internal electric field. Therefore, one needs to consider the optimal electric control at D-A interface for the effective carrier separation.

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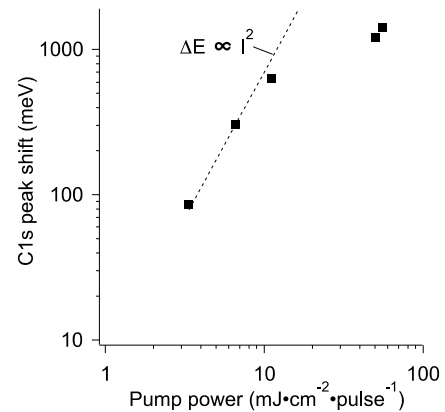


Fig. 3 Spectral shift of C1s photoelectron (ΔE) as a function of the power of the excitation laser in double logarithmic plot. The dashed lines are linear fits to the experimental results. Power law dependencies on the pump pulse power (I) are indicated.

FIRST OBSERVATION OF MODULATED ELECTRONIC STATES IN ACCESS REGION OF GRAPHENE TRANSISTOR

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The linear band dispersion makes zero effective carrier mass in graphene, which is the source of graphene's excellent electronic properties. Unfortunately, however, graphene-based devices, such as graphene field-effect transistor, has not been exhibited nice device performances, as anticipated from excellent electronic properties, such as giant carrier mobility up to 200,000 cm²/Vs. For instance, we have successfully grown high-quality epitaxial graphene whose grain size is > 50 μm, larger than one order of magnitude of epitaxial graphene previous reported [1]. A GFET using our epitaxial graphene showed extrinsic carrier mobility of 4,000 cm²/Vs, and after removing parasitic resistances situated in so-called access region which is in between gate and source/drain electrodes, such as contact resistance, the intrinsic carrier mobility is estimated to be up to 100,000 cm²/Vs. This clearly demonstrate that we cannot ignore the contribution of device interfaces which bring about the parasitic resistances. In other words, spatially-averaged traditional spectroscopy is inefficient for device research and development.

For this reason, spectromicroscopy is recently becoming much attention. However, just spectromicroscopy is not enough for device research and development because it has not observed devices in operation. We have exploited for the first time operando spectromicroscopy using PEEM, which in fact enabled to electronic states of device interfaces through the utilization of nanoscopic X-ray absorption spectroscopy (XAS) [2]. Unfortunately, analysis of XAS is in some cases difficult owing to final-state effects. To overcome this issue, we have exploited operando spectromicroscopy and succeeded in observing linear band of graphene working as a channel of GFET [3].

In this work, we have operando spectromicroscopy using 3D nano-ESCA to observe electronic states of access region which degrades device performances. GFET used in this study is a top-gate transistor, as shown in Fig. 1. The reason for the adoption of the top gate is to avoid the effect of substrate which degrades high-speed response. In between the gate and source/drain electrodes, access regions of about 4 μm in length exist.

In the access region near the source, the unintentional hole doping clearly occurs, as demonstrated in the C1s core-level peak shift of epitaxial graphene (Fig. 2). This is attributed to a charge transfer arising from the difference in the Fermi level. The broadening of the charge transfer region is due to the limited density of states near the Dirac point. A similar charge transfer region is observed in GFET by using non-operando 3D nano-ESCA [4]. The charge transfer region does not vary with the gate bias, as shown in Fig. 2. This is explained by the fact that the source is grounded.

Additionally, an intentional doping is observed near the gate electrode, as shown in Fig. 3. Such an intentional doping has not been observed before. The width of the unintentionally-doped region is smaller, compared to that of the charge transfer region near

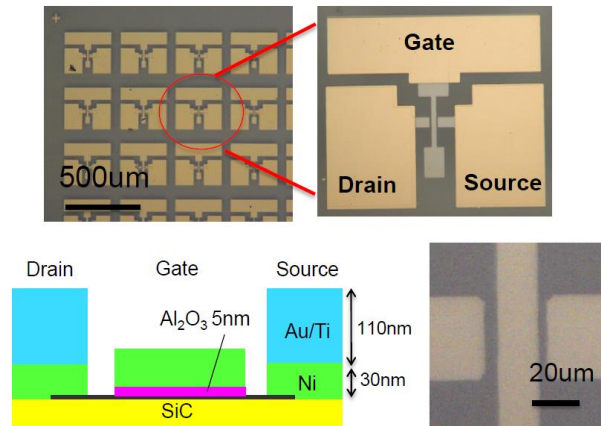


Figure 1 Schematics of the observed top-gate GFET.

the source electrode. Stray electric field is supposed to be the cause of this unintentional doping. We have done a device simulation which reproduce this supposition well.

In conclusion, we have successfully performed operando spectromicroscopy using 3D nano-SCA for the realistic device, e.g. top-gate epitaxial graphene transistor. The obtained results enables to acquire information which is never accessible by spatially-averaged traditional spectroscopy and electrical characterization. Our work is useful for the designation of high-performance GFET.

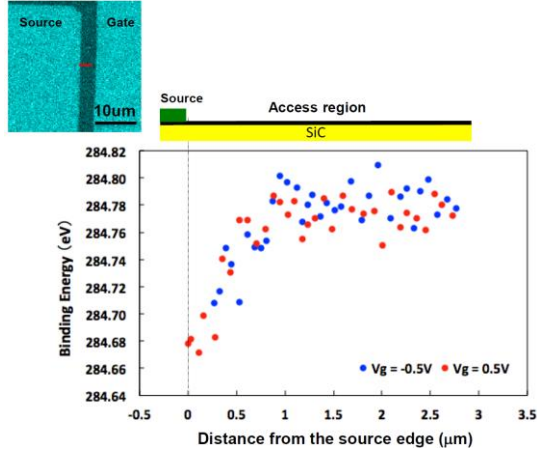


Figure 2 C1s graphene peak shift near the source electrode.

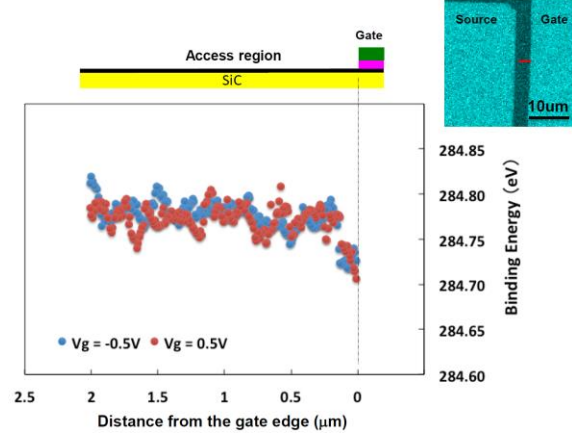


Figure 3 C1s graphene peak shift near the gate electrode.

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Development of Measurement System for RIXS in Magnetic Field

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Resonant inelastic x-ray scattering (RIXS) is a photon-in/photon-out x-ray spectroscopy in which one measures scattered x-ray photons inelastically off matter. It can be therefore applied in electric and magnetic field as well as provides bulk electronic structure of materials [1]. Very few results are however reported for RIXS in magnetic field because of the limitation and difficulty for installing a magnet to an experimental endstation. In this study, to demonstrate the potential of RIXS in magnetic field, we installed a set of magnet system (magnet, positioning mechanism and sample transfer system) to HORNET in SPring-8 BL07LSU and measured RIXS in magnetic field of $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$, which shows giant magnetostriction.

Fig. 1(a) shows a magnet circuit originally designed and fabricated for HORNET station and Fig. 1(b) shows the whole picture of the magnet system including positioning mechanism. The magnetic circuit is consisted of neodymium magnets, which are the strongest type of permanent magnets commercially available, and Iron Yoke and cones for homogeneous and strong magnetic field in the gap. The gap distance is set to 11 mm balancing the field strength against the room for the sample. This magnet system achieves field strengths of over 2500 gauss at the center of the gap. Both the magnetic poles have the 2 mm ϕ holes so as to pass x-ray and apply the magnetic field parallel as well as 45 degree to x-ray. For this magnet system, a new sample stage and a dedicated sample transfer system were developed.

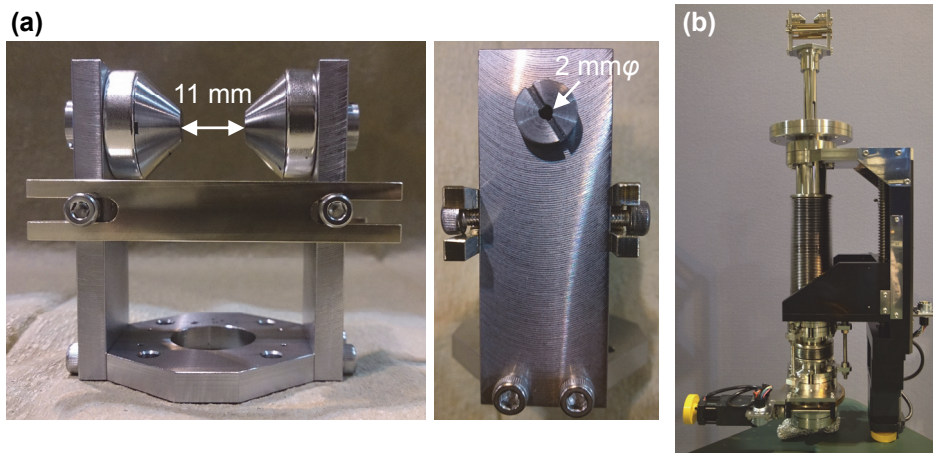


Fig. 1 Photographs of magnet system. (a) Magnetic circuit consisted of neodymium magnets and iron Yoke and cones. (b) Photograph of magnet with positioning system.

$\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$ is a giant magnetostrictive material, showing the largest magnetostriction of 2000 ppm at 2000 gauss [2]. It is already commercialized as actuators and sensors and is applied to the various fields. The giant magnetostriction of $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$ is commonly understood as the distortion of the crystal structure induced by the modification of the crystal field in rare-earth elements resulted from aligned orbital magnetic moments to magnetic field [3]: The microscopic origin of the giant magnetostriction was proposed to be local

crystal distortion caused by the change of crystal field and orbital overlap of the rare-earth elements in magnetic field [4]. Indeed an extended x-ray absorption fine structure (EXAFS) spectroscopy recently observed the local distortion at the atomic scale and the interpretation in terms of the crystal field was experimentally evidenced [5]. Here, we report RIXS of $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$ in magnetic field. RIXS is expected to examine the revolution of crystal field and orbital overlap and enable to interpret the mechanism driving magnetostriction in terms of electronic structure.

Fig. 2(a) shows x-ray absorption spectroscopy (XAS) and RIXS of $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$ in the magnetic field along [111], which is an easy axis of magnetization. XAS in total electron yield (TEY) mode shows a shoulder structure due to surface oxidation, but XAS in partial electron yield (PFY) mode displays a non-splitting peak, indicating Fe is metallic. X-ray magnetic circular dichroism (XMCD) is observed only in the metallic peak at $h\nu = 708.1$ eV, not in the shoulder peak, suggesting bulk Fe is magnetized parallel to the magnetic field. Fig. 2(b) exhibits RIXS measured at $h\nu = 708.1$ eV. No inelastic peak was detected and almost symmetric peak was observed. The RIXS spectral shape does not change over the measured whole energy range and coincides the fluorescent peaks collected with off-resonance excitation energy. This result implies $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$ is weakly correlated electronic system [6]. RIXS was measured with and without magnetic field, but no discernible difference was found. MCD in RIXS is as much as expected from XMCD in PFY mode. All the results support Fe 3d-electron itinerancy in $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$ and imply that Fe 3d-electrons are not responsible for the magnetostriction.

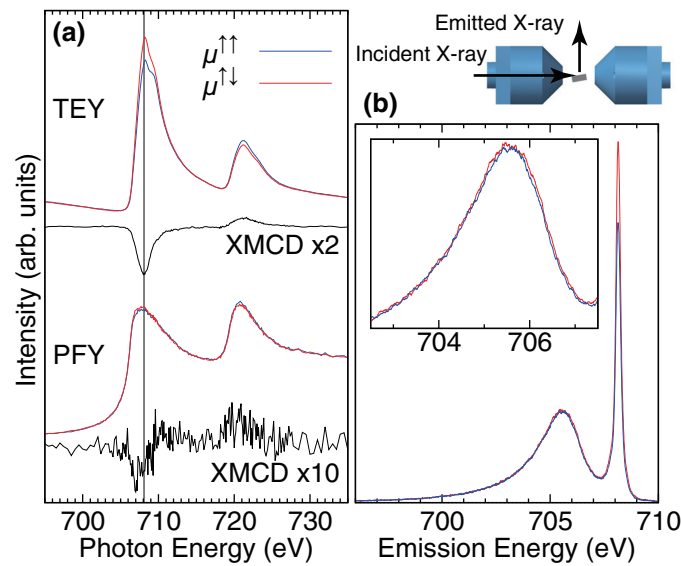


Fig. 2 MCD in XAS and RIXS of $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2$. Sketch depicts the experimental configuration. (a) XAS and XMCD measured in TEY and PFY mode. (b) RIXS measured at $h\nu = 708.1$ eV. Inset: enlarged plot of the peaks at ~ 705.5 eV.

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An *operando* Co 2p soft x-ray emission/absorption study of LiCoO₂

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LiCoO₂ is the most famous cathode material for Li-ion battery. In the charge-discharge processes, the average valence of Co should change between Co³⁺ (for the open circuit voltage (OCV)) and Co^{3.5+} (for the charged state: Li_{0.5}CoO₂). There are many reports about this Co 3d electronic-structure change, e.g. by means of hard x-ray absorption spectroscopy at the Co K edge,² *ex situ* soft x-ray absorption spectroscopy (XAS) at the Co L edge,³ etc. In order to investigate the electronic-structure change in more detail, we tried to perform *operando* soft x-ray emission spectroscopy (XES) and XAS for LiCoO₂ by a similar manner to Ref. 4.

The *in situ* cell consists of the LiCoO₂ thin-film cathode, a Li-metal counter electrode and an organic electrolyte solution. The *in situ* cell was assembled in a grove box filled with Ar gas. Cyclic voltammetry (CV) was employed for the charge-discharge experiment. The scan rate was set to 0.5 mV/s. The *operando* XES and XAS experiments were carried out using ultrahigh-resolution x-ray emission spectrometer, HORNET⁵ at BL07LSU of SPring-8. An excitation energy E_{in} of 780 eV corresponding to the main peak position of the Co L₃-edge absorption spectrum was used for XES. For the XAS measurements, partial-fluorescence-yield (PFY) detection mode was employed. All the XES/XAS measurements were performed at room temperature.

Figure 1 shows the Co 2p resonant XES of LiCoO₂ for the open-circuit voltage (OCV) before charge, charged, and discharged states. The OCV spectrum exhibits *dd*-excitation structure, charge-transfer (CT) excitation below 775 eV, and shoulder-like structures between them. The line shape is more explicit than that in previous XES results for LiCoO₂⁶ due to the high resolution. The electron configuration should be Co³⁺ low-spin (LS) state (t_{2g}^6) according to the Co L₃-edge absorption spectrum.

In going to the charged state, the XES profile was almost unchanged, suggesting that the Co³⁺ state should not be oxidized. Indeed, the CV curves exhibited very small anodic peaks during the charge process (not shown here). Most likely, the oxidation reaction would be suppressed by a high resistivity originated from the *in situ* cell.

The discharged state should be slightly different from the OCV and charged states. The shoulder structure around 779.5 eV and the intensity at 777.8 eV slightly decreased in the XES results. We also performed *operando* Co 2p XAS at the discharged state

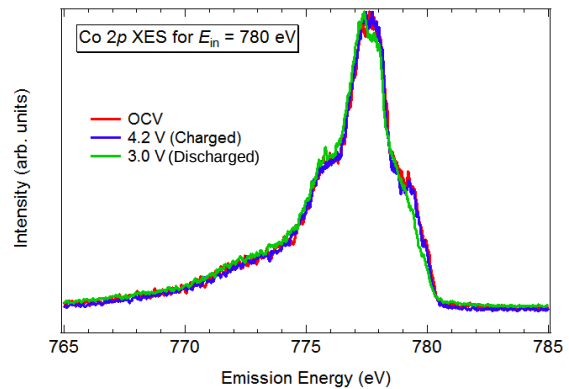


Fig. 1. *Operando* Co 2p XES for LiCoO₂ for E_{in} = 780 eV.

after the XES experiments (Fig. 2). The XAS profile indicates that the main fraction is composed of the Co^{3+} LS state³ and the shoulder structures at 778-779 eV should be of Co^{2+} state. The small change observed in the XES results might be explained by the existence of Co^{2+} state.

The CV and XES results suggest that the charge-discharge experiments were less successful than our previous *operando* experiments for LiMn_2O_4 .⁴ However, the first accomplishment of *operando* Co 2p XAS with applying a voltage is fruitful. In the near future, we will refine the *in situ* cell and LiCoO_2 thin-film cathode to successfully perform the charge-discharge experiments. The combination of *operando* XES and XAS will become the most powerful tool to investigate the electronic-structure change of cathode materials.

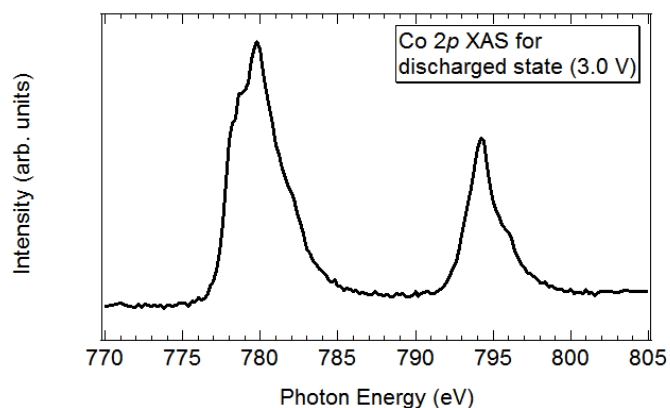


Fig. 2. *Operando* Co 2p PFY XAS for LiCoO_2 (for the discharged state).

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ANALYSIS OF STRUCTURES AND ELECTRONIC STATES OF TRANSITION METAL COMPOUNDS BY MICROSCOPIC HIGH-RESOLUTION TWO-DIMENSIONAL PHOTOELECTRON SPECTROSCOPY

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NiO has played a very important role in clarifying the electronic structure of transition-metal (TM) oxides. It has set a framework for understanding the rich physical properties of TM compounds. For a long time, NiO was thought to be a prototype Mott insulator in which the insulating gap is caused by on-site Coulomb energy U . Zaanen, Sawatzky, and Allen redefined NiO as a charge-transfer insulator.[1] Motivated by resonant valence band (VB) PES, it was shown that the first ionization state is of mainly $3d^8\bar{L}$ character and $3d^7$ -like states (lower Hubbard band) occur at a higher binding energy.[2,3] This picture indicated that the O $2p$ band appears between the lower and upper Hubbard bands, and the insulating gap is formed between the O $2p$ and the upper Hubbard $3d$ bands. The angle-resolved photoelectron spectroscopy (ARPES) study on NiO by Shen *et al.* constituted an important next step.[4] Despite the successes of the localized approach, these data revealed that the electronic structure of NiO is surprisingly band-like. Especially at higher binding energies, rather well-defined dispersing states were observed, which seemed to be naturally explained from conventional band structure theory rather than from a local, strongly correlated point of view. On the other hand, theoretical and experimental studies of the valence band electronic structure have shown that the two lowest energy electron removal states are Zhang-Rice (ZR) doublet bound states.[5-7]

The main purpose of the present study is to observe the Zhang-Rice doublet bound state on the top of the valence band, the dispersive O $2p$ band and lower Hubbard band and to clarify the details of the band structure of NiO by using two-dimensional microscopic photoelectron spectroscopy so-called DELMA.

Two-dimensional photoelectron intensity angular distribution (2D-PIAD) measurements were performed at the free port of BL07LSU in SPring-8. The Display-type Ellipsoidal Mesh Analyser (DELMA) combined with an energy analyser (VG SCIENTA R4000) was used to obtain 2D-PIAD patterns. Figure 1 shows the 2D-PIAD patterns from NiO. A Ni LMM Auger PIAD pattern around $E_{kin} = 700$ eV was taken with Ni $2p \rightarrow 3d$ resonant photon energy of $h\nu = 852$ eV [Fig. 1(c)]. The pattern shows 4-fold symmetry, consistent with the NaCl crystal structure of NiO. It is consistent with the previously measured PIAD pattern by Display-type spherical mirror analyzer (DIANA) at BL25SU, confirming the performance of DELMA.

Next, we have measured k -resolved valence band structure by taking the photoelectron diffraction patterns of the valence band. Figure 2 (b) shows a three dimensional band structure (3D-BS) map of NiO. By slicing the 3D-BS along some specific directions, we have also obtained ARPES spectra, as shown in Fig.2 (c). It confirmed that three dimensional ARPES spectra were successfully obtained by DELMA. Furthermore, we have obtained direct evidence of Zhang-Rice flat band and dispersive O $2p$ bands

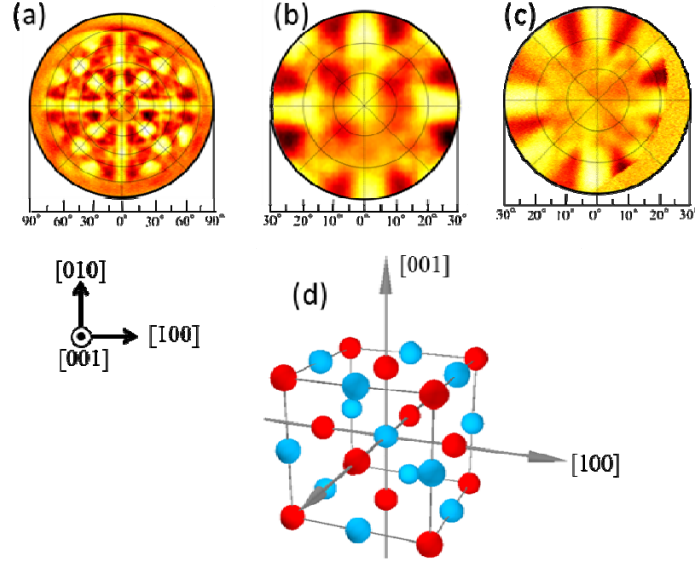


Fig. 1: Comparison of 2D-PIAD patterns obtained by DIANA and DELMA. (a) Wide-angle PED pattern from Ni sites measured by DIANA. (b) Expanded PED pattern from Ni site measured by DIANA. (c) PED pattern from Ni site measured by DELMA

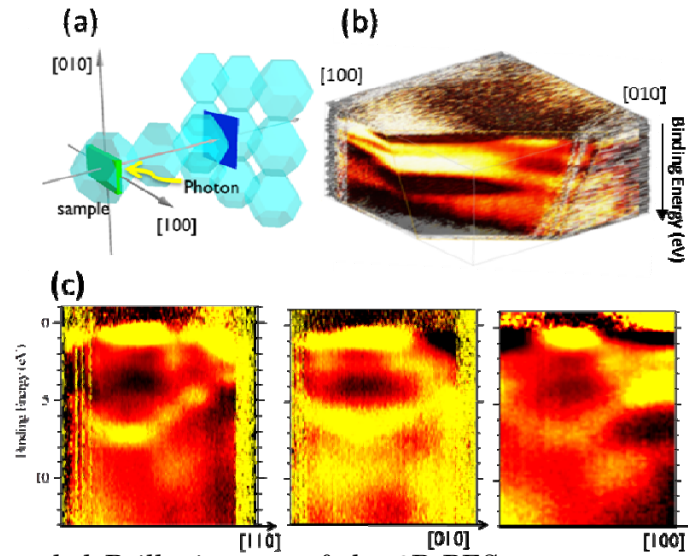


Fig. 2: (a) An extended Brillouin zone of the 2D-PES measurement for NiO. (b) Observed three dimensional band map of NiO obtained by DELMA. (c) Band structures, taken by slicing the three dimensional band map in (b) along [110], [010] and [100] directions.

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STUDY OF THE PHOTO-INDUCED PEIERLS TRANSITION AT THE IN/Si(111) SURFACE

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INTRODUCTION

A periodic array of the indium atomic wires on the Si(111) surface, the Si(111)4x1-In surface, has been one of the intriguing low-dimensional systems to study the Peierls transition. Recently, the metal(4x1)-to-insulator(8x2) transition was reported to be triggered by optical pulses by scanning tunneling microscopy (STM)[1]. It was modeled that the driving force is likely due to doping of the photoexcited carriers to the electronic states of the indium atomic wires by the surface photovoltage (SPV) effect[1]. Generation and relaxation of such surface photovoltage effects at the In/Si(111) surfaces have been by soft X-ray time-resolved photoemission spectroscopy (TRPES). While it of interests to track carrier dynamics during the transition by means of TRPES, one should confirm if the microscopic information, such as STM, can be also observed by the macroscopic observation, i.e. PES. In the present report, we investigated the transition at the In/Si surface by means of electron diffraction and PES.

EXPERIMENT

The electron diffraction and PES experiments with a laser were carried out at the SPring-8 beamline BL07LSU and at the laboratory. The CW laser ($\lambda = 637$ nm) with a pulse trigger switch (< 2 ns, up to ~ 100 MHz) was chosen for enough repetition frequency of the band mapping.

RESULTS

Figure 1 shows reflection high-energy electron diffraction (RHEED) patterns of (a) the 8x2 phase at 60 K and (b) the 4x1 phase with the laser irradiation at temperature just above the $T_c = 120$ K. With the laser power density of 5.4 mW/cm², we observed no photo-induced Peierls transition to the 8x2 phase, as shown in Fig.1(b).

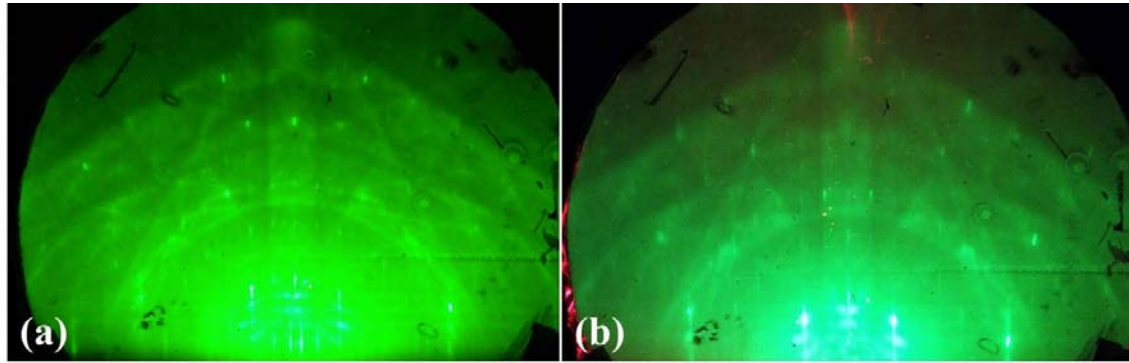


Figure 1 RHEED patterns of (a) the 8x2 phase at 60 K and (b) the 4x1 phase under the laser irradiation at temperature just above the transition temperature of $T_c = 120$ K.

Figure 2 shows PES energy shift of the Si 2p core-level of the Si(111)4x1-In at 18 K under the laser irradiation. The energy shift is referred from the position when laser is off. We observed no notable energy shift due to the SPV effect.

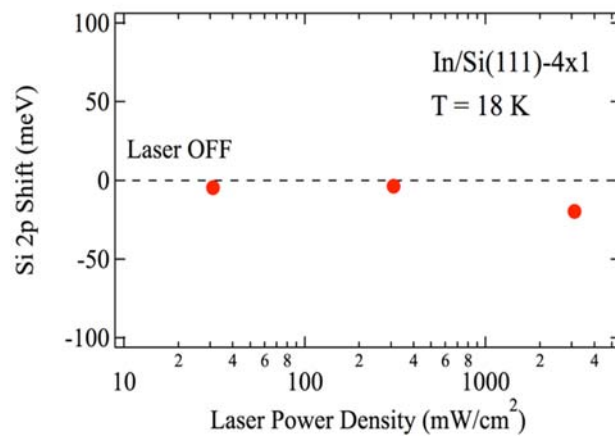


Figure 2 The Si 2p core-level shift of the Si(111)4x1-In at 18 K under various laser

CONCLUSION

Under the present experimental condition of electron diffraction and PES, we were unable to reproduce the photo-induced transition that was reported by STM [1]. We also notice that the surface transition temperature is easily changed by the surface treatment and even by the doping condition of a Si wafer.

ACKNOWLEDGEMENT

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SOFT X-RAY RESONANT INELASTIC SCATTERING FOR CROMIUM DIOXIDE IN MAGNETIC FIELD

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CrO₂ is a well known material as a candidate for the half-metallic ferromagnet with $T_C \sim 395$ K. Since the spin polarization is predicted to be 100 % at the E_F [1, 2], it is extensively studied from the viewpoint of application to spintronics. Although the spin-polarized photoemission is expected to be very powerful to determine the electronic structure of the half-metallic materials, only few works have been reported for CrO₂ [3] because the surface of CrO₂ is unstable and easily forms the antiferromagnetic Cr₂O₃. Even the hard-X-ray photoemission spectrum is noticeably influenced by the contribution from the Cr₂O₃ [4].

In this study, we have performed the photon-in and photon-out spectroscopies to directly reveal the electronic structure of the buried CrO₂. As shown in Figure 1, the O K-edge absorption spectra measured by means of the partial fluorescent yield enable one to probe the unoccupied electronic structure of the CrO₂ without any surface treatment. Especially the peak A at ~ 528.5 eV is free from the Cr₂O₃ component with the strong linear polarization dependence, representing the anisotropy of the electronic structure in CrO₂. This polarization dependence is consistent with the prediction of the configuration-interaction cluster calculation, suggesting the spin-polarization of the peak A due to the charge transfer between the O 2*p* and Cr 3*d* states [5].

To reveal the electronic structures of the Cr 3*d* states, we have performed soft-X-ray resonant inelastic scattering (SXRIXS) at Cr L-edges for CrO₂ and Cr₂O₃. This spectroscopy is powerful to probe the element specific electron excitation from the occupied to the unoccupied *d* states, called *dd*-excitation thanks to the resonant excitation process. The SXRIXS experiments were performed at SPring-8 BL07LSU *Hornet*

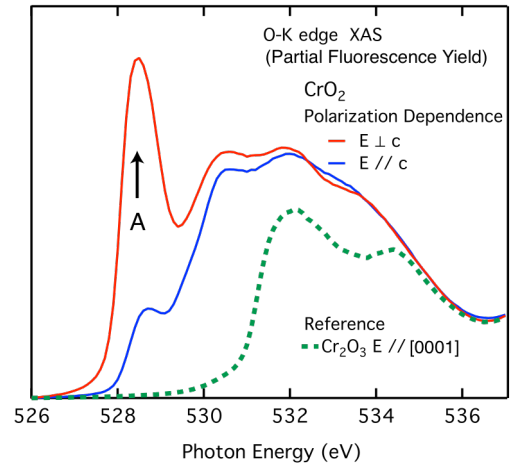


Fig. 1 O-K XAS spectra of CrO₂ and Cr₂O₃

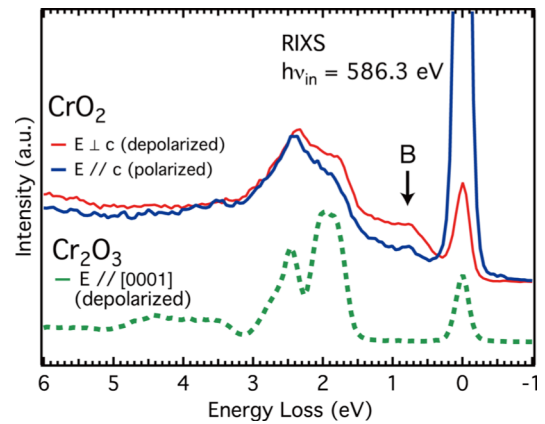


Fig.2 Cr-L RIXS spectra for CrO₂ and Cr₂O₃

end-station, where the high resolution SXRIXS spectrometer was installed. The energy resolution was set to 200 meV at the Cr L-edge. Figure 2 shows the results for CrO₂ (top) and Cr₂O₃ (bottom). There is no clear excitation in the spectrum of Cr₂O₃ in the range of 0 to 1.5 eV, while the spectra of CrO₂ show the *dd*-excitation around 0.9 eV (B) with strong linear polarization dependence. This pronounced excitation in the $E \perp c$ geometry is well correlated with the linear polarization dependence in the O K-edge XAS, suggesting the spin selective inelastic energy loss excitation in the SXRIXS process.

To elucidate the spin polarized electronic structures for CrO₂, we have further performed the SXRIXS under the magnetic field of 0.25 T parallel to the incoming circularly polarized light. The incident angle of the right and left circularly polarized light was set to 10 degree from the sample surface, substantially increasing the magnetic circular dichroism (MCD). Figure 3 shows the light helicity dependence of the SXRIXS spectra under the magnetic field. In contrast to the spectra recorded at $h\nu = 579.2$ eV without any polarization dependence ranging from 0 to 1.5 eV, the strong MCD is observed at $h\nu = 581.4$ eV for the 0.9 eV-peak (C), representing the spin-selective excitations in the 3*d*-states.

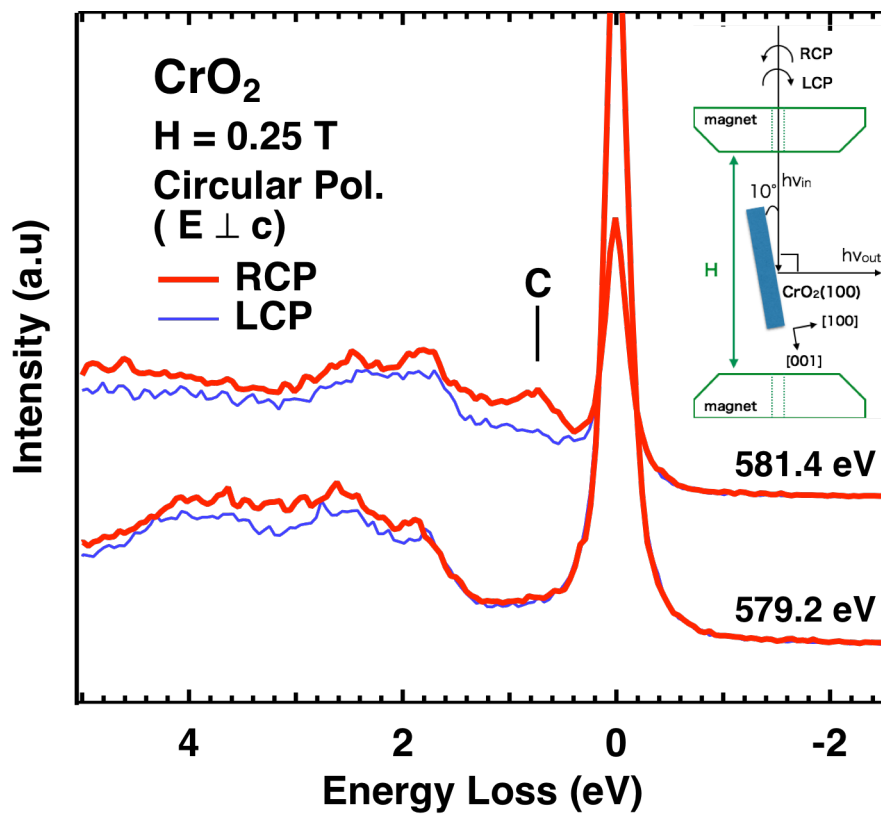


Fig.3 SXRIXS spectra with right and left circular polarized lights for CrO₂ under the magnetic field. The inset shows the experimental geometry under the magnetic field.

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Study of temporal relaxation of the Photo-Dember effect on InN surfaces

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Indium nitride InN is a semiconductor with a narrow band gap ~ 0.7 eV, which has drawn a lot of attention for applications in high efficiency solar cells and high-speed electronic devices. The key issue for understanding InN-based device applications has been proposed to be correlated to the unusual phenomenon of strong electron accumulation and downward band bending at as-grown InN surfaces, no matter N-polar or In-polar [1]. Leyla Colakerol *et al.* [2] found the electrons in the accumulation layer of InN to exist in the discrete quantum well states derived from conduction band. Nevertheless, Kuo *et al.* [3] discovered the flat band from N-polar InN surface through the combined treatment of ex situ chemical wet etching and in situ annealing. On the other hand, surface photovoltage effect on semiconductor surfaces has been a center of interest due to its close relation to photovoltaic and photocatalytic mechanisms that directly lead to solving several of global energy issues [4].

In the beamtime at beamline BL07LSU in SPring-8 (Oct.22 2013 – Oct.25 2013), we carried out the experiment on the N-polar InN surface with downward band bending. We discovered the time-resolved behavior completely distinct from that expected from a SPV picture. Fig. 1(a) shows the energy shift of In 4d core level as a function of delay time at a fixed laser power 8 μ W. As opposed to the behavior that the energy shift would eventually decrease back to zero, the energy shift increase in negative direction initially and then turns to change largely in positive direction over longer time scale up to 10 ns. It appears that there are two different mechanisms competing with each other after the formation of electron-hole pair, excited by the pumped laser. Actually InN itself, with its narrow gap of 0.7 eV, is a degenerate semiconductor, in the space charge layer, in which Photo-Dember effect dominates. This effect has been well known to be responsible for generating terahertz light. Usually, there are two photovoltage effects at a semiconductor surface, surface photovoltage effect (drift-induced) and Photo-Dember effect (diffusion induced). And the surfaces of semiconductors with narrow band gaps are more akin to the latter. The result of that beamtime indicates a great opportunity to depict the complete time-resolved behavior of Photo-Dember effect from InN surfaces by the high- resolution time-resolved photoemission for the first time. We have carried out the simulation research to study the detailed dynamics of the carriers on the InN surface. Currently, we obtained simulation results at the initial stage (picoseconds-time scale) that indicates the Photo-Dember effect, as shown in Fig.1(b). In order to understand the whole relaxation picture (nanoseconds-time scale), much data from the time-resolved photoemission experiments is highly called for.

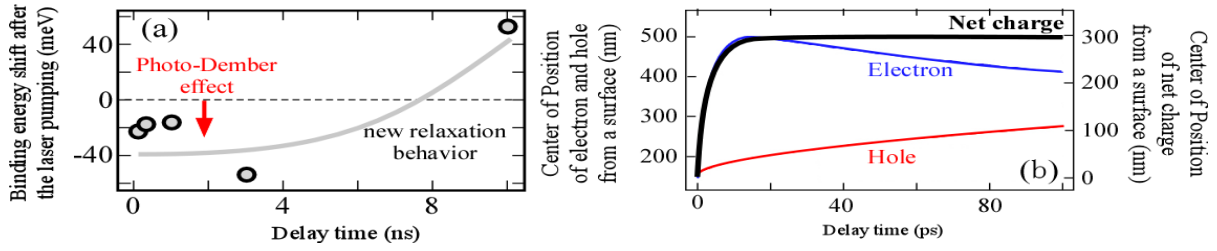


Fig.1: (a) The energy shift of In 4d core level as a function of delay time at the pumping laser power of 8 μ W and (b) numerical simulation results on an InN surface: more holes at surface and more electrons in the bulk, indicating the photo-Dember effect.

In the last beamtime at beamline BL07LSU in SPring-8 (Dec.4 2014 – Dec 9. 2014), we wanted to verify the result indicated from the beamtime in 2013 that there is Photo-Dember effect dictating the electron-hole pair relaxation in InN surface. Therefore, we tried to get more time-dependent data point within larger time scale to nano-seconds in order to confirm the long relaxation time associated with the diffusion mechanism of charge carriers for Photo-Dember effect.

Fig.2 (a) shows the binding energy of In 4d core level peak as a function of pumping laser power. In order to measure the long relaxation behavior of peak shifts, we chose the laser power equal to 356 nW, which corresponds to maximum peak shift in Fig.2 (a). Fig.2 (b) shows the random fluctuation of In 4d peak shift versus delay time. In order to understand the fluctuation, we compare two energy distribution curves (EDCs) with the largest energy difference at delay time 0.35 ns and 3 ns, respectively, as shown in Fig. 3. As observed, the whole lineshapes of two EDCs match each other in spite of the energy difference ~ 0.2 eV extracted by the local peak positions, indicating that random fluctuation can be due to the error of fitting result.

In summary, our experimental results in the last beamtime didn't reveal evident surface photon voltage effect nor Photo-Dember effect on InN surface. It may have to do with the narrow band gap of InN because the previous time-resolved study of hydrogen-terminated SrTiO₃, also a narrow gap semiconductor, shows similar behavior.

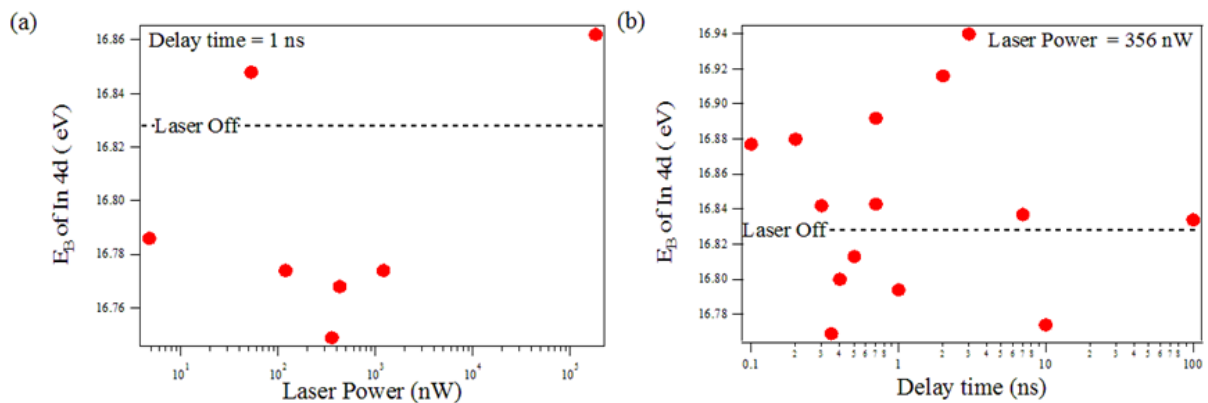


Fig.2: (a) Laser-power dependence of peak shift and (b) delay-time dependence of peak shift for In 4d core level

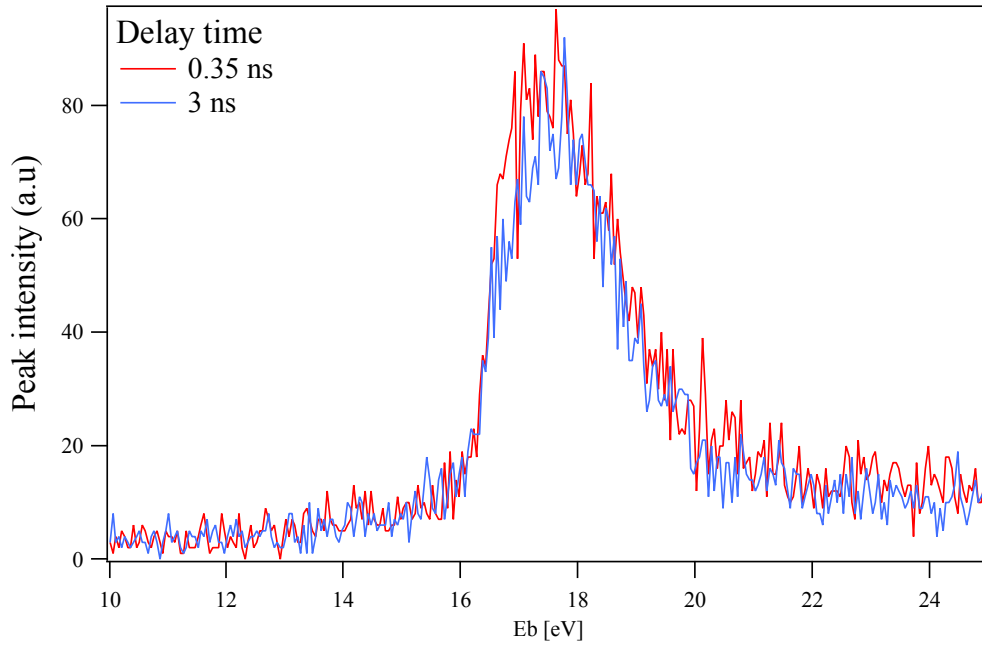


Fig.3: The comparison of two EDCs corresponding to largest energy difference.

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CHARGE INJECTION IN PROTOTYPE SOLAR CELLS SAMPLED BY FAST XPS

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The aim of the experiment was to explore charge injection from light-harvesting core-shell quantum dots (QDs) into an *n*-type TiO₂ substrate. This prototype heterojunction forms part of a new solar cell being developed for microgeneration. We aimed to selectively photoexcite the QDs (but not TiO₂) using a fs laser and time-resolved XPS at BL07LSU to measure the decay of the surface photovoltage (SPV) shift created in TiO₂ by injection of charge into the surface depletion layer. An additional aim was to use synchrotron radiation (SR) depth-profiling XPS to characterise the core-shell structure of the QDs.

As our QD sample, we selected surface-passivated 5 nm PbS/CdS QDs. Recent work by our collaborators has shown that the introduction of a possible CdS outer shell to PbS QDs leads to an improvement in open cell voltage in a hybrid solar cell device (attributed to a reduction in recombination rate) [1]. By combining this approach with additional surface passivation (using a recently reported route using halide anions and bifunctional organic ligands), they have obtained power conversion efficiencies of around 6% in a prototype cell [1]. In order bond the QDs to the substrate for XPS measurements, the initial capping ligand (oleic acid) was exchanged for 3-mercaptopropionic (MPA) acid, and the dots assembled *ex-situ* onto the surface from solution via carboxylate linkages [3]. SR-depth-profiling XPS at BL07LSU was used to probe the ligands and distribution of Cd within the QDs.

Pump-probe experiments at BL07LSU initially used the frequency-doubled output of the Odin-II amplifier at 407 nm and around 300 mW power to photoexcite a UHV-cleaned TiO₂ (110) substrate. Following this, the fundamental at 815 nm and 90 mW - 1 W power was used to excite the QDs attached to the TiO₂ substrate. Spectra were recorded using the ARTof analyser in snapshot mode, allowing the dynamics of the SPV at the surface to be probed using time delays ranging from 0.3 ns to >1 ms.

Depth-profiling XPS at BL07LSU revealed the presence of strong S 2p peaks due to uncoordinated MPA ligands at the surface of the QDs (Figure 1 a & b). Nevertheless, using previous reference spectra where this signal was absent (recorded at ELETTRA and SOLEIL), it was possible to fit the data. Importantly, measurement of the Cd:Pb ratio as a function of sampling depth (from analysis of both Cd 3d/Pb 4f signals and S 2p signals) confirms that Cd is present predominantly at the surfaces of the QDs, previously only inferred from the effect of cation exchange on the cell characteristics [1] (Figure 1c). This is important information that is difficult to obtain by other routes. The analysis showed relatively low levels of Pb oxide/hydroxide contamination compared with PbS QDs [4,5]; together with other data showing low levels of surface sulfate/sulfite (recorded elsewhere), this suggests that the introduction of a Cd shell is important in passivating the surfaces.

Time-resolved measurements were hampered by a poorer than anticipated signal-to-noise ratio, which made it very difficult to probe the TiO₂/QD system within the beamtime available. However, in measurements from the clean TiO₂ substrate using 407 nm to induce direct photoexcitation of the substrate, an SPV shift of the Ti 2p core level of -150 meV (shift to lower binding energy (BE)) at 0.3 ns time delay was reproducibly obtained. This is consistent in direction with the data of Ozawa *et al.* for this surface, and suggests the presence of an electron accumulation layer on the clean substrate [6]. Following attachment of the QDs, the Ti 2p energy was monitored, while photoexciting using 815 nm irradiation (sufficient only to excite the QDs). Unfortunately, the signal-to-noise ratio in this experiment was too

poor to reach any definitive conclusions, with apparent shifts in BE to both higher and lower BE measured. The predominant shift was to higher BE, which may suggest that the adsorption of QDs has changed the surface band-bending, inducing a surface depletion layer. However, a repeated experiment using much longer accumulation times would be necessary before this could be confirmed.

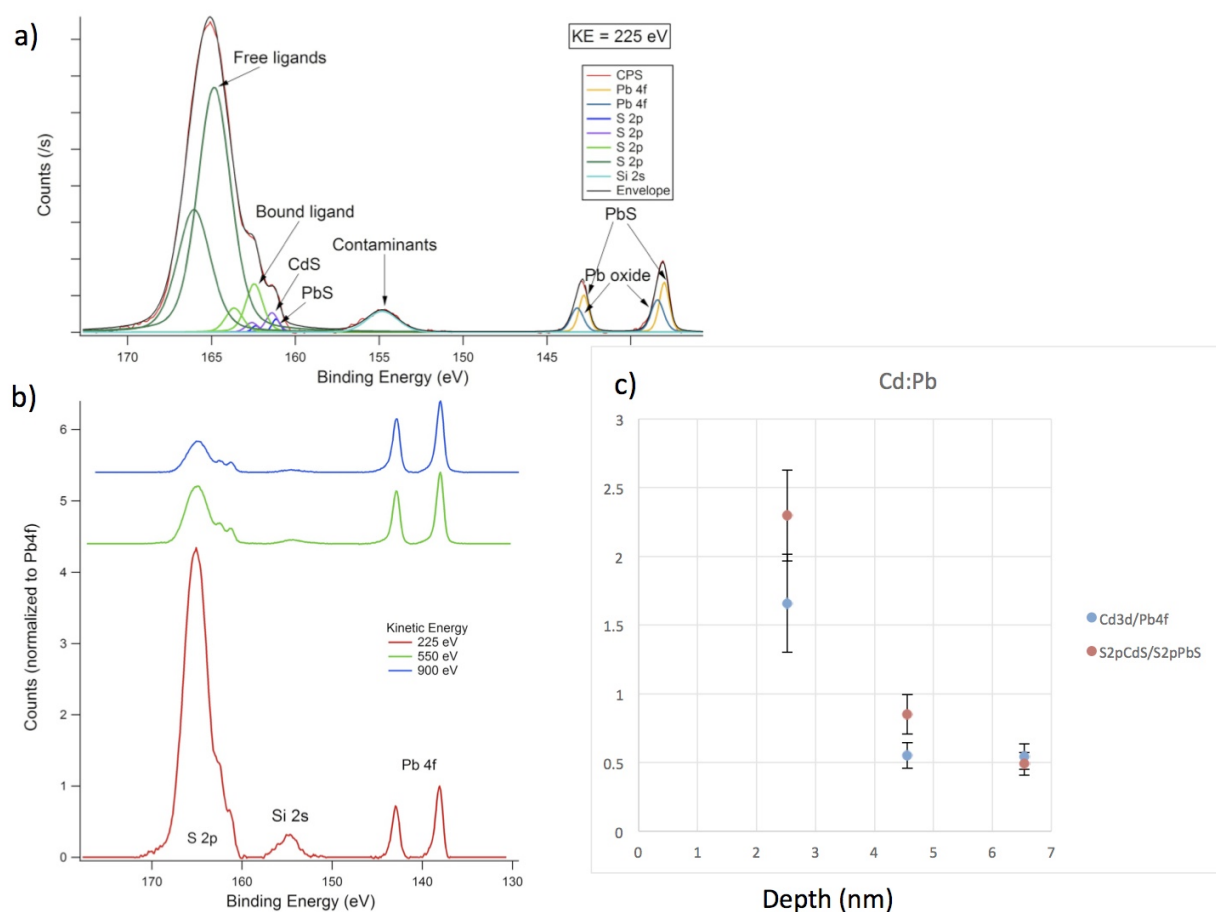


Figure 1: SR-excited depth-profiling XPS of PbSCdS QDs: a) assignment of Pb 4f and S 2p features; b) spectra of this region as a function of photoelectron kinetic energy; c) the elemental ratios obtained as a function of sampling depth, showing Cd is present predominantly at the surfaces of the QDs.

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THE SURFACE REACTION OF CO₂ ON Cu(997) STUDIED BY AMBIENT PRESSURE X-RAY PHOTOELECTRON SPECTROSCOPY

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Hydrogenation of CO₂ is an important chemical reaction in the efficient use of CO₂ as a chemical feedstock [1, 2]. So far, methanol synthesis on a Cu/ZnO catalyst has been widely studied, and already developed industrially [3]. However, the reaction kinetics of CO₂ on the Cu surface is not fully understood yet. In this study, we investigated the reaction process of CO₂ on the Cu(997) surface at 340 K using ambient pressure X-ray photoelectron spectroscopy (AP-XPS).

AP-XPS is a powerful tool for investigating electronic structures and chemical states of adsorbates and substrates under reactant-gas atmosphere. We have newly designed and constructed the ambient pressure X-ray photoelectron spectroscopy system for the “Freeport” of the soft X-ray undulator beamline BL07LSU of SPring-8 (Figure 1). This AP-XPS system consists of four interconnected UHV chambers; an analysis chamber, a preparation chamber, a load-lock chamber, and a fast-entry chamber. The analysis chamber is used for XPS measurements both in UHV and at ambient conditions. The preparation chamber is equipped with an ion source and low energy electron diffraction (LEED) optics. The load-lock chamber and the fast-entry chamber allow the introduction of samples from the air into the UHV system.

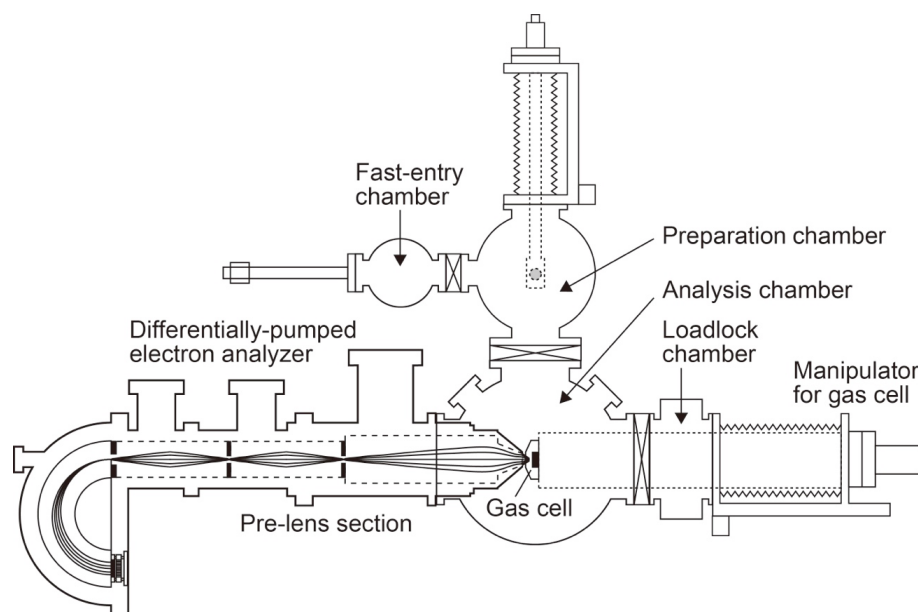


Figure 1. AP-XPS system at SPring-8 BL07LSU

AP-XPS measurements were carried out using a differentially pumped electron analyzer (SPECS, PHOIBOS 150 NAP) with an ambient-pressure gas cell. The Cu(997) surface was cleaned by cycles of Ar⁺ sputtering and annealing to 670 K. After the cleaning, the sample was transferred to the ambient-pressure gas cell. CO₂ gas (99.995% purity) and H₂ gas (99.99999 %) were introduced into the gas cell using each mass flow controller. The sample temperature was monitored by a chromel-alumel (K-type) thermocouple attached to the stainless steel plate beneath the sample. Successive O 1s and C 1s measurements under

ambient conditions were conducted at a photon energy of 630 eV.

Figure 2 shows a series of (a) O 1s and (b) C 1s AP-XPS spectra of Cu(997) at 340 K under ($\text{CO}_2 + \text{H}_2$) gas mixture (total pressure of 1.2 mbar) as a function of elapsed time. Only selected spectra from the whole series are shown. CO_2 gas (0.8 mbar) was introduced in the gas cell at $t = 0$ s, and H_2 gas (0.4 mbar) was added to the gas cell at $t = 240$ s

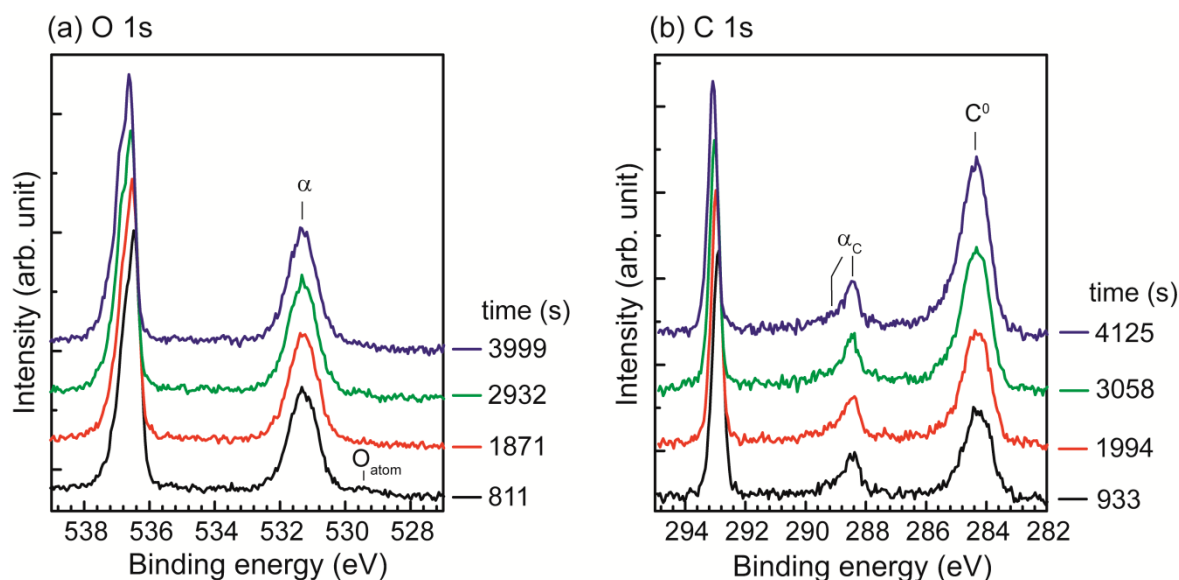


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The peak α in O 1s (Fig. 2a) and the peak α_c in C 1s (Fig. 2b) are assigned to carbonate species, judging from the composition ratio between oxygen and carbon ($\text{O/C} \sim 3$) which is calculated from the area intensities of the O 1s peak (α) and the C 1s peaks (α_c) as compared with those of gaseous CO_2 .

At the CO_2 pressure of 0.8 mbar, carbonate is formed on the surface by the reaction of CO_2 with atomic oxygen, which is produced by CO_2 dissociation. The hydrogenation of carbonate was not observed when 0.4 mbar H_2 was added to the CO_2 gas.

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反射高速陽電子回折 (RHEPD) による Ag(111) 表面上のシリセンの構造決定

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