

Surface, Interface and Thin Films





# Soft X-Ray Absorption Spectroscopy of 1,3,5-Trithia-2,4,6-Triazapentalenyl Thin Film on Ag(111)

K. Eguchi<sup>1</sup>, K. Awaga<sup>1, 2</sup>, Y. Takagi<sup>3,4</sup> and T. Yokoyama<sup>3,4</sup>

<sup>1</sup>Graduate school of Science, Nagoya University, Nagoya 464-8602, Japan

<sup>2</sup>CREST, JST, Kawaguchi 332-0012, Japan

<sup>3</sup>Institute for Molecular Science, Okazaki 444-8585, Japan <sup>4</sup>School of Physical Sciences, The Graduate University for Advanced Studies (SOKENDAI), Okazaki 444-8585,

Japan

Organic radicals, which are open-shell molecules, have been attracting significant attention because of their potential applications in organic electronics and spintronics. Because of its magnetic bistability at room temperature, 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA; Fig. 1(a)) is a candidate for such applications [1]. Although its crystal structures as well as the thermally induced and photo-induced magnetic phase transitions in single crystals have been widely studied, few studies have investigated the structures and electronic and magnetic states of TTTA in thin films. In this study, we measure the angular dependence of X-ray absorption spectra (XAS) of a TTTA thin film prepared on Ag(111) using linearly polarized X-rays.

The sample was prepared on Ag(111) by exposure of gaseous TTTA under ultra-high vacuum condition (~6  $\times$  10<sup>-8</sup> Pa) at room temperature and subsequent annealing at 500 K. XAS were measured at the end station of the bending magnet beamline 4B using an Xcircular rav magnetic dichroism (XMCD) measurement chamber in total electron yield detection mode. Linearly polarized X-rays were irradiated to the sample at incident angles between 0° (normal) and 60° (grazing) in increments of 10° with respect to the substrate normal. Energy resolutions were set to  $E/\Delta E$ = 2000 and 4000 at N K- and S L-edge, respectively.

Figure 1(b) shows angle-dependent N K-edge XAS of the TTTA thin film on Ag(111). Four peaks labeled A–D were mainly observed in this region, and they increased with the X-ray incidence angle, indicating that molecules adsorbed with a relatively flat-lying orientation because of the  $\pi$ \* bonding characters of the singly occupied molecular orbit (SOMO) and lowest unoccupied molecular orbit (LUMO) of TTTA. Judging from the peak intensities and energy levels, peaks A and B can be assigned to SOMO and LUMO, respectively, indicating that the radical in TTTA can survive in the thin film.

Figure 1(c) shows angle-dependent S L-edge XAS of the TTTA thin film. Five peaks, labeled A–E, were observed. Although the intensity of peaks B–E decreased with increasing X-ray incidence angle, peak A showed an opposite polarization dependence. Therefore, peak A can be attributed to the transition from the  $2p_{3/2}$  to the  $\sigma^*$  orbital, as observed in thiophene [2], suggesting less contribution of the S 3d orbitals to the SOMO of TTTA.



Fig. 1. (a) Chemical structure of TTTA. (b) N K-edge and (c) S L-edge XAS of the TTTA thin film on Ag(111) taken at 220 K.

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#### Potassium Doping into Single Crystalline Organic Monolayer

T. Hosokai<sup>1</sup>, Y. Hasegawa<sup>2</sup>, M. Yano<sup>2</sup>, K. R. Koswattage<sup>3</sup> amd Y. Yamada<sup>2</sup>

<sup>1</sup>National Institute of Advanced Industrial Technology and Science, Tsukuba 305-8568, Japan

<sup>2</sup>Institute of Applied Physics, University of Tsukuba, Tsukuba 305-8573, Japan

<sup>3</sup>Institute for Molecular Science, Department of Photo-Molecular Science, Okazaki 444-8585, Japan

Metal doping into organic semiconducting thin films (OTFs) is practically relevant technology in *Organic Electronics*. Potassium (K) is known as a very low workfunction (WF) metal showing around 2.3 eV and is often used as the dopant. K-doped OTF systems often show new electronic states within the band gap of the bare OTFs [1]. This is usually interpreted by filling the lowest unoccupied molecular orbital (LUMO) of OTFs by electron-transfer from the doped K atoms. For such experiments bulk OTFs have been often employed. Owing to this, the discussion on the electronic structure of the doped-OTFs with respect to the doped structure in a molecular level was hindered.

To overcome this issue, we will study the single crystalline K-doped organic monolayers fabricated on Au(111) surface by using angle-resolved ultraviolet photoelectron spectroscopy (UPS). Previously, we found a well-ordered monolayer is formed by depositing K atoms onto two kind of organic monolayer of picene ( $C_{22}H_{14}$ , Fig. 1(a)) and coronene ( $C_{24}H_{12}$ , Fig. 1(b)) [2]. For these doped monolayer systems, here we applied ARUPS to reveal the physics behind the K-doped OTFs.

All the experiments were conducted at BL2B. After preparing a clean Au(111) with conventional Ar sputtering and annealing process, picene, coronene, or K was thermally grown on the substrate. The deposition amount is controlled by a quartz microbalance and is confirmed by a change in WF of the systems. For the well-ordered doped monolayers, K was deposited step-by-step onto the picene or coronene monolayer. ARUPS was measured with a photoelectron emission angle  $\theta = -5 \sim 15^{\circ}$ , hv = 28 eV. All the depositions and measurements were performed at room temperature.

Figures 1(a) and 1(b) show the ARUP spectra of bare Au(111), picene or coronene monolayer, K-doped picene or coronene monolayer, K/Au(111), respectively. The surface state (SS) near the Fermi level in the substrate (top) spectra is vanished by the molecular monolayer formation (second top spectra). The highest occupied MO (HOMO: H) is located at 1.36 eV for picene and 1.57 eV for coronene. The K doping into the films results in the appearance of new states at 0.31 eV for picene and 0.52 eV for coronene. As seen in the K/Au(111) spectra (bottom ones), the new states observed by the K doping are differed to one originating from pure K atoms, which is located at 0.92 eV.

The new states formed in the K/picene and K/coronene systems near the Fermi level can be ascribed to the former LUMO (L') bands. X-ray

photoelectron spectroscopy showed a large chemical shift of C1s in the systems towards higher binding energy side due to electron transfer from K atoms [2]. The resemble features have been observed for other organic/metal systems, such as PTCDA and DIP [3]. The position of L' state is depending on filling amount of the LUMO by electrons. It can be considered that LUMO of picene thin films is partially filled since the L' feature is partly cut at the Fermi level. On the other hand, the L' feature for the K/coronene system is located at higher binding energy side, implying more electrons are transferred to LUMO of coronene. However, the question arises why the doping amount of the electrons are differed between picene and coronene. In previous, a complete filling of LUMO level was reported for the K doped-thick picene and coronene films (thickness is 5 nm) [4]. In this sense, presence of the Au(111) substrate as well as the low dimensional organic monolayer may play the role. To understand this, theoretical investigations based on the ordering model as determined by STM [2] is required.



Fig. 1. (a) ARUPS of Au(111), picene monolayer/Au(111), K-doped/picene, and K/Au(111). (b) ARUPS of Au(111), coronene monolayer/Au(111), K-doped/coronene, and K/Au(111).

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### **Electronic Structures of Thienyl-Porphyrin Derivatives**

Y. Nakayama<sup>1</sup>, A. Nakagawa<sup>1</sup>, K. R. Koswattage<sup>2</sup>, T. Aikawa<sup>1</sup>, T. Kondo<sup>1</sup> and M. Yuasa<sup>1</sup>

<sup>1</sup>Department of Pure and Applied Chemistry, Graduate School of Science and Technology,

Tokyo University of Science, Noda 278-8510, Japan

<sup>2</sup>Center for Frontier Science, Chiba University, Chiba 263-8522, Japan

Porphyrin is a representative bio-functional unit of a large  $\pi$ -conjugated ring and has been attracting much attention of both physico-chemical and bio-medical points of view. Porphyrins functionalized by thiophenes, typical organic semiconductors, are therefore of particular interests for bio-electronics applications [1]. In the present study, we elucidated the electronic structures of two thienyl-porphyrin derivatives, 5,10,15,20-tetra(2-thienyl)porphyrin (2T) and 5,10,15,20-tetra(3-thienyl)porphyrin (3T) (Fig. 1), by means of photoelectron spectroscopy (PES).

Procedures for synthesizing 2T and 3T are found elsewhere [2]. Thin films of 2T and 3T were prepared by vacuum evaporation onto Au-coated Si substrates, where their thicknesses were monitored with a quartz microbalance. PES measurements were conducted at BL2B of UVSOR. The work function of the present electron analyzer (VG-Scienta, R3000) was determined to be 4.40 eV after accurate calibration of the photon energy by using second-order light.

Figure 2 shows wide range PES spectra of *bulk* (16 nm-thick) films of 2T and 3T. The spectral profiles are respectively well reproduced by density-of-states curves which are simulated from each orbital energy distribution. The electronic structures in the highest occupied regions evolve on step-by-step deposition of 2T and 3T as shown in Fig. 3. For both cases, peaks derived from the highest occupied orbitals move toward the Fermi level as the films become thinner. This trend to reduce substantial hole injection barrier (HIB) heights may be attributed to a common screening effect at metal-organic interfaces.

Changes in the work function (WF), HIB, and the ionization potential (IP) values are summarized in Figs. 3(a), (b), and (c), respectively, plotted as a function of the 2T or 3T thickness. These results imply that orientation of the side groups merely gives minor impacts, if any, to the charge carrier conduction characteristics of these thienyl-porphyrin derivatives.



Fig. 1. Molecular structures of (a) 2T and (b) 3T.



Fig. 2. (Top panel) Quantum chemical calculation results of 2T (blue) and 3T (red) molecules. (Bottom) PES spectra of 16 nm-thick films of 2T and 3T.



Fig. 3. Evolution of the PES spectra of 2T (left) and 3T (right) thin films grown on Au substrates.



Fig. 4. (a) Work functions (WF), (b) HIB, and (c) ionization potentials (IP) of the 2T (blue) and 3T (red) thin films plotted as a function of the thickness.

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# Molecular Orientation of Pentacene Thin Film on Silane-SAM with Different Growth Condition

K. K. Okudaira and Y. Tuboi

Association of Graduate Schools of Science and Technology, Chiba University, Chiba 263-8522, Japan

Recently, organic thin-film transistors (OTFT's) with field-effect mobility and on/off current ratio comparable to hydrogenated amorphous silicon thin-film transistors. OTFT's have been fabricated using pentacene as the active material.

Since the interface between the organic active material and the gate dielectric material is a critical part of the field-effect device, control of this interface is important. The characteristics of pentacene TFT's can be improved by using a self-organizing material like octadecyltrichlorosilane (OTS) between the SiO<sub>2</sub> gate dielectric and the pentacene active layer [1].

To achieve optimum control over SAM growth, a new, efficient, and humidity controlled method of growing highly ordered OTS SAMs has been reported. OTFT field-effect mobility and contact angle of the surface of the SAM show strong dependence of the growth condition such as humidity [2]. The characteristics of OTFT such as mobility are considered to be dependence on not only the electronic structure but also the molecular orientation of organic molecule.

In this work we used OTS SAMs for substrate and examined the molecular orientation of pentacene thin films thermally deposited on these SAM surfaces by angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) measurements. In the ARUPS take-off angle dependence of HOMO peak for  $\pi$ -conjugated organic molecule provides an important information on the molecular orientation [3].

ARUPS measurements were performed at the beam line BL2B of the UVSOR storage ring at the Institute for Molecular Science. The take-off angle ( $\theta$ ) dependencies of photoelectron spectra were measured with the photon energy (hv) of 28 eV. We use octadecyltrichlorosilane (OTS) as coupling agent for SAM. The SAMs were prepared using a dipping method at room temperatures. To fabricate humidity-controlled SAM growth was performed under ambient conditions in a controlled atmosphere glovebox at varied relative humidity levels with 10%, 60%, and 80%. Pentacene thin film was deposited on these SAMs.

We observed take-off angle ( $\theta$ ) dependence of HOMO peak in UPS of pentacene thin film (thickness of about 1.5 nm on OTS-SAMs with different growth condition, expressed by humidity (10%) and (60%) (Figs.1(a) and (b)). The HOMO peaks of pentacene on OTS-SAM(with humidity 10%) and 60%) appear at binding energy of about 2 eV. The HOMO peaks of pentacene on both OTS-SAM (10%) and on OTS-

SAM(60%) show intense peaks at normal take-off angle ( $\theta = 0^{\circ}$ ), and at grazing angle these intensities become small. At grazing angle ( $\theta = 60^{\circ}$ ) the intensity of HOMO peak of pentacene on OTS-SAM (10%) remains, while the pentacene HOMO peak on OTS-SAM(60%) almost disappears. Take-off angle dependence of HOMO peak on OTS-SAM(10%) is different from that on OTS-SAM (60%). It indicates that the molecular orientation of pentacene on OTS-SAM(10%) is different from that on OTS-SAM(60%). The surface conditions of OTS-SAM due to the growth condition of SAM such as humidity affect the molecular orientation of organic semiconductor layer, which would have an effect on the characteristics of OTFT such as mobility.



Fig. 1. Take-off angle ( $\theta$ ) dependences of ultraviolet photoelectron spectra with HOMO region of pentacene (1.5nm)/OTS-SAM (with humidity of 10%) (a) and pentacene(1.5nm)/OTS-SAM (with humidity of 60%) (b).

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#### A Surface Study of CsK2Sb Multi-Alkali Photocathode by UPS

M. Urano<sup>1</sup>, M. Kuriki<sup>1</sup>, K. Negishi<sup>1</sup>, A. Yokota<sup>1</sup>, T. Konomi<sup>2</sup> and Y. Seimiya<sup>2</sup>

<sup>1</sup>Graduate school of Advanced Science of Matter, Hiroshima University, Higashi-hiroshima 739-8530, Japan <sup>2</sup>Hight Energy Accelerator Research Organization, Tsukuba 305-0801, Japan

Linear accelerator based facilities such as X-FEL, ERL, Linear colliders break the limitations of the circular accelerators such as 3rd generation light source, ring colliders, etc. In the linear accelerator, high quality and high average current beam has to be provided because of no circulation. Laser photocathode can provide such beam, but conventional cathode material such as metal, GaAs, Cs2Te are not ideal. CsK2Sb multi-alkali photocathode is the candidate of the ideal cathode due to the high quantum efficiency (QE), and high robustness, and green laser driver for photo-electron effect. Many experimental efforts has been made to obtain the CsK2Sb photocathode optimized for the photo-cathode purpose, but it is on the way. In this study, we perform UPS analysis of the CsK2Sb cathode to reveal the cathode performance and the surface states.

Figure 1 shows QE (405nm) evolution during the cathode activation (Sb, K, and Cs evaporation on Si substrate (Si 100) in this order). Typical pressure was  $1.0 \times 10^{-7}$  Pa.

Amount of Sb, K, and Cs are shown as thickness measured by quartz monitor. The sample is in situ and is transferred to UPS chamber by transfer rod. Amplitude (cross section) ratio of Cs 5s and Cs 5p as a function of QE with laser (405nm) are shown in Fig. 2. Different color shows different samples. QE variation is due to the degradation in time for each sample. According to the results, the small ratio gives a large QE for each sample, but the sample dependence is large. According to a similar measurement for Cs<sub>3</sub>Sb [1], the low ratio is interpreted as that Cs is bound to Sb as Cs+ ion. From this observation, the bound state of Sb and Cs is a good index to examine the photocathode performance. This is the first observation for the relation between the cathode performance and the Cs-Sb bound state.



Fig. 1. QE evolution during CsK2Sb activation.



Fig. 2. Cs 5s/5p ratio as a function of QE.

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**Ⅲ-4** 

BL3U

### Operando Observation of Cobalt Catalyst for Oxygen Evolution Reaction by Soft X-Ray Absorption Spectroscopy

M. Yoshida<sup>1,2,\*</sup>, Y. Mitsutomi<sup>1</sup>, S. Onishi<sup>1</sup>, F. Yamamoto<sup>1</sup>, M. Nagasaka<sup>3</sup>, H. Yuzawa<sup>3</sup>, N. Kosugi<sup>3</sup> and H. Kondoh<sup>1</sup>

<sup>1</sup>Department of Chemistry, Keio University, Yokohama 223-8522, Japan

<sup>2</sup>Cooperative Research Fellow, Institute for Catalysis, Hokkaido University, Japan

<sup>3</sup>Institute for Molecular Science, Okazaki 444-8585, Japan

Recently, hydrogen production by electrochemical water splitting using renewable energy sources such as solar, wind, and hydroelectric powers attracts attention from the viewpoint of the realization of a sustainable society that does not depend on fossil fuels. For practical applications, the improvement of overall water splitting efficiency has been required by the development of highly active oxygen evolution electrocatalyst. In this situation, Nocera et al. reported that cobalt oxides electrodeposited from a dilute Co<sup>2+</sup> solution in phosphate or borate buffered electrolyte (Co-P<sub>i</sub> or Co-B<sub>i</sub>, respectively) are efficient electrocatalysts for oxygen evolution reaction (OER) [1]. The local structures of Co species in the Co-P<sub>i</sub> and Co-Bi catalysts were investigated by X-ray absorption fine structure (XAFS) spectroscopy and pair distribution function (PDF) analysis, and it was found that the Co-P<sub>i</sub> and Co-B<sub>i</sub> thin films form a nano-sized cluster (ca. 2-3 nm and 3-4 nm, respectively) with an edge-sharing CoO<sub>6</sub> octahedral structure [2]. However, the detailed information about oxygen species in these electrocatalysts under working condition is not yet obtained. Thus, we have investigated the reaction mechanism by measuring operando O K-edge XAFS spectra for Co-Pi and Co-Bi under electrochemical potential control.

Electrochemical O K-edge XAFS measurements with transmission mode using soft X-rays were performed at BL3U in the UVSOR Synchrotron, according to the previous work [3]. A home-made electrochemical cell was used with Au/Cr/SiC thin film substrates as working electrodes, a Pt counter electrode, and a Ag/AgCl reference electrode. Co-P<sub>i</sub> or Co-B<sub>i</sub> electrocatalyst was electrodeposited on the Au/Cr/SiC working electrode at 1.0 V in 0.1 M phosphate or borate buffered electrolyte containing 0.5 mM Co(NO<sub>3</sub>)<sub>2</sub>.

The OER activities of Co-P<sub>i</sub> and Co-B<sub>i</sub> were tested by the linear sweep voltammograms in phosphate and borate buffered electrolytes, respectively. The result exhibited that the OER current for Co-P<sub>i</sub> electrode was higher than that for Co-B<sub>i</sub>, which means that Co-P<sub>i</sub> is a more efficient OER electrocatalyst compared with Co-B<sub>i</sub>. Next, the operando O K-edge XAFS spectra for Co-P<sub>i</sub> catalyst were taken under electrode potential control in a phosphate buffered electrolyte, as shown in Fig. 1. At 0.0 V, an absorption peak derived from oxygen species of CoOOH was observed around 531 eV. When the electrode potential was changed from 0.0 to 1.1 V, a new absorption peak attributed to oxygen species of CoO<sub>2</sub> was observed around 529 eV, meaning that the part of CoOOH cluster was oxidized to CoO<sub>2</sub> with the high-valent cobalt species (Co<sup>4+</sup>) (Fig. 2). Meanwhile, when the similar measurements were tested for Co-B<sub>i</sub>, the fraction of generated CoO<sub>2</sub> against CoOOH for Co-B<sub>i</sub> was slightly smaller than that for Co-P<sub>i</sub>. Therefore, we found that Co-P<sub>i</sub> can function as a highly active OER electrocatalyst due to the presence of many CoO<sub>2</sub> species.



Fig. 1. Operando O K-edge XAFS spectra of Co-P<sub>i</sub> electrocatalyst at various electrode potentials in 0.1 M phosphate buffered electrolyte.



Fig. 2. Proposed reaction mechanism for  $Co-P_i$  and  $Co-B_i$  OER electrocatalysts.

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#### BL3B

# Effects of Ion Implantation and Thermal Annealing on PL due to Cr<sup>3+</sup> in LaAlO<sub>3</sub>

M. Harima, T. Morimoto and Y. Ohki Waseda University, Tokyo 169-8555, Japan

High permittivity (high-k) dielectrics such as LaAlO<sub>3</sub> are expected as a gate insulator in advanced MOS devices. In the manufacturing process of semiconductors, ion implantation and thermal annealing are often used [1]. However, few reports have been published on the influences of such processing procedures on point defects in LaAlO<sub>3</sub>.

In the present study, single crystal LaAlO<sub>3</sub> was implanted with  $B^+$  ions and then annealed in O<sub>2</sub> at 900°C. The effects of such treatments were examined by measuring optical absorption, X-ray diffraction (XRD), and photoluminescence (PL).

Figure 1 shows optical absorption spectra. The sharp increase in the absorption from around 5.0 eV is caused by the bandgap absorption [2]. This absorption becomes weak by the ion implantation, whereas the following thermal annealing increases the absorption in nearly the whole energy range.

Figure 2 shows in-plane XRD spectra. A sharp peak is seen at  $2\theta_{\chi} = 23.5^{\circ}$ , which corresponds to the diffraction on (012) planes of crystalline LaAlO<sub>3</sub> [3]. The XRD intensity decreases by about 40 percent after the ion implantation. The annealing given following the implantation increases the intensity to almost the same level as the untreated sample. This indicates that the crystallinity of single crystal LaAlO<sub>3</sub> is degraded by the ion implantation and is recovered by the thermal annealing after the ion implantation.

Figure 3 shows PL spectra excited by 6.0-eV photons. A PL, which has three sharp components at 1.62, 1.65, and 1.69 eV, is observable. This PL is due to  $Cr^{3+}$  present in LaAlO<sub>3</sub> as an impurity [4]. After the ion implantation, the total intensity of this PL



Fig. 1. Optical absorption spectra observed for LaAlO<sub>3</sub> samples with a thickness of about 0.5 mm at room temperature before any treatment (1), after implantation of B<sup>+</sup> ions at a fluence of  $10^{15}$  cm<sup>-2</sup> (2), and after thermal annealing in O<sub>2</sub> at 900 °C given following the B<sup>+</sup> implantation (3).

decreases by about 79% compared with the untreated sample. When the sample was implanted with  $B^+$  ions and then annealed at 900°C, the intensity of this PL increases to almost the same level as the untreated sample. Since this PL is sensitive to the crystallinity of LaAlO<sub>3</sub> [5], the decrease of the PL intensity is due to degradation of crystallinity.

These results indicate that the crystallinity of  $LaAlO_3$  is collapsed by the ion implantation and is recovered by the thermal annealing after the ion implantation.



Fig. 2. In-plane XRD pattern. The notations of symbols and curves are the same as those in Fig. 1.



Fig. 3. PL spectra induced by the irradiation of photons with energies of 6.0 eV. The notations of symbols and curves are the same as those in Fig. 1.

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BL4U

# STXM Analysis of Adsorbent for Effective Recovery of Radioactive Elements

Y. Sano, S. Watanabe and S. Kibe Japan Atomic Energy Agency (JAEA), Tokai 319-1194, Japan

Spent nuclear fuels generated from nuclear power plants contain U and Pu which can be reused, and several long-lived radioactive elements. It will be quite important for effective utilization of energy and environmental loading reduction to process the spent fuel adequately. JAEA has been developing the selective recovery process of radioactive elements, which uses adsorbents of SiO<sub>2</sub> supports coated with styrene-divinylbenzene (SDB) copolymer (SiO<sub>2</sub>-P) and extractants on its surface. Our recent work shows that the separation and recovery abilities of adsorbent, i.e. adsorption/elution behavior of radioactive elements, in this process are strongly dependent on the condition of its surface in which polymer and extractants are impregnated [1]. In this study, some information about the adsorbent surface, such as thickness of polymer and uniformity of extractants, were investigated by scanning transmission X-ray microscope (STXM).

Some adsorbents with different crosslinking degree of polymer (CDP) were synthesized and octyl (phenyl)-N, N-diisobutylcarbonoylmethylphosphine oxide (CMPO) was impregnated as an extractant by the flowsheet reported by Wei *et al.* [2]. The average diameter and pore size of the SiO<sub>2</sub> supports were 50 $\mu$ m and 600nm, respectively (Fig.1). These adsorbents were sliced to 300nm in thickness by focused ion beam (FIB), and were supplied to STXM analysis.

Figure 2 shows the change of C-NEXAFS spectra (C-K edge) with CDP, which were obtained near the pore surface on the cross section of the sliced adsorbents. The intensity of the peak at 285 eV (which must be attributed to C  $1s \rightarrow \pi^*$  transition of aromatic C=C) changed with CDP and the impregnation of CMPO. Figure 3 show the colorized composition maps on the cross section of sliced SiO<sub>2</sub>-P (CDP=10%) and SiO<sub>2</sub>-P (CDP=15%) with 20wt% CMPO, which were calculated by fitting C-NEXAFS spectra with those of SDB polymer and CMPO. The SDB polymer and CMPO were distributed within several hundred nanometers from the pore surface, and their distributions were spread by the increase of CDP and CMPO.

The excess increase of the region with SDB polymer and CMPO in the pore may disturb the fluid flow through the pore, and this will give some interpretation of our previous experiment, in which it was more difficult to elute adsorbed metal ions from the adsorbent with higher CDP [1]. It should be required for effective recovery of radioactive elements to compare the STXM data and adsorption/elution behavior, and to optimize the distributions of SDB polymer, i.e. polymer thickness, and extractants.



Fig. 1. Photo of the SiO<sub>2</sub> supports.







Fig. 3. Colorized composition maps (light green;  $SiO_2$ , red; SDB, blue; CMPO (purple; mixture of red and blue) ).

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**Ⅲ-4** 

## Pd *M*-Edge X-Ray Magnetic Circular Dichroism in Perpendicularly Magnetized Co/Pd Multilayers

J. Okabayashi<sup>1\*</sup> and H. Munekata<sup>2</sup>

<sup>1</sup>Research Center for Spectrochemistry, University of Tokyo, Tokyo 113-0033, Japan <sup>2</sup>Imaging Science and Engineering Laboratory, Tokyo Institute of Technology, Yokohama 226-8503

CoPd is a candidate for the spintronics materials possessing perpendicular magnetic anisotropy (PMA) which can be utilized for the low power operation devices [1]. The 4*d* transition metal (TM) system of Pd is well recognized as the sustainable elements of 5*d* TM system in Pt toward the PMA materials combined with the magnetic 3*d* TMs. In order to understand the mechanism of PMA in CoPd, the contributions of orbital magnetic moments of each element have to be clarified explicitly. Bruno theoretically proposed the orbital moment anisotropy in transition-metal multilayers as a second perturbation of spin-orbit interaction [2]. However, even in the strong spin-orbit coupled cases using 4*d* or 5*d* TMs, the applicability of this formula has been still debated [3].

We reveal the anisotropic orbital magnetic moments in Co/Pd multilayers using angular-dependent x-ray magnetic circular dichroism (XMCD) and their spectral analysis. Core-level X-ray absorption spectra (XAS) of Pd *M*-edge appears at around 530 eV which overlaps with the O *K*-edge absorption. In order to detect the Pd *M*-edge absorption signals, the surface oxide components have to be removed, which enables to measure both Pd *M*-edge and Co *L*-edge absorption at the same experimental condition. Our aim in this study is to discuss both orbital and spin moments of Co and Pd for PMA and in-plane anisotropy samples.

We prepared two kinds of samples of Co/Pd multilayered structures: Co (0.69 nm)/Pd (1.62 nm) for PMA and Co (1.03 nm)/Pd (1.62 nm) for in-plane anisotropy with stacking five periods on the Si substrates [4]. Sample surfaces were sputtered by Ar ions before the XMCD measurements in order to remove the oxygen contamination. We performed XMCD experiments at BL4B, UVSOR, Institute of Molecular Science. Total electron yield mode by directly detecting the sample current was adopted. A magnetic field of  $\pm 5$  T was applied along the direction of the incident polarized soft x-ray.

We successfully observed clear XMCD signals in Pd *M*-edges after the removal of surface contamination as shown in Fig. 1. Although the XAS line shapes overlap with those of O *K*-edge absorption, clear XMCD signals induced by the proximity with Co layers are observed. The Pd *M*-edge XMCD line shapes in both PMA and in-plane samples almost remain unchanged. Unfortunately, conventional magneto-optical sum rule analysis, which is defined in the TM *L*-edge absorption, cannot be applicable for *M*-edge XMCD [5]. Precise XAS line shapes in Pd *M*-edges are necessary for the determination of absolute

values of spin and orbital moments. On the other hand, clear Co *L*-edge XAS and XMCD with angular dependence reveal the enhancement of orbital moments in the surface normal direction because of PMA.

Considering these results, we discuss the PMA in Co/Pd multilayers. The Co atoms possess large spin moments and the Pd atoms possess large spin-orbit interaction. The orbital moments in Co is enhanced through the proximity with Pd which induces the spin-orbit coupling. On the other hand, magnetic moments are induced in Pd through the proximity with Co. These collaborate at the interfaces, which enhances the PMA in Co/Pd multilayers. In case of thick Co, the shape anisotropy in Co governs the in- plane anisotropy. Therefore, we propose that the origin of the PMA in Co/Pd interface can be explained by the *orbital moment transfer* at the interface, which opens up new research fields of '*Spin-Orbitronics*'.

We acknowledge to Prof. T. Yokoyama, Dr. Y. Takagi, and Ms. M. Uozumi for the technical supports at BL4B.



Fig. 1. XAS and XMCD of Pd *M*-edge and Co *L*-edge in perpendicularly magnetized Co (0.69 nm)/Pd (1.62 nm) multilayer.

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\*e-mail: jun@chem.s.u-tokyo.ac.jp

## A Monatomic Layer Iron Nitride Magnetically Coupled with Chromium Nano-Clusters

T. Miyamachi<sup>1</sup>, Y. Takahashi<sup>1</sup>, S. Nakashima<sup>1</sup>, Y. Takagi<sup>2,3</sup>, M. Uozumi<sup>2,3</sup>,

T. Yokoyama<sup>2,3</sup> and F. Komori<sup>1</sup>

<sup>1</sup>Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8581, Japan

<sup>2</sup>Department of Materials Molecular Science, Institute for Molecular Science, Okazaki 444-8585, Japan

<sup>3</sup>Department of Structural Molecular Science, The Graduate University for Advanced Studies (SOKENDAI),

Okazaki 444-8585, Japan

An iron nitride compound,  $Fe_4N$ , in the ferromagnetic phase is a promising candidate for rareearth free permanent magnets for their large magnetic anisotropy and high coercivity. The crystal structure of the Fe<sub>4</sub>N is composed of so called Fe-plane and Fe<sub>2</sub>N plane in the fcc Fe sublattice with a N atom centered in the cubic cell [1].

We have previously investigated atomic scale structural and electronic properties of a monatomic Fe<sub>4</sub>N layer grown on a Cu(001) using scanning tunneling microscopy (STM). The surface of the monatomic Fe<sub>4</sub>N is composed of the Fe<sub>2</sub>N plane with  $p4gm(2\times2)$  surface reconstructed structure, but its appearance alters between  $p4gm(2\times2)$  and c(2×2) ones in the STM image due to an orbital selective tunneling process [2]

Magnetic properties of the monatomic Fe<sub>4</sub>N layer (Fe<sub>2</sub>N layer) have been clarified by x-ray adsorption spectroscopy and x-ray magnetic circular dichroism (XAS/XMCD) conducted at BL4B in UVSOR [3]. We find that the fundamental magnetic properties, such as magnetic moments, magnetic anisotropy and the Curie temperature, rely on the surface quality, being considerably lowered by atomic defects on the surface [4]. In this work, we have further grown Cr nanoclusters on the Fe<sub>2</sub>N layer and investigated their influence on the magnetism of the Fe<sub>2</sub>N layer.

To grow the Fe<sub>2</sub>N layer on Cu(001), N<sup>+</sup> ions with an energy of 0.5 keV were firstly bombarded to the clean Cu surface and Fe was additionally deposited at room temperature. By subsequent annealing at 570 K, wellordered Fe<sub>2</sub>N layer can be obtained on the surface. The high-quality Fe<sub>2</sub>N layer on Cu(001) is achieved by the strict control of the growth condition especially for the amount of deposited Fe and annealing temperature. Thereafter, the Cr deposition is done at room temperature, resulting in the formation of bilayer Cr nano-clusters with an almost identical lateral size of ~ 3 nm, which is confirmed by STM in advance of XAS/XMCD measurements.

The measurements were performed at BL4B in UVSOR by total electron yield mode at  $B = \pm 5$  T and T = 7.2 K. In the in-plane ( $\theta = 55^{\circ}$ ) and the out-of-plane ( $\theta = 0^{\circ}$ ) geometries, the XMCD spectra are obtained by detecting  $\mu_{+} - \mu_{-}$ , where  $\mu_{+} (\mu_{-})$  denotes the XAS at Fe and Cr L-adsorption edges with the photon helicity parallel (antiparallel) to the sample magnetization.

Note that  $\theta$  is the angle between the sample normal and the incident x-ray.

We find no significant difference in the Cr  $\mu_+$  and  $\mu_-$ , and thus the minute XMCD signal from the bilayer Cr nano-cluster. Combined with the structural characterization by STM, the results suggest that the antiferromagnetic coupling between the first and second layers in the Cr nano-cluster. The XMCD spectrum at Fe L-adsorption edges reveals the modification of magnetic properties of the Fe<sub>2</sub>N layer. While the magnetic easy axis of the Fe<sub>2</sub>N layer with Cr nano-clusters is towards in-plane direction as in the case of the bare  $Fe_2N$  layer [3, 4], the reduction of the XMCD signal is observed, indicating the influence of the antiferromagnetic Cr nano-clusters through the magnetic coupling.

Quantitative analyses of the XMCD spectra giving magnetic moments, magnetic anisotropy and the Curie temperature of the system will unravel the details of the magnetic coupling between the Cr nano-clusters and  $Fe_2N$  layer.

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# Magnetism of Single and Double Layer Co Films on W(112)

Y. Takamura<sup>1</sup>, S. Mizuno<sup>1</sup>, T. Nakagawa<sup>1</sup>, Y. Takagi<sup>2</sup> and T. Yokoyama<sup>2</sup> <sup>1</sup>Department of Molecular and Material Sciences, Kyushu University, Fukuoka, 816-8580, Japan

<sup>2</sup>Institute for Molecular Sciences, Kyushu Omversity, Fukuoka, 810-8580, Jap

Magnetic thin films on heavy metal surfaces show large anisotropy and coercivity due to their strong spin orbit coupling in the heavy metals [1,2]. Magnetic anisotropy and coercivity can also be enhanced on anisotropic surface structures. bcc(112) surfaces, such as W(112), are good candidates for the highly anisotropic structure since they has ridge and furrow (Fig.1(a)), which would exhibit high magnetic anisotropy. Few investigations of magnetic overlayers on bcc(112) have been examined so far [3]. We have prepared Co nano structures on W(112) surface and investigated their magnetic properties.

X-ray magnetic circular dichroism (XMCD) measurements were done at BL4B using high field and low temperature end station ( $T_s \sim 5$  K,  $H \sim 6$  T). All the sample preparation and measurements were performed *in situ* under the vacuum of  $1 \times 10^{-10}$  Torr.

Figure 1 shows single and double layer Co on W(112) observed by scanning tunneling microscope (STM). We observed Co atomic wires along [11-1], and found no evidences for W-Co alloy formation. The 1st Co layer as well as the 2nd Co layer keep the same surface structure as W(112), 1×1 structure, irrespective of the large size mismatch between Co and W (~10%).

Figure 2(a) shows Co *L* edge XAS for 0.6 ML Co/W(112) and its XMCD, which does not show any dichroic signal even at  $T_s = 6$  K and the magnetic field of ±5 T. The absence of the XMCD signal means that the surface is not ferromagnetic. As in Fig. 2(b), increasing the Co thickness above 1 ML exhibits dichroic signal, corresponding to magnetic moment of 0.4  $\mu_B$ , which is rather small compared with that of bulk Co (1.6  $\mu_B$ ). The second layer Co is ferromagnetic, which is not ferromagnetically coupled with the 1st layer Co.

Figure 3 shows a magnetization curve (*M*-*H* curve) for 1.5 ML Co/W(112), which was measured by monitoring Co  $L_3$  edge XAS intensity as a function of the magnetic field. The *M*-*H* curve along the [11-1] direction shows hysteresis with large coercivity of 3 T.

The absence of ferromagnetism in the first Co layer on W(112) is attributed to strong electronic hybridization between Co and W, caused by the reduced bond length. The bond length between Co and W is 0.239 nm, as determined by low energy electron diffraction, which is 8% shorter than that for the hard share model (0.260 nm).



Fig. 1. STM images for (a) Co(0.6 ML)/W(112) and (b) Co/(1.2 ML). The inset in (a) shows a structure model.



Fig. 2. Co  $L_{2,3}$ -edge XAS and XMCD spectra for (a) Co(0.6 ML)/W(112) and (b) Co(1.5 ML). The spectra are taken at  $H = \pm 5$  T.



Fig. 3. In-plane magnetization curve for Co(1.5 ML)/W(112) taken along the [11-1] direction.

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# X-Ray Magnetic Circular Dichroism of a Copper-Phthalocyanine Monolayer on Si(111)- $(\sqrt{7} \times \sqrt{3})$ -In

S. Yoshizawa and T. Uchihashi

International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan

The reconstruction surface Si(111)-( $\sqrt{7} \times \sqrt{3}$ )-In [hereafter  $(\sqrt{7} \times \sqrt{3})$ -In] exhibits superconductivity below about 3 K [1]. The Cooper pairs of this superconductor reside in the surface atomic layer of indium and are sensitive to the surface environment [2]. Our electrical transport measurements have shown that the superconducting characteristics of  $(\sqrt{7} \times \sqrt{3})$ -In can be modified by covering the surface with selfassembly layers of various transition-metal phthalocyanines (Pcs). To clarify the mechanism we need to determine the magnetic moments of the Pcs on  $(\sqrt{7}\times\sqrt{3})$ -In, because both the electrostatic and magnetic interactions are expected to be involved. We have already performed X-ray magnetic circular dichroism (XMCD) experiments on MnPc and FePc [3, 4], and this time we focus on CuPc to complete the data sets.

The experiments were carried out at the BL4B XMCD system. ( $\sqrt{7} \times \sqrt{3}$ )-In samples were prepared *in*situ by depositing indium onto a clean Si(111) surface followed by an annealing at about 400°C. The growth of the  $\sqrt{7} \times \sqrt{3}$  phase was confirmed with low-energy electron diffraction. CuPc was thermally deposited from a Knudsen cell onto the  $(\sqrt{7} \times \sqrt{3})$ -In surface held at room temperature. The molecular coverage was adjusted to be less than 1 monolayer (ML) for avoiding a second-layer formation. Then, the samples were cooled down to ~7 K and X-ray absorption spectra (XAS) were measured by using a circularly polarized light with ~60% polarization. XMCD signals were obtained from the difference of XAS measured in magnetic fields of  $B = \pm 5$  T applied in the direction parallel to the incoming light.

Before going to the XMCD measurement, the adsorption geometry of CuPc was checked from XAS at the K edge of nitrogen (Fig. 1). The sharp peaks at around 400 eV in the XAS curve at  $\theta = 55^{\circ}$  are assigned to transitions from the nitrogen 1s orbital to  $\pi^*$  molecular orbitals [5]. Their disappearance at  $\theta = 0^{\circ}$  (normal incidence) demonstrates that the molecular framework of CuPc is nearly parallel to the surface.

Figure 2 shows the XAS and the XMCD at the L<sub>2,3</sub> edges of copper. By using XMCD sum rules, we estimated the effective spin moments as  $\langle S_{eff} \rangle = 0.7\pm0.2\mu_B$  for  $\theta = 0^\circ$  and  $\langle S_{eff} \rangle = 0.5\pm0.2\mu_B$  for  $\theta = 55^\circ$ . Here,  $\langle S_{eff} \rangle$  is a sum the spin moment and the intraatomic magnetic dipolar moment. Since the latter contribution goes to zero at  $\theta \sim 55^\circ$  for molecular orbitals with  $C_4$  symmetry [6], the non-zero  $\langle S_{eff} \rangle$  at  $\theta = 55^\circ$  obtained here clearly indicates the presence of

spins in CuPc molecules adsorbed on the  $(\sqrt{7} \times \sqrt{3})$ -In surface. The present results give important clues for understanding the function of a CuPc monolayer on superconducting  $(\sqrt{7} \times \sqrt{3})$ -In.



Fig. 1. XAS at the N K edge. The coverage of CuPc is about 0.7 ML.



Fig. 2. XAS and XMCD at the Cu  $L_{2,3}$  edges. The coverage of CuPc is about 0.7 ML.

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# Vacuum Ultraviolet Transmission Spectra of Amorphous Arsenic Chalcogenide Thin Films

#### K. Hayashi

#### Department of Electrical, Electronic and Computer Engineering, Gifu University, Gifu 501-1193, Japan

It is well-known that amorphous chalcogenide materials exhibit a variety of photoinduced phenomena by irradiation of light with energy corresponding to the optical band gap [1]. Photoinduced changes observed in amorphous chalcogenide materials are classified into two types, irreversible and reversible changes. Reversible changes can be induced optically in amorphous bulk materials and well-annealed evaporated thin films, in which the changes can be removed by annealing to the glass-transition temperature. The reversible photodarkening arising from the red-shift of the optical absorption edge is a photoinduced phenomenon. typical reversible Irreversible changes are induced in as-deposited evaporated thin films. The irreversible photodarkening in as-deposited amorphous films is an irreversible change, it is believed that it occurred by photopolymerization. The irreversible change observed in EXAFS [2] and IR [3] is interpreted by rearrangement of bonding configurations of molecular species within as-deposited evaporated films.

To our knowledge, little attention has been given to photoinduced changes at the vacuum ultra-violet (VUV) absorption spectrum. In this report, we measure the VUV transmission spectra on asdeposited evaporated amorphous arsenic chalcogenide films.

Samples used for the measurement of the VUV transmission spectra were amorphous arsenic chalcogenide (a-As<sub>x</sub>Se<sub>1-x</sub>) thin films prepared onto aluminum thin films by conventional evaporation technique. Using different bulk glass of the composition as a source material, different amorphous film of the compositions was prepared. Typical thickness of the amorphous film and the aluminum film were around 200 nm and 100 nm, respectively. The aluminum film of the thickness of 100 nm was also used in order to eliminate the higher order light from the monochromator in the VUV region. The measurements were carried out at room temperature at the BL5B beam line of the UVSOR facility of the Institute for Molecular Science. And the spectrum was measured by using the silicon photodiode as a detector. Two pinholes of 1.5 mm in a diameter were inserted between the monochromator and sample to remove stray light. The intensity of the VUV light was monitored by measuring the TPEY of a gold mesh. The positions of the core levels for the samples were calibrated by referencing to the 2p core level absorption peak of the aluminum film.

Figure 1 shows the VUV transmission spectra of as-

deposited a-As<sub>0.3</sub>Se<sub>0.7</sub>, a-As<sub>0.4</sub>Se<sub>0.6</sub>, and a-As<sub>0.5</sub>Se<sub>0.5</sub> films. Two main absorption peaks were observed in this wavelength region. One absorption peak around 22 nm corresponds to the 3d core level of selenium atom. Another absorption peak around 28 nm corresponds to the 3d core level of arsenic atom. As shown in the figure, the ratio of the two main absorption peaks changes depending on composition. The spectrum shape also changes depending on composition. We think that those changes are related to the local structures of the amorphous network. We will observe the composition dependence of the change in the spectrum before and after irradiation of light in future. And we are going to investigate the relations between those changes.



Fig. 1. The VUV transmission spectra of as-deposited a-As\_{0.3}Se\_{0.7}, a-As\_{0.4}Se\_{0.6}, and a-As\_{0.5}Se\_{0.5} films.

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**III-4** 

BL5B

# Study of *M*-Edge Resonant Magneto Optical Effect of Fe Ultrathin Films with Large Perpendicular Magnetic Anisotropy Induced by Rashba-Type Spin-Orbit Interaction

Sh. Yamamoto<sup>1</sup>, K. Yamamoto<sup>1</sup>, K. Takubo<sup>1</sup>, K. Fukuta<sup>2</sup>, D. Oshima<sup>3</sup>, T. Kato<sup>2</sup>, S. Iwata<sup>3</sup>, H. Wadati<sup>1</sup> and I. Matsuda<sup>1</sup>

<sup>1</sup> Institute for Solid State Physics, The University of Tokyo, Kashiwa 277-8581, Japan <sup>2</sup>Department of Electrical Engineering and Computer Science, Nagoya University, Nagoya 464-8603, Japan <sup>3</sup>Nagoya University, Massaya 464, 8603, Japan

<sup>3</sup>Nagoya University, IMaSS, Nagoya 464-8603, Japan

Magneto-optical Kerr effect (MOKE) in visible region has been widely utilized in condensed matter physics, especially in the field of magnetism. We have been developing a measurement scheme for resonant MOKE (RMOKE), in which an energy for incident light is tuned to particular absorption edge of target element composed of samples [1], and applied to thin ferromagnetic metals, ferrimagnetic alloys, and artificial multilayers, for examples. For exploring the applicability in terms of its sensitivity of this method, we focus on ultrathin ferromagnetic films here. In such systems. interfacial properties contribute to perpendicular magnetic anisotropy (PMA) of ultrathin films. PMA has been one of the important features in spintronics field due to its potential for developing a non-volatile device with higher density. However, its mechanism has not been understood from microscopic point of view. Therefore in order to access such systems, it is essential to probe the ultrathin magnetic systems in methodological point of view. Recently, a novel scheme considering Rashba-type spin-orbit interaction has been shown to explain the existence of PMA and its electric-field dependence as a result of competition with exchange interaction of magnetic systems as an analogy of Dzyaloshinskii-Moriya interaction [2]. The Rashba effect has been known to emerge in the system without inversion symmetry such as surface or interface. In the new scheme, effective Rashba field acts at an interface between a noble metal or an insulator and ultrathin ferromagnetic films.

In this research, at UVSOR BL5B, we conducted Fe *M*-edge RMOKE measurement of the Fe film that was sandwiched by films of noble metal, Au, and insulator, MgO. We synthesized the sample using molecular beam epitaxy method. The structure of the sample is Au (2 nm)/MgO (2 nm)/Fe (0.29 nm)/Au (25 nm)/Cr (5 nm)/MgO(001, substrate). Fe thickness of 0.29 nm corresponds to  $\sim 2$  monolayer assuming that this layer takes body-centered cubic structure. In measuring RMOKE, rotating-analyzer ellipsometry has been utilized for obtaining Kerr rotation angle at each energy point [1]. The measurement has been conducted at room temperature and external magnetic field (± 0.47 T) that was in perpendicular to sample surface was applied using permanent magnet. The incident light angle was set to 45 degrees.

In Fig. 1, RMOKE spectrum around Fe *M*-edge is shown with error bars  $\pm 0.5$  degrees. There are mainly two structures in the spectrum. One is around the region in 54 – 55 eV that corresponds to Fe *M* absorption edge,  $3p \rightarrow 3d$  transition. The other appears to be broader compared to the former, which can be observed around the region in 60 – 65 eV. This corresponds to Au  $O_3$  edge.

It is shown that this method has sensitivity even for the ultrathin ferromagnetic systems. Furthermore this measurement has been preliminary experiment for time-resolved measurement [3]. It was found that energy around 54 - 55 eV was suitable for tracing dynamics of Fe of this system. Ultrafast spin dynamics of this system has been attracting because this system can be used for investigating effects of spin-orbit interaction at interfaces on its dynamics in subpicoseconds timescale.



Fig. 1. Fe (0.29 nm) M-edge resonant magneto optical Kerr effect spectrum.

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**III-4** 

## Various Electronic Structures of SnCl<sub>2</sub>Pc Film on Graphite

K. Yonezawa<sup>1</sup>, T. Ueba<sup>2</sup>, R. Shiraishi<sup>2</sup>, H. Yamane<sup>2</sup>, N. Kosugi<sup>2</sup> and S. Kera<sup>1,2</sup>

<sup>1</sup> Department of Nanomaterial Science, Graduate School of Advanced Integration Science, Chiba University,

Chiba 263-8522, Japan

<sup>2</sup> Department of Photomolecular Science, Institute of Molecular Science, Okazaki 444-8585, Japan,

Organic  $\pi$ -conjugated molecular solid is consisted by a weak intermolecular interaction. Thus, the film structure could be easily modified by a thermal impact, leading a wide variety in the electronic property of the molecular solid. Tin phthalocyanine dichloride (SnCl<sub>2</sub>Pc) is a  $\pi$ -conjugated molecule which has been reported as an n-type semiconductor property [Fig. 1(a)]. Since SnCl<sub>2</sub>Pc is non-planer molecule, the film structure is considered to be variable depending on the preparation conditions. In this work, we studied impacts of the thermal annealing on the electronic structure of the SnCl<sub>2</sub>Pc film prepared on graphite by angle-resolved UPS (ARUPS) and XPS.

The clean surface of graphite was obtained by cleaving a HOPG under the air and subsequent annealing in the UHV chamber. SnCl<sub>2</sub>Pc is purified by sublimation method twice. After preparing the monolayer film (0.5 nm) on the graphite at room temperature, valence-band and secondary electron cutoff were measured at 45 eV, and Sn 4d, C 1s, Cl 2p and N 1s core levels were measured at 60 eV, 335 eV, 335 eV and 500 eV, respectively.

In Fig. 1(b), the intense peak at 1.8 eV (label a) and the weak peak at 1.4 eV (label a') are observed for asdeposited film. The peak a is assigned to HOMO. The peak a' must be originated from the electronic structure of SnCl<sub>2</sub>Pc, not from that of impurities nor surface contaminations. Upon annealing the film at 343 K for 9h, the spectrum changes drastically from the asdeposited one. New features at 1.6 eV (label b) and 1.2 eV (label b') are observed in addition to the peaks a and a' found for the as-deposited film. Furthermore, weaker features (labels  $\alpha$ ' and  $\beta$ ') at around 0.3 eV are observed after the annealing. From the intensity analysis of ARUPS, the angular dependences of the peaks b, b' and  $\beta$ ' are very similar one another, while it is different from those of the peaks a, a' and  $\alpha'(not$ shown), indicating two kinds of molecular orientation exist in the film.

It has been reported that dissociation of the Cl atom of SnCl<sub>2</sub>Pc has occurred for the monolayer film on Ag(111) after the annealing [1], thus one may consider the peaks b, b' and  $\beta'$  might be ascribed to HOMO of SnPc or SnClPc (radical) etc, which may be formed after the surface chemical reaction upon the annealing. However, the XPS spectra of Cl 2p are nearly identical before/after the annealing (Fig. 1 (c)), indicating almost all the Cl atoms have remained in the film. Therefore, peaks b, b' and  $\beta'$  should be originated from the electronic states of SnCl<sub>2</sub>Pc with another molecular orientation or aggregation. Figure 1 (d) shows Sn 4d states. In contrast to Cl 2p, new features are observed at low-binding energy side of the main peaks of the as-deposited film by 0.33 eV. The spectra of C 1s and N 1s indicate the same trend to Sn 4d, while the energy differences of new features are not equal (not shown). The results indicate the energy shift found in Sn 4d, C 1s, and N 1s could be caused by the charge redistribution at the Pc ring.

The electronic structure of the SnCl<sub>2</sub>Pc film on graphite is clearly modified by the annealing, namely rearrangement of the molecular orientation and aggregation. Finally we would assume the origin of various peaks, though further experiments are requested to conclude. The peaks a' and  $\alpha'$  (b' and  $\beta'$ ) are possible to be originated from HOMO and LUMO of anion states of SnCl<sub>2</sub>Pc. The wave-function localization in the film would be a key to understand the non-trivial features because adsorption distance of Pc ring could be longer by Cl as a spacer.



Fig. 1. (a) Chemical structure of  $SnCl_2Pc$ . (b) Valence-band spectra for the as-deposited (black) and the annealed at 343 K for 9 h (magenta). (c) Cl 2p XPS spectra. (d) Sn 4d XPS spectra. In (c) and (d), as-deposited spectra (pale gray) are shown with the annealed one for comparison.

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## Orbital Energy Rearrangement by the Organic–Metal Interaction: Perfluoropentacene on Ag(111)

T. Ueba<sup>1</sup>, K. Yonezawa<sup>2</sup>, H. Yamane<sup>1</sup>, N. Kosugi<sup>1</sup> and S. Kera<sup>1,2</sup>

<sup>1</sup> Department of Photomolecular Science, Institute of Molecular Science, Okazaki, 444-8585, Japan, <sup>2</sup> Department of Nanomaterial Science, Graduate School of Advanced Integration Science, Chiba University, Chiba 263-8522, Japan

Understanding the *weak* interaction at organicmetal interface, including intermolecular interaction and molecule-metal interaction, is of great importance. Even such weak interaction can cause the rearrangement of molecular orbitals both in energy and space, which defines the electronic properties at interfaces.

Perfluoropentacene (PFP), an organic semiconductor, gives us an interesting example. The energy gap between the HOMO and HOMO–1 of PFP monolayer adsorbed on highly oriented pyrolytic graphite (HOPG), observed by ultraviolet photoelectron spectroscopy (UPS), is identical to gaseous PFP (2.42 eV), while it is 70-meV narrower for PFP on Ag(111) [1]. Because PFP adsorbs on both surfaces in a "physisorptive" manner, namely, without chemical bonding nor charge transfer, the orbital energy rearrangement is a consequence of the *weak* interaction at the interface. In this work, we performed photoemission spectroscopy to examine the origin of the orbital energy rearrangement of PFP/Ag(111), by comparing with PFP/HOPG.

The Ag(111) surface was purified by repeated cycles of Ar<sup>+</sup> sputtering and subsequent annealing. The cleanliness was confirmed by the low-energy electron diffraction (LEED) and the appearance of the Shockley state in angle-resolved UPS. After multilayer deposition on Ag(111), the sample was annealed at 130 K for 5 minutes for obtaining the monolayer [2]. The clean HOPG surface was obtained by cleaving in air and by annealing in the UHV chamber. Valence band and secondary cut-off was measured at a photon energy (*hv*) of 45 eV, and the C1s and F1s core levels at *hv* = 335 eV and 730 eV, respectively.

Figure 1 shows the valence-band spectra. For PFP/Ag(111), the ordered/disordered phase transition at  $T_c \sim 145$  K is reported [2]. However, our results detected no temperature dependence in the HOMO-HOMO-1 gap energy, indicating that the narrower gap arises from the molecule-metal interaction, not the intermolecular interaction.

Figure 2 shows the core-level spectra. The binding energy of the C1s peaks (C-C and C-F) for PFP/ Ag(111) are higher than those for PFP/HOPG, as found in the valence band. However, the C-F peak appears at rather similar energy for both films, as compared with the C-C peak. The energy difference of the F1s peak between PFP/Ag(111) and PFP/HOPG is also reasonably less than the C-C peak.

According to the X-ray standing wave analysis [3],

PFP adsorbs on Ag(111) with the flat-lying geometry. Hence, such core-level shift cannot be explained only with the photohole screening by the substrate or with the surface potential. The result can be taking into account the intramolecular charge redistribution, most likely arising from the change in molecular structure upon the weak molecule- substrate interaction. Indeed, our high-resolution electron energy loss spectroscopy (HREELS) for PFP/Ag(111) resolved the change in vibrational energies as compared with PFP/HOPG (not shown). The result clearly indicates the very slight modification in the molecular structure upon adsorption on Ag(111), which probably causes intramolecular charge redistribution and consequently the orbital energy rearrangement.



Fig. 1. Valence-band spectra of PFP/Ag(111) (top) and PFP/HOPG (bottom) measured at 45 eV.



Fig. 2. A comparison of the C1s (left) and F1s (right) core level energies.

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## Lateral Intermolecular $\pi$ -Band Dispersion in the Superstructure of Perylene Monolayer Physisorbed on Au(111)

H. Yamane<sup>1,2</sup> and N. Kosugi<sup>1,2</sup>

<sup>1</sup> Institute for Molecular Science, Okazaki 444-8585, Japan <sup>2</sup> The Graduate University for Advanced Studies (SOKENDAI), Okazaki 444-8585, Japan

Using angle-resolved photoemission spectroscopy (ARPES), we have recently investigated the lateral intermolecular  $\pi$ -band dispersion in superstructure monolayers of polycyclic aromatic hydrocarbons (PAHs) physisorbed on Au(111), e.g., coronene( $4 \times 4$ ) /Au(111), hexa-peri-hexabenzocoronene (HBC)(5×5) R0°/Au(111), and HBC( $3\sqrt{3}\times3\sqrt{3}$ )R30°/Au(111) [1]. This systematic investigation has revealed that the observed lateral  $\pi$ -band dispersion is dependent on the monolayer's surface Brillouin zone (SBZ) but not on the substrate's SBZ [1]. This finding suggests that the observed  $\pi$ -band dispersion at the PAHs/Au(111) interface is introduced not by a substrate-mediated intermolecular interaction [2,3] but by a genuine lateral intermolecular interaction. In the present work, in order to investigate the impact of the intermolecular space on the lateral intermolecular  $\pi$ -band dispersion, we study the electronic structure of the smaller PAHs of perylene, which also forms the  $(4 \times 4)$ superstructure on Au(111) depending on the film growth condition in the monolayer coverage [4].

The experiment was performed at the in-vacuum undulator beamline BL6U. The clean Au(111) surface was obtained by the repeated cycles of the  $Ar^+$  sputtering and the subsequent annealing at 700 K, as confirmed by the low-energy electron diffraction (LEED) and the Shockley state in ARPES.

Figure 1 shows (a) a LEED image at 20 K and (b) the corresponding SBZ of the perylene monolayer on Au(111). The LEED image shows the  $(4\times4)$  super-

structure with respect to the Au(111) hexagonal lattice, as reported in Ref. [4]. The ARPES spectra were measured by considering the high symmetric point of  $\Gamma$ ', K', and M' in the monolayer's SBZ [blue hexagon in Fig. 1(b)].

The *E*-*k* map of perylene( $4 \times 4$ )/Au(111) along the  $\Gamma$ '-K' and  $\Gamma$ '-M' ( $k_{\Gamma K}$  and  $k_{\Gamma M}$ ) directions, obtained from ARPES, is shown in Fig. 1(c) and 1(d), respectively. The  $\pi$ -type highest occupied molecular orbital (HOMO)-derived peak of perylene is observed at the binding energy of ca. 1.15 eV. Although no direct intermolecular  $\pi$ - $\pi$  overlap exist in the flat-lying monolayer, the HOMO peak shows a very weak lateral  $\pi$ -band dispersion by 20 meV at  $\Gamma$ '-K' and by <10 meV at  $\Gamma$ '-M'. The observed  $\pi$ -band dispersion at perylene( $4 \times 4$ )/Au(111) is narrower than that at the comparable interface of  $coronene(4 \times 4)/Au(111)$  [1]. This difference can be explained by the larger intermolecular space in the perylene monolayer than that in the coronene monolayer due to the molecular size. The observed  $\pi$ -band dispersion is ascribed to the longrange lateral intermolecular interaction through the intermolecular space.

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Fig. 1. (a) LEED of the perylene(4×4)/Au(111) at 20 K, wherein the red dot indicates the substrate's spot. The molecular structure of perylene is also shown. (b) SBZ of the Au(111) (black) and the perylene(4×4)/Au(111) (blue). The red line indicates the scanned region in ARPES. (c,d) The *E*-**k** maps of the perylene(4×4)/Au(111) at 20 K along the  $\mathbf{k}_{\Gamma K}$  and  $\mathbf{k}_{\Gamma M}$  directions and the energy distribution curves.

## A High Hole-Mobility Molecular Layer Formed by Strong Electron Acceptor F4TCNQ on Gold Electrode

H. Yamane<sup>1,2</sup> and N. Kosugi<sup>1,2</sup>

<sup>1</sup> Institute for Molecular Science, Okazaki 444-8585, Japan <sup>2</sup> The Graduate University for Advanced Studies (SOKENDAI), Okazaki 444-8585, Japan

Because of the large electron affinity, 2,3,5,6-tetra fluoro-7,7,8,8-tetracyanoquinodimethane (F<sub>4</sub>TCNQ) is well known as a strong electron-accepting molecule, and has been applied for the *p*-type doping of organic semiconductors [1] and for the work-function control of metal electrodes [2]. It is understood that the cyano group in the molecule plays a crucial role in the chargetransfer (CT) interaction. In particular, at the  $F_4TCNQ/Au(111)$  interface, the  $F_4TCNQ$  molecule forms a two-dimensional network via the cyano group and the segregated Au atom from the substrate [3]. In the present work, in order to investigate the electronic structure of the F<sub>4</sub>TCNQ-Au network, we studied the TCNQ/Au(111) and F<sub>4</sub>TCNQ/Au(111) interfaces by angle-resolved photoemission spectroscopy (ARPES) and low-energy electron diffraction (LEED).

The experiment was performed at the in-vacuum undulator beamline BL6U. The clean Au(111) surface was obtained by the repeated cycles of the Ar<sup>+</sup> sputtering and the subsequent annealing at 700 K, as confirmed by LEED and the Shockley state in ARPES. In order to obtain the ordered monolayer film, the sample was heated at the multilayer desorption temperature of *ca.* 380–390 K, which is slightly lower than the desorption temperature of the TCNQ and F<sub>4</sub>TCNQ monolayers on Au(111), as confirmed by the temperature-dependent ARPES.

Figure 1 shows the normal-emission ARPES and LEED data of TCNQ/Au(111) and F<sub>4</sub>TCNQ/Au(111). Upon the TCNQ monolayer formation, the Shockley state of Au(111) just below  $E_{\rm F}$  (labeled S) is survived with the lower-energy shift. The LEED image of TCNQ/Au(111) shows the  $22 \times \sqrt{3}$  herringbone pattern of Au(111) just around the 0,0 spot. These ARPES and LEED characteristics of TCNQ/Au(111) indicate the weak physisorption at the interface. On the other hand, both the Shockley state in ARPES and the  $22 \times \sqrt{3}$ herringbone pattern in LEED are quenched at F4TCNQ/Au(111). These evidences in ARPES and LEED of F<sub>4</sub>TCNQ/Au(111) can be explained by the Au-atom segregation from the Au(111) surface by the strong chemisorption at the interface, which induces the formation of the F4TCNQ-Au network and the resultant CT-derived peak in ARPES ( $CT_1$  and  $CT_2$ ). The different interfacial interaction between TCNQ /Au(111) and F<sub>4</sub>TCNQ /Au(111) is supported by the N 1s photoemission spectra (not shown here).

Figure 2 shows the *E*-k map of the F<sub>4</sub>TCNQ-Au network on Au(111) at 20 K. Peaks CT<sub>1</sub> and CT<sub>2</sub>, originating from the lowest-unoccupied molecular orbital (LUMO) and highest-occupied molecular

orbital (HOMO) as considered in the neutral  $F_4TCNQ$  molecule, respectively, show the large dispersion by the 0.3-eV bandwidth for LUMO and by the 0.4-eV bandwidth for HOMO with the same *k* periodicity. These band dispersions are observable even at 300 K, and can be ascribed to the adatom(Au)-mediated intermolecular interaction, which is not observable at the physisorbed TCNQ/Au(111) interface.



Fig. 1. Normal-emission ARPES and LEED data of TCNQ/Au(111) and F<sub>4</sub>TCNQ/Au(111).



Fig. 2. The *E*-k map and the selected energy distribution curves of the F<sub>4</sub>TCNQ-Au network on Au(111) at 20 K along the  $\Gamma$ -K direction.

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# Site-Specific Organic/Metal Interactions Revealed from the Analysis of Shockley-Type Interface State

H. Yamane<sup>1,2</sup> and N. Kosugi<sup>1,2</sup>

<sup>1</sup> Institute for Molecular Science, Okazaki 444-8585, Japan <sup>2</sup> The Graduate University for Advanced Studies (SOKENDAI), Okazaki 444-8585, Japan

The Shockley state is a well-known surface state associated with the breakdown of the periodic crystal potential at the surface, and can be observed as a parabolic dispersion for normal metals and semiconductors by using angle-resolved photoemission spectroscopy (ARPES). The origin of the Shockley state is also valid for adsorbed-surface systems. Indeed, the Shockley state has been reported for metal surfaces adsorbed with metals, rare gases, and molecules with modified band dispersions, and has recently been applied to the determination of the interfacial bonding strength [1]. In the present work, we have applied the Shockley-state measurement to the well-ordered monolayer of cobalt phthalocyanine (CoPc) on Au(111), for the quantitative study of the site-specific interfacial interaction.

The experiment was performed at the in-vacuum undulator beamline BL6U. The clean Au(111) surface was obtained by the repeated cycles of the  $Ar^+$  sputtering and the subsequent annealing at 700 K, as confirmed by the low-energy electron diffraction (LEED) and the Shockley state in ARPES.

In Fig. 1, the Shockley state of CoPc/Au(111) is compared with that of H<sub>2</sub>Pc/Au(111) and that of the clean Au(111) at 23 K. The Shockley state of both CoPc/Au(111) and H<sub>2</sub>Pc/Au(111), labeled S', shows the lower-energy shift from that of the clean Au(111). The upshift of the Shockley state originates from the Pauli repulsion (exchange interaction) of surface electrons by adsorbates. Furthermore, one more dispersive band just below the Fermi level ( $E_F$ ) is observed for CoPc/Au(111), labeled X, which cannot be observed for H<sub>2</sub>Pc/Au(111).

As shown in the inset of Fig. 2, the CoPc/Au(111) interface forms an interface state of the Co 3d character (labeled H'), just above the original highest- occupied molecular orbital of the C 2p character (HOMO, labeled H), due to the strong interaction between the Co atom in the molecule and the Au surface, and is not observed for H<sub>2</sub>Pc/Au(111). The observed dispersive band X in Fig. 1 might thus originate from the site-specific Co-Au interaction at the CoPc/Au(111) interface. On the other hand, band S' mainly originates from the interfacial interaction between the Pc-ring site and the Au surface.

In order to examine the site-specific interfacial interaction, we measured the temperature dependence of the Shockley state of CoPc/Au(111) at the  $\Gamma$  point ( $\mathbf{k}_{\Gamma M} = 0 \text{ Å}^{-1}$ ). The Shockley state of the clean Au(111), labeled S, shows the higher-energy shift with

decreasing the temperature due to the contraction of the bulk-crystal lattice constant. A similar behavior is observed for peak S' of CoPc /Au(111). However, the amounts of the energy shift is different;  $\Delta E(S) = 60$ meV for the clean Au(111) and  $\Delta E(S') = 42$  meV for CoPc/Au(111) at 299 $\rightarrow$ 23 K. The energy difference by  $\Delta E(S') - \Delta E(S) = -18$  meV is ascribed to the difference in the Pauli repulsion at the interface due to the narrowing of the bonding distance between the Pc ring and the Au surface with decreasing the temperature. Peak X shows the lower- energy shift with decreasing the temperature by  $\Delta E(X) = -25$  meV, indicating the stronger interaction at the Co site than the Pc-ring site with the Au surface. From the present observation and Ref. [1], the interfacial bonding strength of CoPc/Au(111) at 23 K is determined as 13.0 meV/Å<sup>2</sup> at the Pc-ring site and 45.9 meV/Å<sup>2</sup> at the Co site.



Fig. 1. The *E*-*k* map around the Shockley state for CoPc/Au(111) and H<sub>2</sub>Pc/Au(111) at 23 K, together with the best-fit curve of the Shockley state for the clean Au(111) at 23 K (black dashed curve).



Fig. 2. Temperature dependence of the Shockley state of CoPc /Au(111) and Au(111) at the  $\Gamma$  point. The ARPES near the HOMO are shown in the inset.

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#### **Band Structure Modification of Graphene by Bi Intercalation**

Y. Sohn<sup>1,2</sup>, S. W. Jung<sup>1,2</sup>, M. Huh<sup>1,2</sup>, K. Kwon<sup>1</sup>, H. Yamane<sup>3</sup>, N. Kosugi<sup>3</sup> and K. S. Kim<sup>1,2</sup> <sup>1</sup>Department of Physics, Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea

<sup>2</sup>Center for Artificial Low Dimensional Electronic Systems, Institute for Basic Science (IBS), Pohang 37673, Republic of Korea

<sup>3</sup>Department of Photo-Molecular Science, Institute for Molecular Science, Okazaki 444-8585, Japan

Graphene, a two-dimensional atomic crystal with the Dirac band structure, can be grown on the surface of SiC(0001) [1]. It has been well known that intercalating atoms between the epitaxial graphene layer and SiC(0001) can not only decouple graphene from the substrate, but also modify the low-energy band structure such as doping level, band gap, and spin splitting [2-4]. In this report, we have investigated the band structure of graphene modified by the intercalation of heavy-Z atoms with angle- resolved photoemission spectroscopy (ARPES).

We first prepared zero-layer graphene samples, where a single graphitic layer is strongly bonded to the surface atoms of SiC(0001) and lacks the well-known linear  $\pi$  bands. The zero-layer sample was fabricated by thermal sublimation of surface Si atoms out of the SiC(0001) substrate at high temperature. Bismuth (Bi) was then deposited on the zero-layer sample at room temperature followed by mild annealing at elevated temperatures. ARPES and core-level spectroscopy measurement were performed at the in-vacuum undulator beamline BL6U, UVSOR, equipped with a high-performance hemispherical electron analyzer. The overall energy and momentum resolutions were better than 0.02 eV and 0.002 Å<sup>-1</sup>, respectively. Data were collected at 60 K with the photon energy of 100 eV.

We checked the intercalation of Bi by using lowenergy electron diffraction (LEED) and core-level spectroscopy. After intercalation we observed that  $(1 \times 1)$  spot of SiC(0001) is suppressed, while that of graphene layer remains unchanged.  $(6\sqrt{3}\times6\sqrt{3})R30^{\circ}$ spot, which originates from the lattice mismatch between SiC(0001) and the graphene layer is also suppressed. Bi  $5d_{5/2}$  core-level spectra is observed to be shifted by 0.18 eV after intercalation, and the peak position does not change with the sample annealed up to 1200°C. Figure 1 shows a wide-scale ARPES data of Bi-intercalated graphene, taken near the Fermi energy along the FK direction of the hexagonal Brillouin zone. Graphene  $\pi$  bands clearly appear after intercalation, demonstrating that graphene is effectively decoupled from the SiC(0001) substrate. From the above facts, we concluded that Bi is successfully intercalated beneath the graphene layer. Further ARPES studies are underway to observe the systematic evolution of the band structure.



Fig. 1. Band dispersion along the  $\Gamma K$  direction of Biintercalated graphene.

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### Angle Resolved Photoelectron Spectroscopy on the Clean Surface of the Pentacene Single Crystal

M. Hikasa<sup>1</sup>, Y. Mizuno<sup>2</sup>, S. Ideta<sup>3</sup>, K. Tanaka<sup>3</sup>, H. Ishii<sup>2,4</sup> and Y. Nakayama<sup>1</sup>

<sup>1</sup>Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, Noda 278-8510, Japan

<sup>2</sup>Graduate School of Advanced Integration Science, Chiba University, Chiba 263-8522, Japan

<sup>3</sup>UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan

<sup>4</sup>Center for Frontier Science, Chiba University, Chiba 263-8522, Japan

Pentacene (C<sub>22</sub>H<sub>14</sub>) single crystal (Pn-SC) is a representative p-type organic field effect transistor material, which indicating a high charge carrier mobility larger than 30 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> at room temperature [1]. Therefore, its valence band structures are of particular interest. As reported previously [2], our group succeeded in valence band dispersion measurements of the Pn-SC by angle-resolved photoelectron spectroscopy (ARPES). However, previous ARPES results were obtained on Pn-SC samples which had exposed to ambient air and thus are known to be contaminated by several percent of oxide at their surfaces [3]. On the other hand, in the case of the single crystal of tetracene, a sister molecule of pentacene, existence of the "surface band" was predicted because of surface relaxation [4]. Therefore, ARPES measurements on the clean surface are required in order to clarify the true valence band structures of Pn-SC.

In the present study, photoconductivity-assisted ARPES measurements [5] were performed on the Pn-SC clean surface prepared by vacuum cleavage. Extraction of a spectral contribution of the surface bands was attempted through excitation energy dependent measurements.

Plate-shaped (typically several mm<sup>2</sup> wide and a few um thick) Pn-SCs were produced by a physical vapor transport technique, which were selected and posted onto conductive carbon tape individually. Ag glue was additionally pasted at the rim of each crystal to ensure good electric conductivity. A strip of adhesive tape was carefully attached onto the top side of the Pn-SC sample prior to introduction into the ultra-high vacuum condition. The Pn-SC clean surface was obtained by cleaving that top side off together with the adhesive tape in vacuum. ARPES measurements were carried out at BL7U of UVSOR. The excitation photon energy (hv) was set at 8.0 eV and 21.2 eV in this study. In order to cancel sample charging, the sample was shined by continuous wave laser light (405 nm) during the measurements [2-4, 6]. All ARPES measurements were performed at room temperature.

Figures 1(a) and (b) show the ARPES spectra of Pn-SC (measured with the excitation energy of 8.0 eV and 21.2 eV respectively. The former spectra transform by changing emission angle as seen in Fig. 1(a). The probing depth at the valence band region in this

condition is known to be several nanometer [7]. In other words, energy dispersion of the valence bands of the Pn-SC clean surface was observed in a bulk sensitive condition.

In contrast, the ARPES spectra taken at hv = 21.2 eV do not exhibit apparent dependence on the emission angle. Note that the probing depth in this condition is in the order of sub-nm, namely shallower than one molecular layer of Pn-SC. This implies a shrinkage of the surface valence bands with respect to the bulk ones as predicted in the literature [4]. More precise excitation energy dependence is anticipated in order to clarify the detailed structures of the surface valence bands.



Fig. 1. (a) Bulk-sensitive (hv = 8.0 eV) and (b) surface-sensitive (21.2 eV) ARPES spectra of Pn-SC.

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#### **Electronic Structure of a Monolayer h-BN**

Y. Sugiyama<sup>1</sup>, Y. Okuyama<sup>1</sup>, C. Bernard<sup>2</sup>, S. Ideta<sup>3</sup>, K. Tanaka<sup>3</sup>, T. Greber<sup>2</sup> and T. Hirahara<sup>1</sup>

<sup>1</sup>Department of Physics, Tokyo Institute of Technology, Tokyo 152-8551, Japan

<sup>2</sup>Physik-Institut, Universit ät Zu rich, CH 8057 Zu rich, Switzerland

<sup>3</sup>UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan

Silicene is a monolayer sheet of silicon and believed to host Dirac electrons similar to graphene [1,2]. Experimental studies have been extensively performed recently to reveal the presence of the Dirac-cone-type bands and associated intriguing properties. However, the strong substrate-silicene interaction hinders the exotic properties related to the Dirac physics. For example, we have previously shown that when we try to grown silicene on Ag(111), the Ag atoms from the substrate segregate to the surface of the deposited Si film and the well-known Si(111) $\sqrt{3x}\sqrt{3}$ -Ag structure is formed [3].

One way to get around this problem is to use a substrate that weakly interacts with Si. Usually an insulating material is the right choice. In this respect, hexagonal boron-nitride (h-BN), which is a large gap insulator, should be an ideal substrate. It has been utilized as a substrate for graphene and this graphene/h-BN system was shown to host fascinating physical properties [4]. Furthermore, silicene formed on h-BN was shown by first-principles calculations to maintain the Dirac-like dispersion [5].

In the present study, we have measured the electronic structure of a monolayer h-BN formed on Rh(111) with high-resolution angle-resolved photoemission spectroscopy (ARPES). The samples were prepared in an ultrahigh vacuum (UHV) system in Switzerland and taken out into air. After they were transported to Japan, they were installed in an UHV chamber and annealed at ~500°C for 30 minutes. Lowenergy electron diffraction (LEED) measurements showed sharp spots corresponding to h-BN. Rh(111). as well as the superstructure. Then the h-BN/Rh(111) samples were hydrogenated to flatten the h-BN since the original h-BN/Rh(111) system is buckled due to the interaction among h-BN and Rh(111) [6]. Figure 1 shows the band dispersion of the flattened h-BN measure with ARPES. One can find states near the Fermi level that correspond to the substrate Rh. Below the binding energy of 5eV, one can find  $\sigma$  and  $\pi$  states that originate from the h-BN. Thus we have succeeded in preparing an atomically flat h-BN, and thus hope to actually grow silicene and other group IV and V monolayer systems.



Fig. 1. The band dispersion of h-Bn/Rh(111) system measured at hv = 21 eV with *p*-polarization.

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BL7U

# Scattering of Photoelectrons from Graphite via Organic Molecular Monolayer

T. Yamaguchi<sup>1, 2</sup>, F. Bussolotti<sup>2</sup>, K. Kimura<sup>3</sup>, M. Matsunami<sup>2,3</sup>, S. Ideta<sup>2,3</sup>, K. Tanaka<sup>2,3</sup>, T. Ueba<sup>2,3</sup> and S. Kera<sup>1, 2, 3</sup>

<sup>1</sup>Graduate School of Advanced Integration Science, Chiba University, Chiba 263-8522, Japan <sup>2</sup>Institute for Molecular Science, Okazaki 444-8585, Japan <sup>3</sup>School of Physical Sciences, SOKENDAI, Okazaki 444-8585, Japan kera@ims.ac.jp

Electron scattering governs fundamental properties in solids, such as thermal and electron conductivity. Recently, photoelectron scattering by phonons of graphite was discovered by low-energy angle resolved ultraviolet photoelectron spectroscopy (LE-ARUPS) [1]. In this work, we observed scattering phenomena of the photoelectron from graphite via organic monolayer interfaces using LE-ARUPS at beam line BL7U.

Figure 1 (a) shows LE-ARUPS intensity maps along  $\Gamma$ -K axis for a clean single crystal graphite (SCG). depict pentacene (PEN), Fig.1 (b-h) zinc phthalocyanine (ZnPc) and tin phthalocyanine dichloride (SnCl<sub>2</sub>Pc) monolayers prepared either on SCG or highly oriented pyrolytic graphite (HOPG) substrates. Several linearly dispersive bands with the same slope parameter to the clean SCG band are observed in Fig.1 (b-h), indicating that the origin of these features is photoelectron scattering of graphite  $\pi$ bands by molecular film. The scattering vector depends on the molecule and the measured temperature. We suggest that the features reflect reciprocal vectors of molecular unit cell of monolayer films. However, there are 6 domains for PEN and general Pc-type molecules on the graphite, which means reciprocal vectors do not match to the graphite ones [2, 3], leading to complicated scattering process. To understand a pure nature of these features, a commensurate superstructure of molecular system should be measured.

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Fig. 1. E(k) intensity maps taken at hv=40eV for (a)bare SCG at room temperature (RT) and at 11eV for the monolayers; (b)ZnPc/SCG at 166K, SnCl<sub>2</sub>Pc/SCG at (c)11K and (d)164K, ZnPc/HOPG at (e)11K and (f)142K, and PEN/HOPG at (g)14K and (h)145K. The image was obtained along  $\Gamma$ -K direction for (a-d). Inset spectra show momentum distribution curves at Fermi energy ( $E_{\rm F}$ ) integrated  $E_{\rm F}$ ±25meV. Dashed lines represent the linearly dispersive band with the same slope to the SCG band. The numbers in the maps indicate the momentum (Å<sup>-1</sup>) where the linearly dispersive band crosses the  $E_{\rm F}$ .

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BL7U

#### **ARPES of a Kondo Insulator YbB12(001) Surface**

K. Hagiwara<sup>1</sup>, Y. Ohtsubo<sup>1, 2</sup>, J. Kishi<sup>1</sup>, M. Matunami<sup>3</sup>, S. Ideta<sup>3</sup>, K. Tanaka<sup>3</sup>, T. Ito<sup>4</sup>,

H. Miyazaki<sup>5</sup>, F. Iga<sup>6</sup> and S. Kimura<sup>1, 2</sup>

<sup>1</sup>Graduate School of Science, Osaka University, Toyonaka 565-0043, Japan

<sup>2</sup>Graduate School of Frontier Biosciences, Osaka University, Suita 565-0871, Japan <sup>3</sup>UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan

<sup>4</sup>Department of Materials Engineering, Nagoya University, Nagoya 464-8603, Japan

<sup>5</sup>Department of Frontier Materials, Nagoya Institute of Technology, Nagoya 466-8555, Japan

<sup>6</sup>Department of Physics, Ibaraki University, Mito 310-8512, Japan

Recently, non-trivial topology of the electronic states on Kondo insulator (KI), so-called topological Kondo insulator (TKI) [1], is one of hot topics in solid-state physics as a synergy effect between strong electron correlation and spin-orbit interaction. SmB<sub>6</sub>, a well-known KI, is firstly argued as a candidate of TKI. Earlier angle-resolved photoelectron spectroscopy (ARPES) experiments revealed metallic surface states on SmB<sub>6</sub> [2], but its origin and the topological order of SmB<sub>6</sub> is still under debate [3]. Therefore, a survey of another material is desirable to provide further insight into the origin of metallic surface states on KIs.

In this work, we performed high-resolution ARPES experiments of the surface electronic structure of another Kondo insulator,  $YbB_{12}(001)$  [4] at BL7U of UVSOR-III. We prepared the well-ordered surfaces of  $YbB_{12}$  (001) by heating the sample up to 1600 K in a preparation chamber at the BL7U end station. The quality of the clean surface was checked by low-energy electron diffraction (LEED) as well as ARPES.

Figure 1 is the band dispersions along [100]. A band with steep dispersion below 100 meV would be a conduction band. This band becomes less dispersive around 35 meV, probably due to the hybridization with localized Yb<sup>2+</sup> 4*f* bands. Such hybridization between conduction and 4*f* bands would be driven by the Kondo effect.

In addition to these states, we observed another state clearly crossing  $E_{\rm F}$  at  $k_{//[100]} \sim 0.18$  Å<sup>-1</sup>, as shown by the momentum distribution curve in Fig. 1. Since the bulk electronic structure of YbB<sub>12</sub> has a bandgap at this temperature (~20 K), this metallic band originates from surface electronic structure. This metallic surface state can be a cause of the remnant conduction path of YbB<sub>12</sub> observed at low temperature.

Figure 2 is the constant energy contour at  $E_{\rm F}$  (±10 meV). It shows closed Fermi contour surrounding the  $\overline{\Gamma}$ , a time-reversal-invariant momentum. This behavior of the metallic surface state suggests its origin from the topological order.

These results at low temperatures agree with what is expected for a surface state on a theory of the topological Kondo insulator [1].



Fig. 1. ARPES intensity plots along [100] near  $E_F$  taken with 16.5 eV photons (bottom) and momentum distribution curves at  $E_F$  (±10 meV) (top). Lines in the bottom figure are guides the eyes. Each data are divided by the Fermi distribution function at the sample temperature (20 K) convolved with the instrumental resolution.



Fig. 2. Constant energy contour at  $E_F$  (±10 meV) taken with 16.5 eV photons at 14 K.

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#### Surface Electronic Structure Studies of High Quality CrO<sub>2</sub>(001) Films

H. Fujiwara<sup>1</sup>, M. Sunagawa<sup>1</sup>, K. Terashima<sup>1,2</sup>, T. Nagayama<sup>1</sup>, T. Kittaka<sup>1</sup>, M. Ogata<sup>1</sup>,

S. Ideta<sup>3</sup>, K. Tanaka<sup>3</sup>, T. Wakita<sup>1,2</sup>, Y. Muraoka<sup>1,2</sup> and T. Yokoya<sup>1,2</sup>

<sup>1</sup>Research Laboratory for Surface Science and Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan

<sup>2</sup>Research Center of New Functional Materials for Energy Production, Storage, and Transport, Okayama

University, Okayama 700-8530, Japan

<sup>3</sup>UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan

Chromium dioxide, CrO<sub>2</sub>, is a half-metallic ferromagnet whose spin polarization at Fermi energy is 100% [1]. Previous studies of spin-resolved photoemission spectroscopy (spin-resolved PES) on CrO<sub>2</sub> films reported insulating-like photoemission spectra [2], while the temperature-dependence of resistivity of CrO<sub>2</sub> is metallic. As the reason of the insulating-like Fermi edge, reconstructions of CrO<sub>2</sub>(001) surface has been theoretically suggested. However, it is also known that the surface of CrO<sub>2</sub> easily transforms into antiferromagnetic insulator  $Cr_2O_3$  [3]. Due to the existence of  $Cr_2O_3$ , it has been difficult to discuss the intrinsic electronic states of Recently, our group has  $CrO_2(001)$  surface. succeeded in preparing high quality CrO<sub>2</sub>(100) films by the closed system chemical vapor deposition (CVD) method using Cr<sub>8</sub>O<sub>21</sub> as a precursor [4]. The photoemission spectrum of our CrO<sub>2</sub>(100) film shows a peak at 1 eV with a clear Fermi edge, indicating that there are few contaminants of Cr<sub>2</sub>O<sub>3</sub> on the surface of our sample. In this study, we prepared  $CrO_2(001)$ epitaxial films on TiO<sub>2</sub> substrates with the closed system CVD method and investigated the electronic structure of the CrO<sub>2</sub>(001) surface by PES with synchrotron radiation. In this report, we show photon energy dependence of PES spectra and discuss the surface-metallicity of CrO<sub>2</sub>(001) films.

The PES measurements were carried out at BL-7U in UVSOR. The photon energies between 15 eV and 33 eV were used in our measurement. The energy resolution was approximately 15 meV when photon energy of 21 eV.

Figure 1(a) shows the near- $E_{\rm F}$  valence band PES spectra taken at hv = 15 eV and 33 eV. Both spectra show clear Fermi edge. In the spectrum taken at hv = 33 eV, the intensity is higher than one of spectrum taken at hv = 15 eV because of the difference in cross-section of Cr 3d and O 2p bands, indicating that the Cr 3d and O 2p bands are hybridized at least in the energy region between  $E_{\rm B} = 0.7$  eV and  $E_{\rm F}$ .

Figure 1(b) shows difference spectrum of hv = 33 eV with hv = 15 eV in order to emphasize the surface components of the CrO<sub>2</sub>(001) film. As seen in Fig. 1(b), two peaks at  $E_B = 0.5$  eV and at  $E_F$  were observed, indicating that these structures are surface derived bands. It should be noted that the observation of clear Fermi edge indicates existence of metallic (001) surface states, which has not been predicted in band

calculations [5] assuming that oxygen atoms in  $CrO_2(001)$  surface is reconstructed into tetrahedral arrangement. On the other hand, the observed surface states are consistent with band calculations [6] assuming that the oxygen atoms remain in octahedral arrangement, which indicates that the surface reconstruction does not occur.

In summary, we investigated the photon energy dependence of photoemission spectra of  $CrO_2(001)$  film in order to clarify the surface electronic states. The metallic surface states were observed, consistent with the band calculations not considering surface reconstruction.



Fig. 1. (a) Near- $E_{\rm F}$  valence band PES spectra of the CrO<sub>2</sub>(001) film at 15 K taken at hv = 15 eV and 33 eV. These spectra are normalized at  $E_{\rm B} = 0.7$  eV. (b) The surface states of the CrO<sub>2</sub>(001) film determined from the difference between spectra taken at 33 eV and 15 eV.

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BL7B

#### **Development of Photoconductive Detector Based on LaF<sub>3</sub> Thin Film**

S. Otani, R. Yamazaki, S. Kokuryu, K. Toyama and S. Ono Nagoya Institute of Technology, Nagoya 466-8555, Japan

According to increase in application of vacuum ultraviolet (VUV) light source, the detector for monitoring the light source is required. Consequently, the spectral response of the detector is demanded to optimize for each light source. The spectral response of the detector varies according to band gap of the material. Therefore, our group is proceeding to development of the VUV detectors by using fluorides which have extremely wide band gap [1, 2]. In our past study, the detectors based on  $BaF_2$  and  $YF_3$  show response below 147 nm and 170 nm, respectively. Here, we report on the development of filterless VUV photoconductive detector by using LaF<sub>3</sub> thin film.

LaF<sub>3</sub> thin film was deposited by pulsed laser deposition (PLD) on the MgF<sub>2</sub> single crystal substrate. LaF<sub>3</sub> ceramic target was irradiated with the femtosecond laser pulses (wavelength: 790 nm, laser fluence: 16.1 mJ/cm<sup>2</sup>). The deposition was carried out 4 h under high vacuum condition ( $2 \times 10^{-4}$  Pa). The temperature of the substrate was controlled at 670 K. Figure 1 is scanning electron microscope (SEM) images of YbF<sub>3</sub> thin film. A sub-micron-sized particulates make up the majority of the deposition layer.

To evaluate these thin films as photoconductive detectors, a pair of interdigitated aluminum electrodes was fabricated onto the thin film by vacuum deposition. Photoconductivity of the detector was evaluated by measuring variation of the amperage by VUV irradiation. The amperage increased 1-digit by VUV irradiation as showan in Fig. 2. Additionally, transmission spectrum and spectral response of the detector were measured. The transmission edge was around 115 nm in wavelength. The detector showed photoconductivity below 161 nm in wavelength and the response signal increased as the radiation wavelength decreases (Fig. 3). Furthermore, response speed of the detector was evaluated by measuring temporal response of a VUV pulse by a flash lamp (pulse duration: 10.1 µs). As a result, the temporal waveform by the detector was equivalent to that of a commercially available detector based on diamond.

In summary, we achieved filterless VUV photoconductive detector meeting practical performance by applying LaF<sub>3</sub> thin film grown by PLD.



Fig. 1. SEM images of the surface and section of  $LaF_3$  thin films.



Fig. 2. I-V characteristic of LaF<sub>3</sub> thin film.



Fig. 3. Transmission spectrum and spectral response of the detector.

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