Formation of Active Mo Species Supported on SiO₂-Al₂O₃ for Dehydroaromatization: Mo L₃-edge XANES Study

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MoO₃-modified H-MFI shows high activity for dehydroaromatization of methane, although strong deactivation cannot be avoided during the reaction. In this reaction, many workers have been revealed reduction of Mo species is brought about in contact with methane in the initial step. Deoxidated Mo ions react methane to form carbide species, Mo₂C, in the second stage. The carbide species is active for dehydroaromatization of methane to form benzene, however, deactivation is brought about by carbon deposition on the catalyst surface at the same time. It is likely the catalytic activity and its deactivation rate depend on the type of silica-alumina supports. Relation between silica-alumina support and active Mo species formed in the reaction is important to clarify the formation process of highly active Mo species and its red-ox behavior during the reaction. In fact, molybdena species supported on amorphous silica-alumina shows dehydroaromatization activity while it is very lower than that on H-MFI support. By comparing H-MFI with amorphous silica-alumina supports, reduction behavior of Mo ions before/after the reaction can be provided. Characterization of those species by means of Mo L-edge XANES is appropriate for clarification of Mo ions with different valences. In this report, local structure of supported Mo ions on H-MFI and amorphous silica-alumina (SAH-1) and their redox changes after dehydroaromatization of methane or ethane at 973 K for 3 h is evaluated by Mo L₃-edge XANES.

Experimental

Mo L₃-edge XANES spectra were measured in BL1A of UVSOR-IMS in total-electron yield (TEY) mode, using the Ge(111) double-crystal monochromator (2d = 0.6532 nm). The photon energy was calibrated by using Mo metal sample at Mo L₃-edge (2520 eV).

Results and Discussion

Fig. 1 shows the XANES spectra of authentic Mo samples. It is clear that both intensity and energy positions of two white-lines are different between Na₂MoO₄ (consist of Mo⁶⁺O₄ tetrahedra, Tₐ) and MoO₃ (Mo⁶⁺-O₆ octahedra, distorted O₆) because of local symmetry around Mo⁶⁺ ions. In cases of Mo₂C (Mo⁷⁺) and Mo metal, edge energy values of those XANES are lower than Mo⁶⁺ samples, however, difference of edge energy is unclear between Mo₂C and Mo metal. To clarify the difference, second derivative XANES were introduced, as shown in Fig. 2. As for the 2nd derivative waves, minimum peaks are due to peak components of original XANES. The difference of energy value is significantly between Mo₂C (2524.2 eV as lowest energy) and Mo metal (2523.5 eV). The assignment can be applied to the catalyst samples with reduced Mo ions. Fig. 3 shows the XANES spectra of MoO₃/SAH-1 and MoO₃/H-MFI catalysts before/after the reaction with CH₄ or C₂H₄ at 973 K. For MoO₃/SAH-1, it is concluded that reduced Mo species are formed after C₂H₄ reaction but not formed after CH₄ reaction. In case of MoO₃/H-MFI, which shows high catalytic activity for converting CH₄ to C₆H₆, several components due to Mo²⁺ and Mo⁶⁺ (peak at 2526.5 eV) species are overlapped after CH₄ reaction. This result suggests the formation of so-called “oxy-carbide species” as catalytically active species for dehydroaromatization of CH₄. After C₂H₄ reaction, Mo²⁺-species is only formed and the component due to Mo⁶⁺-species is scarcely seen. The reactivity for converting C₂H₄ to C₆H₆ is higher in MoO₃/SAH-1 than in MoO₃/H-MFI. In addition, crystallinity of MFI-phase in MoO₃/H-MFI became low only by the reaction with C₂H₄ by XRD analysis, suggesting catalytic deactivation during the reaction. Thus it is concluded that difference between H-MFI and SAH-1 supports gives the formation of Mo species with different reduction state after the reaction with CH₄. Partly reduced oxy-carbide species coexisting Mo²⁺ and Mo⁶⁺ ions are formed on H-MFI support after contact with CH₄, and this species can act as highly active species for CH₄ dehydroaromatization.
The alternatives to LiCoO$_2$ cathode material have been extensively searched due to small natural deposits of Co and its toxicity in the field of Li-ion rechargeable batteries. Recently, LiNi$_{0.5}$Mn$_{0.5}$O$_2$ and LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ have been proposed as a new promising candidate. The cell performance using Li exhibited good cyclability, and a reversible capacity of 150 mAh/g within the voltage range of 3.0 to 4.3 V, which corresponds to one-half of theoretical capacity (280 mAh/g). We have employed the X-ray diffraction and XAFS measurement using synchrotron radiation source to investigate the structural change and the charging process of these materials. In this study, the electronic structural change and the charging mechanism were investigated by XANES spectra of Co, Ni, Mn K- and L-edges, and O K-edge respectively.

Experiment

LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ was synthesized in air at 1273 K for 24 h using appropriate molar ratios of LiOH·H$_2$O, Mn(CH$_3$COO)$_2$·6H$_2$O, Ni(CH$_3$COO)$_2$·6H$_2$O, and Co(CH$_3$COO)$_2$·6H$_2$O and de-lithiated samples were electrochemically prepared using coin-type cells with Li/1M LiPF$_6$ in EC:DEC(1:1)/samples. The Ni/Mn/Co valence states of samples were determined by the Ni/Mn/Co K-edge XANES spectra. X-ray absorption measurements at the Co, Ni, Mn L-edges and O K-edge by total electron yield were performed on BL1A and BL8B1.

Results and Discussions

LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ showed a single phase adopted the α-NaFeO$_2$ structure like as LiCoO$_2$. The results of the Ni, Mn and Co K-edge XANES spectra showed that LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ could be represented as Li(Ni$^{2+}$,$^{1/3}$Mn$^{4+}$,$^{1/3}$Co$^{3+}$)O$_2$. On the other hand, Neutron diffraction measurements demonstrated that the lattice parameters of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ are $a = 2.860$ Å and $c = 14.22$ Å and that the chemical composition can be expressed as [Li$_{0.07}$Ni$_{0.03}$]$_3$[Li$_{0.03}$Mn$_{0.33}$Ni$_{0.30}$Co$_{0.33}$]$_3$O$_2$, referring to the Wyckoff positions 3a and 3b with space group R3m. Figure 1 shows the XANES spectra of Ni L-edge for charged Li$_{1-x}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$. A continuous chemical peak shifts corresponding to $L_0$, $L_2$ to higher energy was observed up to $x = 0.7$ for showing charge capacity of 194 mAh/g. The results of K-edge were observed in the same way. In addition, that of Co L-edge showed a slightly higher shift and that of Mn L- and K-edges showed no chemical shifts for all the samples. However, a systematic change was not clearly observed in O K-edge absorption. On the basis of these results, we are constructing the band structure and investigating the charging mechanism for this material.
Porous materials are of scientific and technological interest because of their ability to interact with atoms, ions and molecules not only at their surfaces, but also throughout the bulk of the material [1]. These materials are extremely useful in catalysis and separation technologies [2]. Recently, novel porous morph-genetic ceramics synthesized from natural materials such as wood, fibers, surfaces of leaves, has recently attained particular interest [3, 4], because natural materials exhibit a hierarchically built anatomy optimized in the genetic evolution process, compared to artificial synthetic templates, and are abundant, cheap, renewable and environmentally conscious.

The porous morph-genetic ceramics is generally fabricated through sintering treatment at high temperature, after infiltrating various organic or inorganic solutions to the bio-template. Therefore, clarifying the mechanism of sintering process is indispensable for obtaining desired porous morph-genetic ceramics, because the sintering treatment plays a critical role for transforming the hierarchical cellular structure of bio-template into porous ceramics with specific functional properties.

Unfortunately, it is impossible to reveal the dynamic transition during sintering process by using conventional analysis techniques such as scanning electron microscopy or X-ray diffraction. It is well known that extended X-ray absorption fine structure (EXAFS) is a powerful technique for determining the local structure with atomic selectivity in both crystalline and amorphous states. Therefore, we believe that it is possible to reveal the dynamic transition during sintering process by studying the local structure of atoms. However, to our best knowledge, no study of local structural properties of the porous morph-genetic ceramics has been reported up to now.

In this work, we investigate the local structural properties of the novel porous morph-genetic silicon carbide sintered at different temperatures by EXAFS for the first time. By measuring and analyzing Si K-edge EXAFS, it is found that the coordination number of nearest Si-Si shell dramatically changes when the structure is transformed from amorphous into crystalline, indicating the EXAFS technique is a useful tool to elucidate the synthesis mechanism for these novel porous morph-genetic ceramics.
It has been well established that the X-ray absorption near-edge fine structure (NEXAFS) measurement is a powerful tool to analyze electronic structures of materials, because spectral fine structure of the NEXAFS spectrum is very sensitive to a change in chemical environment. Recently we have succeeded the chemical state analysis of the ultradilute Ga dopant at a level of atomic p.p.m in MgO matrix by combined use of the experimental NEXAFS analysis and the first-principles calculations [1]. For the chemical state analysis of lighter dopant elements by the NEXAFS within the soft X-ray region, we have performed preliminary NEXAFS measurement and the first-principles calculations for Al₂O₃ and AlN at Al K-edge. Our present calculations could quantitatively reproduce both a) spectral fine structure and b) transition energy of the experimental NEXAFS.

**Experiments and calculations**

High-resolution X-ray absorption spectra at the Al K-edge of Al₂O₃ and AlN were measured using the BL1A beamline at UVSOR. The NEXAFS spectra were collected by the total electron yield (TEY) method. The incident photon beam was monochromatized using a KTP (2d₀₋₁=10.954Å) double-crystal monochromator. Commercially available high purity powders with corundum and wurtzite types of structures for Al₂O₃ and AlN, respectively, were attached to the first photocathode of the electron multiplier using adhesive carbon tape. The crystal structures and contaminants of the sample employed here were checked by the X-ray diffraction (XRD) measurements, which revealed the presence of only small amounts of contaminants.

The first-principles density functional theory (DFT) calculations were carried out by using the full-potential linearized augmented plane wave package, WIEN2k [2]. The core-hole effect was fully introduced in our present calculations by using the 2x2x1 and 3x3x2 supercells for Al₂O₃ (120 atoms) and AlN (72 atoms), respectively. The theoretical NEXAFS spectra were calculated within the electronic-dipole-allowed transitions in the core-hole state. Product of the radial transition probability and corresponding projected partial densities of the states (p-PDOS) represents the theoretical NEXAFS spectrum.

**Results**

The observed NEXAFS spectra of Al₂O₃ and AlN at Al K-edge are shown in Fig. 1(a). Seven peaks, labeled as peaks A to G for Al₂O₃ and peaks J to P for AlN, were found within this energy regime in both Al₂O₃ and AlN. Theoretical NEXAFS spectra are shown in Fig. 1(b). As shown in this figure, the theoretical spectral features showed fairly good agreements with experimental ones. It is noted that experimental threshold energy shift, i.e., chemical shift, by 4.3 eV was also well reproduced by our present calculations, although absolute transition energies were slightly overestimated by 4.0 eV (ΔE/E = + 0.25%).

In summary, we have carried out the NEXAFS measurements of Al₂O₃ and AlN at Al K-edge and the first-principles DFT calculations to interpret the spectral features and transition energy of experimental NEXAFS. Our present theoretical approach could give a quantitative reproduction of the experimental spectral fine structures and transition energies. This type of combined use of the experimental NEXAFS and the first-principles calculations must be a powerful tool for systematic and quantitative analysis of the chemical environment of the materials.

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The metallotetraphenylporphyrins (MTPPs) is of particular interest due to many possible applications, such as catalysts, electronic devices, gas sensors, and electroluminescent displays. MTPP have a large p-conjugated aromatic system. In order to elucidate chemical and physical properties of MTPP, it is necessary to determine their electronic structure [1]. In this work, we applied X-ray absorption near edge structure (XANES) spectroscopy to two type porphyrins, FeTPP-Cl and MnTPP-Cl. The results of the measurement indicate unoccupied and occupied electronic structure of MTPPs. The X-ray absorption spectra were measured at BL1A of the UVSOR in the Institute of Molecular Science, Okazaki [2]. The ring energy of the UVSOR storage ring was 750MeV and the stored current was 110-230 mA. Cl K-edge absorption spectra were recorded in the regions of 2533-3733eV by use of two Ge(111) crystals. The absorption was monitored by the total electron yield using a photomultiplier.

The Cl K-edge XANES spectra for the MTPPs are shown in Figs. 1 and 2. A remarkable change of the spectral patterns was observed for the FeTPP-Cl and MnTPP-Cl. Comparison of observed and calculated spectra revealed that metal 3d and 4p orbits contribute to peak A and B. But, MnTPP-Cl did not contain contribution from the Cl4p and Cl5p orbits.

The Measurement of \( \gamma \) and Soft X-ray Excited Optical Luminescence of a Silica Glass

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In the present work, we have made in-situ luminescence measurements of silica glasses induced by \( \gamma \)-ray and soft X-ray, on silica. The main objects of this report are to clarify of the dynamic damaging process in silica which should be induced by the electron excitation, as well as the difference of the radiation effects between \( \gamma \)-ray and soft X-ray irradiations.

Experimental

The measurement of luminescence of the fused silica glass induced by soft X-ray irradiation (1.8-1.9 keV) was carried out on the beam line 7A at UVSOR, Institute for Molecular Science with a stored current of 100-200 mA. The size of soft X-ray beam was ca. 2 x 10 mm, and the flux was ca. \( 1 \times 10^9 \) photons / mm\(^2\) / sec / 100 mA. The luminescence was focused by a lens in the UHV chamber to the monochromator and detected by a multi-channel analyser.

Results and Discussion

Fig. 1 shows the soft X-ray induced luminescence of the fused silica glass. The 3.1 eV band attributed to \( \text{B}_2 \text{E} \) center was observed. One notes the significant deviation of the 3.1 eV band intensity profile for the different excitation energies of the incident soft X-ray. Irrespective of the incident energy of soft X-ray, fundamentally the same evolutions were observed. The intensity of the 3.1 eV band slightly increased in the early stage of the irradiation and then decayed gradually with irradiation time, similarly to the change of the 3.1 eV emission band in the \( \gamma \)-ray induced luminescence.

The normalized luminescence yields of the 3.1 eV band thus obtained are plotted against the absorbed dose in Fig. 2. One can note that all normalized yields show similar dependence on the absorbed dose, in spite of the large difference between \( \gamma \)- and soft X-rays energies. The normalized intensities rapidly increased and reached the maximum at around 3.5 kGy, followed by a gradual decrease. It is noteworthy that all the normalized yields are within a factor of 10, which is far less than the energy difference of \( \gamma \)-ray and X-ray (three order's of magnitude). This means that the luminescence is controlled by the absorbed dose, in other words, the luminescence is induced by the electron excitation from secondary electrons and photons with low energies, but not by the direct excitation of primary (Compton) or high energy electrons and photons.
Photoemission Study for Initial Oxidation and Nitridation of ZrB$_2$


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Transition metal diborides are attractive materials due to its hardness, high-melting point and chemical stability. Among them, zirconium diboride (ZrB$_2$) has the hexagonal symmetry of the AlB$_2$-type structure with an in-plane lattice constant of 0.3168 nm which is very close to that of GaN. Recently, epitaxial growth of GaN film on ZrB$_2$ substrate has succeeded using the metal-organic vapor phase epitaxial method. In order to obtain epitaxial GaN film with good crystallinity, it is indispensable to elucidate the initial oxidation and nitridation processes. In addition, after the unexpected discovery of high temperature superconductivity in MgB$_2$, diborides have attracted renewed attentions. In this work, we have performed the photoemission study for clean ZrB$_2$(0001) surface obtained by in-situ annealing treatment and its initial oxidation and nitridation processes.

Experimental

Experiments have been performed at beamline BL2B1. The ZrB$_2$(0001) single crystalline sample was grown by floating-zone method. The ZrB$_2$(0001) sample was fixed on the molybdenum tile using a small molybdenum clip. The clean surface was obtained by the repetition of flash annealing around 1850ºC. The base pressure of the measurement chamber was about 2×10$^{-8}$ Pa. The pressure during the flash annealing was kept better than 5×10$^{-7}$ Pa. The O$_2$ and N$_2$ were exposed up to 100 Langmuir (1L = 1×10$^{-6}$ Torr×s) at 650ºC. The photoemission spectra were obtained using the double-pass cylindrical mirror analyzer. The overall energy resolution was about 1.3 eV.

Results and Discussions

Figure 1 shows the photoemission spectra for B 1s and Zr 3d core-levels. The peaks at 179.0, 181.3 and 187.7 eV in binding energy correspond to Zr 3d$_{3/2}$, Zr 3d$_{5/2}$ and B 1s core-levels, respectively. Since the spectrum for the clean surface shows no structure originated from the oxidized component, we conclude that contamination free surface can be obtained using our cleaning procedure. The sample showed sharp hexagonal low-energy electron diffraction pattern after the cleaning procedure. We have also performed separated UPS measurements for clean ZrB$_2$(0001) surface. The work function of the clean ZrB$_2$(0001) surface is determined from the width of the photoemission spectra to be 5.1±0.1 eV, which is much larger than that of polycrystalline boron (4.5 eV). On a LaB$_4$(100) surface, the charge transfer occurs form La to B atoms and the dipole moment is directed from the surface into the bulk since the outermost layer of the LaB$_4$(001) surface consists of La atoms. As a result, the work function of LaB$_4$(001) is as small as 2.5 eV. From our result, it is considered that the clean surface of ZrB$_2$(0001) is terminated by graphitic-boron layer and the charge transfer form the second Zr layer to the first B layer exist. Because of the B atom at the ZrB$_2$(0001) surface, the dipole moment is directed outward, and the work function is increased. As shown in Fig.1, the new components appear at 182.0 and 184.3 eV in binding energy after a 11 L O$_2$ exposure at 650ºC. The chemical displacement of +3.0 eV is smaller than that between Zr and ZrO$_2$. The literature value of chemical shift is 4.2 eV for Zr 3d$_{5/2}$ between Zr and ZrO$_2$. On the other hand, the new components appear at lower binding energy after a N$_2$ exposure at 650ºC. It is found that the chemical displacement of Zr 3d$_{5/2}$ core-level is -0.7 eV. We have also performed the X-ray absorption measurement in the N 1s-2p threshold region for 10 L N$_2$ exposed surface. It is found that the X-ray absorption spectra show the dependence on the indent photon direction. In order to clarify the bonding orientation of the chemisorbed N atoms on ZrB$_2$(0001) surface, more detailed measurements is needed.

Fig. 1. Photoemission spectra for B 1s and Zr 3d core-levels.
The characterization of electronic states near Fermi level of DNA duplexes has been desired to clarify the mechanisms of long-range charge migration in DNA, from the viewpoint of not only biochemistry but also molecular device materialization. With the recent progress in nanotechnology, the electric conductivity of DNA has directly been measured in molecular scale. However, these characterizations of the electric property are still indefinite, and there is no significant observation on the electronic states near Fermi level of DNA for understanding of the charge migration mechanism. In this study, therefore, we carried out resonant photoemission spectroscopy (RPES) experiments near Fermi level with resonance from N 1s to unoccupied states for both poly(dG)·poly(dC) (GC) and poly(dA)·poly(dT) (AT) DNA duplexes.

**Experimental**

Experiments were performed at the beamline BL4B of the UVSOR facility, in which the end-station (ultrahigh vacuum systems) is equipped with an electron energy analyzer and a retarding-field electron detector for XAS. We prepared thick GC- and AT-DNA films on SiO₂/p-Si(111) substrates in the atmosphere. The film thickness prepared was estimated to be 100 - 200 nm. These samples were introduced into the ultrahigh vacuum via a sample entry system from the atmosphere, without baking procedures.

**Results and Discussion**

An N K-edge X-ray absorption (XA) spectrum of GC DNA is shown in the inset of Fig. 1. In the XA spectrum, two 1s - π* resonant peaks at 399.7 eV and 401.9 eV and a broad 1s - σ* resonant peak at 407 eV were observed. The off- / on-RPE spectra near the Fermi level of GC DNA are shown in Fig. 1 as a function of kinetic energy. The RPE spectra were measured at each resonant absorption peak marked on the XA spectrum shown in the inset. On the comparison to the off-RPE spectrum, the on-RPE spectra are obviously involving additional components which is attributed to the N-KLL Auger electrons.

The Auger signals could be extracted from the on-RPE spectra by subtracting the off-RPE spectra in binding energy plots, as the dotted lines in Fig. 1. The differential spectra commonly show a broad bump. Normally, the Auger electrons keep an identical distribution in kinetic energy, independently of excitation photon energies. The obtained Auger signals were, however, strongly affected by excitation energy; the lower photon energy light provides a higher kinetic energy distribution. This indicates that the excited electrons locate in the unoccupied states for, at least, a time scale of Auger transition and affect its final state of the transition.

In addition, an appended component was observed at the first π* resonance, as marked by a dagger in Fig. 1. We attribute the additional component to those of participant Auger transition. This finding again indicates that the excited electrons locate in the π* states for, at least, the time scale of Auger transition.

In the case of the molecules chemisorbed on metals, their RPE spectra do not show the drastic peak shift of Auger electrons in kinetic energy and also the participant Auger electrons. These are explained as that the molecular orbitals rehybridized with metal electronic states are delocalized, and the excited electrons in the chemisorbed molecules diffuse into the metal, immediately. In contrast, all features of the observed RPE spectra of DNA, as mentioned above, clearly show that the excited electron is localized at the excited orbitals. In other words, the unoccupied states of the bases in DNA duplexes are not delocalized. Hence, we conclude that the charge hopping model is suitable for electric conduction in DNA duplexes rather than the charge transfer model via delocalized states, when electrons pass through the π* states of the DNA bases.
Rydberg states in condensed phase are of interest since they are sensitive to external perturbation due to their large orbital radii. Several studies have been carried out on surrounding effects in the \( \text{Ar} \, 2p \) excited states using rare gas matrixes. Changes of the spectral features between another condensed phases are explained by the competition of two effects, namely, (i) the polarization stabilization of the ionization threshold, and (ii) the exchange repulsion of the Rydberg electron due to the valence electrons of the neighboring atoms/molecules. \cite{1} In the present study, temperature dependence of the peak position of the bulk \( \text{Ar} \, 2p_{3/2}-4s \) band has been measured to reveal the latter effect. The exchange repulsion is mainly influenced by the inter-atomic distance between the neighboring atoms. Different temperatures of \( \text{Ar} \) solid make different inter-atomic distances of neighboring \( \text{Ar} \). The different inter-atomic distance between the neighboring \( \text{Ar} \) should reveal the effect.

The \( \text{Ar} \) solid was prepared by dosing \( \text{Ar} \) gas approx. 30 L to the gold coated copper plate of a cryostat at ~8K. The temperature of the \( \text{Ar} \) solid was monitored using a silicon diode thermostat and was adjusted to 8K or 16K by using a ceramic heater. Photoabsorption spectra were measured by a partial electron yield (Auger yield) method using an MCP detector with a retarding mesh (-180V). All spectra were taken at grazing incidence angle of 15 degree. The photoabsorption spectra were taken for several times since there was an energy drifting (~7 meV per hour) caused by the instability of the beamline monochromator.

Fig. 1 shows the observed energy position of the \( \text{Ar} \, 2p_{3/2} - 4s \) for bulk \( \text{Ar} \) atom measured at different temperatures, 8K and 16K. The typical spectra for 8K and 16K are also shown as inset. Photon energy was calibrated by using the bulk \( \text{Ar} \, 2p_{3/2} - 4s \) band (245.06eV) for 8K \( \text{Ar} \) solid. \cite{1} As shown in the inset, the main band is observed with a shoulder structure at the lower photon energy side. The main band is assigned to the transition from \( \text{Ar} \, 2p_{3/2} \) to 4s band of bulk \( \text{Ar} \) atom and the shoulder structure is assigned to that of surface \( \text{Ar} \) atoms. \cite{1} Comparing with the main bands for 8K and 16K spectra, it is clearly seen that the spectral features are very similar but the bulk band shows different excitation energy. To obtain the excitation energies of the \( 2p_{3/2} - 4s \) band of the bulk \( \text{Ar} \) atom for 16K, the photoabsorption spectra were taken for several times and the bands are fitted with two Voigt functions. In Fig. 1, the vertical axis indicates the uncalibrated energy positions of the \( \text{Ar} \, 2p_{3/2} - 4s \) band. The horizontal axis indicates the measuring time. Error bars indicate 2\( \sigma \) of the peak fittings. The blue and red lines indicate the linear fittings for the energy driftings for 8K and 16K, respectively. The difference between the sections for both lines gives the excitation energy difference of 5 \( \pm 1.5 \) meV.

The temperature increase causes an expansion of the lattice constant of the \( \text{Ar} \) solid. The \( \text{Ar} \) solid has a face-centered cubic structure with the lattice constants of 5.2890 Å and 5.2941 Å for 8K and 16K, respectively. \cite{2} Neighboring \( \text{Ar} \) atoms with shorter inter-atomic distance are expected to have stronger perturbation (exchange repulsion) because the excited electron in 4s-Rydberg states is pushed to higher energy side by closer potential of the surrounding \( \text{Ar} \) atoms. This can be explained as stronger exchange repulsion by the surrounding atoms arisen from shorter inter-atomic distance of 8K than 16K. The bulk \( \text{Ar} \, 2p_{3/2}-4s \) band at 8 K shows blue shift of 5 \( \pm 1.5 \) meV from that at 16 K because of the increase of the exchange repulsion caused by the reducing the inter-atomic distance.

Fig. 1. The peak position of \( \text{Ar} \) 4s (bulk)

\[\text{[1]} \text{T. Hatsui, M. Nagasono, N. Kosugi, J. Electron Spectrosc. Relat. Phenom., in press.}\]
High-resolution Angle-resolved Photoemission Spectroscopy on CeSb

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The anomalously complicated magnetic phase transition on CeSb has been intensively studied by both experiment and calculation. The origin has long been believed to be understood under the framework of Ce 4f-Sb 5p mixing model (pf mixing model) [1,2]. On the other hand, the recent optical and magneto-optical experiments suggest the importance of the Ce 5d-Sb 5p mixing effect from the comparison with the band structure calculation based on the pf+pd mixing model [3,4]. Thus, we have performed high-resolution angle-resolved photoemission spectroscopy (ARPES) on CeSb at the para- and type-IA antiferro magnetic (AF) phase to elucidate the appropriate starting point of the complicated magnetic phase transition.

ARPES measurements were carried out using a MBS Toyama A-1 electron analyzer with a GAMMADATA discharge lamp and a toroidal grating MBS Toyama A-1 electron analyzer with a phase transition. Appropriate starting point of the complicated magnetic type-IA antiferro magnetic (AF) phase to elucidate the transition on CeSb has been intensively studied by magneto-optical experiments suggest the importance of the Ce 5d-Sb 5p mixing effect with the band structure calculation based on the pf+pd mixing model [2], the latter is not explained by the model, since the band B is suggestive of the band energy-splitting, which has not been expected by the pf mixing model. On the other hand, we have found a qualitative agreement between the experiment and the recent calculation based on pf+pd mixing model [4], where the band energy-splitting originating in the pf+pd mixing effect along the ΓX axis has been expected. This result suggests the importance of the pd mixing effect to interpret the exact mechanism of the magnetic phase transition in CeSb other than the pf mixing effect.

Fig. 1 (a, b) Comparison of the valence band structure of paramagnetic CeSb obtained by ARPES spectra with hv=115 eV (a) and 122 eV (b) photons.
(c) Comparison of normal emission ARPES spectra with hv=115 eV (blue line) and 122 eV (red line) CeSb.

Fig. 2 (a, b) Experimental band structure of para- (a) and AF- magnetic (b) CeSb derived by ARPES. Dashed lines are guide for eyes.
(c) Comparison of normal emission ARPES spectra between AF- (blue line) and para-magnetic (red line) CeSb.

Bulk metallic glasses have received much attention as new materials which possess useful engineering properties such as high mechanical strength, good ductility, and high corrosion resistance. In order to understand the origins of the large glass formation ability and unique properties of the bulk metallic glass from the microscopic point of view, we have studied the electronic structure of a Zr$_{55}$Al$_{10}$Cu$_{30}$Ni$_{5}$ bulk metallic glass [1] by photoelectron spectroscopy.

**Experimental**

Photoelectron spectra were recorded under an ultrahigh vacuum of $2 \times 10^{-8}$ Pa at low temperatures with a high-resolution energy analyzer at BL5U. Total energy resolution and the origin of the binding energy $E_B$, i.e., the Fermi level $E_F$, were determined by the Fermi edge of an evaporated Au film.

Specimens were cut from an ingot of Zr$_{55}$Al$_{10}$Cu$_{30}$Ni$_{5}$ into a size of 3x3x2 mm$^3$ and attached on a copper plate by conductive glue. Clean surfaces for the photoelectron measurement were prepared by in situ scraping the specimen with a diamond file.

**Results and Discussion**

Figure 1 shows typical valence-band photoelectron spectra of Zr$_{55}$Al$_{10}$Cu$_{30}$Ni$_{5}$ recorded at 20 K with various excitation photon energies $h \nu$. They are normalized by the intensity integrated up to the binding energy $E_B = 10$ eV (exceptionally 7 eV for $h \nu \approx 22.3$ eV). Three features at $E_B \approx 0.6$, ~2.0, and ~3.7 eV in the valence band region are ascribed to the Zr 4$d$, Ni 3$d$, and Cu 3$d$ states, respectively, because of their $h \nu$ dependence [2]. An Auger line is also found at $E_B \approx 8$ eV for $h \nu = 66.8$ eV.

Remarkable feature of the observed spectra is the highly symmetric shape of the transition metal d bands with the high binding energy and the narrow width in comparison with those of the crystalline transition metals. The Cu and Ni 3d band widths decrease from ~2 eV for crystalline Cu and Ni metals to ~1 eV for the glass. This is mainly due to the reduction in the neighboring atoms to hybridize with those transition metals in the glass. The symmetric shape may also arise from the lack of the crystalline periodicity.

In Fig. 2, high-resolution spectra recorded with a He I light source ($h \nu = 21.2$ eV) are presented for the valence-bands near $E_F$ of the metallic glass and reference Au. Compared with Au, the intensity is reduced below $E_B \approx 0.12$ eV for the metallic glass. This suggests that a pseudo-gap is formed in this metallic glass, which may stabilize the glass phase and contribute to its large glass formation ability.

At present, however, it is not clear whether these aspects are intrinsic for the glass phase of this alloy or not. Further study is intended on the crystalline counterpart and the glass with different compositions.
Evaluation of Thermoelectric Power in the Al-Mn-Re-Si 1/1-1/1-1/1 Approximant Using High-resolution Photoemission Spectroscopy

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It has been widely believed that metallic compounds are inappropriate for their use as thermoelectric devices because their thermoelectric power, in general, possesses extremely small magnitude as low as a few $\mu$V/K. Recently, however, some metallic compounds such as quasicrystals and cobalt oxides were reported to show a large magnitude in the thermoelectric power. These experimental observations strongly motivated us to investigate the mechanism leading to the large thermoelectric power coupled with metallic electrical conduction.

Thermoelectric power of the metallic electrical conduction can be well explained by

$$S(T) = \frac{1}{eT} \left( \frac{\partial \sigma(\varepsilon)}{\partial \varepsilon} - \frac{\partial f(\varepsilon)}{\partial \varepsilon} \right)$$

where $\sigma(\varepsilon)$, $\mu$, and $f(\varepsilon)$ indicate electrical conductivity, chemical potential, and Fermi-Dirac distribution function, respectively. Electrical conductivity in an isotropic system is determined by the following equation with in the context of the Boltzmann transport theory.

$$\sigma(\varepsilon) = \frac{e^2}{12\pi^2\hbar} N(\varepsilon) \nu(\varepsilon) \tau(\varepsilon) = \frac{e^2}{3\pi} N(\varepsilon) \nu^2(\varepsilon) \tau(\varepsilon)$$

Here $N(\varepsilon)$, $\nu(\varepsilon)$, and $\tau(\varepsilon)$ represent electronic density of states, group velocity, and relaxation time, respectively. If $\nu(\varepsilon)$ and $\tau(\varepsilon)$ can be regarded as energy-independent in a narrow energy range where $\partial f(\varepsilon)/\partial \varepsilon$ has nonzero value while it turns out to possess negligibly small value at the outside of the energy range, $\sigma(\varepsilon)$ in eq.(1) can be simply replaced by $N(\varepsilon)$. In such a case, thermoelectric power can be evaluated using information about $N(\varepsilon)$. In this study, we employed high energy-resolution photoemission spectroscopy to investigate $N(\varepsilon)$ of the Al$_{74.6}$Mn$_{8.7}$Re$_{8.7}$Si$_{8}$ 1/1-1/1-1/1 approximant of the icosahedral quasicrystal. Thermoelectric power in the approximant was evaluated by the measured photoemission spectrum. The energy resolution of the present measurements was better than 20 meV.

Photoemission spectra, in general, are believed to have information only about the valence band below the Fermi level ($E_F$). However, those measured at high temperature contain information about the conduction band up to a few above $E_F$. If the measured spectrum is divided by $f(\varepsilon)$, the resulting spectrum ($N'(\varepsilon)$) gives us information about electronic density of states across $E_F$.

We calculate the thermoelectric power by using eq.(1) and the deduced $N'(\varepsilon)$. Although its magnitude stays less than half of the observed value, the calculated $S(T)$ shows almost the same temperature dependence as that of the measured one. If we take an energy independent contribution of the surface or grain boundaries into account, the magnitude of $S(T)$ is increased and the thermoelectric power can be perfectly determined from experimentally determined density of states. We have already applied this method for the layered cobalt oxides and the layered cuprates of the metallic electrical conduction and succeed in quantitatively evaluating their thermoelectric power.

As a result of these analyses on the thermoelectric power in terms of the electronic structure near $E_F$, we concluded that the large thermoelectric power with metallic electrical conduction is brought about by the characteristic electronic structure near $E_F$ and is predictable if the electronic structure is precisely determined.
Dynamic Final-State Effect on the Core-Level Photoemission of Surface-Passivated Au Nanoparticles on the Graphite Substrates

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Recently, the surface-passivated nanoparticles have been chemically synthesized in the solution including surfactants. These surface-passivated nanoparticles exhibit closed-packed nanoparticle self-assemblies on the single-crystalline substrates, and therefore it is considered that they could be important constituents of future nanostructured devices. In order to elucidate their detailed intriguing properties and to develop the future devices, it is indispensable to understand the interactions with the substrates supporting the nanoparticles as well as their electronic structures. In this work, we have carried out a photoemission study of dodecanethiolate- (DT-) passivated Au nanoparticles.

The synthesis procedure of DT-passivated Au nanoparticles has been described elsewhere [1-3]. Photoemission measurements were carried out at BL-5A of UVSOR Facility. For the photoemission measurements, the synthesized DT-passivated Au nanoparticles were supported on HOPG substrates by evaporating the solvent (toluene) from the dispersion of DT-passivated Au nanoparticles on the single-crystalline HOPG cleaved surface in a nitrogen-filled glove bag directly connected to the ultrahigh-vacuum chamber. Photoemission measurements were performed with the incident photon energy of 180 eV at room temperature.

The Au 4f core-level spectra of DT-passivated Au nanoparticles consist of the two components, and the components with lower binding energy and higher binding energy originate from the inner Au atoms of Au nanoparticles (bulk component) and the surface Au atoms of Au nanoparticles bonded to surface-passivants of DT molecules (surface component), respectively [2]. An important point to note here is that the bulk components shift to higher binding energy side with decreasing the nanoparticle diameter (not given here). In our previous work [1], we have reported that the photoemission spectra in the vicinity of Fermi-level of DT-passivated Ag nanoparticles on the HOPG substrates are well characterized by the dynamic final-state effect due to the photohole with a finite lifetime left behind in the nanoparticles in the photoemission final state. This finite lifetime is determined by the coupling strength between the nanoparticle and substrate. Since the chemical states of both bulk components observed in the Au 4f core-level spectra for bulk Au crystallite and DT-passivated Au nanoparticles are considered to be equivalent, the bulk components in the DT-passivated Au nanoparticles on the HOPG substrates correspond to the shifted ones of bulk component observed in the bulk Au crystallite due to the dynamic final-state effect. In order to analyze the present Au 4f core-level photoemission spectra of DT-passivated Au nanoparticles on the HOPG substrates, we apply the dynamic final-state model to Au 4f core-level photoemission spectra again. Figure 1 shows the comparison of experimental bulk component in the Au 4f/2 core-level spectrum of DT-passivated Au nanoparticles with mean diameter of 3 nm on the HOPG substrates and calculated one from the experimental bulk component of bulk Au crystallite using dynamic final-state effect model. At the middle spectra in Fig. 1, the decomposed component denoted by red line shows the bulk component. The bottom spectrum shows the calculated bulk component based on the dynamic final-state effect on the bulk component of bulk Au crystallite. As shown in Fig. 1, the calculated bulk component reproduces the experimental one of DT-passivated Au nanoparticle on the HOPG substrate fairly well. Therefore, it is concluded that the experimental core-level photoemission spectral features of the present DT-passivated Au nanoparticles on the HOPG substrates can be also quantitatively characterized by the dynamic final-state effect model.

Fig. 1. Comparison of experimental Au 4f/2 core-level spectrum of DT-passivated Au nanoparticles on the HOPG substrates and calculated one using dynamic final-state effect model.

In present society, infrastructures of communication are demanded to expand in the speed and the quantity. One of future devices in this field is a spin-related device. Several candidates are considered and a part of those starts in fundamental research. Theoretical study also reveals the possibility of dilute magnetic semiconductor that exhibits ferromagnetism at room temperature and predicted that GaN-based dilute magnetic semiconductors, especially Cr-doped GaN, are highly potential candidates for those materials. This material, Cr doped wide gap semiconductor, shows ferromagnetic properties even at 400K experimentally. This is one of highest Curie temperatures at present in dilute magnetic semiconductors. Furthermore, GaCrN substance emits luminescence at the energy of near the band gap of Ga. We have, thus, three independent characters for GaCrN, semiconductor nature, ferromagnetism, and optical feature.

Here, we observed the absorption spectra around N K-edge and Ga L_{III,II}-edge to try to reveal the origin of ferromagnetism of GaCrN. Figure 1 shows the absorption spectra around N K-edge. We found a weak peak at 398eV lower than the fundamental N K-shell absorption edge for high Cr concentration specimens studied here. A blue arrow in Fig.1 indicates the peak. The intensity of the peak increases with the concentration of Cr atom. The 3d-orbitals of the doped Cr atom partially hybridize with the N 2p-orbitals to construct a valence band of GaCrN (Fig.2), and the other part makes a state in the band gap of GaCrN as the result of crystal field splitting. We tentatively assign the peak to a transition to the 3d-orbitals of Cr atom making the in-band gap state, which is essentially dipole-forbidden, but becomes partially dipole-allowed owing to the hybridization with the N p-orbital. The electrons in the in-band gap state may play the main role of ferromagnetism of GaCrN in connection of the hole of the valence band.

On the other hand, while a slight modification of the spectrum was found, indicated by a blue arrow, we did not observe the large change in the absorption spectrum around Ga L_{III} and L_{II}-edges as shown in Fig.3. This observation means that the Ga and N s-orbital constructing the conduction band of GaCrN are not strongly affected by doping the Cr atom. By the way, the doped Cr atom states as trivalent ion in the GaN and constructs the alloy GaCrN. The configuration circumstance around the Cr ion has been elucidated with XAFS measurement, and the analysis indicates that the Cr ion locates substitutionally, but the first nearest neighbor configuration is somewhat complex.

![Fig.1 Absorption spectra around N K-edge of GaCrN.](image1)

![Fig.2 Schematic DOS of GaCrN and optical transition.](image2)

![Fig.3 Absorption spectra around Ga L_{III} and L_{II}-edge of GaCrN.](image3)
Study of Ar Cluster Ion Incident Angle for Super Hard Diamond Like Carbon Film Deposition

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We have demonstrated that gas cluster ion beam (GCIB) assisted deposition was useful for forming super hard DLC films (> 50 GPa) with a smooth surface and low content of $sp^2$ orbital at room temperature [1,2].

In our case, the DLC films were formed with irradiation of Ar cluster ion beam during evaporating $C_60$ as a carbon source. These films were deposited with a perpendicular irradiation of Ar cluster ions [3]. In this paper, effects of the irradiation angle of the Ar cluster ion beam on carbon film properties were studied, in order to develop this deposition technique and to optimize the angles for the super hard DLC film formation.

Result and Discussion

Figure 1 shows the NEXAFS spectra of the films irradiated with various incident angles of Ar cluster ion at the acceleration energy of 5 keV. Additionally, the spectra of the conventional DLC film formed with RF plasma and a diamond film formed with microwave plasma are also shown as references.

A significant difference of the spectra between DLC films and the diamond film was the pre-edge peak at 285.3 eV. This pre-edge resonance is due to transitions from a C 1s orbital to an unoccupied $\pi^*$ orbital originating in $sp$ and $sp^2$ orbitals. Thus, the NEXAFS spectrum of the diamond film, which has no- $sp^2$ orbital, did not present the pre-edge peak at all. This pre-edge peak is usually considered as a marker for presence of the $sp^2$ orbital, as the $sp$ orbital is unstable. The increasing of the $sp^2$ content in the DLC film indicates the increasing the graphitic bond in the film. Therefore, in order to obtain higher hardness, the fraction of the $sp^2$ content in the DLC film should decrease. In the DLC films deposited with Ar cluster ion beam assistance, the peak shape at pre-edge of 285.3 eV was different between 0° and 60°. In comparison with the film at the normal incidence, the spectra of the film formed with incident angle of 60° presented an increase of the peak width with the same peak intensity. Therefore, from Fig.1, the $sp^2$ content at 60° was higher than that at normal incident angle. At 40°, the shoulder peak around 287 eV was also higher than that at normal. This increase is also concerned with increasing of $sp^2$ content, because the spectrum of the diamond does not have this shoulder peak. Thus, increasing of the incident angle increased the $sp^2$ content. Additionally, it should be noted that the $sp^2$ content of the film formed with normal incident angle was lower than that of RF plasma film.

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Figure 1: NEXAFS spectra of DLC films formed by Ar cluster ion beam assisted irradiation with oblique incident angles.

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Angle-resolved UV Photoelectron Spectra of Thin Films of Perylene-3,4,9,10-tetracarboxylic Bisimidazole on GeS(001)

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Recently, we observed the intermolecular energy-band dispersion of the oriented perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) multilayer[1]. The observed energy-band dispersion gave that the transfer integral for the $\sigma$-$\sigma$ interaction ($0.05$ eV), the effective mass of HOMO hole ($5.28$ $m_0$), and the hole mobility ($>3.8$ cm$^2$/V s, when $\tau > h/k_B T$), which are the fundamental basis for the understanding of electronic and optical properties of organic solids[1]. This was the first observation of the intermolecular energy-band dispersion of a conventional single-component organic semiconductor only with the weak intermolecular van der Waals interaction.

In this work, in order to obtain information on the intermolecular interaction of perylene-3,4,9,10-tetracarboxylic bisimidazole (PTCBI), we characterized the film structure of PTCBI thin films prepared on GeS(001) single crystal surface by measuring the take-off angle ($\theta$) and the azimuthal ($\phi$) dependencies of angle-resolved UV photoelectron spectroscopy (ARUPS).

Experiments
A GeS(001) was cleaved in UHV. The cleanliness of GeS(001) was confirmed by measuring ARUPS and low-energy electron diffraction (LEED). The purified PTCBI was carefully evaporated onto GeS(001). The film thickness and the deposition rate (<1.0 Å/min.) were measured with a quartz microbalance.

Results and Discussion
Figure 1 (a) shows $\theta$ dependence of ARUPS of PTCBI (3Å) on GeS(001) substrate surface, where the intensity is normalized to the incidence photon flux, and the binding energy ($E_B$) is measured from the Fermi level of the substrate ($E_F^{\text{sub}}$). $\theta$ dependencies of ARUPS spectra are clearly seen. From MO calculation, the highest occupied molecular orbital (HOMO, $E_B = 1.8$ eV) band is assigned to a single $\pi$ MO as shown in Fig. 1. This HOMO-band intensity showed maximum at $\theta = 30 \sim 33^\circ$.

Figure 1 (b) shows the comparison between observed and calculated $\theta$ dependencies of the HOMO-band intensities with the SS/MO (PM3) for the molecular tilt angle of $\beta = 0^\circ$, which gave the best agreement with the observed $\theta$ pattern. It indicates that PTCBI molecules orient with their molecular plane parallel to the GeS(001) substrate surface. Furthermore, LEED measurements showed similar pattern from 3Å- to 50Å-PTCBI (not shown). Therefore, the strong intermolecular $\pi$-$\pi$ interaction in PTCBI multilayer can be expected.

In order to obtain the energy-band dispersion in PTCBI multilayer, the measurements of $\theta$, $\phi$, and $h\nu$ dependencies as a function of PTCBI deposition amounts are now in progress.