Soft x-ray irradiation induced metallization of layered TiNCl

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Abstract
We have performed soft x-ray spectroscopy in order to study the photoirradiation time dependence of the valence band structure and chemical states of layered transition metal nitride chloride TiNCl. Under the soft x-ray irradiation, the intensities of the states near the Fermi level (EF) and the Ti3+ component increased, while the Cl 2p intensity decreased. Ti 2p–3d resonance photoemission spectroscopy confirmed a distinctive Fermi edge with Ti 3d character. These results indicate the photo-induced metallization originates from deintercalation due to Cl desorption, and thus provide a new carrier doping method that controls the conducting properties of TiNCl.

Keywords: photoemission spectroscopy, layered nitride halides, carrier doping method

1. Introduction
TiNCl is an interesting layered material that belongs to a family of layered nitride halides MNX (M = Ti, Zr, Hf and X = Cl, Br, I) systems with two polymorphs, the FeOCl-type crystal structure (α-form) and the SmSI-type crystal structure (β-form) [1, 2]. TiNCl is known to take only the FeOCl-type crystal structure [2], consisting of a stack of orthogonal M–N layers located between two X layers. TiNCl is a band insulator with a direct band gap of approximately 0.5–3 eV [3, 4], and theoretical studies have proposed its application to optoelectronic devices [4], photocatalysts [5], and spin devices [6]. Upon Na intercalation between TiNCl layers, TiNCl becomes a superconductor with a relatively high superconducting transition temperature of ~16 K [7]. As electron-doped β-form HfNCl and ZrNCl [8–20], electron-doped TiNCl is considered a candidate for unconventional superconductors, where exotic mediation forces for Cooper pairing other than phonon are discussed [21–25].

In order to further explore the physical properties of this remarkable material, it is essential to control carrier concentrations. In the β-form MNX, the carrier control has been performed by intercalation of an alkali- or alkaline-earth-metal [8, 9, 15, 16], and/or off stoichiometry or deintercalation of X [26]. As for TiNCl, to the best of our knowledge, carrier control by neither element substitution nor off stoichiometry has been reported. This may be due to the fact that TiNCl is easily thermally decomposed into TiN by annealing [27–29]. The intercalation of alkali metal atoms and/or organic molecules between layers is the only method way for doping carriers. However, intercalated samples are unstable in a humid air, and precise carrier controlling is challenging, which prevents the systematic investigations of physical properties systematically.

One of the techniques to create conductive samples is photo-irradiation-induced metallization by breaking chemical bonds [30–36]. In SrTiO3 and TiO2, a metallic state called two-dimensional electron gases is created on the surface by photoirradiation. Two-dimensional electron gases have
attracted extensive attention owing to unique physical properties [30–35, 37–39], providing opportunities for the development of next generation of electronic and photonic devices. If photo-induced bond breaking is also effective in TiNCl, it can be established as a new method to control the physical properties of TiNCl. Therefore, it is one of the important challenges to investigate whether TiNCl is metallized by photoirradiation.

In this paper, we performed valence and core level photoelectron spectroscopy (PES), x-ray absorption spectroscopy (XAS), and Ti 2p–3d resonance photoelectron spectroscopy (RPES) of layered transition metal nitride chloride TiNCl. It was found that soft x-ray irradiation induced the metallization of TiNCl, and the metallization was closely related to the Cl desorption. This is the first report of electron-doped TiNCl due to Cl desorption.

2. Experiment

The highly crystalline TiNCl was grown by a method described elsewhere [7]. It was pelletized into disk shape in an Ar filled glove box. Subsequently, the pellet was transferred to an ultrahigh vacuum chamber for PES without being exposed to the humid air for a long time. The experiments were performed at the soft x-ray beam line BL23SU of SPring-8 [40] using a photoemission spectrometer equipped with a Gammadata-Scienta SES-2002 electron analyzer. In the RPES measurement, the energy resolution was set to 80 meV, and in the other PES measurements, it was set to less than 200 meV. To reduce a possibility for pyrolysis of TiNCl, we cooled down the sample and measured it at 100 K instead of at 300 K. We performed PES measurements using a photon energy of 1000 eV. For calibration of the binding energy, we used the Fermi edge of a gold film, which was located close to the sample and had a good electrical contact to the sample.

The irradiation light of \( h\nu = 1000 \text{ eV} \) was used, and the detector angle was set to 90’. Sets of Ti 2p, N 1s, Cl 2p, and valence spectra were also measured at \( h\nu = 1000 \text{ eV} \) in the time interval of 25 min without changing the measured location of the sample surface. The irradiation time includes the time of the PES measurements. Though it took 8 min to take a set of Ti, N, Cl, and valence spectra, we refer to the irradiation time as the time when we started the measurement of Ti. The spot size of the excitation light was 100 \( \times 200 \mu\text{m}^2 \), and the photon flux was \( 2 \times 10^{12} \text{ Photons/s} \) [40]. The illustration of the experimental geometry is shown in figure 1. The intensity of PES spectra was normalized by the area intensity of Ti 2p core-level spectra, while those of RPES were normalized by the photocurrent. XAS spectrum was measured using the total electron yield mode. To obtain a clean surface, the TiNCl pellet was fractured at 100 K under an ultrahigh vacuum of 1.5 \( \times 10^{-8} \text{ Pa} \).

3. Results and discussion

Figure 2 shows the soft x-ray irradiation time dependence of the valence band PES spectra of TiNCl. The background of an iterative Shirley method [41, 42] was subtracted from the raw spectra. The initial valence band spectrum of TiNCl had a peak at 6 eV with a shoulder structure at 4 eV, and there was almost no intensity in the near-\( E_F \) region. The overall spectral shape is consistent with that of the previous study [25], and thus the states of approximately 6 and 4 eV can be ascribed to Cl 3p and N 2p orbitals, respectively.

The peak intensities at 6 eV and 4 eV were decreased gradually. In contrast, the spectral intensity in the region between \( E_F \) and \( \sim 1.5 \text{ eV} \) appears to be increased, as illustrated in the inset that shows a blowup of the spectra near \( E_F \). The intensity near \( E_F \) of the initial spectrum can be ascribed to the states induced by the soft x-ray irradiation during the measurement and/or may be assigned to impurity states. In the spectrum after 150 min irradiation, a clear Fermi edge structure was observed, suggesting the metallic nature of the measured region of the sample surface. The change in the valence band and the intensity near \( E_F \) due to the soft x-ray irradiation is very similar to the change due to the photoirradiation effect of SrTiO\(_3\) [30].

To spectroscopically confirm the metallization and the character of the states at \( E_F \), we performed RPES of irradiated TiNCl at the Ti 2p–3d absorption threshold. The photon energies for the RPES measurement were chosen based on the Ti \( L_3 \) XAS spectrum, as shown in the inset of figure 3. Ti \( L_3 \) XAS spectrum had sharp absorption peaks at 457.4 eV, 458.5 eV, and 460.1 eV in the region of Ti 2p\(_{3/2}\)–3d absorption edge. In the octahedral structure, the 3d level was split into \( e_g \) and \( t_{2g} \).
states by the crystal field effect. However, since the Ti ions in TiNCl are in a distorted octahedral structure [7], the degeneracy was further removed by the static Jahn–Teller effect, leading to the observed three-peak structure. We measured RPES spectra of TiNCl in the off-resonance \((\hbar \nu = 454.0 \text{ eV})\) and on-resonance \((\hbar \nu = 457.4 \text{ eV})\) conditions after the irradiation. The soft x-rays for 4 h. While the spectral intensity at \(E_F\) in the off-resonance spectrum was almost negligible, the one in the on-resonance spectrum exhibited a distinctive Fermi edge, and was considerably enhanced. The resonance enhancement of the near-\(E_F\) structure indicates that its orbital character is Ti 3d. Furthermore, the presence of the distinctive Fermi edge indicates that the soft x-ray irradiation indeed induces the metallization of TiNCl.

To understand the mechanism of the metallization induced by soft x-ray irradiation in terms of chemical states, we have measured the core level spectra of TiNCl with different irradiation conditions. Figure 4(a) shows soft x-ray irradiation time dependence of the Ti 2p core-level spectra, and figure 4(b) represents the initial and 150 min difference spectra. The peaks at 457.5 eV and 463.5 eV are spin–orbit split Ti 2p, namely Ti 2p\(3/2\) and Ti 2p\(1/2\), respectively [43]. The initial Ti 2p spectrum showed a sharp Ti\(^{3+}\) peak at 457.5 eV [25] and a small shoulder structure at 456.5 eV. In the Ti 2p spectrum, as the irradiation time increased, the peak area of Ti\(^{4+}\) decreased compared to the initial value. In addition, the intensity of the shoulder structure at 456.5 eV clearly increased gradually. This binding energy is different from that of TiN (455.2 ± 0.2 eV) [44, 45], but is very similar to the week Ti 2p spectral component of electron-doped SrTiO\(_3\) and electron-doped anatase-TiO\(_2\), which is assigned to the component of Ti\(^{3+}\) state [30, 31, 46–48]. Thus, the observation indicates that the soft x-ray irradiation on TiNCl induces the changes Ti\(^{4+}\) in the valance state of the Ti ion from the Ti\(^{3+}\) state to the Ti\(^{3+}\) state. We performed spectral fitting using two components. The area intensities of Ti\(^{3+}\) and Ti\(^{4+}\) components at each irradiation time are summarized in table 1.

Figure 4(c) compares the spectra of the N 1s core level at each soft x-ray irradiation time. These spectra had peaks at 396.5 eV, and were almost identical, suggesting that there was no significant change in the spectral shape due to soft x-ray irradiation. The Cl 2p core-level spectra consist of Cl 2p\(3/2\) (198.4 eV) and Cl 2p\(1/2\) (200.1 eV) spin–orbit split peaks. The intensity of the Cl 2p spectrum after the soft x-ray irradiation of 150 min decreased gradually, which suggests the desorption of Cl atoms from the surface is induced by the soft x-ray irradiation. This is consistent with the observed reduction of the valence band spectra, which reflects a dominant Cl 3p contribution.

Here, we discuss the relationship between the observed results. Figure 5 shows the soft x-ray irradiation time dependence of the intensity of N 1s and Cl 2p core-level PES spectra, the PES intensity between \(E_F\) and 1.5 eV, and the Ti\(^{3+}\) ratio (Ti\(^{3+}\)/(Ti\(^{3+}\) + Ti\(^{4+}\))) of Ti 2p core-level PES spectrum. We normalized their initial values to unity. The intensity of N 1s core-level PES does not show a marked change depending on the soft x-ray irradiation time of soft x-ray. In a comparison with that of the N 1s core-level PES, the intensity of the Cl 2p core-level PES decreased more rapidly with increasing irradiation time. Furthermore, simultaneously with a decrease in Cl, the areas of the Ti\(^{3+}\) component and of the states near \(E_F\) increased in a similar manner. A smaller increase in near \(E_F\) intensity may be attributed to a more complicated orbital character of states near \(E_F\) than that of the Ti\(^{3+}\) core level. These observations suggest the close relationship of the desorption of Cl atoms and an increase in the intensity near \(E_F\) with an increase in the Ti\(^{3+}\) component. We consider that the desorption of a portion of the Cl atoms from the TiNCl layers introduces electron carriers into the layers, making the
The TiNCl is considered to be an ionic insulator composed of the TiNCl is considered to be an ionic insulator composed of tation of core electrons and is applicable to ion bonding. Since it may be well for covalent bonds. The KF model involves the core level spectra (left axis), and an increase ratio in area intensity (change, the data for Ti³⁺ in Ti 2p core level spectra (right axis). The initial values were normalized to 1.

Figure 5. Soft x-ray irradiation time dependence of the core-level and near-E_F intensities of TiNCl. Area intensity of N 1s and Cl 2p core-level spectra (left axis), and an increase ratio in area intensity (near E_F and Ti³⁺ in Ti 2p core level spectra (right axis). The initial values were normalized to 1.

layer conductive, which is inferred from the observation of the metallic Fermi edge. Therefore, to estimate the time of change, the data for Ti³⁺ and Cl 2p, which are more intense than the near-E_F data, were fitted with an exponential function (A exp(−t/λ) + B for Ti³⁺ and C exp(−t/λ) + D for Cl 2p, where t and λ are time and lifetime, respectively). The obtained lifetimes of Ti³⁺ and Cl 2p were 119 ± 29 and 96 ± 31 min, respectively. This provided a value of 100 min as the order estimate of the time of change for this experiment.

There are two possible causes of the desorption of Cl atoms. One of them is a pyrolysis. TiNCl has been reported to be decomposed completely into TiN when it is heated above 550 °C [27–29]. In the present experiment, however, the sample was kept at 100 K during the measurement, and therefore this possibility can be ruled out. The other possible cause is photon stimulated desorption [49–51]. There are primarily two mechanisms for photon stimulated desorption, which are distinguished by the process induced by photon irradiation: the Menzel, Gomer, and Redhead (MGR) model and the Knotek and Feibelman (KF) model [49, 50]. The MGR model involves the excitation of valence electrons and works reasonably well for covalent bonds. The KF model involves the excitation of core electrons and is applicable to ion bonding. Since the TiNCl is considered to be an ionic insulator composed of Ti³⁺ and Cl⁻ [23], we assumed that this mechanism is involved in the Cl desorption of TiNCl. In the case of TiO₂, photoinduced desorption is explained by the KF model in terms of Coulomb expulsion between Ti³⁺ and O⁺ that are induced by emitting Auger electrons after the relaxation of electrons in O 2p levels to create photo-holes in the Ti 3p levels [48]. If the KF mechanism is involved in the present case, the electron transfer that leads to Coulomb expulsion may occur from Cl 3p (valence band) to Ti 3p. Further experiments are needed to confirm the KF mechanism, as it is we think beyond the scope of the present study.

With photon stimulated Cl desorption, the final products may be TiN or Cl deficient TiNCl₁₋δ, depending on the amount of Cl deficiency. However, from the Ti 2p photoelectron spectrum, no sharp TiN peak was observed at 455 ± 0.3 eV [44, 45], suggesting the formation of TiNCl₁₋δ, rather than TiN. In β-(Hf or Zr) NCl, Cl deficiency is called deintercalation, which is one of the methods of electron doping to the system. Deintercalated HfNCl₀.7 is a metallic system that also exhibits superconductivity below 24 K [26]. However, since electron doping utilizing the Cl deintercalation into α-MNX has never been reported, the present study is the first experimental realization of deintercalated electron doped α-MNX. Further Cl deintercalation by the soft x-ray irradiation would make the system superconductive, like β-form compounds.

Lastly, we discuss the benefits of methodologies and findings. Regarding pyrolysis, bond breaking by heat cannot be confined within a small area because of the diffusion of heat in a solid. In addition, temperature controlling of a sample is severe for a target material located in a narrow temperature region of a complicated phase diagram. In contrast, bond breaking by light irradiation occurs only in the place where light is irradiated. In particular, when core-levels excitation are important in the bond-breaking process as in the KF model, element/chemical site-selective bond breaking is possible by setting the excitation energy to a specific element/chemical site [52, 53]. This site-selective bond breaking is called a molecular scalpel and is mainly studied in surface adsorption molecular systems. Such a characteristic, combined with sub-micrometer scale spot sizes in third-generation synchrotron facilities, might be used to make sub-micron scale conducting paths at any place on the surface. Photo-induced metallization of TiNCl has enabled detailed electronic-structure investigation studies of metallic (even superconductive) TiNCl by controlling the carrier concentration in a small single crystal.
In summary, the irradiation time dependence of the valence
band and core-level spectra of TiNCl was studied by PES and Ti 2p–3d RIES. Using soft x-ray irradiation, the intensity of the valence band structure origination from Cl 3p and N 2p states decreased while the intensity near \( E_F \) increased. The intensity near \( E_F \) exhibited resonant enhancement, and the Fermi edge was clearly observed by Ti 2p–3d RIES. The analyses of core-level and near-\( E_F \) PES spectral intensities as a function of the soft x-ray irradiation time revealed that the desorption of Cl atoms, the increase in the intensity of the Ti\(^{3+} \) component, and increase of the spectral weight in the vicinity of \( E_F \) exhibit strong correlations. These results indicate that photoirradiation induced metallization of TiNCl occurs due to electron doping through Cl desorption. As estimated from Cl 2p and Ti\(^{3+} \) data, the order of the time-of-
changes is 100 min. This technique can be used to further explore the conducting properties, especially the unconventional superconductivity, of TiNCl.

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**References**

[1] Yamanaka S 2000 High-\( T_c \) superconductivity in electron-doped layer structured nitrides *Annu. Rev. Mater. Sci.* 30 53
[2] Juzar R and Henes J 1964 Über Nitridhalogenide des Titans und Zirkons Z. Anorg. Allg. Chem. 332 159
[3] Woodward P M and Vogt T 1998 Electronic band structure calculations of the \( MNX \) (\( M = Zr, Ti; X = Cl, Br, I \)) system and its superconducting member, Li-doped \( \beta \)-ZrNCl *J. Solid State Chem.* 138 207
[4] Liang Y, Dai Y, Ma Y, Ju L, Wei W and Huang B 2018 Novel titanium nitride halide TiNX (\( X = F, Cl, Br \)) monolayers: potential materials for highly efficient excitonic solar cells *J. Mater. Chem. A* 6 2073
[5] Zhou L, Zhuo Z, Kou L, Du A and Tretiak S 2017 Computational dissection of two-dimensional rectangular titanium mononitride TiN: auxetics and promises for photocatalysis *Nano Lett.* 17 4466
[6] Wang A, Wang Z, Du A and Zhao M 2016 Band inversion and topological aspects in a TiN monolayer *Phys. Chem. Chem. Phys.* 18 22154
[7] Yamanaka S, Yasunaga T, Yamaguchi K and Tagawa M 2009 Structure and superconductivity of the intercalation compounds of TiNCl with pyridine and alkali metals as intercalants *J. Mater. Chem.* 19 2573
[8] Yamanaka S, Kawai H, Hotohama K-i and Ohashi M 1996 A new layer-structured nitride superconductor. Lithium-intercalated \( \beta \)-zirconium nitride chloride, Li\(_{2}\)ZrNCl *Adv. Mater.* 8 771
[9] Yamanaka S, Hotohama H and Kawai H 1998 Superconductivity at 25.5 K in electron-doped layered hafnium nitride *Nature* 392 580
[10] Tou H, Maniwa Y, Koiwasaki T and Yamanaka S 2001 Unconventional superconductivity in electron-doped layered Li\(_4\)In(THF)\(_2\)HfNCl *Phys. Rev. Lett.* 86 5775
[11] Yokoya T et al 2001 Changes of electronic structure across the insulator-to-metal transition of quasi-two-dimensional \( Na_2\beta\)HfNCl studied by photoemission and x-ray absorption *Phys. Rev. B* 64 153107
[12] Takeuchi T et al 2003 Soft x-ray emission and high-resolution photoemission study of quasi-two-dimensional superconductor \( Na_2\beta\)HfNCl *Physica C* 392–396 127
[13] Yokoya T et al 2004 Valence-band photoemission study of \( \beta \)-ZrNCl and the quasi-two-dimensional superconductor \( Na_2\beta\)ZrNCl *Phys. Rev. B.* 70 193103
[14] Tou H, Maniwa Y and Yamanaka S 2003 Superconducting characteristics in electron-doped layered hafnium nitride: \( ^{11}\)N isotope effect studies *Phys. Rev. B* 67 100509(R)
[15] Taguchi Y, Kitora A and Iwasa Y 2006 Increase in \( T_c \) upon reduction of doping in Li\(_2\)ZrNCl superconductors *Phys. Rev. Lett.* 97 107001
[16] Takano T, Kishiiume T, Taguchi Y and Isawa Y 2008 Interlayer-spacing dependence of \( T_c \) in \( Li_2M_n\beta\)HfNCl (\( M = \) molecule) superconductors *Phys. Rev. Lett.* 100 247005
[17] Kasahara Y, Kishiiume T, Kobayashi K, Taguchi Y and Iwasa Y 2010 Superconductivity in molecule-intercalated Li\(_2\)ZrNCl with variable interlayer spacing *Phys. Rev. B* 82 054504
[18] Kuroki K 2010 Spin-fluctuation-mediated \( d + id' \) pairing mechanism in doped \( \beta \)-MNCI (\( M = Hf, Zr \)) superconductors *Phys. Rev. B* 81 104502
[19] Saito Y, Kasahara Y, Ye J, Iwasa Y and Nojima T 2015 Metallic ground state in an ion-gated two-dimensional superconductor *Science* 350 409
[20] Nakagawa Y et al 2018 Gated-controlled low carrier density superconductors: toward the two-dimensional BCS-BEC crossover *Phys. Rev. B* 98 064512
[21] Zhang S, Tanaka M and Yamanaka S 2012 Superconductivity in electron-doped layered TiNCl with variable interlayer coupling *Phys. Rev. B* 86 024516
[22] Sugimoto A, Shohara K, Ekinio T, Zheng Z and Yamanaka S 2012 Nanoscale electronic structure of the layered nitride superconductors \( \alpha \)-K,TiNCl and \( \beta \)-HfNCl, observed by scanning tunneling microscopy and spectroscopy *Phys. Rev. B* 85 144517
[23] Yin Q, Ylvisaker ER and Pickett WE 2011 Spin and charge fluctuations in \( \alpha \)-structure layered nitride superconductors *Phys. Rev. B* 83 014509
[24] Harshman D R and Fiory A T 2014 Comment on ‘Superconductivity in electron-doped layered TiNCl with variable interlayer coupling’ *Phys. Rev. B* 90 186501
[25] Kataoka N et al 2019 μ-PES studies on TiNCl and quasi-two-dimensional superconductor Na-intercalated TiNCl J. Phys. Soc. Japan 88 104709

[26] Zhu L and Yamakawa S 2003 Preparation and superconductivity of chlorine-deintercalated crystals β-MNC11−x (M = Zr, Hf) Chem. Mater. 15 1897

[27] Saeki Y, Matsuzaki R, Yajima A and Akiyama M 1982 Reaction process of titanium tetrachloride with ammonia in the vapor phase and properties of the titanium nitride formed Bull. Chem. Soc. Jpn. 55 3193

[28] Sosnov E A, Malkov A A and Malygin A A 2015 Chemical transformations at the silica surface upon sequential interactions with titanium tetrachloride and ammonia vapors Russ. J. Gen. Chem. 85 2533

[29] Hegde R I, Fiordalice R W and Tobin P J 1993 TiNCl formation during low-temperature, low-pressure chemical vapor deposition of TiN Appl. Phys. Lett. 62 2236

[30] Plumb N C et al 2014 Mixed dimensionality of confined conducting electrons in the surface region of SrTiO3 Phys. Rev. Lett. 113 086801

[31] Plumb N C et al 2017 Evolution of the SrTiO3 surface electronic state as a function of LaAlO3 overlayer thickness Appl. Surf. Sci. 412 271

[32] Meevasana W et al 2011 Creation and control of a two-dimensional electron liquid at the bare SrTiO3 surface Nat. Mater. 10 114

[33] Reckers P et al 2012 Deep and shallow TiO2 gap states on cleaved anatase single crystal (101) surfaces, nanocrystalline anatase films, and ALD titania ante and post annealing J. Phys. Chem C 119 9890

[34] Rödel T C et al 2015 Engineering two-dimensional electron gases at the (001) and (101) surfaces of TiO2 anatase using light Phys. Rev. B 92 041106(R)

[35] Wang Z et al 2017 Atomically precise lateral modulation of a two-dimensional electron liquid in anatase TiO2 thin films Nano Lett. 17 2561

[36] King P et al 2012 Subband structure of a two-dimensional electron gas formed at the polar surface of the strong spin–orbit perovskite KTiO3 Phys. Rev. Lett. 108 117602

[37] Santander-Syro A et al 2011 Two-dimensional electron gas with universal subbands at the surface of SrTiO3 Nature 469 189

[38] Santander-Syro A et al 2014 Giant spin splitting of the two-dimensional electron gas at the surface of SrTiO3 Nat. Mater. 13 1085

[39] King P et al 2014 Quasiparticle dynamics and spin–orbital texture of the SrTiO3 two-dimensional electron gas Nat. Commun. 5 3414

[40] Saitoh Y et al 2012 Performance upgrade in the JAEA actinide science beamline BL23SU at SPring-8 with a new twin-helical undulator J. Synchrotron Radiat. 19 388

[41] Shirley D 1972 High-resolution x-ray photoemission spectrum of the valence bands of gold Phys. Rev. B 5 4709

[42] Proctor A and Sherwood P M A 1982 Data analysis techniques in x-ray photoelectron spectroscopy Anal. Chem. 54 13

[43] The binding energies of Ti 2p and Cl 2p of the present study are slightly lower by 0.4 eV and 0.2 eV than those in reference [25], respectively. The two experiments were performed in SPring-8 but on the different beam lines BL23SU (present study) and BL25SU (reference [25]). We assume that there are three reasons for this difference: charging up, difference in metallization, and calibration of the spectrometer. Since the photon flux density of BL25SU is higher than that of BL23SU, larger binding energies of BL25SU data may be explained by charging up and/or difference in metallization. We do not have the clear answer, however the difference does not change the conclusion of the present study.

[44] Saha N C and Tompkins H G 1992 Titanium nitride oxidation chemistry: an x-ray photoelectron spectroscopy study J. Appl. Phys. 72 3072

[45] Jaeger D and Patscheider J 2012 A complete and self-consistent evaluation of XPS spectra of TiN J. Electron Spectrosc. Relat. Phenom. 185 523

[46] Ishida Y et al 2008 Coherent and incoherent excitations of electron-doped SrTiO3 Phys. Rev. Lett. 100 056401

[47] Sing M et al 2009 Profiling the interface electron gas of LaAlO3/SrTiO3 heterostructures with hard x-ray photoelectron spectroscopy Phys. Rev. Lett. 102 176805

[48] Yukawa R et al 2018 Control of two-dimensional electronic states at anatase TiO2 (001) surface by K adsorption Phys. Rev. B 97 165428

[49] Knotek M L and Feibelman P J 1978 Ion desorption by core-hole Auger decay Phys. Rev. Lett. 40 964

[50] Ramaker D E, White C T and Murday J S 1982 On Auger induced decomposition/desorption of covalent and ionic systems Phys. Lett. A 89 211

[51] Segovia J 1995 A review of electron stimulated desorption processes influencing the measurement of pressure or gas composition in ultra high vacuum systems Vacuum 47 333

[52] Eberhardt W et al 1983 Site-specific fragmentation of small molecules following soft-x-ray excitation Phys. Rev. Lett. 50 1957

[53] Wada S et al 2006 Selective chemical bond breaking characteristically induced by resonant core excitation of ester compounds on a surface J. Phys.: Condens. Matter. 18 S1629