

Ion desorption from single-walled carbon nanotubes  
induced by soft X-ray illumination

Y. Mera<sup>1</sup>, T. Fujiwara<sup>1</sup>, K. Ishizaki<sup>1</sup>, R. Xiang<sup>2</sup>, J. Shiomi<sup>2</sup>, S. Maruyama<sup>2</sup>,

T. Kakiuchi<sup>3</sup>, K. Mase<sup>3</sup> and K. Maeda<sup>1</sup>

<sup>1</sup>Department of Applied Physics, The University of Tokyo, Hongo, Bunko-ku, Tokyo  
113-8656, Japan

<sup>2</sup>Department of Mechanical Engineering, The University of Tokyo, Hongo, Bunko-ku,  
Tokyo 113-8656, Japan

<sup>3</sup>Institute of Materials Structure Science, KEK, Tsukuba, Ibaraki 305-0801, Japan

E-mail [mera@exp.t.u-tokyo.ac.jp](mailto:mera@exp.t.u-tokyo.ac.jp)

**Abstract**

We have investigated ion desorption from single-walled carbon nanotubes (SWNTs) that is induced by soft X-ray illumination in the C 1s core-excitation energy range in order to have insight to the mechanism of defect formation caused by the similar excitation. The mass of desorbed ions was analyzed by a time of flight (TOF) spectrometer and the photon energy

dependence of the ion yield or the desorption efficiency spectra were measured as a function of the monochromatic photon energy used for illumination. Experimental results exclude the simple detachment of carbon atoms constituting the nanotubes from the cause of the defect formation. Also the photo-induced etching of carbon atoms associated with C-H bond rupture is ruled out from the defect formation mechanism. Auger mechanisms to explain the photo-induced desorption are discussed.

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## Introduction

Single-walled carbon nanotubes (SWNTs) [1] are promising materials for many potential applications owing to their unique structures and properties. Especially, their electronic structures are strongly dependent on how the graphene sheets are folded [2]. One of the issues of technological importance as well as of fundamental interest in SWNTs is structural defects because physical properties of SWNTs should be strongly affected by the presence of imperfections in the quasi-one-dimensional structures [3-5]. In fact, it is known experimentally that defects in SWNTs play a significant role in nano-scale devices based on SWNTs [6]. However, in practice so far, we have no good control of defects in SWNTs, not only in the as-grown stage but also in the subsequent processing stages.

It is known in crystals that point defects can be intentionally generated by irradiating the crystal with energetic particles such as ions and electrons which have energies exceeding the knock-on damage threshold and hence can transfer a sufficient momentum to the target atoms to kick-out them from the lattice site. However, recent studies [7] showed that some defects in SWNTs can be introduced by irradiation with electrons of energies far below

the knock-on damage threshold. More recently, it was also found [8, 9] that defects are generated in SWNTs even by illumination with photons which have no significant momentum. The generation of the defects was detected by an increase of the defect-related D-band intensity in Raman spectra in the sample after illumination with an intense light from a synchrotron radiation ring. The photo-induced damage threshold was found to be reducible down to 6 eV in the ultraviolet range in which light illumination gives rise to low-energy luminescence [10] due to triplet excitation states in SWNTs [11]. It is quite likely that such defect formation induced by low energy photo-excitation shares a common mechanism with a more recently found phenomenon that defects are generated in SWNTs by low energy electron injection from probe tips of scanning tunneling microscopes [12, 13].

For higher energy excitations, it had been reported that structural changes can be induced in carbon materials, not limited to SWNTs, by light illumination in the soft X-ray range that can excite core electrons. Ma et al. [14] conducted pioneering soft X-ray spectroscopic experiments on crystalline diamond and graphite in the core-exciting photon energy range, and showed that the spectrum of X-ray emission induced by resonant core excitations at a

specific energy exhibits an anomalous tail extending to low energies, which signifies the occurrence of considerable displacements of carbon atoms from the lattice sites within the short lifetime of C 1s core excitons. Theoretically, the phenomenon can be well explained by the pseudo-Jahn-Teller (PJT) mechanism that operates in the core-excitonic state [14, 15], which was supported by firmer experimental evidence [16] for the symmetry-breaking atomic displacements expected from the PJT mechanism.

While the atomic displacements in crystalline diamond and graphite mentioned above are temporal and the crystal is reversibly recovered after the core exciton vanishes, atomic displacements caused by soft X-ray illumination in general are not necessarily reversible. It was found that irreversible structural changes are induced by core-exciting illumination in amorphous carbon [17] and most recently in SWNTs [18, 19] as well. What is common in the core-excitation-induced structural changes is the resonant feature of the efficiency spectrum that exhibits a peak between  $\pi^*$  and  $\sigma^*$  peaks of X-ray absorption spectrum (XAS) [17, 19]. Although the origin of this resonant peak, at 289 eV in SWNT [19], is not established, it is often claimed that anti-bonding C-H  $\sigma^*$  states give rise to a resonant XAS peak

between  $\pi^*$  and  $\sigma^*$  peaks [20-23]. The mechanism of atomic displacements induced by core electronic excitations is not limited to the core-excitonic mechanism. A mechanism often invoked to explain the resonant core-excitation-induced atomic desorption, not defect formation, is one that operates in a spectator Auger final state. In a spectator Auger process a core electron is excited to an unoccupied orbital while an electron transitions into the core-hole and another electron is emitted as a spectator Auger electron. When the initially unoccupied orbital has an antibonding character, not only the two holes but also the excited electron contribute to the bond scission that is initiated by the atomic displacements in the core-excitonic mechanism. Therefore, a possible hypothesis one may consider in the resonant defect formation in SWNT is that the defects are generated by desorption of carbon atoms induced by the spectator Auger mechanism that follows the excitation of a C 1s electron to the anti-bonding C-H  $\sigma^*$  state.

In the present study, we have investigated the ion desorption from SWNTs that is induced by soft X-ray illumination in the C 1s core-excitation energy range. We present experimental results of time-of-flight (TOF) of desorbed species from SWNTs, where we pay special attention to carbon ions that

would be present if the defect formation is associated with desorption of carbon atoms constituting the nanotube. Also we examine the TOF spectra obtained for  $^{13}\text{C}$ -enriched SWNT samples as well as ordinary  $^{12}\text{C}$  SWNTs in order to check if the defects are formed as a result of photo-induced etching of carbon atoms in the SWNTs by contaminant molecules chemisorbed on the nanotubes. We also check the hypothesis of the spectator Auger mechanism induced by C-H  $\sigma^*$  excitations by comparing the defect formation efficiency spectrum with the ion yield spectrum of hydrogen the latter of which should represent the C-H  $\sigma^*$  excitation spectrum. Some discussion is made on possible mechanisms based on the experimental facts.

## **Experimental Method**

Vertically aligned SWNT arrays were grown on quartz substrates by alcohol catalytic chemical vapor deposition using Co/Mo bimetal as a catalyst, with details reported elsewhere [24]. SWNT arrays enriched with  $^{13}\text{C}$  isotopes were synthesized by a same process using  $^{13}\text{C}$  labeled (99% replaced with  $^{13}\text{C}$ ) ethanol as a carbon source. The quality of the SWNT films was characterized by resonance Raman spectroscopy [25]. These vertically

aligned SWNT films were detached from the quartz substrates and mounted onto crystalline silicon substrates [26].

Commercial SWNTs powder from Aldrich was also used for measurements of desorption efficiency spectra, XAS spectra and Auger spectra. The powder was refluxed in hot hydrogen peroxide (95°C) for 3 hours in order to reduce amorphous carbon and defective nanotubes, and then was dispersed in dichloroethane by sonication treatments. The dispersed solution was deposited onto a silicon substrate followed by a drying process.

The soft X-ray experiments were conducted at the beamline 13C in Photon Factory at Tsukuba. Monochromatic soft X-rays of  $10^{10}$  photons/s·cm<sup>2</sup> in intensity on the sample was obtained from the undulator device inserted in the synchrotron radiation ring operated in the single-bunch mode. The photon energy  $E$  diffracted from the equipped monochromator had a resolution of  $E/\Delta E = \sim 6000$  and its scale was corrected by assuming the  $\pi^*$  XAS peak of highly oriented pyrolytic graphite at  $E = 285.3$  eV [27]. The intensity of the photons was monitored by measuring the mesh current, a current flowing out of a gold mesh placed in front of the sample. The soft X-ray beam of 0.8 mm<sup>2</sup> in cross section was incident onto a sample with an



angle of  $84^\circ$  from the surface normal.

The mass of desorbed ions was analyzed by a TOF spectrometer coaxially installed within a cylindrical mirror analyzer (CMA) of electrons and ions emitted from the sample with specific energies [28]. To collect the desorbed ions, a voltage of -900 V was applied to the entrance slit of the TOF tube with respect to the sample. Ion desorption efficiency spectra were measured for total ions collected by the TOF tube of another analyzer of the same type but with less mass resolution [29]. X-ray absorption spectra in the photo-electron yield (PEY) mode and Auger spectra were also acquired using this second analyzer. All the experiments were conducted at room temperature under an ultra high vacuum (UHV) condition ( $< 3 \times 10^{-7}$  Pa).

## **Results and Discussion**

Figure 1(a) shows a typical TOF spectrum obtained when the sample was illuminated at  $E = 292$  eV. Because the interval of successive soft X-ray pulses (624 ns) was not long enough for all the flight times of desorbed ions to be separated, the raw TOF spectrum is a superposition of periodically

shifted TOF spectra. In order to check whether the ion signals arose from physisorbed species or not, the sample was heated at a few hundreds °C by Joule heating of the silicon substrate in the UHV sample chamber. The TOF spectra before and after the sample baking were almost the same (not shown), which means that the desorbed species observed in the TOF spectra originated mostly in chemical groups decorating the SWNTs rather than weakly bound physisorbates.

By careful analysis of systematic peak shifts with the voltages applied to the analyzer electrodes, desorbed species in the TOF spectrum in Fig. 1(a) were assigned to ions such as  $\text{H}^+$  ( $m = 1$ ),  $\text{H}_2^+$  ( $m = 2$ ),  $\text{O}_2^+$  ( $m = 32$ )  $\text{COO}^+$  ( $m = 44$ ) and  $\text{NO}^+$  ( $m = 30$ ). An important fact to be stressed here is that monocarbon  $\text{C}^+$  ( $m = 12$ ) and dicarbon  $\text{C}_2^+$  ( $m = 24$ ) ions were *not* detected in the experiments. This means that the simple detachment of carbon atoms *in* the nanotubes is not the mechanism of the defect formation by soft X-ray illumination.

The desorbed species from the commercial sample were essentially the same as those in Fig. 1(a). It is known that sidewalls of SWNTs can be decorated with chemical groups [30]. Those chemisorbed groups can be

desorbed together with carbon atoms constituting the nanotubes leaving vacancy defects on the sidewalls. In order to check this possibility, we measured TOF spectra of desorbed ions from  $^{13}\text{C}$ -enriched SWNTs. Figure 1(b) shows the TOF spectrum of  $^{13}\text{C}$ -SWNTs, which shows that the desorbed species were basically the same to those in the spectrum of ordinary  $^{12}\text{C}$ -SWNTs and no desorbed species including  $^{13}\text{C}$  were observed. Since the peak of  $m = 14$  that could be assigned to  $^{12}\text{CH}_2^+$  or  $^{13}\text{CH}^+$  in Fig. 1(b) was observed in the TOF spectrum obtained also for a bare Si substrate (not shown), we can consider that the peak represents  $^{12}\text{CH}_2^+$  rather than  $^{13}\text{CH}^+$ . This result indicates that desorption induced by photo-etching is not the cause of the soft X-ray induced defect formation.

Figure 2(a) shows the desorption yield spectrum of all ion species from the commercial SWNTs sample and 259 eV Auger electron excitation spectrum acquired by the second analyzer [29], where the vertical scale are divided by the mesh current that represents the X-ray intensity used for the photo-induced desorption. The kinetic energy of the collected photo-electron (259 eV) is the peak energy of the Auger electron spectrum which corresponds to the energy of a valence electron emitted to the vacuum on the

Auger recombination of another valence electron with the core hole. For comparison, Fig. 2(a) also cites the X-ray absorption spectrum (XAS) obtained by dividing the total photoelectron yield with the mesh current. The curve in Fig. 2(b) shows the spectrum of the desorption efficiency that was obtained by dividing total counts of desorbed ions in (a) with the counts of Auger electrons. The spectrum in (b) exhibits a resonant structure near the C 1s core absorption edge (287 eV) and a non-resonant component at energies higher than 290 eV.

Figure 3 shows the ion yield spectra of H<sup>+</sup>, O<sup>+</sup> and CO<sup>+</sup> ions desorbed from the commercial SWNTs sample. These spectra were obtained by estimating the area of the corresponding peak of the TOF spectra at various photon energies used for desorption. The species other than hydrogen were selected because only their peaks, observed in the less-resolved TOF spectra acquired by the second analyzer, are sufficiently separated from each other allowing the deduction of respective ion yield spectra.

As shown in Fig. 2(a), the ion yield spectrum exhibits some similarity to the yield spectrum of Auger electrons. The leveling of the desorption efficiency in Fig. 2(b) at high energy region (above 290 eV) suggests that the

ion desorption occurs in coincidence with the Auger electron emission. Since the Auger electrons of 259 eV in energy emitted as a consequence of core excitation above 290 eV in photon energy are normal Auger electrons in SWNTs, it appears that the ion desorption in this energy range is triggered by normal Auger processes which are non-resonant in nature. In other words, the mechanism operating in the high energy range is considered to be the X-ray induced electron-stimulated ion desorption (XESD) [31], in which it is the localized formation of multiple holes that induces the ion desorption with a rate proportional to the yield of normal Auger electrons.

The desorption efficiency spectrum in Figs. 2(b), however, has also a resonant feature at the photon energy of 287 eV which is above the  $\pi^*$  peak but below the  $\sigma^*$  band in the XAS spectrum. As mentioned above, the XAS peak observed between the  $\pi^*$  peak and the  $\sigma^*$  band in graphitic carbon is often attributed to a resonant core excitation to the empty anti-bonding C-H  $\sigma^*$  state [20-23]. The ion yield spectrum of  $H^+$  ions in Fig. 3 shows a distinct resonant peak at 287 eV while the ion yield spectra for other species have no peak at this energy, from which we identify the XAS peak located at 287 eV as the core excitation to the empty C-H  $\sigma^*$  state. Therefore, the most

plausible mechanism for the resonant desorption of  $H^+$  ions at 287 eV is a spectator Auger process involving the C-H  $\sigma^*$  state.

The resonant peak energy of 289 ~ 290 eV in soft X-ray induced defect formation of SWNTs [19] is considerably higher by ~ 3 eV than the C-H  $\sigma^*$  resonance at 287 eV as shown in Fig. 3. This fact also excludes the carbon desorption associated with C-H bond rupture from the mechanism of soft X-ray induced resonant defect formation in SWNTs.

## Summary

We have investigated the ion desorption from SWNTs that is induced by soft X-ray illumination in the C 1s core-excitation energy range. Experiments using ordinary  $^{12}\text{C}$ -SWNTs sample and SWNTs sample consisting of  $^{13}\text{C}$  isotopes showed that various species including  $H^+$  as the dominant ions are desorbed from the SWNT samples. From the fact that  $C^+$  and  $C_2^+$  ions and species containing  $^{13}\text{C}$  atoms were not detected, we could conclude that the defect formation by soft X-ray illumination is caused neither by the detachment nor by the photo-induced etching of carbon atoms in the nanotubes. The desorption efficiency spectrum divided by Auger

electron yield exhibit a resonant structure near the C 1s core absorption edge and a non-resonant constant component at higher energies. The resonant desorption at the photon energy of 287 eV is dominated by desorption of H<sup>+</sup> ions and is well accounted for by the spectator Auger process involving the C-H  $\sigma^*$  state. The photoelectron-photoion coincidence measurements developed by one of the present authors (Mase) [32] would provide more direct evidence for the mechanism if the ion yield is sufficient to conduct such experiments. The discrepancy of  $\sim 3$  eV in the peak energy between the yield spectrum of H<sup>+</sup> desorption and the efficiency spectrum of defect formation also rules out the C-H bond rupture model for the mechanism of the soft X-ray induced defect formation.

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## Figure Captions

### Fig. 1

Typical TOF spectrum of desorbed ions obtained from SWNTs synthesized from  $^{12}\text{C}$ -isotopes (a) and from SWNTs 100%-enriched with  $^{13}\text{C}$ -isotopes (b) that were illuminated with soft X-rays of 292 eV in energy. Due to the short interval of triggers for TOF measurements, the spectra shown are superpositions of TOF spectra periodically shifted by 624 ns. The slight difference in the time scale between (a) and (b) is due to a small difference in the sample position and therefore has no physical significance. The sharp signals around 600 ns in (a) and (b) are instrumental artifacts. Note the absence of  $\text{C}^+$  and  $\text{C}_2^+$  ions and no desorbed species containing  $^{13}\text{C}$  were detected in (b).

### Fig. 2

(a) Desorption yield spectrum of total ions from the commercial SWNTs sample, the yield spectrum of Auger electrons in energy of 259 eV, and the X-ray absorption spectrum. All the spectral intensities are normalized by the

mesh current that represents the soft X-ray intensity. (b) Desorption efficiency spectrum obtained by dividing the desorption yield spectrum in (a) with the Auger spectrum. Note in (b) a resonant structure at 287 eV and the non-resonant feature at energies higher than 290 eV.

**Fig. 3**

Normalized ion yield spectra of desorbed species separately detected in the commercial SWNTs sample by the second TOF analyzer. Note the peak at 287 eV in the desorption spectrum of H<sup>+</sup> ions is absent in the spectra of other ions. The 287 eV peak position differs from the peak position at 289 eV in the resonant defect formation induced by soft X-ray illumination [18].

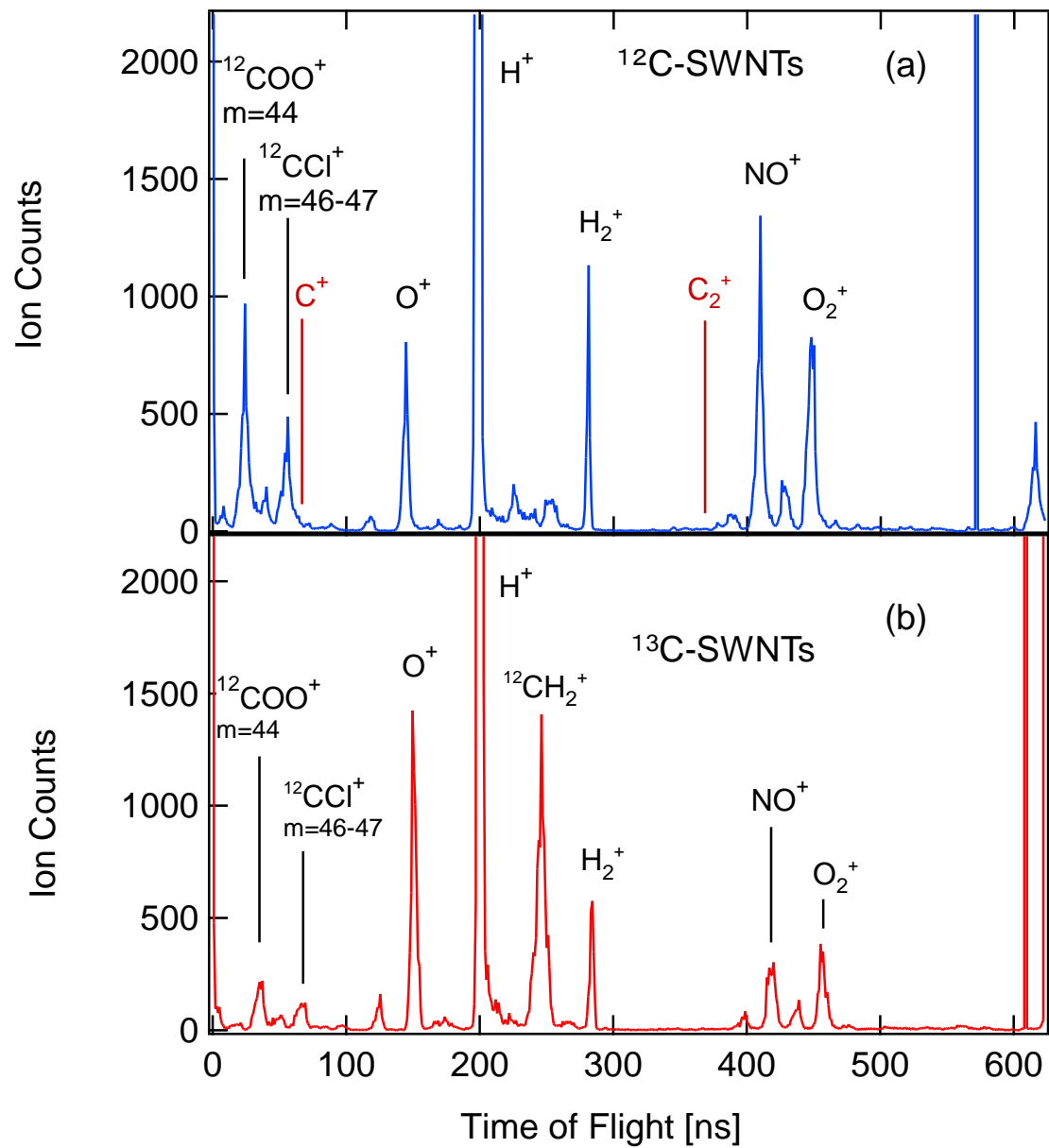


Fig.1

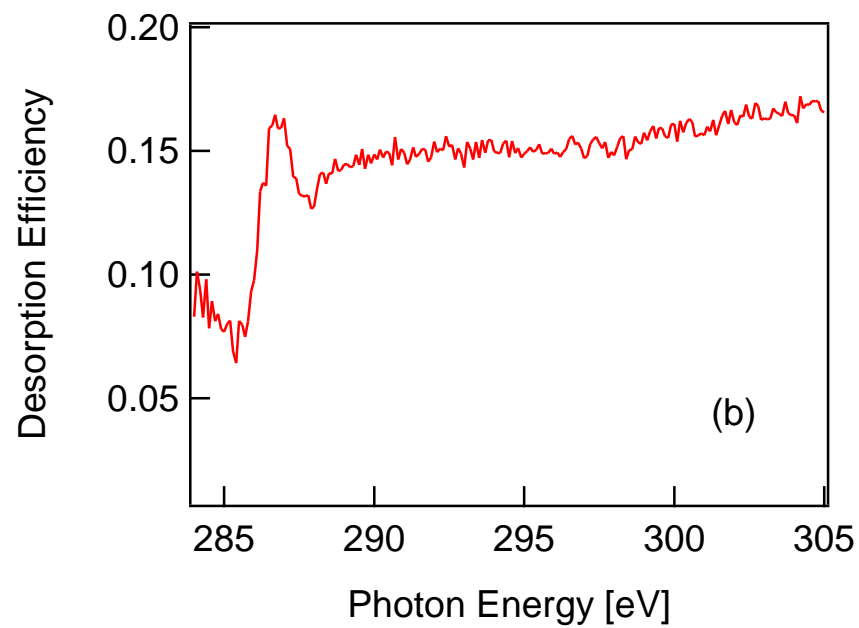
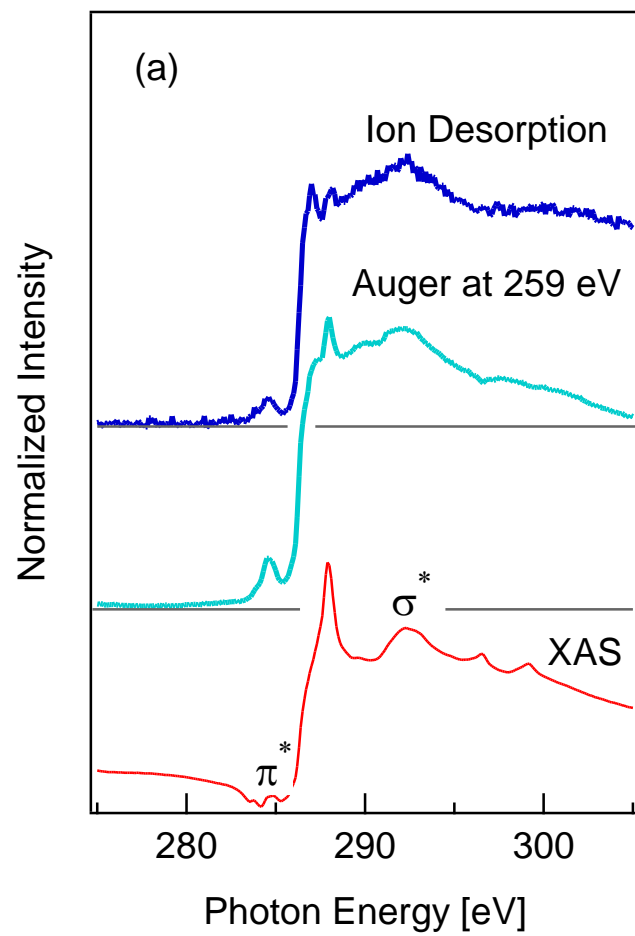


Fig.2

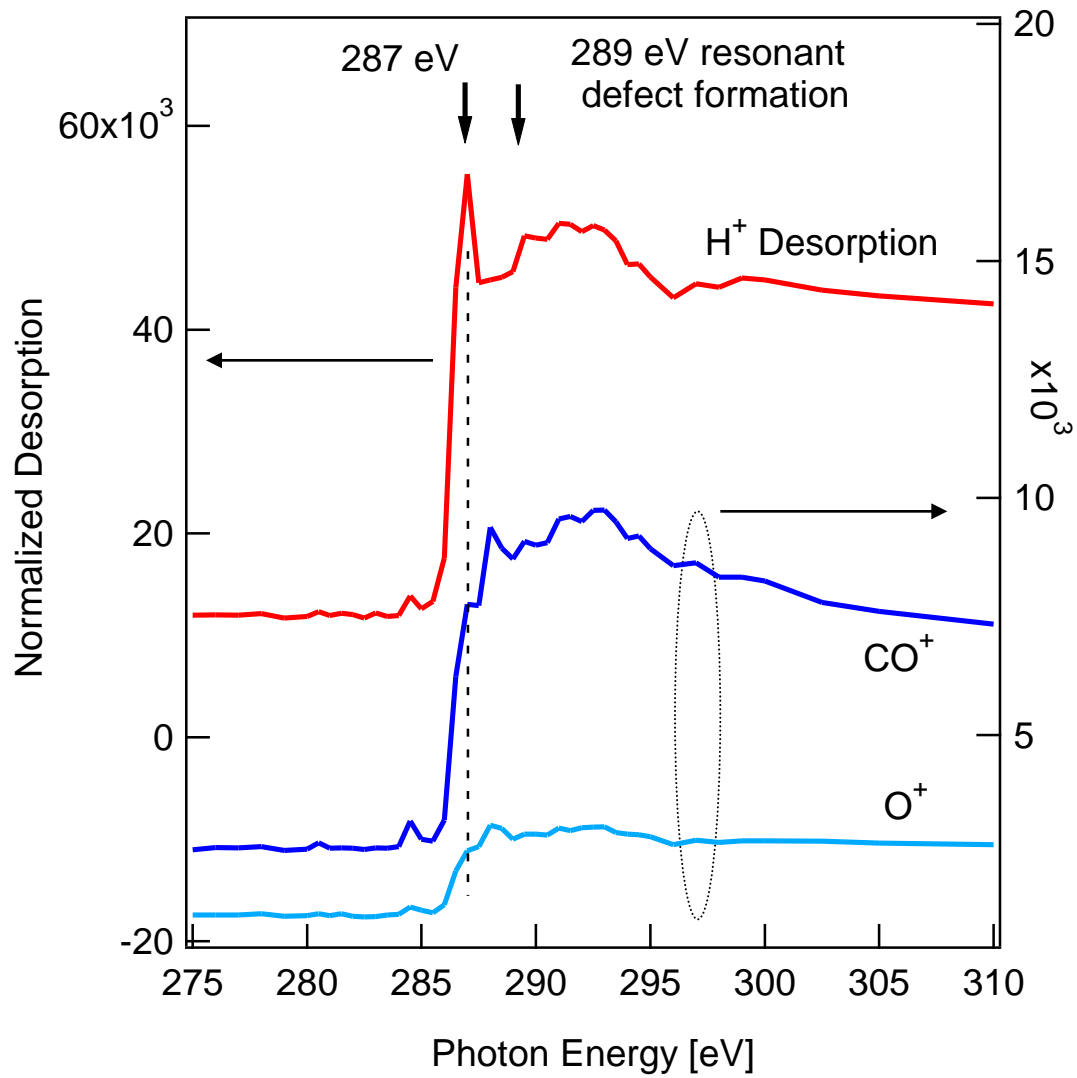


Fig. 3