Site specific photochemical reaction by core electron excitation: carbon and oxygen K-edge fine structure of PMMA

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Abstract

The photon energy dependence of ion desorption from thin films of PMMA was measured in the 250–700 eV photon energy range to investigate the primary steps in radiation induced decomposition using monochromatic pulsed-synchrotron radiation. The desorption of the most intense ions; CH\textsuperscript{2+}, H\textsuperscript{+}, CH\textsuperscript{+} and CHO\textsuperscript{+}, depends on the nature of the electronic state created in the primary excitation process. The fragmentation occurs specifically around the site of the atom where the optical excitation took place. The very localized desorption of CH\textsuperscript{2+} at 288.7 and 535.6 eV, and of CHO\textsuperscript{+} at 539.3 eV can be very useful for lithographic applications or for future molecular electronic devices fabrication.

1. Introduction

There is recent interest in using soft X-rays to replicate patterns lithographically as a step in the fabrication of densely packed microcircuits. The pattern is recorded in a photoresist such as poly(methylmethacrylate) (PMMA) [1] by degrading the main chain and turning the polymer more susceptible to dissolution in weak solvents. A better understanding of the interaction of the incident photon with the resist is very important to determine resolution and sensitivity of polymers used as pattern replication media. Etching rate investigations are normally performed using white radiation. Even though longer exposure times are necessary when using monochromatized radiation, more controlled or sensitive etching is expected to occur. Although the photochemical decomposition of polymer solids by ionizing radiation has been widely used in X-ray and electron beam lithography the knowledge on the decomposition mechanism is very limited. In general, the photochemical decomposition of polymers was investigated by measuring the etching rate [2], the absorption coefficient [3] and the effects of interactions with electrons [4], bombarded ions [5], and infrared- and UV-photons [6]. The photoexcitation in the soft X-ray energy range is characterized by an inner shell electron transition to Rydberg states, unoccupied states or to the ionization continuum. The decay process following

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the primary excitation can proceed through different energy decay paths involving photon, electron, ion or neutral fragments emission [7]. The fragmentation products of the excited molecule are expected to reflect a chemical-bond scission near the atom involved in the initial photoexcitation step.

Electronic states involving excitation and ionization of inner-shell electrons are localized and sensitive to the environment in the region of the core hole. Considering this localized character of core excitations, one can think about its applicability as an active agent to promote very localized decomposition of molecules [8]. In the VUV region (8–40 eV) [9], significant differences were observed between the photon energy dependencies of photoion and photoelectron yields. Preliminary results using synchrotron radiation in the 250–700 eV energy range have indicated the possibility of site specific fragmentation [10]. In the present research, partial ion yield (PIY) spectra from solid films of poly(methylmethacrylate) were measured to investigate the primary steps in radiation induced decomposition following carbon and oxygen ls electron excitations. It was clearly found that the decomposition depends on the nature of the electronic states created in the excited molecule. The ionic fragmentation of PMMA induced by monochromatized soft X-rays is discussed with regard to the possibility of site-selective fragmentation via core excited states. Better etching patterns are expected to be produced by using more controlled photo-excited reactions using monochromatized radiation.

2. Experiment

The experiments were performed at the soft X-ray beam line BL13C at the Photon Factory of The National Laboratory for High Energy Physics. This beam line [11] was designed based on a cylindrical element monochromator (CEM) concept [12] using undulator radiation from a 27-pole multipole wiggler/undulator. The TOF spectrometer was mounted in a UHV chamber [13] which consists of two ultrahigh vacuum (below $5 \times 10^{-8}$ Pa) chambers, a chemical reaction cell, and a multisample introduction port. The TOF spectrometer [10] is located at the normal direction from the sample surface at an angle of 54.7° (magic angle) with respect to the incident photon beam. During single bunch operation of the storage ring, a soft X-ray pulse with a turn time of 624 ns and a width of 100 ps was incident on the sample through a photon-flux monitor of Cu grid. The incident flux spectrum was recorded simultaneously as the photo current at the Cu grid. All spectra were normalized by this flux spectrum to correct for fluctuations in beam intensity.

Thin films of PMMA were prepared by spin-casting from a methyl isobutyl ketone solution on an Au-evaporated Si(100) wafer. The thickness of the PMMA films was estimated to be less than 100 Å as measured by a DEKTAK 3030 surface profiler. In this work the charging up effect was considered negligible and since no significant alteration of the mass spectra was observed even after long X-ray exposures, 8 hours, the X-ray damage effect was judged insignificant. The pressure in the measurement chamber was $3 \times 10^{-7}$ Pa during the measurements, all performed at room temperature.

3. Results and discussion

The partial ion yield spectra (C K-shell excitation spectra) of the main ions $H^+$, $CH^+_2$, $CH^+_2$ and CHO$^+$ near C K-edge are shown in Fig. 1. Six absorption features can be observed. Outka and Stöhr have shown that the C ls NEXAFS of PMMA can be predicted by the ISEELS of model molecules formic acid and methyl formate using the building block approach [14]. The first strong peak at 288.7 eV (feature 2) was first considered as due mainly to the C(C=O) ls $\rightarrow \pi^*$(C=O) transition as reported earlier in electron energy loss studies (EELS) of carboxylic acids [15]. There is a shoulder at 287.5 eV which is assigned to main chain ls transitions to a $\sigma^*$ state mainly localized in the main chain carbons [16]. The shoulder at 289.7 eV is a mixture of C 1s(main chain) $\rightarrow \sigma^*$(C–H), and C 1s(O–CH$_3$) $\rightarrow \sigma^*$(C–H). The broad maxima (features 4, 5 and 6) at 292.3, 296.3, and 303.2 eV in the continuum are at-
tributed to the $\sigma^*(C-C, C-H)$ [17], $\sigma^*(C-O)$ and $\sigma^*(C=O)$ resonances.

Ritsko et al. [16] have compared electron energy loss and photoemission spectra of PMMA to calculated results from all-valence-electron CNDO/S molecular orbital calculations of 2,2-dimethylmethylpropionate (DMMP). From these calculations, the peak at 288.7 eV can be assigned to several nearly degenerate components. The strongest consists of a transition from the carbonyl carbon ($C=O$) to the first empty molecular orbital $\pi^*(C=O)$. The other significant contributions consist of transitions from the main chain carbon to the third, fourth, and fifth empty molecular orbitals mainly localized in the t-butyl as well as from the methoxy carbon to the fourth empty state mainly localized in the methoxy methyl group. The CK-shell excitation spectrum of $CH_3^+$ differs from that of other fragments chiefly by a prominent peak at 288.7 eV. For this ion this peak is consistent with a transition of $C 1s$(main chain) $\rightarrow \sigma^*(C-C)$ and $C 1s$(OCH$_3$) $\rightarrow \sigma^*(O-CH_3)$ at the methoxy group. This prominent peak at 288.7 eV especially in the curve which corresponds to the methyl group fragmentation, can be taken as a strong indication of the higher efficiency of ion production by $\sigma^*$ excitation. Similar results were observed in polystyrene films which show that $\pi^*$ transitions of the benzene ring do not result in bond rupture and ion desorption [18].

The oxygen K-shell excitation spectra of the main ions $H^+$, $CH_3^+$, $CH_3^+$ and $CHO^+$ are shown in Fig. 2. There are 6 common features in all spectra. The first strong peak at 531.5 eV is due to the $O 1s$(C=O) to $\pi^*(C=O)$ transition as reported earlier in electron energy loss studies (EELS) of methyl formate and propanoic acid [15]. The second peak at 534.3 eV can be assigned to a mixture of $O 1s$(OCH$_3$) $\rightarrow \pi^*(C=O)$ charge transfer transition and $O 1s$(C=O) $\rightarrow \sigma^*(C=O-CH_3)$. Peak 3 at 535.6 eV can be assigned to $O 1s$(OCH$_3$) $\rightarrow \sigma^*(O-C=O)$ resonance. The higher energy features 4, 5 and 6 are attributed to unresolved $O 1s$(OCH$_3$) $\rightarrow$ Rydberg/$\sigma^*(C=O-CH_3)$, $O 1s$(C=O) $\rightarrow \sigma^*(C=O)$ and shake up $\pi(C=O) \rightarrow \pi^*(C=O)$ transitions, respectively [19]. In the PMMA OK-edge there is also an overall agreement with the NEXAFS main features of condensed propanoic acid: the $C=O \pi^*$ resonance at 532.8 eV, the $C-O \sigma^*$ resonance at approximately 540.1 eV, and $C=O \sigma^*$ resonance at 544.4 eV consistent with species containing a carboxyl group. The clear qualitative differences found among the different fragments can be related in a simple manner to the localized transitions which originate the fragmenta-
tion. The third feature at 535.6 eV is notably prominent in the spectra of CH$_2^+$ and CH$_3^+$. The efficient production of these ions can be understood as a result of the C–O bond breaking of the methoxy group as a result of the O ls(OCH$_3$) $\rightarrow$ $\sigma^*(C-OCH$_3$)$ transition. The dominant feature in the CHO$^+$ spectrum at 539.3 eV is considered as a result of the O ls(OCH$_3$) $\rightarrow$ $\sigma^*(C-OCH$_3$)$ transition. These interesting differences observed among the spectra of the fragments indicate that the fragmentation process is very sensitive to the unoccupied electronic structure in the immediate vicinity of the oxygen atoms.

The energy decay mechanism after the primary core excitation can be directly investigated by ion yield detection. After the primary excitation and the following Auger decay [20] the ion desorption can proceed for those ions which have sufficient energy to overcome the surface potential barrier. Only those ions that survive reneutralization will escape into vacuum. This explains the small desorption rates in the ion yield spectra which have hindered the application of ion yield detection to near edge absorption fine structure measurements (NEXAFS). In this research, the possibility of measuring partial ion yield spectra for PMMA has proven to be very useful for investigation of ion desorption mechanisms.

The partial ion yield spectra near the carbon edge are all very similar, with an exception made to CH$_2^+$. As has been observed before, this strong peak was assigned to transitions localized mainly in the main chain C–C bondings and in the methoxy group. These experiments alone cannot distinguish the origin of these CH$_2^+$ ions from the main chain or from the methoxy group fragmentation. Further experiments with similar polymers are planned for this purpose.

![Fig. 3. CH$_2^+$ and CHO$^+$ production by localized excitation.](image-url)
Unlike the carbon K-edge, the partial ion yield spectra near the oxygen K-edge are remarkably different. The CH\textsubscript{2}\textsuperscript{+} and CH\textsubscript{3}\textsuperscript{+} spectra are characterized by a stronger peak at 535.6 eV. The CHO\textsuperscript{+} spectrum is dominated by the peak at 539.3 eV.

The core excitation and ionization of gaseous HBr, CH\textsubscript{3}Br, HI, and CH\textsubscript{3}I, have been shown to be a two step relaxation process involving a fast neutral dissociation followed by the autoionization of the excited fragments [21]. For heavier fragments such as those measured in PMMA this phenomenon is considered to disappear. The observed site specific character in the partial ion yield spectra of PMMA can be explained as the selective measurement of those ions produced by fast reactions at the outermost part of the surface that still retain the localized character of the first core excitation process and are more likely to survive neutralization. In the gas phase, the reneutralization path is less probable and all the produced ions, either from fast or slow reaction are collected by ion detection, the resultant spectrum being an average of all decomposition paths. Taking advantage of the more selective character of ion desorption from solid materials, ion detection for solid samples may prove to be a valuable detection technique to assist in peak assignments and in mechanistic investigations.

4. Conclusions

In the present work, interesting information about the photon stimulated ion desorption mechanism (PSID) from thin films of poly(methylmethacrylate) (PMMA) has been obtained by carbon and oxygen K-shell excitations. The most intense ions correspond to CH\textsubscript{2}\textsuperscript{+}, H\textsuperscript{+}, CH\textsubscript{3}\textsuperscript{+}, and CHO\textsuperscript{+} ions. Using soft X-rays, the ion desorption mechanism of PMMA was shown to be directly related to scission of bondings after excitation from 1s core electrons at specific atomic sites to unoccupied orbitals at the bondings responsible for the ion generation. Near the carbon K-edge the strong peak at 288.7 eV was assigned to a mixture of carbon 1s transitions to unoccupied molecular orbitals, mainly, a \pi* state localized at the carbonyl group and \sigma* state localized at the main chain carbon. The efficient production of CH\textsubscript{2} at this energy, is taken as evidence of the localized contribution of the \sigma* state at the main chain carbons. Near the oxygen K-edge, the strong peak localized at 537.7 eV can be understood as an efficient production of CH\textsubscript{2}\textsuperscript{+}, and CH\textsubscript{3}\textsuperscript{+} ions by the excitation of O 1s electrons to \sigma* states localized at the methoxy group. The broader feature at 539.3 eV can be assigned to transitions from the methoxy O 1s to the \sigma* state of the carbonyl–methoxy C–O bonding. This would explain the good efficiency of production of CHO\textsuperscript{+} ions observed at this energy.

This work has also demonstrated the viability of applying ion detection as a powerful technique for investigation of core excitation and decomposition mechanisms. The extension of this research to different molecules is planned in a near future especially to investigate the origin of CH\textsubscript{2} and CH\textsubscript{3} ions. This work demonstrates the viability of using core excitation as a means to localized decomposition of the well known resist PMMA. The reactivity and products distributions are notably dependent on photon energy. High resolution etching patterns will probably be obtained controlling the degradation reactions by choosing suitable monochromatized synchrotron radiation. These results can also be directly applied for the construction of future molecular electronic devices [22] in which the ability of performing very localized transitions is one of the fundamental aspects.

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