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X-ray Photoelectron Spectroscopy Study of an Ion Sputtering Process of Fluoro Polymers Using Monte Carlo Simulation

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Received May 21, 1986

ABSTRACT: The sputtering of Ar ion bombarded poly(tetrafluoroethylene) (PTFE) and poly(vinylidene fluoride) (PVDF) was studied by X-ray photoelectron spectroscopy (XPS). Monte Carlo simulation of the Ar ion sputtering process of both polymers is performed to understand the variation of XPS spectra during sputtering. In both polymer systems, fluorine atoms are preferentially sputtered away from the polymer chains, leaving carbon atoms behind. The damaged layer produced by the process has a homogeneous composition within the sampling depth of XPS. Observed XPS spectra of both polymers are explained by random elimination of fluorine atoms from a polymer chain, although better fitting is acquired by also taking a double fluorine atom elimination mechanism into account.

Introduction

Ion sputtering is frequently used in surface analysis. It is used to obtain signals in secondary ion mass spectroscopy (SIMS) and also for surface cleaning and depth profiling in X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and ultraviolet photoelectron spectroscopy (UPS). It is important to obtain new information for better understanding of the sputtering mechanism in SIMS, especially for organic polymers. It is also desirable to have detailed knowledge of the change of surface composition in depth profiling or in cleaning by sputtering, especially in quantitative analysis.

XPS is expected to be a useful tool for investigation of the change of surface composition induced by the ion sputtering process because of its good surface sensitivity and capability of providing chemical bonding information. The effects on inorganic materials induced by ion sputtering have already been studied in detail by XPS by many authors.[1-10] On the other hand, not many studies[5,11-13] have concerned ion sputtering on organic materials. An understanding of the mechanism of sputtering is particularly important for SIMS measurement of polymer materials;[13-17] however, it is far from satisfactory.

In this paper, we examine the change of chemical composition on the surface of poly(tetrafluoroethylene) (PTFE) and poly(vinylidene fluoride) (PVDF) by Ar ion bombardment with XPS because these fluoro polymers have already been extensively studied by XPS[18-22] and SIMS.[13,15,17] Thickness of a damaged layer on the sputtered polymer surface is estimated by the photoelectron takeoff angle variation measurement of XPS. Change of XPS spectra of the polymers by Ar ion bombardment is interpreted by a simple calculation based on Monte Carlo simulation.

Experimental Section

PTFE and PVDF used in this study are commercially available as 50-μm-thick sheets. These sheets were washed well with an ultrasonic cleaner in *n*-heptane to remove organic contamination from the surface before use.[23] A sample was attached to a holder by double-sided adhesive tape. The AEI-Kokusai Denki Model ES-200 was used for the XPS study with an Al $K\alpha_{1,2}$ X-ray source ($h\nu$ = 1486.6 eV) in a vacuum of 1×10^{-8} Torr.

XPS spectra were recorded at the takeoff angle of 90° in the ordinary measurement and at takeoff angles of 90°, 60°, 40°, 30°, and 20° in the angle-resolved measurement. The takeoff angle here is the angle of observation of photoelectrons relative to the sample surface. All XPS spectra were collected and stored with 1.0-eV steps using a Kratos Model DS-300 data system based on a PDP11/03 computer from Digital Equipment Corp. Sputtering was done by using an ion beam with a 500 nA/cm^2 density and a 1-keV energy at 2×10^{-4} Torr of Ar pressure in the preparation chamber of the ES-200.

Models of Sputtering Process for Monte Carlo Simulation

The simulation is executed on a cyclic polymer chain containing 2500 monomeric units, which is safely considered to be large enough for statistical calculation. It is assumed that only fluorine atoms are sputtered away, whereas all carbon atoms are left intact because of the great difference in their sputtering rates. Another model based on simultaneous elimination of both fluorine and carbon with different rates is also tried but showed little difference from the simpler one. Sputtering of hydrogen atoms in the PVDF system is also neglected since hydrogen cannot be detected in XPS measurement and its elimination brings about very little chemical shift on a carbon atom.[24]

Ar ion sputtering is simulated with the two models shown in Figure 1. In model A, elimination of only a single fluorine atom by one encounter with an activated particle is assumed; that is, any fluorine atom in a polymer chain is independently sputtered away in complete randomness. On the other hand, in model B, it is assumed that both single and double fluorine atom elimination concurrently occur, where the second process happens in a probability of r%. The double elimination here means that two fluorine atoms bonding to a carbon atom are broken off

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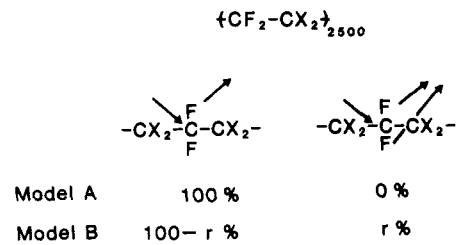

Figure 1. Models of sputtering processes of polymer chains for Monte Carlo simulation, where X represents a fluorine atom in PTFE and a hydrogen atom in PVDF, respectively.

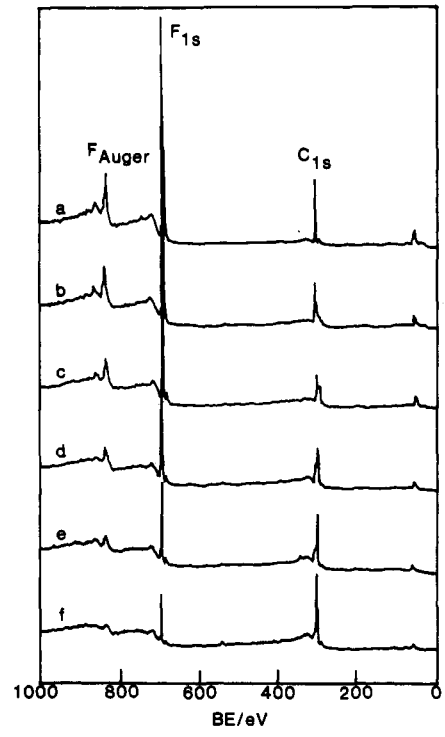

Figure 2. XPS wide-scan spectra of PTFE sputtered by Ar ions. Sputtering times are (a) 0, (b) 10, (c) 30, (d) 60, (e) 120, and (f) 300 s.

together from a polymer chain by one encounter with a single activated particle. An activated particle can be an Ar ion itself, an electron, or another ion generated in the sputtering process.

Actual calculation of the Monte Carlo simulation is carried out by using the two models explained above with the following procedure. A segment of the polymer is picked up by a random integer of uniform distribution over the range from 1 to 2500. The integer is generated with a random number function and it corresponds to one encounter by an activated particle. In model A, one fluorine atom leaves from the segment. In model B, two fluorine atoms leave with probability of r%, and one fluorine atom elimination takes place with probability of $100 - r$%. A series of calculations is repeated until the atomic ratio F/C reaches the value that corresponds to the one determined by the XPS experiment.

C1s chemical shift values of all possible chemical structures after partial and complete removal of fluorine atoms from a polymer chain in both simulation models are shown in Table I. These chemical shift values are estimated on the basis of experimental data of a fluorine polymer series[18] taking the diad effect of the fluorine atom into account. We determined the distribution of residual structures from those chemical shifts at each stage of the simulated sputtering process.

Table I
C1s Chemical Shifts of All Possible Chemical Structures of Sputtered PTFE and PVDF[a]

chemical structure	ΔE, eV	chemical structure	ΔE, eV
C–C*–C	0.00	CF–C*F–CF_2	3.95
C–C*–CF	0.35	CF_2–C*F–CF_2	4.30
C–C*–CF_2, CF–C*–CF	0.70	C–C*F_2–C	5.80
		C–C*F_2–CF	6.15
CF–C*–CF_2	1.05	C–C*F_2–CF_2, CF–C*F_2–CF	6.50
CF_2–C*–CF_2	1.40	CF–C*F_2–CF_2	6.85
C–C*F–C	2.90	CF_2–C*F_2–CF_2	7.20
C–C*F–CF	3.25		
C–C*F–CF_2, CF–C*F–CF	3.60		

[a] Hydrogen atoms in PVDF are neglected because of their very small effect on C1s chemical shift.

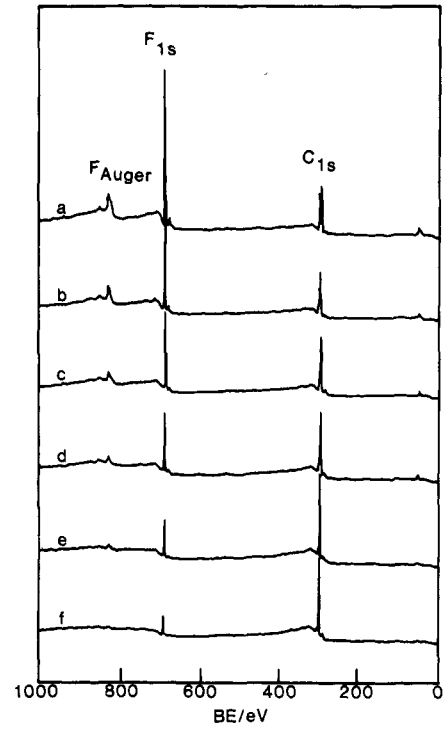

Figure 3. XPS wide-scan spectra of PVDF sputtered by Ar ions. Sputtering times are (a) 0, (b) 2, (c) 5, (d) 10, (e) 20, and (f) 30 s.

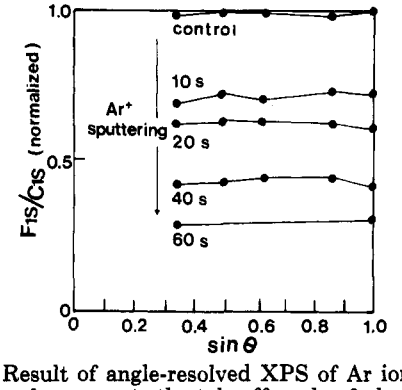

Figure 4. Result of angle-resolved XPS of Ar ion sputtered PTFE, where θ represents the takeoff angle of photoelectrons. F1s/C1s(normalized) in the vertical axis means a peak area ratio of F1s to C1s normalized by that of the control sample before Ar ion sputtering.

Results and Discussion

Surface Composition of Sputtered Polymers. The variation of the XPS wide-scan spectra of PTFE and PVDF by sputtering is shown in Figures 2 and 3. The

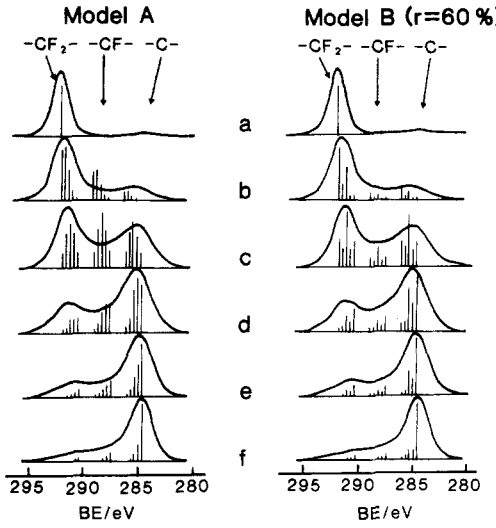

Figure 5. Observed (solid line) and simulated (bar graph) XPS C1s spectra of PTFE after Ar ion sputtering. Sputtering times, fractions of sputtered fluorine, and atomic ratios (F/C) are (a) 0 s, 0%, and 2.00, (b) 10 s, 25%, and 1.50, (c) 30 s, 50%, and 1.00, (d) 60 s, 70%, and 0.60, (e) 120 s, 80%, and 0.40, and (f) 300 s, 90%, and 0.20.

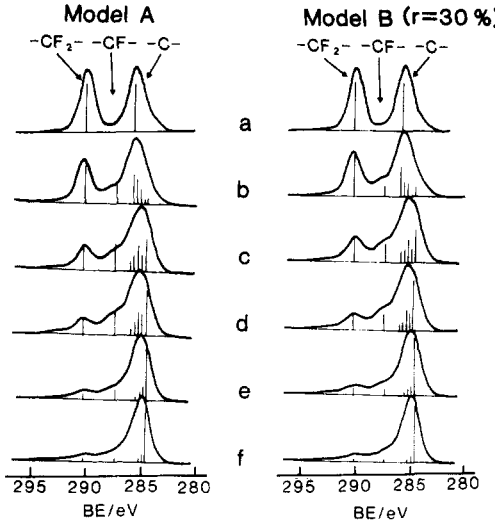

Figure 6. Observed (solid line) and simulated (bar graph) XPS C1s spectra of PVDF after Ar ion sputtering. Sputtering times, fractions of sputtered fluorine, and atomic ratios (F/C) are (a) 0 s, 0%, and 1.00, (b) 2 s, 22%, and 0.78, (c) 5 s, 50%, and 0.50, (d) 10 s, 63%, and 0.37, (e) 20 s, 82%, and 0.18, and (f) 30 s, 90%, and 0.10.

rapid decrease of fluorine peaks in both spectra indicates that fluorine atoms are preferentially sputtered away from polymer chains, leaving carbon atoms behind in both polymer systems.

The result of the angle-resolved XPS measurement of sputtered PTFE is indicated in Figure 4. The photoelectron mean free path is estimated to be a few score angstroms in an XPS measurement of polymer materials.[25] The sampling depth on the surface is proportional to sin θ, where θ is the takeoff angle of photoelectrons.[26] The chemical composition represented by F1s/C1s is independent of sin θ at any sputtering stage. The result suggests that the damaged layer of the bombarded PTFE has a homogeneous composition within the sampling depth of XPS. This ensures that XPS is seeding a homogeneous layer produced by Ar ion sputtering.

The C1s spectra of sputtered PTFE and PVDF are shown by solid lines in Figures 5 and 6. Surfaces of both polymers show broad C1s spectra because of many overlapping peaks of different chemical shifts which depend on the number of fluorine atoms bonding to the carbon atom. The shift of C1s by elimination of fluorine atoms is significant because of the large electronegativity of fluorine. A major component of the C1s spectra comes from the $-CF_2-$ species in earlier stages of the sputtering process of PTFE, while in later stages it comes from the –C– species after removal of all fluorine atoms. The $-CF_2-$ species also gradually decrease in sputtering of PVDF. These C1s spectra are expected to provide information about the mechanism of sputtering of fluorine atoms from the polymer chains.

Monte Carlo Simulation. The simulated and observed C1s spectra of sputtered PTFE are compared in Figure 5. Bar graphs and solid lines show simulated and observed C1s spectra, respectively. The simulated spectra by model A are in good agreement with the observed spectra after more than 80% of the fluorine is sputtered away, but they are in poor agreement for the earlier stages before 50% of the fluorine leaves, especially in the chemical shift region of the –CF– group. In order to improve the fitting, model B with the double elimination of fluorine is added stepwise with increasing probability, r, in 10% intervals from 10% to 100%. Model B with an r value of 60% presents the best fitting for every stage. This simulation reveals that broadening of C1s spectra in the earlier stages of sputtering is due to generation of various kinds of chemical species, and renarrowing in the later stages is due to a decrease in the variety of species.

The result of a similar procedure on PVDF is indicated in Figure 6. The C1s spectra simulated by model A are in better agreement with the observed spectra for all stages than they are with PTFE. Model B with an r value of 30% best explains the observed C1s spectra of sputtered PVDF. The presence of a methylene group in the vicinity seems to work in favor of single elimination of fluorine. The electron-donating effect of a methylene group possibly stabilizes the –CF– species produced in single elimination of a fluorine atom.

The residual chemical structure left behind in polymer chains after elimination of fluorine atoms by sputtering may have unsaturated bonds, cross-links, and also radicals and ions that are composed of carbon atoms. Evidence for the existence of such chemical species is gathered from the following observations. Surface oxygen concentration of PTFE bombarded by Ar ions for 300 s and then exposed to air for a day is found to be 0.11 in O1s/C1s parameter, probably because of radical or ion quenching by oxygen and water in air. In the C1s spectrum of PTFE sputtered for 300 s, a tailing component is observed in the higher binding energy region between 290 and 295 eV. It can be assigned as a π–π^* shake-up satellite from the linear and cyclic unsaturated systems.[27]

Conclusions

XPS is found to be useful for examining the residual composition of ion-sputtered surfaces of polymers. Sputtered PTFE has a damaged layer with a homogeneous composition within the sampling depth of XPS. Monte Carlo simulation has proved to be helpful in understanding the sputtering process of polymer materials. Observed XPS spectra are well explained by random elimination of fluorine atoms from polymer chains of PTFE and PVDF, and even better fitting is achieved by assuming a double fluorine atom elimination mechanism.

Acknowledgment. This study was performed through Special Coordination Funds for Promoting Science and

Technology of the Science and Technology Agency of the Japanese Government.

Registry No. PTFE, 9002-84-0; PVDF, 24937-79-9.

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Time-of-Flight Secondary Ion Mass Spectrometry of Polymers in the Mass Range 500–10 000

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ABSTRACT: Secondary ion mass spectra of a poly(dimethylsiloxane), a polyurethane, and polystyrenes are presented. The spectra were obtained by a time-of-flight secondary ion mass spectrometer equipped with a mass-selected primary ion source, an angle- and time-focusing time-of-flight analyzer, and a single-ion-counting detector. Fragmentation in the low-mass range ($m/z \leq 500$) provided structural information about the repeat unit. Ag^+ and Na^+ cationization of polymer fragments and intact polymer molecules containing large numbers of repeat units in the high-mass range (m/z 500–10 000) allowed identification of the polymers studied. Fragmentation patterns were unique for polymers having different repeat units but of equal mass; distinguishing between such polymers was possible. Oligomer distributions for polystyrene standards obtained from the mass spectrum compared well with distributions determined by other techniques (e.g., gel permeation chromatography).

Introduction

Polymers typically exhibit low volatility and, therefore, pose serious problems for ion formation in mass spectrometry (MS). To date, volatilization methods coupled to MS for characterization of polymers primarily involved pyrolysis (PY-MS). Pyrolysis degrades polymers such that characteristic fragment ions can be used for polymer identification.[1] PY-MS has been used to characterize polymers, polymer blends, and additives;[2] when PY-MS was coupled to gas chromatography, the composition[3] and head-to-head or head-to-tail additions[4,5] for styrene/methacrylate copolymers could be determined. Copolymers have been differentiated from homopolymer mixtures with PY-MS by detection of dimer and trimer fragments.[6] Polyurethanes have been studied by PY-MS; some information about the nature of polyols and isocyanates could be deduced.[7]

A major concern in the PY-MS experiment is reproducibility because decomposition processes are time and temperature dependent. If the pyrolysis temperature is too low, incomplete decomposition occurs. Secondary reactions during pyrolysis are also troublesome because they alter the primary fragments and complicate interpretation of the mass spectrum. If the pyrolysis temperature is too high, noncharacteristic low m/z fragments dominate the mass spectrum. Even at the optimum temperature, the highly energetic pyrolytic processes produce low m/z fragments. These fragments are usually common to a class of polymers, and therefore identification of polymers with similar repeat units often becomes difficult.

The invention of softer volatilization and ionization sources, combined with instrumental advances, has expanded MS to a higher mass range so that sequences of repeat units and oligomer distributions can be observed.[9,10] Field desorption mass spectrometry (FDMS) has been applied extensively to the analysis of polymers.[8,9] Quasi-molecular ions from FDMS exhibit high intensity compared to that of low m/z fragments; FDMS can be used for the determination of oligomer distributions. Accurate molecular weight averages of low molecular weight poly-

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