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# Quantitative Chemical Derivatization Technique in Time-of-Flight Secondary Ion Mass Spectrometry for Surface Amine Groups on Plasma-Polymerized Ethylenediamine Film

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A chemical derivatization technique in time-of-flight secondary ion mass spectrometry (TOF-SIMS) has been developed to quantify the surface density of amine groups of plasma-polymerized ethylenediamine thin film deposited on a glass surface by inductively coupled plasma chemical vapor deposition. Chemical tags of 4-nitrobenzaldehyde or pentafluorobenzaldehyde were hybridized with the surface amine groups and were detected in TOF-SIMS spectra as characteristic molecular secondary ions. The surface amine density was controlled in a reproducible manner as a function of deposition plasma power and was also quantified using UV–visible spectroscopy. A good linear correlation was observed between the results of TOF-SIMS and UV–visible measurements as a function of plasma power. This shows that the chemical derivatization technique in TOF-SIMS analysis would be useful in quantifying the surface density of specific functional groups that exist on the organic surface.

Controlling the surface density and selectivity of specific functional groups that exist on the surface is crucial in biomaterial applications, since functional groups control the immobilization of proteins or cells.<sup>1</sup> A chemical derivatization technique in X-ray photoelectron spectroscopy (XPS), called “derivatization XPS”, has been shown to be a very useful method of identifying and quantifying a specific surface-bound functional group from a complicated multifunctionalized polymer surface.<sup>2–9</sup> Compared to

derivatization XPS, there are few systematic quantification studies of static secondary ion mass spectrometry (SIMS) applications using chemical tagging molecules.<sup>10</sup>

Due to high molecular specificity and surface sensitivity, static SIMS has been used to characterize numerous types of organic/bio surfaces, such as self-assembled monolayers (SAMs),<sup>11</sup> Langmuir–Blodgett (LB) overlayers,<sup>12</sup> conventional polymers<sup>10,13–19</sup> and its modified surfaces,<sup>4,20,21</sup> plasma-deposited films (PDFs),<sup>5–7,22–25</sup> adsorbed proteins,<sup>26–28</sup> and cells.<sup>29–31</sup> In particular, surface char-

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acterization of polymers, including PDFs, has been studied using static SIMS,<sup>4–7,10,13–25</sup> which has improved drastically in terms of signal sensitivity, mass resolution, and range. However, the static SIMS technique has played only an ancillary role in the quantification analysis of specific surface chemical compositions or in the analysis of functional groups using X-ray photoelectron spectroscopy.<sup>4,6,10,19</sup> This is mainly due to the complex matrix effect and low molecular secondary ion efficiency from organic/bio materials.<sup>32</sup> Despite these shortcomings, several quantification studies of polymers using static SIMS have been reported in conjunction with XPS,<sup>5,7,10,20,33,34</sup> spectrochemical titration,<sup>18</sup> bulk concentration,<sup>35–44</sup> and optical waveguide lightmode spectroscopy.<sup>45</sup>

Plasma-deposited organic thin films are pinhole-free, mechanically and chemically stable, and strongly adhere to glass slides due to their highly cross-linked network structures.<sup>46–49</sup> In addition, in PDFs, the thickness and functional group density, as well as the uniformity, can be highly controlled during deposition, all within relatively short periods of time, to produce a high-quality amine-functionalized glass surface for the immobilization of proteins.<sup>50</sup>

For the present work, we used a chemical derivatization technique in time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis to quantify the surface density of amine groups that existed on plasma-polymerized ethylenediamine (PPEDA) film. As a chemical tag, 4-nitrobenzaldehyde (4-NBA) or pentafluorobenzaldehyde (PFBA) was used to hybridize with the surface amine group. The surface amine density was systematically changed as a function of plasma power and independently determined by UV–visible absorption spectroscopy. The results of TOF-SIMS and UV–visible measurements were compared and correlated to obtain a correlation curve for quantification analysis.

## EXPERIMENTAL SECTION

Details of PPEDA films deposited on glass slides are reported elsewhere.<sup>50</sup> The following is a brief description. PPEDA film was

deposited at the substrate at room temperature with a deposition pressure of 30 mTorr, deposition time of 2 min, and an Ar flow rate of 30 sccm. Ethylenediamine was used as the monomer and was put in a stainless steel bubbler, which was heated to 50 °C for vaporization. Two plasmas were used to produce a high-quality amine surface. The inductively coupled plasma (ICP) power varied from 3 to 70 W and was generated around the shower ring by a circular coil, which was connected to a 13.56-MHz radio frequency (RF) generator through a matching box. The 3 W of fixed substrate bias (SB) was generated from another RF generator and was put into a substrate holder for plasma around the glass slide. The wall of the deposition chamber was grounded, and the base pressure of the deposition chamber was  $<10^{-6}$  Torr when pumped with a turbo molecular pump.

To determine the surface amine density of the PPEDA film, UV–visible absorption spectrometry was used, with minor changes, as discussed in Park et al.<sup>51</sup> In a nitrogen atmosphere, a PPEDA-coated slide glass ( $1.5 \times 2.5 \text{ cm}^2$ ) was allowed to react with excess 4-nitrobenzaldehyde (10 mg) anhydrous ethanol solution (25 mL) overnight at 50 °C. After the Schiff base reaction, the substrate was thoroughly washed and sonicated with absolute ethanol, methylene chloride, acetone, and hexane for 3 min each sequentially and dried in a vacuum. The same procedures were applied to the hybridization reaction with pentafluorobenzaldehyde (1 mg). At this stage, the chemically tagged substrate was submitted for TOF-SIMS analysis before hydrolysis. For hydrolysis, the imine-formed substrate was immersed in 1 mL volume of water overnight at 50 °C. The aqueous solution of hydrolyzed 4-NBA ( $\epsilon_{\text{max}} = 1.45 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ) was measured with a HP 8453 UV–visible spectrophotometer (Hewlett-Packard). All spectra were recorded after baseline correction and converted to surface amine density in accordance with Beer's law.

TOF-SIMS measurements were obtained with a TOF-SIMS V instrument (ION-TOF GmbH, Germany) using 25-keV Au<sup>+</sup> primary ions (average current 0.8 pA, pulse width 16.8 ns, repetition rate 5 kHz) at high-current bunched mode. The analysis area of  $100 \times 100 \mu\text{m}^2$  was randomly rastered by primary ions and was charge-compensated by low-energy electron flooding. The primary ion dose was kept below  $10^{12}$  ions/cm<sup>2</sup> to ensure static SIMS condition. Mass resolution was usually higher than 5000 at positive and negative modes. The mass calibration of positive and negative ion spectra was internally performed by using H<sup>+</sup>, H<sub>2</sub><sup>+</sup>, CH<sub>3</sub><sup>+</sup>, C<sub>2</sub>H<sub>3</sub><sup>+</sup>, and C<sub>3</sub>H<sub>4</sub><sup>+</sup> peaks and H<sup>−</sup>, C<sup>−</sup>, CH<sup>−</sup>, C<sub>2</sub><sup>−</sup>, and C<sub>2</sub>H<sup>−</sup> peaks, respectively.

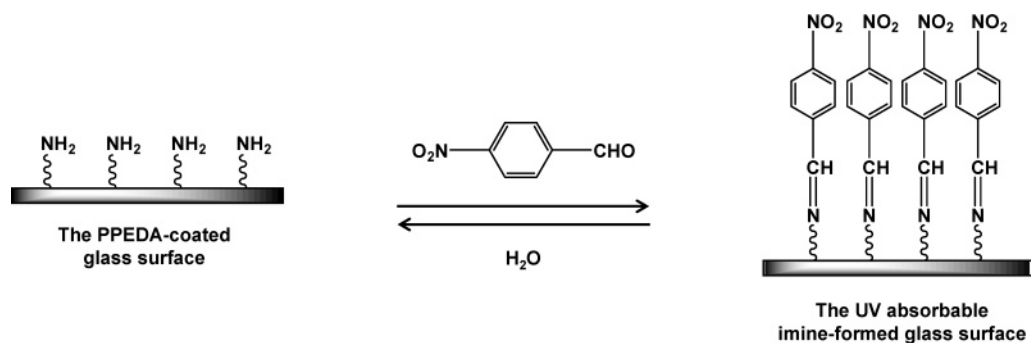
## RESULTS AND DISCUSSION

**UV–Visible Absorption Spectrometric Study.** To study the usefulness of chemical derivatization in TOF-SIMS applications, it is necessary to first determine the surface density of the amine groups on PPEDA thin film. Park et al.<sup>51</sup> used a UV–visible spectroscopic method to successfully measure the surface density of the amine groups that lie on aminosilylated thin layers by converting the nonabsorbing amine group into a UV–visible detectable nitrobenzyl substituted imine. Basically, a large excess of 4-NBA is allowed to react with an amine group to form an imine (Scheme 1), which is hydrolyzed in a known volume of water to

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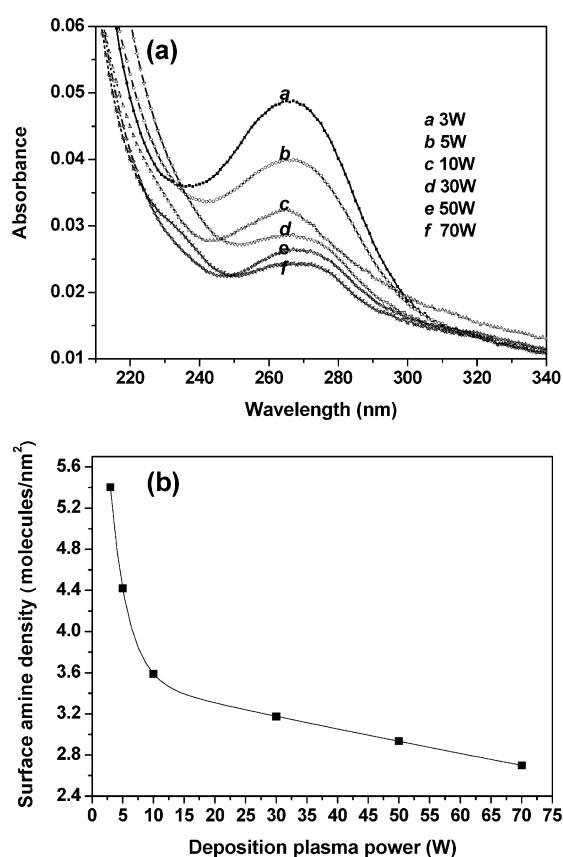
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## Scheme 1



reproduce 4-NBA. The absorbance of the reproduced 4-NBA molecules is subsequently measured to calculate the surface density of the reactive amine groups on the known surface area of the substrates.

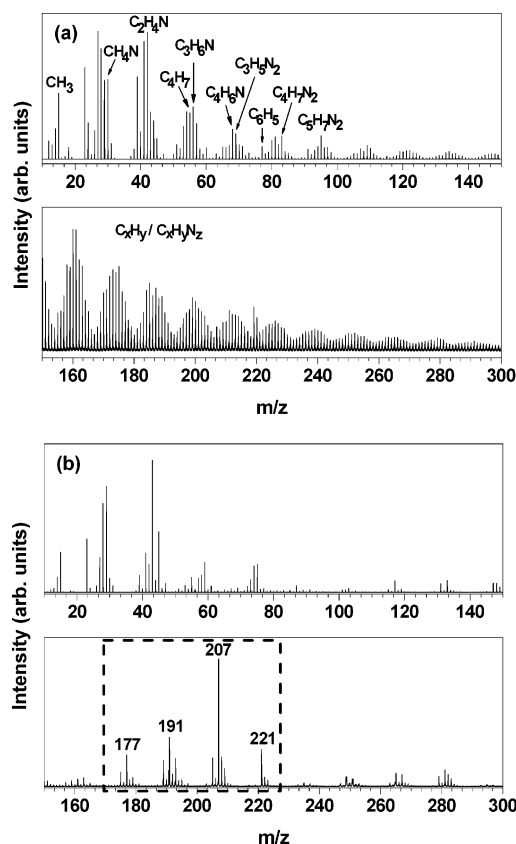
We applied Park's UV-visible spectrometric method to analyze our PPEDA-coated surfaces, which were made in six different ICP powers, namely, 3, 5, 10, 30, 50, and 70 W. The absorbance of 4-NBA molecules reproduced from PPEDA surface appeared at  $\sim 267$  nm and decreased as the plasma power for PPEDA coating increased from 3 to 70 W, as shown in Figure 1a. With a known surface area and volume of water, the absorbance data can be converted to surface amine density by using Beer's law. Figure 1b shows the calculated surface densities of the reactive amine groups as a function of plasma power, changing from 5.4 amine groups/ $\text{nm}^2$  at 3 W to 2.7 amine groups/ $\text{nm}^2$  at 70 W. The surface

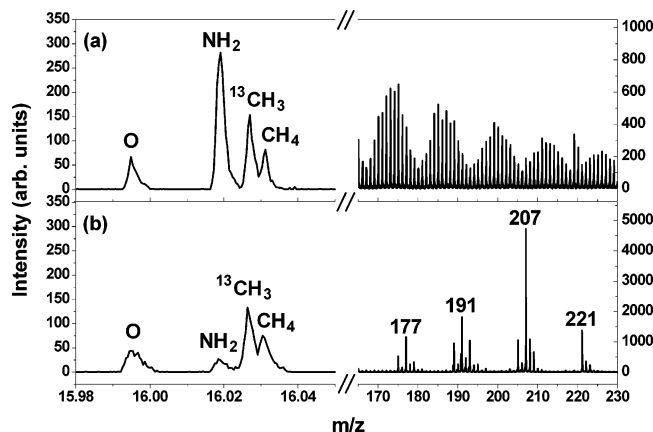


**Figure 1.** (a) Absorbance and (b) surface amine densities of PPEDA thin films as a function of deposition plasma power: 3 (a), 5 (b), 10 (c), 30 (d), 50 (e), and 70 W (f).

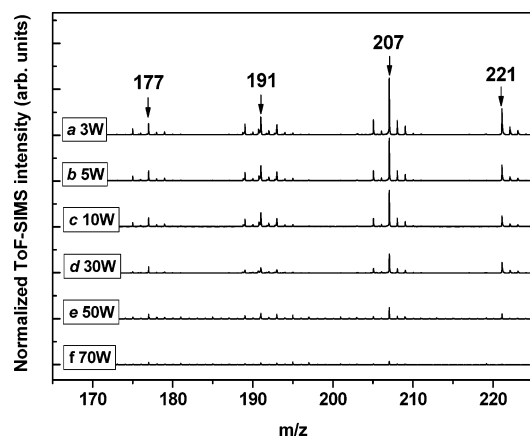
densities of reactive amine groups were used as reference numbers to make a correlation with the TOF-SIMS measurements.

**Chemical Derivatization Technique in TOF-SIMS Study.** Six different PPEDA-coated thin films were allowed to react with 4-NBA or PFBA and were measured in detail using TOF-SIMS. The full spectra of PPEDA films obtained before and after the chemical tagging reaction with 4-NBA are shown in Figure 2a and b, respectively. As a typical case, we have included the full spectrum only for the positive ion spectra of PPEDA made at 10-W plasma power. As expected, there are many peaks related to the aliphatic hydrocarbon ( $\text{C}_x\text{H}_y^+$ ) and the aliphatic hydrocarbon containing nitrogen ( $\text{C}_x\text{H}_y\text{N}_z^+$ ) in TOF-SIMS spectrum of the PPEDA film (Figure 2a).<sup>15</sup> Interestingly, after a chemical tagging reaction with 4-NBA, several new peaks appear in the mass range from  $m/z$  170 to 230, which is indicated by a dashed box in Figure 2b.





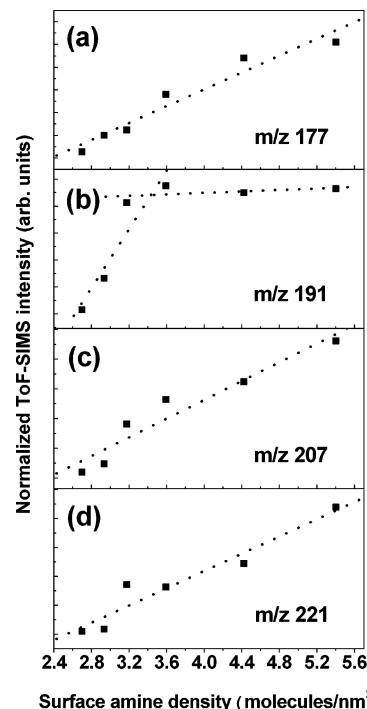
**Figure 3.** Expanded spectra of Figure 2 at  $m/z \sim 16$  and from  $m/z$  170 to 230 (a) before and (b) after chemical tagging with 4-NBA.



**Figure 4.** Normalized positive TOF-SIMS spectra of PPEDA films after chemical tagging with 4-NBA as a function of deposition plasma power: 3 (a), 5 (b), 10 (c), 30 (d), 50 (e), and 70 W (f).

To compare two TOF-SIMS spectra in detail, two interesting regions of the full spectra in Figure 2 are shown in Figure 3. They clearly show that the intensity of the amine functional group,  $-\text{NH}_2$ , is drastically reduced after the chemical derivatization. In addition, new ions are clearly observed at  $m/z$  177, 191, 207, and 221. The intensities of these new ions decreased when the plasma power for making PPEDA film increased as shown in Figure 4. According to the UV-visible absorption spectrometric study, the surface density of amine groups on PPEDA film also decreased as plasma power increased (Figure 1). Similar behavior in UV-visible and TOF-SIMS studies indicates that new ions originate from the chemical tag molecules, 4-NBA. Thus, this suggests that there is a direct correlation between each amine group and the chemical tag molecule, 4-NBA. In other words, the more reactive amine groups on the surface, the more chemical tagging 4-NBA molecules hybridized with amine functional groups on the surface.

Assuming that the amine group on the PPEDA surface is successfully hybridized with the aldehyde group of 4-NBA to make an imine covalent bond formation, we tentatively assigned the major new ions to  $\text{C}_9\text{H}_9\text{N}_2\text{O}_2^+$  (exact  $m/z$  177.066, observed  $m/z$  176.980),  $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_2^+$  (exact  $m/z$  191.082, observed  $m/z$  190.996),  $\text{C}_9\text{H}_{11}\text{N}_4\text{O}_2^+$  (exact  $m/z$  207.088, observed  $m/z$  207.036), and  $\text{C}_{10}\text{H}_{13}\text{N}_4\text{O}_2^+$  (exact  $m/z$  221.104, observed  $m/z$  221.109). The ripped-off mechanism of the tag molecule during ion bombardment may be explained by the high-energy events that are followed by collision cascades.<sup>52</sup>



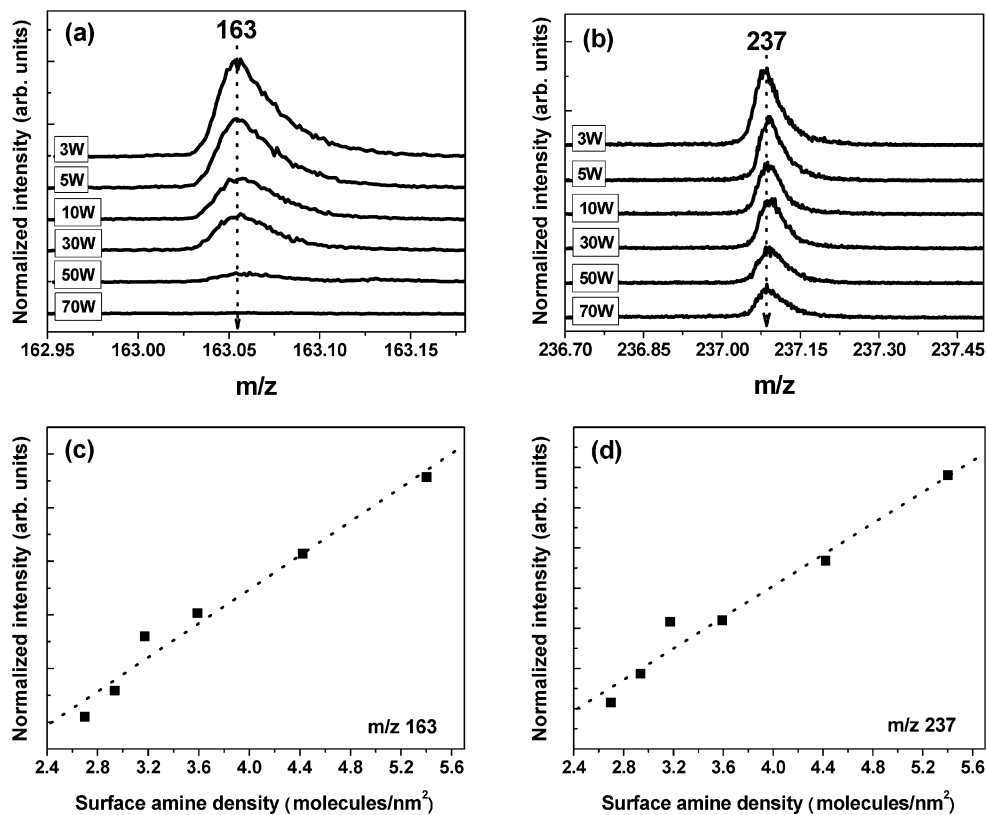
**Figure 5.** Correlation between normalized intensities of (a)  $m/z$  177, (b)  $m/z$  191, (c)  $m/z$  207, and (d)  $m/z$  221 and the surface amine densities determined by the UV-visible method.

**Comparison between UV-Visible and TOF-SIMS Measurements.** For quantitative analysis, the normalized intensities of four new positive ions are correlated with the surface densities of amine groups determined by UV-visible study. These are shown in Figure 5. The silicon peak was used as a reference peak for normalization. The signals of secondary ions observed at  $m/z$  177, 207, and 221, except  $m/z$  191, have a good linear correlation ( $R^2 = 0.94$ ,  $0.92$ , and  $0.93$  for  $m/z$  177, 207, and 221, respectively) with the surface amine densities, despite the possibility that the desorption mechanism could be changed due to molecule-molecule interactions as the coverage of amine groups increases. The good linear correlation may be related to the insignificant change in the surface configuration of the tag molecules as a function of amine density, since the tag molecules would be in a standing-up geometry on the surface after the imine double bond formation. The reason for poor linear correlation observed for  $m/z$  191 in Figure 5b is not clear at this point. The different secondary ion formation mechanism of  $m/z$  191 from those of  $m/z$  177, 207, and 221 may produce a different correlation between TOF-SIMS intensities and surface amine densities.

For the negative mode in TOF-SIMS measurements, two new ions gave a good linear correlation curve. One was observed at  $m/z$  163 after a chemical tagging reaction with 4-NBA, and the other was observed at  $m/z$  237 after a chemical tagging reaction with PFBA. Figure 6a and b shows the normalized peaks of  $m/z$  163 and 237 secondary ions as a function of plasma power, respectively. The corresponding correlation curves are shown in Figure 6c for  $m/z$  163 and d for  $m/z$  237. These also show a good linear correlation ( $R^2 = 0.97$  for both secondary ions). New ions of  $m/z$  163 and 237 were tentatively assigned to  $\text{C}_8\text{H}_7\text{N}_2\text{O}_2^-$  (exact

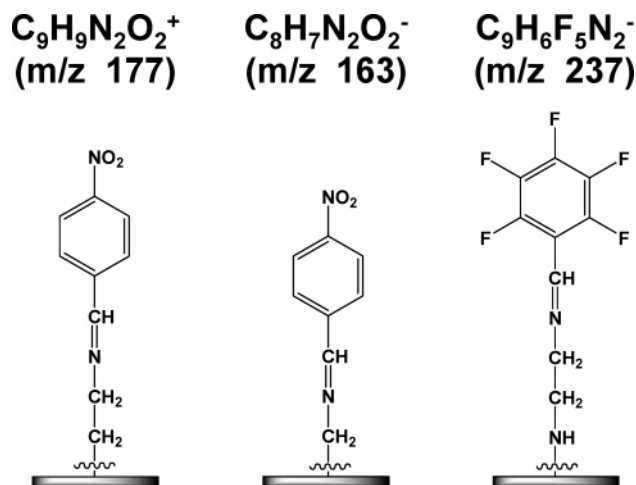
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**Figure 6.** Normalized negative TOF-SIMS spectra of (a)  $m/z$  163 from PPEDA film after reaction with 4-NBA and (b)  $m/z$  237 from PPEDA film after reaction with PFBA. Corresponding correlation curves are shown in (c)  $m/z$  163 and (d)  $m/z$  237.

## Scheme 2



$m/z$  163.051, observed  $m/z$  163.052) and  $\text{C}_9\text{H}_6\text{F}_5\text{N}_2^-$  (exact  $m/z$  237.045, observed  $m/z$  237.086), respectively. Although it is difficult to know the exact chemical structures of the surface layer and its secondary ions without ab initio theoretical calculations, our tentative guesses of the chemical structures of the surface layer for  $\text{C}_9\text{H}_9\text{N}_2\text{O}_2^+$ ,  $\text{C}_8\text{H}_7\text{N}_2\text{O}_2^-$ , and  $\text{C}_9\text{H}_6\text{F}_5\text{N}_2^-$  are shown in Scheme 2.

A good correlation between surface amine densities and secondary ion intensities of the chemical tag molecules indicates that it is feasible to do quantitative analysis of surface amine density using chemical derivatization in TOF-SIMS application. Of course, due to the different normalization, substrate, and matrix effects, etc., the details of a correlation curve will vary according

to the type of sample surface, such as the self-assembled monolayer on a gold surface. However, the general idea of using a chemical derivatization technique in TOF-SIMS studies would still be useful for a quantitative analysis of the surface density of any types of functional groups that exist on general samples, as has already been shown in many XPS studies on the usefulness of chemical derivatization technique.<sup>2–10</sup>

## CONCLUSION

We have shown that the chemical derivatization technique in TOF-SIMS studies is a useful way of quantifying the surface density of amine groups on PPEDA films. The surface density of amine groups on plasma-polymerized ethylenediamine thin film was varied as a function of deposition plasma power and quantitatively and independently determined by UV–visible absorption spectrometry. These densities were compared to results of TOF-SIMS measurements using the chemical derivatization technique. We found good linear correlations between the surface densities of the amine groups and the normalized intensities of each new secondary ion. Tentative chemical formulas and structures of new ions are suggested.

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