

Research Article

Infrared Absorption Spectroscopic Study on Reaction between Self-Assembled Monolayers and Atmospheric-Pressure Plasma

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Received 31 October 2014; Revised 25 December 2014; Accepted 8 January 2015

Academic Editor: Renata Diniz

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Plasma is becoming increasingly adopted in bioapplications such as plasma medicine and agriculture. This study investigates the interaction between plasma and molecules in living tissues, focusing on plasma-protein interactions. To this end, the reaction of air-pressure air plasma with NH_2 -terminated self-assembled monolayer is investigated by infrared spectroscopy in multiple internal reflection geometry. The atmospheric-pressure plasma decomposed the NH_2 components, the characteristic units of proteins. The decomposition is attributed to water clusters generated in the plasma, indicating that protein decomposition by plasma requires humid air.

1. Introduction

Plasma technology has been adopted in Si-based semiconductor technologies [1–5]. Plasma processing is controlled at the nanoscale in semiconductor device development and is now being applied to new fields [6–9]. Among the promising plasma applications proposed is plasma bioapplication such as plasma medicine [10–14] and plasma agriculture [15, 16]. To realize these applications, atmospheric-pressure plasma has been developed [14, 17–19]. In addition, we must optimize the plasma effects on organic systems such as human and animal bodies, plants, and seeds. There are numerous cell types containing various proteins, carbohydrates, and adipose molecules. Although plasma bioapplications have been extensively investigated [10–16], the plasma effect is optimized by multiple repeat experiments, the so-called “trial-and-error” approach. However, this approach is unsuitable for various biomaterials, because each approach requires a protracted timeframe. Furthermore, trial-and-error approach has failed to clarify the detailed reaction mechanisms of plasma with biomolecules. Understanding these mechanisms will certainly enhance the benefit of plasma bioapplications because a comprehensive understanding will lead to comprehensive methodologies. The major

impediment is the difficulty in treating biomolecules because of their great variety, complicated structures, and high molecular weights.

On the other hand, significant information can be gleaned by constructing biomolecule models. Biomolecules with small molecular weights are preferable [20], but it is difficult to analyze their reactions to plasma, because their molecules still have complicated structures with various function groups such as N–H, C–H, and C=O bonds. As test molecules for evaluating how plasma reacts with biological tissues, we focus on self-assembled monolayers (SAMs) [21–24], assemblages of monomers deposited on substrate. There are numerous SAMs, each with definitive chemical states and structures and terminated with specific functional group. Furthermore, adipose tissue, proteins, carbohydrates, and other organic molecules contain $-\text{CH}_2-$ chains and $-\text{C}-\text{C}-$ bonds, whereas proteins are characterized by the amino ($\text{O}=\text{C}-\text{N}-\text{H}$, $-\text{R}$, (R: alkyl)) and amine (N–H) groups. We focus on the amine group (N–H) because of its simple structure. We consider that reactions between plasma and carbohydrate or adipose molecules could be understood by reacting plasma with SAMs that are composed of $-\text{CH}_2-$ bonds; similarly, we can understand plasma-protein reactions by reacting plasma with amino-terminated SAMs. Therefore, SAMs present as

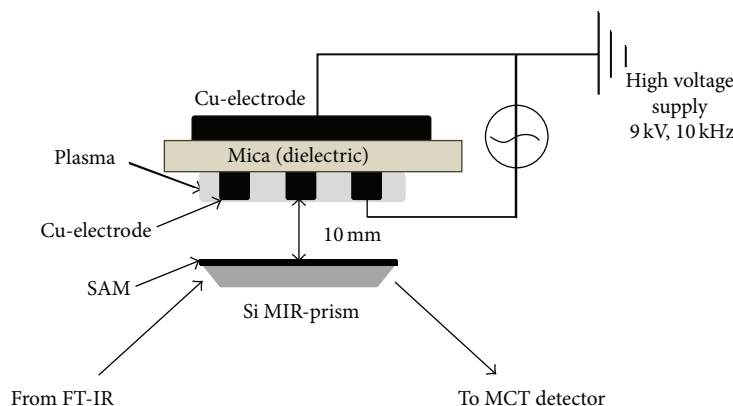


FIGURE 1: Experimental setup.

an ideal tool for research into plasma bioapplications. However, despite elaborate reports of how SAMs interact with plasma generated under low pressure [25–27], the reactions of these mechanisms remain unclear. In particular, unclear are the reactions of NH_2 -terminated SAM with air plasma at atmospheric pressures. Atmospheric plasma is commonly adopted in bioapplications or plasma medical applications, because living cells naturally exist in atmospheric rather than vacuum conditions. There are not so many papers about interaction between atmospheric-pressure plasma and SAM, although there are elaborate papers about low-pressure plasma treatment on SAMs [28, 29].

In this study, we modeled proteins and fats/carbohydrates by NH_2 -terminated SAM and CH_3 -terminated SAM, respectively. Appropriate monomers can form SAMs on a Si surface by siloxane (Si–O) bonds [21]. This advantage is particularly beneficial for us, because we have developed “infrared absorption spectroscopy in multiple internal reflection geometry” (MIR-IRAS) using MIR prism made from a Si wafer [30–34]. The study investigates the reaction of atmospheric-air plasma with the abovementioned SAM using MIR-IRAS. This technique is suitable to investigate reactions between plasma and SAMs deposited on Si-wafer-based MIR prisms because IR does not interfere with plasma and is too weak to alter the chemical states of SAM.

2. Experiments

The MIR-IRAS was monitored by a Fourier-transform IR (FTIR) spectrometer (JASCO FT-6100) and a mercury-cadmium-telluride detector. The MIR prisms were made from n-type p-doped double-sided polished Si(100) wafers with an approximate resistivity of $10 \Omega\text{-cm}$. The prism dimensions were $10 \text{ mm} \times 40 \text{ mm} \times 0.5 \text{ mm}$, with 45° bevels on each short edge. Each Si prism was cleaned by conventional RCA cleaning, and its surface was covered with chemical oxides produced in a boiled $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ solution. The chemical oxide-covered surface provided the reference spectrum for the IRAS spectrum acquisition. Once the reference data were acquired, the MIR prism surface was recleaned in boiled $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ and

deposited with two types of SAM. The first was CH_3 -terminated SAM, obtained by dropping a solution of 2.5 mM octadecyltrichlorosilane (OTS: $\text{Cl}_3\text{SiC}_{17}\text{H}_{34}\text{CH}_3$, Tokyo Chemical Industry, Tokyo, Japan) in toluene onto the prism surface at RT, followed by sequential rinsing with toluene. Hereafter, this SAM is referred to as OTS-SAM. The second was NH_2 -terminated SAM, which was obtained in four steps. First, the MIR prism was immersed in 47 mM 3-(2-aminoethylamino)-propyldimethoxymethylsilane ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_2\text{CH}_3$, Tokyo Chemical Industry, Tokyo, Japan) dissolved in pure water (this step was performed at RT). Second, the sample was dried by annealing at 150°C for 1 h in air. Third, the sample was rinsed with water to remove residual molecules. Fourth, the sample was dried again by annealing for 1 h in air at 150°C .

Atmospheric-pressure air plasma source was generated by barrier discharge. For this purpose, a Cu plate and a W-shaped Cu wire were affixed to opposite sides of a mica sheet measuring $10 \text{ mm} \times 40 \text{ mm}$. The discharge was applied to the side of the W-shaped wire, which faced the MIR prism, as shown in Figure 1. The W fits into a $10 \text{ mm} \times 10 \text{ mm}$ square. The barrier discharge was generated in ambient standard air, dry air, or N_2 . The dry air was generated by an air compressor equipped with an air dryer (SLP-15EED, Annet Iwata, Yokohama, Japan). The humidity of the dry air should decrease into less than 25%. SAMs on the MIR prism faced to the grounded electrode, because we want to know mild reaction without irregular atmospheric discharge [18]. The plasma source was set above the MIR prism. During plasma exposure, 80 infrared spectra were acquired at the rate of approximately 1 min per spectrum. The spectra resolution was 4.0 cm^{-1} .

3. Results and Discussions

Figure 2 shows the IR absorption spectrum of the CH_3 -terminated SAM prepared with OTS in the C–H and O–H stretching vibration regions. Three peaks are observed at 2850 , 2920 , and 2950 cm^{-1} . The peaks at 2850 and 2920 cm^{-1} are attributed to the CH_2 components [35] of the OTS-SAM, while that at 2950 cm^{-1} is attributed to CH_3 components [35].

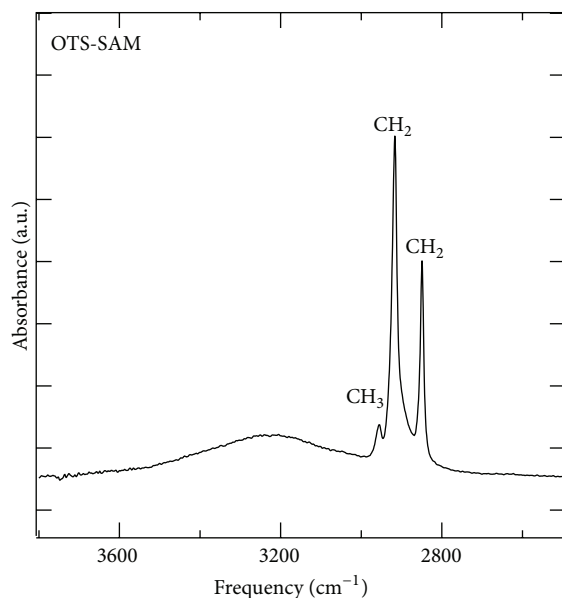


FIGURE 2: Infrared absorption spectrum of OTS-SAM.

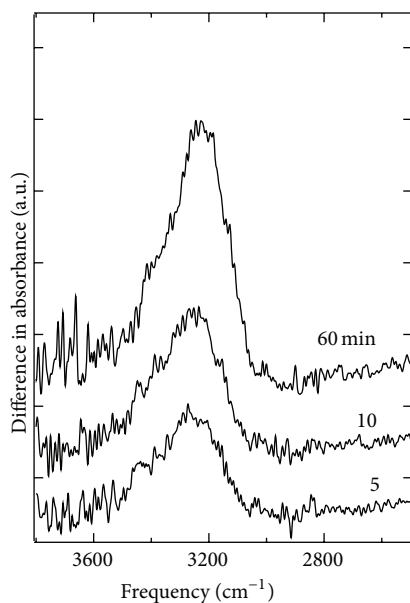


FIGURE 3: Differences between the infrared absorption spectra of the OTS-SAM obtained before and after exposure to air-pressure air plasma (exposure time in minutes).

The CH_3 peak is considerably less intense than the CH_2 peaks. This intensity disparity reflects the chemical bonding structure of the OTS-SAM; each of its monomers comprises 17 CH_2 components and one CH_3 component. The peak at 3200 cm^{-1} is attributed to OH [35], which is absent in the monomers, so the peak must arise from adsorption of water in air during the measurement.

Figure 3 shows the IR absorption spectra of the OTS-SAM exposed to atmospheric-pressure air plasma for various periods, in comparison with the spectrum of the SAM before

plasma exposure, in order to clarify spectral changes. The vertical axis indicates absorbance differences with respect to the spectrum of the SAM before plasma exposure. The figure shows the absorbance differences between the two spectra (vertical axis). The peak between 3200 and 3300 cm^{-1} , whose location is consistent with hydrogen-bonded water, becomes more intense after the exposure. We suggest that water clusters are generated by the atmospheric-pressure air plasma and become adsorbed on the OTS-SAM, although we need cross-checking with other methods such as mass spectroscopy. We will perform checking in the near future. This proposition is consistent with previous reports, in which clustered water was generated in air by electrical discharge [36–38]. On the other hand, these changes are absent in the CH stretching vibration region (between 2800 and 3000 cm^{-1}). This indicates that the $-\text{CH}_2-$ and $-\text{CH}_3$ components in the OTS-SAM are stable against charged water clusters generated in the atmospheric-pressure air plasma. This finding nullifies the rapid generation of oxidizing species such as oxygen radicals in the atmospheric-pressure air plasma because such species would affect the $-\text{CH}_3$ and $-\text{CH}_2-$ chains. We have confirmed that the CH_3 and CH_2 components in the OTS-SAM are etched by the oxygen plasma exposure generated in low pressure oxygen ambience, although the experimental condition is different. The details are described in another paper [39]. We speculate that the atmospheric-pressure plasma generates not only oxygen radicals but also water cluster. We need to know the generated species beside water cluster and their density; moreover for the plasma itself we need to know how much power is consumed by plasma and what is gas temperature. We will investigate them in the near future.

Figure 4 shows the IR absorption spectrum of the NH_2 -terminated SAM prepared in this study. In Figure 4(a), a broad band is observed between 3000 and 3500 cm^{-1} , which is attributed to N–H and O–H stretching vibrations. This band is broadened by the O–H vibration modes which, as observed in Figure 2, are attributed to O–H of water adsorbed from the air. The other broad band between 1200 and 1600 cm^{-1} (Figure 4(b)) is attributed to the bending modes of N–H and O–H. The prominent peaks at 1480 and 1580 cm^{-1} arise from the bending modes of N–H [35]. It might be hardly capable to form well-defined monolayer because of the fact that the source monomer is short-chain molecules. And also the SAM contains both NH_2 and NH groups in different positions within the backbone. We might not be able to elucidate the detailed interaction between NH_2 and atmospheric-pressure plasma because of these reasons. However, we can investigate the reactivity of N–H bonds, included in NH and NH_2 , respective to the plasma, with MIR-IRAS. The reactivity is very important to proteins that include N–H bonds. We consider that the SAM used in this study is suitable to investigate the reaction of N–H bonds with atmospheric-pressure plasma in the present.

Figure 5 compares the IR absorption spectra of the NH_2 -terminated SAM before and after exposure to the atmospheric-pressure air plasma. As in Figure 3, the vertical axis indicates the absorbance differences between the spectra. Figure 5(a) shows the C–H, O–H, and N–H stretching

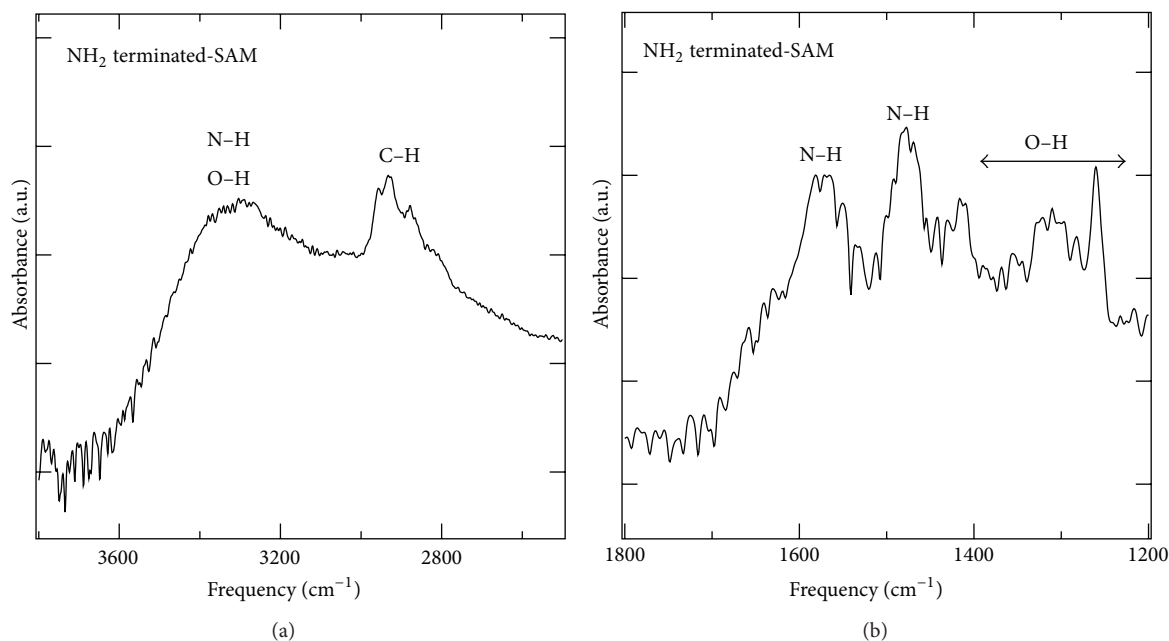


FIGURE 4: Infrared absorption spectrum of NH₂-terminated SAM: (a) in the bending and deformation vibration region and (b) in the stretching vibration region.

vibration regions between 2700 and 3700 cm⁻¹. Following exposure to plasma, the peak intensity between 3200 and 3400 cm⁻¹ decreases, while that between 3000 and 3200 cm⁻¹ increases. The former and latter peaks are attributed to primary amines (NH₂) and OH, respectively. The OH peak is observed between 3200 and 3400 cm⁻¹ in the plasma-exposed OTS-SAM (Figure 3), suggesting that the OH peak shifts to the lower vibration region. The peak of OH adjacent to N atoms shifts into the lower vibration region. Thus, we can assign the peak between 3000 and 3200 cm⁻¹ to the O-H of oximes (OH-N=C-R, H) [27]. The number of N-H groups decreased after plasma exposure, while that of OH groups bonded to N atoms increased. The peak intensity attributed to N-H decreased after less than 10 minutes of plasma exposure and remained relatively steady thereafter (up to 60 min exposure). On the other hand, the intensity of the oxime O-H peak gradually increased throughout the 60-minute exposure period. The bending mode region between 1200 and 1800 cm⁻¹ is visible in Figure 5(b). The doublet peaks at 1540 and 1480 cm⁻¹ are attributed to the N-H bending mode, and the broad peak between 1300 and 1400 cm⁻¹ is attributed to the O-H bending modes. The intensity of the peak attributed to NH components remarkably decreased during the first 5 minutes of exposure but remained steady thereafter. On the other hand, the intensity of the peaks attributed to O-H components gradually and steadily increased throughout the exposure period. The intensity changes in the N-H and O-H peaks exhibit the same behavior in Figures 5(a) and 5(b), indicating that NH is decomposed before the OH is adsorbed. When water clusters reach the NH₂-terminated SAM, the NH₂ group might become dehydrated by an oxidation process, with formation of OH-N bonds such as oximes. Moreover, the N-H peak reduces before the O-H

peak increases, suggesting that the N-H group decomposed before O-H adsorption. The OTS-SAM results confirmed that water clusters were generated in the applied atmospheric-pressure air plasma. Therefore, we can interpret plasma reactions with NH₂-terminated SAM in terms of the charged water clusters generated during plasma exposure. Of course, uncharged water clusters would not have decomposed the NH₂-terminated SAM, because the SAM is produced in water.

Given the importance of humid air in the proposed reaction model of NH₂-terminated SAM-plasma interactions, we altered the plasma atmosphere from air to dry air or N₂ gas. Note that humid air contains humidity of more than 50%, while dry air contains that of less than 25% as described in Experiment section. Figure 6 shows the infrared absorption spectra of NH₂-terminated SAM exposed to plasma generated in air, dry air, or N₂ gas for 60 min. The N-H peak decreased only under an air atmosphere. Although the O-H peak formed under both dry air and N₂, the N-H peak remained stable in these atmospheres. In dry air and N₂ gas, OH formation is attributed to the oxidation of the SAM by O₂ and residual oxygen, respectively, but the NH₂ groups remain intact. These results confirm that charged water clusters are required for decomposition of amine components. This study suggested that humid air is required for sterilization due to atmospheric-pressure plasma, because of the decomposition of amine group characteristic to proteins inevitable to a living thing such as virus and bacteria.

4. Conclusions

The reactions between plasma and two SAM types were investigated using infrared absorption spectroscopy in multiple internal reflection geometry. Atmospheric-pressure air

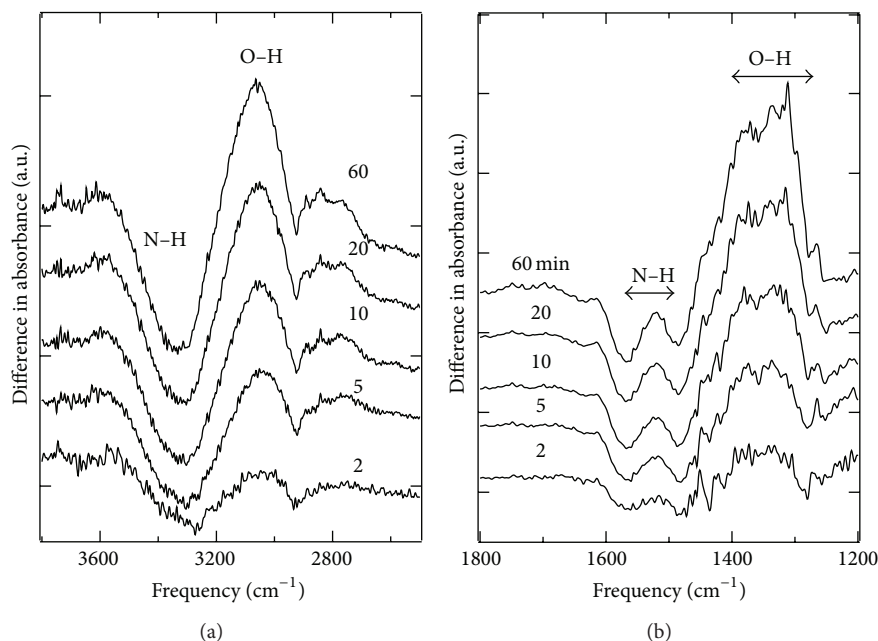


FIGURE 5: Differences between the infrared absorption spectra of the NH_2 -terminated SAM obtained before and after exposure to air-pressure plasma (exposure time in minutes): (a) in the stretching vibration region and (b) in the bending and deformation vibration regions.

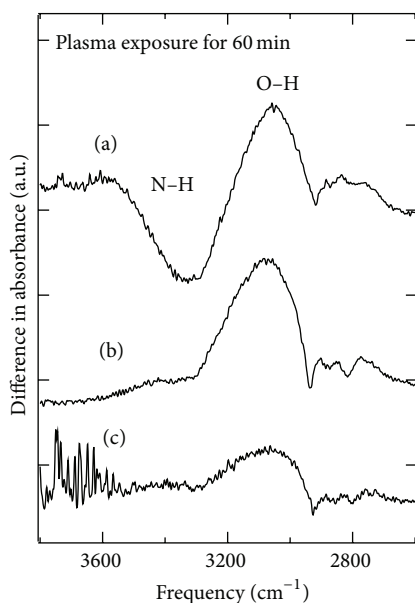


FIGURE 6: Differences between the infrared absorption spectra of NH_2 -terminated SAM in the stretching vibration region, obtained before and after a 30 min exposure to air-pressure plasma generated under different atmospheres: (a) standard air, (b) dry air, and (c) N_2 gas.

plasma generated hydrogen-bonded water by barrier discharge in air. Plasma exposure did not affect the CH_3 terminated OTS-SAM film but oxidized the NH_2 -terminated SAM; in the latter SAM, the number of O-H components was increased at the expense of the N-H groups. We also clarified

that humid air is required for decomposition of amine groups by the applied plasma. This study indicates that humid air is required for sterilization due to air pressure plasma.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

Parts of this work were supported by the following grants from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) and Japan Society for the Promotion of Science (JSPS): a Grant-in-Aid for Scientific Research on Innovative Areas (Material design), MEXT KAKENHI Grant no. 25104720 (2013–2016), a Grant-in-Aid for Scientific Research (B) JSPS KAKENHI Grant no. 24340144 (2012–2015), and Grants-in-Aid for Scientific Research on Innovative Areas (Plasma–nano interface) (MEXT KAKENHI Grant no. 22110511 (2010–2012) and no. 24110716 (2012–2014)).

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