Superhydrophilization of Si Surface by Atmospheric-Pressure Plasma Jet Irradiation: Analysis by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)

Hiroshi Kuwahata*
Department of Electrical and Electronics Engineering, School of Engineering, Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan

Takeshi Haraki
Technology Joint Management Office, Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan

Ikko Mikami
Department of Chemistry, School of Science, Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan

(Received 10 December 2012; Accepted 15 February 2013; Published 16 March 2013)

The superhydrophilization of a silicon (Si) surface by atmospheric-pressure plasma jet irradiation was analyzed by time-of-flight secondary ion mass spectrometry (TOF-SIMS). The Si surface was irradiated with an atmospheric-pressure argon (Ar) plasma jet in air for 5 s. The contact angle of a water drop on the Si surface decreased from 77 to 7° as a result of plasma jet irradiation, meaning that the Si surface became superhydrophilic. TOF-SIMS analysis indicated that the superhydrophilization was due to the removal of hydrophobic polydimethyl siloxane (PDMS) adsorbed on the Si surface and the increase in the amount of the hydrophilic silanol (SiOH) group. Emission spectral analysis of the plasma jet indicated that the SiOH group was formed when hydroxyl (OH) radicals, generated by collisions between high-energy electrons in the plasma and water molecules in air, bond to Si atoms on the surface.

[I DOI: 10.1380/ejssnt.2013.36]

Keywords: Plasma processing; silicon; TOF-SIMS; superhydrophilization; PDMS

I. INTRODUCTION

Recently, atmospheric-pressure plasma has been used for the surface modification of various materials, such as glass, semiconductors, and polymers [1–4].

In our previous study [5], the contact angle of a water drop on quartz glass decreased from 70 to 7° when the quartz glass surface was irradiated with an argon (Ar) atmospheric-pressure plasma jet [6] in air for 10 s, meaning that the surface became superhydrophilic. From the results of X-ray photoelectron spectroscopy (XPS), we confirmed that the superhydrophilization was due to the removal of hydrophobic organic compounds adsorbed on the quartz glass surface.

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) has been employed for the investigation of organic contaminants on surfaces of industrial materials [7–11].

In this paper, we report changes in the hydrophilicity of a silicon (Si) surface when it is irradiated with an atmospheric-pressure Ar plasma jet in air. TOF-SIMS analysis was also carried out to clarify the reason behind the changes in hydrophilicity.

II. EXPERIMENTAL

Figure 1 shows a schematic of our experimental setup. In this setup, a copper tube (inner diameter, 4 mm; outer diameter, 6 mm) used as a discharge electrode is inserted into a dielectric quartz tube (length, 50 mm; inner diameter, 6 mm; outer diameter, 8 mm), around which copper foil (thickness, 0.05 mm; width, 10 mm) is wrapped as a grounding electrode. When a high AC voltage is applied, dielectric barrier discharge is induced in the quartz tube between these electrodes, and the inflowing argon gas is excited to form a plasma that is then released into the atmosphere.

A plasma jet was generated at an argon gas flow rate of 10 L/min using a high-voltage power source (LHV-10AC, Logy Electric Co., Ltd.) with a frequency of 9 kHz and an applied voltage of 10 kV. Under these conditions, the plasma jet extended approximately 30 mm from the end of the quartz tube [12], and its maximum diameter was approximately 6 mm.

[FIG. 1: Schematic of experimental setup.]

*Corresponding author: kuwahata@keyaki.cc.u-tokai.ac.jp

ISSN 1348-0391 © 2013 The Surface Science Society of Japan (http://www.sssj.org/ejssnt) 36
A Si surface was irradiated with an Ar plasma jet in air for 5 s. The distance between the end of the quartz tube and the Si surface was approximately 2 mm. A mirror-polished Si wafer with a size of 30 mm × 30 mm was used as a specimen in this study. The specimen was ultrasonically cleaned with acetone for 10 min before plasma jet irradiation. The contact angle of a water drop on the Si surface was measured using an automatic contact angle meter (Kyowa Interface Science Co., Ltd., CA-V) to evaluate the hydrophilicity of the Si surface. The elements and organic compounds on the Si surface were analyzed using a TOF secondary ion mass spectrometer (ION-TOF GmbH, TOF-SIMS IV) and $^{69}$Ga$^+$ primary ions with a beam energy of 15 keV. A multichannel spectrometer (StellarNet, Inc., EPP2000-UV-VIS) was used in the emission spectral analysis of the plasma jet. The light-receiving part was fixed at a position approximately 2 mm from the end of the quartz tube in the vertical direction and 10 mm from the plasma jet in the horizontal direction.

III. RESULTS AND DISCUSSION

Figure 2 shows the plasma jet irradiation of the Si surface. The plasma jet does not expand when it reaches the Si surface, and the diameter of the plasma jet appears to be almost the same as that of the quartz tube.

The contact angle of a water drop was measured to evaluate the change in the hydrophilicity of the Si surface as a result of plasma jet irradiation. Figure 3 shows water drops on the Si surface before and after plasma jet irradiation. As shown in Fig. 3(a), the water drop on the Si surface appeared to be hemispherical before irradiation, and the contact angle was 77°. Houston and Maboudian have reported that the contact angle of a water drop on a hydrofluoric-acid-treated Si surface was 76.0° [13]. Zhang et al. have reported that the contact angle of a water drop on a hydrogen-terminated Si surface was 79° [14]. As shown in Fig. 3(b), however, the contact angle was 7° after 5 s plasma jet irradiation, meaning that the Si surface became superhydrophilic [15].

TOF-SIMS analysis was carried out to clarify the cause of the superhydrophilization of the Si surface as a result of plasma jet irradiation. Figures 4(a) and 4(b) show the TOF-SIMS spectra of positive ions originating from Si before and after 5 s plasma jet irradiation, respectively. In the spectrum obtained before plasma jet irradiation, peaks were observed at mass-to-charge ratios of 28, 43, 59, 73, 147, 207, and 221. The peak at the mass-to-charge ratio of 28 corresponds to Si$^+$, the peaks at mass-to-charge ratios of 43, 59, 73, 147, 207, and 221 correspond to SiC$_2$H$_7^+$, SiC$_3$H$_7^+$, Si$_2$O$_5$C$_5$H$_{15}^+$, and Si$_3$O$_2$C$_7$H$_{21}^+$, respectively, which are the fragment ions of hydrophobic polydimethyl siloxane (PDMS) [7, 8, 10, 11]. Poleunis et al. have analyzed organic contaminants on a Si surface by TOF-SIMS and observed peaks at mass-to-charge ratios of 28, 43, 57, and 71, similar to those in our study [10]. These results indicate that PDMS was adsorbed on the Si surface before plasma jet irradiation. PDMS is generally used in mold-releasing agents used for plastics. In this study, Si was stored in a plastic case, which may have allowed PDMS on the inside of the plastic case to become adsorbed on the Si surface. Therefore, it is considered that, before plasma jet irradiation, hydrophobic PDMS adsorbed on the Si surface repelled water, resulting in the high contact angle of a water drop. In the TOF-SIMS spectrum after 5 s plasma jet irradiation, peaks were observed at mass-to-charge ratios of 28 and 45. The peak at a mass-to-charge ratio of 28 corresponds to SiOH$^+$. This result indicates that the hydrophilic silanol (SiOH) group was formed on the surface. The inset of each figure shows the peak at a mass-to-charge ratio of 17. The peak corresponds to OH$^+$, which is a fragment ion of SiOH$^+$.

Figure 5 shows the changes in the TOF-SIMS peak intensities upon 5 s plasma jet irradiation. The above peak intensities were normalized using that corresponding to

![Figure 2: Plasma jet irradiation of Si surface.](http://www.sssj.org/ejssnt)

![Figure 3: Water drops on Si surface (a) before and (b) after plasma jet irradiation.](http://www.sssj.org/ejssnt)
FIG. 4: TOF-SIMS spectra of positive ions from Si (a) before and (b) after plasma jet irradiation. The molecular structure of PDMS is also shown in Fig. 4(a). ** represents the peaks corresponding to PDMS.

FIG. 5: Changes in TOF-SIMS peak intensities upon 5 s plasma jet irradiation.

FIG. 6: Emission spectrum of plasma jet.

$^{29}$Si$^+$ to compare the peak intensities before and after plasma jet irradiation. As a result of plasma jet irradiation, the peak intensities for OH$^+$ and SiOH$^+$ increased by factors of 16 and 3, respectively. In contrast, the peak intensities for SiCH$_3^+$, SiC$_2$H$_5^+$, Si$_2$OC$_5$H$_{15}^+$, Si$_3$O$_2$C$_5$H$_{15}^+$, and Si$_3$O$_2$C$_7$H$_{21}^+$ decreased by 96, 97, 95, 96, 97, and 97%, respectively. These results reveal that the PDMS adsorbed on the Si surface was almost completely removed and that the amount of the SiOH group increased. Therefore, the superhydrophilization of the Si surface by plasma jet irradiation was due to the removal of hydrophobic PDMS adsorbed on the Si surface and the increase in the amount of the hydrophilic SiOH group.

Emission spectral analysis of the plasma jet was carried out to clarify the origin of the OH$^+$ and SiOH$^+$, the amounts of which increased as a result of plasma jet irradiation. Figure 6 shows the emission spectrum of the plasma jet. In the emission spectrum, spectral bands were observed in the wavelength ranges of 300-400 and 700-850 nm. The spectral band in the wavelength range of...
300-400 nm corresponds to the emission from the second positive system of nitrogen molecules (N$_2$) [16], which are considered to originate from air. The spectral band in the wavelength range of 700-850 nm corresponds to the emission from the excited Ar atoms [12, 17]. These results indicate that the plasma jet contains high-energy particles such as excited Ar atoms and N$_2$. Moreover, a peak corresponding to hydroxyl (OH) radicals was observed at a wavelength of 309 nm in the emission spectrum [18, 19]. This means that OH radicals are contained in the plasma jet. High-energy electrons (e$^-$) exist in the plasma jet. These electrons collide with water molecules (H$_2$O) in air to generate OH radicals (-OH) and H radicals (-H) as follows.

$$\text{H}_2\text{O} + e^- \rightarrow \cdot\text{OH} + \cdot\text{H} + e^-.$$  \hspace{1cm} (1)

Thus, the emission from the OH radicals observed in the emission spectrum is considered to be that from the OH radicals generated by the reaction between the electrons in the plasma jet and water molecules in air. OH radicals are considered to oxidize and remove hydrophobic PDMS adsorbed on the Si surface because of their high oxidation potential of 2.85 V [20] and strong oxidative power. In contrast, the peak intensities for OH$^+$ and SiOH$^+$ increased by factors of 16 and 3, respectively. This result indicates that the SiOH groups were formed on the Si surface. Therefore, the superhydrophilization of the Si surface by plasma jet irradiation was due to the oxygenation by OH radicals generated by collisions between high-energy electrons in the plasma and water molecules in air. The SiOH group is considered to be formed when OH radicals bond to Si atoms on the surface.

IV. CONCLUSIONS

An atmospheric-pressure Ar plasma jet was generated at a frequency of 9 kHz, applied voltage of 10 kV, and Ar gas flow rate of 10 L/min. The Si surface was irradiated with this plasma jet in air for 5 s. The contact angle of a water drop on the Si surface decreased from 77 to 7$^\circ$ as a result of plasma jet irradiation, meaning that the Si surface became superhydrophilic. TOF-SIMS analysis indicated that hydrophobic PDMS was adsorbed on the Si surface before plasma jet irradiation. After 5 s plasma jet irradiation, the peak intensities for SiCH$_3^+$, SiC$_2$H$_7^+$, SiC$_3$H$_7^+$, Si$_2$OC$_2$H$_7^+$, Si$_3$O$_2$C$_2$H$_{15}^+$, and Si$_3$O$_2$C$_7$H$_{21}^+$, which are the fragment ions of PDMS, decreased by 96, 97, 95, 96, 97, and 97%, respectively. In contrast, the peak intensities for OH$^+$ and SiOH$^+$ increased by factors of 16 and 3, respectively. This result indicates that the SiOH groups were formed on the Si surface. Therefore, the superhydrophilization of the Si surface by plasma jet irradiation was due to the removal of hydrophobic PDMS adsorbed on the Si surface and the increase in the amount of the hydrophilic SiOH group. Emission spectral analysis of the plasma jet indicated that OH radicals are contained in the plasma jet. Therefore, it was found that the removal of PDMS adsorbed on the Si surface as a result of plasma jet irradiation was due to oxidation by OH radicals generated by collisions between high-energy electrons in the plasma and water molecules in air. The SiOH group is considered to be formed when OH radicals bond to Si atoms on the surface.

Acknowledgments

The authors are grateful to Professor Y. Nishi of Tokai University for his cooperation in the contact angle measurement, Mr. Y. Miyamoto of the Technology Joint Management Office, Tokai University, for his cooperation in the TOF-SIMS measurement, and Professor R. Ohyama of Tokai University for his valuable advice.