Superhydrophilization of Surface of Aluminum Thin Film by Atmospheric-Pressure Plasma Jet Irradiation

Hiroshi Kuwahata,* Yuki Murata, Naoki Hashimoto, and Riyuya Segawa

Department of Electrical and Electronic Engineering, School of Engineering, Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan

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An atmospheric-pressure argon (Ar) plasma jet was generated with a frequency of 10 kHz, an applied voltage of 4 kV, and an Ar gas flow rate of 10 L/min. When an aluminum (Al) thin film that was vacuum-deposited on a glass substrate was irradiated with the atmospheric-pressure Ar plasma jet in air for 60 s at an irradiation distance of 2 mm, the surface of the Al thin film was hydrophilized in a circular area with a diameter of 23 mm, which was larger than that of the plasma (6 mm). It was found that the superhydrophilization first occurred at the periphery of the irradiated area (∼5–10 mm from the center of the irradiated area) and then in the area irradiated directly by the plasma (∼≤5 mm from the center of the irradiated area) on the Al thin film. In the previous research on the atmospheric-pressure plasma jet irradiation of Al, the plasma reached Al, and it was reported that the hydrophilicity only improved in the area irradiated directly by the plasma. On the other hand, our plasma in this study did not reach Al. In spite of this, the hydrophilicity improved in the area irradiated directly by the plasma and in the periphery of the irradiated area. On the basis of the results of X-ray photoelectron spectroscopy (XPS), the hydrophobic organic compounds that adsorbed on the surface of the Al thin film are considered to have been removed by the ozone (O3) generated by the interaction between the plasma and oxygen (O2) molecules in air. From the O3 concentration distribution obtained using O3 test strips, the reason for the faster superhydrophilization in the peripheral area than in the irradiated area was found to be that the peripheral area had the higher concentration of O3.

Keywords: Plasma processing; Aluminum; Metallic surfaces; Wetting; X-ray photoelectron spectroscopy

I. INTRODUCTION

Research on surface modification using atmospheric-pressure plasma has been carried out using various materials, such as metals [1–3], semiconductors [4, 5], glass [6–9], and polymer resins [10–12]. Surface modification of metals has been carried out to improve the hydrophilicity (wettability), the bondability between metals, the adhesion between a metal and a polymer, and the adhesion between a coating material and an adhesive. To evaluate hydrophilicity, the contact angle of water on the surface is often used [1–11]. Kim et al. irradiated an aluminum (Al) surface [1] and a stainless-steel surface [2] with an atmospheric-pressure nitrogen/oxygen (N2/O2) plasma jet, which was generated at a frequency of 16–20 kHz and an applied voltage of 10 kV and moved at a speed of 5 mm/s, and measured the contact angle of water. They reported that the contact angle on the Al surface decreased from 66.1 to 19.6° and the contact angle on the stainless-steel surface decreased from 50 to 15° upon plasma jet irradiation, demonstrating that the hydrophilicity of these surfaces was improved. However, the surfaces did not reach the superhydrophilic state, in which the contact angle is ≤10°. Yamamoto et al. used three types of atmospheric-pressure plasma jet generator in their experiment [3]. First, the surface of an Al plate was irradiated with an atmospheric-pressure air plasma jet generated at a frequency of 60 Hz and an applied voltage of 10 kV for 5 s, and the contact angle of water on the surface was measured. They reported that the contact angle decreased from 65–70 to 7° and that the surface became superhydrophilic after plasma jet irradiation. Note that the temperature of the Al surface during the plasma jet irradiation was ∼100°C. Second, when the surface of an Al plate was irradiated with an atmospheric-pressure helium (He) plasma jet generated at a frequency of 13.56 MHz and an applied power of 250 W for 1 min, the contact angle became 6°, indicating that the surface had become superhydrophilic after plasma jet irradiation. Note that the temperature of the Al surface during the plasma jet irradiation was ∼110°C. Third, when the surface of an Al plate was irradiated with a pulse corona plasma generated at a frequency of 300 Hz, an applied voltage of 30 kV, and a pulse width of 200 ns for 3 min, the contact angle became 7°, indicating that the surface became superhydrophilic after plasma jet irradiation. In this case, the temperature of the Al surface remained the same.

In our previous studies, quartz glass was irradiated with an atmospheric-pressure Ar plasma jet generated at a frequency of 10 kHz with an applied voltage of 10 kV and an Ar gas flow rate of 10 L/min for 5 s. As a result, the contact angle of water on the irradiated area decreased from 70 to 10°, showing that the quartz glass surface became superhydrophilic [13]. From X-ray photoelectron spectroscopy (XPS) results, the number of carbon (C) atoms was found to decrease. We concluded that the quartz glass surface became superhydrophilic because the hydrophobic organic compounds adsorbed onto the quartz glass surface were removed by the plasma jet irradiation. We also reported that when a silicon (Si) surface was irradiated with the above-mentioned Ar plasma jet for 5 s, the contact angle of water decreased from 77 to 7°, revealing that the Si surface became superhydrophilic [14]. From the results of time-of-flight secondary ion mass spectroscopy (TOF-SIMS), we found that the amount of hydrophobic polydimethylsiloxane (PDMS) [15–17] adsorbed onto the Si surface decreased and that the number of hydrophilic silanol (SiOH) and hydroxyl (OH) groups on the Si surface increased after plasma jet irradiation. We concluded that the Si surface became superhydrophilic because the...
hydrophobic PDMS was removed by oxidation decomposition in the presence of OH radicals and the number of hydrophilic groups on the Si surface increased.

To the best of our knowledge, the number of reports on atmospheric-pressure plasma jet irradiation on metals is limited. Also, the hydrophilization of metal surfaces by atmospheric-pressure plasma jet irradiation has been reported only for the area irradiated with a plasma jet and has not included the peripheral area. Examining the area of hydrophilization including the peripheral area is important to determine the area affected by plasma jet irradiation.

In this study, an Al thin film deposited on a glass substrate was irradiated with an atmospheric-pressure Ar plasma jet in air. The contact angle of water on the surface was measured and XPS spectra were obtained to examine the change in hydrophilicity of not only the irradiated area but also the peripheral area. In addition, scanning probe microscopy (SPM) was carried out to evaluate the damage on the surface of the Al thin film caused by plasma jet irradiation. To examine the cause of the change in hydrophilicity, emission spectra of the plasma were obtained and the temperature on the surface of the Al thin film during plasma jet irradiation was measured using a thermographic camera. In addition, the concentration and distribution of ozone \( \text{O}_3 \) were measured using \( \text{O}_3 \) test strips to examine the generation of \( \text{O}_3 \).

II. EXPERIMENT

In the unit employed to generate the plasma jet, a copper tube (inner diameter, 4 mm; outer diameter, 6 mm) was used as the discharge electrode with 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) was wrapped as the ground electrode [14, 18]. A high AC voltage was applied to the electrodes to induce dielectric barrier discharge inside the quartz tube between the electrodes and to convert the introduced Ar gas to plasma, which was ejected into the air in the form of a jet. A high-voltage power supply (LHV-10AC, Logy Electric Co., Ltd.) was used to generate the Ar plasma jet (frequency, 10 kHz; applied voltage, 4 kV; Ar gas flow rate, 10 L/min). An Al thin film deposited on a glass substrate was irradiated with the Ar plasma jet for 5–60 s. The distance from the end of the quartz tube to the Al thin film (irradiation distance) was 2 mm.

The voltage and current were measured using a high-voltage probe (P6015A, Tektronix, Inc.) and a current probe (A621, Tektronix, Inc.), respectively, connected to a digital oscilloscope (TDS1001B, Tektronix, Inc.). The gas flow rate was adjusted using a gas flow meter (RK-1250, Kofloc Kyoto, Kojima Instruments Inc.). The Al thin film was formed on a glass substrate (76 × 26 × 1.2 mm\(^3\)) using a vacuum deposition system (VPC-260F, ULVAC KIKO Inc.).

A scanning probe microscope (SPM-9700, Shimadzu Corporation) was used for SPM. The measurement was carried out in the tapping mode using a Si probe (20–80 N/m). A contact angle meter (CA-V, Kyowa Interface Science Co., Ltd.) was used to measure the contact angle of water on the surface. For XPS, a Quantera II spectrometer (ULVAC-PHI Inc.) was used. To obtain emission spectra, a multichannel spectrometer (QE65000, Ocean Optics) was used. The temperature of the surface of the Al thin film during plasma jet irradiation was measured using a thermometer (Thermo Shot F30, Nippon Avionics Co., Ltd.). For the measurement of the \( \text{O}_3 \) concentration, the emission spectra of the plasma jet inside and outside the quartz tube were obtained, as shown in FIG. 2.
FIG. 3. Thermography images of Al thin film: (a) before irradiation, (b) after irradiation for 30 s, and (c) after irradiation for 60 s. There was a quartz tube and an Al thin film at the positions indicated by the white dashed line and the plus symbol, respectively. The temperature of the surface of the Al thin film is shown in the lower left of each image. The room temperature was 28°C during measurement.

FIG. 4. 3D images of the surface of an Al thin film (1000 × 1000 nm$^2$) obtained by SPM: (a) before plasma irradiation and (b) after plasma irradiation for 60 s.

centration distribution, 16 O$_3$ test strips (10 × 8 mm$^2$ each, Macherey-Nagel) that were arranged in a rectangular shape (4 × 4) on a plastic plate were used.

III. RESULTS AND DISCUSSION

Figure 1 shows photographs of the Ar plasma jet ejected onto an Al thin film and an Al thin film deposited on a glass substrate. As shown in Fig. 1(a), the generated plasma did not extend outside the quartz tube and the plasma jet did not appear to reach the Al thin film because light-purple emission was only observed at the lower part of the ground electrode. At an applied voltage of ≤3 kV, no plasma was generated. The Al thin film in Fig. 1(b) had an area of 40 × 16 mm$^2$ and a thickness of 3.5 µm. As shown in Fig. 1(c), the surface of the Al thin film irradiated with the Ar plasma jet for 60 s appeared to be undamaged.

To determine whether or not the Ar plasma extended outside the quartz tube, the emission spectra of the plasma inside and outside the quartz tube were obtained.

The measurement was performed inside the quartz tube (∼10 mm above the bottom of the quartz tube) and outside the quartz tube (∼5 mm below the bottom of the quartz tube). Figure 2 shows the emission spectra of the plasma jet inside and outside the quartz tube. In the emission spectrum obtained from inside the quartz tube [Fig. 2(a)], a peak corresponding to OH radicals was observed at a wavelength of 309 nm [19–22]. The OH radicals were generated as a result of the dissociation of water (H$_2$O) molecules into hydrogen (H) atoms and OH when electrons in the plasma collided with H$_2$O molecules in air. The peaks at 313, 335, and 355 nm correspond to the second positive system of the nitrogen (N$_2$) molecule [23–26]. These emissions occurred when electrons in the plasma collided with N$_2$ molecules in air, providing energy to the electrons of the N$_2$ molecules, then the excited electrons relaxed to the ground state. The peaks at 700–850 nm correspond to the emission from excited Ar atoms [27, 28]. From the above findings, a small amount of air is considered to have been present in the quartz tube. It is considered that oxygen (O$_2$) molecules in air were dissociated to form O radicals and O$_3$ in the quartz tube. In
FIG. 5. Distribution of water droplets on Al thin film: (a) before irradiation, (b) after plasma irradiation for 10 s, (c) after plasma irradiation for 30 s, and (d) after plasma irradiation for 60 s, and photographs of a water droplet on the Al thin film: (e) before irradiation and (f) after plasma irradiation for 60 s.

the emission spectrum obtained outside the quartz tube [Fig. 2(b)], no peak was observed, indicating that there was no plasma outside the quartz tube.

Figure 3 shows thermography images of Al thin films. The colors of the quartz tube and Al thin film are similar to that of the peripheral area in all images. This finding indicates that the plasma jet and Al thin film were at room temperature. The surface temperature of the Al thin film was 28.3 °C before plasma jet irradiation [Fig. 3(a)] and 28.1 and 28.0 °C after plasma jet irradiation for 30 [Fig. 3(b)] and 60 s [Fig. 3(c)], respectively. Thus, the surface temperature slightly decreased with increasing plasma irradiation time. This is because room-temperature Ar plasma jet [28] was ejected onto the surface of Al the thin film to draw heat from the surface. From this finding, the temperature of the plasma was judged to be to less than or equal to room temperature.

Figure 4 shows three-dimensional (3D) images of the surface of an Al thin film obtained by SPM. The root-mean-square roughness (Rq = Rms) was 1.626 and 1.570 nm in Fig. 4(a) and Fig. 4(b), respectively. The image of the surface irradiated with the Ar plasma jet for 60 s [Fig. 4(b)] is similar to that before plasma jet irradiation, indicating that the plasma jet irradiation for 60 s caused no damage to the surface.

Figure 5 shows the distribution of water droplets on an Al thin film and the results for the contact angle of water on the Al thin film. Distilled water was sprayed on the surface of the Al thin film. Before plasma jet irradiation [Fig. 5(a)], many water droplets were observed on the Al thin film, indicating that the surface of the film had low hydrophilicity and repelled water droplets. After plasma jet irradiation for 10 s [Fig. 5(b)], a circular area (diameter, ~16 mm) within which water spread as a film without water droplets, was observed on the Al thin film. The diameters of the circular area were ~19 and ~23 mm after plasma jet irradiation for 30 [Fig. 5(c)] and 60 s [Fig. 5(d)], respectively, i.e., the diameter of the hydrophilic area increased with increasing plasma irradiation time. The hydrophilicity in the circular area is considered to have been increased by plasma irradiation. This finding indicates that hydrophilization occurred even when the area was not directly irradiated with the plasma jet. From this finding, hydrophilization is considered to have occurred not directly owing to the plasma jet but because of active oxygen species, such as O radicals and O₃, generated as a result of the interaction between the...
plasma and O\textsubscript{2} molecules in air. It is difficult for O radicals to move a distance of \(\sim 10\) mm (which corresponds to the diameter of the above circle) in air even when O radicals are generated in the vicinity of the quartz tube, because radicals have high reactivity and bind to other substances in a very short period of time \([29, 30]\). On the basis of this fact, O\textsubscript{3}, which has a relatively long lifetime, may have induced the hydrophilization of the surface. O\textsubscript{3} has a high oxidation potential of 2.07 V \([31–33]\) and oxidizes and decomposes other substances. As shown in Fig. 5(e), the contact angle before irradiation was 55°. In contrast, it was 10° after plasma irradiation for 60 s, as shown in Fig. 5(f), indicating that the surface became superhydrophilic. This result shows that the surface of the Al thin film became superhydrophilic when irradiated with the atmospheric-pressure Ar plasma jet generated at an applied voltage of 4 kV for 60 s.

Figure 6 shows the distribution of the contact angle of water on the Al thin film. As shown in Fig. 6(a), the contact angles at the center of the irradiated area and in the peripheral area (\(\sim 5\) mm from the center) were 53 and 55–58°, respectively, before irradiation. After plasma irradiation for 5 s [Fig. 6(b)], the contact angles decreased slightly to 35 and 36–38°, respectively, indicating increases in hydrophilicity. After plasma irradiation for 10 s [Fig. 6(c)], the contact angles decreased further to 34 and 25–31°, respectively. After plasma irradiation for 15 s [Fig. 6(d)], the contact angles at the center of the irradiated area and in the peripheral area were 27 and 13–18°, respectively. The contact angle in the peripheral area decreased faster than that at the center of the irradiated area. After plasma irradiation for 30 s [Fig. 6(e)], the contact angles at the center of the irradiated area and in the peripheral area were 22 and 8–14°, respectively. The peripheral area became superhydrophilic before the center of the irradiated area. After plasma irradiation for 60 s [Fig. 6(f)], the contact angles were 10 and 7–10°, respectively, indicating that not only the peripheral area but also the center of the irradiated area became superhydrophilic. Yamamoto \textit{et al.} also reported that an Al surface became superhydrophilic after atmospheric-pressure plasma jet irradiation \([3]\). However, they did not describe the change in hydrophilicity in the periphery of the irradiated area. In Fig. 6(g), the open circles indicate the contact angles at the center of the irradiated area and the crosses indicate the contact angles in the peripheral area (\(\sim 5\) mm to the right of the center). With increasing plasma irradiation time, the contact angle decreased faster in the peripheral area than at the center of the irradiated area. The time required for the peripheral area to become superhydrophilic was 30 s and that for the center of the irradiated area was 60 s, which is double the time required for the former. From this finding, the hydrophilization of the surface of the Al thin film irradiated with the Ar plasma jet occurred faster in the peripheral area (\(\sim 5\) mm from the center) than at the center of the irradiated area.

Figure 7 shows XPS spectra of an Al thin film at the...
FIG. 8. Change in intensity of XPS narrow spectra with plasma irradiation time at center of irradiated area on Al thin film: (a) Al 2s and Al 2p peaks, (b) O 1s peak, and (c) C 1s peak.

center of the irradiated area. Before plasma irradiation [Fig. 7(a)], peaks were observed at binding energies of 73.0 and 118.0 eV, which correspond to Al 2p and Al 2s, respectively [1, 34–39]. In addition, a peak corresponding to O 1s was observed at 531 eV [1, 36–39]. Furthermore, a peak corresponding to C 1s was observed at 284 eV [1, 36–39]. These findings indicate that O and C atoms existed on the surface of the Al thin film. On the surface of the Al thin film, there was a natural oxide film with a thickness of 10–20 Å [35, 37, 40]. The O atoms in the natural oxide film and C atoms in organic compounds adsorbed onto the surface of Al thin film as contaminants as observed by XPS [13, 41, 42]. Yamamoto et al. [39] and Kim et al. [1] reported that these C atoms originate from CO₂ and CO in air. In general, contaminants are hydrophobic and repel water [13, 43]. Therefore, the high contact angle

FIG. 9. Dependence of peak intensity on plasma irradiation time at center of irradiated area on Al thin film: (a) Al 2s peak intensity, (b) O 1s peak intensity, and (c) C 1s peak intensity. (d) Ratios of change in the peak intensities of Al 2s, O 1s, and C 1s at center of irradiated area after plasma irradiation for 60 s.
plasma irradiation for 60 s. The intensities of the higher binding energy side in Al 2s and Al 2p peaks also increased. This suggests that the thickness of the natural oxide film increased. As shown in Fig. 8(b), the intensity of the peak corresponding to O 1s slightly increased with increasing plasma irradiation time. As shown in Fig. 8(c), a high-intensity peak was observed at a binding energy of 284 eV and a low-intensity peak was observed at a binding energy of 288 eV, which is considered to correspond to O=C–O [37]. The intensity of the peak corresponding to C 1s decreased with increasing plasma irradiation time.

Figure 9 shows the dependence of the peak intensity at the center of the irradiated area on the plasma irradiation time. As shown in Fig. 9(a), the intensity of the peak corresponding to Al 2s sharply increased after plasma irradiation for 10 s and then gradually increased with increasing plasma irradiation time. As shown in Fig. 9(b), the intensity of the peak corresponding to O 1s also sharply increased after plasma irradiation for 10 s and then gradually increased. On the other hand, the intensity of the peak corresponding to C 1s in Fig. 9(c) sharply decreased upon irradiation for 10 s and then gradually decreased. These tendencies are similar to the dependence of the contact angle of water on the plasma irradiation time [Fig. 6(g)]. This finding indicates that the increase in hydrophilicity at the surface of the Al thin film is related to the decrease in the number of C atoms present on the surface. Fig. 9(d) shows the ratios of the change in the peak intensities of Al 2s, O 1s, and C 1s at the center of the irradiated area after plasma irradiation for 60 s. The ratios of the change in the peak intensities of Al and O atoms increased to ~116%, whereas that of C atoms decreased to ~58% upon irradiation for 60 s. This finding indicates that C atoms (contaminants) adsorbed on the surface of the Al thin film were removed from the surface by plasma irradiation and that Al atoms were exposed because the number of Al atoms on the Al thin film did not increase upon plasma irradiation. It is interesting that the ratio of the change in the peak intensity of Al was the same as that of O atoms. This finding indicates that C atoms (contaminants) adsorbed on O atoms were also removed by plasma irradiation.

The rate of hydrophilization at the center of the irradiated area (≤5 mm from the center of the irradiated area) was different from that at the peripheral area (5–10 mm from the center of the irradiated area), as shown in Fig. 6. To understand the mechanism behind the faster hydrophilization in the peripheral area than at the center of the irradiated area, XPS spectra were obtained at three positions: at the center, 10 mm to the right of the center, and 20 mm to the right of the center.

Figure 10 shows the dependence of the ratio of the change in the peak intensity on the position of XPS observation, i.e., the distance from the center. As shown in Fig. 10(a), the relative intensity of the peak corresponding to O 1s was ≥100% regardless of the distance from the center after plasma irradiation for 30 s, and decreased linearly with increasing distance from the center. The peak corresponding to O 1s is attributable to O atoms that were covered by adsorbed C atoms before irradiation and were removed after irradiation because C atoms were removed from the surface of the Al thin film. Therefore, the finding in Fig. 10(a) indicates that C atoms were removed from the surface of the Al thin film after plasma irradiation. 

Kim et al. reported similar changes in XPS spectra of Al upon atmospheric-pressure plasma irradiation [1]. In their experiment, the surface of an Al thin film was irradiated with an atmospheric-pressure N2/O2 plasma jet, which moved at a speed of 5 mm/s. They reported that the intensity of the peak corresponding to C decreased, whereas the intensities of the peaks corresponding to O 1s, Al 2p, and Al 2s increased.

Figure 8 shows the change in the intensity of XPS narrow spectra at the center of the irradiated area with plasma irradiation time. As shown in Fig. 8(a), there were two peaks corresponding to Al 2s at 115.5 and 118 eV and two peaks corresponding to Al 2p at 70.5 and 73 eV. The peaks at the lower binding energy correspond to Al–Al and those at the higher binding energy correspond to Al–O [37, 38]. This finding indicates that O atoms existed on the surface of the Al thin film, demonstrating the existence of an oxide film. The intensities of the peaks corresponding to Al 2s and Al 2p slightly increased after plasma irradiation for 60 s. The intensities of the higher binding energy side in Al 2s and Al 2p peaks also increased. This suggests that the thickness of the natural oxide film increased. As shown in Fig. 8(b), the intensity of the peak corresponding to O 1s slightly increased with increasing plasma irradiation time. As shown in Fig. 8(c), a high-intensity peak was observed at a binding energy of 284 eV and a low-intensity peak was observed at a binding energy of 288 eV, which is considered to correspond to O=C–O [37]. The intensity of the peak corresponding to C 1s decreased with increasing plasma irradiation time.

FIG. 10. Dependence of relative peak intensity on position of XPS observation: (a) O 1s peak intensity and (b) C 1s peak intensity.

[55°, Fig. 5(e)] was caused by the repulsion of water by contaminants on the surface. The peak corresponding to C 1s in this study has also been observed in XPS spectra of the surfaces of copper (Cu) [1], stainless steel [1], quartz glass [13], and Si [4, 41]. After plasma irradiation for 60 s [Fig. 7(b)], the intensity of the peak corresponding to C 1s decreased, whereas the intensities of the peaks corresponding to O 1s, Al 2p, and Al 2s increased.

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The rate of hydrophilization at the center of the irradiated area (≤5 mm from the center of the irradiated area) was different from that at the peripheral area (5–10 mm from the center of the irradiated area), as shown in Fig. 6. To understand the mechanism behind the faster hydrophilization in the peripheral area than at the center of the irradiated area, XPS spectra were obtained at three positions: at the center, 10 mm to the right of the center, and 20 mm to the right of the center.

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ation for 30 s regardless of the distance from the center and that the number of C atoms removed decreased linearly with increasing distance from the center. The ratio of the change in the peak intensity of O 1s after plasma irradiation for 60 s was higher than that after plasma irradiation for 30 s regardless of the distance from the center. This finding indicates that the number of C atoms removed from the surface of the Al thin film was higher after plasma irradiation for 60 s than that after plasma irradiation for 30 s. Therefore, the ratio of the change in the peak intensity of C 1s was expected to linearly increase with increasing distance from the center. However, as shown in Fig. 10(b), the ratio of the change in the peak intensity of C 1s did not show this tendency and was ≤100% regardless of the distance from the center after plasma irradiation for 30 s. This finding indicates that C atoms were removed from the surface of the Al thin film at all distances from the center after plasma irradiation for 30 s. The ratio of the change in the peak intensity of C 1s did not linearly increase with increasing distance from the center; it was lowest at 10 mm to the right of the center. This finding indicates that the number of C atoms removed from the surface of the Al thin film was greatest at a distance of 10 mm to the right of the center. On the other hand, after plasma irradiation for 60 s, the ratio of the change in the peak intensity of C 1s increased with increasing distance from the center. This finding indicates that the number of C atoms removed from the surface of the Al thin film linearly increased with increasing distance from the center.

The reason for the faster hydrophilization in the peripheral area (≈5–10 mm from the center of the irradiated area) than in the irradiated area (≤≈5 mm from the center of the irradiated area) may be the removal of a large number of C atoms after plasma irradiation for 30 s. As explained before, if it is assumed that C atoms were removed via oxidative decomposition of the organic compounds adsorbed onto the surface of the Al thin film by O3, the concentration of O3 may have been higher in the peripheral area than in the irradiated area.

To confirm this, the O3 concentration distribution was determined using O3 test strips. Figure 11 shows the O3 test strips and a color chart. The O3 concentration was determined by comparing the color of the O3 test strip with that in the color chart. When this O3 test strip is exposed to O3, the color turns brown. As shown in Fig. 11(a), the O3 test strips were white before irradiation. After plasma irradiation for 60 s [Fig. 11(b)], a light-brown ring with an outer diameter of ≈20 mm and an inner diameter of ≈10 mm appeared; the peripheral area of the ring was also very light brown. The concentration of O3 was low inside the ring; it was the highest (90–150 µg/m²) on the ring itself and <90 µg/m² outside the ring. From this finding, our prediction that the concentration of O3 would be low in the irradiated area and high in the peripheral area was confirmed.

From the above findings, the reason for the faster hydrophilization in the peripheral area than at the center is the high concentration of O3 in the peripheral area.

IV. CONCLUSIONS

An atmospheric-pressure Ar plasma jet (diameter, 6 mm) was generated at a frequency of 10 kHz, an applied voltage of 4 kV, and an Ar gas flow rate of 10 L/min. An Al thin film vacuum-deposited on a glass substrate was irradiated with the atmospheric-pressure Ar plasma jet in air for 10–60 s at an irradiation distance of 2 mm. The surface of the Al thin film was hydrophilized in a circular shape; the diameter of the circle increased from ~16 to ~23 mm with increasing plasma irradiation time. The contact angle of water on the surface decreased from 55 to 10° after plasma irradiation for 60 s, indicating that the surface of the Al thin film became superhydrophilic. The results of SPM indicate that the surface of the superhydrophilized Al thin film was not damaged by plasma jet irradiation. It was found that the peripheral area became superhydrophilic faster than the irradiated area on the Al thin film. On the basis of the obtained XPS spectra, the hydrophobic organic compounds adsorbed on the surface of Al thin film are considered to have been removed by...
the O$_3$ generated as a result of the interaction between the plasma and O$_2$ molecules in air. The measurement of the O$_3$ concentration distribution using O$_3$ test strips revealed that the reason for the faster superhydrophilization in the peripheral area than in the irradiated area was the high O$_3$ concentration (90–150 µg/m$^3$) in the peripheral area.

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