Open-air-type Ar + H2O plasma treatment of polytetrafluoroethylene for improving Ag/PTFE adhesion strength: application to highly adhesive Ag direct wiring patterns

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We performed an open-air-type plasma treatment of polytetrafluoroethylene (PTFE) at atmospheric pressure to increase the adhesion strength between PTFE and an Ag metal film obtained from Ag ink. When PTFE was Ar plasma-treated without H2O addition for 600 s, the coloration of the PTFE surface occurred, and the Ag/PTFE adhesion strength was 0.06 N mm\(^{-1}\). This adhesion strength was the same as that of the as-received PTFE (0.04 N mm\(^{-1}\)). When the PTFE was Ar plasma-treated with the H2O addition of ca. 0.1% for 600 s, coloration did not occur, and the Ag/PTFE adhesion strength increased to 1.03 N mm\(^{-1}\). The effects of H2O addition to the Ar plasma on the Ag/PTFE adhesion strength, surface chemical composition, surface morphology, and the surface hardness were investigated and discussed in this study.

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1. Introduction

In an alternating current circuit, the direction of current flow changes with time; it is equivalent to switching the positive and negative electrodes of a direct current power supply with time. In a printed wiring board (PWB), which consists of a resin substrate and an electrically conducting wire material such as copper (Cu) or silver (Ag), the frequency represents the number of positive and negative electrode switching cycles per second. When the frequency is low, current flows uniformly in the metal wiring. In contrast, when the frequency is high, current does not flow in the central part of the metal wiring because of the generation of eddy currents. At very high frequencies, the current flows only at the air/metal and metal/resin interfaces; this phenomenon is known as the skin effect.\(^{1,2}\) The higher the frequency in a PWB, the greater the amount of information transmitted by a single signal. Consequently, PWBs that operate at even higher frequencies are expected to be developed owing to the increasing the amount of digital data transferred worldwide. However, transmission loss increases with increasing frequency in PWBs; therefore, reducing the transmission loss in PWBs at high frequencies is an ongoing research objective. Using a resin substrate with low relative dielectric constant and low dielectric loss tangent is one of the methods for decreasing the transmission loss in PWBs. Among the resins investigated thus far, polytetrafluoroethylene (PTFE) has shown the lowest relative dielectric constant and the lowest dielectric loss tangent.\(^{3,4}\) PTFE is therefore considered a suitable substrate material for PWBs designed to operate at higher frequencies. However, PTFE is difficult to adhere to other materials because of its low surface energy\(^{5,6}\) and its weak boundary layer (WBL).\(^{7,8}\) Sodium-containing corrosive materials have been used to improve its adhesion property to other materials\(^{9-11}\) because these materials both etch and induce the formation of oxygen-containing functional groups at the PTFE surface. Although the adhesion property of PTFE considerably improves upon treatment in sodium-containing corrosive solutions, its surface roughness also increases. An increase in the surface roughness of the treated PTFE means an increase in the interface roughness between the metal wiring and PTFE in PWBs, which leads to an increase in transmission loss in PWBs at high frequencies because of the skin effect and an extension of the transmission path. Thus, a technique is urgently needed to improve the adhesion property of PTFE for use in PWBs for high-frequency operation, without increasing its surface roughness.

In addition to sodium-containing corrosive solutions, other surface treatment methods based on dry processes have been investigated, including ion-radiation irradiation, ultraviolet (UV) irradiation, electron-beam (EB) irradiation, synchrotron radiation (SR) irradiation, and plasma irradiation. Yumoto et al. used a nitrogen-ion-beam to irradiate PTFE sheet\(^{12-14}\) and determined that the adhesion strength between PTFE and glass-cloth tape using an epoxy-based adhesive increased from 0.02 to 0.9 N mm\(^{-1}\).\(^{14}\) However, to our knowledge, the literature contains no reports that ion-beam irradiation can induce adhesive-free strong adhesion between PTFE and a metal. Murahara and Toyoda have reported that UV light can be used to irradiate a PTFE sheet and that the adhesion strength between the PTFE and a stainless steel plate using an epoxy-based adhesive increased from <0.02 to 12.7 MPa.\(^{15}\) Hopp et al. irradiated a PTFE sheet with UV light and reported that the adhesion strength between PTFE and polymethylmethacrylate (PMMA) using an epoxy-based adhesive increased from ca. 0.03 to ca. 10 MPa.\(^{16}\) However, there is no report that UV light irradiation leads to adhesive-free strong adhesion between PTFE and a metal. Nishi et al. used an EB to irradiate PTFE sheet and reported that the adhesion strength between PTFE and polydimethylsiloxane (PDMS) in the absence of an adhesive increased from <0.0002 to 0.11 N mm\(^{-1}\).\(^{17}\) and that the adhesion strength between PTFE and carbon fiber-reinforced epoxy...
polymer in the absence of an adhesive increased from <0.02 to >0.08 N mm\(^{-1}\).

In these cases, although the adhesive-free adhesion strengths were increased, both adhesion strengths were extremely low. To the best of our knowledge, the literature contains no report of EB irradiation leading to adhesive-free strong adhesion between PTFE and a metal. Okubo et al. have reported that SR irradiation of PTFE sheets leads to enhanced adhesion strength between PTFE and PTFE in the absence of an adhesive; however, they did not report adhesion strengths. To our knowledge, no account of SR irradiation leading to adhesive-free strong adhesion between PTFE and a metal has been reported. Some studies have reported on plasma being used to irradiate PTFE sheet; however, the adhesion strength between the PTFE and metals was low (<0.4 N mm\(^{-1}\)). Ohkubo et al. investigated the simultaneous plasma and heat treatment of PTFE sheet and the adhesion strength between the PTFE and various materials, including epoxy-based adhesives, un-vulcanized isobutylene isoprene rubber (IR), un-vulcanized natural rubber, Ag films, and plasma-treated PDMS. This process is known as heat-assisted plasma (HAP) treatment. Plasma treatment has been reported to result in adhesive-free strong adhesion between PTFE and a metal. Although the HAP treatment realized adhesion strengths of >1 N mm\(^{-1}\), HAP treatment is not an open-air-type plasma treatment, i.e. low process throughput remains a problem with HAP treatment.

Improving the process throughput of the HAP process requires a transition from conventional plasma treatment in an evacuated chamber to open-air-type plasma treatment. To our knowledge, the literature contains no reports of a drastic improvement of the adhesion property of PTFE (e.g. adhesion strength between PTFE and other materials to be greater than 1 N mm\(^{-1}\)) using an open-air-type plasma treatment. We previously performed open-air-type plasma treatment with the microaddition of oxygen or hydrogen gas. Although the surface roughness remained almost unchanged, the adhesion strength between PTFE and an Ag film, which was prepared by sintering a Ag salt ink, was 0.64 N mm\(^{-1}\). This value is insufficient for use in practical industrial applications because the Ag/PTFE adhesion strength was less than the target value of 0.70 N mm\(^{-1}\), which is the Japan Electronics Packaging and Circuits Association (JPCA) standard value. In some cases, 0.8 or 0.9 or 1.0 N mm\(^{-1}\) is set up as the target value of PCBs by some companies. In summary, >1 N mm\(^{-1}\) is a sufficiently high value in PCB industries. We therefore investigated the possibility of further improving the Ag/PTFE adhesion strength via the addition of a small amount of gas to the main gas of Ar. When O\(_2\) gas was added to the Ar gas, the adhesion strength decreased to 0.00 N mm\(^{-1}\) with increasing oxygen concentration. Oxygen molecules in the Ar plasma are transformed to oxygen atoms, which demonstrate high etching performance for PTFE. Thus, the surface of the PTFE excessively etched with oxygen atoms in plasma looking similar to an untreated PTFE surface, exhibiting poor adhesion properties. When H\(_2\) gas was added to the Ar gas, the adhesion strength increased from 0.06 to 0.55 N mm\(^{-1}\). Hydrogen molecules in Ar plasma are transformed to atomic H. The H atoms reacted with carbon radicals, resulting in the formation of C–H bonds. Although C–F bonds on the PTFE surface were converted to C–H bonds, the adhesion strength was still poor. We speculated that C–OH bonds are necessary for improving the Ag/PTFE adhesion strength further. Furthermore, we speculated that the addition of H\(_2\)O vapor to the main Ar gas would improve the adhesion property of PTFE because OH radicals (OH\(^{−}\)), OH\(^{+}\), and OH\(^{·}\) are formed in the plasma containing H\(_2\)O vapor. However, these previously reported articles do not address the effect of H\(_2\)O addition to inert gas on the adhesion property of PTFE. Van Deynze et al. previously reported the influence of Ar + H\(_2\)O plasma for improving the wettability of polyethylene (PE), but they also did not address adhesion properties. In a similar study, Rodriguez-Santiago et al. reported the addition of H\(_2\)O vapor to the main He gas for improving the adhesion property of PTFE. In this case, the adhesion property of PTFE was improved, but the adhesion strength between PTFE and the urethane adhesive was <0.4 N mm\(^{-1}\), which is unsatisfactory. We speculated that a low adhesion strength was obtained in this case because they did not consider air contamination (air has an O\(_2\) content of ca. 20%). We confirmed that air contamination adversely affects the adhesion property of PTFE. Therefore, in the present study, for improving the adhesion property of PTFE and achieving >1 N mm\(^{-1}\) of Ag/PTFE adhesion strength using open-air-type plasma treatment equipment, we added H\(_2\)O vapor to the main Ar gas without O\(_2\) gas to increase the formation of C–OH bonds while avoiding excessive etching. The relationship among plasma treatment conditions and adhesion property was listed in Table I.

### Table I. Relationship among plasma treatment conditions and adhesion property.

| Gas species | Heating | Open-air-type | Air contamination | Adhesion | References |
|-------------|---------|---------------|-------------------|----------|------------|
| He          | No      | No            | No                | <0.2 N mm\(^{-1}\) | 23–27      |
| He          | Yes     | No            | No                | >1.0 N mm\(^{-1}\) | 23–27      |
| He + H\(_2\)O | No     | Yes           | Yes               | 0.2–0.7 N mm\(^{-1}\) | 33         |
| He + Air(H\(_2\)O) | No     | Yes           | Yes (purposely)   | No data | 31         |
| He + Air(H\(_2\)O) | Yes    | No            | Yes (purposely)   | <0.2 N mm\(^{-1}\) | 34         |
| Ar          | No      | Yes           | No                | <0.2 N mm\(^{-1}\) | 28         |
| Ar + O\(_2\) | No      | Yes           | No                | <0.2 N mm\(^{-1}\) | 28         |
| Ar + H\(_2\) | No      | Yes           | Yes               | 0.2–0.7 N mm\(^{-1}\) | 28         |
| Ar + H\(_2\) | No      | Yes           | No                | No data | 30, 32     |
| Ar + H\(_2\)O | No     | Yes           | No                | This work | This work |
| Ar + H\(_2\)O | Yes    | Yes           | No                | No data | No report  |

2. Experimental methods

2.1. Plasma treatment

Rolled PTFE sheets with a width of 300 mm and thickness of 0.2 mm (NITOFLON® No. 900UL, Nitto Denko, Japan) were
cut to dimensions of 140 mm × 200 mm and used as fluoropolymer samples. Prior to plasma treatment, the PTFE sheets were washed with acetone (99.5%, Kishida Chemical, Japan) and pure water using an ultrasonic bath (US-4R, AS-ONE, Japan) for 1 min, respectively. The washed PTFE sheets were dried by a gun-type air blower with N₂ gas (99.99%, Iwatani Fine Gas, Japan).

The washed and dried PTFE samples were then plasma-treated using an open-air-type plasma treatment system (AP-T05-L150, SEIKISUI CHEMICAL, Japan) with a pulsed bipolar power supply. The pulse frequency was fixed at 30 kHz. Two process gases—pure Ar (99.99%, Iwatani Fine Gas, Japan) and Ar + H₂O (H₂O concentration: 0.1%–0.35%)—were used in this study. The total gas flow rate was maintained at 151 min⁻¹, and the concentration of H₂O was controlled by constant adjustment using a float-type area flow meter (RK1500–15-D, KOFLOC, Japan). The gas mixtures were made from pure Ar, to which H₂O gas was added using a mass flow meter (FC-770AC and FC-260E, Hitachi Metals, Japan). The dew point at the Ar + H₂O gas line was measured using an electrostatic-capacity-type dew point meter (TK-100, TEKHNE, Japan). The saturated water vapor pressure E was calculated using Eq. (1), which is known as Temtens’s formula.35

\[ E = \frac{107.5t}{237.3 + t} \]  

(1)

The amount of moisture M was calculated by dividing the saturated water vapor pressure E by the ambient environmental pressure E′:

\[ M = \frac{E}{E'} \times 100. \]  

(2)

When the Ar + H₂O plasma treatment was performed, the applied voltage was 107 V (output voltage of 10.7 kV·p−p), and the applied current was 2.10 A (output current of 0.80 A). When the pure Ar plasma treatment was performed, the applied voltage was 80 V (output voltage of 8.0 kV·p−p), and the applied current was 1.77 A (output current of 0.76 A). The reason for different plasma conditions between the pure Ar plasma and the Ar + H₂O plasma treatments was both to preserve a stable glow discharge and to prevent streamer discharge. Prior to plasma treatment, Ar gas was flowed into the plasma irradiation area for 60 s to decrease the oxygen concentration from >210 000 to 50 ppm or lower because a high oxygen concentration during plasma treatment has been reported to lead to poor adhesion properties of PTFE via high etching speed.34 The oxygen concentration at the plasma irradiation area was confirmed using a zirconia-type oxygen densitometer (LC-300, Toray Engineering, Japan). The oxygen concentration at the plasma irradiation area was confirmed to be <20 ppm, as shown in the Fig. A-1.

To obtain optical emission spectroscopy (OES) spectra during plasma treatment, a combination of a multichannel spectrometer (HR-4000CG-UV-NIR, Ocean Optics, USA) and a light fiber (P400-2-VIS/NIR, Ocean Optics, USA) was used. The measurement range was 200–1100 nm, and the measurement period was 1 s. We confirmed that the peak indexed to OH radicals appeared at 309 nm when H₂O was added to the main Ar gas, as shown in the Fig. B-1.

### 2.2. Formation of Ag film on PTFE

Ag salt ink (AC-3I, NOF, Japan) was used to form an Ag metal film on a PTFE sheet. Prior to use, the Ag ink was filtered using a disposable syringe (2-4031-01, AS-ONE, Japan) with a syringe filter (13CFP202AN, Advantec, Japan). A plasma-treated PTFE sheet was fixed onto a silicon (Si) wafer using a polyimide double-sided tape. The plasma-treated PTFE sample on a Si wafer was attached to a spin coater (1H-D7, Mikasa, Japan) with a vacuum chuck. The filtered Ag ink (0.40 ml) was dropped onto the plasma-treated PTFE sample. The Ag ink was spread using a two-stage rotation process; the plasma-treated PTFE sample was thus uniformly coated with the Ag ink film. In the first stage, the rotation speed was 200 rpm, and the rotation period was 10 s. In the second stage, the rotation speed was 2000 rpm, and the rotation period was 10 s. The Ag ink on the plasma-treated PTFE sample was sintered using a ceramic heater (HHP-170D, AS-ONE, Japan) at 120 °C for 10 min. Finally, an Ag metal film with a thickness of 100–200 nm was formed on the plasma-treated PTFE samples.

When Ag wiring patterns were formed on the plasma-treated PTFE sample, an inkjet printer (DMP-2831, FUJIFILM, Japan) was used instead of a spin coater.

### 2.3. Characterization

The adhesion strengths between the Ag metal film and the plasma-treated PTFE sample were measured using a 90° peel test. The as-formed Ag metal film was too thin to peel off; therefore, a two-component epoxy-based adhesive (epoxy resin AV-138 and hardener HV-998, mass ratio of AV-138/HV-998 = 5/2, Nagase Chemtex, Japan) was used as an interlayer between the Ag metal film and the support material (stainless steel square bar, 5 mm × 160 mm × 10 mm). We prepared adhesion test samples as follows. The Ag surface of an Ag/PTFE sample with a width of ca. 10 mm was adhered to two stainless steel square bars using an epoxy-based adhesive and heated at 80 °C for 30 min using a hotplate (HHP-170D, AS-ONE, Japan). Thus, an adhesion test sample comprised four layers: the plasma-treated PTFE film, an Ag metal film, an epoxy-based adhesive, and a stainless steel bar. The stainless steel bar of the adhesion test sample was fixed to an electrically driven test stand (MX-500N, IMADA, Japan), and the PTFE film was peeled off at a sweep rate of 30 mm min⁻¹. The tensile strength was measured using a commercially available peel tester (ZP-200, IMADA, Japan). The adhesion strength was calculated by dividing the tensile strength by the width of the Ag/PTFE samples (ca. 10 mm). Six samples for each plasma condition were prepared under each set of the same condition, and then the average of the values for the six samples was calculated as the Ag/PTFE adhesion strength. All error bars show the standard error of the mean of n = 6. The standard intervals are 95%.

To investigate the change in the chemical bonding state of the PTFE samples plasma-treated with or without H₂O addition, Cls-XPS spectra were obtained between 280 and 296 eV using a scanning ESCA microprobe system (Quantum 2000, ULVAC-PHI, Japan) attached to an Al-Kα X-ray source with a 45° take-off angle. The binding energies of as-received and plasma-treated PTFE were corrected to the peak indexed to −CF₂−CF₂− at 292.5 eV36,37 and
agad the mean value of more than 50 indentation hardness measurements.

3. Results and discussion

3.1. Difference in Ar and Ar + H2O plasma treatments

Figure 1 shows the Ag/PTFE adhesion strength of the PTFE samples plasma-treated with or without H2O addition. The Ag/PTFE adhesion strength of the Ar plasma-treated PTFE sample (0.06 N mm\(^{-1}\)) was approximately the same as that of the as-received PTFE sample (0.04 N mm\(^{-1}\)). However, the Ag/PTFE adhesion strength of Ar + H2O plasma-treated PTFE sample was greater than 1 N mm\(^{-1}\), which is sufficient for use in practical industrial applications. Figure 2 shows the Ag wiring patterns on the Ar + H2O plasma-treated PTFE sample using an inkjet printer.

Ag wiring patterns on the Ar + H2O plasma-treated PTFE sample were not peeled off from the surface of the Ar + H2O plasma-treated PTFE at all when the PTFE sample was repeatedly bent from ca. 90° to >150° by hand 10 times. The effect of adding H2O to the Ar plasma on the adhesion strength was clear.

To clarify the reasons for the difference in the Ag/PTFE adhesion strength between Ar and Ar + H2O plasma treatments, we examined the plasma-treated PTFE surfaces. First, the coloration of the plasma-treated PTFE surface was observed. Figure 3 shows the photographs of PTFE samples before and after plasma treatment. Although reddish-yellow coloration was observed for the Ar plasma-treated PTFE surface, no such coloration was observed when Ar + H2O was used for the plasma treatment. We previously observed that the coloration occurred because the plasma-treated PTFE surface was covered with a reddish-yellow deposition layer of CxFy monomers and/or polymers. The deposition layer was readily peeled from the PTFE sheet, i.e., this deposition layer decreased the Ag/PTFE adhesion strength. Because of the coloration, an extremely low Ag/PTFE adhesion strength was obtained for the Ar plasma-treated PTFE sample. The addition of H2O prevented the deposition, resulting in an extremely high Ag/PTFE adhesion strength for the Ar + H2O plasma-treated PTFE sample.

Second, the surface chemical composition of the plasma-treated PTFE surface was examined. Figure 4 shows the C1s-XPS spectra of the PTFE samples plasma-treated with or without H2O addition for 600 s. For the as-received PTFE, only the peak indexed to −CF\(_2\)− at 292.5 eV was detected. In contrast, for the Ar plasma-treated and Ar + H2O plasma-treated PTFEs, oxygen-containing functional groups (O=C=O, O=C=O, C=O) appeared at 290–286 eV. For the Ar plasma-treated PTFE, the intensity of the peak indexed to CF\(_2\) decreased compared with that of the as-received PTFE, and the peak indexed to −CF\(_3\) at 294.1 eV also appeared. For the Ar + H2O plasma-treated PTFE, the intensity of the peak indexed to −CF\(_2\)− decreased, and the peak indexed to −CF\(_3\) at 294.1 eV slightly appeared; however, the intensity of the peak indexed to −CF\(_3\) for the Ar + H2O plasma-treated PTFE was lower than that of the
peak indexed to $-\text{CF}_2-\text{CF}_2-$ for Ar plasma-treated PTFE. These results indicate that H$_2$O addition to Ar plasma prevented the deposition of F atoms and C$_x$F$_y$ monomers and/or polymers because H atoms and/or OH radicals, which were generated from H$_2$O dissociation in the Ar plasma, reacted with C$_x$F$_y$ radicals such as ·CF$_3$ and ·C$_2$F$_5$, as shown in Fig. 5.

Third, the surface morphology of the plasma-treated PTFE was observed. Figure 6 shows the SEM images of the PTFE samples with or without Ar plasma treatment and with or without H$_2$O addition for 600 s. For the as-received PTFE, numerous cutting scratches and pits are observed [Fig. 6(a)]. This result indicates that as-received PTFE has a WBL, which is introduced to the PTFE surface during the cutting process. For the Ar plasma-treated PTFE, the number of cutting scratches and pits decreased, but some remained. Moreover, the surface roughness apparently decreased because of the deposition of C$_x$F$_y$ monomers and/or polymers [Fig. 6(b)]. For the Ar + H$_2$O plasma-treated PTFE, no cutting scratches or pits were observed [Fig. 6(c)]. These results indicate that the addition of H$_2$O to the Ar plasma promoted both the removal of the WBL and the prevention of deposition of C$_x$F$_y$ monomers and/or polymers.

Figure 7 shows the AFM images of the PTFE samples with or without Ar plasma treatment and with or without H$_2$O addition for 600 s. The surface roughness of both the Ar plasma-treated and Ar + H$_2$O plasma-treated PTFE was lower than that of the as-received PTFE; however, the change on the surface morphology differed between Ar plasma-treated and Ar + H$_2$O plasma PTFE surfaces. In the case of PTFE Ar plasma-treated without the H$_2$O addition for 600 s, the surface was smooth, and fine protuberances were not
observed. The surface without fine protuberances was apparently obtained because of the deposition of CₓFᵧ monomers and/or polymers. When Ar was plasma-treated with H₂O addition for 600 s, fine protuberances were observed; however, the surface roughness slightly decreased compared with that of the as-received sample. This result indicates that surface roughness was not a critical point for a drastic increase in the Ag/PTFE adhesion strength.

Lastly, the surface hardness of the plasma-treated PTFE was evaluated. Figure 8 shows the histograms of the surface hardness of the PTFE samples with or without Ar plasma treatment and with or without H₂O addition for 600 s. The surface hardness of the as-received PTFE was the lowest, which indicated that WBL existed on the PTFE surface before plasma treatment. The surface hardness increased from <110 MPa to >150 MPa via Ar plasma treatment with or without H₂O addition. The difference in surface hardness between the Ar plasma-treated and the Ar + H₂O plasma-treated PTFE surfaces was low. This result indicates that H₂O addition did not affect the etching rate of PTFE or the surface hardness, i.e., these results indicate that metastable-excited Ar atoms play a role in etching the WBL of the PTFE surface.

3.2. Influence of plasma treatment time on Ag/PTFE adhesion strength

Figure 9 shows the relationship between plasma treatment time and Ag/PTFE adhesion strength of the Ar + H₂O plasma-treated PTFE samples. When the plasma treatment time was <300 s, the Ag/PTFE adhesion strengths were less than the target value of 0.70 N mm⁻¹, which is the JPCA standard value. When the plasma treatment time was >600 s, the Ag/PTFE adhesion strengths were much greater than 0.70 N mm⁻¹. These results indicate that the Ag/PTFE adhesion strength increased with increasing plasma treatment time and saturated for more than 600 s. In previous reports, PTFE was found to exhibit poor adhesion when WBL remained on the PTFE surface. PTFE with a WBL
requires sufficient time for etching and/or recovery of the WBL. In the present study, sufficient etching and/or recovery of the WBL required more than 600 s.

3.3. Influence of H2O concentration on the Ag/PTFE adhesion strength

Figure 10 shows the relationship between flow rate of Ar+H2O gas and Ag/PTFE adhesion strength of the Ar+H2O plasma-treated PTFE sample. When the flow rate of the Ar+H2O gas mixture was 1, 3, and 5 l min⁻¹, and the H2O concentrations were 0.10%, 0.23%, and 0.35%, respectively. All of the Ag/PTFE adhesion strengths of Ar+H2O plasma-treated PTFE samples reached greater than 0.70 N mm⁻¹, which is the JCPA standard value ²⁹) for application to PCBs. However, the Ag/PTFE adhesion strengths of Ar+H2O plasma-treated PTFE samples decreased with increase in flow rate of Ar+H2O gas, i.e. Ag/PTFE adhesion strengths of Ar+H2O plasma-treated PTFE samples gradually decreased with increasing H2O concentration. We predicted that the consumption rate of applied power for H2O dissociation increased and the consumption rate of applied power for the generation of metastable-excited Ar atoms decreased when the H2O concentration was increased. This result indicates that the addition of excessive H2O to the Ar main gas adversely affects the adhesion property of PTFE and that a suitable H2O concentration exists for achieving the maximum adhesion property of PTFE.

4. Conclusions

We achieved a drastic improvement in the adhesion property of PTFE for an Ag metal film, with a slightly decreased surface roughness of PTFE. The keys to using an open-air-type plasma treatment system were twofold. The first key is preventing contamination by air containing O₂ gas. In this study, the O₂ concentration at the plasma irradiation space was maintained at < 20 ppm because O₂ gas is converted to O atoms in the plasma, which induces excessive etching of the PTFE surface containing a surface-modified layer. The second key is the addition of H2O gas to the Ar plasma. H2O gas is converted into OH and H atoms in the plasma, which results in both prevention from CxFy deposition and formation of C–OH groups. The process developed in this study does not require a vacuum pump or a time-consuming evacuation process, which reduces costs, conserves space, and promotes high throughput. Although the challenge of decreasing the plasma treatment time remains, this study represents an advancement in the practical use of open-air-type plasma treatment.

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Appendix

Figure A·1: Relation between O₂ concentration in the plasma irradiation area and gas flowing time before plasma treatment.

Fig. 9. (Color online) Ag/PTFE adhesion strength of Ar+H2O plasma-treated PTFE samples with different plasma treatment times. The error bar shows the standard error of the mean of n = 6. The standard intervals are 95%.

Fig. 10. (Color online) Ag/PTFE adhesion strength of Ar+H2O plasma-treated PTFE samples with different flow rates of Ar+H2O gas. The error bar shows the standard error of the mean of n = 6. The standard intervals are 95%.

Fig. A·1. (Color online) Relation between O₂ concentration in the plasma irradiation area and gas flowing time before plasma treatment.
Fig. B·1. (Color online) Representative OES spectra of plasma-treated PTFE samples with or without H\textsubscript{2}O addition for 600 s. (a) Ar plasma and (b) Ar + H\textsubscript{2}O plasma. The peaks indexed to C\textsubscript{2}(d-a) disappeared at 400–700 nm, in contrast the sharp peak indexed to OH radicals appeared at 309 nm when H\textsubscript{2}O was added to Ar main gas.

Fig. B·1: Representative OES spectra of plasma-treated PTFE samples with or without H\textsubscript{2}O addition for 600 s.

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