Research Papers

Surface Modification of Fluoropolymer Using Open-Air Plasma Treatment at Atmospheric Pressure with Ar, Ar + O_2, and Ar + H_2 for Application in High-Adhesion Metal Wiring Patterns

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We performed open-air plasma treatment of polytetrafluoroethylene (PTFE) at atmospheric pressure to increase the adhesion strength between PTFE and an Ag metal film formed from Ag ink. Coloration of the PTFE surface occurred during 600 s treatment with Ar plasma. The Ag/PTFE adhesion strength was 0.06 N/mm. To resolve the problem of coloration and to improve the adhesion strength, O_2 or H_2 gas was added. During treatment with Ar + O_2 plasma with O_2 content of 0.33% for 600 s, no coloration occurred but the adhesion strength decreased to zero. During treatment with Ar + H_2 plasma for 600 s, coloration did not occur. Moreover, the adhesion strength increased to 0.25-0.55 N/mm. These results showed that H_2 addition was effective for preventing coloration and improving adhesion strength during long-period plasma treatment. Furthermore, the uniformity of surface treatment with Ar + H_2 plasma was higher than that for Ar plasma.

Keywords : Adhesion, Ag Ink, Atmospheric Plasma Treatment, Polytetrafluoroethylene (PTFE), Printed Circuit Board for High-Frequency

1. Introduction

In recent years, opportunities to process large amounts of data have increased with the development of the information and communications society. Therefore, high-speed communications are in demand, and it is necessary to transmit more digital data interactively. In order to achieve high-speed data transfer, the frequency of digital signals has been increased.[1),2)] In general, an electronic device is manufactured by assembling electronic components such as capacitors and diodes on a printed circuit board (PCB), which involves printing a metal wiring pattern on a resin material.[3)–7)] When an alternating current flows in a metal wiring pattern on a PCB, energy is lost and heat is generated. The lower are the dielectric constant and the dielectric tangent loss of the resin substrate used as the resin material in a PCB, the smaller the energy loss becomes. Epoxy resin containing glass fibers has been used as a resin substrate for PCBs, but there has been concern about its undesirable influence on the performance of devices owing to the generation of heat in the presence of digital signals with high frequencies such as the GHz region.[8)–13)] Therefore, attention has been focused on polytetrafluoroethylene (PTFE), which has the lowest dielectric constant and dielectric tangent loss of any material.[14)–16)] However, PTFE has poor adhesion properties owing to its low surface energy, which is caused by the abundance of C-F bonds, and it is thus difficult to manufacture a metal wiring pattern with high adhesion to PTFE.[17),18)] Surface treatment of PTFE is essential to improve the strength of adhesion between a PTFE substrate and a metal wiring pattern.

Surface treatment by wet etching involving Na metal has been performed on PTFE as a conventional method, which could improve its adhesion properties for two reasons: the introduction of hydrophilic functional groups onto the PTFE surface via the removal of fluorine atoms by metallic Na and an anchoring effect due to an increase in surface roughness. However, methods using corrosive solutions containing sodium (Na) such as Na-naphthalene and Na-NH_3 complexes have two disadvantages, of which the first comprises the negative effects on the environment that arise because the corrosive solutions are used. The second disadvantage is an increase in transmission losses because of the increase in interfacial roughness between PTFE and metal wiring, in particular in the case of high-frequency signals.[19)–21)]

Surface treatment based on plasma irradiation of fluoropolymers has been considered against such a background.[22)–27)] Plasma is used for dry etching at low pressure, which involves some drawbacks, namely, the need for bulky processing equipment and vacuum exhaust systems and low throughput. Therefore, the use of plasma at atmospheric pressure has attracted attention in recent years.[28)–33)] In addition, direct patterning of metal wiring using metal inks and/or pastes has been studied and developed instead of conventional processes such as electroless copper plating and photolithography to decrease the number and duration of the stages in PCB manufacture.[34)–40)] Therefore, we suggest a process that combines open-air plasma treatment at atmospheric pressure and the formation of a metal film on a PTFE sheet using a metal ink. **Fig. 1** shows a schematic diagram of the entire process flow, which consists of four steps: 1) the formation of C radicals by cleaving C-F bonds on a PTFE surface upon plasma irradiation at atmospheric pressure; 2) the formation of peroxy radicals on the PTFE surface by exposure to air; 3) the coating of the PTFE surface with Ag ink using a spin coater; and 4) the formation of an Ag ink film on PTFE by heating and sintering the Ag ink. By this process, we can modify a PTFE surface without damaging it or increasing its surface roughness and can increase the strength of adhesion between the plasma-treated PTFE and the Ag ink film. In addition, the process avoids the use of vacuum equipment

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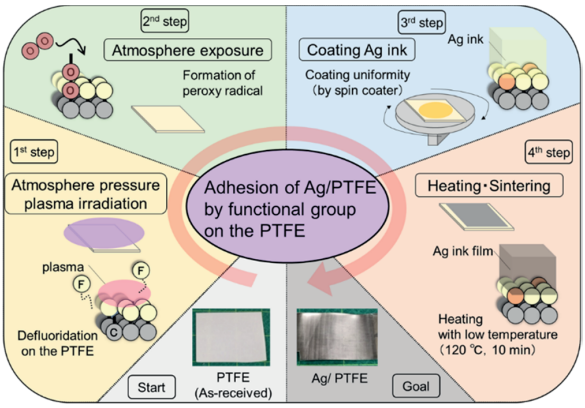

Fig. 1 Process of plasma treatment and metalization of PTFE, which includes four steps: (1) plasma irradiation at atmospheric pressure, (2) atmospheric exposure, (3) coating with Ag ink, and (4) heating and sintering.

by carrying out open-air plasma treatment at atmospheric pressure. Open-air plasma treatment is compatible with roll-to-roll systems, which would lead to high throughput, and represents a major advantage for industrial applications. However, we have not achieved the high adhesion strength necessary for applications in electronic devices, and we will therefore study to further increase the adhesion strength of Ag/PTFE.

In this study, we experimented with the use of three kinds of process gas, namely, Ar, Ar + O_2, and Ar + H_2, in atmospheric-pressure plasma irradiation, because changes in the active species generated in plasma have a major influence on plasma treatment. We also investigated the plasma-treated PTFE surfaces to determine the differences in surface modification that resulted from the addition of very small amounts of O_2 and H_2 to the Ar gas used for plasma irradiation. Then we aimed to increase the adhesion strength of Ag/PTFE.

2. Experimental Section

2. 1 Samples

PTFE sheets (NITOFLON® No. 900UL, Nitto Denko, Japan; thickness: 0.2 mm, roll width: 300 mm) were cut to dimensions of 140 mm × 200 mm and used as samples. The sheets were cleaned with acetone (99.5%, Kishida Chemical, Japan) and pure water in an ultrasonic bath (US-4R, AS-ONE, Japan) for 1 min in each case and then dried using an air blower with N_2 gas (99.99%, Iwatani Fine Gas, Japan) before plasma treatment.

2. 2 Open-air Plasma Treatment

2. 2. 1 Plasma Treatment Equipment

The PTFE samples were treated with plasma using an open-air plasma treatment system (AP-T05-L150, Sekisui Chemical, Japan). The plasma source was generated using a pulsed bipolar power supply. The pulse frequency was 30 kHz, and the voltage was 8 kVp-p. In this study, three kinds of process gas, namely, pure Ar (99.99%, Iwatani Fine Gas, Japan), Ar + O_2 (O_2: 0-0.67%, Iwatani Fine Gas, Japan), and Ar + H_2 (H_2: 0-3.0%, Iwatani Fine Gas, Japan), were used. The total gas flow rate was maintained at 15 L/min and the concentrations of O_2 and H_2 were 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 O_2 or H_2 gas was added using a mass flow meter (FC-770AC, FC-260E, Hitachi Metals, Japan).

2. 2. 2 Optical Emission Spectroscopy

Optical emission spectra were recorded during plasma treatment using a multichannel spectrometer (HR-4000CG-UV-NIR, Ocean Optics, USA) with a wavelength resolution of 0.02 nm and a light fiber (QP400-2-VIS/NIR, Ocean Optics, USA). The measurement range was 200-1100 nm, and the measurement period was 0.25 or 10 s.

2. 3 Formation of Ag Film

2. 3. 1 Spin Coating Method

Ag ink (AC-3I, NOF, Japan) was used to prepare an Ag ink film after being filtered using a plastic disposable syringe (2-4031-01, AS-ONE, Japan) with a syringe filter (13CP020AN, Advantec, Japan). Then 0.40 mL filtered Ag ink was dropped onto the plasma-treated PTFE samples, which were fixed on a Si wafer with polyimide tape before being spin coated. Then the samples were coated with the Ag ink uniformly using a spin coater (1H-D7, Mikasa, Japan) in a two-stage rotation process: in the first stage the rotation speed was 200 rpm and the rotation period was 10 s, and in the second stage the rotation speed was 2000 rpm and the rotation period was 10 s.

2. 3. 2 Sintering of Ag Ink

The PTFE samples coated with Ag ink were heated using a ceramic heater (HHP-170D, AS-ONE, Japan) at 120 °C for 10 min. An Ag ink film with a thickness of about 100-200 nm was formed on the PTFE samples.

2. 4 Measurements of Adhesion Strength

2. 4. 1 Sample Preparation for Peel Test

The adhesion strength between Ag ink films and PTFE samples was measured by a 90° peel test, for which we prepared test samples as follows. Firstly, the Ag surface of an Ag/PTFE sample was adhered to an SUS plate (5 × 160 × 3 mm) using two pack-curing epoxy adhesives (AV138 and HV998, Nagase Chemtex, Japan) and heated at 80 °C for 30 min. In summary, samples comprising four layers, namely, PTFE, an Ag film, epoxy adhesive, and an SUS plate, were prepared, because the Ag film was too thin to peel off. Therefore, the epoxy adhesive was used as an interlayer between the Ag film and the support material (SUS plate).[41)]

2. 4. 2 Peel Test

This test was conducted at a sweep rate of 30 mm/min according to ISO 8510-1 using a commercially available peel tester (ZP-200, IMADA, Japan) and an electrically driven test stand (MX-500N, IMADA, Japan).[42),43)] In the test, the SUS plate was fixed and the PTFE layer was peeled off. All Ag/PTFE adhesion strengths were calculated as the average of the values for six samples under each set of conditions.

2. 5 Sample Analysis

2. 5. 1 Photographic Images of Samples

Images of the sample surfaces were taken with a digital camera (Coolpix P510, Nikon, Japan) before and after plasma treatment.

2. 5. 2 X-ray Photoelectron Spectroscopy

The chemical compositions of untreated and plasma-treated PTFE samples were investigated by X-ray photoelectron spectroscopy (XPS; Quantum 2000, ULVAC-PHI, Japan) using an Al Kα X-ray source with a take-off angle of 45°. In this study, we recorded the C1s XPS spectra of PTFE samples before and after plasma treatment and investigated the peaks indexed to fluorine (CF_3, CF_2, C-F), oxygen (C=O, C-O), nitrogen (C-N), and carbon (C-C, C-H, C=C) groups. In this analysis, several peaks due to CF_3, CF_2, C-F, O-C=O, C=O, C-O, C-N, and C-C (C-H)

groups appeared at 293.5, 291.8, 289.8, 289.2, 288.0, 286.5, 286.3 and 284.6 eV, respectively.[44),45)]

2. 5. 3 Surface Morphology

The morphology of the PTFE surfaces was observed using atomic force microscopy (AFM; SPM-9700, Shimadzu, Japan), which was performed before and after irradiation with Ar or Ar + O_2 plasma in dynamic mode with a Si cantilever. The measured areas had dimensions of 10 μm × 10 μm.

2. 5. 4 Electron Spin Resonance Measurements

Peroxy radicals that formed on the plasma-treated PTFE surface were characterized using an electron spin resonance (ESR) spectrometer (JES-FA100, JEOL, Japan) in the X-band at room temperature. The microwave power was 10 mW, the applied frequency was set to 10 GHz, and the measurement range extended from 329 to 341 mT. The radical density ratio was calculated by double integration of the spectrum. The g-value was measured by comparison with the fourth signal of Mn^{2+} ions in MgO, which was used as a reference and had a g-value of 1.981.[46),47)]

2. 5. 5 Surface Wettability

The wettability of PTFE surfaces before and after plasma irradiation was determined by measuring the static contact angle using a water contact angle tester (Drop Master 300, Kyowa Interface Science, Japan). Samples of 3.0 μL pure water were dropped onto 15 different points on each sample. The water contact angle was calculated as the average of the values for 13 points, excluding the maximum and minimum values.

3. Results and Discussion

3. 1 Treatment with Ar Plasma

3. 1. 1 Sample Coloration and Analysis of Its Causes

Fig. 2 (a) shows the C1s-XPS spectra of PTFE surfaces treated with Ar plasma for different irradiation periods. **Table 1** shows the atomic percentages of PTFE surfaces before and after irradiation with Ar plasma. The intensity of the peak indexed to CF_2 groups (291.8 eV) in **Fig. 2** (a) decreased with an increase in the plasma irradiation period. This showed that fluorine was desorbed from the PTFE surfaces upon plasma irradiation. Peaks indexed

Table 1 Atomic percentages of PTFE surfaces before and after irradiation with Ar, Ar + O_2, Ar + H_2 plasma determined by survey XPS spectra. In Ar plasma treatment, the voltage was 8.0 kVp-p and the electrode gap was 0.5 mm. In Ar + O_2 plasma treatment, the plasma irradiation period was fixed at 600 s, the voltage was 6.0 kVp-p, and the electrode gap was 1.0 mm. In Ar + H_2 plasma treatment, the plasma irradiation period was fixed at 600 s, the voltage was 8.0 kVp-p, and the electrode gap was 0.5 mm. The atomic percentages were calculated using MultiPak 8.2 software (ULVAC-PHI, Japan).

		C (%)	N (%)	O (%)	F (%)	N/C	O/C	F/C
As-received		32.56	0.03	0.29	67.12	0.001	0.009	2.1
Plasma-treated	1 a)	36.24	0.31	1.26	62.19	0.009	0.035	1.7
(Ar)	10 a)	38.98	0.47	1.01	59.54	0.012	0.026	1.5
	20 a)	38.63	0.98	1.00	59.40	0.025	0.026	1.5
	60 a)	40.78	1.53	1.16	56.53	0.038	0.028	1.4
	600 a)	37.95	0.67	0.83	60.54	0.018	0.022	1.6
Plasma-treated	0.00 b)	43.40	1.94	1.67	52.98	0.045	0.038	1.2
(Ar + O_2)	0.0067 b)	45.10	2.88	2.29	49.72	0.064	0.051	1.1
	0.033 b)	48.30	3.35	2.83	45.51	0.069	0.059	0.9
	0.067 b)	46.78	3.47	3.07	46.68	0.074	0.066	1.0
	0.33 b)	32.19	0.15	0.11	67.56	0.005	0.003	2.1
	0.67 b)	32.05	0.09	0.10	67.75	0.003	0.003	2.1
Plasma-treated	0.00 c)	46.01	1.83	1.68	50.47	0.040	0.037	1.1
(Ar + H_2)	0.05 c)	83.66	0.86	4.63	10.84	0.010	0.055	0.1
	0.20 c)	70.91	0.70	5.13	23.26	0.010	0.072	0.3
	0.50 c)	65.59	0.41	4.54	29.47	0.006	0.069	0.4
	1.50 c)	64.04	0.20	4.06	31.70	0.003	0.063	0.5
	3.00 c)	63.58	0.00	4.13	32.28	0.000	0.065	0.5

a) Treatment period (s), b) O_2 content (%), c) H_2 content (%)

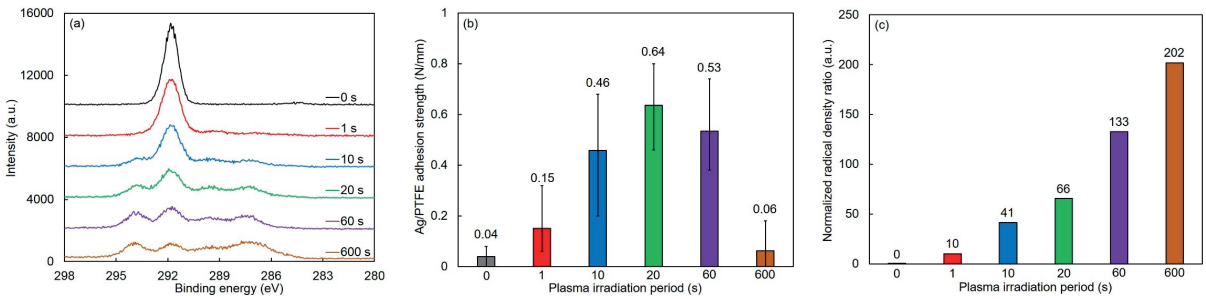

Fig. 2 (a) C1s-XPS spectra of PTFE surfaces before and after irradiation with Ar plasma. (b) Ag/PTFE adhesion strengths for different Ar plasma irradiation periods. (c) The corresponding normalized radical density ratios. We calculated the relative amount of peroxy radicals with reference to PTFE sheets treated with Ar plasma for 10 s. The voltage was 8.0 kVp-p, and the electrode gap was 0.5 mm.

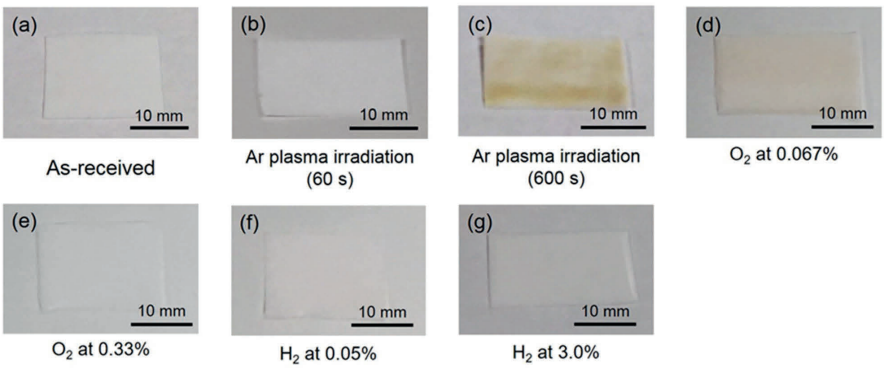

Fig. 3 Photographs of plasma-treated PTFE surfaces: (a) as-received, treatment with Ar plasma for (b) 60 s and (c) 600 s at a voltage of 8.0 kVp-p with an electrode gap of 0.5 mm, treatment with Ar plasma with an O_2 content of (d) 0.067% and (e) 0.33% for a period of 600 s at a voltage of 6.0 kVp-p with an electrode gap of 1.0 mm, and treatment with Ar plasma with an H_2 content of (f) 0.05% and (g) 3.0% for a period of 600 s at a voltage of 8.0 kVp-p with an electrode gap of 0.5 mm.

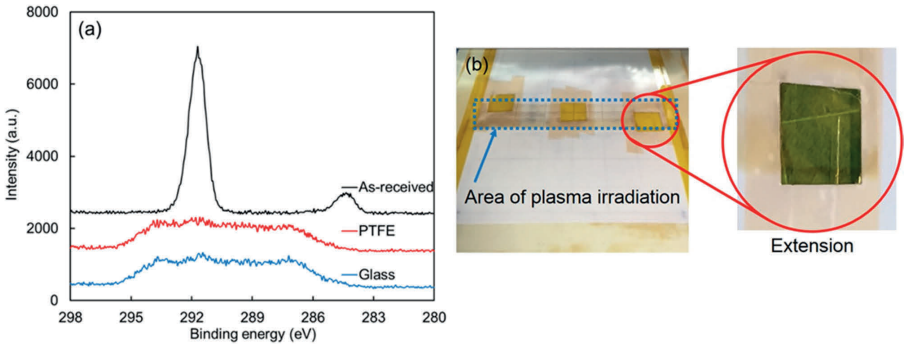

Fig. 4 (a) C1s-XPS spectra and (b) photographs of the surfaces of glass samples used for studying plasma deposition. The plasma irradiation period was 1200 s, the voltage was 8.0 kVp-p, and the electrode gap was 1.0 mm.

to CF_3, O-C=O, C=O, C-O, and C-N groups appeared at 293.5, 289.2, 288.0, 286.5, and 286.3 eV, respectively, for the plasma-treated PTFE surfaces. These peaks increased in intensity with an increase in the plasma irradiation period. In the case of prolonged irradiation with Ar plasma (600 s), the color of the PTFE surface changed from white to reddish-yellow (**Fig. 3** (c)). To discover the reason for this coloration, a glass plate (20 mm × 20 mm × 0.18 mm, 1-9648-02, AS-ONE, Japan) was placed in the cut PTFE sheet and treated with plasma for 1200 s. XPS measurements were then performed on the glass plate. **Fig. 4** (a) shows the C1s-XPS spectra of the glass plate and a PTFE sheet after plasma irradiation for 1200 s. A reddish-yellow coloration was observed on both surfaces (**Fig. 4** (b)), and the C1s-XPS spectra of the glass plate and PTFE sheet had similar shapes. From these results, it was confirmed that the plasma-treated PTFE surface was covered with a reddish-yellow deposition layer. C-N-type deposition involving N=N bonds or C-F-type deposition involving O-F bonds was considered to be the reason for the change in coloration from white to reddish-yellow, according to previous reports.[48)–55)] Emission spectroscopy was also performed during plasma treatment to clarify the reason for the change in coloration. An optical emission spectrum derived from C-F components such as C-N and C_2 was observed in the case of a measurement time of 10 s. Hence, it was thought that an etching reaction occurred on the PTFE surface as a result of treatment with Ar plasma. From these results, it was suggested that three reactions occurred successively when Ar plasma was used to treat PTFE: 1) a polymer and/or monomer consisting of C, F, O, and N atoms was detached from the PTFE surface; 2) this underwent further reactions in the Ar plasma; and 3) precursors of the colored layer, which consisted of C, F, O, and N atoms, were deposited on the PTFE surface.

3. 1. 2 Effect of Coloration of PTFE Surface on Ag/PTFE Adhesion Strength

Fig. 2 (b) shows the adhesion strength of Ag/PTFE samples for different Ar plasma irradiation periods. The maximum adhesion strength was 0.64 N/mm when the irradiation period was 20 s. In addition, the Ag/PTFE adhesion strength increased with an increase in the irradiation period when this was less than 20 s, but decreased with an increase in the irradiation period when this exceeded 20 s. The reasons for the increase and decrease in the Ag/PTFE adhesion strength were considered to be the increase in the amount of peroxy radicals (**Fig. 2** (c)) and the coloration that occurred as a result of deposition, respectively. The latter was because the deposition layer interacted weakly with the base PTFE sheets. In addition, if the irradiation period was prolonged, it is suggested that the thickness of the colored layer would increase and the Ag/PTFE adhesion strength would decrease.

3. 2 Treatment with Ar + O_2 Plasma

3. 2. 1 Influence of Addition of O_2 to Ar Plasma on Chemical Composition of PTFE Surface

To investigate whether coloration of the PTFE surfaces occurred, O_2 was added to the Ar plasma. The voltage was 6.0 kVp-p and the plasma irradiation period was 600 s, because coloration of PTFE occurred when the period of irradiation with pure Ar plasma was 600 s. **Fig. 5** (a) shows the C1s-XPS spectra

of PTFE surfaces treated with Ar + O_2 plasma at different O_2 contents. **Table 1** shows the atomic percentages of PTFE surfaces before and after irradiation with Ar + O_2 plasma. When an O_2 content of less than 0.067% was used, peaks indexed to CF_3, CF_2, O-C=O, C=O, C-O, and C-N groups were observed (**Fig. 5**(a)). In contrast, peaks indexed to CF_3 and CF_2 groups were observed when an O_2 content of greater than 0.33% was used (**Fig. 5**(a)). In addition, the F/C ratio in plasma-treated PTFE when the O_2 content exceeded 0.33% was higher than that in as-received PTFE (**Table 1**). These results suggested that O atoms in the plasma only reacted with C atoms on the PTFE surface, so that the proportion of F atoms increased. This reaction comprised two processes in gas phase, as expressed in the following Equations 1 and 2:

$$C(-F_2) + O \rightarrow CO(-F) \quad \cdots\cdots (1)$$

$$CO(-F) + O \rightarrow CO_2 \quad \cdots\cdots (2)$$

Fig. 6 shows AFM images of PTFE surfaces treated with Ar + O_2 plasma at different O_2 contents. It was confirmed that minute irregularities in shape were formed with an increase in the O_2 content. The surface roughness of plasma-treated PTFE was higher than that of as-received PTFE when the O_2 content exceeded 0.033%. These results indicated that O atoms induced selective etching of C atoms on the PTFE surface so that the F/C ratio increased.

3. 2. 2 Adhesion Strength of PTFE Surface

Fig. 5(b) shows the Ag/PTFE adhesion strength for PTFE samples treated with plasma with different O_2 contents. The adhesion strength decreased with an increase in the O_2 content, and eventually it became impossible to measure the adhesion strength when the O_2 content exceeded 0.33%. **Figs. 3**(d) and **3**(e) show photographs of PTFE surfaces treated with Ar + O_2 plasma with O_2 contents of 0.067% and 0.33%, respectively. Coloration of the PTFE surface was seen at an O_2 content of less than 0.067%, but was not seen when the O_2 content exceeded 0.33%. Preferential etching of C element in the PTFE surface increased with an increase in the O_2 content, so that the amount of adhesive functional groups such as C-O bonds decreased. **Fig. 5**(c) shows

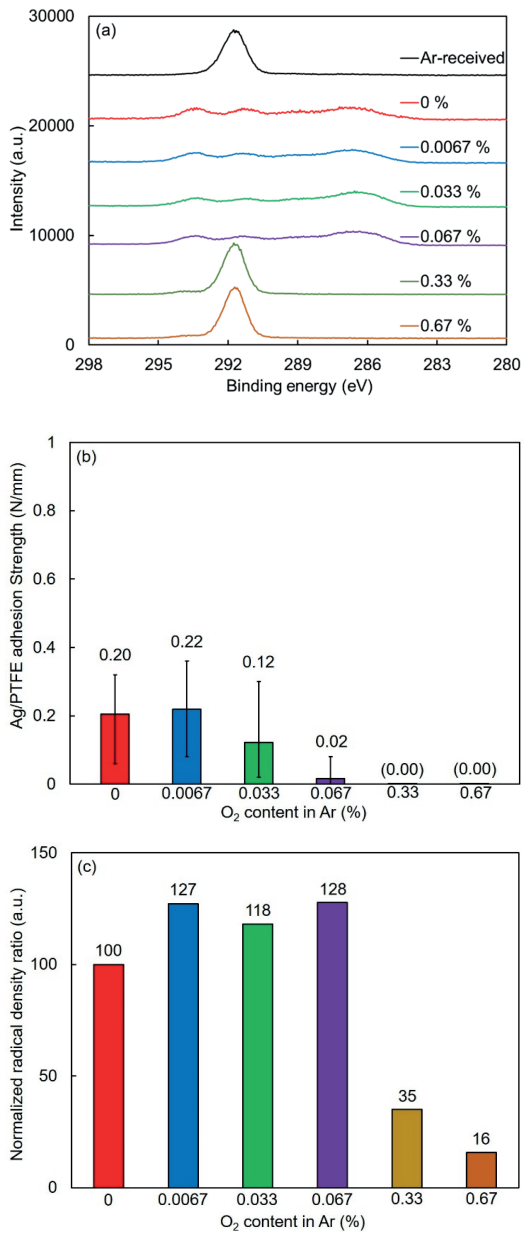

Fig. 5 (a) C1s-XPS spectra of PTFE surfaces before and after irradiation with Ar + O_2 plasma at different O_2 contents. (b) Ag/PTFE adhesion strengths for plasma treatment with Ar with different O_2 contents. (c) The corresponding normalized radical density ratios. We calculated the relative amount of peroxy radicals with reference to PTFE treated with Ar plasma. The plasma irradiation period was fixed at 600 s, the voltage was 6.0 kVp-p, and the electrode gap was 1.0 mm

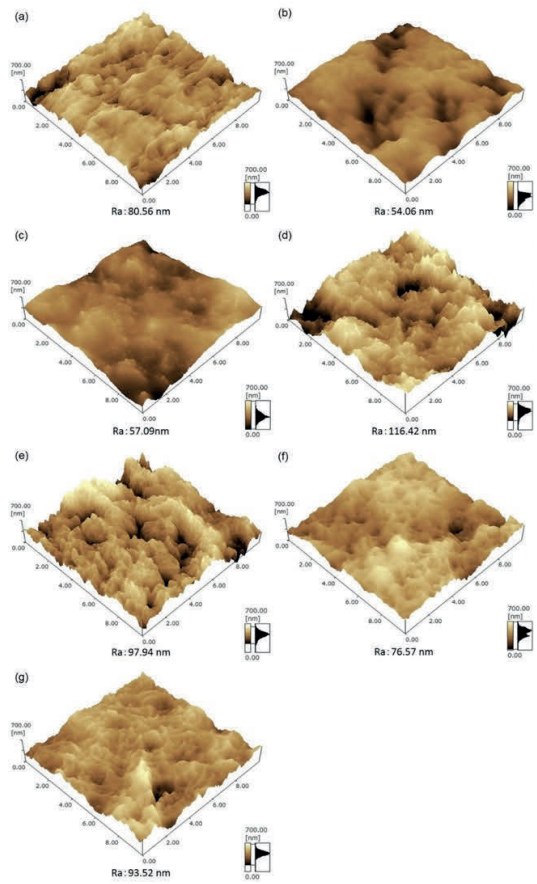

Fig. 6 AFM images of an untreated PTFE surface and PTFE surfaces treated with plasma with different O_2 contents: (a) as-received, (b) 0% O_2, (c) 0.0067% O_2, (d) 0.033% O_2, (e) 0.067% O_2, (f) 0.33% O_2, and (g) 0.67% O_2. The plasma irradiation period was fixed at 600 s, the voltage was 6.0 kVp-p, and the electrode gap was 1.0 mm.

the ESR results for PTFE samples treated with Ar + O_2 plasma with different O_2 contents. The radical density ratio drastically decreased when the O_2 content exceeded 0.33%. From the above-mentioned results, because selective etching of C atoms occurred in the PTFE surface when the O_2 content increased, the number of F atoms became excessive, which would result in a drastic decrease in adhesion strength. These results suggested that it is necessary to ensure lower O_2 contents in the plasma irradiation of PTFE in order to improve its adhesion properties.

3. 3 Treatment with Ar + H_2 Plasma

3. 3. 1 Influence of Addition of H_2 to Plasma

Figs. 3(f) and **3**(g) show photographs of PTFE surfaces treated with Ar + H_2 plasma with H_2 contents of 0.05% and 3.0%, respectively. When H_2 was added to the Ar plasma, no coloration of the plasma-treated PTFE surface was observed. **Fig. 7**(a) shows the C1s-XPS spectra of PTFE surfaces treated with Ar + H_2 plasma with different H_2 contents. **Table 1** shows the atomic percentages of PTFE surfaces before and after irradiation with Ar + H_2 plasma. When the H_2 content was 0%, peaks indexed to CF_3, CF_2, O-C=O, C=O, C-O, and C-N groups were observed (**Fig. 7**(a)). In contrast, peaks indexed to C-F, O-C=O, C=O, C-O, C-C, and C-H groups were observed when the H_2 content exceeded 0.05%. From these results, it was suggested that H_2 molecules dissociated into H atoms in the Ar plasma. The H atoms then reacted with precursors of the colored layer generated by etching with Ar plasma, which inactivated these precursors. In addition, when the H_2 content decreased the C percentage also decreased, but the F percentage increased (**Table 1**). In the case of low H_2 contents, the Ar content increased in the plasma and scission of C-F bonds was likely to occur so that the generation of C radicals increased, which would promote reactions between C radicals and H atoms. In contrast, in the case of high H_2 contents the Ar content decreased in the plasma and the energy available for cleaving C-F bonds decreased, which would decrease the amount of functional groups on PTFE. In summary, the addition of a suitable amount of H_2 was effective in preventing the formation of the fluorine-containing deposits that caused the coloration.

3. 3. 2 Adhesion Strength of PTFE Surface

Fig. 7(b) shows the Ag/PTFE adhesion strength for PTFE samples treated with Ar + H_2 plasma with different H_2 contents. The maximum adhesion strength was 0.55 N/mm when the H_2 content was 0.5%, and it was hence possible to maintain high adhesion strength after plasma treatment for a prolonged period such as 600 s. In addition, upon increases in the H_2 content the adhesion strength increased when the H_2 content was less than 0.5% but decreased when the H_2 content exceeded 0.5%. These results implied that C-H bonds were more likely to be generated on the PTFE surface than C-F bonds when the H_2 content was less than 0.5%. However, C-F bonds were likely to remain on the PTFE surface when the H_2 content exceeded 0.5% because plasma energy would be devoted to the dissociation of H_2 and the scission of C-F bonds would decrease. Hence, it was suggested that high adhesion strength would be achieved in PTFE after prolonged treatment with plasma if the H_2 content were maintained at an appropriate value. **Fig. 7**(c) shows the ESR results for PTFE samples treated with Ar + H_2 plasma with different H_2 contents. The radical density ratio decreased with an increase in the H_2 content. The generation of peroxy radicals consisted of three reactions: (1) the scission of C-F bonds by the Ar plasma; (2) the generation of C radicals; and (3) exposure to air. The reasons for the decrease in the radical density ratio that occurred when the H_2 content increased were the decrease in the scission of C-F bonds by the Ar plasma and the increase in the generation of C-H bonds due to the increase in the H content in the Ar plasma.

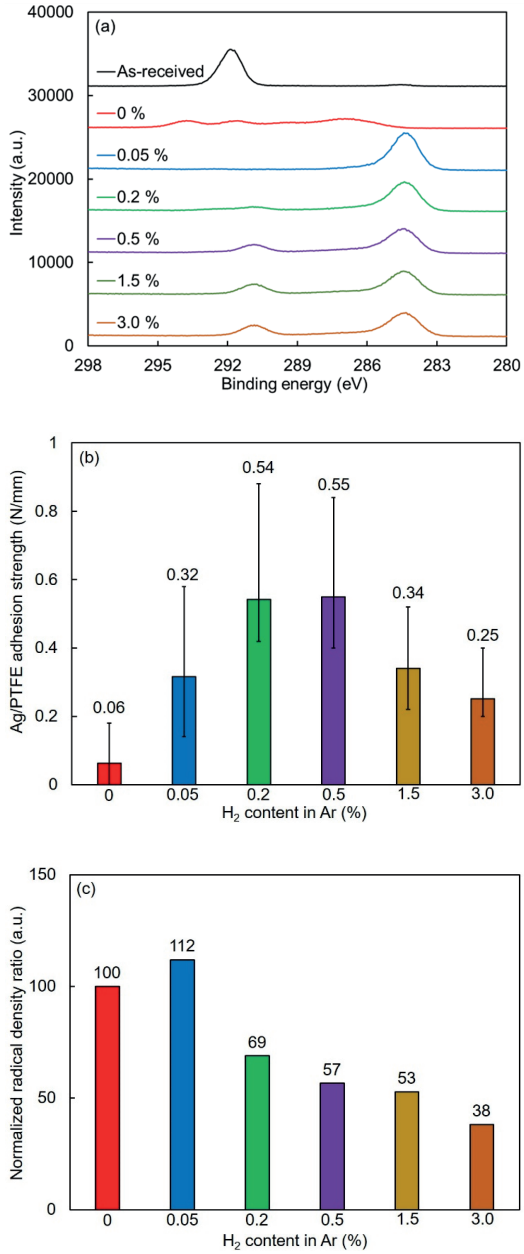

Fig. 7 (a) C1s-XPS spectra of PTFE surfaces treated with Ar + H_2 plasma with different H_2 contents. (b) Ag/PTFE adhesion strengths for irradiation with Ar + H_2 plasma with different H_2 contents. (c) The corresponding normalized radical density ratios. We calculated the relative amount of peroxy radicals with reference to PTFE treated with Ar plasma. The plasma irradiation period was fixed at 600 s, the voltage was 8.0 kVp-p, and the electrode gap was 0.5 mm.

These results indicated that the deposition of precursors of the colored layer was prevented by the addition of H_2 to Ar plasma, and the Ag/PTFE adhesion strength was maintained even after plasma irradiation for a prolonged period such as 600 s. In addition, it was suggested that the adhesion strength could be improved by reducing the formation of C-H bonds on the PTFE

surface by controlling the H_2 content.

3. 4 Comparison between H_2 and O_2 in Ar Plasma Treatment

As a result of irradiation with three kinds of plasma, namely, Ar, Ar + O_2, and Ar + H_2, it was confirmed that although coloration occurred on the PTFE surface treated with Ar plasma, coloration did not occur on PTFE treated with Ar + O_2 plasma with an O_2 content of greater than 0.67% or on PTFE treated with Ar + H_2 plasma with an H_2 content of 0.05-3.0%, as shown in **Fig. 3**. These results indicated that the addition of a small amount of O_2 or H_2 gas to an Ar plasma could greatly change the characteristics of a PTFE surface. **Fig. 8** shows the static water contact angles of an as-received PTFE sample and PTFE samples treated with three kinds of plasma. The static water contact angles of as-received PTFE, PTFE treated with Ar plasma, PTFE treated with Ar + O_2 plasma, and PTFE treated with Ar + H_2 plasma were 119.5°, 125.0°, 125.6°, and 61.1°, respectively. Hence, it was confirmed that the hydrophobicity of the surface increased slightly upon irradiation with Ar + O_2 plasma, but, on the other hand, the hydrophilicity of the surface increased upon irradiation with Ar + H_2 plasma. The reasons for the increase in hydrophobicity were an increase in the content of CF_3 groups and an increase in surface roughness upon treatment with Ar + O_2 plasma. In contrast, the reason for the increase in hydrophilicity was the increase in the contents of both C-H groups and O-containing functional groups upon treatment with Ar + H_2 plasma.

The uniformity of plasma treatment with Ar or Ar + H_2 gas was compared. **Fig. 9**(a) shows a schematic diagram of the area irradiated with plasma and the direction of the peel test. In the peel tests of which the results are shown in **Figs. 2**(b), **5**(b), and **7**(b), the direction of peeling was perpendicular to the flow direction of the process gas. **Fig. 9**(b) shows curves of the Ag/PTFE adhesion strength for PTFE samples that underwent plasma treatment using Ar and Ar + H_2 gas. The direction of peeling was parallel to the flow direction of the process gas. For PTFE treated with Ar plasma, the Ag/PTFE adhesion strength increased when the distance was 0-13 mm but decreased when the distance was 15-30 mm, which indicated that treatment with Ar plasma had low uniformity. In contrast, the Ag/PTFE adhesion strength remained virtually unchanged for PTFE treated with Ar + H_2 plasma when the distance was 0-30 mm, which indicated that treatment with Ar + H_2 plasma had high uniformity. In summary, these results indicated that the uniformity of treatment with Ar + H_2 plasma was superior to that of treatment with Ar plasma. Ar + H_2 plasma should therefore be used as a process gas from the point of view of industrial applications.

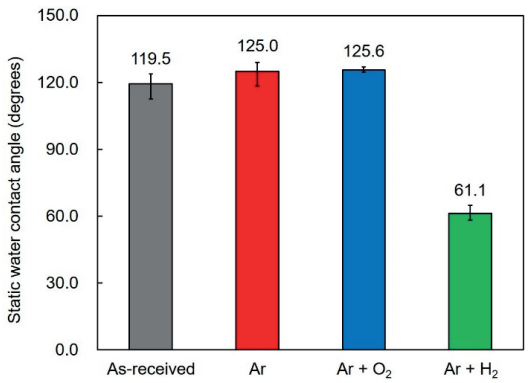

Fig. 8 Water contact angles of PTFE surfaces: as-received, treated with Ar plasma, treated with Ar + O_2 plasma, and treated with Ar + H_2 plasma.

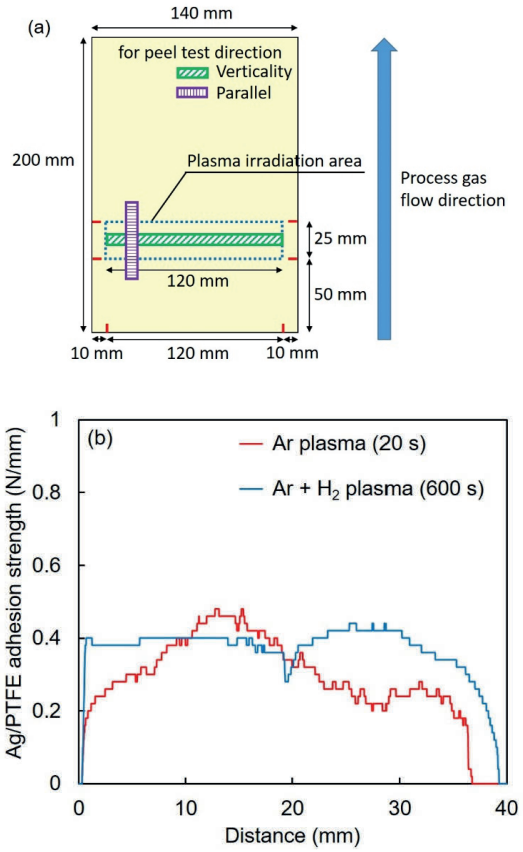

Fig. 9 (a) Area treated by plasma irradiation and direction of peel test. (b) Curves of the Ag/PTFE adhesion strength of samples treated with Ar and Ar + H_2 plasma when peeling was carried out parallel to the flow direction of the process gas. The voltage was 8.0 kVp-p, the electrode gap was 0.5 mm, and the H_2 content was 0.5%.

4. Conclusions

Our aim was to produce a metal wiring pattern with high adhesion to PTFE. We suggested the combination of surface treatment of PTFE using open-air plasma treatment at atmospheric pressure and inkjet printing with Ag ink, which allowed curing at low temperatures. In the case of treatment with pure Ar plasma, the maximum Ag/PTFE adhesion strength of 0.64 N/mm was achieved when the plasma treatment period was 20 s. However, the uniformity was low, and the adhesion strength decreased to 0.06 N/mm and coloration of PTFE occurred when the plasma treatment period was increased to 600 s. To prevent this coloration and increase the adhesion strength further, a small amount of O_2 or H_2 was added to the main Ar gas flow. In the case of treatment with Ar + O_2 plasma, coloration did not occur but the adhesion strength decreased to zero when the O_2 content exceeded 0.33% because of an increase in the number of CF_3 groups on the PTFE surface. In contrast, in the case of treatment with Ar + H_2 plasma, coloration did not occur and high adhesion strength (0.55 N/mm) was achieved when the plasma treatment period was increased to 600 s. We successfully achieved an increase in Ag/PTFE adhesion strength in the case of prolonged treatment with plasma and prevented coloration of the PTFE surface by controlling the H_2 content in the Ar plasma. In addition,

it was confirmed that the uniformity of surface treatment with Ar + H_2 plasma was superior to that of treatment with Ar plasma. In other words, treatment with Ar + H_2 plasma would have major advantages in the case of continuous plasma treatment in practical applications. The addition of a very small amount of a gas additive to the main gas flow in plasma treatment would be effective for not only PTFE but also other fluoropolymers such as PFA (tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer) and FEP (tetrafluoroethylene-hexafluoropropylene copolymer).

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References

1) Y. Nakasha, S. Shiba, Y. Kawano, T. Takahashi ; *Fujitsu Sci. & Tech. J.*, **53**, (3), 9 (2017).
2) F. Ellinger, D, Fritsche, G. Tretter, J. D. Leufker, U. Yodprasit, C. Carta ; *Frequenz*, **71**, (1), 1 (2017).
3) A. R. Djordjević, R. M. Biljić, V. D. Likar-Smiljanić, T.K. Sarkar ; *IEEE T. Electromagn. C*, **43**, 662 (2001).
4) J. Fan, J. L. Drewniak, J. L. Knighten, N. W. Smith, A. Orlandi, T. P. Van Doren, T. H. Hubing, R. E. DuBroff ; *IEEE T. Electromagn. C*, **43**, 588 (2001).
5) A. Koul, M. Y. Koledintseva, S. Hinaga, J. L. Drewniak ; *IEEE T. Electromagn. C*, **54**, 421 (2012).
6) A. C. Siegel, S. T. Phillips, M. D. Dickey, N. Lu, Z. Suo, G. M. Whitesides ; *Adv. Funct. Mater.*, **20**, 28 (2010).
7) K. Cheng, M.-H. Yang, W. W. W. Chiu, C.-Y. Huang, J. Chang, T.-F. Ying, Y. Yang ; *Macromol. Rapid. Comm.*, **26**, 247 (2005).
8) Y. J. Cheng, X. L. Liu ; *IEEE T. Microw. Theory*, **64**, 599 (2016).
9) I. Kharrat, P. Xavier, T.-P. Vuong, J.-M. Duchamp, P. Benech, G. E. P. Tourtollet ; *IEEE Antenn. Wirel. Pr.*, **14**, 1400 (2015).
10) M. Y. Koledintseva, A. V. Rakov, A. I. Koledintsev, J. L. Drewniak, S. Hinaga ; *IEEE T. Electromagn. C*, **56**, 1559 (2014).
11) H. Toyoda, S. Nishimura, H. Kanai, H. Kudou, H. Tanaka ; *Electron. Comm. Jpn.*, **88**, 847 (2005).
12) V. N. Egorov, V. L. Masalov, Y. A. Nefyodov, A. F. Shevchun, M. R. Trunin, V. E. Zhitomirsky, M. McLean ; *IEEE T. Microw. Theory*, **53**, 627 (2005).
13) A. R. Djordjević, R. M. Biljić, V. D. Likar-Smiljanić, T. K. Sarkar ; *IEEE T. Electromagn. C*, **43**, 662 (2001).
14) J. Krupka ; *IEEE Microw. Wirel. Co.*, **26**, 464 (2016).
15) S. Rajesh, V. S. Nisa, K. P. Murali, R. Ratheesh ; *J. Alloy. Compd.*, **477**, 677 (2009).
16) Y. Araki ; *J. Appl. Polym. Sci.*, **9**, 3575 (1965).
17) S. Yang, Q. Xia, L. Zhu, J. Xue, Q. Wang ; Q-M. Chen, *Appl. Surf. Sci.*, **257**, 4956 (2011).
18) R. R. Rye ; *Langmuir*, **6**, 338 (1990).
19) R. R. Rye, G. W. Arnold ; *Langmuir*, **5**, 1331 (1989).
20) L. Kavan, P. Janda, J. Weber ; *J. Mater. Sci.*, **36**, 879 (2001).
21) L. Kavan, F. P. Dousek, P. Janda, J. Weber ; *Chem. Mater.*, **11**, 329 (1999).
22) C. Kubo, A. Yagi, M. Kanda, Y. Nishi ; *Mater. Trans.*, **56**, 529 (2015).
23) Y. Miyazawa, M. Uyama, S. Ishii, M. Kanda, Y. Nishi ; *Mater. Trans.*, **54**, 1166 (2013).
24) R. K. Y. Fu, Y. F. Mei, G. J. Wan, G. G. Siu, P. K. Chu, Y. X. Huang, X. B. Tian, S. Q. Yang, J. Y. Chen ; *Surf. Sci.*, **573**, 426 (2004).
25) L. Guzman, B.Y. Man, A. Miotello, M. Adami, P.M. Ossi ; *Thin Solid Films*, **420**, 565 (2002).
26) R. Guoa, G. Yina, X. Shaa, Q. Zhaob, L. Weia, H. WangaaKey ; *Appl. Surf. Sci.*, **341**, 13 (2015).
27) J. Zhang, C. Q. Cui, T. B. Lim, E. -T. Kang, K. G. Neoh ; *Surf. Interface Anal.*, **28**, 235 (1999).
28) K. Furuse, Y. Sawada, K. Takahashi, M. Kogoma, K. Tanaka ; *J. Photopolym. Sci. Tec.*, **28**, 465 (2015).
29) T. Dufour, J. Hubert, P. Viville, C. Y. Duluard, S. Desbief, R. Lazzaroni, F. Reniers ; *Plasma Process. Polym.*, **9**, 820 (2012).
30) M. Okubo, M. Tahara, Y. Aburatani, T. Kuroki, T. Hibino ; *IEEE T. Ind. Appl.*, **46**, 1715 (2010).
31) C. Sarra-Bournet, G. Ayotte, S. Turgeon, F. Massines, G. Laroche ; *Langmuir*, **25**, 9432 (2009).
32) A. Sarani, N. D. Geyter, A. Y. Nikiforov, R. Morent, C. Leys, J. Hubert, F. Reniers ; *Surf. Coat. Tech.*, **206**, 2226 (2012).
33) V. Rodriguez-Santiago, A. A. Bujanda, B. E. Stein, D. D. Pappas ; *Plasma Process. Polym.*, **8**, 631 (2011).
34) H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, M. Inbasekaran, W. Wu, E. P. Woo ; *Science*, **290**, 2123 (2000).
35) H. Yan, Z. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dötz, M. Kastler, A. Facchetti ; *Nature*, **457**, 679 (2009).
36) M. Kaempgen, C. K. Chan, J. Ma, Y. Cui, G. Gruner ; *Nano Lett.*, **9**, 1872 (2009).
37) H. Minemawari, T. Yamada, H. Matsui, J. -Y. Tsutsumi, S. Haas, R. Chiba, R. Kumai, T. Hasegawa ; *Nature*, **475**, 364 (2011).
38) T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, T. Someya ; *Nat. Mater.*, **8**, 494 (2009).
39) D. Tobjörk, R. Österbacka ; *Adv. Mater.*, **23**, 1935 (2011).
40) F. Torrisi, T. Hasan, W. Wu, Z. Sun, A. Lombardo, T. S. Kulmala, G. -W. Hsieh, S. Jung, F. Bonaccorso, P. J. Paul, D. Chu, A. C. Ferrari ; *ACS Nano*, **6**, 2992 (2012).
41) N. Zettsu, K. Yamamura, Y. Idutsu, H. Wagata, S. Oishi, K. Teshima ; *J. Surf. Finish. Soc. Jpn.*, **65,** 227 (2014).
42) N. Vandencasteele, F. Reniers ; *J. Electron Spectrosc.*, **178**, 394 (2010).
43) T. -K. Lin, S. -J. Wu, C. -K. Pengc, C. -H. Yeh ; *Polym Int.*, **58**, 46 (2009).
44) D. J. Wilson, R. L. Williams, R. C. Pond ; *Surf. Interface Ansl.*, **31**, 385 (2001).
45) N. Vandencasteele, F. Reniers ; *J. Electron Spectrosc.*, **178**, 394 (2010).
46) M. Kuzuya, H. Ito, S. Kondo, N. Noda, A. Noguchi ; *Macromolecules*, **24**, 6612 (1991).
47) Y. Momose, Y. Tamura, M. Ogino, S. Okazaki, M. Hirayama ; *J. Vac. Sci. Technol. A*, **10**, 229 (1992).
48) W. Chen, Z. Wang, Z. Cui, Z. Meng, M. Huang, D. Pan; *Fiber. Polym.*, **15**, 966 (2014).
49) Z. Chunlong, M. Nianchun, L. Liyun ; *Dyes. Pigments*, **23**, 13 (1993).
50) W. Kufer, H. Scheer ; *Tetrahedron*, **39**, 1887 (1983).
51) J. Burdon, B. Emson, A. J. Edwards ; *J. Fluorine. Chem.*, **34**, 471 (1987).
52) B. B. Çarbaş, A. Kivrak, A. M. Önal ; *Electrochim. Acta.*, **58**, 223 (2011).
53) L. Zhang, S. Hu, J. Chen, Z. Chen, H. Wu, J. Peng, Y. Cao ; *Adv. Funct. Mater.*, **21**, 3760 (2011).
54) S. Lou, J. Yu, Y. Jiang, G. Guo, Q. Zhang ; *Chinese Sci. Bull.*, **53**, 2940 (2008).
55) C. S. Barrett, L. Meyer, J. Wasserman ; *J. Chem. Phys.*, **47**, 740 (1967).