Surface modification of PTFE for a high adhesive Cu layer by open-air type plasma treatment with graft copolymerization

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Abstract

Recently, the demand for high-frequency transmission signals has increased. Fluoropolymer has excellent high-frequency properties because of its low dielectric constant and low dielectric loss factor in GHz band. However, fluoropolymer is a chemically stable polymer, and therefore surface metallization is very difficult to achieve various industrial requirements. In our previous work, we have demonstrated a surface modification technique for improving the adhesion strength of electroless copper layer on polytetrafluoroethylene (PTFE). The process of surface Cu metallization involved a combination of atmospheric pressure He plasma irradiation with graft co-polymerization. Through this process, the adhesion strength of Cu layer on PTFE reached ca. 0.6 N/mm, which was sufficient for practical use. In this study, we improved the surface treatment process for more practical use. In the plasma treatment process, we used an open-type plasma system and low cost gas such as air, N_2, and Ar. We evaluated each plasma effect using electron spin resonance (ESR) analysis and measured the adhesion strength of a Cu layer on PTFE.

Key words: fluoropolymer, atmospheric pressure plasma, graft co-polymerization, adhesion strength

1. Introduction

Over the last few decades, the demand for transmission signals of higher frequency has increased. Therefore, materials with excellent high-frequency properties are required for printed circuit boards. Fluoropolymers have a low dielectric loss factor and low dielectric constant, and thus are widely used as materials for high frequency application. However, fluoropolymers are chemically stable, and forming a highly adhesive layer on their surface is difficult. In general, a sodium-naphthalene complex solution is used as an etchant to improve the adhesion strength between two different materials, but this process has main three problems. The first is that sodium-naphthalene complex solution is harmful to the human body. The second is the waste disposal cost of sodium-naphthalene complex is expensive. The third is the surface roughness of PTFE treated using sodium-naphthalene complex solutions becomes as large as the micrometer order. Large surface roughness causes electron scattering at the metal/fluoropolymer interface, which degrades the high-frequency properties of fluoropolymers.

To resolve these problems, we have demonstrated a surface modification technique for improving the adhesion strength of Cu layer on the polytetrafluoroethylene (PTFE) without roughening the surface [1]. The Cu metallization process of PTFE involved the following five steps: (1) formation of peroxy radicals on the substrate through atmospheric-pressure He plasma irradiation; (2) graft copolymerization on the activated PTFE surface; (3) deposition of Pd/Sn catalyst particles onto the grafted PTFE surface; (4) activation of catalyst by the reduction of Pd(II) to Pd(0) and the removal of tin; (5) electroless Cu plating on the PTFE surface. Figure 1 shows schematic of our process. Through this process, we achieved improvement of the adhesion strength of Cu layer on PTFE for practical use. However, this process is not suitable for industrial use because it requires the use of a chamber and He gas in the plasma process. The use of a chamber makes it difficult to treat the PTFE surface on a large scale and to need a high-cost vacuum apparatus. In addition, He gas is expensive. Not only we but also some researchers reported on surface modification processes for PTFE, but their reports required a reaction chamber [2] or a complicated experimental setup [3].

In this study, we used an open-type plasma system and low cost gases such as air, N_2, and Ar in order to improve the surface treatment process for more practical. Using this method, we would be able to form highly an adhesive metal layer on the chemically inert polymer, PTFE, through a low-cost and environmentally friendly process.

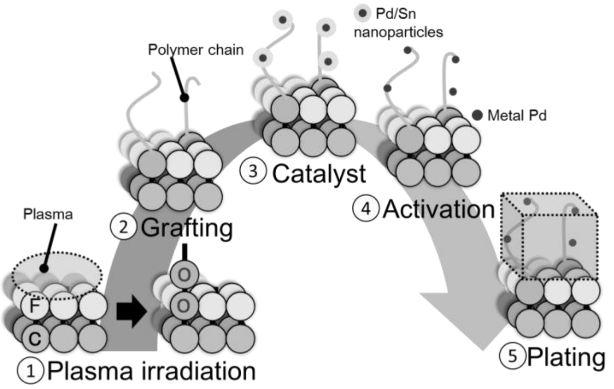

Fig. 1 Surface metallization process of PTFE

2. Experimental section

Commercially available PTFE sheets with a thickness of 0.2 mm were used as substrate materials. They were cut into substrates of 60 × 90 mm^2. These substrates were washed with acetone and pure water for 1 min each in an ultrasonic bath.

The entire plasma treatment process was performed by open-type plasma treatment system (AP-T05-L150, Sekisui Chemical, Inc., Japan). Atmospheric pressure plasma was generated by applying pulsed bipolar

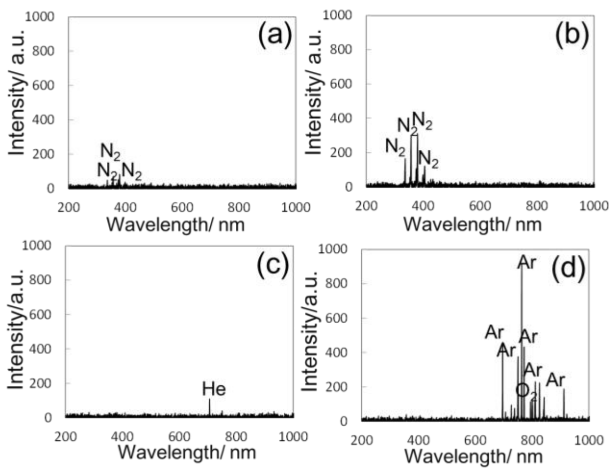

Fig. 2 Optical emission spectra of four kinds of plasma at atmospheric pressure. (a) air, (b) N_2, (c) He, (d) Ar.

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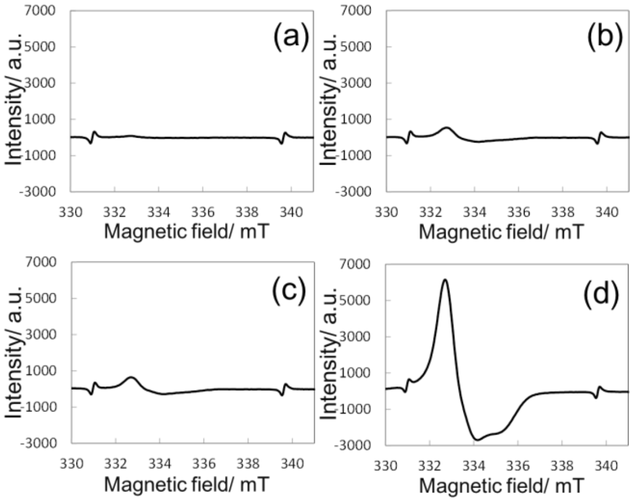

Fig. 3 ESR spectra of PTFE surface irradiated with four kinds of plasma at atmospheric pressure. (a) air, (b) N_2, (c) He, (d) Ar. Each plasma irradiation time was 20 min.

power supply. The pulse frequency was 30 kHz, and the pulse width was 9 μs. The voltage was 15 kVp-v for N_2 and air plasma, 5 kVp-v for He and Ar plasma. The process gas flow rate was maintained at 1.1 L/min. Optical emission spectra of the plasma were measured by a multichannel spectrometer (HR-4000CG-UV-NIR Ocean Optics, Inc., Japan) and a light fiber (P600-2-SR, Ocean Optics, Inc., Japan). Peroxy radicals formed on the PTFE surface were characterized by electron spin resonance (ESR) spectroscopy. ESR spectra were obtained at room temperature using an ESR spectrometer (JES-FA100, JEOL, Inc., Japan) with an X-band and 100 kHz field modulation. The microwave power used in the ESR measurement was 10 mW. The ESR spectral intensity was determined by double integration of the spectra. The *g*-value was measured relative to the fourth signal from the lower magnetic field (g =1.981) of Mn^{2+} in MgO. Mn^{2+} was used as reference.

Aminated acrylic polymer (Polyment, Mw: 10-30 K, NK-100PM, Nippon Shokubai, Inc., Japan) was dissolved in ultrapure water. After plasma irradiation, the PTFE substrate was dipped into the Polyment solution (10 wt%) for graft co-polymerization and then ultrasonically washed with ultrapure water for 10 min to remove excessive Polyment. Finally, the grafted PTFE surface was metalized through electroless Cu plating.

The adhesion strengths of a Cu layer on PTFE were measured using a commercially available peel tester (ZP-200, IMADA, Inc., Japan) according to JIS K 6854-1.

3 Results and discussion

3.1 Optical emission spectra of four kinds of plasma

Figure 2 shows optical emission spectra of four kinds of plasma. For air plasma, optical emission from N_2 was observed. For N_2, He, and Ar plasma, highest optical emission intensity was observed in each

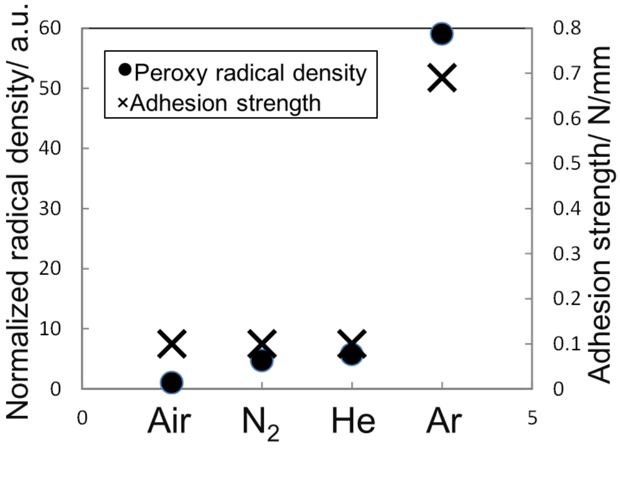

Fig. 4 Effect of gas type on peroxy radical density and adhesion strength of Cu layer on PTFE. Each plasma irradiation time was 20 min.

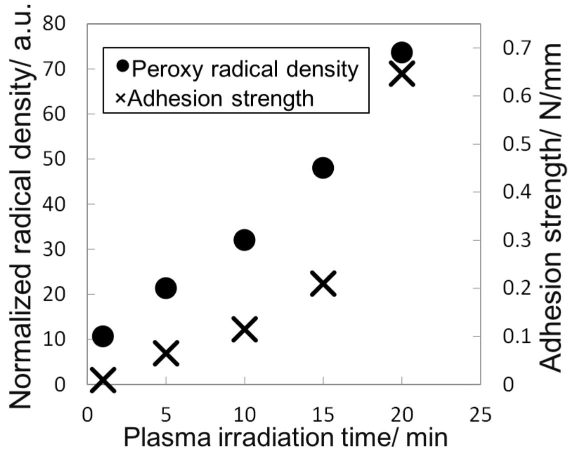

Fig. 5 Effect of Ar plasma treatment time on peroxy radical density and adhesion strength of Cu layer on PTFE.

383.8 nm, 763.5 nm and 706.5 nm, and they are in accord with typical optical emission spectrum of each gas. Optical emission intensity of air plasma was lower than N_2 plasma. For air plasma, since O_2 which is electronegative gas captured free electrons [4]. Optical emission intensity of Ar plasma was higher than that of He plasma. It is considered that ionization potential of Ar (15.8 eV) is lower than that of He (24.6 eV), so Ar gas was easily ionized and optical emission intensity of it was high.

3.2 Effect of gas species

Figure 3 shows ESR spectra of PTFE surface irradiated with four kinds of plasma. Absorption peak of peroxy radicals were observed in all ESR spectra from 332 mT to 336 mT [5]. Absorption peaks observed from 330 mT to 332 mT and from 339 mT to 341 mT were Mn^{2+} reference. Figure 4 shows the normalized peroxy radical densities and adhesion strengths of Cu layer for the PTFE substrates irradiated with different four kinds of plasma. All peroxy radical densities in Fig. 4 were normalized to the peroxy radical density of PTFE irradiated with air plasma. Normalized radical density of PTFE irradiated with Ar plasma was 10 times higher than that of the others. In addition, the adhesion strength was 7 times higher than that of the others. Taking account of optical emission intensity shown in Fig. 2, Ar plasma contains highest density of activated species, so peroxy radical was formed on PTFE surface easier than the other plasmas. And, when the peroxy radical density on PTFE surface increased, the graft density also increased [6], and therefore the adhesion strength of Cu layer on PTFE increased.

3.3 Effect of Ar plasma irradiation time

Figure 5 shows the normalized peroxy radical densities and adhesion strengths of Cu layer for the PTFE substrates irradiated with different Ar plasma irradiation time. All peroxy radical densities were normalized to the peroxy radical density of Ar plasma irradiated for 1 min. As plasma irradiation time was increased, the normalized peroxy radical density and the adhesion strength of Cu layer on PTFE also increased. Since the activated species from Ar plasma reached to substrate easily and the peroxy radical density was increased, which resulted in increases in the graft density and the adhesion strength. When plasma irradiation time was 20 min, the adhesion strength of Cu layer on PTFE was 0.69 N/mm.

4. Summary

We demonstrated effect of four kinds of gas (air, N_2, He and Ar) of plasma for use of low cost gas with an open-type plasma system.

1) The optical emission intensity, normalized peroxy radical density, and adhesion strength varied according to the kinds of gas in plasma treatment. Most effective gas of them was Ar gas.
2) Peroxy radical density and adhesion strength of Cu layer on PTFE increased with increase in Ar plasma irradiation time.
3) Through open-air type plasma irradiation step with low-cost gas and graft copolymerization step, we successfully formed a highly adhesive Cu layer on PTFE. The highest adhesion strength of Cu layer on the PTFE irradiated with Ar plasma was 0.69 N/mm, which was sufficient for practical use.

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