Production of Hydrogen Gas in Atmospheric Pressure Plasma for Surface Modification of Polytetrafluoroethylene
大気圧プラズマによるポリテトラフルオロエチレン表面改質と水素ガスの発生

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Polytetrafluoroethylene (PTFE) was irradiated to atmospheric pressure plasma for hydrophilization of the surface. The atmospheric pressure plasma was generated by dielectric barrier discharge in argon (Ar) gas flow with additional water vapor and/or ethanol vapor. The water contact angle was dramatically decreased by irradiation to Ar with ethanol plasma. Analysis of gas composition in the atmospheric plasma was carried out using quadrupole mass spectroscopy. It was found that hydrogen (H_2) was produced in the plasma from the additive gas when the PTFE surface became hydrophilic.

1. Introduction

Polytetrafluoroethylene (PTFE) is an excellent material in heat resistance and chemical resistance, and has been used for flexible electronic circuit board. Due to its extremely hydrophobic surface and poor adhesiveness, however, it is necessary to prepare hydrophilic surface for some applications. Atmospheric pressure plasma (APP) treatment is an effective processing technique for hydrophilization of PTFE surface with high through put and with small environmental load.

It has been reported that PTFE surface has been modified to hydrophilic by low pressure hydrogen plasma[1] and by APP treatment using He gas mixed with water vapor or organic solvent vapor[2]. It has been considered that, as a possible mechanism for the effective hydrophilization, F atoms were extracted from PTFE surface due to reactive hydrogen radicals generated in the plasma.

In this study, PTFE surface was treated by APP using Ar gas for discharge with water vapor and/or ethanol vapor as the process gas[3-5]. The composition of the gas in APP was analyzed by quadrupole mass spectrometer (QMS) with differential pumping through a thin glass capillary. It was found that hydrogen gas was produced in the plasma from the process gas. In this report, the relationship between the hydrogen production in the plasma and the hydrophilization of PTFE surface is presented.

2. Experimental

Figure 1 shows the experimental setup for APP treatment of PTFE specimens. As the discharge gas, Ar was bubbled in water(H_2O), ethanol(C_2H_5OH), or H_2O/C_2H_5OH mixture in a bottle at a controlled temperature. The mixture gas was introduced into a discharge cell consisting of a pair of glass plates (0.3 mm in thickness) with a gap of 2 mm. A PTFE specimen of 1 mm in thickness was placed in the discharge cell. APP was generated by dielectric barrier discharge using a pair of electrodes 10mm x 10mm in each size put on the glass plates and a sinusoidal wave high voltage source of 10 kV and 25 kHz.

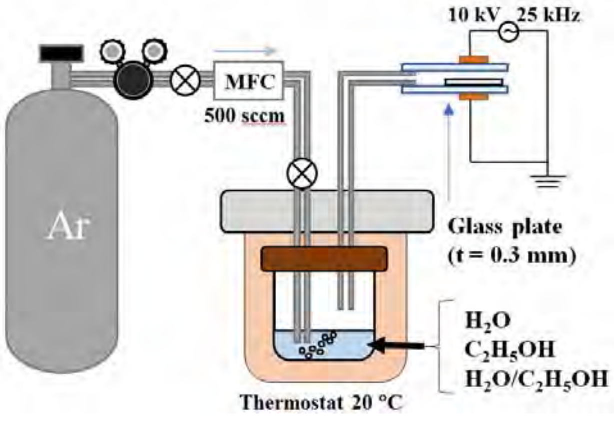

Fig. 1. Experimental setup for plasma treatment.

Figure 2 shows the experimental setup for gas composition analysis using a QMS (ANELVA, M-200QA-M) with a differential pumping system. The reaction gas in the discharge cell was sampled through a thin glass capillary of 35 μm inner diameter.

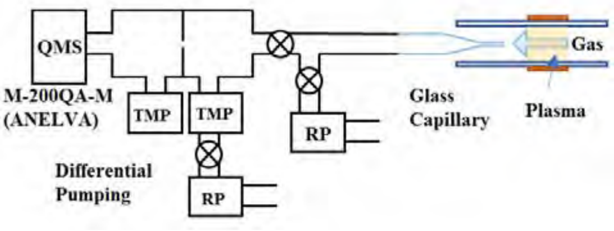

Fig. 2. Experimental setup for gas analysis.

3. Results and Discussion

Figure 3 shows plots of water contact angles (WCA) after H_2O/Ar APP treatment with variation of partial pressure of water vapor. The concentration of water vapor was varied by changing the water temperature or by diluting with pure Ar after bubbling, and the partial pressure was estimated from the saturated vapor pressure at the temperature and the dilution ratio. The WCA decreased from 112° of the original PTFE specimen to below 80° at the water vapor pressure more than 0.01 atm.

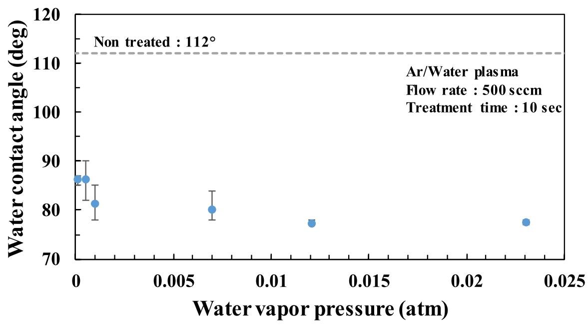

Fig. 3. Water contact angle after H_2O/Ar plasma treatment with variation of water vapor pressure.

Figure 4 shows increase of QMS current for m/e = 2 (I_2) reflecting production of hydrogen molecule (H_2) in the plasma. The I_2 intensity for outgas from the vacuum system was subtracted from the observed spectrum. When the gas in the discharge cell was introduced into the QMS chamber, I_2 slightly increased due to the cracking pattern of H_2O introduced in the gas. When the discharge was turned on, I_2 further increased due to production of H_2 in the plasma.

The production of H_2 in the plasma from water vapor increased with increasing water vapor pressure until 0.01 atm. At 0.023 atm, I_2 slightly decreased. The trends in decreasing of WCA and in increasing of I_2 look like similar to each other.

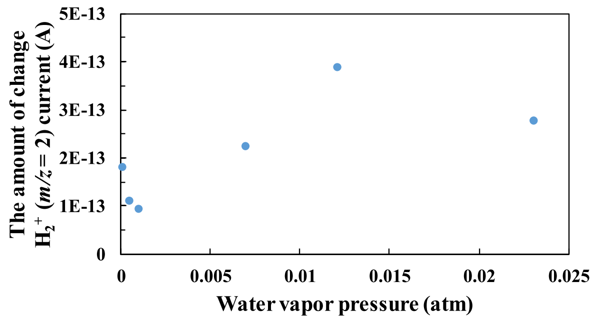

Fig. 4. Increase of QMS current for m/e=2 with variation of water vapor pressure.

It is reasonable to assume that hydrogen radial (H atom) produced from the reaction gas (H_2O, and/or C_2H_5OH) is effectively treat the PTFE surface to hydrophilic. By increasing the water vapor pressure until 0.01 atm, the production of hydrogen radical increased with resulting in decreasing WCA. The increase of hydrogen radicals in the plasma was detected as the increase of hydrogen molecules.

At higher water vapor pressure more than 0.02 atm, however, production of hydrogen radical was saturated possibly due to shortage of plasma reaction at the limited electrical power.

4. Summary

Production of hydrogen in the atmospheric pressure Ar plasma with additional water vapor and/or ethanol vapor was confirmed by QMS analysis. The water contact angle of PTFE surface was decreased with increase of hydrogen production in the plasma.

References

[1] N. Inagaki et al., J. Appl. Polym. Sci., Vol. 83, 340 (2002).
[2] M. Shibahara et al., J. Surf. Finish. Soc. Jpn., Vol. 58, No. 7, 420 (2007) (in Japanese).
[3] H. Yajima et al., in Proc. Plasma Conf. 2017, Hyogo, Japan, 2017, 21P-119.
[4] H. Yajima et al., in Proc. The 65th JSAP Spring Meeting, Tokyo, Japan, 2018, 07-126.
[5] H. Yajima et al., in Proc. The 79th JSAP Autumn Meeting, Nagoya, Japan, 2018, 07-075.