

## 論文内容の要旨

In many applications of plasmas and gas discharge, atmospheric pressure conditions are beneficial due to contains abundant of high reactivity species while not requiring vacuum system. These plasmas play an important role in plasma processing of materials, plasma medicine and agriculture. This study presents the development of dielectric barrier discharge (DBD) plasma for polytetrafluoroethylene (PTFE) surface modification and study of novel method to generate atmospheric pressure gas discharge induced by photoemission. The aims of this study are to enhance surface free energy of PTFE by means of improving its surface wettability and to generate stable atmospheric pressure gas discharge induced by photoemission using air for medical and agriculture applications.

In the first part of this work, atmospheric pressure plasma was generated by the dielectric barrier discharge of a water-ethanol vapor mixture with argon or nitrogen gas. Quadrupole mass spectroscopy (QMS) was employed to analyze gas composition of the plasma. The results revealed that atmospheric pressure plasma promoted the decomposition of ethanol and produced H<sub>2</sub>, CH<sub>4</sub> and CO in case of argon gas. In case of nitrogen gas, beside these species, NH<sub>3</sub> was found. The modified PTFE surface was influenced by the ethanol concentration. Plasma treatment with 3%, 5% and 9% ethanol diluted in argon gas resulted in a significant reduction in the water contact angle (WCA) from 115° to 16.5 ± 2.8° after 10 s of treatment. On the other hand, significant improvement of wettability was occurred when the ethanol concentration 5%, 9%, 50% and 100% diluted in nitrogen gas from 115° to 11.8 ± 2.4° after 10 s treatment. However, when treatment was increased, the WCA degraded up to around 80°. The surface analysis was done by using atomic force microscope (AFM) for morphological examination and using X-ray photoelectron spectroscopy (XPS) for chemical composition measurement. However, the surface morphology showed less significant changes, comparing before and after plasma treatment. In contrast, XPS revealed that oxygen-containing (argon case) functional groups and nitrogen-containing functional groups (nitrogen case), namely hydroxyl, carbonyl, and carboxyl, amine, amide groups, formed on the plasma-treated PTFE surface, reflecting the hydrophilization of PTFE. At the beginning of the plasma treatment, the water vapor induced the breaking of the CF<sub>2</sub> chain, and the additional ethanol vapor generated oxygen-containing polar groups on the PTFE surface. In addition to the modification of the PTFE surface itself, a low-molecular-weight oxidized material layer was deposited over the surface, which prevented further surface modification, and the deposited layer exhibited excellent wettability. The deposited low-molecular-weight oxidized material layer was easily removed by immersion in deionized water, and the exposed modified PTFE surface exhibited stable wettability with water contact angle of 52.7 ± 3.5°. Nevertheless, this phenomenon was occurred seriously for nitrogen + water - ethanol.

In the second part of this work, generation of the atmospheric pressure plasma induced by photoemission was studied. APP was generated using two electrodes from aluminum as an anode and quartz glass - deposited gold thin film as a cathode with a gap of 1 mm. The gold thin film was back illuminated with UV light (Xe\* lamp 172 nm, Hg lamp 256 nm, LED 254 nm) which caused free electron emission in the gap. The optimum gold thickness for gold thin film as photoemitter was found at 9 nm. The current generated by the photocathode was monitored by biasing the gold thin film negatively with respect to the ground. The I-V graph shows that by applying bias voltage up to 1400 V to the discharge cell (argon as gas discharge), stable current up to 30 · A, 12 · A, and 5 · A was obtained for UV 172 nm, UV 256 nm, UV 254 nm, respectively. The free electrons produced by photocathode play

an important role as electron seed for electrical breakdown. However, sufficient intensity of electrons is necessary to obtain stable discharge. It is suggested that in low bias voltage ( $< 600$  V) the obtained current was due to photoemission from cathode, whereas at bias voltage  $> 600$  V, the current was due to photoemission and electron avalanches from ionization process which for UV 265 nm and UV 254 nm two order lower than UV 172 nm. This result also supported by evaluation of photon intensity dependency. In low bias voltage, current has linear correlation. On the other hand, in high bias voltage, current has power correlation with photon intensity. Examination on different gas discharge showed that, for air as gas discharge, it was required higher bias voltage by four times to obtain the same current value as argon gas. Nevertheless, analysis of gas chemical reaction by means of absorbance measurement, showed that air atmospheric pressure plasma induced by UV 172 nm produced reactive oxygen and nitrogen species which is key point for medical and agriculture application.