

In situ Electron Spin Resonance Study of Plasma-Surface Interactions

電子スピン共鳴測定によるプラズマ表面相互作用のその場観察

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During the plasma processes, simultaneous irradiation of electrons, ions, radicals, and photons is occurred and therefore individual contributions of each of these species must be elucidated with atomic level. We have focused on direct observation of the formation and destruction of dangling bonds for this purpose. Actually the real time in situ electron spin resonance (ESR) technique was demonstrated elucidation of plasma-surface interaction on polymer materials as examples for soft- and bio-materials. This opens a new experimental approach to the microscopic understanding of chemical reactions on surfaces with gaseous radicals during plasma processes.

1. Introduction

Plasma discharge had been utilized in various applications such as plasma-enhanced chemical vapor deposition, plasma etching, plasma-induced surface modification, plasma medicine, and so on. Material-synthesis or chemical-functionalization by employing plasmas has recently become a hot-topic in material science fields. Meanwhile, to control those plasma induced damages and to improve their process performance, chemical reactions under plasma are needed to understand comprehensively. During the plasma processes simultaneous irradiation of electrons, ions, radicals, and photons is occurred. Therefore, the individual contributions of each of these species in the plasma must be elucidated.

Recently, the surface treatment of organic materials using atmospheric pressure plasmas has attracted much attention. For example, there is considerable interest in changing the surface hydrophobicity of poly(tetrafluoroethylene) (PTFE) or poly(methylmethacrylate)(PMMA) using treatments such as UV radiation under vacuum at room temperature, oxygen plasma exposure at low-pressure, or surface modification using an atmospheric pressure He plasma. In addition, not only photochemical processes with plasma-induced emission but also synergistic photo- and radical processes play important roles in the utilization of plasma.

To understand the dynamic changes in bonding configurations during processing and surface reactions, direct observation of the formation and destruction of dangling bonds will provide important information. Originally, Westenberg

reported that chemical reactions could be analyzed using the electron spin resonance (ESR) technique [1]. Previously Yamasaki *et al.* succeeded in attempts measure dangling bonds in situ during silicon film growth using ESR [2]. Subsequently we have investigated the plasma processes for plasma etching of dielectric materials and diamonds using *in vacuo* and in line ESR technique [3]. Recently we have reported synergistic formation of radicals by irradiation with both vacuum ultraviolet and atomic hydrogen by using a real-time *in situ* ESR [4].

In this study, we focused on *in situ* ESR measurements performed during plasma processes using an ESR cavity and remote plasma system. PTFE has C-F bonds with a relatively high bond-energy of approximately 5 eV; therefore, it is difficult for photochemical oxidation to occur. Using plasma discharge, C dangling bond was generated during and after surface modification. Dominant pathways under given conditions will be presented with a tentative interpretation of their dynamic changes which observed by ESR signals from both the solid and gas phases.

2. Experimental

An ESR system was connected to a plasma discharge system using a quartz tube with an inner diameter of approximately 9 mm, as shown in Fig. 1. A microwave (2.45 GHz) power supply of 50 W from a generator was used to generate plasma inside of the quartz tube. Hydrogen gas was flowed into the quartz tube at a flow rate of 50 sccm, and the pressure was maintained at approximately 10 Pa

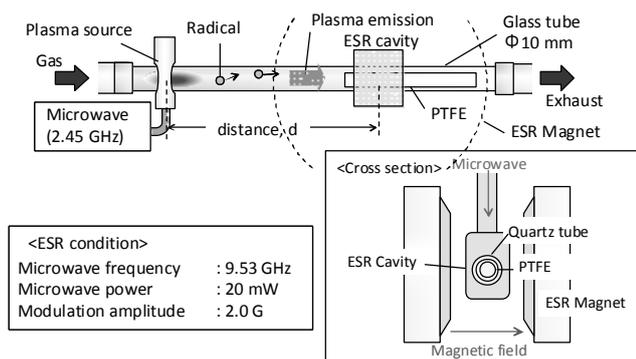


Fig. 1. Schematic of the experimental setup

in the down-flow region.

ESR measurements were conducted using a standard X-band (9 GHz) spectrometer with a microwave resonator. ESR spectra were recorded with microwave power of 2 mW, a field modulation of 0.2 mT, and a modulation frequency of 100 kHz. All experiments were performed at room temperature. The quartz tube and polymer film sample were inserted inside of the ESR cavity in the down-flow region, typically 20 cm from the plasma discharge. The sample used was a 0.1 mm thick PTFE film. Both gaseous reactive species and surface radicals on the PTFE film were simultaneously detected in situ.

Individual contributions from reactive species in gas phase and plasma emission light have been studied in the manner using pallets for plasma process evaluation (PAPE). Since the sample set at the down-flow region, no effect of ion bombardment was observed in this study because the distance from the discharge was sufficiently large and charged particles such as electrons and ions were immediately diminished by recombination. To limit interactions of plasma emissions with the sample, a U-shaped quartz tube and light shade were used as shown in Fig. 2. Neutral reactive species such as atoms and radicals in the gas-phase are relatively long-lived; therefore a sufficient amount of neutral species were transported to interact. In addition, inter-actions

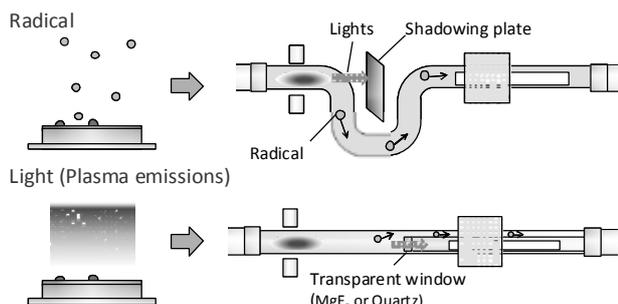


Fig. 2. Irradiation for only radical (upper), and only light (lower)

with only plasma emissions were clarified using the transparent MgF_2 window, which can transmit wavelengths above approximately 115 nm.

Individual roles for atomic H or plasma emission

When the sample was irradiated with only atomic hydrogen, no C-DB was negligible to detect. The lack of C-DB formation was due to the high bond-dissociation energy for C-F of approximately 5 eV.

For VUV irradiation, strong absorption energy of approximately 7.8 eV, which corresponds to a VUV wave-length of 160 nm, was reported. When the MgF_2 window material was used, there was formation of C-DB as shown in Fig. 4. However, when the window material was changed to a quartz window that cut the wavelengths to as low as 250 nm, there was no formation of C-DB.

Notably, for irradiation with both atomic H and VUV, significant acceleration in the rate of C-DB formation was observed at the beginning of irradiation. This behavior can be interpreted that atomic hydrogen may play a scavenging role in reaction with atomic fluorine which is released from C-F bonds. This process is represented by

$$\frac{d[DB]}{dt} \propto k(1-[DB])[H] \quad [DB] \propto (1 - e^{-k[H]t}) \quad (1)$$

where k is rate coefficient. From this, synergistic formation of surface C-DB occurred close to the surface due to the scission of C-F bonds and was accelerated by VUV illumination and ruptured F atom scavenging by H atom to form HF. This surface C-DB produced immediately changed to peroxy radicals when the treated PTFE films were exposed to air. This suggests that high reactivity of C-DB with oxygen and that the peroxy radical species can contribute to enhancement of the surface biocompatibility.

3. Conclusion

The in situ real time ESR technique was demonstrated as a new experimental approach to the microscopic understanding of chemical reactions on surfaces with gaseous radicals during plasma processes.

Acknowledgments

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