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# Hydrocarbon plasma induced surface reaction, considered with multiple-internal-reflection infrared absorption spectroscopy

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Hydrocarbon plasmas are useful for deposition of a lot kinds of carbon films, which are useful to many fields. Of course, it important to control hydrocarbon plasma process for the deposition Thereby, it is important to know and understand hydrocarbon plasma process at an atomic level. Although there have been many reports about hydrocarbon plasma plasmas, especially about gas-phase reactions, thus far, there have not been so many reports about surface reactions during hydrocarbon plasma. To control plasma process, the surface reaction during plasma should be understood. The aim of this study is the elucidation of surface reactions during hydrocarbon plasma, between ethylene plasma, and methane plasma.

It is difficult to investigate surface reactions during plasma, because plasma is ionized gas with charged particles, such as ions and electrons, and also plasma has gas flow. Thereby, it is hard to use surface analysis technique such as XPS (X-ray photoemission spectroscopy), SPM (Scanning Probe Microscope) and so on. While the analysis methods require high vacuum or static environments, infrared absorption spectroscopy (IRAS) is one of promising methods of surface reactions during plasma. To improve the detection sensitivity, MIR (multiple-internal-reflection) configuration is adopted. This is because IR light reflects at Si-prism surface many times. Surface reactions have been investigated with MIR-IRAS method. An MIR-IRAS monitoring system was installed into PECVD (plasma enhanced chemical deposition) chamber. Our vacuum chamber has also RF (13.56MHz) plasma source with a coil-winding glass-tube, and vacuum pumping system with a turbo-molecular pump. After IR light exited from FTIR (FT/IR6100, JASCO Ltd.) came into Si prism in the vacuum chamber, IR light traveled in the Si prism with internal reflections and then focused into liquid-$N_2$ cooled MCT (Mercury Cadmium Telluride) detector. All IR light path expect vacuum environment was not exposed to air but was filled with dried $CO_2$-free air.

After ethylene/methane gas was fed into vacuum chamber with 1 sccm, the pressure of vacuum chamber was set at 50 mTorr. Ethylene plasma was generated by applying RF power of 30 W to the coil. IR absorption spectra of the prism surface were acquired during plasma with neither substrate heating nor substrate bias. Then, IR spectra were affected by hydrocarbon plasma, because the surface reaction was slow and ion effects were excluded. Plasma reaction can be also elucidated from surface reaction.

Fig. 1 shows the IR spectrum of the prism surface exposed to ethylene plasma and that exposed to methane plasma. Peaks at less than 3000 $cm^{-1}$ can be attributed to

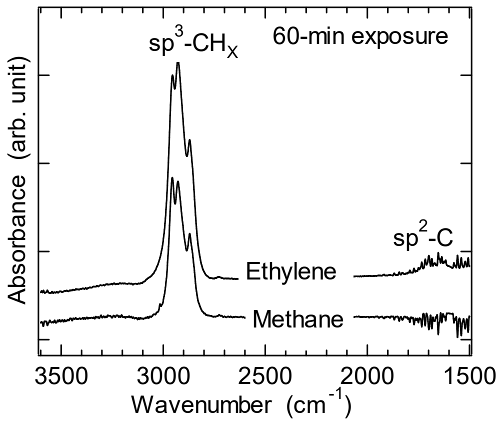


Fig. 1 IR absorption spectra of Si prism surface exposed to methane plasma, ethylene plasma

$sp^3$-hydrocarbon components, while peaks at more than 3000 $cm^{-1}$ can be attributed to sp- or $sp^2$-hydrocarbon components. The $sp^3$-hydrocarbon components were formed with either plasma. According to previous paper[(1)], $C_2H_n$ (n=3-4) species are generated in ethylene plasma, while $CH_n$ (n=3-4) species are generated in methane plasma. Different chemical species are generated in plasma, but the similar chemical components were deposited on the prism. While the $CH_4$ is exhausted as neutral gas, the $CH_3$ is reactive and main species in the methane plasma. Therefore, $CH_3$ is adsorbed on dangling bonds generated by hydrogen abstraction, as described by Keudell [(2)]. While the $C_2H_2$ and $C_2H_4$ are exhausted as neutral gas, the $C_2H_3$ is reactive and main species in the ethylene plasma. C=C bond contained in $C_2H_3$ is altered into C-C bond on the prism. Then, $C_2H_3$ is adsorbed on more than two dangling bonds generated by hydrogen abstraction; as a result, the C=C bonds, $sp^2$-hydrocarbon components disappear in the adsorbed components

We also measured the contact angles of the deposited films to pure water. The angle of ethylene-plasma deposited film is small, compared with that of methane-plasma deposited film. Saturated hydrocarbon components are easily formed in the adsorption during methane plasma, because the $CH_3$ is saturated at the adsorbed surface. On the other hand, dangling bonds are generated in the deposited film, because $C_2H_3$, generated in ethylene plasma, is unsaturated species.

**References**

(1) Ch. Deschenaux, et al., J. Phys. D, **32**, 1876 (1999).
(2) A. von Keudell, Thin Solid Films, **402**, 1 (2002).