Structural characterization of carbon materials fluorinated in CF_4 plasma
（CF_4プラズマ中でフッ素化したカーボン材料の構造評価）

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Carbon nanotube (CNT) is one of the most important materials in many aspects. For functionalizing carbon nanotubes for applications, various processes have been proposed. Among them, plasma processing for fluorination has gained much attention recently. Nevertheless, there have been much less structural studies on the plasma processed CNTs. In this dissertation, I have systematically studied the structural properties of CNTs as well as graphite, diamond, and fullerite, which are plasma processed for fluorination, by means of transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy.

Plasma ions are produced in a reactive ion etcher (RIE), filled with CF_4 gas, with capacitively driven radio frequency (RF) diodes at 13.56 MHz. Electrons, oscillated by the RF driving voltage, collide with neutral CF_4 molecules, dissociate them and induce plasma ions that are dominated by CF_3^+ ions. CF_3^+ ions, which are accelerated by the electric field in a sheath, flow toward the RF electrode, and finally collide with the carbon materials set on the RF electrode. Plasma fluorination condition such as the energy and the density of CF_3^+ ion is systematically controlled by changing the RF power and the flow rate of CF_4 gas.

I have shown that fluorination proceeds on graphite layers of single wall CNTs (SWCNTs) when the energy of the ions is sufficiently low. The intensity of the XPS spectrum that corresponds to covalent C-F bonds increases with the dose of ions. This indicates that fluorine is covalently bonded to SWCNTs while the tube structure is preserved after the fluorination. Raman spectroscopy supports the conclusion above qualitatively. Plasma fluorination with CF_3^+ ions of higher energy gives rise to amorphization partially on the graphite layer. With the further increase of energy of CF_3^+ ions, amorphous fluorocarbon compounds are formed.

I have also examined the fluorination process of double wall CNTs (DWCNTs), triple wall CNTs (TWCNTs), quadra wall CNTs (QWCNTs), and multi wall CNTs (MWCNTs). TEM analysis shows that plasma fluorination is initiated on the outermost wall and proceeds to inner walls. The tolerance to plasma fluorination increases with increasing the number of graphite walls. Accordingly, graphite shows the most tolerant of plasma fluorination. In the fluorination of diamond, no significant change is detected on the surface presumably due to more stable sp^3 bonds. Fullerites are easily collapsed by the plasma fluorination process, forming amorphous fluorocarbon compounds.

In summary, the atomistic process of plasma fluorination in carbon materials has been described systematically. In addition, the plasma fluorination condition of SWCNTs has been established. The study is the most probably useful for functionalizing CNTs for future applications.