## Structure and property control of cluster diamond by fluorination

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Fluorination is one of the most effective chemical methods to modify and control structural and physicochemical properties of carbon materials, and we have so far attempted to property control of new forms of carbon materials such as fullerenes and carbon nanotubes by fluorination<sup>1,2)</sup>. In this paper, we report fluorination of cluster diamond (CD). Structure and surface chemistry of fluorinated CD were investigated by means of TEM, XPS, FT-IR XRD, and elemental analyses. Nitrogen gas adsorption at 77K and tribological properties of fluorinated CD were also investigated.

Cluster diamond prepared by an explosion method was fluorinated in a temperature range 300-500  $^{\circ}\!\mathrm{C}$  using 1 atm elemental fluorine. The cluster diamond is a coalescence of ultra-fine crystalline diamond (average size: 5 nm) whose outer surfaces are covered by onion-like carbon layers. Fig. 1 shows C1s XPS spectra of pristine and fluorinated CD. After the treatment with fluorine, the peak of sp<sup>3</sup>-hybridized carbon atoms of pristine CD shifted from 284.6 to 286.2 eV, and new shoulders are observed at 288.0 and 289.4 eV. These shoulders are assigned to covalent C-F and  $-C = F_2$ bonds, respectively. The formation of CF, CF<sub>2</sub> and CF<sub>3</sub> groups are also confirmed by IR-spectra of fluorinated CD. Both XPS and elemental analyses of fluorinated CD showed the same F/C value 0.2, indicating that cluater diamond is a coalescence of ultra fine diamond particles on a nanometer scale. Fig. 2 shows TEM images of pristine and fluorinated CD at 500°C for 10 days. The (111) lattice fringe of nano-diamond is clearly observed for fluorinated CD, and (002) lattice fringe of onion-like carbon layers also becomes clear. These changes in TEM images by fluorination are ascribed to the elimination of amorphous carbon phase by high temperature fluorination. Upon fluorination, the average size of the coalescence 40  $\mu$  m was reduced to 200 nm, and pore size



Fig. 1 XPS spectra of pristine CD and Fluorinated CD. F500-10D: fluorinated CD at  $500^{\circ}$ C for 10 days, F500-5D: fluorinated at  $500^{\circ}$ C for 5 days.

distribution curve showed a sharp peak at ca. 1 nm, indicating micropore formation.

Fig. 3 shows friction coefficient of PTFET, pristine CD and fluorinated CD powder. The fluorinated CD showed improved tribological properties due to nano-ball bearing effect and the formation of the surfaces with lower surface energy.

## References

H. Touhara and F. Okino, *Carbon*, **38** (2000) 242.
H. Touhara et al., *J. Fluorine Chem.*, **114** (2002).

a b

Fig.2. TEM images of pristine CD (a) and fluorinated CD (b) at  $500^{\circ}$ C for 10 days.



Fig.3. Friction coefficient under applied loads for PTFE, CD-PTFE, and fluorinated CD-PTFE powders.