

## WETTABILITY CONTROL OF SURFACE BY FLUORINATION IN COLD PLASMA

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It is well known that the surfaces of polytetrafluoroethylene (PTFE) and of fluorinated graphite ((CF)<sub>n</sub>) are very hydrophobic. The contact angle ( $\theta$ ) of a water drop has the value of  $110^\circ$  (PTFE) or  $145^\circ$  ((CF)<sub>n</sub>)<sup>(1)</sup>. Fig.1<sup>(2)</sup> shows that the various plastic and graphite surfaces easily changed to hydrophobic surfaces due to the treatment in CF<sub>4</sub> plasma (13.56 MHz). On the other hand, oxygen or air plasma treatment has been used to get a wettable surface on plastic films for printing or adhesion. So we examined a mixture of O<sub>2</sub>-CF<sub>4</sub> as a plasma gas to control the plastic surface wettability. As shown in Fig.2, any desired surface wettability of a plastic surface can be produced<sup>(3)</sup> by changing the plasma gas concentration. The method of O<sub>2</sub>-CF<sub>4</sub> plasma for control of wettability suited not only polyethersulfone (PES) but many other plastics such as polyetheretherketone (PEEK), polyetherimide (PEI), polyethyleneterephthalate (PET), polyimide (PI, Kapton) and polypropylene (PP).

The plasma treatment of surfaces gave some reduction of mass due to the ion etching and/or the formation of gas products, as shown by the open marks in Fig.3. The use of the 3rd electrode of metal mesh which has the same electric potential as the sample electrode gave the results shown by the black marks in Fig. 3. It is clear that the reduction of film mass can be mostly attributed to chemical etching due to the formation of gas product except for the case of a CF<sub>4</sub> concentration of 100 %. The results of observations by SEM showed that the roughness of treated film surfaces in plasma are the largest in 50% of CF<sub>4</sub> concentration, while in 100 % O<sub>2</sub> and 100 % CF<sub>4</sub> concentrations the surfaces are very smooth. In addition, the use of metal mesh gave a clearly smoother surface than the surface obtained after the treatment which did not use metal mesh. So we can conclude that the effects of O<sub>2</sub>-CF<sub>4</sub> plasma treatment on wettability of plastic films are attributable<sup>(4)</sup> to the degrees of surface oxidation and fluorination. As Fig. 4 shows, the use of metal mesh has given about the same contact angle values as obtained for no metal mesh. The surface roughness by etching had no effect directly on the wettability in this experiment.

Many studies about the production of carbon films: the diamond film and/or the amorphous carbon film (a-carbon, i-carbon) from the gaseous phase have been reported. The double treatments (carbon film + fluorination) are a very useful method<sup>(5)</sup> to produce the hydrophobic and hard surface. On the other hand the surface structure of these carbon films is not yet clear. So the states of these carbon films after the CF<sub>4</sub> plasma treatment of only one minute are shown in Fig. 5. The figure shows the relation of the change of contact angle and fluorine content ratio in C<sub>1s</sub> peak of ESCA spectra. These results can be classified according to the amorphous or crystalline structure of the materials. The surface structure of the base material affects the nature of surface wettability after the fluorination. We used the carbon films produced by various methods: D1 (Diamond, micro wave), D2(CVD), D3(Ion sputter), A1(Amorphous carbon, C<sup>-</sup> ion bombardment), A2(Ion plating), A3(Ion sputter), G(Graphite). <sup>(1)</sup> N. Watanabe et al., Nippon Kagaku Kaishi, 1655(1975); <sup>(2)</sup> K. Takahashi et al., *ibid.*, 1916 (1985); <sup>(3)</sup> S. Okazaki et al. Patent applied for No.60-277652 Japan; <sup>(4)</sup> M. Kogoma et al., Plasma Chem.& Plasma Process., accepted; <sup>(5)</sup> S. Okazaki et al., Patent applied for No. 60-78981 Japan.

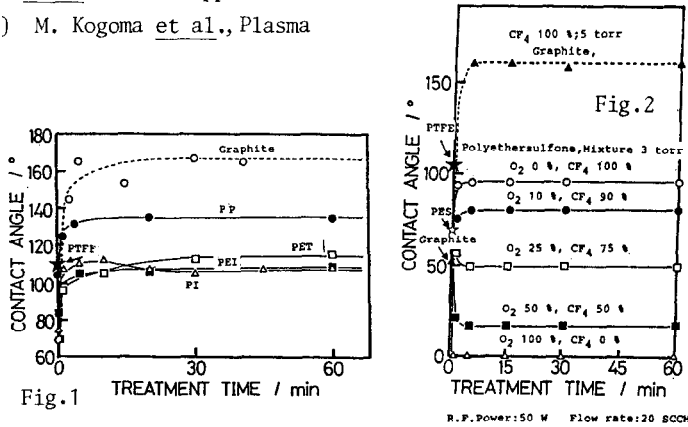


Fig.1

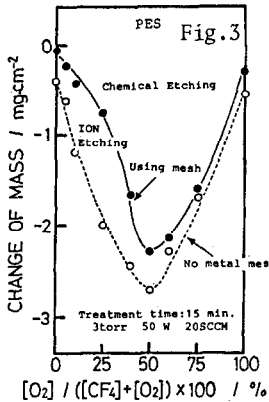


Fig.3

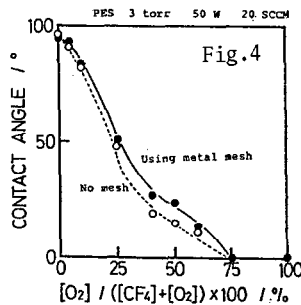


Fig.4

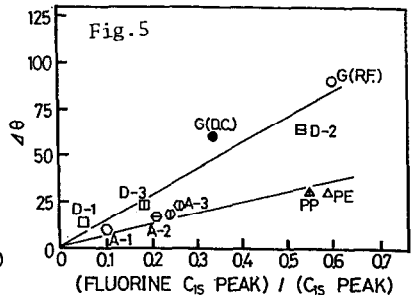


Fig.5