

Chemical Modification of Diamond Surfaces with Fluorine-Containing Functionalities

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Photolysis of perfluoroazooctane with diamond, such as diamond powders, films and nanodiamond films, led to a chemical modification of the surface so that perfluorooctyl functional groups could be introduced, and was confirmed by FT-IR, XPS, Raman and TOF-SIMS measurements. The diamond films modified with fluorine moieties showed an improvement in frictional properties and a reduction of surface energy, which was evaluated by the contact angle with water compared with pristine diamond and nanodiamond films. The contact angle and friction coefficient of a chemically modified diamond film are 118° and 0.1, respectively. In the case of modified nanodiamond films, contact angle measurements showed a highly water-repulsive behavior, to be valued as 124° against water. The results of the values of water contact angle depending on irradiation time are consistent with those of the F/C ratio of fluorinated nanodiamond films monitored with XPS.

1. Introduction

Diamond has been widely investigated because of its various unique electrical, thermal, biological and mechanical properties.⁽¹⁾ Chemical modifications of diamond surfaces have been expected to lead to improvements in its original behaviors while maintaining the bulk properties of diamond.⁽²⁻⁴⁾ Recent studies on the introduction of organic functional groups such as benzyloxy,⁽⁵⁾ cyano,⁽⁶⁾ DNA molecules⁽⁷⁾ and alkyl substituents⁽⁸⁾ on the surface of diamond films and powders terminated with hydrogen or oxygen using photo- and

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thermochemical methods have been reported.

Fluorine-containing organic compounds have attracted much attention in the field of medicinal chemistry and materials science because of their unique properties derived from the presence of fluorine atoms, namely, their biological activity and water/oil repellent properties.⁽⁹⁾ Previously we reported that photolysis of perfluoroazooctane (**1**) produced perfluorooctyl radicals effectively in solution under mild conditions for perfluoroalkylation of organic compounds.⁽¹⁰⁾ The introduction of substituents containing fluorine atoms would improve the behavior of diamond surfaces by enhancing their lubricity and stability under extreme conditions.⁽¹¹⁾ The fluorination of diamond surfaces has been studied by using F₂ gas,⁽¹²⁾ CF₄ plasma⁽¹³⁾ and X-ray irradiation.⁽¹⁴⁾ These methods have problems with the handling of the reactions, and makes it necessary to use special vessels. In this paper, we report on a useful method for a chemical modification of diamond powders, films and nanodiamond films with perfluoroalkyl substituents using the photolysis of **1** under mild conditions.

2. Materials and Methods

2.1 Samples and reagents

Diamond powders (MD500, particle size 500 nm) are commercially available from Tomei Diamond Industry Co., Ltd. Diamond films on Si substrates were purchased from Sumitomo Electric Industries Co., Ltd. as polycrystalline films grown by CVD. Nanodiamond films on Si substrates and on glass were fabricated as described elsewhere.⁽¹⁵⁾ Perfluoroazooctane (**1**) was prepared according to the literature.⁽¹⁶⁾ Perfluorohexane and n-hexane were obtained from Lancaster Synthesis Inc. and from Kanto Chemical Co., Inc., respectively, and used without further purification.

2.2 Perfluoroalkylation of diamond surfaces

Azo compound **1** (3.7 mg) in perfluorohexane (4 ml) was irradiated with a 60 W low-pressure mercury lamp (Eikosha EL-S-SQ-60) at room temperature in the presence of diamond powders (10 mg) and films (8 × 8 mm²) and an argon atmosphere, with stirring. In the case of nanodiamond modification, a Xe excimer lamp (172 nm) was used as a light source. After washing with three 2 ml portions of perfluorohexane and with one 2 ml portion of hexane to remove unreacted starting material, the samples were analyzed by Fourier transform infrared spectroscopy using reflection absorption spectroscopy (RAS FT-IR), X-ray photoelectron spectroscopy (XPS), a time-of-flight secondary ionization mass spectrometer (TOF-SIMS) and Raman spectroscopy. The irradiation time dependence of perfluoroalkylation on nanodiamond film surfaces was investigated by monitoring with XPS.

2.3 Measurements

FT-IR spectra were recorded with a Shimadzu FTIR-8700 using a microscope attachment for diamond powders and a JASCO FT/IR-680 Plus spectrometer using an RAS attachment for diamond films. XPS was measured by a PHI ESCA model 5800 using aluminum K α radiation. The fluorinated sample was analyzed by TOF-SIMS (Physical Electronics TFS-

2000). Primary ion bombardment was carried out with 15 kV Ga⁺ ions. The width of each ion pulse was 12 ns. Water contact angle measurements were carried out with an Elma G-1-1000. Sliding tests were performed with a reciprocating sliding tester in air at 55% humidity and 25°C. Stainless steel balls (SUS440C) were used as opposing specimens against the diamond films. Raman spectra were measured either with a JASCO Laser Raman Spectrometer NRS-2100 or NRS-1000UV using the 514.5 or 244 nm line of an argon ion or UV laser, respectively, with a power of 100 mW. Scanning electron microscopy (SEM) was used to examine surface morphology before and after irradiation. Samples were mounted on an Al stub using conducting carbon paste before examination in a Hitachi S-5000.

3. Results and Discussion

3.1 Chemical modification of O-terminated diamond powders

Figure 1 shows FT-IR spectra of the diamond powders before and after treatment by irradiation with **1**. In the sample after the photoreaction we can observe a new peak at 1196 cm⁻¹ for C-F stretching bands and a red shift of the carbonyl stretching vibration from 1792 to 1751 cm⁻¹. It is known that the surfaces of untreated diamond powders have carbonyl groups such as carboxylic acid and cyclic ketone.⁽¹⁷⁾ These results suggest that perfluorooctyl radicals generated by the photolysis of **1** abstracted hydrogen from carboxylic acid and/or reacted with ketone to give perfluorooctyl ether, after which the reaction of another C₈F₁₇ radical with a carboxyl radical gave perfluorooctyl ester on the surface of the diamond powders (Fig. 2).

As shown in Fig. 3, XPS spectra of the diamond powders were measured before and after treatment of perfluorooctylation, showing that a new peak at 694.4 eV of fluorine 1s appeared after irradiation. In the carbon 1s region, a strong peak appeared at 293.1 eV, with higher binding energies ascribed to carbon atoms bound to fluorine atoms than in the case

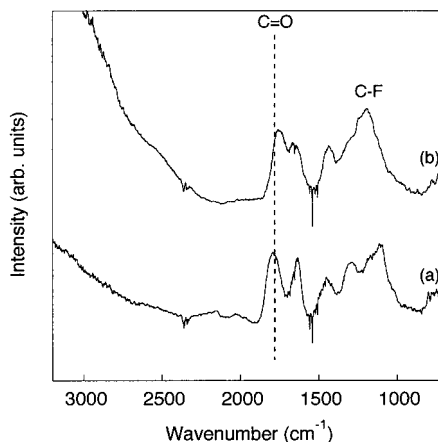


Fig. 1. FT-IR spectra of (a) untreated diamond powders and (b) diamond powders after perfluorooctylation treatment.

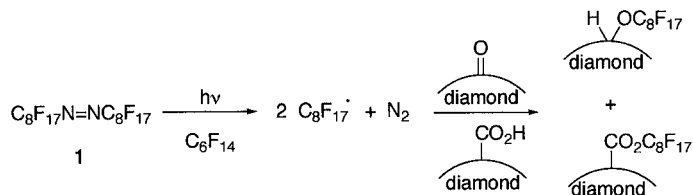


Fig. 2. Reaction mechanism of the chemical modification of diamond powders with fluorine functionalities.

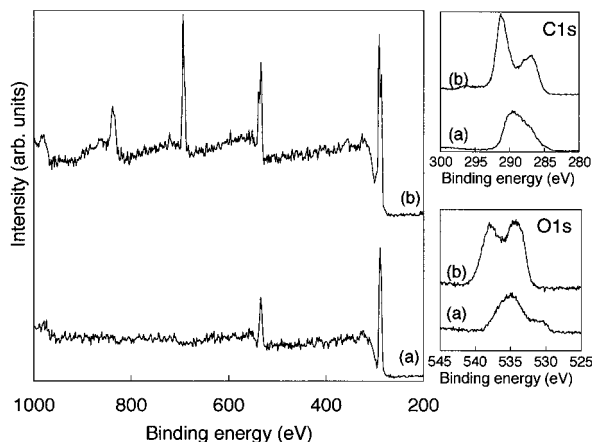


Fig. 3. XPS spectra of diamond powders (a) before and (b) after irradiation with perfluoroazooctane (**1**).

of the untreated diamond powders. Additionally, binding energies of 534.6 and 538.0 eV of oxygen 1s were also observed due to the C=O and C-O bonds, respectively.

3.2 Chemical modification of H-terminated diamond films

Figure 4 shows RAS FT-IR spectra of the diamond films before and after treatment by irradiation with **1**. The sample after the photoreaction shows a new peak at 1142 cm^{-1} for the C-F stretching band and the disappearance of a C-H stretching vibration at 2920 and 2851 cm^{-1} , which were derived from pristine diamond film. It is known that the surface of as-grown CVD diamond films is terminated with hydrogen.⁽¹⁸⁻²⁶⁾ These results suggest that the perfluorooctyl radical generated by the photolysis of **1** with the elimination of nitrogen abstracts hydrogen atoms from the diamond surface to produce $\text{C}_8\text{F}_{17}\text{H}$, and then the reaction of another C_8F_{17} radical with the remaining carbon radical on the diamond surface gives a perfluorooctyl substituent on the surface (Fig. 5).

As shown in Fig. 6, XPS spectra of the diamond films were measured before and after the perfluorooctylation treatment, showing that a new fluorine 1s peak at 687.9 eV appeared after irradiation. In the carbon 1s region, a new peak at 290.9 eV, with higher binding energies ascribed to the carbon atom bound to the fluorine atom, was observed, accompanied by a diamond C1s peak at 286.4 eV.

In order to investigate the influences on the formation of perfluorooctyl functionality on

a diamond surface, the fluorinated material was analyzed with Raman spectroscopy. As shown in Fig. 7, a characteristic diamond peak was observed at 1337 cm^{-1} in the case of fluorinated material, which was shifted and broadened compared with a pristine diamond film (1333 cm^{-1}). Vouagner *et al.* reported that UV-laser irradiation to diamond films caused surface structural transformations correlating to stress vibrations in diamond, along with

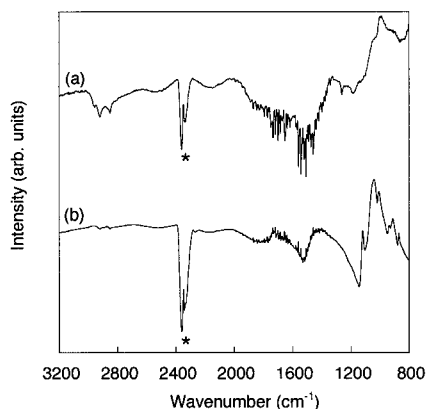


Fig. 4. FT-IR spectra of (a) untreated diamond films and (b) diamond films after perfluorooctylation treatment.

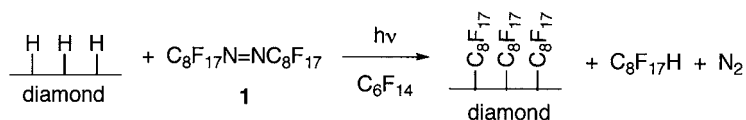


Fig. 5. Reaction mechanism for the surface modification of diamond films using photolysis of azo compound **1**.

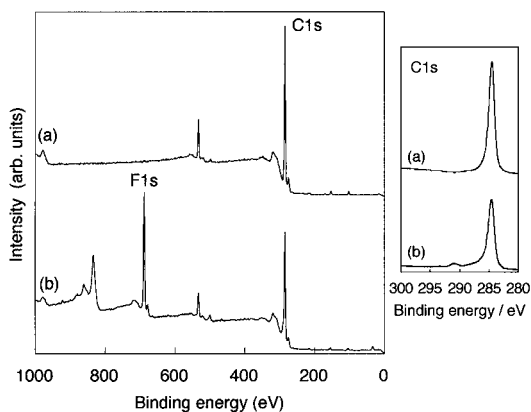


Fig. 6. XPS spectra of diamond films (a) before and (b) after irradiation with perfluoroazooctane (**1**).

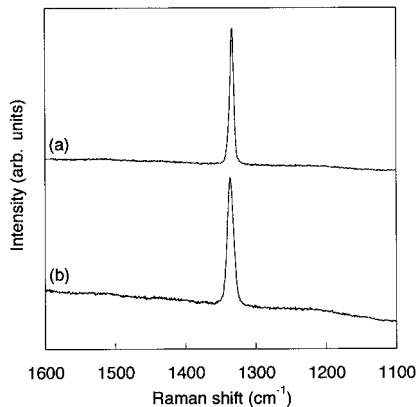


Fig. 7. Raman spectra of (a) pristine diamond films and (b) diamond films after perfluorooctylation treatment.

Raman peak shifts and broadening.⁽²⁷⁾ In this reaction, the characteristic diamond peak was shifted and broadened in a similar manner to that in the previous report.

In addition, the presence of the fluorinated surface on the diamond film was characterized with TOF-SIMS measurements for further confirmation. The positive spectrum shown in Fig. 8 exhibited peaks of m/z 12 (C^+), 31 (CF^+), 50 (CF_2^+), 69 (CF_3^+), 100 ($C_2F_4^+$), 119 ($C_2F_5^+$), 131 ($C_3F_5^+$), 169 ($C_3F_7^+$), 193 ($C_5F_7^+$) and 243 ($C_6F_9^+$), which are characteristic fragments from perfluoroalkyl groups.

The introduction of a fluorine moiety would be expected to decrease the surface energy. Surface properties were investigated by measuring the contact angles of the fluorinated diamond film with water. As shown in Figs. 9(a) and 9(b), the contact angle of the C_8F_{17} -modified diamond film was 118° , whereas the angle of the untreated diamond film was 81° . The fluorine-modified diamond surface provided water repulsion behavior comparable to polytetrafluoroethylene (PTFE), the contact angle of which is 103° .⁽²⁸⁾ It is known that the value of the contact angle depends on surface morphology together with surface chemical structure. In order to investigate the influence of the surface morphology of a C_8F_{17} -modified diamond surface, SEM images of pristine and treated diamond films were observed. As shown in Figs. 9(c) and 9(d), surface morphologies of diamond films did not change after modification with C_8F_{17} moieties. These results indicate that the water repulsion behavior of the fluorinated diamond surface was derived from the introduction of C_8F_{17} moieties.

Diamond has good tribological properties: namely, low friction and high wear resistance.^(29,30) It is expected that chemical modification of a diamond surface with fluorine functionalities would result in improvements in its friction properties. In order to investigate the mechanical properties of diamond films with C_8F_{17} moieties, friction tests were carried out, showing that at a load of 9.8 mN the friction coefficient of the chemically modified diamond film is 0.1 and that of the pristine diamond film is 0.2 (Fig. 10). The introduction of C_8F_{17} functional groups also provides a change in the friction properties at a low load.

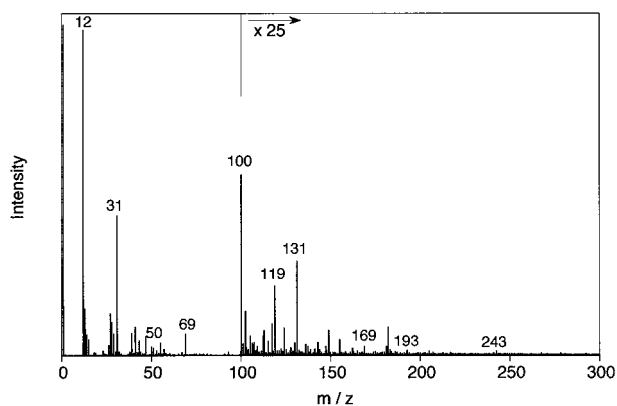


Fig. 8. TOF-SIMS spectrum of a fluorinated diamond film.

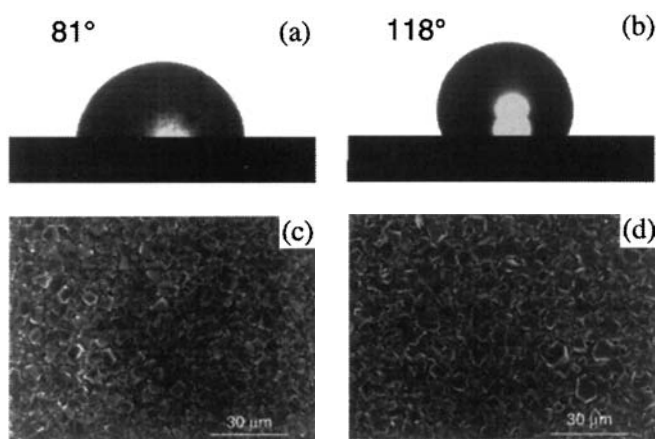


Fig. 9. Water contact angles of (a) pristine and (b) fluorinated diamond films. SEM images of (c) untreated and (d) diamond films after perfluorooctylation treatment.

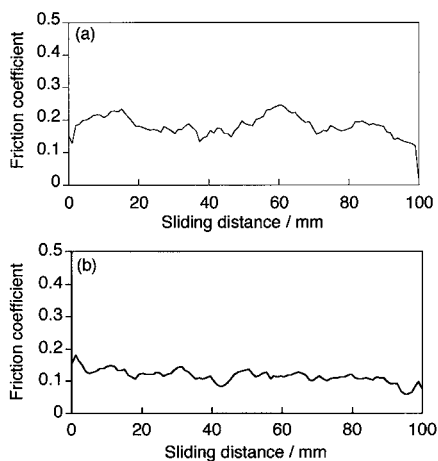


Fig. 10. Friction coefficients of (a) pristine and (b) fluorinated diamond films.

3.3 Chemical modification of O-terminated nanodiamond films

A RAS FT-IR spectrum of the nanodiamond films before irradiation with **1** shows the presence of -OH and C-H stretching bands, indicating that the nanodiamond film surfaces have mainly O-termination (Fig. 11(a)). The sample after the photoreaction indicates observations of a new peak at 1108 cm^{-1} for the C-F band, the C-H vibrations at 2919 and 2851 cm^{-1} disappear, and the OH stretching band decreases (Fig. 11(b)). These results suggest that perfluorooctyl radicals generated by the photolysis of **1** abstracted hydrogen atoms from C-H or -OH on nanodiamond surfaces to produce $\text{C}_8\text{F}_{17}\text{H}$, and then the reaction of another C_8F_{17} radical with the remaining carbon or oxygen radical on the nanodiamond surface gave perfluorooctyl substituents on the surface (Fig. 12).

As shown in Fig. 13, XPS spectra of the nanodiamond films were measured before and after perfluorooctylation treatment, showing that a new fluorine 1s peak at 690.0 appeared after irradiation, accompanied by C1s and O1s peaks. In the carbon 1s region, a new peak at 290.9 eV , with higher binding energies ascribed to carbon atoms bound to fluorine atoms, was observed, accompanied by nanodiamond C1s peak at 285.1 eV .

In order to investigate the influence on the formation of perfluorooctyl functionality on a nanodiamond surface, the fluorinated material was analyzed with Raman spectroscopy. As shown in Fig. 14, a characteristic diamond peak was observed at 1326 cm^{-1} with a broad peak from a graphite component at 1586 cm^{-1} . This photoreaction did not influence the bulk properties of the nanodiamond and led to a surface modification with fluorine functionalities.

Surface properties were investigated by measurements of the contact angles of the fluorinated nanodiamond films to water. As shown in Fig. 15, the contact angle of the C_8F_{17} -modified nanodiamond film is 124° , whereas that of untreated nanodiamond film is 54.5° . A fluorine-modified nanodiamond surface provided water repulsion behavior. These results indicate that this water repulsion behavior was derived from the introduction of C_8F_{17} moieties.

The nanodiamond films are transparent when deposited on glass substrates (Fig. 16(a)). The influence of nanodiamond surface modification with fluorine moieties was investigated using UV-vis measurements. As shown in Fig. 16(b), this chemical modification did not influence the transparency of the nanodiamond films, which showed $>87\%$ transmittance in the region of wavelengths $>400\text{ nm}$.

Furthermore, these surface properties depend on the F/C area ratio of XPS in Fig. 17. Irradiation time dependence of the formation of perfluorooctyl moieties on nanodiamond surfaces was investigated by monitoring them with XPS. The diamond C1s peak at 285.1 eV binding energy was used as an internal standard. Figure 17 shows the ratio of the area of the F1s signal to that of the total signal as a function of irradiation time. Due to the formation of C_8F_{17} moieties on the nanodiamond surface, the value for the fluorine atom increased with increasing irradiation time up to 30 min, while the value decreased with longer irradiation times. The tendency of changes in contact angle as a function of irradiation time is similar to that of the F/C ratio.

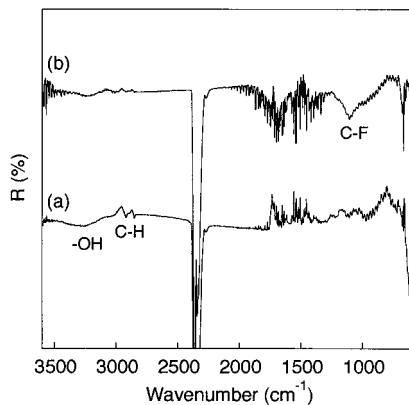


Fig. 11. FT-IR spectra of (a) untreated nanodiamond film and (b) nanodiamond film after perfluorooctylation treatment.

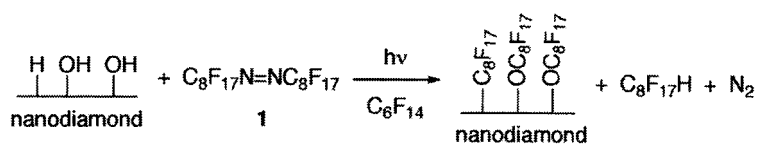


Fig. 12. Reaction mechanism for the surface modification of nanodiamond films using photolysis of azo compound **1**.

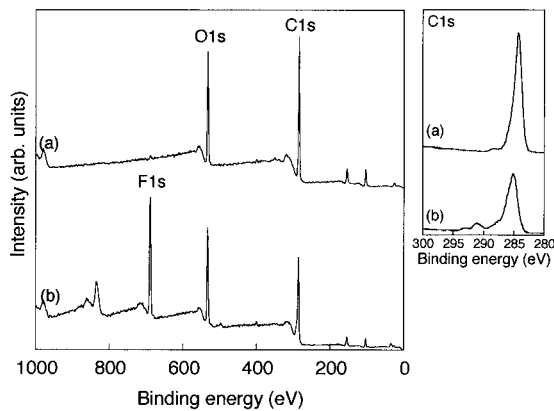


Fig. 13. XPS spectra of nanodiamond films (a) before and (b) after irradiation with perfluoroazooctane (**1**).

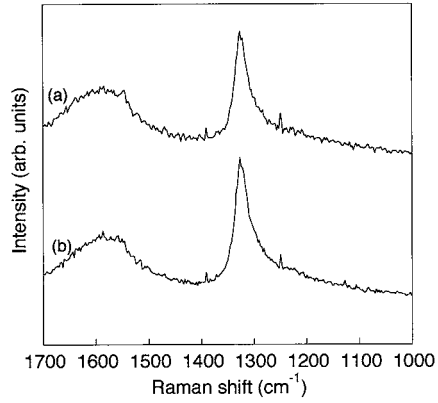


Fig. 14. Raman spectra of (a) pristine nanodiamond films and (b) nanodiamond films after perfluorooctylation treatment.

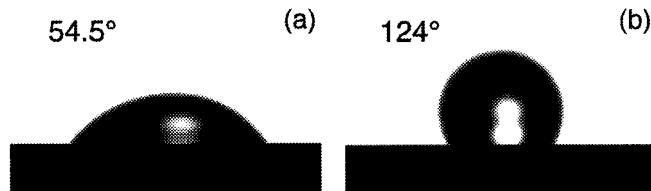


Fig. 15. Water contact angle of (a) pristine and (b) fluorinated nanodiamond films.

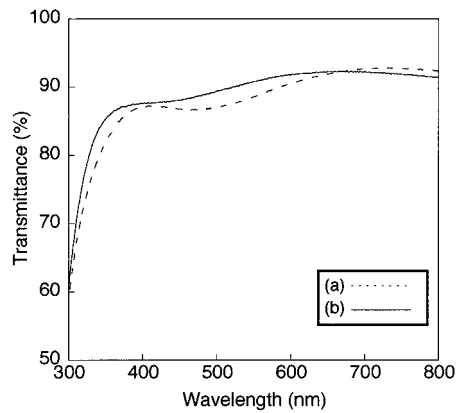


Fig. 16. UV-vis spectra of nanodiamond films (a) before and (b) after chemical modification with fluorine functionalities.

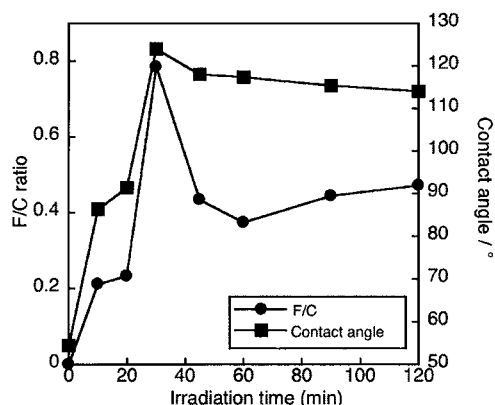


Fig. 17. Irradiation time dependence of F/C area ratio from XPS measurements and of contact angles of functionalized nanodiamond films.

4. Conclusions

Photolysis of perfluoroazooctane with diamond powders, films and nanodiamond films led to a chemical modification of the surface to form perfluorooctyl ester and ether functional groups. The introduction of the perfluoroalkyl substituents was confirmed by FT-IR, XPS and TOF-SIMS measurements. The diamond films modified with fluorine moieties showed improvements in frictional properties and a reduction of the surface energy, evaluated by measuring their contact angles with water compared with pristine diamond films. The contact angle and friction coefficient of chemically modified diamond film are 118° and 0.1, respectively. In the case of modified nanodiamond films, contact angle measurements show a highly water-repulsive behavior valued at 124° . This chemical modification did not influence the bulk properties of diamond as measured using Raman and UV-vis measurements. The values of the contact angle as a function of irradiation time are consistent with those of the F/C ratio of fluorinated nanodiamond films monitored with XPS.

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