

Direct Thermal Fluorination of Diamond Surfaces

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Introduction

Chemisorption on diamond surfaces is of interest due to its integral role in diamond crystal growth from the vapor phase. Investigation of the chemical reactivity of diamond surfaces leads to the understanding of the growth mechanism and development of the processes. The crucial factor in diamond growth is to prevent surface carbon atoms from forming the graphitic phase. Fluorine is expected to have a similar role as hydrogen for maintaining sp^3 hybridization of carbon atoms on the diamond surface, because fluorine reacts with graphite to give graphite fluorides $(CF)_n$ and $(C_2F)_n$.

Previously, we have reported on the hydrogenation,¹ oxidation,² chlorination³ and plasma-fluorination⁴ of diamond surfaces using diffuse-reflectance infrared Fourier-transform (DRIFT) and temperature-programmed desorption (TPD) spectroscopies. Recently, we have carried out fluorination of diamond surfaces with elemental fluorine.^{5,6} In this paper, the reactivity of hydrogenated and oxidized diamond powder surfaces with elemental fluorine and the stability of the

fluorinated diamond surfaces are discussed.

Experimental

Commercially available synthetic diamond powder less than $0.5 \mu\text{m}$ in diameter was used. Hydrogenated and oxidized diamond powder surfaces were prepared for our investigation of fluorination. The oxidized diamond was prepared by the liquid phase-treatment in a boiling acid mixture ($H_2SO_4 + HNO_3$), and the hydrogenated diamond was prepared by the vapor-phase treatment in a pure molecular hydrogen environment at 900°C . Fluorination was carried out under 1 atm of F_2 at -10°C to $+500^\circ\text{C}$ for 24 hours. DRIFT spectra were recorded on a Bio-Rad Digilab FTS-45 FTIR instrument equipped with a liquid nitrogen cooled MCT detector in the region $4000 - 500 \text{ cm}^{-1}$.

Results and Discussion

DRIFT spectra of C-H and C-F stretching regions

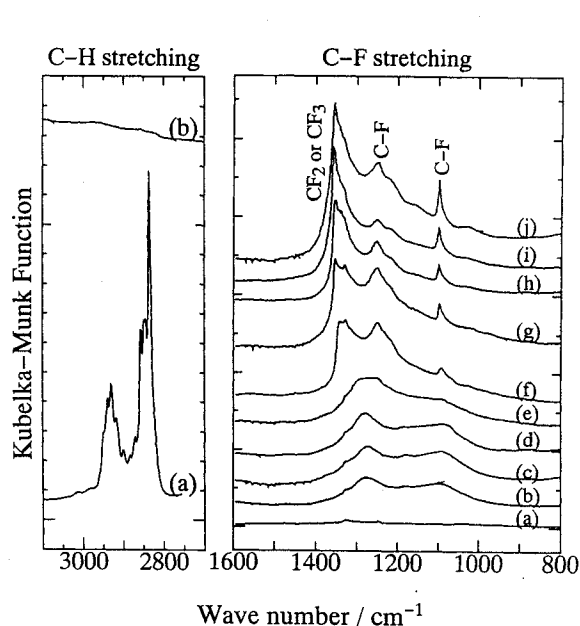


Figure 1 DRIFT spectra of the hydrogenated diamond powder surface before and after fluorination. (a) Before treatment, (b) treated with F_2 at -10°C , (c) 0°C , (d) 10°C , (e) 35°C , (f) 100°C , (g) 200°C , (h) 300°C , (i) 400°C , and (j) 500°C .

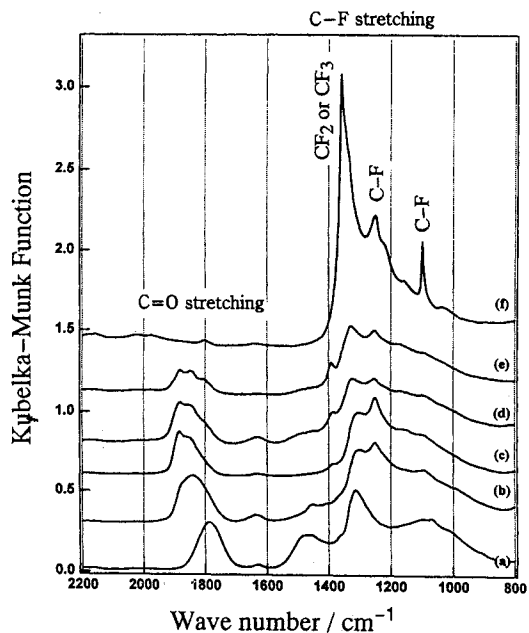


Figure 2 Fluorination temperature dependence of DRIFT spectra of the oxidized diamond powder surface. (a) Before treatment, (b) treated with F_2 at 100°C , (c) 200°C , (d) 300°C , (e) 400°C , and (f) 500°C .

of fluorinated samples are shown in Figure 1 as a function of the reaction temperature. The initial spectrum of the pre-hydrogenated diamond surface before treatment contains several peaks in the region $2800 - 2970 \text{ cm}^{-1}$ [Spectrum (a)]. These are ascribed to the C-H stretching vibrations of sp^3 hybridized bonding. After treatment with fluorine at -10°C , no C-H stretching vibrations were observed [Spectrum (b)], whereas new peaks appeared in the region $1000 - 1400 \text{ cm}^{-1}$ with two maxima at 1085 and 1277 cm^{-1} . These are due to C-F stretching vibrations. These results indicate that substitution of hydrogen by elemental fluorine occurred even at -10°C .

Figure 2 shows the results of the fluorination of the oxidized diamond powder surface. Before treatment, the DRIFT spectrum shows a peak at 1788 cm^{-1} , which is due to C=O stretching vibration of carboxylic anhydride, carboxylic acid or cyclic ketone structure, and several peaks at 1080 , 1316 , and 1470 cm^{-1} , which are due to C-O stretching vibrations. After treatment in fluorine above 100°C , the peak at 1788 cm^{-1} significantly shifted to a higher frequency region. This indicates that C=O stretching vibrations are affected by fluorine atoms. In contrast to the fluorination of hydrogenated diamond surface, most of the oxygen chemisorbed on the diamond surface remains on the surface below 200°C .

Figure 3 shows the reaction time dependence of

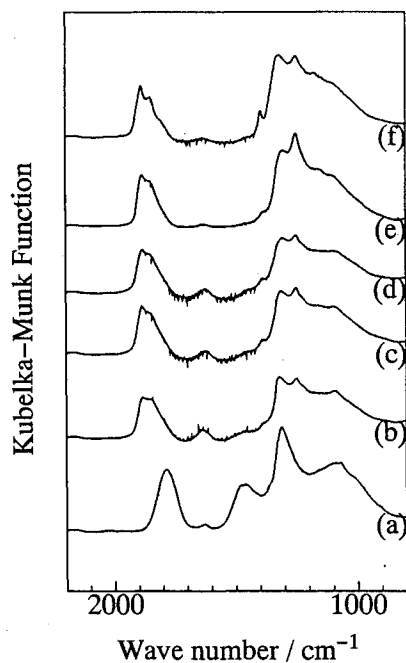


Figure 3 Fluorination time dependence of DRIFT spectra of the oxidized diamond powder surface. (a) Before treatment, (b) treated with F_2 at 200°C for 15 min, (c) 40 min, (d) 12 hrs, (e) 24 hrs, and (f) 7 days.

fluorination of the oxidized diamond surfaces. The results indicate that partial fluorination of the oxidized diamond occurs within 15 minutes at 200°C . Even after 7 days, however, the C=O peak at *ca.* 1800 cm^{-1} did not diminish grossly, indicating that the complete depletion of oxygen requires more than 7 days at 200°C or, probably, higher temperatures above 400°C as Figure 3 indicates.

The fluorinated diamond surface is quite stable in air at room temperature, while the chlorinated diamond surface is very reactive even at low temperatures.³ After fluorination at 500°C , the diamond was treated in H_2 at various temperatures. Little change was observed below 500°C . By treatments above 525°C , peaks due to C-F stretching vibrations reduced and peaks due to C-H stretching vibrations appeared and grew in the region $2800 - 3000 \text{ cm}^{-1}$. The re-hydrogenation was completed at 650°C to give C-H species.

Conclusions

This study confirms that fluorine can abstract hydrogen from the diamond powder surface even at low temperature ($T = -10^\circ\text{C}$) resulting in fluorine chemisorption on the diamond surface. Raising the fluorination temperature ($T > 100^\circ\text{C}$) increases the coverage of fluorine to produce CF_3 species. The oxidized diamond powder surface shows less reactivity toward elemental fluorine than the hydrogenated surface. The fluorinated diamond surface is stable in air at room temperature and reacts with H_2 above 525°C .

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