

# F<sub>2</sub>, H<sub>2</sub>O, and O<sub>2</sub> etching rates of diamond and the effects of F<sub>2</sub>, HF and H<sub>2</sub>O on the molecular O<sub>2</sub> etching of (110) diamond

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## Abstract

Oxidation kinetics of natural (110) diamond by oxygen and water were investigated using in situ Fizeau interferometry. Apparent activation energies of 53 and 26 kcal mol<sup>-1</sup> were obtained for the etching of (110) type Ia diamond by O<sub>2</sub> and H<sub>2</sub>O respectively. The etch rate was found to follow second-order kinetics with respect to O<sub>2</sub> pressure in the pressure range 0.04–10 Torr. For water over the vapour pressure range 0.1–2 Torr, the reaction has a reaction order near unity. The diamond (110) surface was impervious to etching by molecular fluorine at all temperatures up to 1300 °C. Fluorine, hydrogen fluoride and water were found to inhibit the molecular oxygen etching of diamond. Below 900 °C, oxidation is inhibited by the addition of F<sub>2</sub> and HF presumably by blocking reactive sites on the diamond surface through formation of C–F bonds. Above 900 °C, the fluorine is thought to desorb from the diamond (110) surface, rendering the surface susceptible to further oxidation. Addition of water below 800 °C was found to retard etching by molecular oxygen. This is attributed to the formation of C–OH bonds, analogous to C–F.

**Keywords:** Diamond; Etching; Fluorine; Oxygen

## 1. Introduction

One of the properties of diamond which is of interest to many of its applications is its chemical reactivity, particularly with respect to oxygen. Many diamond CVD processes include oxygen whether in the form of molecular oxygen, water, or CO<sub>2</sub> along with the carbon source and hydrogen. The presence of oxygen is thought to enhance the quality of CVD diamond through selective etching of sp<sup>2</sup> carbon. Rawles and D'Evelyn [1] have studied the growth rates of CVD diamond in a hot filament reactor using 0.5–1% methane and 0–0.44% oxygen. They reported that at low concentrations of oxygen, the growth rate was enhanced below 800 °C while etching of diamond was observed above 900 °C.

In the presence of oxygen, diamond is known to readily etch at temperatures above 600 °C. Etching rates of natural diamond are known to exhibit strong orientation dependence [2], with the (111) surface exhibiting the highest oxidation rate, followed by (110) with (100) being the lowest [3]. Effective activation energies of 55 kcal mol<sup>-1</sup> were reported by Evans for the three low index faces of diamond in the temperature range of 600 to 750 °C [1]. The etching of hot filament CVD polycrystalline diamond films and MPCVD films has been

investigated by several research groups and the activation energy is found to vary from 35.6 kcal mol<sup>-1</sup> to as high as 70 kcal mol<sup>-1</sup>, depending on factors such as the morphology of the film, crystal defects such as presence of twinning, and the amorphous carbon content of the film [4–9]. Etch rates of polycrystalline diamond can be close to those of graphite or natural (100) diamond, depending on the amorphous carbon content and the orientation of the crystallites in the film. In general, the etch rate increases as the diamond film quality decreases with respect to amorphous carbon content. In this paper we report the etching rates of natural diamond Ia wafers in the presence of fluorine, hydrogen fluoride, oxygen and water. We have also investigated the effects of fluorine, hydrogen fluoride and water on the etching of diamond by molecular oxygen.

## 2. Experimental

In this thermochemical etching study, natural (110) diamond crystals are evaluated using a Fizeau interferometer for in situ etching measurements. The chemical etchants are water and molecular oxygen. Fluorine and



HF are also added to investigate their possible etching of diamond as well as their effect on molecular oxygen etching rates. The experiments are conducted under vacuum with partial pressures of oxygen and water from 0.04 to 15 Torr and at temperatures from 600 to 1000 °C. Natural (110) type Ia diamond chips were obtained from Harris Diamond Corporation and polished before use on a Crystallite 2000 r.p.m. lapping machine. A schematic of the reactor used for the etching studies is shown in Fig. 1. Gases are introduced into the reactor chamber using mass flow controllers through concentric nickel tubes. The gas flows directly over the diamond substrates mounted on a platinum substrate heater. The polished (110) diamond chip is firmly mounted by spot welding two small platinum pieces in the centre of a platinum strip with a 1 mm hole for back illumination by a HeNe laser beam. The platinum substrate heater is connected to water-cooled electrodes which resistively heat the platinum and the diamond substrate to the desired reaction temperatures. A platinum-13% rhodium thermocouple is spot welded to the platinum heater adjacent to the diamond to monitor the substrate temperature. In order to ensure the temperature stability needed for in situ fringe monitoring, a variable output temperature controller was used.

Etching rates of the diamond substrates are obtained through direct in situ measurements using a Fizeau interferometer to monitor changes in the diamond thickness, and thus etch rates. The Fizeau interferometer utilizes the fringes due to interference patterns generated by a helium–neon laser on a diamond chip. A schematic of the fringe monitoring system is illustrated in Fig. 2. A detail description of the development of the Fizeau interferometer is found elsewhere [10]. Interference fringes occur when there is a difference in the optical paths travelled by successive beams originating from a single light source. By maintaining the same refractive index, an interferometer can measure small changes in the geometric thickness of an object. A smooth diamond

chip for which the two faces are not perfectly parallel to each other will produce interference fringes. Any change in the thickness of the diamond will lead to movements of the fringes. Such changes can also result from heating or cooling and growing or etching of the substrate. By monitoring the substrate thickness change as a function of time, the rate of the thickness change can be determined. Growth or etching are distinguished from the direction of fringe movement.

The light source for the interferometer is a 1.0 mW linearly polarized Uniphase HeNe gas laser with a 633 nm beam, which after being passed through a filter and a beam-focusing lens was positioned on the back of the diamond substrate. The resulting interference patterns of bands, or fringes, are recorded with a high-performance CCD camera. Images from the camera were recorded with a VCR and also captured on a Macintosh computer using a Scion video frame-grabber for further analysis. With appropriate image magnification and capture with a video camera, image analysis can provide measurement accuracy of 1/100 of a complete fringe shift. This corresponds to a sensitivity of 1.3 nm thickness change with a 633 nm HeNe laser and the 2.4 refractive index of diamond. This interferometer has permitted the sequential variation of processing parameters in a single experiment and the determination of very small etching rates within 10–15 min time periods.

### 3. Results and discussion

For monochromatic light and nearly perpendicular incident light, the thickness change of a diamond substrate  $\Delta D$  in time  $\Delta t$  can be determined from the following relationship:

$$\Delta D = \pm \left( \frac{\lambda}{2n} \right) \left( m \frac{\Delta x}{\Delta S} \right) \quad (1)$$

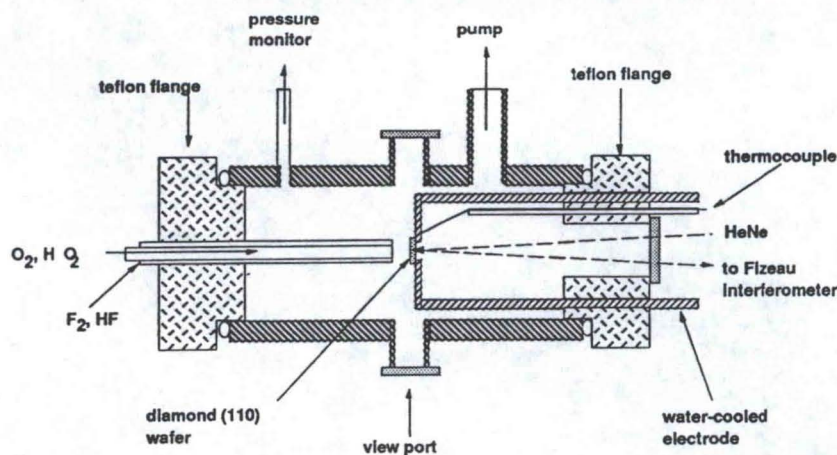


Fig. 1. Reaction chamber.



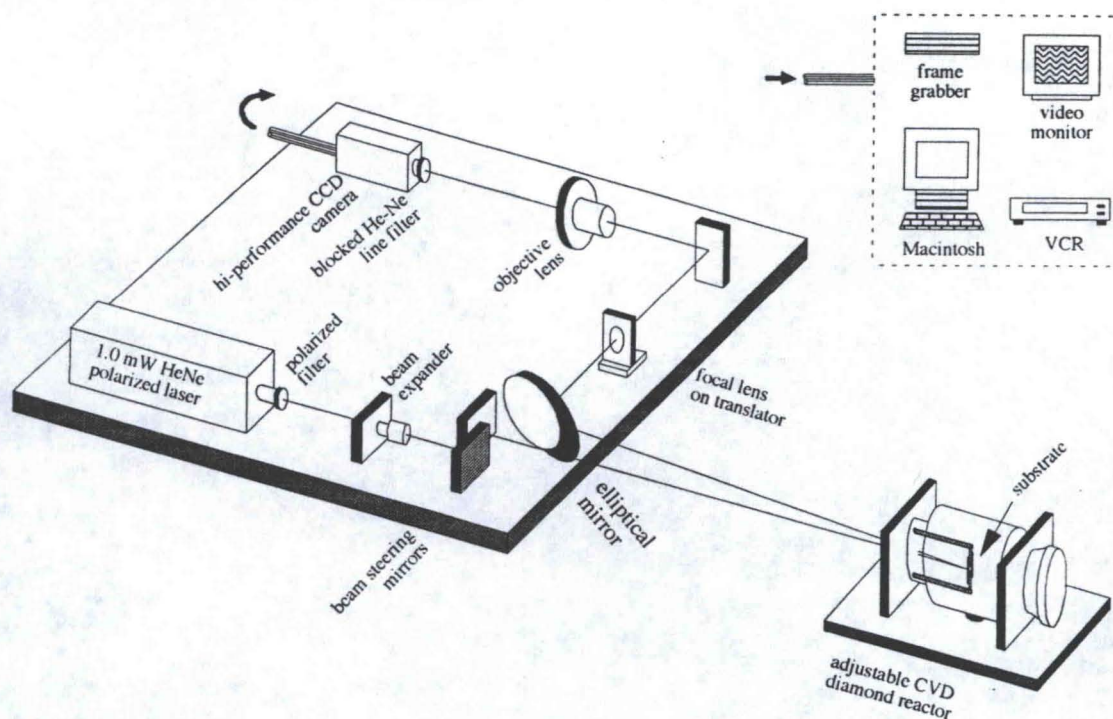


Fig. 2. Fizeau interferometer.

where  $\lambda$  is the wavelength of the laser line and  $n$  is the refractive index of the diamond substrate, which is 2.4 at room temperature.  $m$  represents the total number of complete fringe cycles,  $\Delta x/\Delta S$  is the remaining fraction of a fringe cycle, and  $\Delta S$  is the spacing in pixels between two neighbouring fringes. The sign on the right-hand side of the equation corresponds to diamond growing or etching. Because of its small temperature dependence ( $(1/n)(dn/dT)_p = 4.04 \times 10^{-6} \text{ K}^{-1}$ ) [11], the refractive index of diamond increases by <3% when the temperature of diamond increases from room temperature to 1000 K. Therefore 2.4 is assumed for the refractive index of diamond at all experimental temperatures. At constant temperature, a shift of one fringe indicates  $0.13 \mu$  thickness change in the diamond.

The fringe movement of the diamond substrate was continuously monitored by the Fizeau interferometer. A typical fringe pattern of the diamond substrate prior to oxidation is illustrated in Fig. 3. Etching of the diamond substrate causes the fringes to move in the same direction as cooling of the substrate. For example, after 70 min at  $900^\circ\text{C}$  and under 15 Torr pressure of oxygen, a total of 81 complete fringe cycles was observed by the interferometer. By assuming  $n=2.4$  in Eq. (1), 81 complete fringe cycles correspond to  $10.7 \mu\text{m}$  etching of the diamond substrate. The thicknesses of the diamond substrate before and after oxidation were determined by the FTIR interferometry technique to be 475.6 and  $465.3 \mu\text{m}$ , respectively. The resulting thickness change of  $10.7 \mu\text{m}$  by the Fizeau interferometer vs.  $10.3 \mu\text{m}$  by the FTIR interferometry technique [12] demonstrates excellent

agreement within the expected error limits of the FTIR total thickness measurement.

### 3.1. Etching by oxygen and water

Etching of the (110) diamond chip was carried out from  $650$  to  $850^\circ\text{C}$  under 15 Torr pressure of oxygen and from  $925$  to  $1000^\circ\text{C}$  under 15 Torr of  $\text{H}_2\text{O}$  pressure. The etch by water was much slower and required a higher temperature for observation. The etch rate data in terms of  $\mu\text{m h}^{-1}$  are presented in Table 1. Molecular oxygen is observed to etch (110) diamond at much higher rates than water. The rate data are presented in the form of an Arrhenius plot in Fig. 4. The apparent activation energies calculated from the slopes are  $53$  and  $26 \text{ kcal mol}^{-1}$  respectively for oxygen and water. The finding for oxygen is in agreement with that reported by Evans and Phaal [2].

The variation of reaction rate with pressure is presented in Fig. 5 for oxygen at  $850^\circ\text{C}$  and in Fig. 6 for water at  $1000^\circ\text{C}$ . The apparent reaction order calculated from the slopes of the plots is found to be second-order over much of the intermediate pressure range with respect to oxygen pressure, indicating bimolecular reaction kinetics. A reaction order near unity was found for water. A comparison of the apparent reaction order for the diamond–oxygen reaction with values obtained by other research groups is presented in Table 2. The discrepancies in the reaction orders appear to be due to the differences in the pressure ranges of the different research groups. The second-order kinetics for oxygen



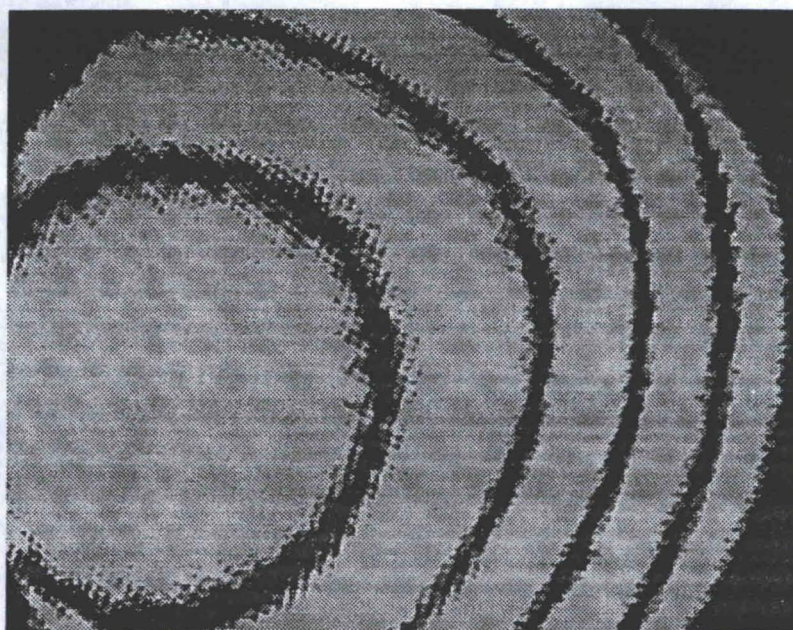


Fig. 3. Fringe pattern of a polished (110) diamond wafer before experiment.

Table 1  
Etch rates of (110) diamond wafer by oxygen and water

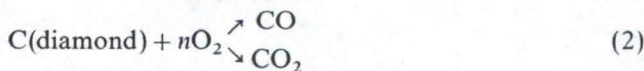
Temperature (°C)	Etch rate ( $\mu\text{m h}^{-1}$ ) at oxygen pressure of 15 Torr	Temperature (°C)	Etch rate ( $\mu\text{m h}^{-1}$ ) at water pressure of 15 Torr
653	0.37	925	1.14
703	1.37	950	1.44
751	6.15	975	1.73
802	10.31	1000	2.16
850	69.01		

is different from that of Evans and Phaal who found the diamond–oxygen reaction to follow first-order kinetics. However, our results do not necessarily disagree with their finding, since the pressure ranges studied by Evans and Phaal are in the range of 0.1–0.5 Torr, which is the lower limit of our studies. Our results also appear to indicate a lower reaction order at low pressures. This is illustrated in Fig. 5, which compares our data with those of Evans and Phaal. The findings of Alam and Sun are in a pressure range much higher than our studies. At pressures above 15 Torr we have found that the reaction rate begins to slow, presumably due to the saturation of reactive sites on the diamond surface. Presently there are no literature data available on the diamond–water reaction, which we have found to follow a near unity reaction order in the range of 0.1–1.6 Torr. Above 2 Torr of water vapour pressure, the reaction rate is insensitive to variations in water vapour pressure.

Clearly, etching proceeds by different mechanisms for oxygen and water, as indicated by a factor of two difference in the observed activation energies. Etching by water is not observed until 900 °C, whereas oxidation

by molecular oxygen initiates at <600 °C. The saturation pressure for oxygen occurs near 15 Torr, while the water etching reaction rate approaches saturation at 2 Torr of water pressure.

The reaction of diamond and oxygen can be thought of in terms of combustion of carbon, i.e.



Temperature-programmed desorption (TPD) of diamond powder oxidized by molecular oxygen at temperatures from 25 to 554 °C was studied by Matsumoto et al. [13]. Two desorption peaks attributed to CO and CO<sub>2</sub> were observed whose maximum desorption temperature varied from 500 to 600 °C depending on the initial oxidation temperature of the samples. Oxidation at higher temperatures favoured the formation of carbon–oxygen groups, which led to the desorption of CO rather than CO<sub>2</sub>. For diamond powder oxidized at the higher temperature of 554 °C, CO desorption was 12 times more abundant than CO<sub>2</sub>. TPD studies by Ando et al.



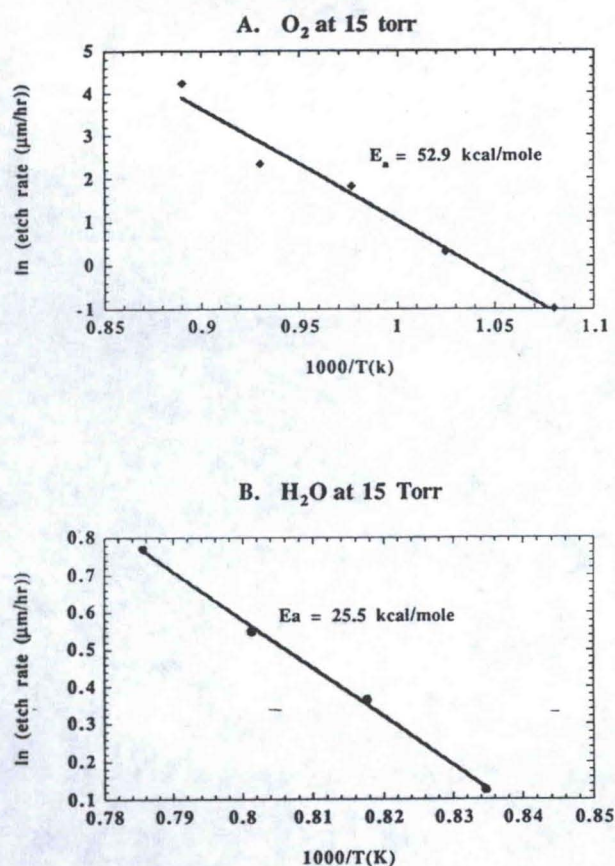


Fig. 4. Arrhenius plot of the etch rate of (110) diamond

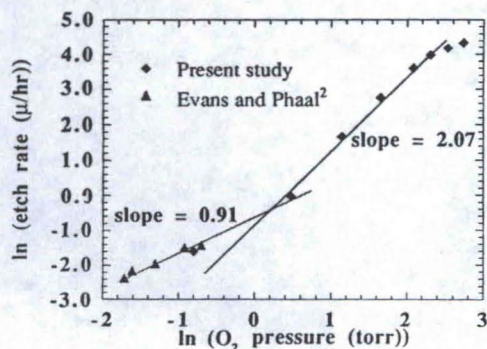
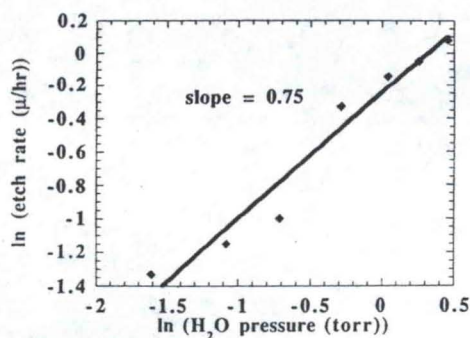
Fig. 5. Etching of (110) diamond by O<sub>2</sub> at 850 °C.Fig. 6. Etching of (110) diamond by H<sub>2</sub>O at 1000 °C.

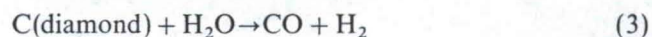
Table 2

Apparent reaction orders for the diamond-oxygen reaction

Source	Pressure range (Torr)	Reaction order
Present study	0.04-15	2.1
Evans and Phaal [2]	0.1-0.5	1.0
Alam and Sun [5]	165-760	0.6

[14] indicated that the desorption of CO corresponded to the loss of C=O vibrations of strain-free cyclic ketones in the infrared spectra of the oxidized samples. The desorption of CO<sub>2</sub> corresponded to the loss of C=O stretching vibrations of carboxylic anhydride, lactones or strained cyclic ketone structures, which are not favoured during oxidation at higher temperatures. Rather, the desorption of CO<sub>2</sub> from samples oxidized at higher temperatures is postulated by Matsumoto to be through the secondary reactions of initially desorbed CO with surface oxygen. In our present study, a larger amount of CO<sub>2</sub> relative to CO is expected as a result of higher O<sub>2</sub> pressures. In situ gas sampling near the diamond surface was not performed, since CO<sub>2</sub> is also the expected product due to the presence of Pt, the substrate holder and heater, which is known to catalyse the oxidation of CO by molecular oxygen to CO<sub>2</sub>. The activation energy of CO desorption from an oxygen-terminated diamond (100) surface was measured by Thomas et al. [15] to be approximately 44 kcal mol<sup>-1</sup>, while the activation energy for CO<sub>2</sub> desorption was 21 kcal mol<sup>-1</sup>. Our studies indicate that the activation energy is not dependent on pressure even though the reaction converts from first-order at low pressures to second-order at intermediate pressures. We believe that this indicates that the same intermediate activation complex is involved over the entire pressure range. The difference results from increased probability for CO<sub>2</sub> formation due to reaction of adjacent carbonyl groups, a Langmuir-Henzelwood reaction mechanism, or reaction of molecular oxygen with an activated surface carbonyl group, a Eley-Rida reaction mechanism. In either case the reaction to produce CO<sub>2</sub> is second-order in O<sub>2</sub> if the surface concentration of carbonyl has a first order dependence on O<sub>2</sub>. In any case the second-order reaction of oxygen with a carbon surface is a very important reaction path for all surface-controlled combustion of carbon solids.

The reaction of diamond with water is different from that of diamond-oxygen in that hydrogen is involved. The products should include H<sub>2</sub> and CO, i.e.



Matsumoto et al. [16] have studied the thermal desorption of diamond powder treated with water from room temperature to 1400 °C and found CO and H<sub>2</sub> to be major desorption products. Desorption of CO<sub>2</sub> was



not observed. This CO and H<sub>2</sub> desorption occurs at higher temperatures than that of diamond powder oxidized with molecular oxygen. Desorption of CO and H<sub>2</sub> initiates at 800 °C, with CO maximizing at 900 °C and H<sub>2</sub> at 1000 °C. This higher temperature requirement correlates with our observations of the diamond-water reaction that it is not measurable until at least 850 °C. Thomas et al. [15] have also observed the desorption of CO and H<sub>2</sub> at 900 °C from TPD studies of oxygen saturated (100) diamond surface annealed in an atomic hydrogen flux. The source of CO is expected to be different from that of the diamond-oxygen reaction, which occurs at much lower temperatures. Ando's [14] diffuse reflectance FTIR studies of oxidized diamond powder hydrogenated at 400-800 °C indicated the predominance of C-O-C absorptions at 800 °C and the reduction of C=O absorptions at lower temperatures. HREELS of the oxidized diamond (100) surface showed that heating reduced the carbonyl and hydroxyl intensities more rapidly than C-O-C intensities [17]. The formation of ether C-O-C groups may be the predominant intermediate of high-temperature CO in the diamond-water reaction, since they are readily formed through the elimination of H<sub>2</sub> from C-OH and C-H groups on the diamond surface. The fact that the activation energy is lower than that of the diamond-oxygen reaction may be attributed to the presence of hydrogen on the diamond surface, which readily stabilizes the carbon dangling bonds created during CO desorption, thus lowering the activation energy of the reaction.

Since diamond is not etched by water until a much higher temperature, it can stabilize the diamond surface with respect to etching by molecular oxygen at temperatures below 900 °C. The results of three sets of experiments illustrating the effects of water on diamond oxidation by molecular oxygen are presented in Table 3. For example, at 800 °C and an oxygen partial pressure of 0.51 Torr, the addition of 0.14 Torr of water decreased the etch rate from 2.44 to 0.07 μm h<sup>-1</sup>. These experiments indicate that water is a good oxidation inhibitor at temperatures below 850 °C, possibly due to the formation of C-OH bonds at active sites. This inhibition of the diamond-oxygen reaction by water has also been observed by other research groups [2,7].

### 3.2. Effects of H<sub>2</sub>O, F<sub>2</sub>, HF addition on diamond etching by molecular oxygen

During fluorine-activated diamond CVD growth studies [18], it was observed that the presence of graphitic or amorphous carbon during the growth process can be eliminated by cyclic additions of F<sub>2</sub>, which preferentially etches graphite in the presence of diamond. Rosner and Strakey [19] have studied the kinetics of pyrolytic graphite gasification by molecular fluorine in the temperature range 1036-1715 K and found that

Table 3  
Effects of water on oxidation of (110) diamond surface

#### Experiment A<sup>a</sup>

Total P (Torr)	O <sub>2</sub> P (Torr)	H <sub>2</sub> O P (Torr)	Etch rate (μm h <sup>-1</sup> ) at 800 °C
0.51	0.51	0	2.44
0.65	0.51	0.14	0.07
0.54	0.51	0.03	0.77

<sup>a</sup> O<sub>2</sub> flow set at 8 sccm.

#### Experiment B<sup>b</sup>

Total P (Torr)	O <sub>2</sub> P (Torr)	H <sub>2</sub> O P (Torr)	Etch rate (μm h <sup>-1</sup> ) at 800 °C
18.79	18.79	0	13.86
19.54	18.79	0.75	1.13
22.22	18.79	3.43	0.93

<sup>b</sup> O<sub>2</sub> flow set at 8 sccm.

#### Experiment C<sup>c</sup>

Total P (Torr)	O <sub>2</sub> P (Torr)	H <sub>2</sub> O P (Torr)	Etch rate (μm h <sup>-1</sup> ) at 850 °C
2.58	2.58	0	10.68
4.06	2.58	1.48	4.41
5.19	2.67	2.52	5.49
6.27	2.67	3.60	5.98
2.67	2.67	0	13.20

<sup>c</sup> O<sub>2</sub> flow set at 8 sccm.

carbon atoms are removed preferentially from the edge planes of pyrolytic graphite by F<sub>2</sub>. We have studied the stability of diamond (110) surface under 5 Torr of F<sub>2</sub> atmosphere and found it to be impervious to molecular fluorine in the temperature range 900-1600 K. Freedman [20] found fluorine to adsorb on diamond (100) and (111) surfaces at 300 K. Desorption occurred over a wide range of temperatures from 500-1200 K without etching diamond.

We have investigated the effects of molecular fluorine and hydrogen fluoride on the diamond-oxygen reaction. The results for F<sub>2</sub> addition are presented in Table 4. At 700 °C and 15 Torr of oxygen with a continual flow of 8 sccm, the etch rate of a diamond IA (110) wafer was established at 0.98 μm h<sup>-1</sup>. Addition of 0.01 Torr of F<sub>2</sub> was accomplished by introducing F<sub>2</sub> at a flow rate of 1.5 sccm for 2 min into the reaction chamber. At 700 °C and 15 Torr of oxygen, the etch rate was reduced from 0.98 μm h<sup>-1</sup> to 0 μm h<sup>-1</sup>. This etching inhibition was observed to be instantaneous by the cessation of fringe movement in the Fizeau interferometer. The diamond wafer temperature was then increased and held at 750 °C for 10 min and the etch rate remained at 0 μm h<sup>-1</sup> even though the expected etch rate at 750 °C in the absence of F<sub>2</sub> is 4.40 μm h<sup>-1</sup>. As the diamond substrate temper-



Table 4  
Effects of F<sub>2</sub> on oxidation of (110) diamond

Time (min)	O <sub>2</sub> P (Torr)	F <sub>2</sub> P (Torr)	Temp. (°C)	Etch rate (μm h <sup>-1</sup> )	Expected etch rate without F <sub>2</sub> (μm h <sup>-1</sup> )
0	15.00	0	700	0.98	—
16	15.00	0.01	700	0.00	0.98
30	15.00	0	750	0.00	4.40
40	15.00	0	800	3.91	7.38
50	15.00	0	850	32.56	49.36
53	15.00	0	750	2.35	4.40
60	15.00	0	700	0.58	0.98

\* O<sub>2</sub> flow set at 8 sccm.

ature was increased to 800 °C, the etch rate increased from 0 to 3.91 μm h<sup>-1</sup>, which is still less than the expected etch rate of 7.38 μm h<sup>-1</sup>. We believe this indicates that surface fluorine has partially desorbed from the diamond surface, rendering the diamond susceptible to oxygen attack. The presence of surface fluorine is evident even at 850 °C, since the observed etch rate of 32.56 μm h<sup>-1</sup> is still less than the expected etch rate of 49.36 μm h<sup>-1</sup> without F<sub>2</sub>. After a sustained period at 850 °C, the temperature of the diamond wafer was reduced to 700 °C, the starting temperature. Some etching inhibition still remained at the end of the experiment, as indicated by the etching rate of 0.58 μm h<sup>-1</sup>, which is lower than the expected rate of 0.98 μm h<sup>-1</sup> without F<sub>2</sub> addition. No fluorine inhibition was observed above 900 °C.

The effects of HF addition on the etching rate of diamond by molecular oxygen are presented in Table 5. At the beginning of the experiment, the etch rate by molecular oxygen of a (110) type IA diamond wafer was established as 1.80 μm h<sup>-1</sup> at 700 °C and 14.91 Torr of oxygen with a constant flow of 8 sccm. Upon the addition of 0.98 Torr of HF, the etch rate was reduced to 0.15 μm h<sup>-1</sup>. Thus 6% HF had an etching inhibition efficiency of 92% at 700 °C, while in the F<sub>2</sub> addition experiment, 0.07% F<sub>2</sub> had an etching inhibition efficiency

Table 5  
Effects of HF on oxidation of (110) diamond

Temp (°C)	O <sub>2</sub> P (Torr) <sup>a</sup>	HF pressure (Torr)	Etch rate (μm h <sup>-1</sup> )	Expected etch rate without HF (μm h <sup>-1</sup> )
700	14.91	0	1.80	—
700	14.91	0.98	0.15	1.80
750	14.91	1.14	0.83	8.08
800	14.91	1.14	5.94	13.55
800	14.91	2.72	2.26	13.55
800	14.91	6.54	1.58	13.55
800	14.91	15.04	0.79	13.55
800	14.91	0	13.86	13.55

\* O<sub>2</sub> flow set at 8 sccm.

of 100% at 700 °C. Molecular fluorine is therefore a much better inhibitor of the diamond–oxygen reaction than HF. This is further illustrated by the results at 800 °C in Table 5. When HF was eliminated at the end of the experiment, the etching rate of diamond returned to that of the expected etch rate in the absence of HF. A comparison of Tables 4 and 5 shows that the effect of HF on diamond etching by molecular oxygen is not as pronounced as molecular fluorine. This is expected, owing to the much higher reactivity of elemental fluorine.

A comparison of the effectiveness of HF to that of water as an inhibitor for the diamond–oxygen reaction is illustrated in Table 6. At 800 °C and 14.91 Torr of oxygen, 6% HF was required to reduce the etching rate of diamond by a factor of 2.3. At 800 °C and 18.79 Torr of oxygen, only 3.8% of H<sub>2</sub>O was required to reduce the etching rate of diamond by a factor of 12. Clearly water is a better etching inhibitor than HF by a factor of 5 at 800 °C. However, above 850 °C, water loses its usefulness as an inhibitor, since more than 40% water was required to achieve an etching reduction factor of 2. At this temperature, only molecular fluorine retains its effectiveness as an inhibitor of etching by molecular oxygen.

#### 4. Summary

Etching of natural (110) diamond by oxygen and water was investigated using in situ Fizeau interferometry. Apparent activation energies of 53 and 26 kcal mol<sup>-1</sup> were obtained for the oxidation of (110) type Ia diamond by O<sub>2</sub> and H<sub>2</sub>O respectively. The etch rate was found to follow second-order kinetics with respect to O<sub>2</sub> pressure in the pressure range 0.04–10 Torr. For water over the vapour pressure range of 0.1–2 Torr the reaction has a reaction order near unity. Different mechanisms are postulated for the diamond–oxygen and diamond–water reaction, with the formation of CO<sub>2</sub> as the major mechanism of diamond etching by molecular oxygen at intermediate pressures and the desorption of CO and H<sub>2</sub> at higher temperatures as the etching mechanism for the diamond–water reaction. Fluorine was found not to etch diamond at all temperatures up to 1300 °C.

Table 6  
Comparison of H<sub>2</sub>O and HF's effectiveness as oxidation inhibitors

O <sub>2</sub> pressure (Torr)	Temp. (°C)	%H <sub>2</sub> O	Reduction factor
18.79	800	3.84	12.27
18.79	800	15.44	14.90
O <sub>2</sub> pressure (Torr)	Temp. (°C)	%HF	Reduction factor
14.91	800	5.8	2.33
14.91	800	13.7	6.13



Fluorine, hydrogen fluoride and water were found to inhibit the diamond-oxygen reaction. Below 900 °C, etching of diamond is inhibited by the addition of F<sub>2</sub> and HF presumably by blocking reactive sites on the diamond surface through the formation of C-F bonds. Molecular fluorine is a better oxidation inhibitor than HF. Above 900 °C, fluorine desorbs from the diamond (110) surface, rendering the surface susceptible to further etching by oxygen. Addition of water below 800 °C was found to retard etching by molecular oxygen. This is attributed to the formation of C-OH bonds, analogous to C-F.

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