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FLUORINATED DIAMOND FILMS
FOR TRIBOLOGICAL APPLICATIONS

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1. INTRODUCTION

Diamond thin films produced by vapor phase deposition are potentially important materials for tribological applications. To obtain optimum performance from these materials, it is necessary to controllably modify the characteristics of the surface and near surface layers. The research described in this report demonstrates the feasibility of a novel fluorination process aimed at chemically passivating the diamond surface.

Current fluorination processes are hampered by several problems. These fluorination processes require high substrate temperatures (500-800 K) and high pressures of molecular fluorine (1 atm). This presents a substantial gas handling problem as well as corrosion and erosion problems in the processing equipment. Furthermore, control of factors critical to tribological performance - e.g., the composition of surface and near-surface layers - is extremely difficult under these conditions. Finally, these high pressure processes are becoming increasingly incompatible with the low pressure diamond deposition techniques which are being developed. This is an important short-coming since it seriously limits the possibility of process integration.

An alternative approach to the fluorination of diamond thin films for tribological applications, developed here, is to use F atoms produced by low pressure discharges similar, in many respects, to those used to deposit the diamond thin films themselves. Because such free radical species have much higher reactivities than their parent molecules the severity of the conditions

required to perform the fluorination process is reduced and process efficiencies are enhanced.

The objective of the Phase I study was to provide information needed to demonstrate the feasibility of this approach to the fluorination of diamond thin films for tribological applications. Data were obtained in the following areas:

- The fluorination kinetics of diamond by F radicals;
- The composition and structure of the surface and near surface layers of fluorinated diamond;
- The effects of diamond thin film temperature on the fluorination process;
- The thermal stability of the fluorination products; and
- The stability of the fluorinated diamond in various environments (oxygen and hydrogen).

The detailed results of these studies are presented in the next section in the form of a first draft of a manuscript which will be submitted for publication in the Journal of Vacuum Science and Technology. As a result, the format is rather concise and avoids many extraneous details normally found in final reports. The last section of this report will focus more heavily on the ramifications of this work for tribological coatings, diamond thin film growth, and diamond processing.

2. FLUORINATION OF DIAMOND (100) BY ATOMIC AND MOLECULAR BEAMS

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ABSTRACT

Diamond (100) substrates have been fluorinated with both atomic and molecular fluorine under ultrahigh vacuum conditions using molecular beams. X-ray photoelectron spectra of the resulting samples indicate that atomic fluorine, F, reacts with an initial accommodation coefficient of 0.25 (± 0.1) at 298 K; a saturation coverage of about three quarters of a monolayer is obtained. The carbon fluoride adlayer is thermally stable to 700 K, but slowly desorbs at temperatures above this. In contrast, molecular fluorine, F₂, reacts quite slowly; a saturation coverage of less than one fifth of a monolayer after several hundred monolayers exposure to F₂ at temperatures from 300 K to 700 K is achieved. In addition, diamond substrates saturated with fluorine atoms showed no loss of fluorine after exposure to beams of H₂ and O₂ at temperatures between 300 K and 700 K.

INTRODUCTION

The recent development of new techniques for the production of homo- and heteroepitaxial diamond thin films has revealed a host of possible applications for such films. Foremost among these applications are extremely fast, radiation-hard, and temperature resistant electronic circuits and coatings for

moving parts whose performance is enhanced by low coefficients of friction and improved wear characteristics.¹⁻³

A study of diamond fluorination is relevant in several respects to both electronics and tribological applications. First, fluorine has been implicated as an essential ingredient in a new (and evidently efficient) growth technique which utilizes CF_4 and fluorine (and no hydrogen).⁴ If fluorine atoms play a role in the growth process similar to that expected of atomic hydrogen (etchant of non-diamond substances), the comparative ease of their production (vis-a-vis atomic hydrogen) may make a significant impact on further development in this area. Second, there is a need for processing diamond by chemical or reactive ion etching. Fluorine atoms might be attractive in this respect. Fluorination has also been suggested as a solution to the fact that diamond surfaces show high coefficients of friction when adsorbed water or oxygen is present.⁶ Fluorine atoms are expected to passivate the surface, forming a hydrophobic and oxidation resistant adlayer.

We have studied the fluorination of the diamond (100) surface using a beam of fluorine atoms in an ultrahigh vacuum environment using x-ray photoelectron spectroscopy. These studies show that fluorination to saturation occurs efficiently at room temperature and that the resulting adlayer is thermally stable up to 700 K and is resistant to attack by oxygen and hydrogen. The results will be compared to that obtained for molecular fluorine and to previous studies using XeF_2 as a fluorinating agent on the diamond (111) surface.^{7,8}

EXPERIMENTAL

The experimental apparatus used in these studies is shown in Figure 1. It comprises a turbomolecular pumped, liquid nitrogen trapped ultrahigh vacuum cell (ultimate vacuum - 3×10^{-10} torr) interfaced to an ion/sublimation pumped analysis chamber. The diagnostics available in the analysis chamber

are x-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). The sample is transferred between chambers using a linear motion feedthrough with sample heating (1200 K) and cooling (120 K) capabilities.

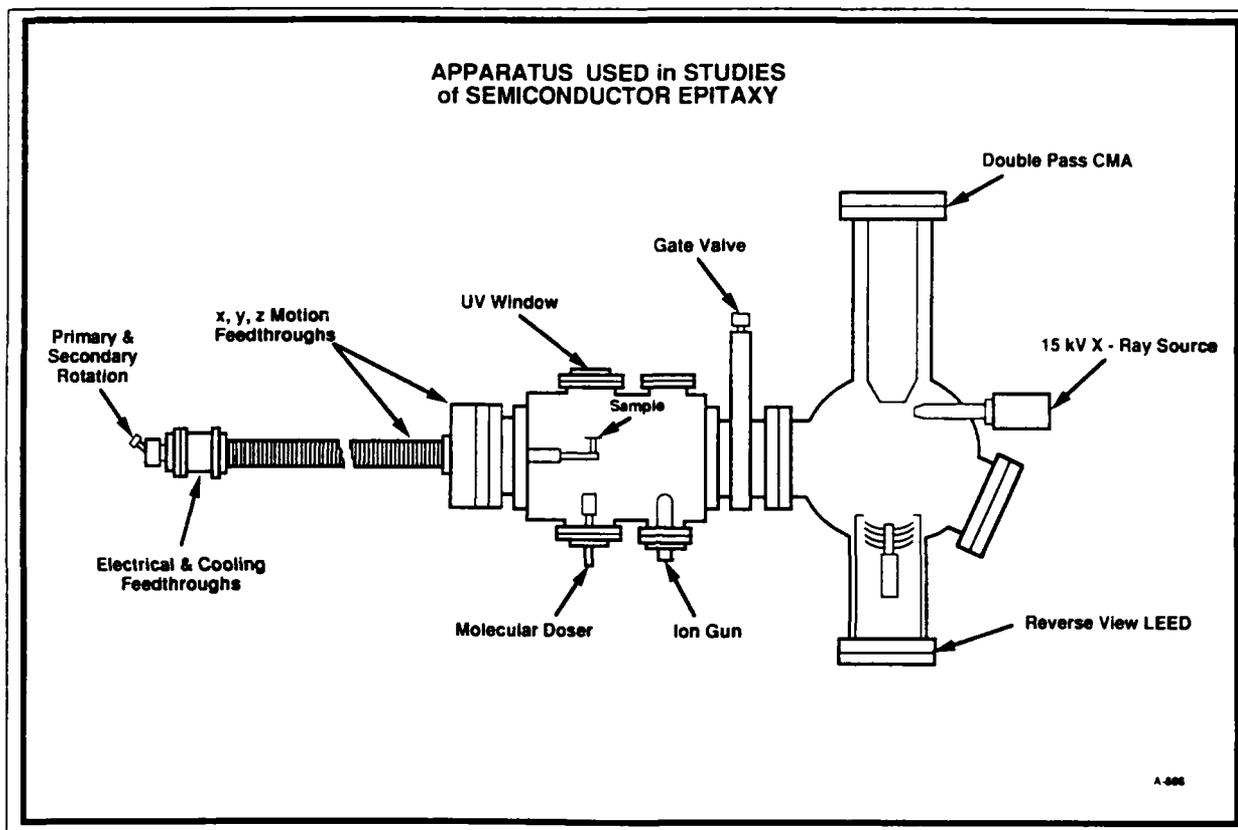


Figure 1. Experimental Apparatus - The Halogen Atom. Source is not shown.

The $5 \times 5 \text{ mm}^2$ (0.25 mm thick) diamond substrate was used as provided by Dubbledee; x-ray diffraction results confirmed the assignment of the crystal order. Annealing the diamond at 1200 K in vacuo removed all traces of oxygen and fluorine contaminants within the 0.5% sensitivity of the XPS diagnostic.

No ion etching was used as this produced graphitization of the diamond surface. Simple 1X1 LEED patterns were observed at beam voltages as low as 85 eV.

The fluorine atom source has been described in detail elsewhere.^{9,10} Briefly, it consists of a miniature fast flow tube whose output is sampled by a small aperture (40 μm). A schematic of the source is shown in Figure 2. A 5% fluorine in argon gas mixture (2 Torr) is flowed (500 sccm) through the alumina tube which is surrounded by an Evenson-type microwave cavity. The flow tube exhaust is sent through a co-annular passage and pumped by a 16 cfm chemical plasma mechanical pump (Alcatel). Running the discharge at 70 W power produces 100% dissociation of the fluorine. The alumina flow tube is readily passivated and no recombination of F atoms in the gas or on the walls is seen when the beam is sampled by a mass spectrometer.⁹ Dosing of the substrate with other gases (H_2 , O_2) is accomplished using a separate effusive beam.

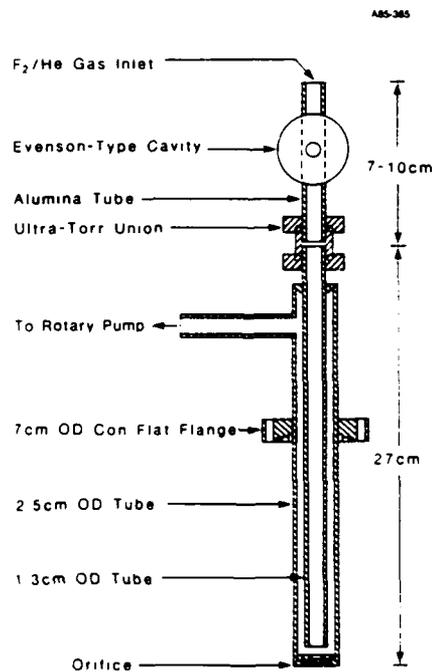


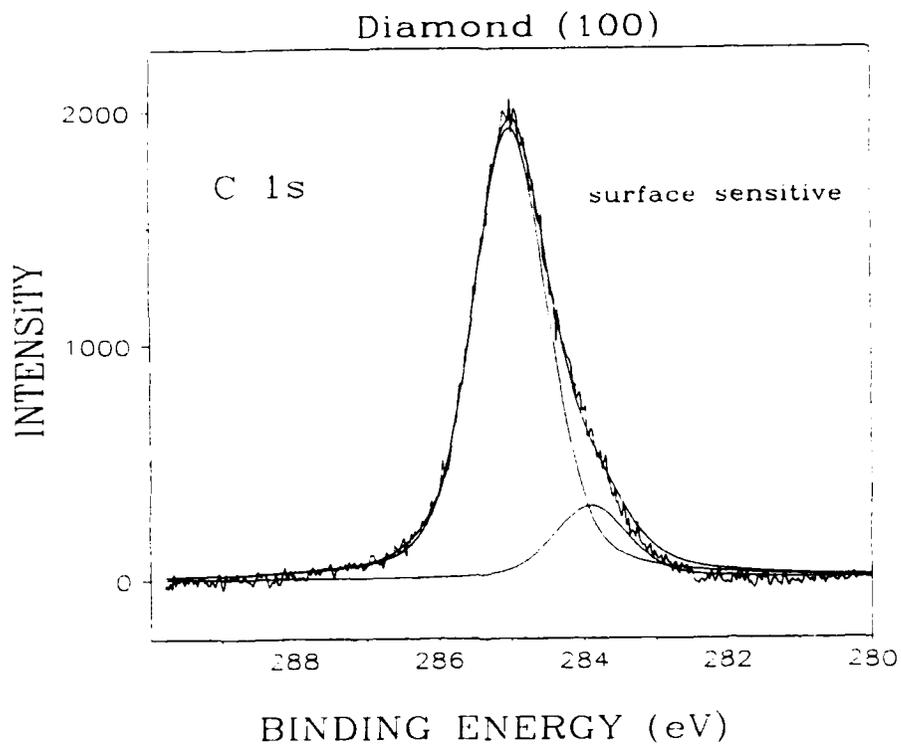
Figure 2. Halogen Atom Source

The XPS analyses were performed using a PHI 15 keV, Mg K_{α} x-ray source and a PHI double pass cylindrical mirror electron energy analyzer operated at a pass energy of 25 eV. The analyzer was calibrated using the Au $4f_{7/2}$ peak at 83.8 eV and is accurate to ± 0.2 eV. Due to the insulating properties of the diamond sample, significant charging effects were observed. For this reason, all spectra presented here are referenced to the C 1s peak (285.0 eV) of bulk diamond. We note that the 1.4 eV FWHM of this peak is the narrowest we have ever observed on this apparatus and that its assignment is never ambiguous.

RESULTS

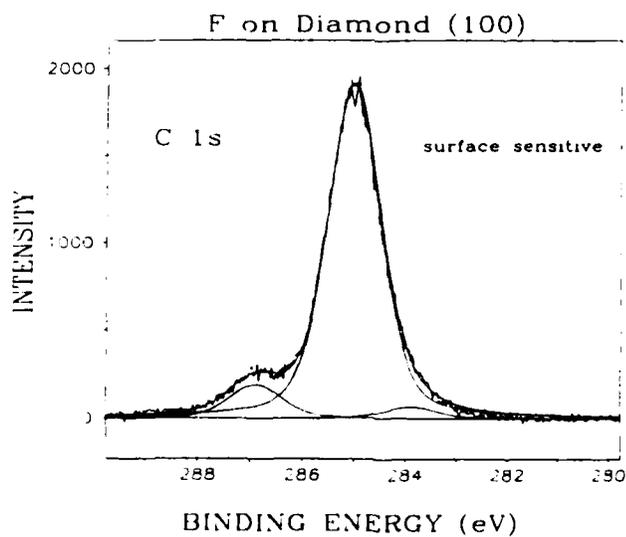
F-Atoms:

Figure 3 presents a C 1s spectrum of an annealed diamond sample taken at a substrate temperature of 298 K recorded in a surface sensitive mode (in which electrons escaping from the topmost layers are detected preferentially to those which derive from the bulk.) This spectrum consist of a bulk peak at 285.0 eV and a shoulder at lower binding energy associated with a diamond surface state.^{7,11} Figure 4 (also in a surface sensitive mode) shows the effect of exposing this surface at 298 K to a fluence of 40 ML (1 ML = 1.6×10^{15} atoms cm^{-2}) of F atoms. It is evident that the intensity of the peak associated with the surface state is reduced and a new peak on the high binding energy side of the bulk peak is formed as a result of the fluorination process. Figure 5 presents a subtraction spectrum which unambiguously identifies the annealed diamond surface state at 1.1 eV below the binding energy of the bulk diamond peak and the fluorinated diamond state at 1.8 eV above the bulk peak energy. Within experimental uncertainty, ± 0.2 eV, these values agree well with previous results on the diamond (111) surface.^{7,8} The single narrow peak for fluorinated diamond is consistent with the formation of a carbon-monofluoride species on the surface. It is clear from Figure 4 that the saturated surface is not completely fluorinated since there is still a remnant of a surface peak. The saturation coverage can be estimated by simply comparing the integrated



13e c.p.t

Figure 3. XPS Spectrum of Diamond (100) Annealed at 1200 K. The spectrum has been recorded in a surface sensitive mode.



11f c.p.t

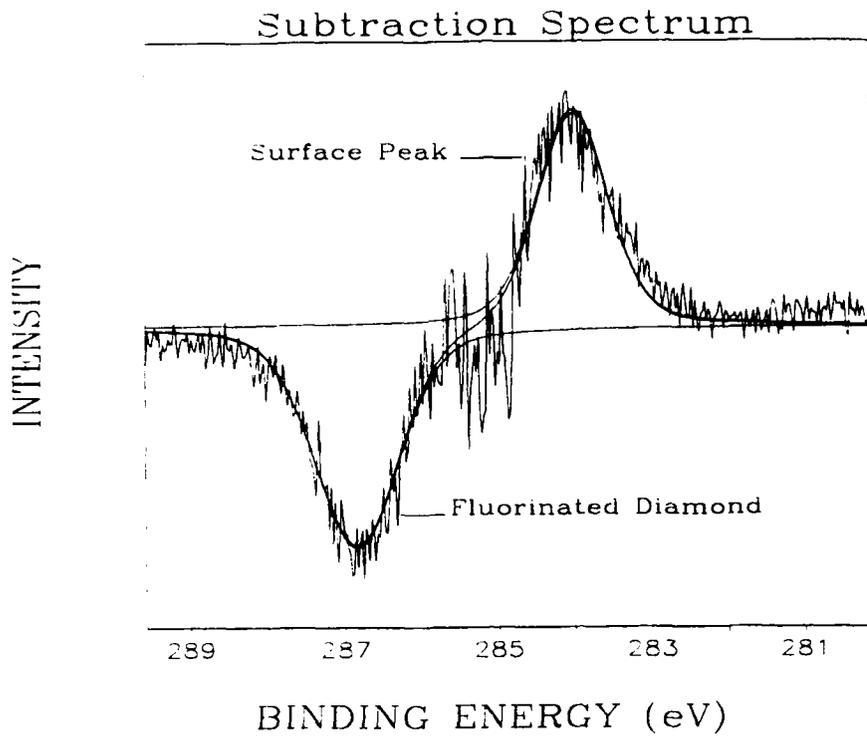
Figure 4. XPS Spectrum of Diamond (100) Which Has Been Exposed to 40 ML (Monolayers) Dose of F Atoms at 298 K. This spectrum has been recorded in a surface sensitive mode.

surface XPS peaks and correcting for attenuation of the fluorinated peak by fluorine atoms. Using an apparent attenuation of 8%, a coverage of approximately three fourths of a monolayer at 298 K is obtained.

XPS spectra of the fluorine 1s peak are shown in Figure 6 as a function of exposure to fluorine atoms. Figure 7 provides an uptake curve for a substrate temperature of 298 K; the integrated fluorine signal has been normalized to the integrated carbon signal. Saturation of the surface occurs at approximately 40 monolayers (ML). From the slope of the uptake curve, an initial accommodation coefficient of ~ 0.25 can be obtained. When the fluorination process is performed at elevated temperatures, it is observed that saturation levels remain constant for substrate temperatures up to 700 K; above this temperature, however they start to fall off. This can be explained by the data in Figure 8 which shows the effect of heating a substrate which had been saturated with fluorine at room temperature. The carbon monofluoride surface layer is quite resistant to desorption up to 700 K, whereupon fluorine (in some form) starts to desorb until all traces of fluorine are removed above 1000 K. It is possible that the desorption process involves a temperature dependent conversion of the carbon monofluoride to more volatile species such as CF_2 . Any conclusions about this process await identification of the gas phase desorption products.

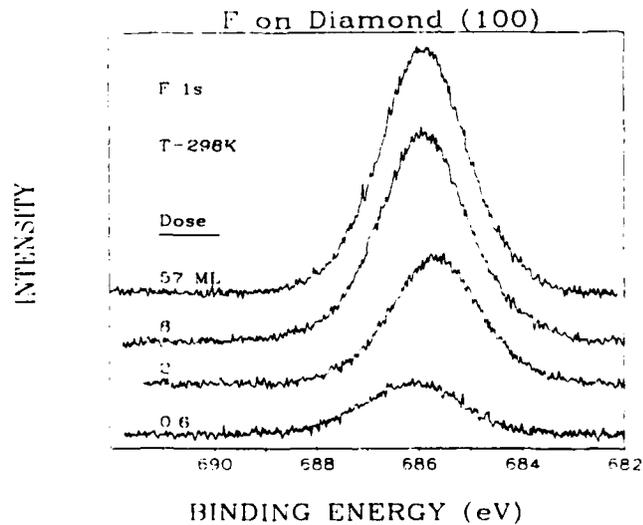
F₂ Molecules

Fluorine molecules fluorinate the diamond (100) surface with much lower efficiency than atomic fluorine. Fluorine uptake at 298 K slowly rises to a fluorine to carbon (F/C) ratio of 0.13 after 240 ML exposure (one fifth the limiting value seen with F atoms); atomic fluorine reaches this uptake level in less than 1 ML exposure. Increasing the substrate temperature does not significantly affect the uptake at 240 ML exposure, which increases to a F/C ratio of 0.17 at 700 K and decreases to 0.04 at 900 K. Evidently, accommodation of F₂ molecules is limited by the number of reactive surface sites and not by thermodynamic considerations.



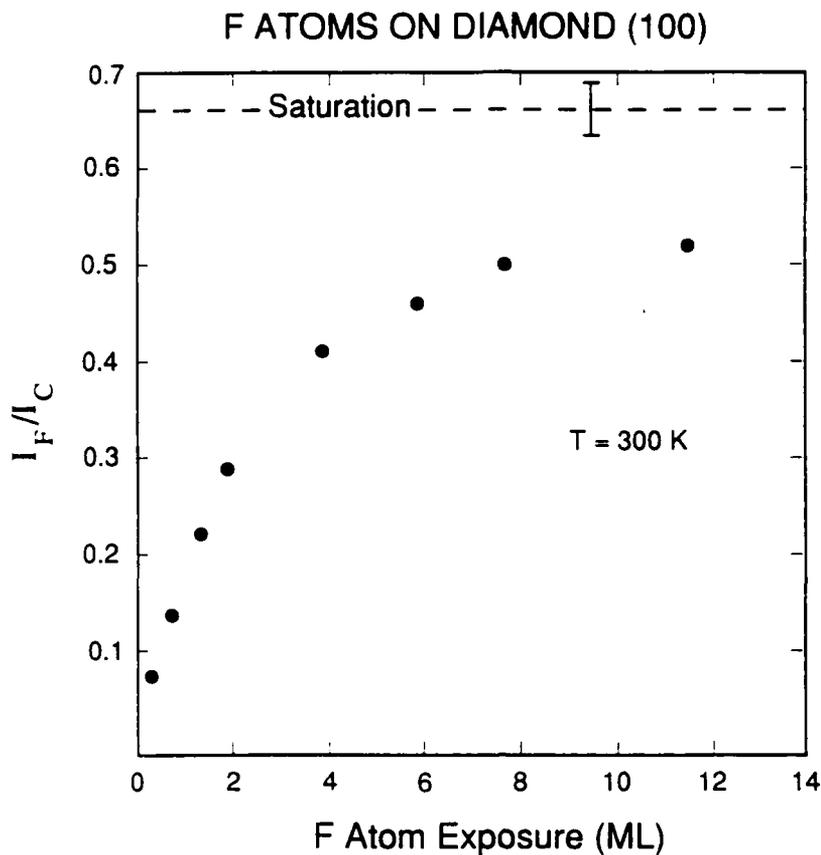
sub.plt

Figure 5. Subtraction Spectrum of Fluorinated and Annealed Diamond (100) Samples



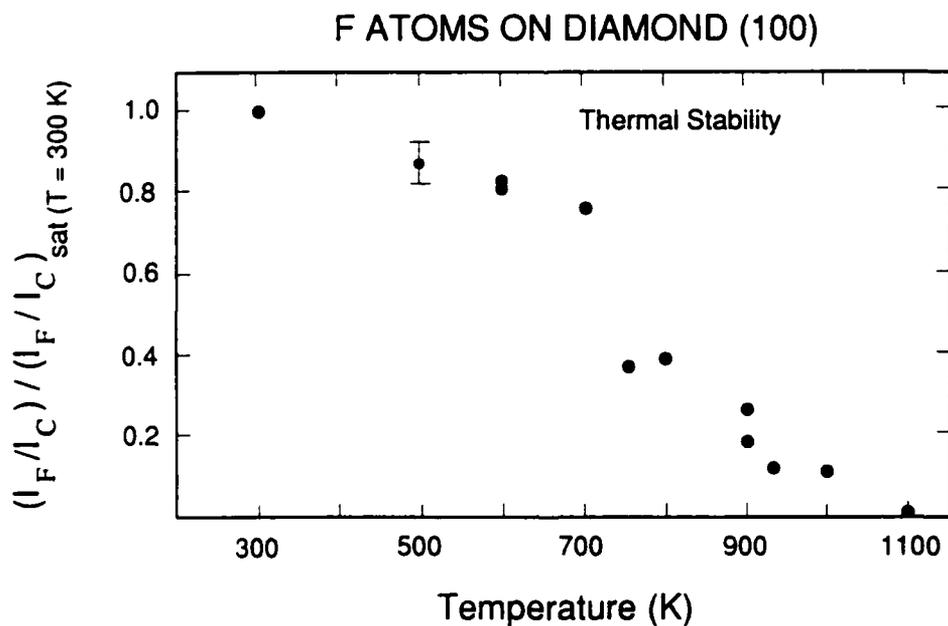
fplot.plt

Figure 6. XPS Spectra of Fluorine As a Function of Exposure to F Atoms at 198 K. Binding energies are references to the bulk diamond peak at 285.0 eV.



M89-193

Figure 7. Uptake Curve of Fluorine As a Function of F Atom Exposure at 298 K. The integrated fluorine signal has been normalized to the integrated carbon signal. Saturation occurs at approximately three quarters of a monolayer.



M89-194b

Figure 8. Thermal Stability of Fluorinated Diamond Layer. The substrate was fluorinated to saturation at room temperature before heating.

Thin Film Reactivity

Diamond substrates which had been fluorinated to saturation at 298 K were exposed to molecular beams of hydrogen and oxygen at temperatures ranging from 298 K to 700 K and examined for loss of fluorine or change in the carbon XPS spectra. Exposure to 15000 ML of H₂ and 4000 ML of O₂ produced no apparent loss of fluorine or change in the carbon spectra. Exposure of the unfluorinated diamond surface to these chemicals also resulted in no observable changes in the XPS spectra.

DISCUSSION

The initial reaction of the diamond (100) surface with fluorine atoms appears to be quite efficient, and reaches a saturation coverage of three-quarters of a monolayer in only 40 ML exposure. The resulting carbon monofluoride layer is quite stable up to 700 K and resists attack by molecular oxygen and hydrogen. This is in stark contrast to the behavior of the thermodynamically more stable carbon allotrope, graphite. Recent XPS studies of atomic fluorine interactions with graphite at room temperatures indicate that a substantial reaction product layer is formed with strong evidence for multiple fluorination.¹² Of course, at high temperatures (> 1000 K), graphite is rapidly attacked and etched by both atomic and molecular fluorine.¹³

The comparative inertness of the diamond surface is due to its structure. The sp³ hybridization of the diamond lattice results in each surface carbon atom being bound to three other carbon atoms, leaving only one "dangling" bond for reaction. Fluorine atoms (as well as hydrogen atoms) apparently passivate the surface by strongly bonding at this reaction site. There is no evidence for any chemical etching of diamond by fluorine or hydrogen atoms at low temperatures; this may be due to the inability of either radical to penetrate the surface layer to form volatile species (an issue discussed below). It is interesting to note the dynamic equilibrium of the carbon-fluoride adlayer with the surface reconstruction which produces the "surface" state seen in the

XPS spectra. The desorption of the fluorinated adlayer occurs over a wide temperature range (700-1000 K), suggesting that the desorption process involves a gradual change in the fluorine surface carbon bonding. This may have a bearing on recent work that has shown that homoepitaxial growth of diamond films can be achieved using a CF_4/F_2 mixture at substrate temperatures of 1150 K.³ While the addition of F_2 probably serves to efficiently etch non-diamond growth components, it is reasonable to speculate that high concentrations of fluorine atoms also serve to maintain the bulk diamond structure at the surface, leading to efficient growth. Thus, one might expect that growth temperatures for this process could be substantially reduced if the CF_4 and F_2 were converted to CF_x and F radicals by thermal pyrolysis or discharge techniques prior to surface exposure.

The behavior of diamond (100) and (111) upon fluorination with either F or XeF_2 is also quite different from that found on the Si(111) surface.^{14,15} Si(111) surface at room temperature is rapidly penetrated by fluorine atoms to form a SiF_x reaction product layer which eventually produces volatile species such as SiF_2 and SiF_4 . Bagus and co-workers have indicated that this effect is due to the highly ionic nature of the silicon-fluorine bond.^{16,17} The F^- anion strongly polarizes the silicon substrate, allowing the F atom to penetrate the surface without generating an activation barrier due to Pauli repulsion. Hydrogen, a much smaller anion, cannot penetrate due to the covalent nature of its bonding to silicon. Chlorine atoms, while interacting ionically are simply too large to penetrate without generating a substantial barrier. Using this logic, the diamond lattice is not open to fluorine atom penetration for two reasons. First, the surface density of atoms is more than twice as large in diamond as in silicon; and second, the carbon fluorine interaction is much less ionic than the silicon fluorine bonding. (The Pauling electronegativity of Si, C, and F is 1.8, 2.5, and 4.0, respectively.) Thus one would expect a substantial energy barrier to fluorine penetration in the case of diamond.

These results provide information in three areas of practical concern: diamond thin film growth, tribological coatings, and diamond etching. The first observation, important in all these areas, is that fluorination of diamond surfaces can be accomplished at room temperature and with minimal exposures using atomic fluorine, which does not hold true with molecular fluorine. As mentioned previously, atomic fluorine may promote diamond thin film growth at lower temperatures than is needed with F₂ (and perhaps hydrogen). Second, the resultant submonolayer is quite stable with respect to desorption upon substrate heating and chemical attack by oxygen and hydrogen. Thus fluorination may promote the lubricating and wear properties of diamond thin films in both atmospheric and space environments. Third, atomic fluorine, while highly "reactive", is not a strong chemical etchant and thus ideal as a component in reactive ion beam etching scheme. The fluorine atoms would attack any exposed diamond surface, but etching would occur only where an ion beam strikes the substrate creating anisotropic etching. An added benefit would be that only the surface layer is contaminated by the fluorination process. Given the ease with which fluorine atoms are generated, either by discharge or thermal techniques, they should provide an attractive alternative to hydrogen in diamond processing technologies.

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3. CONCLUSIONS

3.1 Summary of Experimental Results

X-ray photoelectron spectroscopy studies of the fluorination of diamond(100) crystals have shown that atomic fluorine reacts efficiently with diamond at 298 K to form a carbon-monofluoride layer which is thermally stable to above 700 K and resistant to attack by molecular oxygen and hydrogen. Molecular fluorine, in contrast, reacts quite slowly at room and elevated temperatures and never completely fluorinates the diamond surface under the conditions of this study.

3.2 Technological Ramifications

3.2.1 Tribological Coatings

It is clear that the proposal technology for fluorinating diamond thin films is ideal for current production facilities utilizing microwave or RF discharges. Fluorine atoms are easily produced using these techniques and their efficacy in fluorinating diamond allows an exceedingly low concentration of fluorine to be used. The fact that the fluorination technique proceeds rapidly at room temperature also avoids many complications. In comparison, the use of molecular fluorine at high pressures and temperatures poses many safety problems. We note that discharges of fluorine containing gases are used on a regular basis in plasma etching, a commercial dry etching technique for semiconductor materials. Fluorine atoms may also be produced thermally,

but this would pose a comparatively severe materials problem. Thus, the fluorination of diamond films with atomic fluorine may be difficult to integrate into tungsten filament apparatuses. But fluorination of diamond films produced in this manner could be handled as an add-on process.

It is difficult to ascertain exactly what effects fluorination will have on tribological characteristics of diamond films. The most important characteristic of these state-of-the-art films is their morphology, (e.g., grain size). Recent results have shown that very fine grained ($\leq 3000 \text{ \AA}$) films with excellent adherence can be deposited on quartz slides. The measured coefficient of friction is less than 0.05 with no observed wear. If these results can be extended to other substrates, fluorination may provide a significant improvement by keeping the diamond surface completely inert in the oxidizing and high temperature environments typically found in situations where lubrication is required. In a vacuum environment (outer space), the passivation of the diamond lattice should prevent the seizing associated with typical lubricants such as graphite which exhibit strong self attachment without the presence of water vapor.

3.2.2 Novel Diamond Growth Techniques

According to the current understanding of diamond growth processes, atomic hydrogen, whether produced by a hot filament or gas discharge plays several roles. Its main role appears to be that of a chemical etchant of non-diamond substances, mainly graphite. We note that fluorine atoms are an extremely efficient etchant of graphite and do not apparently etch diamond. A novel growth technique developed at RTI utilizing CF_4 and F_2 at high substrate temperatures has produced satisfactory diamond homoepitaxy. This process should be ideally suited for RF or microwave discharges where CF_x and F radicals can be generated without the need for high temperatures. Even in more typical hydrocarbon deposition systems, F atoms could not only act to

etch graphite, but would also serve to abstract H atoms off the hydrocarbon feedstock gas to produce the reactive free radicals necessary for film growth.

3.2.3 Dry Etching on Diamond Substrates

If useful electronic devices structures are to be constructed of diamond thin films, etching techniques must be developed. This is a non-trivial task given the chemical inertness of diamond. The dry etching technique currently being developed at Lincoln Laboratories involves a reactive ion beam etching technique where an argon ion beam is combined with nitrogen dioxide to etch diamond. Presumably, the nitrogen dioxide is a source of reactive oxygen atoms, whose presence enhances the etching rate. This technique provides anisotropic etching (high depth to width ratio) because the production of oxygen atoms occurs only where the highly directional ion beam is striking. Unfortunately, nitrogen dioxide has a very low sticking coefficient and the substrate must be cooled to insure sufficient concentrations for efficient etching. Fluorine atoms are a logical alternative. They react very efficiently with diamond at room temperature without penetrating the surface, and thus, are not being prone to "under-cutting". Their ability to etch is thus dependent on the presence of the ion beam thus achieving anisotropic etching. Moreover, they will leave behind a chemically passivated surface layer which is relatively unreactive with the ambient atmosphere (especially water).