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## Foreign Atoms At the Diamond (100) Surface:

1. The Fluorine Passivated Surface
2. Is Subcutaneous Passivation a Possibility?

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## Surface Passivator Effects:

### H and F on the Diamond (100) Surface

#### I. INTRODUCTION

With a goal towards an understanding of how nucleation of diamond growth can be beneficially enhanced, our research has concentrated on how different types of surface passivator might positively impact diamond nucleation and growth. We have focused these studies on the fluorinated and hydrogenated (100) surface for several reasons:

(1) both fluorine and hydrogen form single bonds with carbon atoms, so fluorinated and hydrogenated diamond surfaces are expected to have some qualitative similarities. (2) due to differences in size, electronegativity and bond energies, equilibrium surface passivator concentrations and surface geometries will be different, (3) there has been some experimental work by the Rice group indicating promising results with fluorine assisted diamond growth, (4) the (100) surface may be susceptible to short range repulsions between neighboring surface passivators, an effect which may be very different for H and F.

#### II. MODELS TO BE STUDIED.

The models used in our studies of the passivated (100) surface extend from isolated crystallites [ $C_{21}F_6H_{20}$ ] to ten-layer periodic slabs of free standing fluorinated diamond films. For purposes of comparison, we also carried out calculations on analogous models of the hydrogenated (100) surface. The cluster calculations were performed within the density-functional framework using linear-combinations of atomic orbitals

(LCAO) codes, while the film studies used the linear augmented plane wave (LAPW) computational method. The cluster calculations were used to produce reasonable geometries as input to the more numerically intensive film calculations, which are more representative of high coverage situations.

We considered two geometries of a monofluoride surface. The first surface, which would be best described as an ideal 1x1 surface with a monolayer of ionically bonded fluorines, is metallic. However, the second surface, which exhibits a 2x1 reconstruction with chemically bonded fluorines, is found to be insulating. To aid in the phenomenological characterization of the fluorinated (100) surface, we have compared theoretical carbon-core-level shifts with experimental values. The double-hump feature observed experimentally in the core level spectrum [A. Freedman and C. D. Stinespring, *Appl. Phys. Lett.* 57, 1194 (1990)] can be accounted for by a surface consisting of high and low-density fluorinated islands on the surface.

### III. FLUORINATED DIAMOND CRYSTALLITES

To study surfaces with a low density of adsorbed fluorine atoms or islands of fluorine atoms, it is either necessary to use very large unit cells with periodic boundary conditions or to model the infinite surface by a diamond crystallite (cluster) with adsorbed fluorine atoms. We have elected to use the latter approach. The low-adsorbate-density limit is modelled by six fluorine passivators bonded to six surface carbon atoms which are themselves bonded to a diamond fragment consisting of the nearest fifteen subsurface carbon atoms (initially on an ideal diamond lattice). The fifteen subsurface carbon atoms were four-fold coordinated by hydrogen atoms and other carbon atoms.

We then placed three pairs of dimerized carbon atoms on the surface and allowed these six carbon atoms to bond with fluorine atoms. To obtain the relaxed geometry,

we allowed the epilayer of fluorine atoms and two layers of carbon atoms to adjust themselves to minimize the energy. These potentially time-consuming procedures were facilitated by using our new, accurate algorithms for calculations of forces. The resulting surface C-C bonds are significantly stretched in comparison to ideal single bonds or to those found on a similar hydrogenated surface (discussed below). We find that these bondlengths are stretched to 3.7 (3.2) a.u. for the central (outer) dimers. These carbon separations are noticeably larger than normal single C-C bonds (2.9 a.u.) but quite a bit shorter than the C-C separation of an ideally cleaved (100) surface (4.77 a.u., the second nearest-neighbor distance in diamond). As expected from experimental gas-phase data on hydrofluorocarbon molecules, we find equilibrium C-F bondlengths of 2.70 and 2.76 a.u. for the central and outer bonds respectively. With respect to the ideal diamond lattice, we find that the surface carbon layer relaxes toward the bulk by approximately 0.2 a.u..

To determine differences between the fluorinated and hydrogenated surface, we also performed a geometrical optimization of the hydrogenated surface cluster. After a partial geometrical optimization a trend toward enhanced surface dimerization became apparent. The central and outer C-C surface bondlengths were only of 3.2 and 3.0 a.u. respectively.

The reduced surface reconstruction in the fluorinated cluster is primarily due to long range Coulomb repulsions that are present on the fluorinated surface and absent on the hydrogenated surface. The repulsion arises due to charging of the fluorine atoms, each of which attracts 0.25 electrons from the neighboring carbon atom. In addition, short-range Van der Waal's (steric) repulsions are also partially responsible. Evidence for these repulsions was observed by noting that the C-F bonds bent away from one another to increase the distance between adjacent fluorine atoms. The carbon-atom charge state in each layer was obtained by comparison with the diamond

bulk. We found a significant reduction of charge ( 0.25 electron) in the first layer of carbon atoms.

While the resulting geometry is expected to be realistic for the isolated cluster and for a diamond surface with a small concentration of adsorbed fluorine atoms, a great deal of insight can be obtained by "borrowing" the crystallite geometry to construct a periodic 2x1 reconstructed (100) surface with a monolayer of fluorine atoms. Upon doing so, we find that the fluorine atoms in different unit cells would be very close to one another with F-F separations as small as 2.54 a.u.. Since the equilibrium bondlength of a gaseous fluorine molecule is only 2.68 a.u., the fluorine atoms in neighboring unit cells would either form a molecule and leave the surface or repel one another. Since hydrogen is less electronegative and has a smaller radius, this type of adsorbate induced surface strain is less prominent in the hydrogenated surface.

In accord with the experimental findings of Stinespring and Freedman, the presence of adsorbate induced surface strain suggests that a full monolayer of fluorine on the (100) surface (which is actually two fluorine atoms per carbon atom) is not very probable. The actual fluorinated system will relax to alleviate these strains. We now discuss how this occurs.

#### IV. FLUORINATED MONOLAYERS ON DIAMOND FILMS: 1X1 OR 2X1?

At least three reasonable geometries exist for a monolayer of fluorine adsorbed on the diamond (100) surface. The first is a 2x1 dimerized surface with bond angles that are less obtuse than those observed in the relaxed crystallite. A second is the limit of orthogonal C-C-F bonds. Under this circumstance, it is possible that the bonds between pairs of surface carbon atoms could break causing a relaxation of the 2x1 to an ideally cleaved 1x1 surface with fluorine atoms directly above each surface carbon.

A third possibility is a 1x1 surface with a physisorbed, rather than chemisorbed, layer of fluorine ions located directly above each hollow on the (100) surface. While we consider this third possibility surface to be the least probable we discuss it first.

For the 1x1 monolayer with fluorine ions directly above the pseudo four-fold hollows of a perfectly cleaved (100) surface, we have placed the ten layers of carbon atoms at their ideal lattice sites and then monitored the total energy as the height of the fluorine monolayer is varied. The equilibrium height is found to be 2.18 a.u. above the diamond surface which corresponds to a C-F nearest-neighbor distance of 4.02 a.u.. Since there is one fluorine atom per surface carbon atom in this case, it is possible that each fluorine will attract one dangling bond electron and become a closed shell  $F^{-1}$  ion. This does not happen. We find there are partially occupied surface bands, involving both dangling bonds and F p states, so the resulting surface is metallic. The carbon surface core states are shifted downward by 1.29 eV indicating some charge transfer from the surface C atoms to the F atoms, but nothing close to a full electron is transferred.

We have also performed two calculations on ten layer free standing films with chemically bound fluorines and find that a 2x1 dimerized reconstruction is more stable than an ideally cleaved 1x1 surface with chemically bonded fluorine. We have proved this by performing calculations on two 2x1 surfaces, one with moderate dimerization and one that is only slightly relaxed away from a ideal 1x1 surface. After performing a self-consistent calculation on the slightly dimerized surface, we examined the interatomic forces and found that the surface strongly prefers a greater degree of dimerization, indicating the instability of the 1x1 surface.

The resulting band structure shows a (local density) bandgap of 3.0 eV, which suggests a true gap of the order of 5 eV. [Local density calculations typically underestimate bandgaps by such an amount.] This gap is strongly dependent on the degree of

surface dimerization. Experimental observation of the gap of the fluorinated diamond surface would be very useful in furthering our understanding of this surface.

## V. ANALYSIS

The results discussed in the previous sections suggest that the repulsions between neighboring fluorine atoms are not strong enough to inhibit surface dimerization. However, a detailed comparison of the 1s-core level shifts observed in the crystallite and slab calculations shows that, due to the coulomb repulsion in the full monolayer, the system responds and decreases the ionicity of the fluorine atoms. By decreasing the charge transfer, the coulomb repulsions between surface atoms is decreased at the expense of a comparable decrease in the C-F bond energy. The decrease in the C-F bond energy enhances the possibility of desorption of the fluorine atoms. By decreasing the C-F bond strength, the adsorbate surface density is expected to decrease as well. An alternative way for the system to respond is to allow some of the fluorine atoms to desorb and have coexisting phases of isolated fluorinated islands, dangling bonds, and reasonably large regions that look like an ideal monolayer. This point is in accord with the experimental measurements of Freedman and Stinespring, who clearly see the presence of surface dangling bonds in their core-state absorption spectrum.

To make further contact with experiment, we note that Freedman and Stinespring have measured the C 1s core-level shifts and find a large bump at  $1.8 \pm 0.2$  eV and a shoulder at approximately 1.3 eV. The experimental absorption spectrum is in excellent agreement with our theoretically derived core level absorption spectrum if we assume the system consists of coexisting phases of (more or less) isolated fluorine atoms and (2x1) fluorine monolayer regions.

# Be, B, and F Atoms At the Diamond (100) Surface: Is Subcutaneous Passivation a Possibility?

## I. INTRODUCTION

With a view towards alternative passivation of the diamond surface, we have initiated work on boron-doped and beryllium-doped diamond (100) surfaces. The idea here was to investigate how atoms other than carbon could maintain an unreconstructed diamond (100) surface but lead to better growth and nucleation rates. The working assumption is that better growth rates will be obtained if passivators with some or all of the following characteristics can be found:

(1) The passivator (P) prevents surface reconstruction (bonding between next-nearest neighbor carbon atoms) but, in contrast to hydrogen, does not reside at or near the dangling bonds that would be occupied by the next layer of carbon atoms.

(2) If the passivator bonds to carbon atoms in a similar way as hydrogen, the equilibrium density of passivated sites is decreased due to a favorable combination of passivator size and ionicity and the C-P bond strength.

(3) The propensity of an individual passivator to remain bonded to or near the surface is automatically decreased if/when a new carbon atom is adsorbed at a bonding site that is in the neighborhood of that passivator.

Before discussing the calculations that we have performed, we further motivate this work by discussing a very simple growth model that would lead to good growth rates IF a passivator with certain idealized characteristics could be found. The interstices at or within a diamond surface are quite small and unreactive, and our calculations have shown that it is energetically unfavorable for a hydrogen atom to reside in one of these sites. However, if one could induce a concentration of inert

atoms (such as helium or beryllium) into hollows at the (100) surface, the presence of these "hard spheres" would prevent the surface atoms from bonding to one another due to the van der Waals repulsion between the surface carbon atoms and the hard spheres. This would leave dangling carbon bonds at the surface available to bond to gaseous carbon atoms. Moreover, once a new layer of carbon atoms is added to the surface, the "hard spheres" would, under most conditions, automatically float from a subsurface interstice to a surface hollow.

It is likely to be easy to find an atom that would preferentially migrate from a subsurface interstice to a surface hollow. The trick is rather to find an atom that would sit in a surface hollow rather than diffuse out into the vapor. Our calculations are aimed at analyzing this possibility.

## II. BERYLLIUM, BORON AND FLUORINE AS HARD SPHERE PASSIVATORS

To investigate the possibility of a hard sphere passivator we have used an opened adamantane molecule as a model for a hollow near the diamond (100) surface. This model consists of seven carbon atoms, which reside in three different planes of an ideally cleaved (100) surface. Eight hydrogen atoms are added to ensure that the subsurface carbon atoms are four-fold coordinated. Four of the carbon atoms form a square tied off from below by carbon atoms or hydrogen atoms. The two carbon atoms below the square are bonded from below by a single carbon atom that forms the bottom of the hollow. In analogy to the diamond (100) surface, the surface carbon atoms are only two-fold coordinated and would reconstruct and bind to one another if left to their own devices.

We have considered a boron atom along an axis going through the center of the pseudo 4-fold site, and varied the height of the boron atom to minimize the energy. We find that it is energetically unfavorable to submerge the boron atom

below (or even near) the plane of carbon atoms and that the boron atom would like to reside approximately 0.1 Angstroms below the plane of the new layer of carbons. Momentarily sidestepping the question of local stability of the boron atom at the center of a pseudo 4-fold site, we simulated the addition of a new layer by placing two three-fold coordinated carbon atoms at the nearest empty carbon sites. Upon doing so, we find that the boron atom floats up through the new plane of carbon atoms and forms a bond to the two new carbon atoms.

While the latter effect (B-C bond formation with a boron atom occupying a new vacant surface site) is less than ideal, the former effect explicitly shows that an automatic ejection mechanism for passivators can occur as a result of diamond growth. Since the boron atom readily bonds to the two new carbon atoms, we have discarded it as a candidate for a hard sphere passivator. However, in a later paragraph we discuss other features that may help with diamond growth.

We have repeated this calculation for beryllium (a closed shell atom) and find two important differences. First, while the expulsion of a subcutaneous Be passivator from a surface hollow is exothermic as it was for boron, the expulsion energy, measured with respect to the plane of the subsurface, is lower by a factor of two with the beryllium atom. Secondly, the beryllium atom does not squeeze out as easily vertically, since it must overcome a 0.25 eV energy barrier. We expect that rather than diffusing out vertically, a beryllium atom would diffuse out at a 45 degree angle and avoid passing between two carbon atoms. Diffusion along this pathway is exactly what is needed to place the beryllium atoms above a pseudo 4-fold site of the new diamond layer.

We conclude that beryllium will act as a hard sphere passivator if the following conditions are met:

- (1) The beryllium atoms prefer to reside at the center of a pseudo four-fold site rather than forming a bridge bond between two carbon atoms.

(2) The beryllium atoms can be induced to occupy these positions instead of migrating into the vapor.

These conditions are in no way guaranteed and must be tested by additional calculations. As an example of what can go wrong in a search for a hard sphere passivator, we briefly discuss what was found for the case of fluorine, for which we have also performed such calculations. A fluorine atom will adsorb at a pseudo 4-fold site rather than escape into the vapor. In excellent agreement with LAPW slab calculations of a periodic array of F atoms on a diamond (001) surface (reported above), our LCAO adamantine model predicts that the fluorine atoms will reside 2.23 a.u. above the surface. However, additional calculations have shown, not surprisingly, that the fluorine atoms prefer to form single C-F bonds on a dimerized (reconstructed) surface.

### III. BORON AS A SUBSURFACE SUBSTITUTIONAL PASSIVATOR

It is well known that boron acts as an electron acceptor when doped into diamond films. This behavior may also be a useful quality of a subsurface substitutional passivator. To study this possibility we have again used an adamantine-like model to look at how the force on an unsaturated surface carbon atom will change when the subsurface consists of a boron rather than carbon atom. The geometry we have used corresponds to the equilibrium geometry of adamantine (as calculated in the local density approximation), which looks similar to the (100) surface and consists of ten four-fold coordinated carbon atoms. The idea here is place an unsaturated carbon atom at the precise location that it would reside if fully coordinated and see if the subsurface can be doped in a way that stabilizes the atom at that point. We use atomic forces and the density of states at the Fermi level to characterize this stability.

As compared to carbon, we find that a subsurface of boron favorably stabilizes

• the surface carbon atoms. The force on a surface carbon atom is four times smaller when the subsurface consists of boron rather than carbon atoms. Further, the boron density of states clearly shows that the boron atom steals part of the dangling bond electron from the surface carbon atoms thereby inhibiting bond formation between next-nearest-neighbor carbon atoms (i.e. dimerization type of reconstruction).

While the results of this calculation strongly suggest that subsurface boron would stabilize the diamond (100) surface, such a growth scheme will only be useful if a low energy B-C exchange mechanism would allow the boron atoms to bubble to the top as diamond grows. [Note: experimentalists at Stanford University (still unpublished?) have found that boron stabilizes the diamond surface.]

A portion of this work is in press:

M. R. Pederson and W. E. Pickett, "Theoretical Investigations of Fluorinated and Hydrogenated Diamond (100) Films." Proc. Spring MRS Meeting, April 1992 (MRS. Pittsburgh, 1992), in press.