Fluorine and carbon fluoride interaction with a diamond surface: quantum-chemical modeling

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Abstract

Our study provides the results of quantum-chemical calculations of the interaction of fluorine atoms F, as well as CF_2 and CF_3 particles, with the ordered and defective C(100)-(2×1) diamond surfaces. We discuss the possible degree of fluorine coating for an ordered C(100)-(2×1) surface. It is shown that difluoride states on an ordered diamond surface are single complexes surrounded by monofluoride states. This paper includes the estimated values of activation energies of the particles adsorption and desorption, which determine the surface chemical etching mechanism. It is shown that fluorine atoms in the gas phase, along with vacancies on the surface, reduce the activation energy of difluoride states formation and increase the etching rate, while the CF_2 and CF_3 fragments in the gas mixture impede atomic fluorine etching of the surface.

Keywords: C(100)-(2×1) diamond surface, reactive gas phase, quantum-chemical modeling, point defects, adsorption, chemical etching.

1. Introduction

Synthetic diamond single crystals are an important material for many high-tech areas. Diamonds are used as monochromators in X-ray optics [1,2], ultrahigh-reflectance mirrors [3], refractive lenses for high-power X-ray synchrotron radiation [4,5], in extreme and power electronics devices [6-8], and in acoustics [9,10]. A necessary condition for reliable operation of the synthetic-diamond elements is high perfection of their surface. Another important objective is to provide surface relief structures with desired geometrical characteristics. Currently, reactive ion etching (RIE) is a promising method in the diamond surface preparation.

It is known that the C(100) diamond surface is reconstructed in a 2×1 structure, and it is a surface with rows of symmetrical dimers [11,12]. The dimer atoms are adsorption sites on the atomically clean

(100)-(2×1) diamond surface. The dimers are symmetric both in the geometry and electronic state of the atoms, the bond in the dimer is a double one, the C=C bond length is about 1.40 Å [12-15].

Plasma with different composition and content of components was used for reactive ion etching of diamond surfaces (100) and (111). A mixture of carbon tetrafluoride and oxygen was used in a number of works [16-18]. According to the experimental data, surface roughness of the single-crystal diamond and diamond films grown by chemical vapor deposition decreases with increasing the CF_4 content. Sulfur hexafluoride was used in the plasma for etching the surface of mono-, polycrystalline, and ultrananocrystalline diamonds [19,20]. In all cases, the SF_6 addition to an Ar/O_2 gas mixture allowed to reduce the surface roughness.

The SF_6/CF_4 plasma composition has been studied experimentally in the works [21,22]. According to [22], atomic fluorine, as well as the SF_5^+, SF_3^+, CF_3^+ and CF_2^+ fragments, is present in the SF_6/CF_4 gas mixture in the highest concentration. Research in [23] provides a theoretical and experimental study of the SF_6 plasma composition. The proposed model presents the neutral fragments SF_6, F, F_2, and SF_4, as well as SF_5^+ ad F^- radicals as the main products of the decomposition reactions in the plasma. The authors of [24] simulated plasma chemical etching of silicon in a SF_6/O_2 gas mixture. It was found that when the mixture contains no oxygen, the main components of the plasma are SF_6, F and SF_5 particles. Silicon tetrafluoride SiF_4 was the main etching reaction product.

The authors of [25,26] developed and examined the RIE treatment of the (001) surface of synthetic single-crystal diamond applying a two-step process. The treatment process consisted of alternating steps of etching in SF_6 and passivation in CF_4. According to [26], physical sputtering is carried out mainly by heavy ions SF_5^+, while chemical etching of the surface involves atomic fluorine. A $(CF_2)_n$ film appears on the surface as a result of passivation, and it consists of CF_4 decomposition products [25]. In [27] the authors studied the CF_3 radicals interaction with a hydrogenated diamond surface C(100)-(2×1) using *ab initio* calculations. It has been shown that the reaction of a CF_3 difluoride complex bonding to a surface dimer is exothermic and may be one of the stages in the reaction sequence of diamond CVD growth from CF_3 radicals.

Thus, according to the available experimental data, diamond surface treatment by reactive ion etching in sulfur hexafluoride and carbon tetrafluoride results in the planarization of the diamond surface. Active particles involved in the chemical interaction with the surface, in this case, are atomic fluorine, CF_2 and CF_3. However, atomic mechanisms of interaction with surface defects that inevitably arise in the process of etching remain insufficiently studied.

In this paper, we used the quantum chemistry methods to investigate the chemical interaction of F, CF_2 and CF_3 with point defects on the reconstructed diamond surface C(100)-(2×1): single vacancies and divacancies.

2. Methodology

Simulation of a clean reconstructed diamond surface C(100)-(2×1) was carried out on a $C_{195}H_{112}$ cluster using a semiempirical technique involving a MOPAC software package [28]. The initial cluster contained 5 atomic layers. The dangling bonds of carbon atoms going into bulk at the edge of the cluster were saturated with hydrogen atoms (a monovalent pseudoatom model). The first atomic layer of the surface remained clean; modeling of particle adsorption was carried out on the carbon atoms of the first cluster layer, applying calculation of the reaction coordinate. The distance between the particle and the adsorption center on the surface was set as a reaction coordinate *r* (Fig. 1a). Description of the reaction coordinate and potential surface calculation is provided in [29].

Simulation of point defects (monovacancies, divacancies) was carried out by removing the carbon atoms from the central dimers on the cluster surface. In the stationary points of the system, the gradients on the atoms did not exceed 3 kcal/Å. We calculated the total energy of the cluster, atom bond orders, population of the atomic orbitals, and molecular localized orbitals.

As test calculations, we simulated monovacancies and a divacancy in the central dimer row of the cluster, as well as a fully fluorinated surface. In the simulation of a fully fluorinated surface C(100)-(2×1), each of the surface dimer atoms formed a bond with a single F atom (Fig. 1b). The PM3 method resulted in the geometric and energy characteristics of the simulated systems that showed a close match with the published literature [30,31]. Thus, we used the PM3 approximation to further simulate the interaction of the particles with the C(100) surface.

3. Results and discussion

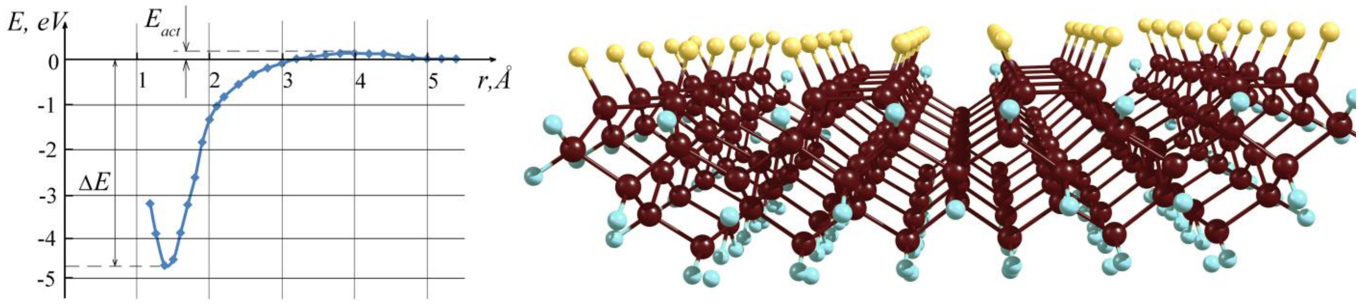
According to [24], reactive ion etching is accompanied by the following necessary processes: formation of reactive radicals; diffusion of particles to the surface; adsorption on the surface; particle interaction with the surface (etching and sputtering); desorption of the reaction products; diffusion in the gas phase. In addition, the chemical etching rate depends only on the frequency (probability) of desorption acts.

3.1. Interaction of particles with an ordered C(100)-(2×1) surface

We selected fluorine atoms and CF_2, CF_3 fragments as adsorbate particles to simulate the interaction with the surface, which is consistent with the experimental conditions in [25].

3.1.1. Interaction of F with the surface

Quantum-chemical calculations of sequential adsorption of atomic fluorine on a clean orderly C(100)-(2×1) surface suggest that carbon atoms of the surface dimers can equally be adsorption sites. Chemisorption of the first fluorine atom requires activation energy E_{act}=0.13 eV (Fig. 1a), which is due to



a) b)

Fig. 1. The dependence of the total energy of the "cluster - fluorine" system on reaction coordinate for adsorption of a F atom on a clean ordered surface (a); the C(100)-(2×1) surface covered with a monolayer of fluorine (1 ML) (b). The zero point is the total energy of system of the non-interacting cluster and a fluorine atom.

a π-bond rupture in the dimer and re-hybridization of the carbon atom orbitals to create a covalent bond with fluorine. Adsorption of the second fluorine atom takes place on the adjacent atom in the dimer without activation. Thus, a clean ordered diamond surface (100)-(2×1) is covered by a monolayer of fluorine (1 ML). Such a surface (Fig. 1b) preserves the 2×1 structure which is characterized by rows of surface dimers. However, each carbon atom in the dimer is in an sp^3-hybrid state and is bonded with one fluorine atom (monofluoride state).

In the simulation of a fully fluorinated surface, we calculated the heat of adsorption E_{ads} of the fluorine on the surface according to the formula:

$$E_{ads} = \left(E_{C_M H_N} + nE_{F_2}/2 - E_{C_M H_N F_n}\right)/n \tag{1}$$

where $E_{C_M H_N}$ and $E_{C_M H_N F_n}$ are total energies of the $C_M H_N$ cluster simulating a clean C(100)-(2×1) surface, and the cluster with n atoms of fluorine adsorbed, respectively The value of E_{F_2} corresponds to the energy of the F_2 molecule. For this configuration, we obtained E_{ads}=3.85 eV, which agrees well with the similar value of 3.94 eV in [31].

Upon further interaction with fluorine atoms with the surface coated with a fluorine monolayer, the following processes can occur (Fig. 2): adsorption of fluorine on the carbon atoms of the surface dimers to form difluoride states; binding of the gas phase fluorine atom with fluorine adsorbed on the surface, and desorption of the F_2 molecule; binding of one or two gas phase fluorine atoms to the surface CF-complex and desorption of CF_2 or CF_3 fragments. We simulated all of the above processes. The values of activation energy are 2.9 eV, 2.2 eV and 6.4 - 5.8 eV, while the energy changes by -0.20, +3.15, +3.41 and -1.00 eV, respectively.

Transition from monofluoride to difluoride state requires activation energy of 2.90 eV and reduces the total energy of the "surface - 1ML + F" system by ΔE = -0.20 eV (Fig. 2b). The resulting surface

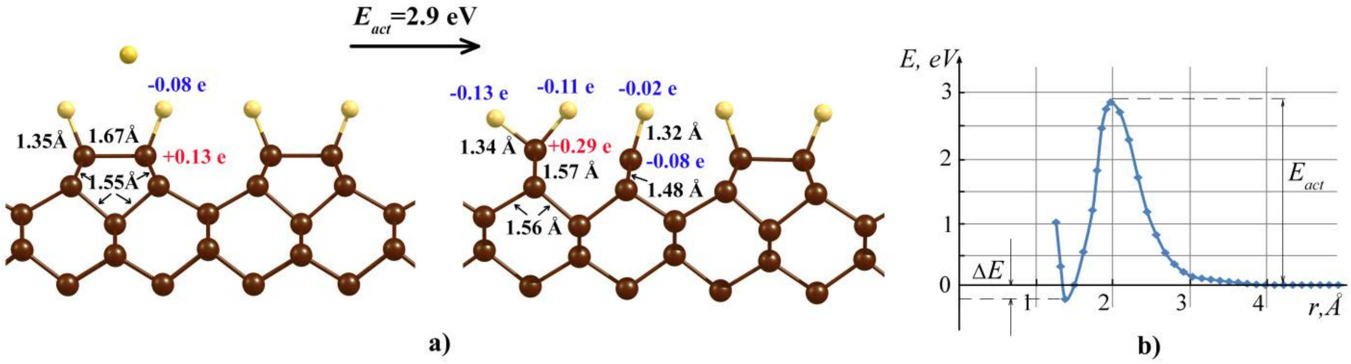


Fig. 2. A monofluoride to difluoride state transition model, side view (a); dependence of the total energy of the "cluster - fluorine" system on reaction coordinate for adsorption of F atom on a monolayer of fluorine (1 ML) surface (b).

condition is the destruction of the surface dimer and formation of adjacent mono- (CF) and difluoride (CF_2) complexes (Fig. 2a). The difluoride complex carbon atom is located in the sp^3-hybrid state, and the carbon atom orbitals in the surface complex CF rehybridize from sp^3- into sp^2 + *p* state. An unfilled *p*-orbital of the carbon atom in the monofluoride CF complex is parallel to the surface along the line of the destroyed dimer bond. It should be noted that such monofluoride states have been described in the work [32] devoted to the study of fluorine interaction with a silicon surface using *ab initio* calculations and molecular dynamics. The paper noted that a monolayer of fluorine atoms on silicon prevents further increase in the degree of fluorination, despite the presence of unfilled *p*-orbitals. In our case, an unfilled *p*-orbital and the stresses arising on the surface due to the difluoride formation obviously cause a slight decrease in the total energy by surface adsorption.

Thus, steric repulsion of fluorine atoms prevents the formation of alternating difluoride and monofluoride states on the diamond surface. Such a layer (called 1.5 ML) of fluorine adsorbed on the of the Si(100)-(2×1) reconstructed silicon surface has also been studied in the work [32]. It has been determined that such a structure is stable at 0 K, but at 300 K the 1.5 ML layer ordering is broken. The same paper studied the structure and stability of the 1.25 ML and 2 ML layers. It has been found that 1.25 ML is an ordered arrangement of mono- and difluoride complexes separated by F-Si-Si-F dimers. This structure is stable at room temperature. An idealized 2.0 ML ordered structure consisting only of difluoride states is unstable due to the high energy of repulsion between the neighboring SiF_2 complexes. Given the fact that the C-C and C- F bond lengths in diamond are substantially shorter than in silicon, it can be assumed that repulsion of the neighboring fluorine atoms adsorbed on C(100)-(2×1) will be notable with a lower degree of fluorine coating than on silicon.

The difficulty of the adjacent dihydride CH_2 states formation on the C(100)-(2×1) surface is also highlighted in a number of works [33-36,11]. It is known that the dihydride states formation on the C(100)-(2×1) surface is accompanied by a range of features associated with an increase in the surface energy due to its change from (2×1) to (1×1), and as a consequence, a close (~ 1.4 Å) location of hydrogen atoms in the neighboring dihydride states. However, in [11] it has been discovered that, a 1.33 ML layer on the C(100) surface, consisting of alternating monohydride-state dimers and dihydride complexes, is a more stable configuration than 1 ML.

Our calculations show that after a single difluoride complex is formed, the next adjacent difluoride complex on the adjacent carbon atom is energetically unfavorable, as it requires a 3.4 eV activation energy and is accompanied by an increase in the (cluster + F) system energy by 0.74 eV. When the second difluoride complex appears on the carbon atom of the adjacent dimer of the same row, the energy increases by 2.65 eV and 2.29 eV, depending on the relative position of fluorine atom pairs. If the second difluoride complex appears in the neighboring dimer row (for "staggered" arrangement), the energy increases by 1.95 eV. Thus, we have found that the structure of an ordered layer of 1.25 ML and more is unstable because of the fluorine atoms steric repulsion, both in the same and in the neighboring difluoride complexes, and as a consequence, the stresses and strains (tensile and compressive deformations) in the interatomic distances on the surface. Probably, difluoride states on an ordered diamond surface are segregate complexes surrounded by monofluoride states.

The papers [37,38] provide a TDS study of fluorine desorption form diamond surfaces (100) and (111). The thermal desorption data [37] show fluorine desorption over a wide temperature range (500–1200 K) on both surfaces indicating binding sites with a range of energies. The [38] data show that fluorine desorbs at temperatures above 830°C. The highest desorption temperature is proposed for fluorine desorption from monofluoride states. The theoretical study [13] uses *ab initio* methods to calculate the C-F binding energy during chemisorption of the first fluorine atom E_b=485 kJ/mol (4.99 eV) and shows that when a monolayer is formed, the C-F binding energy value is reduced due to steric repulsion of fluorine atoms. According to the data of [37] diamond surface must be free of fluorine at a temperature above 1200 K. Based on the data of [35], which investigated hydrogen desorption from the (100) surface, at 1260 K, those particles desorbed for which the desorption activation energy was 80 kcal/mol=3.44 eV. The authors of [12] have estimated the heats of dehydrogenation of the C(100)-2×1:H surface, providing the following values: 359-311 kJ/mol =3.72-3.22 eV. For plasma chemical etching of diamond, it is important that CF_x fragments got desorbed instead of atoms (molecules) of fluorine from the surface. The desorption activation energies for the CF_x fragments should be lower than those for fluorine desorption.

We have calculated the values of the activation energy of desorption from the CF_2 difluoride complex surface: E_{des}=1.89 eV. The fluorine atoms in the gas phase cause a decrease in the desorption activation energy value. The atomic fluorine interaction with the surface difluoride complex CF_2 enables the CF_3 fragment or a CF_4 carbon tetrafluoride molecule desorption into the gas phase or according the reactions:

$$C_MH_NF_n + F \rightarrow C_{M-1}H_NF_{n-2} + CF_3 \qquad \text{or} \qquad C_MH_NF_n + 2F \rightarrow C_{M-1}H_NF_{n-2} + CF_4.$$

The first reaction requires a 1.63 eV activation energy, which can be observed at temperatures above 580 K. The second reaction requires a 0.56 eV activation energy and can be observed at lower temperatures. Both reactions require the presence of atomic fluorine in the gas phase. This once again highlights the importance of the atomic fluorine presence in the gas phase, acting as a basic element for the surface chemical etching.

In both cases, desorption resulted in the (cluster + xF) system total energy decrease by 0.80 and 5.66 eV, respectively, and a single vacancy remained in the place of the difluoride complex (Fig. 3).

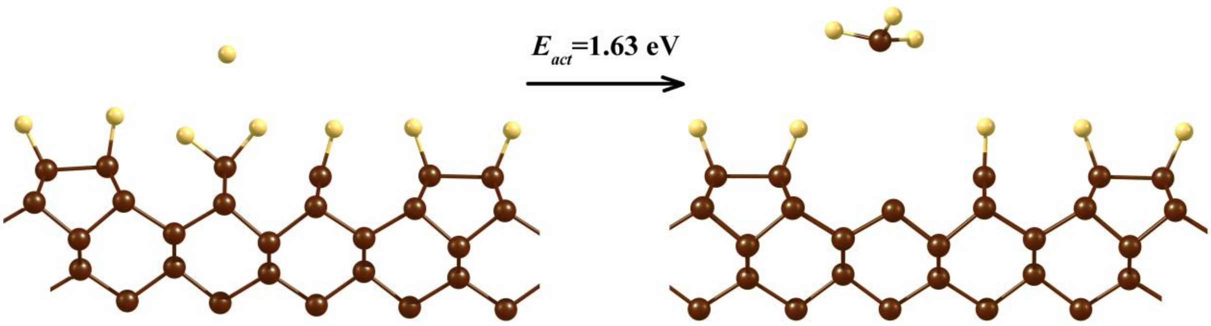


Fig 3. Model of a CF_3 fragment desorption into the gas phase as a result of atomic fluorine interaction with the surface difluoride complex CF_2 (side view).

The reaction of atomic fluorine with the CF monofluoride complex located next to the difluoride complex CF_2 enables the desorption of CF_2, CF_3 fragments or CF_4 carbon tetrafluoride molecules into the gas phase according to the reactions:

$C_MH_NF_n + F \rightarrow C_{M-1}H_NF_{n-1} + CF_2$,

$C_MH_NF_n + 2F \rightarrow C_{M-1}H_NF_{n-1} + CF_3$,

$C_MH_NF_n + 3F \rightarrow C_{M-1}H_NF_{n-1} + CF_4$.

The activation energy of the first reaction is 2.40 eV, while for the second and the third reactions the activation energy values are 1.9 - 1.7 eV. As a result, a single vacancy and a difluoride complex remain on the surface.

Thus, it can be concluded that for a clean ordered C(100)-(2×1) surface, the reaction of difluoride complexes formation of monofluoride ones requires the largest value of activation energy E_{act}=2.90 eV. It be noted that this is accompanied by the FC-CF surface dimer destruction, and there are two potential centers of CF_x fragments desorption (x=2,3,4) from a diamond surface: a CF monofluoride complex and a CF_2 difluoride complex (Fig. 2). Analysis of molecular orbitals (MO energies, bond orders, etc.), and the activation energies of desorption indicates a greater probability of CF_x fragments desorption from CF_2 difluoride complexes on the (100) diamond surface. Desorption of CF_3 and CF_4 particles during CF_2

difluoride complexes binding with atomic fluorine requires significantly less energy (1.63 - 0.56 eV) compared to the energy of a CF_2 difluoride complex formation. Therefore, it is the probability of difluoride complexes formation that will determine the kinetics of the C(100)-(2×1) ordered surface etching.

Thus, the main results of the simulation of the atomic fluorine interaction with the diamond surface C(100) leading to the etched surfaces are: 1) difluoride states formation from monofluoride ones and surface dimers destruction (E_{act}=2.90 eV); 2) a decrease in the activation energy of the CF_x fragments desorption from the surface in the presence of fluorine in the gas phase (E_{des}=2.4 - 0.56 eV).

3.1.2. Interaction of CF_2 and CF_3 with the ordered surface

When we simulated the interaction of particles with the surface, we assumed that the gas mixture contains both fluorine atoms and CF_2 and CF_3 fragments.

When the CF_2 and CF_3 radicals with dangling bonds react with a fluorinated surface, they can facilitate the desorption of F from the surface. A CF_2 interaction with the monofluoride states on fluorinated surface may lead to the formation of a CF_3 fragment or a CF_4 molecule by the reactions:

$C_MH_NF_n + CF_2 \rightarrow C_MH_NF_{n-1} + CF_3$ or $C_MH_NF_n + CF_2 \rightarrow C_MH_NF_{n-2} + CF_4$.

For the former of these processes, when there are only monofluoride states on the surface, one of the two dangling bonds of a CF_2 fragment saturates and there is an increase in the (cluster + CF_2) system energy by 0.39 eV. For the latter process, when a pair of fluorine atoms from the neighboring dimers of one row is desorbed, the energy also increases by 0.69 eV. A very low probability of such reactions is indicated by values of their activation energies: 3.5 eV or higher.

Calculations have shown that the most likely process is the CF_3 radicals interaction with the 1 ML layer by the reaction:

$C_MH_NF_n + CF_3 \rightarrow C_MH_NF_{n-1} + CF_4$.

The value of the activation energy for this reaction is E_a=1.24 eV. After desorption, some carbon atoms remain on the surface, and either fluorine atoms or CF_2 particles may adsorb on them. In the latter case, a CF_2 surface complex is formed, it includes an adatom.

Unlike monofluoride states, desorption of a single fluorine atom from difluoride state with CF_2 and CF_3 radicals requires activation energies of 1.8 eV and 0.3 eV, and there is a decrease in energy by 2.82 eV and 3.25 eV. The result is a CF_3 fragment or a CF_4 molecule (Fig. 4) and the surface dimer with monofluoride states of carbon atoms is restored.

Thus, the CF_2 and CF_3 particles in the gas phase impede the process of the ordered surface etching with atomic fluorine. In our opinion, the CF_3 particles involved in the transformation of difluoride states

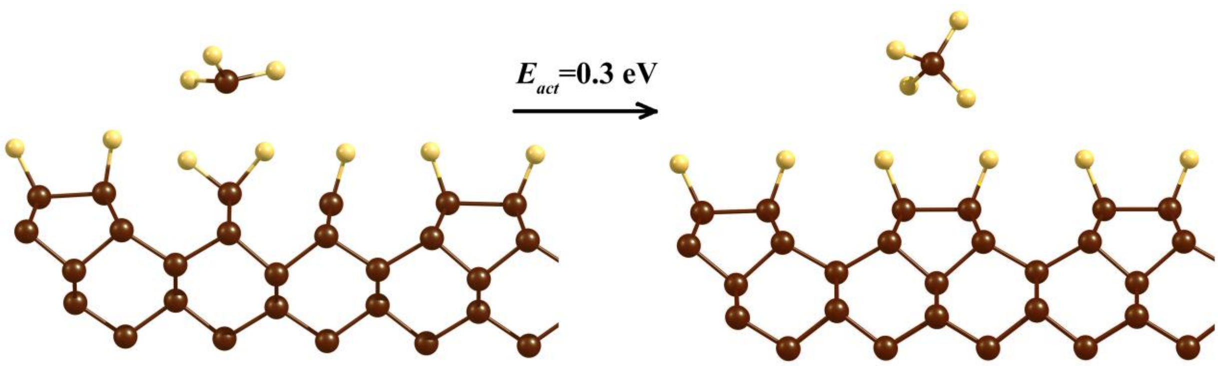


Fig. 4. Model of a CF_4 molecule desorption into the gas phase by the CF_3 radical reaction with the CF_2 difluoride surface complex (side view).

of carbon atoms to monofluoride ones and consequently complicating the orderly surface etching process.

3.2. Interaction of particles with vacancy defects

3.2.1. F interaction with a monovacancy

Fig. 5a illustrates a cluster fragment simulating fluorinated surface with a vacancy defect. Coating a clean C(100) surface with fluorine near a monovacancy requires a 0.1-0.2 eV adsorption activation We have calculated the activation energy value for the $C1F_2$ difluoride complex desorption from the 1 ML fluorine-coated surface (Fig. 5a): E_{des}=1.65 eV, which is by 0.24 eV lower than the similar values for the ordered surface. Fluorine atoms in the gas phase reduce the desorption activation energy value, in the same manner that we observed for the ordered surface.

When a difluoride complex on the C1 atom bonds with one fluorine atom from gas phase, a CF_3 particle can be desorbed, and it requires activation energy E_{des}=1.28 eV, while the total energy of the system decreases by 1.36 eV. When a difluoride complex on the C1 atom bonds with two fluorine atoms from the gas phase, a CF_4 molecule can be desorbed, and it requires activation energy E_{des}=0.42 eV, a decrease in energy in this etching is equal to 2.97 eV. The result is a divacancy defect on the surface (Fig. 5b).

Thus, a CF_x particle desorption from the surface in the $C1F_2$ difluoride state requires activation energies of 1.65 eV, 1.28 eV and 0.42 eV for x = 2,3,4, respectively.

Analysis of the reaction coordinate calculations showed that the monofluoride to difluoride state transition on the carbon atoms of the surface dimers, neighboring to a single vacancy, requires activation energy E_{act}=1.85-2.28 eV, which is smaller than such value for an ordered surface while the total energy of the system decreases by 0.46-0.74 eV. Moreover, for the carbon atoms (C6, C7, Fig.5a) of the same dimer row where the vacancy is located E_{act}=1.85 eV, indicating a greater likelihood of difluoride states

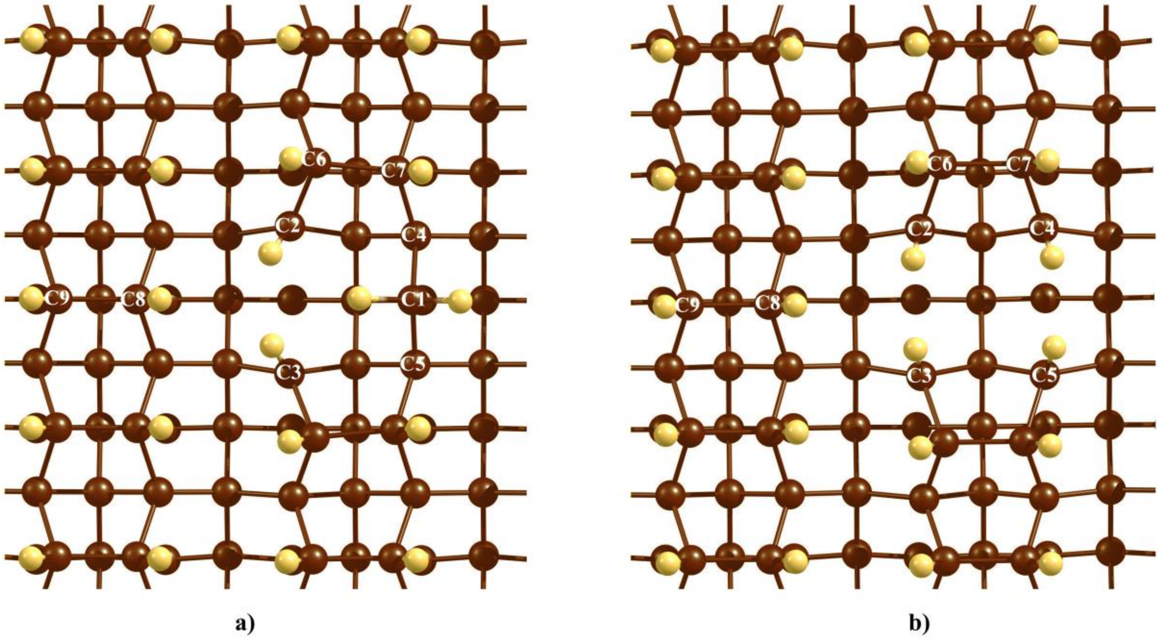


Fig. 5. A fragment of C_{195} cluster covered with a monolayer of fluorine (1 ML) and containing a monovacancy (a), divacancy (b) (top view).

on these atoms, and this is the determining step in the surface chemical etching mechanism (formation of volatile CF_x fragments and their desorption from the surface). For a carbon atom (C8, Fig.5a) of the dimer row adjacent to the vacancy E_{act}=2.28 eV.

Thus, a vacancy on the surface leads to a decrease in the activation energy of difluoride state formation on the atoms of the neighboring dimers of the same dimer row where the vacancy is located. According to preliminary calculations, we can assume that during diamond etching in the atomic fluorine atmosphere, vacancies on the C(100)-(2×1) surface initiate further formation of linear defects in the form of “empty” dimer rows.

3.2.2. CF_2 and CF_3 interaction with vacancies

Let us consider the interaction of a fluorinated monovacancy (1 ML, Fig 5a) with a CF_2 radical. A CF_4 molecule can form during fluorine atom pairs desorption from C2 and C3 atoms, or from C1 atom. These reactions require activation energies of 0.64 eV and 2.99 eV, and they are accompanied by a decrease in the (cluster + CF_2) system energy by 4.12 eV and 0.32 eV, respectively. However, fluorine atoms bonded to the C1 atom are more prone to the desorption of a single F atom according to reactions:

$C_MH_NF_n + CF_2 \rightarrow C_MH_NF_{n-1} + CF_3$, and $C_MH_NF_n + CF_3 \rightarrow C_MH_NF_{n-1} + CF_4$.

The activation energy of the first reaction is 1.90 eV, while for the second reaction E_{act}=0.43 eV and the energy is reduced by 1.17 eV and 1.70 eV, respectively. As a result, the difluoride complex on the surface is converted to a monofluoride one.

If, due to fluorine desorption, the C2 and C3 atoms in the vacancy area became free adsorption sites, fluorine atoms can bond again with the remaining dangling bonds, and the system returns to its previous state. However, if a CF_2 fragment joins the C2 and C3 vacancy atoms (E_{act}=1.20 eV), the orderly surface will restore. It should be noted that the CF_2 binding to the C2 and C3 atoms is accompanied by a decrease in energy only in the presence of one fluorine atom adsorbed on C1. In case there is a difluoride state on C1 atom, the CF_2 fragment is not adsorbed on the vacancy atoms, because this process is accompanied by a considerable increase in the adsorption activation energy (E_{act}=3.14 eV) and energy rising by 0.47 eV. Increasing energy in this case is related to the steric repulsion of the two difluoride complexes on the adjacent carbon atoms of the surface.

Similarly, the C2-C5 atoms in the divacancy area can become free adsorption sites (Fig. 5b). In case a CF_2 fragment joins the free atoms C2, C3, E_{act}=0.78 eV. The result is a single vacancy involving a difluoride complex. The second CF_2 fragment is not binding to the atoms C4, C5 due to steric repulsion and the corresponding increase in energy. A more likely process is free fluorine binding to these atoms. Thereafter, the vacancy defect comes to a state described above, and the ordered surface is restored involving CF_2 fragments.

Thus, the CF_2 and CF_3 particles are involved in difluoride to monofluoride state transition of carbon atoms, and therefore, they may reduce the etching speed in the vacancy area. Besides, the quantum-chemical calculations indicate a possibility of a diamond surface ordering with CF_2 radicals adsorption from the gas mixture. This result is consistent with experimental data [16-18].

3.2.3. F interaction with a divacancy

Let us consider the possibility of further etching the surface having a divacancy formed due to the impact of the considered particles with the adsorbed fluorine atoms (Fig. 5b). Such a defect will accelerate the etching rate compared to the ordered surface, if a difluoride state appears on one of the carbon atoms in the immediate vicinity from the divacancy. We considered the following possible positions of a difluoride complex: on the carbon atom of a dimer following the divacancy in the same dimer row (atoms C6, C7, Fig. 5b); on the nearest C atom of the neighboring dimer row (atom C8, Fig. 5b); on the next C atom separated from the vacancy by a monofluoride state (atom C9, Fig. 5b). For these configurations, the (cluster + F) system energy change was equal to +0.35, -0.36 and +0.03 eV, respectively.

Calculations have shown that the most likely process is desorption of CF_2 or CF_3 fragments from the neighboring dimer in the same row with the divacancy (atoms C6, C7, Fig. 5b). This reaction involves bonding of one or two fluorine atoms from the gas phase with monofluoride states of C6F, C7F on the surface; desorption activation energy is 2.10-1.74 eV. As a result of desorption, for example, of a single $C6F_x$ fragment, a complex defect is formed on the surface consisting of a divacancy and a monovacancy

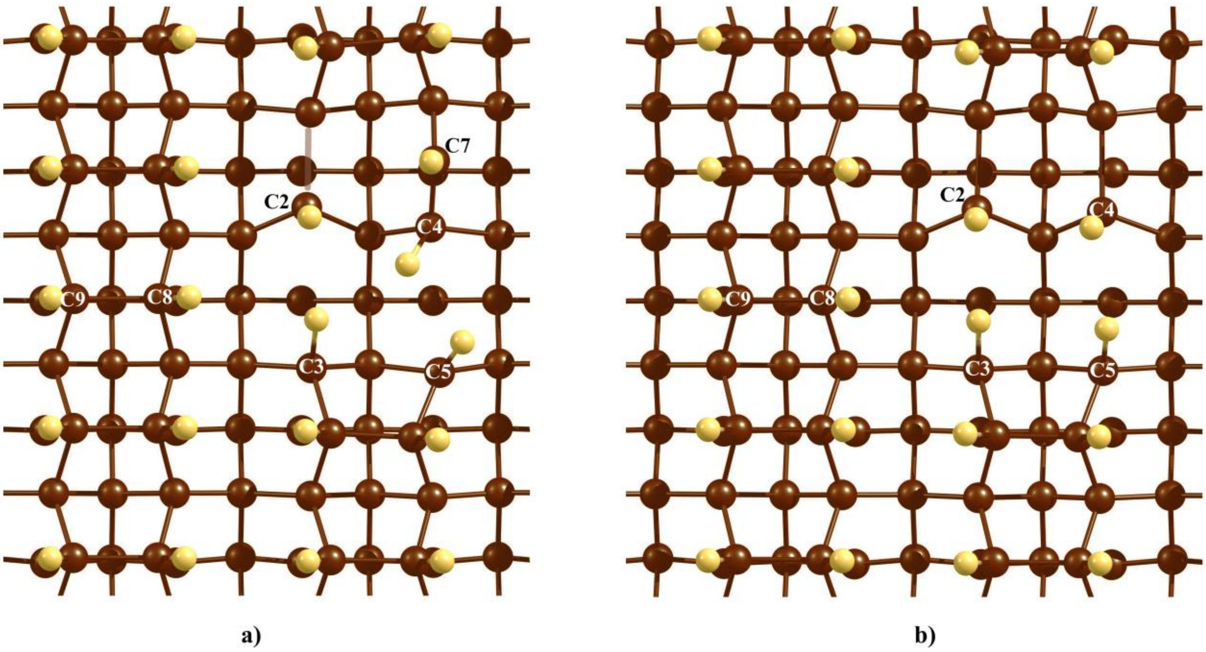


Fig. 6. A complex of divacancy and monovacancy in the same dimer row (a); a pair of divacancies (b) (top view).

in the same dimeric row (Fig. 6a); the corresponding reduction of energy is 2.82 eV. Desorption of a C7F_2 fragment formed of the monofluoride C7F and a free fluorine atom requires activation energy of 0.99 eV and is accompanied by a decrease in energy by 3.42 eV, while a pair of divacancies remains on the surface (Fig. 6b).

Unlike a single divacancy joining of a CF_2 fragment to such a defect (Fig. 6b) is energetically not favorable (energy increases by 0.43 eV), since it is accompanied by a significant distortion of the structure. It can be assumed that reactive etching of diamond in atomic fluorine atmosphere produces a lot of vacancies, and they initiate further formation of linear defects in the form of "empty" dimer rows.

4. Conclusion

Analyzing the quantum-chemical calculations results for the energy characteristics of the fluorine atoms and CF_2 and CF_3 particles interaction with the C(100)-(2×1) diamond surface, we can conclude on the following:

- Formation of difluoride states of carbon atoms on an ordered diamond surface in the atomic fluorine atmosphere requires a 2.9 eV activation energy and leads to the destruction of surface dimers. As a result, there appear two types of potential centers of CF_x fragments desorption on the surface involving gas phase fluorine atoms: a difluoride and a monofluoride one.
- CF_4 molecules desorption from the surface involving a surface difluoride complex and two fluorine atoms of the gas phase requires activation energy of 0.56 eV and 0.42 eV (for the ordered and defective surface, respectively). This is the most likely reaction of surface etching by atomic fluorine.

Table 1

Energy characteristics of fluorine atoms and CF_2, CF_3 particles interaction with the C(100)-(2×1) diamond surface.

Process / Surface	Adsorption: Particle from the gas phase	Adsorption: E_{act}, eV	Adsorption: ΔE, eV	Adsorption result	Desorption: Particle leaving the surface	Desorption: E_{des}, eV	Desorption: ΔE, eV	Desorption result
Clean ordered surface	F	0-0.13	-4.67	1 ML	*			
1 ML, monofluoride states only	F	2.90	-0.20	Difluoride state CF_2	CF_2	1.89	-0.26	Monovacancy
	CF_2	→			CF_3	>3.5	+0.39	Dangling bond on a surface carbon atom
	CF_3	→			CF_4	1.24	+0.44	
1 ML with a difluoride state					CF_2	1.89	-0.26	Monovacancy
	F	→			CF_3	1.63	-0.80	Monovacancy
	2F	→			CF_4	0.56	-5.66	Monovacancy
	CF_2	→			CF_3	1.80	-2.82	Monofluoride state
	CF_3	→			CF_4	0.31	-3.25	
1 ML, with a monovacancy defect					CF_2	1.65	-0.45	Divacancy
	F	→			CF_3	1.28	-1.36	
	2 F	→			CF_4	0.42	-2.97	
	CF_2	→			CF_3	1.90	-1.27	Monofluoride state on C1
		1.20	-0.69	Ordered surface, 1 ML				
	CF_3	→			CF_4	0.43	-1.70	Monofluoride state on C1
1 ML, with a divacancy defect	F	→			CF_2	2.10-1.74	-2.82	A complex defect
	CF_2	0.78	-0.87	Mono-vacancy				
1 ML, with a complex defect	CF_2	*	+3.00	Divacancy	CF_2	0.99	-3.42	A pair of divacancies

Symbols in the Table: * - there was no simulation of this process; → - the next process involves the particles from the previous row. ΔE, eV – total energy changes are marked by "-" if the resulting state has a lower energy than the initial one.

- CF_2 and CF_3 particles in the gaseous mixture impedes the atomic fluorine etching process for the surface due to their high reactivity for converting difluoride states of carbon atoms to monofluoride ones.

- A vacancy on the surface leads to a decrease in the activation energy (E_{act}=1.85 eV) of difluoride states formation on the atoms of the neighboring dimers in the same dimer row where the vacancy is located. This suggests that vacancies on the C(100)-(2×1) surface trigger further formation of linear defects in the form of "empty" dimer rows.

- Adsorption of CF_2 particles on the surface with a vacancy and divacancy defect can lead to the restoration of the ordered surface. This result is consistent with experimental data [16-18], pointing to the possibility of leveling the diamond surface during CF_2 radicals adsorption from the gas mixture.

- CF_4 molecules and CF_3 fragments are the main etching products for the investigated processes.

Acknowledgements

This work was supported by the Ministry of Education and Science of the Russian Federation, Grant 14.577.21.0159 (project ID RFMEFI57715X0113).

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