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Modeling of fluorine atoms interaction with the fluorinated diamond C(100)-(2 × 1) surface

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ABSTRACT

This study provides the results of quantum-chemical modeling of atomic fluorine chemisorption reactions on the C(100)-(2 × 1) diamond surface comprising mono- and difluoride states. These reactions have resulted in the emergence of vacancy defects, which in turn significantly affect the energetics and kinetics of chemical etching. We have analyzed the changes in the electronic state of mono- and difluoride states in the presence of fluorine atoms of the gas phase. This research presents theoretical evidence that difluoride state weakens the surface C—C bonds, and thus promotes CF_x fragments desorption.

1. Introduction

An important goal in the diamond-based tools manufacturing technology is to prepare the diamond surface. At present, plasma-chemical treatment is an effective method of polishing and creating relief structures. Processes of reactive ion etching provide a qualitatively higher level of solving many technical problems in the production of electronic equipment. Such gases as CF_4 and SF_6 are used as main etchants of (100) and (111) diamond surfaces [1–7]. During discharge in the gaseous phase, some SF_5, SF_3, CF_3 and CF_2 fragments are formed along with fluorine atoms and ions [8]. Fluorine is the main component that performs chemical etching of the surface [2].

We have recently published an article [9] which focuses on simulating a series of reactions that occur on the diamond surface during ion etching in the atomic fluorine atmosphere. We have found that both mono- and difluoride states may form on the diamond surface, and the CF_2 difluoride state formation probability determines the C(100)-(2 × 1) surface etching kinetics. We have estimated the value of the activation energy of the difluoride states formation from monofluoride ones on the ordered surface $E_{act} = 2.9$ eV. A vacancy defect on the surface results in the low value of difluoride state formation energy on the carbon atom of the defective dimer (next to the vacancy) and to a decrease in the difluoride state formation energy $E_{act} = 1.85$ eV on the carbon atoms in the dimers neighboring the vacancy in the same dimeric row.

However, a number of theoretical aspects remain insufficiently investigated, including examination of individual acts of diamond surface etching by fluorine at the level of changes in the surface geometric parameters and electronic state of the atoms involved in the reaction. The surface electronic structure has an impact on both geometry and reactivity of the surface. The aim of this work is to study the mechanisms of fluorine adsorption and CF_x fragments desorption from the C(100)-(2 × 1) diamond surface at the atomic level.

Quantum-chemical calculations of atomic fluorine sequential adsorption on a clean orderly C(100)-(2 × 1) surface allow us to conclude that carbon atoms of the surface dimers are equal adsorption sites [9, 10]. Chemisorption of the first fluorine atom requires activation energy $E_{act} = 0.13$ eV, which is due to the π-bond rupture in the dimer and carbon atom orbitals re-hybridization to create a covalent bond with fluorine [9]. Adsorption of the second fluorine atom on the adjacent atom in the dimer occurs without activation. Thus, monofluoride states form on the ordered C(100)-(2 × 1) diamond surface, and the degree of fluorine termination can increase rapidly up to a monolayer termination – 1 ML.

The authors of [10] investigated theoretically the properties of the C(001)-(2 × 1) diamond surface with varying degrees of fluorine termination using DFT-calculation. It was found that the adsorption energy was only weakly dependent on coverage in the 25–100% coverage range. This result indicates a rather low steric repulsion between

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monofluoride complexes. The paper concluded on the stability of the fully fluorinated (1 ML) diamond surfaces (001), (111) and (110) up to high temperatures.

Increasing the degree of fluorine or hydrogen termination of the C(001)-(2 × 1) surface to over 100% (1 ML) is associated with the appearance of surface complexes in which a carbon atom bonds to two adsorbed atoms (of dihydride or difluoride states). 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 [11–14]. It is known that the dihydride state 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 and a significant electron density overlap of the corresponding pairs of H atoms. According to calculations in [11], a single dihydride complex formation out of a monohydride complex requires activation energy of ~2 eV. When the hydrogen termination degree increases up to >133%, the hydrogenated surface becomes unstable against spontaneous formation of CH_4 [12]. The 1 × 1 surface containing only dihydride states is energetically unstable relative to H_2 desorption [15,16].

Mono- and difluoride states have been described in the work [17] 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. It has been found that 1.25 ML (a 125% fluorine termination) 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. In our study [9] we have found that the structure of an ordered F layer of 1.25 ML and more on the C(100)-(2 × 1) diamond surface 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.

In this paper, continuing our article [9], we have investigated and described the reaction of atomic fluorine chemisorption on the C(100) diamond surface coated with a 1 ML fluorine monolayer (containing monofluoride states), which results in the $CF + F = CF_2$ difluoride state formation, and a CF_3 fragment desorption from the surface by the surface difluoride state reaction with a gas phase fluorine atom $CF_2 + F = CF_3\uparrow$. These reactions on the ordered diamond surface have resulted in the emergence of vacancy defects, which, in their turn, have a significant impact on the energy and kinetics of the surface chemical etching.

In this study we pursued the following objectives: to analyze the changes in the electronic state of the monofluoride and difluoride states in the presence of a gas phase fluorine atom and to demonstrate theoretically that the presence of a difluoride state leads to the C—C bonds weakening and the possibility of CF_x fragments desorption from the surface, while the fluorine atoms in the gas phase near difluoride state loosen the difluoride state binding with the surface.

2. Calculation

Simulation of a clean reconstructed C(100)-(2 × 1) diamond surface was carried out on a $C_{195}H_{112}$ cluster using semi-empirical quantum chemical methods by the MOPAC software package [18], and *ab-initio* methods of the Firefly QC package [19], which is partially based on the GAMESS (US) [20] source code. The starting cluster contained 5 atomic layers. The dangling bonds of carbon atoms at the edge of the cluster going into bulk were saturated with hydrogen atoms (a monovalent pseudoatom model). 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, atomic bond orders, atomic orbitals population, molecular and localized orbitals.

We used the Mulliken population analysis to describe the electronic state of the surface. It is well known that the values of the Mulliken charges are highly dependent on the used basis sets [21]. The PM3 method involves a minimum basis set consisting of a maximum of one atomic orbital (AO) for each angular quantum number. The normal basis set for any atom consists of one *s* (φ_s) and three *p* orbitals (φ_{Px}, φ_{Py} and φ_{Pz}).

In this paper, the s-component of the hybrid orbitals was defined as follows. Binding between the atoms of the cluster involves the mixed- (hybrid-) type φ_i orbitals, constructed as a linear combination of its atomic orbitals (AO):

$$\varphi_i = a_i\varphi_{is} + b_i\varphi_{ip_x} + c_i\varphi_{ip_y} + d_i\varphi_{ip_z}$$

where a_i, b_i, c_i, d_i are coefficients by the AO. *s*-Components of localized orbitals are calculated according to the formula:

$$\kappa_s = \frac{a_i^2}{a_i^2 + b_i^2 + c_i^2 + d_i^2}$$

where k_s is *s*-component of the hybrid orbital, a_i, b_i, c_i, d_i are coefficients by the AO, taken from the resulting file of the system geometry optimization calculation, they are the solutions of the Roothaan equations.

As test calculations, we have simulated a vacancy and divacancy in the central dimer row of the C(100)-(2 × 1) diamond surface, and a fully fluorinated surface. Calculations were carried out using semiempirical MNDO, PM3 and PM6 methods. A PM3 method provided the results with the highest correspondence between the obtained geometric and energy characteristics of the simulated systems with the published data [10,22]. For example: in the simulation of a fully fluorinated surface, we calculated the heat of adsorption E_{ads} of the fluorine on the surface. We obtained $E_{ads} = 3.85$ eV, which agrees well with the similar value of 3.94 eV in [10]. When we used the PM6 approximation, we received the underestimating values for the heat of adsorption E_{ads} of the fluorine on the surface, the MNDO method results in overestimating.

Thus, for further analysis and modeling of the particle interaction with the C(100) surface, we used the PM3 approximation. To assess the impact of the system size on the results obtained, we made a comparative study, using the $C_{198}H_{100}$ and $C_{141}H_{84}$ clusters (8 and 5 layers of carbon atoms, respectively). For the fully fluorinated surfaces of these clusters, we obtained the values of the binding energy per fluorine atom (E_b) 3.86 eV and 3.77 eV for the C_{198} and C_{141}, respectively. Previously, we have identified E_b for the C_{195} cluster as 3.85 eV [9]. Thus, reducing the number of carbon atoms in the cluster lowers the binding energy of fluorine with the surface as compared with the literature data [10]. Since the difference in E_b for C_{195} and C_{198} clusters did not exceed 0.01 eV, for further research, we chose the C_{195} structure with the largest number of dimer rows on the surface.

Modeling the fluorine atoms adsorption on a diamond surface with a 1 ML fluorine termination was carried out using reaction coordinate calculations. The technique is described in detail in [23,24].

3. Results and discussion

3.1. Fluorine interaction with monofluoride states on the diamond surface

Let us consider fluorine interaction with a diamond surface containing monofluoride states (1 ML fluorine termination). This surface (Fig. 1) preserves the (2 × 1) structure characterized by rows of surface dimers. Each carbon atom in the dimer is in an sp^3-hybrid state and is bonded with one fluorine atom. We aim to investigate the changes in the lengths and orders of the C—C and C—F bonds; in the charges localized on the surface atoms; in hybridization of atomic orbitals (AO) of the atoms involved in the reaction of difluoride states formation from