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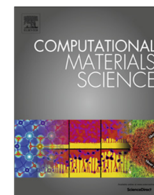

Fluorine and carbon fluoride interaction with a diamond surface: Quantum-chemical modeling

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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(1 0 0)-(2 × 1) diamond surfaces. We discuss the possible degree of fluorine coating for an ordered C(1 0 0)-(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 particle 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 state 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.

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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 was 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(1 0 0) 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 (1 0 0)-(2 × 1) diamond surface. The dimers are symmetric in the both geometry and electronic state of the atoms, the bond in the dimer is a double one, and the C═C bond length is about 1.40 Å [12–15].

Plasma with different compositions and contents of components was used for reactive ion etching of diamond surfaces (1 0 0) and (1 1 1). 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 monocrystalline, 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 (0 0 1) surface of synthetic single-crystal diamond applying a two-step process. The treatment process consisted of

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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(1 0 0)-(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(1 0 0)-(2 × 1): single vacancies and divacancies.

2. Methodology

Simulation of a clean reconstructed diamond surface C(1 0 0)-(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 atom 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 (1 0 0)-(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(1 0 0) 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(1 0 0)-(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(1 0 0)-(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 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 (1 0 0)-(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:

$$E_{ads} = \left(E_{C_MH_N} + nE_{F_2}/2 - E_{C_MH_NF_n}\right)/n \qquad (1)$$

where $E_{C_MH_N}$ and $E_{C_MH_NF_n}$ are total energies of the C_MH_N cluster simulating a clean C(1 0 0)-(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.

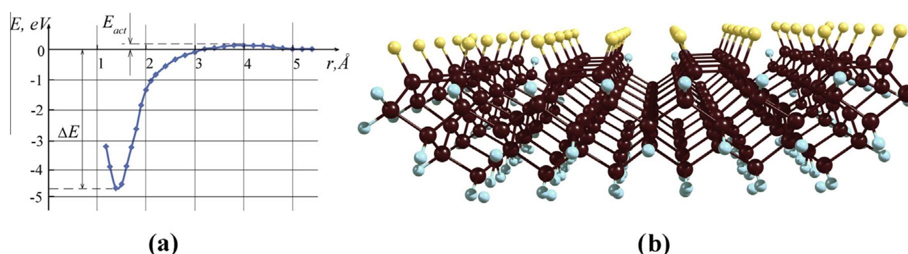

Fig. 1. The dependence of the total energy of the "cluster - fluorine" system on reaction coordinate for adsorption of a F atom on a clean ordered surface (a); the C(1 0 0)-(2 × 1) surface covered with a monolayer of fluorine (1 ML) (b). The zero point is the total energy of system of the non-interacting cluster and a fluorine atom.

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