

Modeling the hydrogen and oxygen atoms interaction with the defects on a diamond surface

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ABSTRACT

This paper analyzes the values of adsorption and desorption activation energy, bonding energy and the results of interaction between the particles (H, O, CH₂ and CO) with point defects on the reconstructed hydrogenated diamond surface C(100)-(2×1): a monovacancy and adatom. The study describes the most probable single acts of etching and restoration of an ordered surface.

Keywords: C(100)-(2×1) diamond surface, quantum-chemical simulation, adsorption properties, point defects

1 INTRODUCTION

Today, diamond constitutes a promising class of materials for many high-tech areas. Intense research is focused on synthetic diamond mono- and polycrystals. The combination of unique properties such as high hardness, wear resistance and thermal conductivity makes diamond a non-conventional material for extreme and power electronics [1-3], X-ray optics [4-6], and acoustics [7,8]. However, preparing a diamond surface with a high degree of perfection is a complicated task due to the high diamond strength combined with its low reactivity. Creating a high-quality surface, up to an atomically smooth one, is an important condition for the manufacture of reliably functioning components of synthetic diamond.

Reactive ion etching in a plasma environment of different gas composition is an effective method of smoothing the diamond surface [9-12]. The authors of [13] developed a controlled roughness reduction technique for ultrananocrystalline diamond films by the use of H₂/O₂ plasma. Pure oxygen, pure hydrogen and a hydrogen-oxygen mixture were used as an active gas environment. It has been found that the most effective method is to use hydrogen-oxygen plasma, with hydrogen as a main component. This study also provides a mechanism for the plasma particles interaction with the peaks and valleys of the ultrananocrystalline diamond surface. The active particles involved in the chemical interaction with the surface, in this case, are hydrogen, oxygen, as well as hydrocarbon radicals and CO_x particles. However, the atomic mechanisms of interaction with the surface defects

that inevitably arise in the process of etching remain understudied.

The work [13] focused on the study of ultrananocrystalline diamond films grown by vapor deposition (CVD). It is known that one of the most critical surfaces of a CVD-diamond is the C(100) surface [14]. A clean C(100) surface re-structures to a 2×1 configuration, a feature of which is the formation of π -bound C-C dimers [15]. A fully hydrogenated C(100)-(2×1):H surface corresponds to a structure in which each of the symmetric surface dimer atoms binds with a single H atom [16].

In this paper, we use the quantum chemistry methods to investigate the chemical interaction of H, O, CH₂ and CO with point defects on the reconstructed hydrogenated diamond surface C(100)-(2×1): a single vacancy and adatom. The selected types of point defects are analogues of the larger-scale surface irregularities - valleys and peaks - interacting with an active gas environment.

2 CALCULATION

Simulation of the clean reconstructed C(100)-(2×1) diamond surface was carried out on a C₁₉₈H₁₀₀ cluster using semi-empirical quantum chemical methods implemented in a MOPAC software package [17]. The starting cluster contained five layers composed of carbon atoms. The dangling bonds of the carbon atoms at the edge of the cluster, going into the bulk, were saturated with hydrogen atoms (a monovalent pseudoatom model). The optimized cluster geometry corresponding to the system energy minimum was determined by the Baker's Eigen Following (EF) method. The forces on the atoms did not exceed 3 kcal/Å in the stationary points of the system. We calculated the total energy of the cluster, atomic bond orders, population of the atomic orbitals, and molecular, localized orbitals. Simulation of the point defects involved removing one or several carbon atoms of the cluster or adding some C atoms to the surface.

Previously, for test calculations using several approximations, we simulated a vacancy and a divacancy on a C(100)-(2×1) diamond surface and a fully fluorinated surface [18]. The PM3 method provided the best concordance of the obtained geometric and energy characteristics of the simulated systems with the published

data [19]. Thus, in this paper, we used the PM3 approach to simulate the defects in the surface layers. In the simulation of a fully hydrogenated surface C(100)-(2×1), each of the surface dimer atoms formed a bond with a single H atom. Calculations within the semi-empirical method are described comprehensively in [18,20,21].

To simulate the processes of adsorption and desorption of molecules and fragments, we used the reaction coordinate calculation, for which we selected the distance between the particles and C atoms. The surface-particle binding energy (the heat of adsorption) E_b was calculated by the following formula:

$$E_b = (E_C + E_p) - E_{sys}$$

where E_C and E_p are full energies of the pure cluster and an isolated particle, E_{sys} is the (cluster + adsorbed particle) system total energy.

The calculations resulted in a 4.26 eV value of E_b for a hydrogen atom on a fully hydrogenated ordered surface containing only monohydride complexes. This resulting value is in good agreement with the 4.39 eV desorption energy in [22].

3 INTERACTION OF PARTICLES WITH A MONOVACANCY

3.1 O Adsorption

The study [13] applies a mixture of hydrogen/oxygen (19:1 v/v) as reactant gases to etch the surface of ultrananocrystalline diamond films. In this paper, we used a cluster with a fully hydrogenated surface as a model object. Figure 1a illustrates a monovalent defect in the upper layer, the C1 atom of the defective dimer is in the dihydride state. Atoms C2, C3 of the vacancy region have some dangling bonds, and oxygen atoms (Figure 1a) or hydrogen (Figure 1b) from the gas phase can be adsorbed on them. The O atom adsorption requires activation energy $E_{act}=0.44$ eV. In the bound state, oxygen forms two covalent O-C2 (C3) bonds, the heat of adsorption is equal to 8.93 eV.

When a single oxygen atom binds to the C1 atom, a double C-O bond is formed ($E_b=9.60$ eV), the activation energy is practically absent. Consequently, a single oxygen atom interaction with a monovacancy defect would most probably result in the formation of a monoxide complex of C1O.

3.2 H Adsorption

Unlike oxygen, the adsorption two hydrogen atoms leads to the formation of two single bonds with the C1 atoms. The activation energy for the H atom attachment is equal to 0.55 eV, the adsorption heat is 4.26 eV per one hydrogen atom. For hydrogen atoms bind to the carbon atoms of the vacancy region (C2, C3), the bond energy with

the cluster is lower: 3.97 eV. In addition, the activation energy is higher: 0.58 eV. The difference in energy characteristics is due to the mutual repulsion of the H atoms adsorbed on the C2, C3 atoms and, as a consequence, the additional compression/expansion stresses of the interatomic bonds in the carbon atoms of the nearest environment.

3.3 CO Adsorption

Earlier, the research [23] experimentally determined that the most probable chemical reaction of the oxygen interaction with a CVD diamond surface is the formation of a CO molecule. In the present study, we have considered the inverse process - the addition of a CO molecule to a vacancy defect. The most likely result of adsorption ($E_b=3.91$ eV, $E_{act}=1.27$ eV) is the restoration of the ordered surface, accompanied by the formation of two C-C bonds between the carbon atoms of the molecule and the cluster (C2, C3). There appears a monoxide state on the attached carbon atom.

3.4 CH₂ Adsorption

As an alternative process, we considered the CH₂ fragment adsorption from the gas phase. We determined that the values of E_{act} and E_b are 0.60 eV and 9.41 eV, respectively. Thus, the results of calculations show that the adsorption of a hydrocarbon fragment on a vacancy is more probable than the addition of a CO molecule. However, it should be noted that such a process is possible only in case there is a monohydride state on the C1 atom.

3.5 CO Desorption

Further, we investigated desorption of a CO molecule and a CH₂ fragment from the configurations considered. Such processes can be regarded as single etching acts which result in the formation of vacancy defects on the surface. We studied how a CO molecule forms of C2 and O atoms (Figure 1a). The activation energy is 10.58 eV, the energy of the system increases by 9.93 eV as a result of desorption. Thus, such a process should be considered as an improbable one. Desorption of a CO molecule formed from a monoxide complex on the C1 atom also requires high activation energy: $E_{act}=6.62$ eV, the change in the total energy $\Delta E=+4.50$ eV.

3.6 CH₂ Desorption

The CH₂ fragment desorption was considered in the separation of a C1 atom containing a dihydride complex (Figure 1b). The results of calculations showed that, similar to a monoxide complex (see Section 3.5), formation of a divacancy defect from a single vacancy is energetically unfavorable. For the process we address, $E_{act}>10$ eV, $\Delta E=+9.09$ eV.

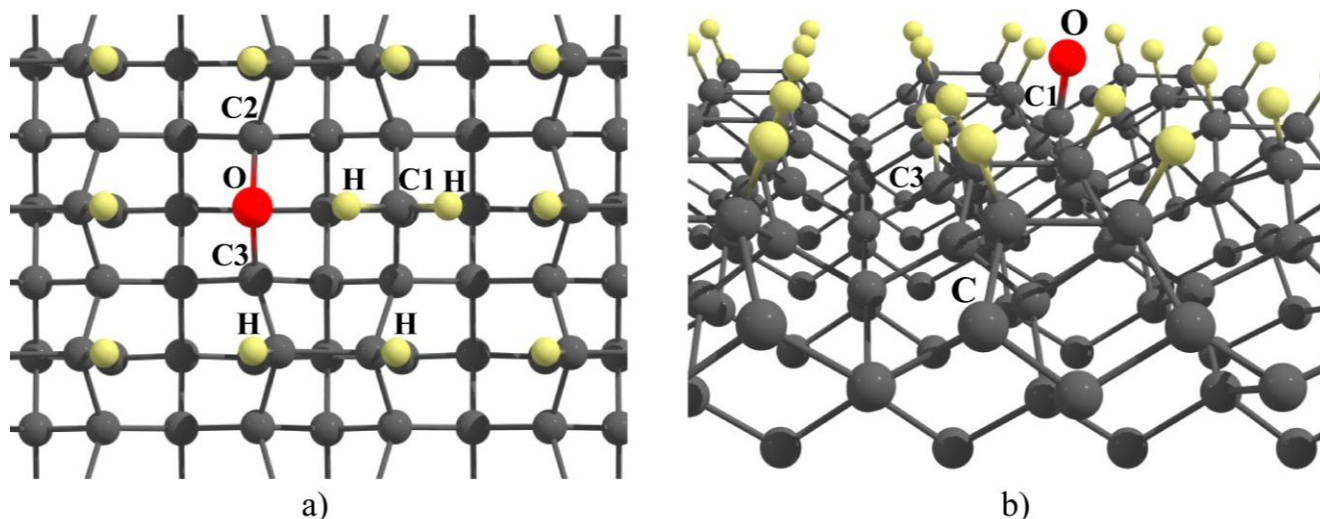


Figure 1: Result of oxygen chemisorption onto the monovacancy : a) on C2, C3 atoms; b) on C1 atom.

The energy characteristics of the considered processes are summarized in Table 1. The ΔE value corresponds to the change in the total energy of the "surface+particle" system due to the adsorption/desorption processes. A positive ΔE value indicates an increase in the energy of the system.

Particle, process	Process result (to Figure 1)	E_{act} , eV	ΔE , eV
O adsorption	Ads. to C1	<0.10	-9.60
O adsorption	Ads. to C2,C3	0.44	-8.93
H adsorption	Ads. to C1	0.55	-4.26
H adsorption	Ads. to C2,C3	0.58	-3.97
CO adsorption	Ordered surface	1.27	-3.91
CH ₂ adsorption	Ordered surface	0.60	-9.41
CO desorption	Divacancy	6.62	+4.50
CH ₂ desorption	Divacancy	>10	+9.09

Table 1: Energy characteristics of particle interaction with a monovacancy in the upper layer.

4 INTERACTION OF PARTICLES WITH ADATOMS

4.1 O Adsorption

Figure 2 illustrates a portion of the C(100)-2×1 hydrogenated surface containing an adatom with adsorbed particles. A single adatom (without attached particles) forms two covalent bonds with the surface dimer atoms, the total energy of which is 5.19 eV. An oxygen atom is adsorbed practically without activation, while the energy of the "cluster+particle" system decreases by 9.63 eV. As a result, a monoxide complex containing a double C-O bond is formed on the C4 carbon atom.

4.2 H Adsorption

Unlike oxygen adsorption, the addition of a single hydrogen atom to the adatom requires a 0.48 eV activation energy. The binding energy per hydrogen atom from the C4H dihydride complex (Figure 2b) is 4.56 eV. This value is greater than for an ordered fully hydrogenated surface (4.26 eV). The increase in the binding energy can be explained by the lower values of the tension/compression stresses for interatomic bonds "adatom-surface" compared to the surface carbon atoms.

4.3 CO Desorption

The processes of desorption of particles containing adatoms from the surface, similarly to the ones with monovacancies, can be regarded as single etching events. However, unlike the processes discussed above, desorption does not cause the appearance of additional defects, it leads to the restoration of an ordered surface. The C4O molecule formation and its transfer to the gas phase is accompanied by an increase in energy by 1.71 eV and requires activation energy of 2.38 eV. The E_{act} value obtained in the present study is in good agreement with the experimentally determined [23] activation energy for the oxidation of CVD diamond films (232 kJ/mole). The E_{act} value for desorption of CO molecules from surface areas containing adatoms is much lower than for desorption from monovacancy defects (Section 3.5).

4.4 CH₂ Desorption

Calculations showed that, in comparison with the desorption of an integral CO molecule, the separation of the C4H₂ dihydride surface complex is difficult:

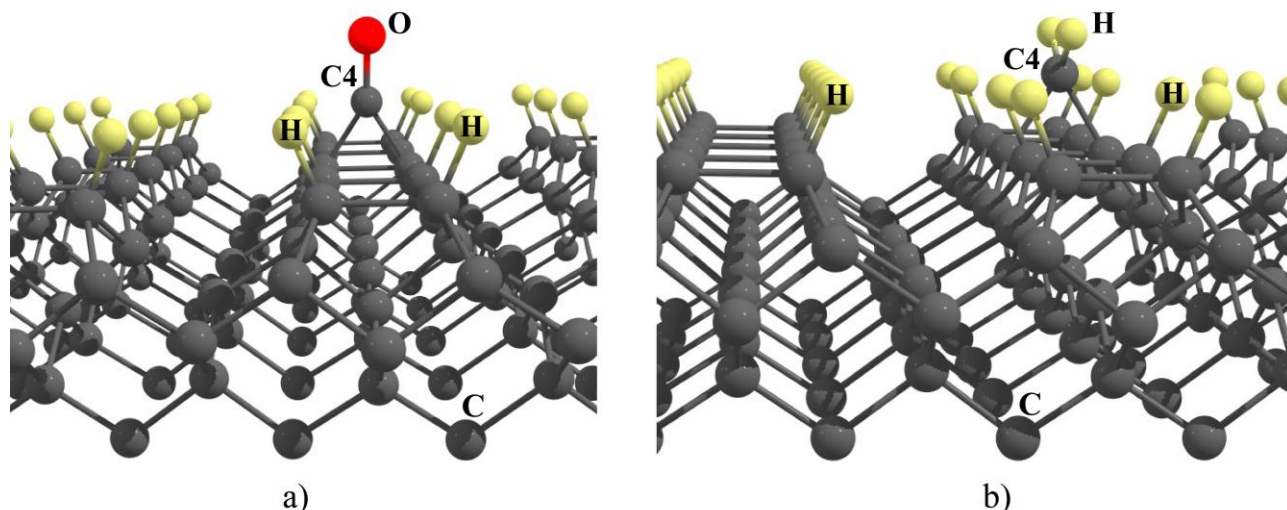


Figure 2: Result of chemisorption onto the adatom: a) O atom; b) H atoms.

$E_{act}=5.11$ eV, $\Delta E =+6.23$ eV. Consequently, the role of hydrogen in this case can be considered insignificant.

The energy characteristics of these processes are summarized in Table 2. A positive ΔE value indicates an increase in the energy of the system.

Particle, process	Process result (to Figure 2)	E_{act} , eV	ΔE , eV
O adsorption	Ads. to adatom	<0.10	-9.63
H adsorption	Ads. to adatom	0.48	-4.56
CO desorption	Ordered surface	2.38	+1.54
CH ₂ desorption	Ordered surface	6.42	+6.23

Table 2: Energy characteristics of particle interaction with an adatom.

5 CONCLUSION

The energy characteristics and the results of the interaction of particles (H and O atoms, CO molecules, CH₂ fragment) with defects (monovacancy, adatom) on the ordered fully hydrogenated surface C(100)-(2×1):H are analyzed. The above results allow us to draw the following conclusions:

- the most active particles interacting with the surface atoms with dangling bonds are atomic oxygen;
- the most likely single etching acts among the considered processes is the formation of CO molecules from adatoms and oxygen from the gas phase;
- the most effective process of restoring an ordered surface is the attachment of CH₂ fragments to monovacancy defects.

The work was supported by the Ministry of Education and Science of the Russian Federation, scientific project #14.580.21.0003 (RFMEFI58015X0003).

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