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The divacancy V_2 and V – C = C – V configurations on the diamond surface: quantum-chemical simulation

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This paper presents the results for the quantum-chemical modeling of V_2 and $V-C=C-V$ divacancy defects configurations on the $C(111)-2\times1$ diamond surface. We provide calculations for the geometric, electronic, and energy characteristics for these configurations. Energy characteristics of water and hydrogen molecule adsorption on the surface with divacancy defects are estimated. The presence of V_2 and $V-C=C-V$ divacancy defects are shown to change the mechanism and energy characteristics of molecular adsorption.

Keywords: diamond surface, divacancy defect, electronic properties, adsorption properties.

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1. Introduction

The properties of diamond are largely determined by its defects, both from its formation and arising during subsequent processing, ion implantation [1]. Vacancy defects are among the most important ones, as they not only have a significant impact on diamond growth, but also can change its optical and electronic properties. When a defect is formed, certain effects such as surface reconstruction, local re-hybridization of electron states, or even binding and bond rupture of the surface atoms may significantly affect the energy and the dynamics of heterogeneous chemical reactions and greatly complicate the existing models of adsorption and desorption. Experimental and theoretical works have mainly been devoted to studying the stability and influence of the vacancy and divacancy defects on the bulk properties of diamonds. Therefore, it is vital to have a comprehensive study of surface defects at the atomic level. Surface point defects can significantly modify the properties of dielectrics and wide-band gap semiconductors. However, it is not always possible to clearly define the structure and properties of the defects based on experimental data. In such a situation, quantum-chemical modeling is of particular interest.

Single vacancies and divacancies on the $C(100)-2\times1$ diamond surface have been previously studied using density functional theory (DFT) calculations [2]. Calculations indicated that the formation energy of a monovacancy is 2.97 eV, whereas that of a divacancy is 1.28 eV. A theoretical paper [3] found a metastable monovacancy state, and provided research on the adsorption of atomic and molecular hydrogen in the vicinity of the vacancy defects. The results for quantum-chemical calculations of structural, electronic, and energy characteristics of the water chemisorption on the $C(100)-2\times1$ diamond surface with a vacancy defect are outlined in [4]. The authors of [5] used DFT methods to study the impact of vacancies on the structure of diamond nanoparticles and indicate graphitization of the area around the vacancy. In [6], results were presented for the study of bulk defects in diamond grown by chemical vapor deposition (CVD), using optical absorption, luminescence, and electron spin resonance techniques. The vacancy was shown to lead to the appearance of some permitted levels in the band gap of diamond (E_c – 3.2 eV) and optical absorption, 1.63 eV for vacancies and 2.543 eV for divacancies.

V – C = C – V divacancies in bulk diamond have been investigated in [7] by DFT calculation. An isolated V – C = C – V divacancy was found to be very stable and was separated by a high barrier of 5 eV from the divacancy of two missing adjacent carbons, V_2. The appearance of these defects on the surface of radiation-damaged diamond is accompanied by the formation of graphitic sp^2-bonds in the material [1, 5]. Nevertheless, the question of the sp^2-bond formation effect on the properties of radiation-damaged diamond still remains open.

This paper presents results for calculations of the geometric, electronic, and energy characteristics, adsorption properties of V_2 and V – C = C – V divacancy defects on the diamond (111) – 2×1 surface.

We used a $C_{123}H_{79}$ cluster that reproduces a clean reconstructed C(111) – 2×1 surface and comprises six atomic layers. The dangling bonds of carbon atoms at the edge of the cluster, spreading into volume, were saturated with hydrogen atoms (a monovalent pseudoatom model). Quantum-chemical simulation was performed using the quantum chemical methods: semiempirical – PM6 (MOPAC software package) and Hartree-Fock *ab initio* (PC GAMESS software package). Geometry optimization was carried out by finding the minimum of the total energy by a gradient method. *Ab initio* calculations were performed using RHF approximation which does not lead to the ground state of the system, so the results are estimates. The aim of this work is a comparative calculation of electronic and energy characteristics of divacancy defect configurations on the C(111) – 2×1 surface, as well as energy characteristics of water and hydrogen molecule adsorption on a surface containing divacancy defects. The methodology for this calculation is described in detail in [3, 4].

2. Clean reconstructed C(111) – 2×1 surface

The reconstruction of a clean C(111) diamond surface was found to be in agreement with the model of π-bound Pandey chains [8]. Fig. 1a shows a model of the C(111) – 2×1 surface with Pandey chains (top view). The length of the bonds between the atoms in the chain on the surface is the same for all atoms (1.47 Å), the distance between the chains is 4.37 Å. This leads to a weaker interaction between the atoms of different chains than in the middle of the same chain. The length of the bonds between the atoms in the second-layer chain is 1.56 Å [2].

On the (111) diamond surface, no significant charge sharing between the atoms of the first and second layers is observed. On the surface chain atoms, there is a negative charge $-(0.010-0.018)e$, on the second-layer chain atoms there is a positive charge $+(0.008-0.016)e$. The bond orders between the carbon atoms in the surface chains are $\sim$ $(1.080 - 1.106)$, in the second-layer rows $\sim$ $(0.952 - 0.966)$, the valence is $3.947 - 3.966$.

The orbitals of the atoms in the surface chain have a hybridization close to an $sp^2 + p$ type: 3 low-energy sp^2-hybrid orbitals with a high s-component form covalent σ-bonds with the adjacent atoms, and a practically unhybridized high-energy p-orbital oriented perpendicular to the plane of the surface is involved in forming a delocalized electron cloud as a result of orbital overlap with first-layer neighboring atoms. Thus, the atoms in the surface chains are bound to each other by π-bonds with the presence of $\pi - \pi$ conjugation. The atoms in the second-layer chains have sp^3-type hybridization, orbitals with a high s-component form 4 covalent σ-bonds with the neighboring atoms, similar in characteristics to the bonds in a bulk diamond structure.

3. V_2 divacancy defect and V – C = C – V defect on the C(111) – 2×1 surface

A V_2 divacancy defect on a C(111) – 2×1 surface was simulated by the removal of two carbon atoms of the neighboring nodes of the cluster and the subsequent geometry optimization.

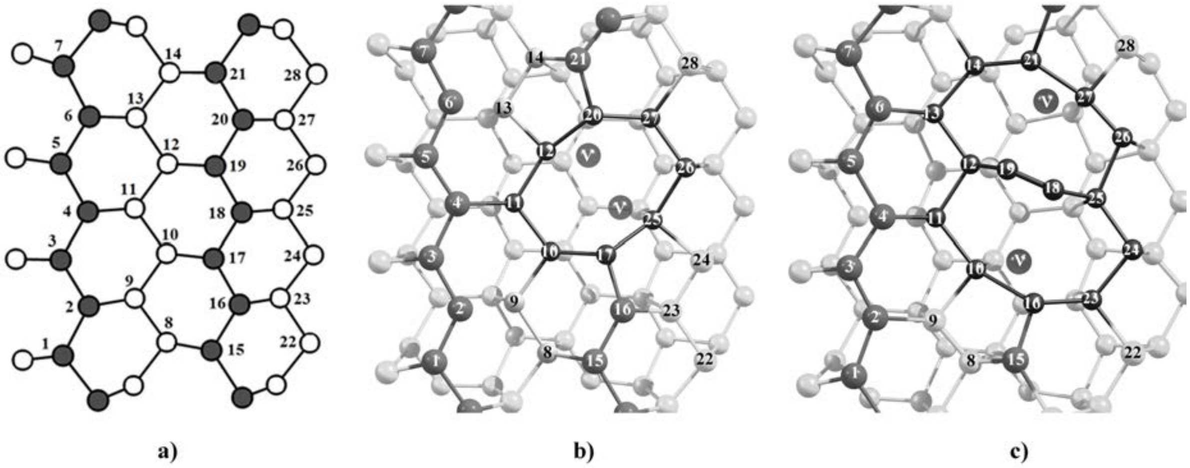

FIG. 1. Fragment of a cluster simulating the $C(111)-2\times 1$ surface: a) a model of a reconstructed $C(111)-2\times l$ surface with Pandey chains; b) with a V_2 defect, A-configuration; c) with a $V-C=C-V$ defect. Light-gray color indicates the carbon atoms of the cluster, dark-gray indicates the upper surface Pandey chain atoms, black highlights the atoms in the defect, V are vacancies in the upper surface Pandey chain

The search for equilibrium defect geometries was implemented by varying the positions of the atoms surrounding the divacancy within the first and the second atomic layer in directions perpendicular to and along the surface.

We built divacancy models where the vacancies were located in various surface chains. So, we considered the following configurations:

A – the vacancies are located in the neighboring 18 and 19 nodes of the top Pandey chain (V18 and V19); B – in the neighboring nodes of the lower Pandey chain V11 and V12; C – V11 and V in the third layer; D – in the nodes of the upper and lower chains V19 and V12.

Of all the configurations under investigation, the A-configuration had the minimum energy (Fig. 1b). In the B-configuration, the total energy of the surface was 1.67 eV higher, in the C-configuration it was higher by 5.69 eV, and in the D-configuration – by 3.32 eV. Calculation of the activation energy of a V_2 defect migration from the D-configuration to the A-configuration resulted in a value of ~ 4.47 eV.

Now, we consider V_2 vacancy defects in configuration A on the $C(111)-2\times 1$ surface (Fig. 1b). When a divacancy appears, it restructures the surface area around the divacancy, which mainly affects the atoms of the two surface layers, that is, the atoms of the upper and lower Pandey chains. There were two new bonds $C12-C20$ and $C17-C25$ between the atoms of the upper and lower chains. It can be assumed that there is greater mobility for atoms in the chains compared to the deeper layers of the surface and the absence of dangling bonds in the A-configuration divacancy which is the cause for the minimum value of the total energy for this configuration.

The lengths of the $C-C$ bonds on the V_2 divacancy perimeter are $d = 1.51 - 1.58$ Å. The $C20-C21$ and $C17-C16$ double bonds have an order of 1.43 and a length of $d = 1.41$ Å. There is a charge distribution in such a way that a $-(0.38-0.42)e$ negative charge is localized on the C20 and C17 atoms, respectively, and a positive one $+(0.17-0.25)e$ is localized on the neighboring atoms. There has been no change in the orbital hybridization of atoms around V_2: the upper chain atoms C16 ... C21 are in sp^2+p hybrid state, while the lower chain atoms are in sp^3-hybridization. However, both the charge distribution between the atoms and the existence of high-energy p-orbitals in the C17 and C20 atoms are involved in the formation of π-bonds with the C16 and C21 atoms positions these atoms as potential adsorption centers.

When we simulated the V – C = C – V defect, we considered the configurations in which: carbon atoms C19 = C18 and vacancies V_20 and V17 are in the upper surface chain nodes (Fig. 1c); carbon atoms C11 = C12 and vacancies V10 and V13 are in the lower surface chain nodes; carbon atoms C11 = C12 are in the lower chain and vacancies V4 and V19 are in the nodes of different upper chains; carbon atoms C19=C18 are in the upper chain, V17 is in the upper chain and V12 is in the lower chain.

The total energy values for the V – C = C – V defect configuration vary in the range of 3.5 eV, the minimum energy corresponds to the configuration shown in Fig. 1 (both carbon atoms and vacancies are in the upper chain).

The lengths of the C – C bonds on the V – C = C – V defect perimeter are $d = 1.42 - 1.64$ Å. The C18 – C19 bond has an order of 2.79 and a length $d = 1.22$ Å indicating a triple bond. It should be noted that there is a slight charge distribution between the carbon atoms in the vacancy. On the atoms belonging to the upper chain, there is a negative charge of $-(0.01 - 0.08)e$, while on the lower chain atoms, there is a positive charge $+(0.03 - 0.10)e$. The orbital hybridization of atoms C18 and C19, having a triple bond between them, is close to the $sp + 2p$ type, and atoms of the upper chain C10 and C21 are in an $sp^2 + p$ hybrid state, while the lower chain atoms have sp^3-hybridization. Thus, the existence of high-energy p-orbitals involved in the formation of π-bonds between the atoms C18 and C19 makes them preferential sites for active adsorption.

The value of the total energy of the surface with the V_2 defect is 3.8 eV lower than the total energy of the surface with the V – C = C – V defect. In this study, we simulated the transformation (transition) of the V – C = C – V defect into the V_2 divacancy. The activation energy of the transition is 8 – 10 eV, which indicates a very low probability of the V – C = C – V to V_2 conversion by thermal motion of the atoms or even as a result of annealing.

4. Interaction of molecules with divacancy defects

To simulate the adsorption properties of the C(111) – 2×1 surface with vacancy defects, we selected a nonpolar hydrogen molecule and a dipolar water molecule as adsorbate particles. Adsorption modeling was performed for the ground states of defects shown in Fig. 1b,c.

Adsorption of an H2 molecule on the ordered C(111) – 2×1 surface occurs dissociatively, hydrogen atoms form bonds either with the neighboring atoms of the upper surface Pandey chain ($E_{act} = 2.03$ eV, $q = -0.47$ eV), or with carbon atoms of the adjacent upper Pandey chains ($E_{act} = 2.37$ eV, $q = -0.69$ eV).

For dissociative adsorption of molecular hydrogen onto the carbon atoms in the V_2 divacancy region, an activation energy $E_{act} = 1.16$ eV is required for adsorption on the atoms C17 and C20; $E_{act} = 1.66$ eV for adsorption on the atoms C17, C16 (C20, C21) and 1.45 eV for adsorption on the atoms C17, C4 (C20, C4). All calculated values of activation energy of hydrogen chemisorption are much lower than the binding energy in the H_2 molecule ($E_b = 4.47$ eV), which indicates that there is a weakening (loosening) of chemical bonds in the molecule at the surface. Moreover, in the divacancy area, the weakening of H – H bond in a hydrogen molecule is more pronounced than on an ordered surface.

For dissociative chemisorption of a water molecule, the same pairs of the atoms were chosen as adsorption sites as in the previous case (for a hydrogen molecule). The results for the calculations of energy adsorption characteristics are presented in Table 1.

TABLE 1. Energy characteristics of adsorption of molecules on the C(111) – 2 × 1 surface with a V_2 divacancy

Molecule / Ads. centers	C17 and C20		C17 and C16		C17 and C4	
	E_{act} (eV)	q (eV)	E_{act} (eV)	q (eV)	E_{act} (eV)	q (eV)
H_2	1.16	−1.42	1.66	−1.18	1.45	−1.28
H_2O	0.31	−1.65	0.43	−1.47	0.40	−1.58

We detected a state of physical adsorption of a water molecule at a distance $r(\text{C} - \text{O}) = 3.7$ Å, characterized by the activation value $E_{act} = 0.10$ eV, and the heat of adsorption $q = -0.12$ eV. It should be noted that physical adsorption of water molecules for the ordered C(111) – 2×1 surface is not observed.

Let us consider the dissociative chemisorption of the molecules on the C(111) – 2×1 surface with a V – C = C – V defect. The C18 and C19 atoms may form both mono- and dihydride states. In a monohydride state (Fig. 2a), each of the carbon atoms is bonded to one atom of hydrogen and the C18 – C19 connection becomes a double bond. When a dihydride state forms, for example, on a C18 atom, the C18 – C19 bond becomes single, and the C19 atom forms a new bond with C21, while C18 forms two bonds with hydrogen (Fig. 2b). This state is characterized by the highest value of the heat of adsorption (Table 2).

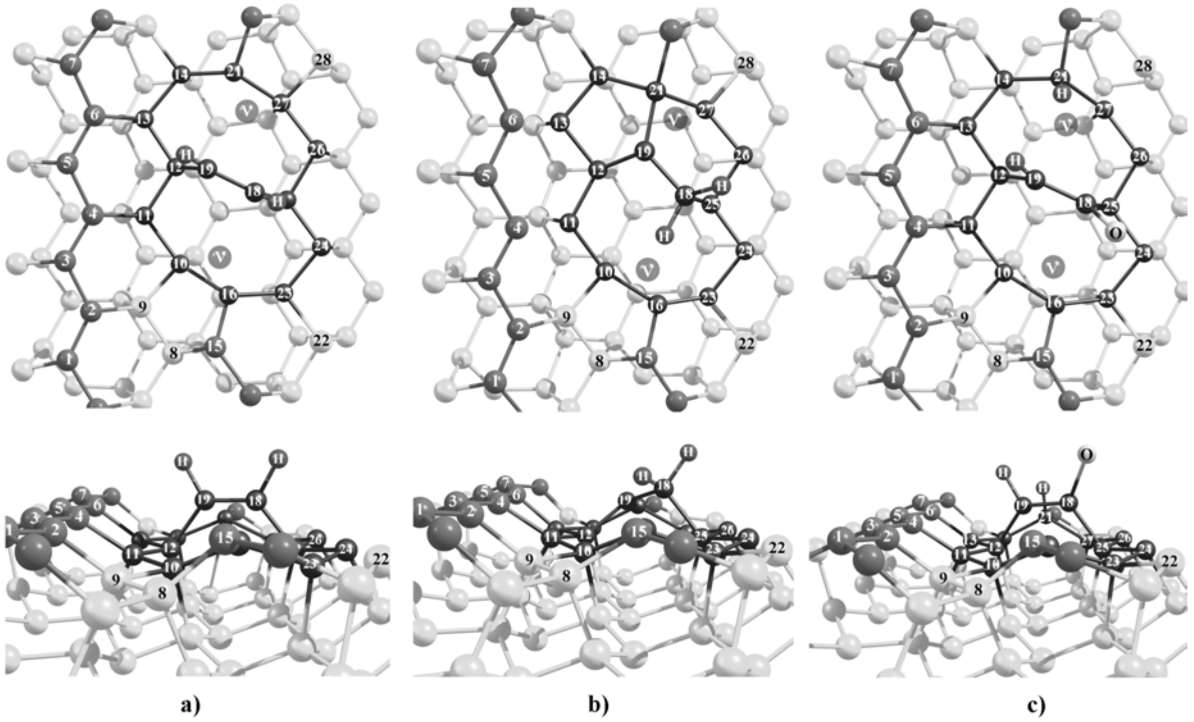

FIG. 2. Fragment of a cluster modeling a C(111) – 2 × 1 surface with a V – C = C – V defect: a) monohydride states of atoms C18 and C19; b) dihydride state of the atom C18; c) results of water chemisorption by the $H_2O \to O + H + H$ mechanism. Light-gray color indicates carbon atoms of the cluster, dark-gray stands for the upper surface Pandey chain atoms, black – atoms in the defect, V are vacancies in the upper surface Pandey chain

TABLE 2. Energy characteristics of adsorption of molecules on the C(111)-2×1 surface with a $V-C=C-V$ defect

Molecule / Ads. centers	C18 and C19		C19 and C21		C18 and C16		C18, dihydride	
	E_{act} (eV)	q (eV)	E_{act} (eV)	q(eV)	E_{act} (eV)	q (eV)	E_{act} (eV)	q (eV)
H_2	1.41	−2.71	1.53	−2.54	1.65	−2.23	1.63	−2.85
H_2O	0.12	−3.1	0.09	−2.82	0.07	−2.90	—	—

Dissociative chemisorption of a water molecule by the $H_2O \rightarrow OH+H$ mechanism on the $V-C=C-V$ defect requires little activation energy (Table 2), indicating the high chemical reactivity of the atoms acting as adsorption sites. The $H_2O \rightarrow O+H+H$ chemisorption of water is available, however, this process requires an activation energy $E_{act} = 0.52$ eV and heat of adsorption $q = -4.48$ eV. In this case, oxygen binds to one of the C18(C19) atoms forming a double bond with it, and hydrogens saturate the bonds of the neighboring atoms in the defect region (Fig. 2c).

5. Conclusion

Thus, the search for stable configurations of the V_2 and $V-C=C-V$ divacancy defects on the C(111)-2×1 diamond surface leads to states with a minimal total energy where the vacancies are located in the upper surface chain. The total energy of the surface with a V_2 divacancy is nearly 3.8 eV lower than the total energy of the surface with a $V-C=C-V$ defect. However, the divacancy configuration transition from the V_2 to $V-C=C-V$ is not possible due to atomic thermal motion, possibly even as a result of annealing.

Divacancy defects on a diamond surface have an increased reactivity in comparison to an ordered surface. Potential adsorption centers are atoms in the area of divacancies with unsaturated bonds (involved in the formation of delocalized electron clouds) and atoms with a double (triple) bond. It has been found that the C(111)-2×1 diamond surface with a $V - C = C - V$ defect allows for the creation of both monohydride and dihydride states.

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