

Quantum-chemical Simulation of Divacancy Defects on C(100)-(2×1) Diamond Surface

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The paper presents the results of the quantum-chemical simulation of the divacancy defect V_2 and the "split" divacancy V-C-V in the surface layers of C(100)-(2×1) diamond. Calculations were performed using the semi-empirical PM3 method realized in a MOPAC software package and ab initio methods implemented in Firefly (known as PC GAMESS). Six configurations of the divacancy defect V_2 are considered. It is shown that the position of the divacancy in the first layer of the surface is the most energetically favorable. The calculations of geometric and electronic characteristics of the divacancy in the ground state are performed. The energy characteristics of atomic hydrogen adsorption on the surface containing divacancies are estimated. It is shown that the divacancy defect V_2 on the diamond surface has an increased chemical activity as compared with an ordered surface. Potential adsorption sites are atoms in the divacancy V_2 region with double bonds. The formation of the "split" V-C-V divacancy is more energetically favorable than the formation of the divacancy V_2 in 3-4 layers of the surface. It is explained by the formation of graphene-like surface structures (Hexagons) from atoms of the first two surface layers caused by the existence of vacancies in the third layer of the cluster under dimer row. The formation of such a defect is accompanied by a change in the bond orders, hybridization of atomic orbitals and adsorption activation energy for hydrogen atoms compared with the ordered surface. Thus, the divacancy defects in the C(100)-2×1 diamond surface layers cause significant changes in the geometry and electronic state of the surface. Depending on the location of the defect, the active or passive chemisorption centers may be formed affecting the mechanism and energy of the process.

Keywords: C(100)-(2×1) diamond surface, Quantum-chemical simulation, Divacancy defect, V-C-V defect, Electronic properties, Hydrogen adsorption.

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1. INTRODUCTION

Vacancies are important defects that affect the electrical, optical, adsorption, and tribological properties of the diamond surface layers [1-4]. Basically, the structure and properties of surface layers are crucial for the functioning of devices and components based on thin diamond films and nanodiamonds. The most important surfaces of diamond, formed by chemical vapor deposition (CVD) method, are the C(100) and C(111) surfaces [5]. The use of diamond-based devices in extreme conditions causes the appearance of radiation defects, among which may be divacancy and multivacancy. However, a large number of theoretical [6, 7] and experimental [8, 9] studies are mainly devoted to the study of vacancy defects in the bulk of diamond, and studies of divacancy defects in the surface layers are currently lacking.

The structure and relative stability of vacancy defects on reconstructed C(111) and C(100) diamond surfaces were studied by molecular dynamics methods in [10, 11]. In the framework of the electron density functional theory (DFT), the authors of [12] showed that the energy of divacancy formation in the first layer of the C(100)-(2×1) surface is equal to $E_{dv} = 1.28$ eV, and the formation energy of monovacancies is significantly higher – $E_{mv} = 2.97$ eV. The diffusion of monovacancies from the first layer to the second layer is associated with an increase in the surface energy of about 3 eV and, therefore, is energetically unfavorable. However, these studies are limited to considering the position of vacancies in 1-2 surface layers only. In the presence of

vacancy defects, a local reconstruction of the surface occurs accompanied by rehybridization of electronic states, breaking the existed bonds and the formation of new bonds between surface atoms. These processes can significantly affect the spectral characteristics and energy parameters of adsorption and desorption of particles on the surface. The aim of this work is to establish the geometrical parameters and to study the electronic state of divacancy defects in 1-4 subsurface layers of C(100)-(2×1) diamond surface using semi-empirical methods of quantum chemistry.

2. CALCULATION PROCEDURE

The simulation of a clean reconstructed diamond surface C(100)-(2×1) was carried out on the $C_{195}H_{112}$ and $C_{126}H_{91}$ clusters using semi-empirical quantum chemical methods implemented in the MOPAC software package and ab initio methods implemented in Firefly (known as PC GAMESS). The initial clusters contain 5 atomic layers. Dangling bonds of carbon atoms on the edge of the clusters were saturated with hydrogen atoms (monovalent pseudoatomic model). The use of the semi-empirical PM3 method allowed to achieve the maximum correspondence of the obtained geometric and energy characteristics of the C(100)-2×1 surface to the published literature data [12].

When simulating vacancy defects in the surface layers of diamond, carbon atoms were removed from the lattice points of 1-4 layers of the central part of the $C_{195}H_{112}$ cluster (Fig. 1). The search for equilibrium geometrical configurations of defects was carried out by

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varying the positions of the atoms surrounding the divacancy defect.

The Davidson-Fletcher-Powell method was used to determine the optimized geometry of the system that meets the minimum total energy. At stationary points of the system, the gradients on the atoms did not exceed 3 kcal/Å. The total cluster energy, atomic bond orders, valences, value of the electron density, atom orbital populations, atomic charges, localized molecular orbitals and hybridization of atomic orbitals were calculated. To simulate the processes of hydrogen adsorption, the calculation of the reaction coordinates was used. For “atomic hydrogen – surface” interaction the distance between the hydrogen atom and one of the surface carbon atoms was chosen as the reaction coordinate. The coordinates of all other atoms of the system were optimized freely.

3. RESULTS AND DISCUSSION

In the case of random collisions of individual vacancies they can be combined into pairs – divacancy. Their total surface decreases, and the corresponding gain in surface energy ensures the stability of the divacancy. In the bulk of a solid, the concentration of divacancies depends on the concentration of monovacancies and the binding energy for a pair of vacancies. In the surface layers, the stability of various vacancy defects, which are formed, for example, by ion implantation or irradiation, may be caused by a large value of the migration energy or transformation of the defect, which may be a reason for its localization.

The characteristic of the reconstructed C(100)-(2×1) diamond surface is the rows of surface dimers. Each dimer carbon atom on the C(100)-(2×1) surface forms two covalent σ bonds with neighboring atoms of the second layer and dimeric bonds with the atom-neighbor of the first layer. The dimer bond is double and is formed by the overlap of two hybrid orbitals of atoms-forming the dimer; its length is 1.40 Å. A strong σ -bond

formed by the overlap of low-energy atomic orbitals (s -component $\sim 35\%$). The other weaker π -bond is formed by overlap of high-energy atomic orbitals with a high p -component (s -component $\sim 3\%$) that are oriented perpendicularly to the surface plane. During the adsorption of particles on the C(100)-(2×1) surface, the π -bond will first be destroyed, and the activation energy of adsorption on carbon atoms of surface dimers will depend on the energy required for the destruction of the π -bond in dimer. An example of such a dimer is the C17-C18 dimer in Fig. 1a and in Table 1.

3.1 The Divacancy Defect V_2

Divacancy defect V_2 in diamond is the absence of two adjacent carbon atoms in the lattice points. The divacancy defect V_2 on the C(100)-(2×1) surface was simulated by removing two carbon atoms from neighboring cluster points and subsequent optimization of the surface geometry. In Fig. 1a, for clarity, a schematic model of the C(100)-(2×1) surface (top view) is shown with numerization of atoms in 1-3 surface layers.

Six configurations of the divacancy defect were constructed, in which vacancies (V) were located in adjacent points of 1-4 surface layers. For example, V_1 means that the vacancy is located instead of atom 1 indicated in Fig. 1:

A – in the points of the first (upper) dimer rows 1 and 2 (V_1 and V_2)

B – in the sites of the first and second layers of the cluster V_2 and V_8 ;

C – in the points of the second and third layers of the cluster V_8 and V_{14} ;

D – in the points of the third and fourth layers of the cluster V_{14} and V of the 4-th layer;

E – in the points of the second and third layers of the cluster V_8 and V_{13} ;

F – in the sites of the third and fourth layers of the cluster V_{13} and V of the 4-th layer.

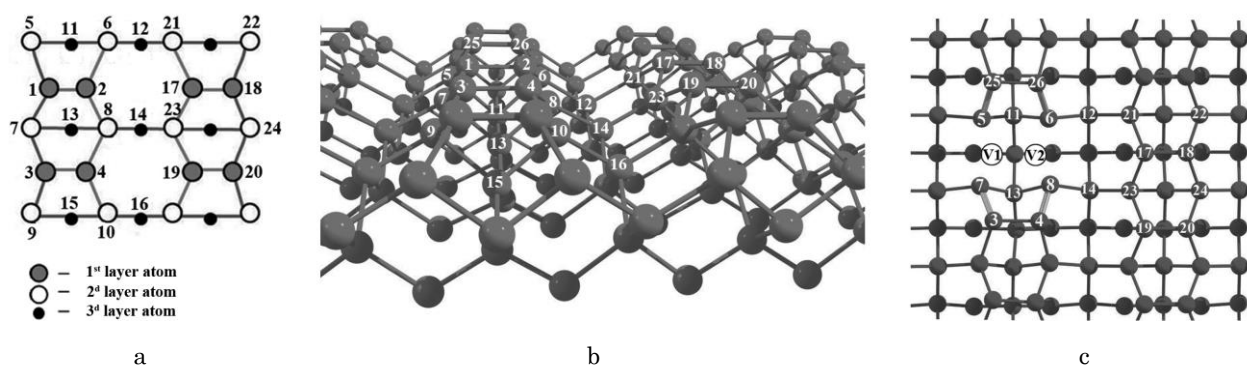


Fig. 1 – Schematic model of the C(100)-2×1 surface, top view (a), a fragment of the $C_{195}H_{112}$ cluster simulating the ordered diamond surface C(100)-2×1 (b), a cluster fragment simulating the C(100)-2×1 surface with defect V_2 in the ground state – configuration **A**, the top view (c)

From all the considered configurations of divacancy V_2 , configuration **A** has the minimum energy. Fig. 1c presents a fragment of a cluster, which shows the numbers of carbon atoms in the cluster and the positions of divacancy V_2 in the ground state (the ground state corresponds to configuration **A**). The relative values of the total energy of the surface with a divacancy

of various configurations are shown in the diagram (Fig. 2). The zero point is the total energy of the cluster with a divacancy V_2 in the configuration **A**.

Let's consider the ground state (configuration **A**) of the V_2 defect on the C(100)-2×1 surface. The appearance of the divacancy results in a local surface rearrangement: the lengths and bond orders of atoms around the

divacancy change, which reflects changes in the rehybridisation of these atoms orbitals. The dimer bonds C3-C4 and C25-C26 near the divacancy V_2 become single, their length increases in comparison with the ordered surface and is equal to $d = 1.517 \text{ \AA} - 1.518 \text{ \AA}$ (Table 1). The bonds between atoms of the first and second layers C5-C25, C6-C26, C3-C7 and C4-C8 become double, have a bond order 1.44 and a length $d = 1.443 \text{ \AA} - 1.445 \text{ \AA}$. This is due to the reorientation of active orbitals with a high p -component

of the atoms of the first layer C3-C4, C25-C26 from dimer bonds to bonds with the atoms of the second layer. It can be assumed that the absence of dangling bonds in configuration **A** is a result of the double bonds formation between atoms around the divacancy and the cause of the minimum value of the total energy for this configuration. The value of charge redistribution on atoms in the divacancy region is insignificant; therefore, such a divacancy defect will be considered uncharged.

Table 1 – Geometric and electronic characteristics of the C(100)-(2×1) surface with a divacancy in the first layer (configuration **A**, as shown in Fig. 1c)

No	Q_N, e	P_{NN}	M	P_{MM}	Q_M, e	P_{NM}	$R_{NM}, \text{ \AA}$	s-comp. $LO_N, \%$	s-comp. $LO_M, \%$
8	+ 0.043	3.93	4	3.95	- 0.021	1.44	1.443	40.5	38.5
			13	3.96	+ 0.101	0.98	1.518	38.4	31.8
			14	3.96	+ 0.090	0.95	1.517	41.7	29.9
			4	3.95	- 0.021	1.44	1.443	5.0	4.6
4	- 0.021	3.95	8	3.93	+ 0.043	1.44	1.443	40.1	39.3
			3	3.95	- 0.041	0.96	1.517	38.2	32.7
			10	3.95	+ 0.022	0.95	1.521	42.5	29.7
			8	3.93	+ 0.043	1.44	1.443	4.6	5.0
17	+ 0.008	3.96	18	3.90	- 0.012	1.82	1.402	36.0	35.3
			21	3.93	- 0.054	0.96	1.521	38.2	30.7
			23	3.94	+ 0.022	0.96	1.542	40.5	28.8
			18	3.90	- 0.012	1.82	1.402	3.1	3.4

Designations in Table 1: N, M are the number of an atom in a cluster; Q_N, Q_M are the charges on the atom; P_{NN}, P_{MM} are valences; R_{NM} is the interatomic distance; P_{NM} is the bond order, s-comp. LO_N is the s-component of N atom localized orbital

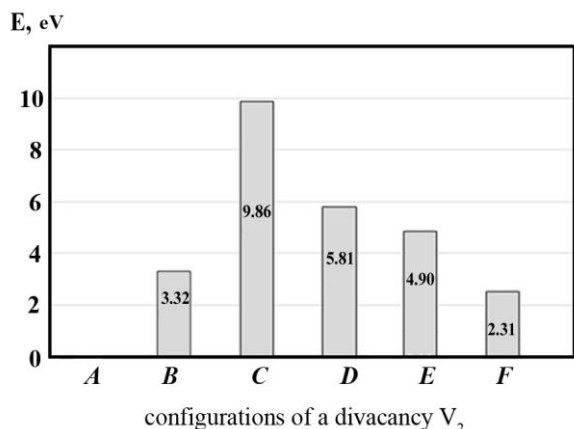


Fig. 2 – A diagram of the total energy values of the surface with defect V_2 on the C(100)-2×1 surface in **A-F** configurations

There are no significant changes in the hybridization of atomic orbitals around the V_2 defect – the atoms of the second layer C5, C6, C7 and C8 are in the sp^3 -hybrid state, but the hybrid orbital which takes part in the π -coupling with the atoms of the first layer has a high p component (s-component is about 5%). It can be assumed that the presence of a weak π -bond of C5-C25, C6-C26, C3-C7, and C4-C8 atoms makes these atoms active adsorption centers. To test this assumption, we have carried out a simulation of the adsorption of atomic hydrogen onto atoms surrounding a divacancy defect. As a result of calculations of reaction coordinates between the hydrogen atom and the C3, C4, C7 and C8 atoms, the values of the adsorption activation energy

E_a and the heat of adsorption q were obtained (Table 2). For adsorption on atoms in divacancy region, the value of the activation energy is lower than for adsorption on an ordered part of the surface (C18 atom).

Thus, atoms around a divacancy are preferred adsorption centers. However, chemisorption of hydrogen on atoms of the second layer has a greater value of the heat of adsorption and does not lead to the formation of dangling bonds on the surface, as compared to chemisorption on atoms of the first layer of C25, C26, C3 and C4.

For example, chemisorption of hydrogen atoms on C5, C6, C7 and C8 centers causes the formation of strong C-H covalent bonds. Thus, all the bonds of the second layer atoms will be saturated. The double bonds of these atoms with the atoms of the first layer C25, C26, C3 and C4 will be destroyed. These atoms will also restore the double bonds between themselves in the C25-C26 and C3-C4 surface dimers. All bonds of surface atoms will be saturated (Fig. 3).

The value of the total energy of a surface with a divacancy in configuration **F** is 2.31 eV, which is more than in configuration **A** and less than in configurations **B-E**.

Table 2 – The energy characteristic values of hydrogen adsorption on a diamond surface containing a divacancy (configuration **A**, as shown in Fig. 1c and Fig. 3)

Surface atom	E_a, eV	q, eV
C3	0.36	4.18
C4	0.37	4.14
C7	0.38	4.65
C8	0.37	4.63
C18	0.68	4.02

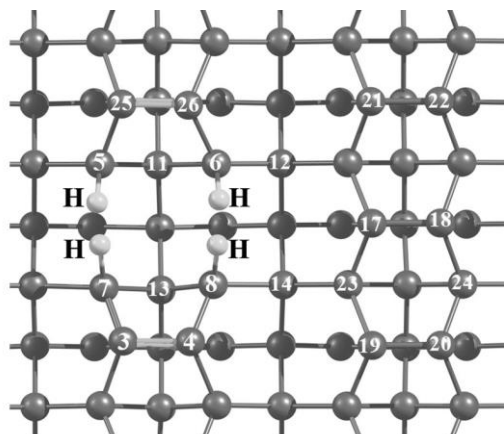


Fig. 3 – A fragment of the $C_{196}H_{100}$ cluster, simulating the $C(100)-2\times 1$ surface with the hydrogen saturated defect V_2 in the ground state (configuration **A**), the top view

A specific feature of the **F** configuration is that the vacancy in the third V_{13} layer causes the formation of a Hexagon from $C1-C2-C8-C4-C3-C7$ atoms on the surface, which suggests the absence of dangling bonds on the surface. A vacancy in the lattice point of the fourth layer leads to the formation of dangling covalent bonds, which increases the value of the total surface energy in this configuration.

According to calculations by the molecular dynamics [10] and ab initio [12] methods, an uncharged divacancy in the first layer of the $C(100)-2\times 1$ diamond surface is a more energetically favorable defect than two separate neutral vacancies. In the present work, it was found that the value of the total energy of the surface with the divacancy V_2 in the first layer (configuration **A**) is 2.8 eV lower than the total energy of the surface with two separate vacancies in the first layer. In this regard, it is worth to find out whether this ratio will remain for the third layer.

3.2 The V-C-V “Splitted” Divacancy

A defect similar to divacancy was formed by removing two nearest carbon atoms under one dimer row in the third layer of the surface. Thus, the V-C-V “splitted” divacancy in the third layer was obtained. In the “splitted” V-C-V divacancy, vacancies are not located in the neighboring lattice points, there is a carbon atom between them, in this case – it is a carbon atom of the fourth surface layer. Our calculations have shown that the value of the total energy of a surface with a divacancy (configuration **F**) is 2.21 eV higher than the value of the total energy of the surface with a “splitted” V-C-V divacancy in the third layer of the cluster and is 2.18 eV higher than the value of the total energy of the surface with two separate vacancies in the third layer. Therefore, the formation of a V-C-V defect or the existence of two separate vacancies in the third layer is more energetically favorable than the formation of divacancy V_2 in 3-4 layers. This can be explained by the formation of Hexagons from atoms of the first two surface layers caused by the existence of a vacancy in the third layer of the cluster under a dimer row [13].

The location of the vacancy in the third layer of the cluster under the dimer row leads to the appearance of dangling bonds of the second layer atoms $C7$ and $C8$, they change their location and “pull up” to the atoms of the first layer, thus forming the hexagonal structure $C1-C2-C8-C4-C3-C7$ (Fig. 4b).

Hybridization of Hexagon atoms is the same and is close to sp^2+p ; π -conjugation is formed by p -orbitals. The order of bonds between Hexagon atoms differs significantly from the order of bonds of the same atoms on ordered diamond surface and is close by the value to the order of carbon bonds in graphene [13]. This may significantly affect the adsorption energy characteristics of particles on the graphene-like surface region.

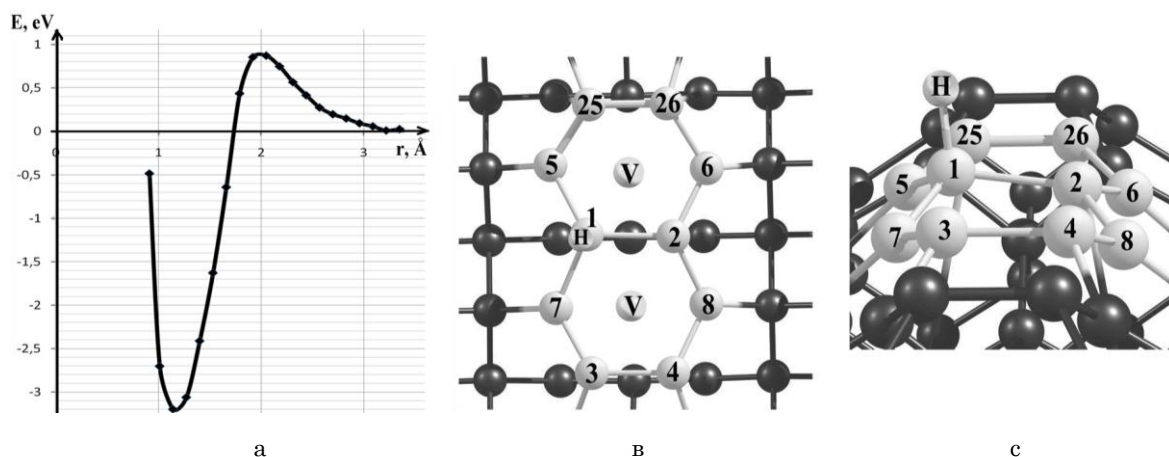


Fig. 4 – The total energy of the “surface + hydrogen” system as a function of the H-C1 reaction coordinate (a), a cluster fragment with adsorbed hydrogen on a $C1$ atom – top (b) and side (c) view. Hexagon atoms are shown in gray color

Let’s consider the adsorption process of atomic hydrogen on the diamond surface containing divacancies V-C-V in the third layer of the cluster. Atomic hydrogen adsorption was simulated by calculating the reaction coordinates (Fig. 4a) for each Hexagon atom as an adsorption center. In Fig. 4, carbon Hexagon atoms are shown in gray color. According to the change in the total

energy of the “surface + hydrogen” system, the values of the activation energy of adsorption E_a and the hydrogen heat of adsorption q (Table 3) were estimated.

The chemisorption of atomic hydrogen on $C1-C2$ and $C3-C4$ atoms requires an activation energy of $E_a = 0.91$ eV- 0.95 eV, and on the $C7$ and $C8$ atoms – $E_a = 1.28$ eV- 1.31 eV. The $C7$ and $C8$ atoms have high

bond order values and small bond lengths with Hexagon neighbors compared with C1-C2 and C3-C4 atoms. In addition, the chemisorption of hydrogen causes more significant changes in the location of these atoms (C7 and C8), which explains the higher value of the activation energy of hydrogen chemisorption for these adsorption centers.

Comparison of the values for the activation energy of atomic hydrogen adsorption $E_a = 0.91$ eV-1.31 eV for a hexagonal graphene-like structure on the surface with a divacancy V-C-V in the third layer obtained in this work with other calculations [14, 15] suggests that the chemisorption of hydrogen primarily occurs in ordered surface regions where the adsorption centers are surface dimer atoms ($E_a = 0.65$ eV [14], $E_a = 0.67$ eV [15]), and then on Hexagon atoms, mainly on C1, C2, C3 and C4 atoms, for which the adsorption activation energy of the first hydrogen atom is equal to $E_a = 0.91$ eV.

Table 3 – Energy characteristic values of hydrogen atom adsorption on the diamond surface containing the V-C-V divacancy in the third cluster layer

Surface atoms	E_a , eV	q , eV	d C-H, Å
C1	0.91	3.23	1.105
C2	0.95	3.34	1.102
C3	0.93	3.31	1.106
C4	0.94	3.37	1.103
C7	1.28	3.10	1.111
C8	1.31	3.02	1.114

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Квантово-хімічне моделювання дивакансійних дефектів на поверхні алмазу C(100)-2×1

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У роботі представлені результати квантово-хімічного моделювання дивакансійного дефекту V_2 та "розщепленої" дивакансії V-C-V у приповерхневих шарах алмазу C(100)-(2×1). Розрахунки проводилися за допомогою напівемпіричного методу РМЗ, реалізованого у програмному пакеті MORAC та *ab initio* методів, реалізованих у програмному продукті Firefly. Розглянуті шість конфігурацій дивакансійного дефекту V_2 . Показано, що положення дивакансії в першому шарі поверхні є найбільш енергетично вигідним. Проведені розрахунки геометричних та електронних характеристик дивакансії в основному стані. Оцінені енергетичні параметри адсорбції атомарного водню на поверхні, що містить дивакансію. Показано, що дивакансійний дефект V_2 на поверхні алмазу має підвищену хімічну активність у порівнянні з упорядкованою поверхнею. Потенційними центрами адсорбції є атоми в області дивакансії V_2 з подвійними зв'язками. Утворення "розщепленої" дивакансії V-C-V у третьому шарі поверхні є більш енергетично вигідним, ніж утворення дивакансії V_2 у 3-4 приповерхневих шарах. Це пояснюється утворенням графеноподібних приповерхневих структур (гексагонів) з атомів перших двох

поверхневих шарів. Формування гексагонів на поверхні алмазу спричинено наявністю вакансій у третьому шарі кластера під димерним рядом. Формування такого дефекту супроводжується зміною порядків зв'язків, гібридизації атомних орбіталей та збільшенням значення енергії активації адсорбції для атомів водню порівняно з упорядкованою поверхнею. Таким чином, дивакансійні дефекти в поверхневих шарах алмазу C(100)-2×1 обумовлюють суттєві зміни в геометрії та електронному стані поверхні. В залежності від місця розташування дефекту на поверхні алмазу можуть утворюватися активні або пасивні центри хемосорбції, що впливатимуть на механізм і енергетику процесу.

Ключові слова: Поверхня алмазу C(100)-(2×1), Квантово-хімічне моделювання, Дивакансійний дефект, Дефект V-C-V, Електронні властивості, Адсорбція водню.