

Hemisorption of hydrogen on the diamond surface containing a “boron + vacancy” defect

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PACS 68.43.-h, 81.05.ug, 03.67.Lx

DOI 10.17586/2220-8054-2018-9-1-61-63

In this paper, we present the results of quantum-chemical modeling for atomic hydrogen adsorption on the C(100)-(2 × 1) diamond surface containing a “boron + monovacancy” complex defect. We also provide a comparison of the energy characteristics of adsorption (activation energy and adsorption heat) for an ordered diamond surface, graphene surface, and a surface containing a “boron + monovacancy” complex defect.

Keywords: C(100)-(2 × 1) diamond surface, quantum-chemical modeling, complex defect, BV-complex, adsorption.

Received: 19 June 2017

Revised: 18 October 2017

1. Introduction

Boron-doped diamond is a *p*-type semiconductor and due to its unique natural properties, it is a promising material for microelectronics [1]. Goss and coworkers studied boron aggregates in diamond [2]. According to *ab initio* calculations, the B₄V- and BV-complexes correspond to the lowest energy of formation attributed to a single B atom. In [3], the authors study the electronic structure of a BV-center in diamond for its various charge states – BV⁰, BV⁺¹, BV⁻¹ and BV⁻² – using first-principles calculations. The charge state of the BV⁻¹ complex defect is stable and is suitable for qubit realization. However, for the reconstructed C(100)-(2 × 1) surface, the BV-complexes remain insufficiently studied. Such a complex defect located on the surface or in the near-surface layers can lead to local surface restructuring, to the charge distribution between the atoms around the defect, and can influence the energy of particle adsorption. Atomic hydrogen takes part in the growth mechanisms of CVD diamonds [4], in diamond etching for use in microelectronics [5].

In this paper, we investigate the energy characteristics of hydrogen adsorption on a C(100)-(2 × 1) diamond surface with BV-complexes by quantum-chemistry methods.

2. Calculation technique

A clean reconstructed C(100)-(2 × 1) diamond surface was reproduced with use of C₁₉₅H₁₁₂ and C₁₉₈H₁₀₀ cluster models containing 5 and 8 atomic layers, respectively. Calculations involved semi-empirical quantum-chemical methods implemented in the MOPAC software package [6]. The distance between the hydrogen atom and the surface carbon atom was chosen as the reaction coordinate for calculation of H adsorption. The calculation procedure is described in detail in [7].

3. Adsorption of atomic hydrogen on the diamond surface with a BV-complex

Calculations carried out for the cluster surface models have shown [8] that the lowest energy belongs to the state of a complex defect in which boron is in the fourth layer, and the vacancy is in the third layer (Fig. 1, defect 1). The position of boron in the first layer, with the same position of the vacancy in the third layer, is less energetically favorable (Fig. 1, defect 2). The feature of defect 1 is the formation of C1–C6 hexagonal structure on the surface [8]. The order of bonds between the “hexagon” atoms differs significantly from the order of these atomic bonds on the ordered surface and is close to the bond order of carbon atoms in graphene (Table 1). Two types of adsorption centers can be distinguished among atoms of the “hexagon” on the surface: they are C1–C2 and C3–C4 atoms (initially, atoms of the surface dimers) and C5 and C6 atoms (initially, the second-layer atoms). In the structure of defect 2, replacing the C5 carbon atom by the B boron atom resulted in distortion of the “graphene-like” structure: all sides of the “hexagon” have different lengths. The most bound pairs of atoms are C1–C6 and C4–C3.

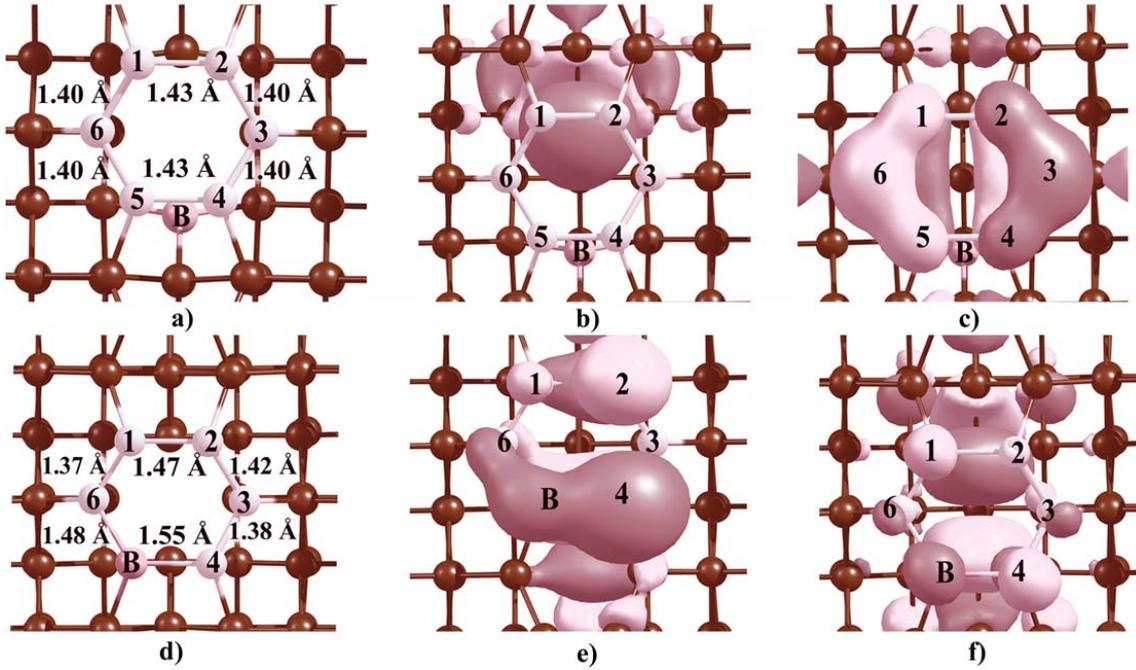


FIG. 1. a), d) defect 1 and defect 2; b), e) HOMO electron density isosurfaces; c) isosurface of the electron density of MO localized on the atoms of the “hexagon”; f) LUMO electron density isosurfaces. Atoms of the “hexagon” are shown in light gray color

TABLE 1. Bond orders (b.o) and interatomic distances (d) of carbon atoms on the C(100)-(2 × 1) diamond surface containing a “boron+vacancy” complex, and in graphene

Atoms	Ordered surface		Defect 1		Defect 2		Graphene [9, 10]	
	b.o	d , Å	b.o	d , Å	b.o	d , Å	b.o	d , Å
C1–C2	1.85	1.400	1.35	1.430	1.15	1.472	1.32	1.420
C2–C3	0.96	1.508	1.39	1.402	1.29	1.421	1.32	
C3–C4	0.96	1.508	1.39	1.401	1.53	1.383	1.32	
C5(B)–C4	1.85	1.400	1.35	1.431	1.04	1.550	1.32	
C5(B)–C6	0.96	1.508	1.38	1.401	1.13	1.482	1.32	
C1–C6	0.96	1.508	1.39	1.403	1.60	1.371	1.32	

The energy of the dimeric π -bond on the C(100)-(2 × 1) surface was estimated by *ab initio* methods in [11], and for different cluster models it was 0.67 – 1.17 eV. The authors of [12] estimated the activation energy of atomic hydrogen chemisorption on the surface dimer atoms as $E_{act} = 0.65$ eV using semiempirical quantum chemistry methods. Comparison of the $E_{act} = 0.85$ – 1.11 eV values obtained in this work for a hexagonal graphene-like structure on the surface with a BV-complex (defect 1) with the data of [11, 12] suggests that the chemisorption of hydrogen will primarily occur on the ordered areas of the surface where surface dimer atoms are the adsorption centers ($E_{act} = 0.65$ eV), and only then on hexagon atoms – predominantly on the C1, C2, C4 and C5 atoms, for which the activation energy of the first hydrogen atom adsorption is $E_{act} = 0.85$ eV (Table 2).

All hexagon atoms in defect 2 can be called adsorption centers of different types; they are characterized by different interatomic distances with neighboring atoms, different values for the charge localized on the atom and of the energy characteristics of chemisorption (Table 2). Comparison of $E_{act} = 0.40$ – 0.78 eV for a hexagonal graphene-like structure on the surface with a BV-complex (defect 2) with the literature data [11, 12] suggests that the chemisorption of hydrogen will primarily occur on the C1, C2 and C4 atoms of the “hexagon”, for which the

TABLE 2. The geometry and energy characteristics of a hydrogen atom adsorption on the diamond surface containing a “boron + vacancy” complex

Surface atom	E_{act} (eV)		Heat of adsorption q (eV)		C (B) – H distance d , Å	
	Defect 1	Defect 2	Defect 1	Defect 2	Defect 1	Defect 2
C1	0.85	0.43	3.18	2.74	1.102	1.115
C2	0.85	0.41	3.24	3.54	1.103	1.110
C3	1.10	0.64	2.64	2.43	1.116	1.134
C4	0.86	0.40	3.23	3.60	1.103	1.109
C5 (B)	0.86	0.52	3.20	2.98	1.118	1.160
C6	1.11	0.78	2.72	3.22	1.124	1.125

activation energy of the first hydrogen atom adsorption is $E_{act} = 0.40 - 0.43$ eV, and only next on the dimer atoms in the ordered surface areas ($E_{act} = 0.65$ eV).

Thus, BV-complexes in the near-surface layers of C(100)–(2 × 1) diamond lead to a significant change in the geometry and electronic state of the surface: there appear some active centers of chemisorption that affect the mechanism and energy of the whole process.

Acknowledgements

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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