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Formation energy of dangling bonds on hydrogenated diamond surfaces: A first-principles study

G. Zilibotti,[1,2,*] S. Corni,[2] and M. C. Righi[1,2]
[1]*Università di Modena e Reggio Emilia, Dipartimento di Fisica, Via Campi 213/A, I-41125 Modena, Italy*
[2]*Centro S^3, CNR-Istituto Nanoscienze, Via Campi 213/A, I-41125 Modena, Italy*

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We calculate the energy cost to create dangling bonds on hydrogenated diamond (001) surfaces by means of spin-polarized first-principle calculations. We demonstrate that the dangling bond formation energy depends on both the density and the arrangement of the dangling bonds already present on the surface. In particular, at low dangling bond density, hydrogen removal is less energetically costly than at high dangling bond density. We also find that adjacent dangling bonds are more stable in the antiferromagnetic configuration than in the ferromagnetic one. We provide quantitative information and a physical rationale of these phenomena.

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Introduction. The exceptional physical, mechanical, and electronic properties of diamond have attracted great interest from the scientific and industrial communities. Diamond films are used for applications in tribology, device technology, and for microelectronics operating in biological environments. The synthesis of diamond films is currently performed very actively. In particular, high quality diamond films are obtained by chemical vapor deposition (CVD). The usual chemical sources are hydrogen atoms and hydrocarbon-based species. Hydrogen has a fundamental role in the CVD process, since it enhances the growth rate and improves the quality of the obtained diamond films.[1,2] In fact, hydrogen is able to promote the diamond sp^3 bonding and remove the graphitic (sp^2) bonding in the films.[2,3] Atomic hydrogen has been demonstrated to improve also diamond epitaxy, which is, on the contrary, limited by the H desorption. Thus, most of the diamond films artificially grown contain hydrogen. It is known that hydrogen-covered diamond surfaces exhibit significant negative electron affinity.[4] Moreover, the hydrogen termination reduces the adhesion and greatly improves the tribological performances of sliding diamond surfaces.[5–8] Since hydrogen is such a critical element in determining the properties of diamond films, several experimental and theoretical investigations on the interactions between hydrogen and diamond surfaces have been performed, in particular on hydrogen adsorption and desorption reactions. Experiments of temperature-programmed desorption (TPD), isothermal desorption, and photon stimulated desorption[1,2,9] provided information on the kinetics of the hydrogen desorption reactions. Theoretically, the energetics of the adsorption and desorption reactions have been analyzed by different approaches, such as molecular mechanics,[10] semiempirical methods,[11] and *ab initio* calculations.[12–15] These studies focused in particular on the (001) surface of diamond, which is of interest because of the advantages in CVD growth process to obtain atomically smooth thin films.[10] The clean (001) diamond surface presents a (2×1) reconstruction, where surface carbon atoms form π-bonded dimers along the [110] direction. When the surface is hydrogenated, it mostly maintains the (2×1) reconstruction consisting of hydrogenated carbon dimers.[2,4,10,16–18] It has been demonstrated by means of *ab initio* calculations that the energy barrier for hydrogen desorption from the monohydride C(001) diamond surface is higher than from the dihydride C(001) surface, confirming that the monohydride phase is the most stable.[12,13]

Here we study hydrogen desorption from hydrogenated diamond C(001) surfaces in the monohydride phase by means of *ab initio* calculations. We calculate the reaction energy, E_R, associated with hydrogen desorption and show that E_R depends on both the density and the arrangement of the dangling bonds (DBs) present on the surface. In agreement with previous studies,[1,2] we find that the energy cost to create the first DB on a fully saturated dimer is higher than that necessary to create the second DB, producing in this way a bare C=C dimer. Furthermore, we demonstrate that the electrostatic repulsion between neighboring polar CH groups favors the formation of isolated DBs. For adjacent DBs, the antiferromagnetic (AFM) arrangement of spins is favored with respect to the ferromagnetic (FM) one.

Method. Calculations are carried out within density functional theory (DFT)[19] using generalized gradient approximation (GGA) in the PBE parametrization for exchange-correlation potential.[20] Ionic species are described by ultrasoft pseudopotentials[21] and electronic wavefunctions are expanded in a plane-wave basis set. On the basis of test calculations, we use a cutoff of 30 Ry to truncate the expansion. The C(001) surface is modeled using periodic supercells, containing a ten-layer-thick diamond slab and a 20 Å-thick vacuum region. A (2×2) in-plane size, consisting of four C surface atoms (2 dimers), is used to simulate different DBs concentrations and arrangements. The atoms belonging to the bottom layer of the slab are arranged in a (2×1) dimer configuration. A (5×5×1) Monkhorst-Pack grid[22] is adopted to sample the Brillouin zone (BZ). We take into account different hydrogen coverages ranging from 100%, where both the dimers of the cell are saturated with hydrogen, to 0%, where both the dimers are clean and the C atoms form C=C double bonds. We optimize the geometry of each system and obtain the corresponding total energy. During the relaxation, all the atoms are allowed to move until any atomic forces become smaller than 0.03 eV/Å and the total energy variation is less than 0.001 eV. The reaction energy for DBs formation is calculated as $E_R = (E_{N-1} + \mu_H) - E_N$, where E_N is the total energy of the system containing N hydrogen atoms and μ_H is the chemical potential of hydrogen. μ_H can assume different values depending on temperature and partial pressure. We have described the changes of E_R as a function of the hydrogen chemical potential in Ref. 5. In the present calculations, we assume $\mu_H = \frac{1}{2}E_{H_2}$, where E_{H_2} is the total energy of an isolated hydrogen molecule. In CVD processes, H atoms are removed via abstraction by radical species, for example, H atoms to form H_2 molecules. To obtain the energy related to this process, it is necessary to add to E_R, besides the thermal contributions, the quantity $\frac{1}{2}E_{H_2} - E_H^{\text{isolated}}$, representing half of the formation enthalpy of a H_2 molecule (-2.26 eV at $T = 298$ K[23]).

Zero point energies corrections (ZPEc) are not included in the calculations. They would not change the relative order of results.[24] The reaction energies are given at $T = 0$ K. All the calculations take into account the spin polarization. In this way, variations of E_R due to the changes in total magnetization of the system, M, can be evaluated. To investigate the polarization of surface bonds, we perform the Löwdin population analysis[25] on each structure, obtaining the net charges present on C and H atoms of the different considered structures.

Results. The reaction energy associated with the desorption of a hydrogen atom from the H-terminated diamond surfaces is calculated taking into account different concentrations and relative arrangements of DBs. The value of E_R is affected both by the presence of another DB on the same dimer and by the presence of DBs on adjacent dimers. In fact, the stability of the surface is governed by the electrostatic and exchange interactions between atoms, which change as a function of the number of DBs and their relative positions within the cell.

We first consider the H desorption from a fully passivated dimer (Fig. 1). The second dimer present in the (2×2) cell is considered fully passivated (a), partially passivated [(b) and (c)], and bare (d). The hydrogen coverages of initial states are thus 100% (a), 75% [(b) and (c)], and 50% (d). The final configurations differ from the initial ones only for one missing H atom. All the calculated values of E_R are positive, indicating that the hydrogen desorption is an endothermic reaction. The lowest energy cost, $E_R = 2.208$ eV, corresponds to the case represented in Fig. 1(a): the hydrogen atom is removed from a fully hydrogenated surface, giving rise to one isolated dangling bond per cell. The initial state has total magnetization $M_i = 0$ and the final one has total magnetization $M_f = 1\ \mu_B$, i.e., what is expected for paired and unpaired electrons, respectively. To explain the fact that the reaction of Fig. 1(a) is the less energetically unfavored we can observe that the formation of a DB, i.e., the removal of a CH group, reduces the electrostatic repulsion between CH groups. In fact, as we will describe in the following, CH groups have laterally aligned dipole moments, which is electrostatically unfavorable.

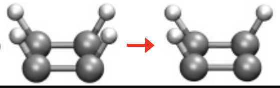
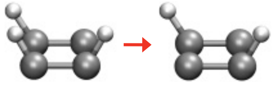
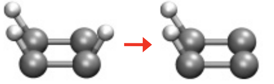
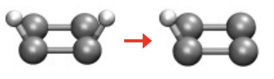
initial state final state	M_i , M_f	E_R
(a) 	0 , 1	2.208
(b) 	1 , 0	2.234
	1 , 2	2.235
(c) 	1 , 0	2.214
	1 , 2	2.251
(d) 	0 , 1	2.262

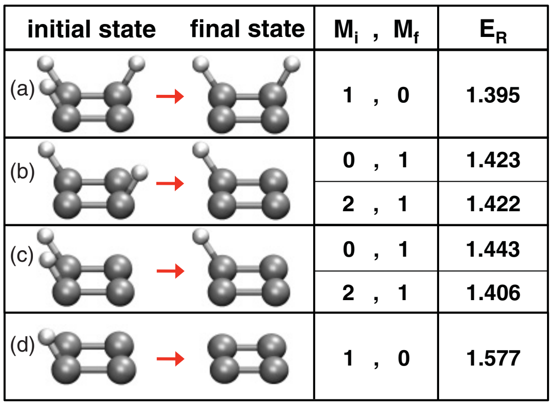
FIG. 1. (Color online) Schematic representation of hydrogen desorption reactions from fully hydrogenated dimers. The carbon and hydrogen atoms are represented in gray and white, respectively. The total magnetization of the initial (M_i) and final (M_f) configurations are reported in units of μ_B and the reaction energy, E_R, is given in eV. Periodic boundary conditions are applied, although not represented.

When a dangling bond is already present in the (2×2) cell, the repulsion between CH polar groups is lower than at full H coverage; thus, the H desorption requires higher energy [Figs. 1(b) and 1(c)]. The final states of the two reactions have the same number of hydrogen atoms, but differ in the relative position of dangling bonds, which can be arranged in a zig-zag configuration [Fig. 1(b)] or create an infinite wire of DBs [Fig. 1(c)]. For both the structures we consider the cases of antiparallel or parallel configurations of the spins. That is an antiferromagnetic order, with $M_f = 0$, or a ferromagnetic order, with $M_f = 2\ \mu_B$. The reaction energies associated with the formation of AFM final states are the lowest ones; thus, the AFM order is energetically favored over the FM one in both zig-zag and wire configurations. This is due to the exchange interaction between DBs likely mediated by the atoms they are both bonded to. The spin coupling increases by decreasing the distance and the number of bonds separating the DBs: we obtain a negligible difference between the energies of FM and AFM structures in the case of zig-zag arrangement, $E_{FM} - E_{AFM} = 1$ meV, where the distance between dangling bonds is $d_{DB} = 3.5$ Å (separated by 3 bonds), while in the case of DB wire, where $d_{DB} = 3$ Å (separated by 2 bonds), $E_{FM} - E_{AFM} = 37$ meV. The latter value is in agreement with the calculations of J.-H. Cho and J.-H. Choi,[26] who found a difference of 31 meV between the FM and the AFM configurations of a H-terminated C(001) surface containing an infinite DB wire.

The sum of the reaction energies of Figs. 1(a) and 1(c) gives the energy needed to create a wire of dangling bonds on a fully hydrogenated surface. If we consider the most stable configuration for the final state, i.e., the AFM one, we obtain $E_R = 4.422$ eV. The same reaction has been studied by Y. Okamoto[14] with hybrid-density-functional theory, using the B3LYP exchange-correlation form, obtaining $E_R = 5.43$ eV without considering the spin polarization. S. P. Walch *et al.*[15] calculated similar energetics in (2×1) cells, finding $E_R = 4.349$ eV. Moreover, experimental study of H_2 desorption from diamond, performed by Koleske *et al.*[1] using temperature-programed desorption (TPD), estimated $E_R = 4.16$ eV.

In Fig. 1(d), we consider hydrogen desorption from a fully passivated dimer, in the presence of an adjacent bare dimer. The final state presents an isolated DB, in analogy with the final structure of the reaction in Fig. 1(a). This reaction is, however, more unfavorable than Fig. 1(a) because the initial state is more stable. The higher stability is due to a lower electrostatic repulsion associated with the lower density of CH polar groups.

As a next step in our analysis, we consider the desorption of a H atom from a partially hydrogenated dimer (Fig. 2), producing a bare dimer. Since the reactions include the



initial state → final state	M_i , M_f	E_R
(a)	1 , 0	1.395
(b)	0 , 1	1.423
	2 , 1	1.422
(c)	0 , 1	1.443
	2 , 1	1.406
(d)	1 , 0	1.577

FIG. 2. (Color online) Diagram of hydrogen desorption reactions from partially hydrogenated dimers. As before, C and H atoms are represented in gray and white, respectively. The total magnetization of the initial (M_i) and final (M_f) configurations are reported in units of μ_B and the reaction energy, E_R, is given in eV. Periodic boundary conditions are applied, although not represented.

formation of C=C double bonds, which stabilize the final structures, we obtain lower reaction energies than those of Fig. 1. The formation of a bare dimer adjacent to a fully hydrogenated dimer, Fig. 2(a), has an energy cost of 1.395 eV. The presence of a double C=C bond makes this structure more stable than the previously considered structures containing the same number of hydrogen atoms, as discussed later. The relative reaction energies of the processes represented in Figs. 2(b) and 2(c) can been explained as the corresponding reactions of Figs. 1(b) and 1(c): The highest values of E_R occur when initial states are the most stable, i.e., those with DBs in AFM configuration. As shown for reactions of Fig. 1, in the presence of high hydrogen coverage, the H desorption is less unfavorable than in low H-coverage conditions.

By comparing the reactions in Figs. 1(b), 1(c), and 2(a), which have the same initial state, it is possible to determine the relative stability of structures containing two H atoms per cell with different arrangements. The final state of the reaction of Fig. 2(a), where the H atoms belong to the same dimer, is more stable than the structures containing two partially passivated dimers per cell [Figs. 1(b) and 1(c)]. In fact, we obtain $E_R[2(a)] - E_R[1(b)] = -0.839$ eV and $E_R[2(a)] - E_R[1(c)] = -0.819$ eV for AFM order. Therefore, the final configurations of Figs. 1(b) and 1(c) will tend to rearrange to that of Fig. 2(a).

In Fig. 3, the relaxed geometries corresponding to the final states of Figs. 1(a)–1(c), and 2(a) are shown. Along with the structural parameters, we show the net Löwdin charges δ present on the surface atoms. The values of δ are expressed in units of the electron charge in absolute value, |e|. Thus, the + sign indicates an electron depletion, while the − sign indicates an excess of electrons. The Löwdin population analysis reveals the charge displacement along CH bonds: the hydrogen atoms are positively charged and the corresponding carbon atoms are negatively charged.[6,7,27,28] Thus, CH bonds constitute electric dipole moments, oriented from the C atom to the H atom of each group as represented by black arrows in Fig. 3(a). The electrostatic repulsion between these polar groups makes the H desorption at high hydrogen coverage less unfavorable than at low hydrogen coverage. On the contrary, C atoms bearing a dangling bond are always close to neutral (max $|\delta| = 0.02$). In the structures shown in Figs. 3(a)–3(c), we observe a small buckling of the partially hydrogenated dimers, which is similar in all the DBs configurations. The fully hydrogenated and the bare dimers do not present any buckling. Regarding the bond lengths, we can observe that different dimer lengths highlight different nature of the bonds: the shortest length of the bare dimer in Fig. 3(d) reveals the presence of the double C=C bond.

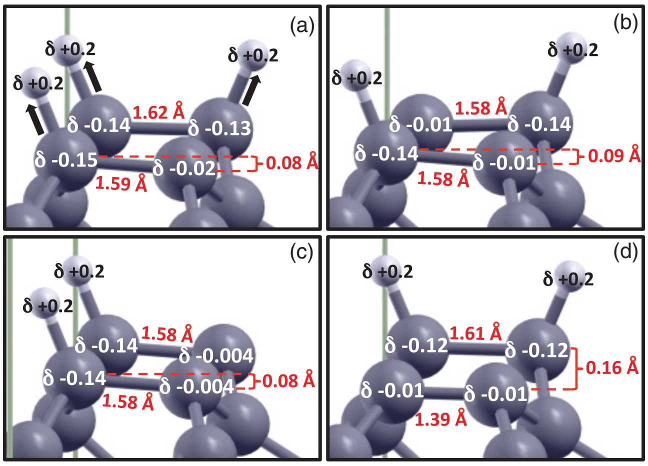


FIG. 3. (Color online) Ball and stick representation of the relaxed configurations of the C(001) surface at different H coverages. The dimer lengths and buckling are reported as well as the net charges (δ) on the surface atoms. The black arrows in panel a represent the electric dipole moments of the CH groups. For clarity, they are omitted in the other panels. Periodic boundary conditions are applied, although not represented.

Conclusions. In this work, we calculated the reaction energy required to desorb a hydrogen atom from a hydrogenated diamond (001) surface by means of *ab initio* calculations. We found that this energy depends on several factors, such as the coverage and the polarization of the surfaces. All the possible initial and final configurations of a (2×2) cell were considered. The energy cost to create a dangling bond on a fully hydrogenated dimer is higher than on a partially passivated dimer. In the latter case, in fact, the final state consists in a double C=C bond, which stabilizes the structure. The differences between reaction energies are governed by electrostatic and exchange interactions. The electrostatic repulsion between polar CH groups decreases the stability of initial configurations with high H coverage and, consequently, the energy required for H desorption. The role of exchange coupling is particularly evident when more than one dangling bond is present in the (2×2) cell. These structures are more stable in the antiferromagnetic configuration with respect to the ferromagnetic one. The overall picture can be summarized as follow: the hydrogen desorption reaction is energetically less unfavorable at high H coverage; thus, H desorption preferably produces structures containing isolated dangling bonds or isolated bare dimers.

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*giovanna.zilibotti@unimore.it

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[24] The largest contribution to ZPE correction (ZPEc) to E_R in Figs. 1 and 2 comes from the highest vibration frequency of the bond that dissociates in the reaction, i.e., the C–H bond stretching ν. In fact, when the C–H bond dissociates its ZPE is lost, as well as its effect on the ZPE of the remaining C–H groups. Since C–H vibrations may couple, their ν and the corresponding ZPEc depend on their relative C–H arrangements, yielding different ZPEc's for different structures (ΔZPEc). One can get an upper bound estimate of ΔZPEc considering a situation where the coupling between C–H vibrations is maximal, i.e., when two H belong to the same C–C dimer: the symmetric-antisymmetric stretching split is $\sim$50 cm^{-1},[29] showing that the C–H/C–H coupling can affect ZPE up to $\sim$2–3 meV. ΔZPEc among reactions within Figs. 1 and 2, respectively, should be lower, since the structures differ for the arrangements of C–H groups belonging to another dimer with respect to the dissociating C–H group.

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