Structure of diamond(100) stepped surfaces from *ab initio* calculations

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Abstract. We present theoretical studies of relaxations of monoatomic S_A, S_B(b) and S_B(n) steps on the diamond(100)-(2×1) surface employing an *ab initio* molecular dynamics simulation method that is based on density functional theory. Stable dimer structures are found in the upper and lower planes of the step surfaces in agreement with experiment. Significant atomic relaxations occur near the step edges of S_B(b) and S_B(n) stepped surfaces induced by the creation of the steps. Atomic H adsorption on these step surfaces to form monohydride structures is energetically favourable. We also simulate the presence of radical sites near the step edges of S_A, S_B(n) and S_B(b) and local reconstruction involving the dimer containing the radical sites is found. Electronic charge density profiles of the filled states near the Fermi level show features associated with the dimer structures.

1. Introduction

The diamond surfaces are probably some of the most widely studied surfaces of a solid [1, 2]. Basic science and the search for optimal conditions that allow synthesis of good quality diamond films at high deposition rate have motivated efforts to elucidate the properties of the surfaces of these materials. Presently, the combination of experimental and theoretical work has begun to shed light on the characteristics of diamond surfaces [3–15]. Diamond has three prominent low-index faces: (100), (111) and (110). The (100) surface reconstructs into an energetically favourable (2×1) structure, while the (111) substrate exhibits the Pandey-chain configuration [3–6, 12–15]. The (110) face which is found to be the most rapidly growing phase during chemical vapour deposition (CVD) growth assumes a stable (1×1) configuration [3, 14, 15]. The monohydride terminated (100)-(2×1) surface is found to have negative electron affinity, while the corresponding bare surface exhibits positive electron affinity [7]. The clean surfaces exhibit gap levels in their electronic density of states due to dangling bonds, which disappear upon termination of the substrates with hydrogen atoms [8, 9, 14, 15]. Recently, surface phonon modes have been identified and attributed to the excitations of the surface atoms [10, 11, 14].

   Despite all these efforts, little is known about the structure of the surface near a step. In reality, the diamond surface is rough and found to contain steps which were discovered to considerably affect the behaviour of the diamond surface at elevated temperature during CVD growth [16–19]. The large number of atoms that are typically required to represent the step surfaces has so far hampered exhaustive theoretical treatment of the their properties.

The first attempts at complete characterization are the empirical tight-binding studies of Davidson and Pickett [15]. An alternative methodology is interatomic interaction derived from first principles combined with slab supercells that realistically model the step surfaces. In this paper we present an *ab initio* molecular dynamics calculation of monatomic height steps at the diamond(100) surfaces using supercell geometries approaching 200 atoms. Our methodology is capable of predicting fully relaxed structures of our simulation systems. We find stable rows of dimer structures on the upper and lower planes of the step surfaces consistent with experiments. Significant geometry induced relaxation of edge atoms occurs for the S_B-type surfaces. Interaction of hydrogen with the steps' dangling bonds to form monohydride structures is an energetically favourable process. Abstraction of a hydrogen from an edge dimer of the monohydride structure results into local buckling of that dimer. Our methodology, likewise, permits calculation of charge densities of states near the Fermi level. Features due to the dimer structures are identified giving rise to a line-shape-like pattern along the dimer rows, in qualitative agreement with scanning tunnelling microscopy (STM) measurement.

2. Methodology

The first-principles molecular dynamics simulations scheme developed by Sankey and Niklewski is employed in this work [20]. The method is based on density functional theory (DFT) and its suitability for covalent systems such as C and Si is well proven and documented [21, 22]. In particular, the method has been applied to study the structural, electronic and vibrational properties of the ideal flat diamond(100), (111) and (110) surfaces and yielded results in good agreement with available data from experiments and self-consistent plane wave calculations [14]. Moreover, we also successfully employed this scheme to investigate adsorption of various hydrocarbon molecules on the diamond surfaces [23]. We will briefly summarize the main features of this scheme. The reader is referred to [20] for a more detailed description of this methodology. First, it employs the spin unpolarized (with doubly occupied orbitals) non-self-consistent version of the DFT using the Harris functional [24]. The LDA exchange correlation term assumes the Ceperley–Alder form as parametrized by Perdew and Zunger [25, 26]. Second, the non-local, norm conserving pseudopotentials of Bachelet–Hamman–Schlüter type [27] are employed to approximate the core electrons. Third, it uses a minimal basis set where the local orbitals (1s and 3p functions per site) have compact support, reflecting a confinement boundary condition. The orbital confinement radii, r_c (i.e. the radii where the atomic orbitals vanish), for C and H are 4.1 and 3.8 au respectively [20, 28]. The motivation behind the imposition of the confinement boundary condition is to reduce the range of interactions between the atomic orbitals and, hence, make the calculations less computationally intensive. Notice that the values of r_c are chosen such that they are well past the peak of the atomic wavefunction and, therefore, do not significantly modify their main features [20].

The stepped (100) diamond substrates were modelled as slabs with periodic boundary conditions in the two directions parallel to the surface (infinite in two dimensions). The S_A and S_B step types were created on a properly dimerized surface. Employing Chadi's convention [29], S_A represents a single-atom step whose upper terrace contains dimers oriented perpendicular to the step edges, while S_B indicates a single-layer step with dimers on the upper terrace oriented parallel to the step edge. Two types of S_B structure are considered in this work. One is the non-bonded type $S_B(n)$ with no rebonded atoms on the lower terrace, while the bonded type $S_B(b)$ has rebonded atoms present on the lower edge. The stepped structure models are five carbon layers deep where the bottom layer is

terminated by H atoms. Structures with S_A and S_B step edges have horizontal dimensions of 7×4 and 8×4 atoms per layer respectively. We used the Γ point ($k = 0$) to sample the small electronic Brillouin zone of the slab model for the stepped structures.

The minimum energy configurations of our simulation systems were obtained using a dynamical quenching technique. Except for the bottom C layer of the supercells we employed in this work, all the atoms were allowed to relax to their equilibrium structures. To reduce computational demands, each slab is first relaxed using semiclassical molecular dynamics simulations based on Tersoff–Brenner semiempirical potential expressions for the hydrocarbon system [30]. We then take this initially relaxed structure and further minimize it using the *ab initio* scheme until the systems attain their equilibrium structures. This two-step minimization using the semiempirical potential initially and relaxing the slab to its ground state using the first-principles method was also adopted with success in previous work [14].

3. Results and discussion

The equilibrium structure of step S_A (see figure 1(a)) yielded a stable configuration where strongly sp^2 hybridized dimers are present on both upper and lower terraces. Unlike the corresponding silicon S_A step surface, the dimers are symmetric and no geometry or electronically induced dimer buckling is found. The edge of S_A has structure that is close to that of the flat surface; i.e. it is not strongly reconstructed. The CC dimer bondlengths have an average value of 1.37 Å, comparable to those on the flat (100)-(2×1) surface [14] and lying between typical CC single and double bondlengths (1.54 and 1.34 Å, respectively). Figures 1(b) and (c) show the equilibrated S_B(n) and S_B(b) surfaces. Similar to S_A, the dimers on both S_B type steps are symmetric and sp^2 hybridized. Unlike S_A, there is, however, a significant reconstruction of the atoms at the edge. For the S_B(n), the strong reconstruction is partly attributed to the edge atoms (labelled $1'-4'$ in figure 1(b)) that have sp^2 hybridization resulting from the creation of the step. Notice that these particular edge atoms are fourfold coordinated or sp^3 hybridized in the flat surface. The dimers at the first row of the lower terrace have bondlengths comparable to those from S_A while, interestingly, those at the edge of the upper terrace have increased bondlengths of ∼1.48 Å. These strained bonds lie between the diamond bulk CC bondlength of 1.57 Å and the graphite CC bondlength of about 1.42 Å. Moreover, several upper-plane subsurface bonds (labelled 1–4 in figure 1(b)) have bondlengths stretched by about 11% with respect to the diamond bulk CC bond. In the case of S_B(b), the pronounced movement of the edge atoms may also induced by the geometry of the step edge. The edge dimers on the upper plane are displaced vertically towards the bulk by about ∼0.2 Å, relative to those from S_B(n), although the bondlengths are approximately preserved. Several lower-plane subsurface CC bonds (labelled 1–8 in figure 1(c)) are stretched by more than 13% relative to the diamond CC bulk bondlength.

In a typical CVD growth chamber, hydrogen atoms are present in the gas phase which are postulated to be producers of radical sites and suppressors of graphitic sp^2 structures on the growing substrate [1, 2]. To investigate the effect of hydrogen adsorption, we terminated the surface dangling bonds of each step surface with atomic H to form monohydride structures. We then relaxed the simulation systems to their minimum energy configurations using the *ab initio* technique outlined previously. Figures 2(a)–(c) show the equilbrium structures of these monohydride substrates. As intuitively expected, hydrogen atoms interact with the stepped surface carbon atoms to form single C–H bonds. We find that atomic H adsorption on all the step surfaces is energetically favourable with respect to the unhydrogenated
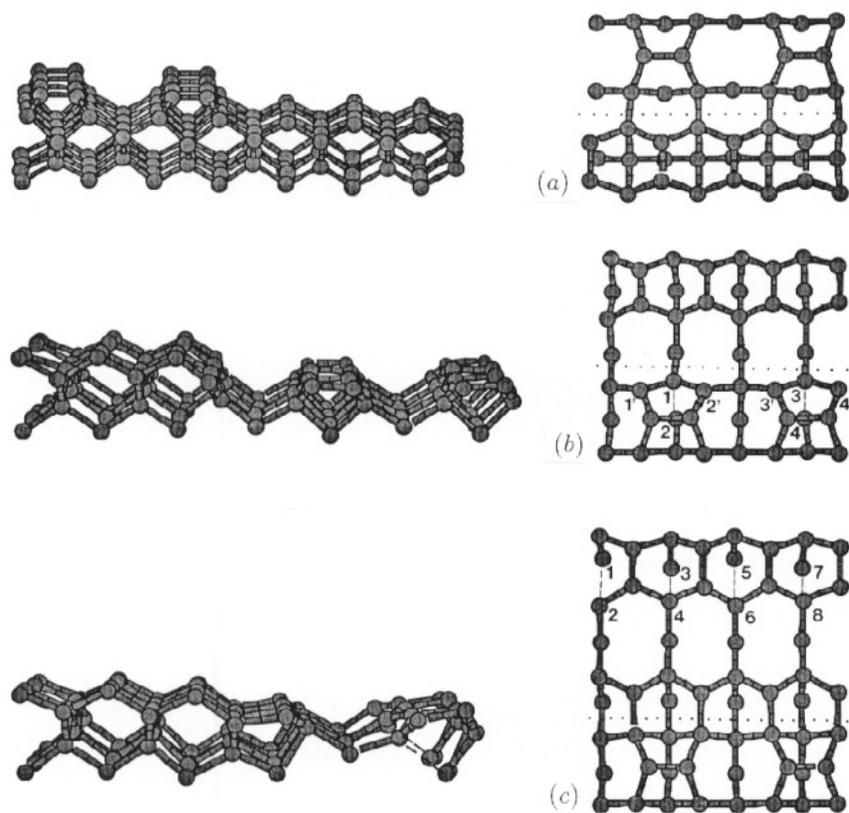
Figure 1. Minimum energy configurations for clean (a) S_A, (b) $S_B(n)$ and (c) $S_B(b)$ step surfaces. Clusters shown are portions of the unit cell employed in this work. For the step edges shown in the right panel, the region above the dotted lines are the lower plane of the substrates. Grey circles represent C atoms.

substrate and H_2 molecules by an average of $\sim$1.5 eV/(surface CH bond). The CH bonds have distances from 1.16 to 1.18 Å, which is about 8–10% larger than the sum of the Bohr radii of C and H. In general, the CH bonds on the dimers are tilted by about 24°, with respect to the surface normal. The most prominent effect of H adsorption on the step substrates is on the reconstruction of the surface dimers. In the clean cases, these structures have significant sp^2 hybridization which is removed by the addition of H atoms. The unbuckled configuration of the dimers is still preserved, but the bondlengths increase to 1.61 Å, due to the decrease in the bond order between carbon atoms making up each dimer. Moreover some of the previously mentioned subsurface CC bonds of the S_B type surfaces that are found to be significantly stretched now approach the bondlength of bulk CC diamond when the surfaces are H terminated.

The single-atomic-layer heights of the various step surfaces (i.e. the height difference between upper and lower terraces' dimer rows) are $\sim$0.8–1.0 Å. Our results are in good agreement with the the scanning tunnelling microscopy works of Tsuno *et al* [4] and Fraunheim *et al* [5], where they find S_A and S_B type steps with monatomic heights in the range 0.89–1.1 Å. To simulate the presence of reactive sites near the step edges, we remove an H atom from an edge dimer residing on the upper plane of each step surface
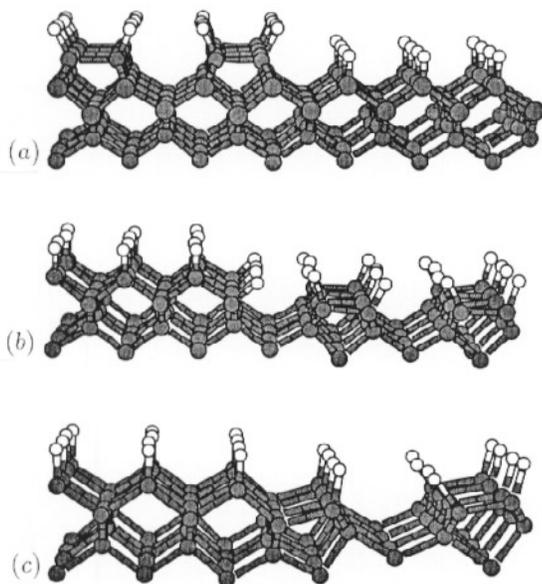
Figure 2. Minimum energy configurations for hydrogenated (a) S_A, (b) S_B(n) and (c) S_B(b) step surfaces. Clusters shown are portion of the unit cell employed in this work. Grey and white circles represent C and H atoms, respectively.

and equilibrate the slab. In general, local buckling of the undercoordinated dimers with an amplitude of about 0.1 Åis found. Moreover, the decrease in the coordination of the dimer gives rise to the contraction of the C–C dimer bondlength to ∼1.56 Å from 1.61– 1.62 Å. Removing the second H from the these particular edge dimers causes them to assume symmetric configurations with bondlengths comparable to those dimers found on the clean step surfaces.

Finally, we elucidate the electronic charge densities for filled states near the Fermi level by plotting the isodensity profile in the plane containing the surface [31]. For most of the studied geometries, we find a similar qualitative difference between the isodensity plot of clean and monohydride surfaces. In this paper, we discuss the results we obtained for the clean and monohydride S_A surfaces as an example. For both cases, isodensity plots were calculated using an energy interval of ∼1.0 eV at the top of the Fermi level (i.e. isodensity plots were calculated for filled energy states lying from the top and ∼1.0 eV below the Fermi level). Figure 3(a) shows the profile for the clean S_A. The positions of the maxima of the isosurface along the z axis correspond to the upper-plane dimers, while local maxima appear to be situated on the lower-plane dimers. Features due to the subsurface carbons directly underneath and bonded to the dimer carbons are also evident. Minima appear to be situated between the neighbouring rows resulting in a line-shape-type pattern along the dimer rows. Figure 3(b) depicts the isodensity plot for the monohydride S_A. Reduction of features on the surface dimer fragments caused by formation of CH bonds is evident. Similar to the clean case, the features on the dimers qualitatively gives rise to a line-shaped pattern running along the dimer rows. Moreover, the isodensity plots for both surfaces yielded, at the step edge, parallel 'lines' (due to dimer rows) on the upper and lower planes that are perpendicular to each other. These results are in qualitative agreement with scanning tunnelling microscopy of the monatomic step structures found in the (100) surface

of diamond [4, 5]. Lines at the step edge appear in two directions which are perpendicular to each other. The authors of these works identified in their STM images upper-plane lines (signature of dimer rows) in the direction parallel and perpendicular to the step edge (S_A and S_B, respectively), as did we. The resolution of their STM images, however, precludes us from inferring whether the step surfaces they investigated are hydrogenated or not.
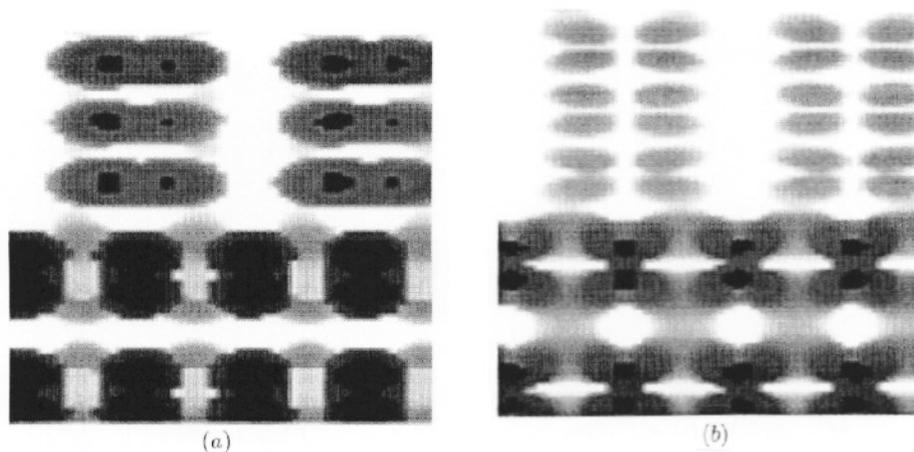

Figure 3. Isodensity plots of (a) clean S_A and (b) hydrogenated S_A step surfaces.

4. Conclusions

We have performed the first *ab initio* theoretical investigation of the structures of the clean and monohydride diamond(100) surfaces using very large supercells to model the surfaces. We find significant relaxations of the bonding structure highly localized near step edges of the monoatomic $S_B(n)$ and $S_B(b)$ step surfaces. The formation of monohydride S_A, $S_B(b)$ and $S_B(n)$ structures is energetically favourable. The presence of a radical site on the dimer near the step edge causes local buckling of the dimer. Analysis of the valence charge isodensity plots for the filled states of clean and monohydride S_A structures is presented. Features due to dimer structures are identified for the clean substrate which become less intense when the surface is terminated by hydrogen.

Acknowledgments

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