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Ab initio study of diamond C(100) surfaces

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We use *ab initio* local-density-approximation methods to study the electronic and geometrical structure of the various C(100) surfaces. The calculated densities of states suggest that the surface states observed for the (2×1) surface are attributable only to the clean C(100)(2×1), not the C(100)(2×1):H. The hypothetical C(100)(1×1):2H is found to be energetically unstable. The C(100)(3×1):1.33H is found to be favored over the C(100)(2×1):H. H desorption energies are calculated.

Diamond is an interesting material with useful physical properties; high thermal conductivity, chemical inertness, low friction coefficient, hardness, and possible use as a high-temperature semiconductor. Surfaces of diamond have received considerable attention in the last decade due to advances in thin-film growth by chemical vapor deposition (CVD) methods.

Among the three prominent surfaces of diamond, (100), (110), and (111), the C(100) is unique in having two dangling bonds per bulk-terminated surface atom, while on the (110) and (111) surfaces, there is only one dangling bond per surface atom. Moreover, nearly atomically smooth surface growth has been possible primarily on the C(100) surface in homoepitaxial CVD.[1] Thus, the C(100) surface has unique appeal for theoretical modeling and experimental growth studies.

According to experimental results, a 1×1 low-energy electron diffraction (LEED) pattern appears when a polished C(100) surface is heated from 500 to 700 K.[2] At temperatures above 1300 K hydrogen desorbs from the surface and a 2×1 LEED pattern is observed.[2] Hamza, Kubiak, and Stulen assumed the 1×1 reconstructed surface to be the C(100)(1×1):2H dihydride, which has two H atoms chemisorbed per surface atom, and the 2×1 reconstructed surface to be either the C(100)(2×1):H monohydride or clean C(100)(2×1) surface, which has one H or no H atom on each surface atom, respectively.[2] Ultraviolet photoemission spectroscopy (UPS) experiments found filled surface states within the band gap near the valence-band edge for the 2×1 reconstructed surface, but no surface states for the 1×1 reconstructed surface.[2]

At present, only empirical or semiempirical calculations[1,3–6] have been used to study the structure of the C(100) surfaces. These theoretical studies generally agreed that dimers form on the clean C(100)(2×1) and C(100)(2×1):H surfaces. However, considerable disagreement still exists as to the qualitative details. For example, it is unclear whether or not the dimer of the clean (2×1) surface is buckled or symmetric, or if the C(100)(1×1):2H dihydride structure is responsible for the 1×1 LEED pattern.[1] The desorption energy calculated for H atoms on C(100) surfaces in general varies more than 1 eV per surface H atom, and the dimer bond length on the clean (2×1) surface differs by more than 0.2 Å among the calculations. At present, there are insufficient experimental data to discriminate between the existing methods. This ambiguity in the theoretical results motivates this *ab initio* study.

The theoretical foundation of this method is the local-density approximation (LDA) within density-functional theory (DFT).[7] In addition to the LDA, further approximations are incorporated in this method. First, it uses a non-self-consistent version of DFT by using a linearized form of the Kohn-Sham equations due to Harris,[8] and Foulkes and Haydock.[9] Second, it expresses the one-electron energy eigenstates as a linear combination of pseudoatomic orbitals, computed from a self-consistent Herman-Skillman–type program[10] with orbital confinement radius R_c of C and H chosen to be 3.47 and 2.65 a.u., respectively.

Applications of this method to Si (Ref. 7) and C (Ref. 11) clusters, surfaces,[12] and bulk structures yielded structures, bond lengths, and vibrational frequencies in very close agreement to fully self-consistent LDA calculations. The lattice constant and bulk modulus of diamond are found to be 3.616 Å and 4.406 Mbars. The experimental values are 3.567 Å and 4.43 Mbars, respectively.

To model a diamond surface, 32 special k points were employed to sample the Brillouin zone of a supercell, which included a slab consisting of twelve C layers with two C atoms per plane, plus one layer of H atoms at the bottom to tie up the dangling bonds. All atoms were allowed to move freely, except the C atoms at the bottom layer, which were fixed in space. The passivation of dangling bonds on the bottom surface was found to be very important to the final results. For example, the difference

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in the dimer bond length of the clean C(100)(2×1) surface was off by 0.2 Å without the proper passivation.

The surface valence- and conduction-band edges were determined by looking at the charge localization for states near the Fermi level.[13] The valence-band maximum was taken to be the highest-energy occupied eigenvalue with its associated and extended eigenstate. In a similar way, the conduction-band minimum was chosen to be the lowest-energy extended eigenvalue above the Fermi level. Surface states are unambiguously identified by a large amount of charge localization on the surface.

Clean 2×1 surface

Table I and Fig. 1 summarize the results of the theoretical studies on the clean C(100)(2×1) surface. Considerable distortions from the bulk positions were seen down to the seventh C layer after the reconstruction. This suggests that the slab size has to be at least eight C layers to study the surface reconstruction thoroughly.

The C═C dimer length of the clean 2×1 reconstructed surface was found to be 1.40 Å in this study, slightly bigger than 1.38 Å, the C═C double bond length of an isolated C_2H_4 molecule. Since a surface dimer is formed by sharing two dangling bonds of a surface atom with those of its neighboring surface atom, the dimer length is expected to be close to, but slightly larger than, the ideal C═C double bond length, due to the strain of the bulk. Results on dimer bond lengths in a variety of calculations are given in Table I.

In this study the dimer was found to be buckled and symmetric with the two top C atoms moving inwards by 0.25 and 0.10 Å (see Fig. 1). The atoms on the second layer moved outward uniformly by 0.04 Å from the ideal bulk positions, resulting in a contraction of the first interlayer spacing by 24% as compared to the bulk spacing. The atoms at the third and fourth layers are also found to be buckled with buckling amplitudes of 0.26 and 0.18 Å, respectively.

The energy density of states (EDOS) has been calculated for this clean C(100)(2×1) structure, as shown in Fig. 2. Note that surface states are found in the band gap near the valence edge, and they are associated with the dangling bonds of the dimerized surface atoms. This agrees well with the photoemission studies of Hamza, Kubiak, and Stulen for the 2×1 reconstructed surface.[1]

Monohydride surface

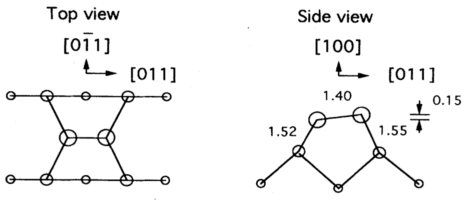
In this study, dimer bond length on the C(100)(2×1):H monohydride surface is calculated to be 1.67 Å, slightly larger than the C—C bulk bond of 1.57 Å, increased by 0.27 Å from the C═C of the clean C(100)(2×1) surface above. The dimer bond length agrees well with that of other work (see Table I). The C—H bond was found to be tilted 24° from the surface normal, facing away from the other C—H bonds of the same dimer.

Unlike the clean C(100)(2×1), no buckling was found for the surface atoms. The first interplanar distance uniformly contracted by 3% with respect to the bulk spacing, which was much smaller than that of the clean surface (24%). This is attributed to the formation of a C—H bond on the surface, which reduces the strain on the bulk by partially breaking the distorted C═C double bond of a clean surface dimer.

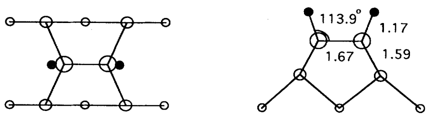
We define the desorption or binding energy as

TABLE I. Properties of optimal structures. ΔE is the relaxation energy per surface dimer with respect to the bulk-terminated structure. r_{dimer} is the dimer bond length. Δd_{nm} is the percent change of interplanar spacing on average between the nth and mth C layers with respect to the bulk spacing. $r_{\text{C—H}}$ is the surface C—H bond length. $\theta_{\text{C—H}}$ is its angle with respect to the surface normal. ΔE_{H} is the desorption energy of a H atom from the C(100)(2×1):H to the C(100)(2×1) [from the C(100)(3×1):1.33H to the C(100)(2×1):H]. Our desorption energies in parentheses were obtained by considering experimental bonding energies on the surface layers and a rescaled energy contributed from total lattice distortions [see Eq. (2)]. The values for other studies can be found in Refs. 4, 3, 5, 1, and 6, respectively.

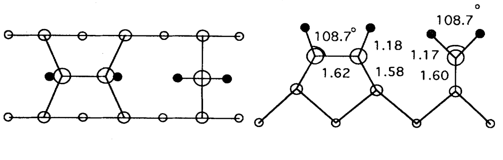
	Verwoerd	Mehandru and Anderson	Zheng and Smith	Yang and D'Evelyn	Brenner	This work
			C(100)(2×1)			
ΔE (eV)	3.09	3.68(2.52)	7.86	2.57	5.49(5.20)	3.64
r_{dimer} (Å)	1.434	1.58(1.40)	1.38	1.46	1.38(1.43)	1.40
Δd_{12} (%)	27	−16.9(−21.4)	−38	−13.5		−24
Δd_{23} (%)		6.7(9.0)	4			3
Δd_{34} (%)		−3.4(−3.4)	0.2			−0.6
			C(100)(2×1):H			
ΔE_{H} (eV)	4.39	6.63	6.32	3.27	3.74(3.62)	6.2(3.5)
r_{dimer} (Å)	1.67	1.73	1.56	1.63	1.63(1.60)	1.67
$r_{\text{C—H}}$ (Å)	1.1	1.08	1.13	1.11		1.17
$\theta_{\text{C—H}}$ (deg)	19	21	21.6	23.3		24.0
Δd_{12} (%)	−9	−3	−15			−3
Δd_{23} (%)			0.3			−0.3
			C(100)(3×1):1.33H			
ΔE_{H} (eV)				2.60		3.9(2.8)



(a) Clean C(100)(2x1)



(b) C(100)(2x1):H



(c) C(100)(3x1):1.33H

FIG. 1. The optimized structures of the clean C(100)(2×1), C(100)(2×1):H, and C(100)(3×1):1.33 H. The open circles correspond to C atoms of the top, second, and third layers in the order of size, respectively. The filled circles correspond to the H atom.

$$\delta E = (E_{\text{substrate}} + E_{\text{adsorbate}}) - E_{\text{system}} , \qquad (1)$$

where $E_{\text{substrate}}$ is the energy of the relaxed substrate [the clean (2×1) surface in this case], $E_{\text{adsorbate}}$ is the energy of the isolated adsorbate (either an atomic hydrogen or a hydrogen molecule), and E_{system} is the relaxed energy of the adsorbate on the surface [the relaxed C(100)(2×1):H monohydride]. Since the shortest distance between H atoms on the C(100)(2×1):H (2.56 Å) is much larger than the calculated H_2 molecular bonding distance of 0.68 Å, it seems likely that desorption occurs by an atomic H mechanism, rather than by a H_2 mechanism. However, bombardment by atomic H could of course alter the mechanism. The desorption energies are provided in Table I. Note that these energies always refer to lower bounds of the actual desorption energies because these desorption energy values have been calculated based only on the initial and final states. The existence of a possible energy barrier during a desorption process has been completely ignored, which is probably reasonable. The desorption energy of a H atom with respect to the clean C(100)(2×1) is found to be 6.18 eV per H atom as shown in the table.

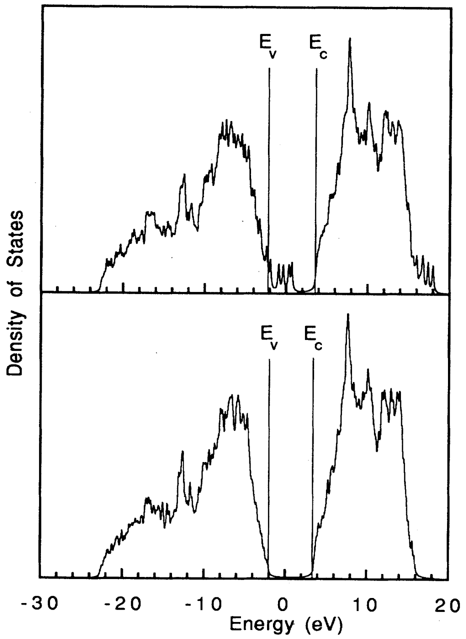


FIG. 2. EDOS of the clean C(100)(2×1) (top) and C(100)(2×1):H (bottom). The EDOS of the C(100)(3×1):1.33H is essentially the same as that of the C(100)(2×1):H. No surface states were found inside the gap of the C(100)(2×1):H or C(100)(3×1):1.33H.

A heuristic understanding of the desorption energy may be gained by partitioning bonding energy contributions from the surface layer and total lattice distortions,

$$\delta E = -2E_{\text{C—H}} + (E_{\text{C=C}} - E_{\text{C—C}}) + E_{\text{distortion}} . \qquad (2)$$

Using 6.18 eV for δE and performing simple calculations for $E_{\text{C—H}}$, $E_{\text{C=C}}$, and $E_{\text{C—C}}$ bonding energies from various structures (CH_y, C_2H_4, bulk diamond), the energy contribution from the distortions $E_{\text{distortion}}$ was calculated to be 1.0 eV per H atom, which implied that atoms in the lattice distorted significantly during the desorption process.

However, experimental bond energies for C—H, C—C, and C=C are about 32–44 % smaller than our calculated values (this discrepancy is readily attributed to LDA errors, artificially increased binding from orbital confinements, and ambiguity in computing bond energy). Therefore, it is more realistic to interpret our results by using experimental values in Eq. (2), with a rescaled value of $E_{\text{distortion}} = 0.64$ eV. This yields $\delta E = 3.5$ eV per H atom.

Figure 2 shows the calculated EDOS for the C(100)(2×1):H monohydride, in which no surface states are found inside the band gap. Note that there were surface states found for the clean C(100)(2×1). The hydrogens on the C(100)(2×1):H removed the surface states inside the gap by terminating the dangling bonds of the clean C(100)(2×1) surface. This suggests that only the clean C(100)(2×1) surface is responsible for the surface states in the band gap observed by Hamza, Kubiak, and Stulen for the 2×1 LEED patterned surface. This indicates that there were some regions on the 2×1 C(100) sample which were not hydrogenated at all in the experiment, although there might also have been some monohydrogenated regions.

LEED 1×1 surface

There are some disagreements among theoretical models as to whether or not the C(100)(1×1):2H dihydride model really corresponds to the C(100) surface which exhibits the (1×1) LEED pattern.[1] In this study, the formation of the C(100)(1×1):2H dihydride phase was inhibited by the high repulsive interactions between H atoms on adjacent units. The ideal bulk-terminated structure with two H atoms on the dangling sites was unstable, and relaxed to the monohydrogenated surface.

On the other hand, Yang and D'Evelyn suggested that a disordered dihydride with a $(2n+1)\times 1$ surface is a possible structure which gives rise to a (1×1) LEED pattern.[1] This $(2n+1)\times 1$ structure, which consists of n dimers separated by a dihydride unit, is expected to be energetically stable because the large steric repulsion caused by the hydrogens on the dihydride C(100) surface is greatly reduced by the presence of the dimers. Note that a high-quality diamond surface is not easily prepared because conventional surface treatments such as ion sputtering and annealing may easily change the surface into the graphitic structure. Therefore, the surface of a polished C(100) sample is considered to be disordered with many defective regions including many steps. Thus, disordered patches of $(2n+1)\times 1$ structures may yield the 1×1 pattern seen by LEED, due to the underlying lattice as viewed through the disordered top layer.

In particular, we studied the 3×1 structure, which consists of alternating the monohydride and dihydride unit (see Fig. 1). The dimer length and C—H bond angle of its monohydride unit (with respect to the normal surface) are found to be 1.62 Å and 18.7°, slightly smaller than the corresponding values of the C(100)(2×1):H (1.67 Å, 23.9°). The changes in the bond length and bond angle are presumably due to H repulsions between the dihydride and monohydride unit.

The desorption energy of a H atom is calculated to be 3.90 eV with respect to the C(100)(2×1):H. Note that this C(100)(3×1) is the most stable structure among the clean C(100)(2×1) and C(100)(2×1):H, implying that it would be the most commonly observed structure during typical CVD conditions.

The desorption energy of 3.9 eV would correspond to a desorption temperature of 1560 K for the H atom (i.e., 3×1 to 2×1:H). By using experimental values (and a rescaled $E_{\text{distortion}}$) in Eq. (2) a desorption energy was calculated to be 2.8 eV per H atom (1120 K). Since the data of Hamza, Kubiak, and Stulen (1300 K) lie between these two desorption temperatures, this suggests that our results are reasonable, both qualitatively and semiquantitatively. In other words, the $(2n+1)\times 1$ structure does appear to be the true optimal structure at low temperature.

The calculated EDOS is shown in Fig. 2. In the EDOS calculated for the 3×1 structure, the surface states are not seen inside the band gap, which is consistent with the UPS results by Hamza, Kubiak, and Stulen, in which no filled surface states were observed inside the 5.5-eV band gap for the surface exhibiting the (1×1) LEED pattern.[2] This consistency of EDOS with experiment and the energetic stability of this C(100)(3×1):1.33H structure increases the possibility of the $(2n+1)\times 1$ structure being the 1×1 LEED patterned surface. However, further studies need to be carried out.

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