Surface structures and electron affinities of bare and hydrogenated diamond C(100) surfaces

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The structure and electronic properties of bare and H-terminated C(100)-2×1 surfaces have been studied by *ab initio* molecular dynamics. Stable 2×1 structures were found for both clean and monohydride-terminated surfaces. The 1×1 dihydride phase is energetically unstable relative to H_2 desorption, although a local minimum, consisting of canted dihydride pairs, was found. The bare diamond (100)-2×1 surface has a positive electron affinity, while a negative electron affinity is obtained for both the 2×1:H and 1×1:2H surfaces. The existence of negative electron affinity for the diamond (100)-2×1:H surface is in good agreement with recent experimental data.

I. INTRODUCTION

Among the three low-index surfaces of diamond, only the (100) orientation sustains high-quality growth of homoepitaxial and heteroepitaxial films.[1-5] The flatness of the surfaces grown in this direction can be on a nanometer-to-micrometer scale, making C(100) a good candidate for applications. Recently, the C(100)-2×1:H surface has been found to have a negative electron affinity (NEA), a property that has strong technical and scientific appeal, Normally, a polished C(100) surface shows a 1×1 low-energy-electron diffraction (LEED) pattern when heated from 500 to 700 K in an UHV environment. At temperatures above 1300 K the surface reconstructs to a 2×1 structure.[6] The 2×1 phase is believed to be either monohydride terminated (a single H atom per surface C atom) or bare, depending on its preparation and annealing conditions. While no consensus has been reached on the observed 1×1 structure, it has been suggested that it is either dihydride-terminated 1×1 or a disordered 2×1 structure.

Previous theoretical work has mainly used tight-binding and related approximation,[7-9] although an approximate local-density-based calculation has been published recently.[10] The 2×1 phase is believed to be stable with or without adsorbed hydrogen. However, most workers believe that a full dihydride coverage cannot be responsible for the observed 1×1 structure,[8,10] since the calculated steric repulsions are large. Although most calculations find that the dihydride structure is still locally stable,[7-9,11] in the calculations of Ref. 10 the H atoms spontaneously dissociated and formed a H_2 molecule. The original experimental work, utilizing electron stimulated desorption and time-of-flight (ESD-TOF) spectra[6] found two distinct velocities of ions emerging from the 1×1 surface, which would indicate the existence of CH_2 dihydride unit. The slower peak, which persisted to higher temperatures ($\sim$1530 K) and followed an appearance of a 2×1 reconstruction, was attributed to the hydrogen desorption from monohydride pairs. However, oxygen was also found on the initial 1×1 surface, which might have inhibited the reconstruction of this sur-

face.[6,12] A more stable 1×1 structure, consisting of alternating dihydride and monohydride units was studied theoretically by Frauenheim *et al.*,[13] who used semi-empirical simulated annealing molecular-dynamic techniques. Davidson and Pickett[7] have also considered the possibility of a half hydride for the 2×1 surface. Frauenheim *et al.* simulations indicate that the 2×1 monohydride structure is stable at $\sim$1200 K.[13]

The hydrogenated diamond (111) surface has long been known to exhibit NEA, i.e., its conduction band edge is above the vacuum level, thus allowing conduction-band electrons to be emitted into vacuum. The NEA can be unambiguously detected in photoemission by a presence of a distinct peak at the low-energy end of the spectrum.[14] The NEA effect could potentially make diamond useful in applications, such as cold cathode emitters and UV detectors. For C(111), NEA is associated with the 1×1 phase, whereas the (2×1) reconstructed phase exhibits a positive electron affinity.[15] Recently, it was found by a combination of UV photoemission experiments and theoretical calculations that the hydrogenated C(100)-2×1 surface exhibits negative electron affinity while the C(100)-1×1 surface does not.[16] In general the measured electron affinity has contributions from two different mechanisms, band bending due to the space charge, and surface dipole adjustment. Band bending occurs over a range of about 1000 Å from the surface and is due to the occupation of surface states by impurity and defect-induced carriers from the solid.[17,18] Surface dipole adjustment occurs on the atomic scale and strongly depends on the surface structure and the adsorbed atoms.

This paper describes the results of extensive *ab initio* molecular-dynamics studies of the structure of the bare and hydrogenated diamond (100) surfaces and of their electron affinities. The calculated electron affinities, in conjunction with experimental measurements, also provide information about the surface structure that has led to the identification of the NEA-active diamond (100) surface.[16]

II. METHODOLOGY

Ab initio molecular dynamics (Car-Parrinello method) utilizes the Lagrangian[19]

$$L = \sum_i \tfrac{1}{2}\mu \int_\Omega d^3r |\dot\psi_i|^2 + \sum_I \tfrac{1}{2}M_I \dot{\mathbf{R}}_I^2 + \sum_v \tfrac{1}{2}\mu_v \alpha_v^2$$
$$-E[\{\psi_i\},\{\mathbf{R}_I\},\{\alpha_v\}] , \tag{1}$$

where ψ_i denotes the electronic wave functions that depend also on constraints $\{\alpha_v\}$, $\mathbf{R}_I$ the ionic coordinates, and E is the total energy of the system in the local-density approximation.[20] The masses μ and μ_v are associated with the fictitious dynamics of the electronic wave functions and the constraints, respectively. The resulting equations of motion are

$$\mu \ddot\psi_i(\mathbf{r},t) = -\delta E/\delta \psi_i^*(\mathbf{r},t) + \sum_k \Lambda_{ik}\psi_k(\mathbf{r},t) , \tag{2a}$$

$$M_I \ddot{\mathbf{R}}_I = -\Delta_{\mathbf{R}_I} E , \tag{2b}$$

$$\mu_v \ddot\alpha_v = -(\delta E/\delta\alpha_v) , \tag{2c}$$

where Λ_{ik} are the Lagrange multipliers associated with the orthonormality constraints of the wave functions. After a suitable initialization, the molecular dynamics proceeds while the temperature of the system is slowly reduced to zero. At this point the time derivatives of the wave functions are all zero and Eq. (2a) are identical, within a unitary transformation, to the well-known Kohn-Sham equations derived variationally from the local-density expression for the total energy.[21]

This formulation allows for band-structure calculations, optimization of atomic geometries, as well as truly time-dependent quantum molecular-dynamics simulations. The ability to perform time-dependent simulations is also useful in geometry optimization. For example, we have developed a fast relaxation method in which the atoms follow Newtonian dynamics in the presence of a special friction force.[22] This method is substantially faster than either steepest descents or conjugate gradient techniques. It has been used in the present work to relax the various surface structures.

The calculations were carried out using plane waves and soft-core, norm-conserving pseudopotentials, generated using Hamann's procedure.[23] The kinetic-energy cutoff in the plane-wave expansion was 35 Ry. The diamond surfaces were modeled by a supercell containing ten layers of diamond and a 10-Å vacuum region, in order to avoid interactions between the periodically repeated slab images. Both surfaces of the slab were kept equivalent, thereby avoiding dipole interactions between the surfaces. The clean C(100)-2×1 surface supercell contained eight atoms per layer, or a total of 80 carbon atoms. The monohydride C(100)-2×1:H surface contained 12 carbon atoms per layer. One hydrogen atom was attached to every surface carbon atoms. For the C(100)-1×1:2H dihydride surface, two hydrogen atoms were attached to each of the surface carbon atoms. Due to the sizes of the supercell, only the Γ point was used for k-space sampling. Starting from an estimated structure, the equilibrium geometries were obtained by a combination of the steepest descents and fast relaxation methods.[22]

The electron affinity of a semiconductor surface is defined as the energy difference between the conduction-band minimum inside the solid and the vacuum level. Normally, two factors affect the value of the electron affinity: the surface dipole moment, defined as the potential drop across the first few atomic layers of the surface, and the space charge due to the occupation of surface states by electrons or holes from the bulk. The effect of hydrogen adsorption on the surface states and on the dipole moment can be directly analyzed using the present calculations. However, the space charge, which extends hundreds of angstroms from the surface and depends on bulk doping, must be studied by a different formalism.

By definition, the electron affinity of a semiconductor is

$$\chi = V(\infty) - E_c , \tag{3}$$

where $V(\infty)$ is the position of vacuum level and E_c denotes the conduction-band edge. The formula (3) is easily rewritten as

$$\chi = D - (E_c - V_{\text{bulk}}) , \tag{4}$$

where $D = [V(\infty) - V_{\text{bulk}}]$ is defined as the surface dipole strength that determines the relative positions of the bulk electron states and the vacuum level,[24] and $(E_c - V_{\text{bulk}})$ is the position of the conduction-band edge relative to the bulk averaged electrostatic potential V_{bulk} and is purely a bulk property. To minimize computational errors, we computed the position of the valence-band maximum E_v using a bulk diamond calculation, which gives the value of $(E_v - V_{\text{bulk}})$. E_c was then determined by using the experimental band gap (5.47 eV), since the local-density theory underestimates the value of the band gap. The dipole strength D can be obtained directly from the difference of the electrostatic potential across the surface. More illustratively, D can also be calculated by integrating the one-dimensional Poisson equation:

$$d^2V/dz^2 = -4\pi\rho(z) ,$$

where $\rho(z)$ is the plane-averaged total (electronic and nuclear) charge density.

III. RESULTS AND DISCUSSION

Surface geometries and energetics

Both clean and monohydride surfaces can have stable 2×1 structures (Fig. 1), but the C-C dimer bond length is shorter at the clean surface (1.38 Å) than at the monohydride surface (1.63 Å). This difference is in the expected range for typical C-C double and single bond lengths. Much larger vertical relaxations were found for the clean surface than for the hydrogenated surfaces. For the 2×1 bare, 2×1 monohydrogenated, and 1×1 dihydrogenated surfaces, the spacing between the first and second layers is compressed by 27%, 10%, and 6.7%, respectively, while the spacing between second and third layers is stretched by 5.6%, 1.1%, and 2.2%, relative to the bulk spacing of 0.89 Å (see Table I). However, only small displacements (less than 0.02 Å) from the ideal bulk positions were found at the third and fourth layers—an indication that the ten-layer slab used in the calculation is
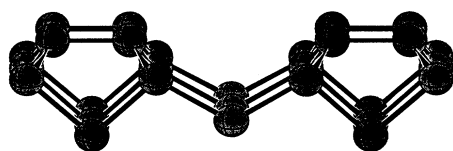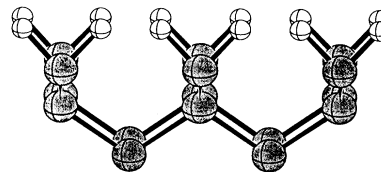
a) The clean C(100)-2x1
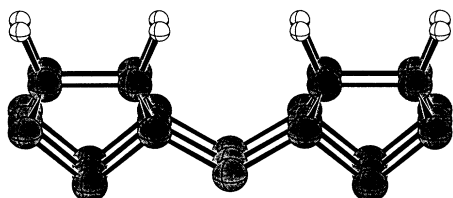
b) C(100)-2x1:H

FIG. 1. Relaxed structure of clean C(100)-2×1 and C(100)-2×1:H surfaces. The large spheres denote carbon atoms and the small ones hydrogen atoms.

a) symmetric

b) canted

FIG. 2. Structure of C(100)-1×1:2H. (a) Symmetric dihydride, obtained by steepest-descent calculation from an originally symmetric geometry. (b) Canted dihydride, the structure after simulated annealing.

adequate for studying atomic relaxations of these surfaces.

Due to steric repulsion, bonded hydrogen atoms tend to avoid each other. This is the reason for the change in angle between the C-H bond and the surface normal on the monohydride surface from its starting value of 54.7° to its relaxed value of 23.1°. On the dihydride surface the steric repulsion is even stronger. Starting from symmetric initial positions and using the method of steepest descents, a symmetric dihydride structure was obtained [Fig. 2(a)]. The stability of the dihydride surface was then examined by a finite temperature simulation where the surface was heated to 300 K for about 0.02 ps (about three periods of C-H vibrations). During the simulation the hydrogen atoms deviated from the symmetric positions but no dissociation from the surface was observed. This is in contrast to the results of Ref. 10, where the dihydride structure was found to be unstable, leading to

dissociation of H_2 molecules from the surface upon geometry optimization. Starting from the "annealed" structure, we performed a steepest descent quench that led to a canted and twisted structure that is lower by 0.12 eV in energy per 1×1 cell than the symmetric structure. Similar twisting of the dihydride pairs was found by Yang and D'Evelyn.[25,26] Due to the prohibitive computational cost, we did not attempt higher-temperature simulations or a search for a global minimum for the hihydride surface.

The hydrogen removal energies δE_H for the monohydride and dihydride surfaces were computed as differences in total energies between the fully relaxed hydrogenated configurations (2×1:H and 1×1:2H) and the relaxed surfaces containing one less H atom per surface unit cell. The results are tabulated in Table II, together with those obtained by previous workers. A large difference (4.36 eV/H atom) in the δE_H was found between the monohydride and the dihydride surfaces. In particular, the dihydride surface is energetically unfavorable by 2.3 eV/H_2 with respect to H_2 desorption, although it is still favored by 1.13 eV relative to desorption to atomic H. Due to a lower δE_H, the desorption of hydrogen from the dihydride surface should occur at a much lower temperature than from the monohydride surface. This is in qualitative agreement with the ESD-TOF measurements.[6] However, the above values were computed by removing an entire hydrogen layer from the surface, rather than a single atom. Furthermore, the measured desorption temperatures reflect the energy barriers for the various desorption paths. Dynamic simulations are thus necessary to make quantitative comparisons to the measured desorption temperatures.

Accurate experimental measurements of hydrogen coverage on diamond (100) surfaces are not currently available, possibly due to experimental difficulties.[6,26] In the

TABLE I. Calculated C(100) surface geometries. r_{dimer} is the surface dimer length and r_{CH} and C-H bond length. α (dimer-H) and θ (H-C-H) are, respectively, the angle between the dimer and the C-H bond on the monohydride surface, and the H-C-H angle on the dihydride surface. Δx_{ij} is the spacing between ith and jth layers. An average is taken for Δx_{ij} on the 1×1:2H annealed surface, since it is not flat.

	2×1:clean	2×1:H	1×1:2H (symm)	1×1:2H (annealed)
r_{dimer} (Å)	1.38	1.63		
r_{CH} (Å)		1.11	1.06	1.04–1.13
α (dimer-H)		113.1°		
θ (H-C-H)			84.72°	93°–96°
Δx_{12} (Å)	0.65	0.80	0.83	0.88
Δx_{23} (Å)	0.94	0.90	0.91	0.90
Δx_{34} (Å)	0.87	0.89	0.89	0.87

TABLE II. Energetics of hydrogen binding for C(100)-2×1:H and C(100)-1×1:2H surfaces. Also listed are results of previous studies (Refs. 8–10 and 31).

Surface (eV)	This work	Mehandru and Anderson (Ref. 9)	Yang and D'Evelyn (Ref. 8)	Yang, Drabold, and Adams (Ref. 10)	Zheng and Smith (Ref. 31)
δE_{H-mono}	5.49	6.63	3.27	6.18	6.32
δE_{H-di}	1.13		1.19		4.11

cases of Si(100) surfaces, Cheng and Yates[27] found a saturation coverage of 1.9 ML (1 ML is defined as one H per surface Si atom) and suggested that the Si(100)-1×1 surface was a disordered phase containing monohydride, dihydride, and trihydride structures. Compared to silicon, the diamond lattice constant is 34% smaller. Thus, the larger steric repulsion will inhibit high-density coverage. Yang and D'Evelyn[25,26] suggested that a disordered dihydride with a local (2+1)×1 structure will most likely give rise to a 1×1 LEED pattern.[6] This model eliminates the large repulsion between two adjacent dihydride units and implies a maximum hydrogen coverage of 1.33 ML, at which a 3×1 structure results. In principle, although the steric repulsion is very high for the dihydride surface, it could still exist at zero temperature, since our calculations indicate that it is lower in energy relative to the bare surface and free H atoms. Moreover, a barrier exists for H_2 desorption. However, the conditions required for this phase to occur may be very different from normal laboratory conditions.

Electronic structure

The electronic wave functions were analyzed by examining their Mullikan populations and plane-averaged square moduli. Information about the charge distribution and the bond orientations was obtained from s- and p-projected Mullikan populations. Surface states were identified by the wave functions being largely localized in the surface region.

Figure 3(a) and 3(b) shows schematically the electronic levels of the bare and monohydride C(100)-2×1 surfaces in the band-gap region. At the bare surface both filled and empty surface states exist in the forbidden gap. They mainly consist of π bonding and antibonding orbitals on the dimer atoms. The energy separation between the filled and empty surfaces states is 1.5 eV. For the monohydride surface, no occupied surface states were found in the band gap. The C-H bonding states lie about 4 eV below valence-band maximum (VBM). However, a broad band of unoccupied states, consisting mostly of C-H antibonding orbitals, lies between 1.5 an 2.5 eV below the conduction-band edge. Due to the well-known inadequacy of local-density approximation (LDA) in describing excited states, the position of these states cannot be precisely determined.

In their tight-binding calculation for the bare C(100)-2×1 surface, Davidson and Pickett[7] found a 2-eV gap between the highest occupied and the lowest unoccupied states, similar to our value of 1.5 eV. However, Yang, Drabold, and Adams[10] and Mehandru and Anderson[9]

found the bare surface to be nearly metallic. While the unoccupied states inside the band gap did not appear in the calculations of Ref. 9 for the monohydride surface, our results are very similar to theoretical and experimental findings on the monohydride Si(100)-2×1:H surface. Hammers, Avouris, and Bozso[28] attributed the peak at 1.0 eV above E_f, obtained in their STM spectroscopy, to Si-H antibonding states previously predicted by Ciraci et al.,[29] using the empirical tight-binding method. Although a strong C-H bond should lead to a large separation between the bonding and antibonding states (typically ∼9 eV in small molecules, such as CH_4), the interactions with the surface broaden the band so that the empty states drop below the conduction-band edge.

Experimentally, for the 2×1 diamond (100) surface, Hamza, Kubiak, and Stulen[6] found occupied states over a 1.5 eV range of the energies above the valence-band maximum and no empty states from 1.2 to 5.5 eV above the

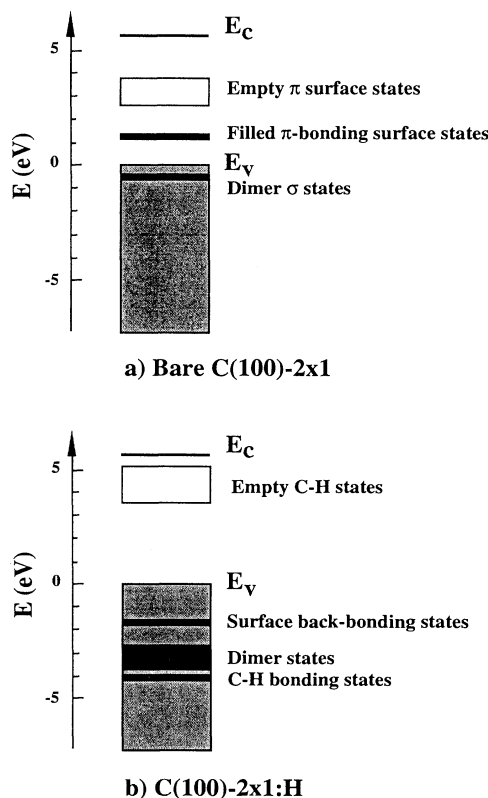a) Bare C(100)-2x1

b) C(100)-2x1:H

FIG. 3. The electronic structure of 2×1 diamond surfaces: (a) bare C(100)-2×1; (b) monohydride C(100)-2×1:H. Zero of energy was set at the valence-band maximum (E_v).

Fermi level. Neither of the present calculations for the ideal 2×1 surface (clean or monohydride) results in the electronic structure that exactly matches these data. Since there is a clear indication of occupied gap states, we conclude that the actual surface is at least partially bare. Based on their tight-binding calculations, Davidson and Pickett[7] have shown that a half-hydride structure, with partially filled gap states, would best fit the photoemission data.

The electronic structure of the symmetric dihydride surface is schematically shown in Fig. 4. The highest occupied states are surface states induced by hydrogen adatoms. These states extend the VBM. A broad band of empty surface states exists 1.5 eV above VBM and is of C-H antibonding character. Although the interactions between the dihydride units are strong, the surface remains insulating. This is in qualitative agreement with the tight-binding calculations of Davidson and Pickett.[7] However, in his self-consistent tight-binding calculation,[30] Gavrilenko found the dihydride surface to be metallic. His calculations placed some of the C-H bonding states at the conduction edge, which is more than 5 eV above VBM, where the remaining part of C-H bonding states reside. This is against our intuition, since C-H bonding states should at least be lower in energy than the surface dangling bonds, usually found near the middle of the gap. Regardless of these findings, the existence of a dihydride phase remains controversial.

Electron affinity

In Fig. 5, we plot the plane-averaged self-consistent potentials for the bare, monohydride, and the symmetric dihydride surfaces. For plotting purposes it is convenient to align the potentials inside the bulk. The vacuum level thus appears different for each of the three surfaces, since each of them has a different potential barrier to vacuum. All the potentials agree well inside the bulk and all flatten out in the vacuum region, indicating good convergence with respect to the number of diamond layers and the size of the vacuum included in the calculations. The bare $C(100)$-2×1 surface has the largest potential barrier (i.e., the largest surface dipole D). Its vacuum level lies above the conduction band edge E_c, giving an electron affinity of $+0.8$ eV. Compared to the bare $C(100)$-2×1 surface,
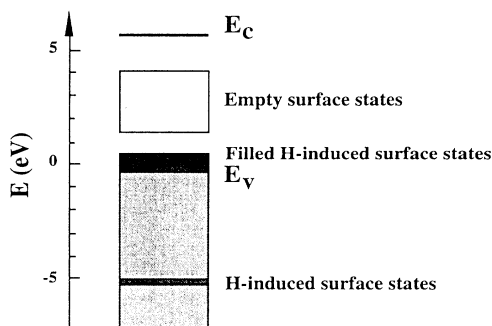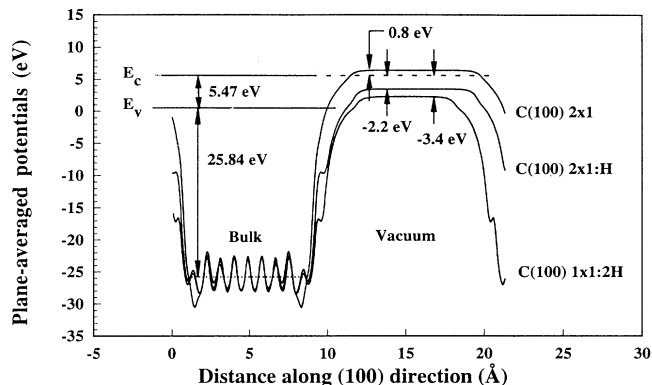
FIG. 5. Plane-averaged self-consistent potential for $C(100)$-2×1, $C(100)$-2×1:H, and $C(100)$-2×1:2H surfaces. The energies of the band edges and the electron affinities are indicated by arrows. See text.

the hydrogenated surfaces have less electronic charge spilling into the vacuum, because hydrogen atoms have saturated the dangling bonds. The net effect is that of an additional dipole layer in the opposite direction to the bare surface dipole D. Hence, the total potential barrier is reduced and the vacuum level lies below the bottom of the conduction band for both the monohydride and the dihydride surfaces. The calculated electron affinities are -2.2 eV and -3.4 eV, respectively.

In the UV photoemission measurements, it was found[16] that the occurrence of NEA was coincident with 2×1 reconstruction, which followed a $1050\,°C$ anneal. While hydrogen cannot be seen in the UV photoemission measurement, we concluded from a comparison between the experimental and our calculated results that hydrogen is present on the 2×1 surface. This is supported by additional experiments,[16] which show that exposure to atomic hydrogen does not significantly alter the ultraviolet photoemission spectroscopy (UPS) spectrum. As for the 1×1 unannealed surface, the UPS spectrum does not show the NEA peak and Auger measurements indicate the presence of oxygen. The atomic structure of this surface is yet to be determined.

IV. SUMMARY

We have investigated the atomic and electronic structure of bare and hydrogenated diamond (100) surfaces by *ab initio* molecular dynamics. Stable structures have been found for both clean and 2×1 H-terminated surfaces. The 1×1 dihydride surface exhibits large steric interactions and it is energetically unfavorable relative to H_2 desorption. However, a finite temperature simulation at 300 K indicates that a local minimum involving canted and tilted dihydride pairs exists.

The hydrogen desorption energies have been calculated. The desorption energy for the dihydride surface is significantly smaller than that of the monohydride, in agreement with the ESD-TOF experiments and previous calculations. The electronic states were analyzed by computing their s- and p-projected Mullikan populations and

FIG. 4. The electronic structure of $C(100)$-1×1:2H surface.

by direct examination of the wave-function shape and extent. The clean 2×1 surface has both filled and empty states within the forbidden gap, while for the monohydride surface only empty states appear in the gap. The dihydride surface has a 1-eV gap between the filled and empty states, despite the overcrowding of hydrogen atoms.

Negative electron affinities of 2.2 and 3.4 eV were found, for monohydride and dihydride surfaces, respectively, while the clean 2×1 surface has a positive electron affinity of 0.8 eV. The occurrence of the negative electron affinity is due to surface dipole changes, which lead

to smaller potential barriers for electrons at the hydrogenated surfaces. From these results, we conclude that the C(100)-2×1 surfaces that exhibit NEA in photoemission experiments are hydrogenated.

ACKNOWLEDGMENTS

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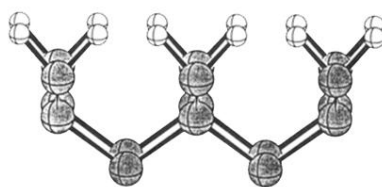[31] X. M. Zheng and P. V. Smith, Surf. Sci. **261**, 395 (1991).
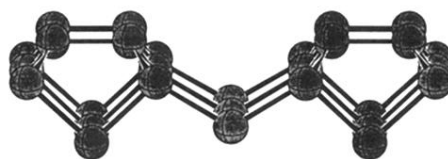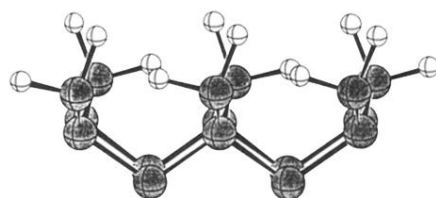
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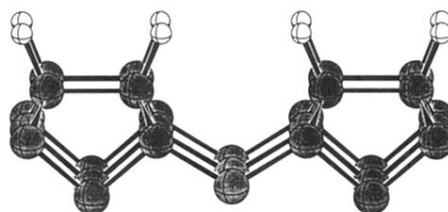
b) C(100)-2x1:H

FIG. 1. Relaxed structure of clean C(100)-2×1 and C(100)-2×1:H surfaces. The large spheres denote carbon atoms and the small ones hydrogen atoms.
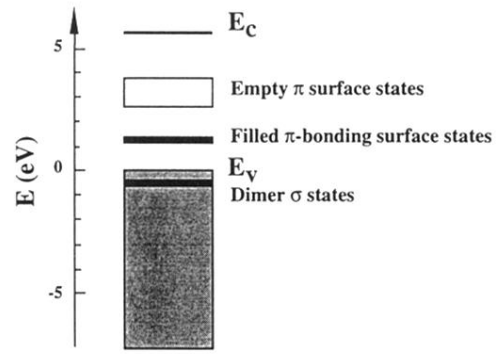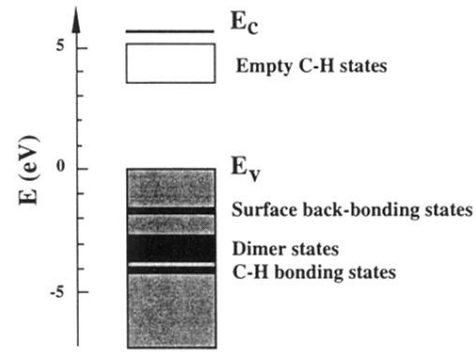
a) symmetric

b) canted

FIG. 2. Structure of C(100)-1×1:2H. (a) Symmetric dihy-
dride, obtained by steepest-descent calculation from an original-
ly symmetric geometry. (b) Canted dihydride, the structure
after simulated annealing.

a) Bare C(100)-2x1

b) C(100)-2x1:H

FIG. 3. The electronic structure of 2×1 diamond surfaces: (a) bare C(100)-2×1; (b) monohydride C(100)-2×1:H. Zero of energy was set at the valence-band maximum (E_v).
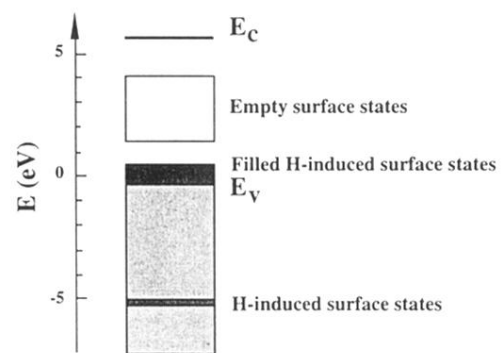
FIG. 4. The electronic structure of C(100)-1×1:2H surface.