Reconstruction of the Diamond (111) Surface

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The (2×1) reconstruction of the (111) surface of diamond has been characterized via a series of first principles molecular dynamics calculations. The reconstructed clean surface is found to consist of dimerized π-bonded chains with no buckling and to be stable against thermal fluctuations up to about 2500 K. Our results for the atomic and electronic structure agree well with the experimental information available.

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There is a growing demand for an accurate understanding of the physical properties of the (111) surface of diamond. As a matter of principle, one would like to draw a comparison with the well established physics of Si(111) and Ge(111), and to understand similarities and differences. On the practical side, C(111) is a growth plane for chemical-vapor-deposited carbon films and its structural characteristics may play an important role in determining the morphology of these systems [1]. Moreover current attempts to fabricate diamond/Si and diamond/transition-metal interfaces require a good understanding of the starting surfaces.

The (111) surfaces of diamond, Si, and Ge are unstable against reconstruction [1]. Whereas those of Si and Ge are by now well characterized [2–4], the current understanding of the C(111) reconstruction is incomplete and controversial, in spite of several experimental and theoretical investigations [1,5–15]. Only the symmetry of the reconstructed surface is well established: LEED patterns [1, 5] with apparent (2×2) symmetry are now known to arise from the superposition of three (2×1) rotational domains. Ion scattering data [6], together with independent spectroscopic findings [7–9] support a π-bonded chain model [10] for the reconstructed geometry. There is, however, no consensus about the precise structural properties of the surface, such as intrachain dimerization, chain buckling amplitude, and multilayer relaxations, nor about the nature of the large surface electronic gap. Electron-energy-loss spectroscopy (EELS) data [11] show an optical transition at $\simeq 2$ eV, which may be attributed to the presence of a surface gap, due to either buckling or dimerization. Tight-binding [10, 12] and slab-MINDO [13] calculations indicate that surface π-bonded chains are dimerized and that this is responsible for the opening of the gap. By contrast, in more elaborate, though not fully self-consistent, local density (LD) calculations by Vanderbilt and Louie [14], an undimerized π-bonded chain is found to be energetically favored.

In this Letter we present the first fully self-consistent *ab initio* molecular dynamics [16] study of the (111) surface of diamond. We have carried out a series of calculations based on a LD pseudopotential description of the electronic states, which yield a clear picture of the stable (2×1) reconstructed state of the clean surface. It consists of *dimerized* π-bonded chains with no buckling. The reconstructed geometry exhibits multilayer relaxations and is stable against thermal fluctuations up to about 2500 K, where a noticeable decrease of dimerization is found. The computed electronic structure of the surface relates directly to several experimental findings [7, 8, 11].

In our calculations, the C(111) surface was represented by periodically repeated slabs of C atoms (eight layers in the unreconstructed geometry), with one side terminated by hydrogens and the other followed by a vacuum region of $\simeq 9$ Å. The interaction between C ionic cores and valence electrons was described by a fully nonlocal pseudopotential with s-only nonlocality [17]. Single particle orbitals and charge density were expanded in plane waves with kinetic energy cutoffs (E_{cut}) up to 35 and 140 Ry, respectively. In one set of computations we considered 8 atoms per layer (64-atom slab) and Bloch functions only at the $\overline{\Gamma}$ point of the supercell surface Brillouin zone (SBZ); this corresponds to including the points $\overline{\Gamma}$, $\overline{J}/2$, and $\overline{J}$ of the primitive cell SBZ. In another set of calculations we used instead 2 atoms per layer (16-atom slab) but single particle orbitals at various sets of k points (up to 32) of the primitive cell SBZ. Various strategies were adopted to search for the most stable structure at $T = 0$. Using the 64-atom slab geometry and $E_{\mathrm{cut}} = 20$ Ry, we performed two successive annealing cycles. In the first one, we started from a (2×1) Pandey model [10], with equidistant surface atoms and a substantial buckling (0.13 Å) of the chains. This initial configuration (c0) has a total energy considerably lower than that of the ideal surface. The system was heated up to 1000 K and cooled down to about 300 K. The most stable structure at $T = 0$ was then found using a steepest descent (SD) algorithm. The resulting structure (c1) was considered as the starting point for a second annealing cycle, during which the system was brought to $\simeq 2700$ K, equilibrated for 0.5 ps, cooled down to $T \simeq 300$ K, and relaxed to $T = 0$ by steepest descent. The atomic arrangement obtained in this way (c2) was basically the same as c1, and has a total energy considerably lower ($\simeq 0.12$ eV/surface atom) than c0. This indicated that a reliable and stable minimum had been found. Starting from c2, the SD procedure was repeated with an increased energy cutoff ($E_{\text{cut}} = 35$ Ry), leading to a geometry qualitatively similar to c2, with all the characteristics of the surface reconstruction unchanged. Bond lengths become slightly smaller ($\simeq 2\%$) with the higher cutoff, as found in several other carbon systems [18]. As a final refinement of our results, we performed a further SD optimization using a 16-atom slab ($E_{\text{cut}} = 35$ Ry) and an improved sampling of the SBZ. As suggested in Ref. [14], we considered a set of 32 k points which becomes denser as the $\overline{J}\,\overline{K}$ zone boundary is approached. Once more we did not find qualitative differences with respect to the c2 geometry, but only small quantitative changes.

Figure 1 shows our final surface geometry which consists of dimerized π-bonded chains with no buckling [19]. The optimal dimerization parameter $d = (l_1 - l_2)/(l_1 + l_2)$ (l_1 and l_2 are the two nonequivalent nearest neighbor distances in the top chain) is found to be 1.4%. Although comparison with experimental findings is not yet possible, this amount of dimerization is compatible with current interpretations of both LEED [1, 5] and ion scattering structural data [6]. Our computed d value is considerably smaller than those obtained in tight-binding (27%) [12] and slab-MINDO studies (4%–6%). We also note that in polyacetylene—which is another example of a π-bonded chain carbon system—the measured value of d ranges from 1.6% [20] to 2% [21], quantitatively close to ours. The unbuckled dimerization of chains on (2×1) C(111) is in sharp contrast with the undimerized buckling of the corresponding Si(111) and Ge(111) surfaces [3]. This can be explained as follows. The buckled state is partly ionic and implies a charge transfer between the raised and the lowered atoms. This is more costly in C, than in either Si or Ge, due to a stronger intra-atomic Coulomb repulsion, thus favoring dimerization in C. This distinctive feature of C is also reflected in the fact that stable adatom-type reconstructions, which involve a sizable charge transfer from adatom to restatom, are absent in C(111) but present and stable in Si (7 × 7) and in Ge (2 × 8).

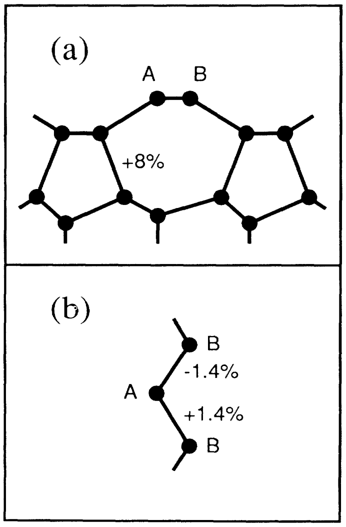

FIG. 1. C(111) (2×1) reconstructed surface as obtained from our calculations: (a) side view; (b) top view (see text).

Additional features of the computed optimal surface structure are (i) an average π bond length $l_0 = (l_1 + l_2)/2$ of 1.44 Å; (ii) an expansion $\Delta d_3/d_3 = 8\%$ of the spacing between the first and second bylayer; and (iii) all other bond lengths within 1%–2% of that of bulk diamond. Our results are in good agreement with the corresponding experimental numbers ($l_0 = 1.45$ Å and $\Delta d_3/d_3 = 8.1\%$) extracted from LEED data [5]. These structural parameters are also close to those of Vanderbilt and Louie [14], except for dimerization which is found to be zero in their calculation.

In our simulations, the reconstructed surface geometry is very stable against thermal fluctuations, up to 2500 K. At this temperature the distance between the first and second bylayer grows, becoming considerably larger than at $T = 0$. The value of d correspondingly decreases by roughly 50%. The topology of the π-bonded chain reconstruction also starts being modified. This might indicate a tendency towards a structural transition, e.g., graphitization of the surface, found to occur experimentally [8, 22] after ion bombardment or after annealing at very high temperature. The shape and size of our MD cell prevents, however, a complete characterization of this transition: This would require MD simulations of several hundreds of atoms.

The surface electronic structure of reconstructed C(111) calculated at $T = 0$ is shown in Fig. 2. It is qualitatively similar to those of (2×1) Si(111) and Ge(111), in spite of differences in the reconstruction of the three surfaces. Its main features are (i) the presence of occupied and unoccupied surface bands associated with bonding and antibonding p_z orbitals of the first layer atoms, and (ii) a gap between these bands at the zone edge $\overline{J}\,\overline{K}$, caused by dimerization. For $k_{||}$ (k parallel to the surface) lying between $\overline{J}/2$ and $\overline{J}$ we find the highest occupied (HO) and lowest unoccupied (LU) states mostly localized on the uppermost chains and not interacting with bulk states [see Figs. 3(b) and 3(d)]. For $k_{||}$ lying between $\overline{\Gamma}$ and $\overline{J}/2$ we observe instead some mixing of HO and LU states with bulk valence and conduction edges, which is more pronounced for the occupied state.

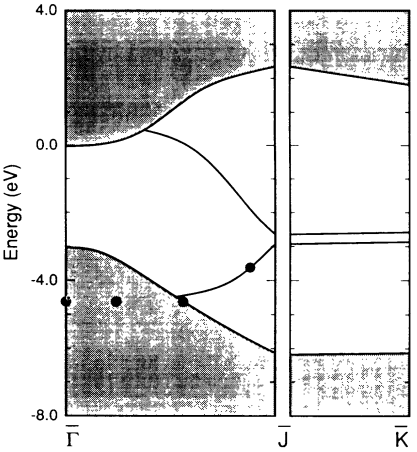

FIG. 2. Computed surface band structure along the directions $\overline{\Gamma}\ \overline{J}$ and $\overline{J}\ \overline{K}$ of the SBZ. The shaded regions correspond to bulk states. Dots indicate the positions of photoemission peaks as measured with AR spectroscopy by Himpsel *et al.* [7].

In particular at $\overline{\Gamma}$ the HO wave function is partly delocalized on the second layer chains [see Figs. 3(a) and 3(c)]. Comparison with ARUPS [7] and AR two-photon spectroscopy [8] is delicate since in the experiments multiple (2×1) rotational domains are sampled, as pointed out in Ref. [8]. However, these measurements clearly indicate the presence of an occupied and an empty surface state with p_z character, as found here [23], and are in good agreement with the band structure of Fig. 2. The quantitative agreement between computed and measured band gaps is quite poor, as expected from any LD calculation. The gaps that we find at $\overline{\Gamma}$ (3.0 eV) and $\overline{J}$ (0.3 eV) are both smaller than the corresponding experimental quantities by about 1.5–2.0 eV. Also the band gaps of bulk diamond as obtained in LD calculations are underestimated by approximately the same amount. Only an accurate treatment of strong correlation effects which lies beyond LD could fix this discrepancy.

It has been suggested [14, 15] that antiferromagnetic spin ordering (AFSO) may be an alternative mechanism to surface chain dimerization, which can open a gap along the SBZ boundary $\overline{J}\ \overline{K}$. We note from Fig. 2 that the π state dispersion along $\overline{J}\ \overline{K}$ is extremely small, indicating that the surface chains interact very weakly and can therefore be regarded as a quasi-one-dimensional (1D) system. A 1D antiferromagnetic deformable chain would be intrinsically unstable (spin Peierls instability) and spontaneously dimerize, thus leading to a singlet ground state with precisely the same symmetry as our LD state. Therefore we believe that the symmetry of the surface chain ground state considered in our LD calculation is correct. AFSO is apparently supported by C *KVV* Auger measurements [15], where a strong reduction of the ($\pi - \pi$) line-shape intensity relative to the ($\sigma - \pi$) intensity is observed. We note that the suppression of the Auger ($\pi - \pi$) process certainly indicates strong electronic correlations but does not imply long-range antiferromagnetic ordering.

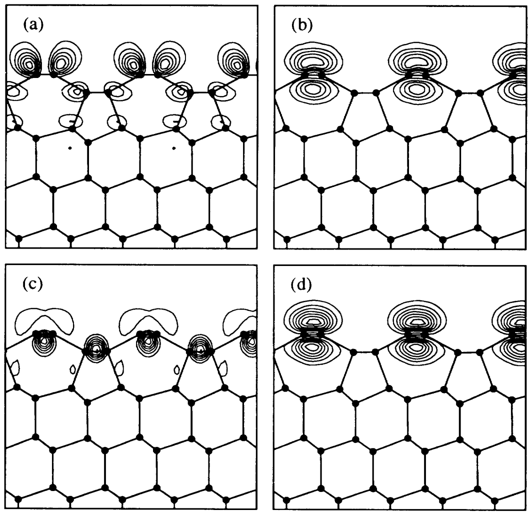

FIG. 3. Square modulus of the wave functions of the lowest unoccupied [(a),(b); upper panel] and highest occupied [(c),(d); lower panel] states of the reconstructed surface, represented in a plane perpendicular to the surface and to the direction of the chains, and intersecting the π-bonded chains in the middle of a π bond. The right and left panels show the states at the $\overline{\Gamma}$ and $\overline{J}$ points of the SBZ, respectively. Lines of equal density are separated by 0.002 (a.u.).

In summary, we have presented the first fully self-consistent *ab initio* calculation of the (2×1) reconstruction of diamond (111). In order to keep our approach as unbiased as possible, we have used various global minimization procedures to find the most stable structure at $T = 0$ and first principles MD simulations to investigate the stability of the reconstructed surface as a function of temperature. The reconstructed geometry at $T = 0$ consists of dimerized π-bonded chains: This inequivalence of first neighbor distances is responsible for the opening of a gap at the SBZ boundary $\overline{J}$. The reconstructed surface is stable up to $T \simeq 2500$ K, temperature at which a tendency towards a structural transformation is observed, foreshadowing a graphitization of the surface.

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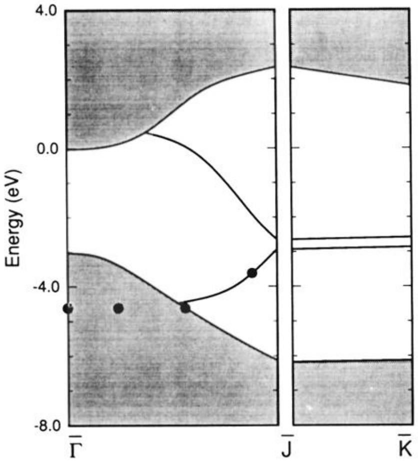

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