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Graphite-layer formation at a diamond (111) surface step

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Relaxation of a stepped (111) diamond surface is studied using an accurate, total-energy tight-binding method. We determined that the bare surface will become sp^2 bonded near a step. This spontaneous graphitization is accompanied by a large increase in spacing between the surface layers. Band structures of the ideal and relaxed surfaces indicate that surface states are removed from the gap upon relaxation, but additional gap states arise from the lower layers. Addition of hydrogen to the surface will force the C atoms to revert back to sp^3 bonding. These results are significant towards the understanding of the behavior of a stepped surface under conditions of film growth or even the possibility of diamond nucleation from graphite.

Even cleaved and polished diamond surfaces in reality are not flat, but are rough, and may contain height variations of hundreds of angstroms. It is not surprising then that the C(111) surface of diamond films, grown by chemical vapor deposition (CVD), contain grooves,[1] hillocks, and steps.[2,3] Hu *et al.*[1] used reflection electron microscopy (REM) to determine that not only did their surface contain single atom steps, but that epitaxial growth involved the lateral motion of these steps. In fact, diamond growth mechanisms have been proposed that begin with the formation of a single atom step on the C(111) surface,[4,5] but Sun *et al.*[3] found that there were already many steps on their (111) surface, and that the creation of a step was not the reaction bottleneck but rather the proper concentration of hydrocarbons above the surface. An alternative identification of the predominate factor in determining the growth rate was given by Enckervort *et al.*,[2] who concluded from their scanning tunneling and REM data that the rate limiting step for (H-F assisted) CVD diamond growth is the diffusion of growth units towards the surface steps. Despite these proposed mechanisms and observations, very little is known about the actual chemistry of the diamond surface near a step. An understanding of the behavior of the steps would most certainly be a prerequisite to determining their role in diamond growth.

The purpose of this paper is to show that the bare C(111) surface near a step will graphitize and that the addition of H will return the surface back to sp^3 bonding. It has been observed that a roughened diamond (111) surface will graphitize at temperatures above 1500 °C (Refs. 6–8) after H has desorbed from the surface. In addition, there are indications that graphitization may be related to diamond nucleation. X-ray photoemission data taken during diamond growth reveal that diamond nucleation is preceded by the formation of graphitic carbon.[9,10] Lambrecht *et al.*[11] have proposed that diamond nucleation can occur in the prism plane at the edge of graphite particles, and have presented a model that could lead to growth in the (111) direction. A graphitized surface at a step would be a region where this could occur.

We employ a tight-binding total energy formalism that has been optimized for both the diamond and graphite phases of carbon.[12] This approach is much faster than *ab initio* methods without much loss in accuracy and allows us to consider the large unit cells required to model surface steps. Our total-energy functional uses a parametrized tight-binding Hamiltonian matrix to generate the electronic levels and an analytical function to model the remaining repulsive terms. The total energy is written as

$$E_{\text{total}} = E_{\text{rep}} + E_{\text{bs}} + E_{\text{charge}}. \tag{1}$$

The repulsive energy E_{rep} is a functional of a pair potential between the ions. The band-structure energy E_{bs} is a sum of the occupied eigenvalues of an orthogonal sp^3 basis Hamiltonian. A positive charge term E_{charge} is added to account for charge transfer. The functional form of E_{rep} and the scaling of the two-center terms in the Hamiltonian has been suggested by Goodwin *et al.*[13] who applied a similar approach to Si:

$$h(r) = h_0\left(\frac{r_0}{r}\right)^n \exp\left[n\left\{\left(\frac{r_0}{r_c}\right)^m - \left(\frac{r}{r_c}\right)^m\right\}\right]. \tag{2}$$

The parameters for C are taken from the fit by Xu *et al.*[12] Their parameters were obtained by fitting to the total energies, calculated with density functional (DF) theory, of diamond, graphite and an infinite linear chain over a range of lattice constants. The resulting total-energy expression has been applied to the energetics and dynamics of large fullerenes[14] and *a*-C.[15] Reference 12 contains the parameters and gives the resulting phonon frequencies, bulk modulus, and Grüneisen parameters for diamond and graphite. We have also applied this parametrization to the study of the C(111), C(100), and C(110) surfaces[16] and found that it is in good agreement with DF results, where they exist. The additional C-H parameters were calculated from a fit to DF forces and energies[17] of small hydrocarbons over a range of C-H bond lengths. The parameters for the C-H bond are given in Ref. 16 along with a comprehensive description of how we obtained these parameters. These parameters accurately reproduce the length, vibrations, and anharmonicity of the H bond on the C(111) surface.

The surface is modeled as slabs (infinite in two dimensions) with 60 C atoms per unit cell. The steps in our periodic cells are separated by seven surface C bond lengths. The supercells have inversion symmetry about the middle. The thickness was chosen such that the surface states on the top and bottom would not significantly

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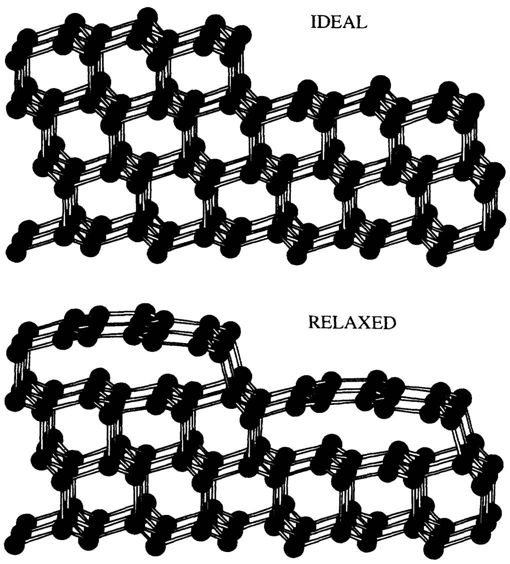

FIG. 1. Graphitization of C(111) step upon relaxation. The ideal surface (top) has diamond bond lengths. The relaxed surface has surface bond lengths less than 1.45 Å. Atoms are darkened to highlight the transformation of the sp^3 chair configuration into graphitic hexagons indicating sp^2-like bonding.

mix. For the band structure energy, a 28 $\vec{k}$-point integration mesh in the reduced Brillion zone is used for the bare surfaces and an 8 $\vec{k}$-point integration mesh is used for the H covered surface. Partially hydrogenated surfaces required a 16 $\vec{k}$-point mesh. Since the bare surface is metallic, we smear the occupation of the levels with a Fermi-Dirac distribution with a width of 0.01 eV. We allowed six layers plus the H atoms (when present) and their mirror images to fully relax. The remainder of the cell was held fixed. The forces below the sixth layer are small.

The starting configuration, shown at the top of Fig. 1, is a (110) step on a C(111) surface with ideal, bulk terminated bond lengths and angles. We allow this surface to relax using steepest descents. Upon complete relaxation at $T = 0$ (no input of additional energy), we find that the top layer forms a graphiticlike sheet (bottom of Fig. 1). The relaxed step terrace is nearly flat and sp^2 bonded. Figure 2 is a side view of the step, indicating the new bond lengths. The average bond length in the surface plane is 1.437 Å, which is close to the bond length of graphite (1.42 Å). With the exception of the one stretched bond of 1.62 Å attached to the bottom of the step, the second layer has an average bond length of 1.50 Å, approximately halfway between graphite and diamond. The spacing between the first and second layer has increased to $\sim$2.0 Å. The atoms in the second layer are now essentially threefold coordinated since the upper bond has stretched by almost 30%, but their bonding has remained sp^3 in character. It is of interest to note that transmission electron microscopy images indicate that when diamond is heated, the graphite that appears is oriented with the c axis along the (111) direction and the a axis along the (110) direction.[6]

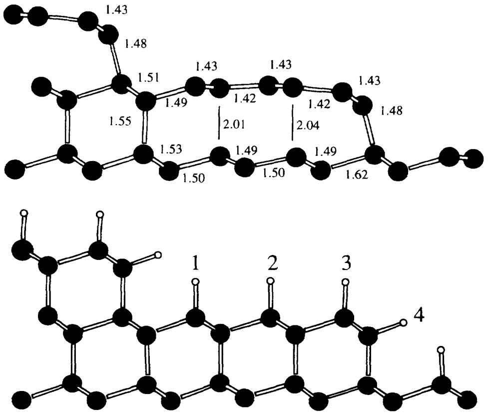

FIG. 2. Side view of the bare (top) and hydrogenated relaxed steps. Bond lengths are in angstroms. The H atoms in the lower figure are shown as open circles. All C-C bond lengths for the relaxed hydrogenated surface are between 1.52 Å and 1.54 Å. The darkened atoms correspond to the darkened atoms in Fig. 1.

Table I lists the relative gain or loss from the relaxation of the atomic coordinates of the three terms contributing to the total-energy expression in Eq. (1). The lowering of the band structure energy $E_{\rm bs}$ outweighs the increase in energy from both the repulsive and charge terms and can be understood in terms of the surface states in the gap. The dangling bonds on a ideal flat (1×1) C(111) surface are on second-neighbor atoms. These dangling bonds create defect states in the gap. Since these dangling bonds can still interact, there is a bandwidth to these gap states, which we calculated to be approximately 1.2 eV.[16] The surface of our unit cell contains four dangling bonds, which are distinguished as two different types: terrace and step, labeled in Fig. 2 as numbers 1-2 and 3-4, respectively. On the terrace we have the same environment as the ideal C(111) surface, but at the top corner of the step, which is the (110) surface, there are dangling bonds on nearest-neighbor atoms. Since these dangling bonds are on nearest-neighbor atoms, we expect an increase in the interaction between them and therefore a larger splitting between the states. This can be seen below in Fig. 3 where we show the band structure near the Fermi level for both the ideal and the relaxed step. At the Γ point the two terrace surface states are 0.4 eV apart, centered near the Fermi level at 2.82 eV. The dangling bonds at the top of the steps have a larger splitting, separating into a fully occupied level at 2.4 eV and a partially occupied level at 4.2 eV. The surface states show very little dispersion across the steps (in the J direction) which is indicative that states from neighboring steps are not interacting. In the direction parallel to the

TABLE I. Energy gain or loss per surface atom from relaxation of C(111) step as compared with ideal surface step, which has bond lengths and geometry consistent with bulk diamond. Energy terms correspond to Eq. (1).

Energy term	Gain or loss (eV)
total	-0.694
repulsive	+8.632
band structure	-9.346
charge term	+0.020

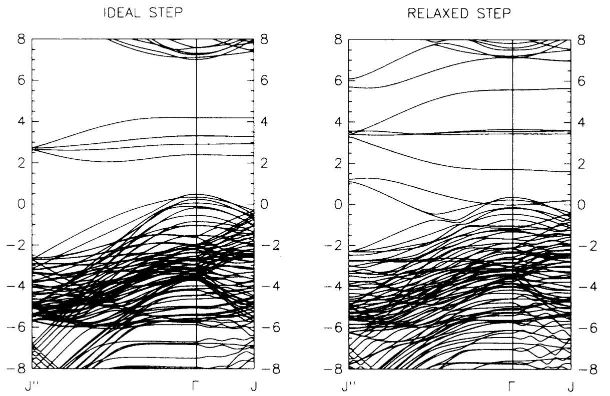

FIG. 3. Band structure near gap of the 111 steps (shown in Fig. 1). The zero energy is arbitrary and the top of the valence band is approximately 0.5 eV. The Fermi level for the ideal step is at 2.82 eV and for the relaxed step is at 3.45 eV. J direction is across the steps and J'' direction is along the steps.

steps (J'' direction) there is small dispersion, and the states become degenerate at the zone edge. (This is why the antibonding step state is partially occupied.)

The band structure of the relaxed step is more complicated due to bond breaking and to the large decrease in bond lengths. There are three things occurring at the zone center: (1) A decrease in the separation of the step dangling bonds results in an increase in the splitting of step states now located at 1.6 eV and 5.6 eV, (2) the change of the sp^3 bonding of the terrace states to sp^2 bonding with the shorter bond lengths removes the terrace states from the gap at the zone center, and (3) the introduction of "surface" states associated with the second layer, which are grouped near the Fermi level and arise from the separation of the first layer from the second. We have found a large increase in energy of the atoms in the second layer due to these newly formed surface states, which we believe could result in further graphitization of the lower layers at higher temperatures. Though the tight-binding electronic parameters were not optimized to yield highly accurate electronic states, particularly above the Fermi level, the qualitative features of the band structure should be correct. Even with the creation of the additional gap states in the second layer, which can be considered to be transferred from the terrace, the decrease in energy from effectively removing the terrace states from the gap drives the graphitization of the surface. The states at the top of the step are not as important for this relaxation as is the additional room the step provides to relieve any steric hindrance to forming planar sp^2 bonds.

Exposure of a (2×1) reconstructed C(111) surface to atomic H will revert the surface back to (1×1).[18,19] Similarly, we placed H atoms above the graphitized step approximately above the original (bulk ideal) surface bonds. This configuration was allowed to relax using steepest descents. The H bonds that formed on the terrace and steps transformed the surface back to sp^3 bonding. This result is consistent with the calculations of Mehandru *et al.*[20] who reported that the addition of H to a planar graphite cluster can cause the C atoms to buckle into chair configurations associated with sp^3 bonding. A diagram of the relaxed, fully hydrogenated step is shown in Fig. 1. All the carbon bond lengths have returned to approximately the bulk diamond value between 1.53 Å and 1.54 Å. The terrace H bonds (labeled 1 and 2) are 1.126 Å and the step H bonds (labeled 3 and 4) are slightly shorter at 1.124 Å.

Sun *et al.*[3] monitored the H stretch vibrations on the C(111) surface and observed both perpendicular and parallel components, which they assumed were attributed to H attached to the (111) faces and (110) face steps, respectively. Upon dosing the surfaces with atomic deuterium, they concluded that the H atoms on the (111) faces are replaced before the H bonds on the (110) steps. As a test of their assumption, and to compare H bond strengths, we removed one H from a single site and fully relaxed the coordinates. This was similarly repeated for the four distinct H bonds and the energy differences of the final resulting structures are given in Table II. According to this analysis, the surface H bond at the corner of the step, shown in Fig. 1 as site 4, is the strongest H bond. The weaker H bonds, which would be more likely to break, are the ones attached to terrace atoms, labeled as sites 1 and 2. These results are consistent with the interpretation of Sun *et al.*[3] of their deuterium data. In our calculation, when a H atom is removed, the corresponding surface C moves into the bulk and its nearest-neighbor bond lengths in the surface plane shrink to ~1.49 Å. The local flattening of the surface C bilayer results in an increase in spacing below the terrace. Continuing to remove H atoms from the surface allows the surface to relax back into the graphitic structure shown in the bottom of Fig. 1 and described above.

In summary, we have applied a tight-binding Hamiltonian to the relaxation of a C(111) surface step, and have shown how the bare surface will graphitize. This relaxation can be understood in terms of the behavior of the gap states on the terrace atoms and the steric freedom introduced by the step. There are indications from the increase in the layer spacing, which causes gap states below the surface layer, that the process of graphitization could continue in the lower layers at finite temperatures. Considering the growth mechanism proposed by Lambrecht *et al.*,[11] these graphite layers could become regions of diamond nucleation or lead to further graphitization at higher temperatures. Addition of H to this relaxed

TABLE II. Comparison of the relative energies of the relaxed stepped surfaces with one of the H atoms (labeled in Fig. 1) removed. Zero point in energy is chosen as the configuration with H bond 4 removed. A lower energy indicates a more likely structure.

Site	Energy difference (eV)
1	-0.061
2	-0.076
3	-0.020
4	0.000

graphitic surface step will return the surface back to diamondlike bonding. Using the same energy functional, we have now begun studying specific growth mechanisms at steps and flat surfaces.

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