Enhancement of Surface Hardness: Boron on Diamond (111)

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(Received 26 September 1997)

We have performed *ab initio* pseudopotential calculations for the diamond (111) surface with nitrogen or boron replacing the surface carbon atoms. Surface boron atoms form planar sp^2 bonds with carbon atoms and the compressive stress from the underlying bulk diamond lattice squeezes the B-C bonds significantly. Bulk and shear moduli in the surface region increase substantially, surpassing those of bulk diamond. In contrast, for the nitrogen-covered surface, N-C bonds are elongated because of the tensile stress from bulk diamond and the elastic stiffness decreases. [S0031-9007(97)05216-2]

PACS numbers: 62.20.Qp, 62.20.Dc, 71.15.Hx

Carbon, nitrogen, and boron in their strong covalent bonding configurations have unusually high hardness and wear resistance and have been widely used as coating materials. Although diamond has long been known to be the hardest material, there has been an ongoing effort to fabricate a material as hard as or harder than diamond. Since plastic (indentation) hardness is not easy to study using *ab initio* computational methods, theoretical studies usually focus on analyzing elastic stiffness constants (bulk and shear moduli) which are indicators of hardness and are computationally tractable. After the original suggestion that carbon nitrides might be candidates for a material comparable to or harder than diamond [1], a cubic form of C_3N_4 with its bulk modulus comparable to that of diamond was predicted to exist using theoretical calculations [2,3]. However, fabricating this material has proved difficult and despite many experimental reports of synthesis, there is no general consensus [4]. Using the concepts that short bond lengths and small charge transfer are conducive for achieving high elastic stiffness, we propose here a somewhat less ambitious strategy. The goal is to strengthen diamond by replacing some carbon atoms by other elements locally to explore the possibility of achieving a higher elastic modulus in the limited region where the replacement occurs.

The surface is the easiest place to make substitution for the carbon atoms without disturbing the strong sp^3-bonding network of the diamond lattice. Furthermore, if we use nitrogen or boron atoms to replace surface carbon atoms on the diamond (111) surface, each N or B atom forms covalent bonds with three carbon atoms below it and such a bonding environment is compatible with the tendency of N or B to have 3-fold coordination. Motivated by this idea, we have performed *ab initio* pseudopotential calculations for the N- or B-covered diamond (111) surface. We find that boron atoms replacing the diamond (111) surface monolayer substantially increase the bulk and shear moduli in the surface region beyond those of bulk diamond, whereas the monolayer nitrogen atoms decrease the moduli.

The calculation involves the use of a supercell of a 12-layer diamond slab separated by an 11 Å thick vacuum region to simulate the diamond surface. The surface regions of the model systems are shown in Fig. 1. Monolayer coating is achieved by replacing carbon atoms in the top and bottom layers of the diamond (111) slab by nitrogen or boron atoms as indicated in Fig. 1(a). The hydrogenated surface and (2×1) reconstructed surface (known as Pandey's π-bonded chain structure [5]) are shown in Figs. 1(b) and 1(c), respectively. Experimentally, the (2×1) reconstructed structure is obtained by annealing the sample. Hereafter, the nitrogen(boron)-coated and hydrogenated surfaces will be abbreviated as N(B)/C(111) and H/C(111), respectively.

The plane-wave-based *ab initio* pseudopotential total energy method [6] is employed. The fully separable [7] nonlocal pseudopotentials are generated with the Troullier-Martins method [8] and the Ceperley-Alder exchange-correlation potential [9] as parametrized by Perdew and Zunger [10] is used. Because of the deep pseudopotential of N, a large energy cutoff of 90 Ry is needed for the N/C(111) surface, compared with 50 Ry for other systems. Nine and eight **k** points are sampled for integration in the surface Brillouin zone of (1×1) and (2×1) surfaces, respectively. The internal stress tensor σ_{ij} is calculated [11] with a normalization factor of (supercell volume)/(slab volume). The internal coordinates of all atoms and surface lattice vectors are relaxed using the conjugate-gradient method so that Hellmann-Feynman forces and stress tensors are converged to within 10^{-4} Ry/a_B and 10^{-5} Ry/a_B^3, respectively. The relaxation of the structure is performed within the given symmetry for each. Since we intend to study a realistic surface which is connected to a macroscopic volume of bulk diamond below, equilibrium lattice vectors in the xy plane are constrained to be those of bulk diamond. The theoretical

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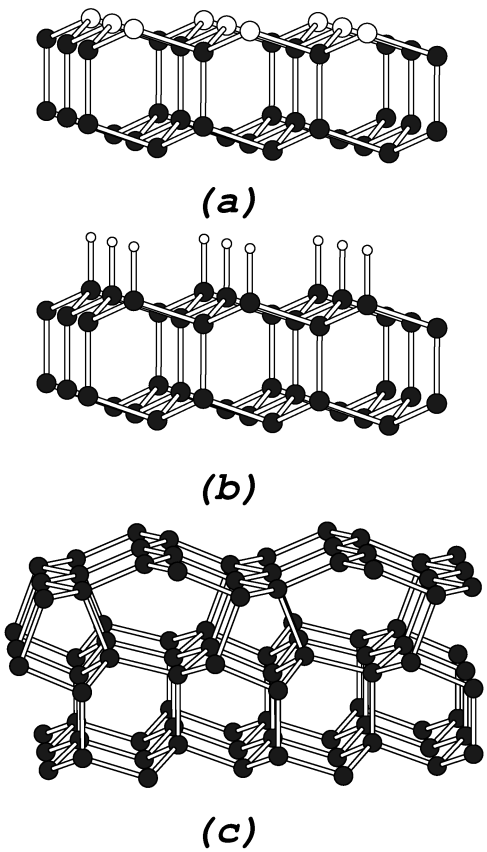

FIG. 1. Geometry of top layers of (a) nitrogen coated or boron coated, (b) hydrogenated (1 × 1), and (c) (2 × 1) reconstructed C(111) surfaces. Black circles are carbon atoms. White circles are nitrogen or boron atoms in (a) and hydrogen atoms in (b), respectively.

equilibrium lattice constant of bulk diamond is 3.571 Å compared with the experimental value of 3.567 Å.

First, we compare equilibrium geometries of various (1 × 1) surfaces. Distances between layers near the surface are shown in Table I. Our equilibrium geometry of the H/C(111) surface agrees with other calculations [12,13] to within 1%. It also agrees with the results of LEED studies [14] for the C(111) surface. Structural parameters of the N/C(111) surface are remarkably close to those of the H/C(111) surface as shown in the table. The N-C bond length here is 1.53 Å which is larger than the typical N-C bond length of 1.45 Å in most model C_3N_4 compounds [15], and is very close to the C-C bond length of bulk diamond (1.54 Å). On the other hand, the geometry of the B/C(111) surface is quite different. The distance between the first and second layer is greatly reduced and the C-B-C bond angle increases from the tetrahedral angle of 109.5° to 117.8° which is closer to the ideal sp^2 angle of 120°. The expansion by 0.07 Å between the second and third layers indicates the weakened sp^3 bonding between these layers, and this is consistent with the above observation of sp^2 bond formation. The B-C bond length is 1.47 Å, which is smaller than the usual B-C bond length (e.g., 1.55 Å for BC_3 [16] or 1.64 Å for B_4C [17]).

We mention above that we keep the lattice constant in the xy plane the same as the equilibrium lattice constant of bulk diamond to simulate a realistic situation for a macroscopic dimension of bulk diamond beneath the surface. Consequently, atoms near the surface are under stress and it is interesting to calculate the extra stress needed for this constraint. In Table II, relevant components of the stress are shown in each case [18]. It is noteworthy that the sign of the B/C(111) surface is positive, opposite to other model surfaces. This means that the B/C(111) surface is under compressive stress in the surface tangential directions, while other surfaces are under tensile stress. A similar trend has been found on the Si(111) surface [19]. Formation of an sp^2 type bonding between B and C within a diamond lattice makes the surface tend to expand in the xy plane; hence the positive constraining stress (compressive stress) is exerted to retain the bulk lattice constant. The smallest stress for the H/C(111) surface indicates that the bonding properties of bulk diamond are best preserved in the hydrogenated (1 × 1) surface.

The bulk modulus and its pressure derivative for each structure are obtained by fitting the P-V relation to Birch's equation of state [20] taking into account the above constraining stress. Various fitted parameters are presented in Table III. The bulk modulus of the H/C(111) or N/C(111) *slab* system studied here is fairly similar to that of *bulk* diamond. The same calculation for bulk diamond yields 441 GPa in agreement with the experimental value of 443 GPa. The pressure derivative of the bulk modulus, B_0', is especially large for the N/C(111) slab geometry, consistent with the fact that the N-C bond is elongated in the present configuration and the bulk modulus will increase very rapidly as the system is compressed and the strong N-C bond is restored. Perhaps the most interesting feature is that the bulk modulus of the B/C(111) slab system is greater than that of bulk diamond. It is well known that

TABLE I. Structural relaxation for the (1 × 1) surfaces in the absence of hydrostatic pressure. $d_{i,i+1}$ means the distance between the ith and $(i+1)$th layers. All distances are in Å.

Structure	$d_{\text{H-C}}$	d_{12}	d_{23}	d_{34}
H/C(111)[a]	1.113	0.487	1.540	0.514
H/C(111)[b]	1.125	0.485	1.546	0.514
N/C(111)		0.483	1.536	0.509
B/C(111)		0.219	1.607	0.506

[a]This work.
[b]Reference [12].

TABLE II. External stress needed in constraining the surface lattice vectors to those of bulk diamond. The unit is 10^{-3} Ry/a_B^3.

Structure	σ_{xx}	σ_{yy}	σ_{xy}
H/C(111)	−0.76	−0.76	0.00
N/C(111)	−2.43	−2.43	0.00
B/C(111)	1.75	1.75	0.00
C(111)-(2 × 1)	−1.78	−1.82	0.17

the B-C bond in a solid is weaker than the C-C bond because of its ionic character and a larger bond length. In the diamond (111) surface, with monolayer boron atoms replacing the surface carbon atoms, the constraining stress exerted by the underlying bulk diamond squeezes the bond and makes it much stiffer. The only alternative to maintain a longer B-C bond on top of the shorter bulk diamond lattice would be the buckling of the boron atoms above the surface, but this is suppressed by the strong tendency of boron atoms to form planar sp^2 bonds with three nearest neighbor carbon atoms. This result does not mean that the actually measured bulk modulus of a *macroscopic* sample of diamond would increase with the boron replacement. The bulk modulus calculated here is for a thin slab geometry and the true bulk modulus is the weighted average contributed from the entire macroscopic volume of a sample; the surface effect on the bulk modulus of a macroscopic sample is quite small. Furthermore, since surface boron atoms exert, as a reaction, a tensile stress to the bulk diamond, there is an opposing contribution from the bulk. However, the enhancement of hardness in the surface region is real. If we consider six topmost layers from the surface as studied above, the fractional volume change (i.e., compressibility) for a given pressure is almost 20% less than that of diamond in the bulk region. Therefore, while N-C bonds may possibly enhance the bulk hardness as predicted for C_3N_4, B-C bonds enhance the surface hardness of diamond.

For certain materials, it has been found experimentally that the shear modulus correlates better than the bulk modulus with the indentation hardness [21]. A basic explanation is that the shear modulus is a measure of the mechanical hardness involving the shape change (indentation) which depends on lateral bond breaking and rebonding along the path of the dislocation motion, whereas the bulk modulus is related to the isotropic bond compression. We have calculated the surface tangential component of the shear modulus, C'_{44}, for each surface. This component is related to the elastic stiffness components of the cubic crystal in the following way:

$$C'_{44} = \tfrac{1}{6}(C_{11} - C_{12}) + \tfrac{2}{3}C_{44}\,. \qquad (1)$$

The results are presented in Table III. Again, the calculated shear modulus C'_{44} for the B/C(111) slab geometry is significantly greater than that of bulk diamond. All other slab geometries have a lower C'_{44} than bulk diamond. We note here that the surface region is important for practical applications of hard materials. A greater surface shear modulus implies a stronger resistance against the yield of the material because the yield in the indentation experiment presumably starts at the surface. Especially in nanotribology or thin-film coating, the action tends to take place in a small region near the surface.

TABLE III. Bulk modulus, its pressure derivative, and shear modulus for various model systems. Note that surfaces here mean 12-layer [or 14-layer in the case of H/C(111)] slabs with two surfaces.

Structure	B_0 (GPa)	B'_0	C'_{44} (GPa)
H/C(111)	436	1.8	487
N/C(111)	426	6.2	507
B/C(111)	521	2.9	588
C(111)-(2 × 1)	397	3.6	526
Bulk diamond (calc.)	441	3.7	533
Bulk diamond (expt.)	443	4.0	543

The calculated surface band structures of the N/C(111) and B/C(111) slab geometries near the Fermi level are shown in Fig. 2. Both systems are insulators as expected from electron number counting. The top two valence bands of the N/C(111) slab consist of lone pairs of mainly p_z character at N sites. Two bands originate from the two surfaces of our model. They are almost degenerate except near the $\bar{\Gamma}$ point, indicating that the interaction between the two surfaces is reasonably small and our supercell geometry does mimic isolated surfaces. These N lone-pair states are chemically inactive and spatially localized at atomic sites resulting in relatively flat bands. In Fig. 2(b), the lowest unoccupied bands of the B/C(111) slab which are well separated from other bands above and below also consist of p_z orbitals at B sites. These orbitals are almost noninteracting and form even narrower bands than the N-covered surface in Fig. 2(a).

Total valence electron charge density plots of the N/C(111) and B/C(111) surfaces are presented in Fig. 3. A characteristic feature in the charge density of the N/C(111) surface in Fig. 3(a) is the lone pair localized at the N atom. Otherwise, the charge density of the N/C(111) system is almost identical to bulk diamond. On the other hand, the charge density of the B/C(111) system in Fig. 3(b) shows the sp^2 bonding near the surface. Also, the ionic character of the B-C bond is seen in Fig. 3(b). Because of this charge rearrangement, the bond between the second and third layers is affected and becomes weaker as shown in the figure. The perturbation in the charge density is appreciable up to this point and the sp^3 covalent character of bulk diamond is preserved

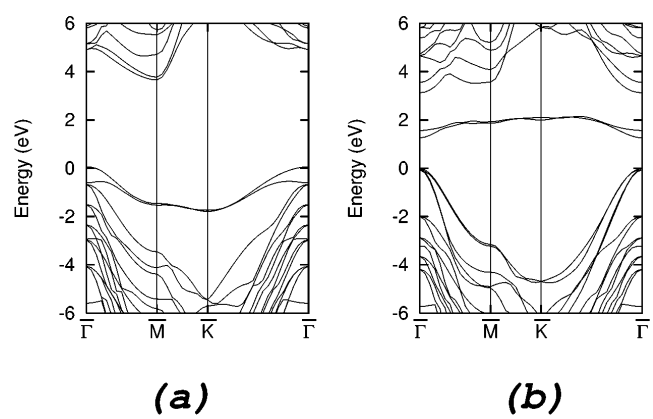

FIG. 2. Band structure in the surface Brillouin zone of (a) N/C(111) and (b) B/C(111). The top of the valence band is set to 0 eV.

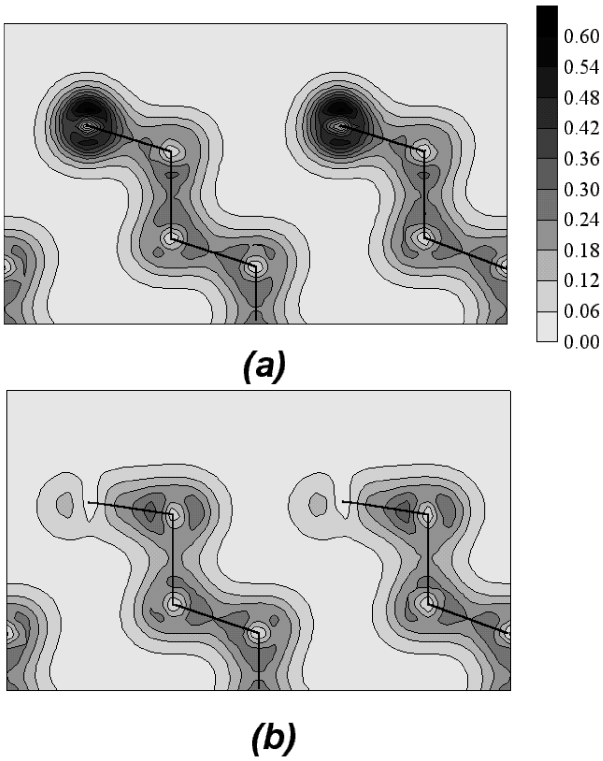

FIG. 3. Valence electron charge density of (a) N/C(111) and (b) B/C(111) in the [010] plane perpendicular to the surface. The unit of gray scale bar is electrons/a_B^3. Solid lines indicate bonding between atoms.

below the third layer. We also calculate the cohesive energies of these systems. The cohesive energies are 8.18, 8.27, and 8.55 eV/atom for nitrogen-coated, boron-coated, and (2×1) reconstructed C(111) 12-layer slab systems, respectively [22]. For comparison, the same calculational setting yields 8.43 and 8.69 eV for the unreconstructed (without hydrogen) (1×1) slab and bulk diamond.

We expect that the B/C(111) surface may be realized first by cleaning the diamond surface in UHV and depositing a monolayer of boron by laser ablation or molecular-beam epitaxy. Another possibility is to use the arc-discharge plasma with hafnium boride as a source. The stability (i.e., exothermic nature) of the B chemisorption here makes this procedure very plausible. Calculations show that replacing the surface carbon of the H/C(111) surface by boron and releasing hydrocarbons is strongly exothermic ($\sim$2.2 eV/B atom), whereas the same replacement by N is endothermic. We further note that oxygen and carbon are around in usual experimental situations. Since the calculated binding energy of a hypothetical B-H bond on the B/C(111) surface is $\sim$2.5 eV at most (about the same as the H-H binding energy per atom), compared with 4–5 eV for O-H or C-H bonds, H is not likely to bind to the B/C(111) surface and reduce the hardness.

In summary, we have studied the effect of boron and nitrogen monolayer coating on the diamond (111) surface. In spite of the small but finite ionic bonding character, the bulk and shear moduli in the surface region of the B/C(111) slab are larger than any other systems studied and even exceed those of diamond. This is a consequence of the constraining force from the underlying diamond lattice that compresses the sp^2 bonds between B and C atoms. Since the elastic moduli and mechanical hardness are closely related for covalent materials, we believe that the present findings are potentially important for applications to materials with high surface hardness and wear resistance.

S. H. and J. I. are supported by the BSRI Program of the MOE of Korea, the KOSEF through the SRC program, the LG Yonam Foundation, and the LG Semicon through the SNI. S. G. L. and M. L. C. are supported by NSF Grant No. DMR-9520554 and the U.S. DOE under Contract No. DE-AC03-76SF00098. Supercomputer time was provided by the NERSC.

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