Diamond Nucleation on Hexagonal Boron Nitride: A Theoretical Investigation of the Influence of Nearest Substituents

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The effect of electronegative substituents on the diamond nucleation on hexagonal boron nitride (h-BN) was investigated theoretically by using the DFT method. Fluorine and hydroxyl were used as substituents on zigzag edge atoms of the basal plane. Outgrowths corresponding to diamond nuclei were calculated to be energetically more stable than the corresponding growth of graphite nuclei for both types of substituents. A comparison between the nucleation of diamond on H-terminated and substituted h-BN edges showed only small energy differences. The effect of the larger electronegativities and radii of F and OH on the stabilization energy of the diamond nucleation was found to be minimized by the lengthening of the substituent-ring distance and by distortion of the geometry.

Introduction

Diamond is a very good candidate material for use in both electronic and wear resistant coating applications because of its extreme hardness, high thermal conductivity and electric resistivity, optical transparency, and chemical inertness. Fabrication of diamond electronic devices of particular interest includes high-power/high-frequency devices and devices to be used in high-temperature, high-radiation flux environments. Recent developments in the gas-phase synthesis of thin (nm) diamond films, under conditions where graphite is the thermodynamically most stable form of carbon, have increased the interest in these types of diamond devices. Diamond films are rarely epitaxial with the substrate except when grown on bulk diamond. However, evidence of heteroepitaxial growth of diamond on substrates with similar cell parameters, e.g., BeO,[1] Si,[2−4] Ni,[5] Cu,[6] *c*-BN,[7−13] and *β*-SiC1,[4,15] has been obtained. By use of the experiences of heteroepitaxial growth of diamond on different substrates, complex composites could be produced that may become more efficient than conventional tools for various industrial applications. For instance, the possibility of creating a composite material consisting of the two hardest material phases now in existence, diamond and *c*-BN, is obviously particularly attractive.

It is well established that graphite is a proper substrate for diamond growth.[16−19] Hexagonal boron nitride (h-BN) is another good candidate as substrate for the diamond growth. It has a structure that is almost identical with the graphite one but where every other carbon atom has been replaced by a boron and a nitrogen atom, respectively. The bond length r_{B-N} of h-BN is 1.45 Å, which is quite close to the corresponding bond length in graphite ($r_{C-C} = 1.42$ Å). This structure provides two zigzag edges (boron atoms on the (100) edge and nitrogen atoms on the (−100) edge) and an armchair edge (alternate boron and nitrogen atoms on the (110) edge).

Both experimental[20,21] and theoretical investigations[22] have been performed regarding nucleation of diamond on the hexagonal BN substrate. The experimental investigations reported high nucleus densities of diamond on polycrystalline substrates. A nucleus density of 1×10^4 nuclei/cm^2 was obtained after a 3 h deposition in the work by Johansson.[21] Lidlbauer et al.[22] reported a nucleus density of 5×10^5 nuclei/cm^2 after 5 h of diamond deposition. The hot filament technique was used in both investigations.

The ab initio study by Johansson et al.[23] confirmed the possibility of growing diamond on a graphite-like substrate such as h-BN. Outgrowths corresponding to diamond nuclei were calculated to be energetically more stable (at 0 K) than the corresponding growth of graphite nuclei for all different edges of the h-BN (001) plane. A comparison between the nucleation of diamond on these three edges with the nucleation of diamond on the corresponding edges of the basal plane of graphite was also made. The relative energy for a chair formation (corresponding to a diamond nucleus) in the different edges of the basal plane of h-BN was then numerically similar to the results of the corresponding diamond nucleation on the edges of the graphite basal plane.

In the present work, a comparative structural and energetic investigation is made in order to study the influence of electronegative substituents (−F and −OH) on the diamond growth on h-BN. The nucleation of diamond on the zigzag edge atoms of h-BN, using a cluster approach and the density functional theory (DFT), is then especially investigated. The species F and OH is assumed to terminate the edge atoms, then to become the closest neighbors to the outgrowths. The effect of these substituents on the stability of buckled outgrowths (diamond nuclei) on the two zigzag edges of h-BN (100 and −100) will, in the present investigation, be presented and discussed in relation to the graphitic planar forms of outgrowth and to the H-terminated h-BN edges.

Method

The nucleation of diamond on the different types and configurations of edge atoms of the hexagonal BN (001) plane was investigated within the framework of density functional theory, using the program system CASTEP from Biosym/Molecular Simulation Technologies of San Diego. The ap-

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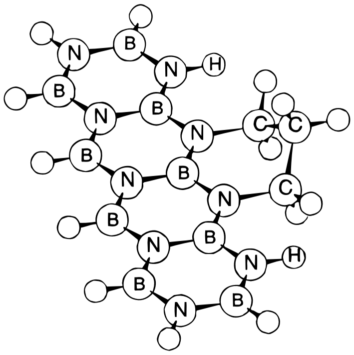

Figure 1. Illustration of the template used in the calculations of the diamond nucleation stabilization energy. A diamond outgrowth from the zigzag edges of the h-BN basal plane is sketched. Four h-BN rings are then used. The two central ones carry the carbon outgrowth, while the outer ones carry the substituent (H in the present illustration). The composition of the diamond outgrowth is C_3H_6.

proximation method used is the gradient-corrected LDA version as developed by Perdew et al.[29] The electronic relaxation is achieved by minimization of the total energy. The electronic wave functions are expanded using a plane wave basis set, and the expansion coefficients are varied in order to minimize the total energy, with an independent optimization of each wave function. We employed a plane-waves basis set with kinetic energy cutoff up to 10 Ry, corresponding to 3500−3700 plane waves in the unit cell. The electron−ion interaction is described by using pseudopotentials generated using the scheme of Lin et al.,[30] which ensures the transferability of the potentials. The pseudopotentials are then used in the Kleynman−Bylander separable, norm-conserving form.[31]

The calculations are fully self-consistent with eigenvalues obtained using either 1, 4, or 8 k-points. The primary method of k-points generation is the Monkhorst−Pack scheme,[32] which produces a uniform mesh of k-points in the reciprocal space. The quality of the representation has been verified by increasing the density of k-points used in the mesh. A quantity of 1, 4, and 8 k-points have been used for a specific system. However, the relative total energies for the different outgrowths became quite similar, and 1 k-point was used for the other calculations in the present investigation.

The presence of substituents on both sides of the carbon outgrowths implies a template consisting of four aligned aromatic rings. The two central rings carry the carbon outgrowth, while the outer rings carry the substituents (Figure 1). A supercell approach is used in the calculations. The four-ring template is included in a unit cell with vacuum regions of 7 Å in the (001) and (100) directions while keeping the periodicity in the (110) direction.

The total energy of two different types of outgrowths from the two edges of the h-BN basal plane was calculated for a saturated carbon ring system and the graphitic counterpart. The aim of these calculations was to obtain relative total energies for these two types of outgrowths. The relative energies are balanced by the total energy of two hydrogen atoms, since the buckled form of the outgrowth contains two more atoms than the graphitic one (the composition of the diamond and graphitic outgrowth is C_3H_6 and C_3H_4, respectively). The energy of the two hydrogen atoms has been calculated by including them in a unit cell of the same size as for the template and at a distance similar to the one they have in the diamond outgrowth. All geometrical parameters of the different types of outgrowths from the edge atoms of the hexagonal BN (001) plane were allowed to be fully relaxed, as well as the substituents and the two atoms bonded to the carbon outgrowths.

TABLE 1: Total and Relative Energies for the Growth of Buckled and Planar Ring Systems on the (100) and (−100) Edges of the h-BN Basal Plane[a]

substituent	E_{buckled} (eV)	E_{planar} (eV)	ΔE (kJ/mol)
	B-Rich Edge		
−H	−3183.34	−3152.63	560
−F	−4260.09	−4229.68	531
−OH	−3960.60	−3930.10	541
	N-Rich Edge		
−H	−3182.34	−3151.37	584
−F	−4256.52	−4225.96	545
−OH	−3957.96	−3927.45	541
−OH (4 k-points)	−3957.96	−3927.05	530
−OH (8 k-points)	−3956.88	−3926.52	525

[a] Calculations are performed with 1 k-point and with different substituents. In addition, calculations were also performed with 4 and 8 k-points, respectively, for the substituent −OH.

Results and Discussion

A. General. The assumed mechanism for diamond nucleation on the zigzag edge of the basal plane of h-BN involves a combination of abstraction of terminating substituents and adsorption of hydrocarbon species. These individual steps will result in a completion of a buckled six-membered ring containing three sp^3-hybridized carbon atoms (Figure 1). The three other members of this partially saturated outgrowth from the zigzag edge atoms of h-BN are sp^2-hybridized boron and nitrogen atoms. On the boron-rich (100) edge, two boron atoms are bonded to the carbon atoms and a nitrogen atom completes the ring. Two nitrogen atoms are bonded to the carbon atoms on the nitrogen-rich edge. In the graphitic counterparts two of the three added carbon atoms are sp^2-hybridized, while the third is sp^3-hybridized. An alternative approach would have been to choose an sp^2-hybridized carbon radical system instead of the sp^3-hybridized carbon atom. However, the possibility for this sp^2-hybridized carbon atom to undergo an H adsorption reaction, resulting in an sp^3-hybridized carbon atom, is very large in the growth environment in a hot filament reactor.

B. Stabilization Energy. The relative total energies for the buckled and planar ring systems are given in Table 1. These relative adsorption energies will hereafter be referred to as stabilization energies of diamond nucleation. The effect of a different number of k-points on the stabilization energy has been tested for the system with −OH substituents on the N-rich edge. The results reported in Table 1 show an energy difference of about 10 and 15 kJ/mol for a scheme with 1 k-point compared to 4 and 8 k-points, respectively. These differences are, hence, less than 3% of the total stabilization energies. A quantity of 1 k-point was chosen to be used for all investigated systems.

To be able to investigate the effect of electronegative substituents on the stabilization energy of diamond nucleation, calculations have been carried out on corresponding H-terminated templates. Similar to the results in a previous paper,[23] outgrowths corresponding to diamond nuclei are calculated in the present work to be more stable than the graphitic counterparts. Furthermore, a comparison of stabilization energies for the two zigzag edges (B- and N-rich, respectively) does not show any significant differences.

In addition to the large differences in electronegativities of F/O (in OH) and H, there is a rather large variation in the radii. The covalent radii of F and OH are larger than for H (0.72, 0.96, and 0.20 Å, respectively). Both these factors (electronegativities and radii) may influence the diamond nucleation. The latter will influence by introducing steric hindrances. The influence of electronegative differences on, for example, adsorption and nucleation on H- and F-terminated diamond surfaces

TABLE 2: Bond Distances between the Edge N Atoms and the Substituents and Carbon Outgrowths, Respectively[a]

B-Rich Edge

substituent	$r_{B-substituent}$ (Å)	r_{B-C1} (Å)	r_{B-C2} (Å)
$-H_{(buckled)}$	1.236	1.700	1.701
$-F_{(buckled)}$			
$-OH_{(buckled)}$	1.629	1.715	1.702
$-H_{(planar)}$	1.240	1.699	1.652
$-F_{(planar)}$	1.640	1.701	1.643
$-OH_{(planar)}$	1.660	1.702	1.635

N-Rich Edge

substituent	$r_{N-substituent}$ (Å)	r_{N-C1} (Å)	r_{N-C2} (Å)
$-H_{(buckled)}$	1.129	1.910	1.939
$-F_{(buckled)}$	2.004	1.939	1.939
$-OH_{(buckled)}$	2.000	1.941	1.913
$-H_{(planar)}$	1.131	1.910	1.897
$-F_{(planar)}$	1.967	1.970	1.897
$-OH_{(planar)}$	1.965	1.985	1.913

[a] The carbon atoms C1 and C2 (bonded to the edge atoms) are two of three atoms in the carbon outgrowth.

TABLE 3: Total Atomic Charges Obtained from Mulliken Population Analysis, Based on the MP2/6-31g Theory**[c]

	X	A	B	C
H (graphite)[a]	−0.08	0.50	−0.76	0.74
F (graphite)[a]	−0.51	0.86	−0.79	0.78
OH (graphite)[a]	−0.76 (O) 0.31 (H)	0.84	−0.79	0.77
H (diamond)[a]	−0.11	0.48	−0.75	0.75
F (diamond)[a]	−0.49	0.84	−0.76	0.75
OH (diamond[a]	−0.74 (O) 0.30 (H)	0.79	−0.75	0.74
H (graphite)[b]	0.17	−0.64	0.76	−0.68
F (graphite)[b]	−0.32	−0.35	0.80	−0.76
OH (graphite)[b]	−0.43 (O) 0.38 (H)	−0.48	0.76	−0.73
H (diamond)[b]	0.26	−0.76	0.80	−0.75
F (diamond)[b]	−0.38	−0.32	0.78	−0.74
OH (diamond)[b]	−0.49 (O) 0.35 (H)	−0.48	0.79	−0.72

[a] B-rich edge. [b] N-rich edge. [c] X is the substituent. A is the nitrogen edge atom bonded to the substituent X. C is one of the surface atoms that are being bonded to the carbon outgrowth (the closest one with respect to the X substituent). B is the edge boron atom between the A and C atoms.

has earlier been investigated theoretically.[33−35] Charge transfer from the surface, and specific adsorbates, to the electronegative terminating F species was then also discussed. No corresponding withdrawing effect was observed when terminating the surface with H atoms.

As can be seen in Table 1, the influence of the substituents on the stabilization energies is very similar despite large differences in electronegativites and/or covalent radii. The stabilization energies are all included within a range of 40 kJ/mol. Structural geometries of the region close to the outgrowth, as well-as electron densities, may give further information.

C. Structural Geometries. The different edges involved in the present investigation include two zigzag edges (boron atoms on the (100) edge and nitrogen atom on the (−100) edge). These edges are assumed to be terminated with H, F, or OH. The two edges, including diamond outgrowths, are illustrated in Figure 1. Information about the geometrical structures (e.g., bond lengths) of the different substituents on both edges are shown in Table 2. The B−H and N−H distances are rather similar (1.24 vs 1.13 Å). This is not the situation for the substituents −F and −OH. The N−F and N−O distances are about 2.0 Å, while the corresponding B−F and B−O distances are about 1.6 Å. In contrast, the distances between N and these electronegative substituents are expected to be smaller that the corresponding distances for B.[36] Furthermore, the ring structure of h-BN was found to be rather distorted by the presence of −F or −OH. Although the overall geometry is rather flat for a H-terminated edge, the ring atoms attached to the carbon outgrowths as well as the substituents −F or −OH are buckled. The −F and −OH substitutents are then bent out of the h-BN plane by about 40°. The −OH substituents are also bent away from the outgrowth by about 109°. The presence of differently hybridized carbon atoms in the graphitic outgrowths results in a structural asymmetry with different C−C bond lengths (∼1.4 and 1.7 Å).

It is then possible to draw the conclusion that the effect of the electronegativities and radii of the substituents on the stabilization energies of diamond nucleation may be minimized by lengthening of the ring-substituent distance and by distortion of the structural geometry close to the outgrowth. When the N−F and N−O bonds are forced to a shorter distance of 1.6 Å, a decrease in stabilization energy of about 100 kJ/mol was obtained.

D. Electron Densities. Electron deformation densities were calculated for all three substituents −H, −F, and −OH and for both type of edges (B- and N-rich zigzag edges). The deformation density is the difference between the molecular and the unrelaxed atomic charge densities. No change in charge distribution within the h-BN ring formation was observed for the different types of outgrowths and for the different substituents. The largest electron densities are localized within the N−B bonds, polarized toward the nitrogen atoms, independent of type of edge. Large electron densities are also localized between the sp^2-hybridized carbon atoms in the graphitic outgrowth, as well as on the substituents −F and −OH. In the case of graphitic outgrowths, the six-membered ring (containing C, B, and N) are well included in the aromatic system with electrons equally delocalized over all five rings. Hence, edges including graphitic outgrowths will gain the energy of an extra aromatic ring, with a stalibization of the graphitic outgrowth compared to the diamond one.

Total atomic charges were furthermore calculated in order to study the influences of different substituents more in detail. Mulliken population analysis was then used, based on the MP2/6-31g** level of theory.[37] The total charges of the substituent and for three of its closest edge atoms are presented in Table 3. As can be seen in Table 3, the effects of the different substituents on the total charge of the atom N/B bonded to the outgrowth are almost identical. The variation in charges obtained for a specific edge decreases quickly when going from the substituent-binding edge atom to the atoms bonded to the carbon-containing outgrowth. This is to be compared with an earlier study,[33] where diamond growth on diamond (111) surfaces were investiagted. Neighboring surface-terminating F atoms were then found to influence the charges of the adsorbant-binding surface atoms more than corresponding H neighbors do. These differences in total atomic charges were found to correlate with differences in adsorption energies. One of the major differences between the present investigation and the former one is the aromaticity of hexagonal BN. This aromaticity may play a certain role in minimizing the effect of an electronegative subsitutent.

The results in Table 3 strongly support the results of the calculated adsorption energies in Table 1.

Summary

The effect of different electronegative substituents on the stabilization energy of diamond nucleation on the zigzag edges of h-BN has structurally and energetically been investigated using a cluster approach and the DFT method. The investigation has been carried out on the (100) and (−100) edges of the basal plane, using F and OH as substituents. These nucleation processeses have been compared with corresponding processes involving hydrogen. In addition to large differences in electronegativities of F, O (in OH), and H, there are large variations in covalent radii. Both of these factors are generally assumed to influence the diamond nucleation.

The calculations in the present investigation show that the presence of H, or the electronegative species F and OH, does not substantially alter the diamond stabilization energy (or the atomic charges). This is in contrast to earlier investigations where growth processes on diamond surfaces were studied.[34−36] For instance, the adsorption of a growth species (CH_3), being the first step in a nucleation process, was found to be influenced differently by neighboring surface-bonded F vs H species.[34] Both the adsorption energy and the total atomic charges close to the structural region of adsorption varied.

Different factors are assumed to be responsible for the minimization of the effects of electronegativity and induced steric hindrances, respectively. One is the observed lengthening of the substituents−ring distance and distortion of structural geometry close to the outgrowth. An electrostatic interaction between the substituent −OH and the diamond outgrowth is then included in this type of factor. Another factor is the aromaticity of the hexagonal BN substrate.

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