

Diamond Nucleation on Hexagonal Boron Nitride: A Theoretical Investigation of the Influence of CH₃ and Na Substituents

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The effect of CH₃ and Na on diamond nucleation on hexagonal boron nitride (h-BN) was investigated theoretically by using the DFT method. The methyl and sodium species 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. Only small energy differences were obtained for diamond nucleation on Na and CH₃ substituted h-BN edges, respectively.

Introduction

Within the past decade there has been a substantial increase in the interest of gas-phase synthesis of diamond under conditions where graphite is the thermodynamically most stable form of carbon. It has become possible to deposit diamond films by several methods at relatively high rates.¹ The combination of the exceptional properties of diamond (e.g., extreme hardness, high thermal conductivity and electric resistivity, optical transparency, and chemical inertness) makes it one of the best candidates for several applications, such as fabrication of wear-resistant protective coatings, abrasives, heat sinks, and high-temperature semiconducting and optical devices.

For growth of diamond of high quality, there is a need for detailed understanding at the molecular level of the growth process occurring on various substrates and surfaces of different crystallographic orientations. Especially, basic knowledge of the nucleation process on different substrate surfaces is essential, since the film growth is strongly dependent on the nucleation. It has been shown that under appropriate growth conditions diamond can be grown on nondiamond substrates. Diamond films are in fact 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,² Si,^{3–5} Ni,⁶ Cu,⁷ c-BN,^{8–14} β -SiC^{15,16}) has been obtained.

It is well established that unsaturated aromatic (sp²) compounds and graphite can serve as sites for diamond nucleation.^{17–21} In a comparative study of diamond growth on Ni and Monel substrates, Johansson *et al.*¹⁷ have shown that diamond nucleates faster on substrates with predeposited graphite Angus *et al.*¹⁸ have also shown that diamond nucleation is enhanced by the addition of powdered graphite or nonvolatile graphitelike compounds to silicon substrates. Microwave plasma-assisted chemical vapor deposition by Dubray *et al.*¹⁹ has also proved that it is almost impossible to nucleate diamond directly on this (001) plane of highly oriented graphite. This is most probably due to the low reactivity of the basal plane toward gas-phase species. An *ab initio* study by Larsson *et*

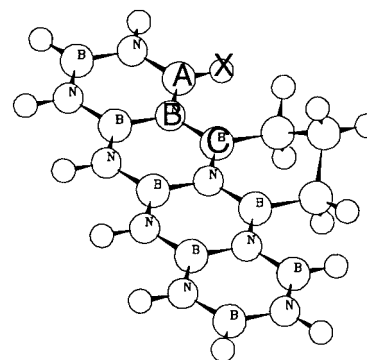


Figure 1. Illustration of the template used in the calculations of the diamond nucleation stabilization energy. A diamond outgrowth from the zigzag edges of the h-BN basal plane is sketched. Four h-BN rings are then used. The two central ones carry the carbon outgrowth, while the outer ones carry the substituent (H in the present illustration). The composition of the diamond outgrowth is C₃H₆.

*al.*²⁰ confirmed the higher stability of diamond nucleation compared to that of graphitic nucleation on the edge atoms of the basal plane of graphite.

Hexagonal boron nitride (h-BN) is another good candidate as substrate for diamond growth. It is isostructural to graphite where every other carbon atom has been replaced by a boron and a nitrogen atom, respectively. The bond length $r_{\text{B-N}}$ of h-BN is 1.45 Å, which is quite close to the corresponding bond length in graphite ($r_{\text{C-C}} = 1.42$ Å). As can be seen in Figure 1, 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). Johansson *et al.* investigated the possibility for diamond growth on hexagonal BN, using *ab initio* quantum chemistry mechanical methods.²¹ Outgrowths corresponding to diamond nuclei were calculated to be energetically more stable than the corresponding growth of graphite nuclei, for all the edges of the h-BN (001) plane.

Several researchers have suggested that diamond can also be grown from gas mixtures of halogens or halogenated methane.^{22–27} The presence of fluorine has been found to lower the substrate temperature by several hundred degrees compared to hydrogen based processes.^{22,25,27} This is particularly useful

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for those substrate materials which cannot tolerate high temperatures. Carbone *et al.*²⁴ made a comparative structural and energetic investigation in order to determine the influence of electronegative substituents (F and OH) on diamond nucleation on zigzag edge atoms of the h-BN (001) plane. A cluster approach and a gradient corrected LDA method were then used. These substituents were bonded to the edge atoms closest to the carbon outgrowths. Furthermore, the saturated carbon outgrowths were assumed to act as precursors for diamond formation. It was found that the stabilization energy of diamond nucleation will not significantly be affected by the presence of neighboring electronegative substituents.

In contrast to electronegative substituents, a highly electropositive substituent is generally expected to induce an electron donating process. It would, hence, be of great interest to investigate the possibility for any influence of electropositive substituents (e.g., Na) on the diamond nucleation process on the edges of the c-BN (001) plane. Larger substituents (e.g., CH₃) may also be of a great interest to study since they may influence the diamond nucleation due to large induced sterical hindrances. The methyl species is regarded as one of the most important growth species in conventional chemical vapor deposition of diamond. It is, hence, possible that CH₃ will act also as a substituent during diamond nucleation and deposition.

The purpose with the present study is to investigate the influence of the substituents CH₃ and Na, on the stability of buckled outgrowths (diamond nuclei) on the two zigzag edges of h-BN (B-rich (100) and N-rich (−100)). The results will be presented and discussed in relation to the corresponding effects of H, and the more electronegative species F, and OH, which have been presented in a recent paper by the present authors.²⁴

Method

The nucleation of diamond on different types and configurations of edge atoms of the hexagonal BN (001) plane has been investigated within the framework of density functional theory using the program system CASTEP from Molecular Simulation Inc., San Diego. The approximation method used is the gradient corrected LDA version as developed by Perdew *et al.*²⁸ The wavefunctions are expanded by using a plane wave basis set and the expansion coefficients are varied self-consistently in order to minimize the total energy. A plane wave basis set with kinetic energy cutoff up to 10 Ry (corresponding to 3500–3700 plane waves in the unit cell) has then been used. The *k*-points used in the calculation in the present study are generated in the program according to the Monkhorst–Pack scheme.²⁹ The investigations were carried out by using one *k*-point only. It was found in the earlier investigation by the present authors²⁴ that variations in the diamond nucleation stabilization energy of less than 3% were introduced when using four or eight *k*-points compared to one *k*-point. Hence, the number of *k*-points is concluded to be of no significant importance in the present investigation.

A template consisting of four aligned aromatic rings is modeling the (100) and (−100) edges of h-BN in the present work (Figure 1). The two central rings carry the carbon outgrowth, while the outer rings carry the substituents. In the calculations, a supercell approach is used. A 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. All geometrical parameters of the different types of outgrowths were allowed to be fully relaxed. This was also the situation for the substituents and for the two atoms (B or N) bonded to the carbons in the outgrowths.

TABLE 1: Total Energies, as Well as Relative Energies, Obtained for the Nucleation of Buckled Ring System and Their Planar Counterparts on the (100) and (−100) Edges, Respectively, of the Basal Plane of h-BN

substituents	E_{buckled} , eV	E_{planar} , eV	ΔE , kJ/mol
B-rich edge			
H	−3183.34	−3152.63	560
CH ₃	−3532.87	−3501.35	541
Na	−3166.92	−3136.74	508
N-rich edge			
H	−3182.34	−3151.67	584
CH ₃	−3532.44	−3502.23	511
Na	−3162.86	−3132.74	510

The following formula was used when calculating the stabilization of the diamond (buckled) outgrowth in relation to the graphitic (planar) counterpart;

$$\Delta E = E_{\text{planar}} - E_{\text{buckled}} - 2E_{\text{H}} \quad (1)$$

where E_{planar} and E_{buckled} are the calculated total energies for the planar and buckled outgrowth, respectively, and E_{H} is the total energy for an H atom. The relative energies have to be balanced by the total energy of two hydrogen atoms, since the buckled form of the outgrowth contains two more H atoms than the graphitic one.

The total energy for two different types of outgrowths from the edges of the h-BN basal plane was then calculated; one type of outgrowth consisted of three edge atoms (B and N) and three saturated C atoms (C₃H₆), and the other formed the graphitic counterpart (C₃H₅). The aim with these calculations was to obtain relative total energies for these two types of outgrowths. 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 used and at a distance similar to the one they have in the diamond outgrowth.

Results and Discussion

A. General. The effects of electronegative substituents on diamond nucleation on different zigzag edges atoms of the basal plane of h-BN has recently been investigated theoretically, using a gradient-corrected LDA method.²⁴ It was then found that the presence of electronegative substituents as closest neighbors to the carbon outgrowth does not appreciable change the stabilization energy of diamond nucleation. This was the situation for both types of zigzag edges (the N-rich (100) and B-rich (−100) edges, respectively). Furthermore, the calculated stabilization energies were numerically similar to the corresponding outgrowths from the zigzag edge atoms of the basal plane of graphite.

In the present paper, we apply the gradient-corrected LDA method in order to investigate the influences of a large electropositive substituent (Na), as well as the influence of a sterically hindering substituent (CH₃) on diamond nucleation on the edge atoms of the basal plane of h-BN. Generally, the adsorption of a methyl species to radical edge atoms is viewed as a specific process during diamond growth. The relative total energies for the buckled and planar ring systems are presented in Table 1. The corresponding relative energies obtained when using H as a surface terminating species²⁰ are also presented in Table 1. These relative adsorption energies will hereafter be referred to as diamond nucleation stabilization energies.

The assumed mechanism for diamond nucleation on the zigzag edges of the basal plane of h-BN involves a combination of abstraction of hydrogen (or other substituents that are

terminating the edges) 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. The three other members of this partially saturated outgrowth 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. In the graphitic counterparts two of the three added carbon atoms are sp^2 -hybridized, while the third is sp^3 -hybridized.

B. Stabilization Energy. As can be seen in Table 1, the diamond nucleation stabilization energies are rather similar for both the B- and N-rich edges. This is the situation for all three substituents (H, CH_3 , and Na). The stabilization energies presented in Table 1 are all within a range of about 70 kJ/mol. They are especially similar for the substituents Na and CH_3 (541 (CH_3) versus 508 (Na) kJ/mol for a B-rich (100) edge and 511 (CH_3) versus 510 (Na) kJ/mol for a N-rich (−100) edge). These stabilization energies are lowered in relation to the corresponding stabilization energies obtained, when terminating the edge atoms with H, by about 70 (CH_3 and Na) kJ/mol on a N-rich edge and 20 (CH_3) versus 50 (Na) kJ/mol on a B-rich edge. There is, hence, a tendency for a certain destabilization effect when using CH_3 (or Na) instead of H as a terminating species on the N-rich h-BN edge. On the other hand, the numerical values of the total energies obtained (not relative energies) for the substituents H and Na, were rather different on the different edges. As can be seen in Table 1, the total energies were, with one exception, appreciable smaller for all substituents and for both type of outgrowths on the B-rich edge. A nucleation of diamond, as well as a nucleation of the graphitic counterpart, seems to be energetically favored on the B-rich edge when H, F, or OH are terminating the edge atoms. On the contrary, the formation of a graphitic outgrowth seems to be energetically favored on the N-rich edge when the sterically hindering CH_3 group is terminating the edge atoms. This will explain the difference in relative energies for the different edges (30 kJ/mol).

C. Structural Geometry. The lengths of the bonds formed between the edge atoms and the different substituents (or carbon outgrowths) are demonstrated in Table 2.

The calculated bond distances between the edge atoms and substituents in the present study are for both types of outgrowths about 1.1 (H), 1.9 (CH_3), and 2.2 (Na) Å for the N-rich edge and about 1.2 (H), 1.8 (CH_3) and 2.4 (Na) Å for the B-rich edge. Corresponding bond lengths involving the electronegative substituents F and OH were found to be about 1.6 vs 1.7 Å for the B-rich edge and 2.0 vs 2.0 Å for the N-rich one. The bond distances between edge N atoms and these type of substituents are, however, generally expected to be smaller than the corresponding bond distances including B atoms.³⁰

The geometry optimization of the CH_3 and Na substituents, and the carbon outgrowth resulted in a minimization of the mutual sterical hindrances, induced by both the substituents as well as the outgrowth (buckled or planar). The methyl substituents and the buckled carbon outgrowth were found to be situated on opposite sides with respect to the plane of the h-BN rings. This was also the situation for the graphitic (planar) counterpart. Furthermore, the two methyl substituents were also found to be situated at opposite sides of the ring system. The graphitic ring twisted a few degrees (about 10°) with respect to the h-BN rings.

Moreover, a large displacement of the sodium atoms positions, compared to the other systems in the present investigation, was obtained as a result of the calculations. The Na substituents

TABLE 2: Distances for the Substituents, as Well as for the Carbon Outgrowth, from the Corresponding Ring-Attached Atoms (a) Left Part and (b) Right Part of the Model

substituent	B-Rich Edge		B–C ^a	B–C ^b
	B-substituent ^a	B-substituent ^b		
H(buckled)	1.24	1.25	1.70	1.70
CH_3 (buckled)	1.75	1.24	1.69	1.64
Na(buckled)	2.42	2.49	1.72	1.72
Na(buckled) (z-direction)	1.80	1.46		
H(planar)	1.24	1.25	1.70	1.65
CH_3 (planar)	1.80	1.18	1.70	1.66
Na(planar)	2.40	2.56	1.71	1.67
Na(planar) (z-direction)	2.12	1.46		
substituent	N-Rich Edge		N–C ^a	N–C ^b
	N-substituent ^a	N-substituent ^b		
H(buckled)	1.13	1.25	1.91	1.94
CH_3 (buckled)	1.92	1.92	1.96	1.95
Na(buckled)	2.25	2.17	2.00	1.93
Na(buckled) (z-direction)	1.67	1.19		
H(planar)	1.13	1.25	1.91	1.90
CH_3 (planar)	1.94	1.94	1.96	1.90
Na(planar)	2.17	3.07	1.99	1.91
Na(planar) (z-direction)	1.85	0.88		

neighboring a diamond outgrowth were markedly bent out of the plane of the rings by about 60° and 50° for the N- and B-rich edge, respectively. Some distortions of the geometry also occurs for Na substituents neighboring a graphitic outgrowth. The graphitic ring is then twisted by about 30° with respect to the h-BN ring system. Furthermore, the Na substituents here were also bent out of the plane of the ring system. One Na was shifted toward the graphitic outgrowth, being more pronounced for the N-rich edge. The second Na was instead shifted further away from the graphitic outgrowth. This bonding situation is most probably due to the asymmetry of the graphitic outgrowth since one of the carbon atom in the outgrowth is sp^3 hybridized, while the other two are sp^2 hybridized.

D. Electron Densities. Electron deformation densities were calculated for all substituents as well as for both type of edges in the present investigation. 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 were localized within the N–B bonds, polarized toward the nitrogen atoms and independent of the type of edge. Large electron densities were also localized between sp^2 hybridized carbon atoms in the graphitic outgrowth. In the case of graphitic outgrowths, the six-membered rings (containing C, B, and N) are well included in the aromatic system with electrons equally delocalized over all five rings. Hence, edges including graphitic outgrowth will gain the energy of an extra aromatic ring, with a resulting stabilization of the graphitic outgrowth compared to the diamond one.

Moreover, total atomic charges were calculated in order to study the influences of different substituents in more detail. Mulliken population analysis were then used, based on the MP2/6-31g** level of theory.³¹ The total amount of atomic charges for the substituent, and for three of its closest edge atoms are presented in Table 3. The actual atoms are marked in Figure 1. As can be seen in Table 3, the effects of the different substituents on the total charge of the N (or B) edge atom

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

	X	A	B	C
H(graphite) ^a	-0.08	0.50	-0.76	0.74
Na(graphite) ^a	0.12	0.40	-0.72	0.63
CH ₃ (graphite) ^a	-0.26	0.57	-0.77	0.82
H(diamond) ^a	-0.11	0.48	-0.75	0.75
Na(diamond) ^a	0.08	0.33	-0.75	0.80
CH ₃ (diamond) ^a	-0.23	0.58	-0.76	0.83
H(graphite) ^b	0.29	-0.64	0.76	-0.83
Na(graphite) ^b	0.61	-0.84	0.75	-0.88
CH ₃ (diamond) ^b	-0.18	-0.73	0.75	-0.70
H(diamond) ^b	0.26	-0.76	0.80	-0.75
Na(diamond) ^b	0.62	-0.84	0.73	-0.78
CH ₃ (diamond) ^b	-0.14	-0.72	0.76	-0.70

^a B-rich edge. ^b N-rich edge.

(bonded to the outgrowth) are almost identical. The variation in charges obtained for a specific edge decreases rapidly when going from the substituent-binding edge atom to the atoms bonded to the carbon-containing outgrowth. This is to be compared with the results obtained in an earlier investigation by the present authors.²⁴ It was then found that aromaticity may play a certain role in minimizing the effect of an electronegative substituent. This seems also to be the situation in the present investigation.

The electron densities of the Na substituents were found to be extremely low. The total atomic charges were about +0.10 and +0.61 for a B- and N-rich edge, respectively (Table 3). These positively charged substituents were arranged, as a result of the geometry optimizations, in a way that they can interact with the electrons in the ring system. The positively charged Na substituents close to a diamond outgrowth will bend toward the delocalized π electrons in the ring system. The positively charged Na substituents close to a graphitic outgrowth will interact with a sp^2 hybridized carbon atom. Most probably due to its higher electron density.

Summary

The effect of two different types of substituents (CH₃, Na) on diamond nucleation on the (100) and (-100) edge atoms of the basal plane of h-BN has been structurally and energetically investigated by using a cluster approach and a gradient-corrected LDA method. The Na species is a very electropositive element. The CH₃ species is not only a branched species, it is also a commonly assumed important growth species during diamond growth. This study follows a previous work where the effect of H and two different electronegative substituents (F, OH) on the corresponding nucleation processes has been investigated. Hence, the two investigations cover a large variation in electronegativities as well as in degree of spatially demanding substituents.

The calculations show that the diamond nucleation stabilization energies are rather similar for both the B- and N-rich edges and for the substituents H, CH₃, and Na. However, changes in the optimized structural geometry occur as an effect of type of substituent. This is especially true for the Na substituent. This substituent appears to be bent toward the h-BN rings in order to achieve a better electrostatic interaction.

The adsorption of CH₃ species to a diamond (111) surface was found to be influenced differently by neighboring surface-bonded F, versus H, species in an earlier theoretical study.³² The adsorption energy, as well as the total atomic charges close to the structural region of adsorption, did vary. In the present study, different factors are assumed to be responsible for the minimization of the expected effects of (1) electronegativity of

the different substituents and (2) induced sterical hindrances by the substituents. One is the observed distortion of structural geometry close to the outgrowth. Another factor is the aromaticity of the h-BN substrate.

The calculated total energies indicate a preference for both diamond and graphitic nuclei (to approximately the same extent) on the B-rich (100) edge. As an exception, however, there is a larger preference for a graphitic nuclei, with a CH₃ substituent, on the N-rich (-100) edge.

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