A mechanism for crystal twinning in the growth of diamond by chemical vapour deposition

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A model for the formation of crystal twins in chemical vapour deposited diamond materials is presented. The twinning mechanism originates from the formation of a hydrogen-terminated four carbon atom cluster on a local {111} surface morphology, which also serves as a nucleus to the next layer of growth. Subsequent growth proceeds by reaction at the step edges with one and two carbon atom-containing species. The model also provides an explanation for the high defect concentration observed in {111} growth sectors, the formation of penetration and contact twins, and the dramatic enhancement in polycrystalline diamond growth rates and morphology changes when small amounts of nitrogen are added to the plasma-assisted growth environments.

Keywords: diamond; twinning; chemical vapour deposition; nitrogen

1. Introduction

Diamond chemical vapour deposition (CVD) is now an industrial process producing diamond materials ranging from nanocrystalline thin films to single crystals of higher purity than the best of natural diamonds. The growth of diamond, a metastable form of crystalline carbon relative to graphite, at low pressures (partial vacuum) and relatively low temperature (approx. 50% of its Debye temperature) is a kinetically controlled process driven by reactive species (primarily atomic hydrogen). The complex gaseous chemistry, transport of reactive species and surface chemistry has been summarized previously (Butler et al. 1993; Goodwin & Butler 1997).

Twinned crystal domains are observed very commonly in the CVD of diamond, and can severely impact the properties of diamond materials, mostly in a positive manner for mechanical applications, and mostly negative for optical and electronic applications. Twinned domains are crystallographically rotated from the parent crystal by a single (or multiple) errors (stacking faults) in the normal a-b-c layer stacking of carbon atom layers along the ⟨111⟩ crystal direction. The rotated domains can be macroscopic, easily observed by the change in surface facets with the eye or optical microscope, or microscopic regions only observed with the aid of scanning or transmission electron microscopy (TEM; Angus et al. 1992; Shechtman et al. 1993).

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In the CVD growth of diamond, crystal twinning can result in fascinating local faceting, such as the ‘accordion’ surface faceting shown in figure 1, where crystal domains share a common \{111\} plane that is nearly parallel to the growth direction (Shechtman et al. 1993; Shechtman 1994, 2006). Several of these parallel \{111\} ‘twin’ planes that are offset from one another create surface faceting with re-entrant angles, or the accordion structure. Twinning on the common \{111\} plane rotates the orientation of the twinned crystal 70.5° about the [110] axis.

This has led to the fascinating observation of apparent fivefold axes of symmetry as shown in figure 2 (Carrington et al. 1989; Tamor & Everson 1994). Twinned growth structures can appear on diamond \{100\} as well as \{111\} surfaces. The former are designated as ‘penetration twins’, while the latter are called ‘contact’ twins (Everson et al. 1994; Tamor & Everson 1994; Wild et al. 1994).

A consequence of twin formation is the generation of structural and electronic defects (Kasu et al. 2003). The interface of a parent crystal with its twin ideally can have coherent carbon–carbon bonds across the interface, a \(\Sigma 3\) grain boundary (Shechtman et al. 1993). However, there are four distinct \{111\} planes on which a stacking fault could occur, so domains twinned relative to the twin domain can and will have higher order grain boundaries \(\Sigma 9, \Sigma 27, \ldots, \Sigma 81\) where the bonding cannot be coherent across the interface between the domains. Depending on how these ‘dangling’ bonds stabilize, either with sp\(^2\) bonding, or adatom termination (H, O, N), electronic states will probably occur at energies within the bandgap highest occupied molecular orbital (HOMO)–lowest occupied molecular orbital (LUMO) carbon energy gap of sp\(^3\) carbon–carbon bonding, thus creating scattering centres and electronic traps to transport of charge carriers and optical absorption/emission within the bandgap, i.e. properties detrimental to many intended applications of diamond materials.

Figure 1. A scanning electron microscope image of a region of a polycrystalline diamond film grown by CVD showing the ‘accordion’ like structure due to parallel twin planes. (Photo courtesy of Shechtman (1994).)
Microscopic analysis (mostly by TEM) has shown that \(\{111\}\) growth sectors, i.e. domains of the crystal grown under a \{111\} surface, are highly defective, containing a high density of stacking faults and dislocations. Figure 3 shows TEM results from sections taken from different heights of a crystal containing a central \(\{100\}\) growth sector surrounded by four \(\{111\}\) growth sectors (Steeds et al. 1998). Note the low density of dislocations in the central \(\{100\}\) sector and the high density in the \(\{111\}\) growth sectors.

It has also been observed that trace amounts of nitrogen present in the plasma-assisted growth of diamond can dramatically enhance the growth rate, the formation of macrosteps on the surface of diamond and shift the relative growth rates on \{111\} versus \{100\} surfaces. The rate of deposition of polycrystalline CVD diamond in a microwave plasma can be enhanced by a factor of eight by the addition of nitrogen at a concentration of less than 0.4 N/C in the gaseous reactants, while less than 10 ppm nitrogen is incorporated into the diamond (S. Prawer & J. E. Butler 2007, unpublished data; Muller-Sebert et al. 1996; Hunt 1999). Nitrogen in the growth environment is observed to enhance step bunching on the growing surface (de Theije et al. 2000). Additionally, nitrogen added to the growth environment influences the morphology of the diamond crystals and the crystalline texture of the polycrystalline growth (Locher et al. 1994; Cao et al. 1996; Yan & Vohra 1999).

This work presents an atomistic model of how crystallographic twins are formed during the CVD of diamond, and the role of impurities such as nitrogen on the growth rate and morphology of CVD diamond. For simplicity, we chose to discuss the growth of diamond from gaseous hydrogen and methane.

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precursors, as this captures all the dominant growth chemistry and keeps the discussion focused on the principal features of growth (Butler & Woodin 1993; Goodwin & Butler 1997).

2. Background

Diamond CVD occurs in a complex chemical environment. This environment is summarized briefly here and explained in more detail elsewhere (Butler & Woodin 1993; Goodwin & Butler 1997). Reactants, usually hydrogen and a dilute amount of a hydrocarbon (0.1–4%), are flowed into a reaction environment at pressures between 0.1 and 1500 Torr, but more typically 10–200 Torr. The gases are activated by a hot filament (>2000°C), plasma or combustion flame. The gas activation produces atomic hydrogen (1–50 mol%; and similar radical species). While the gaseous species are being transported from the activation zone (plasma, hot filament, …) to the deposition surface by a combination of forced

Figure 3. 250 kV bright-field plan view transmission electron micrographs of square facetted regions of CVD diamond film looking along {100} resolved by tilting through 60° along the normal to one (a) near the substrate surface, (b) at an intermediate depth in the film of the edge-on fault planes from one close-packed direction and (c) near the growth surface. A typical V-shaped region is arrowed. Reprinted with permission from Steeds et al. (1998). Copyright © Elsevier.
flow, convection and diffusion, various gas phase reactions occur. Since the concentration of the hydrocarbon (usually methane) is dilute, these reactions mostly involve atomic and molecular hydrogen and the hydrocarbon species. Of the reactive hydrocarbon species produced, \( \text{CH}_x \) with \( x = 0 \text{ to } 4 \) and \( \text{C}_2\text{H}_y \) with \( y = 0 \text{ to } 6 \), the single carbon species \( \text{CH}_x \), have been shown to account for the bulk of diamond growth. Of these, the methyl radical, \( \text{CH}_3 \), is generally the most ubiquitous and will be the carbon radical used in the following model. Other single and multiple carbon species may play various ‘minor’ roles in the diamond CVD, which should be obvious in the following discussion.

The flux of reactive species at the growing surface of the diamond is principally atomic \( \text{H} \) and carbon radicals (e.g. methyl radical). The flux of atomic hydrogen to the growing surface will depend on the pressure and the degree of dissociation of the molecular hydrogen, and generally exceeds \( 10^{19} \) hydrogen atoms \( \text{cm}^{-2} \text{s}^{-1} \) and is more typically \( 10^{21} \text{ to } 10^{22} \text{ cm}^{-2} \text{s} \). Since the surface density of carbon atoms is \( 2 \text{ to } 3 \times 10^{15} \) atoms \( \text{cm}^{-2} \), each surface carbon atom sees \( 10^6 \text{ to } 10^7 \) gaseous atomic hydrogen atom collisions per second! The surface is terminated with hydrogen in the form of C–H bonds, which can be abstracted by reaction with the incoming hydrogen atom at the surface temperatures typical of diamond growth (600–1200°C) to form surface radical (dangling bond) sites. The fate of these sites is to react with another incoming radical species (generally atomic hydrogen, and occasionally a gaseous carbon radical) to reform the C–H bond or a C–C bond of a carbon adsorbate. Thus, we see that there is a high turnover rate of the C–H bonds on the surface relative to the occasional carbon adsorbate that might be formed. The net surface C–H bond exchange rate is thus 1000 to 10 000 times the rate of carbon adsorbate formation.

It is also worth noting that at these surface (and bulk) temperatures, the surface is ‘hot’ to bond breaking and formation, i.e. the thermal energy is sufficient to break even strong C–C and C–H bonds on the surface, although the rate is much slower than the atomic hydrogen abstraction and retermination reactions discussed above. Also, the bulk is thermally cold relative to atomic diffusion and rearrangements (approx. 50% of the Debye temperature of diamond). In this temperature range, only interstitial carbon or hydrogen atoms and carbon vacancies are known to diffuse in diamond. Hence, there is little or no diffusion of adsorbates on the surface and adsorbates must be strongly bound to the surface.

Atomistic modelling has been performed of the diamond CVD growth using the kinetic Monte Carlo method (Battaile et al. 1997a,b, 1998). A key observation was that growth rate on the diamond (111) surface was limited by the rate of nucleation of the next layer of growth and that once a step edge exists, growth proceeds rapidly by single and two carbon addition events at the step edges (see figure 4).

### 3. Computational

In order to provide an atomistic insight into twin formation during the CVD growth on (111) surface, we performed density functional theory (DFT) calculations of the atomic structure and energetics of elementary steps of hydrocarbon adsorption and subsequent surface carbon cluster formation on (111) surface. These processes, subsequently discussed in detail, are the important
steps of nucleating carbon seeds for the next layer growth. First-principles DFT calculations were performed using Dmol, a local combination of atomic orbitals (LCAO) all-electron DFT code (Delley 2000). The LCAO basis set, self-consistent convergence criteria, numerical integration grid and other Dmol parameters were carefully studied to get the convergence in energies and in forces better than 0.01 eV per atom and 0.01 eV Å⁻¹, respectively. We used the well-known Becke–Perdew generalized gradient approximation (Becke 1988; Perdew & Wang 1992), which works extremely well in predicting geometries and energetics of hydrocarbon molecules with chemical structures resembling the system of our interest.

One of the distinct features of our calculations is the use of periodic boundary conditions (PBCs) in $x$ and $y$ directions along the (111) surface. The use of PBCs allows us to exclude undesirable effects of the boundaries present in frequently used quantum chemical calculations employing small clusters. Using large dimensions of the surface unit cell, we ensure that there are no interactions between periodic images of the system. In our calculations, the (111) diamond surface has been represented by a periodic slab consisting of five $4 \times 4$ (111) layers, each having 16 carbon atoms. The bottom of the slab has been saturated by hydrogens and both hydrogen and two bottom carbon layers were fixed during geometry optimization of the surface chemical rearrangements. Each structure corresponding to every elementary step of carbon cluster nucleation has been optimized to get the forces on atoms less than 0.01 eV per atom. The heat of reactions reported below do not include the effects of zero-point energy and finite temperature. We expect these energy differences to be considerably small when compared with the energies of bond breaking and remaking occurring during nucleation stages.

Figure 4. Images of a ball and stick representation of steps on hydrogen-terminated {111} diamond surfaces: (a) a step edge with a local {110} like structure requiring a two-atom addition event to continue growth and (b) a step edge with a local {100} dihydride structure requiring only one-atom addition events to continue growth.
4. The model

Models of the hydrogenated diamond \{111\} surface are shown in figure 4, depicting two types of step edges. As was shown in the kinetic Monte Carlo modelling, the step edge sites are the most reactive and growth can occur by one and two carbon growth events at the edge, rapidly growing the layer to completion. The rate-limiting step for growth on the \{111\} surface is the nucleation of the next layer of growth, i.e. a new island on the \{111\} plane. In the following, we propose a plausible mechanism for this island formation or ‘nucleation of the next layer of \{111\} growth’. As discussed earlier, hydrogen abstraction and hydrogen atom adsorption are the dominant events happening at every surface site of the order of microseconds. In the presentation of the model, we will show only these events explicitly as they are relevant to the local surface chemistry and will instead focus on the carbon species adsorption and desorption events. We shall further simplify the model by considering only the C$_1$ growth species, the methyl radical—CH$_3$. These simplifications are justified by data indicating the C$_1$ species account for the bulk of diamond growth, that the carbon flux to the surface is less than 0.01 the atomic H flux, and the rapid conversion of CH$_x$ ($x=0$–2) species on the surface to CH$_3$ by the rapid H atom adsorption.

Figures 5–10 outline a plausible growth sequence for the nucleation of the next layer of growth on a diamond \{111\} surface. A stable island on \{111\} consists of a minimum of four carbon atoms back-bonded to the lower \{111\} layer and bonded to one another (see structure [19] in figure 9). To build such a structure using primarily single carbon species, one must first build C$_2$ adsorbates and a three-carbon bridge. The rate of building such structures, or ‘nucleating’ the next layer of growth, will depend on the lifetime of carbon adsorbates on the surface and the probability of a reactive carbon species from the gas phase finding and reacting with the appropriate adsorbate.

Structure [1] in figure 5a depicts a representation of local region of the hydrogen-terminated diamond \{111\} surface from slightly above the surface where the CH bonds are oriented along the \{111\} crystallographic direction. Figure 5a depicts the reaction sequence to the hydrogen abstracted, ‘dangling bond’ structure [2], and the adsorption of a methyl radical to form a methyl adsorbate [3]. The overall change in energy between two structures is given in eV and (kcal mol$^{-1}$) as computed using the first-principles DFT calculations summarized earlier and is shown in the figure above and between the two model structures. Structure [3] represents a methyl adsorbate on the diamond surface with only a single bond to the lattice and, as such, is not a carbon atom ‘grown’ into the lattice since the reaction between [2] and [3] is reversible and at the high temperature end of the diamond CVD growth (above 800°C), the methyl absorbate can desorb by breaking the carbon–carbon single bond. Ultimately, this reaction and the surface coverage of hydrogen on the surface limit the growth and stabilization of diamond at high temperatures (Butler & Woodin 1993). Figure 5b,c depict the mechanisms for creating two adjacent methyl adsorbates, and a two-carbon adsorbate, the ethyl species, respectively. These are the probable precursors to the eventual formation of the three-carbon bridge species. As one might imagine, the formation and concentration of these structures depend on the relative fluxes of reactant species from the gas phase.

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and the surface temperature, which controls the desorption of adsorbates and the probability of hydrogen abstraction.

Figure 6 depicts an important mechanism for the removal of two (or more) carbon atom containing adsorbates from the surface, the ‘beta-scission’ reaction, sequence \([7]-[8]-[2]\) (Butler & Woodin 1993). In the beta-scission reaction, abstraction of a terminal hydrogen from an adsorbed alkane or alkene can result in the breaking of the carbon bond between the second and third carbon atoms in the chain to form gaseous ethylene or acetylene and a radical site on the surface, structure \([2]\). It is called the beta-scission reaction since the bond severed is the one once removed, i.e. ‘beta’, to the carbon atom where the radical is formed. The net effect of this reaction is to chop two carbon atom species (ethylene or acetylene) off any adsorbed alkanes which might grow on the surface, and to

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lower the probability of ever finding a two- (or more) carbon adsorbate. Since the beta-scission reaction is energy neutral, it becomes increasingly important at higher substrate temperatures. Sequence \([7]-[8]-[9]-[7]\) depicts a radical generation and shuffling sequence that will also be going on in the high H atom flux to the surface and accomplishes nothing towards growth.

At this point, it should be obvious that in the high H-atom flux bombarding the surface there is rapid H exchange with the surface, surface radical (dangling bond) generation and hydrogen retermination, and the generation of carbon adsorbates that are rapidly converted into adsorbed methyl groups by the H flux and beta-scission reactions. Owing to the beta-scission reactions, the lifetime or probability of finding two (or more) carbon containing adsorbates is low and strongly dependent of the flux of carbon species to the surface.

The critical step to nucleating the next layer of growth on the \{111\} surface is the formation of the three-atom bridge between adjacent carbon atom sites on the \{111\} surface, of which one pathway starting from structure \([7]\) is depicted in figure 7. A similar, but alternative pathway could have started from structure \([5]\) of figure 5b.

Once the three-atom bridge is formed on the surface, it rapidly isomerizes between the ‘boat’ and ‘chair’ (stacking fault and normal stacking) of the six-member ring containing the three-atom bridge, figure 8, because the two configurations have essentially the same energy (they only differ in third nearest neighbour interactions) when compared with the thermal energy of the bulk and surface.
To complete the island formation, a fourth carbon (methyl group) must absorb on one side or the other of the rapidly isomerizing three-atom bridge, and be grown in by subsequent hydrogen abstractions and radical recombination reactions. These are depicted in figure 9 to form an island with normal stacking.

Figure 7. Representations of a local region of the \{111\} surface with various adsorbates bonded to the surface carbons of diamond \{111\} as viewed from slightly above the plane: structures [7], [10]–[15], and showing various routes to the formation of the three-atom bridge structure, [15]. The mechanisms are discussed in more detail in the text. Reaction enthalpy changes are shown in eV (kcal mol\(^{-1}\)).

Figure 8. Representations of a local region of the \{111\} surface with various adsorbates bonded to the surface carbons of diamond \{111\} as viewed from slightly above the plane: structures [15] and [15\(^{\prime}\)], and showing the rapid isomerization of the three-atom bridge between the chair (normal stacking) and boat (stacking fault or twin) forms of the six-atom ring. The mechanisms are discussed in more detail in the text. Reaction enthalpy changes are shown in eV (kcal mol\(^{-1}\)).

To complete the island formation, a fourth carbon (methyl group) must absorb on one side or the other of the rapidly isomerizing three-atom bridge, and be grown in by subsequent hydrogen abstractions and radical recombination reactions. These are depicted in figure 9 to form an island with normal stacking.
or untwined growth, and figure 10 to form an island with a stacking fault or twinned to the underlying lattice. This four-atom island on the \{111\} surface has three C–C backbonds to the diamond lattice, it is unlikely to desorb, be etched by hydrogen abstractions and or beta-scission reactions, or to rearrange into the other structure due to the number of bonds that would have to be broken in a concerted manner. Hence, once formed, it is there to stay. And it is created with approximately a 50 : 50 chance of being a twin or stacking fault. This is probably the only mechanism for twin formation during growth of diamond by CVD.

![Figure 9](image-url) Representations of a local region of the \{111\} surface with various adsorbates bonded to the surface carbons of diamond \{111\} as viewed from slightly above the plane: structures [15]–[19], and showing the formation of the stable four-atom island, or nucleation of the next layer of growth on \{111\} surfaces with normal stacking, structure [19]. The mechanisms are discussed in more detail in the text. Reaction enthalpy changes are shown in eV (kcal mol\(^{-1}\)).

![Figure 10](image-url) Representations of a local region of the \{111\} surface with various adsorbates bonded to the surface carbons of diamond \{111\} as viewed from slightly above the plane: structures [15]′–[19]′, and showing the formation of the stable four-atom island, or nucleation of the next layer of growth on \{111\} surfaces with a stacking fault or twin plane, structure [19]′. The mechanisms are discussed in more detail in the text. Reaction enthalpy changes are shown in eV (kcal mol\(^{-1}\)).
(a) Consequences of \{111\} island nucleation

What are the consequences of this four-atom island formation on the \{111\} surface? Once the island is formed on a \{111\} surface, it can rapidly grow out to the edges of the surface or domain by one and two carbon growth events at the edges of the island. The edges of the island are parallel \langle110\rangle directions and a two-carbon atom addition event(s) is required as the first step of the extension of the island edge, followed by one-carbon atom addition along the \langle110\rangle step edge to complete the edge. This process is repeated until the \{111\} layer grows to completion. Since the formation of this island is a highly improbable event, it is generally the rate-limiting step to growth on the \{111\} surfaces, and thus can impact the morphology of isolated and polycrystalline aggregates by changing the relative growth rates on \{111\} versus \{100\} surfaces, or other facets.

If two islands nucleate on the same \{111\} surface, there is a nearly equal chance that one will be twinned relative to the other and when their growth edges collide there will be incommensurate bonding and the formation of defects. Hence growth on large, isolated \{111\} surfaces (or facets) will develop growth sectors under the \{111\} facet which will include a great many defects, as is confirmed experimentally (Steeds et al. 1998). Suppression and minimization of these highly defective and twinned \{111\} growth sectors is an issue in the growth of large single crystal stones by CVD where the morphology and orientation of the seed crystal is carefully selected and those \{111\} growth sectors which do occur are laser trimmed off before subsequent processing.

There is a situation where high quality, low defect \{111\} growth sectors are observed in CVD diamond growth. Often polycrystalline growth develops a preferred crystalline texture relative to the growth direction. When the texture is near a \langle110\rangle or \langle112\rangle axis of the crystallites, an accordion-like surface faceting is observed with re-entrant surfaces alternating between \{111\} and \{100\} (Shechtman 1994, 2006). In this situation, the next layer of growth on the \{111\} surface can nucleate at the re-entrant corner with a two-atom growth event and when this and the subsequent growth events at the step edge are faster than the nucleation of isolated four-atom island on the \{111\} surface, the result is the suppression of twin formation on the growing \{111\} facet and a high-quality growth sector underneath (Steeds et al. 2002).

Penetration twins are often observed on nominal \{100\} surfaces. In this model, they would be formed by nucleation of twinned islands on a local surface region that has \{111\} structure, such as this might occur at etch pits on \{100\} (around dislocations) or macrostep edges (on vicinal \{100\}). As discussed earlier, once formed, these local twinned regions would not go away. They may be suppressed by rapid overgrowth from the \{100\} region surrounding them or they may grow more rapidly with subsequent twin formation on the exposed \{111\} facets of the penetration twin forming the core of growth hillocks observed on \{100\} nominal surfaces, all depending on the local growth environment or the relative growth rates of the slowest growing surfaces (Wild et al. 1993, 1994; Tamor & Everson 1994).

(b) Role of nitrogen in the gaseous growth environment

The impact of molecular nitrogen on the CVD growth of diamond depends strongly on the method of activation of the gas phase reactants: plasma enhanced, hot filament or combustion flame. In hot filament activated growth, there is a very low probability of nitrogen incorporation and only a mild
dependence of growth rate on molecular nitrogen in (added to) the gas phase (Cao et al. 1995). However, in microwave plasma-assisted CVD of diamond, there is a dramatic, almost catalytic, enhancement of the growth rate of polycrystalline diamond films with trace amounts of molecular nitrogen added, increasing by a factor of eight when the nitrogen to carbon ratio is increased from 0.0 to 0.4 in the reactants (S. Prawer & J. E. Butler 2007, unpublished data), while the concentration of substitutional nitrogen in the as-grown films is less than 20 ppm (Hunt 1999). In atmospheric combustion flames, the situation is less clear. Obviously, nitrogen from the air can diffuse into the flame, but there have been no explicit studies of its impact on the growth.

In the microwave plasma-enhanced growth environment, molecular nitrogen is easily cracked by the plasma and reacts with the atomic and molecular hydrogen and the carbon species to form the very stable molecule HCN and radical CN. Optical emission from the CN radical is often used to detect trace amounts of nitrogen in the plasma environment from air leaks or impurities in the reactants. Figures 11 and 12 depict the role the CN radical can play as a two-atom adsorbate in the path to constructing the four-atom island which nucleates the next layer of growth on the \{111\} surface. The key point here is that the CN adsorbate has no terminal hydrogen to be abstracted, which could enable the

![Figure 11](http://rsta.royalsocietypublishing.org/)

Figure 11. Representations of a local region of the \{111\} surface with various adsorbates bonded to the surface carbons of diamond \{111\} as viewed from slightly above the plane: structures [1], [2], [20]–[27] and [27'], and showing the formation of the three-atom bridge based on the CN radical as a two-atom adsorbate forming structures [27] and [27'], which are rapidly isomerizing. The mechanisms are discussed in more detail in the text. Reaction enthalpy changes are shown in eV (kcal mol\(^{-1}\)).
beta-scission reaction. Since the beta-scission channel is blocked for the CN adsorbate, its lifetime on the surface is longer than that of a two- (or more) carbon adsorbate, and the rate of creation of the four-atom island becomes faster and next layer of carbon atom growth is enhanced. Hence, one nitrogen atom (in the form of CN) can dramatically increase the rate of carbon atom growth by enhancing the nucleation of next layer growth on \{111\} surfaces! Other consequences are the increased twinning and defect generation, which are supported by experimental observation (Steeds et al. 1998, 2003; Hunt 1999).

The lifetime of CN adsorbates on the surface will be limited by thermal desorption and hydrogenation reactions, forming \(\text{CH}_x \text{N}_y\) \((x=1, 2; y=1, 2)\) adsorbates, which are then subject to beta-scission reactions. In any case, the lifetime of the CN containing adsorbate is probably longer than that of the two-carbon adsorbate, and thus the growth rate is enhanced.

Once growth of the next layer nucleated from the four-atom island containing nitrogen, structures \([31]\) and \([31']\) in figure 12, the nitrogen in the layer will have no terminal hydrogen. When the following (next) layer of growth is nucleated on the \{111\} surface (presumably somewhere else on the surface) and the growth front at the step edge progresses across the surface, it will encounter the nitrogen site...
which has no terminal hydrogen. This is likely to slow down the kinetics of the one or two carbon addition events by which the growth front propagates, causing pile-up in subsequent growth layers and possibly explaining the ‘macro’ steps often observed on the surface of CVD diamond grown in the presence of nitrogen (Yan & Vohra 1999; de Theije et al. 2000).

5. Summary

This work has presented a model for the formation of crystal twins in CVD diamond materials based on energetically and kinetically plausible reaction steps in the diamond CVD growth environment. The twinning mechanism originates from the formation of a hydrogen-terminated four carbon atom cluster on a local \{111\} surface morphology, which also serves as a nucleus to the next layer of growth. Subsequent growth proceeds by reaction at the step edges with one and two carbon atom containing species. Each cluster has an approximately 50% chance of being a twin, thus the formation of multiple clusters on the same growth plane provides an explanation for the high defect concentration observed in \langle 111 \rangle growth sectors. In addition, the model explains the formation of penetration and contact twins, and the dramatic enhancement in polycrystalline diamond growth rates and morphology changes when small amounts of nitrogen are added to the plasma assisted growth environments.

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Discussion

C. T. B. Foxon (University of Nottingham, UK). Can you improve crystal growth by using off-orientation substrates?

J. E. Butler. Yes, to a limited degree. Use of vicinal cut surfaces obviates the need for creation of the more reactive step edges until all the steps have grown out to a stable surface. This is useful for thin film growth over limited areas, but not for bulk or thick film growth. Eventually, one is back to having to nucleate the next layer of growth and the problems associated with that, e.g. twinning for the \{111\} surfaces.

O. J. Guy (University of Swansea, UK). What is the growth rate of high-quality diamond and how does this compare to the other semiconductors, e.g. silicon carbide?

J. E. Butler. The growth rate of ‘high’ quality diamond can vary from 0.01 to tens of \(\mu\text{m h}^{-1}\) depending on the reactor design and growth recipe and conditions. Generally speaking, slower growth rate is higher quality, but there are significant exceptions to this, particularly of high power density plasmas.

P. W. May (University of Bristol, UK). If nitrogen catalyses the formation of defects on a \{111\} surface, the growth rate should be dependent upon the amount of molecular nitrogen (N\(_2\)) in the gas phase. So why does the growth rate saturate at a N\(_2\) concentration of a few ppm?

J. E. Butler. The growth rate of polycrystalline diamond in a microwave plasma is linear with added nitrogen and it begins to saturate at hundreds of ppm of added nitrogen, which was at about a C/N ratio in the gas phase of approximately 1. There can be many reasons for the saturation in growth rate including the formation HCN and CN in the gas phase lowering the availability of single carbon species like the methyl radical for growth, or reaching a point where the rate-limiting step in growth is not the nucleation of the next layer of growth.

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