

Formation Conditions for Epitaxial Graphene on Diamond (111) Surfaces

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Submitted: 02 Dec 2018; Accepted: 10 Dec 2018; Published: 20 Dec 2018

Abstract

The phase transformation from a non-terminated diamond (111) surface to graphene has in the present study been simulated by using *ab initio* MD calculations at different temperatures and under various reaction conditions. For strict vacuum conditions, the graphitization process was observed to start at about 800 K, with a final graphene-like ad layer obtained at 2500 K. The C-C bonds across the interface were found to be broken gradually with an increase in temperature. The resulting graphene-like ad layer at 2500 K was observed to chemisorb to the underlying diamond surface with 33% of the initial C-C bonds, and with a C-C covalent energy value of 3.4 eV. The corresponding DOS spectra showed a *p*-doped character, as compared with graphene.

When introducing H radicals during the annealing process, a graphene-like ad layer started to be formed at a much lower temperature; 500K. The completeness of the diamond-to-graphene process was found to strongly depend on the concentration of H radicals. When introducing a larger concentration of H radicals into the lattice in the initial part of the annealing process, the formation of a free-standing graphene layer was observed to take place at an even lower H concentration and temperature (1000 K).

Keywords: Diamond, graphene, graphitization, theory, Molecular Dynamics, DFT

Introduction

A monolayer of graphite (i.e., graphene) has recently become a very popular material with very promising electronic properties [1-3]. Graphene is constituted as a two-dimensional hexagonal sheet, in which all C carbons are sp²-hybridized. Today, different types of synthesis techniques for graphene exist; out of which chemical vapor deposition (CVD) of graphene onto Cu (or Pt) surfaces have recently been developed [4-5]. Other examples of techniques include mechanical exfoliation and exfoliation from silicon carbide substrate [6-7]. Within less than 10 years after the first successful synthesis of graphene, a vast number of scientific studies have concentrated on the properties of graphene (e.g., ultrahigh mobility, mass less low-energy excitations, and mechanical strength), as well as of plausible applications for this specific material (e.g., single molecule gas sensor, and electric field effect transistor) [8].

Diamond is a cubic phase of carbon, with quite different properties when compared to graphene (e.g., high break down field, high thermal conductivity, band gap of 5.47 eV). It has theoretically been discussed that diamond (111) surface will be graphitized at a temperature around 2500K [9]. Since the surface atoms of a material have more freedom to move, and also exhibit a higher energy with respect to the bulk material, the upper surface is expected to undergo more severe reconstructions and relaxations with an

increased temperature. For the situation with the graphitization of a diamond (111) surface, there will be an almost perfect lattice matching between an eventually formed graphene structure and the underlying diamond (111) structure. By modeling an interface based on diamond (111) and the basal plane of graphite, a mismatch of less than 2% was calculated. A question may arise if, for well-controlled temperature and pressure parameters, this graphitization process could be controlled in the way to produce epitaxial graphene from the upper surface of diamond (111). The possibility for a diamond-to-graphene formation would be interesting for many applications. For example, a graphene layer adsorbed on a wide band gap diamond substrate can be applied in field effect transistors, which can be designed for various environment working conditions (i.e. bio-compatible sensing, high corrosion condition) but also for RF communication applications [10-11].

Experimental investigations have earlier shown that epitaxial graphene can be formed on a diamond substrate under different experimental setups [12-13]. A multi-layer of graphene was reported to be formed onto diamond under a rapid thermal annealing at low pressure [12]. This transformation of diamond-to-graphene took place on an atomically flat H-terminated single crystalline diamond (111) surface. The reported temperature of the annealing process was 1000 to 1300 °C, and the pressure was ~10⁻³ Pa [12]. In another study, graphene layers were formed on a single crystalline diamond (100) surface in the presence of catalytic Ni, which had initially been deposited onto the diamond surface by e-beam evaporation.

Multilayer graphene were thereafter formed in an annealing process at 800°C, and in an UHV atmosphere [13]. It has also experimentally been shown that epitaxial graphene can be formed by annealing a diamond (111) surface, with iron as a catalyst, under UHV conditions. Iron, Fe, was initially deposited onto the diamond (111) surface by using a thermal deposition technique. With the presence of iron, the graphitization temperature was reduced from 1000 (for a SiC substrate) to 600°C (for the diamond (111) substrate) [14].

In the present study, the condition for forming a monolayer of graphene on the diamond (111) surface has theoretically been investigated using density functional (DFT) calculations under periodic boundary conditions. *Ab initio* molecular dynamics (MD) annealing processes (from 0 K to 2000K) were then used to simulate the geometrical restructuring of the upper diamond (111) surface. The structural evolution process was studied under steady state conditions for each specific temperature chosen, with time steps of 0.15 fs for a total duration of 0.30 ps. All though the total duration of time scale was relatively short, it has here been proven possible to outline the effect by i) temperature, and ii) presence of H radicals, in the initial structural evolution stage of the diamond-to-graphene transformation. The graphitization process was considered under the assumption of three different experimental assumptions. Firstly, a pure thermally induced transformation for diamond (111) to graphene was considered to take place under a strict vacuum condition (i.e. without the presence of gaseous species). Secondly, a sufficient amount of H radicals were introduced to the system during the annealing process. Thirdly, the system was saturated with H radicals prior to the annealing process. The purpose with the present study has also been to elucidate the binding condition over the interface, by calculating the adhesion energy between the developed graphene-like ad layer and the diamond surface. The electronic properties (in the form of partial density of state (DOS) curves) of the hereby constructed epitaxial graphene-like ad layers, have also been of a large interest to investigate, and were in this study calculated and compared with ideal and free-standing graphene.

Methods and Methodology

Density functional theory (DFT) has been used for all of the calculations in the presented work (based on the CASTEP program from BIOVIA [15-17]). Ultra-soft pseudo-potential was applied to describe the core level of atoms under periodic boundary conditions. In previous investigations, graphitization of a diamond (111) surface to graphite has been theoretically studied by using an LDA method, and the result indicated a smooth phase transition from diamond (111) to graphite [18]. In the present investigation, the Perdew-Burke-Ernzerh of (PBE) general gradient approximation (GGA) was used to approximate the exchange and correlation parts of the Hamiltonian [19]. In order to evaluate the different methods of choice, a comparison of calculated equilibrium lattice constants was made (using GGA vs. LDA), and compared Δ with experimental values for both the diamond and graphite lattice. Compared to the Local Density Approximation (LDA), the GGA functional is more accurate since it does not overestimate the bond strengths in the system under investigation. However, GGA has been considered to underestimate the weak interactions across the diamond/graphene structure. Therefore, corrections for these weak interactions were implemented in the study by using dispersive corrections (Tkatchenko-Scheffler scheme) [20]. By using the GGA method with dispersion correction, the lattice parameters of graphite were obtained as $a = b = 2.467 \text{ \AA}$, and $c/a = 1.442$. The LDA method with

dispersion correction resulted in $a = b = 2.448 \text{ \AA}$, and $c/a = 1.432$. The corresponding experimental data of the lattice parameters of graphite are $a = b = 2.461 \text{ \AA}$ and $c/a = 1.363$. It is apparent from this comparison that the GGA method better reproduce the a - and b -axis of the graphite lattice, and hence more correctly describes the in-plane covalent structure of graphite. The LDA method was found to give a better result for the c/a value, indicating that LDA would be a better choice in simulating Van-der-Waals interactions. However, it must be stressed that the difference in c/a value (obtained for both GGA and LDA) is quite small.

For the very large model system used in the present study, the energy cut-off was set to 280 eV, and the generated k-point mesh was selected as $[1 \times 1 \times 1]$ by using the Monkhorst-Pack grid [16]. A serial of higher energy cutoff values (310, 330, 350 eV) were tested in order to evaluate the accuracy of this parameter in the present study. As a result, the difference in energy for these energy cut-off values was less than 0.001 eV/atom. Hence, it was thereby found that a cutoff value of 280 eV is accurate enough for the present system under investigation.

Moreover, *ab-initio* molecular dynamics (MD) were used to evaluate the structural changes of the interfaces, both as a function of time and for various temperatures, in simulating an annealing of the system from 0 K up to 2000 K. An NVT ensemble, in addition to the Nose thermostat, was used for the annealing simulations. The temperatures were thereby set to 0, 300, 500, 800, 1000, 1500 and 2000 K, respectively. The MD time step was set to 1.5 fs, with a total simulation time of 0.3 ps. In order to simulate the cooling down of the system after reaching maximum temperatures, each structure was geometrical optimized (at zero K) with the purpose to elucidate any structural rearrangements that might take place during a rapid cooling stage. Based on these geometry optimized structures, single point calculations were for each temperature used to i) calculate the interlayer adhesion energy, ii) visualize the interfacial C reactivity (by calculating the Fukui functions), and iii) to explore the electronic properties of the interfacial systems.

The adhesion energy between the newly formed “graphene-like ad layer” and the diamond (111) surface was calculated by using equation 1.

$$\Delta E_{\text{adhesion}} = E_{\text{system}} - (E_{\text{graphene}} + E_{\text{lower diamond}}) \quad (1)$$

E_{system} is the total energy of the whole interfacial system, and E_{graphene} and $E_{\text{lower diamond}}$ is the total energy of the graphene-like adlayer and the “new” diamond (111) surface, respectively. As a measure of the averaged adlayer//diamond surface bond strength, the adhesion energy $\Delta E_{\text{adhesion}}$ was thereafter divided by the number of remaining $C_{\text{graphene-like}} - C_{\text{diamond}}$ covalent bonds within the supercell.

Moreover, the Fukui (or frontier) function calculations were performed in the present investigation with the purpose to receive information about the reactivity of the C atoms in the interfacial region [21];

$$f^+(r) = \frac{1}{\Delta N} (\rho_{N+\Delta}(r) - \rho_N(r)) \quad (2)$$

$$f^-(r) = \frac{1}{\Delta N} (\rho_N(r) - \rho_{N-\Delta}(r)) \quad (3)$$

Hence, the f^+ (r) function will visualize the susceptibility towards a nucleophilic attack, and the corresponding f^- (r) function will give information about the susceptibility towards an electrophilic attack. The average of these two functions, f^0 , is of a larger interest in the present investigation since it will show the susceptibility for a radical attack from the gaseous environment (such as radical H species).

Density of state (DOS) spectra for the resulting graphene-like ad layers, were calculated using a $[2 \times 2 \times 1]$ mesh of k-points, and compared to the corresponding DOS spectrum for a monolayer of ideal graphene. The DOS calculations for ideal graphene were using a super cell with an identical number of C atoms as for the graphene-like ad layer, with otherwise identical super cell parameters.

As is the situation for poly-crystalline diamond, the following diamond planes are frequently observed on thin NCD films; [(111), (100) and (110)] (with a preference for the first two types)]. Hence, these three low-index planes have also been included in the present study, in studying the prerequisites for graphene-formation from diamond, and under which conditions the graphitization prefers to take place. However, the present study has concentrated more on the thermally-induced phase transformation for the diamond (111) surface, since the lattice matching between graphene and diamond is most optimal for this specific surface plane. In addition to these perfectly planar terraces, a diamond (111) surface with a mono atomic step edge was also studied in order to investigate the effect

of surface roughness on the diamond-to-graphene transformation (see Fig. 1). The super cell model of a perfectly flat diamond (111) surface does in this work include 432 carbon atoms, distributed over 12 atomic layers with 36 C atoms in each. For the stepped diamond (111) surface model, 396 carbon atoms were distributed over 10 atomic layers with 36 C atoms in each layer. In addition, 18 C atoms were positioned on top of the upper C layer, thereby forming the mono atomic step edge. Careful test-calculations in earlier work by the present research group have shown that these model sizes are adequate to use in the present investigation [22].

For all models used in the present study, a 12 Å thick vacuum layer was added in the super cells. This vacuum layer will ensure that there are no inter-slab interactions that may interfere with the process that has been of interest to investigate in the present study. The thickness of this vacuum layer was tested. A difference of 0.001 eV was found when increasing the vacuum layer to 15 Å. These results showed that the final model was accurate enough for the following geometrical and energetic calculations in the present investigation. Moreover, the lower carbon layer (for all models) was terminated with H atoms in order to saturate the dangling bonds. In order to check if these saturated C atoms will be able to represent a bulk-like diamond structure during the MD-simulations, they were carefully monitored with the purpose to identify any significant displacements during the simulation procedure.

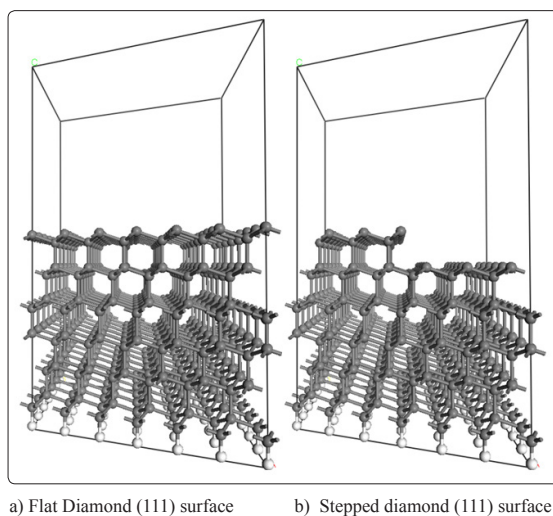


Figure 1: Diamond (111) flat (a) and stepped (b) surface

Results and Discussion

Geometrical Restructuring of the Diamond (111) Surface during Annealing at Low Temperatures

The possibility for graphitization of the upper part of the diamond (111) surface was at first simulated under strict vacuum conditions (i.e., no other gaseous species were present in the models). Two MD calculations (at 300 K and 500 K) were initially performed with the purpose to relax and reconstruct the upper part of the surface. As a result of the geometry relaxation and reconstruction, the upper two C layers within the diamond (111) surface underwent a 2×1 reconstruction towards a Pandey-chain π -binding structure [23]. This process was just initiated at 300 K, and was completely finished at about 500 K (see Fig. 2). The temperature of a Pandey chain structure formation at 500 K was found to be lower than the previous

reported experimental temperatures of 1000 and 1223 K, under UHV conditions [24, 25]. Earlier studies have shown that energy barriers at various extents are needed when transferring diamond (111)- 1×1 to (111)- 2×1 , using highly accurate DFT calculations [22]. It was from those calculations concluded that a Pandey chain reconstruction can take place at quite low temperature for completely non-terminated diamond (111)- 1×1 surface, whilst H-terminated surfaces will require very high temperatures. The (111)- 1×1 to (111)- 2×1 reconstruction requires 0.32 eV for a completely bare surface, and 60 eV for the H-terminated ditto. The energy barriers for (111)- 2×1 to (111)- 1×1 de-reconstruction are even larger. Experimentally, when working at UHV there is certain coverage of H on the surface, and this is most probably the reason to the discrepancy between our observation at 300 K and the experimental one. By considering the

collision frequency of H atoms to the diamond surface, under the assumption of a UHV pressure (10^{-9} Torr), a sticking coefficient of 0.8 and a temperature of 727 C, it will take about 1.8 hours until the diamond (111)-1x1 surface is completely covered with H. Moreover, when considering the larger energy barrier for the (111)-2x1 to (111)-2x1 reconstruction of an H-covered surface, it is understandable that experiments performed at UHV will not give numerical resemblances with theoretical simulations at zero pressure [26].

Based on earlier experimental and theoretical observations, it can here be concluded that a diamond (111) surface reconstruction to a complete Pandey-chain structure is the preferred one at temperatures above (and close to) 500 K, and that this type of reconstruction is likely to completely fill the surface area of diamond (111) [22,24,25,27]. The obtained Pandey-chain reconstruction at these lower temperatures were used as initial structure when continue studying the structural evolution of this system for temperatures above 500 K. For all MD simulations in the present investigation, the total simulation time were chosen to guarantee a stabilized constant of motion (and system total energy) for the part of the simulation where observations were made. To be more specific, the systems did achieve thermal equilibrium at a simulation time of approximately 0.15 ps (see Fig. 3).

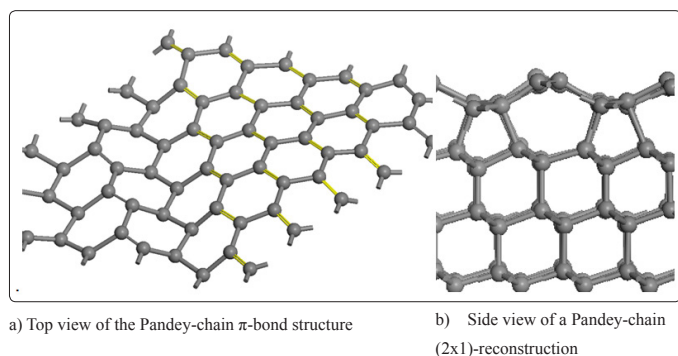


Figure 2: Surface reconstruction obtained at the temperature of 500 K. The top (a) and side (b) views show the transition to a 2x1 Pandey-chain structure

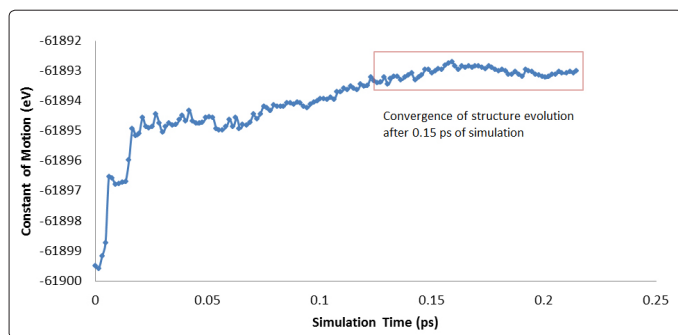


Figure 3: Evolution of the constant of motion during the annealing of a diamond (111) surface at 2000 K

Thermally Induced Transformation of Diamond (111) To Graphene under Strict Vacuum Conditions

In this part of the investigation, a simulation of the diamond-to-graphene formation was performed under the assumption that there are no gaseous species that will interact with the newly formed surfaces (i.e., under strict vacuum condition). The Pandey-chain

reconstructed diamond (111) surface was found to be quite stable, and remained in the same geometry until the temperature was increased to about 800 K. Compared to the results from the *ab initio* MD simulations at 500 K, a geometrical transformation of the upper diamond C layer to graphene-like channels was observed at a temperature of 1000 K. Two nearby-positioned and parallel Pandey chain structures started to merge together, and thereby form this type of single layer graphene channel (with a width of 7 Å and height of 2.5 Å). Hence, an obvious trend was observed in that an increase in temperature (from 500 K to 1000 K) will result in a decrease in number of covalent $C_{\text{diamond}}-C_{\text{graphene-like}}$ bonds between the underlying diamond surface and the graphene-like ad layer. By increasing the temperature to 1500 K, and later on to 2000 K, the graphene-like channels became even more pronounced and well-shaped, and the number of C-C bonds between the two materials decreased even further. In fact, the number of $C_{\text{diamond}}-C_{\text{graphene-like}}$ bonds (in the super cell) that were left between the two structures, decreased from originally 36 (0 K) to 18 (500 K), 14 (1000 K), and 13 (2000 K), respectively. The observed influence of temperature on the diamond (111) surface restructuring, is demonstrated in Figure 4.

The channel-like epitaxial graphene, chemisorbed onto diamond (111), showed a similar structure when compared with the experimental results obtained by Lim et al [28]. This is also the situation with the electronic property of this graphene ad layer, which were observed to be metallic rather than intrinsic graphene (to be discussed further below). Moreover, graphitization of diamond (111) has earlier been studied theoretically by Jung nickel et al [29]. The starting point of a graphitization process on a diamond (111) surface was reported to be the boundary of a twin intersection, which is similar in shape with the reconstructed Pandey-Chain structure used in the present study. As presented in the present study, the 2x1 reconstruction process of non-terminated diamond (111) surface is expected to take place at rather low temperatures (500 to 800K), and will therefore be an important part of the diamond-to-graphene formation when increasing the temperature even further.

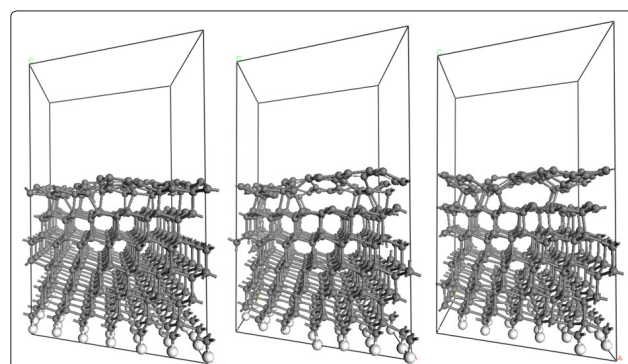


Figure 4: Influence of temperature on surface restructuring for a flat diamond (111) surface; (a) 500 K, (b) 1000 K, and (c) 2000 K.

For the stepped diamond (111) surface, similar changes in surface geometry were observed. A perfect Pandey-chain structure was formed next to the step edge (parallel with the step and on the upper plane) at about 300 K (see Fig. 4a). By increasing the temperature up to 2000K, many of the C-C bonds between the Pandey-chain carbon layer and the lower-laying C layer, were broken. This broader channel, which is 7 Å in width and 2.5 Å in height, was observed at a lower temperature compared to the situation with a perfectly flat diamond (111) surface plane (1000 vs. 2000 K). Due to size-

restrictions when using *ab initio* MD techniques, only very narrow upper terraces can be used in modeling these step edges (as can be seen in Fig. 4). Therefore, the results presented here only gives an indication that for these types of narrow formations, an increase in temperature will cause graphene-like channels that are only connected to the underlying diamond surface at the edges. It is, though, expected that corresponding structural results for broader upper terraces, will be more similar to the above presented results for a perfect diamond (111) plane.

In addition to the Pandey-chain restructuring in parallel with the step edge, a very striking result is the very strong bond formations at the edges of the channel (as shown in Fig. 5). This is a result that is expected for all widths of upper-terraces. The bond strength of these C-C bonds was here calculated to be stronger than the ones between the upper terrace and the lower-lying diamond (111) surface (i.e. more in the middle of the channel); 3.7 vs. 3.4 eV. This explains the difficulties to break these edge bonds during the MD simulation. The reason for having this stronger bond is that the edge C atoms has initially less neighboring carbon atoms, and as such is much more reactive. Therefore, it is more prone to a more local surface reconstruction. Furthermore, for the lower (111) terrace next to the edge, the evolution of a graphene-like channel was formed in the same manner as for a perfect (111) plane.

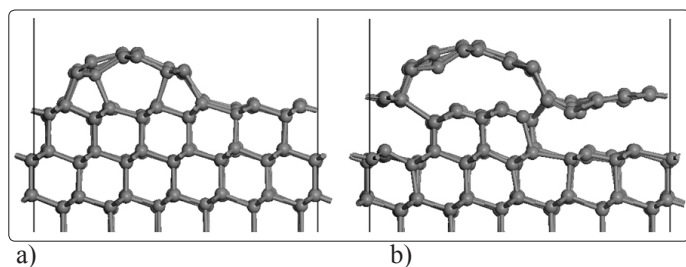


Figure 5: Side views of an annealed diamond (111) stepped surface at (a) 500 K and (b) 2000 K, respectively.

As shown in Figures 4 and 5, the temperature-induced geometrical structure evolution within the phase-pure diamond (111) surface, was observed to start as a local sp^3 to sp^2 transition. By rising the temperature from 500 K to 2000 K, more and more bonds between C atoms (sp^3 hybridized) in the 2nd and 3rd atomic layer were broken to form carbon double bonds (and thereby sp^2 -hybridized C atoms) between the 1st and 2nd atomic C layer. In this procedure, a graphene-like monolayer was gradually formed when increasing the temperature. The average bond lengths for the finally obtained carbon double bonds (within the graphene-like ad layer) were calculated as 1.38 Å for the initially perfectly planar (111) surface, and 1.36 Å for stepped diamond (111) surface. In a previous theoretical work by Ewels et al, the graphitization mechanism at surface dislocation cores within amorphous diamond materials, where studied by using cluster models [30]. The carbon double bonds in their study were found to be somewhat shorter than in the present work; 1.30 Å vs. (1.38/1.36 Å). The main reason to this difference is most probably the fact that the present study is performed with *ab initio* MD simulations at higher temperature, and the results from reference 30 are performed at zero Kelvin. Other contributing to the observed difference in bond length might be the fact that an infinite periodic boundary system was used in the present work, whilst cluster models were used in the previous study [30]. Energetically, it is difficult to make a strict comparison in energies for the previous zero Kelvin calculations

and the molecular dynamic simulations at higher temperatures as presented in the present study.

For comparison, similar simulations were also made for the diamond (100)- 2×1 and (110) surfaces, respectively. The results were found to be completely different in relation to diamond (111). There were no major distortions observed, either for the carbon atom on the surface or further below in the lattice. Similar observations were made for the diamond (110) surface. There was no indication of carbon atom distortion, or C-C bond breakage, up to a temperature of 1000 K.

Introduction of Radical H into the System during the Annealing Processes

In this part of the investigation, a simulation of the diamond-to-graphene formation was performed under the assumption that H is introduced into the system during the annealing process. The temperature used for the H-induced annealing process was set to higher than 1000K. This choice of temperature is in accordance with previous experimental results, where desorption of H from the diamond (111) surface was observed to take place in the temperature interval 900-1300K [26]. When performing MD simulations of the diamond//graphene system at higher temperatures, oscillations of breakages and recombination's of C-C bonds were observed between the diamond (111) surface and the graphene-like ad layer, and also within the respective system (i.e., upper diamond surface and graphene-like ad layer, respectively). It is interesting to note that the occurrences of C-C bond breakage and recombination within the graphene-like layer, and diamond substrate, respectively, were much more frequent than the corresponding processes in between (i.e., within the diamond//graphene interface). In order to explain the reason for this phenomenon, Fukui function, $f^{(0)}$, calculations (i.e. showing the interfacial susceptibility towards a radical attach) were performed for both flat and stepped diamond (111) surfaces at a temperature of 1000 K and 1500 K, respectively. The results from all of these calculations made clear that the C-C bond breakages, which are most often localized in the diamond//graphene-like interface, will cause remaining non-binding diamond (111) carbon atoms that show a large degree of radical reactivity. In the formation of a graphene-like ad layer structure, there is a Pandey chain reconstruction taken place within the upper two diamond (111) C layers. Apparently, the driving force for the formation of these Pandey chain structures, are stronger than the corresponding one for the preservation of the bonds within the initial diamond (111) surface structure. As an effect of the Pandey chain reconstruction, there is a withdrawal of electron density from the interfacial C-C bonds, leaving underlying carbon atoms with a dangling bond (i.e., radical C atoms).

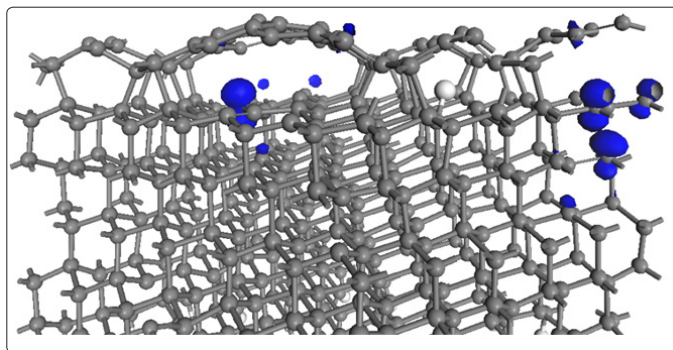


Figure 6: Radical reactivity of C atoms, as calculated by the Fukui functions $f^{(0)}$.

As can be seen in Fig. 6, the most reactive carbon atoms were found in the upper C layers of the newly formed diamond (111) surface. Since these highly reactive C atoms are also very susceptible to a C-C recombination across the diamond//graphene interface, the addition of gaseous radical species is expected to prevent this recombination by terminating the surface and, hence, to make the whole system more thermodynamically stable. It should here be stressed, that gaseous H radicals are small enough to diffuse into the diamond//graphene interface, and to chemisorbs onto the highly reactive surface C atoms on the newly formed, diamond surface.

In order to investigate the structural effect by the H atoms, being introduced into the diamond/graphene system during the annealing process, *ab initio* MD simulations were performed with H radicals positioned interstitially within the interface. The aim was here to model the evolution of the geometrical structure when increasing the temperature, and at the same time introducing more and more H radicals to the interfacial system. Figure 7 shows the result when introducing only one H radical at 1000 K. As a result of the *ab initio* MD simulations at this temperature, the number of remaining C-C bonds between the diamond surface and the graphene-like ad layer, was significantly decreased comparing to the corresponding situation with no H in the system.

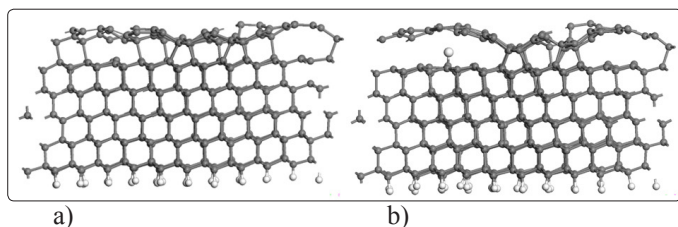


Figure 7: The structural changes of the upper diamond (111) surface at 1000 K without any H radicals (a), and with one H radical in the vicinity to a radical C site within the interface (b).

For the simulations at 1500 and 2000 K with 2, 3 and 4 interstitially positioned H radicals, it was observed that all H radicals will aid in the breakage of $C_{\text{diamond surface}}-C_{\text{graphene}}$ bonds in the interface, and thereby bind to radically active carbon atoms on the newly formed diamond (111) surface. The bond breaking effect by the H radicals was found to be very efficient for the addition of the first H radical into the system (as compared with adding more H radicals to the system). For comparison, an MD simulation was done at the same temperature, but with all radical C atoms saturated with chemisorbed H radicals. An extra H radical was also positioned within the interface. For this highly saturated situation, this extra H radical showed the efficiency to break more C-C bonds than just a single H does (see Figure 8).

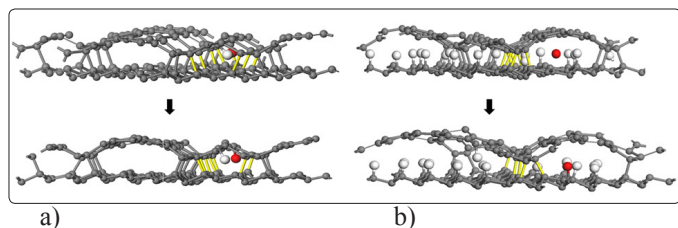


Figure 8: The effect of interstitially positioned H radicals (marked with red color) in an unsaturated (a), and H-saturated (b), diamond-graphene interface. The upper figures show the starting structures, and the lower ones show the resulting structures at thermal equilibrium ($T=1000\text{K}$).

The efficiency of an even larger number of radical H atoms, being present in the upper surface area during the course of the annealing process, has been tested at 1000K. This number of H atoms (33) is assumed to be large enough to saturate the developing C radicals.

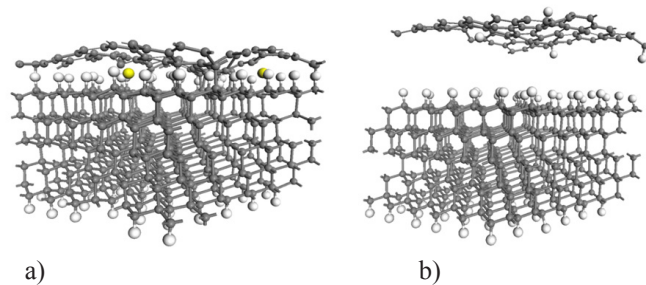


Figure 9: Initial (a), and resulting (b), structure after annealing at 1000 K.

As can be seen in Fig. 9, these H atoms are extremely efficient in causing a complete lift-off of a graphene sheet (although somewhat H-terminated) at 1000K, with no sign of any bonding between the graphene and the resulting diamond (111) surface.

Introduction of a Larger Concentration of H Radicals in the Initial Part of the Annealing Process

In this part of the investigation, a simulation of the diamond-to-graphene formation was performed under the assumption that a larger concentration of H has been introduced to the system in the initial part of the annealing process. A sequentially increased number of H radicals (9, 12 and 17) were then introduced into the initially ideal diamond (111) upper surface (i.e., between C layer 2 and 3). For a temperature at 1000 K, a quite dramatic result was observed when going from 9 to 17 H interstitials. The remaining $C_{\text{diamond}}-C_{\text{graphene}}$ bonds were only 7 when adding 9 H radicals to the lattice. However, this number decreased to 0 when introducing 17 H radicals (H/C_{surface} was 0.47, see Figure 10).

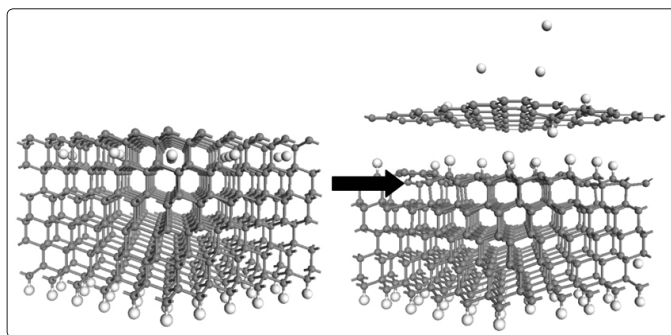


Figure 10: Graphene evolution from the diamond (111) surface, with 17 H radicals in the system at 1000 K.

Adhesion Energy between Graphene and a Diamond Surface

For all of the different temperatures used in the present study, the adhesion energy between the diamond surface and the graphene-like ad layer was calculated by following an *ab initio* MD simulation by geometry optimization at zero Kelvin (as described in the Section 2). The average bond energies for the C-C bonds at the various temperatures were in a range of 3.7 eV (at 500 K) to 3.4 eV (at 2000 K). These values correspond to the bond length range 1.46 Å to 1.66 Å. The corresponding experimental values for a C-C sp^3 bond are 3.6 eV and 1.54 Å. This comparison gives an indication

that, in addition to covalent C-C bonds, there are also dispersion interactions between the diamond surface and the graphene-like allayer (at least at lower temperatures).

Electronic States for the Graphene-like Ad layer

The electronic property of the graphene-like ad layer produced without H at 500 K and with 18 $C_{\text{diamond}}-C_{\text{graphene}}$ bonds left, was in the present study compared with the one for ideal graphene. As can be seen in Fig. 11, the Density of States (DOS) for the graphene-like ad layer (solid line) has a very similar shape as the one for ideal graphene (non-solid line). A DOS minimum at 0 eV (the Fermi level) can be found for both structures. This is an indication that the graphene-like ad layer has also a cone shape band cross at the Fermi level, and will thereby show similar electronic properties as a single layer graphene.

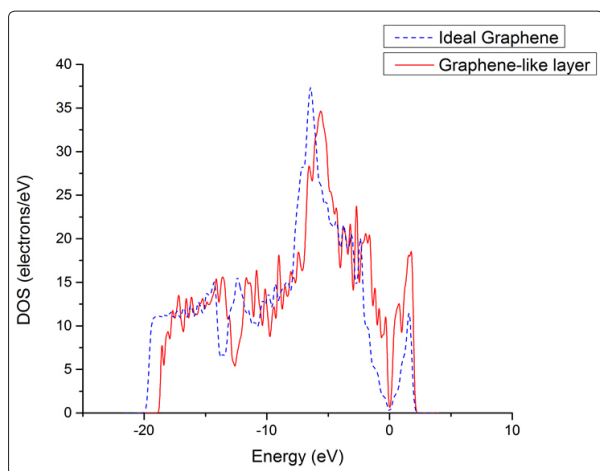


Figure 11: Comparison of DOS spectra for a graphene-like ad layer and an ideal graphene

Summary and Conclusion

The formation conditions for a temperature-induced formation of epitaxial graphene onto a diamond surface, has in the present study been simulated and analyzed using first principle Density Functional Theory techniques. The result showed that graphene can only be formed on a perfectly planar diamond (111) surface. For a perfect vacuum condition, a graphene-like ad layer was formed at about 1500K. The graphitization process was observed to start at about 800 K by forming Pandey chain structures on the diamond (111) surface. In the course of a temperature increase, the extent of C-C bond breakages across the interface, were gradually enlarged. When the temperature reached 2000 K, a graphene-like ad layer was obtained with 33% of the original interfacial C-C bonds. More generally, the interfacial C-C bond energies were calculated to be in the range 3.4 to 3.7 eV, which correspond to the bond lengths 1.66 to 1.46 Å. The weaker C-C bonds were obtained from an annealing at 2000K, whilst the stronger bond strengths were the results of annealing at 500K. Moreover, the topology of this epitaxial graphene was found to be almost identical to ideal graphene, but with the exception that it is not a true 2D structure. The corresponding DOS spectrum of the graphene ad layer showed a p-doped character, which is very similar to the situation graphene.

With the presence of H radicals in the system, two different experimental-like approaches were investigated; a) introduction of H radicals during the annealing process, and b) introduction of

H radicals before the annealing process. For the former situation, the H radical were observed to saturate the radical C formation that takes place within the upper part of the diamond (111) surface during the annealing process. The overall effect by the H radicals were to accelerate the graphitization process within the first and second C layer of the diamond (111) surface, and to stabilize the third and fourth layer of the surface. More specifically, the diamond-to-graphene formation was observed to take place at a substantially lower temperature, as compared with the situation without H in the system. A monolayer of graphene started to be formed at 1000 K, whilst the completeness of the diamond-to-graphene process was found to depend on the concentration of H radicals in the lattice. Up to a certain H concentration, there was a strict relation between the number of H radicals in the super cell and the number of interfacial C-C bond breakages. At the temperature of 1000 K, a complete and free-standing graphene monolayer was formed when introducing 34 H radicals to the system (corresponding to the breakage of 36 interfacial C-C bonds).

For the situation with the introduction of H atoms into the system prior to annealing, an even stronger acceleration in the graphitization process took place. More specifically, the diamond-to-graphene formation was observed to take place. For the temperature of 1000 K, a complete and free-standing graphene monolayer was obtained for only 17 H radicals in the super cell). Hence, this is identical to a reduction in H concentrations with about 50%.

The temperature values presented in this theoretical study are different to the experimentally obtained ones. However, the here presented MD calculations have been performed at strict vacuum conditions (i.e., zero pressure), whilst the experimental investigations have been performed at, at least, UHV conditions, with a non-avoidable extent of surface termination that will change the kinetics, and therefore the temperature, for the diamond-to-graphene processes. Other more plausible causes to the difference in temperature are, e.g., degree of surface roughness (for the experimental investigations). However, it must be stressed that the aim and purpose with the present study has been to show the effect by radical H. An introduction of a certain concentration of H into the diamond system will lower the temperature needed to transform diamond (111) to graphene. In addition, this effect is strongly correlated to the concentration of H.

Acknowledgments

This work was supported by the FP7 Marie Curie ITN network MATCON-238201. The computational results were obtained using Materials Studio from BIOVIA.

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