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Theoretical Study of the Effect of an Fe Interlayer on the Formation of Graphene on a Diamond (1 1 1) Surface

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Abstract

The effect by a catalytic Fe interlayer on the formation of graphene onto a diamond (111) substrate, has been studied by using DFT calculations under perodict boundary conditions. With varying the Fe interlayer thickness from two to five atomic layers, geometry optimized diamond//Fe//graphene multilayer models were obtained. A general result was that the Fe atoms are ontop positioned on both the graphene carbon atoms and on the diamond carbon atoms. Moreover, both the interfacial diamond//Fe and Fe//graphene adhesion energies were calculated and compared. As a result, the interaction between graphene and the iron layer, which was indentified as of an electrostatic nature, was found to be weak (-12.3 to -10.5 kJ/mol per graphene C atom) and propotional to the thickness of the Fe layer. The thicker the Fe interlayer, the stronger was the adhesion energy. On the contrary, the adhesion energy for the binding of a Fe layer on the diamond substrate was calculated as much stronger (-124.5 to -109.0 kJ/mol per diamond C atom), and following an inverse correlation. The thicker the Fe interlayer, the weaker is the interfacial adhesion energy. Calculations of electron density differences and partial Density of States (pDOS´s), will further support the results of a quantum size effect of the iron layer.

Keywords: Materials; Conductivity; Relativity; Polarization; Adhesion energy

Introduction

Graphene, as the pioneer of two dimensional structured materials, possesses many excellent properties, such as high carrier mobility, zero bandgap, high mechanical strength and transparency [1,2]. It has attracted much more attention since the first demonstration of separation from graphite [3]. However, in order to be successful for the various applications, the synthesis of large area, or patterned, graphene has become a challenge topic. Recently, an experimental study of Fe-mediated epitaxial graphene growth on a diamond substrate, has been presented. It was not only shown to be able to lower the temperature of the growth process, but also, with the thin interlayer of Fe, to control the size of epitaxial graphene [4].

As another member of the carbon family, diamond is also a well-known material with enormous excellent properties (such as high thermal conductivity [5], high breakdown voltage, and chemical inertness [6]). Since chemical vapor deposition (CVD) methods have been very successful in synthesizing different forms of diamond [7,8] (e.g. poly-crystalline, nano-crystalline and single crystalline diamond), the different types of applications of diamond have increased dramatically [9-13].

The diamond (111) surface is one of the most common surface planes of CVD synthesized diamond. The surface has a bi-layer structure, with every two carbon layers close to each other in the z-direction. In addition, there is a very low lattice mismatch (2%) when compared with basal plane of graphene. Due to these circumstances, the upper part of the diamond (111) surface has earlier been found to transfer to graphite at a relatively high temperature [14-16]. It was reported to take place at a temperature of at least 900 K under the effect of a catalyst (i.e., Ni, Fe etc.) [4,17].

In the present study, the epitaxial graphene growth on the diamond (111) substrate, with different interlayers of Fe (fcc) as a catalyst, has theoretically been studied using density functional theory (DFT) under periodic boundary conditions. The effect of number of iron atomic layers on the adhesion energies and interlayer structures, of graphene onto the iron interlayer, was especially studied. In addition, the resulting electronic structure of graphene was analyzed by calculating the partial density of states.

Methods and Models

The Density Functional Theory (DFT) method, under periodic boundary conditions, has been used within the present investigation. To be more specific, the CASTEP program within the Materials Studio package (Accelrys, Inc.) has been used for all calculations in the present study [18,19]. As can be seen in Figure 1, the super cell model was built as a multilayer with a diamond (111) surface slab as the bottom layer, followed by an Fe (fcc) (111) layer, and a single graphene layer on top of the Fe interlayer. The purpose with the present study was thereby to simulate the diamond (111)-to-graphene transfer at a high temperature treatment by using the Fe interlayer as a catalytic seave, through which C from diamond will be transported up to the Fe surface and forming a graphene layer. It has earlier been shown experimentally that the size of this graphene layer will be determined by the size of the monocrystalline diamond (111) surface [3]. In addition, the layers of graphene sheets was in reference [3] observed to depend on the duration of the heat treatment. The bottom layer of the diamond slab was saturated with H in order to simulate a continuation into the bulk. For the same reason, it was also kept fixed during the geometry optimization. The diamond (111)//Fe multilayer was built in 4 different Fe layer thicknessess (2, 3, 4 and 5, respectively) with the purpose to investigate the effect of this variation on the graphitization process. For each of these thicknesses,

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the graphene layer was positioned ontop of Fe in two different ways (i.e., either with the graphene C atoms in ontop position relative the diamond surface C atoms, or with the graphene C atoms in the corresponding diamond hollow positions) (Figure 2).

The core level electrons were described by using ultrasoft pseudo-potentials, as suggested by Vanderbilt [20]. In order to check the role of relativistic effects that might be induced by the heavier Fe atoms, an all electrons basis set (with relativistic effects) was used in calculations by using the DFT-based Dmol3 module from Accelrys, Inc. For these calculations, a 1x1 diamond//Fe//graphene supercell was used. The results of these test-calculations showed an energy difference between the CASTEP (non-relativistic effects) and the DMol3 (relativistic effects) of as low as 1 kJ/mol per atom. As a result, it was not found necessary to include relativistic effects for this type of Fe-containing multilayer. Hence, the CASTEP program was used for the rest of the calculations in the present study. Moreover, the Perdew-Burke-Ernzerhof (PBE) general gradient approximation (GGA) was used to approximate the electron exchange and correlation parts of the Hamiltonian [21]. Spin-polarized calculations (GG(S)A) were performed for all systems in the present study since Fe includes non-paired electrons in its d orbitals. In addition, an energy cut-off of 400 eV was used for the plane wave functions. The k-points used for the geometry optimization of the diamond//Fe//graphene supercell were generated as 3x3x1 by using the Monkhorst-Pack scheme [22]. For the electronic properties calculation, 23x23x1 (i.e., in total 265 irreducible k-points) were used for a converted supercell of all structures. The reason to convert the high-symmetry structures into the smallest supercell, was to save computing time. However, a dramatically increased k-points setup had to be used in order to maintain the accuracy of the calculations.

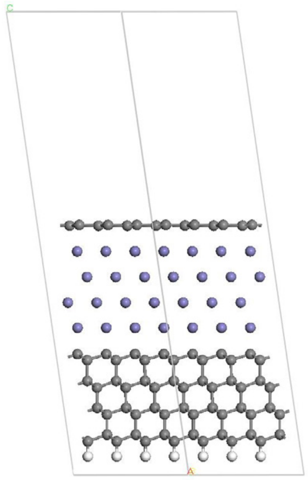

Figure 1: Model of a diamond(111)//Fe//graphene multilayer structure, with 4 atomic layers of Fe(fcc).

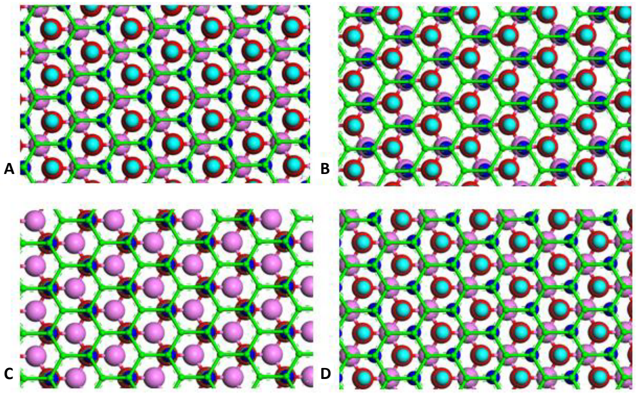

Figure 2: Top views of geometry optimized diamond//Fe//graphene structures with different atomic layers of Fe; 2 (a), 3 (b), 4 (c), and 5 (d). The green layer demonstrates graphene, and the dark blue atoms indicate the upper Fe atoms (closest to graphene). The light blue atoms indicate the lower positioned Fe atoms that are closest to the diamond slab. Moreover, the red and pink atoms representing the first and second layer of diamond.

The adhesion energies have been calculated by using

$$E_{adh\_G\_Fe} = E_{tot} - E_{graphene} - E_{diamond//Fe} \tag{1}$$

$$E_{adh\_Fe\_D} = E_{tot} - E_{graphene//Fe} - E_{diamond} \tag{2}$$

Where, E_{tot} is the total energy of the complete diamond//Fe//graphene system, $E_{graphene}$ is the energy of the graphene monolayer, $E_{G//Fe}$ is the energy of the graphene//Fe interlayer and $E_{diamond//Fe}$ is the energy of the diamond//Fe interlayer.

Results and Discussions

Geometrical structures

It has been of a large interest to also investigate the effect of the Fe layer thickness on the resulting multilayer structure, and especially on the interfacial stabilities. For this purpose, four different atomic layers of Fe has been used: 2,3,4 and 5. Top views of the resulting structures are shown in Figure 2.

At first, the geometrical structure of the diamond//Fe interface, with four atomic layers of Fe, was studied. A series of single point energies (i.e., no geometry optimizations) were performed, where the distance between the upper diamond surface and the lower Fe layer where altered. The purpose was to find the most optimal interfacial distance, with, hence, the strongest interaction energy. This distance was thereafter chosen for the geometry optimization of the whole interface (but with a frozen lower C layer, with its terminating H species). A sideview of the initial and final diamond//Fe structure can be seen in Figure 1.

This optimized diamond//Fe structure was thereafter used in constructing the diamond//Fe//graphene multilayer. A similar procedure was also for this structure performed, where the graphene monolayer were sequentially positioned closer to the upper Fe surface, with the purpose to find the most stable configuration. In this process, two different lateral positions of graphene was used: (i) $C_{graphene}$ ontop Fe, but non-ontop $C_{diamond}$, and (ii) $C_{graphene}$ non-ontop Fe, but ontop $C_{diamond}$. For these structures, Fe refers to an upper surface Fe atom, and $C_{diamond}$ refers to an upper surface diamond C atom. Moreover, a position non-ontop $C_{diamond}$ means that the graphene C atoms are positioned in hollow positions with respect to the upper layer diamond structure (Figure 2).

Figure 2A demonstrates the optimized structure for the situation with $C_{graphene}$ ontop a two-atomic layer thick Fe interlayer, but non-ontop $C_{diamond}$. It is, from this figure, clear that the graphene C atoms prefer to stay ontop the upper Fe atoms. This tendency is even further supported in Figures 2B and 2D, where the initial structure was as well based on $C_{graphene}$ ontop Fe, but non ontop $C_{diamond}$. The only exception was the situation with four atomic layers of iron. Since the Fe (fcc) (001) structure repeat itself every four atomic layers in the z-direction, it was the only case where $C_{graphene}$ was found both on top Fe and ontop $C_{diamond}$

(Figure 2C). As a result of the geometry optimization, the Fe//graphene region relaxes towards $C_{graphene}$ ontop Fe, but non-ontop $C_{diamond}$. It is very interesting to notice that this ontop behaviour between Fe and C is the prefered one for both C phases (i.e., diamond and graphene). The geometrical results, as presented in Figure 2, have from here on been used in the forthcoming diamond//Fe//graphene multilayers (i.e., with $C_{graphene}$ ontop Fe).

As an observation for all Fe thicknesses, the lower Fe atoms were found to be strickly positioned ontop of the surface carbon layer atoms in diamond (111) surface. This was, with one minor exception, also observed for the upper Fe// graphene interface. A slight shift from ontop position of $C_{graphene}$ onto Fe was observed for a 3 atomic layer thick Fe slab.

Since there is an, in principle, strict ontop positioning for C (diamond or graphene) versus Fe, the orientation of $C_{graphene}$ with respect to $C_{diamond}$ was found to depend on the number of Fe layers. Hence, for multilayers with either 2 or 5 Fe atomic layers, the graphene C atoms that were binding to Fe were positioning over diamond hollow positions (Figures 3A and 3D). Moreover, a multilayer with 3 Fe atomic layers, resulted in Fe-binding $C_{graphene}$ to be position above C atoms in the second diamond layer. Finally, a multilayer with 4 Fe atomic layers, resulted in Fe-binding $C_{graphene}$ to be position above C atoms in the first diamond layer. These relative positioning is further demonstrated by the side views of the various multilayer structures (Figure 3).

Adhesion energy

In order to study the effect of iron interlayer thickness, on the growth of epitaxial graphene, the adhesion energies of (i) graphene ontop diamond//Fe, and (ii) graphene //Fe// ontop diamond, have been calculated in the present study.

As can be seen in Figure 4A, the adhesion energies for graphene attached to diamond//Fe was calculated to be within the range -0.109 to -0.127 eV (per carbon atom), depending on the thickness of the iron layer. The smallest adhesion energy (-0.109 eV) was for a two atomic layer thick Fe interlayer, then the adhesion energy increased by following the increased thickness of layers and eventually to -0,127 eV in case of 5 layers of Fe. However, it must be stressed that this difference in adhesion energy is very small. Moreover, 3 layers of Fe interlayer caused slightly higher adhesion energy as -0.122 eV than the case of 4 layers Fe and the reason was, as shown in Figure 2B, that graphene layer had a minor shift from ontop towards bridge position. On the other hand, the adhesion energies for an attached Fe//graphene layer onto diamond (111), were observed to be much stronger than the one between diamond//Fe and graphene. The adhesion energy for a two atomic thick Fe interlayer, was calculated as -1.29 eV (per carbon atom), which is the strongest among all Fe thicknesses investigated. When the number of iron layers was increased to 5, the adhesion energy became -1.13 eV, which is the weakest adhesion of all Fe thicknesses investigated. Moreover, the adhesion energy between the diamond and the Fe//graphene layers, was in strong correlation with $C_{diamond}$-Fe bond distances (Figure 4 vs. Figure 5). It must be stressed that the calculated Fe-C bond lengths will be equal to the distance between those layers, since the Fe atoms were observed to reside strictly ontop of the carbon atoms (Figure 2). This correlation is most probably due to an Fe quantum size effect, which is a circumstance that will be analyzed more in detail in the Section below.

Electronic structure of the system

Electron density difference calculations will result in the changes in electron density distribution when the individual atoms are forming the model system. Hence, it is due to the formation of bonds in the model systems. If a covalent bond is formed between two atoms, therewill

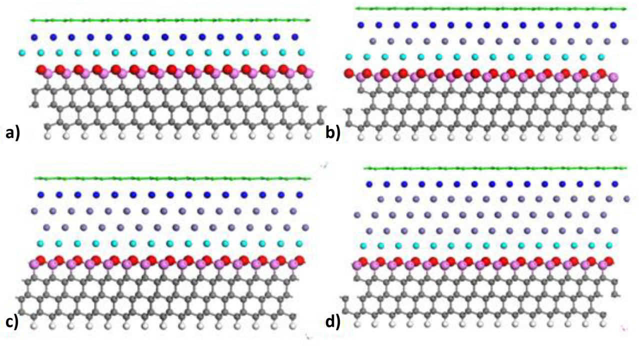

Figure 3: Side views of geometry optimized diamond//Fe//graphene structures with different atomic layers of Fe; 2 (a), 3 (b), 4 (c), and 5 (d). The green layer demonstrates graphene, and the dark blue atoms indicate the upper Fe atoms (closest to graphene). The light blue atoms indicate the lower positioned Fe atoms that are closest to the diamond slab. Moreover, the red and pink atoms representing the first and second layer of diamond.

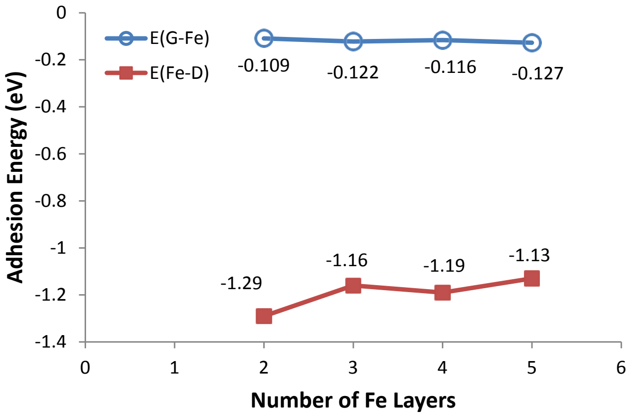

Figure 4: Calculated adhesion energies (per carbon atom) for a) graphene attached Fe//diamond (circles), and b) Fe//graphene attached to diamond (111) (squares).

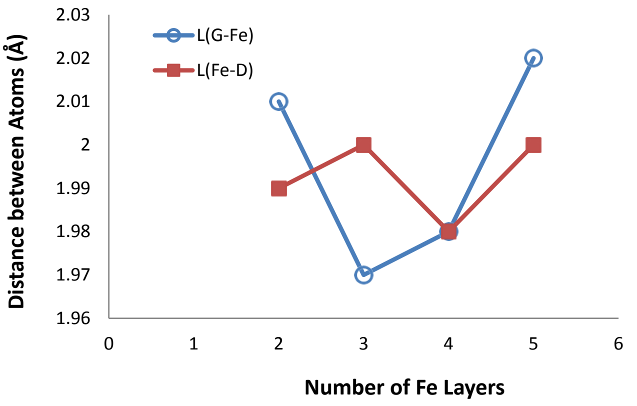

Figure 5: The closest distances between C atoms from graphene and Fe atom and Fe atoms to C atoms from diamond surface

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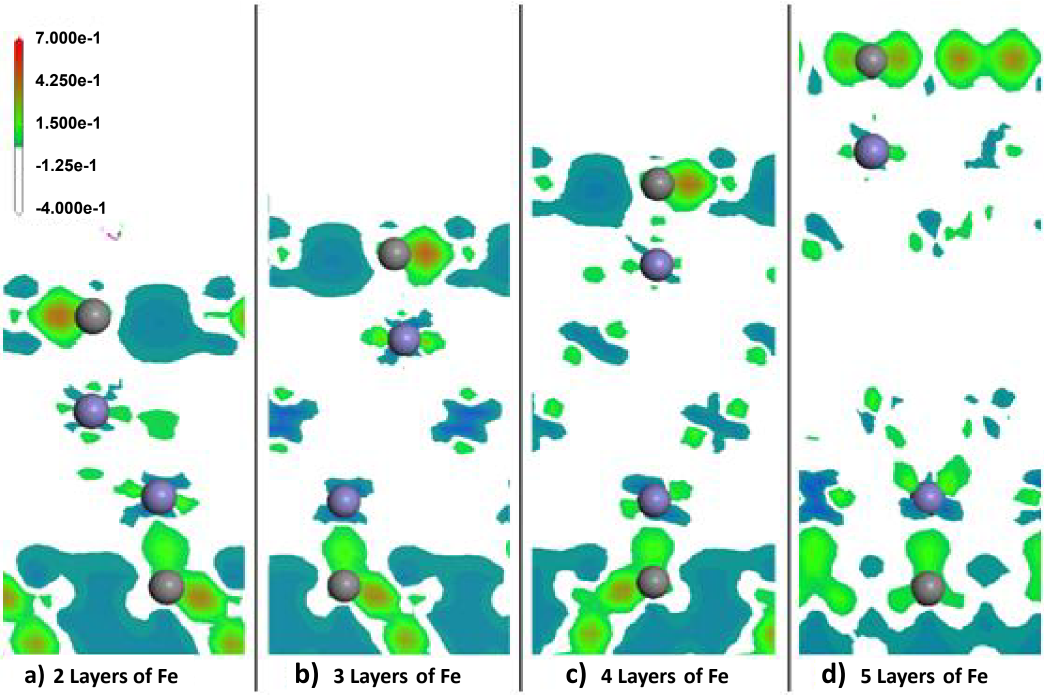
be an electron density gain in between the atoms (e.g. indicating the increased number of electrons in that position). As shown in Figure 6, the electron density coloured red and green (in the upper part of the scales shown in Figure 6), represents the binding area, and the colours from the lower part of the scales indicate electron. As can be seen in Figure 6, within the interface formed by the graphene layer and the Fe surface , the values of electron density difference was found to be minor. On the contrary, the interactions between the diamond substrate and the Fe atoms within the lower interface, the electron difference values were quite larger. The is a result that strongly correlate with the respective adhesion energy, and thereby the interfacial bond strength. It is interesting to see the formations of both p-type like bond formations, in addition to sp^3-hybridized orbitals, could be identified in the area of the carbon atoms.

In addition to the electron density difference calculations, also partial Density of State (pDOS) calculations have been made. The DOS for the graphene adlayer can be seen Figure 7A. For comparison, also the DOS for a freestanding graphene sheet is included in Figure 7A. It is obvious that the graphene adlayers with an Fe layer beneath, have an increased electron density at the Fermi level, thereby showing a metallic property. Moreover, the pDOS spectra show similar features for the different Fe layer thicknesses. For a five atomic thick Fe layer, the pDOS spectra was though slightly shifted to higher energies in the region from approximately -5 eV and upwards. The same trend was also observed for the diamond surface in the energy region close to the Fermi level (Figure 7C) The diamond pDOS spectrum for a five atomic Fe layer also showed an increased intensity close to the Fermi level at an energy of about -1 eV. It must be stressed that no major difference in pDOS spectra was observed for the graphene layer and diamond substrate for the thinner Fe layers (i.e., two, three, and four atomic Fe layers).

The DOS spectra for the Fe interlayer are shown in Figure 7B. As can be seen in this Figure, the with of the DOS spectra decreased with an increase in Fe atomic layers. The underlying reasons to this observation are most probably twofold. One explanation is the quantum size effect, which for this situation is one dimensional. The second factor that most probably will influence the spectra is the bonding with both the diamond substrate and the graphene adlayer. It is well-known that the formation of an interface will affect the DOS spectra for both involved surfaces in the interacting states will either be shifted and/or change in form. This fact is clearly demonstrated for the diamond (111) surface (Figure 7A), and for the graphene adlayer (Figure 7C).

Summary and Conclusion

In the present study, the effect by an interlayer of Fe (fcc) on the diamond-to-graphene formation, has been studied theoretically by using DFT calculations under periodic boundary conditions. The epitaxial formation of graphene onto diamond(111)//Fe were thereby studied with respect to interfacial geometries, interfacial adhesion energies, and electronic structures. The thickness of the Fe interlayer was set from 2 atomic layers up to 5 atomic layers. As a result of the geometry optimization, it was clear that the graphene atoms tend to position ontop of the Fe surface atoms (e.g., C ontop of Fe). Similarly, Fe interlayer atoms were observed to bind to the diamond surface in ontop positions. The only exception was the situation with three layers of Fe, where the orientation of the carbon atoms within the graphene layer was found to be slightly shifted towards bridge positions. A clear correlation was observed between Fe thickness and the adhesion energy between graphene and the diamond//Fe interlayer. By increasing the Fe thickness from 2 to 5 layers, the adhesion energy increased (in absolute values) from 0.109 to 0.127 eV. On the other hand, there was the reverse correlation between Fe layer thickness and the adhesion energy between diamond and Fe//graphene. In absolute values, the adhesion energy decreased from 1.29 to 1.13 eV (these correlations did include the exception by the three atomic Fe layer). The interfacial adhesion energy between diamond//Fe and graphene was electrostatic in nature,



a) 2 Layers of Fe b) 3 Layers of Fe c) 4 Layers of Fe d) 5 Layers of Fe

Figure 6: Electron density differences for various Fe interlayer thicknesses; a) two d) three a) four d) five layers, respectively.

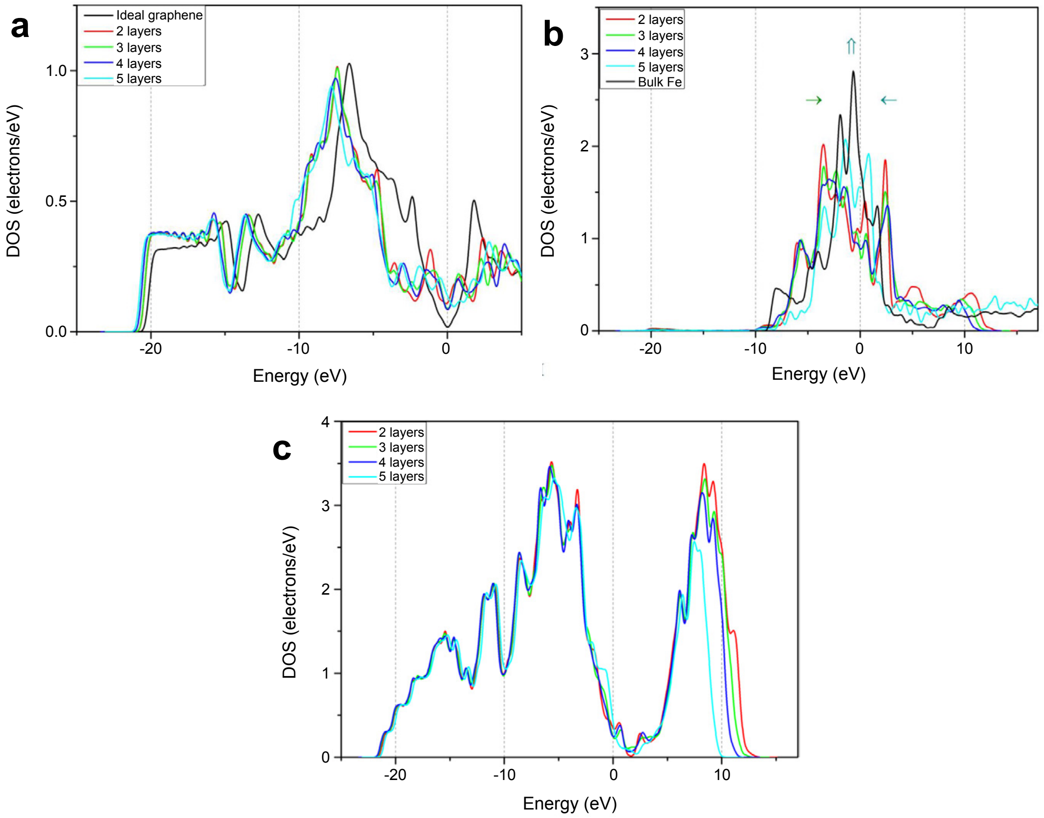


Figure 7: The density of states (DOS) for a) graphene, b) the Fe interlayer, and c) the diamond (111) surface for various numbers of Fe atomic layers.

whilst the adhesion energy between diamond and the Fe//graphene was more of a covalent nature. These results are well supported by the analysis of the respective electron density difference maps.

Density of State (DOS) calculations were performed in order to further analyze the electronic structures for the various systems. As a result, the pDOS spectra of the graphene layers were observed to have a higher electronic density at the Fermi level (as compared to a free-standing graphene sheet). This implied that these graphene adlayers do show a metallic conductivity. Moreover, the pDOS spectra of the Fe interlayer showed a strong dependence by the Fe interlayer thickness. The width of the spectra decreased with an increased number of Fe atomic layers. This indicates a one-dimensional quantum confinement effect. In addition, the binding of the Fe interlayer to both the diamond substrate and the graphene adlayer, is expected to induce a shift and/or broadening of the peaks that are interacting with the diamond surface, and the graphene layer, respectively. This is a circumstance that is proved by the changes in pDOS structure close to the Fermi level, for both the diamond surface and graphene, respectively.

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