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Adsorption of Carbon, Silicon, and Germanium

Adatoms on Graphene Sheet

A thesis submitted in partial satisfaction
of the requirements for the degree Master of Science
in Chemical Engineering

by

Erica Cahyadi

2012

ABSTRACT OF THE THESIS

Adsorption of Carbon, Silicon, and Germanium Adatoms on Graphene Sheet

by

Erica Cahyadi

Master of Science in Chemical Engineering

University of California, Los Angeles, 2012

Professor Jane P. Chang, Chair

Film growth is characterized by the making and breaking of chemical bonds. Other interactions such as Van der Waals and electrostatic forces are secondary if not negligible. The primary purpose of this thesis is to provide an assessment on how epitaxial growth on an inert substrate, i.e. no dangling bonds, can proceed. This is done by calculating the adsorption energy of carbon (C), silicon (Si), and germanium (Ge) adatoms at different sites on graphene sheet and mapping their potential energy surface. We observe that adsorption energy of carbon on graphene is the strongest, 1.45 eV more than that of silicon and 1.56 eV more than germanium. The second part of this thesis is observing how C, Si and Ge dimers behave on graphene. Carbon dimer still displays the strongest interaction with graphene, yet the binding strength of germanium dimer

surpasses that of silicon's in these dimer simulations. All calculations are done by the ab-initio density functional theory.

The thesis of Erica Cahyadi is approved.

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University of California, Los Angeles

2012

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1. Introduction

Epitaxial growth refers to depositing film on top of a crystalline substrate in orderly manner, replicating the atomic arrangement of the substrate. This epitaxy process is important and vastly used in nanoelectronics as it is capable to grow high quality thin films with various compositions. The commonly used methods for epitaxial growth are chemical vapor deposition, vapor phase epitaxy, and molecular beam epitaxy.

There are three modes of epitaxial growth, namely Frank-van der Merwe (FV), Volmer-Weber (VW) and Stranski-Krastanov (SK). FV is growth of films one layer at a time. This is usually the most favorable mode of growth when film stress is negligible. In VW growth, adatoms form islands initially as adatom-adatom interaction is stronger than adatom-surface interaction. The islands eventually coalesce to form film. Islands can take up different shapes depending on the diffusion barriers around them (usually asymmetric). Lastly in SK growth, thin film is formed layer by layer at first before it reaches its critical thickness – depends on chemical and physical properties of the substrate and adatoms [1]– and then VW growth takes over. Growth usually forms strong interaction, i.e ionic or covalent bonds, between diffusing atoms and substrate; when an island of two or more atoms is grown, its position is fixed onto the substrate. [2]

In a chemically inert substrate, dangling bonds are absent. Thus the force that is attracting diffusing atoms to the substrate is either electrostatic or Van der Waals force. These forces, which are relatively weak, are not the same for all elements as they depend on the number of electrons in the valence band and the polarity of an atom. Typically, before reaching the critical

nuclei, adatoms can migrate easily around the substrate as the diffusion barrier is low. Initial growth occurs at the defect sites or surface edges. [2]

Graphene, a two-dimensional honeycomb structure consists of carbon atoms, has been one of the most studied semimetal in nanotechnology since its discovery in 2004. This is mostly due to its stable and unique electronic properties: very high mobility, monolayer thick, zero bandgap and good transporting properties as the charge carrier mobility can go beyond $10^4 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$. The electronic properties of graphene can be altered by different types of adsorbates.

The surface of graphene is very inert. It has a potential field with exceedingly low amplitude of undulation to atoms impinging onto the surface from a source. Once on the surface, the atoms lose sufficient amount of energy giving them almost no chance of desorbing again. These adatoms form equilibrium with the edges of existing 2-dimensional clusters, which are known as nuclei. Under a given substrate temperature, there is always a corresponding density of adatoms, obtained via the rate of detachment (which is exponentially dependent on substrate temperature via activation energy, i.e. the bond energy of edge atoms at the perimeter of 2-D clusters) being equal to the rate of attachment (which is proportional to the density of adatoms). When that happens, the system is said to be in equilibrium. In this thesis, we study the behavior of carbon, silicon and germanium adatoms on graphene sheet. Some description of the choices of adatoms studied in this thesis are presented below.

1.1. Carbon

Carbon is basic element of organic matter. As graphene is made of carbon atoms, it is intuitive to test how carbon adatoms would react on top of it. We would like to observe whether the carbon adatoms will form bonds with the graphene underneath, form another graphene layer, or will just nucleate, forming an island above it.

Another reason to study carbon adatoms is that an additional layer of graphene on an existing one would alter its overall band structure. This simulation can potentially be valuable in the study of a gate tunable band gap in bilayer graphene and even of a gate tunable band overlap in trilayer graphene. [3] Currently, the bilayer graphene field- effect transistor (FET) is extensively being studied. Although a pure bilayer graphene also has zero bandgap energy just like the single layer, electric field can be applied to break the inversion symmetric AB-stacked layers thus inducing non-zero bandgap. Zhang et al. found that the bandgap can be increased up to 250 meV. This tunable bandgap property would be a breakthrough in semiconductor industry as it provides tremendous flexibility in designing devices, especially in the FET applications. [4]

1.2. Silicon

The study of heteroepitaxy on graphene substrate can be a potential revolution in electronics industry. We would like to observe whether graphene can be a flexible atomic template that can enable the fabrication of single crystalline semiconductors over amorphous surfaces.

One of the reasons why silicon is chosen is that it is often called the father of semiconductor industry; is the most used semiconductor material in micro and nanotechnology. Just like carbon, silicon is a group IV element and can also form 2-D honeycomb structure called silicene. [5] Houssa et al. mentions that if one could successfully grow silicene, it would be a more favorable material to nanotechnology than graphene. It is shown that due to the strong bond and low polarity of Si-C bond, it is both thermodynamically and kinetically stable. [6] Thus this is a good reason for us to want to observe how silicon adatoms diffuse on top of graphene sheet and to calculate their binding energy. It should be noted though that in heteroepitaxy, which is growing crystals on top of a different crystalline substrate, lattice mismatch is an important issue that governs how the crystal will grow.

1.3. Germanium

Germanium is the next element on the same column in the periodic table as carbon and silicon. Thus, they are isovalent and can demonstrate strong chemical interaction with graphene [7]. The electron mobility in germanium is twice as fast as that in silicon, yet one of the factors that limits the use of germanium is that it has non-stable oxide. It is also much more expensive than silicon. Germanium is also used in this study as the length of a Ge-Ge bond is the same as the distance between two adjacent carbon atoms in graphene. Along with C and Si, Ge can also form a monolayer honeycomb structure called germene. In this thesis, we would like to look at the strength of Ge-C bonds in a single adatom and dimer systems. This can be advantageous in the study of germanium-based devices. [6] Below is a table summarizing the properties of each element chosen in this thesis.

Table 1 – theoretical bond length and bond strength for molecules that will be presented in this thesis. [8]

Type of bond (single bond)	Bond Length (Å)	Bond Strength (eV)
Si-C	1.54	4.67
Ge-C	1.95	4.76
C-C	1.85	6.29
Si-Si	2.37	3.38
Ge-Ge	2.46	2.73
C-C in graphene	1.42	N/A

2. Computational Method

One of the objectives of this thesis is to map the potential energy surface (PES) of an adatom on graphene. Because the making and breaking of bonds are needed to calculate this potential energy, an accurate quantum mechanical system consisting the many-electron system is a requirement [9]. That is where the first principle calculation, Density Functional Theory (DFT) calculations come into place.

DFT calculates the ground state energy and the force of a system, which is the derivative of the energy. For this entire simulations, Fritz Haber Institute ab-initio molecular simulations package (FHI-aims) are utilized. Fhi-aims is an accurate all-electron, full-potential electronic structure code package for computational materials science including density functional theory, which is used for isolated molecules as well as periodic boundary conditions. [10]

One element that is necessary to understand in DFT is the exchange and correlation. The exchange refers to the difference in energy when two electrons switch coordinates. The correlation part ensures that electrons are not described as individual particles, instead as a collection or “cloud” of electrons, which can then be defined wholly from their electronic density. Conventionally, if the position of one electron is changed, the neighboring electrons will also move in order to maintain the most favorable (low energy) location. However, if we take correlation into accounts, changing the position of one density has no direct influence to the adjacent density. The interaction of individual electron is essentially traded off with this approximation.

We used generalized gradient approximation (GGA) which when compared to local spin density (LSD) favors density inhomogeneity more. It also refines the total and atomization energies, stretches and contracts bonds and improves energy barriers and structural energy differences.

[11] With respect to Local density approximation (LDA), GGA defines band gaps more accurately as LDA tends to underestimate their magnitude by over 50%. DFT calculations usually do not incorporate the electrostatic or the Van der Waals force between atoms.

Fortunately, Van der Waals interaction can be added to our computations. This is important as graphene does not have dangling bonds, so although covalent bonds are still possible with some strain and stress, Van der Waals force is the one that governs the interaction between adatoms and graphene. [12]

2.1. K-grid Setting

A single k point is enough to generate wave functions that characterize electronic wave functions for some k-space region. Boundary conditions for a bulk material set the number and range of k points that allow the existence of electronic states. This range of k points is directly related to the volume of the material and only a finite number of k points are needed for electronic potential and total energy calculation. [13]

This number of k points or grid for our system has to be selected in a way that will give us the maximum accuracy in our energy calculations. We calculate energies for our 1x1 cell at different mesh point setting, 2x2x2, 4x4x2, and so on at an increment of 2 up to 12x12x2. We conclude that the energy is converged at 10x10x2 as the value does not change when we increase the grid to 12. For accuracy purpose, we choose 24 as our grid in a 1x1 cell system as we will go up to 4x4 cell, and still want to retain accuracy in this simulation. We used 8x8x2 for a 3x3 cell and 6x6x2 for a 4x4 cell in the simulations.

2.2. Accuracy setting

In order to have efficiency and accuracy in our numerical computations, a basis set that represents the Hilbert space of the electron is needed [14]. There are a number of basis sets with different complexity in first principle calculations. The two main groups include the atomic orbitals (AO) and molecular orbital (MO) [15]. These basis sets are made of Slater-type orbitals or Gaussian function defined in the discussion of semi-empirical methods. There is usually a

trade-off between the set size for accurate calculation and the numerical algorithms availability for individual basis functions. For our DFT calculation, the basis function we use is the numerically tabulated numeric atom-centered orbital (NAO) which gives us the advantage of flexibility, allowing compact element-dependent basis sets and great accuracy computations within meV convergence scale. [14]

Fhi-aims offers 4 types of accuracy settings to choose: light_194, light, tight, and really tight. Each of them is different in the size of the basis function and numerical implementations such as the k-mesh setting. In order to determine which setting to use, we perform calculations for lattice constant, explained in the next section, for each setting. The data collected shows that the adsorption energies for both light_194 and light are the same, and so do the energies for both tight and really tight (Figure 1). The values for energy between the two groups are significantly different, thus we concluded that light_194 and light are not accurate enough, and really tight is unnecessary as it gives the same result as the tight setting and is computationally more expensive. We use the tight setting for all our simulations.

2.3. Lattice constant and unit cell

By symmetry, a graphene unit cell consists of 2 carbon atoms. We obtain the lattice constant of 2.464 Å by calculating the energy of the system while varying the distance between the 2 carbon atoms from 2.1 to 2.9 Å (0.1 increment). Figure 1 below shows this lattice constant computation results described before using Fhi-aims. These calculations are done using four different accuracy settings – light_194, light, tight and really tight. The lowest energy, or highest negative

value, should be the most desirable distance between the atoms, Thus, we can say that it is the lattice constant of a graphene sheet. After we obtain a value, about 2.5 Å from this plot, we refine our calculation up to 0.01, then 0.001 accuracy. This 2.464 Å is our final value and it agrees with many journal publications. [16]

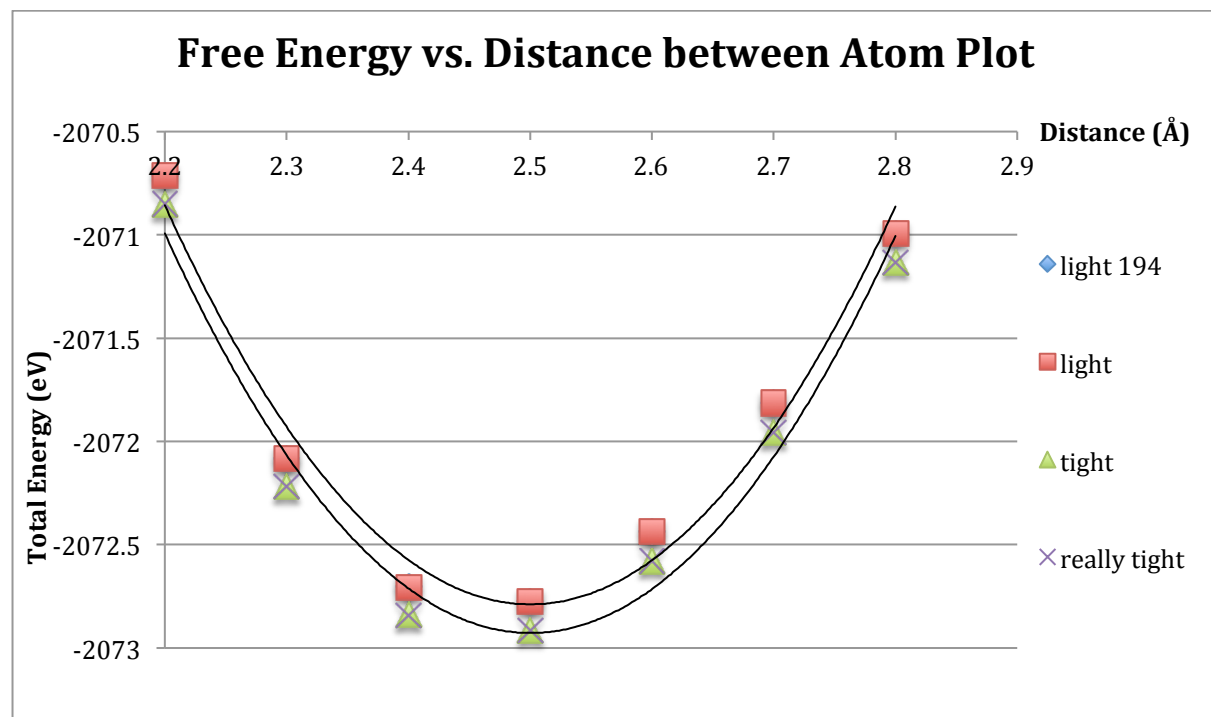


Figure 1 – The free energy vs. distance between two carbon atoms to determine the optimum length of graphene’s lattice spacing.

The next step in our calculation is to determine the optimum size of unit cell to be used throughout our calculations. This is done by placing a single adatom, i.e. silicon adatom, on a graphene sheet with varying sizes. Because there are two carbon atoms in a single or 1x1 unit cell, and because we are using a periodic boundary condition, adding an adatom would result in a 1/2 coverage for silicon adatom. Our next set of simulations is mapping potential energy surface for different adatoms and this 1/2 coverage is too high; there is still interactions from the neighboring adatoms. Thus, we continue to run the same experiment, but keep on increasing the

cell size up to 4x4 (1/32 coverage). The adsorption energy of the single adatom keeps on increasing rapidly as we lower the surface coverage. The adsorption energy tapers at 3x3 cell. The energy still goes down in 4x4, but the difference is only approximately 30 meV (very little) so we conclude that it is accurate enough use the 3x3 cell for our next calculations.

3. Potential Energy Surface

The behavior of C, Si and Ge adatoms diffusing on a graphene sheet can be observed by mapping the surface energy plot. Potential energy surface (PES) is the energy of a molecule as a function of its geometry [17]. Adsorption energy is calculated as follow:

$$E_{tot} = E_{graphene} + E_{isolated\ adatom} + E_b \quad \text{Equation 1}$$

Where E_{tot} is the total energy of the system, $E_{graphene}$ is the energy of graphene only, $E_{isolated\ adatom}$ is the energy of a single adatom, and E_b is the binding energy, which is what we want to find. Arranging the equation, we get:

$$E_b = E_{tot} - E_{graphene} - E_{isolated\ adatom} \quad \text{Equation 2}$$

Adsorption is an exothermic process. Energy is released when an atom is attracted to the substrate hence the negative value of the change in enthalpy and free energy. Potential energy plot is also needed to better understand the diffusion pathways of adatoms, such as recognizing the local and global minima. On this PES plot, minima represents favorable sites for adsorption

while the saddle points determine the activation energy for diffusion along different paths [18]. The diffusion pathways can be guessed by tracking the energy barriers, as an adatom would go for a detour in order to cross the lowest barriers.

3.1. Simulation Set up

All calculations are done by Fhi-aims software described before. We do these PES calculations in a 3x3 cell by fixing the x and y coordinates of the adatom at ten different points in the graphene hexagonal structure and let the z coordinate and graphene underneath to relax. We then calculate the adsorption energy of Ge, Si and C adatom on each of the site. The sites chosen are shown in Figure 2 below. Site A is called the bridge site as it is on the C-C bond. Site J and site D are called the top and the hollow sites respectively. Because graphene has 12 lines of symmetry, it is enough to choose sites from this small triangular portion as MATLAB can be used afterwards to map it to other parts of the hexagon.

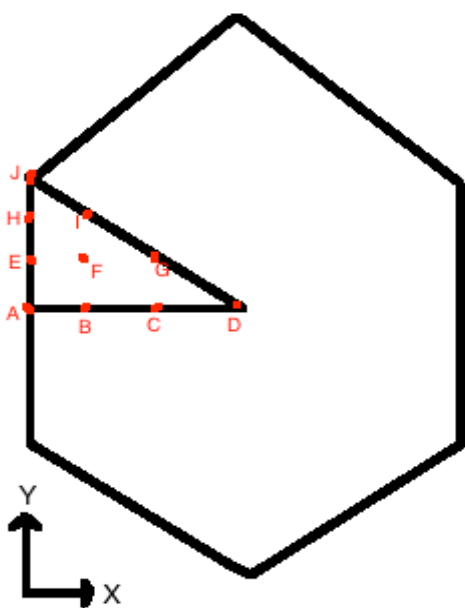


Figure 2 – schematic drawing of graphene with 10 different points chosen.

3.1.1. Carbon

First set of simulation is placing carbon atom on graphene. As the calculations are done in a 3x3 cell, we have a 1/18 coverage of carbon in the system. Table 2 below lists the results, which is the adsorption or binding energy of carbon adatom at ten different sites.

Table 2 – C adsorption energy on the 10 different sites

Site	C Ads. Energy (eV)
A	-2.729
B	-2.594
C	-2.080
D	-0.826
E	-2.704
F	-2.549
G	-1.980
H	-2.439
I	-2.383
J	-2.249

It is clear that the lowest energy value, which refers to the strongest binding energy, is located on the bridge site (site A) of graphene. The adatom makes two bonds with the two carbon atoms underneath, which explains the strong bonds. Adatom at the top site creates a single bond with the carbon atom on the graphene, this is also shown by a relatively low value for the adsorption energy.

The highest energy corresponds to the hollow site of the graphene as the adatom does not bond

with the graphene underneath. The difference between the global maximum and minimum is 1.9 eV, which is extremely large compared to the difference between the minimum and any sites other than the hollow site. The diffusion barrier for this carbon adatom is calculated to be 25 meV.

The next step after obtaining these energy values is to create a potential energy surface plot. With MATLAB, it is possible to replicate results for a single hexagon in graphene to multiple hexagons, nine in this case, in order to have a more complete picture and better understanding of diffusion path of this adatom. Figure 3 below is a 3-D Figure of the binding energy showing the peaks and the troughs, which corresponds to unfavorable and stable sites respectively. All the peaks shown here are the hollow sites of graphene. There is no significant difference in energy for the top and bridge sites of graphene.

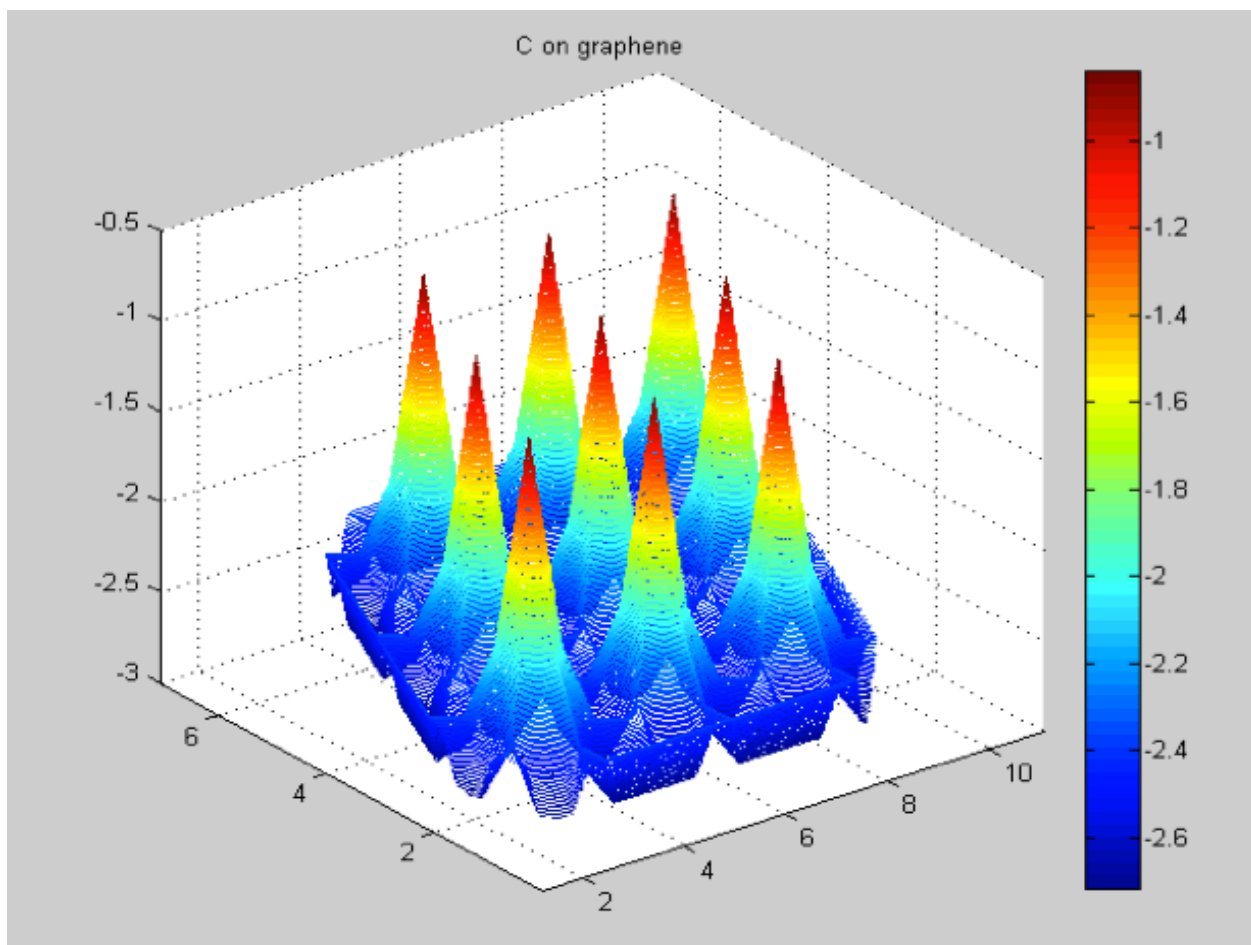


Figure 3– Contour plot mapping the PES of C adatom on graphene

3.1.2. Silicon

The next adatom chosen in this PES study is silicon. The average adsorption energy presented in Table 3 below is noticeably higher than that of carbon adatom, about 1.06 eV. This means that carbon adatom binds stronger to graphene than silicon adatom does. From this table it can also be observed that the trend of binding strength of silicon adatom at each site is similar to the ones for carbon adatom. The highest energy, -0.791 eV corresponds to the hollow site of the graphene, and the two lowest binding energies, 1.279 and 1.277 eV are found where the adatom is close to

the bridge site of graphene. The diffusion barrier of this silicon adatom in the graphene sheet is calculated to be 10 meV.

Table 3 – Si adsorption energy on the 10 different sites

Site	Si Ads. Energy (eV)
A	-1.267
B	-1.277
C	-1.253
D	-0.791
E	-1.249
F	-1.283
G	-1.232
H	-1.209
I	-1.279
J	-1.143

Figure 4 below shows the 3-D plot of the adsorption energy vs. the sites chosen. The same set up as Figure 3 are used in MATLAB. A similar plot is also obtained here. The nine red peaks refer to the hollow site of the graphene sheet and the blue troughs refer to the bridge and top sites of graphene.

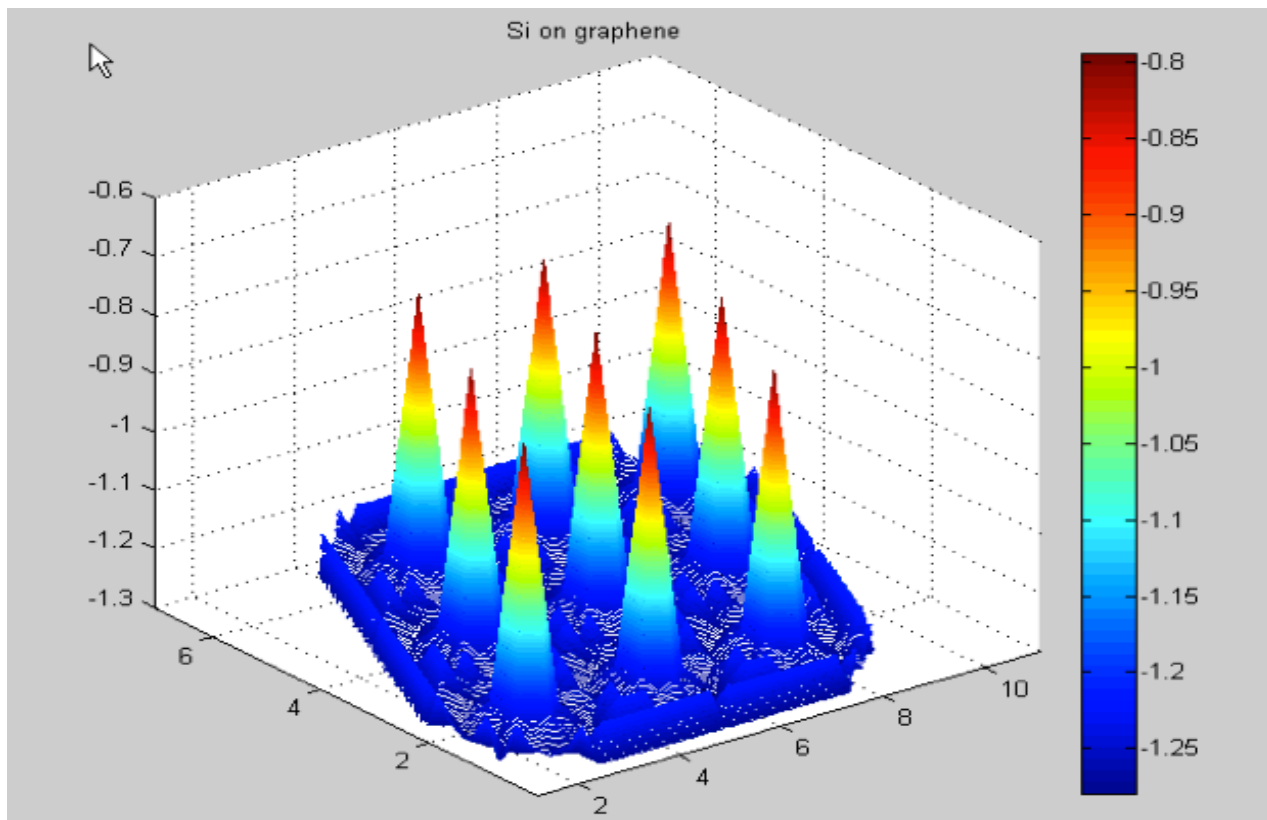


Figure 4 – Contour plot mapping the PES of Si adatom on graphene

3.1.3. Germanium

The adsorption energies are even higher for germanium adatom, with an average of 1.18 eV higher than that of carbon adatom, and 0.13 eV higher than silicon adatom. The distance between Ge adatom and graphene is also higher than that of carbon and silicon adatoms. As the atomic number (molecular weight) increases, the free energy becomes higher. However, the adsorption energy is still negative for all sites, which means that the interaction to graphene underneath is still stable and favorable. This is because heavier atoms tend to be less stable. [19] For germanium adatom, no Ge-C bonds are formed; only Van der Waals interaction exists.

Table 4 below summarizes the adsorption energy for germanium adatoms at ten different sites. The most favorable binding site is also found on the graphene bridge. The diffusion barrier for germanium adatom is 12 meV. We did the same set up to plot the 3-D potential energy surface, shown in Figure 5. We can see a similar plot and trend to the ones for carbon and silicon. – nine red peaks at the hollow sites and blue troughs for all other sites.

Table 4 – Ge adsorption energy on the 10 different sites

Site	Ge Ads. Energy (eV)
A	-1.174
B	-1.162
C	-0.947
D	-0.748
E	-1.158
F	-1.159
G	-1.016
H	-1.116
I	-1.152
J	-1.084

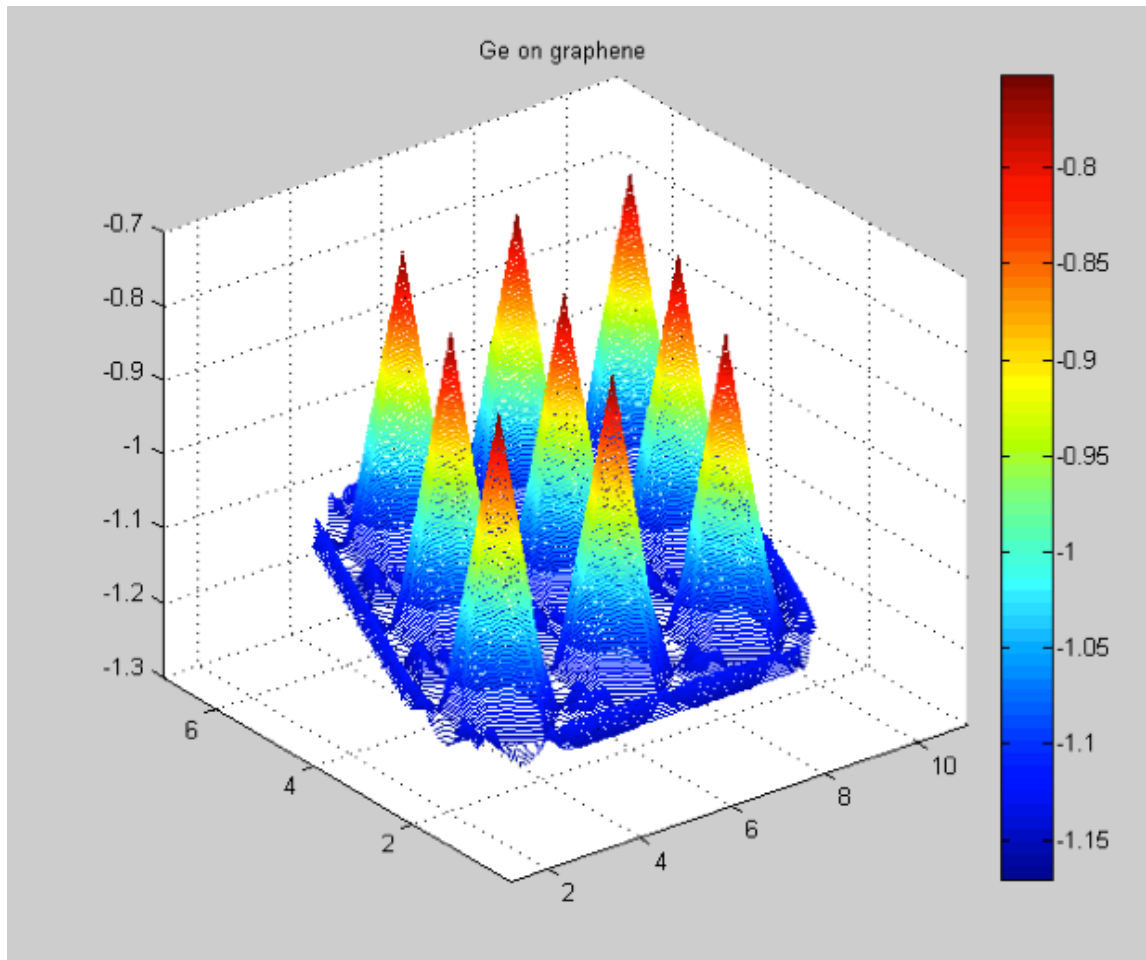


Figure 5 – Contour plot mapping the PES of Ge adatom on graphene

4. Dimer

It is well known in epitaxy that film formation proceeds in a sequence of steps that starts with atoms being trapped in the surface potential well, becoming adatoms. The adatoms diffuse along the surface until they form nuclei of 2-D islands by combining with other adatoms, or attaching to the step edges of existing islands. The nucleation of the two-dimensional islands is typically associated with a nucleation barrier and the corresponding critical nucleus size. Knowledge of the nucleation barrier for a given adatom-surface combination is crucial for controlling the film

morphology and growth kinetics. Specific nucleation barrier can be obtained by considering the energies of clusters of adatoms, e.g. dimers, trimers, etc

The study of dimer can potentially indicate a pattern for atoms nucleation. Aside from the diffusion barrier that adatoms have to overcome, there is no other energy barrier that prevents the formation of dimers. Thus, there is an instant attraction when two adatoms meet. For two silicon adatoms, once they are bonded, the energy to separate them is about 1.33 eV. [20]

In early stage of diffusion, atoms are more likely to relax to the local minimum as they still do not have enough kinetic energy and energy transfer at the shallower site is more effective. [21] When more adatoms reach the adsorbed atoms and form an island, they will try to relax and look for an energetically more favorable site, the global minimum. The pathways of this island depend on how atoms are bonded to one another and how they are attached to the substrate.

In order to have a stable island, the energy of the entire system has to be negative. Initially, when atoms are too few to be stable, there are a lot of dangling bonds, which add positive “boundary free energy” to the system. As more adatoms join to nucleate, the number of unsaturated bonds decrease and the attraction energy among atoms eventually becomes large enough to avoid dissociation; an addition of one more atom will only make the island more stable. [21] The number of atoms needed to form this stable island is often referred to the critical nucleus. When the critical nucleus is reached, island prefers to grow than to shrink. This fact is also one of the reasons why studying dimer is important here. For carbon, it can be intuitively expected that a 6-member ring is the critical nucleus size so a dimer can be viewed as the initial step (likely to be unstable) towards the construction of the 6-member critical nucleus. Future work along this line of research is to build up carbon nuclei from dimer onward to 6-member rings.

4.1. Simulation Set up

Even though we concluded before that an adatom in a 3x3 cell does not interact with another adatom in the next periodic cell, we want to enlarge our cell size to simulate nucleation. This is because we are going to deal with more than one adatom and we still want to isolate them.

Our dimer is arranged by placing one adatom horizontally adjacent to another adatom, 2.464 Å apart (length of a unit cell). In this adsorption energy calculation, ten different sites on graphene sheet, just like any other previous simulations, are explored. The binding energy is calculated as follow:

$$E_b = E_{tot} - E_{graphene} - E_{isolated\ dimer} \quad \text{Equation 3}$$

Unlike in the previous simulation where the adatoms are constrained at specific coordinates, they are allowed to relax to their favorable position in this set of simulations.

4.1.1. Carbon

The first simulation deals with carbon atoms as the dimer. After the dimers are placed in ten different sites, they relaxed to three different final configurations shown in Figure 6 below.

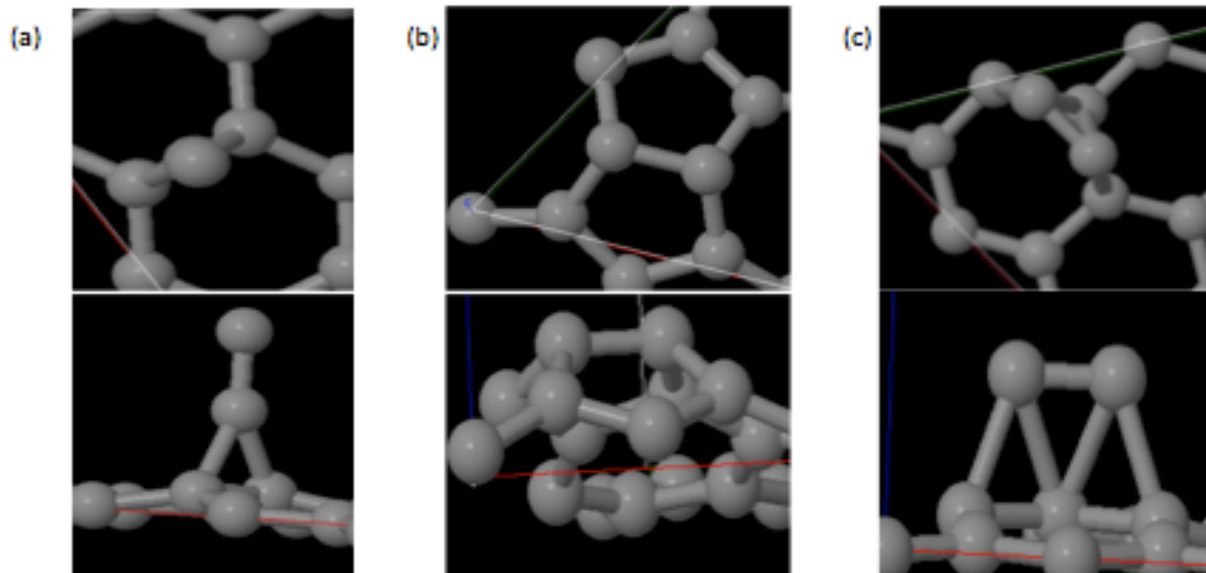


Figure 6 – Top and side views of the three final geometries of carbon dimers

Figure 6(a) shows the first configuration observed. It has adsorption energy of -2.59 eV, which is the lowest among the three configurations. The two adatoms position themselves on top of one another (vertically), with the bottom one bonding to two of the carbon atoms in the graphene sheet. The distance between graphene and dimer is 1.36 Å for the closer adatom and 2.64 Å for the farther one. Observe that the two carbon atoms on the graphene that are bonded with the dimer are slightly pulled upwards.

For the second final configuration, Figure 6(b), the adsorption energy is -2.45 eV. The dimer clearly inserts itself to the graphene's hexagonal structure, forming two carbon pentagons. To better see what happens to the graphene sheet, we also provide the side view of the geometry.

We also observe that the form of the graphene sheet is distorted; the entire graphene sheet is no longer flat here. This deformity might be the cause of the slightly higher adsorption energy

although the entire system is considered favorable (negative value in energy). This is not good for graphene as this final geometry can alter its chemical and electronic properties.

The last configuration for carbon dimer is shown in Figure 6(c). The dimer sits 1.59 Å on top of the bridge sites of the graphene with each of the carbon atom from the dimer bonded with two other carbon atoms from the graphene. Even though the system is still stable and favorable (negative adsorption energy of -1.77 eV), this final geometry possesses the largest energy compared to the other two dimer configurations we explored before.

4.1.2. Silicon

The next dimer in our analysis is silicon dimer. With DFT calculations, we are able to obtain three final relaxed configurations shown in Figure 7 below. The reported theoretical bond length for C-Si is 1.54 Å and for Si-Si is 2.37 Å. [8] We will present the bond lengths obtained from our simulation results below.

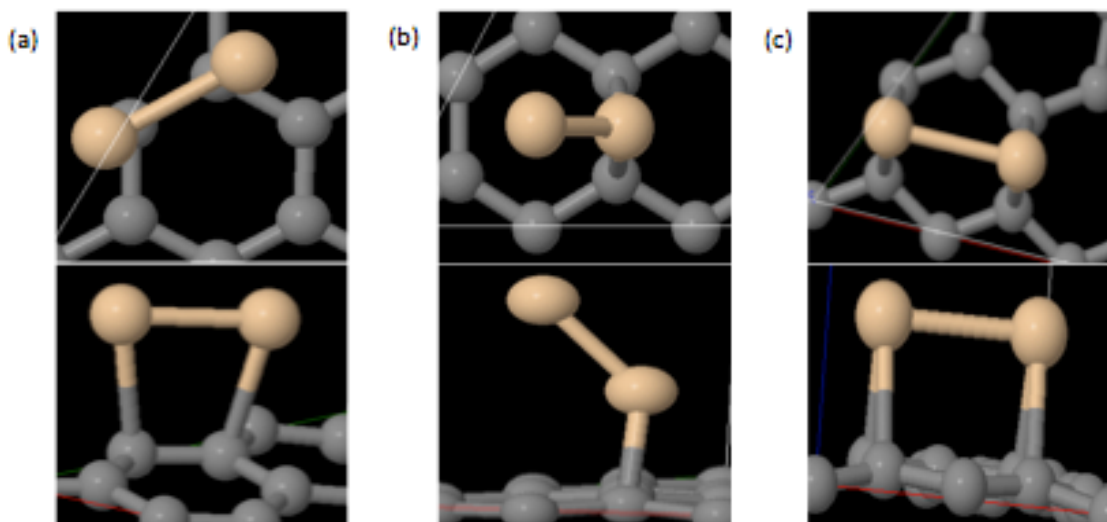


Figure 7 – Top and side views of the three final geometries of silicon dimers

For the first geometry, Figure 7(a), the two silicon adatoms sit on top of the carbon atoms, slightly bent outwards as Si-Si bond is longer than C-C bond. The former overlaps with the latter underneath. With adsorption energy of -0.912 eV, this is the most favorable configuration for silicon dimer on top of graphene. The distance between the dimer and graphene is 2.4 Å, which is about 1 Å higher than the theoretical length.

The second final geometry, which is shown in Figure 7(b) has adsorption energy of -0.389 eV. This is the second most favorable geometry, with one silicon atom sitting at a height of 2.2 Å and the other at 3.9 Å. The lower silicon is located on the bridge site, making bonds with two carbon atoms underneath. The other silicon atom sits on top of the first silicon, protruding to the hollow part of the graphene. Just like the configuration for carbon in Figure 6(b), this system is stable; the slightly higher energy may be caused by not having the dimer exactly vertical.

The third and final configuration, shown in Figure 7(c), has adsorption energy of -0.241 eV. The silicon adatoms sit on top of the bridge site of graphene, bonded with the four carbon atoms underneath. The distance between the dimer and graphene is also 2.2 Å. This is higher than the previous configurations. The reason behind this high energy is because the two silicon atoms are separated 2.464 Å away while the theoretical value for Si-Si bond length is only 2.37 Å. This also may be caused by having the bond on the hollow part of graphene. From the PES calculation, it is shown that atoms do not prefer to be in that region.

4.1.3. Germanium

The germanium dimers on the ten different sites relax to the following four final configurations shown in Figure 8. The energy barrier between the lowest and the second lowest binding energy is calculated to be 40 meV.

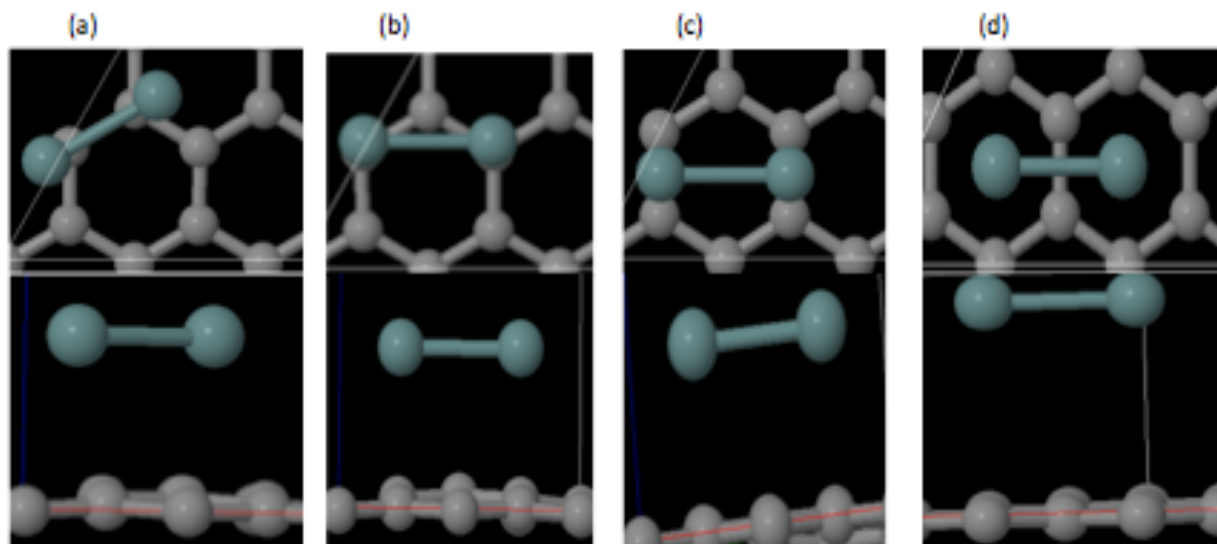


Figure 8 – Top and side views of the four final geometries of germanium dimers

The first configuration shown in Figure 8(a) is similar as Figure 7(a) for silicon dimer. It has adsorption energy of -1.09 eV, which is stable. However, the germanium dimer does not at all make bonds with the graphene underneath; the distance between graphene and dimer is 2.56 Å and the bond length of C-Ge has been reported to be 1.95 Å [8].

This is the most favored configuration as it has the lowest adsorption energy compared to the other three configurations. The two germanium atoms are on top of two carbon atoms in the graphene, slightly stretched outwards as Ge-Ge bond length is longer than the C-C bond in graphene – 2.46 Å compared to 1.42 Å. The bond for the dimer is right on top of one of the

carbon-carbon bond in the ring. The distance between the dimer and graphene is also the shortest here.

Figure 8(b) above is the second most favorable positions for the Ge dimer. The two germanium atoms are still on top of the carbons but this time, the bond is on the hollow part of the graphene. Not having anything underneath may be the cause of the increase in energy. The adsorption energy calculated is -1.05 eV and the distance between graphene and dimer is 2.60 Å

The third configuration shown in Figure 8(c) is the same as Figure 7(c) for silicon adatom. However, the dimer does not bond with the carbon atoms underneath, unlike silicon. The distance between graphene and dimer is also higher up at 2.75 Å. Yet, the adsorption energy is lower, -0.79 eV compared to -0.241 eV of silicon. The adsorption energy for this third configuration is the second to the highest one. The germanium atoms sit on the C-C bonds with the dimer bond across the hollow region. From our PES calculations we show that nothing likes to sit on top of the hollow region.

Figure 8(d) above shows the most unfavorable configurations for germanium dimer, with adsorption energy of -0.68 eV. Now that the adsorption energy gets significantly higher than the previous configurations, the distance between the dimer and graphene is observably larger compared to the other configurations (3.59 Å versus 2.6-2.7 Å). The two germanium atoms sit above the middle (hollow) part of the graphene. From the previous section, it is found that the highest adsorption energy site for the three adatoms is in the middle. This dimer configuration

confirms the finding. Table 5 below summarizes the results for the adsorption energies of the final geometries of C, Si and Ge on graphene sheet.

Table 5 – Binding energies of carbon, silicon and germanium dimers on graphene sorted from lowest (most favored) to highest (least favored) energy.

Carbon	Silicon	Germanium
-2.59	-0.91	-1.09
-2.45	-0.39	-1.05
-1.77	-0.24	-0.79
N/A	N/A	-0.68

5. Conclusion

In this study of epitaxial growth on an extremely inert substrate of graphene, we have shown that three adatoms from group IV, namely carbon, silicon and germanium, in the periodic table can diffuse and nucleate on top of it. We have successfully mapped the potential energy surface for those adatoms on a graphene sheet, which is useful to study the diffusion path for each of them. We have found that for all three adatoms, the preferential site for adsorption on graphene is at the bridge site of the hexagonal structure, and the unfavorable site is at the hollow part. Even though graphene is stable with three bonds for each of the carbon atom, it forms a fourth bond when a single carbon, silicon and germanium are placed above it.

As for dimers, only carbon and silicon sit low enough to form bonds with graphene. This is especially true for carbon dimer as one of the simulation results show that it actually becomes part of graphene and distorts the originally flat graphene structure. One interesting observation, germanium dimers display stronger binding energies to graphene than silicon dimers, contrary to the results for single adatoms system. Germanium dimers do not form bonds with graphene as the theoretical bond length for Ge-C is 1.95 Å, whereas in these simulations, they sit at about 2.56 to 2.59 Å above the graphene. They are only attracted by Van der Waals force. Future work on nucleation, including trimers, tetramers and hexamers are currently being studied. All simulations are done by using Fhi-aims' density functional theory calculation, which is a simplified yet accurate quantum mechanics description to study the energy of a system.

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