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Abstract

With the aim of searching for a promising Anode material for lithium ion batteries, quantum espresso modelling of the introduction of Lithium into the carbon terminated Silicon Carbide (SiC) Surface layers with the bottom layers treated with hydrogen to prevent dangling bond. We employ first principle (Ab-initio) Density functional theory (DFT) calculations with inclusion of gradient correction and periodic boundary conditions to obtain the convergent energies of the different doped structures at the **Surface** and **Near surface** layers of the super cell and also to understand the structural, electronic and lithium absorption properties on the surface. we can show that the absorption of Lithium by silicon Carbide is energetically more stable at the surface than the bulk. Energy differences will turn to decrease as we increase the concentration of Lithium into the vacancies.

Acknowledgement

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I thank my thesis supervisor Dr Eva Rauls at Faculty of Science University of Stavanger for her immense support and guidance throughout this project. The door of her office was always open at all-time whenever I have questions or direction about my research. She consistently allowed this project to be my own work but guided me in the right direction whenever she feels I needed it.

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Finally, I must express my sincere gratitude to my parents and to my wife, Gana Sandrine, for providing me with continuous support and encouragement throughout my years of studies and throughout this research process. Without their valuable support, this accomplishment would not have been possible .

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1. CHAPTER ONE

1.1. INTRODUCTION

Lithium ion batteries have gained enormous grounds for energy storage devices for portable electronic appliances such as laptop computers,Tablet PCs and electronic devices due to its high energy density [Tarascon and Armand, 2001, Whittingham, 2012, Marom et al., 2011]. To meet the energy goals of high capacity and energy density, materials possessing extremely high Lithium capacities are being investigated.Amongst these materials, Silicon has the highest theoretical capacity of Lithium ion storage of $4200 mAhg^{-1}$ [Huang and Tu, 2013, Chan et al., 2007, Magasinski, 2010], far greater than that of the traditional graphite which is often used with capacity $372 mAhg^{-1}$. This is because Silicon has an electrochemical alloying behaviour [Tian et al., 2015] which is not the same as the insertion mechanism for Graphite.

However, incorporating huge amount of lithium in Silicon will lead to an increase in volume. This causes intense lattice strain consequently, particles are pulverized and electrical connections are lost [Huang and Tu, 2013]. Another practical challenge to the high performance of Silicon comes from its semi conductive, approximately $10^{-5} Scm^{-1}$ charge transportation compared with $10^{3} Scm^{-1}$ of Graphite that hinders the electrode redox process and electronic diffusion [Wang and Han, 2010]

Several routes have been taken to accommodate these challenges and hence enhance the performance of these electrodes. These routes include adding different carbon conductive materials such as , graphite [Ma and Zhanyi Hu, 2014], carbon-nano tubes [Chan et al., 2010, Li et al., 2008], graphenes [Lee et al., 2010, Feng, 2015], Silicon carbide composite materials [Magasinski, 2010, Park et al., 2013] and different nano structures such as nano-tubes [Park et al., 2009], nanowires [Chan et al., 2007].
In this Thesis project,Lithium atoms of different concentrations are inserted into different sites of the carbon terminated surface and near surface layer of the 4H silicon carbide Composite structure and the formation energies of the resulting doped structures are calculated using the calculated chemical potentials of each of the elements present.The project begins with a theoretical background knowledge of the methods used to perform these calculations, followed by the the results of each Plane Wave Self-consistency simulations performed in

Quantum espresso and finally ends with the analysis and conclusions of these results. I will also like to mention here that, experimental findings have been carried out to show that Lithium ions can be inserted into Silicon carbide interstitial sites and the Lithium diffusion constant measured.

2. CHAPTER TWO

2.1. THEORETICAL BACKGROUND

In principle,we can obtain the properties of a system by solving the quantum mechanical wave equation governing the system dynamics. For a non relativistic system, this is just the Schrödinger equation.We begin this chapter by examining the Schrödinger equation,which is very successful for a system with one dimension like the hydrogen atom.

2.1.1. Schrödinger equation

This equation which describes the wave behaviour of matter was written down by Erwin Schrödinger. This can be written as [Breinig, 2009]:

$$[\frac{-\hbar^2}{2m}\bigtriangledown^2 + U(\vec{r},t)]\psi(\vec{r},t); = i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) \tag{2.1}$$

Where:
m is the mass of the particle
$U(\vec{r},t)$ is the potential energy of the particle
$\bigtriangledown^2$ is the Laplacian operator and
$\psi(\vec{r},t)$ is the wave function

We can find the ground state energy of any atom by solving the above Schrödinger equation. For a many particle problem in solid, we can use the Born-Approximation which considers the state of the nuclei to be more massive than the electron and so can be considered fixed. In this approximation, we separate the dynamics of the atomic nuclei with that of the electron and write out the wave function in two parts as follows:

$$\psi(R_i,r_j) \rightarrow \psi_n(R_i) \times \psi_e(r_j) \tag{2.2}$$

where:
$\psi_n(R_i)$ wave function that describes the dynamics of the nuclei

$\psi_e(r_j)$ Wave function that describes the dynamics of the electrons
Solving the Schrödinger equation for many particle problem in solid is a tedious exercise due to the many degrees of freedom that arise for different system. For our system, ie Silicon Carbide (SiC), there are 20 electrons, 6 from carbon and 14 from Silicon. For three spatial coordinates for each electronic position, this means we will have a 60 dimensional problem to deal with! In order to simplify our difficulty, we have used the Density functional Theory (DFT).

2.1.2. Density functional theory (DFT)

For relativistic system of many body particles, calculations using Density Functional Theory (DFT) is very successful. It treats the electron density as the central variable rather than the many body wave function. This approach leads to a remarkable reduction of the difficulties encountered in solving a relativistic many body system.
An early density functional theory was proposed by Thomas and Fermi [Dahl and Avery, 2013]. This took the kinetic energy to be a functional of the electron density but in common with the Hartree-Fock methods, only incorporated the electron-electron interactions via a mean field potential: as such, it neglected both exchange and correlation; a subsequent by Dirac [Dirac, 1930]; formulating an expression for the exchange energy in terms of the electron density failed to significantly improve the method. Here we consider the Honhenberg-kohn sham formulation of DFT. This technique is one of the choices applied in electronic structure theory and has been very successful in fields ranging from quantum chemistry to condensed matter Physics. In this description, we will focus on the areas of DFT which is related to this thesis work.

2.1.3. Thomas-Fermi Model

One of the earliest routes taken for solving many electrons problem was proposed by Thomas and Fermi [Plaskett, 1953, Thomas, 1927]. In this Model, we consider the electron density $\vec{\varrho}(r)$.According to this theory, if we have interacting electrons moving with external potential $V(r)$, we can write this density distribution as:

$$\varrho(\vec{r}) = a\left\{U - V_{eff}(r)\right\}^{\frac{3}{2}} \tag{2.3}$$

with

$$a = \frac{1}{3\pi^2}(\frac{2m}{\hbar^2})^{\frac{3}{2}} \tag{2.4}$$

$$V_{eff} \equiv V(\vec{r}) + \int \frac{\varrho(\vec{r'})}{|\vec{r} - \vec{r'}|} dr' \tag{2.5}$$

U is the r independent external potential and the second term in equation 2.5 is the classical electrostatic potential generated by the density $\varrho(r)$

2.1.4. Hohenberg and Kohn Theorem

Theorem 1 :

The external potential $V(\vec{r})$ (except for an additive constant is uniquely determined by the electron density $\varrho(\vec{r})$.

Proof:

Assumption: The exist two different external potential $V(\vec{r}), V'(\vec{r'})$ which yield the same $\varrho(\vec{r})$:

$$\varrho(\vec{r}) \rightarrow \Psi\hat{H} \qquad , \langle\Psi|\Psi\rangle = 1 \tag{2.6}$$

$$\varrho'(\vec{r}) \rightarrow \Psi'\hat{H} \qquad , \langle\Psi'|\Psi'\rangle = 1 \tag{2.7}$$

$$\Longrightarrow E_0 < \langle\Psi'|\hat{H}|\Psi'\rangle = \langle\Psi'|\hat{H}|\Psi'\rangle + \langle\Psi'|\hat{H} - \hat{H}'|\Psi'\rangle = E_0' + \int \varrho(\vec{r})[V(\vec{r}) - V'(\vec{r'})]dr \tag{2.8}$$

$$E_0' < \langle\Psi|\hat{H}'|\Psi\rangle = \langle\Psi|\hat{H}|\Psi\rangle + \langle\Psi|\hat{H}' - \hat{H}|\Psi\rangle = E_0 + \int \varrho(\vec{r})[V'(\vec{r}) - V(\vec{r})]d\vec{r} \tag{2.9}$$

$$E_0 + E_0' < E_0' + E_0 \qquad \Longrightarrow Contradiction$$

The total energy with Hohenberg and Kohn is given by:

$$E_{HK}[\varrho] = T[\varrho] + V_{ke}[\varrho] + V_{ee}[\varrho] \tag{2.10}$$

Or

$$E_{HK}[\varrho] = \int \varrho(\vec{r}) V(\vec{r}) d\vec{r} + F_{HK}[\varrho] \tag{2.11}$$

With:

$$F_{HK}[\varrho] = T[\varrho] + V_{ee}[\varrho] \tag{2.12}$$

$$V_{ee}[\varrho] = J[\varrho] + nonClassicalterm(Exchangecorrelation)$$

$$T[\varrho] = KineticEnergyFunctional$$

$$V_{ee}[\varrho] = Electron - ElectronFunctional$$

$$V_{ke}[\varrho] = \int \varrho(\vec{r}) V(\vec{r}) d\vec{r} = NucleusElectronFunctional$$

$$J[\varrho] = \frac{1}{2} \iint \frac{\varrho(\vec{r}_1)\varrho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 = Coulomb - Functional$$

Theorem 2:

It states that the electron density that minimizes the energy of the overall functional is the true ground state electron density. It is also known as the variational principle for densities

$$E_0 = min_{\varrho'} E_{HK}[\varrho'] \tag{2.13}$$

Constraint :

$$\int \varrho'(\vec{r}) d\vec{r} = N \qquad ; \varrho'(\vec{r}) \geq 0 \tag{2.14}$$

proof:

$$E_0[\varrho_0] = T[\varrho] + V_{ke}[\varrho] + V_{ee}[\varrho] \tag{2.15}$$

with ϱ_0 equals the exact ground state density

$$E_{HF} = T[\varrho'] + V_{ke}[\varrho'] + V_{ee}[\varrho'] \tag{2.16}$$

because of the first Hohenberg-Kohn theorem:

$$\varrho'(\vec{r}) \rightarrow \hat{H}', \Psi' \tag{2.17}$$

$$\Longrightarrow \langle \Psi' | \hat{H} | \Psi' \rangle = T[\varrho'] + \int \varrho'(\vec{r}) V(\vec{r}) d\vec{r} + V_{ee}[\varrho] \tag{2.18}$$

$$= E_{HK}[\varrho'] \geq E_0[\varrho_0] = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \tag{2.19}$$

$$(\Longrightarrow \quad \langle \Psi' | \hat{H} | \Psi' \rangle \geq \langle \Psi_0 | \hat{H} | \Psi_0 \rangle) \tag{2.20}$$

we can define the following energy functionals:

$$E_{HK}[\varrho] = \int \varrho(\vec{r}) V(\vec{r}) d\vec{r} + F_{HK}[\varrho] \tag{2.21}$$

$$F_{HK} = T[\varrho] + J[\varrho] + E_{xc}[\varrho] \tag{2.22}$$

$$J[\varrho] = \frac{1}{2} \int \frac{\varrho(\vec{r}_1)\varrho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \tag{2.23}$$

$$E_{xc}[\varrho] = E_x[\varrho] + E_c[\varrho] \tag{2.24}$$

Where $T[\varrho]$, $E_x[\varrho]$ and $E_c[\varrho]$ are the kinetic, exchange and correlation energies and they are all Unknown

2.1.5. Kohn-Sham Equations

They suggested that we have to calculate the kinetic energy of a density by making an assumption that this density corresponds to a wave function that consist of a single slater determinant, since we already know how to look for the slater determinant (ie this is just the same as the hatree Fock theory). This process is known as the Kohn-Sham Density functional Theory and it is mostly used even though it may not be suitable for large systems computations because of the cost.

In order to perform the Variation, Kohn and Sham proposed the following:

$$E[n] = T_s[n] + \int v(r) n(r)\, d^3r + \frac{1}{2} \int \frac{n(r) n(r')}{|r - r'|}\, d^3r\, d^3r' + E_{xc}[n] \tag{2.25}$$

$T_s[n]$ Stands for the kinetic energy of the non-interacting particles

The variation of this energy leads to the equation of non-interacting particles that moves in the potential $V_{eff}(r)$

$$\frac{\delta E}{\delta n} = \frac{\delta T_s}{\delta n} + \frac{\delta}{\delta n}\left\{\int v(r)n(r)\, d^3r + \frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}\, d^3r\, d^3r' + E_{xc}[n]\right\} \tag{2.26}$$

$$\implies V_{eff} = V(r) + \int \frac{n(r')}{|r-r'|} d^3r' + \frac{\delta E_{xc}}{\delta n} \tag{2.27}$$

In contrast with Hatree and Hatree Fock where we start with an approximation, i.e an ansatz for the wave function and then perform the variation, in this case, we have used the variational principle for the ground state and now we start thinking about approximation. However, we do not know $T_s[n]$, we know only an approximation like in the Thomas Fermi approach. We can't also established whether it exist for all densities but we can assumed it by restricting the range of densities to one which can be represented as:

$$n(r) = \sum_{i=1}^{N} |\Psi_i(r)|^2 \tag{2.28}$$

constructed from the N lowest solution to an arbitrary single particle Hamiltonian. With these densities, we can approximately cover all physically meaningful densities.To calculate the density of non-interacting particles, we solve the Schrödinger equation 2.29

$$\left\{\frac{\nabla^2}{2} + V_{eff}(r)\right\}\Psi_i(r) = \epsilon_i\, \Psi(r) \tag{2.29}$$

We can then calculate $T_s[n]$ via

$$T_s[n] = T_s[\sum_i |\Psi_i(r)|^2] = \sum_{i=1}^{N} \langle\Psi_i| - \frac{\nabla^2}{2}|\Psi_i\rangle \tag{2.30}$$

or

$$T_s[n] = \sum_{i=1}^{N} \epsilon_i - \int V_{eff}(r)n(r)d^3r \tag{2.31}$$

2.1.6. Local Density approximation

There are many schemes developed to obtain approximate forms for the functional for exchange correlation. The error in density functional theory usually arises from these approximate nature of E_{xc}. Local Density Approximation(LDA) is mostly used and is given by (35)

$$E_{xc}^{LD} = \int \varrho_{GS}(r)[\varrho_{GS}(r)]dr \tag{2.32}$$

where $\in_{xc}[\varrho_{GS}(r)]$ is the exchange- correlation energy per electron in a homogeneous electron gas of constant density.

3. CHAPTER THREE

3.1. METHODS

We begin this chapter by looking at a brief description of the silicon carbide structure, and state few reasons why 4H-SiC is preferred over the other poly-types in this project. The chapter summarises with the general iterative process used for the calculations, some computational details performed.

3.1.1. Silicon Carbide

Silicon carbide exist in different polytyptes. While there are many known polytypes of SiC, only few are commonly grown in a reproducible form acceptable for use in building different electronic deviced. The Most commonly grown types of SiC are 3C-SiC, 4H-SiC and the 6H-SiC. The stacking sequences of these three types are shown on figure 1 [Yazdi et al., 2016]

Each of these SiC polytypes exhibits specific electrical and optical properties. In this thesis, we have decided to use the 4H-SiC which has a stacking sequence ABCBABCB... as shown on figure 1.The letter "H" means it is hexagonal and the number "4" before the letter refers to the number of double atomic-layers in one repeating unit, e.g for 4H, we have (ABCB). The 4H-SiC is favorable over the other polytypes for the following reasons:it has higher carrier mobility and shallower dopant ionization energies compared to 6H-SiC, this makes it a useful choice for most SiC electronic devices.
Further more, the 6H-SiC has a property which is directionally dependent, which implies different properties in different directions. This property degrades conduction parallel to the c-axis for the 6H-SiC and favours the 4HSiC which is directionally independent and hence useful for vertical power configurations.

3.1.2. Computaional Details

Given the above advantages of the 4H-SiC, explain why we have chosen this polytype as our system of interest. The system is made up of 96 atoms. To perform first principle DFT calcu-

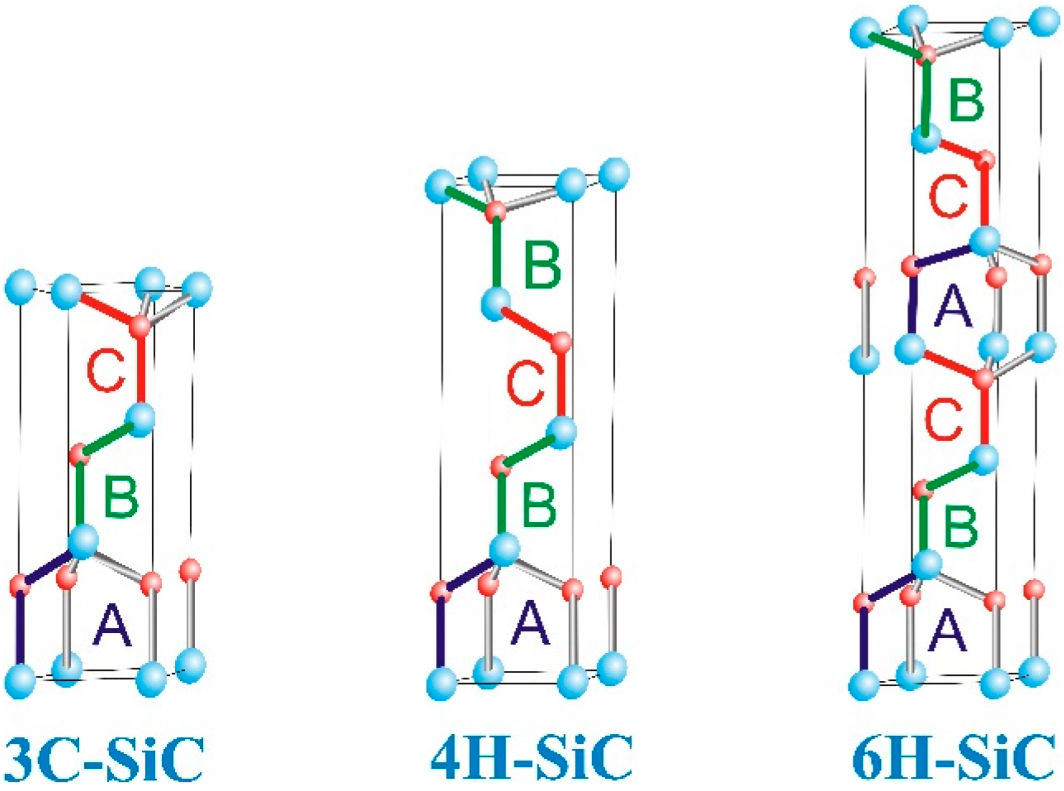


Figure 1: Three Most common Silicon carbide polytypes

lations, we carry out Self-consistent Kohn-Sham energy computations. By self consistently solving the Kohn-Sham one-electron equations we can obtain the ground state of a system composed of many electrons and nuclei.The general Lithiation process was Modelled using DFT as follows:

Create Vacancies at the surface and near surface layer of the 4HSiC input structure

Insert Lithium atoms of different concentrations into these vacancies

Increase the volume and scale coordinates.

We Allow these coordinates to optimize at a constant volume.

We calculate the total energy and repeat the process for all the structures.

The input structure for our calculations consist of 96 atoms built in a supper cell. We added a vacuum of about 10Å along the c-axis(z-direction). Calculations of the coordinates of the atoms along the z-direction were performed to make sure these atoms were not displaced due to the vacuum.We then fixed two layers and make calculations on the first (**surface**) and second (**near surface**) layers of the final structure. The input structure is as shown on figure 2

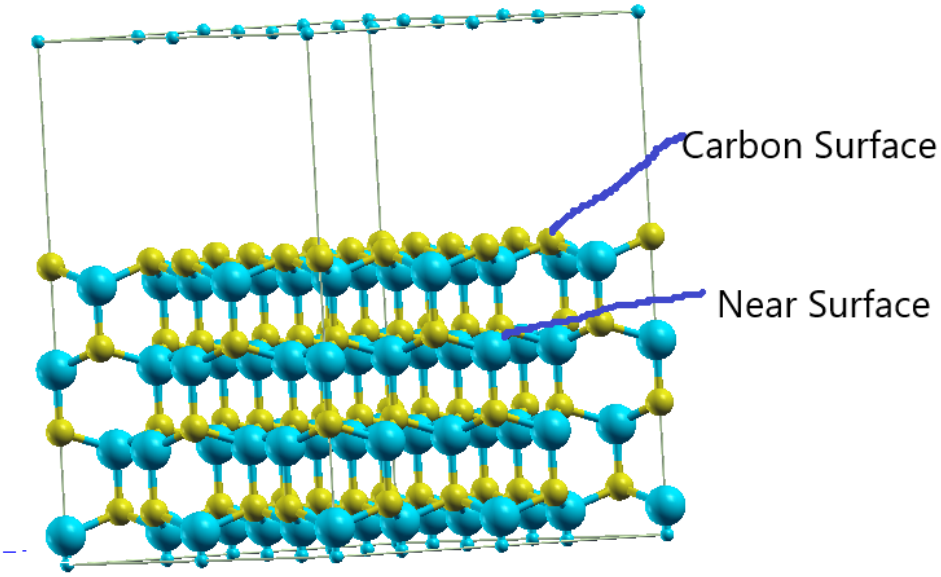


Figure 2: The Input Structure of 4H-SiC

To perform first principle calculations on this input structures, we have set up the energy limit to be 50Ry,(cut-off energy), and use the PBE psudopotential and functional. Smearing condition was also set at 0.1eV. In the first step, the starting configuration with layered arrangement of lithium and silicon atoms were optimized and the convergent energy of this configuration recorded to be $-931.01460868Ry$. we also check convergence of this configuration at different energy limits (cut-off energies) and also at different k-points. Table 1 shows the result for the K-points and table 2 shows the result for convergent energies at different cut-off energy for the 4HSiC input structure.

These results can be shown on the following plots. Figure 3 shows the result for K-points and figure 4 shows the result for the cut-off energy

In the second step, we created vacuums at different sites in the first (Surface) and second (near surface) layers of this configuration and insert lithium atoms of different concentrations. We then applied first principle approach on these configurations to search for optimal structures. We then determine the stabilities of the defected structures by calculating their

K-points	Convergent Energies (Ry)
1 1 1	-931.07652539
2 2 1	-931.01585917
3 3 1	-931.01457763
4 4 1	-931.01460868
5 5 1	-931.01463474
6 6 1	-931.01462672

Table 1: K-point Test for Silicon Carbide Input Structure

Cut-off Energies (Ry)	Convergent Energies (Ry)
40	-930.95340729
50	-931.01574001
60	-931.03887987
70	-931.05512663
80	-931.06200949
90	-931.06468700
100	-931.06627489

Table 2: Cut-off Energy Test for Silicon Carbide

formation energies. To obtain these formation energies, We have made use the convergent energies and the calculated chemical potential for each of the elements (Si, C, and li) to obtain the formation energies for the different modified (lithiated) structures.To obtain these energies, we have used the expression in equation 3.33: [J. Chen et al., 2008]

$$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li} \tag{3.33}$$

E_s = Energy of the structure containing Lithium atom

E_b= Energy of the Silicon Carbide Bulk (structure without Lithium atom)

U_c= chemical potential for Carbon

U_{Li} = Chemical potential for Lithium

U_{Si} = Chemical potential for silicon

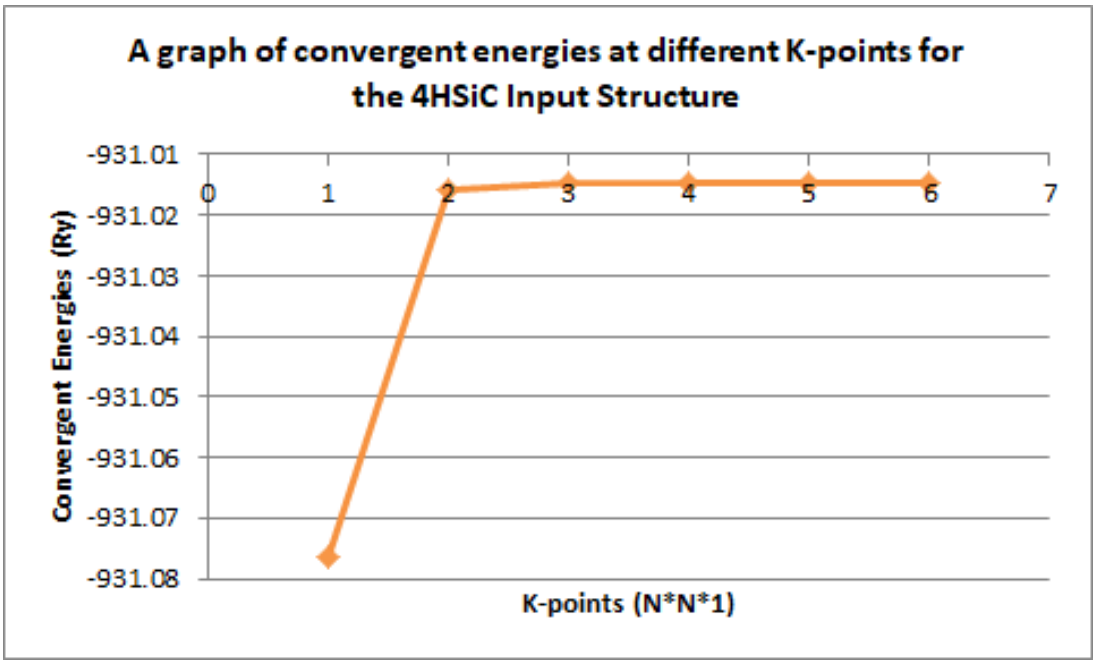


Figure 3: K-point test for 4H-SiC Input structure

E_F = Calculated formation energy for the structure

r = Number of Lithium atoms

p= Number of carbon atoms

q = Number of Silicon atoms

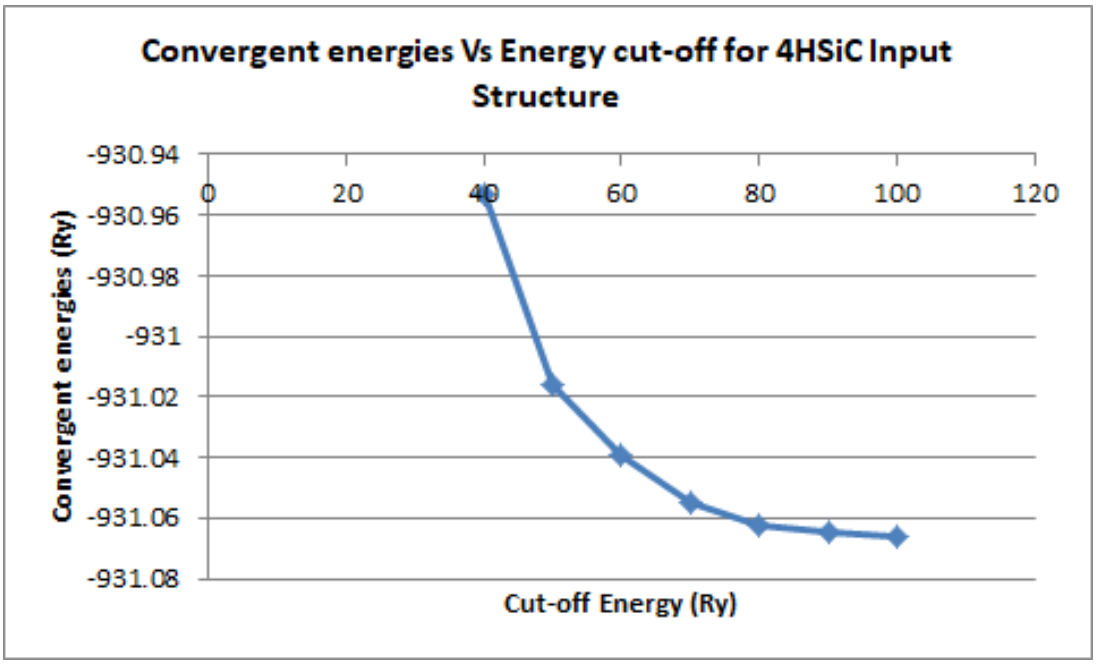


Figure 4: Cut-off energy test for 4H-SiC input structure

4. CHAPTER FOUR

4.1. RESULTS

There are different types of intrinsic defect that can be observed in Silicon carbide crystals, examples are point defects and higher dimensional defects[Claeys and Simoen, 2013]. point defects consist of Silicon vacancies, Carbon vacancies, divacancies and antisite. The presence of these defects can either degrade or improve the performance of SiC-based devices. therefore identification of these defects,knowledge of their characteristics will give a better understanding of the use of Silicon carbide for energy storage in electronic devices.

In this chapter, we shall be looking at the intrinsic point defect on the surface and near surface layer of our Silicon carbide input structure. We start by briefly introducing the chemical potentials of the elements: carbon, silicon and lithium, and finally use these chemical potentials and convergent energies of each structure to calculate the formation energies for each Lithiated structure.

4.1.1. Chemical potential for Lithium

Here we calculated the chemical potential U_{Li} for the lithium atom. we Built an input file for lithium, setting the cut-off energy at 50Ry, we ran a K-point convergence test for the Lithium structure. Table 3 shows the result obtained.

K-points	Convergent Energies (Ry)
1 1 1	-14.10354663
2 2 1	-14.10012590
3 3 1	-14.09990393
4 4 1	-14.09978164
5 5 1	-14.10016895
6 6 1	-14.10011515
7 7 1	-14.10014056
8 8 1	-14.10008469
9 9 1	-14.10007647
10 10 1	-14.10012400

Table 3: Table to show K-point Test for Lithium

To perform the calculation, we choose the chemical potential to be $-14.09978164Ry$ which is the value obtained at K-point 4 4 1.
The graph in figure 5 shows the variation of convergent energies with K-points. The K-point is chosen in the form (N*N*1) where N is a number that ranges from one to Ten.

4.1.2. Chemical potential for Silicon

Calculations of the chemical potential for Silicon is performed the same way as that for Lithium above.We started by building an input file for Silicon, setting the cut-off energy to 50Ry, we tested for k-point convergence of the structure. Table 4 Shows this result.

In our entire calculations for this thesis, we choose the value U_{Si} to be -7.58581405 which corresponds to convergence at K-point 4 4 1. The results of these calculations are shown on

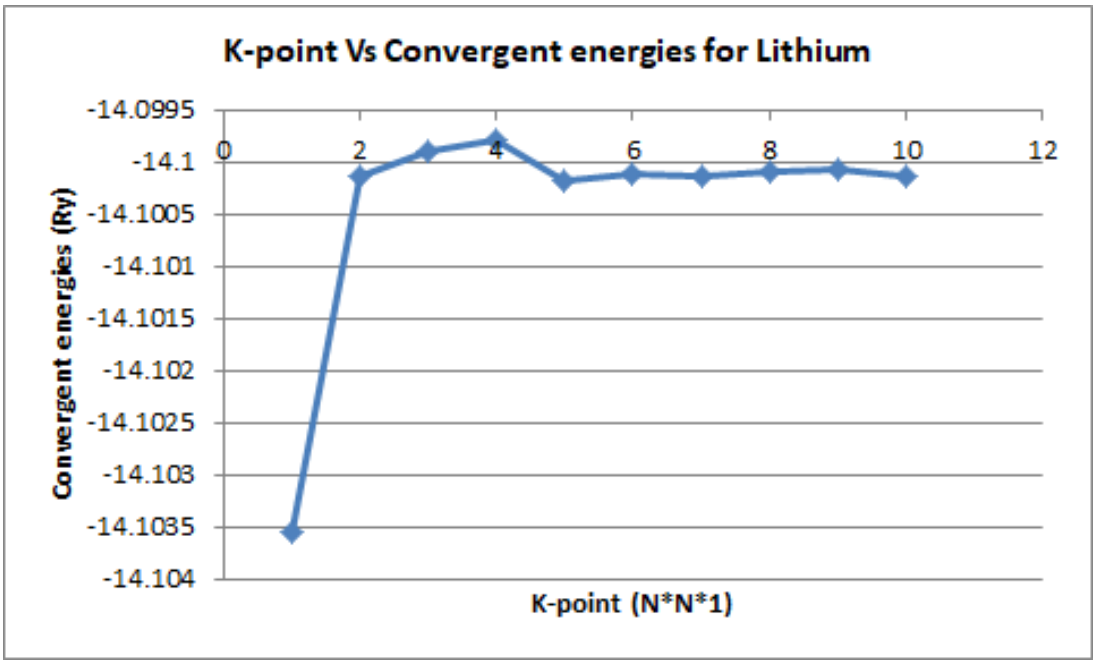


Figure 5: Energy versus K-points for Lithium

K-points	Convergent Energies (Ry)
1 1 1	-7.58569491
2 2 1	-7.58581412
3 3 1	-7.58581408
4 4 1	-7.58581405
5 5 1	-7.58581415
6 6 1	-7.58581413
7 7 1	-7.58581414
8 8 1	-7.58581413
9 9 1	-7.58581412
10 10 1	-7.58581414

Table 4: Table to show K-point Test for Silicon

figure 6

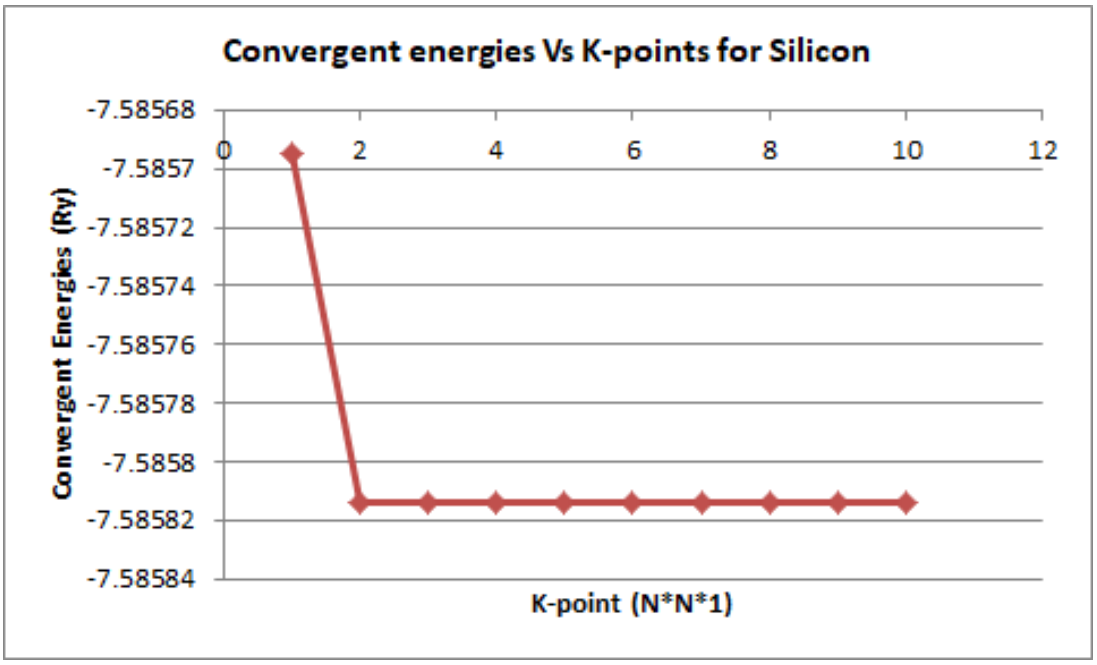


Figure 6: Energy versus K-points for Silicon

4.1.3. Chemical potential for carbon

We constructed a cell made up of two carbon atoms and set the cut-off energy to be 50Ry. We run a convergent test at different K-points. We then obtain the chemical potential for a single atom by dividing the results of the convergent energy obtained at K-point 4 4 1 for Carbon by 2. Table 5 shows the result. It can also be illustrated graphically on figure 7

4.2. Lithium atoms in carbon Vacancies at the surface

For these first set of five structures, we have inserted Lithium atoms of different concentrations into carbon vacancies. The formation energies are calculated according to the formula... given above.

4.2.1. Lithium in a carbon vacancy at the surface

In this case, a carbon vacancy is created at the surface of the Silicon carbide input structure and this vacancy is replaced by a Lithium atom as shown on figure 8

K-points	Convergent Energies (Ry)
1 1 1	-22.55871469
2 2 1	-22.82626666
3 3 1	-23.01304414
4 4 1	-23.01236456
5 5 1	-23.02039735
6 6 1	-23.02020329
7 7 1	-23.01978083
8 8 1	-23.01946151
9 9 1	-23.01925393
10 10 1	-23.01922467

Table 5: Table to show K-point Test for Carbon

The formation energy for this structure is calculated to be $2.503042722eV$

4.2.2. Two Lithium atoms in two carbon vacancies at the surface

In this case , we created two carbon vacancies in the input structure and replaced it with Lithium atoms. The input and output structures are as shown in figure 9

The formation energy is calculated to be $4.659985466eV$

4.2.3. Three Lithium atoms in three carbon vacancies at the surface

In this case, we inserted three Lithium atoms in three carbon vacancies at the surface layer of the silicon carbide input structure. The diagram for the input and output structures are as shown in figure 10

The formation energy for this case is calculated to be $6.546361216eV$

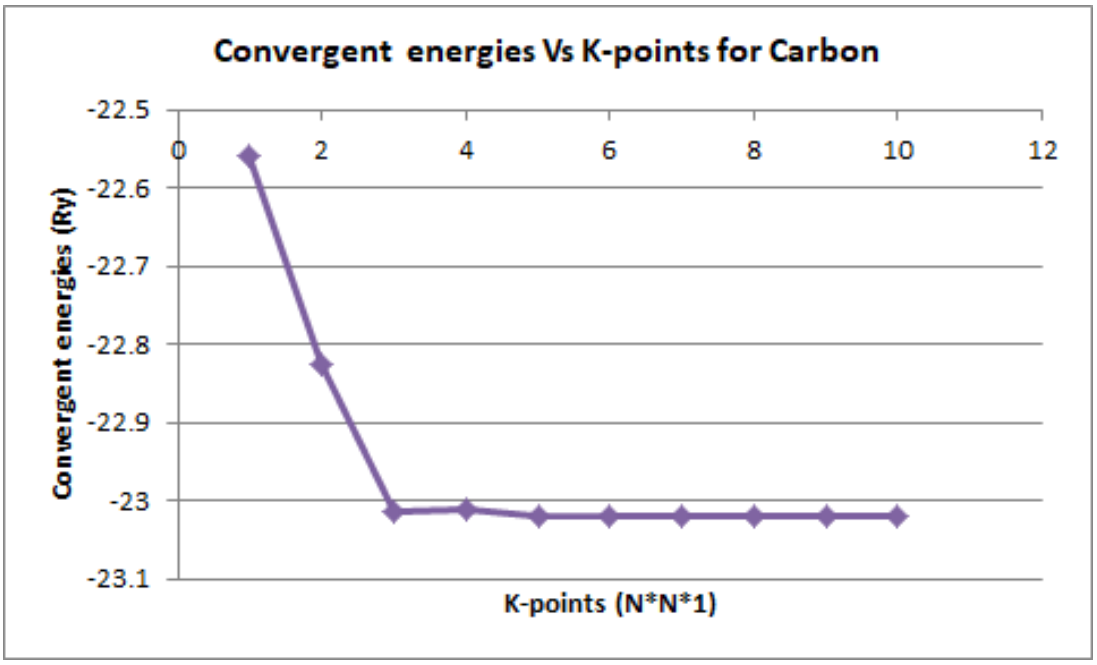


Figure 7: Energy versus K-points for Carbon

4.2.4. Four Lithium atoms in four carbon vacancies at the surface

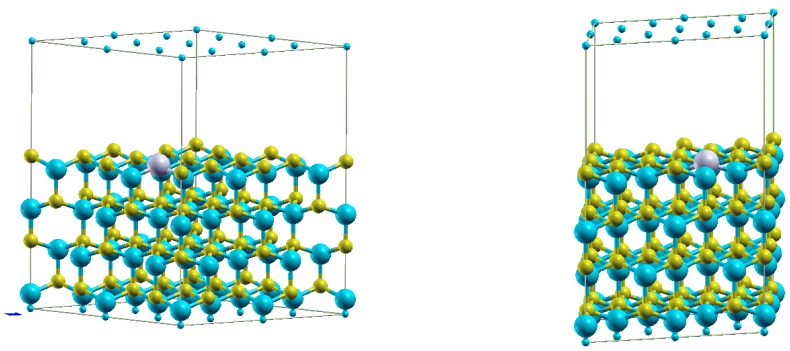
Here we increased the number of vacancies by removing 4 carbon atoms and replacing them with a lithium atom. The input and output structures are as shown in figure 11

The Formation energy for the four Lithium atom is calculated to be $8.423602781eV$

4.2.5. Five Lithium atoms in five carbon vacancies at the surface

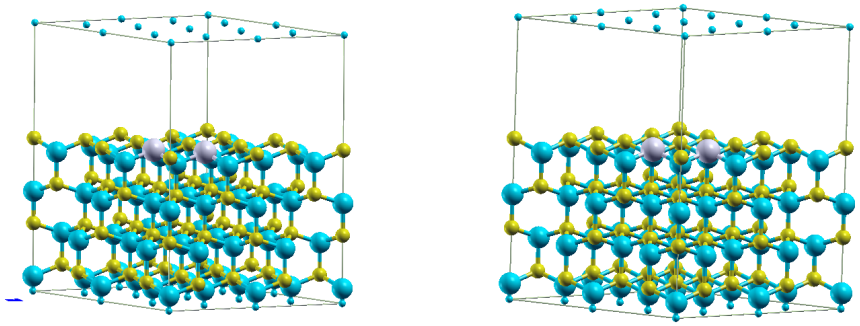
In this case we have replaced five (5) carbon atoms at the surface with Lithium atoms. Bellow are the figures for the input and output structures are as shown in figure 11

The Calculated formation energies for this structure is $10.17443149eV$
The table 6 shows the summary of formation energies for these first five structures and a graph to show the energy trend as we increased the number of lithium atoms on the surface.



a) Input b) Output

Figure 8: Input and Output structures for one Lithium in a carbon vacancy at the surface

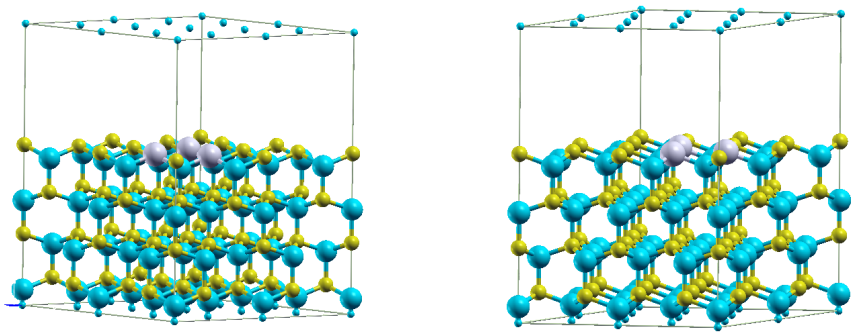


a) Input b) Output

Figure 9: Input and Output structures for Two Lithium atoms in Carbon vacancies at the surface

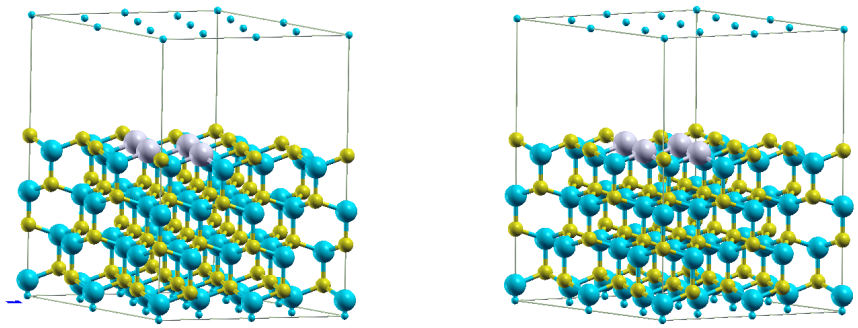
Number of Lithium atoms	Formation Energies (eV)	atoms	Energy differences
1	2.503042722	-	-
2	4.659985466	0ne and two	2.156943
3	6.546361216	Two and three	1.886376
4	8.423602781	Three and four	1.877242
5	10.17443149	Four and five	1.750829

Table 6: Formation Energies and Energy differences for Lithium atoms in Carbon vacancies at the surface



a) Input b) Output

Figure 10: Input and Output structures for three Lithium atoms in carbon vacancies at the surface

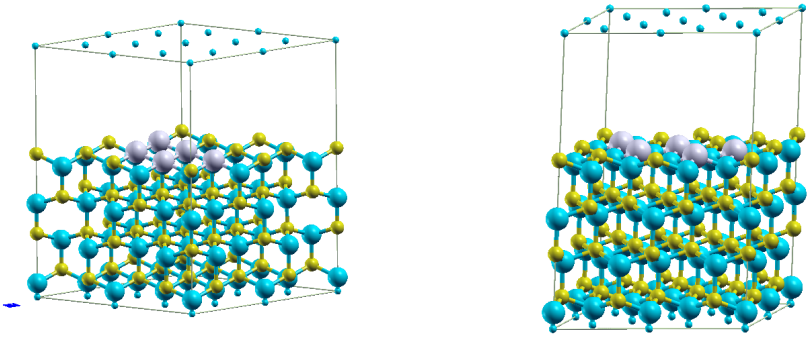


a) Input b) Output

Figure 11: Input and Output structures four Lithium atoms in Carbon vacancies at the surface

4.3. Variation of the concentration of Lithium atom in near surface layer with one lithium atom kept constant in a carbon vacancy at surface

In the next five structures, we will keep a lithium atom fixed at the surface and create carbon vacancies in the layer near the surface. we then substitute Lithium atoms into these vacancies by increasing the concentration and calculate the formation energies of the final structures.

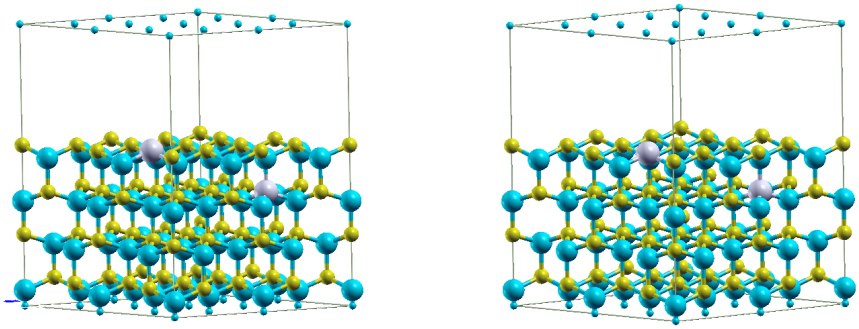


a) Input b) Output

Figure 12: Input and Output structures for Five Lithium atoms in carbon vacancies at the surface

4.3.1. lithium atom in a carbon vacancy at the surface and one lithium in a carbon vacancy at near surface

In this case, we substitute one Lithium atom in a carbon vacancy at the surface and one Lithium atom in a carbon vacancy near surface. The diagram for this first case is as shown on figure 13 :



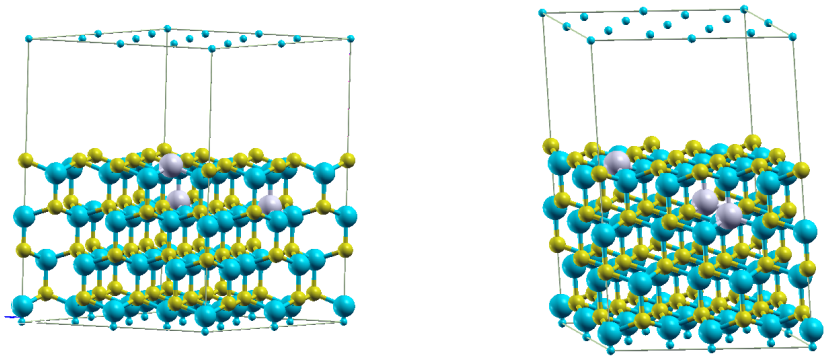
a) Input b) Output

Figure 13: Input and Output structures for one lithium atom in a carbon vacancy at the surface and one lithium in a carbon vacancy at near surface

the formation energy for this case is determined to be $8.819633358eV$

4.3.2. One lithium atom in a carbon vacancy at the surface and two Lithium atoms in a carbon vacancy at the near surface layer

The two structures for the input and output is as shown on figure 14



a) Input b) Output

Figure 14: Input and Output structures for one lithium atom in a carbon vacancy at the surface and two lithium in a carbon vacancy at near surface

the formation energy for the final structure is obtained to be $15.21933576eV$

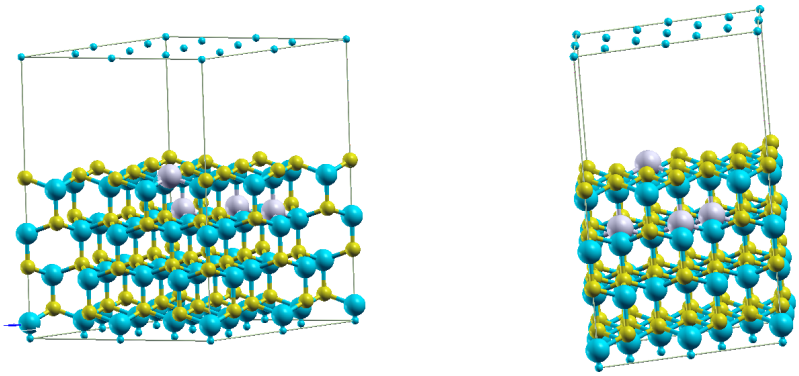
4.3.3. One Lithium in a carbon vacancy at the surface and 3 lithium in a carbon vacancy at the near surface layer

We replaced 3 carbon atoms at the near surface layer with a lithium atom , keeping one lithium atom at the surface in a carbon vacancy fixed. the input and output structures are as shown on figure 15

The final formation energies for this case is determined to be $20.40525384eV$

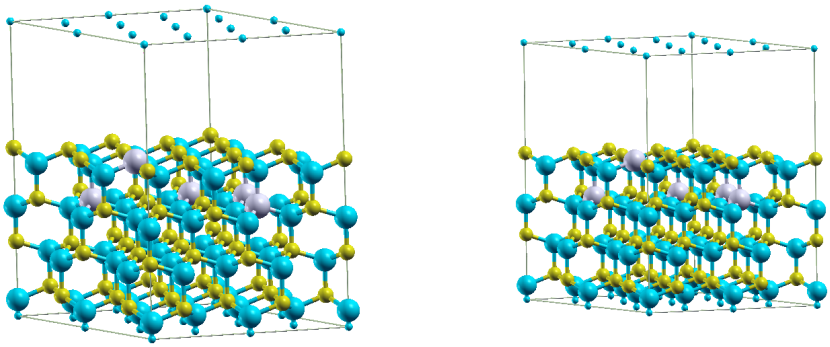
4.3.4. One Lithium in a carbon vacancy at the surface and 4 lithium in a carbon vacancy at the near surface layer

This structure has 4 lithium atoms in 4 carbon vacancies at the near surface and one lithium atom in a carbon Vacancy at the surface The input and Output structures are shown in figure 16



a) Input b) Output

Figure 15: Input and Output structures for one lithium atom in a carbon vacancy at the surface and three lithium in a carbon vacancy at near surface



a) Input b) Output

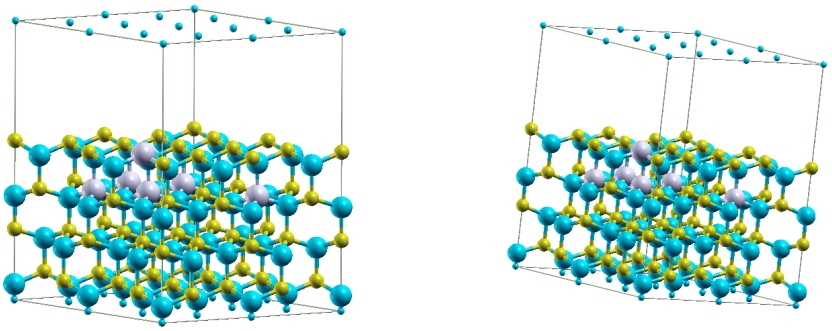
Figure 16: Input and Output structures for one lithium atom in a carbon vacancy at the surface and four lithium in a carbon vacancy at near surface

The formation energy is calculated to be 26.22601461 eV

4.3.5. One Lithium in a carbon vacancy at the surface and 5 lithium in a carbon vacancy at the near surface layer

This structure has 5 lithium atoms in 5 carbon vacancies at the near surface and one lithium atom in a carbon Vacancy at the surface The input and Output structures are shown in figure 17

the formation energy for this structure is calculated to be 30.72341919 eV



a) Input b) Output

Figure 17: Input and Output structures for one lithium atom in a carbon vacancy at the surface and Five lithium in a carbon vacancy at near surface

The results of these energies are summarised on table 7.

Number of Lithium atoms	Formation Energies (eV)	atoms	Energy differences
1	8.819633358	-	-
2	15.21933576	0ne and two	6.399702402
3	20.40525384	Two and three	5.18591808
4	26.22601461	Three and four	5.82076077
5	30.72341919	Four and five	4.49740458

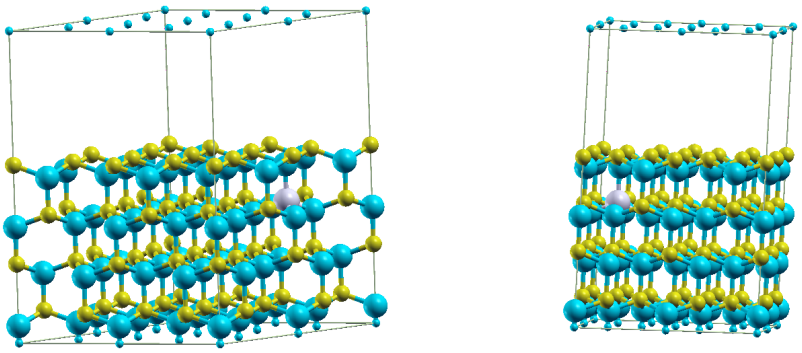
Table 7: Formation Energies and Energy differences for one Lithium atom In a Carbon vacancy at the surface and different concentrations of Lithium atoms in Carbon Vacancies Near Surface

4.4. Variation of the concentration of Lithium atom in carbon vacancy at the near surface

In this section we study the variation of the formation energies at the layer bellow the surface (near surface layer).We created carbon vacancies in this layer in increasing concentration of lithium and calculate energies.

4.4.1. One Lithium atom in a carbon vacancy at the near surface layer

In this first case, we replaced one carbon atom at the near surface layer with a lithium atom as shown on figure 18



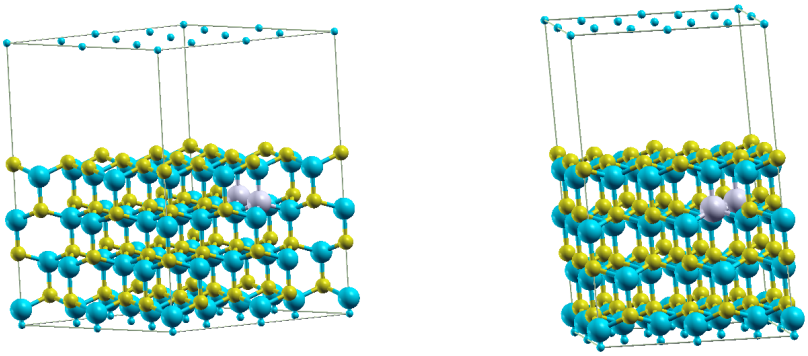
a) Input b) Output

Figure 18: Input and Output structures For One Lithium atom in a carbon vacancy at near surface layer

The formation energy for this first structure is obtained to be $6.231040728eV$

4.4.2. Two Lithium atoms in two carbon vacancies at the near surface layer

The structures for the input and output are as shown on figure 19



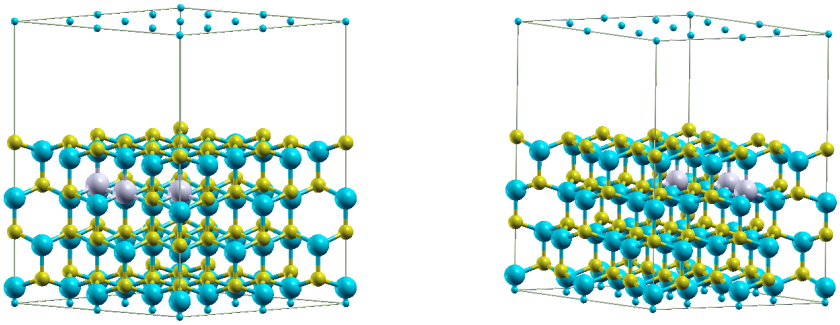
a) Input b) Output

Figure 19: Input and Output structures for two Lithium atom in a carbon vacancy at the near surface layer

The formation energies for this case is obtained to be $11.91619663eV$

4.4.3. Three lithium atoms in three carbon vacancies at the near surface layer

In this case we insert three lithium atom into three carbon vacancies in the near surface layer and calculate the formation energy. The resulting structures are displayed on figure 20



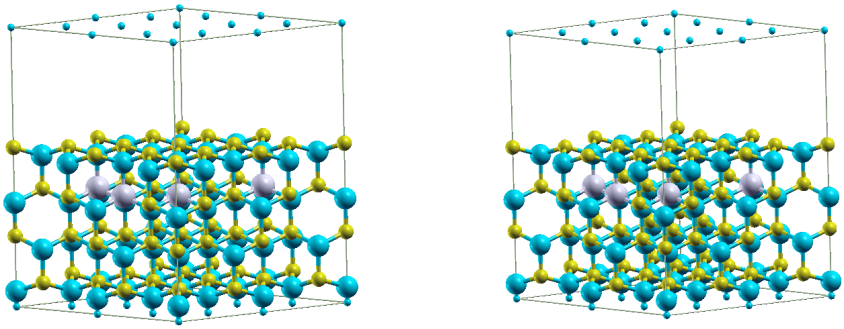
a) Input b) Output

Figure 20: Input and Output structures for three Lithium atom in a carbon vacancy at the near surface layer

The formation energy for this structure is obtained to be 17.65937621eV

4.4.4. Four Lithium atoms in Four carbon vacancies in near surface layer

In this case we replaced four carbon atoms in the layer near the surface as seen on the figure 21



a) Input b) Output

Figure 21: Input and Output structures for four Lithium atom in a carbon vacancy at the near surface layer

we calculate the formation energies in this case to be $23.44381439eV$

Table 8 summarises these results and what we can deduce from the trend

Number of Lithium atoms	Formation Energies (eV)	atoms	Energy differences
1	6.231040728	-	-
2	11.91619663	0ne and two	5.685156
3	17.65937621	Two and three	5.74318
4	23.44381439	Three and four	5.784438

Table 8: Formation Energies and Energy differences for Lithium atoms in Carbon vacancies Near surface

4.5. Mix vacancy at the surface

in this set of next five structures, we decided to create mix vacancies by fixing a lithium atom in a Silicon vacancy at the surface and increase the concentration of lithium atoms in carbon vacancies.

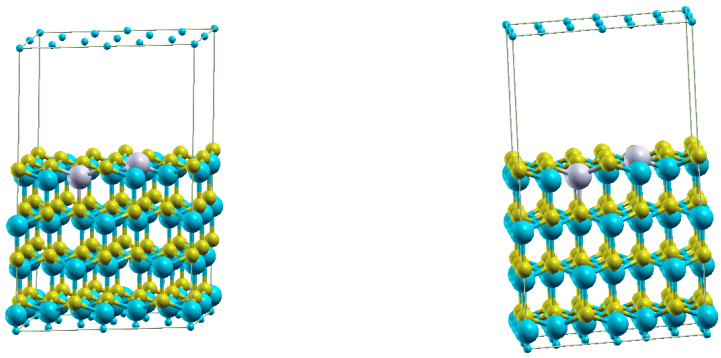
4.5.1. One lithium atom in a carbon vacancy and one lithium atom in a silicon vacancy at the surface layer

In this first case, we have inserted a lithium atom in a Silicon and carbon vacancies as seen on figure 22

The formation energy is deduced to be $10.87237292eV$

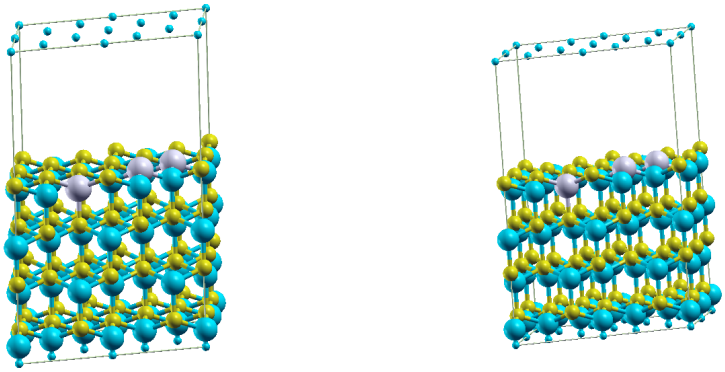
4.5.2. one lithium atom in a silicon vacancy and two lithium atoms in a carbon vacancy at the surface layer

In this case, with a Lithium atom fixed in a silicon vacancy at the surface, we replaced two carbon atoms with two lithium atom as seen on figure 23



a) Input b) Output

Figure 22: Input and Output structures for One lithium atom in a carbon vacancy and one lithium atom in a silicon vacancy at the surface layer



a) Input b) Output

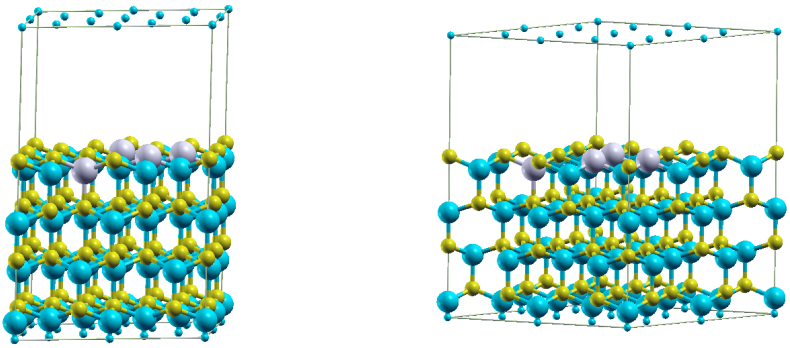
Figure 23: Input and Output structures for one lithium atom in a silicon vacancy and two lithium atoms in a carbon vacancy at the surface layer

The formation energy is calculated to be $12.80108919eV$

4.5.3. One lithium atom in a silicon vacancy and three lithium atoms in three carbon vacancies at the surface layer

With a lithium atom in a silicon vacancy, we have replaced three carbon vacancies with lithium atoms at the surface as seen on figure 24

the formation energy is calculated to be $14.44121446eV$

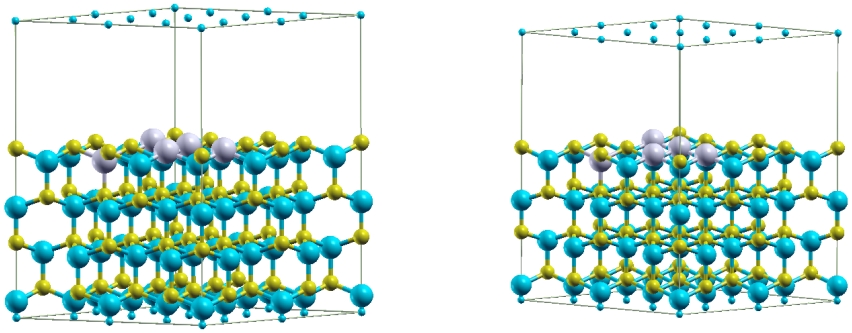


a) Input b) Output

Figure 24: Input and Output structures for one lithium atom in a silicon vacancy and three lithium atoms in a carbon vacancy at the surface layer

4.5.4. One lithium atom in a silicon vacancy and four lithium atoms in four carbon vacancies at the surface layer

In this section we increased the number of lithium atom in the carbon vacancy at the surface to four and maintained one lithium atom in a silicon vacancy. The input and output structures are as shown on figure 25



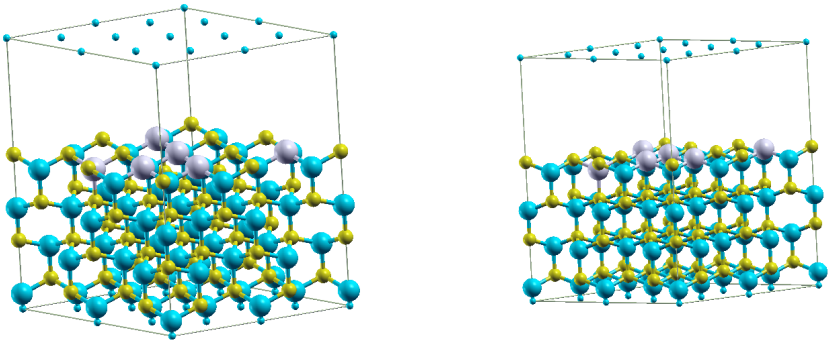
a) Input b) Output

Figure 25: Input and Output structures for one lithium atom in a silicon vacancy and four lithium atoms in a carbon vacancy at the surface layer

the formation energy for this structure is calculated to be 16.38890034eV

4.5.5. One Lithium atom in a Silicon Vacancy and five lithium atoms in a carbon vacancy at the surface

Finally, In this structure we have increased the concentration of the lithium atoms at the surface to five and still maintaining one lithium atom in a silicon vacancy as shown on figure 26



a) Input b) Output

Figure 26: Input and Output structures for one lithium atom in a silicon vacancy and five lithium atoms in a carbon vacancy at the surface layer

we calculate the formation energy of this structure to be 17.86517301eV

The table 9 summarizes the results for these five set of structures

Number of Lithium atoms	Formation Energies (eV)	atoms	Energy differences
1	10.87237292	-	-
2	12.80108919	0ne and two	1.928716
3	14.44121446	Two and three	1.640125
4	16.38890034	Three and four	1.947686
5	17.86517301	Four and five	1.476273

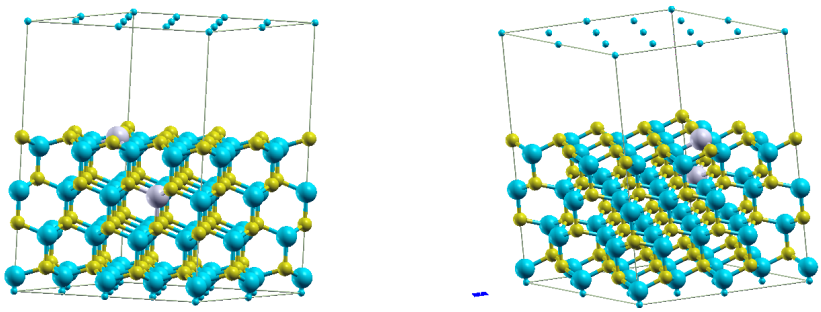
Table 9: Formation Energies and Energy differences for one Lithium atom In a Silicon vacancy at the surface and different concentrations of Lithium atoms in Carbon Vacancies Near Surface

4.6. Mix vacancies at Surface and Near surface layer

in these set of calculations, we have decided to create mix vacancies and study the energy variation as we increase the concentration of lithium atoms on the surface

4.6.1. One lithium atom in a silicon Vacancy near surface and one lithium atom in a Carbon vacancy at the Surface

In this first case, we insert a lithium atom in a silicon vacancy at the near surface layer and a lithium atom in a carbon vacancy at the surface as shown on the input and output diagrams in figure 27



a) Input b) Output

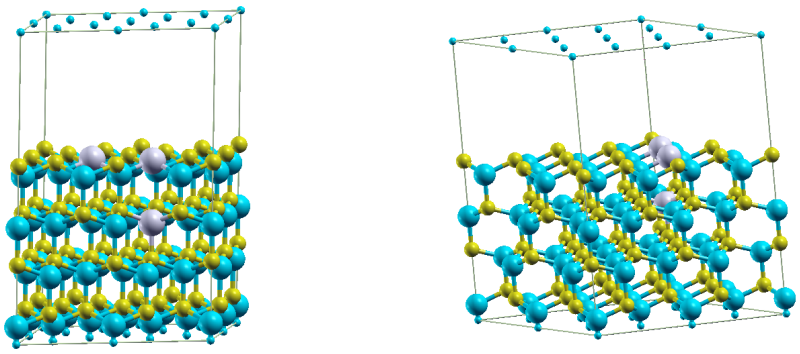
Figure 27: Input and Output structures for One lithium atom in a silicon Vacancy near surface and one lithium atom in a Carbon vacancy at the Surface

the formation energy is calculated to be $10.4889438eV$

4.6.2. One lithium atom in a silicon Vacancy near surface and two lithium atoms in two Carbon vacancies at the Surface

With the Lithium atom fixed in a silicon vacancy at the near surface layer, we increased the number of carbon vacancies at the surface layer to two and replaced them with two lithium atoms as shown on figure 28

The Formation energy is calculated to be $12.38606901eV$

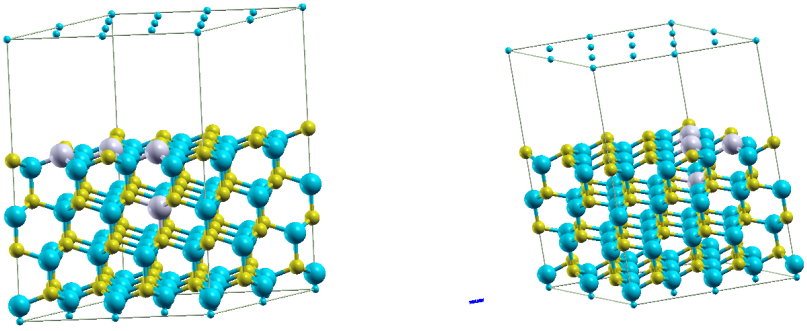


a) Input b) Output

Figure 28: Input and Output structures for One lithium atom in a silicon Vacancy near surface and two lithium atoms in two Carbon vacancies at the Surface

4.6.3. One lithium atom in a silicon Vacancy near surface and three lithium atoms in three Carbon vacancies at the Surface

In this case we make the carbon vacancies at the surface to be three and replaced them with three lithium atoms. one lithium atom is also replaced in a silicon vacancy at the near surface layer as shown on figure 29



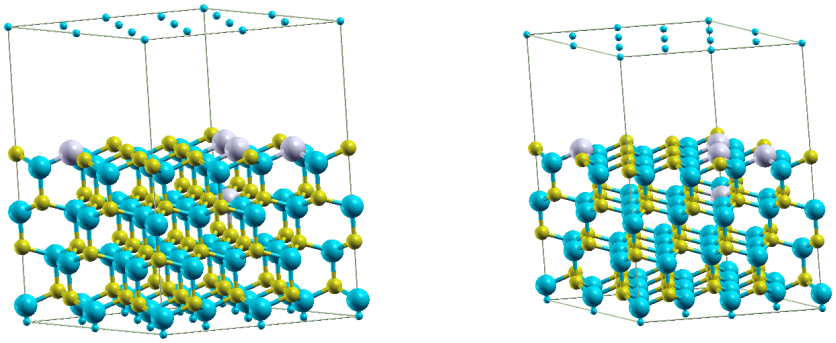
a) Input b) Output

Figure 29: Input and Output structures for One lithium atom in a silicon Vacancy near surface and three lithium atoms in three Carbon vacancies at the Surface

the formation energies for these structures are calculated to be $14.63509783eV$

4.6.4. One lithium atom in a silicon Vacancy near surface and four lithium atoms in four Carbon vacancies at the Surface

we decided to step up the lithium atom in the carbon vacancy at the surface to four and maintained the one lithium atom in the silicon vacancy at the near surface layer as shown on figure 30



a) Input b) Output

Figure 30: Input and Output structures for One lithium atom in a silicon Vacancy near surface and four lithium atoms in four Carbon vacancies at the Surface

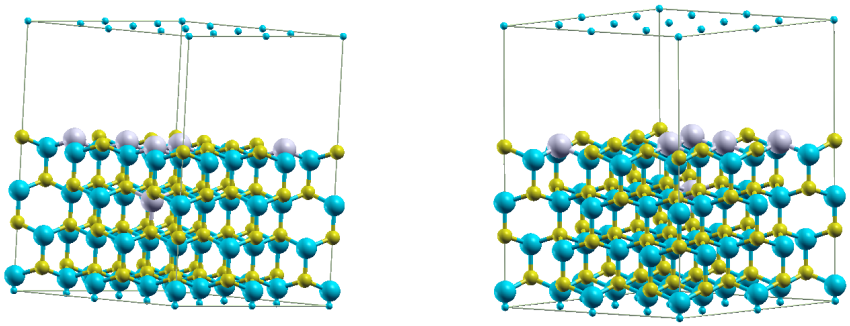
The formation energy for the structures is obtained to be $16.59600152eV$

4.6.5. One lithium atom in a silicon Vacancy near surface and five lithium atoms in five Carbon vacancies at the Surface

Finally we make the carbon vacancy at the surface to five and replaced it with five lithium atoms. One lithium atom is maintained in a silicon vacancy at the near surface layer as shown on figure 31

We calculated the formation energy to be $18.11293807eV$

The Table 10 summarizes the results of these first five structures



a) Input b) Output

Figure 31: Input and Output structures for One lithium atom in a silicon Vacancy near surface and five lithium atoms in five Carbon vacancies at the Surface

Number of Lithium atoms	Formation Energies (eV)	atoms	Energy differences
1	10.4889438	-	-
2	12.38606901	0ne and two	1.897125
3	14.63509783	Two and three	2.249029
4	16.59600152	Three and four	1.960904
5	18.11293807	Four and five	1.516937

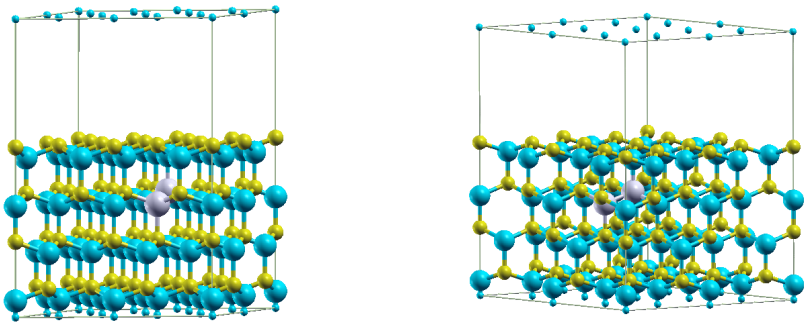
Table 10: Formation Energies and Energy differences for one Lithium atom In a Silicon vacancy at near surface and different concentrations of Lithium atoms in Carbon Vacancies at the Surface

4.7. Mix vacancy at near surface

In these set of calculations, we have created mix vacancies at the near surface layer and replaced these vacancies with lithium atom(s) and the formation energies calculated

4.7.1. One lithium atom in one silicon vacancy and one lithium atom in a carbon vacancy at the near surface layer

This first structure, we have replaced a silicon vacancy and a carbon vacancy by lithium atoms as seen on figure 32



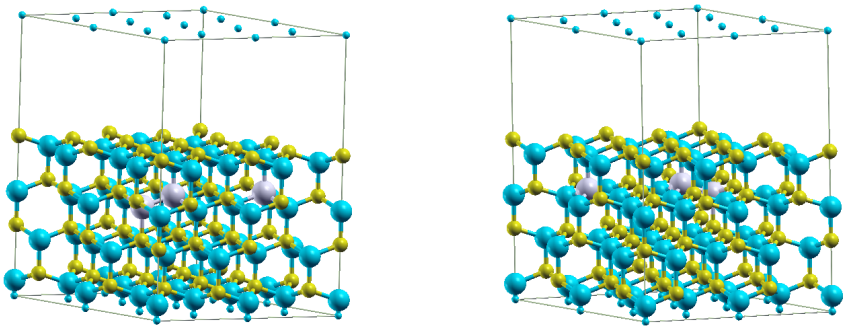
a) Input b) Output

Figure 32: Input and Output structures for One lithium atom in one silicon vacancy and one lithium atom in a carbon vacancy at the near surface layer

the formation energy of this first case is calculated to be 11.23166811eV

4.7.2. one lithium atom in one silicon vacancy and two lithium atoms in two carbon vacancies at the near surface layer

In this case we created two carbon vacancies in the near surface and replaced them by two lithium atoms. With the lithium atom maintained in the Silicon vacancy as shown on figure 33



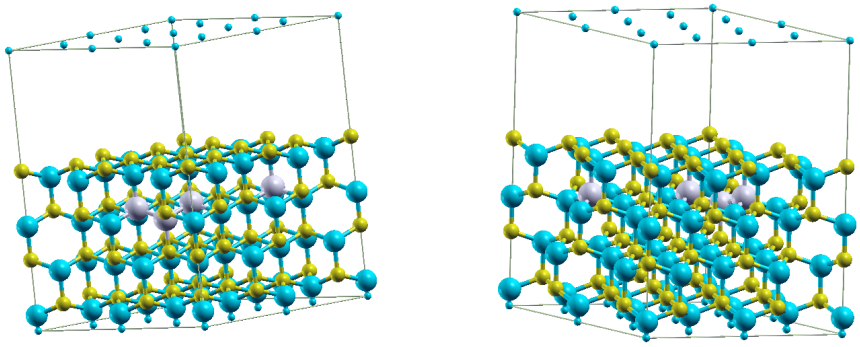
a) Input b) Output

Figure 33: Input and Output structures for one lithium atom in one silicon vacancy and two lithium atoms in two carbon vacancies at the near surface layer

We calculated the formation energy to be 17.42008273

4.7.3. One lithium atom in one silicon vacancy and three lithium atoms in three carbon vacancies at the near surface layer

Here we replaced three carbon vacancies with three lithium atoms at the near surface layer as shown on figure 34



a) Input b) Output

Figure 34: Input and Output structures for one lithium atom in one silicon vacancy and three lithium atoms in three carbon vacancies at the near surface layer

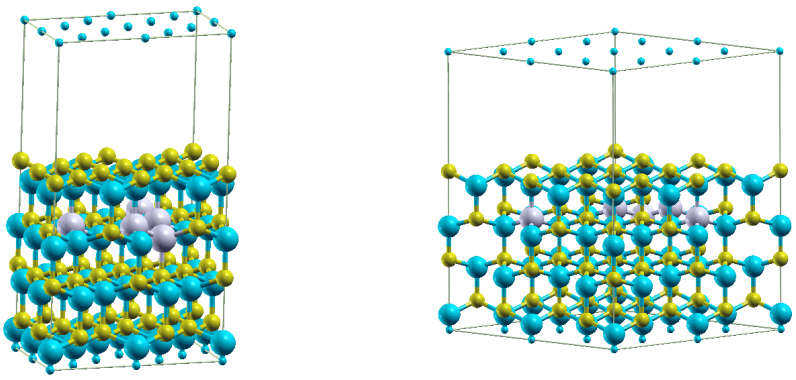
We then calculated the formation energy of this structure to be 20.45124487eV

4.7.4. One lithium atom in one silicon vacancy and four lithium atoms in four carbon vacancies at the near surface layer

We finally created four carbon vacancies at the near surface and replaced them with four lithium atoms.With the one lithium atom maintained in the silicon vacancy, as shown on figure 35

we obtained the formation energy to be 26.23510743eV

The table 11 shows the summary of these set of results.



a) Input b) Output

Figure 35: Input and Output structures for one lithium atom in one silicon vacancy and four lithium atoms in four carbon vacancies at the near surface layer

Number of Lithium atoms	Formation Energies (eV)	atoms	Energy differences
1	11.23166811	-	-
2	17.42008273	0ne and two	6.188415
3	20.45124487	Two and three	3.031162
4	26.23510743	Three and four	5.783863

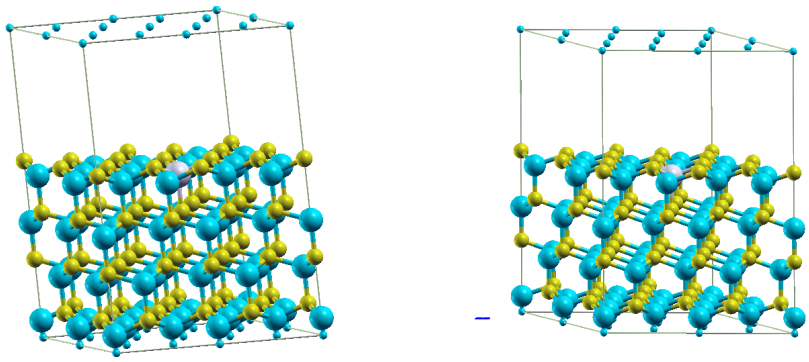
Table 11: Formation Energies and Energy differences for one Lithium atom In a Silicon vacancy at near surface and different concentrations of Lithium atoms in Carbon Vacancies at Near Surface

4.8. Lithium atoms in Silicon vacancies at the surface

In this section we decided to investigate the variation of formation energies by creating Silicon vacancies at the surface and replaced them with Lithium atoms. We Started by inserting one Lithium atoms into a silicon vacancy then increased the concentration to five. The formation energies for each calculation is stated under their respective headings as shown below

4.8.1. One Lithium atom in a silicon Vacancy at the surface

The input and output structures are shown in figure 36



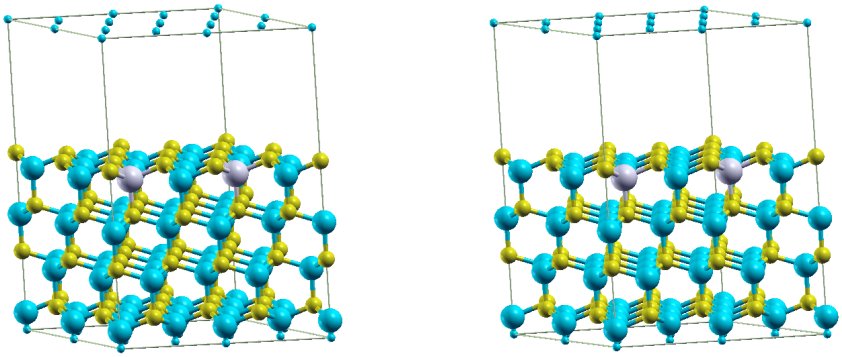
a) Input b) Output

Figure 36: Input and Output structures for One Lithium atom in a silicon Vacancy at the surface

The formation energy for this case is calculated to be 8.386220853eV

4.8.2. Two Lithium atoms in two silicon vacancies at the surface

The Input and Output structures are shown in figure 37



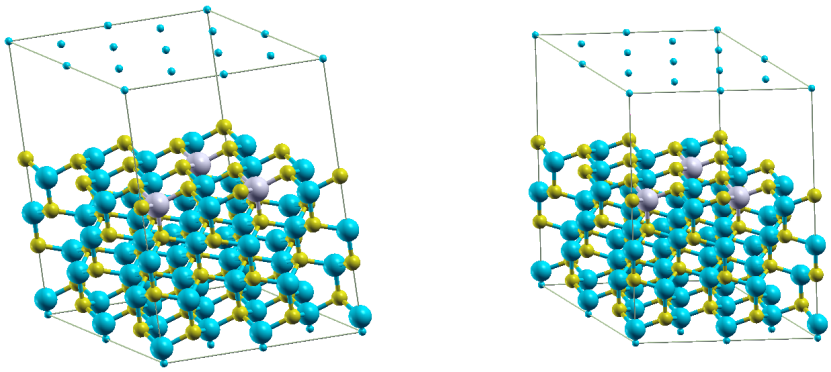
a) Input b) Output

Figure 37: Input and Output structures for Two Lithium atoms in two silicon vacancies at the surface

The formation energy is calculated to be 16.758694eV

4.8.3. Three lithium atoms in Three Silicon Vacancies at the surface

The Input and Output structures are shown in figure 38



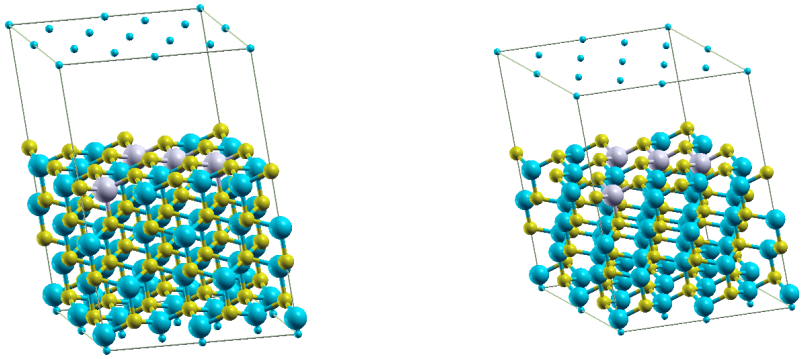
a) Input b) Output

Figure 38: Input and Output structures for three Lithium atoms in three silicon vacancies at the surface

The formation energy is calculated to be 25.1240815eV

4.8.4. Four lithium atoms in Four Silicon vacancies at the surface

The Input and Output structures are shown in figure 39



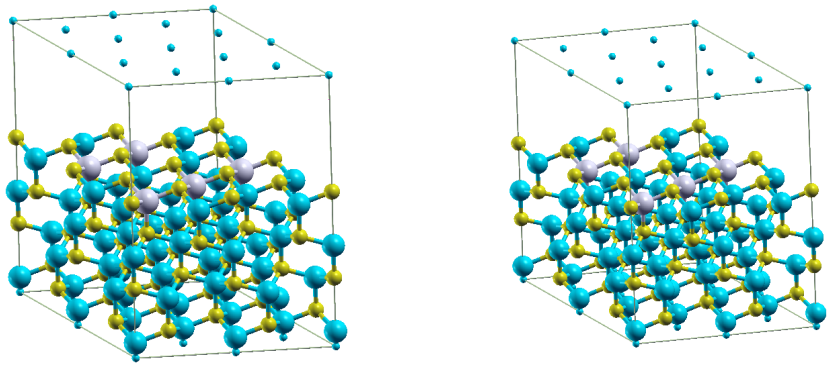
a) Input b) Output

Figure 39: Input and Output structures for four Lithium atoms in four silicon vacancies at the surface

The formation energy is calculated to be 32.61413366eV

4.8.5. Five Lithium atoms in five Silicon Vacancies at the Surface

The Input and Output structures are shown in figure 40



a) Input b) Output

Figure 40: Input and Output structures for five Lithium atoms in five silicon vacancies at the surface

The formation energy is calculated to be 40.63633787eV

A summary on table 12 shows the trend of the stability of the structures with respect to their formation energies.

Number of Lithium atoms	Formation Energies (eV)	atoms	Energy differences
1	8.386220853	-	-
2	16.7586941	0ne and two	8.372473147
3	25.1240815	Two and three	8.3653875
4	32.61413366	Three and four	7.49005216
5	40.63633787	Four and five	8.02220421

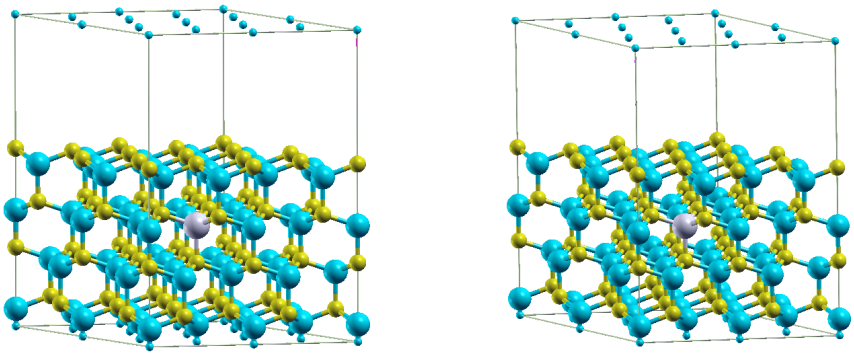
Table 12: Formation Energies and Energy differences for Lithium atoms In Silicon vacancies at the Surface

4.9. Lithium atoms in Silicon vacancies at the Near surface layer

In this next five calculations, we investigate the trend of the formation energies, hence stability as we increased the number of lithium atoms inserted in silicon vacancies at the the layer below the surface. We decided to call it Near Surface layer just for convenience. The results and structures are described under their respective headings below.

4.9.1. One lithium atom in one Silicon vacancy

The input and output structures are shown in figure 41



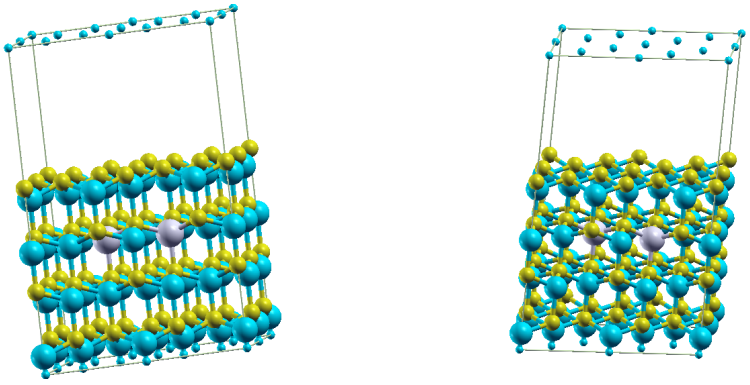
a) Input b) Output

Figure 41: Input and Output structures for One lithium atom in one Silicon vacancy

The formation energy for this case is calculated to be $8.01685894eV$

4.9.2. Two lithium atoms in two silicon Vacancies

The input and output structures are shown in figure 42



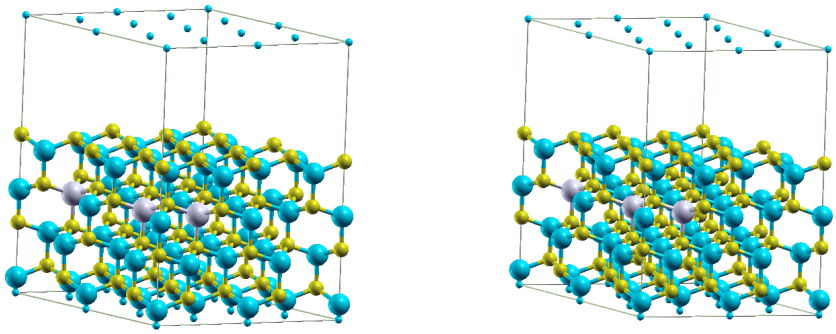
a) Input b) Output

Figure 42: Input and Output structures for two lithium atom in two Silicon vacancy

The formation energy for this case is calculated to be $16.09165271eV$

4.9.3. Three Lithium atoms in Three Silicon Vacancies

The input and output structures are shown in figure 43



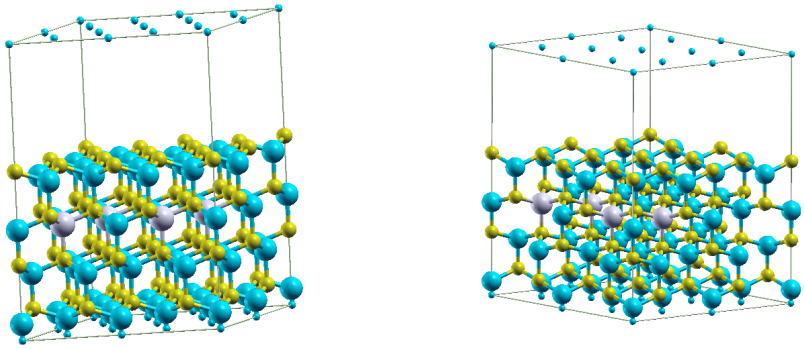
a) Input b) Output

Figure 43: Input and Output structures for three lithium atom in three Silicon vacancies

The formation energy for this case is calculated to be 24.12498924eV

4.9.4. Four Lithium atoms in four Silicon Vacancies

The input and output structures are shown in figure 44



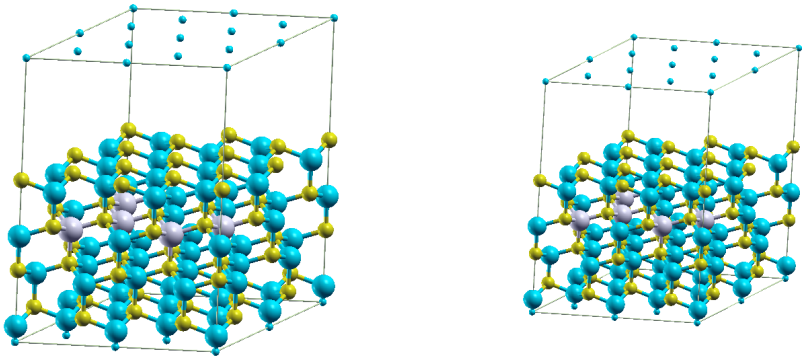
a) Input b) Output

Figure 44: Input and Output structures for four lithium atom in four Silicon vacancies

The formation energy for this case is calculated to be 32.20851039eV

4.9.5. Five Lithium atoms in five Silicon Vacancies

The input and output structures are shown in figure 45



a) Input b) Output

Figure 45: Input and Output structures for five lithium atoms in five Silicon vacancies

The formation energy for this case is calculated to be 39.9851576eV

Table 13 shows the summary of these results.

Number of Lithium atoms	Formation Energies (eV)	atoms	Energy differences
1	8.01685894	-	-
2	16.09165271	0ne and two	8.07479377
3	24.12498924	Two and three	8.03333653
4	32.20851039	Three and four	8.08352115
5	39.9851576	Four and five	7.77664721

Table 13: Formation Energies and Energy differences for Lithium atoms in Silicon vacancies Near surface

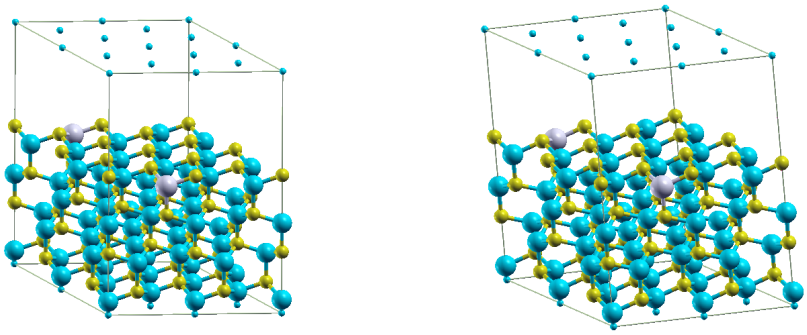
4.10. vacancies in some symmetric positions

In these last six calculations, we decided to create Silicon and Carbon Vacancies in some symmetric positions at the surface and increased concentration of lithium atoms in those

vacancies. we calculated the Formation energies. the results and structures are recorded under the following headings:

4.10.1. one lithium in a silicon Vacancy

The input and output structures are shown in figure 46



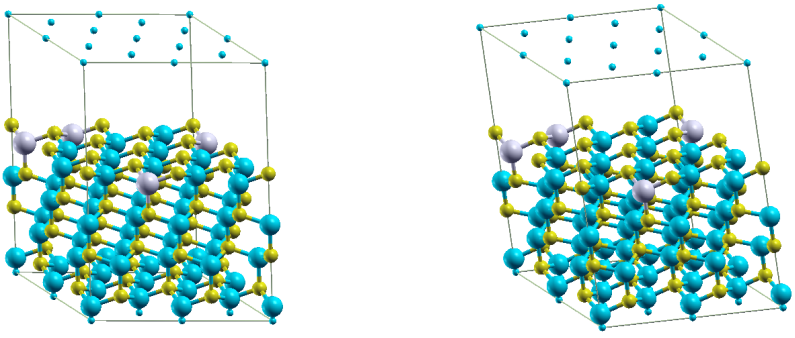
a) Input b) Output

Figure 46: Input and Output structures for one lithium in a silicon Vacancy

The formation energy for this case is calculated to be $8.386220853eV$

4.10.2. Two Lithium atoms in two Silicon Vacancies

The input and output structures are shown in figure 47



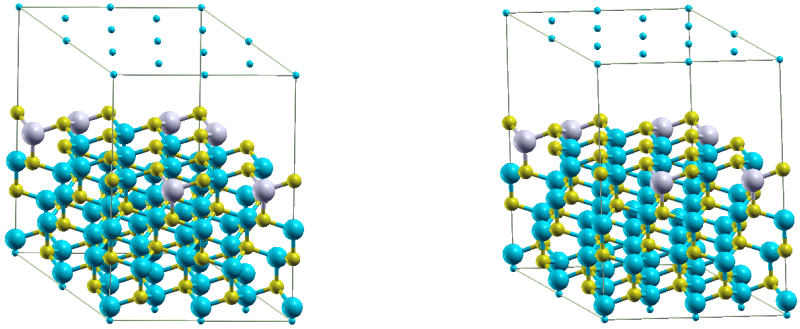
a) Input b) Output

Figure 47: Input and Output structures for Two Lithium atoms in two Silicon Vacancies

The formation energy for this case is calculated to be $16.67783625eV$

4.10.3. three Lithium atoms in three Silicon Vacancies

The input and output structures are shown in figure 48



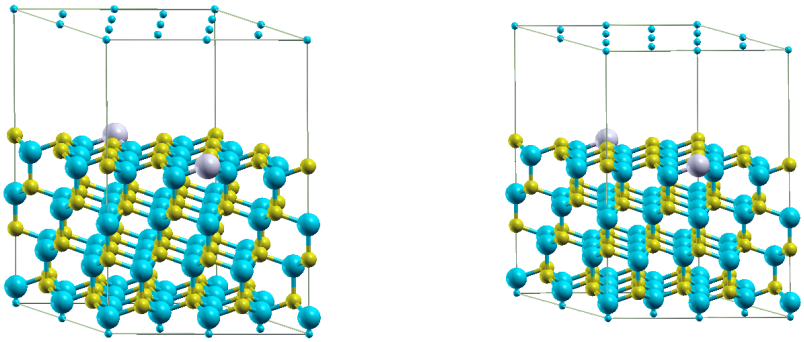
a) Input b) Output

Figure 48: Input and Output structures for three Lithium atoms in three Silicon Vacancies

The formation energy for this case is calculated to be 24.94022063eV

4.10.4. One Lithium atom in one Carbon Vacancy

The input and output structures are shown in figure 49



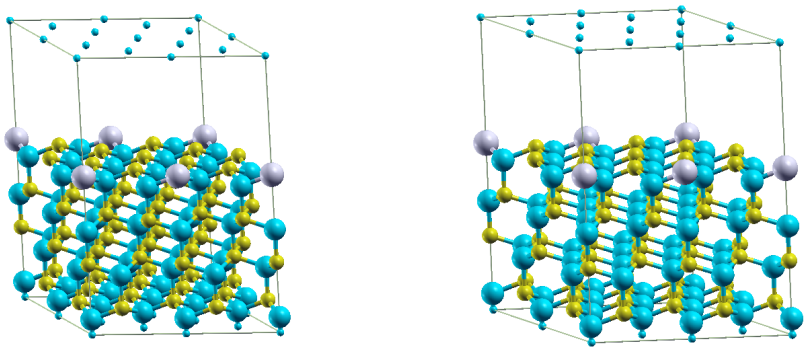
a) Input b) Output

Figure 49: Input and Output structures for One Lithium atom in one Carbon Vacancy

The formation energy for this case is calculated to be 2.503042722eV

4.10.5. two Lithium atoms in two Carbon Vacancies

The input and output structures are shown in figure 50



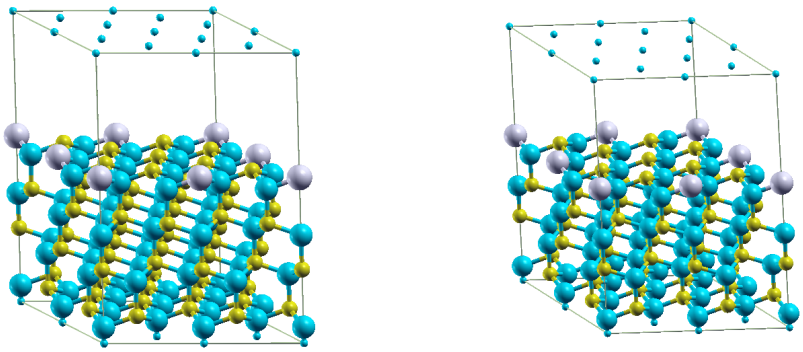
a) Input b) Output

Figure 50: Input and Output structures for two Lithium atoms in two Carbon Vacancies

The formation energy for this case is calculated to be $5.156062279 eV$

4.10.6. Three Lithium atoms in Three Carbon Vacancies

The input and output structures are shown in figure 51



a) Input b) Output

Figure 51: Input and Output structures for three Lithium atoms in three Carbon Vacancies

The formation energy for this case is calculated to be $7.940720229 eV$

A summary on table 14 shows the trend of the stability of the structures with respect to their formation energies.

Number of Lithium atoms	Formation energies (eV)
Silicon Vacancies	
1	8.386220853
2	16.67783625
3	24.94022063
Carbon Vacancies	
1	2.503042722
2	5.156062279
3	7.940720229

Table 14: Formation Energies For Lithium atoms in Carbon and silicon Vacancies for some Symmetric positions at the Surface

5. CHAPTER FIVE

5.1. DISCUSSION

In this section we compare and analyse some of the results of formation energies calculated. We have also used some results from the Masters thesis work of Sushil,[Acharya, 2018] who made calculations on the Bulk 4HSiC structure.we obtain results for calculation of formation energies for carbon and silicon vacancies in bulk. We compare these results and can deduce the following:

5.1.1. comparing Formation energies for Lithiation at the surface for carbon and Silicon vacancies

The Table 15 shows these values and figure 52 shows the variation.

From the energy trend, we can deduce that it is much more favorable to build Lithium atoms in carbon sites at the surface than Silicon sites

Number of Lithium atoms	Formation energies for Carbon sites at Surface	Formation energies for Silicon Sites at Surface
1	2.503042722	8.386220853
2	4.659985466	16.7586941
3	6.546361216	25.1240815
4	8.423602781	32.61413366
5	10.17443149	40.63633787

Table 15: Comparing Formation Energies for Carbon and Silicon sites at surface

5.1.2. Comparing Formation energies for Lithiation at Near Surface for carbon and Silicon

The Table 16 shows these values and figure 53 shows the variation.

From the energy trend, we can deduce that it is still much more favorable to build Lithium

Number of Lithium atoms	formation energies for Carbon sites Near surface	Formation energies for Silicon Sites Near Surface
1	6.231040728	8.386220853
2	11.91619663	16.7586941
3	17.65937621	25.1240815
4	23.44381439	32.61413366
5	-	39.9851576

Table 16: Comparing Formation Energies for Carbon and Silicon sites at Near surface

atoms in carbon sites at the Near surface than Silicon sites at Near Surface

5.1.3. Comparing formation energies at Surface and Bulk for Carbon Sites

The Table 17 shows these values and figure 54 shows the variation.

From the energy trend, we can deduce that it is much more favourable to build Lithium atoms in carbon sites at the surface than in the bulk

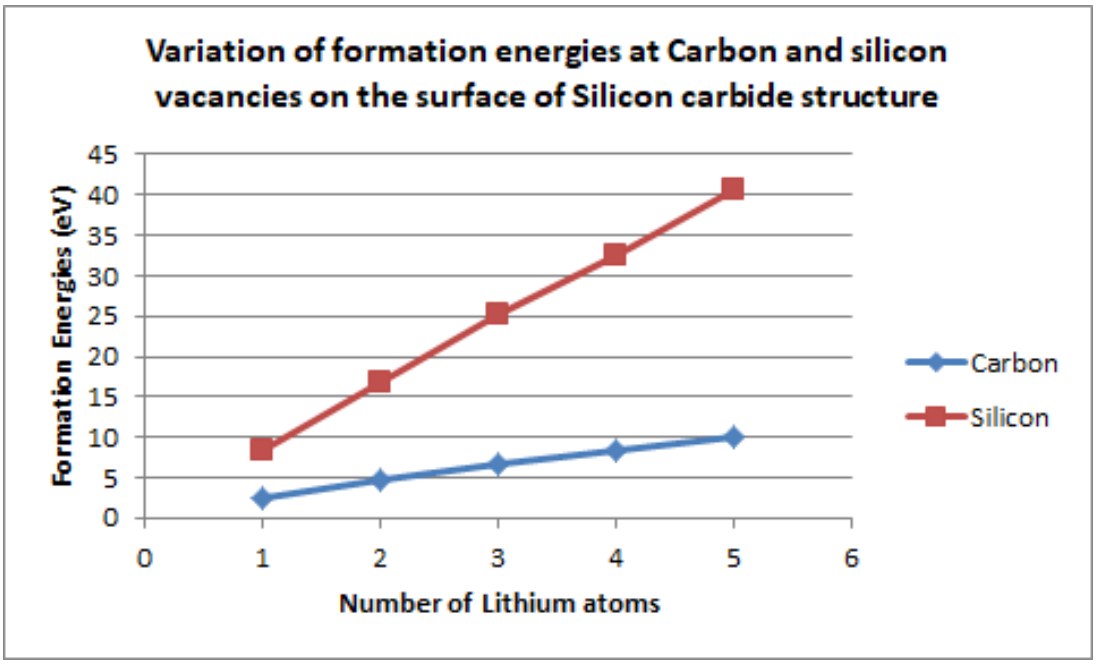


Figure 52: Carbon and Silicon vacancies at the surface

Number of Lithium atoms	formation energies for Carbon sites at Surface	Formation energies for Carbon Sites in the Bulk
1	2.503042722	7.2747
2	4.659985466	9.5898
3	6.546361216	13.5525
4	8.423602781	20.5265
5	10.17443149	20.1442

Table 17: Comparing Formation Energies for Carbon sites at surface and Bulk

5.1.4. Comparing formation energies at Surface and Bulk for Silicon Sites

The Table 18 shows these values and figure 55 shows the variation.

From the energy trend, we can deduce that it is much more favorable to build Lithium atoms in Silicon sites in the Bulk than in Silicon Sites at the Surface.

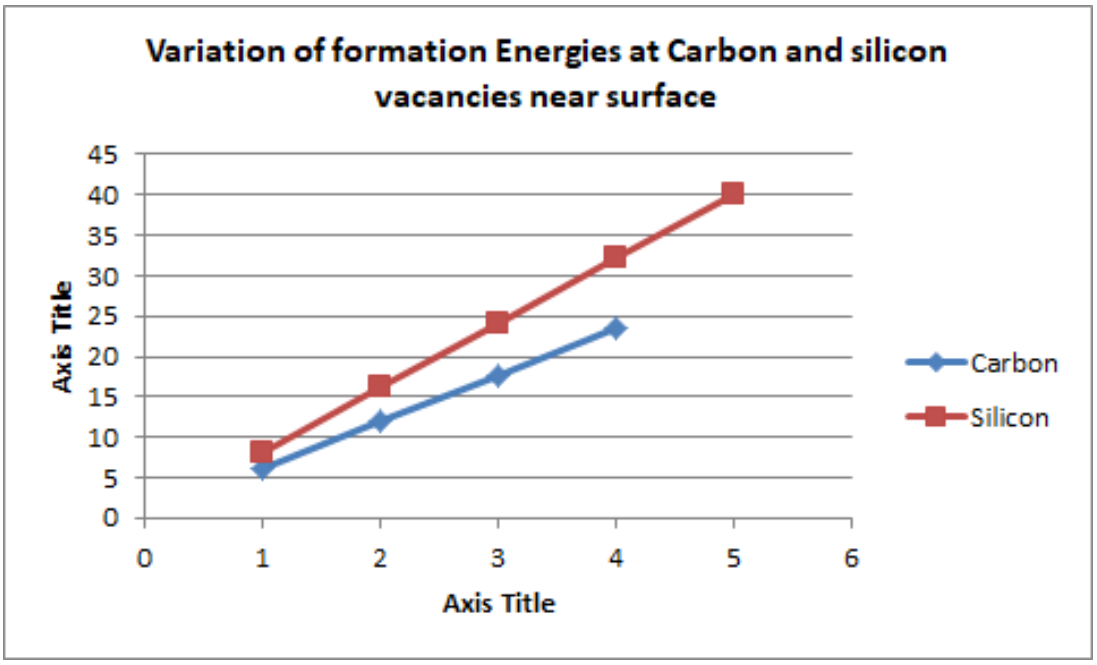


Figure 53: Carbon and Silicon Vacancies Near surface

Number of Lithium atoms	formation energies for Silicon sites at Bulk	Formation energies for Silicon Sites at Surface
1	5.7173	8.386220853
2	9.6861	16.7586941
3	12.8663	25.1240815
4	16.6410	32.61413366
5	21.5187	40.63633787

Table 18: Comparing Formation Energies for Silicon sites at surface Surface and Bulk of 4HSiC

5.1.5. Comparing formation energies for Lithiation of Silicon carbide from Surface to Bulk for the carbon sites

The Table 19 shows these values and figure 56 shows the variation. In this result, we have considered formation energies from Surface, Near Surface and Bulk of the 4HSiC From the energy trend, we can deduce that it is much more favourable to build Lithium atoms in carbon sites from the surface, Bulk and Near surface respectively

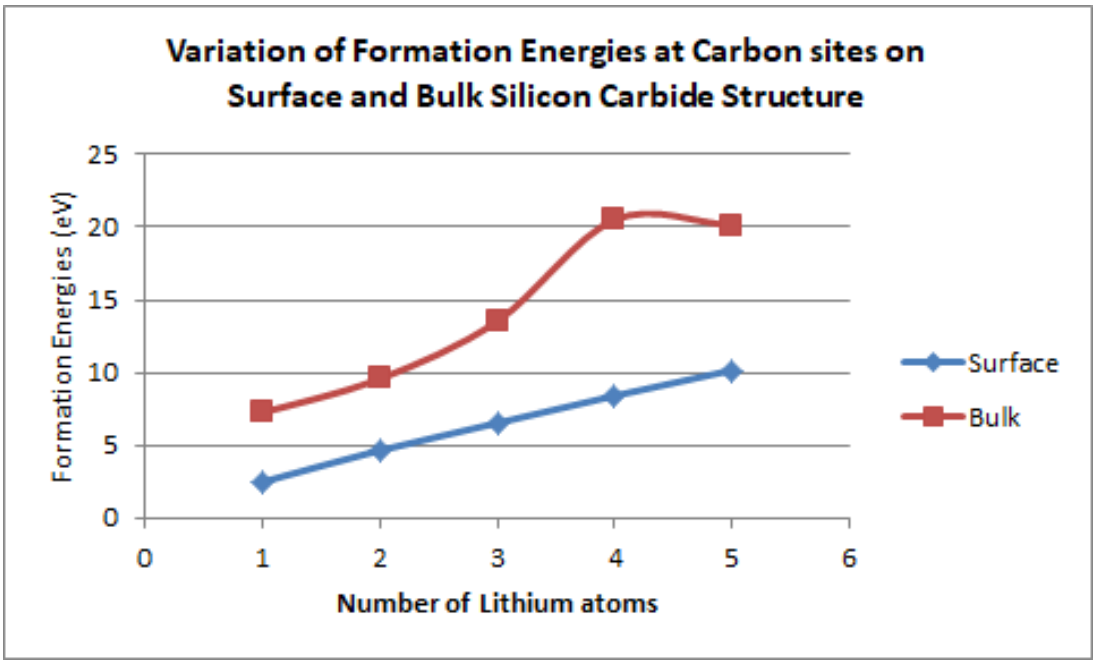


Figure 54: Carbon vacancies at surface and Bulk

Number of Lithium atoms	formation energies for Carbon sites at Surface	Formation energies for Carbon Sites Near Surface	Formation energies for carbon sites in the bulk
1	2.503042722	6.231040728	7.2747
2	4.659985466	11.91619663	9.5898
3	6.546361216	17.65937621	13.5525
4	8.423602781	23.44381439	20.5265
5	10.17443149	-	20.1442

Table 19: Comparing Formation Energies for Carbon sites from surface to bulk of 4HSiC

5.1.6. Comparing formation energies for Lithiation of Silicon carbide from Surface to Bulk for the Silicon sites

The Table 20 shows these values and figure 57 shows the variation. In this result, we have considered formation energies from Surface, Near Surface and Bulk of the 4HSiC From the energy trend, we can deduce that it is much more favourable to build Lithium atoms in Silicon sites from the Bulk, Near surface and surface respectively

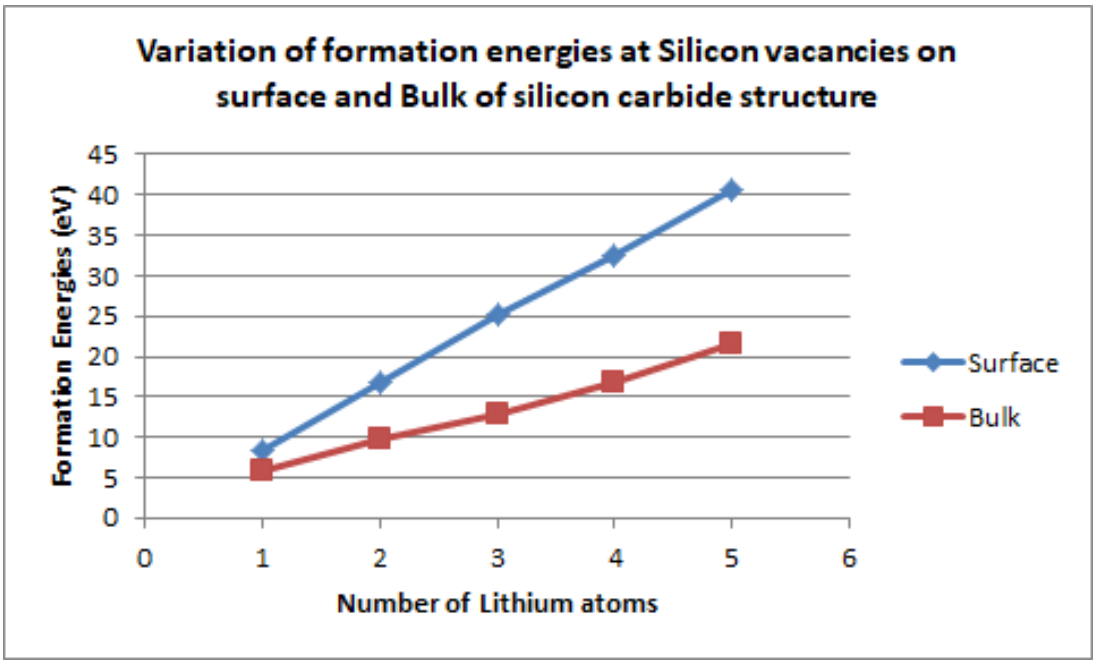


Figure 55: Silicon vacancies at surface and bulk

Number of Lithium atoms	formation energies for Silicon sites at Bulk	Formation energies for Silicon Sites at Surface	Formation energies for Silicon sites Near Surface
1	5.7173	8.386220853	8.01685894
2	9.6861	16.7586941	16.09165271
3	12.8663	25.1240815	24.12498924
4	16.6410	32.61413366	32.20851039
5	21.5187	40.63633787	39.9851576

Table 20: Comparing Formation Energies for Silicon sites from surface to Bulk of 4HSiC

6. CHAPTER SIX

6.1. Conclusion

We Have performed calculations with the 4HSiC involving 96 atoms. We calculated the formation energies and energy differences for the different set of Silicon and carbon vacancies created at the surface and near surface layer of our super cell . From these results, we can make the following conclusions:

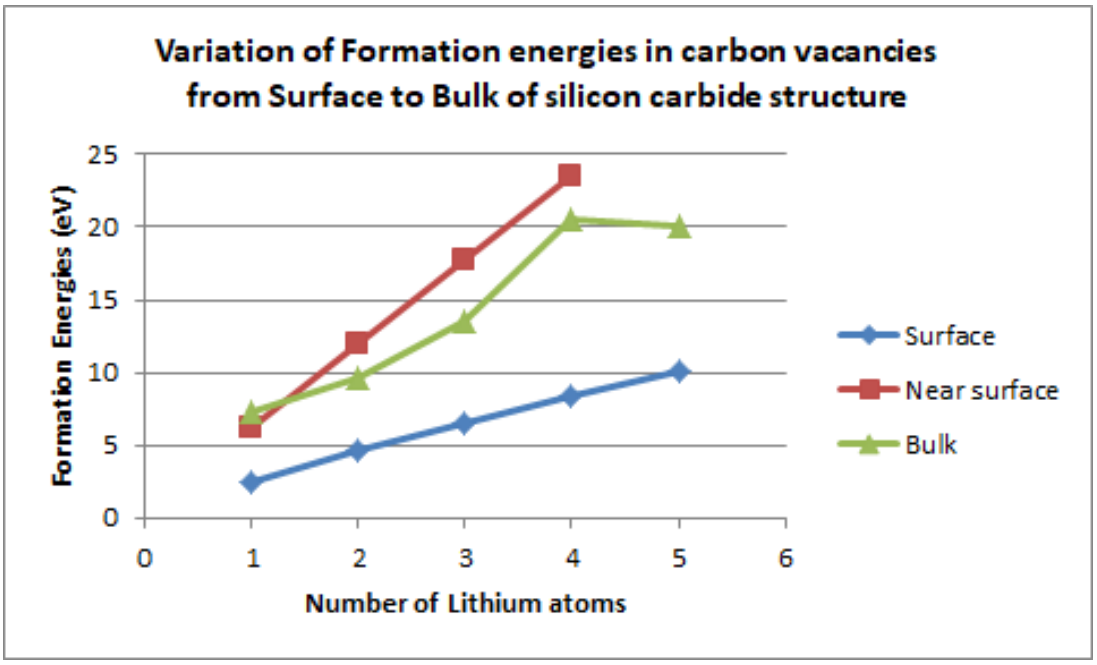


Figure 56: Carbon vacancies from surface to bulk

The results on table 15 and figure 52 show that, it is much more energy favourable to insert Lithium atoms in carbon terminated surface than Silicon

The results on table 19 and figure 56 show that we can adopt a pattern in carefully building inn lithium atoms in Carbon terminated surface of 4H Silicon Carbide. We start putting in the Lithium atoms into Carbon Vacancies From the Surface, then move to the bulk and finally into vacancies near the surface.

This means if we heat the silicon carbide containing Lithium atoms in the bulk to a temperature greater than the activation energies of these Lithium atoms, the Lithium atoms will migrate to the surface and are easily formed at the carbon terminated sites as we have shown in this project. Therefore the next step in this project as a continuation will be calculating this activation energies. This will be a good start for the introduction of Graphene on the surface which involves the intercalation of lithium atoms in it layers.

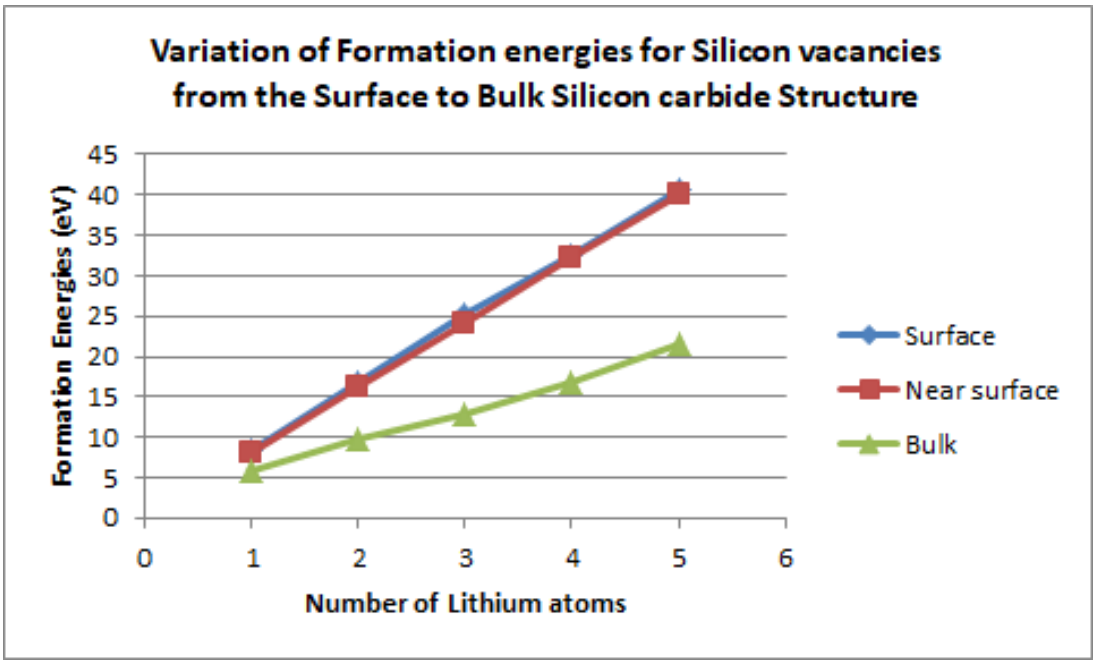


Figure 57: Silicon Vacancies from surface to Bulk

APPENDIX

In this section we present all the mathematical calculations done in the entire thesis Project.We will begin by showing the calculations for the formations energies using the formula in equation 3.33 stated in chapter 3 above. we will start by stating some quantities already defined in chapter 3 :

$E_b = -931.01460868Ry$

$U_c = -11.38075288Ry$

$U_{Li} = -14.09978164Ry$

$U_{Si} = -7.58581405$

$1Ry = 13.6056980659eV$

$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$

Lithium in One Carbon Vacancy at the surface

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -933.54966726 + 931.01460868 - (1 \times 11.38075288) + (1 \times 14.09978164)$$
$$= 0.18397018 Ry$$
$$\implies E_F = 2.503042722\ eV$$

Lithium atoms in two carbon vacancies at the surface

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -936.11016371 + 931.01460868 - (2 \times 11.38075288) + (2 \times 14.09978164)$$
$$= 0.34250249 Ry$$
$$\implies E_F = 4.659985466\ eV$$

Lithium atoms in Three Carbon vacancies at the surface

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -938.69054646 + 931.01460868 - (3 \times 11.38075288) + (3 \times 14.09978164)$$
$$= 0.4811485 Ry$$
$$\implies E_F = 6.546361216\ eV$$

Lithium atoms in Four carbon Vacancies at the surface

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -941.27160056 + 931.01460868 - (4 \times 11.38075288) + (4 \times 14.09978164)$$
$$= 0.61912316 Ry$$
$$\implies E_F = 8.423602781\ eV$$

Lithium atoms in Five Carbon vacancies at the Surface

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -943.86194583 + 931.01460868 - (5 \times 11.38075288) + (5 \times 14.09978164)$$
$$= 0.74780665 Ry$$
$$\implies E_F = 10.17443149\ eV$$

Lithium atom in a carbon vacancy at the surface and One lithium atom in a carbon vacancy near surface

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -935.80443534 + 931.01460868 - (2 \times 11.38075288) + (2 \times 14.09978164)$$
$$= 0.64823086 Ry$$
$$\implies E_F = 8.819633358\ eV$$

Lithium atom in a carbon Vacancy at the surface and two Lithium atoms in two carbon vacancies Near surface

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -938.05309482 + 931.01460868 - (3 \times 11.38075288) + (3 \times 14.09978164)$$
$$= 1.11860014 Ry$$
$$\implies E_F = 15.21933576\ eV$$

Lithium atom in a carbon vacancy at the surface and three Lithium atoms in three carbon vacancies near surface

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -940.39096577 + 931.01460868 - (4 \times 11.38075288) + (4 \times 14.09978164)$$
$$= 1.49975795 Ry$$
$$\implies E_F = 20.40525384\ eV$$

Lithium atom in a carbon vacancy at the surface and four Lithium atoms in four carbon vacancies near surface

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -942.68217666 + 931.01460868 - (5 \times 11.38075288) + (5 \times 14.09978164)$$
$$= 1.92757582 Ry$$
$$\implies E_F = 26.22601461\ eV$$

Lithium atom in a carbon vacancy at the surface and five Lithium atoms in five carbon vacancies near surface

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -945.07065240 + 931.01460868 - (6 \times 11.38075288) + (6 \times 14.09978164)$$
$$= 2.25812884 Ry$$
$$\implies E_F = 30.72341919\ eV$$

Lithium atom in a carbon vacancy at near surface

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -933.27566456 + 931.01460868 - (1 \times 11.38075288) + (1 \times 14.09978164)$$
$$= 0.45797288 Ry$$
$$\implies E_F = 6.231040728\ eV$$

Lithium atoms in two carbon vacancies at near surface

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -935.57684222 + 931.01460868 - (2 \times 11.38075288) + (2 \times 14.09978164)$$
$$= 0.87582398 Ry$$
$$\implies E_F = 11.91619663\ eV$$

lithium atoms in three carbon vacancies at near surface

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -937.87375522 + 931.01460868 - (3 \times 11.38075288) + (3 \times 14.09978164)$$
$$= 1.29793974 Ry$$
$$\implies E_F = 17.65937621\ eV$$

Lithium atoms in four carbon vacancies at near surface

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -940.27566456 + 931.01460868 - (4 \times 11.38075288) + (4 \times 14.09978164)$$
$$= 1.72308795 Ry$$
$$\implies E_F = 23.44381439\ eV$$

Lithium atom in a Silicon vacancy and one Lithium atom in a Carbon vacancy at the surface

$$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$$
$$= -939.44850065 + 931.01460868 - (1 \times 7.58581405) - (1 \times 11.38075288) + (2 \times 14.09978164)$$
$$= 0.79910438 Ry$$
$$\implies E_F = 10.87237292\ eV$$

Lithium atom in a silicon vacancy and Two lithium atoms in two carbon vacancies at the surface

$$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$$
$$= -942.02577143 + 931.01460868 - (1 \times 7.58581405) - (2 \times 11.38075288) + (3 \times 14.09978164)$$
$$= 0.94086236 Ry$$
$$\implies E_F = 12.80108919\ eV$$

Lithium atom in a Silicon vacancy and Three Lithium atoms in Three carbon vacancies at the surface

$$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$$
$$= -944.62425325 + 931.01460868 - (1 \times 7.58581405) - (3 \times 11.38075288) + (4 \times 14.09978164)$$
$$= 1.0614093 Ry$$
$$\implies E_F = 14.44121446\ eV$$

Lithium atom in a Silicon vacancy and four Lithium atoms in four Carbon vacancies at the surface

$$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$$
$$= -947.20012979 + 931.01460868 - (1 \times 7.58581405) - (4 \times 11.38075288) + (5 \times 14.09978164)$$
$$= 1.20456152 Ry$$
$$\implies E_F = 16.38890034\ eV$$

lithium atom in a Silicon vacancy and Five Lithium atoms in Five Carbon vacancies at the surface

$$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$$
$$= -949.81065455 + 931.01460868 - (1 \times 7.58581405) - (5 \times 11.38075288) + (6 \times 14.09978164)$$
$$= 1.31306552 Ry$$
$$\implies E_F = 17.86517301\ eV$$

Lithium atom in a Silicon vacancy near surface and one Lithium atom in a carbon vacancy at the surface

$$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$$
$$= -939.47668216 + 931.01460868 - (1 \times 7.58581405) - (1 \times 11.38075288) + (2 \times 14.09978164)$$
$$= 0.77092287 Ry$$

$\implies E_F = 10.4889438\ eV$

Lithium atom in a Silicon vacancy near Surface and two Lithium atoms in two Carbon vacancies at the Surface

$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$

$= -942.05627484 + 931.01460868 - (1 \times 7.58581405) - (2 \times 11.38075288) + (3 \times 14.09978164)$

$= 0.91035895 Ry$

$\implies E_F = 12.38606901\ eV$

Lithium atom in a Silicon vacancy near Surface and three Lithium atoms in three Carbon vacancies at the Surface

$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$

$= -944.61000309 + 931.01460868 - (1 \times 7.58581405) - (3 \times 11.38075288) + (4 \times 14.09978164)$

$= 1.07565946 Ry$

$\implies E_F = 14.63509783\ eV$

Lithium atom in a Silicon vacancy near Surface and four Lithium atoms in four Carbon vacancies at the Surface

$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$

$= -947.18490814 + 931.01460868 - (1 \times 7.58581405) - (4 \times 11.38075288) + (5 \times 14.09978164)$

$= 1.21978317 Ry$

$\implies E_F = 16.59600152\ eV$

Lithium atom in a Silicon vacancy near Surface and five Lithium atoms in five Carbon vacancies at the Surface

$$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$$
$$= -949.79244416 + 931.01460868 - (1 \times 7.58581405) - (5 \times 11.38075288) + (6 \times 14.09978164)$$
$$= 1.33127591 Ry$$
$$\implies E_F = 18.11293807\ eV$$

Lithium atom in a silicon vacancy and one Lithium atom in a Carbon vacancy at the Near surface

$$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$$
$$= -939.42209295 + 931.01460868 - (1 \times 7.58581405) - (1 \times 11.38075288) + (2 \times 14.09978164)$$
$$= 0.82551208 Ry$$
$$\implies E_F = 11.23166811\ eV$$

Lithium atom in a silicon vacancy and Two Lithium atoms in two Carbon vacancies at the Near surface

$$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$$
$$= -941.68628179 + 931.01460868 - (1 \times 7.58581405) - (2 \times 11.38075288) + (3 \times 14.09978164)$$
$$= 1.280352 Ry$$
$$\implies E_F = 17.42008273\ eV$$

Lithium atom in a silicon vacancy and three Lithium atoms in three Carbon vacancies at the Near surface

$$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$$
$$= -944.18252416 + 931.01460868 - (1 \times 7.58581405) - (3 \times 11.38075288) + (4 \times 14.09978164)$$
$$= 1.50313839 Ry$$

$\implies E_F = 20.45124487\ eV$

Lithium atom in a silicon vacancy and four Lithium atoms in four Carbon vacancies at the Near surface

$E_F = E_s - E_b + p \times U_c + q \times U_{Si} - r \times U_{Li}$

$= -946.47644718 + 931.01460868 - (1 \times 7.58581405) - (4 \times 11.38075288) + (5 \times 14.09978164)$

$= 1.92824413 Ry$

$\implies E_F = 26.23510743\ eV$

Silicon Vacancies

lithium atom in a silicon vacancy at the Surface

$E_F = E_s - E_b + q \times U_{Si} - r \times U_{Li}$

$= -936.91220063 + 931.01460868 - (1 \times 7.58581405) + (1 \times 14.09978164)$

$= 0.61637564 Ry$

$\implies E_F = 8.386220853\ eV$

Lithium atoms in two Silicon vacancies at the surface

$E_F = E_s - E_b + q \times U_{Si} - r \times U_{Li}$

$= -942.81080301 + 931.01460868 - (2 \times 7.58581405) + (2 \times 14.09978164)$

$= 1.23174085 Ry$

$\implies E_F = 16.7586941\ eV$

Lithium atoms in three Silicon vacancies at the surface

$$E_F = E_s - E_b + q \times U_{Si} - r \times U_{Li}$$
$$= -948..70992619 + 931.01460868 - (3 \times 7.58581405) + (3 \times 14.09978164)$$
$$= 1.84658526 Ry$$
$$\Longrightarrow E_F = 25.1240815\ eV$$

Four Lithium atoms in four Silicon vacancies at the surface

$$E_F = E_s - E_b + q \times U_{Si} - r \times U_{Li}$$
$$= -954.67338530 + 931.01460868 - (4 \times 7.58581405) + (4 \times 14.09978164)$$
$$= 2.39709374 Ry$$
$$\Longrightarrow E_F = 32.61413366\ eV$$

Lithium atoms in five Silicon vacancies at the surface

$$E_F = E_s - E_b + q \times U_{Si} - r \times U_{Li}$$
$$= -960.59773197 + 931.01460868 - (5 \times 7.58581405) + (5 \times 14.09978164)$$
$$= 2.98671466 Ry$$
$$\Longrightarrow E_F = 40.63633787\ eV$$

Lithium atom in one Silicon vacancy at near surface

$$E_F = E_s - E_b + q \times U_{Si} - r \times U_{Li}$$
$$= -936.93934822 + 931.01460868 - (1 \times 7.58581405) + (1 \times 14.09978164)$$
$$= 0.58922805 Ry$$
$$\Longrightarrow E_F = 8.01685894\ eV$$

Lithium atoms in two Silicon vacancies at near surface

$$E_F = E_s - E_b + q \times U_{Si} - r \times U_{Li}$$
$$= -942.85982963 + 931.01460868 - (2 \times 7.58581405) + (2 \times 14.09978164)$$
$$= 1.18271423 Ry$$
$$\implies E_F = 16.0916527\ eV$$

Lithium atoms in three Silicon vacancies at near surface

$$E_F = E_s - E_b + q \times U_{Si} - r \times U_{Li}$$
$$= -948.78335809 + 931.01460868 - (3 \times 7.58581405) + (3 \times 14.09978164)$$
$$= 1.77315336 Ry$$
$$\implies E_F = 24.12498924\ eV$$

Lithium atoms in Four Silicon vacancies at near surface

$$E_F = E_s - E_b + q \times U_{Si} - r \times U_{Li}$$
$$= -954.70319805 + 931.01460868 - (4 \times 7.58581405) + (4 \times 14.09978164)$$
$$= 2.36728099 Ry$$
$$\implies E_F = 32.20851039\ eV$$

Lithium atoms in five Silicon vacancies at near surface

$$E_F = E_s - E_b + q \times U_{Si} - r \times U_{Li}$$
$$= -960.64559282 + 931.01460868 - (5 \times 7.58581405) + (5 \times 14.09978164)$$
$$= 2.93885381 Ry$$
$$\implies E_F = 39.9851576\ eV$$

Symmetric positions in carbon and Silicon vacancies at the surface

Lithium atom in one silicon Vacancy

$$E_F = E_s - E_b + q \times U_{Si} - r \times U_{Li}$$
$$= -936.91220063 + 931.01460868 - (1 \times 7.58581405) + (1 \times 14.09978164)$$
$$= 0.61637564 Ry$$
$$\implies E_F = 8.386220853\ eV$$

lithium atoms in two Silicon vacancies

$$E_F = E_s - E_b + q \times U_{Si} - r \times U_{Li}$$
$$= -942.81674595 + 931.01460868 - (2 \times 7.58581405) + (2 \times 14.09978164)$$
$$= 1.22579791 Ry$$
$$\implies E_F = 16.67783625\ eV$$

lithium atoms in three Silicon vacancies

$$E_F = E_s - E_b + q \times U_{Si} - r \times U_{Li}$$
$$= -948.72343971 + 931.01460868 - (3 \times 7.58581405) + (3 \times 14.09978164)$$
$$= 1.83307174 Ry$$
$$\implies E_F = 24.94022063\ eV$$

Lithium atom in a carbon vacancy

$$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$$
$$= -933.54966726 + 931.01460868 - (1 \times 11.38075288) + (1 \times 14.09978164)$$
$$= 0.18397018 Ry$$

$\implies E_F = 2.503042722\ eV$

Lithium atoms in two carbon vacancies

$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$

$= -936.07370275 + 931.01460868 - (2 \times 11.38075288) + (2 \times 14.09978164)$

$= 0.37896345 Ry$

$\implies E_F = 5.156062279\ eV$

Lithium atoms in three carbon vacancies

$E_F = E_s - E_b + p \times U_c - r \times U_{Li}$

$= -938.58806373 + 931.01460868 - (3 \times 11.38075288) + (3 \times 14.09978164)$

$= 0.58363196 Ry$

$\implies E_F = 7.940720229\ eV$

References

[Acharya, 2018] Acharya, S. (2018). Lithiation of silicon carbide. Master's thesis, University of Stavanger.

[Breinig, 2009] Breinig, M. (2009). *Schrodinger Equation*, pages 681–685. Springer Berlin Heidelberg, Berlin, Heidelberg.

[Chan et al., 2010] Chan, C. K., Patel, R. N., O'Connell, M. J., Korgel, B. A., and Cui, Y. (2010). Solution-grown silicon nanowires for lithium-ion battery anodes. *ACS Nano*, 4(3):1443–1450. PMID: 20201547.

[Chan et al., 2007] Chan, C. K. P., Hailin Liu, G. M., Kevin Zhang, X. F. H., and Robert A. Cui, Y. (2007). High-performance lithium battery anodes using silicon nanowires. *Nature Nanotechnology*.

[Claeys and Simoen, 2013] Claeys, C. and Simoen, E. (2013). *Radiation Effects in Advanced Semiconductor Materials and Devices*. Springer Series in Materials Science. Springer Berlin Heidelberg.

[Dahl and Avery, 2013] Dahl, J. and Avery, J. (2013). *Local Density Approximations in Quantum Chemistry and Solid State Physics*. Springer US.

[Dirac, 1930] Dirac, P. A. M. (1930). Note on exchange phenomena in the thomas atom. *Mathematical Proceedings of the Cambridge Philosophical Society*, 26(3):376–385.

[Feng, 2015] Feng, X. (2015). *Nanocarbons For Advanced Energy Storage*. Number v. 1. Wiley.

[Huang and Tu, 2013] Huang, Y. and Tu, K. (2013). *Silicon and Silicide Nanowires: Applications, Fabrication, and Properties*. Pan Stanford.

[J. Chen et al., 2008] J. Chen, Z., Xiao, H., T. Zu, X., and Gao, F. (2008). First-principles calculation of defect formation energies and electronic properties in stannate pyrochlores. *Journal of Applied Physics*, 104:093702 – 093702.

[Lee et al., 2010] Lee, J. K., Smith, K. B., Hayner, C. M., and Kung, H. H. (2010). Silicon nanoparticles–graphene paper composites for li ion battery anodes. *Chem. Commun.*, 46:2025–2027.

[Li et al., 2008] Li, Y., Tan, B., and Wu, Y. (2008). Mesoporous co3o4 nanowire arrays for lithium ion batteries with high capacity and rate capability. *Nano Letters*, 8(1):265–270. PMID: 18072799.

[Ma and Zhanyi Hu, 2014] Ma, D. C. and Zhanyi Hu, A. (2014). Si-based anode materials for li-ion batteries: a mini review. *Jour*.

[Magasinski, 2010] Magasinski, A. Dixon, P. H. B. K. A. A. J. Y. G. (2010). High-performance lithium-ion anodes using a hierarchical bottom-up approach. *Nature Materials*.

[Marom et al., 2011] Marom, R., Amalraj, S. F., Leifer, N., Jacob, D., and Aurbach, D. (2011). A review of advanced and practical lithium battery materials. *J. Mater. Chem.*, 21:9938–9954.

[Park et al., 2009] Park, M.-H., Kim, M. G., Joo, J., Kim, K., Kim, J., Ahn, S., Cui, Y., and Cho, J. (2009). Silicon nanotube battery anodes. *Nano Letters*, 9(11):3844–3847. PMID: 19746961.

[Park et al., 2013] Park, Y., Lee, S., Kim, S.-H., Jang, B. Y., Kim, J. S., Oh, S. M., Kim, J.-Y., Choi, N.-S., Lee, K. T., and Kim, B.-S. (2013). A photo-cross-linkable polymeric binder for silicon anodes in lithium ion batteries. *Rsc adv.*, 3:12625–12630.

[Plaskett, 1953] Plaskett, J. S. (1953). The theory of the thomas-fermi electron density. *Proceedings of the Physical Society. Section A*, 66(2):178–190.

[Tarascon and Armand, 2001] Tarascon, J.-M. and Armand, M. (2001). Issues and challenges facing rechargeable lithium batteries. *Nature*, 414(6861):359–367.

[Thomas, 1927] Thomas, L. H. (1927). The calculation of atomic fields. *Mathematical Proceedings of the Cambridge Philosophical Society*, 23(5):542–548.

[Tian et al., 2015] Tian, H., Xin, F., Wang, X., He, W., and Han, W. (2015). High capacity group-iv elements (si, ge, sn) based anodes for lithium-ion batteries. *Journal of Materiomics*, 1(3):153 – 169.

[Wang and Han, 2010] Wang, X.-L. and Han, W.-Q. (2010). Graphene enhances li storage capacity of porous single-crystalline silicon nanowires. *ACS Applied Materials & Interfaces*, 2(12):3709–3713. PMID: 21114292.

[Whittingham, 2012] Whittingham, M. S. (2012). History, evolution, and future status of energy storage. *Proceedings of the IEEE*, 100(Special Centennial Issue):1518–1534.

[Yazdi et al., 2016] Yazdi, G. R., Iakimov, T., and Yakimova, R. (2016). Epitaxial graphene on sic: A review of growth and characterization. *Crystals*, 6(5).