COMPUTATIONAL STUDY OF ELECTRONIC PROPERTIES OF CARBON- HOMO DOPED SILICENE MONOLAYER

By

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Dedication

This thesis is dedicated to my family.

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Abstract

Silicene, two dimensional form of silicon atom, has attractive considerable attention due to its promising applications in nanoelectronics. This study, investigates how doping carbons at different concentrations alters and improve its properties as well as intensify its applications. Inorder to investigate structural and electronic modifications produced by doping carbon atom in to silicene lattice, we use Density Functional Theory (DFT). Our findings indicate that substituting carbon atoms leads to significant changes, starting with the emergence of a band gap at a dopant concentration of x = 0.22 in super cell of eighteen(18) silicon atoms. This transition converts silicene from a semimetal to a semiconductor. Furthermore, at both carbon dopant concentrations of x= 0.22 and x = 0.33, a direct band gap material is produced.The study provides understanding of how carbon doping influence the electronic properties of silicene, open the way for development of next generation technology.

Key words: silicene, Structural properties, Electronic properties, Density Functional Theory

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Chapter 1

INTRODUCTION

1.1 Background of the Study

2D materials are always fascinating in their own right from a basic physics point of view, as well as in technology. The hottest material in the world of materials is two dimensional graphene. Since its discovery, it has led to many new research ideas due to its unusual properties and it has been found to have great potential for use in future nanoelectronic devices. A band gap opening in grapheme observed by doping in an uncontrollable manner, which makes it incompatible for use in building practical devices. In this situation, researchers have found a replacement for graphene in the form of silicene, a monolayer of silicon atoms forming a two dimensional honey-comb lattice like graphene. Note that silicon to date is the most semiconducting element used in nanotechnology. In contrast to the advantage obtained from graphene, silicene thus may be easily interfaced/integrated with existing micro or nano-electronic devices. This new two dimensional material has been found to be compatible with the present Si based nano electronics industry, both experimentally and theoretically [1].

A graphene-like band structure has been reported for the case of planar silicone

[2]. Silicene has been epitaxially grown on a silver surface Ag (111). A standard computer processor works through the use of silicon based transistors. A transistor can be used for various purposes, such as amplification, logic, and memory. All of these utilities are dependent on the physical properties of the material used to create the transistor. The current rapid advancement in the field of electronics is largely dependent on advances in transistor technology. However, recently transistor technology has reached a plateau. The current methodology is centered about placing more transistors in the same unit area. Through this method the speed and throughput of processors have continued to rise. The speed and efficiency of the processor has changed as well, but if you could dramatically improve the switching speed of a transistor, you could theoretically increase the speed of a processor by an equivalent amount .This thesis will examine a new material that could vastly increase the speed of a transistor. That material is silicene ,which is the silicon version of the well-know material, graphene. The method used will be density functional theory implemented through the software suite Quantum Espresso [3].

Silicene is a two-dimensional buckled lattice of silicon atoms with hexagonal lattice structure. When examining a new material for an application, it is a worth while task to use abinitio calculations to determine the physical properties for that material before investing time and money on manufacture. To that effect the structural and electronic properties of the new structure will be simulated. This simulation will be done using the Quantum Espresso software suite. Quantum Espresso is based on density functional theory, or DFT. Density functional theory relies on many-body theory, among other approximations, to set up the Schrodinger wave equation, abbreviated as SWE. This many-body version of the SWE uses numerous Kohn-Sham equations; they provide the wave function of an electron inside a solid. The Kohn-Sham equations are not solvable analytically. They can, however, be solved by approximation methods using Quantum Espresso . Solid state physics is the largest branch of condensed matter physics. It describes various large-scale properties and how they are determined from the atoms and structures of the crystals and or solids in question. Solid state physics, like any field, has many new topics to consider. One of the most often considered new materials in the field is graphene. Graphene is a two-dimensional carbon crystal that has the same structure as a single layer of graphite. Graphene has shown various unique properties that have drawn the attention of the solid state physics community. However it is silicene and the possible integration of silicene that is the focus of this thesis. Silicene is a relatively new material, one with a wealth of new topics and possible research. Very recently, the formation of silicene was reported on various metallic surfaces, like (111Agsurfaces [4, 5, 6, 7, 8, 9], (0001) ZrB2surfaces [10, 11] and (111) Iron surfaces [12].

The electronic properties of the silicene layer on Ag(111) was investigated using angle-resolved photoemission spectroscopy. These measurements revealed the presence of a linear dispersion in the band structure of silicene (so called Dirac cones) with a Fermi velocity of about $1.3 \times 10^6 m/s$, as theoretically predicted for free-standing silicene. A recent breakthrough paved the way to the possible realization of silicene-based field effect transistors operating at room temperature [13], presenting ambipolar current-voltage characteristics, as expected for a gapless semiconductor. We review here recent theoretical results, based on density-functional theory (DFT) calculations, pertaining to the interaction of silicene with non-metallic surfaces.

From the large variety of two-dimensional (2D) materials that exist today, silicene, the silicon counterpart of graphene has steadily increased its sphere of influence due to its malleable electronic properties and its compatibility with the current silicon-based technology [14]. For instance, the buckled layer geometry of silicene facilitates a band gap engineering and in the presence of an electric field opens a gap transport that makes possible the realization of a field-effect transistor (FET) at room temperature. In the past few years silicene has been gaining considerable interest in the scientific community [15, 16, 17]. Like graphene, silicone has a 2D hexagonal structure with silicon atoms at each lattice site, with two interpenetrating sublattices A and B. Silicene [18] is a single atomic layer of silicon (Si) much like graphene [19]. The interest in silicene is exactly the same as that for graphene, in being two-dimensional (2D) and possessing a Dirac cone [18]. One advantage relies on its possible application in electronics, whereby its natural compatibility with the current Si technology might make fabrication much more of a commercial reality.

1.2 Statement of problem

Recently, silicene has been considered to overcome the band gap issue of graphene. Since the discovery of graphene there were strong efforts to search theoretically and experimentally for similar two-dimensional materials composed of group-IV elements, especially silicon. Silicene was first mentioned in a theoretical study by Takeda and Shiraishi [20] in 1994 and then reinvestigated by Guzman-Verri and co-workers [18]. However, a solid phase of silicon analogous to graphite does not exist in nature. As a consequence, silicene cannot be generated by exfoliation methods but more sophisticated methods have to be considered. Silicene, the silicon-based analogue of graphene, has garnered substantial attention in the scientific community due to its unique structural and electronic properties. However, the inherent limitations of pristine silicene, such as the lack of a sizable band gap and the potential instability of the freestanding material, have motivated researchers to explore various strategies for enhancing and modifying its characteristics. One promising approach is the incorporation of dopant atoms, such as carbon, within the silicene lattice. The substitution of silicon atoms by carbon, known as carbon homo-doping, can introduce structural distortions and alter the electronic properties in the material. Understanding the impact of carbon doping on the structural properties of silicene is crucial for the rational design and optimization of this 2D material for various technological applications. Despite the growing interest in carbon-doped silicene, there is a need for a comprehensive Density Functional Theory (DFT)-based investigation to elucidate the underlying mechanisms governing the structure-property relationships in this system. The key problems such as , how do varying concentrations of carbon doping (e.g., 2C, 4C, 6C) affect the structural distortions of the silicene lattice ? , how does carbon doping influence the electronic band structure and the nature of the electronic states near the Fermi level? ,Can carbon doping lead to the emergence of metallic or conductive behavior in silicene?,what is the relationship between the structural modifications and electronic structure properties of carbon-doped silicene? questions need to be addressed .Addressing these problems through a comprehensive DFT study will provide valuable insights into the fundamental mechanisms governing the interplay between the structural and electronic properties of carbon- homo doped silicene monolayers. This knowledge is essential for the rational design and optimization of this 2D material for various applications, such as electronics, spintronics, sensing, and energy-related

1.3 Objectives

1.3.1 General Objective

To investigate the electronic properties of carbon homo-doped silicene monolayers using Density Functional Theory (DFT) calculations

1.3.2 Specific Objectives

- To Optimize the atomic structure of carbon homo-doped silicene monolayers with varying carbon concentrations (e.g., 2C, 4C, 6C doping).
- To observe the electronic structural properties of silicene
- To understand the influence of carbon substitution on the overall structural properties and distortions of the silicene lattice.
- To examine the changes in the electronic band structure and the nature of the electronic states near the Fermi level
- To investigate the impact of carbon doping on the electronic conductivity and potential metallic behavior of the silicene monolayers.

1.4 Significance of the Study

- Since the study focused on the modification of silicene's properties through carbon doping,this opens up potential uses in electronics, specially in the development of next generation transistors, sensors, and other nanoscale devices.The ability to tailor the material's properties makes it a promising candidate for various advanced technologies.

Generally, this study contributes fundamental knowledge about the structure-property relationships in carbon doped silicene, which is valuable for developing silicene-based electronic and spintronic technologies.

1.5 Thesis Out Line

DFT Study of Structural, Electronic, and Magnetic Properties of Carbon Homo-Doped Silicene Monolayer. The introduction is presented in Chapter I. The literature review is addressed in Chapter II. In Chapter III the methodology and materials are listed. In chapter V result and discussions are investigated.. In addition, the structural, electronic, and magnetic properties of carbon doped silicene are included. The conclusions is given in Chapter V.A list of the references is presented in the end.

Chapter 2

Related Literature Review

2.1 Theoretical Background of Silicene Structure ,Properties and Potential Applications

2.1.1 Structural Properties

Silicene, silicon-based atomically thin 2D sheets, was first proposed based on first-principles total-energy calculations[20].Unlike the planar structure of graphene, however, with sp^2 hybridization configuration, silicon atoms arrange themselves in the form of low buckled structure due to a mixture of sp^2 hybridization and sp^3 hybridization. Silicene has been firstly fabricated on Ag(111) substrate in 2012[4] Silicene is a two-dimensional allotrope of silicon with a low-buckled honeycomb structure, which differentiates it from the planar structure of graphene[21, 5]. It exhibits Dirac-like electronic dispersion near the Fermi level, high carrier mobility, and tunable electronic and magnetic properties, which make it a promising material for electronic and spintronic applications [21] .Theoretical studies suggest that the electronic properties of silicene can be effectively tailored through methods such as doping, strain engineering, and chemical functionalization[16] .For instance, carbon doping has been studied extensively, as it can significantly modify the behavior of 2D materials like silicene (Assistant's previous response on carbon-doped silicene). From a theoretical standpoint, density functional theory (DFT) and other computational methods have played a crucial role in understanding the structural, electronic, and magnetic properties of silicene[22].Pristine silicene adopts a honeycomb-like structure, similar to the structure of graphene. This is supported by both theoretical calculations and experimental observations[21, 4].Unlike the planar structure of graphene, the silicene honeycomb lattice exhibits a slight out-of-plane displacement of the silicon atoms, resulting in a "buckled" or "puckered" structure. This buckling is a consequence of the larger atomic radius of silicon compared to carbon[23]

Electronic and magnetic properties of silicene 2D materials are gaining a lot attention in the nanotechnology space. Of these, graphene is the most widely known, followed by hexagonal boron nitride (dubbed 'white graphene). However, there are many other 2D materials out there. Polyatomic 2D materials such as transition metal dichalcogenides (TMDCs) have been widely documented, but more and more, monoatomic 2D materials are gaining interest. One such material with promise is silicene, and in this thesis we will discuss what it is and why its properties are of interest.

Silicene is a 2-dimensional allotrope of silicon, in a similar way that graphene is an allotrope of carbon atoms[24]. Silicene is monoatomic[10], meaning that it is composed only of silicon. However, unlike graphene and some other 2D materials, silicene is not strictly planar[6]. Instead, it has a buckled honeycomb surface. Silicene is not as widely produced, nor studied, as other 2D materials and it is a lot harder to create than the likes of graphene. This is because its 3D form is a diamond-like lattice, so currently, silicene can only be produced through epitaxial growth, not exfoliation. However, it does appear to have many beneficial properties. For one, in multi-layered silicene, the interactions between the layers are very strong and are much stronger than the individual layers in multi-layered graphene. In addition to pure silicene, there are also oxygenated forms of silicene named 2D silica; and silicene nanoribbons are known to exist. One difference to graphene is that it doesn't have a high dependence on pi-electrons and therefore is not reliant on pi-stacking mechanisms. This has been attributed to filled electronic states lying close to vacant electronic states, giving rise to pseudo Jahn-teller distortions in the 2D lattice.

Like many 2D materials with a high electrical conductivity, silicene is one of the few materials that possesses Dirac cones. Additionally, silicene exhibits a quantum hall spin effect (QHE)[25] and is thought to possess massless Dirac fermions - much like grapheme does[26]. This means that silicene has all the excellent electronic properties that grapheme does, but with a greater spin-orbital coupling and the potential to utilize the QHE at ambient temperatures. Despite its buckled structure, silicene possesses a zero-band gap from the overlap of the conduction and valence bands. However, this band gap is also tuneable. The bonds in a silicene lattice are predominantly sp3 hybridized and this creates a more chemically active surface. Because it is tuneable, silicene can be doped with a wide range of atoms to provide tuneable electronic properties. This allows silicene to be tuned into both a semimetallic material and a semiconducting material. The magnetic properties are also affected by doping. Silicene harbours an internal magnetism arising from the high spin-orbit coupling. Under a magnetic field, the electrons move from the conductance to the valence band. When there is no magnetic field, it displays a quantized Hall conductance.

Doping can have a wide range of effects on the magnetic properties of silicene, inducing a local magnetic moment, transforming silicene into a ferromagnetic semiconductor and introducing tune able magnetic ordering from ferromagnetic to antiferromagnetic. The tune ability of its electronic band gap provides silicene with versatile electronic and thermal properties that make it a highly desirable material for field effect transistor (FET) and miniature electronic applications. Aside from the electronic aspect, silicene appears to be unreactive to oxygen, suggesting that it would be stable enough to be used in the above electronic applications. Its interchangeable magnetic ordering properties could also lead to the development of new spintronic devices.

2.1.2 Electronic Properties

The band structure of silicene exhibits a Dirac cone similar to that of Graphene , with two cones at the K and K' points in the Brillouin zone .The Dirac cones are a result of the linear dispersion of the electronic states near the Fermi level , which gives rise to the unusual electronic properties of silicene . The silicene lattice is hexagonal leading to a hexagonal Brillouin zone. The unique band structure feature of silicene and graphene (in the absence of spin-orbit interaction) is the presence of valence and conduction bands with linear dispersions, so-called Dirac cones, crossing at the Fermi energy and at the K and K' points in the Brillouin zone. The Dirac cones form valleys in the Brillouin zone and the two degenerate bands at a given point originate from the A and B sublattices of the silicene structure.

For graphene, these Dirac electrons originate from the pz states on each sublattice; thus, in a tight-binding (TB) calculation, the Hamiltonian is of order 2 and the Dirac cones can be related to pseudospins. For silicene, due to the lack of mirror symmetry, pz states are coupled to px and py states, as well as s states. The band structure of buckled and at silicene have been compared in a number of papers [3] whereas Lebgue and Eriksson [2] compared silicene to planar Ge; similar calculations were performed by Houssa et al. [27], Wang [28] and Suzuki and Yokomizo [29]. Both forms of silicene have been shown to have electronic properties very similar to graphene [18]in that they both have a zero band gap at the K point. While the Dirac cones have been observed for graphene, it remains a prediction for free-standing silicene [18] and whether it is present for silicene on silver remains a controversy [30, 31, 32, 33, 34] in spite of early claims of observation [35]. All the above calculations were done by ignoring the spin-orbit coupling. Inclusion of the latter effect has shown that silicene would open a small gap of 1.55 meV and, therefore, might be better than graphene at displaying the quantum spin Hall effect (QSHE)[36].

The band structures of silicene as obtained by Sahin et al.[37] are reproduced . Silicene is a single atomic layer of silicon (Si) much like graphene. Early ork, both theoretical[35] and experimental went mostly unnoticed until silicene nanoribbons were reported to have been fabricated on a silver substrate by Kara et al. in [1]. The interest in silicene is exactly the same as that for graphene, in being two-dimensional (2D) and possessing a Dirac cone [4]. One advantage relies on its possible application in electronics, whereby its natural compatibility with the current Si technology might make fabrication much more of a commercial reality. Indeed, a field-effect transistor made out of silicene has finally been demonstrated in 2015 [13]. silicene has large band gap like 1.55meV [38]. Simply silicene is a monolayer of silicon atoms which resembles a honeycomb lattice and relativistic Dirac fermions of graphene [39].

Alike to graphene, the study of electronic properties of silicene is also an important issue for making a better microelectronic devices[11]. It is also observed that silicene exhibits some advantages over graphene in the areas of recent research because of its strong spin orbit interaction (SOI)[40] . With a strong SOI and tunable band gap is expected to be key criteria in the race towards electronic applications. Among of them quantum study of materials is significant. Because silicene is a 2D materials, quantum hall effect and quantum capacitance are the two most striking phenomena in the field of electronic research. Otherwise it is tobe noted that these two properties are solely depended on the corresponding Fermi level energy. As stated earlier Silicene has strong SOI for this it provides mass to the Dirac fermion by applying perpendicular electric field[41].

Silicene also shows integer quantum hall effect when it is subjected to an perpendicular magnetic field [42]. From the large variety of two-dimensional (2D) materials that exist today, silicene, the silicon counterpart of graphene has steadily increased its sphere of influence due to its malleable electronic properties and its compatibility with the current silicon-based technology.[14] For instance, the buckled layer geometry of silicene facilitates a band gap engineering and in the presence of an electric field opens a gap transport that makes possible the realization of a field-effect transistor (FET) at room temperature.[43] Synthesis of silicene is achieved nowadays by surface-assisted epitaxial growth on different substrates;[39] however, during this process, the formation of imperfections on the layer is practically unavoidable, which strongly influences the magnetic and electronic properties of the material [18]. In the context of imperfections, these modifications of the electronic, magnetic, and structural properties imply a fundamental form of disorder.[44] Silicene, which consists of Si atoms, has a single layer of hexagonal honeycomb structure [4].

Unlike graphene, the bonds between Si atoms are sp2-sp3 hybridization and the atoms are puckered rather than perfectly aligned in a single plane [45]. Due to its buckled structure, the properties of silicene can be easily tuned by an electric field or external force [46]. Therefore, silicene has extra potential to be applied in the electronic device industry. The similar properties of silicene and graphene have been observed both experimentally[47]and theoretically[48].The striking similarity between graphene and silicene originates from the basic fact that both carbon (C) and silicon

(Si) belong to the same group in the periodic table of elements. Besides, along the row of the periodic table (C , Si , Ge , Sn), the atomic weight increases from 12 to 119. This implies a strong relativistic effect as the velocity of electrons is proportional to atomic number. This has a two fold effect. Firstly, the low energy physics can be described by a Dirac type energy-momentum relation similar to graphene.

Secondly, there is a significant increase in spin-orbit splitting in comparison to graphene. Thus, like massless Dirac fermions in graphene, silicene has massive Dirac fermions due to the large spin-orbit gap (1.55 eV). Moreover, unlike graphene, silicene is a topological insulator characterized by a full insulating gap in bulk with a helical gapless edge[48]. Again, Si has a larger ionic radius than C, so sp3 hybridization is favorable to Si in contrast to common sp2 hybridization in C. Therefore, the mixing of sp2 and sp3 hybridization in Si results in buckling[2]. This buckling structure in silicene,[45] due to the pseudo Jahn-Teller effect in contrast to graphene, is significantly promising in the sense that the bandgap in such a structure can be easily tuned by application of an external electric field, without the need for any chemical functionalization. In recent work carried out by Jose and Datta[49]. the characteristic chemical and structural properties of silicene have been compared with graphene.

2.1.3 Potential applications of silicene

In terms of potential applications, silicene-based devices could complement or even surpass existing silicon electronics, provided that stability and scalable synthesis issues are adequately addressed[13] .There is also a significant potential for the integration of silicene with other materials and structures, such as silicon nanowires, for developing novel nanoelectronic devices .Due to its Dirac-like electronic structure and high carrier mobility, silicene can be used in field-effect transistors, logic gates, and photodetectors.The strong spin-orbit coupling in silicene enables the manipulation of electron spins, enabling the development of spin-based devices.Silicene can be used in Li-ion batteries, supercapacitors, and catalysts due to its high surface area and tunable electronic properties.The sensitivity of silicene's electronic properties to external stimuli can be exploited in the development of various sensors.Silicene's large surface area and electronic properties could enhance the performance of energy storage devices[50]. Generally, the unique structural and electronic properties of silicene, along with the potential for integration with existing silicon-based technologies, make it a promising 2D material for a wide range of applications.

2.2 The Structural and Electronic Properties of Carbon

Carbon is the second most abundant element in the human body after oxygen and is a key component of all organic molecules[51].It has the atomic number 6 and exists in the ground state with the electronic configuration [He] $2s^2$ $2p^2$[51].This configuration allows carbon to form four covalent bonds, leading to its versatility in forming a wide range of organic and inorganic compounds[52].The carbon atom has a small atomic radius of 0.77 and a high first ionization energy of 1086.5 kJ/mol, indicating its stability and tendency to form strong bonds[53].Carbon can exist in different allotropic forms, such as diamond, graphite, and fullerenes, which have distinct structural and physical properties.

The four valence electrons of the carbon atom can participate in the formation of single, double, or triple covalent bonds with other elements, depending on the specific molecular structure[54].This flexibility allows carbon to form a diverse range of compounds with varying properties.Carbon exhibits a high electronegativity value of 2.55 on the Pauling scale, indicating its ability to attract shared electrons in a covalent bond[55].This property contributes to the formation of polar bonds in many carbon-containing compounds.

2.2.1 Potential Application of Carbon

Carbon-based materials, such as graphite and activated carbon, are used in the production of batteries and supercapacitors for energy storage applications[56].Carbon nanotubes and graphene are being explored for their high surface area and conductivity in advanced energy storage devices[57].Carbon-based semiconductors, such as organic thin-film transistors and carbon nanotube-based electronics, are being developed for flexible, lightweight, and high-performance electronic devices[58].Diamond and diamond-like carbon coatings have applications in microelectronics, optics, and cutting tools due to their hardness, thermal conductivity, and optical properties[59].Activated carbon is widely used for water purification, air filtration, and the removal of organic pollutants from industrial waste streams[60].Carbon-based materials, like graphene oxide and carbon nanotubes, are being explored for adsorption, catalysis, and membrane-based water treatment applications[61].Carbon-based materials, such as graphene and carbon nanotubes, are being investigated for drug delivery, tissue engineering, and biosensing applications due to their unique properties[**?**].Diamond-like carbon coatings are used in medical implants, prosthetics, and surgical instruments due to their biocompatibility and wear resistance[62].

2.3 Theoretical Background of Density Functional Theory (DFT) for the Study of 2D Materials

Density Functional Theory (DFT) is a powerful computational method that has become a widely used tool for the study of 2D materials, such as graphene, silicene, and other novel 2D systems. The theoretical foundation of DFT lies in the Hohenberg-Kohn theorems and the Kohn-Sham equations, which provide a framework for mapping the many-body problem onto a set of effective single-particle equations.The behavior of 2D materials is governed by the complex interactions between the atoms and their electrons, making the direct solution of the many-body Schrdinger equation computationally intractable, especially for larger systems.The Hohenberg-Kohn theorems establish that the ground-state properties of a many-electron system are uniquely determined by its electron density, allowing the replacement of the complicated many-body wavefunction with the simpler electron density as the fundamental variable[63].The Kohn-Sham equations provide a way to map the many-body problem onto a set of effective single-particle equations, enabling the calculation of the ground-state electron density and the total energy of the system[64].The accuracy of DFT calculations relies on the choice of the exchange-correlation functional, which accounts for the quantum mechanical effects of electron-electron interactions. Various functionals have been developed for different applications, such as the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA)[65] .

Density Functional Theory (DFT) has played a crucial role in understanding the structural, electronic, and magnetic properties of 2D materials like silicene.DFT is an efficient computational method that can screen different doping configurations and their effects on the properties of 2D materials prior to experimental synthesis and characterization[63].DFT is a quantum mechanical modelling method used to investigate the electronic structure of many-body systems, such as atoms, molecules, and condensed phases. It is based on the principle that the ground-state properties of a many-electron system can be determined by using functionals, which are functions of the electron density .

In the context of 2D materials, DFT has been widely employed to study the structural stability, electronic band structure, spin-orbit coupling, and the effects of doping, strain, and chemical functionalization on the properties of materials like silicene, graphene, and their heterostructures[65]. The insights gained from DFT calculations have guided experimental efforts and helped in the rational design of novel 2D materials and devices[66].

For those who wish to go more deeply into the formalism of density functional theory there are a number of reviews and books aimed at intermediate and advanced levels available in the literature[67].Where appropriate source articles are referred to in the text.

Chapter 3

Methodology and Materials

In this chapter, will be discussed the computational methods and software that we used for our study. Among the first-principles methods, we apply density functional theory (DFT) for the ground state properties of the system. The softwares we used were Quantum Espresso package.

In the context of computational materials science, ab initio (from first principles) DFT calculations allow the prediction and calculation of material behavior on the basis of quantum mechanical considerations, without requiring higher-order parameters such as fundamental material properties. Density-functional theory (DFT) is a successful theory to calculate the electronic structure of atoms, molecules, and solids[63]. Its goal is the quantitative understanding of material properties from the fundamental laws of quantum mechanics. Traditional electronic structure methods attempt to find approximate solutions to the Schrӧdinger equation of N interacting electrons moving in an external, electrostatic potential (typically the Coulomb potential generated by the atomic nuclei). However, there are serious limitations of this approach: (1) the problem is highly nontrivial, even for very small numbers N and the resulting wave functions are complicated objects and (2) the computational effort grows very rapidly with increasing N, so the description of larger systems becomes prohibitive. A different approach is taken in density-functional theory where, instead of the many-body wave function, the one-body density is used as the fundamental variable. Since the density n(r) is a function of only three spatial coordinates (rather than the 3N coordinates of the wave function), density-functional theory is computationally feasible even for large systems. The Hohenberg-Kohn Theorems are the foundation of Density Functional Theory (DFT) and play a crucial role in the study of 2D materials. These theorems were developed by Walter Hohenberg and Walter Kohn in 1964[63] .

First Hohenberg-Kohn Theorem: The first Hohenberg-Kohn theorem states that the external potential (and hence the total energy) is a unique functional of the electron density. This means that the ground-state properties of a many-electron system are uniquely determined by the electron density. Mathematically, this theorem can be expressed as: "The external potential (up to a constant) is a unique functional of the electron density."

Second Hohenberg-Kohn Theorem: The second Hohenberg-Kohn theorem states that the electron density that minimizes the total energy of the system is the ground-state electron density. Mathematically, this theorem can be expressed as: "The functional that delivers the ground-state energy of the system delivers the correct ground-state density as the function that minimizes this functional."

In summary, the Hohenberg-Kohn theorems are the cornerstone of DFT and have been instrumental in the study of 2D materials, allowing for the simplification of the many-body problem and the efficient calculation of ground-state properties. The foundations of density-functional theory are the Hohenberg-Kohn and Kohn-Sham theorems which will be reviewed in the following section. In the section "Approximations for the exchange-correlation energy," various levels of approximation to the central quantity of DFT are discussed. The section "Results for some selected systems" will present some typical results from DFT calculations for various physical properties that are normally calculated with DFT methods. The original Hohenberg-Kohn and Kohn-Sham theorems can easily be extended from its original formulation to cover a wide variety of physical situations. To perfectly simulate the properties of a material, one must solve the Schrdinger equation (Equation 1) for all the material's electrons and nuclei. The Hamiltonian for this system is given in Equation 2, with the first two terms describing the kinetic energies of the nuclei and electrons, respectively, and the following terms the internuclear, electron-electron and nucleus-electron Coulomb interactions.

$$\hat{H}\Psi(\overrightarrow{R}_\alpha;\overrightarrow{r}_i)=\varepsilon\Psi(\overrightarrow{R}_\alpha;\overrightarrow{r}_i) \tag{3.0.1}$$

$$\hat{H}=-\sum_\alpha\frac{h^2}{2M_\alpha}\nabla^{2_\alpha}-\sum_i\frac{h^2}{2m\nabla^{2_i}}+\frac{e^2}{2}\sum_{\alpha,\beta}\frac{Z_\alpha Z\beta}{\overrightarrow{\mid R_\alpha-\overrightarrow{R_\beta}\mid}}+\frac{e^2}{2}\sum_{i,j}\frac{1}{\overrightarrow{|ri-\overrightarrow{rj}|}}-\frac{e^2}{2}\sum_{i,\alpha}\frac{Z_\alpha}{\overrightarrow{|R_\alpha-\overrightarrow{r_i}}} \tag{3.0.2}$$

3.1 The Solution of the Schrödinger Equation

During the study of this paper, we will be primarily concerned with the calculation of the ground state energy of a collection of atoms. The energy may be computed by the solution of the Schrdinger equation - which, in the time independent, nonrelativistic, Born-Oppenheimer approximation is ;

$$\hat{H}\Psi(r1,r2,...,rN)=E\Psi(r1.r2,...,rN) \tag{3.1.1}$$

The Hamiltonian operator, H, consists of a sum of three terms; the kinetic energy, the interaction with the external potential (Vext) and the electron-electron interaction (Vee). That is;

$$\hat{H}=\frac{1}{2}\sum_i^N\nabla i^2+V_{ext}+\sum_{i<j}^N\frac{1}{|r_i-r_j|}------ \tag{3.1.2}$$

In materials simulation the external potential of interest is simply the interaction of the electrons with

$$V_{ext} = -\sum_{\alpha}^{Nat} \frac{Z_\alpha}{|r_i - R_\alpha|} -------\qquad(3.1.3)$$

Here, r_i is the coordinate of electron i and the charge on the nucleus at $R_\alpha$is Z_α. Note that in order to simplify the notation and to focus the discussion on the main features of DFT the spin coordinate is omitted here and throughout this article. Equation 1 is solved for a set ofΨ subject to the constraint that that the Ψ are antisymmetric - they change sign if the coordinates of any two electrons are interchanged. The lowest energy eigenvalue,E_0, is the ground state energy and the probability density of finding an electron with any particular set of coordinates r_i is $(|\Psi_0|)^2$. The average total energy for a state specified by a particularΨ, not necessarily one of the eigenfunctions of Equation 1, is the expectation value of H, that is

$$E[\Psi]\int \Psi^* \hat{H} \Psi dr \equiv \langle \Psi \left| \hat{H} \right| \Psi \rangle \langle \Psi | \Psi \rangle --------\qquad(3.1.4)$$

The notation $[\Psi]$ emphasises the fact that the energy is a functional of the wavefunction. The energy is higher than that of the ground state unless Y corresponds to Ψ_0 - which is the variational theorem; $E[\Psi] \geq E_0$

3.2 Born-Oppenheimer Approximation

There are many approximations that one must make when dealing with a many-body problem in the realm of solids. The first one is known as the Born- Oppenheimer approximation. This approximation is based on the idea that in a solid the nuclei are not moving as quickly as the electrons. The nuclei, which are approximated as ions in this case, are assumed to be stationary. Since the electrons are much less massive and move at much higher velocities than the nuclei, the positions of the electrons are considered variables and the positions of the ions are considered parameters. In order to examine this situation, we define the general Hamiltonian for a many-body system from the standard Hamiltonian. Remember the basic Hamiltonian in this situation is the potential and the kinetic energy as in,

$$H = T + V, whereT = -\frac{h^2}{2m}\nabla - - - - - - - - - \tag{3.2.1}$$

However, the potential, V, changes based on the potential of the system. There are two kinetic energy terms and three potential energy terms that needed to be added. They can be written as

$$H = \frac{h^2}{2m}\sum_{e}^{n}\nabla i^2 - \frac{h^2}{2m}\sum_{i}^{n}\nabla i^2 - \sum_{i,e}^{n}\frac{Z_i e^2}{4\Pi}\epsilon r_{ei} + \frac{1}{2}\sum_{i,j}^{n}\frac{Z_i Z_j e^2}{4\Pi\epsilon}r_{ij} + \frac{1}{2}\sum_{ee}^{n}\frac{e^2}{4\Pi}\epsilon r_{ee}..... \tag{3.2.2}$$

Where the subscripts (i,j) refer to ions and the subscript (e) refers to the electrons. The key components of the mathematical Born-Oppenheimer approximation are that first the nuclear energy term is left separate and that the positions of the electrons with respect to the ions in the nucleus are considered as parameters. Essentially the fourth term is neglected and the term r_{ei} is changed into a set parameter. This allows a great simplification of the equations when dealing with solids.

3.3 Hartree-Approximations

The Born-Oppenheimer approximation begins the outline a many-body Hamiltonian in a useful manner by reducing out various terms. But the many-body problem is a complex one and the Hamiltonian derived in the Born-Oppenheimer is still not suitable for calculations. There are further approximations that must be made to achieve better accuracy and minimize calculation time. That is what is involved in the derivation of the Hatree-Energy equations The Schrodinger wave equation will be used to solve for the energy of the many-body solid. First, take the Hamiltonian that is defined in the Born-Oppenheimer approximation and put it into the SWE with a new wavefunction. Then to define a wavefunction as a new combination of products of the wave functions that correspond to individual electrons. It can be written as

$$\psi = \varphi_1(r_1)\varphi_2(r_2)\varphi_3(r_3 ... \varphi_n(r_n) ------ \tag{3.3.1}$$

However, this wavefunction cannot be put straight into the Schrodinger wave equation without some analysis and manipulation. The first step is to use the variational principle to analyze and set the energy of a system involving these wavefunctions. Our overall goal is to find the ground state and the variational principle places a limit on the minimum energy of the system. It outlines the equation below, where it is defined as

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|H|\psi\rangle} ------ \tag{3.3.2}$$

Where $E \geq E_0$ and E_0 is the ground state energy of the system. From this it is possible to get an energy minimum. However that minimum is not necessarily the ground state energy. Using these equations and the variational principle it is possible to derive the Hartree Energy equations, however it more useful to include the Pauli-Exclusion principle and show the Hartree-Fock equation as the equations are essentially the same.

3.4 Hartree Fock Approximation

The Hartree energy equations can be useful under some specific circumstances, but they still lack some important characteristics. Primarily, the lack of spin is troubling. It can be included in a post analysis. However, that is an ad-hoc solution and doesn't contain useful information. spin characteristics into the wavefunction from the beginning. It can be done by using what is called the Slater determinant. The Slater determinant,

$$\Psi(x_{1,\ldots x_n}) = 1\frac{1}{\sqrt{n!}}\begin{vmatrix} \Phi_1(x_1) & \Phi_2(x_1) & \ldots & \Phi_n(x_1) \\ \Phi_1(x2) & \Phi_2(x2) & \ldots & \Phi_n(x2) \\ \ldots & \ldots & \ldots & \ldots \\ \Phi_n(xn) & \Phi_n(xn) & \ldots & \Phi_n(xn) \end{vmatrix} \tag{3.4.1}$$

A slater determinant, as in above is an n by n matrix that includes the Pauli exclusion principle, which is essential if each state has to be unique. If

$$\varphi_i = \varphi_j \tag{3.4.2}$$

then two columns of the determinant would be zero. This is desirable as makes sure that a non-physical situation such as the equality of two different states cannot happen. It can be written in a more straightforward fashion with a permutation operator such that,

$$\Psi(x1...xn) = \frac{1}{\sqrt{n!}}\sum_p (-)_p P\Phi_1(x1)\Phi_2(x2)...\Phi_n(xn) ------ \tag{3.4.3}$$

This permutation operator works by switching either the coordinates or the subscripts of the Φ wave functions. Keep in mind that these individual wave functions are orthogonal in a manner such that,

$$\langle\Psi_i(r_k)|\Psi_j(r_k)\rangle = \delta_i ------- \tag{3.4.4}$$

is true. Using this information and methodology it is possible to derive the Hartre-FockEquations, which boil down to

$$\frac{-\hbar^2}{2m} + V(r) + V_{H(r)}(r)\Phi_i(r) = E_i\Phi_i(r) ------- \tag{3.4.5}$$

Where the $V_{H(r})$ term is the Coulomb repulsion term which can be written as,

$$V_{H(r)} = e^2\int\frac{n(r')}{|r-r'|}d^3r' ----- \tag{3.4.6}$$

3.5 Density Functional Theory

Now that the fundamentals of the Hartree-Fock and the Hartree energy equations have been reviewed, there is a system of equations that covers the many-body problem between the electrons and the ions in a solid. The equations that have been derived are correct, but have a large number of variables and are therefore not useful. For example, the wavefunction of each electron in a solid would need to be solved and a solid of any significant volume would have a number of electrons on the order of Avogadro's number. This is an impractical number of equations to solve; so in order to find a useable solution one needs to find a way to condense these equations. Hohenberg, Kohn and Sham together developed a method to deal with the many-body problem. This approach involves a method that relies on electron functionals. The theorem dictates that a potential can be determined uniquely from the ground state electron density. It also goes on to say that the reverse is true. From a known potential one can determine the electron density. One knows this because a definite electron potential fixes the Hamiltonian. Which is known from the existence theorem. The existence theorem states that a density functional uniquely determines the Hamiltonian. The software uses density functional theory as the basis of the solutions. So a functional needs to be defined. A functional takes a function and defines a single number from the function, such as,

$$F[f] = \int_{-1}^{1} f(x)dx - - - - - - - - - - - - \tag{3.5.1}$$

So, the Hohenberg and Kohn's theorem is such that a ground state energy can be expressed as $\hat{n}(r)$ where n(r) is the electron density and hence the reason for the name density functional theory. That means that one needs to come up with an expression n(r). This is where the Thomas-Fermi contribution to the theory needs to be outlined, which will illuminate further practical steps. Thomas and Fermi posited that the electron density is uniquely determined by the potential. To start, one need to know the density of states as in,

$$N = V\sum_{\sigma}\sigma d_{k\rho}(k) = \frac{2}{(2\Pi)^3}\frac{4\Pi}{2\Pi}k^3 fV ------ \qquad (3.5.2)$$

This is a well-known equation. It outlines the amount of energy states that electrons can occupy in a given volume. When one know the density of states one can estimate the kinetic energy of particles in the system. From the kinetic energy it is possible to estimate the potential. However this estimation is not complete, for example there is something called exchange correlation energy that is not included, and that leads to large systematic errors in the final answers. The exchange correlation energy is actually two terms that have been combined into one energy. Both energies are unknown in the current formalism and must be approximated, so to simplify matters they have been combined. An exchange energy refers to the exchange interaction theory. In that theory, particles with overlapping wave functions of identical particles have different energies than expected. The correlation energy is often referred to as the Coulomb correlation and has to do with the coulombic repulsion spatial characteristics of atoms. One of the primary goals of density functional theory is to come up with a good approximation of the exchange-correlation energy, which will be discussed more in the Local Density Approximation section.

3.5.1 Kohn Sham Equations

The Kohn-Sham equations are often broken down into three equations that give essentially the same information as the Hartree and Hartree-Fock equations. However,this new equation is a single equation versus the many-body equations in the previous versions. Keep in mind that these two methods are not equivalent. The Kohn-Sham enable a mapping of the original Hartree-Fock equations that can yield a similar answer. Which is the ground state electron density of the system. Density functional theory is only capable of determining the ground state density of the system. If an excited state is desired it is possible to figure that out from the ground state. The Kohn-Sham equations end up giving a set of equations similar to the Euler-Lagrange equations seen in classical mechanics. However, the variable that would normally be used in the Euler-Lagrange is replaced by a wave function. It can be seen through the variational method that these equations based on the new functional definition of the energy start as,

$$F[n] = F_{kE}[n] + E_{xc}[n] + \frac{e^2}{2}\int n(r)n(r')\frac{d\tau\rho\tau'}{|r-r'|} ------ \tag{3.5.3}$$

Knowing this one can then obtain the Euler-Lagrange equations for this system as

$$\frac{\delta FKE[n]}{\delta_n(r)} + V_{eff}(r) = \mu ------ \tag{3.5.4}$$

Which when one substitutes in,

$$n(r) = \sum_{j=1}^{N} |\varphi_J(r)|^2 --------- \tag{3.5.5}$$

as the electron density, we can then obtain one form of the Kohn-Sham Equation as,

$$(-\frac{1}{2}\nabla^2 + V_{eff}(r - \epsilon_j)\varphi_j(r) = 0 ------- \tag{3.5.6}$$

3.6 Exchange-correlation functional

In materials science, exchange-correlation (XC) functionals are an essential component of Density Functional Theory (DFT) calculations.These functionals are used to approximate the exchange and correlation energy terms in the Kohn-Sham equations, which are crucial for accurately describing the electronic structure of a system The choice of exchange-correlation functional is a critical aspect of DFT calculations for studying doped silicene. For a Silicon we have used si- pbe-n-rrkjus-psl.1.0.0.UPF and for dopant carbon we have used c-pbe-n-kjpaw-psl.1.0.0.UPS. The common exchange-correlation functionals used and their advantages and limitations were discussed below.

3.6.1 Local Density Approximation

This is the simplest XC functional, which assumes that the exchange-correlation energy density at a point depends only on the electron density at that point. This approximation can help to actually calculate the electron density as if it were a uniform electron gas with the density of states as mentioned above. Over a small enough region one can always make this approximation. From a summation over all the regions it is possible to get an approximate expression for the entire solid. So first one wants to write down an effective potential such that,

$$\nu_{eff}(r) = \nu(r) + \int \frac{n(r')}{\|r - r'|} dr' + \nu_{xc}(r) \tag{3.6.1}$$

This is the same effective potential as before.The next step is to write down a new exchange correlation energy for this approximation which can be written as

$$E_{xc}^{LDA} = \int n e_{xc}^{u}[n(r)] dr \tag{3.6.2}$$

Keep in mind that this exchange energy is representative of the energy for each particle. This new energy can be rewritten $\nu_{xc}(r)$ as,

$$\nu_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n(r)} \tag{3.6.3}$$

Which is the final theoretical step one needs before moving these equations into practical applications.

3.6.2 Generalized Gradient Approximation (GGA)

GGA functionals take into account the gradient of the electron density in addition to the density itself. The Perdew-Burke-Ernzerhof (PBE)functional is one of the most widely used GGA functionals in silicene studies.PBE generally provides a good balance between computational cost and accuracy for structural and electronic properties.However, GGA functionals like PBE are known to underestimate the band gap of semiconductor materials, including silicene.In DFT calculations for doped silicene, the choice of basis sets and pseudopotentials is crucial for accurately describing the electronic structure and properties of the system.The plane-wave basis set is defined by a kinetic energy cutoff, which determines the number of plane waves included in the calculation.Convergence with respect to the plane-wave cutoff energy must be carefully tested to ensure the calculated properties are well-converged.For doped silicene, a plane-wave cutoff energy in the range of 30Ry or 408 eV is typically required to achieve good convergence.

3.6.3 Computational Detail for the Calculation of 2D-Carbon Homo-doped Silicene Monolayer

DFT calculations were performed using the Quantum-Espresso (QE) package[68]. The generalized gradient approximation describes the exchange correlation, also known as the GGA with the Perdew-Burke Ernzerhof (PBE) functional[68].We used the ultrasoft pseudopotentials for PBE calculations , which were used for electron-ion interaction. The plane wave energy cutoff was set at 30Ry or 408.17eV to ensure total energy convergence to 0.001 eV per primitive cell.The Broyden Fletcher Goldfarb Shanno (BFGS) [69] algorithm was used for structural optimization. The convergence criterion was set at 3.6×10^9 Ry/cell in energy and 0.4 for mixing . We used a 3 ×3× 1 super cell structure of monolayer 2D-silicene with 18 atoms doped with C for our calculations. During relaxation, the Brillouin zone (BZ) was integrated using a 8×8 × 1 k-point grid,, and the density of state (DOS) was calculated using a 8×8×1 mesh.Our simulation began with a DFT calculation for plane-wave self-consistent field calculation and crystal structure optimization.The band structure and partial density of state of carbon homo-doped 2D silicene are calculated.

3.6.4 Parameter optimization

The optimized crystal structure of silicene monolayer for a) pristine, b) x = 11.11 %,c) x = 22.22%and x=33.33% carbon (C) doped,is shown in chapter 4 along figure 4.2,4.11,4.12 and 4.13 respectively

3.6.5 Plane wave cutoff energy and K-point sampling

We used 2D hexagonal super cell of 3×3 × 1 which made up primitive unit cell of silicene monolayer. Doping is done by substituting carbon atom in place of silicon atom in the super cell 3×3×1. The convergences test is then computed with respect to plane-wave energy cutoff and k-point sampling grid density.They are the critical starting points for any plane-wave self-consistent field (PWSCF) calculations because a poor convergence test always results in an incorrect converged total energy.

The results for results for kinetic energy cutoff and convergence tests with respect to k-points mesh for hexagonal pristine are shown in chapter 4 with figure 4.3.

3.7 Softwares

The majority of studies on doped silicene employ first-principles DFT calculations using plane-wave basis sets and pseudopotentials. Among different DFT software packege ,we have used Quantum ESPRESSO packege for our study .A comprehensive collection of software codes called Quantum-espresso[68], utilizes pseudopotentials to simulate electron-ion interactions, plane wave basis sets for determining electronic structure, and density-functional theory to compute material properties. The GNU General Public License (GPL) governs the distribution of quantum espresso, a free and open source piece of software .The fundamental computations and simulations that can be performed in QE include the computation of the ground-state energies, Kohn-Sham (KS) orbitals, comprehensive structural optimizations, spin-orbit coupling, and noncollinear magnetism .

Chapter 4

Results and Discussion

4.1 Pristine and Super Cell of Silicen

4.1.1 Structural Optimization and Convergence

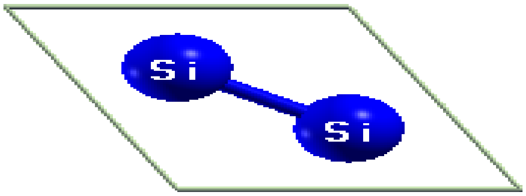


Figure 4.1: Structural Optimizations of Silicene unit cell

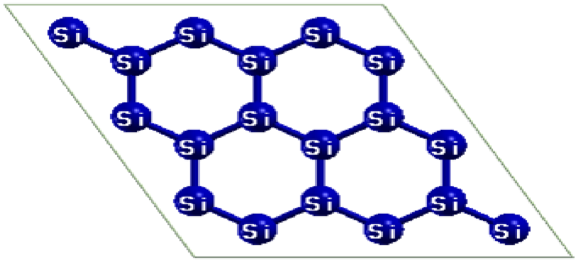
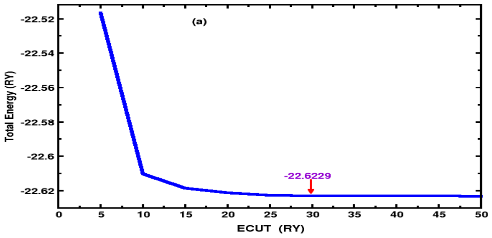


Figure 4.2: Structural Optimizations of super cell of silicene



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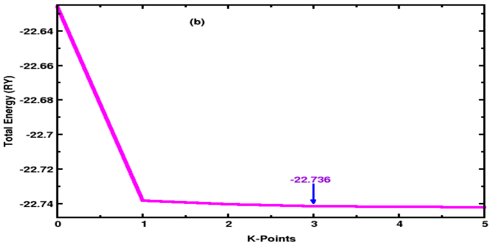

Figure 4.3: Convergence calculation for the cutoff energy of Si and convergence calculation for k-points.

The two figures 4.1 and 4.2 show the crystal structure optimization results for pristine silicene and a super cell of silicene, respectively. Silicene has a buckled structure in contrast to graphene, which has a flat geometryStructural .Optimization was done by optimizing the crystal lattice constant .As shown in figure 4.1 the silicene structure exhibits a hexagonal lattice arrangement with a slight buckling of the silicon atoms. This buckling is a unique structural feature of silicene, differentiating

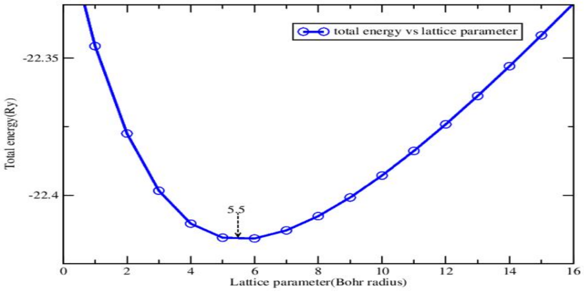

Figure 4.4: Optimized Lattice parameter of silicene

it from the planar structure of graphene.The lattice has a hexagonal structure, with a unit cell highlighted that contains two Si atoms labeled 1X1. The super cell, also comprising eighteen Si atoms, is labeled 3X3, as shown in figures 4.1 and 4.2, respectively. From this graph we see that , Silicene has a buckled structure in contrast to graphene, which has a flat geometry .These structural insights, along with the electronic band structure and density of states analyses, provide a comprehensive understanding of the fundamental properties of silicene and is crucial for exploring the potential applications of silicene in various technological domains, such as nanoelectronics, optoelectronics, and energy-related devices. The total energy is then plotted against the cutoff energy or the k-point mesh generating a curve that converges towards some constant value as in figure 4.3 .The convergence figures shows how the total energy changes as the ecut wave function value is increased.As the ECUT is increased, the total energy decreases rapidly at first, indicating that the system is converging towards a more stable total energy value of -22.629Ry . The energy curve

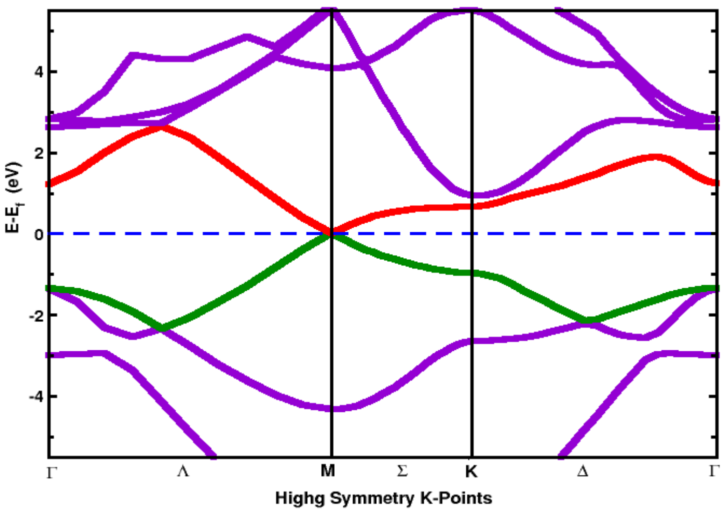

Figure 4.5: Optimized band structure of pristine silicene .The blue dot line shows transformed fermi energy

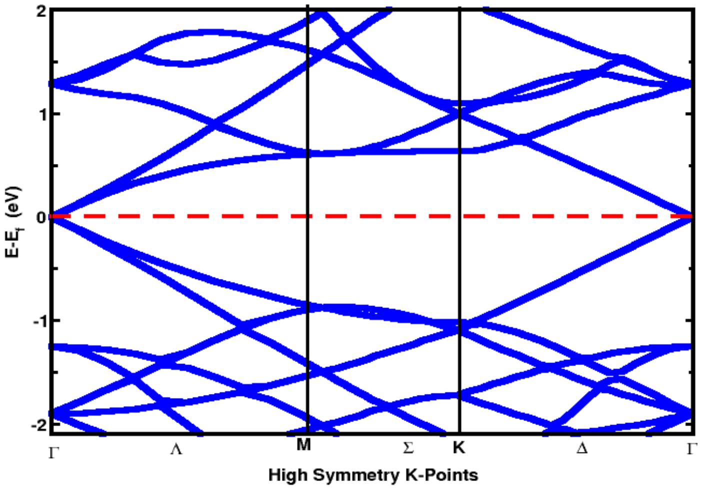

Figure 4.6: Optimized band structure of super cell of silicene

gradually flattens out at higher ECUT values, suggesting that the energy has reached a converged state and further increasing the ECUT did not significantly affect the total energy . The results for convergence tests with respect to kinetic energy cutoff and k-points mesh are shown in Fig. 4.3(a) and (b)respectively. This demonstrates that the variations in energy cutoff become stable after 30 Ry, and thus increasing the energy cutoff from 30 Ry to 50 Ry has no significant effect on total energy. The energy changed significantly as the number of k-points changed until it reached at a point where it remained constant was 3×3 × 1 .

From figure 4.4 the lattice parameter calculate was 5.5 (Bohr) which is slightly similar to theoretical calculations studies, the lattice parameter of pristine silicene monolayer is typically reported to be around 7.34 (Bohr)as cited in ref.[70].When we analyze the comparison between the theoretical value of 7.34 Bohr and our calculation value of 5.5 Bohr , the calculated value of 5.5 Bohr is slightly smaller than the reported value of 7.34 Bohr. This vary slightly depend on computational methods, exchange-correlation functionals, and other parameters used in the theoretical modeling of pristine silicene.

4.1.2 Electronic Band Structure

The band structure of pristine silicene exhibits a Dirac cone at the M point of the Brillouin zone, which is similar to graphene and also exhibits other interesting features, such as the formation of a flat band near the Fermi level as shown in figure 4.5. However, the Dirac cone in silicene is tilted due to the spin-orbit coupling, which breaks the sublattice symmetry and opens a band gap. Figure 4.5 shows the band structure of Silicene calculated along high symmetry lines between the points $\Gamma - M - K - \Gamma$ and illustrates zero band gap energy of silicene .The band structure exhibits Dirac cones at the M points in the Brillouin zone, where the conduction and valence bands touch, forming a linear energy-momentum relationship and pristine silicene is a gapless semimetal material .All these properties make pristine silicene an interesting material for potential applications in electronic and optoelectronic devices, as the unique electronic structure can lead to unique transport and optical properties . However, according to this thesis, these properties may depend on potential doping factor.

In figure 4.6 the conduction band and the valence band touch each other at two high symmetry points Γ . However, the shape of the bands touching points do not exhibit dirac cone shape as like as pristine .

4.1.3 Density of States (TDOS/PDOS)

In figure: 4.9, its TDOS shows there are mobility electrons at low density around energy level .This indicates that, the conducting behavior of super cell structure of silicene .

From 4.7, we can explain that the band gap region is centered around the Fermi level, which is typically set to 0 eV in the plot the TDOS exhibits a characteristic V-shaped or Dirac-cone-like structure, which is a signature of the 2D nature of silicene.The TDOS values are non-zero on both sides of the band gap, indicating the presence of both valence and conduction bands.The density of states plot for pristine silicene in figure 4.7 shows a continuous distribution of states across the Fermi level, indicating a zero band gap material. This is consistent with the semi metallic behavior observed in the band structure of pristine silicene.And exhibits a linear behavior near the Fermi level, which is a characteristic of the Dirac cones in the band structure. This linear DOS is a signature of the massless Dirac fermions in pristine silicene.The density of states plot is symmetric about the Fermi level, reflecting the symmetry of the electronic structure in pristine silicene .The continuous density of states across the Fermi level means that there are no regions with zero density of states,

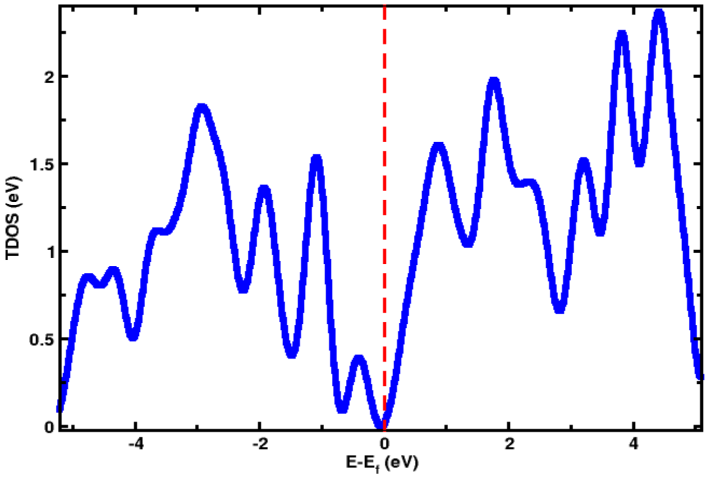

Figure 4.7: The TDOS structure of pristine silicene in unit cell

The total density of state (TDOS) exhibits a peak at energy level of -2.6eV within a

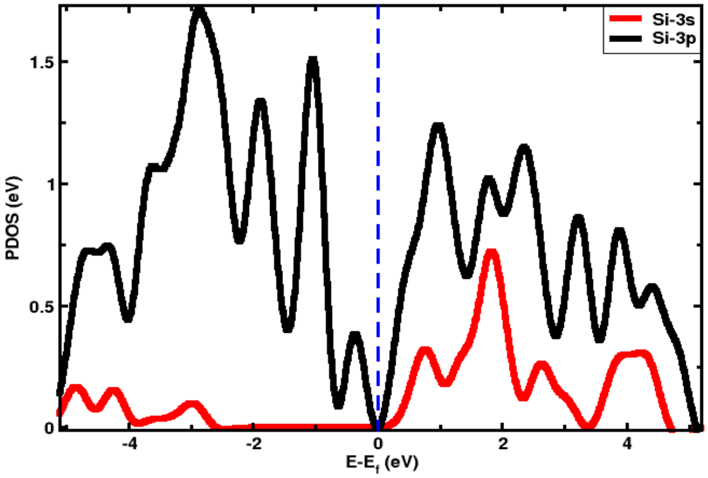

Figure 4.8: The PDOS structure of pristine silicene

balance band of super cell pristine silicene, whereas the total density of state(TDOS) peak at energy of 4.2eV in conducti on band. This change results from the large unit cell size, which alters and modifies the total density of state, thereby affecting the material's electronic properties. As the figure 4.8 and 4.9 illustrated, the DOS structure is symmetry i.e., silicene possesses a zero-band gap from the overlap of the conduction and valence bands. The projected density of states (PDOS) plot for pristine silicene in figure 4.8 shows the contributions of the s-orbitals and p-orbitals to the overall electronic structure. We can understand that the states near the Fermi level are predominantly composed of the p-orbitals of the silicon atoms i.e. the more dominant in valence band and conduction band .This is consistent with the formation of the Dirac cones in the band structure, which are primarily derived from the p-orbitals.But in conduction band Si(s) somewhat rise rather than in valency band . The presence of both s-orbital and p-orbital contributions in the PDOS indicates that the silicon atoms in pristine silicene undergo a hybridization of their valence

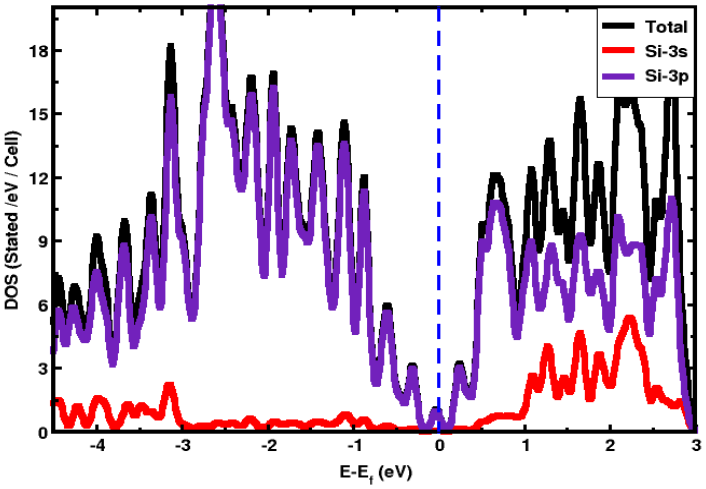

Figure 4.9: The TDOS and PDOS structure of super cell silicene

orbitals, leading to the formation of strong covalent bonds within the honeycomb lattice. The PDOS plot shows a symmetric distribution of the s-orbital and p-orbital contributions about the Fermi level, reflecting the inherent symmetry and degeneracy in the electronic structure of pristine silicene . The electron configuration of silicene can be described as 1s2 2s2 2p63s2 3p2, reflecting the arrangement of electrons in the silicone atoms that make up the material .The valence band of silicone is composed of the 3s and 3p orbitals of the silicone atoms , which together contain four valence electrons. The 1s and 2s/2p orbitals of silicone atoms are fully occupied and do not contribute to the electronic properties of the material. From all these description we understand that pristine silicene has a semi metallic properties .

4.2 Electronic Properties of Carbon doped Silicene

In the case of Carbon homo-doped Silicene , we used DFT to investigate the effects of carbon doping on the properties of Silicene. By comparing the total energy of

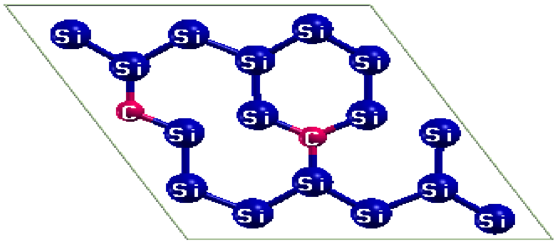

Figure 4.10: Structural Optimizations of 2C doped silicene

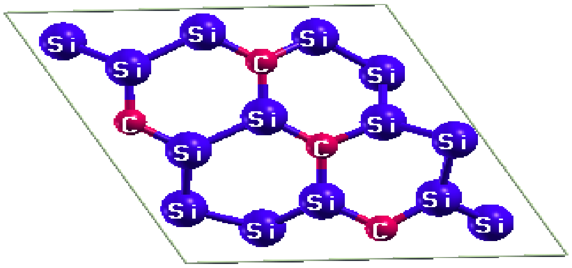

Figure 4.11: Structural Optimizations of 4C doped silicene

the doped system to that of the un doped Silicene monolayer, one can determine whether the carbon dopant stabilizes or destabilizes the structure. A DFT study of Carbon homo-doped Silicene monolayer can provide valuable insights into the effects of carbon doping on the material's structural and electronic properties, which can have important implications for its potential use in various applications. Silicene is a two-dimensional material composed of a single layer of silicon atoms arranged in a honeycomb lattice, similar to graphene.

4.2.1 Carbon Doped h- Silicene with Concentration x=0.11

Figure 4.10 shows that, when 2C atoms doped h-silicene, the bond between silicon atom around carbon dopants atoms, had broken after optimization . The electronic properties of 2c-doped silicene, as indicated by the band structure, suggest it can

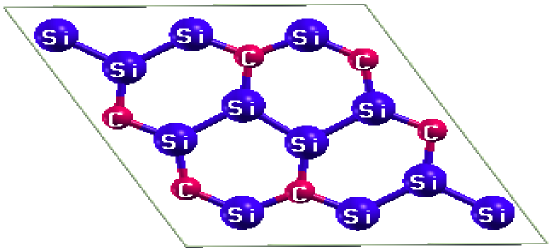

Figure 4.12: Structural Optimizations of 6C doped silicene

exhibit semimetallic characteristics.The band structure of 2C-doped silicene ,illustrated in the figure 4.13 , reveals that the valence band edge slightly crosses the fermi level at points Γ -Λ and touches two edge of bands touched atΔ , similar pattern to the pristine case , but above the fermi level in conduction band . The material remains gapless. In the Figure 4.16 the black line represents the total DOS,showing the overall the distribution of states across different energy levels. The total DOS reaches its highest point between -2 eV, indicating a dense concentration of states at the indicated energy . The Si-3s orbitals make a modest and dispersed contribution, with minor peaks near -2 eV in the valence band and around 2 eV in the conduction band. The C-2s orbitals do not contribute to the valence band, while the Si-3p orbitals contribute significantly to both the valence and conduction bands, especially near the Fermi level.

4.2.2 Carbon Doped h- Silicene with Concentration x=0.22

The crystal structure of carbon doped hexagonal silicene shown in the figure 4.11 the band gap of the doped silicene was tuned by adjusting the concentration of carbon atoms , and the material can exhibit semimetallic and semiconductor behavior depending on the doping level.In this study we observed that the band gap begins to open at carbon atom doping concentration of X=0.22,with small band gap value of 0.25eV as indicated in the figure 4.14 .The band shows that the maximum valence

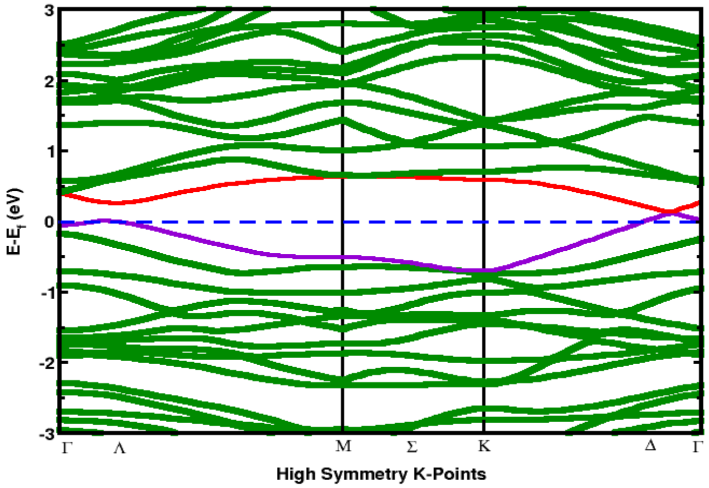

Figure 4.13: The band structure of 2C doped silicene

band and the minimum conduction band occurred at the same K-points, suggesting that the material has direct band gap .From figure 4.17 the si-3s orbital has relatively low contribution throughout the energy range , with smaller peaks appearing below the fermi level.In contrast , the Si-3p orbital exhibits significant contributions , specially near the fermi level, extending into both the valence band and conduction bands. The carbon 2s orbital's contribution is minimal, with all most no states in the valence bands. The carbon 2porbital contributes somewhat, particularly below the fermi level, but it is less prominent than the Si-3p orbital.

4.2.3 Carbon Doped h-Silicene with Concentration X=0.33

The band gap is indicated On the figure 4.15 shown a value of 0.56eV .This is the energy difference between the highest occupied electronic state (valence band) .A band gap of 0.56eV suggests that the material is semiconductor .The band gap of 6C doped silicene increased as the concentration of carbon atoms increase as shown in

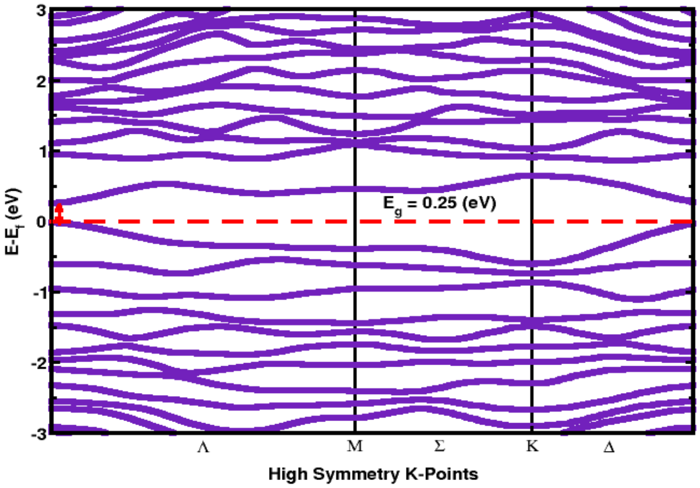

Figure 4.14: The band structure of 4C doped silicene

figure 4.15.That band gap we obtained was 0.56eV.This is also indicate semiconductor properties .The band structure in the figure 4.15, shows that doping with six carbon atoms results in a material with a band gap energy of 0.56eV, which is slightly greater than that of the doped with four carbon atoms.The minimum of the conduction band the maximum of the valence band are located at the same symmetry point, Γ ,indicating that the material exhibits a direct band gap at this doping level, which could be useful for fotoelectronic applications .In figure 4.18, the p-orbitals of Si atoms play the dominant role in forming both the conduction and valence bands. The s-orbitals of carbon atoms and the s-orbitals of silicon atoms hybridized at an energy level of 1.35eV, while the s- and p- orbitals of Si atoms and the p-orbitals of carbon atoms hybridize at 0.3eV when the carbon dopant concentration is X=0.33. This indicates the location of orbitals involved in charge transfer.

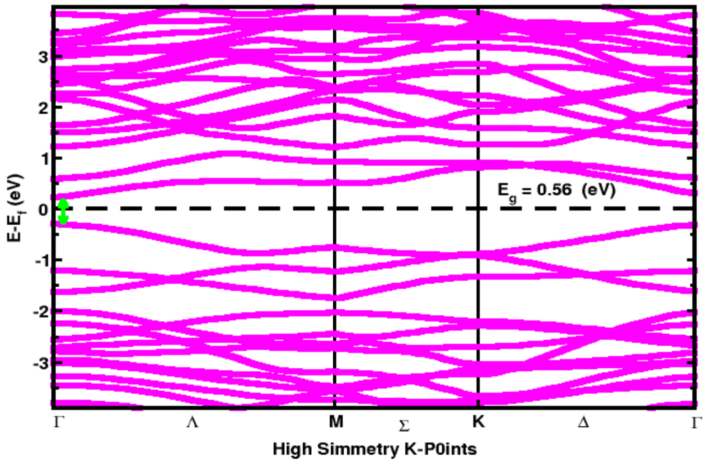

Figure 4.15: The band structure of 6C doped silicene

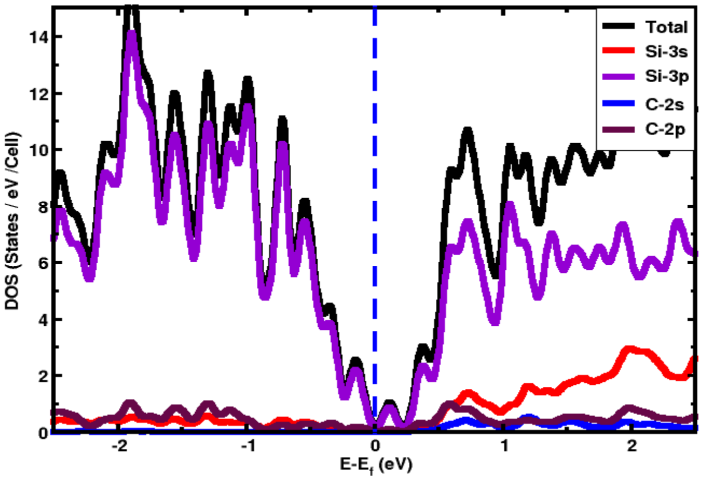

Figure 4.16: The Total Density of States (TDOS) and PDOS for silicene doped with 2C atoms .

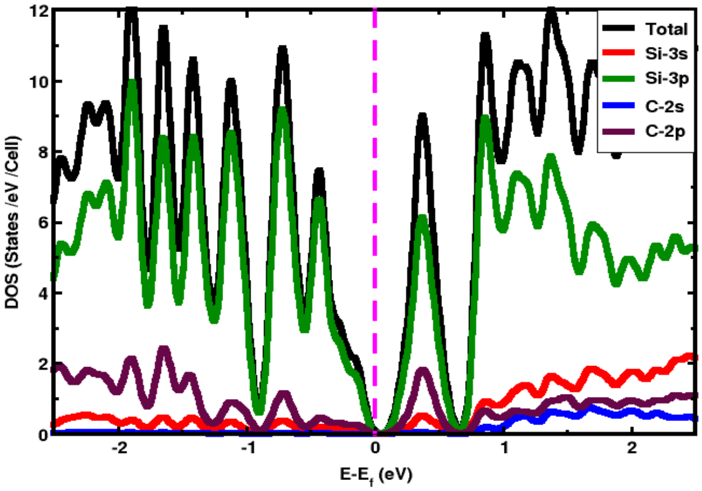

Figure 4.17: The Total Density of States (TDOS) and PDOS for silicene doped with 4C atoms .

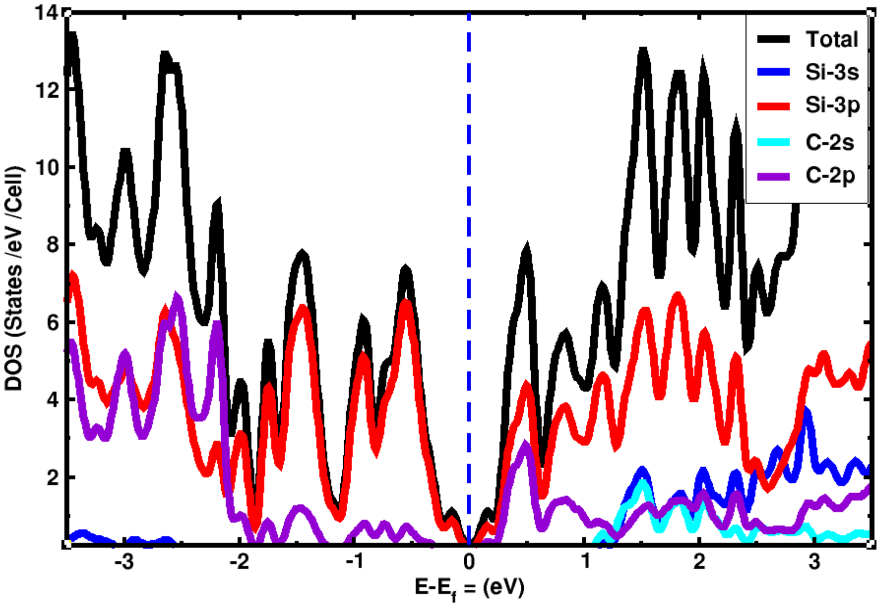

Figure 4.18: The Total Density of States (TDOS) and PDOS for silicene doped with 6C atoms .

Chapter 5

Conclusion and Recommendation

- Density functional theory(DFT) is crucial for investigating the impact of carbon doping on the electronic band structure of silicene . It allows researchers to calculate the band gap and density of states, showing carbon atoms alterthe electronic behavior of silicene, potentially tuning it in to a semiconductor.
- The introduction of carbon atoms into the silicene lattice can cause distortion due to the difference in atomic size between silicon and carbon. This might result in variations in the buckling and bond angles within the silicene sheet, influencing its overall stability and mechanical properties.
- Carbon doping can significantly influence the electronic behavior of silicene. It can modify the band gap, potential turning s ilicene from a semimetal in to a semiconductor. This is particularly important for applications in nanoelectronics, where controlling the band gap is crucial for the development of transistors and other electronic components.
- silicene doped with carbon at concentrations of X=0.22 and 0.33 forms a direct band gap semiconductor matrial.
- The changes in the electronic band structure and the nature of the electronic states near the Fermi level

Overall, this study contributes to the understanding of the fundamental properties of carbon-doped silicene and paves the way for further research into its potential applications in the fields of spintronics, electronics, and optoelectronics.

For future work further investigation and computation would be required to determine the behavior of the material.

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