2010

Ab Initio Simulations of Hydrogen and Lithium Adsorption on Silicene

Tim H. Osborn
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Ab Initio Simulations of Hydrogen and Lithium Adsorption on Silicene

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

By

Timothy H. Osborn
B.S. in Engineering Miami University, 2008

2010
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Timothy H. Osborn ENTITLED Ab Initio Simulations of Hydrogen and Lithium Adsorption on Silicene BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science in Engineering.

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Abstract

Osborn, Timothy Howard. M.S., Department of Mechanical and Materials Engineering, Wright State University, 2010. *Ab Initio Simulations of Hydrogen and Lithium Adsorption on Silicene*

The energies and temperature-dependent dynamics of hydrogen and lithium chemisorption on a silicon nanosheet, called silicene, were studied using density functional theory and molecular-dynamics (MD) simulations. Silicene has a buckled honeycomb structure, and has been fabricated as suspended monolayer sheets and nanoribbons in recent experiments. We calculated the adsorption energies of hydrogen and lithium on silicene for different adsorption ratios between 3.1% and 100%. The studies will clarify the characteristics of these novel and promising nanomaterials, and pave the way for their applications.

For Hydrogen, the adsorption energy had a maximum of 3.01 eV/H for complete hydrogenation, and decreased by 24.5% to 2.27 eV/H for single atom adsorption on a 32-silicon-atom supercell. It was determined that the preferred hydrogen adsorption patterns were clusters. Molecular dynamics simulations revealed the stability of adsorption configurations at 300K. The electronic structure of these stable configurations could be modified and controlled through partial and complete hydrogenations, and a transformation from zero-gap semiconductor to insulator was observed.
For lithium on silicene, the adsorption energy had a maximum of 2.23 eV/Li for 50% lithiation and decreased by 29.6% to 1.57 eV/Li for 100% lithiation. For partial Lithium adsorptions up to 50%, the preferred adsorption sites were hollow sites on top of silicon hexagons. This preference changed as more lithium atoms were introduced. At a 100 % adsorption ratio, the lithium atoms adsorbed to sites directly above or below the silicon atoms. Unlike hydrogenated silicene, the band structure of each partially lithiated structure was shown to be that of a metal.

Combining hydrogen and lithium adsorptions, it was shown that silicene-Li nanocompounds can be considered for hydrogen storage.
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I would like to sincerely thank my advisor Dr. Amir Farajian for providing me with this wonderful research opportunity. His guidance and enthusiasm has instilled in me an insatiable curiosity for my work. I would like to express my appreciation for the work of Dr. James Menart in creating such a relevant and challenging renewable and clean energy degree program. I would also like to extend a special thanks to the members of my research group for their valuable insight and support. And finally I would like to thank the members of my graduate committee Dr. Daniel Young and Dr. Maher S. Amer.
1. Introduction

From Graphene to Silicene

Graphene is a two dimensional carbon sheet composed of atoms arranged in a $sp^2$ hybridized honeycomb lattice. Graphene was first synthesized in 2004 by isolating a single layer of graphite through mechanical exfoliation [1]. Prior to its discovery, two-dimensional structures were believed to be unstable at finite temperatures. The successful synthesis of graphene led to countless papers exploring its properties, and potential applications.

Graphene quickly made its way into the renewable energy field as it opened up new possibilities for hydrogen storage materials, and lithium-ion battery anodes. Due to its unusual electronic properties, graphene has also been regarded as the leading candidate for the next generation of electronic materials.

The recent success of graphene has led to the investigation of other honeycomb monolayers composed of group IV elements such as silicon and germanium. [2] It has been previously shown through simulation that silicon can remain stable in a low buckled honeycomb monolayer called silicene [3].

Unlike graphene, silicene is not stable as a perfectly flat sheet. Because the $sp^3$ hybridization is more stable in silicon than the $sp^2$ hybridization, low buckled silicene is energetically favorable. Density functional theory studies [3] and phonon dispersion calculations [4] have confirmed that this low buckled structure, neither exactly $sp^3$ nor $sp^2$ configuration, is indeed the most stable.
Silicon has a lower $\pi$ bonding energy than carbon which makes the formation of silicon nanotubes and other unique structures less probable. However, experimental evidence of $sp^2$ bonding in single walled silicon nanotubes has been reported. [5] Despite structural differences, graphene and silicene share a unique electronic structure.

**Synthesis of Silicon Monolayers**

Three independent instances of synthesized silicon monolayers have been reported. The first group has demonstrated the synthesis of silicon nanoribbons grown on silver substrates. [6] These ribbons are parallel in alignment to each other and have a magic width of 16 Å and a thickness of only 2 Å.(Figure 1) STM images [7] with near atomic resolution clearly show the honeycomb structure of these silicon nanoribbons (Figure 2)

Figure 1 –Monolayer silicon nanoribbons grown on a silver substrate [6]
The second group [8] reports the synthesis of suspended monolayer silicon sheets doped with magnesium by chemical exfoliation of CaSi$_{1.85}$Mg$_{0.15}$. In this method, CaSi$_{1.85}$Mg$_{0.15}$ is immersed in a solution of propylamine (C$_3$H$_9$N) hydrochloride (HCl). The CaSi$_{1.85}$Mg$_{0.15}$ is then converted into doped silicon sheets and an insoluble black metallic solid. Two dimensional sheets ranging from 200 to 500 nm width have been reported using this method. The third group uses a similar method to produce silicon sheets covered with organic groups by exfoliation of layered polysilane [9].

These experimental observations of silicon nanoribbons, and suspended sheets, strongly support the existence of silicene. With the discovery and synthesis of a new material such as silicene, exciting new research opportunities and potential applications arise.

The existence of a silicon honeycomb monolayer has attracted attention due to silicon’s compatibility with existing electronics infrastructure. Such a material could enable the electronics industry to produce fast nanoscale electronics without retooling to work with carbon-based nanostructures such as graphene.
Recently, the electronic structure of silicene was determined to be that of a metal or a zero-gap semiconductor [10, 11]. Similar work on silicene sheets passivated with hydrogen show a direct bandgap at the Γ point [12]. These results, when compared to each other, clearly show that the electronic properties of silicon sheets can be controlled through hydrogenation. A similar effect was observed in long silicon nanowires, where the structural and electronic properties were found to change after hydrogenation [13].

This phenomenon has been similarly observed in graphene. Recent work shows the transformation of the graphene band gap from a zero-gap semiconductor to an insulator through reversible hydrogenation. This transformation was first proposed by Sofo et al. [14] and experimentally realized by Elias et al [15]. The fully hydrogenated graphene sheet, called graphane, could be restored to its original bare state by annealing the material at 450 °C. The band gap engineering of the graphene to graphane transformation could lead to fast nanoscale transistors, laser diodes, or solar cells.

Does silicene have a place in the field of renewable and clean energy and can it replace graphene as the successor to nanoscale electronic materials? By studying the interactions and energies associated with hydrogen and lithium adsorption on silicene we hope to illuminate band gap transformations while gaining valuable insight into the feasibility of silicene as a hydrogen or lithium storage material. Here we review the motivations for studying new materials for potential applications in nanoscale electronics, hydrogen, and lithium storage.
2. Background

Hydrogen Storage

Hydrogen is the most abundant element in the universe and cleanly burns to provide more energy per mass than existing fuels. The only byproduct of burning hydrogen is water and the quick diffusivity in air makes it safe at low pressures. This energy dense fuel has many benefits and is considered one of the leading alternatives to fossil fuels. However, despite these benefits hydrogen fuel still has two primary obstacles that need to be overcome; hydrogen production and storage.

Hydrogen is not available in its raw form, and needs to be extracted from existing molecules found in fossil fuels, biomass or water. Several different methods of extracting hydrogen from naturally occurring substances such as water have been demonstrated and work continues to progress in order to make hydrogen production more economical.

The second issue concerns hydrogen storage and arises because hydrogen has a low volumetric energy density. This means that hydrogen needs to be stored in high pressure tanks, liquified or stored on other materials to achieve the same performance as a gasoline internal combustion engine. Because of practicality and safety issues associated with compressed and cryogenic hydrogen on automobiles, the preferred method for storage is to adsorb the gas on a solid. An ideal solid material for hydrogen storage
must be able to adsorb a high weight percentage of hydrogen and also be able to release the hydrogen on demand at near room temperatures.

The Department of Energy (DOE) has set a target for hydrogen storage on solid materials of 5.5 wt. % by 2015 with an ultimate goal of 7.5 wt. %. This percentage measures the mass of hydrogen compared to the total (loaded) mass of the material that stores hydrogen. [16] Advancements in nanomaterials have led to new materials and structures capable of storing these amounts of hydrogen, however, releasing the hydrogen at near room temperatures has proven to be difficult. The slow kinetics of high capacity storage materials has consistently been an issue.

There are two possible ways for hydrogen to interact with a surface for storage; chemisorption and physisorption. Chemisorption is defined by a chemical bond between the storage material and hydrogen whereas physisorption is a weak attraction caused by induced dipoles known as Van der Waals forces. Physisorption is advantageous for hydrogen storage because it allows for faster adsorption/desorption cycles, however chemisorption has been shown to allow for higher weight percentages. It has been determined that the adsorption energies corresponding to a desirable release are (~ 0.1 - 0.2 eV). [17] This means that hydrogen is ideally loosely physisorbed to the storage medium and can be released by the addition of small amounts of thermal energy.

Carbon nanotubes and fullerenes have been explored for potential hydrogen storage materials with limited success. Recent work [18] suggest that silicon nanotube arrays have promising hydrogen storage potential. Other methods demonstrated in [19] use a boron doped graphene sheet with adsorbed lithium to reversibly store hydrogen.
(Figure 3) Because lithium does not naturally form strong bonds with graphene, boron is used to effectively enhance the binding energy, allowing for release of hydrogen without the release of lithium.

This work is particularly interesting because lithium bonds more strongly to silicene than it does to graphene. Raising the question, could a silicene-Li nanocompound effectively and reversibly store hydrogen? This question will be investigated in later chapters.

![Figure 3 – Boron doped Li-graphene compound for hydrogen storage [19]](image)

**Lithium Storage**

The recent boom of portable electronic devices, laptops and the resurgence of the electric car has led to increased interest in the development of high energy density batteries. While there are many battery chemistries being used today, lithium and lithium-ion batteries have a superior energy density compared to traditional nickel or lead based chemistries (Figure 4).
Rechargeable lithium-ion batteries operate on the principle of storing and releasing lithium ions. When a battery is charging, ions move through an electrolyte from the cathode to the anode where they insert themselves in the anode material. Current battery technologies typically use an amorphous carbon anode. By increasing the anode lithium storage capacity the overall capacity of the battery can be increased.

It has recently been shown that the capacity of current battery anodes can be theoretically increased by up to 10 times by replacing existing carbon materials with silicon.[21] This stems from the fact that silicon has the largest known charge capacity (4200 mAh/g) of any material [22]. While this capacity increase represents an appealing theoretical maximum, cyclability in silicon anode materials tends to suffer from large volume expansions upon lithium insertion.
Si nanowires and nanotubes have demonstrated better cyclability than bulk silicon [23] but significant advances still need to be made to realize this new anode material commercially. New materials such as silicene should be explored for lithium and lithium ion storage potential.

**Computational Material Science**

Computational methods have been rapidly developing in recent years. Today, computers are widely used to solve theoretical materials science problems by calculating the structural parameters and properties of materials through the use of quantum and classical physics. This powerful field of science and engineering has allowed scientists to further explore the behavior of materials and to predict the existence of materials before they are experimentally realized.

Understanding the properties of a many-particle system can be accomplished by determining its energy and how it changes as atoms are moved around. Quantum mechanics has shown that this can be achieved by solving the Schrödinger equation of $3N$ spatial variables and $N$ spin variables, where $N$ is the number of particles (electrons, neutrons, protons). For many-particle systems, this solution is far too complex for reasonable computations. In fact, quantum mechanical systems beyond that of a simple hydrogen or helium atom have yet to be solved exactly. To minimize this complexity, while still providing meaningful results, several approximations and theories have been developed.

Computational methods for modeling materials can be divided into four basic categories; semi-empirical, molecular mechanics, ab initio, and density functional theory.
Each method has its advantages and disadvantages depending on computational power, the size of the system and the desired accuracy. There is also significant overlap in these categories within various software packages used today.

Semi-empirical methods typically use experimentally obtained data as inputs for the Hartree-Fock formalism, whereas, molecular mechanics strictly uses classical Newtonian mechanics and force fields to model a material’s behavior. Ab initio methods calculate molecular structures by solving for the Schrödinger equation using the exact Hamiltonian and without using any empirical inputs. Instead, this method uses only theoretical principles, fundamental constants, and the atomic number of atoms. A large number of simplifying approximations are typically needed for this method and can be applied as needed based on desired computational time and accuracy.

**Density Functional Theory**

Due to recent advancements in approximations, density functional theory has become the most widely used technique for electronic structure calculations. Density functional theory provides a formulation for quantum mechanics that is simple and computationally efficient.

The basic principles of density functional theory were developed by Hohenberg & Kohn and Kohn & Sham in 1964 and 1965 respectively [23,24]. The Kohn-Sham theorem states that the ground state electron density, uniquely determines the total energy of a system. Mathematically, the electron density $\rho$ at a position in real space defined by coordinates $(x,y,z)$ is given by the function,
\[ \rho = \rho(x,y,z) \]

The total energy, \( E \), of the system can then be written as a functional of electron density

\[ E = E[\rho(x,y,z)] \]

To determine \( E \) the energies can be grouped into three terms as follows,

\[ E[\rho] = T[\rho] + U[\rho] + E_{xc}[\rho] \]

where \( T \) is the kinetic energy of electrons, \( U \) is the Coulomb energy, and \( E_{xc} \) is the electron-electron exchange-correlation energy. The Coulomb energy, \( U \), can be solved for classically and is given by,

\[ U = U_{ne} + U_{nn} + U_{ee} \]

where \( U_{ne} \) is the Coulomb attraction between electrons and nuclei, \( U_{ee} \) is the electron-electron repulsion, and \( U_{nn} \) is the nuclei-nuclei repulsion.

The “effective” kinetic energy of electrons is given by

\[ T = \sum_i n_i \int \nabla^2 \left[ -\frac{\hbar^2}{2m} \right] \psi_i^*(r) \psi_i(r) dr \]

This value can be determined by ab initio methods.

The final term, electron exchange-correlation, \( E_{xc} \), attempts to describe interaction between electrons. Within DFT this exchange correlation energy, as a functional of electron spin density, is the only term that needs to be approximated. Several
approximation methods have been developed to accurately represent this variable. The most commonly used functionals are the local density approximation (LDA) and the generalized gradient approximation (GGA). Here we use GGA based on previous results that suggest that GGA improves total energies, energy barriers, and structural energy differences. [25]. The expression for this approximation is given by,

$$E_{xc}^{GGA} [n] = \int d^3r f(n, \nabla n).$$

By combining the expressions for T, U and a selected E_{xc} expression, An equation for total energy can be determined. An example of this equation for a doubly occupied electronic states is given by [27]

$$E[\{\psi_i\}] = 2\sum_i (-\frac{\hbar^2}{2m})\psi_i \nabla^2 \psi_i d^3r + \int \psi_{ion}(r) \rho(r) d^3r + \frac{e^2}{r} \int \frac{\rho(r) \rho(r')}{|r-r'|} d^3r d^3r' + E_{xc}[\rho(r)] - U_{nn}[\{R_i\}]$$

where $\psi_i$ represents the occupied electronic states and $V_{ion}$ is the static total electron-ion potential.

Numerous codes utilize the basic concepts of density functional theory in slightly different ways. Here we use the SIESTA program [26]. This software utilizes an additional approximation known as pseudopotentials.

Because chemical properties are entirely determined by valence electrons, pseudopotentials are used to generate a pseudo-wavefunctions that are smooth in the core region. This effectively eliminates core electrons thus simplifying calculations and reducing computation time.
Molecular Dynamics

Molecular dynamics allows for computer simulations that run for a designated amount of time at a given temperature or temperature gradient. This method can provide accurate information about the structure, dynamics, and thermodynamics of molecular systems. Essentially the energy of the system is being used to make the system move. A given system of particles having a position, inter-molecular force and velocity can be classically determined using numerical methods.

The position of a given atom in this system can be defined by the position of its nucleus and the positions of its electrons. Because electrons will respond to external changes faster than the nucleus, we can divide the nucleus and the electrons into separate mathematical problems. This separation is known as the Born-Oppenheimer approximation. From here we can assume that the nucleus is fixed in order to calculate the lowest energy state or ground state of the electrons. By separating the electronic and nuclear motion it is possible to visualize molecules as nuclei moving over a potential energy surface created by electrons.

For ab initio Born Oppenheimer molecular dynamics, forces are determined as the simulation runs. A static optimization of electronic structure is performed at each time step within the simulation. This provides the coordinates of each ion for every time step. By using these coordinates, the energy and forces acting upon each ion can be solved for quantum mechanically.

From Newton’s equation of motion and the Born-Oppenheimer approximation we get the result:
\[ M_I \ddot{R}(t) = -\nabla I V_e^{\text{approx}}(R(t)) \]

where \( M_I \) is the mass of the ion I, \( \ddot{R} \) is the acceleration of ion I and \( V_e^{\text{approx}} \) is the effective potential energy. By integrating this equation of motion for the nuclei and including the Nose-Hoover temperature control, one obtains

\[
f_c([P_1]; \{R_1\}) \propto \exp \left[ -\beta \left( \frac{1}{2} \sum_i \frac{P_i}{M_i} + E_0(\{R_i\}) \right) \right]
\]

Where

\[
\beta = \frac{1}{k_B T}
\]

Within SIESTA, this Nose mass or heat bath constant can be set to minimize temperature fluctuations.
3. Method

Parameters

The energies and temperature-dependent dynamics of hydrogen and lithium chemisorption on a silicon nanosheet were studied using density functional theory (DFT) and molecular-dynamics (MD) simulations. These calculations were performed using the SIESTA code [26] with a generalized-gradient approximation (GGA), Perdew-Burke-Ernzerhof (PBE) exchange correlation functional, double zeta polarization (DZP) basis set and norm-conserving pseudopotentials.

Supercells of 2, 8, and 32 atom units were constructed with periodic boundary conditions for all energy calculations. Using larger supercell sizes allowed for more degrees of freedom when exploring adsorption patterns, but has significantly increased computation time. The z-dimension of each cell was set to 15 Å to eliminate interlayer interactions. Structural relaxations were performed using conjugate gradient (CG) methods in which the force tolerance was set to 0.005 eV/Å, and the k-grid cutoff corresponded with 40 Bohr for 2 atom super cells and 80 Bohr for super cells of 8 and 32 atoms. The mesh cutoff was set to 250 Ry.

Procedure

The preferred sites for adsorption on these supercells were explored by testing various hydrogenation and lithiation configurations corresponding to adsorption percentages between 3.1 and 100%. The configurations tested include but are not limited to those shown in Figure 5 for 25, 50, and 75% adsorptions.
Figure 5 – Schematics of partial hydrogen adsorption configurations for 25, 50 and 75 % adsorption ratios. Dots represent hydrogen atoms adsorbed on an 8-silicon-atom supercell.
The lowest energy configurations obtained from these relaxations were then tested for stability at 298 K using Molecular Dynamics (MD) simulations. The MD simulations were performed using a time step of 1 fs over a 1000 fs duration. Simulations were conducted at a near room temperature of 298 K as controlled by a Nosé thermostat [28], where temperature fluctuations were minimized by the Nosé mass or heat bath mass constant to within ± 200 K (Figure 6).

![Figure 6](image)

**Figure 6** – Temperature fluctuation for MD simulations around a set temperature of 298 K as controlled by a Nosé thermostat

For the most stable hydrogenation and lithiation patterns, the adsorption energy of atomic hydrogen and lithium on the silicon sheet was calculated using the following equation:

$$E_{adsorp} = \frac{1}{N_H}(E_{Si} + N_HE_H - E_{H+Si})$$

where $E_{Si}$ is the total energy of the bare silicon sheet, $N_H$ is the number of adsorbed atoms, $E_H$ is the total energy of atomic hydrogen or lithium calculated with spin polarization, and $E_{H+Si}$ is the total energy of the fully saturated silicon sheet.
The band structure for each hydrogenation configuration was investigated along the high symmetry directions in the hexagonal Brillouin zone, i.e., K, Γ, and M. (Figure 7)

![High symmetry points considerd in the hexagonal brillouin zone of silicene](image)

Figure 7 – High symmetry points considered in the hexagonal brillouin zone of silicene

The density of state (DOS) curves were plotted from the resulting eigenvalues and displayed using Gaussian broadening with a width of 0.15 eV.

**Method Verification**

Each input parameter for our code was tuned in order to achieve convergence of the total energy. The parameter that was most crucial to achieving accurate energies was k-grid cutoff. For each sized silicene unit cell, the convergence of total energy was determined against the number of k-points defined by the k-grid cutoff. (Figure 8) This study revealed that a k-grid cutoff of 160 Bohr should be used to guarantee total energy convergence for systems larger than 32 atoms. The downside to using larger k-grid cutoffs is that it significantly increases computation time. This proved limiting and we used a k-grid cutoff of 80 Bohr, that still results in a reasonable convergence.
Figure 8 - Total energy vs. k-grid cutoff for a silicene 32-atom supercell relaxation using Siesta.

The parameters used in these calculations were tested and verified against published geometries and band structure data for graphene, graphane, and silicene. Our results agreed with previous data [12] verifying that our code and parameters were functioning as expected.
4. Silicene: A 2D silicon nanosheet

In order to investigate hydrogen and lithium adsorption on silicene, calculations have been conducted in three steps: First, we determined the stable structure of silicene and fully hydrogenated silicene. We then explored various hydrogen adsorption patterns to find the most favorable configurations for partial hydrogenations. Using these stable configurations, we then plotted the adsorption energies, band structure and density of states. This process was repeated for lithium adsorptions.

Because all calculations were based on silicene, determining the correct relaxed structure was crucial. To test the stability of silicene, the structure was relaxed from three starting positions; A. planar, B. near planar (planar with one atom displaced 0.05 Å out of plane) and C. high buckled (similar to that of the bulk Si (111) surface). (Figure 9)

Figure 9 – Initial geometry of silicene before relaxations (A) planar (B) planar with a single atom displaced by 0.05 Å (C) high buckled
After relaxations, the flat structure of A. remained unchanged while B. and C. both relaxed to the same low buckled structure. While the planar structure in A. remained perfectly flat, it fails to accurately represent the global energy minimum for silicene. Test B clearly shows that a minor displacement of one atom, (i.e. a system experiencing a non-zero temperature), will cause the structure to relax into a low buckled structure. Because of this, we can conclude that silicene is not stable in a planar graphene-like structure. Instead, the most energetically favorable structure is low-buckled. This agrees with, phonon dispersion calculations plotted by [4] showing that planar silicene is not stable.

The relaxed geometric structure for bare silicene is shown in Figure 10. The bare silicene sheet has a buckle height of 0.542 Å with an internal angle of 114.65 degrees and a Si-Si bond length of 2.298 Å. These dimensions are slightly different from the dimensions reported by Cahangirov et al. [4] using plane wave method. Our results, however, are in agreement with those of previously reported structures by Ding and Ni [10] who used both localized atomic orbital and plane wave methods.
Figure 10 – The relaxed structure of bare silicene
5. Hydrogen adsorption on silicene

Structure

When the silicene sheet is fully hydrogenated (Figure 11) the silicon atoms are pulled further out of plane resulting in an increased buckle height and Si-Si bond length of 0.736 Å and 2.359 Å respectively. This fully hydrogenated structure closely resembles that of the bulk Si(111) surface. The Si-H bond has a bond length of 1.519 Å.

Figure 11 – Relaxed geometry of fully hydrogenated silicene
Energetics

For hydrogenation ratios between 3.1% and 100%, numerous adsorption patterns were relaxed. The most energetically favorable configurations were consistently those in which hydrogen atoms clustered on the silicene surface. These hydrogen clusters form the most stable structure when the total number of nearest neighbors with adsorbed hydrogen is maximized.

The adsorption energies associated with these lowest energy clusters for each hydrogenation ratio are plotted in (Figure 12). The graph shows that a fully hydrogenated sheet has the highest hydrogen adsorption energy (3.01 eV/H) and is therefore the most stable. This adsorption energy suggests a strong chemical bond between the silicon and hydrogen atoms. As the hydrogenation ratio is decreased, the adsorption energy per atom also decreases. This shows that hydrogen prefers adsorption on sites adjacent to those already occupied with hydrogen. This preferred clustered hydrogenation pattern for silicene agrees with the predicted clustered hydrogenation pattern for graphene [30].

In (Figure12), each line represents a different sized supercell. As the supercell size increases more hydrogenation patterns become available and higher adsorption energies can be obtained. This is demonstrated in Table 1, where we compare the adsorption energy and band gap data for partial hydrogenation configurations on 8 and 32 atoms supercells.
Table 1- Comparison of the adsorption energies and band gaps for different supercell sizes and hydrogenation ratios.

<table>
<thead>
<tr>
<th>Hydrogenation (Percent)</th>
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<th>Band Gap (eV)</th>
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<td>8 Atom</td>
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<tr>
<td>25</td>
<td>2.63</td>
<td>No Gap</td>
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<td>No Gap</td>
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<td>75</td>
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<td>1.79</td>
</tr>
<tr>
<td>32 Atom</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>2.79</td>
<td>No Gap</td>
</tr>
<tr>
<td>50</td>
<td>2.86</td>
<td>No Gap</td>
</tr>
<tr>
<td>75</td>
<td>2.94</td>
<td>0.256</td>
</tr>
</tbody>
</table>

The 8-atom curve presented in Figure 12 is distinctly different from that of the larger cell sizes because it includes the adsorption of odd numbers of atoms. Each dip in the curve (from left to right) represents the adsorption energy for 1, 3, 5, and 7 hydrogen atoms adsorbed on the surface. These dips can be attributed to lattice curvature, i.e. the fact that clusters of odd numbers of adsorbed atoms distort the lattice more than even numbered clusters. With odd number of hydrogen atoms, there is always an “unpaired” adsorption site. The silicon atom at the unpaired site causes a high-buckled lattice distortion that is not compensated by the deformation owing to a hydrogen adatom on the other side of the silicene sheet. The compensated high-buckled arrangement indicates $sp^3$ hybridization similar to that of bulk silicon, and is stable. Therefore, the adsorption of odd number of hydrogen atoms (per supercell) results in less stable structures observed for the 8 atom supercell in Figure 12.
Electronic Structure

Band structure calculations confirmed that silicene changes from a zero gap semiconductor to an insulator after complete hydrogenation. This electronic structure transformation is shown in Figures 13 and 14. These band structure calculations agree with previous works [11, 12]. To further explore the changes induced in the electronic structure of silicene upon hydrogen adsorption, we investigated partial hydrogenation.

This transformation was further explored for partial hydrogenation by calculating the density of states (DOS) for 25%, 50%, and 75% hydrogenation ratios. The result for the lowest energy configuration for each ratio is depicted in Figure 15. The DOS curves revealed that partial hydrogenation creates an energy gap at the Fermi energy, and this gap widens with increasing hydrogenation ratios.
Figure 13 – The bandstructure of bare silicene

Figure 14 – Band structure of hydrogenated silicene
Figure 15 - Density of states curves for lowest energy configurations of silicene with 0%, 25%, 50%, 75%, and 100% hydrogenations. Fermi energy is shifted to zero.
A similar effect has also been observed in the case of graphene nanoribbons, where partial hydrogenation creates a gap and results in a metal-to-semiconductor transition [30].

We also conducted MD simulations at 300 K to assess the stability of these structures. The lowest energy structures at each hydrogenation ratio were found to be stable over 500 time steps of 1 fs each. The MD simulations revealed that H-Si and Si-Si bond length oscillation periods are approximately 16 and 75 fs, respectively. The finite temperature stability of partially hydrogenated structures is consistent with the large hydrogen adsorption energies (Figure12 and Table 1) that indicate strong chemical bonding between the silicon atoms and the adsorbed hydrogen atoms.
6. Lithium adsorption on silicene

Structure

The structure of fully lithiated silicene is shown in Figure 16. This structure closely resembles that of the fully hydrogenated case. Complete lithium saturation results in a buckle height of 0.68 Å with a Si-Si bond length of 2.32 Å and a Si-Li bond length of 2.649 Å. This buckling is slightly flatter than that of hydrogen adsorption (0.734 Å) but still more buckled than bare silicene (0.54 Å).

Figure 16 – Fully lithiated silicene structure
This fully lithiated structure is unique. For partial lithiation ratios of 50% and less, the hollow cite is the preferred lithium adsorption position, whereas for the fully saturated structure the on-top position is preferred.

Energetics

The maximum adsorption energy of 2.24 eV/Li occurs at a 50% lithiation corresponding to complete saturation of all hollow sites. During 100 % lithiation there are no longer enough hollow cites for atoms to occupy. Instead the lithium atoms remain at the sites directly above silicon atoms. This configuration has significantly lower adsorption energy of 1.57 eV/Li. The adsorption energies are shown in Figure 17 for partial and complete lithiations.

Figure 17 – Lithium adsorption energy on 8 atom silicene supercell versus the adsorption ratio
**Electronic Structure**

Through partial and complete lithiations the band structure of silicene was transformed from a zero-gap semiconductor into a metal. This transformation was explored through lithiations of 25, 50 and 100% adsorption ratios. The band structure and density of states for 100% lithiation is shown in Figure 18. The most energetically favorable configurations are shown in Figure 19 with their corresponding density of states curves.

![Figure 18 – Band Structure and DOS of Fully lithiated Silicene](image-url)
Figure 19 - Density of states curves for lowest energy configurations of silicene with 0%, 25%, 50%, and 100% lithiation

Figure 19 represent a transformation from a zero-gap semiconductor to a metal at very low adsorption ratios. In addition, it shows that the metallic band structure, and thus the conductance of the material, is modified as the adsorption ratio changes.
6. Hydrogen Storage using silicene-Li nanocompounds

Hydrogen chemisorption on bare silicene yields a maximum weight percentage of 3.6% through 3.01 eV binding. These values indicate that bare silicene by itself is not a practical hydrogen storage material. However, through exploring secondary adsorptions on silicene-Li compounds, more promising results have been obtained. In the previous section we show that lithium atoms prefer to adsorb on the hollow sites of silicene at low adsorption ratios with a binding energy of 2.24 eV/Li. This strongly bonded lithium atom may serve as a platform for storing molecular hydrogen. To explore this possibility we calculate the adsorption energies of H$_2$ for the structure shown in Figure 20.

![Figure 20 - Molecular hydrogen adsorbed on silicene-Li compound structure](image)

The preliminary adsorption energy calculations show that the hydrogen binding energy is 0.11 eV/H. This value indicates that the H$_2$ molecules are physisorped to the lithium and should release easily. The weight percentage of this configuration is 3.36% but only represents one lithium-occupied hollow cite. Adding another adsorption
platform to the other side of the silicene structure as demonstrated in the previous section for the 25 % case would increase the weight percent to 6.51 %. Both the binding energy and weight percent values fall within the desired range of values for viable hydrogen storage set forth by the DOE.

Band structure calculations have shown that completely hydrogenated silicene behaves as an insulator and completely lithiated silicene behaves as a metal. By combining the two atoms in a hybrid system a band gap is maintained. (Figure 21) This unique formation consisting of alternating strips of lithium and hydrogen adsorbed on silicene (Figure 22) is derived from the most stable configuration of 50 % hydrogenation with lithium atoms filing the voids.

Figure 21 – Band structure of lithium and hydrogen strips on silicene compound
Figure 22 – Lithium-Hydrogen-Silicene nanocompound
7. Conclusion

We calculated the stable structures of a novel silicon nanosheet, silicene, as well as those of its hydrogenated and lithiated nanocompounds.

It was shown that the binding energy for hydrogen chemisorption on silicene increases with hydrogenation ratio. Partial hydrogenation clusters were shown to be energetically favorable. The band structure transformed from a zero gap semiconductor to an insulator. This transformation was shown through partial hydrogenation steps.

For lithium, it was shown that the adsorption energy on silicene decreases with increasing adsorption ratio. Hollow site saturation was shown to be the most energetically favorable configuration. The metallic band structure of lithiated silicene was explored for the first time.

Secondary adsorptions on silicene were explored for potential hydrogen storage. Preliminary results indicate that the silicene-Li nanocompounds may be promising materials for hydrogen storage worth further consideration.
References


Presentation and publication

Part of this work was presented at the American Physical Society conference in Portland Oregon in March and is being submitted to The Journal of Physical Chemistry Letters.