Computational Design and Characterization of Silicene Nanostructures for Electrical and Thermal Transport Applications

Tim H. Osborn
Wright State University

Follow this and additional works at: https://corescholar.libraries.wright.edu/etd_all

Part of the Engineering Commons

Repository Citation
Osborn, Tim H., "Computational Design and Characterization of Silicene Nanostructures for Electrical and Thermal Transport Applications" (2014). Browse all Theses and Dissertations. 1215.
https://corescholar.libraries.wright.edu/etd_all/1215

This Dissertation is brought to you for free and open access by the Theses and Dissertations at CORE Scholar. It has been accepted for inclusion in Browse all Theses and Dissertations by an authorized administrator of CORE Scholar. For more information, please contact library-corescholar@wright.edu.
COMPUTATIONAL DESIGN AND CHARACTERIZATION OF SILICENE NANOSTRUCTURES FOR ELECTRICAL AND THERMAL TRANSPORT APPLICATIONS

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering: Materials Science and Nanotechnology

By

TIM H. OSBORN
M.S., Wright State University, 2010
B.S., Miami University, 2008

2014
Wright State University
WRIGHT STATE UNIVERSITY
THE GRADUATE SCHOOL

May 15, 2014


________________________________________
Amir A. Farajian, Ph.D.
Dissertation Director

________________________________________
Ramana V. Grandhi, Ph.D.
Director, Ph.D. in Engineering Program

________________________________________
Robert E.W. Fyffe, Ph.D.
Dean of The Graduate School

Committee on Final Examination

________________________________________
Amir A. Farajian, Ph.D.

________________________________________
Khalid Lafi, Ph.D.

________________________________________
Sharmila M. Mukhopadhyay, Ph.D.

________________________________________
Ajit Roy, Ph.D.

________________________________________
H. Daniel Young, Ph.D.
ABSTRACT


Novel silicene-based nanomaterials are designed and characterized by first principle computer simulations to assess the effects of adsorptions and defects on stability, electronic, and thermal properties. To explore quantum thermal transport in nanostructures a general purpose code based on Green’s function formalism is developed.

Specifically, we explore the energetics, temperature dependent dynamics, phonon frequencies, and electronic structure associated with lithium chemisorption on silicene. Our results predict the stability of completely lithiated silicene sheets (silicel) in which lithium atoms adsorb on the atom-down sites on both sides of the silicene sheet. Upon complete lithiation, the band structure of silicene is transformed from a zero-gap semiconductor to a 0.368 eV bandgap semiconductor. This new, uniquely stable, two-atom-thick, semiconductor material could be of interest for nanoscale electronic devices.

We further explore the electronic tunability of silicene through molecular adsorption of CO, CO$_2$, O$_2$, N$_2$, and H$_2$O on nanoribbons for potential gas sensor applications. We find that
quantum conduction is detectibly modified by weak chemisorption of a single CO molecule on a pristine silicene nanoribbon. Moderate binding energies provide an optimal mix of high detectability and recoverability. With Ag contacts attached to a ~ 1 nm silicene nanoribbon, the interface states mask the conductance modulations caused by CO adsorption, emphasizing length effects for sensor applications. The effects of atmospheric gases: nitrogen, oxygen, carbon dioxide, and water, as well as CO adsorption density and edge-dangling bond defects, on sensor functionality are also investigated. Our results reveal pristine silicene nanoribbons as a promising new sensing material with single molecule resolution.

Next, the thermal conductance of silicene nanoribbons with and without defects is explored by Non-Equilibrium Green’s function method as implemented in our ThermTran program that was developed as part of this Ph.D. research. We reveal that the thermal transmission and conductance of pristine silicene ribbons is systematically reduced upon the introduction of hydrogen and silicon vacancy defects. This suggests that defect engineering and/or doping may provide a viable method for tuning the thermal transport of narrow silicene nanoribbons. Our generalized ThermTran program for calculating thermal transport across pristine, defected, contacted, or interfaced, junctions is demonstrated.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. INTRODUCTION ..................................................................................................................</td>
</tr>
<tr>
<td>1.1 Research Aims ..................................................................................................................</td>
</tr>
<tr>
<td>2. LITERATURE SURVEY .........................................................................................................</td>
</tr>
<tr>
<td>2.1 Graphene .........................................................................................................................</td>
</tr>
<tr>
<td>2.2 Boron Nitride Nanosheets ................................................................................................</td>
</tr>
<tr>
<td>2.3 Silicene ..........................................................................................................................</td>
</tr>
<tr>
<td>2.3.1 Synthesis of Silicene ...................................................................................................</td>
</tr>
<tr>
<td>Soft Chemistry ......................................................................................................................</td>
</tr>
<tr>
<td>Silicene Nanoribbons on Silver Substrates .........................................................................</td>
</tr>
<tr>
<td>Silicene Nanoribbons on Au(110) .......................................................................................</td>
</tr>
<tr>
<td>Silicene Nanosheets on Ag (111) .......................................................................................</td>
</tr>
<tr>
<td>Silicene on Zirconium Diboride .........................................................................................</td>
</tr>
<tr>
<td>Chemical Vapor Deposition .................................................................................................</td>
</tr>
<tr>
<td>2.4 Germanene .....................................................................................................................</td>
</tr>
<tr>
<td>2.5 Comparing Properties of 2-D Monolayers ..................................................................</td>
</tr>
<tr>
<td>2.5.1 Physical Structure .....................................................................................................</td>
</tr>
</tbody>
</table>
2.5.2 Electronic Structure........................................................................................................22

2.5.3 Thermal Properties........................................................................................................24

2.5.4 Synthesis..........................................................................................................................24

2.5.5 Property Summary...........................................................................................................25

3. METHODOLOGY .....................................................................................................................27

3.1 Density Functional Theory ................................................................................................28

3.1.1 Born Oppenheimer Approximation .............................................................................28

3.1.2 Hohenberg-Kohn Theorems .........................................................................................29

3.1.3 Kohn-Sham Equations ..................................................................................................30

3.1.4 Exchange Correlation ....................................................................................................32

3.1.5 Pseudopotentials ..........................................................................................................34

3.2 Quantum Molecular Dynamics ..........................................................................................35

3.3 Phonon Dispersion Calculations .........................................................................................37

3.4 Quantum Electronic Transport ..........................................................................................41

4. RESULTS ..................................................................................................................................43

4.1 Silicene Stability ..................................................................................................................43

4.2 Silicene Hydrogenation ........................................................................................................48

4.2.1 Introduction .....................................................................................................................48
4.2.2 Results ..............................................................................................................48

4.3 Silicene Lithiation .................................................................................................54

4.3.1 Introduction .......................................................................................................54

4.3.2 Method ...............................................................................................................56

4.3.3 Results ...............................................................................................................59

Stability .....................................................................................................................63

Molecular Dynamics .................................................................................................66

Phonon Dispersion .....................................................................................................68

Electronic Structure ..................................................................................................69

4.3.4 Summary .........................................................................................................70

4.4 Silicene Nanoribbons as High Resolution Gas Sensors ......................................72

4.4.1 Introduction .....................................................................................................72

4.4.2 Method .............................................................................................................75

4.4.3 Results .............................................................................................................76

CO Adsorption ..........................................................................................................76

Effects of CO Density and Edge Defects .................................................................81

Environmental Gas Adsorption .................................................................................84

Silver Contacts .........................................................................................................87
Silicene on Silver Contacts ................................................................. 88

4.4.4 Summary .................................................................................. 90

4.5 Quantum Thermal Transport in Defected Silicene Nanoribbons ............... 92

4.5.1 Introduction .............................................................................. 93

4.5.2 Method ..................................................................................... 94

4.5.3 Validation ................................................................................ 99

4.5.4 Results .................................................................................... 102

4.5.5 Summary ................................................................................ 108

5. CONCLUSIONS .............................................................................. 109

6. APPENDIX A ................................................................................. 110

A.1 Publications .............................................................................. 110

A.2 Presentations ............................................................................. 111

REFERENCES .................................................................................. 112
LIST OF FIGURES

Figure 1. Model sketch of a single layer of graphite without interlayer interactions as drawn in 1947 \cite{1} ................................................................. 2

Figure 2. TEM images of graphitic flakes as seen by Hanns-Peter Boehm in 1962 \cite{2} ............... 3

Figure 3. AFM image of exfoliated graphene flake as seen by A. Geim and K. Novoselov in 2004 \cite{5} .................................................................................................................. 4

Figure 4. Band structure of silicene from first principles as calculated in 2005 \cite{30} .................. 7

Figure 5. Model of oxygen-free silicon monolayers covered in decylamine groups \cite{36} ............ 10

Figure 6. (a) STM image of linked silicon hexagon formation on Ag(100) surface \cite{45} (b) Si tetramer structures \cite{47} (c) and aligned silicon nanoribbon formation on Ag(110) surface \cite{46} ........................................................................................................ 11

Figure 7. Proposed structure of silicon nanoribbons experimentally grown on Ag(110) substrates by (A) A. Kara \cite{48} et al. (B) C. Lian et al. \cite{49} ........................................................................ 12

Figure 8. (a) STM image \cite{41} and (b) 3d STM image of silicene on Ag(111) \cite{43} ...................... 13

Figure 9. STM image of terraced silicene multilayers as seen by P. Vogt. et al. in 2013 \cite{57} ....... 15

Figure 10. (a) STM image of silicene layer on ZrB$_2$ buffer (b) DFT predicted model of experimentally realized structure (c) Band structure of freestanding reconstructed 3x3 silicene \cite{58} ........................................................................................................ 16

Figure 11. (a) SEM image and (b) TEM image of silicon nanosheets after 30 minutes growth time on Si substrate \cite{59} ........................................................................................................ 17
Figure 12. STM image of Ge tetramers after Ge deposition on Ag(001) surface

Figure 13. Comparison of geometry and electronic band structure for graphene, silicene, germanene and hexagonal boron nitride nanosheets. The band structures shown are results of our calculations within SIESTA and show agreement with previous works.

Figure 14. Illustration of the Kohn-Sham treatment of interacting electron systems

Figure 15. Schematic showing the self-consistent approach to calculating the electron density within the SIESTA code

Figure 16. All-electron wavefunction and potential (dashed) compared with the pseudopotential wavefunction and potential (solid)

Figure 17. Dispersion relation for a linear atomic chain with only nearest neighbor interactions and $K = 1, M = 1$, and $a = 1$

Figure 18. Phonon dispersion of graphene

Figure 19. Source, molecular contact, drain for quantum transport calculations

Figure 20. Relaxed structure of low-buckled silicene sheet

Figure 21. Phonon dispersion results for (a) planar and (b) low-buckled silicene

Figure 22. Average Si-Si bond-length fluctuation over the duration of molecular dynamics simulation at 300 and 1500K

Figure 23. Adsorption energies per hydrogen atom for ortho, para, and meta adsorption configurations, i.e., adsorption on the pair of neighboring Si atoms, opposite Si atoms, or Si atoms separated by one other atom, respectively
**Figure 24.** The lowest energy configurations of silicene with 0%, 25%, 50%, 75%, and 100% hydrogenations and their corresponding band structures. The supercell contains 32 silicon atoms. Fermi energy is shifted to zero.

**Figure 25.** Relaxed Geometric structure of fully lithiated silicene (silicel), obtained by using GGA.

**Figure 26.** The dependence of lithium adsorption energy on lithium content for the lowest energy adsorption configurations on silicene.

**Figure 27.** Change in Gibbs free energy of $Li_xSi_{1-x}$ compound with increasing lithium content, obtained by employing GGA and LDA. Pure bulk Si and pure bulk Li cases are represented by $\delta G = 0$. For fully lithiated silicene, silicel, the difference between LDA and GGA Gibbs free energy changes turns out to be less than 1 meV/atom.

**Figure 28.** Average Si-Si bond length (top) and average Li-Si bond length (bottom) plotted over 3000 fs duration.

**Figure 29.** Phonon dispersion curves for silicene (left) and lithiated silicene (silicel) (right).

**Figure 30.** The band structure for pristine (left) and fully lithiated silicene (right) obtained by using GGA. The supercells contain two Si atoms. Fermi energy is set to zero.

**Figure 31.** Linear dispersion fit at the k-point for silicene (a) and deviation from linearity for silicel (b).

**Figure 32.** Relaxed geometry of pristine 5ASiNR (a), lowest energy structure for CO adsorption "CO-Edge" (b), and second lowest energy structure for CO adsorption.
"CO-Center" (c). Top and side views of monolayer ribbons considered in this study are shown in each panel. .................................................................77

**Figure 33.** Quantum conductance of pristine silicene nanoribbon (blue), CO edge adsorption on nanoribbon (red), and deformed nanoribbon with CO removed (green). Middle of the gap is set at zero. .................................................................78

**Figure 34.** Quantum conductance of pristine silicene nanoribbon (blue), CO center adsorption on nanoribbon (red), and deformed nanoribbon with CO removed (green). Middle of the gap is set at zero. .................................................................79

**Figure 35.** Quantum conductance of pristine silicene nanoribbon (blue), with one CO adsorbed (green), two CO adsorbed on the same side (2 CO-A) (red), and two CO adsorbed on opposite sides (2CO-B) (grey). The conductance changes for the system having one edge-dangling bond defect with (orange) and without (purple) one CO adsorbed are also shown. Middle of the gap is set at zero. .................................................................83

**Figure 36.** Quantum conductance modulation resulting from environmental gas molecules adsorptions on nanoribbon: N$_2$ (blue), O$_2$ (red), CO$_2$ (green) and H$_2$O (purple). Middle of the gap is set at zero. .................................................................85

**Figure 37.** Conductance of fixed contact based on surface Ag(100) layer without (blue) and with CO-adsorbed molecule (red). Fermi energy is set at zero. .................................................................88

**Figure 38.** Conductance of pristine silicene nanoribbon attached to Ag(100) contacts (blue), and silicene nanoribbon with CO-Center (red) and CO-Edge adsorption (green). Red
box indicates interface that was relaxed on the fixed Ag-contact. Fermi energy is set at zero.

**Figure 39.** Graphical user interface of our newly developed ThermTran program.

**Figure 40.** Schematic representation of the system setup for quantum thermal transport calculations (top) and an illustration of a realistic nanoribbon device setup (bottom).

**Figure 41.** Notation for defining the submatrices of $K_{Dynamic}$.

**Figure 42.** Simplified atomic chain matrix to validate ThermTran output.

**Figure 43.** Thermal transmission of simple atomic chain model.

**Figure 44.** Structure of polyethylene chain used for ThermTran validation (top panel) and thermal transmission of Polyethylene chain (bottom panel).

**Figure 45.** Relaxed geometry of pristine silicene nanoribbon (top panel) with a single hydrogen atom removed (middle panel) and with a silicon edge atom removed (bottom panel). These are results of cluster relaxations using Gaussian 09 program.

**Figure 46.** Thermal transmission for pristine silicene nanoribbon (blue curve), with single hydrogen defect (red curve), and single silicon vacancy edge defect (green curve). Note: High frequency contributions ($\sim 2200 \text{ cm}^{-1}$) due to hydrogen modes are not pictured here.

**Figure 47.** Conductance vs. Temperature for Pristine (top panel), hydrogen defected (middle panel), and silicon edge defected (bottom panel) silicene nanoribbons. The curves are *not* shifted along the conductance axis.
LIST OF TABLES

Table 1. Comparison of available property data and references for graphene, silicene and germanene. Values without reference are from our calculations. ..............................................................25

Table 2. Geometry optimization and total energy results for different lithium adsorption configurations and ratios as calculated using GGA and LDA for comparison. Total energies of the most stable structures for each adsorption ratio are set to zero. x is the lithium content in Li$_x$Si$_{(1-x)}$ surface adsorption compounds. .................................................................60

Table 3. Adsorption energy and molecular charge of CO for adsorption at center and edge locations on 5AsiNR. Positive values of charge represent charge transferred from CO to the nanoribbon. .........................................................................................................................81

Table 4. Calculated cohesive energies for silicene nanoribbon systems with and without defects ........................................................................................................................................104
ACKNOWLEDGMENT

I would like to thank my advisor Dr. Amir A. Farajian for his excellent guidance, my committee members for their constructive feedback, and my family members for their continued love and support.

I would also like to thank our funding sources: The National Science Foundation Grant ECCS-0925939 and The Wright State University, Ph.D. In Engineering Program.
1. INTRODUCTION

1.1 Research Aims

The primary aim of this research is to fully understand, by first principles, the stability, electronic, and thermal properties of silicene based nanostructures and how these properties can be altered by chemical adsorptions, doping, and functionalization to create novel new materials for nanoelectronic devices, gas sensors, and thermoelectric devices. In this dissertation we will; discuss relevant literature surrounding the realization of silicene and related 2-d nanomaterials such as graphene, germanene and hexagonal boron nitride nanosheets (BNNS). We will then detail our results on the stability of silicene, reveal our newly designed silicene based semiconductor materials, explore the gas sensing capability of silicene nanoribbons, and demonstrate the utility of our newly created ThermTran program by calculating thermal conductance across defected silicene nanoribbons.
2. LITERATURE SURVEY

2.1 Graphene

Graphite monolayers were first theoretically explored by tight binding approximations in 1947 by P. Wallace. Here he showed the semi-metallic behavior of graphite monolayers (not yet called graphene) as a starting point for studying bulk graphite. The simple sketch from his published work is shown in Figure 1. At the time, graphene was not known to be stable and thus the monolayer properties were given little attention.

![Figure 1](image.png)

**Figure 1.** Model sketch of a single layer of graphite without interlayer interactions as drawn in 1947

Graphite and graphite-oxide monolayers were first observed in 1962 by Hanns-Peter Boehm et al. via transmission electron microscopy (TEM) as shown in Figure 2. He later coined...
the term “graphene” to describe these single layers\textsuperscript{3}. For decades this finding received little attention because the properties of graphene were not well known and the isolated stability not widely accepted.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{graphitic_flakes.png}
\caption{TEM images of graphitic flakes as seen by Hanns-Peter Boehm in 1962\textsuperscript{2}}
\end{figure}

In 2002 B. Jang et al. filed a US patent for the production of nanoscale graphene platelets\textsuperscript{4} and in 2004 A. Geim and K. Novoselov succeeded in mechanically exfoliating and isolating graphene from graphite, demonstrating its stability and electronic properties\textsuperscript{5}. Figure 3 shows an atomic force microscopy (AFM) image of a stable graphene monolayer\textsuperscript{5}. Their work on graphene led to the Nobel Prize in physics in 2010 and opened the door to one of the most highly promising and published materials of the past decade; graphene.
The excitement surrounding graphene begins with its exceptional properties, i.e. flexibility, mechanical strength, electronic transport, and thermal conductivity. We will discuss the properties of graphene and other monolayers in more detail in section 2.5. Based on these properties, promising graphene-based applications such as; flexible electronics, high frequency transistors, logic transistors, photo detectors, composites, paints, coatings, biosensors, gas sensors, drug delivery capsules, and energy storage devices, have been explored.

Since 2004, the development of simple processes for inexpensively producing high quality graphene, has contributed to its rapid evolution. The most common graphene synthesis methods today are chemical vapor deposition (CVD), mechanical exfoliation, molecular assembly, liquid-phase exfoliation, and shear mixing. As outlined by K. Novoselov et al. in
their latest graphene review article, applications for graphene, and other monolayers, are highly dependent on the amount, quality and cost of synthesis. As synthesis methods and manufacturing processes progress, more promising graphene applications are expected.
2.2 Boron Nitride Nanosheets

Analogous to graphene, boron nitride also forms hexagonal nanosheets (BNNS) with strong in-plane sp³ bonding. In contrast to semi-metallic graphene, BNNS are insulators with a bandgap of ~ 5.9 eV\textsuperscript{12} due to a slightly ionic nature. This electronic difference coupled with excellent chemical stability and graphene-like structure, has made BNNS an attractive and promising material for device substrates\textsuperscript{13}, nanoelectronics \textsuperscript{14}, composites \textsuperscript{15,16}, graphene hybrids\textsuperscript{17}, and thermally enhanced polymers\textsuperscript{18,19}.

In multi-layer forms both graphene and h-BN layers interact via weak van der Waals interactions making them highly susceptible to exfoliation. BNNS were first realized by mechanical exfoliation in 2008\textsuperscript{20}. Other methods such as chemical vapor deposition (CVD)\textsuperscript{21,22}, physical vapor deposition (PVD)\textsuperscript{23}, molten hydroxide exfoliation\textsuperscript{24}, plasma deposition\textsuperscript{25} chemical synthesis\textsuperscript{26,27}, nanotube unwrapping\textsuperscript{28} and liquid exfoliation have since been demonstrated as larger-scale production methods.
2.3 Silicene

Two-dimensional, hexagonal, silicon and germanium layers were first theorized by K. Takeda and K. Shiraishi from first principles in 1994\textsuperscript{29}. Here they showed that while carbon prefers a planar 2-d structure silicon and germanium prefer a buckled structure. Theoretical work by X. Yang\textsuperscript{30} and G. Guzman\textsuperscript{31} helped reveal the electronic structure of this buckled silicon monolayer, noting that it is a zero-gap semiconductor that shows linear $\pi$ and $\pi^*$ bands converging at the Fermi level (Figure 4). This indicates that charge carriers would behave as massless fermions (like in graphene); leading to potentially high carrier mobility which is promising for next generation nanoelectronics.

![Band structure of silicene](image)

**Figure 4.** Band structure of silicene from first principles as calculated in 2005\textsuperscript{30}

Later works, using more robust computational methods, confirmed the stability of Si and Ge buckled layers from phonon dispersion calculations and went on to describe other stable
group IV and III-V compound honeycomb monolayers such as SiC, GeC, SnC, SnSi, SnGe. Despite the positive theoretical evidence for silicene, it was not successfully synthesized until 2009.
2.3.1 Synthesis of Silicene

The experimental realization of silicene has proved difficult, especially when compared to graphene, and has led many to shy away from its potential. The reason for this difficulty is rooted in the fact that silicene is significantly less stable than its bulk counterpart (Si-diamond) and does not occur naturally in sp$^2$ layers like graphene. Only through careful deposition (and soft chemistry) techniques has silicene (and its compounds) been synthesized. Here we will review all reports of silicene, and silicene compound synthesis to verify the existence of silicene and to outline various techniques for producing it.

Soft Chemistry

The first silicene-like materials were produced by H. Nakano et al. by soft chemistry techniques. Here they prepared alkyl-modified silicene sheets$^{33}$, silioxene nanosheets$^{34}$, Mg-doped silicon sheets$^{35}$ and oxygen-free silicon sheets covered in organic groups (Figure 5)$^{36,37,38}$ but failed to isolate uncapped silicene layers. For these experimentally realized silicon-compounds, like the silicene-decylamine shown in Figure 5, it is unclear whether the attractive transport and semiconductor behavior is maintained in these modified structures. Therefore, further research is needed to explore the properties of these realized materials.
Figure 5. Model of oxygen-free silicon monolayers covered in decylamine groups.

Silicene Nanoribbons on Silver Substrates

The synthesis of uncapped-silicene was achieved recently through epitaxial growth on silver substrates in the form of nanoribbons and nanosheets. The first attempts at depositing thin layers of Si on Ag(100) at room temperature resulted in an amorphous layer by layer growth of silicon. Upon annealing at 230 °C, two ordered structures were observed, one with linked hexagonal ribbons (1.6 ML Si concentration - Figure 6a) and one with Si tetramer structures (1ML Si concentration- Figure 6b). Depositing Si on the Ag(110) surface at ultra-high vacuum (UHV) conditions yielded highly promising silicon nanowires that were self-aligned having a magic width of 16 Å (Figure 6c).
Figure 6. (a) STM image of linked silicon hexagon formation on Ag(100) surface \textsuperscript{45} (b) Si tetramer structures \textsuperscript{47} (c) and alligned silicon nanoribbon formation on Ag(110) surface \textsuperscript{46}

The aligned nanoribbon structures (Figure 6c) are likely strained due to the differing periodicity between silver and silicene. The resulting nanoribbons are hence asymmetric across their width and compressed by \(\sim 13\%\) along their length; as compared with theoretically predicted pristine silicene. This compression is made possible by an increased silicene buckle height. Two density functional theory (DFT) studies reveal possible nanoribbon geometries. The first study, by A. Kara et al., suggests that the experimentally obtained ribbons are 4-ZNR’s as shown in Figure 7a \textsuperscript{48}. More recent work, by C. Lian et al., proposes 8-ANR’s as an alternative structure (Figure 7b) and agrees better with experiment\textsuperscript{49}. 
Figure 7. Proposed structure of silicon nanoribbons experimentally grown on Ag(110) substrates by (A) A. Kara et al. (B) C. Lian et al.

Silicene Nanoribbons on Au(110)

Due to the similarities between Ag and Au crystal structure and lattice constants, other groups have demonstrated the growth of similar (1.6 nm wide) silicon nanoribbons on the Au(110) surface. However surface alloying has been shown to be highly likely and may require more investigation.
Silicene Nanosheets on Ag (111)

B. Lalmi et al. first reported the synthesis of silicene nanosheets in 2010. Here they evaporated silicon wafers through direct current heating and deposited the resulting silicon atoms on a sputter-cleaned Ag (111) substrate. This synthesis was performed under UHV conditions, at 250 °C, and with careful attention paid to applying the very minimum amount of silicon to create a monolayer. Since this paper was published, several other groups have succeeded in growing silicene on Ag(111) using similar techniques. STM images of their realized materials are collected in Figure 8. Other metallic substrate surfaces such as Ir(111) have successfully facilitated silicene sheet growth as well.

Figure 8. (a) STM image and (b) 3d STM image of silicene on Ag(111)
H. Jamgotchian et al. reported that the formation geometry of the silicon layer is highly dependent on the substrate temperature. Here they demonstrated the synthesis of three separate superstructures, and combinations therein, for Ag temperatures ranging from 150 to 300 °C. Further work by Feng et al. has confirmed this. The intrinsic geometry matching between the four nearest Ag-Ag neighbors (1.156 nm) and three unit cells of Si(111) (1.152 nm) explains the existence of several possible ordered phases. Theoretical results have shown that the low diffusion barrier (~0.16 eV) and the low nucleation barrier for Si on Ag(111) will lead to numerous grain boundaries if temperatures are not carefully controlled.

Further experimental and theoretical results supporting the existence of silicene are presented by P. Vogt et al. While most agree that silicene is formed, the exact timing of the experimental results leading to this conclusion is still widely debated. In more recent work by P. Vogt et al., multilayer silicene terraces are observed for the first time as shown in Figure 9.
This result is unexpected and contrary to many previous studies and thoughts suggesting silicene could not stack. The energetics and mechanisms behind this finding will be of high interest to this field going forward.

**Silicene on Zirconium Diboride**

In addition to epitaxial growth of silicene on silver substrates, A. Fleurence et al. found silicene to spontaneously segregate on a conductive ceramic buffer layer of ZrB$_2$ deposited on a silicon wafer$^{58}$. Here they showed that silicon atoms are arranged in a reconstructed $\sqrt{3} \times \sqrt{3}$ honeycomb structure as shown in Figure 10a.
Figure 10. (a) STM image of silicene layer on ZrB$_2$ buffer (b) DFT predicted model of experimentally realized structure

Not only is this structure (Figure 10b) closer to that of theoretically predicted freestanding silicene, it is also the only experimentally realized silicene structure shown to have a bandgap. This bandgap is thought to open due to the structurally induced strain caused by the diboride film. This work suggests that the degree of buckling is determined by the substrate geometry which, in-turn, controls the band gap. Due to the structural flexibility of silicene it may be possible to further control the electronic structure by choice of growth substrates.
Chemical Vapor Deposition

While isolated silicene has not yet been reported, free standing silicon nanosheets with a thickness $< 2$ nm, not as thin as silicene, have been synthesized by chemical vapor deposition\textsuperscript{59} (Figure 11) The characterization and determination of thickness of these layers has not been rigorously examined and would be of great interest to the silicene community.

Figure 11. (a) SEM image and (b) TEM image of silicon nanosheets after 30 minutes growth time on Si substrate\textsuperscript{59}

After reviewing all known reports of silicene and silicene-like synthesis we can summarize by saying: silicene honeycomb monolayers have been realized but not yet isolated from their substrates or capping layers. Since the primary metallic growth substrate (Ag, Au, and Ir) mask silicene’s electronic properties and deform it into various monolayer superstructures.
The exact interaction between silicene, Ag, and other growth substrates will be important going forward and has been the subject of some recent work. The isolation, or growth of silicene on an insulating material, would be a highly valuable contribution to this field. Hexagonal boron nitride and planar aluminum nitride have both been shown from first principles to be promising candidates as insulating growth substrates for silicene electronics.

As a practical alternative to new growth substrate and material transferring, discovering new ways to stabilize silicene through capping and/or adsorptions while retaining its desirable electronic and thermal properties would also prove highly valuable. Our research explores this possibility by looking at the stability and properties of silicene with and without adsorptions. A more detailed discussion and further background can be found in the results of chapter 4.
2.4 Germanene

Germanene, is the least explored of the group IV monolayers. It was first suggested alongside silicene in 1994 but its stability has been questioned by conflicting phonon dispersion results and it has yet to be synthesized. Multilayer germanane (a graphene analog) has been synthesized by topotactic deintercalation of $\beta$-CaGe2 in aqueous HCl and was shown to be thermodynamically stable and resistant to oxidation.

G. Le Lay, et al. has suggested that their attempts to grow germanene on Au(111) surfaces have yielded honeycomb-like patches or islands but their work has yet to be confirmed or published. Previous attempts to deposit Ge on Ag surfaces have revealed a competition between the Ge-Ge interaction leading to the formation of Ge tetramers on Ag adatoms (Figure 12) and the Ge-Ag interaction leadings to surface alloying.

![Figure 12. STM image of Ge tetramers after Ge deposition on Ag(001) surface](image)

67
The study of germane synthesis is still in its infancy but will undoubtedly become of more interest as silicene research progresses.
2.5 Comparing Properties of 2-D Monolayers

To better understand and design silicene based nanostructures it is logical to comparatively explore the properties of similar monolayer materials such as graphene, h-BN nanosheets, and germanene. This comparison provides immediate context for assessing a material’s application potential versus similar structures. The properties of graphene have been extensively explored both from theory and experiment. For this reason we will use graphene as a baseline to compare other 2-D monolayers properties.

2.5.1 Physical Structure

Graphene has a tight hexagonal planar structure with C-C bond lengths of 1.42 Å, whereas silicene and germanium both have buckled structures with bond lengths of 2.29 Å and 2.44 Å respectively (by our DFT calculations). Boron nitride, is iso-electronic with graphene and has a similar planar structure with B-N bond lengths of 1.44 Å.

Graphene is planar due to the strong, short, π bonds formed between p_z orbitals. As one moves down the periodic table, from C to Si and on to Ge, we see that the bond length increases and the π bonds weaken to the point where they cannot sustain planarity. Instead, silicene, and germanium buckle to form a more sp^3-like hybridization as shown in the top panel of Figure 13.
2.5.2 Electronic Structure

The electronic band structure of graphene was shown to be that of a zero-gap semiconductor with a conical energy spectrum near the dirac point (K). This leads to a linear dispersion relation $E = \hbar k v_f$ where charge carriers in graphene behave as massless relativistic particles with speeds ($v_f$) only 300 times smaller than the speed of light.

Although the lowest energy structures of silicene and germanene differ from graphene, they still show characteristic graphene-like electronic structure, i.e. zero-bandgap semiconductors with massless charge carriers at the K point. BNNS, in contrast, are insulators with a 5.9 eV bandgap. This significant difference is attributed to the slight ionic nature of the B-N interactions. Figure 13 compares the electronic band structures of graphene, silicene, germanene and hexagonal boron nitride nanosheet (BNNS).
Figure 13. Comparison of geometry and electronic band structure for graphene, silicene, germanene and hexagonal boron nitride nanosheets. The band structures shown are results of our calculations within SIESTA and show agreement with previous works.⁶⁸
2.5.3 Thermal Properties

Graphene, silicene, germanene and h-BN structures all show real phonon frequencies indicating thermal stability. While thermal conductivity values for these materials vary significantly from publication to publication, it is safe to say that the planar structures (i.e. graphene and boron nitride) are significantly more thermally conductive than their buckled counterparts (silicene and germanene). Quantitative evaluation of thermal conductivity values are collected in table 1.

2.5.4 Synthesis

In general, layered bulk materials such as graphite and hexagonal boron nitride (h-BN) can be mechanically separated by top down approaches into thinner layers whereas silicon and germanium cannot. This is due the natural existence of bulk layered sp² sheets in graphite, and h-BN. Due in part to this fundamental difference, these 2-d materials are all at very different stages of realization. For example, graphene is currently being produced in relatively large quantities and is making its way into commercial applications, silicene has been experimentally grown on silver substrates but not isolated, pristine germanene has yet to be synthesized, and boron nitride nanosheets have been synthesized by numerous methods similar to graphene. Of the mentioned 2-d nanomaterials discussed here (graphene, silicene, germanene, and BNNS) graphene is clearly at the most advanced stages of production and synthesis.
2.5.5 Property Summary

To compare measurable properties of these three monolayers a table has been constructed below describing the reported (experimental and/or theoretical) properties i.e. mechanical strength, and thermal conductivity for graphene, silicene, germanene and BNNSs.

Table 1. Comparison of available property data and references for graphene, silicene and germanene. Values without reference are from our calculations.

<table>
<thead>
<tr>
<th></th>
<th>Graphene</th>
<th>Silicene</th>
<th>Germanene</th>
<th>h-BN</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cohesive Energy</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(eV/atom)</td>
<td>9.885\textsuperscript{74}</td>
<td>4.57 -5.12\textsuperscript{75}</td>
<td>4.09</td>
<td>8.82\textsuperscript{76}</td>
</tr>
<tr>
<td><strong>Bulk Cohesive Energy</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(eV/atom)</td>
<td>7.37</td>
<td>5.42</td>
<td>3.85</td>
<td>8.82\textsuperscript{76}</td>
</tr>
<tr>
<td><strong>2d-Elastic Constant</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NM\textsuperscript{-1})</td>
<td>342.04\textsuperscript{77}</td>
<td>80.74\textsuperscript{77}</td>
<td>51.26\textsuperscript{77}</td>
<td>258\textsuperscript{74}</td>
</tr>
<tr>
<td><strong>Shear Modulus (NM\textsuperscript{-1})</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>135.01\textsuperscript{77}</td>
<td>28.64\textsuperscript{77}</td>
<td>18.76\textsuperscript{77}</td>
<td>123.95\textsuperscript{77}</td>
</tr>
<tr>
<td><strong>Thermal Cond. In plane (W/mK)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1500-5500\textsuperscript{70,71}</td>
<td>9 - 65\textsuperscript{72}</td>
<td>300-2000\textsuperscript{70}</td>
<td></td>
</tr>
</tbody>
</table>
Here we see that, in theory, silicene and germanene are significantly weaker than graphene and BNNS as indicated by the cohesive energy, 2d-elastic modulus, and shear modulus. Graphene and BNNS are also significantly more thermally conductive than silicene. Electronically the properties of graphene and silicene are very similar; i.e. both are zero-gap semiconductors with high carrier mobility potential. BNNS, in contrast, is an insulator with a band gap \( \sim 5.9 \text{ eV} \). Comparing properties in Table 1 helps illustrate the benefits, weaknesses and potential applications for these materials and possible hybrids.
3. METHODOLOGY

Computational Materials Science

Computational materials science allows us to rapidly design, predict and explore the properties of new materials, like silicene, and/or provide insight into experimental processes that may be difficult to otherwise obtain.

The fundamentals laws of nanoscale physics and chemistry are well described by quantum mechanics. However, the application of these laws to real-world systems (having large numbers of atoms) leads to mathematical complexities that are unsolvable by traditional methods. Today, raw computational power coupled with Nobel-prize-winning formalism, model simplifications, and accurate approximations enable us to predict the properties of complex systems with high accuracy. These calculations can be performed from first principles; i.e. without utilizing empirically obtained inputs. For our calculations just the atom species and approximate atomic positions are required as inputs. As computing power grows, so will our ability to describe complex systems of atoms.

Because the primary results of this work are based on first principles utilizing Density Functional Theory, Quantum Molecular Dynamics, and in-house quantum transport codes, let us begin by introducing the basic principles behind these powerful tools.
3.1 Density Functional Theory

Density functional theory (DFT) emerged out of necessity driven by the fact that solving the time independent Schrödinger equation (Eq. 1) for multi-body problems, larger than the hydrogen atom, requires a prohibitive number of spatial variables.

\[ \hat{H} \psi (r_e, r_n) = E \psi (r_e, r_n) \]  (1)

Density functional theory provides a way of reducing this problem to three spatial dependencies by introducing accurate simplifications and approximations which we will introduce in the following sections.

3.1.1 Born Oppenheimer Approximation

The Born-Oppenheimer approximation is based on the fact that nuclei are significantly more massive than electrons, resulting in a near-instantaneous response of the electrons to nuclear motion. Therefore, it is reasonable to treat the position of the nucleus as fixed while calculating electronic wavefunctions. This allows for the wavefunction of a molecule to be separated into nuclear and electronic coordinates

\[ \psi_{total} = \psi_{electronic} \psi_{nuclear}, \]  (2)

and eliminates the nuclear degrees of freedom in the Hamiltonian which is reduced to

\[ \hat{H} = T_e + V_{ne\ne} + V_{ee\ne}. \]  (3)
Here $T$ represents kinetic energy and $V$ represents potential energy with subscripts $e$ and $n$ indicating electron and nuclear interaction respectively. The Born-Oppenheimer approximation alone is not enough to obtain a solution to the Schrödinger equation for many-body systems. Further simplifications are required.

### 3.1.2 Hohenberg-Kohn Theorems

The foundation of DFT can be traced back to the two Hohenberg-Kohn theorems $^{73}$; of which the first demonstrates that the ground state electron density $\rho(r)$ uniquely determines the ground state wavefunction $\psi$ and total energy $E[\psi]$ of a system as

$$E[\psi] = E[\rho(r)] \quad (4)$$

The second shows that the electron density that minimizes the total energy is the electron density corresponding to the full solution of the Schrödinger equation. In other words, if we can solve for the ground state electron density; $\rho(r)$, we can determine the corresponding wavefunction; thus completely describing the system. Unlike the wavefunction, electron density is an observable and is defined as the number of electrons at a given position per unit volume. This effectively maps the wavefunction definition of a quantum state to an observable electron density.
3.1.3 Kohn-Sham Equations

To calculate the appropriate electron density the Kohn-Sham theorem \(^{74}\) is utilized; which demonstrates that the correct electron density can be found by solving the Kohn-Sham equation of the form:

\[
\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(r)\right) \varphi_i(r) = \varepsilon_i \varphi_i(r) \quad (5)
\]

for a set of non-interacting particles. Here, \(\hbar\) is the reduced Planck constant and \(m\) is particle mass. \(v_{\text{eff}}(r)\) is the Kohn-Sham potential given by:

\[
v_{\text{eff}}(r) = v_{\text{ion}}(r) + v_{H}(r) + v_{XC}(r), \quad (6)
\]

with \(v_{\text{ion}}(r)\) being the total electron-ion potential, \(v_{H}(r)\) a coulomb (or Hartree) potential of electrons, and \(v_{XC}(r)\) the exchange-correlation potential. In a sense, this theory creates a “Kohn-Sham” reference system of simple non-interacting particles within potential \(v_{\text{eff}}(r)\) in order to generate the actual (matching) electron density for interacting particles. This concept is illustrated in Figure 14.
Once $v_{eff}(r)$ is calculated the Kohn Sham orbitals ($\varphi_i$) are obtained from Eq. 5 with corresponding orbital energies ($\varepsilon_i$). From this orbital solution, the electron density is calculated as given by

$$\rho(r) = \sum_{i=1}^{N} f_i |\varphi_i(r)|^2$$  \hspace{1cm} (7)

where $f_i$ is the occupation of orbital $i$. $v_{eff}(r)$ and $\rho(r)$ are calculated self consistently until the electron density that minimizes the total energy as given by:

$$E[\rho(r)] = T_0\{\varphi_i(\rho)\} + V_H(\rho) + E_{XC}(\rho) + V(\rho)$$  \hspace{1cm} (8)

is found. Here $T_0\{\varphi_i(\rho)\}$ is the kinetic energy of non-interacting particles, $V_H(\rho)$ is the hartree energy, $E_{XC}(\rho)$ is the exchange-correlation energy, and $V(\rho)$ is the potential due to the fixed nuclei.
\( T_0\{\varphi_i(\rho)\} \) can be calculated as the sum of the kinetic energies of the non-interacting particles. The coulomb energy term \( V_H(\rho) \) can be calculated for interactions between the electrons assuming that the correct electron potential is known. This leaves us with one unknown: i.e. the exchange correlation term \( E_{XC}[\rho] \) which cannot be solved directly. Instead, high accuracy approximations have been developed as outlined in the next section.

### 3.1.4 Exchange Correlation

The exchange correlation term attempts to describe the electron-electron interaction and cannot be calculated exactly. Instead several high accuracy approximations have been developed. Two widely used functionals are the Localized Density Approximation (LDA); given by

\[
E_{XC}^{LDA}[\rho] = \int \epsilon_{xc}(\rho(r))\rho(\vec{r})d\vec{r} \tag{9}
\]

where \( \epsilon_{xc}(\rho(r)) \) is the exchange correlation energy for a single electron in a homogeneous electron gas of density \( \rho(\vec{r}) \), and the Generalized Gradient Approximation (GGA) given by

\[
E_{XC}^{GGA}[\rho] = \int \epsilon_{xc}(\rho, \nabla \rho)\rho(\vec{r})d\vec{r}, \tag{10}
\]

where, \( \epsilon_{xc}(\rho, \nabla \rho) \) is the exchange correlation energy as a function of density \( \rho \) and gradient \( \nabla \rho \). These functionals have proved to be extremely valuable to the field of
computational materials science and have been extensively explored for accuracy in thousands of different systems. Each approximation has its advantages and inherent inaccuracies. Careful consideration must be given to selecting this approximation based on the type of system being investigated.

Assuming that we can find a correlation functional that suits our needs, we now have all the tools to solve the set of Kohn-Sham equations. By iteratively solving these equations, a self-consistent solution can be found that in turn will minimize the energy of the energy functional thus leading to our desired ground state electron density. Each code has its own way of going about this. For example, the software package called SIESTA performs these calculations. A schematic showing the self-consistent approach to obtaining electron density within SIESTA is displayed in Figure 16.

![Figure 15](image.png)

**Figure 15.** Schematic showing the self-consistent approach to calculating the electron density within the SIESTA code.
3.1.5 Pseudopotentials

Pseudopotentials are used to further simplify calculations by eliminating the core electrons and replacing them with an effective potential. This can be visualized in Figure 16, where the real nuclear potential (dashed line) is replaced by a pseudopotential (solid line) including the effects of core electrons, and correspondingly the core electrons (dashed lines) are effectively replaced by a smooth curve (solid line). This simplification allows computational software such as SIESTA to only deal with the valence electrons that are crucial to the behavior of the material.

![Figure 16. All-electron wavefunction and potential (dashed) compared with the pseudopotential wavefunction and potential (solid) ](image)

76
3.2 Quantum Molecular Dynamics

Molecular dynamics simulations allow us to simulate thermodynamic phenomena for dynamical systems, i.e. system where properties are dependent on nuclear (and electron) motion. These simulation, unlike our electronic structure calculations in section 3.1, require time and temperature inputs.

Quantum MD has several benefits over classical molecular dynamics: i.e. it is more accurate and does not require the use of material or situation specific potentials. In our work classical MD is not a good choice because it does not properly account for chemical bond formation and breaking. The one drawback of this approach is that it is computationally intensive and is not suited for systems much larger than the periodic nanostructures that we consider (2-32 atoms per supercell).

Born Oppenheimer quantum molecular dynamics simulations optimize electronic structures for fixed ion positions at each time step, solve for energies quantum mechanically, and then calculate the forces on ions. An average temperature can be applied to the system utilizing the relationship between average kinetic energy and average particle velocity in the system. Like we discussed for DFT (see section 3.1.2), the Born-Oppenheimer approximation is utilized to decouple the electronic and nuclear motion. This decoupling allows us to treat electron interactions quantum mechanically and ion motion classically. These ion motions
can then be solved for by Newton’s equations of motion based on forces calculated quantum mechanically.

Within our molecular dynamics simulations there are several different ways to regulate the overall energy in the system (and thus average temperature). Here we use a Nose-Hoover Thermostat implemented within SIESTA code. The Nose-Hoover temperature coupling scheme attempts to add and remove energy from the simulation cell to approximate a canonical ensemble. It accomplishes this by adding a fictitious friction coefficient (\( \zeta \)) and effective mass term (\( Q \)) to the equations of motion describing the system. The resulting Hamiltonian of the nose-hoover coupled system is given by

\[
H = \sum \frac{|p_i|^2}{2m} + U(r^N) + \frac{\zeta^2 Q}{2} + 3Nk_BT\ln(s) \tag{11}
\]

Where the first two terms represent the physical system and the second two terms represent the thermostat coupling. Here \( p_i \) is the conjugate momentum, \( m \) the particle mass, \( r \) the position, \( N \) the number of particles, \( k_B \) the Boltzman constant, and additional Hoover coordinate \( s \). The equations of motion can then be defined using this “extended” Hamiltonian. This extended system will drive the microcononical ensemble used in molecular dynamics (where number of atoms, volume, and energy variables (NVE) are kept constant) towards a canonical ensemble in which temperature is controlled instead of energy.
3.3 Phonon Dispersion Calculations

To explore stability and vibrational properties of nanomaterials we explore phonon dispersion calculations. Phonons, are vibrations in the crystal, that propagate through solids in quantized modes; having characteristic frequencies $\omega(q)$ where $q$ is the wave-vector. In solids, atoms are connected by a series of bonds. This means that a displacement in a single atom will have a ripple effect in the surrounding lattice.

To show how this general concept is applied to a basic case, we consider a simple atomic chain model which can be solved analytically. Following along with chapter 22 of Ref. we model this atomic chain as a periodic series of masses that only interact with nearest neighbors and are connected by massless springs. An equation of motion can be easily written for such a system and will have a solution of the form:

$$u(na, t) \propto e^{i(kna-\omega t)} \quad (12)$$

Where $u(na, t)$ is the $n$th displacement from equilibrium with spacing $a$, $k$ is the wavenumber and $\omega$ is the frequency. Substitution into the equation of motion and accounting for boundary conditions yields:

$$-M \omega^2 e^{i(kna-\omega t)} = -2K (1 - \cos ka) e^{i(kna-\omega t)} \quad (13)$$

which can be arranged to give us a clear relation between frequency and wavenumber:
\[ \omega(k) = 2 \sqrt{\frac{K}{M}} \left| \sin \frac{1}{2}ka \right| \]  \hspace{1cm} (14)

where \( K \) is a spring constant and \( M \) is atomic mass. Plotting Eq. 13 with \( K = 1, M = 1 \), and \( a = 1 \), we obtain the dispersion relation as shown in Figure 17.

![Dispersion relation for a linear atomic chain with only nearest neighbor interactions and \( K = 1, M = 1 \), and \( a = 1 \)](image)

**Figure 17.** Dispersion relation for a linear atomic chain with only nearest neighbor interactions and \( K = 1, M = 1 \), and \( a = 1 \)

The group velocity \( v \) of wave propagation is then given by the slope of this dispersion relation and the phase velocity by \( c = \omega/k \). For treating 3-d systems with many more atoms and longer range interactions the complexity of the solutions change but the principles we
have discussed remain the same. Here we use the SIESTA code to calculate force constants and subsequent phonon dispersion relations for 2-d systems.

Phonon dispersion calculations were conducted utilizing large supercells (> 140 atoms). We calculated force constants by displacing individual atoms along three coordinate directions and compiling their effects on all other atoms in a force constant matrix. The phonon spectrum is then computed with a SIESTA utility (VIBRA) that takes the FC matrix and diagonalizes it to get phonon frequencies and corresponding eigenmodes. These eigenmodes are then plotted against wave vectors along high symmetry points in the brillouin zone; i.e. Γ, K, and M for hexagonal monolayers.

![Phonon dispersion of graphene](image)

**Figure 18.** Phonon dispersion of graphene
To establish the validity of this method and parameters, we first conducted benchmark tests for graphene and compared with previously published phonon dispersion results. The phonon dispersion plot for graphene obtained is shown in Figure 18 and agrees well with published results. The effects of mesh cutoff, force tolerance, kgrid cutoff, supercell size, force displacement, and unit cell positioning were tested to ensure phonon dispersion accuracy.
3.4 Quantum Electronic Transport

Quantum transport is calculated using the TARABORD code developed by A. A. Farajian et al. This code uses the nonequilibrium surface Green’s function to calculate conductance of finite systems connected to two semi-infinite contacts (Figure 19).

![Diagram](image)

**Figure 19.** Source, molecular contact, drain for quantum transport calculations

In short, this code calculates the conductance of the molecular junction as described by the Landauer formula,

\[
\mathcal{C}(E,V) = \frac{2e^2}{h} T(E,V),
\]

(15)

Where \( T(E,V) \) is the transmission probability which can be written as

\[
T(E,V) = Tr[I_D G_{TM} I_S G_{TM}^\dagger]
\]

(16)

with
Here, $\Sigma_{D,S}$ is the self-energy of the source and drain respectively, and $G_{TM}$ is the total Green’s function. By using the output of Gaussian 09 electronic structure calculations to obtain the Hamiltonian and overlap matrices the conductance and I-V characteristics can be calculated.

**Limitations**

It is important to note that all of the methods previously discussed are limited by the size of the system that can be considered due to finite computational resources. Larger systems require prohibitive amounts of computational time to achieve high accuracy. In certain instances, educated assumptions have been made to simplify the system and reduce computation time; and will be noted.
4. RESULTS

4.1 Silicene Stability

Previously, we explored the stability of isolated silicene sheets by geometry optimization\textsuperscript{82,83}, reporting that a low-buckled structure (Figure 20) was energetically favorable compared to a perfectly planar (sp\textsuperscript{2}-like) silicene sheet. This finding strengthened the case for the existence of low-buckled silicene while disputing previous claims that silicene was structurally analogous to graphene. Furthermore, this example demonstrated that geometry relaxations alone are not enough to prove the stability of a material.

In this work, we go beyond structural relaxations to devise a multifaceted computational approach for determining stability of nanomaterials via phonon dispersion relations and quantum molecular dynamics simulations.

\textbf{Figure 20.} Relaxed structure of low-buckled silicene sheet\textsuperscript{83}
Here we perform phonon dispersion calculations for planar and low-buckled silicene structures. Results of these calculations are displayed in Figure 21. The phonon dispersion plot for the planar structure (a) has bands at highly negative frequencies. These negative frequencies indicate imaginary phonon frequencies and crystal instability. In contrast, the low-buckled structure (b) has all positive frequencies indicating stability. These conclusions agree with previous work by S. Cahangirov et. al. 

![Phonon dispersion results](image)

**Figure 21.** Phonon dispersion results for (a) planar and (b) low-buckled silicene

To further verify the stability of low buckled silicene, quantum molecular dynamics simulations at temperatures of 300 and 1500 K are performed over a 3 ps duration. At both temperatures silicene retains its structure. The average Si-Si bond length over the duration of the simulation for temperatures of 300K and 1500K are shown in Figure 22. We see that the
average bond length does not deviate more than 4% (at 300 K) and 12 % (at 1500 K), from the equilibrium length of 2.29 Å. These results further demonstrate the stability of low-buckled silicene sheets at room and elevated temperatures.

**Figure 22.** Average Si-Si bond-length fluctuation over the duration of molecular dynamics simulation at 300 and 1500K

This comprehensive approach, (i.e. geometry optimization, phonon dispersion, and quantum molecular dynamic simulations) provides a convincing argument for the stability of silicene. Furthermore, this approach can be used to reliably predict the existence of other novel materials.

The stability of low-buckled silicene has been shown in the absence of environment and on growth substrates. However, it has proved difficult to synthesize and isolate in the lab. This
is mainly due to the fact that silicon prefers sp\(^3\) bonding and does not exist in nature as a layered sp\(^2\) bonded structure (like graphite).

To demonstrate this point we calculate the cohesive energy of a silicene sheet and compare it to bulk silicon (diamond structure). Our results show that the cohesive energy of bulk silicon is 0.812 eV/atom stronger than that of silicene. For comparison, the cohesive energy of carbon (diamond structure) is 1.03 eV/atom weaker than graphene. \(^{84}\) This is consistent with the fact that graphene exists in nature whereas silicene does not. Therefore, in order to realize the ideal properties of silicene, it will need to be carefully grown on a substrate (preferably insulating), or with a capping layer, to avoid the formation of bulk diamond crystals.

In silicene, atoms are only coordinated with three nearest neighbors. Here Si atoms weakly interact through pi bonds formed by the overlapping 3Pz orbitals. This interaction is significantly weaker than in graphene due to much larger atom-atom distances. Introducing certain foreign atoms or molecules to silicene is expected to break these weak pi bonds in favor of chemical adsorptions leading to sp\(^3\) hybridization and Si(111)-like geometry.

To preserve and tune the properties of silicene while stabilizing it away from a substrate we previously studied capping silicene with hydrogen \(^{82}\). This work was later expanded, generalized, and published \(^{83}\). While we had briefly explored lithium adsorption on silicene, as well, we recently discovered a new lowest energy structure, for 100% lithiation of silicene.
that has led to a valuable new investigation as published in our recent article \textsuperscript{85} and described in chapter 4.2.
4.2 Silicene Hydrogenation

4.2.1 Introduction

In our previous work we demonstrated that hydrogen collectively adsorbed in energetically favorable clusters that transform the electronic properties of silicene from a zero-gap semiconductor to a wide gap semiconductor. Following up on this research, using the same methodology as discussed in Ref., we recently revealed new lowest energy hydrogen adsorption configurations and detailed the fundamental mechanism behind these preferential adsorptions. We also calculated the band structure for each new configuration and published this work in Chemical Physics Letters. Our results show that partial hydrogenation, achievable through exposing silicene to hydrogen gas with various densities and/or masking techniques, can be used in engineering silicene's electronic structure and transport properties.

4.2.2 Results

Unlike pristine and fully hydrogenated silicene, partial hydrogenation can result in various isomers. Let us compare the adsorption energies of possible isomers for 25% hydrogenated silicene where, as depicted in Figure 23, two out of eight silicon atoms of the supercell form bonds with hydrogen. We call the three possible isomers ortho, para, and meta, by analogy with benzene and other aromatic hydrocarbons. In alternant π-conjugated systems including silicene, occupying a π-orbital of an atom from one subsystem creates an unpaired
electron in the other subsystem. As follows from the Longuet-Higgins rule \textsuperscript{86,87}, this unpaired electron is delocalized with the highest probability at the atoms next to the hydrogenated one (i.e., in the ortho position), and with second-highest probability at the atoms opposite to the hydrogenated one in the same 6-member ring (i.e., in the para position).

Correspondingly, as presented in Figure 23, we observe that after addition of the second H atom to silicene, the highest adsorption energy is seen in the ortho isomer, and the second-highest adsorption energy is seen in the para isomer. As for the Si atoms in the meta position with respect to the originally hydrogenated Si atom, they have the same parity \textsuperscript{86,87} (i.e., belong to the same subsystem) and thus have no unpaired electron. Hydrogenation of two Si atoms of the same parity creates a system with two unpaired electrons both in the other subsystem that, of course, is highly unstable. This is confirmed by the low adsorption energy of the meta isomer.

For the simplest case of 25\% hydrogenation of an 8 atom supercell the adsorption energy values are presented in Figure 23, for the three adsorption configurations where the hydrogenated silicon atoms are in ortho, para, or meta mutual positions within a hexagon. Notice that choosing any other pair of atoms results in equivalent adsorption configuration in the infinite silicene sheet, as is evident by changing the borders of the supercell.
It has previously been shown that ortho and para hydrogen adsorption pair geometries are energetically favorable for graphene. This is consistent with the fact that graphene is also an alternant π-conjugated system. As explained above, our results show that two hydrogen atoms on silicene exhibit the same preferential ortho/para behavior. For higher adsorption ratios, it was observed that isomers in which the number of hydrogenated Si atoms in one subsystem equals that in the other subsystem, were most stable. One can consider such hydrogenated clusters as composed of connected ortho and/or para hydrogenated Si pairs.
The geometries that resulted in meta configurations, i.e. those in which one subsystem has more hydrogenated Si atoms than the other, produced the least stable results. This preferred clustered hydrogenation pattern for silicene agrees with the predicted clustered hydrogenation pattern for graphene.\textsuperscript{89}

With a more complete understanding of the hydrogen adsorption energetics, we further explore the electronic changes induced by hydrogen adsorption on silicene. To this end, we investigated partial hydrogenation by calculating the band structures for 25, 50, and 75% hydrogenation ratios on a 32-atom supercell. The results for the lowest energy configurations for each ratio are depicted in Figure 24. For the particular case of 25% hydrogenation, according to our calculations, the energy of the arrangement of a hydrogenated patch at the middle of the supercell is 148 meV lower than that of "side hydrogenation" case, in which eight bordering atoms at a side of the supercell are hydrogenated. This can be explained by the fact that middle-patch hydrogenation has two hydrogenated Si atoms with fully hydrogenated neighbors. These two Si atoms, therefore, are in a bulk-like \( sp^3 \) arrangement with lowest energy (and least lattice distortion due to unhydrogenated neighbors).
Figure 24. The lowest energy configurations of silicene with 0%, 25%, 50%, 75%, and 100% hydrogenations and their corresponding band structures. The supercell contains 32 silicon atoms. Fermi energy is shifted to zero.  
\(^82\)
In Figure 24, the band structures reveal a small band gap for 25% hydrogenation and the absence of energy gap for 50 and 75% hydrogenations. It is interesting to note that the latter configurations correspond to continuous hydrogenated regions extending throughout the whole lattice, while the former corresponds to disconnected hydrogenated regions. The emergence of energy gap for disconnected hydrogenated regions and the metallic character of systems with continuous partial hydrogenation is similar to the corresponding cases for graphene, Refs. 90 and 91, respectively, where edge states at the interface of hydrogenated regions were found to be responsible for band structure modulations.
4.3 Silicene Lithiation

We explore the adsorption characteristics and stability of lithium on silicene from first principles. Our work shows that lithium adsorption could provide a unique method for isolating a stable silicene-based material while inducing a bandgap. We explore the energetics, temperature dependent dynamics, phonon frequencies, and electronic structure associated with lithium chemisorption on silicene. Our results predict the stability of completely lithiated silicene sheets (silicel) in which lithium atoms adsorb on the atom-down sites on both sides of the silicene sheet. Stability is confirmed by molecular dynamics simulations conducted at elevated temperatures and real phonon frequencies for all k-values. Upon complete lithiation, the band structure of silicene is transformed from a zero-gap semiconductor to a 0.368 eV bandgap semiconductor. This new, uniquely stable, two-atom-thick, semiconductor material could be of interest for nanoscale electronic devices. Detailed results are discussed below and published in the Journal of Physical Chemistry C. 

4.3.1 Introduction

Silicene, a promising new silicon analog of graphene, has recently been synthesized through epitaxial growth on silver substrates in the form of nanoribbons and nanosheets. Silicene has also been found to spontaneously segregate on a buffer layer of ZrB$_2$ on the Si (111) surface. While isolated silicene has not yet been reported, free standing silicon nanosheets with a thickness < 2 nm, not as thin as silicene, have been
synthesized by chemical vapor deposition\textsuperscript{59}. Recent work has described silicene's electronic and mechanical properties as well as its surprising resistance towards oxidation.\textsuperscript{92} A comprehensive review has been published by Kara et. al.\textsuperscript{93} This newly synthesized material has promising potential due to its unique electronic properties, and compatibility with the existing electronics industry.

Silicene, like graphene, is a zero-gap semiconductor\textsuperscript{31}. In order to realize its potential for most electronic applications, the generation of a band gap is a fundamental necessity. To this end, several groups have explored fully hydrogenated silicene, noting that the band structure is transformed from a zero-gap semiconductor to an insulator upon complete hydrogenation.\textsuperscript{83,94} We previously explored this transformation via partial hydrogenation and observed a metal-semiconductor-insulator transition where the band gap of fully hydrogenated silicene was predicted to be (~ 2.25 eV)\textsuperscript{83}. This value is too large for semiconductor electronic applications. Here we explore ways of creating a stable semiconducting material based on silicene.

To our knowledge, silicene monolayers have yet to be isolated from their growth substrates. Based on previous cohesive energy calculations\textsuperscript{95}, silicene has been shown to be less stable than bulk silicon and therefore unlikely to grow naturally like graphene. Current silicene growth methods use metal substrates, such as silver, which screen the electronic properties of silicene and are therefore not suitable for creating electronic devices. Alternate substrates and capping layers have been explored to create a more stable, isolated, material.\textsuperscript{62,96} Due to
the similarities between silicene and graphene it is important to note that lithium adsorption on graphene has already been explored\(^{97,98}\).

Here we will explore the nature of the interaction between lithium and the silicon analog of graphene; i.e. silicene. We assess the energetics and stability of partially and fully lithiated silicene via structure optimization and molecular dynamics (MD) simulations based on density functional theory (DFT). Subsequently, we explore the electronic and phononic characteristics of the stable lithiated silicene. The results show that, like hydrogenated silicene, lithiated silicene is more stable, relative to its bulk counterpart, than bare silicene. This could provide a method for producing freestanding (lithiated) silicene, with potential application as a uniquely stable, two-atom-thick, semiconductor.

4.3.2 Method

The energies, phonon frequencies, and temperature dependent dynamics of lithiated silicene were studied using DFT and MD simulations. Calculations were performed using the Siesta code\(^{99,75}\) utilizing both generalized-gradient approximations (GGA) with Perdew-Burke-Ernzerhof (PBE) and local density approximation (LDA) with Perdew-Zenger (PZ) exchange correlation functional for comparison. We chose the basis set; double-\(\zeta\) plus polarization orbitals (DZP) and norm-conserving pseudopotentials. Supercells including eight silicon atoms, with various levels of lithiation, and periodic boundary conditions, were used for all energy calculations. For electronic structure and phonon calculations, two atom
supercells were used. Phonon interactions were explored within an expanded 140-atom cell. The z-dimension of each cell was set to 20 Å to eliminate interlayer interactions. Structural relaxations were performed using conjugate gradient (CG) method in which the force tolerance was set to 0.005 eV/Å. Supercell dimensions were allowed to relax, and the \( k \)-grid cutoff corresponded with 120 Bohr. The mesh cutoff was set to 300 Ry. Total energy convergence was tested and achieved through the aforementioned setup. Spin polarization was included for energy calculations of single lithium and silicon atoms. Pristine silicene and lithiated silicene were found not to be spin polarized for the lithiation ratios considered. For verification, we checked spin-polarized vs. non-spin-polarized calculations for one lithium adsorption per supercell; both total energies and geometrical structures were essentially the same.

For \( \text{Li}_x\text{Si}_{(1-x)} \) surface adsorption compounds, Li-Si bond strength was assessed based on the adsorption energy of lithium atoms on both sides of the silicene surface. The adsorption energy, or binding energy, was calculated as follows:

\[
E_{\text{Adsorption}} = \frac{1}{N_{\text{Li}}} (E_{\text{Si}} + N_{\text{Li}} E_{\text{Li}} - E_{\text{Li}+\text{Si}})
\]  

(18)

While this energy value gives us insight into the average Li-Si bond energy, it does not necessarily describe the overall stability of the compound itself. To assess overall stability one needs to compare Gibbs free energies that are defined based on cohesive energies. The cohesive energy is calculated as follows:
\[ E_{\text{cohesive}} = \frac{E_{\text{Li+Sil}}-N_{\text{Li}}E_{\text{Li}}-N_{\text{Si}}E_{\text{Si}}}{N_{\text{Li}}+N_{\text{Si}}} \]  (19)

For Eq. 17 and 18, \( N_{\text{Li}} \) is the number of adsorbed lithium atoms, \( E_{\text{Si}} \) is the total energy of the bare silicon sheet, \( E_{\text{Li}} \) is the total energy of a single lithium atom, \( E_{\text{Li+Sil}} \) is the total energy of the lithiated silicon sheet, and \( E_{\text{Si}} \) is the total energy of a single silicon atom. To obtain the stability relative to Li and Si bulk counterparts we calculated the Gibbs free energy of formation as given by:

\[ \delta G = E_{\text{cohesive}}(x) - xu_{\text{Li}} - (1-x)u_{\text{Si}} \]  (20),

where \( u_{\text{Li}} = -1.589 \) eV/atom and \( u_{\text{Si}} = -5.426 \) eV/atom are the chemical potentials of bulk lithium and silicon, respectively, as calculated using the GGA result for the corresponding cohesive energies. These values differ from those of LDA calculations i.e. \( u_{\text{Li}} = -1.776 \) eV/Atom and \( u_{\text{Si}} = -6.123 \) eV/Atom. The experimental value for chemical potential of bulk silicon is -4.63 eV/Atom. Both GGA and LDA methods are known to over/under estimate cohesive energy, as consistent with other works. Overall, GGA shows better agreement with experiment than LDA and will be the primary focus of this work. However, it should be mentioned that the conclusions of this work are independent of the choice between LDA and GGA.
To further explore the stability of lithiated silicene, molecular dynamic simulations were performed at temperatures of 300 K, 900K, and 1500 K as controlled by a Nosé thermostat over a 3 ps duration. The MD time step was 1 fs. Average length oscillations for both Si-Si and Li-Si bonds were plotted for each temperature. Phonon frequency calculations were performed using both GGA-PBE and LDA-PZ methods. We present the results of the GGA-PBE phonon dispersion in this work.

4.3.3 Results

Adsorption Energy

The relaxed structures for Li$_x$Si$_{1-x}$ surface adsorption compounds corresponding to x values of 0.111, 0.2, 0.333, and 0.5 were determined. These structures are shown in Table 2 alongside the next lowest energy configurations considered.
Table 2. Geometry optimization and total energy results for different lithium adsorption configurations and ratios as calculated using GGA and LDA for comparison. Total energies of the most stable structures for each adsorption ratio are set to zero. $x$ is the lithium content in $\text{Li}_x\text{Si}_{(1-x)}$ surface adsorption compounds.

<table>
<thead>
<tr>
<th>LITHIUM ADSORPTION%</th>
<th>CONFIGURATION A</th>
<th>CONFIGURATION B</th>
<th>CONFIGURATION C</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5 % (1 Li)</td>
<td>0.000 eV</td>
<td>0.258 eV</td>
<td>0.176 eV</td>
</tr>
<tr>
<td>$x=0.11$</td>
<td></td>
<td>0.250 eV LDA</td>
<td>0.236 eV LDA</td>
</tr>
<tr>
<td>25 % (2 Li)</td>
<td>0.000 eV</td>
<td>0.029 eV</td>
<td>0.017 eV</td>
</tr>
<tr>
<td>$x=0.2$</td>
<td></td>
<td>0.130 eV LDA</td>
<td>0.236 eV LDA</td>
</tr>
<tr>
<td>50% (4 Li)</td>
<td>0.000 eV</td>
<td>1.035 eV</td>
<td></td>
</tr>
<tr>
<td>$x=0.33$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 % (8 Li)</td>
<td>0.000 eV</td>
<td>0.760 eV</td>
<td>0.322 eV</td>
</tr>
<tr>
<td>$x=0.5$</td>
<td></td>
<td>0.770 LDA</td>
<td>0.320 LDA</td>
</tr>
</tbody>
</table>

We considered four main possible adsorption sites for a single lithium atom adsorbed on silicene, i.e., hollow, bridge, atom up, and atom down. For a single lithium atom adsorbed on an 8-atom silicene supercell ($x=0.111$ in Table 2), the most energetically favorable position was found to be the hollow site with an adsorption energy of 2.210 eV/Li. The atom-down
relaxation revealed a local minimum while the bridge and atom-up structures relaxed to the hollow site.

For two lithium atoms (x=0.2), there are two lowest energy configurations (whose energies differ by 15 meV/atom); one containing lithium atoms above and below a single hollow site with adsorption energy of 2.318 eV/Li, and another with lithium atoms on alternate atom-down sites with adsorption energy of 2.333 eV/Li. Here we see the first signs of lithium atoms pulling the silicene sheet into a high buckled state.

For four lithium atoms (x=0.333), the lowest energy configuration is also a high buckled atom-down structure. The adsorption energy increases to 2.515 eV/Li. This adsorption ratio leads to a structural transformation from a buckled planar structure to the deformed structure shown in Table 2 for x=0.333.

The most energetically favorable configuration for the adsorption of eight lithium atoms (x=0.5) occurs when the atom-down sites are completely saturated. The optimized geometry and bond length data are presented in Figure 25. This configuration represents a completely lithiated sheet with adsorption energy of 2.394 eV/Li.
Based on the calculated adsorption energies for partial and complete lithiations ranging from 2.210 to 2.515 eV/Li, and the average Si-Li bond length of 2.639 Å, we see that lithium is strongly chemisorbed on the silicene in all cases. While the adsorption energy calculations in Figure 26 show the Li-silicene interaction strength, they do not adequately describe the overall stability of the compound. In particular, although adsorption energy for x=0.333 is the maximum, this lithiation ratio does not represent the most stable structure as we shall see shortly based in Gibbs free energy calculations.
Figure 26. The dependence of lithium adsorption energy on lithium content for the lowest energy adsorption configurations on silicene.

Stability

In order to assess the stability of partial and fully lithiated silicene sheets, we calculated the change in Gibbs free energy for each structure. These values are collected in Figure 27. It is observed that the difference between GGA and LDA results is small (13% maximum difference for pure silicene's \( \delta G \)). This difference does not affect the stability trend and other conclusions presented in this work.
Figure 27. Change in Gibbs free energy of $Li_xSi_{(1-x)}$ compound with increasing lithium content, obtained by employing GGA and LDA. Pure bulk Si and pure bulk Li cases are represented by $\delta G = 0$. For fully lithiated silicene, silicel, the difference between LDA and GGA Gibbs free energy changes turns out to be less than 1 meV/atom.

In Figure 27, $\delta G$ represents the energy of formation for each compound. A positive value indicates that the adsorption is endothermic and yields less stable structures. Figure 27 shows that as the lithium content increases, the structures approach the stability of bulk compounds of the same atomic ratio. The GGA (LDA) energy of formation of 0.004 (0.003) eV for $Li_{0.5}Si_{0.5}$ suggests that fully saturated silicene is essentially as stable as the bulk compound with the same lithium content.
These results also show the relative instability of silicene at lower lithium adsorption ratios (x = 0.111 – 0.333). At x=0.333, the Li-Si adsorption energy is greater as compared with the fully saturated (x=0.5) case. However, the structural transformation caused by this partial lithiation, effectively destabilizes the entire silicene sheet resulting in a less stable structure. Therefore fully lithiated silicene is the most stable Li-Si surface adsorption compound, with the same Gibbs free energy as that of the bulk with the same lithium content. For simplicity we will refer to this fully lithiated silicene sheet as silicel.

Comparing these energy results on lithium adsorption to those for hydrogen adsorption, we see that the energy of formation (Gibbs) is 0.004 eV/Atom for silicel, -0.154 for hydrogenated silicene, and 0.812 for pristine silicene. This indicates that both hydrogenated silicene and silicel are more stable, relative to their bulk counterparts, than pristine silicene and may provide a viable method for isolating a silicene based nanosheet. Previous work by Gao et. al. shows that halogen adsorptions may be even more stable than lithium or hydrogen. The benefit of silicel is that it is a small gap semiconductor.

It is worth commenting on the stability of lithium adsorption in the presence of oxygen. Our results show that lithium bonds with a hydroxyl (OH) with an energy of 3.252 eV/Li as compared to the Si-Li bond energy of 2.394 eV/Li. This indicates that the Li-O bond is stronger than the Si-Li bond which may lead to lithium desorption in oxygen environments. To confirm this, the dynamics of O₂ molecule adsorption on silicel would need to be fully explored, which is deferred for a future publication. For practical applications as a
semiconductor, therefore, silicel may need to be covered and isolated from oxygen in the environment.

**Structure of Silicel**

The relaxed atomic structure of fully lithiated silicene, termed silicel, is shown in Figure 25. The distortion in the lattice due to lithium adsorption is significant. The buckle height increases from 0.54 Å to 1.03 Å and the Si-Si bond-length changes from 2.29 Å to 2.42 Å. This structure differs from the hydrogenated case calculated in our previous work in which the Si-Si bond length is 2.359 Å, and the H-Si bond length is 1.519 Å, with a buckle height of 0.736 Å. Yang et. al. reported the same atom-down adsorption sites were preferred for lithium on graphene. For both silicene and graphene lithium adsorption prefers the atom down site whereas for hydrogen adsorption it prefers the atom-up sites.

**Molecular Dynamics**

To further investigate the stability of silicel, we have conducted MD simulations at 300 K, 900 K, and 1500 K over 3000 fs. Figure 28 shows the average Si-Si and Li-Si bond length variation over time at 300 K, 900 K, and 1500 K. Here we see stability at 300 K and 900 K. While the lithium does not dissociate from the sheet at 900 K we did notice that it undergoes a phase change in the simulation; changing from atom-up adsorptions to hollow site adsorptions. At 1500 K, we observe a dramatic increase in both the Si-Si and Li-Si average bond lengths. The simulation shows that at temperatures near 1500 K, silicel begins
to break apart both through lithium desorption and the destruction of Si-Si bonds. At high temperatures such as this, silicene is not recoverable. Here we also observe, through similar MD simulations (not presented here), that pristine silicene is stable at temperatures near 1500 K. G. Tritsaris et. al.\textsuperscript{104} explored lithium diffusion and cyclability on silicene in further detail concluding that silicene, in contrast to bulk silicon, does not experience detrimental structural changes during lithiation cycles.

\textbf{Figure 28.} Average Si-Si bond length (top) and average Li-Si bond length (bottom) plotted over 3000 fs duration.
Phonon Dispersion

As another method for assessing the overall stability of silicel we explored the phonon frequencies. In Figure 29 we show the phonon band structure of silicene in comparison with that of silicel. Both materials show stability based on the absence of imaginary phonon eigen-frequencies. The effect of adding lithium to silicene on the phonon structure is two-fold: The lithium adsorption introduces six additional modes and reduces the maximum frequency by nearly 100 cm\(^{-1}\).

![Figure 29. Phonon dispersion curves for silicene (left) and lithiated silicene (silicel) (right)](image-url)
Electronic Structure

Here we calculate the electronic band structure of pristine silicene and fully lithiated silicene. We see that upon complete lithiation, the band structure undergoes a transformation from a zero-gap semiconductor to a semiconductor with 0.368 eV band gap. Figure 30 shows the band structures of bare silicene and fully lithiated silicene. Unlike graphene that behaves as a metal upon lithiation, here we see that silicene becomes a semiconductor.

![Figure 30](image)

**Figure 30.** The band structure for pristine (left) and fully lithiated silicene (right) obtained by using GGA. The supercells contain two Si atoms. Fermi energy is set to zero.
It should also be mentioned that while graphene and silicene have a zero-gap and linear dispersion at the K point, silicel does not. Figure 31b shows this minor deviation from linearity upon lithiation of silicene; indicating lower carrier mobility in lithiated silicene.

**Figure 31.** Linear dispersion fit at the k-point for silicene (a) and deviation from linearity for silicel (b)

### 4.3.4 Summary

We demonstrated that Li-silicene compounds are energetically more stable than pristine silicene relative to their bulk counterparts, with fully lithiated silicene being the most stable of the compounds. The stability of the fully lithiated case was further verified by molecular dynamics at 300K and 900K and phonon frequency calculations. The band structure of silicene changes from a zero-gap semiconductor to a 0.368 eV bandgap semiconductor for complete lithium adsorption. Lithiation could provide a unique way of isolating silicene while inducing and tuning its band gap. Furthermore, our results suggest that the stability
and electronic properties of silicene are highly sensitive to atomic adsorptions. This property may lend silicene to applications as high resolution nanosensors.
4.4 Silicene Nanoribbons as High Resolution Gas Sensors

Applications based on silicene as grown on substrates are of high interest toward actual utilization of this unique material. Here we explore, from first principles, the nature of carbon monoxide adsorption on semiconducting silicene nanoribbons and the resulting quantum conduction modulation with and without silver contacts for sensing applications. We find that quantum conduction is detectibly modified by weak chemisorption of a single CO molecule on a pristine silicene nanoribbon. This modification can be attributed to the charge transfer from CO to the silicene nanoribbon and the deformation induced by the CO chemisorption. Moderate binding energies provide an optimal mix of high detectability and recoverability. With Ag contacts attached to a ~ 1 nm silicene nanoribbon, the interface states mask the conductance modulations caused by CO adsorption, emphasizing length effects for sensor applications. The effects of atmospheric gases: nitrogen, oxygen, carbon dioxide, and water, as well as CO adsorption density and edge-dangling bond defects, on sensor functionality are also investigated. Our results reveal pristine silicene nanoribbons as a promising new sensing material with single molecule resolution.

4.4.1 Introduction

Gases such as CO, O₂, H₂, NO, NO₂, and CO₂ need to be closely monitored to prevent air pollution, health hazards, and device contamination. To this end, it is important to create new low-dimension sensors with high sensitivity, selectivity and recoverability. The
emergence of high surface area nanomaterials has led to enhanced gas detection capabilities
at finer resolutions\textsuperscript{105}. Despite recent advances, reliably detecting, identifying, and releasing a
single gas molecule has remained an elusive task.

Notable progress has already been made towards realizing graphene-based CO
nanosensors\textsuperscript{106-107}. However, at low CO concentrations, pristine graphene nanoribbons have
been found to be electronically insensitive to CO adsorptions thus prohibiting detectable
conductance modulation\textsuperscript{108}. Likewise, pristine graphene nanosheets have been shown to
interact weakly with CO via physisorption with a binding energy of \(\sim 0.014\) eV \textsuperscript{106} and
negligible charge transfer. Some groups have noted that the experimentally realized sensing
ability of graphene\textsuperscript{107} must rely heavily on oxygen functionalization, substrate effects and
high defect concentrations\textsuperscript{109}. Further studies have explored doping and functionalization of
graphene to strengthen the CO-graphene interaction and enhance conduction modulation
\textsuperscript{110}. Based on these studies, we see that pristine graphene is not a suitable material for high
resolution sensing of CO by conductance modulation. This shortcoming has led us to
explore alternatives such as silicene.

Silicene, the silicon equivalent of graphene, has been shown to interact more strongly with
foreign molecules and atoms compared to graphene. Previous works have shown that
molecular and atomic adsorptions\textsuperscript{111,83,112} and doping\textsuperscript{113} can significantly modify the
electronic properties of silicene sheets. This stronger interaction (compared to graphene)
can be explained by the lack of a stable \(sp^2\) form of silicene; i.e. silicene prefers complete \(sp^3\)
hybridization which is made possible by various gas adsorptions. Upon molecular
adsorptions, we expect silicene’s buckled structure to allow for strong electronic modulation with moderate binding energies leading to high detectability and recoverability; making it a promising material for molecular sensing by conduction modulation. This application for silicene has yet to be explored.

Silicene-like nanoribbons have recently been synthesized by epitaxial growth on Ag(100)\(^{47,39}\) and Ag(110) substrates\(^{114,39,40}\). On Ag(110), it is believed that these synthesized nanoribbons have armchair edges and a width of 1.6 nm containing 8 silicon rows, hence specified as 8ASiNR\(^{49}\). To our knowledge free-standing silicene nanoribbons have yet to be isolated from their silver growth substrates. Therefore, applications based on silicene as grown on silver surfaces are of high interest. Here we propose that this silver growth substrate can be used to create the essential well-coupled metallic contacts, on either side of the silicene nanoribbon. These silicene nanoribbon sensors could be produced by removing silver from the growth substrate to create a trench, bridged by the nanoribbon. If realized, this would provide a consistent setup for experimental conductance measurement. In this study, we explore the possibility of using novel silicene nanoribbons with and without Ag contacts for building nanoscale sensors capable of detecting a single CO molecule.
4.4.2 Method

Structural optimizations are performed using the generalized gradient approximations (GGA) with the exchange–correlation parameterization of Perdew, Burke, and Ernzerhof (PBE)\textsuperscript{115} as implemented in Siesta package\textsuperscript{99,75}. All nanoribbon structures are relaxed utilizing normal conserving pseudopotentials, a double-\(\zeta\) linear combination of atomic orbitals (LCAO) basis, an energy mesh cutoff of 250 Ry, a \(k\)-grid corresponding to 80 Bohr, and maximum force tolerance of 0.02 eV/Å. Long, non-periodic, silicene nanoribbons are constructed from relaxed periodic unit cells containing 10 silicon atoms and then fully relaxed in an isolated cell with 20 Å of vacuum space in all directions.

Electronic structure calculations are carried out utilizing the Becke-Lee-Yang-Parr (BLYP) method\textsuperscript{116,117} with lanl2dz basis as implemented in Gaussian 09 program\textsuperscript{118}. Quantum conductance is calculated with our TARABORD code\textsuperscript{81} by Green's function method. This quantum transport code utilizes the (nonequilibrium) Green's function to calculate conductance of a finite system connected to two semi-infinite contacts. The code uses Gaussian electronic structure output, and has proved to provide reliable results in agreement with other benchmark studies\textsuperscript{108,81,119}. Within TARABORD, conductance is described by the Landauer formula:

\[
\mathcal{C}(E,V) = \frac{2e^2}{\hbar} T(E,V)
\]

(21)

where \(e\) and \(\hbar\) are the charge carrier energy and Planck's constant respectively and \(T(E,V)\) is the transmission probability written as
Here $G_{t,m}$ is the total Green’s function with

$$ T(E, \nu) = \text{Tr}[i \Gamma_{D,S} G_{t,m} G_{t,m}^+] , $$

and $\Sigma_{D,S}$ is the self-energy of the drain/source. By using Gaussian 09 electronic structure calculations to obtain the Hamiltonian and overlap matrices, the total Green's function (projected onto the junction region) is obtained and conductance is then calculated. By obtaining the conductance curve for each system, with and without CO, we are able to determine the conduction modulation effects of a single CO adsorption.

4.4.3 Results

CO Adsorption

We consider a silicene nanoribbon containing 5 silicon rows (5ASiNR) as our sensing material. The relaxed periodic geometry of this nanoribbon is shown in Figure 32 (a). Ribbons are edge-passivated with hydrogen while the surface is kept pristine. This is consistent with the fact that the edge is more reactive than the surface \cite{120} and that silicene lacks a complete sp$^3$ hybridization \cite{121,32,94}. Therefore, the silicene surface is less reactive than that of, e.g. bulk-like silicon structures. We first expose this nanoribbon to individual gas molecules (CO, N$_2$, O$_2$, CO$_2$, H$_2$O) and calculate the preferred adsorption configurations.
Figure 32. Relaxed geometry of pristine 5ASiNR (a), lowest energy structure for CO adsorption "CO-Edge" (b), and second lowest energy structure for CO adsorption "CO-Center" (c). Top and side views of monolayer ribbons considered in this study are shown in each panel.

For CO adsorption, the lowest energy structure is shown in Figure 32 (b). Here we see that CO prefers adsorption in a vertical C-down orientation on a silicon edge-atom (CO-Edge) with adsorption energy $E_{\text{ads}}=0.99$ eV/CO. The second lowest energy configuration, shown in Figure 32 (c), is a vertical C-down adsorption on an interior atom site (CO-Center) with adsorption energy $E_{\text{ads}}=0.63$ eV/CO. These C-down orientations are consistent with those previously reported for CO adsorptions on a bulk Si(100)-2×1 surface $^{122}$. It is important to note that the CO-Center relaxation results in bowl-like deformation in the nanoribbon whereas the CO-Edge adsorption has less of an effect on the underlying silicene structure.

After obtaining lowest energy adsorption configurations, we calculate the quantum conductance of 5ASiNR before and after adsorption of a single CO molecule. The
conduction curve for a pristine 5ASiNR is shown in Figure 33 (blue curve) and has a small band gap of 0.09 eV. Previous works have shown that unstrained silicene nanoribbons with a width index of $N=3p+2$, where $p$ is an integer, have non-zero bandgaps ($\sim 0.06$ eV for 8ASiNR)\textsuperscript{123}. This result supports our bandgap calculations. Upon adsorption of a single CO molecule (Center-CO or Edge-CO) the band gap is preserved and overall conductance is detectably reduced as demonstrated in Figure 33 and Figure 34 (red curves).

**Figure 33.** Quantum conductance of pristine silicene nanoribbon (blue), CO edge adsorption on nanoribbon (red), and deformed nanoribbon with CO removed (green). Middle of the gap is set at zero.
Figure 34. Quantum conductance of pristine silicene nanoribbon (blue), CO center adsorption on nanoribbon (red), and deformed nanoribbon with CO removed (green). Middle of the gap is set at zero.

To isolate modulation contributions due to nanoribbon deformation, we calculate conductance of a deformed nanoribbon after CO is artificially removed as depicted in Figure 33 and Figure 34 (green curves). For the CO-Edge case in Figure 33, we see significant reduction in conductance from CO adsorption (red curve), without contribution from the deformation (green curve). In contrast, for the CO-Center case in Figure 34, we see that deformation (green curve) plays a more significant role in reducing the overall conductance.
We next calculate the molecular charge transfer between the CO molecule and the 5ASiNR for both CO-Center and CO-Edge adsorptions. Results are collected in Table 3. In both cases, we see that substantial charge (0.406 |e| for CO-Edge and 0.418 |e| for CO-center) is donated from CO to the nanoribbon, which manifests itself as detectable conduction reduction through partial scattering of carrier wavefunctions in both systems. The stronger edge adsorption (CO-Edge) causes less nanoribbon deformation and modulates the conductance primarily by transferring charge to the nanoribbon, whereas the highly deformed center adsorption (CO-Center) modulates conduction with contributions from both deformation and charge transfer. The induced localized states cause scattering and conductance reduction. The more significant disruption of carrier transmission probability for CO-Edge compared to CO-Center, evidenced as lower conduction near Fermi energy in Figure 33 compared to Figure 34, indicates stronger modification of local density of states (LDOS) upon CO adsorption at the edge as compared to LDOS modification upon CO adsorption at the center.
Table 3. Adsorption energy and molecular charge of CO for adsorption at center and edge locations on 5AsiNR. Positive values of charge represent charge transferred from CO to the nanoribbon.

| Molecule Orientation | $E_{\text{ads}}$ (eV/molecule) | Charge ($|e|$) |
|----------------------|-------------------------------|--------------|
| CO-Edge              | 0.99                          | 0.406        |
| CO-Center            | 0.63                          | 0.418        |

Effects of CO Density and Edge Defects

Based on the conduction modulation as a result of one CO adsorption, we can expect more significant changes upon increasing the density of adsorbed molecules. To assess this possibility we double the CO adsorption concentration and calculate conductance modulation. The results are presented in the top panel of Figure 35. Comparing the conductance changes for one and two CO adsorption cases we notice enhanced sensing capability both above and below the gap upon increasing CO density.

The change in quantum conductance does not depend on the specific location of CO adsorption: The single CO adsorption can happen anywhere at the nanoribbon's edge and still result in the same conductance modulation. As for double CO adsorption, the results in
Figure 35 shows that conductance modulation is basically the same for the two possible adsorption cases namely adsorption on the same side (2 CO-A) or on opposite sides (2 CO-B). These indicate reproducibility of sensing results.

To explore the effects of “edge-dangling bond defects” we remove a hydrogen atom from the edge of the ribbon and calculate conductance with and without CO adsorption. The idea is to investigate sensing capability of the nanoribbons in presence of edge-dangling bond defects. It should be mentioned that surface-dangling bond defects, as observed e.g. in silicon nanowires, are much less probable than edge-dangling bond defects as explained in section 3.1. The results of our calculations on sensing by nanoribbons with edge-dangling bond defects are presented in the middle panel of Figure 35. Here we see that conduction is still detectably modified by CO adsorption in presence of a hydrogen passivation defect. In other words, the presence of possible edge-dangling bond defects does not hinder the sensing capability of the silicene nanoribbons.
Figure 35. Quantum conductance of pristine silicene nanoribbon (blue), with one CO adsorbed (green), two CO adsorbed on the same side (2 CO-A) (red), and two CO adsorbed on opposite sides (2CO-B) (grey). The conductance changes for the system having one edge-dangling bond defect with (orange) and without (purple) one CO adsorbed are also shown. Middle of the gap is set at zero.
Environmental Gas Adsorption

Because sensors are typically exposed to environmental gases such as N₂, O₂, CO₂, and H₂O we also consider the effects of these gases on silicene nanoribbon’s conductance. Our calculations show that N₂ interacts with silicene via physisorption with an energy of 0.42 eV/N₂ and is most energetically stable on the edge of the nanoribbon. This N₂ adsorption does not lead to significant deformation in the nanoribbon. Oxygen, on the other hand, interacts strongly with the pristine silicene nanoribbon with adsorption energy of 2.96 eV/O₂. Upon relaxation, the O₂ molecule splits apart in favor of individual Si-O bonds. This large adsorption energy seems to indicate that pristine silicene nanoribbons would easily oxidize at ambient conditions. However, Padova et al. have experimentally demonstrated that silicene nanoribbons (on a silver substrates) resist oxidation up to exposures of 1000 L. Undoubtedly, substrate effects and kinetics are of interest here and will need to be resolved if silicene nanosensors (and other devices) are to be realized for use in oxygen environments. This exploration is beyond the scope of this work.
Figure 36. Quantum conductance modulation resulting from environmental gas molecules adsorptions on nanoribbon: N₂ (blue), O₂ (red), CO₂ (green) and H₂O (purple). Middle of the gap is set at zero.
To explore environmental gas effects on the conductance of the nanoribbon, we calculate conductance before and after the adsorption of O₂ and N₂ molecules. The conduction curves depicted in the top panel of Figure 36 confirm the inert behavior of N₂ (blue curve) showing conductance nearly identical to that of the pristine nanoribbon. For oxygen, we see that conductance is significantly reduced (red curve) while the 0.09 eV band gap is preserved. These results indicate that although CO sensing capability of silicene nanoribbons may diminish in oxygen-containing atmosphere, the capability is preserved in nitrogen-containing atmosphere.

The effects of CO₂ and H₂O adsorption are also investigated. The conductance results are shown in the middle panel of Figure 36 and the structures are presented in the bottom panel of the same figure. For H₂O adsorption, the minimum energy configuration results from water splitting ¹²⁵ and subsequent attachment of H and OH at the edge (with a binding energy of 1.62 eV) while CO₂ adsorsbs via physisorption (with a binding energy of 0.46 eV). Similar to the case of oxygen adsorption, owing to the destructive effect on the nanoribbons structure, water molecules should also be removed from the environment for proper CO sensor functionality.

Interestingly, comparing carbon oxides sensing by graphene nanoribbons ¹⁰⁸ and by silicene nanoribbons, we notice that detection of CO is much more feasible in the presence of CO₂ for silicene nanoribbons as compared with graphene nanoribbons. This is because CO₂ physisorbs on both nanoribbon types whereas CO physisorbs on graphene nanoribbons but chemisorbs on silicene nanoribbons.
**Silver Contacts**

As previously mentioned, a silicene nanosensor needs to be connected to leads via contacts. Here we explore connection to the Ag(001) surface as a contact for the nanosensor. Because silicene has already been successfully grown on Ag(110) and Ag(001), this contact would likely be realizable experimentally. Here we model the top surface of a bulk silver contact with a single fixed layer of Ag(001). (Figure 37)

To explore potential CO adsorptions on the bulk Ag(100) contact itself, we use lowest energy geometry for CO adsorption on Ag(100) as calculated by Qin et al. 126 They report the most energetically favorable configuration to be a vertical C-down adsorption on top of a silver atom with a C-Ag distance of 3.44 Ang. Using this geometry, we calculate the conduction for a pristine Ag ribbon (contact) and an Ag ribbon with a single CO adsorption to obtain the conduction curves shown in Figure 37. Here we see that the overall conduction is only slightly reduced by the presence of a single CO molecule. This demonstrates that CO molecule adsorptions on the contact surface itself may slightly alter the conductance reading of the silicene nanoribbon sensor, however, the conductance change is much less significant than the one arising from CO adsorption on a silicene nanoribbon. This result is expected based on weaker physisorption interaction (0.19 eV/CO) 126 and smaller charge transfer (0.123 |e|) 126 from the CO to similar silver surfaces as reported by Qin et al.
Figure 37. Conductance of fixed contact based on surface Ag(100) layer without (blue) and with CO-adsorbed molecule (red). Fermi energy is set at zero.

Silicene on Silver Contacts

To combine the Ag-contact and the silicene nanoribbon, the Si-Ag interface is relaxed independently to fixed contacts at both ends and then rejoined to the pristine silicene junction region, as depicted in Figure 38 (red box). Initial geometries are taken from G. He et al. Upon relaxation, we see that the periodicity of the silicene nanoribbon is broken by the interaction with the Ag contact edge, i.e. a single boat-like link is formed within the red
box shown in Figure 38. To verify the existence of this boat-like link we re-relax the entire silicene ribbon while fixing the ends to the contact and find that it is indeed preserved.

**Figure 38.** Conductance of pristine silicene nanoribbon attached to Ag(100) contacts (blue), and silicene nanoribbon with CO-Center (red) and CO-Edge adsorption (green). Red box indicates interface that was relaxed on the fixed Ag-contact. Fermi energy is set at zero.
Next, we calculate the conductance for the silver contacted silicene nanoribbon. The conduction results show that over a small energy range (1 eV) near Fermi energy, conductance is modulated but not in a systematic or detectable way. The ribbon-plus-contact system is shown here to be metallic. We consider this as a manifestation of interface states penetrating the silicene bridge as a result of the close proximity of the two Ag contacts. This effectively masks the conductance modulation effects of the CO-nanoribbon interaction. By extending the length of the silicene nanoribbon the behavior will approach that of the pristine nanoribbon that we described earlier, for which detectable conductance modulation effects are expected upon CO adsorption.

Sensor recyclability needs further assessment from a computational standpoint. However, based on the relative stability of silicene (cohesive energy of 4.61 eV/atom) and the adsorption energy of CO on silicene (0.99 eV/CO) it can be estimated that CO would separate before silicene disintegration.

4.4.4 Summary

We have shown that a single carbon monoxide molecule detectably modulates the quantum conductance of silicene nanoribbons. The weak chemisorption of CO on the silicene nanoribbon would enable the silicene sensor to be recovered upon heating. We have also shown that individual environmental gas molecule adsorption events modulate the conduction of pristine silicene nanoribbons in a differentiable manner from CO; while N$_2$
and CO₂ essentially do not affect conductance, O₂ and H₂O can strongly chemisorb and
diminish silicene’s capability to detect CO. Proper functionality of such basic silicene
nanosensors may therefore require removing oxygen and water from silicene environment.
From another perspective, among the gas molecules that we considered (CO, CO₂, O₂, N₂,
H₂O), CO, O₂ and H₂O cause the most significant changes in conductance, and are therefore
predicted to be detectable. Effects of CO adsorption density and edge-dangling bond defects
are also investigated. Silver-contact-coupled sensors are considered and shown not to work
for short (~ 1 nm) silicene segments as they do not exhibit any systematic change in
conductance due to effects of silver contacts in close proximity. This highlights the
importance of using long-enough silicene nanoribbons in which interface states are confined
away from the functional CO-adsorption region. Overall, these results indicate that long
silicene nanoribbons could provide a unique nanosensor capable of single molecule
resolution.
4.5 Quantum Thermal Transport in Defected Silicene Nanoribbons

Having explored the electrical transport properties of silicene for sensing applications, we now turn our attention to thermal transport in similar nanoribbon systems. Here the thermal conductance of silicene nanoribbons with and without defects is explored by Non-Equilibrium Green’s function (NEGF) methods as implemented in our newly developed ThermTran code. We reveal that the thermal transmission and conductance of pristine silicene ribbons is systematically reduced upon the introduction of single hydrogen and silicon vacancy defects. This reduction is primarily driven by phonon scattering. The utility of our ThermTran program for calculating thermal transport across defected, contacted, or interfaced junctions is demonstrated and opens the possibility to explore the thermal transport properties of other realistically imperfect (or engineered) nanostructures.

![Graphical user interface of our newly developed ThermTran program](image)

**Figure 39.** Graphical user interface of our newly developed ThermTran program
4.5.1 Introduction

Understanding thermal transport in nanoscale materials and devices is crucial to the advancement of thermoelectric devices and miniaturization of electronic components. Pristine silicene ribbons have been shown to be a promising candidate for thermoelectric devices based on their low theoretical thermal transport and high theoretical electronic transport\textsuperscript{128,129}. The theoretical thermal conductivity for pristine silicene sheets was recently predicted to be 9.4 W/mK at 300K which is significantly smaller than that of bulk silicon\textsuperscript{72} and much smaller than that of graphene (4000-5500 W/mK\textsuperscript{71}).

Previous studies have explored thermal transport in pristine isolated nanoribbons by classical molecular dynamics\textsuperscript{130}. In general, classical molecular dynamics approaches do not account for important quantum effects and require careful matching of potentials for each system. While previous studies serve to predict the theoretical maximum for thermal transport in pristine silicene nanostructures, defected and/or contacted silicene nanoribbons have yet to be explored. This is especially important for narrow silicene ribbons, where defects are expected to significantly affect thermal conductance. Here, we have developed our own code based on Non-Equilibrium Green’s function (NEGF) and formalisms described by Z-X Xie et al.\textsuperscript{131}, J. Wang et al.\textsuperscript{132} and N. Mingo et. al.\textsuperscript{133} to calculate the ballistic thermal phonon transport of quasi-one-dimensional systems connected between two semi-infinite leads. This approach calculates force constants at a quantum (ab initio) level and is capable of treating nonperiodic structures (i.e. structures with defects, adsorptions, interfaces, or contact couplings). We focus on ballistic thermal transport with the assumption that the phonon
mean free path is much larger than any impurity or local scattering defect within the materials we explore; i.e. phonon-phonon and electron-phonon interactions can be ignored. This is indeed the case for graphene\textsuperscript{134}. Silicene has a smaller phonon mean free path than graphene\textsuperscript{129} and further exploration into other transport regimes may be of interest. Because the silicene ribbons considered here are small gap semiconductors, contributions to thermal transmission are primarily due to phonons. It has been previously shown that phonon transmission is dependent on chiral direction based on differing phonon path lengths for armchair and zigzag directions in silicene ribbons\textsuperscript{135}.

4.5.2 Method

We treat silicene nanoribbons as a junction connected by two semi-infinite leads as shown in Figure 40. Structures are prepared with all defects/adsorptions confined to the junction region and connected by perfectly periodic leads.
Figure 40. Schematic representation of the system setup for quantum thermal transport calculations (top) and an illustration of a realistic nanoribbon device setup (bottom).

Structural DFT relaxations are performed within the Gaussian 09 (G09) suite at a high level of accuracy due to force constant sensitivity to small structural differences. We used the hybrid functional B3LYP method and a 6-31G(d) basis with very fine convergence criteria and ultrafine grids for all relaxations. This combination achieves the best mix of accuracy and computational cost compared with others tested (i.e. blyp/3-21g).

After obtaining relaxed structures, force constants are calculated using the same method, basis, and level of accuracy within Gaussian. As with most commercially available DFT codes, force constants can be generated by moving a single atom and calculating the resultant forces on all other atoms. Here we have specially designed our ThermTran program to interface with Gaussian 09 outputs; utilizing force constant matrices and atomic weights as inputs.
The force constant matrix \( (k_{ij} \text{ the Hessian}) \) is the second derivative of energy with respect to position and is calculated in G09 as

\[
k_{ij} = \frac{\partial^2 E}{\partial u_i \partial u_j}. \tag{24}
\]

For the diagonal terms of this matrix we must ensure that Newton’s third law is satisfied by checking and enforcing the condition

\[
k_{ij} = \sum_{j \neq i} -k_{ij}. \tag{25}
\]

Following along with equation development from N. Mingo et. al.\textsuperscript{133} the dynamical equation can then be written as

\[
(\omega^2 M + K)\ddot{\mathbf{u}} = \mathbf{0} \tag{26}
\]

where \( \omega \) is the frequency, \( M \) is a matrix of atomic masses, \( K \) is the force constant matrix, and \( \ddot{\mathbf{u}} \) is the atomic displacements. In order to resolve the form of this equation for use with Green’s function formalism the elements of the force constant matrix are mass weighted by

\[
\hat{k}_{ij} = \frac{k_{ij}}{\sqrt{m_i m_j}} \tag{27}
\]

yielding a new dynamical equation of the form

\[
(\omega^2 I - \hat{K})\ddot{\mathbf{u}} = \mathbf{0}. \tag{28}
\]
It is important to note that the output Hessian values from Gaussian 09 have dimensions of 3N x 3N where N is the number of atoms in the system. The Gaussian 09 calculations are performed on a cluster resembling the central junction and coupling to the left and right contact unit cells. Beyond the contact unit cells, the cluster also includes redundant parts to avoid open end effects. The assumption is that with large-enough redundant parts the vibrational couplings represent those with semi-infinite contacts. The Hessian therefore includes a redundant left and right part and must be cropped to include only the contacts and junction region. This new matrix is called $K_{\text{Dynamic}}$ and is displayed in Figure 41.

$$K_{\text{dynamic}} = \begin{bmatrix} K^L & V^{LC} & V^{LR} \\ V^{CL} & K^C & V^{CR} \\ V^{RL} & V^{RC} & K^R \end{bmatrix}$$

**Figure 41.** Notation for defining the submatrices of $K_{\text{Dynamic}}$

Here $K^L$, $K^C$, $K^R$ are the sub matrices of the dynamical matrix representing force constants of the left contact, center junction, and right contact respectively. The V matrices represent the overlap between neighboring matrices/regions.
To calculate thermal transport we seek the phonon transmission probability across the junction region. The Green’s functions provide a way to calculate phonon eigenfunctions for a specific energy range depending on temperature. First, the retarded surface green’s function is iteratively determined by using the efficient Lopez-Sancho algorithm\textsuperscript{138} to solve
\begin{equation}
\begin{aligned}
g_{L,R}^r &= [(\omega + i\eta)^2 I - K_{L,R}]^{-1},
\end{aligned}
\end{equation}
where $\omega$ is the frequency, $\eta$ is an infinitesimally small positive value necessary for calculation in the complex frequency plane to avoid the singularities of the Green’s function along the real frequency axis, and $I$ is the identity matrix. The resulting matrix is then used to calculate the self-energies:
\begin{equation}
\Sigma_{L,R} = V_{CL}^R g_{L,R}^r V_{C}^{LRC}.
\end{equation}
Using these self-energies the central green’s function.
\begin{equation}
G_{C}^r(\omega) = [(\omega + i\eta)^2 I - K_{C} - \Sigma_{L}^r - \Sigma_{R}^r]^{-1}
\end{equation}
is calculated\textsuperscript{131,132}. We then find the coupling between the left, (right) and the center lead of the system by:
\begin{equation}
\Gamma_{L,R} = -2\text{Im}\Sigma_{L,R}.
\end{equation}
Combining these results we get the thermal transmission coefficient
\begin{equation}
T(\omega) = \text{Tr}[G_{LM} \Gamma_{L} G_{LM}^\dagger \Gamma_{R}],
\end{equation}
which is related to thermal conductance by phonons as

\[ C_{ph} = \frac{1}{2\pi} \int_0^\infty \hbar \omega \frac{\partial f(\omega)}{\partial T} T(\omega) d\omega. \] (34)

Where \( \hbar \) is Planck’s constant, \( \omega \) is the frequency, and \( f \) is the Bose-Einstein distribution.

Based on the output of our program we can then plot quantum phonon transmission versus frequency and compare thermal conductance as a function of temperature.

4.5.3 Validation

Simple Atomic Chain Model

To validate and troubleshoot our code we create a simple atomic chain force constant matrix in which only nearest neighbor atoms interact and only displacements in the X-direction are considered. This matrix is shown in Figure 42. For our toy model we include 6 atoms. The matrix rows and columns both represent atoms 1-6. A displacement in a row atom has a resultant force on its two nearest neighbor column atoms. For simplicity we take the spring constant between atoms to be unity.

\[
\begin{bmatrix}
2 & -1 & 0 & 0 & 0 & 0 \\
-1 & 2 & -1 & 0 & 0 & 0 \\
0 & -1 & 2 & -1 & 0 & 0 \\
0 & 0 & -1 & 2 & -1 & 0 \\
0 & 0 & 0 & -1 & 2 & -1 \\
0 & 0 & 0 & 0 & -1 & 2 \\
\end{bmatrix}
\]

**Figure 42.** Simplified atomic chain matrix to validate ThermTran output
This simple system can be solved explicitly and compared with the output of our program as displayed in Figure 43. Here we see the transmission is one unit for frequencies up to 2 cm\(^{-1}\) and zero thereafter. This is consistent with analytic result presented in section 3.3 and the validation work of Z. Nan\(^{139}\).

![Figure 43. Thermal transmission of simple atomic chain model](image)

Specifically, inserting \(K=1\) and \(M=1\) for nearest neighbor spring constant and particle mass respectively, in the dispersion relation obtained in section 3.3 for simple atomic chain model we see that there is one and only one band in the frequency region between 0 and 2 cm\(^{-1}\). The single band corresponds to one unit of phonon thermal conduction which is represented by transmission, \(T[\omega] = 1\), for frequencies between 0 and 2 cm\(^{-1}\).
Polyethylene

To validate our code with a real system, we use a polyethylene chain as relaxed using previously described G09 methods. The structure is shown in Figure 44 along with the thermal transmission results of our program. Compared to previously reported transmission plots for polyethylene\textsuperscript{140}, our program shows excellent agreement.

Figure 44. Structure of polyethylene chain used for ThermTran validation (top panel) and thermal transmission of Polyethylene chain (bottom panel)
The phonon transmission is directly proportional to the number of transport channels available in polyethylene. For periodic systems the transmission directly correlates with the number of bands in the phonon dispersion relation at a given frequency. Comparing our result with the phonon dispersion relation\textsuperscript{140}, we see 4 acoustic modes at low frequencies, several optical modes between 750 cm\textsuperscript{-1} and 1500 cm\textsuperscript{-1}, followed by a high frequency optical branch caused by the vibrational modes of the C-H bonds.

It is important to note that while our long chain of polyethylene is relaxed as a cluster (i.e. non-periodic) that there is a minor error at near-zero frequencies caused by the lack of strict translational and rotational invariance of the non-periodic relaxation. Here the transmission should be exactly four at zero frequency; representing the 4 acoustic branches corresponding to 3 translationally + 1 rotationally invariant modes of polyethylene. For small systems our program output deviates slightly. This problem has been solved by B. Mingo et al.\textsuperscript{141} through the implementation of a symmetrization routine. As an alternative approach, we have effectively minimized this error by using a large (18 unit) polyethylene cluster.

4.5.4 Results

Relaxed silicene nanoribbons with and without defects are displayed in Figure 45. The force constants extracted from the central parts of the relaxed systems are used to approximate force constants for the central junction attached to two semi-infinite pristine contacts. For the pristine ribbon, Si-Si bonds on the edge of the ribbon are 2.23 Å (with buckling height of 0.55 Å) as compared with 2.29 Å (0.53 Å) for interior bonds. This edge contraction for
narrow nanoribbons is expected to affect the electronic and thermal transport properties of the system. L. Pan et. al. \textsuperscript{128} have previously illustrated size effects on thermal conductance in silicene nanoribbons by tabulating thermal conductance changes (0.058 nW/K – 0.12 nW/k) for varying widths (7ASiNR-15ASiNR respectively). \textsuperscript{128}

![Figure 45](image)

**Figure 45.** Relaxed geometry of pristine silicene nanoribbon (top panel) with a single hydrogen atom removed (middle panel) and with a silicon edge atom removed (bottom panel). These are results of cluster relaxations using Gaussian 09 program.

Removing a single hydrogen atom from the edge of the ribbon, elongates the Si-Si bond (not parallel to the edge) from 2.29 Å to 2.31 Å. This elongation is accompanied by a localized reduction in buckling height almost to the point of planarity. Removing a single silicon atom
results in the formation of an edge pentagon (in place of a hexagon) and the creation of a boomerang-structure having an interior angle of 157° and a minor twist.

The cohesive energy is calculated for each system and values are collected in Table 4. The cohesive energy predictably drops as the severity of the defect increases. Here we see that the most stable structure is a pristine 5ASiNR (3.905 eV/Atom) followed by the ribbon with a single hydrogen defect (3.887 eV/Atom) and the least stable ribbon containing a silicon edge-defect (3.861 eV/Atom).

Table 4. Calculated cohesive energies for silicene nanoribbon systems with and without defects

<table>
<thead>
<tr>
<th>Cohesive Energy (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
</tr>
<tr>
<td>Hydrogen Defect</td>
</tr>
<tr>
<td>Silicon Defect</td>
</tr>
</tbody>
</table>

The thermal transmission for all three structures are displayed in Figure 46. Here we see that the thermal transport for the pristine ribbons is quantized. These integer values of transmission indicate that ballistic phonon transport can be directly correlated to the number of bands in the phonon dispersion relation. In contrast, the transmissions of the defected nanoribbons are not quantized and overall transmission is reduced by the presence of defects. Comparing the two defected cases we see that at low frequency (acoustic modes), the phonon transmission for the silicon defect case is less than that of the hydrogen defect case. At higher frequencies, however, the silicon defect case has similar transmission.
compared to the hydrogen defect case. This can be attributed to the fact that the Si-defect creates a severe long-range structural deformation (ribbon bending) whereas the H-defect only creates localized deformation.

![Graph showing thermal transmission for pristine silicene nanoribbon (blue curve), with single hydrogen defect (red curve), and single silicon vacancy edge defect (green curve).](image)

**Figure 46.** Thermal transmission for pristine silicene nanoribbon (blue curve), with single hydrogen defect (red curve), and single silicon vacancy edge defect (green curve). Note: High frequency contributions (~2200 cm⁻¹) due to hydrogen modes are not pictured here.

The thermal conduction is modulated (reduced) by atom edge defects. The thermal conductance at 298 K for pristine silicene is 0.059 nW/K and reduces to 0.042 nW/K for H-defect and 0.034 nW/K with a Si-defect present. This value for pristine silicene is in fair
agreement with values reported by L Pan et. al. using a non-equilibrium molecular dynamics approach. Compared to similar sized graphene nanoribbon conductance of 0.630 nW/K\textsuperscript{142}, silicene nanoribbons are an order of magnitude less thermally conductive. To explore the effects of temperature on thermal conductance of all three systems we calculate the thermal conductance at temperatures of 100, 200, 300, 400, and 500 K. Results are plotted in Figure 47. Here we see a larger temperature dependence (greater slope of conductance curve) for pristine silicene between 100 K and 200 K as compared to the defective case. This is due to the low frequency emphasis of the derivative of the Bose-Einstein distribution term in Eq. 34. In all cases we see conductance increases of $\sim$2.5\% between low (100K) and room temperatures (300K).
Figure 47. Conductance vs. Temperature for Pristine (top panel), hydrogen defected (middle panel), and silicon edge defected (bottom panel) silicene nanoribbons. The curves are not shifted along the conductance axis.

Recalling the results from section 4.4.3 we see that the 29% decrease is thermal conductance at room temperature for H-defected ribbons is accompanied by a very slight reduction in
electronic transmission. This reduction in thermal conductance for a small gap semiconductor suggests that accounting for defects may be of interest in assessing thermoelectric utility.

4.5.5 Summary

Silicene nanoribbon thermal transmission has been calculated utilizing our new NEGF-based thermal transport code. Defects in the junction region are shown to reduce the transmission and conductance (at 298 K). The utility of our code is demonstrated on this basic silicene system and is readily expandable to other nanosystems with and without defects, dopings or contact interfaces.
5. CONCLUSIONS

In conclusion, we have demonstrated the stability of silicene from first principles utilizing structural relaxations, phonon dispersion relations and molecular dynamics simulations. To engineer a band gap in silicene and perhaps stabilize it away from growth substrates, we have demonstrated stability and properties of hydrogen and lithium silicene compounds. Furthermore, we demonstrated the utility of silicene nanoribbons as a potential high resolution gas sensor material by conduction modulation. Thermal transmission of these nanoribbons was calculated by developing our own thermal transport code based on non-equilibrium Green’s function formalism. Here we see the effects of defects, almost inevitable during fabrication, on thermal conductance and demonstrated our generalized code for predicting thermal transport properties of defected or contacted nanostructures. We have revealed new silicene based semiconductor compounds, suggested potential sensing application for silicene nanoribbons, and applied a generalized approach for thermal transport in nanomaterials.
6. APPENDIX A

A.1 Publications


A.2 Presentations


2. Tim H. Osborn, Amir A. Farajian; Gas molecule adsorption on silicene nanoribbons: Conductance modulation and contact effects; American Physical Sociesty (APS), Dallas, TX, USA, 2011 March meeting; Abstract S1.00102
REFERENCES


111. Osborn, T. H. & Farajian, A. A. Stability of Lithiated Silicene from First Principles
    Tim H. Osborn*, Amir A. Farajian Department of Mechanical and Materials
    Engineering, Wright State University, Dayton, Ohio 45435, U.S.A. 1–16

112. Gao, N., Zheng, W. T. & Jiang, Q. Density functional theory calculations for two-
    61 (2012).

113. Zheng, F., Zhang, C., Yan, S. & Li, F. Novel electronic and magnetic properties in N
    or B doped silicene nanoribbons. J. Mater. Chem. C 1, 2735 (2013).

114. Enriquez, H., Vizzini, S., Kara, A., Lalmi, B. & Oughaddou, H. Silicene structures on

115. Perdew, J., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made

116. Becke, A. D. Density Functional exchange-energy approximation with the correct

117. Lee, C., Yang, W. & Parr, R. G. Development of the Colle-Salvetti correlation-energy

118. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R.
    Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M.
    Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L.


120. Dávila, M. E. et al. Comparative structural and electronic studies of hydrogen
    interaction with isolated versus ordered silicon nanoribbons grown on Ag(110).
    Nanotechnology 23, 385703 (2012).


122. Bacalzo, F. T., Musaev, D. G. & Lin, M. C. Theoretical Studies of CO Adsorption on
    Si ( 100 ) -2 × 1 Surface. 5647, 2221–2225 (1998).


