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Characterizing effects of defect induction on thermal transport and structural rippling under uniaxial strain of phosphorene through classical molecular dynamics computations

by

Oswaldo Sanchez

A thesis submitted to the graduate faculty in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE

Major: Mechanical Engineering

Program of Study Committee: Ganesh Balasubramanian, Co-Major Professor Sonal Padalkar, Co-Major Professor Liming Xiong

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2017

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ABSTRACT

This analysis includes a literature review analyzing the latest investigations performed on graphene analogous materials, as well as classical molecular dynamics (MD) simulations performed to evaluate defect engineered phosphorene. Extensive studies on thermal transport have been conducted for graphene, both experimental and computational. Recently, other 2D materials have gained popularity as they have been shown to exhibit qualities preferable over graphene. As such, there is an increased utility for conducting a comparatively extensive analysis into the properties of these potential alternatives for graphene. With that in mind, the focus here remains one such material, phosphorene. In particular, the thermal conductivity κ of phosphorene is investigated, with an emphasis on isotope substitution effects. Molecular dynamics (MD) simulations are applied to evaluate the effect of the isotope substitution on thermal transport in phosphorene.

Other desireable properties displayed by phosphorene include observable optical limiting behavior, optical property modification via strain-engineered rippling, and band gap tenability with applied axial strain. The two latter characteristics reveal that inducing strain reveals a notable property modifying behavior in the material that merits further investigations. As such, an investigation was conducted with a focus on property modification via strain application. Previous analysis on pristine phosphorene demonstrated that it exhibits superior structural flexibility in the armchair direction that results in rippling with applied strain. Here we are interested in modulation of this flexibility upon introduction of vacancy defects in the structure. A computational analysis utilizing molecular dynamics (MD) simulations was applied to investigate the effect of applying a uniaxial strain in the armchair and zigzag directions. The vacancies range from mono vacancies (single missing atom) to nano-pores (multiple missing neighboring atoms) of up to seven missing atoms.

CHAPTER 1. OVERVIEW

Modified from "Graphene analogous elemental van der Waals structures in Advances in Nanomaterials (ed. G. Balasubramanian) by Springer, 2017

1.1 Introduction

In recent years, graphene has become a pioneer for investigations involving single atomic layer structures. The idea of 2D materials is not new, since they have been theoretically analyzed for many years. Unfortunately, much of the information was limited to theoretical analysis simply because the creation of these structures had not been possible. The successful synthesis of single-layer graphite allowed the world of 2D materials to become a tangible reality and has paved the way for investigations of varying phenomena occurring in single-atomic layer materials. For many years, graphene was the focus of these investigations since a method of synthesizing other 2D materials was not yet available. In recent years, this has changed as graphene analogous materials have successfully been synthesized, as will be discussed later. The scope of this review focuses on the Group IV elements (C, Si, Ge, and Sn), with emphasis on the non-carbon members of this group.

1.2 Elemental Structure

Although the atomic arrangements of Group IV elements follow the hexagonal honeycomb structure of graphene, only the carbon-based material forms a perfect planar layer. The other elements construct buckled hexagonal structures, as seen in Figure 1². In Figure 1a it is possible to see the buckled structure arrangement, where some of the atoms in a unit cell demonstrate a planar separation. There are different possible lattice arrangements that appear from this buckling behavior. These structures are illustrated in Figure 1b, where the planar separation, or buckling distance, is designated by δ . From the image, the Flat structure demonstrates the planar structure found with graphene. For the boat and washboard structures, it has been found that they are unstable and will converge to the flat structure, while the chair structure demonstrates a greater stability than even that of the flat structure²⁴. Table 1.1 below contains the lattice and buckling parameters for select group IV elemental sheets.

Table 1.1: Structural and elemental structures. Electronic quantities for Group IV elements derived from hybrid exchange correlation functional HSE06 calculations with the inclusion of spin orbit coupling²⁴

| | С | Si | Ge | Sn |
|---|--------|--------|--------|---------------------|
| Lattice constant α (nm) | 0.2468 | 0.3868 | 0.4060 | 0.4673 |
| Bond length d (nm) | 0.1425 | 0.2233 | 0.2344 | 0.2698 |
| Buckling parameter δ (nm) | 0 | 0.045 | 0.069 | 0.085 |
| Effective electron mass $_{M}^{*}$ (m ₀) | 0 | 0.001 | 0.007 | 0.029 |
| Fermi velocity carriers V_F (10 ⁶ ms ⁻¹) | 1.01 | 0.65 | 0.62 | 0.55 |
| Energy gap $E_g \pmod{meV}$ | 0.02 | 1.9 | 33 | 101 |

1.3 Silicene

The discovery of graphene and the tremendous advancements in this field of research have fueled the effort of searching for similar two-dimensional materials composed of group-IV elements, especially with silicon, via theoretical and experimental approaches.

1.3.1 Synthesis

One of the most fundamental but also greatest challenges comes with finding the proper way of synthesizing these 2D materials. Silicene does not seem to exist in nature, nor is there a solid phase as there is with graphene⁴⁴. The synthesis of graphene has been possible via exfoliation of bulk graphite due to weak interlayer interactions²⁶. Unfortunately, this is not the case for silicon, and for this reason, exfoliation methods utilized in synthesizing single-layer graphite could not generate pure 2D silicon layers^{44, 26}. To get 2D silicon layers, researchers must consider the growth or synthesis of silicon with more sophisticated methods⁴⁴. Among the methods, the most widely spread one is to deposit silicon on metal surfaces which do not interact strongly with the Si atoms or form compounds⁴⁴. Many have successfully synthesized Silicene



Figure 1.1: Silicene on Ag (111) surface: Filled state ATM images of a) Ag (100) surface and b) silicene on Ag. c) Schematic overlay describing the observed STM images in (a) and (b) [Figure reproduced^{2, 44}].

on Ag (111) via epitaxial growth^{44, 17, 22}. This is particularly effective due to the interactions, or lack thereof, between Ag and Si. Davila⁵ describes that Ag and Si form atomically abrupt surfaces without intermixing. Figure 2 demonstrates a scanning tunneling microscopic (STM) images of a buckled silicene layer on Ag (111) as synthesized by Vogt et al⁴⁴. There has also been success in synthesizing buckled silicene on Ir (111)²⁶.

1.3.2 Structural Properties

The planar honeycomb structure in silicene has an imaginary frequency in Brillouin zone from the phonon mode analysis. During the structure optimization on a 2 X 2 supercell, there is a tendency to make a cluster in high-buckled structure. For all kinds of silicene structure, the variation of binding energy remains constant. The surface of silicene is very reactive because of its weak interatomic bonds¹⁵. This makes silicene readily absorb chemical species, which forms chemical bonds with silicene¹⁶. Because of the reason, modification is adopted for the surface of silicene with transition metals. For example, with the existence of Ti and Ta in puckered silicene, the material becomes planar structure while NbSi₂ shows the largest mechanical stiffness. For reducing reactiveness from the surface of silicene, doping is also used



Figure 1.2: Band structure of silicene and of Si (111) obtained from TB models^{8, 49}.

for alternative. The buckling in silicene is largely influenced by the carrier concentration 15 .

1.3.3 Electronic Properties

Similar to graphene, the π bands of silicene is not also connected to the bands because of its planar and orbital symmetries³⁸. As far as bands are concerned, the crossings between bands and bands , which occur in graphene, do not occur in silicene due to the lowered down valence bands in silicene⁸. The π band maintains the form as in graphene, however, when the π^* band approaches Γ from the K Γ and the M Γ directions, the band changes⁸. Compared to graphene, the electrons move slower in silicene. The longer atomic distance makes the weaker π bonds in silicene compared to its in graphene because bonds usually involve in the conduction property in each material. It can be shown from Figure 4; the property is symmetry at K point. The π bands are weaken at K. Electrons in around the K point should behave as Dirac massless fermions due to the presence of the Dirac cone in both structures. Compared to the fermi velocities of graphene (10⁶ m/s), fermion velocities in Si (111) (10⁴ m/s) and silicene (10⁵ m/s) is slower. This is because the π interaction is weak in Si(111) and silicene⁸.

1.3.4 Thermal Properties

From the previous studies, it is well-known that graphene has ultra-high thermal conductivities of 3000-5000 WmK^{-1 42}. Compared to it, the recent studies on silicene shows that the in-plane thermal conductivity of silicene at room temperature is in the range of 20-60 WmK⁻¹,



Figure 1.3: (a) The variation of binding energy as a function of lattice constant for PL, LB, and HB honeycomb silicene and germanene and (b) the band structures of PL and LB silicene and germanene⁴

which is almost the 20 percent of that of bulk silicon, as extrapolated from the linear relation in Figure 5⁴¹. Comparably low thermal conductivity enables silicene to be more suitable to the purpose of thermoelectric figure. The large reduction in thermal conductivity of silicene compared to bulk silicone could be attributed to the increased phonon-surface scattering in low-dimensional semiconducting nanostructures. From these findings with excellent electric transport properties, silicene is suitable for the thermoelectric material for power generators or refrigeration application.



Figure 1.4: The inverse of thermal conductivity, λ , versus the inverse of system size, L, for bulk silicon (²⁸Si) and silicene (²⁸Si). The thermal conductivity of infinite system can be obtained by linear extrapolating to $1/L = 0^{33}$



Figure 1.5: Normalized thermal conductivity (λ/λ_0) of silicene as a function of tensile strain $(L-L_0)/L_0$ in the X (armchair) and Y (zigzag) directions. The thermal conductivities increase at small strains and decrease at large strains³³

The thermal conductivity of silicene is largely affected by the strain. With further increasing strain, the thermal conductivity starts to decrease. To explain this concept, at tensile strain of 0.12, the thermal conductivity drops more than 30 percent compared to the strain-free value, as seen in Figure 6^{33} . For graphene, the thermal conductivity of graphene shows the state of decreasing all the way. However, the effect of strain in silicene shows small increase at the beginning phase 33 . This behavior of silicene could be attributed to the initial buckled configuration. The buckled configuration would be less buckled at small tensile strains, and this is because of bond rotation. As a result, we can get in-plane stiffness and an increase in the thermal conductivity in silicene³³. Furthermore, it is also known that defects influence on thermal conductivity from the studies in graphene. Among the defects, vacancy defects are quite unavoidable in 2D materials during growth and processing, and those defects are usually led by stress, irradiation, and sublimation²⁰. Vacancy defects are lattice sites that in a perfect crystal would be occupied, but instead remain vacant. They not only affect electronic properties significantly, but also cause lattice vibration localized around the defects. The localized vibration means that phonon thermal conduction will be reduced in both graphene, and silicene, but similar research is still rarely performed in the field of silicene 20 .

Increasing the concentration and size of the vacancy defects significantly reduces the phonon thermal conductivity of silicon nanosheets. In addition, not only the values of thermal conductivity, but also its anisotropy is influenced by the edge shape of vacancy clusters. This is considered important because of the chiral-angle tailoring of the thermal conductivity of silicene sheets²⁰. Meanwhile, Isotope doping provides an efficient method to tune the thermal conductivity of nanomaterials. To get a result, Isotope doping is simulated by MD simulations. According to the simulation, the thermal conductivity of graphene and silicon nanowires can be dramatically reduced even at a low doping percentage. Moreover, ultra-low thermal conductivity can be achieved if the dopants are arranged into a superlattice structure, as in Figure 8. Isotope doping has the advantage that it would not affect the electronic properties of the nanostructures since all the isotopic atoms have the same electronic structure. Researchers indicates that the bigger the mass difference between isotope atoms, the larger the reduction in thermal conductivity is counted for 10%



Figure 1.6: (a) The atomic configuration of silicene with random doping, where the two different colors represent different isotopes. (b) Thermal conductivity of randomly doped silicene as a function of the percentage of doped isotope atoms³³



Figure 1.7: (a) The atomic configuration of silicene with ordered doping (isotope superlattice), where the two different colors represent different isotopes. (b) Thermal conductivity of ordered doped silicene as a function of the percentage of doped isotope atoms³³

and 23% for Si and Si doping, each³³. In addition, the graph of this result shows somewhat Ushaped change as the thermal conductivity correlated with the concentration of doping atoms. The thermal conductivity decreases initially to a minimum and then increases as the doping concentration changes from 0% to $100\%^{33}$. The minimum of the thermal conductivity occurs at the doping concentration of around 50%. The randomly doped atoms can be considered as distributed impurities in the pure Si silicene lattice ³³. Those impurities cause the phonon scattering and localization of phonon modes, thus reducing the phonon group velocity. Therefore, the thermal conductivity decreases with increasing doping concentration. However, when the doping concentration is above 50%, the doped atoms become the main part of the lattice structure and the Si atoms become the impurities, as seen in Figure 7³³. As a result, the phonon scattering and phonon-modes localization reduce with increasing doping atoms. Consequently, the thermal conductivity increases with increasing doping concentration from 50% to 100%³³.

7

Moreover, ultra-low thermal conductivity can be achieved if the dopants are arranged into a superlattice structure. Isotope doping has the advantage that it would not affect the electronic properties of the nanostructures since all the isotopic atoms have the same electronic structure. In addition to possible application for power generator and refrigerator, silicene can be used as a molecule sensor. Silicene can chemically absorb Nitrogen-based molecules. NO₂ has the largest absorption energy of -1.12 and -1.53 eV per molecule for two absorption configurations, whereas the absorption energies of NO and NH₃ range from -0.46 to -0.60 eV per molecule¹¹. The charge carrier concentrations of silicene are larger than that on graphene. These findings indicate that silicene is a potential candidate for a molecule sensor with high sensitivity for NH₃, NO and NO₂.



Figure 1.8: STM images of germanene sheets grown by several research groups 21, 5, 3, 6, 15. For comparison, all the images have the same size of 4 nm x 4 nm. (A) STM image of germanene $\sqrt{19} \ge \sqrt{19}$ superstructure on Pt (111). (V = 1 V)and I = 0.05 nA)²¹, (B) STM image of the germanene $\sqrt{3} \ge \sqrt{3}$ superstructure on Au(111) (V = -1.12 V and I = 1.58 nA; the Au(111) $\sqrt{7} \ge \sqrt{7}$ unit cell is outlined in $black)^5$, (C) STM image of the germanene honeycomb layer on Ge_2Pt cluster (V = -0.5 V and I = 0.2 nA)³, and (D) STM image of the germanene 3 x 3 superstructure on Al(111) (V = -0.7 V and I = 0.3 $nA)^6$.

1.4 Germanene

One of the novel graphene analogous materials gaining attention is germanene. This material is often connected and compared to silicene when reported in the literature. However, published experimental work on the material is comparably less than its on silicene. This is to be expected, as much of the current electronics technologies involve either silicon, germanium, or a combination of the two. Because of this, silicene and germanene offer opportunities for easy integration to current technologies, as opposed to graphene which would require significant modification before it could be successfully implemented². This, in turn, brings great appeal to investigations on properties and behaviors of silicene and germanene.



Figure 1.9: Electronic band structure of germanene calculated using DFT for different values of the buckling Δ . Zero energy corresponds to the Fermi energy. Blue circles denote the antibonding band crossing the Fermi energy at low buckling values.

1.4.1 Synthesis

Germanene synthesis is even more novel than that of silicene. While Ag has been established as the common substrate for silicene synthesis, the use of Ag would not be plausible for germanene synthesis. At room temperature Ge reactions with Ag form an Ag₂Ge alloy ³². Because of this phenomenon, alternative substrates have been investigated and discovered. Davila et al.⁵ hypothesized that the answer would lie in finding a material that demonstrated a similar behavior with Ge, as that of Ag with Si (with no intermixing); the material that was found to fit these criteria is Au (111)⁵. Once Au was identified as a suitable substrate, the same process of dry epitaxial growth used for the silicene growth was implemented to grow germanene on the gold substrate. As Davila et al⁵ expected, the germanene growth was found to be comparable to the silicene formation on Ag substrates. Continuous germanene layers have also been successfully synthesized on Al (111)⁶ and Pt (111)^{21, 40}.

Unfortunately, the current synthesis methods do not cater to free standing germanene²⁷. Miro et. al.²⁷ mentions that germanane (GeH) does not need a substrate to be stable, however, as of now the synthesis of single-atom germanene is limited to a few substrates¹.

1.4.2 Structural Properties

Currently the structure stability, electronic and vibrational properties have been investigated via ab initio calculations^{25, 37}. As increased interatomic distance, the bonding between atoms in germanene is significantly weaker than its in graphene. This makes less energy distributions between the bonding and antibonding orbitals. It affects the structure of germanene. Because the band structure is deduced from planar germanene as can be seen from Figure 10, the low lying antibonding is staying around Γ -point. It results in a finite density of state at the Fermi level. It is not preferable for its energy, so that achieving a buckled structure by expanding buckling (the vertical separation between two sub-lattices) of the low point group is highly recommended. The vertical distance between two sub-lattices are decided by a balance between the electronic and elastic energies. For free standing germanene, the buckling is ranged from 0.64 to 0.74 Å, and even the value becomes bigger than 2 Åat the total energy landscape. This structural property can be altered by interactions with other substrates. Like graphene, there is also the opening of a band gap induced by the symmetry in sub-lattice of supported germanene¹. Matusalem et. al.²⁵ found that a lower stability is obtained when in the graphene like arrangement, and it becomes more stable in the honeycomb dumbbell arrangement. Acun et.al¹ reported DFT calculations on the buckled honeycomb structure of germanene and found it to be a 2D Dirac fermion system (this has yet to be validated by experiment). This leads to the hypotheses that the quantum spin Hall effect would be present at accessible temperatures ¹. This poses graphene as a promising 2D topological insulator¹⁸.

1.4.3 Electronic Properties

Germanene possesses a semi-metallic band alignment and is predicted to possess similar electronic properties as silicene, including massless Dirac fermions^{10, 19}.

1.4.4 Thermal Properties

Currently there are no available literatures focusing solely on thermal conductivities. This can be expected, as the main use of germanium, and silicon, applications involve thermoelectric properties. These studies are not normally found with graphene because the high thermal conductivity implies poor thermoelectric properties. Yang et. al.⁴⁷ reports on thermal conductance when investigating the thermoelectric figure of merit, however, since the values are evaluated implementing ab initio the system size is very limited. Molecular dynamics simulations would allow for an evaluation of thermal conductivity for larger system sizes.

Unfortunately, there are not currently molecular dynamics studies investigating thermal conductivities or the effects of defects on the thermal properties. Of course, these results require validation by experiment, however, as mentioned previously, current synthesis methods do not cater to free standing germanene so such investigations are unavailable.

1.5 Stanene

Another Group IV graphene analogous material gaining popularity is stanene. An appealing characteristic of stanene stems from the fact that bulk tin is metallic, so there is an interest in exploiting those favorable electronic properties⁴². One of the appealing characteristics at this time is the potential for stanene to be established as a topological insulator^{41, 46}. Essentially, this means good electrical conduction with minimal energy loss due to waste heat. This opens the potential for implementation of this material in electrical circuits.

1.5.1 Synthesis

The novelest synthesis discussed in this paper is that of monolayer tin. Unlike silicene and germanene, there are very few reports of successful synthesis of stanene. While the synthesis of 2D stanene has presented a challenge, there is a report of atomically thick free-standing fewlayer stanene (FLS) that are characterized optically with UV-Vis absorption³⁹. Also, Zhu et. al.⁵⁰ present successful fabrication of stanene with molecular beam epitaxy (MBE) on Bi_2Te_3 (111). This success opens the possibility of experimentally investigating, and validating the current theoretical and computational models that have been developed for stanene.

Due to the novelty of stanene, the available data is limited when it comes to experimental information. Since stanene synthesis is still an area of open investigations, the availability of samples to perform experiments is essentially non-existent. Due to this, much of the available information has resulted from theoretical or computational analysis. Even then, since the focus has been mainly on silicene, and to a lesser extent, germanene, the material available involving stanene is sparse at the moment. There are reports available involving first principle, density functional theory, and Boltzmann transport equation calculations to analyze the thermal and mechanical properties of stanene^{31, 34}. There are even some who are expanding into investigating the tuning of material properties of stanene. Garg et al⁷ performed DFT calculations to investigate the band gap opening in stanene by patterned B-N doping and then implemented MD simulations to confirm the stability of the structure.

1.5.2 Structural Properties

van den Broek et. al.⁴² presented first-principle DFT calculations to investigate the structural, mechanical, and electrical properties of 2D hexagonal tin. First principle molecular dynamics calculations determined the monolayer to be thermally stable at temperatures up to 700K. Mojumder et al implemented MD simulations with the embedded atom model to analyze mechanical properties of stanene. The resulting investigation showed that increased temperature causes a reduction in the fracture strength and strain on stanene. It was also notable that uniaxial loading in the zigzag direction presented a higher fracture strength and strain than that of armchair direction loading, while no noticeable difference was found for biaxial loading ²⁹.

1.5.3 Electronic Properties

Stanene and germanene are very similar and are often compared to silicene together. As was the case for germanene, stanene has a slightly metallic band alignment and is also predicted to possess electronic properties like those found in silicene^{10, 19}.

1.5.4 Thermal Properties

Another area of interest in these 2D materials involves the thermal properties. If there is any hope of establishing stanene as a legitimate option for real applications, the thermal properties must be investigated. While information is limited, there have been some significant studies published on the matter. Peng et. al.³⁴ presented an analysis of phonon transport in stanene via first principles calculations and phonon Boltzmann transport equations to evaluate the materials thermal conductivity. In fact, this analysis coincides with the results obtained by Nissimagoudar et. al.³¹ and establishes stanene as the material with the lowest thermal conductivity amongst all of the group-IV materials. The latter report also mentions the potential for thermal conductivity to be tuned by adjusting the sample size and applying rough surfaces on the edges.

At this time, the analysis on thermal conductivity remains limited to pure stanene. Currently, there appears to be a lack of information on the effects of defects on thermal conductivity. Also, there are currently no molecular dynamics simulations available that model the thermal conductivity in this material. This can be attributed to the fact that there has not been a parameterization of suitable potentials for MD simulations.

1.6 Phosphorene

1.6.1 Configuration

Single-layer phosphorene forms a puckered honeycomb lattice and is composed of two atomic layers of P atoms. It varies from graphene in the fact that it exhibits armchair and zigzag configurations in the x and y directions, respectively. The sp^3 hybridized P atoms dominate the intralayer bonding. It has been proposed that PBE-G06 and optB86b-vdW provide the best description for the phosphorene structure⁵⁰. The semi-empirical potential (DFT-D) based PBE-G06, and nonlocal correlation functional (vdW-DF) based optB86b-vdW, both describe weak interactions between phosphorene layers²⁸. The DFT-D semi-empirical treatment of dispersion interactions makes it less expensive than vdW-DF. However, this is counterbalanced by the fact that optB86b-vdW generally less significant errors than other functionals when applied to geometry optimization and is adaptable to more varied applications².

1.6.2 Structural Properties

Phosphorene exhibits interesting properties, which can be attributed to its distinctive structural properties. The Youngs modulus of phosphorene has been shown to be anisotropic via DFT-PBE computations³³. In particular, the in-plane Youngs modulus in the x and y directions were found to be 44 and 166 GPa, respectively; this revealed the puckered x direction to be more pliable. Wei et al. implemented first principles DFT computations to demonstrate a potential endurance of 30 and 27% tensile strain in the x and y directions, respectively, for monolayer phosphorene²¹. Interestingly, phosphorene demonstrates a negative Poissons ratio due to its puckered structure, which separates it from other 2D materials²⁴. Jiang et al.¹⁴, via *ab initio* calculations, demonstrated that the puckered structure introduces negative Poissons ratio in the out-of-plane direction when deformed in the y direction. This increase in thickness in the direction perpendicular to the stretching direction reveals phosphorene as a potential 2D auxetic material. Due to previous experimental agreement of DFT-D on pressure coefficient and elastic constants for bulk black phosphorus⁴⁴, utilizing DFT to predict mechanical properties of phosphorene is also viable.

1.6.3 Electronic Properties

As a relatively novel material, it is of interest to see if phosphorene offers any unseen electronic properties. In order to make this analysis, there have been a number of theoretical investigations to understand the electronic properties of phosphorene. The GW method has been established as more accurate than DFT in determining the bandgap of semiconductors, since DFT is known to underestimate the bandgap values. Based on the Greens function (G) and screened Coulomb interactions (W) the GW method allows accurate description of the ground and excited states, while DFT is limited to only the ground state. G_0W_0 is particularly effective in computing bandgap of semiconductors and insulators composed of light elements ⁵. The G_0W_0 is based on the local-density approximation (LDA) and generalized gradient approximation (GGA) single particle Hamiltonian H0. Tran et al. used the G_0W_0 method resulting in a band cap prediction of ~2.0 eV³. This band gap value was also reported by Liang et al. implementing scanning tunneling microscopy (STM)^{3, 6}. Hence, the GW method is shown to be very effective in accurate descriptions of band structure. Unfortunately, it is also highly computationally expensive, which limits the potential applications of this method.

In an effort to find a middle ground between the underestimation of pure DFT and the high computer cost of the GW method, a hybrid DFT has been adopted. For determination of bandgap in semiconductors, the currently preferred method is the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional based on the PBEh hybrid functional. The HSE exchange-correlation energy is expressed below¹⁵:

$$E_{XC}^{HSE} = aE_x^{HF,SR}(\omega) + (1-a)E_x^{\omega PBE,SR}(\omega) + E_x^{\omega PBE,LR} + E_c^{PBE}$$
(1.1)

Where $E_x^{HF,SR}$ is the short range Hartree Fock (HF) exchange, $E_x^{\omega PBE,SR}$ and $E_x^{\omega PBE,LR}$ are the short and long range components of the PBE exchange functional, ω is the splitting parameter, and is the HF mixing constant. Adjusting the value of ω allows for reasonable bandgap calculations. For the HSE06 functional, ω is often set to 0.2. Utilizing the HSE06 functional provided a value of ~1.5 eV^{50, 26} for the bandgap, which is still lower than the values obtained experimentally and with the GW method.

Despite underestimating the bandgap, pure DFT and hybrid DFT offer the same physical picture as the GW method. Similar to the GW method, both PBE (DFT) and HSE06 (hybrid DFT) computations show phosphorene is semiconducting with a quasi-direct bandgap, with the conduction band minimum (CBM) at the Γ point and the valence band maximum (VBM) located near the Γ point^{50, 17}. Despite the VBM location, phosphorene can still be considered a direct band gap semiconductor since the energy difference between the Γ and the VBM is less than 10 meV.

From band diagrams it is possible to see conduction and valence bands in the textity direction are more flat than in the x direction, which shows a highly asymmetric band structure that contributes to anisotropic excitons and effective mass in different directions^{22, 16}. HSE06 computations show effective mass in x direction is .15 m₀ for holes and .17 m₀ for electrons, while in the y direction the effective mass is 6.35 m₀ for holes and 1.12 m₀ for electrons ⁵⁰. Anisotropic effective masses for electrons and holes indicate the possibility of anisotropic carrier mobility in the x and y directions, which is another important factor for semiconductors in device applications.

To evaluate carrier mobility of semiconductors computationally, Barden and Shockleys deformation potential (DP) can be utilized³⁸. According to DP, energies of CBM and VBM have a linear relation with the lattice dilation or compression. Carrier mobility for 2D materials is given by the following expression⁵⁰:

$$\mu = \frac{(2e\hbar^3 C)}{3k_B T |m^*|^2 E_1^2} \tag{1.2}$$

Where \hbar is Plancks constant, k_B is the Boltzmann constant, T is temperature, m^* is effective mass, E_1 is the DP constant, and C is in plane stiffness of the 2D material.

Using HSE06, Qiao et al. found x direction electron mobility to be about 1100-1140 cm²/Vs, almost 14 times greater than in the y direction ($\sim 80 \text{ cm}^2/\text{Vs}$)⁵⁰. However, x direction hole mobility (640-700 cm²/Vs) is 16-38 times lower than y direction values of 10,000-26,000 cm²/Vs. This shows high mobility transport anisotropy in phosphorene. For comparison, MoS₂ only reports a value of $\sim 200 \text{ cm}^2/\text{Vs}^8$ which is considerably lower than that reported for phosphorene. This places phosphorene as a promising candidate for transistor fabrication.

It is notable that the band structure of phosphorene is significantly sensitive to the number of layers. In fact, computational and experimental results have shown a layer dependent direct band gap in phosphorene^{3, 42}. In particular, as layer thickness increases, there is a monotonic decrease in the band gap of phosphorene^{50, 3, 41}. It has been suggested that this dependence is a result of the repulsive interlayer hopping effect²⁰. In addition to layer thickness, it was demonstrated theoretically that phosphorenes electronic properties also depend on the stacking patterns⁴², hence these properties can be adjusted by varying the thickness and stacking patterns.

1.6.4 Property Tuning

Modifications to the surface of phosphorene is an effective way of tailoring the materials properties. During preparation, it is virtually impossible to avoid vacancy or topological defects that can affect the properties of phosphorene²⁵. It has been theoretically demonstrated that a monovacancy defect can induce magnetization in phosphorene while divacancy defects in phosphorene maintain remain nonmagnetic³⁷. Adsorption of B, N, F, Fe, Co, Cr, or Au adatoms can also make phosphorene magnetic[?], but the magnetic states for transition metal (TM) atom doped phosphorene behave differently. Codoped phosphorene is non-magnetic, but Ti-, V-, Cr-, Mn-, Fe-, or Ni-doped phosphorene are all magnetic¹⁹. Also, substituting P with N, F, Si, S, and Cl (non-metallic elements) can also induce magnetic moments^{10, 47}. It was also found that B, C, N, and F will induce mid-gap states and yield metallic transverse tunneling characteristics, while oxygen does not modify the bandgap of phosphorene¹⁰.

The HSE06 scheme was used to analyze properties of native point defects in few-layer phosphorene⁴⁶. The results showed that vacancy and interstitial defects are more stable in the outer layer than the inner layer. Also formation and transition energies for vacancy and self-interstitial P defect decrease as film thickness increases, but vacancies and self-interstitials could act as shallow acceptors.

CHAPTER 2. THERMAL TRANSPORT INVESTIGATION OF ISOTOPE SUBSTITUTION IN PHOSPHORENE

2.1 Introduction

Extensive studies on thermal transport have been conducted for graphene, both experimental and computational. Recently, other 2D materials have gained popularity as they have been shown to exhibit qualities preferable over graphene. As such, there is an increased utility for conducting a comparatively extensive analysis into the properties of these potential alternatives for graphene. With that in mind, the focus here remains one such material, phosphorene. In particular, the thermal conductivity κ of phosphorene is investigated, with an emphasis on isotope substitution effects. Molecular dynamics (MD) simulations are applied to evaluate the effect of the isotope substitution on thermal transport in phosphorene.

First-principles calculations for phosphorene at 300 K have predicted κ along the armchair and zigzag directions to be 36 and 110 W·m⁻¹·K⁻¹, respectively¹³. Additionally, a phonon Boltzmann transport equation (BTE) solution produced a computed value of 13.65 and 30.15 W·m⁻¹·K⁻¹, respectively, for κ at 300 K along the armchair and zigzag directions³⁶. While such first-principles analyses have been successful, and are known for their high modeling accuracy, their modeling ability is quite limited. Due to their high computational cost, such calculation require sample sizes and simulation times to remain small.

Fortunately, molecular dynamics (MD) offers a reasonable alternative that produces reasonable accuracy while allowing for significantly larger simulation size and duration at a more moderate computational cost. This work presents the effects of isotope substitution on the thermal conductivities of a 2D phosphorene sheet as assessed by a large scale MD simulation. Periodic boundary conditions are implemented along each direction to remove the effect size would have on the system. A non-equilibrium molecular dynamics approach is used for the thermal conductivity characterization. This analysis is done at a temperature of 300 K with isotope concentrations ranging from 0 - 5% (as greater concentrations were found to be unstable).

2.2 Methodology

For this work, all simulations were performed using the open source molecular dynamics code and large-scale atomic/molecular massively parallel simulator (LAMMPS)³⁵. All structures were constructed using the MOLTEMPLATE text-based molecule builder for LAMMPS. The phosphorene sheets are all constructed to be pristine initially, and the isotope substitution is done within the LAMMPS MD code, before any time has passed in the simulation.

Jiang et al.¹⁴ has successfully parameterized a Stillinger-Weber (SW) potential that considers the inter-atomic interactions in monolayer phosphorene, and accounts for the puckered nature of phosphorene by including interactions from pucker to pucker. The above SW potential is utilized for minimizing and equilibrating the simulated structures. The phosphorene sheets are then subjected to the Muller-Plathe method to evaluate the thermal conductivity of the system. Muller-Plathe is a very useful method that is not very difficult to implement, and is further explained below.

2.2.1 Isotope Substitution and Minimization

As mentioned above, for this system the Stillinger-Weber (SW) potentials were utilized for equilibrating and minimizing the energy. Stillinger-Weber is often used because it accounts for non-linear effects with reasonably fast computational time. These potentials are found with the sum of two terms. A two-body term (Eq. 2.1) is used to account for bond stretching, and a three-body term (Eq. 2.1) accounts for angle bending.

$$V_2 = \varepsilon A (B_L \sigma^p r_{ij}^{-p} - \sigma^q r_{ij}^{-q}) \exp\left[\frac{\sigma}{r_{ij} - a\sigma}\right]$$
(2.1)

$$V_3 = \varepsilon \lambda [\cos \theta_{jik} - \cos \theta_0]^2 \exp \left[\gamma \sigma (r_{ij} - a\sigma)^{-1} + \gamma \sigma (r_{jk} - a\sigma)^{-1} \right]$$
(2.2)

The potential interactions for all atoms within the cutoff distance are considered for each atom pair/trio, where the cutoff distance is determined by $a\sigma$. The parameters necessary for each of these equations were taken from the parametrization presented by Jiang¹⁴.

In order to achieve thermal equilibrium, 7 ns isobaric-isothermal (NPT: constant particle number, constant pressure constant temperature), 7 ns canonical ensemble (NVT: constant particle number, constant volume, constant temperature), and 2 ns micro-canonical (NVE: constant particle number, constant volume, constant energy) calculations are performed. The duration of the NPT calculations is effective for simulating experimental conditions, then the NVT allows for surface atom relaxation to prepare for the temperature gradient calculations. Then NVE releases the restrictions on pressure and temperature to achieve thermal equilibrium. (A more detailed list of parameters for these simulations can be found on Table B.1). After reaching thermal equilibrium, the Muller-Plathe method is implemented.

2.2.2 Muller-Plathe Method

To find the thermal conductivity of the system, a temperature gradient is created within the system. This is done using a Muller-Plathe algorithm³⁰ to swap the kinetic energy of two particles at different locations in the simulated system. This method of computing thermal conductivity is often referred to as non-equillibrium MD (reverse NEMD). In traditional NEMD simulations the imposed condition is the temperature gradient and the response evaluated from the system presents the heat flux. With the Muller-Plathe method, the imposed condition is the heat flux, and the evaluated response is the temperature gradient.

Essentially, the simulation box is divided into a number of bins to represent different sections, or locations, of the material. Then, the kinetic energies of two atoms in different sections/bins are swapped every N iterations (set by user). By selecting the hottest atom in bin 1 and the coldest atom in the center bin this creates the temperature gradient across the system (this is process is visualized in Fig. A.4). This is done for a duration of .5 ns to create the gradient, then an additional .1 ns during which the properties of the system are collected for analysis. This was done three more times to collect three data sets per isotope concentration.

Then, utilizing the sum of all the energy swaps, the heat flux can be calculated using Eq. 2.3.

$$\dot{Q} = E/2t \tag{2.3}$$

Utilizing a combination of Eq. 2.3 and Fourier's Law (2.4) then allows us to easily compute the thermal conductivity of the system using Eq. 2.5.

$$\dot{Q} = -\kappa A \Delta T \tag{2.4}$$

$$\kappa = \frac{E}{2At|\frac{\partial T}{\partial r}|} \tag{2.5}$$

Where κ is the thermal conductivity, E is the total sum of the swapped energies, A is the cross sectional area, t is the time elapsed while running the algorithm, and $\frac{\partial T}{\partial x}$ is the temperature gradient. To assess the temperature gradient, the slope is computed from each side of the center bin, and averaged. This is shown visually in Figures A.5.

A code was written in C language that read in the output file given from the LAMMPS simulations and selected out the temperature values throughout the simulated system to evaluate the temperature gradient. The three data sets for each simulated structure were imported and analyzed to solve Eq. 2.5 to produce the thermal conductivity value. Along with this, each data set was plotted to allow for a visual representation and analysis of the temperature gradient, as was shown in Figures A.5.

2.3 Results and Discussion

Thermal conductivity of pristine phosphorene was found to coincide with previous simulations performed in the same manner⁹. The resulting thermal conductivity values for isotope concentrations varying from 0 - 5% can be seen in Table 2.1. As isotope concentration increases, there is a sharp drop in thermal conductivity. Introducing isotopes of greater mass has been shown to decrease thermal conductivity⁴⁸. This thermal conductivity reduction may prove useful as a way to improve the thermoelectric performance, as the way to change the temperature-independent figure-of-merit, ZT, without modifying the Seebeck coefficient S, or the electrical conductivity, σ is by inserting atoms of greater mass²³. Phosphorene demonstrates promise for potential application in nanoscale thermoelectric materials.

| Isotope Substituted Phosphorene | | | |
|---------------------------------|--|--|--|
| Isotope Concentration (%) | Thermal Conductivity $(W \cdot m^{-1} \cdot K^{-1})$ | | |
| 0.0 | 102.15 | | |
| 1.0 | 103.95 | | |
| 2.0 | 106.27 | | |
| 3.0 | 153.51 | | |
| 3.5 | 25.08 | | |
| 4.0 | 20.89 | | |
| 5.0 | 28.113 | | |

Table 2.1: This table shows the data resulting from applying the Muller-Plathe method to calculate thermal conductivity (κ).

CHAPTER 3. EFFECTS OF STRAIN ON STRUCTURAL RIPPLING IN PHOSPHORENE

Work done while an AFRL Summer Research Facility Intern (Summer 2016).

3.1 Introduction

As discussed previously, graphene analogous materials have been shown to present desirable properties that could make them a superior alternative to graphene in certain applications. Some such properties found in phosphorene include an observable optical limiting behavior, optical property modification via strain-engineered rippling, and band gap tenability with applied axial strain. The two latter characteristics reveal that inducing strain reveals a notable property modifying behavior in the material that merits further investigations. As such, this research remained focused on property modification via strain application.

In particular, this report focuses on the structural flexibility of phosphorene with defects. Previous analysis on pristine phosphorene demonstrated that it exhibits superior structural flexibility in the armchair direction due to its puckered nature (shown in Fig. 3.1). This opens the possibility of fabricating devices with complex shapes including folded phosphorene. Here we are interested in modulation of this flexibility upon introduction of vacancy defects in the structure. A computational analysis utilizing molecular dynamics (MD) simulations was applied to investigate the effect of applying a uniaxial strain in the armchair and zigzag directions. The structures measure 15 nm in length in the strain direction and 13 nm in the other direction. The vacancies range from mono vacancies (single missing atom) to nano-pores (multiple missing neighboring atoms) of up to seven missing atoms. Structures were found to remain stable despite removal of up to 7 atoms, and the buckling behavior from applied uniaxial strain remains unchanged despite the missing atoms. Additionally, introduction of vacancies presents negligible effects on rippling amplitudes.



Figure 3.1: Illustrates the configuration and puckered nature of phosphorene which allows for exceptional structural flexibility.

3.2 Methodology

Simulations for these investigation were completed using the open source molecular dynamics code and large-scale atomic/molecular massively parallel simulator (LAMMPS)³⁵. All structures were created by applying the MOLTEMPLATE text-based molecule builder for LAMMPS. The phosphorene sheets are all constructed to be pristine initially, and the vacancies are induced within the LAMMPS MD code, prior to system equilibration or energy minimization. The Stillinger-Weber (SW) potential parameterized by /citetJiang was applied to account for inter-atomic interactions, including pucker to pucker interactions (additional details on this SW potential can be seen in Sect. 2.2.1.The above SW potential is utilized for minimizing and equilibrating the simulated structures. Following minimization, each structure was equilibrated to a thermally stable state using the canonical ensemble (NVT), followed by the isothermal-isobaric ensemble (NPT) for 2.5 nanoseconds each. Then the system a uniaxial strain was applied.

3.2.1 Uniaxial Strain

Strain is induced within the LAMMPS code upon each structure after energy minimization and system equilibration. The strain is applied at a constant strain rate of 10^{-4} ps⁻¹ up to a maximum strain of 80%. Here strain is defined as the length of the simulation box has changed size compared to its original length expressed as a percentage (e.g. 80% strain in the x direction



Figure 3.2: A) Buckling from 10% applied strain in the zigzag direction B) Rippling induced by 80% strain in the armchair direction.

means the simulation box has been compressed 80% of its original x length.) The simulation box length in the strain direction is determined by Eq. 3.1.

$$L(t) = L_0(1 + e_{rate} \cdot dt) \tag{3.1}$$

Where L(t) is the length in the strain direction at some time t, L_0 is the initial length in the strain direction, e_{rate} is the strain rate, and dt is the elapsed time. (Full parameters found in Table B.2).

3.3 Results and Discussion

The behavior exhibited by the selected simulated structures is in good agreement with previous simulations⁴⁵. As seen in Figure 3.2, the phosphorene fractures at relatively low strain when uniaxial strain is applied in the zigzag direction, and ripples when the strain is applied in the armchair direction.

3.3.1 Objective 1: Determine effect of strain and cell size on structural properties of pristine phosphorene

Initially, the reaction to uniaxial strain was investigated on structures of varying length (in the strain direction). Smaller simulation boxes result in lower tolerable strain when applied in the armchair direction, as seen in Table B.3 (As such, structures of (number x number) were utilized for Objective 2).



Figure 3.3: Rippling amplitudes for A) uncompressed equilibrated structures and B) compressive strain-induced structures of of pristine phosphorene of varied cell size.

Additionally, the rippling amplitude of these structures demonstrated a dependence on simulation box size. Shown in Figure 3.3 relation appears almost linear and occurs in the uncompressed structures as well as the compressed structures. Despite a search in the literature, information about this phenomenon was not explained or documented.

3.3.2 Objective 2: Explain and predict structural response in defective phosphorene with applied strain

From our investigations of the defective structures we found that they remained stable despite removal of up to seven atoms. It was also found that the buckling behavior remains unchanged (low strain, around 10%, still results in fracturing of the structure when applied in the zigzag direction, but strain up to 80% results in rippling). Additionally, as demonstrated in Figure 3.4, the introduction of vacancies presented negligible effects in the rippling amplitudes for both compressed and uncompressed structures, which is consistent with results found in the literature¹². The formation energies range from .5 to 1.4 eV for vacancies ranging from 1-7 missing atoms. However, the effects of vacancy and topological defects on generation of midgap states, has not yet been determined.

3.3.3 Future Work

The current goal is to expand on the previously conducted research by introducing additional defect types, and evaluating their effects by applying the aforementioned technique⁴³. Also,



Figure 3.4: Rippling amplictudes for A) uncompressed equilibrated structures and B) compressive strain-induced structures of vacancy induced phosphorene of varied cell size.

the effects of higher defect concentration on electronic and structural properties provides a potential area of further investigations in the future. Additionally, expanding the research by applying Density Functional Theory (DFT) calculations to evaluate electronic and optical properties is of great interest, as these properties would be key in deciding which applications phosphorene would be best suited for.

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Figure A.1: a) Buckled hexagonal crystal structure of 2D elemental sheets (X = Si, Ge, and Sn). Darker shaded atoms are at a slightly higher horizontal plane than the lighter shaded atoms. b) Various hexagonal plane buckled structures of X. The buckling parameter δ is the vertical distance between the two planes of X of atoms. c) Puckered hexagonal crystal structure of phosphorene



Figure A.2: Atomic structures of stanene on Bi_2Te_3 . (a) Top view (upper) and side view (lower) of the crystal structure of stanene. (b) RHEED pattern of stanene film. (c) RHEED intensity as a function of growth time. The blue arrow marks the deposition time for stanene. (d, e) STM topography of Bi_2Te_3 (111) (d) and Sn films of more than single biatomic layer coverage (e). The corresponding deposition time is marked by the black arrow in (c). (f)Height line profile in (e). (g) Large-scale STM topography of stanene film. (h) Zoom-in STM image of stanene. (i) Atomically resolved STM image of stanene. (j, k) Height line profiles in (g) and (i). (l) Atomically resolved STM image of top and bottom atomic layers of stanene. Blue dots mark the lattice of the top Sn atoms. Red dots mark the lattice of the bottom Sn atoms. The two lattices do not coincide. (m) Height line profile in (l). [Figure reproduced with permission 50]



Figure A.3: (a) Band structure of stanene and (b) DOS for different values of applied strain in the presence of SOC^{28} .



Figure A.4: Muller-Plathe method visualized. (a) Shows how they system is divided into bins, each with an energy distribution within them. (b) Illustrates how the atoms are selected and swapped between the bins. (c) Demonstrates the desired distribution after the Muller-Plathe algorithm has been applied.



Figure A.5: Muller-Plathe method data analysis. (a) This plot shows the temperature data collected after performing the Muller-Plathe method. (b) This plot shows the temperature data selected on either side of the bin to determine. (c) The slope depicted here is utilized for calculating the thermal conductivity in Eq. 2.5.



Figure A.6: Phosphorene structures utilized in the molecular dynamics simulations including pristine phosphorene and vacancies varying in size from 1-7 atoms

APPENDIX B. SUPLEMENTAL TABLES

Table B.1: This table shows the parameters utilized for the molecular dynamics (MD) simulations discussed in Chapter 2.

| MD Parameters | | |
|----------------------------|-------------------------|--|
| Simulator: | LAMMPS | |
| Potential: | Stillinger-Weber | |
| Boundaries: | Periodic | |
| Isobaric-Isothermal (NPT): | $7 \mathrm{ns}$ | |
| Canonical (NVT): | $7 \mathrm{ns}$ | |
| Microcanonical (NVE): | 2 ns | |
| Timestep: | $1 \mathrm{fs}$ | |
| Box Thickness: | 20 nm | |
| Armchair (x) Dimension: | ${\sim}140~\mathrm{nm}$ | |
| Zigzag (y) Dimension: | ${\sim}4$ nm Å | |

| MD Parameters | | |
|----------------------------|---------------------------|--|
| Simulator: | LAMMPS | |
| Potential: | Stillinger-Weber | |
| Boundaries: | Periodic | |
| Canonical (NVT): | $2500 \mathrm{\ ps}$ | |
| Isobaric-Isothermal (NPT): | $2500 \mathrm{\ ps}$ | |
| Strain Rate: | 10^{-4} ps^{-1} | |
| Max Strain: | 80% | |
| Timestep: | $0.5 \mathrm{fs}$ | |
| Box Thickness: | 20 nm | |
| Strain Direction: | ${\sim}60$ - 160 Å | |
| Lateral Direction: | ${\sim}130$ Å | |

Table B.2: This table shows the parameters utilized for the molecular dynamics (MD) simulations discussed in Chapter 3.

| a) | Zigzag | b) A | Armchair |
|---------------------|---------------------|---------------------|---------------------|
| Cell Size (Å) | Buckling Strain (%) | Cell Size (Å) | Buckling Strain (%) |
| 131.84 x 63.61 | 8.0 | 61.80 x 133.92 | 38 |
| $131.84 \ge 73.66$ | 8.5 | $70.04 \ge 133.92$ | 42.5 |
| $131.84 \ge 83.70$ | 7.5 | $78.28 \ge 133.92$ | 47 |
| $131.84 \ge 93.74$ | 7.0 | $90.64 \ge 133.92$ | 69 |
| 131.84 x 103.79 | 9.0 | $98.88 \ge 133.92$ | 74 |
| $131.84 \ge 113.83$ | 8.5 | $107.12 \ge 133.92$ | 79 |
| $131.84 \ge 123.88$ | 8.5 | $123.60 \ge 133.92$ | No Buckling |
| $131.84 \ge 133.92$ | 9.5 | $131.84 \ge 133.92$ | No Buckling |
| $131.84 \ge 143.96$ | 8.5 | $140.08 \ge 133.92$ | No Buckling |
| $131.84 \ge 157.36$ | 10 | $152.44 \ge 133.92$ | No Buckling |

Table B.3: This table shows the amount of strain (up to 80%) resulting in buckling of the structure when applied in the a) zigzag direction b) armchair direction.