Global Journal of Researches in Engineering: F
Electrical and Electronics Engineering
Volume 18 Issue 5 Version 1.0 Year 2018
Type: Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals
Online ISSN: 2249-4596 & Print ISSN: 0975-5861

Vibrational Properties of Disorder Silicene

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Abstract- A large amount of work has been devoted to the calculation of the phonon density of states (PDOSs) in disordered systems. However, very little is known about the actual nature of phonon states. By analogy with the corresponding problem of electrons in disordered systems, one expect that for strong disorder, phonon states will be localized excitations in the Anderson sense .Phonon localization in one-dimensional solids has been considered by Ishii and Jackle .Numerical studies has been considered by Nagel, Rahman, and Grest, for Lenrand-Jones glasses The glasses were prepared by means of molecular dynamics simulations of rapid cooling from the liquid state. One a glass was formed, the normal modes of vibration were studied numerically. It was found that above a certain frequency the modes were localized, as expected from the general ideas of Anderson localization. The structural and vibrational properties of two-dimensional hexagonal silicon (silicene) are investigated by means of first-principles calculations. It is predicted that the silicene structure with a small buckling of 0.44 Å (0.7 Å) and bond lengths of 2.28 Å (2.44 Å) is energetically the most favourable, and it does not exhibit imaginary phonon mode.

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GJRE-F Classification: *FOR Code: 290903*

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Keywords: phonon density of state; defects; raman spectrum; lattice structure;brillouin zone.

I. INTRODUCTION

The field of nanomaterials has become one of the most quickly growing areas in science due to the unique properties and potential applications of these materials in electronics, medicine, consumer goods, defence, amongst others. Nanomaterials come in different shapes including zero-dimensional (0D), one-dimensional (1D) and two-dimensional (2D) forms. They are classified by having at least one of their dimensions less than 100 nm in size. The class of 2D nanomaterials are characterised by large lateral dimensions and small thicknesses of the order of less than, typically, several nanometres. They are often referred to as Nano sheets and can be considered akin to extremely thin sheets of paper. A wide variety of materials can be grown as 2D nanomaterials and can be composed of one or multiple elements. The elemental 2D nanomaterials usually have names ending in 'ene', namely silicene. Silicene is a crystalline two-dimensional (2D) nanomaterial composed entirely of silicon (Si) atoms. The atoms in this single layer are arranged in a hexagonal honeycomb structure which, when viewed from the side, are buckled [1].

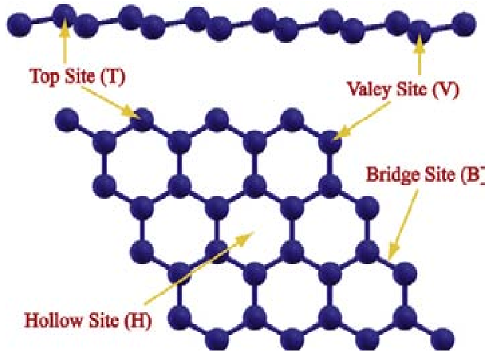

Figure 1: A (4 × 4) super cell of hexagonal buckled silicene structure

In fact, in view of the unique electronic properties found for the widest studied 2D material, graphene, researchers are looking for similar or even better properties in other layered materials, which could be eventually integrated into the current Nano electronics technology. Silicon is nowadays the most important semiconducting element used in this technology. Thus, the idea of having the silicon counterpart of graphene (silicene), is at the same time fascinating from the physical point of view, but also very attractive by virtue its possible integration into Nano electronics devices.

a) *Objectives*

We use force vibrational method for numerical analysis induced by Williams and Marris [121.s] and it is applicable for any disordered 2D material systems. We can apply this method as the field of

- A large complex disordered system.
- In low frequency regime we can calculate the DOS.

The main objectives of our thesis are:

- Develop a model based on FV method to determine vibrational properties of disordered silicene.
- To determine the Phonon Density of States (PDOS) of silicene.

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b) Geometrical Structure

Silicon is the most commonly used material in the semiconductor industry and is made of sp3-hybridized silicon (Si) atoms adopting the three dimensional diamond structure (figure 2.1(a)).

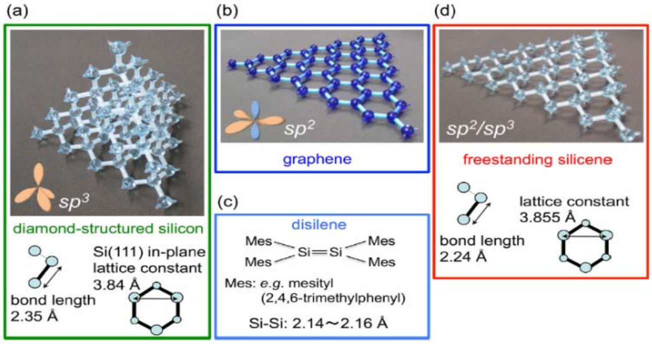

Figure 2: Structures and structural parameters of (a) diamond- structured silicon, (b) graphene (c) disilene [5], and (d) hypothetical, freestanding silicene [9]. In the insets, the sp^2andsp^3 type of hybridization are sketch.

c) Lattice Structure

The lattice vectors of the hexagonal lattice with respect to the frame of reference used in the software Quantum Espresso are as follows: [16]

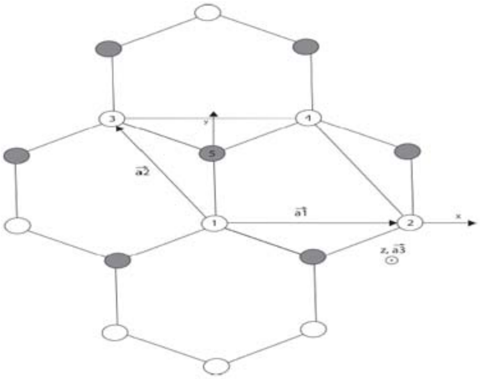

Figure 3: Lattice structure of silicene

$$\vec{a}_1 = a\hat{\imath}, \quad (1)$$

$$\vec{a}_2 = -\frac{a}{2}\hat{\imath} + \frac{\sqrt{3}a}{2}\hat{\jmath} \quad (2)$$

$$\vec{a}_3 = \hat{k} \quad (3)$$

The distance of this buckling parameter (Δz) is often given as 0.44 °A. [17] While silicene may seem three-dimensional due to the buckling parameter, it is more like a pseudo two-dimensional structure. The structure is actually two-dimensional except for that buckling parameter. Vector a_3 is only present for calculation reasons in the case of the two-dimensional structures. The buckling amount will be verified in the calculations section. Notice the buckling amount will vary when introduced into the bilayer and super lattice structure. But the buckling amount of stand-alone silicene will be verified so that Quantum Espresso can be proven effective.

d) Band Structure

Once the lattice structure is determined, the next step is to determine the band diagrams of these silicene-graphene composites. To accomplish that one needs to construct the Brillouin zone of this hexagonal lattice. The Brillouin zone has some symmetry points that will be used to plot the band structure. The equations for the reciprocal vectors as well as the equations for the points in the Brillouin zone used to plot the band structure are,

$$\vec{b}_1 = \frac{2\pi}{a\sqrt{3}}\left(\sqrt{3\hat{k}x} + \hat{k}y\right) \quad (4)$$

$$\vec{b}_2 = \frac{4\pi}{a\sqrt{3}}\hat{k}y \quad (5)$$

$$\vec{b}_3 = 2\pi\hat{k}z \quad (6)$$

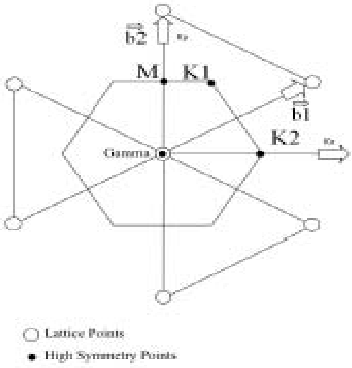

Figure 4: The Brillouin zone of silicene

The high symmetry points in the Brillouin zone will be written in this frame of reference. The units of $\frac{2\pi}{a}$ are pulled out to the front.Brillouin zone of the two materials will be the same.

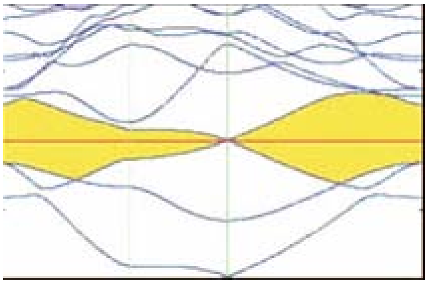

Figure 5: DFT band structure of silicene.

e) Phonons

Silicene has a flexural mode, as does graphene. However, because of the symmetry reduction due to the buckling, this mode for silicene has both a z and a xy component.

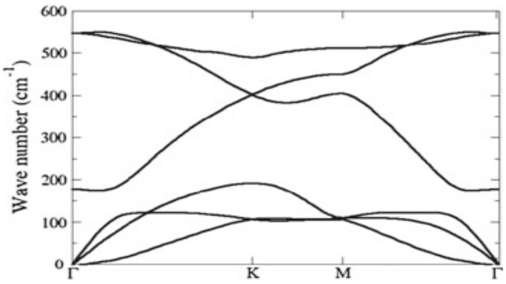

Figure 6: Phonon spectrum for silicene

f) Defects

When silicene-based materials have been fabricated experimentally, they will have some vacancy and atoms-vacancy defects [27]. Vacancies have a striking effect on the electronic structure. In particular, it is well known that vacancies induce localized states with associated resonant peaks at the Dirac point, and that state in the vicinity of the Dirac point has an enhanced tendency for localization, as revealed by an enhancement of the electronic inverse participation ratio [28].Variety of defects can exist in silicene and the impact on certain physical properties.

Single vacancies [33] and di-vacancies induce small gaps in silicene. Si atoms induce long-range spin polarization and a band gap, thus achieving an all-silicon magnetic semiconductor. Small defects were found to have a tendency to coalescence forming highly stable vacancy clusters [34].Stone-Wales defect is a topological defect formed by the 90° rotation of a dimer bond which results in four hexagons turning into two pairs of pentagon-heptagon rings.

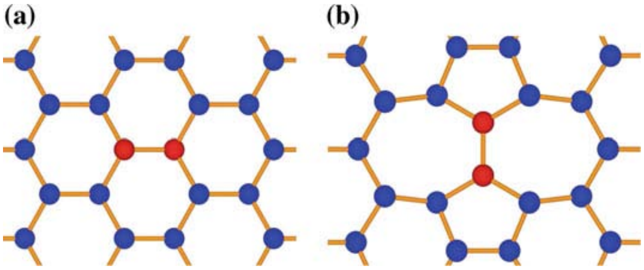

Figure 7: Representation of a stone-wales defect in silicene.

In particular, it was found that the formation energy and kinetic barrier are lower in silicene than in graphene. A band gap of 0.01 eV is created. The effect of vacancies and Stone-Wales defects on the mechanical properties has been studied using molecular dynamic finite element method with Turnoff potential [33]. They found that pristine and lowly defective silicene sheets exhibit almost the same elastic nature up to the fracture points. However, a single defect significantly weakened the silicene sheet, leading to a considerable reduction in the fracture strength. Thus, one 2-atom vacancy in the reduced the fracture stress by 1820 % and the fracture strain by 3335 %. The weakening effects of Stone-Wales defects varied with the tensile direction and the orientation of these defects.

A defect that is particular to 2D materials but absent for graphene is the buckling interface formed between two pieces of silicene with oppositely oriented buckling [34].This leads to a line defect that has a low formation energy but has a higher reactivity than the pristine silicene itself. The latter was deduced by studying the adsorption of a single gold atom and they turn out to have a binding energy of −3.50 eV.

II. METHODOLOGY

a) Numerical method

The equation of motion of the masses is

$$M_l \ddot{u}_l(t) = -\sum_{\acute{l}} \emptyset_{l\acute{l}} u_{\acute{l}}(t) \qquad (7)$$

Where, M_1 andu_l (t) are the mass and displacement of the l_th mass and Ø_ (ll ́) describes the strength of the spring coupling atoms l and l ́. The displacement can be decomposed into a set of normal modes according to

$$u_l(\mathrm{t}) = \sum_\lambda Q_\lambda\,(t)\,\frac{e_\lambda(t)}{\sqrt{M_l}}, \tag{8}$$

Where Q_λ is the amplitude of the normal mode λ and e_l (λ) is the displacement pattern or "polarization" vector of the mode λ. The {e_l (λ)} and the frequencies {ω_λ } satisfy the equations

$$\sum_{\acute{l}} \phi_{l\acute{l}}(M_l M_{\acute{l}})^{-\frac{1}{2}} e_{\acute{l}}(\lambda) = \omega_\lambda^2 e_l(\lambda) \tag{9}$$

Thus, to find the frequencies and displacement patterns of the normal modes one has to find the eigenvalues and eigenvectors of an N×N matrix. Conventional methods require a large amount of computer time as N becomes large. Thus, one has to find another approach.

b) *Method for the Density of States*

Start with each atom at rest and with zero displacement then apply a force on each atom given by $F_l \cos(\Omega \mathrm{t})$Where F_l is independent of time. After a time, large compared to the typical period of oscillation of the atoms, the total energy of the atom is,

$$E = \frac{1}{2}\sum_\lambda [\sum_l \frac{F_l e_l(\lambda)}{\sqrt{M_l}}]^2 \frac{\sin\{[(\omega_l - \Omega)/2]t\}^2}{(\omega_\lambda - \Omega)^2} \tag{10}$$

Thus, for large times the periodic force excites only those modes whose frequency is close to Ω.

$$F_l = F_0\sqrt{M_l}\cos\Phi_l \tag{11}$$

Where F_0 is a constant and ϕ_l is a random quantity. If we average over all possible values of Φ_l we find that the average value of E is

$$\langle E\rangle = \frac{F_0{}^2}{4}\sum_\lambda \frac{\sin\{[(\omega_l - \Omega)/2]t\}^2}{(\omega_\lambda - \Omega)^2} \tag{12}$$

We have used the orthonormality of the mode patterns:

$$\sum_l e_l(\lambda) e_l(\acute{\lambda}) = \delta_{\lambda\acute{\lambda}} \tag{13}$$

The modes which contribute to the sum in equation 3.6 are those whose frequencies lie within about $\pm\left(\frac{2\pi}{t}\right)$ of Ω . Let us choose t such that

$$\Omega t \gg 1\ , \tag{14}$$

$$\frac{4\pi N}{\omega_m t} \gg 1 \tag{15}$$

Where ω_m is the maximum frequency of the system. Equation (3.8) means that only modes in a narrow band of frequency on the scale of Ω contribution to the sum, equation (3.9) ensures that the number of such modes is much larger than unity. Thus, if there conditions are met we have

$$\langle E\rangle \approx \frac{\pi t F_0{}^2}{8}\sum_\lambda \delta(\omega_\lambda - \Omega) = \frac{\pi t F_o{}^2 N g(\Omega)}{8} \tag{16}$$

Where g(Ω) is the phonon density of states. Thus, provided that a way can be found to carry out the time development in the presence of the periodic force, we can find

$$\mathrm{g}(\Omega) = \frac{8\langle E\rangle}{\pi t F_o{}^2} \tag{17}$$

For a sufficiently large system, one expects that it will not be necessary to carry out explicitly the average over all values of the make one random choice of the $\{\phi_l\}$.

c) *Numerical Algorithm*

The problem thus reduces to the solution of the equations of motion of the system in the presence of a periodic force. These equations can be written as,

$$v_l{}^{\cdot} = M_l{}^{-1}[\phi_{l\acute{l}}.u_{\acute{l}}(t) + F_l\cos(\Omega t)] \tag{18}$$

$$\dot{u}_l(t) = v_l(t) \tag{19}$$

The standard approach to the time development is to replace t by nτ where τ is a small time step, and n an integer. Then a time development algorithm is

$$v_1(n+1) = v_l(n) + M_l{}^{-1}[\phi_{l\acute{l}}.u_{\acute{l}}(t) + F_l\, cos(\Omega t)]\tau \tag{20}$$

$$u_1(n+1) = u_n + v_l(n)\,\tau \tag{21}$$

Normally one would choose τ to be small scale of the system, i.e. the period τ_m of the highest frequency mode.

The initial set at t= 0 is prepared in which all atoms are at rest and have zero displacements. A random force is applied to each atom at rest, which is given by:

$$F_l\cos(\Omega t) = F_0\surd M_l\cos(\phi l)\cos(\Omega t) \tag{22}$$

Where F_0 is a constant and ϕl varies from 0 to 2π. The corresponding equation of motion of the system becomes:

$$M_l\ddot{u}_l + \sum_{\acute{l}} \emptyset l\acute{l}\, u_{\acute{l}}(t) = F_0\surd M_l\cos(\emptyset l)\cos(\Omega t) \tag{23}$$

The total energy of the system can be written as the summation of kinetic and potential energy as follows:

$$E(t) = K + U$$

$$= \frac{1}{2}\sum_l M_l\,\dot{u}_l{}^2(t) + \frac{1}{2}\sum_l\sum_{\acute{l}} u_l(t)\,\emptyset l\acute{l} u_{\acute{l}}(t)$$

$$= \frac{1}{2}(\sum_l M_l\,\dot{u}_l{}^2(t) + \sum_l\sum_{\acute{l}} u_l(t)\,\emptyset l\acute{l} u_{\acute{l}}(t)) \tag{24}$$

Thus, for large times the periodic external force excites only those modes whose frequency is close to. When average all possible values of ϕ_l and used the ortho-normality of the eigen-vector$\Omega e_l(\lambda)$, the average value of energy $\langle E\rangle$becomes,

$$\langle E\rangle = \frac{F_0{}^2}{4}\sum_\lambda \frac{\sin\{(\Omega - \omega_\lambda)/2^t\}^2}{(\Omega - \omega_\lambda)^2} \tag{25}$$

If we choose t such that

$$\frac{1}{\Omega} \ll t \ll \frac{4\pi N}{\omega_{max}} \tag{26}$$

Therefore, from Eq. 3.10, we can write:

$$\langle E(\Omega)\rangle = \frac{\pi t {F_0}^2}{8} \sum_\lambda \delta(\omega_\lambda - \Omega) \tag{27}$$

The density of states are related with the delta function by the following equation:

$$g(\Omega) = \frac{1}{N} \sum_\lambda \delta(\omega_\lambda - \Omega) \tag{28}$$

Therefore, we can write the density of the states of the system is

$$\langle E(\Omega)\rangle = \frac{\pi t {F_0}^2 N g(\Omega)}{8} \tag{29}$$

$$g(\Omega) = \frac{8\langle E(\Omega)\rangle}{\pi t {F_0}^2 N} \tag{30}$$

Thus, it could be obtained phonon density of states to carry out the time development in the presence of external force.

d) Raman Spectroscopy

Raman spectroscopy is a widely used experimental technique to identify the characteristic vibrational modes of materials. It is one of the most used optical techniques for the characterization of 2D materials like graphene. Several properties can be derived from the analysis of the Raman spectra, e.g., the shift in frequency of the Raman peaks has been successfully used to analysis flakes of layered materials such as 〖MoS〗 _2and quantify the number of layers [40, 41]; similarly the Raman spectrum of graphene flakes has been used not only for the identification of the number of layers, but also to estimate the quality (in term of defects) of the graphene sheets [42, 43].

Note however that the splitting of the iTO and iLO at Γ could be due to an artifact of the DFT calculation and particularly to the slightly different bond length $a \neq b$ predicted by using the nonlinear core correction. Nevertheless, the iTO mode is very close to the LiO mode and its Raman spectra show only one peak at around 575 cm–1, as shown in Fig. 3.1 below.

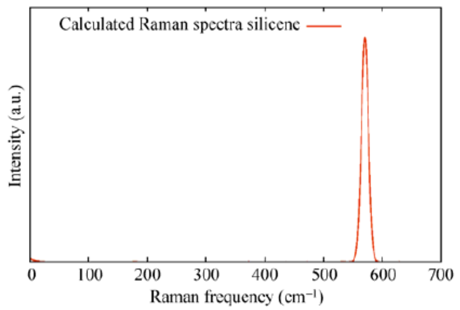

Figure 8: Raman spectrum of silicene obtained by the calculated vibrational spectrum convoluted with a uniform Gaussian broadening having 10 cm^{-1} width.

III. RESULT AND DISCUSSION

We have calculated phonon density of states of silicene, g(ω) for lattice of 1000 atoms in the array respectively 40×40 and we analysis for 5%,10% and 15% defects.We also have calculated phono density of states of silicene, g(ω) for lattice of 2000 atoms in the array respectively 50×50. We consider same 5%,10% and 15% defects for this lattice structure.

a) Force constants calculation

As the force constants are effective in three planes such that in the radius plane, in the inner plane, and in the outer plane. The force constants are as given following table 4.1[44].

Table 1: The force constants in three effective plane

Neighbour	Φ_{ra}	Φ_{tin}	Φ_{to}
1st	2.032544	15.9965	0.3814
2nd	-0.882486	0.9010	0.0683
3rd	0.249645	-0.9737	0.1396
4th	0.295442	-0.1067	0.1006

b) Results

Phonon Density of states of Silicene for different atom numbers:

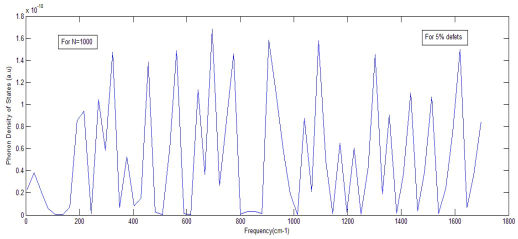

Figure 9: Phonon Density of States of silicene for 1000 atoms with 5% defects.

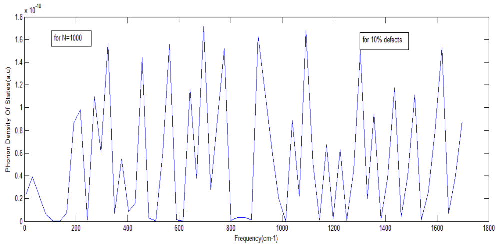

Figure 10: Phonon Density of States of silicene for 1000 atoms with 10% defects

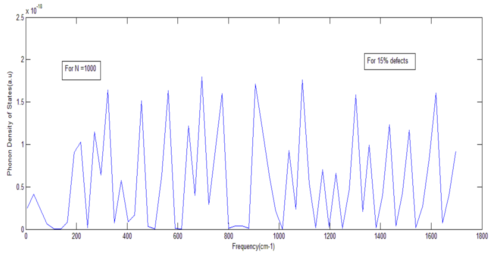

Figure 11: Phonon Density of States of silicene for 1000 atoms with 15% defects.

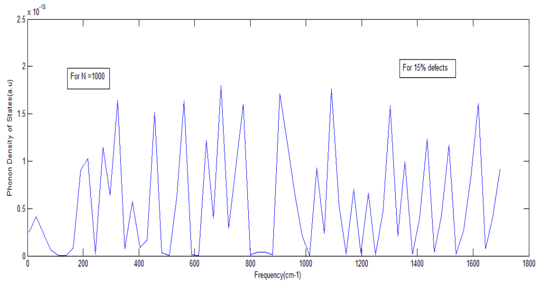

Figure 12: Phonon Density of States of silicene for 2000 atoms with 5% defets.

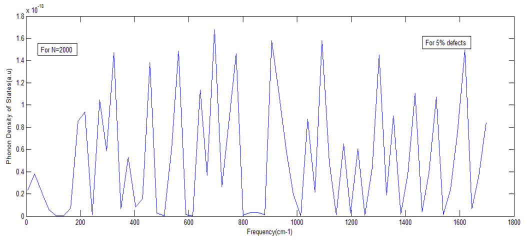

Figure 13: Phonon Density of States of silicene for 2007 atoms with 10% defects

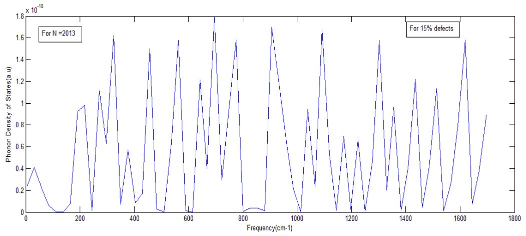

Figure 14: Phonon Density of States of silicene for 2013 atoms with 15% defects

IV. CONCLUSIONS AND FUTURE WORK

Silicene is a single layer of silicon atoms with *sp3* bonds in the honeycomb lattice structure. More compatibility of the Silicene with the current semiconducting technology and some other advantages such as a new and promising alternative for the spintronic and the Nano-magnetic materials have attracted considerable scientific attention in very recent years. In addition, despite the single layer Graphene which owns zero band gap in the Dirac point, Silicene owns a tunable band gap from zero to semiconducting region, which make it better choice for the FET technology. However, stability of this material was an issue that the recent experimental studies showed that it could be stable with a small buckling. However, its electronic properties such as the density of states, the total carriers and the conductance as well as their temperature dependence and comparison with the electronic properties of the Graphene have been being investigating analytically.

We studied the Phonon Density of states (PDOSs) of disorder silicene, we belief that this thesis work will help to investigate the electronic properties of silicene. Of course, the work on silicene is still a growing area of research and there are many questions yet to be answered about the potential of this material. We are very excited to be part of the discoveries in this area and look forward to seeing where this material will go in the future. We hope that you as the reader will share in our passion for science and 2D nanomaterials!

The simulating analysis of vibrational properties like phonon density of states have been studied and found phonon density of states for lattice atoms disorder. There have been considered the normal mode of vibration. At the same time, there have been several important issues in the field that remain to be addressed.

We have performed the mathematical calculation on basis of a 2d dimensional model. The method developed in this dissertation can be extended to the three dimension for calculating the vibrational properties of multi-layer silicene. We can further calculate the layered structure of silicene and, further investigation of many-body interactions and electron-phonon scattering effect, calculation of Raman intensities, quantitative analysis of specific structural defects such as Stone-walse defects in silicene samples, and an harmonic effects responsible for the thermal conductivity in the silicene sheet. The electron-phonon interactions can be further calculated. The harmonic effects and thermal conductivity in the silicene sheet can be studied in a more systematic way.

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