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Electronic and Magnetic Properties of Two-dimensional Nanomaterials beyond Graphene and Their Gas Sensing Applications: Silicene, Germanene, and Boron Carbide

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

ELECTRONIC AND MAGNETIC PROPERTIES OF TWO-DIMENSIONAL
NANOMATERIALS BEYOND GRAPHENE AND THEIR GAS SENSING
APPLICATIONS: SILICENE, GERMANENE, AND BORON CARBIDE

A dissertation submitted in partial fulfillment of

the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

ELECTRICAL ENGINEERING

by

Sadegh Mehdi Aghaei

2017

To: Interim Dean Ranu Jung
College of Engineering and Computing

This dissertation, written by Sadegh Mehdi Aghaei, and entitled Electronic and Magnetic Properties of Two-dimensional Nanomaterials beyond Graphene and Their Gas Sensing Applications: Silicene, Germanene, and Boron Carbide having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this dissertation and recommend that it be approved.

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Florida International University, 2017

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DEDICATION

I would like to dedicate this dissertation to my beloved parents, Ali and Lida, and to my brother, Saeb. The completion of this work would not have been possible without their encouragement, support, wisdom, understating, patient, and most of all love.

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ABSTRACT OF THE DISSERTATION

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APPLICATIONS: SILICENE, GERMANENE, AND BORON CARBIDE

by

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Florida International University, 2017

Miami, Florida

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The popularity of graphene owing to its unique properties has triggered huge interest in other two-dimensional (2D) nanomaterials. Among them, silicene shows considerable promise for electronic devices due to the expected compatibility with silicon electronics. However, the high-end potential application of silicene in electronic devices is limited owing to the lack of an energy band gap. Hence, the principal objective of this research is to tune the electronic and magnetic properties of silicene related nanomaterials through first-principles models.

I first explored the impact of edge functionalization and doping on the stabilities, electronic, and magnetic properties of silicene nanoribbons (SiNRs) and revealed that the modified structures indicate remarkable spin gapless semiconductor and half-metal behaviors. In order to open and tune a band gap in silicene, SiNRs were perforated with periodic nanoholes. It was found that the band gap varies based on the nanoribbon's width, nanohole's repeat periodicity, and nanohole's position due to the quantum

confinement effect. To continue to take advantage of quantum confinement, I also studied the electronic and magnetic properties of hydrogenated silicene nanoflakes (SiNFs). It was discovered that half-hydrogenated SiNFs produce a large spin moment that is directly proportional to the square of the flake's size.

Next, I studied the adsorption behavior of various gas molecules on SiNRs. Based on my results, the SiNR could serve as a highly sensitive gas sensor for CO and NH₃ detection and a disposable gas sensor for NO, NO₂, and SO₂. I also considered adsorption behavior of toxic gas molecules on boron carbide (BC₃) and found that unlike graphene, BC₃ has good sensitivity to the gas molecules due to the presence of active B atoms. My findings divulged the promising potential of BC₃ as a highly sensitive molecular sensor for NO and NH₃ detection and a catalyst for NO₂ dissociation. Finally, I scrutinized the interactions of CO₂ with lithium-functionalized germanene. It was discovered that although a single CO₂ molecule was weakly physisorbed on pristine germanene, a significant improvement on its adsorption energy was found by utilizing Li-functionalized germanene as the adsorbent. My results suggest that Li-functionalized germanene shows promise for CO₂ capture.

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LIST OF ACRONYMS & ABBREVIATIONS

FET	Field-effect transistor
FinFET	Fin field-effect transistor
3D	Three-dimensional
2D	Two-dimensional
1D	One-dimensional
0D	Zero-dimensional
SiNR	Silicene nanoribbon
ASiNR	Armchair silicene nanoribbon
ZSiNR	Zigzag silicene nanoribbon
SiNF	Silicene nanoflake
GNR	Graphene nanoribbon
AGNR	Armchair graphene nanoribbon
GO	Graphene oxide
CNT	Carbon nanotube
SOC	Spin-orbit coupling
NM	Nonmagnetic
FM	Ferromagnetic
AFM	Antiferromagnetic
vdW	van der Waals

BZ	Brillouin zone
PDOS	Partial density of states
CBM	Conduction band minimum
VBM	Valence band maximum
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
DFT	Density functional theory
NEGF	Non-equilibrium Green's function
LDA	Local density approximation
PZ	Perdew-Zunger
PW	Perdew-Wang
VWN	Vosko-Wilk-Nusair
GGA	Generalized gradient approximation
PW91	Perdew-Wang 1991
PBE	Perdew-Burke-Ernzerhof
B3LYP	Becke, 3-parameter, Lee-Yang-Parr
TPSS	Tao-Perdew-Staroverov-Scuseria
HSE06	Heyd-Scuseria-Ernzerhof 06
BSSE	Basis set superposition errors
LCAP	Linear combination of atomic orbitals
cp	Counterpoise

ATK	ATOMISTIX TOOLKIT
TEM	Transmission electron microscopy
STM	Scanning tunneling microscopy
SNOM	Scanning near field microscopy
AFM	Atomic force microscopy
RHEPD	Reflection high-energy positron diffraction
AREPS	Angle-resolved photoelectron emission spectroscopy
LEED	Low energy electron diffraction
UHV	Ultra-high vacuum
CVD	Chemical vapor deposition
MBE	Molecular beam epitaxy
UV	Ultraviolet

CHAPTER 1

Introduction

1.1 Motivation

Semiconductors are the foundation of modern solid-state and electronic devices [1]. Based on an observation known as Moore's law, the number of transistors per square inch on integrated circuits doubles every year [2]. A myriad of improvements to semiconducting materials, their properties, and the device fabrication processes have steadily decreased the size of the devices at a rate comparable to that predicted by Moore's law [3]. This decrement in device size has led to huge improvements in their performance and efficiency.

Silicon (Si), as a semiconducting material, is one of the most valuable materials of semiconductor technology because of its superior physical and technological properties, abundance in Earth's crust, easy fabrication processes, easy tuning of electronic properties, and current-carrying properties [3, 4]. Microprocessors currently have circuit features down to 10 nm. In April 2017, Samsung started shipping their new smartphone named Galaxy S8 that uses 10 nm fin field-effect transistor (FinFET) process technology. However, keeping pace with Moore's law has become increasingly challenging due to the physical limits of Si technology [5-7]. In February 2017, Intel announced that Fab 42 in Arizona would produce microprocessing using 7 nm node technology [8], but they would move away from silicon at this node [9]. IBM has built the first functional transistors with 7 nm technology using silicon-germanium process [10]. The 5 nm node might be the end of Moore's law for microprocessors created by three-dimensional (3D) materials. Many issues arise when devices reach this size. First of all, heat is unavoidable when

more and more silicon circuitry is packed tightly into a same small area. Secondly, the transistors of this size will experience quantum tunneling from the source to the drain [3]. Third, the band gap of the 3D materials starts to speedily increase by reducing their size to the nanometer scale because of the quantum confinement effect. Last but not least, when the size of 3D materials decreases, the impacts of surface states caused by surface roughness and dangling bonds become much greater. As a result, these hurdles significantly hinder creating 3D-based devices at the nanoscales. The first question is what will be the next silicon?

The second motivation for this dissertation comes from the market where the demand for new electronic devices is growing daily. Today, most electronic devices come in the form of rigid chips, while the demand for very thin and flexible devices which can be rolled up like paper is fast increasing. Unfortunately, Si cannot be wrapped on a flexible platform or used to cover a large area which hinders its potential toward new electronic devices. Consequently, to respond to the market demands, Si technology requires new alternatives that can be fabricated cheaply and easily in large scale and also can be easily integrated into Si-based electronics.

Gas sensing is a crucial need for controlling of chemical processes, to prevent health hazards and air pollution, device contamination, and for medical diagnosis. Much effort has been devoted to developing novel platforms for gas sensing with high sensitivity, selectivity, stability, and fast response and recovery. In principle, a gas sensor works by transforming the gas adsorption into detectable signals. Conductance-based gas sensors have attracted significant attention due to their relatively low cost and high performance. The popular metal oxide-based gas sensors have been extensively

investigated in the past few decades due to their relatively low cost and high sensitivities [11]. However, to obtain a high response to targeted gases, a relatively high operating temperature would be adopted, which not only increases the power consumption but also causes thermal safety problems, thus hindering their practical applications. Developing novel gas-sensing materials with ultrahigh surface-to-volume ratios and strong surface activities is a strikingly primary and reliable approach for fabricating gas sensors operated at low or room temperature. This is the third motivation for me in this dissertation.

Today, two-dimensional (2D) nanomaterials, a class of single-atom thick materials, could overcome these hurdles. They offer numerous benefits for further miniaturization of nano-electronic devices and can develop high-mobility, low-power, large-area, flexible, and low-cost electronic devices [12, 13]. Their inherently thin nature makes them sturdy against quantum confinement effects. Moreover, 2D materials do not suffer from surface roughness and dangling bonds issues. Hence, nano-electronic devices based on 2D nanomaterials have the potential to revolutionize the global market because of their remarkable properties. As an example, a transistor with a 1 nm gate was created with a MoS₂ bilayer channel and a single-walled carbon nanotube gate electrode in 2016 [14].

2D layered nanomaterials have aroused tremendous interest due to their excellent semiconducting performance and unique thickness dependent physical and chemical properties, including ultra-large surface-to-volume ratios, high surface activities, *etc* [15-17]. Furthermore, 2D layered nanomaterials can be easily fabricated as field-effect transistors (FETs) that have low power consumption and good thermal safety. Such

advantages of 2D layered nanomaterials distinguish them from conventional metal oxides and render them a promising future in the development of ultrahigh sensitive and low-power-consumption sensor platforms.

Although graphene was the first 2D material to be discovered in 2004 [18, 19], physicists believe that around five hundred 2D materials might be found in future [20]. While graphene cannot take the place of Si; however, it can combine with Si in the fabrication of specific devices in order to compensate for the shortcoming of Si [21, 22]. The 2D materials beyond graphene have garnered growing interest in recent years [23-28]. Molybdenum disulfide (MoS_2) was graphene's first descendant that attracts attention [29]. The 2D form of other cousins of MoS_2 , so-called transition metal dichalcogenides (or TMD), have been widely investigated [15, 30, 31]. Silicene, germanene, and stanene (the graphene equivalent for silicon, germanium, and tin) are the members of another class of 2D materials drawing the attention of scientific community because they closely resemble graphene [26-28].

1.2 General Statement of Problem Area

Graphene has drawn enormous attention from various scientific communities owing to its extremely high carrier mobility. This desired property in electronic technology originated from linear energy-momentum dispersion within 1 eV around the Fermi level at the high symmetric K points in the Brillouin zone [18]. However, the high-end potential applications of graphene in electronic devices such as gas sensors, FETs, and digital logic circuits are limited due to the semi-metallic nature of graphene [32]. In order to open and tune a band gap in graphene, different methods have been proposed such as chemical modifications [33, 34], substrate interactions [35], nanostructuring into bilayers [36, 37],

and nanoribbons [38, 39]. However, utilizing these methods might result in severe degradation of carrier mobility.

A new 2D nanomaterial is another route to address this problem. Silicene and germanene have attracted great interest in this regard because of their appreciable direct band gap induced by spin-orbit coupling (SOC). The values of the SOC-induced band gap in germanene, silicene, and graphene are 23.9 meV, 1.55 meV, and 0.024 meV, respectively. [40, 41]. The other advantage of silicene and germanene over graphene is that they are more compatible with Si-based electronic devices, making them outstanding candidates for future electronic applications. To open and tune the band gap in a silicene or germanene sheet, several methods have been applied, including nanoribbons [42], applying a perpendicular electric field [12, 43, 44], chemical functionalization [45-47], surface adsorption [48-50], substitution [51], substrate interactions [52, 53], or introducing nanoholes on the sheet [54].

On the one hand, graphene shows low sensitivity toward gas molecules adsorption [55], however, its sensing ability can be improved by introducing dopants or defects in the structure [56-58]. Excitingly, dissimilar to the flat graphene sheet, the silicene and germanene honeycomb structures are puckered [59] due to the tendency of silicon atoms to adopt sp^3 and sp^2 hybridization rather than only sp^2 hybridization [60]. Therefore, silicene and germanen are expected to show a considerably higher chemical reactivity for molecules adsorption compared to graphene due to their buckled formation, making them promising materials for gas molecules detection [61-64].

On the other hand, conductance-based nanoscale gas sensors based on semiconducting materials exhibit better sensitivity in comparison with metallic materials because adsorption of gas molecules has a much smaller effect on the electronic properties of metals. The semiconducting armchair ribbons of 2D materials could solve this problem.

1.3 Research Objectives

This dissertation aims to explore the electronic, magnetic properties and gas sensing performance of 2D nanomaterials beyond graphene such as silicene, germanene, and boron carbide through first-principles models.

As mentioned in the previous section, semiconducting materials show better sensitivity to the gas molecules. However, the pristine graphene, silicene, and germanene sheets are semimetals in the absence of SOC. Nanoribbons are introduced as effective methods to open a band gap in the sheets. For silicene, I will focus on the following aspects:

- (1) The electronic and magnetic properties of the nanoribbons with different edge types including armchair, zigzag, Klein, reconstructed Klein, reconstructed pentagon-heptagon, and their combinations.
- (2) The effects of edge functionalization on the electronic and magnetic properties of the nanoribbons.
- (3) The impacts of doping on the stability, electronic, and magnetic properties of the edge-functionalized nanoribbons.
- (4) Band gap tunability of silicene by perforating periodic nanoholes in its nanoribbon.

(5) The tunability of the electronic, transport and magnetic properties of silicene through hydrogenation of silicene nanoflakes.

Moreover, to understand the mechanism of conductance-based gas sensors, I will carry out the following research:

(6) The gas molecules adsorption capability of silicene, germanene, and boron carbide by studying the most stable adsorption configurations, adsorption sites, adsorption energies, charge transfer, quantum conductance modulation, and electronic properties of all studied gas molecules on adsorbents.

(7) The influences of introducing dopants, defects, and functionalization on the sensitivity of the adsorbents.

1.4 Organization of This Dissertation

The remainder of this dissertation is organized as follows:

Chapter 2 provides a literature review of graphene, silicene, and germanene. It also explains the gas sensing mechanism for 2D layered nanomaterials and the configurations of gas-sensing devices. Chapter 3 expresses the methods used in this dissertation. In chapter 4, the influence of edge functionalization on the structural stabilities, electronic and magnetic properties of silicene nanoribbons (SiNRs) are studied in depth. Moreover, the effects of N or B doping on the stability, electronic and magnetic properties of hydrogenated and fluorinated SiNRs are considered. In chapter 5, the band gap tunability of SiNRs by perforating periodic nanoholes is scrutinized. Chapter 6 describes the electronic and magnetic properties of pristine and hydrogenated silicene nanoflakes (SiNFs) in order to induce a robust magnetism in silicene. Chapter 7-9 focuses on the gas sensing capability of silicene, germanene, and BC_3 sheet. In chapter 7, the

adsorption of gas molecules (N_2 , NO , NO_2 , NH_3 , CO , CO_2 , CH_4 , SO_2 , and H_2S) on SiNRs are examined. In Chapter 8, the adsorption of toxic gas molecules (NO , NO_2 , NH_3 , and CO) on BC_3 sheet is investigated. In Chapter 9, the interaction of CO_2 gas molecules with pristine and lithium-functionalized germanene is discussed in order to evaluate the CO_2 capture capability of germanene. Finally, *chapter 10 summarizes the dissertation outcomes and makes recommendations for the future works.*

CHAPTER 2

Background and State of the Art

2.1 Graphene

A planar monolayer of carbon atoms packed in a 2D honeycomb crystal lattice is called graphene. As an allotrope of carbon, graphene is the building block of various carbon allotropes [21]. Graphene layer can be stacked into 3D graphite [65], can be rolled to form one-dimensional (1D) carbon nanotube (CNT) [66], or wrapped up into zero-dimensional (0D) fullerene [67], as shown in Figure 2.1 [21, 68].

Figure 2.1 Graphene is the building block for carbon allotropes. It can be wrapped up into 0D fullerene (left), rolled into 1D nanotubes (middle), or stacked into 3D graphite (right). Figure is extracted with permission from Ref. [21].

Graphite monolayers were first realized using Tight-Binding Approximation in 1947 by Wallace *et al.* [69]. Ruess and Vogt published the earliest transmission electron microscopy (TEM) images of few layers graphite in 1948 [70]. However, the first experimental observation of monolayer flakes of reduced graphite oxide *via* TEM was reported by Hanns-Peter Boehm *et al.* in 1962, as shown in Figure 2.2 [71].

Figure 2.2 TEM image of graphitic flakes as seen by Hanns-Peter Boehm *et al.* in 1962. Figure is extracted with permission from Ref. [71].

In 2002, Jang *et al.* filed a US patent for the production of nano-scaled graphene plate material [72]. Two years later, graphene was extracted from bulk graphite using mechanical exfoliation by Geim *et al.* [18, 21]. They received the 2010 Nobel Prize in Physics for their groundbreaking work. An atomic force microscopy (AFM) image of a stable graphene monolayer is depicted in Figure 2.3.

Figure 2.3 AFM image of exfoliated graphene as seen by Geim *et al.* in 2004. Figure is extracted with permission from Ref. [18].

There is a tremendous amount of scientific papers published on graphene and graphene-based devices since its discovery in 2004. The properties of graphene (which defines its application) are strongly dependent on the method of production. The most common methods for mass-production of graphene are chemical vapor deposition (CVD), mechanical exfoliation, molecular assembly, liquid phase exfoliation, and synthesis on SiC [22]. These methods can be categorized regarding the quality, size, and price, as shown in Figure 2.4 [22].

Each carbon has four valence electrons. The carbon atoms in a flat graphene sheet have sp^2 hybridization. In this hybridization, the 2s orbital mixes with only two of the three available 2p ($2p_x$ and $2p_y$) orbitals. Consequently, each carbon atom is strongly bonded to its three neighbors by sp^2 or σ -bond. Furthermore, each carbon atom has one electron (p_z) weakly bonded (π -bonding) that determines charge carrier transport. The resultant orbitals are oriented in the XY-plane with an angle of 120° [73].

Figure 2.4 Methods for mass-production of graphene. Figure is extracted with permission from Ref. [22].

The honeycomb lattice structure of graphene is presented in Figure 2.5(a). The honeycomb lattice is not a Bravais lattice. However, the sublattices A and B together form a triangular Bravais lattice. The bond length (a) of C-C is 1.42 Å. The three vectors which connect the sublattice A to the nearest sublattices B are:

$$\delta_1 = \frac{a}{2}(\hat{i} + \sqrt{3}\hat{j}), \delta_2 = \frac{a}{2}(\hat{i} - \sqrt{3}\hat{j}), \delta_3 = -a\hat{i} \quad (2.1)$$

Here, $\hat{i}$ and $\hat{j}$ are the unit vectors attributed to X and Y axes, respectively. Therefore, the basis vectors of triangular Bravais lattice are defined as:

$$\mathbf{a}_1 = \frac{3}{2}a(\hat{i} + \frac{1}{\sqrt{3}}\hat{j}), \mathbf{a}_2 = \frac{3}{2}a(\hat{i} - \frac{1}{\sqrt{3}}\hat{j}) \quad (2.2)$$

The lattice constant is equal to 2.46 Å. Moreover, the primitive vectors of the reciprocal lattice of graphene are:

$$\mathbf{b}_1 = \frac{2\pi}{3a}(\hat{i} + \sqrt{3}\hat{j}), \mathbf{b}_2 = \frac{2\pi}{3a}(\hat{i} - \sqrt{3}\hat{j}) \quad (2.3)$$

The reciprocal lattice of a triangular lattice of graphene is depicted in Figure 2.5(b). The first Brillouin zone (BZ) is a hexagon with the center of Γ -point and two inequivalent corners of K- and K'-points (Dirac points) which their positions in momentum space are:

$$K = \frac{2\pi}{3a}(\hat{i} + \frac{1}{\sqrt{3}}\hat{j}), K' = \frac{2\pi}{3a}(\hat{i} - \frac{1}{\sqrt{3}}\hat{j}) \quad (2.4)$$

Figure 2.5 (a) Honeycomb lattice of graphene and (b) its corresponding Brillouin zone. $\mathbf{a}_1$ and $\mathbf{a}_2$ are the lattice unit vectors. δ_i ($i=1,2, \text{ and } 3$) are the nearest-neighbor vectors. $\mathbf{b}_1$ and $\mathbf{b}_2$ are the primitive vectors of the reciprocal lattice. The Dirac cones are located at K and K' points. Figure is extracted with permission from Ref. [73].

While the π electrons are responsible for electronic properties at low energies, the energy bands far from Fermi level is defined by σ electrons. Graphene is a zero-gap semimetal because the conduction and valence bands meet at the Dirac point. As reported by Wallace *et al.*, the wave function of graphene can be expressed as linear combination of Bloch functions of sublattice A (B) [69]. Therefore, the energy eigenvalues, only considering the nearest neighbor integrations can be stated as [69, 73]:

$$E(\mathbf{k}) = \pm t \sqrt{3 + f(\mathbf{k})} - t' f(\mathbf{k}) \quad (2.5)$$

$$f(\mathbf{k}) = 2 \cos(\sqrt{3} k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2} k_y a\right) \cos\left(\frac{\sqrt{3}}{2} k_x a\right) \quad (2.6)$$

Here, t is the nearest-neighbor hopping energy and t' is the next nearest-neighbor hopping energy. k_x and k_y are the wave vectors in X- and Y-planes, respectively. Plus sign corresponds to upper (π^*) and the minus sign to lower (π) band. Figure 2.6 illustrates the energy dispersion in the honeycomb lattice. The upper and lower bands meet at K and K' where the energy dispersion vanishes (Fermi level). One can see that there is a linear dispersion relation near the Dirac points (within 1 eV of the Dirac energy). This relationship can be expressed as follows [69, 73]:

$$E(\mathbf{k}) = \pm v_f |\mathbf{k}| \quad (2.7)$$

Here, v_f is the Fermi velocity (10^6 m/s). This energy dispersion near the Dirac points makes the Fermions in graphene behave as massless electrons.

Figure 2.6 (a) Energy dispersion of graphene as a function of k_x and k_y . Left: Energy spectrum for $t = 2.7$ eV and $t' = -0.2t$. Right: Zoom in of the energy bands near the one the Dirac points. Figure is extracted with permission from Ref. [73].

2.2 Silicene

Silicene is the silicon equivalent of graphene. The name silicene was coined by Guzmán-Verri and Lew Yan Voon in 2007 [59]. However, the 2D hexagonal layers of silicon and germanium were first studied by Takeda and Shiraishi from first-principles in 1994 [74]. They found that while carbon prefers a flat 2D structure due to sp^2 hybridization, silicon and germanium desire corrugated structure due to the mixture of sp^2 and sp^3 hybridization. It can be argued that Si atoms have larger separation compared to C atoms, resulting in a weakening of the π bond [43]. This phenomenon can also be explained by pseudo Jahn-Teller effect with the coupling of the ground state to next one by a vibrational mode [75]. Figure 2.7 shows a monolayer of silicene with the corrugated arrangement of silicon atoms. The lattice constant of silicene was found to be 3.855 Å [74] and the Si-Si bond length is 2.28 Å [76]. Moreover, the buckling distance (Δ) of the Si atom was calculated to be 0.53 Å by Ding *et al.* [77], 0.44 Å by Cahangirov *et al.* [42],

and 0.45 Å by Lew Yan Voon *et al.* [45]. Similar to graphene, the linear π and π^* bands convergence is observable at the Fermi level of silicene's electronic structure [59, 78]. As a result, the charge carriers behave as massless fermions, bringing about high carrier mobility for silicene [59, 78]. However, the Fermi velocity was found to be 10^5 m/s for silicene, an order smaller than that for graphene [59].

Figure 2.7 Top and side view of the honeycomb lattice of silicene. The primitive cell is distinguished by the red rhombus. The two equivalent Si atoms, A and B, have a buckled arrangement. Δ is the buckling distance. Figure is extracted with permission from Ref. [12].

It should be noted that when the SOC is considered in the density functional theory (DFT) calculations, silicene is predicted to have a band gap of 1.55 meV [40] which is much higher than that of graphene (0.024 meV) [41]. Interestingly, heavy metals such as Au, Ti, Pb, and Hg are able to enhance SOC [79]. Also, decoration of silicene by transition metal can create new phases like quantum anomalous Hall state [80-83]. More

excitingly, a band gap can be opened at K-points of silicene by applying an electric field perpendicular to its plane because of the natural buckling of the sheet [12, 43, 84-86]. As a matter of fact, the electric field breaks the inversion-symmetry in the system because of the charge transfer between the top and bottom Si atoms. A sizable band gap can also be obtained by functionalization [45, 46, 87-93], surface adsorption [48, 49, 79, 94], substitution [51], substrate interaction [52, 53, 95, 96], defects [54, 97-101], *etc.*

Silicene is significantly less stable compared to 3D silicon bulk. Therefore, the experimental realization of silicene is very challenging in comparison with graphene. In 2010, Lalmi *et al.* reported the epitaxial growth of silicene on Ag (111) with nearly planar (0.02 nm of buckling distance) honeycomb structure and very short Si-Si bond lengths (0.2 nm) [102]. However, their results are severely doubted and were not reproduced by others [103]. In 2012, several groups in parallel reported the experimental synthesis of silicene. Vogt *et al.* [60], Lin *et al.* [104], Feng *et al.* [105], and Chen *et al.* [106] reported the growth of silicene on Ag (111), while, Fleurence *et al.* reported the synthesis of silicene on ZrBr₂ [107]. As underlined by Jamgotchian *et al.*, the final structure of silicene filmed is highly reliant on the temperature of the substrate [108]. Based on insights from theoretical studies, temperature fluctuations can create numerous grain boundaries due to the low diffusion and nucleation barriers of Ag (111) against Si [109]. Below 400 °K, Si atoms tend to form clusters or disordered structures on Ag (111) [105]. While, above 400 °K, silicene forms a variety of ordered phases with various superstructures on Ag (111): T phase, 4×4 , $\sqrt{13} \times \sqrt{13}$, $2\sqrt{3} \times 2\sqrt{3}$, and finally $\sqrt{3} \times \sqrt{3}$ phases with increasing substrate's temperature [60, 104-106]. One possible reason for these several ordered phases is the perfect matching between the reconstructed 3×3

silicene lattice (1.152 nm) and 4×4 supercell of Ag (111) (1.156 nm) [110]. The Si-Si bond lengths within the 3×3 supercell of silicene are close to those obtained for free-standing silicene (2.25 Å) [42]. However, the buckling distance is increased from 0.44 Å for free-standing silicene to 0.83 Å. Fukaya *et al.* confirmed these atomic arrangements using reflection high-energy positron diffraction (RHEPD) [111]. Fleurence *et al.* experimentally found that silicene grown on ZrB₂ has a band gap [107]. The induced strain on silicene caused by ZrB₂ film is the possible reason for this band gap. This work proposed that the degree of buckling which is affected by substrate controls the band gap. Therefore, it is feasible to tune the electronic structure of silicene by choice of the substrate owing to the structural flexibility of silicene [107].

As reported by Feng *et al.* [105], the preparation of silicene needs an ultra-high vacuum (UHV) chamber combined with a home-built low-temperature scanning tunneling microscopy (STM) owing to the high sensitivity of Si toward oxidation. The Ag (111) substrates were cleaned by repeated argon ion sputtering and annealing process. Si atoms were deposited from a pure Si source using thermal evaporation system. They found that several reconstructed phases can be obtained by carefully changing the temperature of the substrate. The $\sqrt{13}\times\sqrt{13}$, 4×4 , $\sqrt{7}\times\sqrt{7}$, and $\sqrt{3}\times\sqrt{3}$ reconstruction appeared on the Ag (111) when the temperature of the substrate is in the range from 400-530 °K, 400-470 °K, 470-530 °K, and a narrow temperature window higher than 530 °K, respectively, as shown in Figure 2.8.

Figure 2.8 Large scale (upper panels) and high resolution (lower panels) STM images of (a) $\sqrt{13} \times \sqrt{13}$, (b) 4×4 , and (c) $\sqrt{7} \times \sqrt{7}$ silicene superlattice on Ag (111). Red balls represent highly buckled. Figure is extracted with permission from Ref. [105] and [112].

Vogt *et al.* have also provided the compelling experimental evidence for successful silicene synthesis on Ag (111) [60]. Two major experimental techniques, angle-resolved photoelectron emission spectroscopy (ARPES) and STM, have been used to study the electronic structure of silicene. While the Ag substrate was kept at a temperature between 220-260 °C, the STM characterizations were performed at room temperature. They formed a 4×4 silicene layer on the Ag (111) surface, as shown in Figure 2.9. Figure 2.9(a) and (b) show the bare Ag (111) surface and 2D Si adlayer. Based on the model of silicene on Ag (111) in Figure 9 (c), silicene unit cells accord with

a 4×4 Ag (111)-(1 $\times$ 1) area. The obtained Si-Si bond length and buckling distances are 0.22 and 0.292 nm, respectively. Moreover, the linear dispersive bands were also observed by ARPES measurement.

Figure 2.9 The STM images of (a) the clean Ag (111)-(1 $\times$ 1) surface and (b) 4×4 silicene sheet. (c) Model of silicene on Ag (111). Figure is extracted with permission from Ref. [60]

Silicene monolayer has been also grown on other substrates such as Ir [113], Al [114], MoS₂ [115], ZrC [116], *etc.* From first-principles calculations, hexagonal boron nitride [12] and planar aluminum nitride [117] are introduced as promising candidates for being used as insulating growth substrates.

Figure 2.10 STM image of first 3×3 silicene layer on Ag (111) and three well-ordered terraces of silicene multilayers. Inset: LEED pattern of the surface. Figure is extracted with permission from Ref. [118]

Although monolayer of silicene can only survive for few minutes in the air, multilayers of silicene are resistant for at least 24 hours because an ultra-thin native oxide protects the rest of silicene film [119]. Multilayer silicene was grown epitaxially by

deposition of Si atoms on a 3×3 silicene layer-Ag (111) by Padova *et al.* [[118-121](#)]. Figure 2.10 presents STM image of silicene multilayers. They found that each layer of silicene has a $(\sqrt{3}\times\sqrt{3})R30^\circ$ symmetry found by low energy electron diffraction (LEED) system. They also proposed that Si layers are van der Waals (vdW) packed in multilayer silicene [[118](#)]. More excitingly, they revealed that the multilayer silicene host Dirac fermions [[121](#)]. Nevertheless, Mannix *et al.* showed that the structure of multilayer of silicene is identical to bulk silicon [[122](#)].

Asymmetry owing to A and B sublattices as well as reconstructions can eventually result in opening a band gap [[107](#)]. The reactivity of silicene is expected to be more than that of graphene to the partially sp^3 hybridization. Ergo, the band gap opening can be further facilitated by hydrogenation of silicene. There have been quite a number of experimental studies on the hydrogenation of silicene in the literature [[123-127](#)]. Qiu *et al.* studied the hydrogenation of monolayer of (3×3) silicene sheet on Ag (111) using STM and DFT calculations [[123](#)]. Their proposed theoretical method was perfectly matched with the experimental results, as shown in Figure 2.11. Interestingly, clean silicene layer can be fully recovered by increasing the temperature to 450 °K.

Figure 2.11 (a) STM image of the hydrogenated (3×3) silicene. The white rhombus represents a unit cell of the structure. (b) The clean silicene surface which is fully recovered after annealing at 450 °K. (c) Structural model and simulated STM image of hydrogenated silicene. Figure is extracted with permission from Ref. [123].

SiNR have also been synthesized on Ag (110) and Au (110) surfaces [110, 128-130]. Highly uniform single nanoribbons with a width of 1.7 nm arranged in a parallel have already been grown on Ag (110) surface by Aufray *et al.*, as shown in Figure 2.12 [128]. They found that the achieved nanoribbons are compressed by 13% along their edge, in comparison with DFT calculations, and are asymmetric across their width because of the difference in the periodicity of silicene and Ag. In two different studies, Kara *et al.* [131] and Lian *et al.* [132] employed DFT calculations and suggested that the

achieved nanoribbons are zigzag SiNR (ZSiNR) with a width of 4 and armchair SiNR (ASiNR) with a width of 8, respectively. However, the latter agrees better with the experiment.

Figure 2.12 STM image of parallel SiNRs grown on Ag (110) surface. Figure is extracted with permission from Ref. [128].

The practical applications of silicene were already revealed by Akiwande *et al.* [133]. They fabricated a silicene FET with room temperature mobility of $100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The schematic of the fabrication process of a FET with silicene channel and Ag electrodes is shown in Figure 2.13. After epitaxial growth of silicene on Ag (111) on mica, the Al_2O_3 capping layer was deposited *in-situ*. Then, the structure was detached and flipped. Next, the encapsulated silicene was transferred onto a SiO_2 substrate, and the source and drain contacts were formed by electron beam lithography followed by etching

to produce back-gate silicene FET. Their encapsulated delamination transfer method and native Ag contacts preserve silicene during the fabrication process. The low carrier density and high gate modulation compared to graphene suggest a small band gap for silicene [133].

Figure 2.13 Schematic of silicene FET fabrication process. Figure is extracted with permission from Ref. [133].

2.3 Germanene

Germanene, the germanium-based cousin of graphene, was first predicted by Takeda and Shiraishi [74] in 1994. They believed that the planar germanene might not exist [74] and its stability has been questioned by contradictory phonon dispersion data [42, 134, 135]. Cahangirov *et al.* discovered that low-buckled germanene seems to be stable and behaves as a semi-metal [42]. The Ge-Ge bond length and buckling distances are 2.38 and 0.64 Å, respectively [42]. The electronic structure of germanene is quite similar to that of graphene and silicene [42, 59, 74]. Germanene is ambipolar and hosts massless Dirac fermions [42]. More interestingly, the Fermi velocity of germanene is $5.6 \times 10^5 \text{ ms}^{-1}$ and carrier-phonons interactions are 25 times less than graphene [136]. Germanium has a much stronger SOC compared to silicon and carbon due to the larger atomic number of

germanium. A small buckling distance will increase the SOC by the orders of magnitude which lead to a small band gap at the Dirac points. The SOC band gap in germanene is 23.9 meV which is much larger than that of graphene (0.024 meV) and silicene (1.55 meV) [40, 41, 137-139]. More excitingly, giant magnetoresistance [140], quantum spin Hall [141, 142], quantum anomalous Hall [83, 143], quantum spin/valley effects [144], and large thermoelectric figure of merit [145] have been reported for germanene.

Hydrogen-terminated germanene (GeH or germanane) was first synthesized from the topochemical deintercalation of CaGe_2 [146]. It was found that germanene is very stable at ambient conditions and only oxidizes after several months. To date germanene has been reported to be grown on various substrates such as Pt (111) [147], Au (111) [27], Al (111) [148], Cu (111) [149], and AlN/Ag (111) [150]. The first paper on the synthesis of germanene was published by Li *et al.* in 2014 [147]. They reported the growth of germanene on Pt (111). Ge atoms were deposited using an electron-beam evaporator under UHV and at room temperature, and then the Pt substrate was annealed at a temperature in the range of 600-750 °K for 30 min. They found that the germanene has a $\sqrt{19} \times \sqrt{19}$ superstructure with a buckling distance of 0.6 Å as obtained by STM and LEED. Figure 2.14 presents the STM image of the germanium adlayer formed on Pt (111) surface. It is important to mention that the STM image is not at atomic resolution; however, it could provide the atomic model of germanene. The value of the periodicity for the obtained structure (12 Å) is close to the lattice constant of the germanene 3×3 superlattice (11.91-12.06 Å).

Figure 2.14 (a) Large-scale STM image of a $\sqrt{19} \times \sqrt{19}$ superstructure of the germanene on Pt (111) surface. (b) Zoomed-in STM image. (c) Line profile along the dashed line in (b), showing the periodicity of the germane. Figure is extracted with permission from Ref. [147]

Davila *et al.* have grown germanene on Au (111) using molecular beam epitaxy (MBE) and characterized their samples by STM and LEED [27]. The $\sqrt{3} \times \sqrt{3}$ reconstructed germanene layer with a flat honeycomb structure in conjunction with a $\sqrt{7} \times \sqrt{7}$ reconstructed Au (111) supercell was identified by synchrotron radiation core-level spectroscopy and advanced DFT calculations. Bampoulis *et al.* also discovered that the deposition of few monolayer of Pt on Ge (110) and subsequently annealing the sample at 1100 °K forms Pt/Ge crystals which have a honeycomb structure at the outermost layer [151]. The buckling distance and nearest-neighbor distance of the obtained germanene are 0.2 and 2.5 ± 0.1 Å, respectively [151]. The scanning tunneling spectra revealed that the germanene shows a metallic behavior due to the hybridization of electronic states of germanene with the underlying substrate. Recently, d’Acapito *et al.* have deposited germanene on Ag (111) with AlN buffer layer [150]. The germanene

produces a 4×4 superstructure with respect to AlN buffer layer, and the Ge-Ge bond length is 2.38 Å which is equal to the bond length of freestanding germanene. On the other hand, the deposition of Ge atoms on Ag (111) will lead to formation of the bulk of Ge [150]. Zhang *et al.* reported the successful synthesis of germanene on MoS₂ [152] which is a band gap material. It was discovered that germanene islands prefer to nucleate at preexisting defects of MoS₂ substrate. In addition to the V shape π bands at the K points, two parabolic bands cross the Fermi level at Γ point and subsequently suppress the 2D Dirac properties [152].

2.4 Comparing Properties of Graphene, Silicene, and Germanene

In this section, the properties of the group IV honeycomb crystals graphene, silicene, and germanene are compared. This comparison could provide insight into the potential applications of these materials.

The atomic weight of group IV (C→Si→Ge) increases from top to bottom (12.01→28.08→72.64), signifying a considerable increase of relativistic effects on the motion of the electrons. As mentioned before, unlike flat graphene sheet, silicene and germanene honeycomb lattices are buckled [45]. The bond lengths (d), lattice constants ($a = \sqrt{3}d$), and buckling distances (Δ) of graphene, silicene, and germanene are listed in Table 2.1. It is clear that all these parameters increase along the row graphene, silicene, and germanene.

Although, C atoms in planar graphene sheet have sp^2 bonding, Si atoms in silicene and Ge atoms in germanene have sp^2 - sp^3 bonding. The deviation from pure sp^2 hybridization brings about the corrugation in the structure. The sp^3 character augments

along the row C, Si, and Ge, resulting in highest buckling distance for germanene followed by silicene [153].

The Fermi velocities of graphene, silicene, and germanene calculated by Heyd-Scuseria-Ernzerhof 06 (HSE06) functional [154-156] are summarized in Table 2.1. As can be seen, the Fermi velocity decreases along the row graphene, silicene, and germanene. The Fermi velocity obtained by HSE06 ($1.01 \times 10^6 \text{ m/s}$) for freestanding graphene is comparable to that obtained experimentally ($1.1 \times 10^6 \text{ m/s}$) [157]. However, the value of Fermi velocity for silicene grown on Ag (111) was found to be $1.3 \times 10^6 \text{ m/s}$ [60] which is larger than the theoretical value ($0.65 \times 10^6 \text{ m/s}$) most probably because of the silicene-substrate interactions.

Without the SOC, all the aforementioned 2D structures are zero-gap semiconductors with linear dispersion around K point, as shown in Figure 2.15. The SOC can induce a substantial band gap in silicene (1.55 meV) [40] and germanene (23.9 meV) [40], as shown in Figure 2.15. However, the SOC-induced band gap in graphene is tiny (0.024 meV) [41]. These gaps for silicene and germanene will result in massive Dirac particles around K point because of a direct relationship between effective mass and the band gap:

$$m^* = \frac{E_g}{2v_F^2} \quad (2.8)$$

The dispersion relation of massive Dirac relativistic particles near K point can be expressed as:

$$\varepsilon_{\pm}(\mathbf{k}) = \pm \sqrt{\left(\frac{E_g}{2}\right)^2 + (\hbar v_F \Delta \mathbf{k})^2} \quad (2.9)$$

Here, $\Delta \mathbf{k}$ is the derivation of the 2D wavevector from its value, as shown in the insets of Figure 2.15.

Figure 2.15 Band structures of (a) graphene, (b) silicene, and (c) germanene using the HSE06 functional with spin-orbit interaction. The inset shows a magnification of the electronic band structure around the Dirac obtained without SOC (solid black lines). Figure is extracted with permission from Ref. [153].

The total thermal conductivity κ of a system is defined as:

$$\kappa = \kappa_e + \kappa_p \quad (2.10)$$

where κ_e and κ_p are the electron and phonon contributions, respectively. The thermal conductivity of silicene (9-65 $\text{Wm}^{-1}\text{K}^{-1}$) is much lower than that of graphene (1500-5500 $\text{Wm}^{-1}\text{K}^{-1}$) owing to short phonon mean-free path in silicene [158]. In other words, multitude scattering centers are available for acoustic phonons in silicene which lead to a lower thermal conductivity. The thermoelectric effect is the conversion of the temperature difference to an electric current, and its efficiency is evaluated by the thermoelectric figure of merit ZT [145]:

$$ZT = \frac{\sigma S^2 T}{\kappa} \quad (2.11)$$

where σ is the electrical conductance, S represents Seebeck coefficient, and T is the absolute temperature. While a material with $ZT \approx 1$ can be considered as a good thermoelectric material, materials with ZT approaching or larger than three could rival the conventional energy conversion techniques [159]. It is clear that a material with large σ and S and low κ have a higher ZT . It is found that graphene is not an efficient thermoelectric material owing to its high κ [145, 159, 160]. Nevertheless, silicene and germanene could be promising materials for the next generation energy conversion technologies not only for their low κ but also for their excellent compatibility with silicon-based devices. The ZT of silicene is predicted to be ~ 1.88 , however it could be increased up to 2.8 by appropriate n- and p-type doping of the SiNRs [159]. More excitingly, this value can be further increased to 4.9 if the applied temperature is enhanced to 600 °K [159].

In order to assess the mechanical properties of graphene, silicene, and germanene, their in-plane stiffness and shear modulus are also collected in Table 2.1. From graphene to silicene to germanene, the stiffness and the shear modulus decrease. Graphene shows an exceptional mechanical strength because of the sp^2 hybridization of carbon atoms in the structure [161]. Hu *et al.* reported the superior mechanical flexibility of silicene compared to that of graphene [162]. Hence, silicene holds great promise in flexible nanoelectronics.

Table 2.1 Structural, electronic, and mechanical parameters of graphene, silicene, and germanene

	Graphene (C)	Silicene (Si)	Germanene (Ge)
Lattice Constant a (Å)	2.45-2.47 [73, 153, 163]	3.86-3.91 [42, 153, 164, 165]	4.06-4.10 [135, 147, 153]
Bond Length d (Å)	1.41-1.43 [73, 153, 163]	2.22-2.26 [42, 153, 164]	2.34-2.45 [135, 147, 153]
Buckling Distance Δ (Å)	0.00 [153, 166]	0.45-0.55 [42, 97, 153, 165]	0.66-0.69 [42, 147, 153, 167]
Effective Electron Mass $m^*(m_0)$	0.00 [153]	0.001 [153]	0.007 [153]
Fermi Velocity v_f (10^6 ms^{-1})	1.01 [153]	0.65 [153]	0.62 [153]
Energy gap E_g with SOC (meV)	0.024 [41, 153, 166]	1.55 [12, 40, 43, 153, 168]	23.9 [40, 142, 153, 169]
Cohesive Energy (eV/atom)	7.37-7.81 [170]	4.57-5.12 [171]	3.09 [170]
Bulk Cohesive Energy (eV/atom)	7.37 [172]	4.63 [172, 173]	3.85 [172]
In-plane Stiffness C (Jm^{-2})	-	100 [161]	53 [161]
Shear Modulus (Nm^{-1})	135.01 [174]	28.64 [174]	18.76 [174]
Thermal Conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)	1500-5500 [175, 176]	9-65 [177]	-

2.5 Two-dimensional Based Gas Molecules Sensors

2D nanomaterials show huge promise in the development of ultrahigh sensitive and low-power consumption gas sensors because of their exceptional properties such as ultra-large surface-to-volume ratio, high surface activities, excellent conductivity, and high sensitivity to external stimulants [15-17, 178, 179]. Up to now, the sensing capability of different 2D materials such as graphene [180-182], MoS₂ [183-189], WS₂ [190-193], MoSe₂ [194-196], MoTe₂ [197], SnS₂ [198, 199], VS₂ [200], WO₃ [201], ZnO [202, 203], NiO [204], black phosphorus [205-208], hexagonal boron nitride (h-BN) [209], and graphitic carbon nitride (g-C₃N₄) [210] toward various gas molecules detection have been experimentally investigated.

2.5.1 Gas-sensing Mechanism for 2D Layered Nanomaterials

The sensing mechanism of 2D materials is based on charge transfer between adsorbates and adsorbents [186-188, 211]. Upon exposure to reactive gases, the resistance of the

sensors changes due to the adsorption of the gas species on the surface of sensing materials. However, the resistance of the sensors reverts upon exposure to the air or an inert environment because of desorption of gas species from the sensing materials. A typical example of this mechanism is the interactions between gas molecules (NO_2 and NH_3) with CVD-grown monolayer MoS_2 (n-type semiconductor) [188]. Upon adsorption of NO_2 molecule, an unpaired electron of N atom in NO_2 behaves as strong oxidizer and tends to withdraw electrons from the MoS_2 , as shown in Figure 2.16 (a). This charge transfer induces a reduced carrier concentration and consequently degraded electrical conductivity. On the other hand, NH_3 has a lone electron pair which makes it to acts as an electron donor. Therefore, the electrons are transferred from NH_3 to the conduction band of MoS_2 , leading to an increased carrier concentration and enhanced electrical conductivity in MoS_2 , as presented in Figure 2.16 (b).

The sensitivity of a sensor can be expressed as:

$$S = \frac{R_g - R_{N_2}}{R_{N_2}} \quad (2.12)$$

Here, R_g and R_{N_2} are the values of sensor resistance under target gas and in N_2 dry environment, respectively. In principle, gas molecules could interact with solid surfaces *via* either the vdW attraction or a chemical reaction. Although both would vary the conductance of the solid, the vdW interaction could be used for the gas sensing applications, while the chemical reaction would be more suitable for catalysis.

Figure 2.16 Schematics of the charge transfer processes for a monolayer of MoS₂ in the presence of (a) NO₂ and (b) NH₃ molecules. Figure is extracted with permission from Ref. [188].

2.5.2 Configurations of Gas-sensing Devices

The chemiresistor-type gas sensor is the class of chemical sensor in which the resistance of the sensing material changes as a result of chemical interactions with analytes. Simple fabrication, easy operation, and direct measurements are the main advantages of this type of sensor [212-214]. A typical structure of a chemiresistive gas sensor is illustrated in Figure 2.17. This sensor was fabricated by dropping the dispersed solution containing sensing materials onto a ceramic plate which was previously coated with Au electrodes and RuO₂ layer as heater using screen printing techniques [215]. This type of gas sensors has been widely used for several gas species such as NO₂, NH₃, H₂S, H₂, ethanol (C₂H₆O), formaldehyde (CH₂O), *etc* [185, 198, 199, 208, 210, 211, 215-234].

Figure 2.17 (a) The schematic illustration of a chemiresistive gas sensor. Photographs of (b) the blank sensor and (c) the sensors coated with the sensing material. Figure is extracted with permission from Ref. [215].

Another important type of electronic gas sensor is FET [235]. The drain current (I_{DS}) of a FET-based sensor is governed by the gate voltage (V_G) and it can be effectively tuned upon exposure of gas molecules. The on/off current ratio defines the performance of a FET-based gas sensor. The higher on/off current ratios usually offer higher sensitivity [236]. Various 2D nanomaterials have shown potential to be served as channel materials for FET-based gas sensors owing to their outstanding semiconducting properties and large lateral size [183, 184, 186, 187, 189, 194, 206, 237-245]. Figure 2.18 (a) presents a schematic diagram of the MoS₂ FET-based sensor for detection of NO₂ and NH₃ [187]. The optical image of the device with Ti/Au electrodes and the MoS₂ channel is shown in Figure 2.18 (b). Upon exposure to reactive gas molecules, they are adsorbed on the surface of the MoS₂, resulting in a change of the charge carrier concentration. This

alternation could be monitored by measuring the current variations. Figure 2.18 (c) and (d) plots I_{DS} - V_{DS} of the device upon exposure to 400 parts per billion (ppb) of NO_2 and 500 parts per million (ppm) of NH_3 . The device was initially turned on ($V_G = 30$ V) and turned off ($V_G = 0$ V) before NO_2 and NH_3 exposure, respectively. A conductance decrease (increase) by a factor of 174 (1218) has been observed after exposure to NO_2 (NH_3). Figure 2.18 (e) and (f) illustrates the real time conductance variations of the MoS_2 -based FET toward exposure to NO_2 and NH_3 at different concentrations. A sufficiently large response $\sim 20\%$ (40%) was obtained for 20 ppb (1 ppm) of NO_2 (NH_3) [187].

Figure 2.18 (a) Schematic and (b) optical image of the MoS_2 -based FET with Ti/Au electrodes and back-gate. The dotted triangle in (c) indicates the MoS_2 flake. Conductance changes of the device upon exposure to (a) 400 ppb of NO_2 and (d) 500 ppm of NH_3 . In (c), the device was turned on at $V_G = 30$ V, and the device turned off at $V_G = 0$ in (d). Real-time conductance changes of the device as a function of time of exposure to (e) NO_2 and (f) NH_3 at different concentrations. Figure is extracted with permission from Ref. [187].

2.5.3 Graphene-based Gas Sensors

Graphene-based nanosensors have drawn massive attention due to graphene's high surface-volume ratio, low electronic temperature noise, remarkably high carrier mobility, high chemical and thermal stability, and fast response time [180-182, 246]. These astonishing properties of graphene make it ultrasensitive to gas adsorption even down to a single molecule [247, 248]. The potential application of graphene for gas sensors has been widely studied experimentally [219, 237, 238, 249-251] and theoretically [55-57, 182, 252-254]. In 2007, Novoselov *et al.* developed a gas sensor using mechanically exfoliated graphene with a limit of detection down to the ppb level [249]. Although the quality of the graphene prepared by the mechanical exfoliation method is high, the size of the produced films is usually below $1000\mu\text{m}^2$. High quality and large area graphene can be obtained using CVD method. In 2015, Jang *et al.* fabricated a self-activated transparent CVD graphene-based gas sensor with endurance to mechanical bending and humidity [237]. Figure 2.19 (a) and (b) shows the fabrication procedure and the photograph of the sensor, respectively. First, the CVD-grown graphene on Cu foil was patterned. Then, poly (methyl methacrylate) (PMMA) was coated on top of the patterned graphene in order to protect it through the transfer step. Subsequently, the Cu foil was removed using FeCl_3 etchant, and the patterned graphene was transferred onto a polyimide (PI) substrate. Finally, the PMMA was removed using acetone and subsequent heat treatment. Upon exposure to three consecutive pulses of NO_2 at 5 ppm, the device indicated an improvement in its recovery and response time with increasing bias voltage, as presented in Figure 2.19 (b). The performance of the sensor in dry (0% RH) atmosphere was compared with that in humid (50% RH) atmosphere, as shown in

Figure 2.19 (c). It was revealed that the impact of humidity on the performance of the device is negligible. Because of the graphene's flexibility, the fabricated sensor presented a reliable operation under mechanical bending, as displayed in Figure 2.19 (d).

Figure 2.19 (a) Fabrication procedure of CVD graphene-based gas sensor. (b) Photograph of the device. (c) Response curves of the device to three consecutive pulses of 5 ppm NO_2 (c) under the increased bias voltage, (d) under 0% and 50% humidity conditions at 60 V, and (e) without and with the bending strain. Figure is extracted with permission from Ref. [237].

The pristine graphene shows low sensitivity to common gas molecules [55-57] which limits its potential for detection of the individual gas molecule [255, 256]. Graphene oxide (GO) as a cost-effective method for mass-producing of graphene-based devices [257-259] contains an abundance of reactive sites for gas adsorption (oxygen contacting functional groups) [260-262]. However, it is almost insulator which limits its practical application in electronic devices. Chemically reduction processes can partially restore the conductivity of GO. Excitingly, the reduced GO (rGO) contains some defects and vacancies which could act as adsorption sites [263-265]. The high-performance gas sensors based on rGO have been developed [220-223, 255, 266]. Functionalization of graphene with micro/nanomaterials has been proven to be an effective approach to further

improve the sensing performances of the graphene thank to the diverse functionalities and synergistic effects in the composites. To this reason, various functional materials such as metals [[224-226](#), [267-270](#)], metal oxides [[214](#), [227](#), [228](#), [239](#), [271](#)], CNTs [[240](#)], polymers [[229-231](#), [241](#), [272](#), [273](#)] have been incorporated into graphene structures.

CHAPTER 3

Methodology

Computational materials science expands our understating of the properties of new materials and phenomena related to their design, synthesis, and processing, and also provides new insights into their experimental processes that might otherwise be difficult to obtain. Classical mechanics fails in describing the physical and electronic properties of nanoscale systems such as atoms, molecules, condensed phase materials, *etc.* Hence, quantum mechanics developed out of this failure to adequately describe such systems. Nonetheless, the application of quantum mechanics to real-world systems having a myriad of atoms results in mathematical equations that seem unsolvable by traditional methods. Model simplifications, accurate approximations, and new formalism help us to predict the properties of the complex systems with high accuracy. Nowadays, these predictions can be accomplished using first-principles that calculate physical quantities without utilizing assumptions such as empirical or fitted parameters. The only required inputs for these calculations are atom species and approximate atomic positions. One of the most famous examples is ab *initio* quantum mechanical calculations which are based on the use of Schrödinger's equation within a set of approximations and are independent of any experimental data. In this dissertation, I employed first-principles method based on non-equilibrium Green's function (NEGF) combined with DFT. In this chapter, the basic principles behind these powerful tools are introduced.

3.1 Density Functional Theory

As we know from quantum mechanics, all information about a given system is contained in its wave function, Ψ . The wave function for a single electron moving in a potential energy $V(r)$ is calculated from nonrelativistic Schrödinger's equation:

$$\hat{H}\Psi(r) = \left[-\frac{\hbar^2 \nabla^2}{2m} + V(r)\right]\Psi(r) = E\Psi(r) \quad (3.1)$$

Here, $\hat{H}$ is the Hamiltonian operator, r is the position vector, $\hbar$ is the reduced Planck constant, m is particle mass, ∇^2 is the Laplacian, and E is the energy of state Ψ . For more than one electron (multi-body problems) the Schrödinger's equation becomes:

$$\begin{aligned} & \left[\sum_i^N \left(-\frac{\hbar^2 \nabla_i^2}{2m} + V(r_i) \right) + \sum_{i < j} U(r_i, r_j) \right] \Psi(r_1, r_2, \dots, r_N) \\ & = E \Psi(r_1, r_2, \dots, r_N) \end{aligned} \quad (3.2)$$

Here, N is the number of electrons and $U(r_i, r_j)$ is electron-electron interaction. Numerous powerful methods for solving Schrödinger's equation for multi-body problems have been developed; however, it seems impossible to apply them to large and complex systems. DFT provides a way of reducing this problem to three spatial dependencies by presenting precise simplifications and approximations which will be introduced in the following sections. The DFT method was first introduced in two influential papers in the 60's [274, 275]. Walter Kohn was awarded the Nobel Prize in Chemistry in 1998 for his development of the DFT.

3.2 Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is defined based on the nuclei-electrons interactions. Because the nuclei are considerably more massive than electrons, the response of electrons to the nuclear motion is instantaneousness. It is reasonable to consider the position of the nucleus fixed when calculating the electronic wavefunctions. As a result, the wavefunctions of a molecule can be separated into nuclear and electrons [276]:

$$\Psi_{total} = \psi_{electronics} \times \psi_{nuclear} \quad (3.3)$$

Furthermore, the nuclear degrees of freedom in the Hamiltonian are eliminated:

$$\hat{H} = T_e + V_{n \Leftrightarrow e} + V_{e \Leftrightarrow e} \quad (3.4)$$

Here, V and T denote potential energy and kinetic energy, respectively. Moreover, e and n represent electron and nuclear interaction, correspondingly. It is worth nothing that the Born-Oppenheimer approximation alone is not adequate to solve the Schrödinger's equation, and further simplifications are necessary.

3.3 Hohenberg-Kohn Theorems

The two theorems proved by Hohenberg and Kohn in 1964 [274], make DFT existence possible. The first Hohenberg-Kohn theorem states that the external potential is a unique function of the electron density $\rho(r)$. It means that the ground state wavefunction ψ and total energy $E[(\psi)]$ of a system can be distinctively determined by the ground state electron density:

$$E[(\psi)] = E[\rho(r)] \quad (3.5)$$

The second theorem indicates that the ground state electron density is the exact density that minimizes the total energy. In other words, if Schrödinger's equation is solved for the ground state electron density, the corresponding wavefunction can be determined. In this way, the unobservable wavefunction is interpreted by the observable electron density which is the number of electrons at a specific location. As a result, the system can be fully described. Although the Hohenberg-Kohn theorems are tremendously powerful, the ground state density cannot be computed using them.

3.4 Kohn-Sham Equations

The Kohn-Sham theorem offers an amazing way to compute the electron density by solving the Schrödinger's equation of a fictitious system of non-interacting particles in the form of [\[275\]](#):

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + V_{eff}(r)\right] \psi_\alpha(r) = \varepsilon_\alpha \psi_\alpha(r) \quad (3.6)$$

Here, ε_α is the orbital energy of the corresponding Kohn-Sham orbital, ψ_α . Furthermore, $V_{eff}(r)$ represents the Kohn-Sham potential in which the non-interacting particles move and has three contributions:

$$V_{eff}(r) = V_H(r) + V_{xc}(r) + V_{ext}(r) \quad (3.7)$$

The first two terms are related to the interactions with other electrons. $V_H(r)$ is the Hartree potential owing to the mean-field electrostatic interaction, and $V_{xc}(r)$ represents the exchange-correlation potential caused by the quantum mechanical nature of the electrons. The Hartree potential as classical electrostatic potential can be calculated from the electron density:

$$\nabla^2 V_H(r) = -4\pi\rho(r) \quad (3.8)$$

Additionally, the exchange-correlation potential is:

$$V_{xc}(r) = -\frac{\delta E_{xc}(\rho)}{\delta\rho(r)} \quad (3.9)$$

Here, $E_{xc}(\rho)$ represents the exchange-correlation energy which will be introduced in detail later. The third term $V_{ext}(r)$ is associated with any other electrostatic interactions in the system. This term can be caused by the ion potentials (described by norm-conserving pseudopotentials) and electrostatic interactions with the external electrostatic field. Pseudopotential is an attempt to simplify the calculations by replacing the effects of core electrons of an atom with an effective potential. This approximation was first introduced by Hans Hellmann in 1934 [277]. As can be seen in Figure 3.1 [278], the wave function oscillates rapidly in the core electrons region because of the strong ionic potential. By replacing the real potential (red solid line) with a weaker pseudopotential (blue dashed line), a pseudo wavefunction with a smooth curve is constructed [278].

As a result, the Kohn-Sham theorem considers a fictitious system of non-interacting particles within an effective potential to study a real system in which particles interact within an external potential [279].

Figure 3.1 A potential and its corresponding wavefunction of all-electron (blue) compared to that of pseudoelectron (red). Here, r_c is the radius at which all-electron and pseudopotential values match [278].

3.5 Electron Density

The electron density of a closed or periodic system with N -particles can be defined based on the occupied eigenstates as:

$$\rho(r) = \sum_{\alpha=1}^N |\psi_{\alpha}(r)|^2 f\left(\frac{\epsilon_{\alpha} - \epsilon_f}{kT}\right) \quad (3.10)$$

Here, $f(x) = 1/(1 + e^x)$ is the Fermi function, ε_f is the Fermi energy, T is the electron temperature, and k is the Boltzmann constant. Conveniently, electron density can be presented in term of density matrix (D_{ij}):

$$\rho(r) = \sum_{\alpha} D_{ij} \phi_i(r) \phi_j(r) \quad (3.11)$$

where D_{ij} is defined by basis set expansion coefficients

$$D_{ij} = \sum_{\alpha} c_{\alpha i}^* c_{\alpha j} f\left(\frac{\varepsilon_{\alpha} - \varepsilon_f}{kT}\right) \quad (3.12)$$

Moreover, the electron difference density can be calculated by comparing the electron density with a superposition of atom based densities:

$$\Delta\rho(r) = \rho(r) - \sum_{\mu} \rho^{atom}(r - r_{\mu}) \quad (3.13)$$

3.6 Total Energy

The Kohn-Sham potential and electron density are self-consistently calculated up until the electron density which minimizes the total energy found. The total energy of a system as a function of electron density is expressed as follows:

$$E(\rho) = T(\rho) + E_H(\rho) + E_{ex}(\rho) + E_{xc}(\rho) \quad (3.14)$$

Here, $T(\rho)$ is the kinetic energy of non-interacting particles which is described as:

$$T_s(\rho) = \sum_{\alpha=1}^N \int dr \psi_{\alpha}^*(r) \left(-\frac{\hbar^2}{2m} \nabla^2\right) \psi_{\alpha}(r) f\left(\frac{\varepsilon_{\alpha} - \varepsilon_f}{kT}\right) \quad (3.15)$$

$E_H(\rho)$ is the Hartree energy which can be expressed as:

$$E_H(\rho) = \frac{e^2}{2} \int dr \int dr' \frac{\rho(r)\rho(r')}{|r-r'|} \quad (3.16)$$

$E_{ext}(\rho)$ is the energy related to interactions with the pseudopotential ions and other electrostatic external potentials and given by:

$$E_{ext}(\rho) = \int dr V_{ext}(r) \rho(r) \quad (3.17)$$

3.7 Exchange-correlation Energy

The quantum mechanical effect of the other electrons in the system is included in the exchange-correlation energy term. There are various approximations for the exchange-correlation energy. The choice of the appropriate functional greatly depends on the system at hand. Experience and benchmarking are required to find the best choice. The local density approximation (LDA) is the lowest rung on Jacob's ladder of approximations [280, 281], in which the exchange-correlational energy depends only on the electronic density at a point in space [275]. The LDA for the exchange-correlation energy is given by:

$$E_{xc}^{LDA}(\rho) = \int \rho(\vec{r}) \varepsilon_{xc}(\rho(r)) dr \quad (3.18)$$

Here, $\varepsilon_{xc}(\rho(r))$ is the exchange-correlation energy of a homogeneous electron gas with density of $\rho(r)$.

Although the exact exchange energy for the homogeneous electron gas, so-called Dirac-Block exchange, can be calculated, the correlation energy needs some approximation to be calculated. To this end, a number of approximations such as Perdew-Zunger (PZ) [282] and Perdew-Wang (PW) [283], and Vosko-Wilk-Nusair (VWN) [284] have been used.

The generalized gradient approximation (GGA) is a functional in which both the density and its gradient at each point are considered. With this additional information, GGA is usually more accurate than LDA. The GGA for the exchange-correlation energy is:

$$E_{xc}^{GGA}(\rho) = \int \rho(\vec{r}) \varepsilon_{xc}(\rho(r), \nabla \rho) dr \quad (3.19)$$

Here, $\varepsilon_{xc}(\rho(r), \nabla \rho)$ is the exchange-correlation energy as a function of density and its gradient. Different parameterizations of GGA are reported in the literature such as Perdew-Wang 1991 (PW91) [285], Perdew-Burke-Ernzerhof (PBE) [286], and BLYP (from the name Becke for the exchange part and Lee, Yang and Parr for the correlation part) [287, 288]. Another functional is meta-GGA which uses the Laplacian of the density in addition to the density and its gradient. The Tao-Perdew-Staroverov-Scuseria (TPSS) is a function of this type [289]. Hybrid functionals are another class of approximations to the exchange-correlation energy that uses a fraction of exact exchange from Hartree-Fock theory as well as exchange and correlation from other sources such as *ab initio* or empirical. B3LYP (Becke, 3-parameter, Lee-Yang-Parr) is one the most frequently used functionals of this type [290, 291]. The exchange-correlation energy of B3LYP functional is expressed as:

$$E_{xc}^{B3LYP} = E_x^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + E_c^{LDA} + a_c(E_c^{GGA} - E_c^{LDA}) \quad (3.20)$$

Here, a_0 , a_x , and a_c are 0.20, 0.72, and 0.81, respectively. E_x^{LDA} and E_x^{GGA} are the exchange energies of LDA-VWN [284] and GGA-Beke 88 [287], correspondingly. E_c^{LDA} and E_c^{GGA} represent the correlation energies of LDA-VWN and GGA-Beke 88 functionals, respectively. E_c^{HF} is the Hartree-Fock energy which can be expressed as:

$$E_x^{Hf} = -\frac{1}{2} \sum_{i,j} \iint \psi_i^*(r_1) \psi_j^*(r_1) \frac{1}{r_{12}} \psi_i(r_2) \psi_j(r_2) dr_1 dr_2 \quad (3.21)$$

3.8 Self-consistent Loop in DFT

A schematic representing a self-consistent loop in DFT method for obtaining electron density is illustrated in Figure 3.2. First, an initial guess for the electron density is assumed. By repetitively solving the Kohn-Sham equations using the appropriate exchange-correlation functional, one can obtain a self-consistent solution that minimizes the total energy, resulting in a desired ground state electron density.

Figure 3.2 A flow chart of the iteration scheme in DFT method for calculating electron density and total energy.

3.9 Transport Properties

In order to investigate the electronic structure and electronic transport for systems connected to semi-infinite electrodes under a voltage bias, the DFT combined with NEGF method is used. The detailed explanation of this method can be found in the literature [292-295]. The device system is divided into three regions: two electrode regions (left and right) and a central region, as illustrated in Figure 3.3.

Figure 3.3 Geometry of a device configuration with two electrodes. The system is periodic in the left and right electrodes. The central region is seamlessly connected to the electrodes. The parts of the central region where the atoms have the same arrangement as the electrodes are called the left and right electrode extension. Figure is extracted from Ref. [296].

The system is periodic in the left and right electrodes. To match the effective potential of the central region with bulk electrodes, the perturbation of the scattering region should be screened out. To this end, a sufficient fraction of the electrode regions should be repeated in the central region. As a result, the effective potential of the outermost part of the central region is similar to that of bulk electrodes.

To calculate the non-equilibrium electron distribution in the central region, the NEGF method is employed. First, the density matrix is divided into left and right contributions:

$$D = D^L + D^R \quad (3.22)$$

where $D^{L(R)}$ is calculated using NEGF theory by [293]

$$D^{L(R)} = \int \rho^{L(R)}(\varepsilon) f\left(\frac{\varepsilon - \mu_{L(R)}}{k_B T_{L(R)}}\right) d\varepsilon \quad (3.23)$$

Where $\rho^{L(R)}(\varepsilon)$, the spectral density matrix is

$$\rho^{L(R)}(\varepsilon) \equiv \frac{1}{2\pi} G(\varepsilon) \Gamma^{L(R)}(\varepsilon) G^\dagger(\varepsilon) \quad (3.24)$$

Here $\Gamma^{L(R)}$ is the broadening function of the left (right) electrode which defines as

$$\Gamma^{L(R)} = \frac{1}{i} (\sum^{L(R)} - (\sum^{L(R)})^\dagger) \quad (3.25)$$

where $\sum^{L(R)}$, the left (right) electrode self-energy is

$$\sum^{L(R)} = V_{S/L(R)} g_{L(R)} V_{L(R)/S} \quad (3.26)$$

Here, $g_{L(R)}$ is the surface Green's function for the semi-infinite electrodes and $V_{L(R)/S} = V_{S/L(R)}^\dagger$ are the coupling matrix elements between electrodes and the scattering region. Furthermore, the key quantity to calculate is G , the retarded Green's function matrix,

$$G(\varepsilon) = \frac{1}{(\varepsilon + i\delta_+)S - H} \quad (3.27)$$

where δ_+ is an infinitesimal positive number. S and H are the overlap and Hamiltonian matrices of the entire system, respectively. The Green's function is only required for the central region and can be calculated from the Hamiltonian of the central region by adding the electrode self-energies:

$$G(\varepsilon) = [(\varepsilon + i\delta_+)S - H - \sum^L(\varepsilon) - \sum^R(\varepsilon)]^{-1} \quad (3.28)$$

The transmission amplitude t_k , defines the fraction of a scattering state k propagating through a device. The transmission coefficient at energy ε is obtained by summing up the transmission from all the states at this energy,

$$T(\varepsilon) = \sum_k t_k^\dagger t_k \delta(\varepsilon - \varepsilon_k) \quad (3.29)$$

The transmission coefficient may also be obtained from the retarded Green's function using

$$T(\varepsilon) = G(\varepsilon)\Gamma^L(\varepsilon)G^\dagger(\varepsilon)\Gamma^R(\varepsilon) \quad (3.30)$$

At $T_R = T_L = 0$ (electron temperature) the conductance is determined by the transmission coefficient at the Fermi Level,

$$C(\varepsilon) = G_0 T(\varepsilon) \quad (3.31)$$

where $G_0 = 2e^2 / h$ is the quantum conductance, in which e is the electron charge and h is Planck's constant.

CHAPTER 4

Edge Functionalization and Doping Effects on Stability, Electronic and Magnetic Properties of Silicene Nanoribbons

In this chapter, through DFT the impacts of edge functionalization on the structural stabilities, electronic and magnetic properties of SiNRs are investigated. $-H$, $-F$, $-Cl$, $-Br$, and $-I$ edge functionalization of armchair, zigzag, Klein, reconstructed Klein, reconstructed pentagon-heptagon edge types, and their combinations are examined. Furthermore, the effects of N or B doping on the stability, electronic and magnetic properties of hydrogenated and fluorinated SiNRs are studied. My results encourage further experimental investigations in the development of SiNRs-based nanoelectronics with spin tuning. These results were published in RSC Advances [297] and Journal of Nanomaterials [298].

4.1 Overview

SiNR as a method to open a band gap in a silicene sheet [42, 299] has already been grown on different substrates such as Ag (110) and Au (110) [110, 128-130]. Similar to graphene [300], armchair and zigzag/Klein edges can be formed by cutting the silicene honeycomb lattice along $\langle 1\bar{1}10 \rangle$ and $\langle 2\bar{1}\bar{1}0 \rangle$ directions, respectively. Mixtures of different edge types give rise to intermediate orientations, so-called chiral edges. Recently, several studies have probed the electronic and magnetic properties of SiNRs [97, 99, 299, 301-306]. Dávila *et al.* [302] demonstrated that hydrogen could alter the geometry and electronic properties of isolated and self-assembled SiNRs grown on Ag (110) substrate. On

the basis of DFT calculations, Ding *et al.* [299] studied the completely hydrogenated armchair SiNRs (ASiNRs) and zigzag SiNRs (ZSiNRs), finding that the band gap of ASiNRs decreases with increasing the ribbon width while oscillates with a period of three and ZSiNRs exhibit antiferromagnetic (AFM) semiconducting behavior. Like zigzag edge graphene nanoribbons (GNRs) in which having ferromagnetic (FM) semiconducting behavior is desirable for spintronics applications [307, 308], it is important to discover approaches that induce ferromagnetism in the ZSiNRs while retaining its semiconducting behavior. It was proven that edge states could dramatically modify the electronic and magnetic properties of GNRs [300, 309-315]. Edge functionalization is an attractive method to tailor the properties of SiNRs and can convert the system into spin gapless semiconductors (SGS), intrinsic half-metals, or FM metals [316-320].

Recently, the effects of chemical doping on the electronic and magnetic properties of SiNRs have been investigated [321-326]. Particular attention was paid to 2p elements such as B, N, and P atoms due to their chemical propinquity to silicon [327]. A spectacular SGS character with 100% spin polarized currents around the Fermi level was observed in ZSiNRs doped with N atom at the edge [321, 322]. While ASiNRs experience a semiconductor-metal transition when doped with B or N atoms at the edges [322]. When a B-N pair is introduced into SiNRs, the ASiNRs remain semiconductor, while for the ZSiNRs, it causes a transition from nonmagnetic (NM) to spin-polarized state and SGS [323]. Fang *et al.* found that the ZSiNRs doped with N or P atoms can become half-metal under a perpendicular electric field [316]. Interestingly, a bipolar magnetic semiconducting

behavior was found in asymmetric hydrogenated ZSiNRs, which can be converted to half-metal by B or P doping [317].

However, to the best of my knowledge, no in-depth study to this point has comprehensively explored the full range of SiNRs edge types with different functional addends. In this chapter, I employ first-principles method based on DFT to investigate the effects of edge hydrogenation (-H) and halogenation (-F, -Cl, -Br, and -I) on the geometry, stability, electronic and magnetic properties of different SiNRs edge types. Additionally, the impacts of N or B atoms on the stability, electronic and magnetic properties of different SiNRs functionalized with a hydrogen atom or halogen atoms are explored. My results serve as a useful guide for experimental synthesis groups and theoretical studies in tuning the electronic and magnetic properties of stable SiNRs.

4.2 Computational Details

Calculations are performed using the first-principles method based on self-consistent DFT combined with NEGF, carried out using ATOMISTIX TOOLKIT (ATK) [293, 296, 328]. The PBE parameterized GGA exchange-correlation with a double- ζ polarized basis set and a density mesh cut-off of 150 Rydberg are utilized to solve Kohn-Sham equation and expand electronic density. All the structures are treated with periodic boundary conditions. In order to suppress any interactions between the structure and its periodic image, a vacuum space of 15 Å is considered on each side of the supercell. In addition, the electronic temperature of the structures is kept constant at 300 °K. Prior to the calculations, all the atomic positions and lattice constants are allowed to relax until the force and stress on

them become less than 0.05 eV/Å and 0.001 eV/ Å³, respectively. A k mesh of $1 \times 1 \times 11$ is used for sampling of the Brillouin zone during the optimization. In order to extract accurate electronic and magnetic properties of the structures, the k mesh is increased to $1 \times 1 \times 121$.

4.3 Free-standing Silicene Sheet

Although the 2D structures of silicene and graphene appear quite similar, they have significant differences. While both are hexagonally shaped, unlike a flat graphene sheet in which sp^2 hybridization is more favorable for C, the stable silicene sheet is low-buckled (See Figure 4.1(a)) because the Si-Si bonds are formed by a mixture of sp^2 and sp^3 hybridization. The silicene flat sheet and the buckled sheet have a total energy difference of 0.1 eV/atom [329]. Another difference is that silicene cannot exist in graphitic form due to the fact that a covalent Si-Si bond doesn't have π -stacking unlike the C-C bond [164]. After optimization, the silicene sheet is found to have a buckling distance of about 0.5 Å and lattice constant of 3.86 Å, both in agreement with previous work [43, 330]. Figure 4.1(b) shows the conduction band and valence band crossing at the Fermi level in the Brillouin zone indicating that the silicene sheet has no band gap.

As reported previously for graphene sheet [331], it is predicted that cutting silicene sheets along $\langle 1\bar{1}10 \rangle$ and $\langle 2\bar{1}\bar{1}0 \rangle$ directions results in armchair and parallel zigzag/Klein edges, respectively, as shown in Figure 4.2 Furthermore, silicene edges are expected to undergo reconstruction of Klein edges in order to enhance their stability.

Figure 4.1 (a) Top and side view of the optimized structure of a silicene sheet illustrating its natural buckled hexagonal structure, cyan balls represent Si atoms. The lattice constant and buckling distance are indicated by “ a ” and “ Δ ”, respectively. (b) The corresponding band structure for a pristine silicene sheet shows a zero band gap at the K-point.

All intermediate orientations, which are made by altering parts of edge orientations or mixing different edge types together, are called chiral edges. In order to distinguish the various functionalized edge configurations of SiNRs, a nomenclature similar to the Ref. [309] is used as follows: a : armchair, z : zigzag, k : Klein, and rk : reconstructed Klein. Additionally, the subscripts denote the number of hydrogen or halogen atoms attached to each silicon edge atom along the periodic direction in the supercell, and the hyphen between numbers in the subscripts separate the number of hydrogen or halogen atoms attached to one edge

from another. Here, a detailed theoretical report is given on the impacts of edge-functionalization on the electronic and magnetic properties of ASiNR, ZSiNR, and all chiral edges with a width of 7. For this reason, X atoms (X = H, F, Cl, Br, and I) with different densities are attached to the silicon edge atoms. Finally, the influence of N or B doping on the electronic and magnetic properties of SiNRs are studied.

Figure 4.2 Cutting a silicene sheet *along* the $\langle 1\bar{1}00 \rangle$ and $\langle 2\bar{1}\bar{1}0 \rangle$ directions create armchair (blue solid stars) and zigzag (black solid squares) or Klein (red solid circles) edges, respectively.

4.4 Armchair Silicene Nanoribbons

Three common forms of edge hydrogenation and halogenation are studied: mono-atom on both edges (a_{11}), diatoms on both edges (a_{22}), and diatoms on one edge and mono-atom on the other edge (a_{22-11}), as shown in Figure 4.3. In addition, we considered the a_{21} structure in which silicon atoms are periodically attached to mono-hydrogen (-halogen) and di-hydrogen (-halogen) and a_{2211} structure which is a mix of a_{22} and a_{11} structures.

Figure 4.3 Schematic structural models of the different edge-functionalized 7-ASiNRs. L is the periodic length of the structure. The primitive supercell is marked by a dashed black box. The cyan and red balls represent Si and functional addends (H, F, Cl, Br, and I), respectively.

4.4.1 Stability of Armchair Silicene Nanoribbons

The stability of edge-functionalized ASiNRs can be determined by calculating formation energies. If the nanoribbon segment in one supercell contains n_{Si} silicon atoms and n_{X} hydrogen or halogen atoms, the average edge formation energy of functionalized SiNRs is expressed as

$$E_{\text{edge}} = (E_{\text{ribbon}} - n_{\text{Si}} \times E_{\text{Si}} - (n_{\text{X}} / 2) \times E_{\text{X}_2}) / 2L \quad (4.1)$$

where E_{Ribbon} represents the total energy of the functionalized SiNR in a supercell. E_{Si} and E_{X_2} are the total energy of free Si and isolated hydrogen or halogen molecule, respectively. n_{Si} and n_{X} are the number of Si atoms in the supercell and the number of hydrogen or halogen atoms attached to the edges, respectively. L is the periodic length of the nanoribbon and 2 accounts for two edges of the nanoribbon. The negative values of E_{edge} correspond to an exothermic process in perfect vacuum conditions around free-standing SiNRs. The edge formation energies, band gap energy, and magnetic edge states of various ASiNRs configurations are listed in Table 4.1. The ASiNR with bare edges is unstable (+ 0.33 eV/Å). The precise edge functionalizing of SiNR is one way to increase

its stability. Among all configurations of hydrogenated ASiNR, a_{22} (-0.13 eV/Å) is the most stable one. The stability of ASiNRs has been even increased by halogenation, for instance, the value of formation energy of a_{22} when functionalized with fluorine atoms has been decreased up to -2.48 eV/Å, which is 19 times more stable than hydrogenated a_{22} . The stability of halogenated ASiNRs decreases as the atomic number of the halogen atoms increases. However, they are still much more stable than hydrogenated ASiNRs.

Figure 4.4 Edge formation energy of a_{22} for different ratios of H:F attached to Si edge atoms. Insets show schematic models of functionalized a_{22} with different H:F ratios. The cyan, red, green balls represent Si, H and F atoms, respectively.

To consolidate the obtained results, the stability of the a_{22} functionalized with a combination of hydrogen and fluorine atoms is investigated. Figure 4.4 shows the edge formation energy changes of edge-functionalized a_{22} for different combinations of H and

F atoms on the edges. It is clear that the edge formation energy decreases with increased F atoms attached to Si edge atoms confirming our findings that the halogenation would enhance the stability of the structures.

In order to consider the influence of experimental conditions, temperature and gas pressure, on the stability of functionalized SiNRs, the calculated edge formation energy can be compared to the chemical potential (μ_{X_2}) of the hydrogen or halogen molecule. For this purpose, we calculate the edge free energy $G_{X_2}(T, P)$ using the following formula [332, 333]

$$G_{X_2}(T, p) = E_{\text{edge}} - \frac{1}{2} \times \rho_X \times (\mu_{X_2}(T, p) - E_{X_2}) \quad (4.2)$$

Here, $\rho_X = n_X / 2L$ is the hydrogen or halogen edge density. The hydrogen or halogen chemical potential μ_{X_2} depends on the experiment's temperature and gas pressure according to the following formula [332, 333]

$$\mu_{X_2}(T, p) = E_{X_2} + \mu^o_{X_2}(T, p) \quad (4.3)$$

The zero reference state of $\mu_{X_2}(T, P)$ is chosen to be the total energy of an isolated hydrogen or halogen molecule E_{X_2} at $T = 0$, *i.e.*, $\mu_{X_2}(0, p) = E_{X_2} \equiv 0$. With respect to this zero, the temperature and pressure dependence contribution to the chemical potential is then given by [332, 333]

$$\mu^o_{X_2}(T, p) = H^o(T) - H^o(0) - TS^o(T) + k_B T \ln(p/p^o) \quad (4.4)$$

Here, $H^\circ(S^\circ)$ is the enthalpy (entropy) of hydrogen or halogen molecule at the pressure $p^\circ = 1$ bar, which is obtained from Ref. [334]. It is important to define the thermodynamic limits of hydrogen's or halogen's chemical potential. The upper limits are defined by the chemical potential at which hydrogen or halogen molecule is formed, which is equal to the total energy of an isolated molecule at $T = 0$ °K.

$$\max[\mu_{X_2}(T, p)] = E_{X_2} \quad (4.5)$$

The lower limits are chosen for those hydrogen or halogen potentials that are accessible experimentally at very high temperature (900K).

$$\min[\mu_{X_2}(900, p)] = E_{X_2} + \mu_{X_2}^\circ(900, p) \quad (4.6)$$

Using Ref. [334], the value of the second term for hydrogen and fluorine molecules at a pressure of 1 bar is -1.52 eV and -2.24 eV, respectively. Therefore, the allowed range of the chemical potential, considering E_{X_2} as zero reference, for the hydrogen molecule is

$$-1.52 \prec \mu_{H_2}(T, p) - E_{H_2} \prec 0 \quad (4.7)$$

and for the fluorine molecule is

$$-2.24 \prec \mu_{F_2}(T, p) - E_{F_2} \prec 0 \quad (4.8)$$

The variations of edge free energy with respect to chemical potential of, for example, the H_2 molecule, using E_{H_2} as zero reference, for different ASiNRs configurations are calculated, as shown in Figure 4.5. Under H-poor conditions with $\mu_{H_2} < -1.419$ eV, the a_{11} is favorable for ASiNRs. While, when $\mu_{H_2} \geq -1.419$ eV, the a_{22} becomes more stable than other configurations. Interestingly, under ambient conditions, i.e., 300 °K and 5×10^{-7} bar ($\mu_{H_2} = -0.694$ eV), a_{22} has minimum energy. It should be added that for fluorine, a_{22} edge structure is always the most stable structure. (See Figure 4.6).

Figure 4.5 Edge free energy G_{H_2} of hydrogenated edge ASiNRs studied as a function of hydrogen chemical potential μ_{H_2} , using E_{H_2} as the zero reference. The bottom inset axis represents the pressure (bar), of molecular H_2 corresponding to μ_{H_2} when $T = 300$ °K.

Figure 4.6 (a) Edge free energy G_{F_2} as a function of fluorine chemical potential μ_{F_2} , using E_{F_2} as the zero reference, for different fluorinated edge ASiNRs.

4.4.2 Energy Band Gap of Armchair Silicene Nanoribbons

Figure 4.7 (a) shows the variations of band gap of hydrogenated a_{11} , a_{22} , and a_{22-11} with respect to the ribbon width (N). Similar to the trend of the band gap energy in the most widely studied case, hydrogenated a_{11} , the band gap of all configurations oscillate with $3N$ periodicity [42, 301, 324]. They can be classified into three branches with width $3N - 1$, $3N$, and $3N + 1$, where N is an integer. Similar to armchair GNRs, the three branches with decaying profiles in band gaps originate from the quantum size effect which has been already proved in the literature [335, 336]. Interestingly, comparing the variations of band gap of a_{22} and a_{22-11} with a_{11} , a shift is visible. The values of band gap for a_{11} , a_{22-11} ,

and a_{22} with a width of N , $N + 1$, and $N + 2$ are almost equal. A Si atom shares four valence electrons ($Ne\ 2s^2 2p^2$) in the ribbon. Since the contributions of s orbitals are too small near the Fermi level, only p_z orbitals should be considered. For a_{11} , each Si atom at the edge is connected to two Si atoms and one H by sp^2 hybridization; therefore, p_z orbitals of all the edge and inner Si atoms contribute to the band gap. However, for a_{22} , Si atoms at the edge are bonded to two Si atoms and two H atoms by sp^3 hybridization. Therefore, p_z orbitals are not available anymore. This means that dihydrogenation of one armchair edge of the ribbon decreases the ribbon width (N) of a_{11} by one due to the reduction of the sp^2 hybridization of the edge silicon atom. For example, an a_{22} with a width of $N + 2$ can be modeled as a combination of two edges with sp^3 hybridization that makes a large band gap due to strong quantum confinement and an internal ASiNR with sp^2 hybridization, with a width of N , with a much smaller band gap that is equal to value of band gap of a_{11} . The band gap of this combination is defined by the latter which is equal to the band gap of a_{11} . These findings have previously been observed for graphene [97, 315, 336].

As can be seen in Table 4.1, the nanoribbons functionalized with hydrogen have comparable edge formation energies for a_{22-11} and a_{2211} configurations (-0.02 eV), however, these configurations have different energy band gaps (0.446 eV and 0.308 eV, respectively). The primitive supercell of a_{22-11} includes 14 Si atoms and 6 H atoms, while there are 28 Si atoms and 12 H atoms in the primitive supercell of a_{2211} , as shown in Figure 4.3. If the supercell size of a_{22-11} is doubled, the number of Si and H atoms in the new supercell of a_{22-11} and the primitive supercell of a_{2211} would be equal. The edge formation energies of both nanoribbons would be almost equal since there are 4

dihydrogenated Si edge atoms and 4 mono-hydrogenated Si edge atoms in both supercells. However, as mentioned before, the band gap would be defined by the size of the quantum confinement effect which strongly depends on the width of the nanoribbon. Also, it was revealed that the dihydrogenation would decrease the effective ribbon width by one. As a result, while, the two structures have the same edge formation energies, their energy band gap values are different because of different the quantum confinement strengths.

Figure 4.7 (a) The energy band gap changes versus nanoribbon width for hydrogenated a_{11} , a_{22-11} , and a_{22} (b) The energy band gap variations of hydrogenated and halogenated a_{11} with nanoribbon width (c) effective electron (m_e^*) and hole (m_h^*) mass changes of hydrogenated a_{11} , a_{22-11} , and a_{22} with respect to nanoribbon width at the Γ -point.

Furthermore, the band gap changes of hydrogenated and halogenated a_{11} with nanoribbon width are compared in Figure 4.7 (b). It is clear that halogenation results in a reduction of band gap values. However, it maintains the oscillatory behavior which is found in the hydrogenated case. In hydrogenated ASiNR, the Si-H bond is covalent. The electrons of hydrogen occupy the empty lowest conduction band of silicene, leaving the Si-Si bonds unchanged [337]. Nonetheless, in the halogenated ASiNR, the Si-X (X = F, Cl, Br, and I) bond shows ionic characteristics. The values of Pauling electronegativity of X are 3.98,

3.16, 2.96, and 2.66, respectively, much larger than that of silicon which is 1.90. The vdW for hydrogen and X atoms are 1.20, 1.47, 1.75, 1.85, and 1.98 Å, respectively. In a perfect ASiNR, the Si-Si bond length (2.28 Å) is almost twice that of hydrogen vdW, suggesting that steric hindrance can be ignored in pristine ASiNRs. However, steric hindrance should be accounted for in halogenated ASiNRs. The steric hindrance effect becomes noticeably stronger with increasing atomic number of halogens due to increasing of van der Waals radii. As a result, the ionic characteristic of the Si-X bond and interaction between Si and functional atoms make the Si-Si bond weaker. They also reduce the electron population in the bonding orbitals of Si, bonding-antibonding splitting, and consequently the energy band gap of ASiNRs [46, 315].

Variations of electron and hole effective masses of hydrogenated a_{11} , a_{22} , and a_{22-11} with respect to nanoribbon width are also calculated, as plotted in Figure 4.7 (c). Similar to the band gap's trend, effective masses of hydrogenated a_{11} oscillate with $3N$ periodicity and shift when one edge is dihydrogenated. The larger band gaps associated with larger carrier effective masses and thus lower mobilities at the band edges, suggesting that functionalization is an effective approach to control the transport properties of SiNRs. The results are in good agreement with previous observations for graphene [315].

Table 4.1 Edge formation energy E_{edge} (eV), band gap E_g (eV), magnetic state, the energy difference between the FM and AFM state $\Delta E_{\text{FM-AFM}}$ (eV), total magnetic moment M_{total} (μ_B), and spin-polarized band gap (eV) for different armchair edge SiNRs functionalized with hydrogen and halogens.

Edge Type	Edge Atom	E_{edge} (eV/A)	E_g (eV)	Magnetic State	Magnetic Edge State		
					ΔE (meV)	E_g (eV)	M_{Total} (μ_B)
a_{11}	Bare	+0.330	0.357 (in)	NM	-	-	-
	H	-0.082	0.581 (d)	NM	-	-	-
	F	-1.032	0.514 (d)	NM	-	-	-
	Cl	-0.433	0.411 (d)	NM	-	-	-
	Br	-0.314	0.218 (d)	NM	-	-	-
	I	-0.183	0.201 (d)	NM	-	-	-
a_{22}	Bare	+0.330	0.357 (in)	NM	-	-	-
	H	-0.129	0.096 (d)	NM	-	-	-
	F	-2.483	0.118 (d)	NM	-	-	-
	Cl	-1.219	0.026 (d)	NM	-	-	-
	Br	-0.985	0.034 (d)	NM	-	-	-
	I	-0.689	0.109 (d)	NM	-	-	-
a_{22-11}	Bare	+0.330	0.357 (d)	NM	-	-	-
	H	-0.025	0.446 (d)	NM	-	-	-
	F	-1.759	0.452 (d)	NM	-	-	-
	Cl	-0.822	0.498 (d)	NM	-	-	-
	Br	-0.652	0.558 (d)	NM	-	-	-
	I	-0.439	0.584 (d)	NM	-	-	-
a_{21}	Bare	+0.330	0.357 (in)	NM	-	-	-
	H	+0.058	0.00	FM-S	-86.55	Up (0.888) (d) Down (0.697) (in)	1.99
	F	-1.695	0.00	AFM-M	+6.38	0.00	0.00
	Cl	-0.762	0.00	FM-S	-18.12	Up (0.650) (d) Down (0.55) (in)	1.96
	Br	-0.603	0.00	FM-S	-34.02	Up (0.664) (d) Down (0.584) (in)	1.79
	I	-0.394	0.00	FM-S	-56.99	Up (0.659) (d) Down (0.551) (in)	1.99
a_{2211}	Bare	+0.330	0.357 (in)	NM	-	-	-
	H	-0.021	0.334 (d)	NM	-	-	-
	F	-1.749	0.308 (d)	NM	-	-	-
	Cl	-0.761	0.378 (d)	NM	-	-	-
	Br	-0.659	0.397 (d)	NM	-	-	-
	I	-0.446	0.370 (d)	NM	-	-	-

a : armchair, z : zigzag, k : Klein, rk : reconstructed Klein, subscripts: the number of fictional atoms attached to Si edge atom, NM: non-magnetic, FM: ferromagnetic, AFM: antiferromagnetic, S: semiconductor, M: metal, SGS: spin-gapless semiconductor, HF: half-metal, d: direct band gap, in: indirect band gap, ΔE : $E_{\text{FM}} - E_{\text{AFM}}$.

4.4.3 Magnetic Properties of Armchair Silicene Nanoribbons

The spin-polarized calculations show that all a_{11} , a_{22} , and a_{2211} configurations are NM, exceptionally, unlike other configurations of ASiNRs, the hydrogenated or

halogenated a_{21} structure shows metallic behavior. The spin-polarized calculations of hydrogenated a_{21} demonstrate that they are FM semiconductors with a direct band gap of 0.888 eV for spin-up channel and the indirect band gap of 0.697 eV for the spin-down channel, as shown in Figure 4.8. The energy difference between FM and AFM states ($\Delta E_{\text{FM-AFM}}$) is -86.55 meV. However, the fluorinated a_{21} is an AFM metal considering spin polarization.

Figure 4.8 Band structures of hydrogenated a_{21} in the (a) NM and (b) FM states. The Fermi energy is set at zero. α (black solid line) and β (red dashed line) represent spin-up and spin-down bands, respectively.

4.5 Zigzag / Klein Edge Silicene Nanoribbons

The $\langle 2\bar{1}\bar{1}0 \rangle$ orientation along is much more complicated than $\langle 1\bar{1}10 \rangle$. As can be seen in Figure 4.2, there are two primary parallel possibilities for SiNRs in the $\langle 2\bar{1}\bar{1}0 \rangle$ direction, calling the zigzag edge and the Klein edge. The bare ZSiNR is highly unstable ($+0.38$ eV/Å). Various forms of edge functionalization with hydrogen and halogens are considered to improve the stability of ZSiNRs. In addition to well-known structures of z_1 , z_2 , and z_{2-1} , some other possible forms of

edge functionalization of ZSiNRs are considered, including z_{21} , z_{211} , and z_{221} , as seen in Figure 4.9. The edge formation energies, band gap energies, and magnetic edge states of various ZSiNRs are listed in Table 4.2.

Figure 4.9 Different edge structures of functionalized SiNRs along $\langle 2\bar{1}\bar{1}0 \rangle$ direction. L is the periodic length of the structure. The primitive supercell is marked by a dashed black box. The cyan and red balls represent Si and functional addends (H, F, Cl, Br, and I), respectively.

Table 4.2 E_{edge} (eV), E_g (eV), magnetic state, $\Delta E_{\text{FM-AFM}}$ (eV), total magnetic moment M_{total} (μ_B), and spin-polarized band gap (eV) for different zigzag edge SiNRs functionalized with hydrogen and halogens.

Edge Type	Edge Atom	E_{edge} (eV/A)	E_g (eV)	Magnetic State	Magnetic Edge State		
					ΔE (meV)	E_g (eV)	M_{Total} (μ_B)
z_1	Bare	+0.381	0.00	NM	-	-	-
	H	+0.097	0.00	AFM-S	+5.08	0.313 (d)	0.00
	F	-0.871	0.00	AFM-S	+4.23	0.281 (d)	0.00
	Cl	-0.362	0.00	AFM-S	+4.05	0.271 (d)	0.00
	Br	-0.282	0.00	AFM-S	+4.01	0.269 (d)	0.00
	I	-0.165	0.00	AFM-S	+3.71	0.253 (d)	0.00
z_2	Bare	+0.381	0.00	NM	-	-	-
	H	-0.101	0.036(in)	AFM-S	+34.46	0.414 (in)	0.00
	F	-2.064	0.00	AFM-S	+25.44	0.312 (in)	0.00
	Cl	-0.951	0.00	AFM-S	+14.29	0.174 (in)	0.00
	Br	-0.766	0.00	AFM-S	+16.26	0.184 (in)	0.00
	I	-0.469	0.00	AFM-S	+21.39	0.267 (in)	0.00
z_{2-1}	Bare	+0.381	0.00	NM	-	-	-
	H	+0.053	0.00	FM-S	-12.14	Up (0.540) (d) Down (0.541) (d)	1.00
	F	-1.460	0.00	FM-M	-8.12	0.00	0.981
	Cl	-0.658	0.00	FM-SGS	-6.17	Up (0.505) (in) Down (0.277) (in)	0.909
	Br	-0.529	0.00	FM-SGS	-5.99	Up (0.495) (in) Down (0.273) (in)	0.913
	I	-0.346	0.00	FM-M	-3.20	0.00	0.932
z_{21}	Bare	+0.372	0.00	NM	-	-	-
	H	+0.002	0.175 (d)	NM	-	-	-
	F	-1.515	0.159 (d)	NM	-	-	-
	Cl	-0.699	0.162 (d)	NM	-	-	-
	Br	-0.568	0.156 (d)	NM	-	-	-
	I	-0.385	0.156 (d)	NM	-	-	-
z_{211}	Bare	+0.350	0.00	NM	-	-	-
	H	-0.003	0.160 (d)	NM	-	-	-
	F	-1.698	0.091 (d)	NM	-	-	-
	Cl	-0.786	0.110 (d)	NM	-	-	-
	Br	-0.637	0.109 (d)	NM	-	-	-
	I	-0.431	0.118 (d)	NM	-	-	-
z_{221}	Bare	+0.383	0.00	NM	-	-	-
	H	-0.402	0.140 (d)	AFM-S	+48.31	0.285 (in)	0.00
	F	-0.648	0.024 (in)	AFM-S	+10.56	0.078 (in)	0.00
	Cl	-0.199	0.025 (in)	AFM-S	+14.47	0.079 (in)	0.00
	Br	-0.152	0.040 (in)	AFM-S	+18.77	0.101 (in)	0.00
	I	-0.085	0.058 (in)	AFM-S	+22.01	0.133 (in)	0.00

4.5.1 Stability of Zigzag / Klein Edge Silicene Nanoribbons

Among all possible edge hydrogenation forms of ZSiNRs, the z_2 (-0.009 eV/Å) is found as the most stable. However, it is about 13.5 times less stable than the most stable hydrogenated ASiNR (a_{22}). The order of structure stability for different configurations of ZSiNRs is $z_2 > z_{221} > z_{21} > z_{211} > z_{2-1} > z_1$. The possible reason is that Si atoms prefer to accept sp^3 hybridizations over sp^2 in silicene; therefore, dihydrogenation could increase the stability of the structures. In addition, similar to ASiNRs, halogenating would increase the stability of the ZSiNRs. The stability of fluorinated z_2 (-2.064 eV/Å) is 215 times more than the hydrogenated z_2 and 0.84 less than the fluorinated a_{22} . Similar to ASiNRs, the stability of halogenated ZSiNRs decreases with increasing the atomic number of halogen atoms.

The bare pristine Klein edge is also unstable ($+0.38$ eV/Å). It is found that hydrogenated k_1 ($+0.40$ eV/Å) and k_2 ($+0.25$ eV/Å) are still unstable. However, fluorinated k_1 (-0.65 eV/Å) and k_2 (-1.84 eV/Å) are stabilized. Interestingly, while hydrogenated k_3 (-0.72 eV/Å) shows metastable behavior, fluorinated k_3 (-3.23 eV/Å) is highly stable due to the preference of sp^3 hybridization of Si edge atoms over sp^2 . It is revealed that trifluorinated Klein edge (k_3) is the most stable edge structure among all edge structures of SiNRs. Furthermore, the hydrogenated k_3 can become more stable by periodically inserting a Klein vacancy terminated with two functionalization atoms $k_{33} + z_2$ (-0.10 eV/Å) resulting in stabilities approaching that of hydrogenated a_{22} . It is important to mention that the bare Klein edge can undergo a reconstruction to a pentagon-terminated Klein edge (rk) or to a pentagon-heptagon zigzag edge (5-7), which are 0.05 and 0.03 eV/Å more stable

than bare Klein edge. Although the hydrogenated $(5-7)_{11}$ is unstable ($+ 0.16 \text{ eV/\AA}$), the hydrogenated $(5-7)_{22}$ is almost stable ($- 0.026 \text{ eV/\AA}$). Interestingly enough, when the edges of $(5-7)$ SiNRs are terminated with one and two fluorine atoms the formation energies are decreased to $- 0.80$ and $- 2.07 \text{ eV/\AA}$ which are more stable than those of hydrogenated. In addition, the edge configurations of hydrogenated rk_{11} ($+ 0.15 \text{ eV/\AA}$) and rk_{21} ($+ 0.81 \text{ eV/\AA}$) are unstable. However, the hydrogenated rk_{22} is energetically more favorable with formation energy of $- 0.069 \text{ eV/\AA}$. Even more interesting is that fluorinated rk_{11} and rk_{22} are both stable with edge formation energy of $- 0.798 \text{ eV/\AA}$ and $- 2.104 \text{ eV/\AA}$, respectively, emphasizing that halogenating is a decent way to increase the stability of SiNRs. Similar to $k_{33} + z_2$ structure, rk_{22} can be more stabilized by periodically inserting a Klein edge vacancy which results in a double hydrogenated or halogenated zigzag edge site. The hydrogenated $rk_{22} + z_2$ ($- 0.083 \text{ eV/\AA}$) is a slightly more stable than rk_{22} (for more details see Table 4.3).

Finally, the combinations of zigzag and reconstructed Klein edges are also investigated. For this reason, one edge is zigzag and the other one is reconstructed Klein. Based on the different possible edge functionalization, four types of edge functionalization are chosen as follows: a) $rk_{22} - z_{22}$ kind, b) $rk_{11} - z_{11}$ kind, c) $rk_{22} - z_{11}$ kind, and d) $rk_{11} - z_{22}$ kind [318]. The unterminated $rk - z$ is unstable ($+ 0.35 \text{ eV/\AA}$). The edge formation energy of hydrogenated a, b, c, and d kinds are $- 0.035$, $+ 0.12$, $+ 0.014$, and $+ 0.009 \text{ eV/\AA}$, respectively. The edge formation energy of a, b, c, and d kinds decreased to $- 2.081$, $- 0.833$, $- 1.485$, and $- 1.428 \text{ eV/\AA}$,

respectively, using fluorine as the functionalization atom (for more details see Table 4.4).

Table 4.3 E_{edge} (eV), E_g (eV), magnetic state, $\Delta E_{\text{FM-AFM}}$ (eV), total magnetic moment M_{total} (μ_B), and spin-polarized band gap (eV) for different Klein edge SiNRs functionalized with hydrogen and halogens.

Edge Type	Edge Atom	E_{edge} (eV/A)	E_g (eV)	Magnetic State	Magnetic Edge State		
					ΔE (meV)	E_g (eV)	M_{Total} (μ_B)
k_2	Bare	+0.383	0.00	NM	-	-	-
	H	+0.255	0.00	NM	-	-	-
	F	-1.837	0.00	NM	-	-	-
	Cl	-0.812	0.00	NM	-	-	-
	Br	-0.628	0.00	NM	-	-	-
	I	-0.426	0.00	NM	-	-	-
k_3	Bare	+0.383	0.00	NM	-	-	-
	H	-0.072	0.00	AFM-S	+4.60	0.290 (d)	0.00
	F	-3.237	0.00	AFM-S	+4.55	0.273 (in)	0.00
	Cl	-1.477	0.00	AFM-S	+5.10	0.278 (in)	0.00
	Br	-1.154	0.00	AFM-S	+4.53	0.200 (in)	0.00
	I	-0.763	0.00	AFM-S	+1.01	0.101 (in)	0.00
$k_{33}+z_2$	Bare	+0.334	0.00	NM	-	-	-
	H	-0.103	0.161 (d)	NM	-	-	-
	F	-2.901	0.157 (d)	NM	-	-	-
	Cl	-1.390	0.156 (d)	NM	-	-	-
	Br	-1.103	0.159 (d)	NM	-	-	-
	I	-0.797	0.112 (d)	NM	-	-	-
$(5-7)_{22}$	Bare	+0.354	0.00	NM	-	-	-
	H	-0.020	0.00	NM	-	-	-
	F	-2.076	0.00	NM	-	-	-
	Cl	-0.970	0.00	NM	-	-	-
	Br	-0.372	0.00	NM	-	-	-
	I	-0.288	0.00	NM	-	-	-
rk_{22}	Bare	+0.338	0.00	NM	-	-	-
	H	-0.069	0.00	AFM-S	+8.80	0.281 (d)	0.00
	F	-2.104	0.00	AFM-S	+8.64	0.284 (d)	0.00
	Cl	-1.011	0.00	AFM-S	+8.44	0.275 (d)	0.00
	Br	-0.827	0.00	AFM-S	+8.49	0.276 (d)	0.00
	I	-0.584	0.00	AFM-S	+8.14	0.289 (in)	0.00
$rk_{22}+z_2$	Bare	+0.333	0.00	NM	-	-	-
	H	-0.083	0.160 (d)	NM	-	-	-
	F	-2.120	0.150 (d)	NM	-	-	-
	Cl	-1.014	0.151 (d)	NM	-	-	-
	Br	-0.835	0.141 (d)	NM	-	-	-
	I	-0.588	0.144 (d)	NM	-	-	-

Table 4.4 E_{edge} (eV), E_g (eV), magnetic state, $\Delta E_{\text{FM-AFM}}$ (eV), total magnetic moment M_{total} (μ_B), and spin-polarized band gap (eV) for different Klein edge and zigzag SiNRs combinations functionalized with hydrogen and halogens.

Edge Type	Edge Atom	E_{edge} (eV/A)	E_g (eV)	Magnetic State	Magnetic Edge State		
					ΔE (meV)	E_g (eV)	Moment (μ_B)
rk ₂₂ -z ₂₂	Bare	+0.355	0.00	NM	-	-	-
	H	-0.036	0.00	FM-S	-22.46	Up (0.524) (in) Down (0.473) (in)	2.003
	F	-2.082	0.00	FM-M	-14.71	0.00	1.607
	Cl	-0.982	0.00	FM-S	-13.26	Up (0.528) (in) Down (0.270) (in)	1.660
	Br	-0.799	0.00	FM-S	-13.96	Up (0.520) (in) Down (0.276) (in)	1.875
	I	-0.557	0.00	FM-M	-4.66	0.00	0.492
	Bare	+0.355	0.00	NM	-	-	-
rk ₁₁ -z ₁₁	H	+0.127	0.00	FM-M	-6.94	0.00	0.921
	F	-0.834	0.00	FM-M	-4.04	0.00	1.037
	Cl	-0.329	0.00	FM-M	-4.43	0.00	1.016
	Br	-0.248	0.00	FM-M	-3.67	0.00	1.031
	I	-0.158	0.00	FM-M	-1.21	0.00	1.012
	Bare	+0.355	0.00	NM	-	-	-
rk ₂₂ -z ₁₁	H	+0.015	0.00	AFM-S	+9.5	Up (0.297) (d) Down (0.301) (d)	0.00
	F	-1.486	0.00	AFM-S	+8.04	Up (0.343) (d) Down (0.198) (d)	0.00
	Cl	-0.685	0.00	AFM-S	+8.02	Up (0.328) (d) Down (0.200) (d)	0.00
	Br	-0.554	0.00	AFM-S	+7.94	Up (0.326) (d) Down (0.201) (d)	0.00
	I	-0.365	0.00	AFM-S	+7.52	Up (0.310) (d) Down (0.188) (d)	0.00
	Bare	+0.355	0.00	NM	-	-	-
rk ₁₁ -z ₂₂	H	+0.009	0.00	AFM-M	+8.2	0.00	0.00
	F	-1.429	0.00	AFM-M	+6.69	0.00	0.00
	Cl	-0.627	0.00	AFM-M	+2.12	0.00	0.00
	Br	-0.496	0.00	AFM-M	+1.23	0.00	0.00
	I	-0.341	0.00	AFM-M	+0.091	0.00	0.00
	Bare	+0.355	0.00	NM	-	-	-

Based on the calculated edge formation energies, k_3 and $k_{33} + z_2$ edges are found to be the most stable edge structures. In order to account for the experimental conditions, the edge free energies of the aforementioned hydrogenated edge structures are calculated and plotted in Figure 4.10. For low hydrogen chemical potential $\mu_{\text{H}_2} < -2$ eV, the z_1 has minimum energy. When -2 eV $\leq \mu_{\text{H}_2} < -1.4$ eV, several different edge structures have almost same

amount of energy. Further increase of μ_{H_2} up to -0.2 eV, $rk_{22} + z_2$ is most favorable. For $-0.2 \text{ eV} \leq \mu_{\text{H}_2} < +0.5 \text{ eV}$, $k_{33} + z_2$ is the most stable edge structure. The edge free energy for $k_{33} + z_2$ and k_3 is almost equal for $0.5 \text{ eV} \leq \mu_{\text{H}_2} < +1 \text{ eV}$. Finally, for $\mu_{\text{H}_2} \geq +1 \text{ eV}$, the k_3 edge structure is found as the most stable structure.

Figure 4.10 Edge free energy G_{H_2} of different edge structures of hydrogenated SiNRs along $\langle 2\bar{1}\bar{1}0 \rangle$ versus hydrogen chemical potential μ_{H_2} , using E_{H_2} as the zero reference. The allowed range for hydrogen chemical potential is indicated by vertical dotted lines. The bottom inset axis represents the pressure, in bar, of molecular H_2 corresponding to μ_{H_2} when $T = 300$ °K.

For fluorine, for $\mu_{\text{F}_2} < -1.9$ eV the $(5-7)_{22}$ is the most stable edge structure, while when $\mu_{\text{F}_2} \geq -1.9$ eV it is k_3 (See Figure 4.11). Under ambient

conditions, i.e., 300 K and 5×10^{-7} bar, the stable edges are hydrogenated $rk_{22} + z_2$ (at $\mu_{H_2} = -0.694$ eV) and fluorinated k_3 (at $\mu_{F_2} = -0.933$ eV).

Figure 4.11 (a) Edge free energy G_{F_2} as a function of fluorine chemical potential μ_{F_2} , using E_{F_2} as the zero reference, for different edge structures of fluorinated SiNRs along $\langle 2\bar{1}\bar{1}0 \rangle$ directions.

To sum up, for ASiNRs, the a_{22} structure is the most stable structure in perfect vacuum conditions and experimentally under ambient conditions. For the hydrogenated edge SiNRs along the $\langle 2\bar{1}\bar{1}0 \rangle$ direction, $k_{33} + z_2$ in perfect vacuum conditions and $rk_{22} + z_2$ under experimental ambient conditions are the most stable structures. Furthermore, if the edges along the $\langle 2\bar{1}\bar{1}0 \rangle$ direction were functionalized with fluorine atoms, the k_3 structure is found as the most stable structure in both vacuum and experimental conditions.

4.5.2 Magnetic Properties of Zigzag / Klein Edge Silicene Nanoribbons

The non-spin-polarized calculations of hydrogenated z_1 show that the valence top π band meets the conduction bottom π^* band at Fermi level and the bands flatten, as shown in Figure 4.12. It has been found that the flat bands which cause metallicity in z_1 are induced by the p_z orbital of the outer Si atoms and are referred as to edge states. On the other hand, spin-polarized calculations of hydrogenated z_1 demonstrate that the total energies of AFM and FM states are 43.15 and 38.07 meV, lower than that of the NM state, pointing out that the AFM state is the ground state. Furthermore, the spin-up and spin-down bands are fully degenerated, and a band gap of 0.313 meV is opened at the Fermi level in AFM state, demonstrating AFM semiconducting behavior, as seen in Figure 4.12(b). The results are in excellent agreement with previous findings [316, 318]. It should be mentioned that all halogenated z_1 structures are also AFM semiconductors.

The non-spin-polarized band structure of hydrogenated z_2 shows that it is a semiconductor with a small indirect band gap of 0.037 eV, however, the halogenated z_2 structures exhibit metallic behavior. Considering spin-polarization, the total energy of AFM and FM states are 86.66 meV and 52.2 meV lower than that of NM state, suggesting that the AFM state is the ground state. Comparing the $\Delta E_{\text{FM-AFM}}$ of hydrogenated z_2 (34.46 meV) and hydrogenated z_1 (5.06 meV) shows that dihydrogenation enhances the stability of the AFM state. The AFM state of z_2 is also an indirect semiconductor with a band gap of 0.41 eV which is much larger than that of NM, as shown in Figure 4.12(c) and (d). There is a good match between these results and Ref. [316].

Figure 4.12 Band structures of hydrogenated z_1 in the (a) NM and (b) AFM states, hydrogenated z_2 in the (c) NM and (d) AFM states.

The non-spin-polarized calculations of asymmetrically hydrogenated z_{2-1} indicate that there is a flat band throughout the Brillouin zone, showing a metallic behavior, as depicted in Figure 4.13(a). Similar to zigzag edge GNRs [312], the edge Si atoms which are attached to two hydrogen atoms have negligible contributions around Fermi level, while the adjacent atoms undertake the role of edge states, bands flattening in the range of $0 < k \leq 2\pi/3$. For the zigzag edge with mono-hydrogen termination, the p_z orbitals of the edge Si atoms have a significant contribution to the Fermi level, making the bands flat in the range of $2\pi/3 < k \leq \pi$. Considering the spin-polarized calculations of hydrogenated z_{2-1} , it has been found

that the AFM state is metallic while becoming an indirect semiconductor (0.54 eV) with spin-up (-down) fully occupied (unoccupied) in the FM state. The hydrogenated z_{2-1} shows a bipolar magnetic behavior because of fully spin-polarized states with opposite orientations around the Fermi level, as shown in Figure 4.13(b). The value of $\Delta E_{\text{FM-AFM}}$ for hydrogenated z_{2-1} is -12.14 meV, suggesting that the FM state is the ground state. In addition, the total magnetic moment of stable FM state is $1 \mu\text{B}$ per unit cell. The results are confirmed in Refs. [316] and [317]. In addition, the spin-polarized band structures of the z_{2-1} functionalized with F and I show that they are FM metals, while, functionalization of z_{2-1} structure with Cl or Br atom yields FM semiconducting behavior. The value of indirect band gaps for spin-up (down) channel for Cl and Br are 0.505 (0.277) eV and 0.495 (0.273) eV, respectively. Interestingly, the top valence band of spin-up touches the bottom band of spin-down at Fermi level, showing the SGS feature, as presented in Figure 4.13(d) for Cl.

Hydrogenated z_{21} and z_{211} are direct semiconductors with band gaps of 0.175 eV and 0.160 eV, respectively. The spin-polarized calculations show that they are NM. The stable hydrogenated z_{221} structure is also a direct semiconductor with a band gap of 0.140 eV. However, the halogenated z_{221} structures have small indirect band gaps in the range of 2 - 6 meV. If spin-polarization is taken into account, the AFM state will match with the ground state, where $\Delta E_{\text{FM-AFM}}$ for hydrogenated z_{221} is equal to 48.31 meV which is more stable than that of z_1 , z_2 , and z_{2-1} structures. Furthermore, hydrogenated z_{221} becomes an indirect semiconductor (0.285 eV) when spin-polarization is considered.

Figure 4.13 Band structures of hydrogenated z_{2-1} in the (a) NM and (b) FM states, chlorinated z_{2-1} in the (c) NM and (d) FM states.

The unstable hydrogenated k_1 and k_2 have metallic behaviors with no sign of magnetism when spin-polarized calculations are performed. Interestingly, the stable hydrogenated k_3 is still metal (Figure 4.14(a)), but tri-hydrogenation of edge Si atoms induced magnetism when spin-polarization is considered. The AFM state is the ground state ($\Delta E_{\text{FM-AFM}}$ has a small value of 4.6 meV), and a direct band gap of 0.29 eV is opened at the Fermi level, showing semiconducting behavior, as seen in Figure 4.14(b). In addition, periodically inserting Klein vacancy in k_3 , creating $k_{33} + z_2$, makes k_3 more stable, as mentioned before, and transforms it to a semiconductor with a band gap of 0.162 eV. Moreover, the spin-polarized calculations of hydrogenated $k_{33} + z_2$ show that it is not magnetic. The stable

hydrogenated (5-7)₂₂ shows a metallic behavior without magnetism when taking into consideration spin-polarization.

Figure 4.14 Band structures of hydrogenated k_3 in the (a) NM and (b) AFM states, hydrogenated rk_{22} in the (c) NM and (d) AFM states.

The non-spin-polarized calculation of the stable hydrogenated rk_{22} shows that it is a metal (Figure 4.14(c)), and becomes magnetic when considering polarization. The value of $\Delta E_{\text{FM-AFM}}$ is 8.8 meV, showing that the AFM state is the ground state. Also, a band gap opening with a value of 0.282 eV occurs at Fermi level, demonstrating semiconducting behavior, as shown in Figure 4.14(d). It should be noted that similar to hydrogenated z_2 the metallicity origin in non-spin-polarized calculations comes from the flat band located around the Fermi level.

The p_z orbitals of edge Si atoms with two attached hydrogen atoms corresponds to bands which are deep in the valance bands, while the p_z orbitals of Si atoms next to edge Si atoms, the zigzag edge, ascribe to the flat bands. These flat bands give rise to magnetism in rk_{22} due to the stoner effect. The results correspond well with the literature [318]. Similar to k_3 , periodically inserting dihydrogenated zigzag edge between reconstructed Klein edges, $rk_{22} + z_2$, cause a metal to semiconductor transformation which has a direct band gap of 0.16 eV at Γ -point. It should be mentioned that stabilizing rk_{22} via periodic injection of z_2 suppresses magnetism in spin-polarized calculations. The halogenated k_3 , $k_{33} + z_2$, $(5-7)_{22}$, rk_{22} , and $rk_{22} + z_2$ structures shows a similar behavior as mentioned for hydrogenated structures, as seen in Table 4.3.

The combinations of Klein and zigzag edges may result in attractive magnetic properties. The non-spin-polarized calculations of previously mentioned combinations show that they are all metallic. Taking spin-polarization into account, the hydrogenated $rk_{22} - z_{11}$ is still an AFM semiconductor. However, different from rk_{22} and z_1 , the band gap is spin-resolved, resulting in a band gap of 0.297 and 0.301 eV for spin-up and spin-down, respectively. The value of ΔE_{FM-AFM} is 9.5 meV which is larger than that of rk_{22} and z_1 . Moreover, the total magnetic moment is still 0 μ_B . The halogenated $rk_{22} - z_{11}$ exhibits similar behavior as hydrogenated, as seen in Table 4.4. For spin-polarized hydrogenated $rk_{11} - z_{11}$ and $rk_{11} - z_{22}$ combinations, FM and AFM metallic behaviors are found in the ground state, respectively. The spin-polarized calculations of rk_{11} prove that it is not magnetic; hence it eliminates the magnetism from one edge side of the nanoribbons, as shown in Figure 4.15(c). It means that the zigzag edge of the

nanoribbons determines the total magnetic moment, as shown in Figure 4.15(a) and (b), which is 0.92 μ_B for the z_{11} case and 0 μ_B for the z_{22} one.

Figure 4.15 Spin-charge density distributions of (a) z_2 , (b) z_1 , (c) rk_{11} and (d) rk_{22} . The green and blue regions correspond to the isosurfaces of spin-up and spin-down channels with a spin value of 0.001 $e/\text{\AA}^3$. The band structures of hydrogenated rk_{22} - z_{22} in the (e) NM and (f) FM states.

As discussed earlier, in z_{22} case, the atom next to the Si edge atom plays a key role in magnetism, the distribution of spin densities are different for two above case, causing a difference in magnetic status. For the hydrogenated rk_{22} - z_{22} case, both edges are involved in magnetism, as shown in Figure 4.15(a) and (d), resulting in a FM ground state with a total magnetic moment of 2.003 μ_B and $\Delta E_{\text{FM-AFM}}$ of -22.46 meV. In addition, the whole bottom conduction band and the entire top valence bands have

opposite spin orientations, showing a bipolar magnetic semiconducting behavior. The value of indirect band gap for spin-up (-down) is 0.524 (0.473) eV, see Figure 4.15(f). Similar results are reported in Ref. [318]. Functionalization with Cl and Br also give rise to FM semiconductor behavior in $rk_{22} - z_{22}$. Nonetheless, for the $rk_{22} - z_{22}$ case functionalized with F and I, the results show that a weak FM metallic behavior appears in the structure.

4.6 Armchair Silicene Nanoribbons Doped by N or B Atoms

The electronic and magnetic properties of SiNRs can be effectively tuned by doping. The effects of doping of SiNRs with N or B impurity have been investigated. Theoretically, a single N or B atom can be substituted with Si atom in different sites of the nanoribbon. To further clarify which site is experimentally more likely to occur, the formation energy of the N or B impurity is calculated

$$E_f = E_{\text{doped}} - \left(E_{\text{Pristine}} - (m + n) E_{\text{Si}} + m E_{\text{N}} + n E_{\text{B}} \right) \quad (4.9)$$

Here, E_{doped} and E_{Pristine} are the total energy of doped SiNRs with N or B impurity and the total energy of pristine SiNR, respectively. The E_{Si} , E_{N} , and E_{B} are the total energy of free Si, N, and B impurity, respectively. m and n are the number of N and B impurities in the doped SiNR, respectively. Based on the definition, the more negative value of E_f is, the more favorable the system would be. Figure 4.16 shows the preferred N- or B-doped positions in different edge-functionalized ASiNRs.

Figure 4.16 Schematic structural models of the different edge-functionalized ASiNRs doped with a N or B atom, in which the most stable substitution configurations are indicated. The cyan and red balls represent Si and functional addends (H, F, Cl, Br, and I), respectively, and the blue solid circle shows a N or B atom.

It has been found that the formation energy of a single substitution at the edge site is lower than other sites in the nanoribbon, indicating that the possibility of substitution of Si atoms with dopants is higher at the edges of the nanoribbons [321-325]. However, other metastable sites can be considered for practical thermodynamical conditions due to the small difference in the amount of their formation energies [324]. The edge formation energies, band gaps, and magnetic edge states of hydrogenated and fluorinated ASiNRs doped with N or B atom are listed in Table 4.5.

The formation energy of B-doped ASiNRs is found to be lower than that of N-doped ASiNRs, suggesting that B impurity is easier to substitute in ASiNRs. It can also be due to the larger Pauling electronegativity (3.04) and smaller covalent radius (0.75 Å) of the N atom compared to the B atom (Pauling electronegativity of 2.04 and covalent radius of 0.82 Å) [338]. To gain better insight on the reason behind this, the bond lengths of atoms in pristine and doped ASiNRs, for instance, a_{11} , are calculated. The optimized pristine Si-Si bond length and Si-H bond length are 2.28 and 1.50 Å, respectively. In addition, the calculated Si-N bond length (1.74 Å) and N-H bond length (1.02 Å) in N-doped a_{11} are found to be shorter than Si-B bond length (1.92 Å) and B-H bond length

(1.21 Å) in B-doped a_{11} . It means that the values of bond length for B-doped ASiNR are more similar to values of bond length for pristine ASiNR than the N-doped ASiNR counterpart, resulting in less lattice distortion and a more stable structure.

Table 4.5 E_{edge} (eV), E_g (eV), magnetic state, $\Delta E_{\text{FM-AFM}}$ (eV), and spin-polarized band gap (eV) for different N- and B-doped armchair edge SiNRs functionalized with hydrogen and fluorine.

Edge Type	Edge Atom	Dopant	E_{edge} (eV/Å)	E_g (eV)	Magnetic State	Magnetic Edge State	
						ΔE (meV)	E_g (eV)
a_{11}	H	N	-1.005	0.00	FM-S	-0.31	Up (0.137) (in) Down (0.540) (d)
	H	B	-4.401	0.00	NM	-	-
	F	N	-2.301	0.00	FM-SGS	-0.10	Up (0.092) (in) Down (0.463) (d)
	F	B	-4.662	0.00	FM-SGS	-0.09	Up (0.481) (in) Down (0.259) (in)
a_{22}	H	N	-0.683	0.00	NM	-	-
	H	B	-4.412	0.00	NM	-	-
	F	N	-1.170	0.00	NM	-	-
	F	B	-4.662	0.00	NM	-	-
a_{22-11}	H	N	-1.026	0.00	NM	-	-
	H	B	-4.403	0.00	NM	-	-
	F	N	-1.344	0.00	NM	-	-
	F	B	-4.584	0.00	NM	-	-
a_{21}	H	N	-2.067	0.00	FM-S	-170.91	Up (0.310) (d) Down (0.188) (d)
	H	B	-4.864	0.00	FM-S	-180.46	Up (0.44) (d) Down (0.630) (in)
	F	N	-1.87	0.00	AFM-S	+43.59	Up (0.248) (in) Down (0.241) (d)
	F	B	-5.123	0.00	AFM-S	+4.57	Up (0.103) (in) Down (0.221) (in)

The band structures of N- or B-doped ASiNRs show that there is a half-filled band near the Fermi level, resulting in a semiconductor-metal transition, as seen in Figure 4.17 (a) and (c). Interestingly, the band introduced by N dopant lies closer to the conduction band, while the band induced by B dopant is located near valence band. The reason behind this is that the value of ionic electronegativity of the Si atom is higher (lower) than the B (N), and hence the orbit energies of B (N) are higher (lower) than

those of Si. As a result, the B (N) impurity shifts the band levels of SiNRs up (down) [322, 323]. It should be noted that the impurity states mostly stem from the hybridized interactions between N or B impurity and their Si atom neighbors. Besides, the spin-polarized calculations show that the N- or B-doped a_{22} and a_{22-11} have a null magnetic moment, which is in agreement with pristine ASiNRs [322].

Figure 4.17 Band structures of N-doped hydrogenated a_{11} in the (a) NM and (b) FM states, N-doped fluorinated a_{11} in the (c) NM and (d) FM states.

4.7 Zigzag / Klein edge Silicene Nanoribbons Doped by N or B Atom

Similar to ASiNRs, the N or B impurity prefers to be substituted for the edge Si atoms to interior ones due to the lower formation energy of edge doped SiNRs in $\langle 2\bar{1}\bar{1}0 \rangle$

direction. The underlying reason can be attributed to the decay of edge states in ZSiNRs, as reported for GNRs [338]. Figure 4.18 indicates the preferred N- or B-doped positions in functionalized SiNRs along $\langle 2\bar{1}\bar{1}0 \rangle$ direction.

Figure 4.18 Different edge structures of functionalized SiNRs along the $\langle 2\bar{1}\bar{1}0 \rangle$ direction doped with a N or B atom, in which the most stable substitution configurations are indicated. The cyan and red balls represent Si and functional addends (H, F, Cl, Br, and I), respectively, and the solid blue circle shows a N or B atom.

The non-spin-polarized calculations of doped SiNRs in the $\langle 2\bar{1}\bar{1}0 \rangle$ direction show that they are all metallic. First, I studied the effect of N or B doping on the zigzag edge SiNRs. The spin-resolved band structure of N- or B-doped hydrogenated z_1 shows that the introduction of dopants at the edge of the hydrogenated z_1 gives rise to asymmetrical spin-up and spin-down bands around E_f , suggesting that the spin degeneracy of AFM - z_1 disappeared and the mirror symmetry is broken. For the N- (B-)

doped case, both spin-up and spin-down channels show semiconducting behaviors with direct band gaps of 0.161 and 0.219 eV (0.219 and 0.106 eV), respectively, as shown in Figure 4.19(a)-(d). The origin of spin-degeneracy in pristine hydrogenated z_1 is considered to be the unpaired spin-up π band and spin-down π^* band at the edge of the nanoribbons. The introduction of N or B impurity at the edge of the ZSiNR injects an additional electron or hole into the SiNR, and they would occupy the unpaired spin orbital, causing the degeneracy of bands to break. This fact that the electrons and holes tend to inject into the edge π and π^* states more than interior states can be related to the local structure distortion caused by impurities at the edge of the nanoribbon [322, 323]. To obtain a deeper insight into the reason of breaking degeneracy of hydrogenated z_1 , the spin-density distribution of N-doped hydrogenated z_1 is plotted in Figure 4.19(e). As can be seen, the spin-polarization at the Si edge of the SiNR which is substituted by the N impurity is fully suppressed, proving that there are no unpaired spins on the N atom. However, the spin polarization of the un-doped edge is less affected, and it is similar to the spin polarization of the pristine hydrogenated z_1 . The reason should be attributed to the less affected bond lengths of Si atoms in the un-doped edge. For both N and B cases, the total magnetic moment is 1 μ_B per supercell. It should be added that the fluorinated z_1 doped by N or B atoms are also semiconductors with band gap of 0.159 (0.155) eV and 0.198 (0.84) eV for spin-up (-down) channels, respectively. These results are in excellent agreement with previous studies [322, 323].

Figure 4.19 Band structures of N-doped hydrogenated z_1 in the (a) NM and (b) AFM states, B-doped hydrogenated z_1 in the (c) NM and (d) FM states. (e) The spin-charge density distributions of N-doped hydrogenated z_1 . The purple ball represents N atom. The green and blue regions correspond to the isosurfaces of spin-up and spin-down channels with a spin value of $0.001 \text{ e}/\text{\AA}^3$.

The spin-polarized band structure of N- or B-doped z_2 shows that similar to the doped z_1 , the spin degeneracy of AFM - z_2 is broken, and it becomes an AFM semiconductor with asymmetrical spin-up and spin-down bands. The value of band gaps for hydrogenated z_2 doped with N and B are 0.365 (0.352) eV and 0.444 (0.243) eV for spin-up (-down) channels, respectively. As mentioned before, there are flat bands near the Fermi level in the whole Brillouin zone for both spin-up and spin-down channels in spin-polarized band structures of asymmetric z_{2-1} . So that, the hydrogenated and fluorinated z_{2-1} are FM direct semiconductor and FM metal, respectively. If the Fermi level shifts down to meet the top valence band, the z_{2-1} would be transformed to a half-metal with the spin-down channel conducting. While, if the Fermi level shifts up to cross the bottom conduction band, the spin-up channel takes the role of the conductive channel, and the spin-down channel shows an insulating behavior. One approach to moving the

Fermi level up (down) is injecting electrons (holes) by n-type (p-type) doping [317]. The N- or B-doped hydrogenated z_{2-1} becomes a FM indirect semiconductor with band gaps of 0.486 (0.200) eV and 0.238 (0.373) eV for spin-up (-down) channels, respectively. While, when N is doped at the edge of the fluorinated z_{2-1} , it is semiconducting in the spin-down channel with a direct band gap of 0.174 eV, and conducting in spin-up channel, showing a half-metallic behavior. Interestingly, when B is doped in fluorinated z_{2-1} , the structure keeps its FM metallic behavior, as shown in Figure 4.20.

Figure 4.20 Band structures of N-doped fluorinated z_{2-1} in the (a) NM and (b) FM states, B-doped fluorinated z_{2-1} in the (c) NM and (d) FM states.

When N or B atom is doped in z_{221} edge structure, the AFM indirect semiconductor - z_{221} converts into a different state depending on the dopant type and

functionalization atoms. The N- or B-doped hydrogenated z_{221} is still a semiconductor; however, the spin degeneracy disappears. For the N-doped, there is a direct band gap of 0.163 eV in the spin-up channel and an indirect band gap of 0.252 eV in the spin-down channel. The B-doped hydrogenated z_{221} has a direct band gap of 0.372 (0.111) eV for both spin-up (-down) channel. Moreover, the fluorinated z_{221} doped with N atom is transformed into metal. However, the B-doped fluorinated z_{221} is indirectly semiconducting (0.238 eV) in the spin-up channel, and conducting in the spin-down channel.

I also address the effect of N or B doping in Klein edge SiNRs. The hydrogenated AFM direct semiconductor k_3 keeps its semiconducting character when it is doped with N or B atoms. However, doping causes the spin degeneracy to disappear. The energy band gaps for N- or B-doped hydrogenated k_3 are 0.158 (0.170) eV and 0.202 (0.089) eV for spin-up (-down) channels. The fluorinated AFM indirect semiconductor k_3 is still semiconductor when it is doped with N atom. There is a direct band gap (0.149 eV) in the spin-up channel and an indirect band gap (0.134 eV) in the spin-down channel. Though B-doped fluorinated k_3 is semiconducting (0.221 eV) in the spin-up channel, it is conducting in the spin-down channel. The effects of doping on AFM direct semiconductor rk_{22} are more straightforward. In both hydrogenated and fluorinated cases, the semiconducting character remains after doping, while, the spin degeneracy of bands collapses. It is found that the doping decreases the energy band gap of hydrogenated or fluorinated rk_{22} .

Finally, I investigated the influence of the N or B doing on the magnetic properties of the combinations of zigzag and reconstructed Klein edges. The

hydrogenated and fluorinated AFM direct semiconductor $rk_{22} - z_{11}$ are transformed into FM metals when they are doped with N or B atom on the edge sites. The hydrogenated AFM metal $rk_{11} - z_{22}$ is turned into a semiconductor with direct band gap of 0.320 eV for spin-up channel and an indirect band gap of 0.178 eV for spin-down channel when doped with a N atom, and becomes indirect semiconductor with band gap of 0.082 (0.124) eV for spin-up (-down) channel when a Si atom is replaced with a B atom. The fluorinated $rk_{11} - z_{22}$ shows half-metallic behavior when it is doped with N or B atom. The N-doped $rk_{11} - z_{22}$ is semiconducting (0.178 eV) in the spin-up channel, and conducting in the spin-down channel. But the situation is reversed when it is doped with a B atom. The spin-up channel shows metallic behavior, while the spin-down channel is a semiconductor with a direct band gap of 0.307 eV. In FM metal $rk_{11} - z_{11}$ case, the B atoms do not change its characteristic. However, the hydrogenated and fluorinated $rk_{11} - z_{11}$ become semiconductors when they are doped with N atom. The N-doped hydrogenated $rk_{11} - z_{11}$ has an indirect band gap of 0.423 (0.416) eV around its Fermi level for spin-up (-down) channel. As mentioned before, the hydrogenated $rk_{22} - z_{22}$ is a FM indirect semiconductor. It is found that the N or B doping keeps its semiconducting behavior, while the band gap values experience a small change. The situation is a little bit different for the FM metal fluorinated $rk_{22} - z_{22}$ case. It experiences a metal to semiconductor transformation when it is doped with N atom. A direct band gap of 0.479 eV in the spin-up channel and an indirect band gap of 0.395 eV are found around its Fermi level. A half-metallic behavior is observed in the B-doped fluorinated $rk_{22} - z_{22}$ structure. While the spin-up channel is conducting, the spin-down channel is semiconducting with a band gap of 0.353 eV (For more details see Tables 4.6 and 4.7).

Table 4.6 E_{edge} (eV), E_g (eV), magnetic state, $\Delta E_{\text{FM-AFM}}$ (eV), and spin-polarized band gap (eV) for different N- and B-doped zigzag edge SiNRs and Klein edge SiNRs functionalized with hydrogen and fluorine.

Edge Type	Edge Atom	Dopant	E_{edge} (eV/A)	E_g (eV)	Magnetic State	Magnetic Edge State	
						ΔE (meV)	E_g (eV)
z_1	H	N	-1.251	0.00	AFM-S	+0.001	Up (0.161) (d) Down (0.191) (d)
	H	B	-4.765	0.00	AFM-S	+0.001	Up (0.219) (d) Down (0.106) (d)
	F	N	-2.699	0.00	AFM-S	+0.009	Up (0.159) (d) Down (0.155) (d)
	F	B	-5.050	0.00	AFM-S	+0.002	Up (0.198) (d) Down (0.840) (d)
z_2	H	N	-1.452	0.00	AFM-S	+99.79	Up (0.365) (d) Down (0.352) (in)
	H	B	-4.598	0.00	AFM-S	+93.55	Up (0.444) (in) Down (0.243) (in)
	F	N	-2.386	0.00	AFM-S	+5.94	Up (0.131) (in) Down (0.035) (in)
	F	B	-4.700	0.00	AFM-S	+7.62	Up (0.184) (in) Down (0.031) (d)
z_{2-1}	H	N	-1.725	0.00	FM-S	-28.43	Up (0.486) (in) Down (0.200) (in)
	H	B	-4.849	0.00	FM-S	-20.96	Up (0.238) (in) Down (0.373) (in)
	F	N	-2.416	0.00	FM-HM	-8.42	Up (0.00) Down (0.174) (d)
	F	B	-4.709	0.00	FM-M	-7.59	0.00
z_{221}	H	N	-2.187	0.00	AFM-SGS	+0.008	Up (0.163) (d) Down (0.252) (in)
	H	B	-5.508	0.00	AFM-S	+0.007	Up (0.372) (d) Down (0.111) (d)
	F	N	-2.069	0.00	AFM-M	+0.003	0.00
	F	B	-4.637	0.00	AFM-HM	+0.002	Up (0.238) (in) Down (0.00)
k_3	H	N	-1.904	0.00	FM-S	-0.010	Up (0.158) (d) Down (0.170) (d)
	H	B	-5.310	0.00	FM-S	-0.011	Up (0.202) (d) Down (0.089) (d)
	F	N	-2.682	0.00	FM-S	-0.020	Up (0.149) (d) Down (0.134) (in)
	F	B	-6.066	0.00	FM-HM	-0.015	Up (0.221) (d) Down (0.00)
rk_{22}	H	N	-1.171	0.00	FM-S	-0.011	Up (0.129) (d) Down (0.186) (d)
	H	B	-4.590	0.00	FM-S	-0.020	Up (0.198) (d) Down (0.072) (d)
	F	N	-1.893	0.00	FM-S	-0.013	Up (0.123) (d) Down (0.183) (d)
	F	B	-4.648	0.00	FM-S	-0.022	Up (0.203) (d) Down (0.073) (d)

Table 4.7 E_{edge} (eV), E_g (eV), magnetic state, $\Delta_{\text{EFM-AFM}}$ (eV), and spin-polarized band gap (eV) for different N- and B-doped reconstructed Klein edge and zigzag edge SiNRs functionalized with hydrogen and fluorine.

Edge Type	Edge Atom	Dopant	E_{edge} (eV/A)	Band gap (eV)	Magnetic State	Magnetic Edge State	
						ΔE (meV)	Band gap (eV)
rk ₂₂ -Z ₂₂	H	N	-1.710	0.00	FM-S	-13.660	Up (0.424) (in) Down (0.383) (in)
	H	B	-4.590	0.00	FM-S	-12.530	Up (0.186) (in) Down (0.483) (d)
	F	N	-1.893	0.00	FM-S	-13.360	Up (0.479) (d) Down (0.395) (in)
	F	B	-4.648	0.00	FM-HM	-1.810	Up (0.00) Down (0.353) (d)
rk ₁₁ -Z ₁₁	H	N	-1.543	0.00	FM-S	-10.150	Up (0.423) (in) Down (0.416) (in)
	H	B	-4.522	0.00	FM-M	-0.110	0.00
	F	N	-1.915	0.00	FM-S	-8.230	Up (0.384) (in) Down (0.423) (d)
	F	B	-5.154	0.00	FM-M	-0.080	0.00
rk ₂₂ -Z ₁₁	H	N	-0.517	0.00	AFM-M	+0.007	0.00
	H	B	-4.397	0.00	AFM-M	+0.005	0.00
	F	N	-0.999	0.00	AFM-M	+0.002	0.00
	F	B	-4.569	0.00	AFM-M	+0.001	0.00
rk ₁₁ -Z ₂₂	H	N	-0.556	0.00	FM-S	-12.41	Up (0.320) (d) Down (0.178) (in)
	H	B	-3.504	0.00	FM-SGS	-6.070	Up (0.082) (in) Down (0.124) (in)
	F	N	-0.940	0.00	FM-HM	-11.03	Up (0.178) (d) Down (0.00)
	F	B	-5.199	0.00	FM-HM	-5.84	Up (0.00) Down (0.307) (d)

4.8 Summary

First-principles calculations based on DFT were used to investigate the geometry, stability, electronic and magnetic properties of different edge-functionalized (-H, -F, -Cl, -Br, and -I) SiNR types, including armchair, zigzag, Klein, reconstructed Klein, reconstructed pentagon-heptagon, and their combinations. Halogenated edge SiNRs are found much more stable than those of hydrogenated edge. Although the edge stability of halogenated edge SiNRs decreases with increasing atomic number of halogen atoms, they

are still more favorable than hydrogenated edge SiNRs due to their lower formation energies. Experimentally under ambient conditions, a_{22} structure along the along $\langle 1\bar{1}10 \rangle$ direction and hydrogenated $rk_{22}+z_2$ and fluorinated k_3 structures along the $\langle 2\bar{1}\bar{1}0 \rangle$ direction are found as the most stable structures. It was revealed that the asymmetry in edge functionalization of two edges of ZSiNRs induces fantastic SGS and ferromagnetic metal behaviors into ZSiNRs owing to breaking of the spin degeneracy of two edge states. Furthermore, the combinations of reconstructed Klein edge and zigzag edge result in various magnetic states depending on type and density of edge functional addend.

It was discovered that N or B dopant energetically tends to be substituted for the Si edge atoms, suppressing the spin polarization of edge Si states. When a N or B atom is doped into the fluorinated a_{11} structure, a NM semiconductor to FM SGS transition occurs. In addition, the half-metal character was also found in fluorinated z_{2-1} and k_3 when they are doped with N and B atoms, respectively. It was also observed that several peculiar magnetic states, such as ferromagnetic metal, AFM metal, half-metal, and SGS, can be obtained in the combinations of reconstructed Klein edge and zigzag edge depending on dopant atom and edge functional atom and its density. These predicted properties of SiNRs will have potential applications in the advancement of nanoelectronics and spintronics.

CHAPTER 5

Band Gap Tuning of Armchair Silicene Nanoribbons Using Periodic Hexagonal Holes

In this chapter, using first-principle calculations based on DFT, the electronic properties of ASiNR with periodic nanoholes (ASiNRPNHs) are investigated. It is found that ASiNRPNHs' band gaps change based on the nanoribbon's width, nanohole's repeat periodicity and position relative to the nanoribbon's edge compared to pristine ASiNRs because of changes in quantum confinement strength. My results are expected to be a felicitous reference for theoretical and experimental studies in tuning band gap of silicene. These results were published in Journal of Applied Physics [97], MRS Advances [98], and IEEE Southeast Conference 2015 [99].

5.1 Overview

The potential applications of graphene have been limited in modern electronic devices such as FETs because its zero band gap restricts achievable on-off current ratio [339]. Utilizing quantum confinement and edge effects found in graphene nanoribbon structures are important approaches to open appreciable band gaps in graphene [38, 335]. Their electronic properties not only depend on their size and edge shapes but are also susceptible to defects which can be introduced during their fabrication, such as Stone-Wales defects [340], vacancies [341], nanoholes [342], or substitutions [343].

Inspired by the outstanding properties of graphene, other 2D monolayer materials beyond graphene, such as silicene, have attracted great interest [23]. In 2015, the first silicene FETs were demonstrated by Tao *et al.* the reported carrier mobility for these initial devices was around $100 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$. Though the value of carrier mobility is less

than expected, it would be improved by tuning the band structure and enhancing the charge transport of silicene [133]. Nonetheless, silicene like graphene lacks a band gap around its Fermi level [59]; therefore, opening a band gap in a silicene sheet may create new possibilities in the fabrication of high-performance nanoscale devices such as FETs [330]. It should be mentioned that spin-orbit coupling of silicene opens a small band gap of 23.9 meV, which is much higher than that of graphene [133]. To open a band gap in a silicene sheet, several methods have been applied, including by cutting a silicene sheet into SiNRs [12, 42, 77], applying a perpendicular electric field to the silicene sheet [43, 85], chemical functionalization of silicene sheets [45, 46], surface adsorption [48, 49, 79, 344, 345], substitution [51], silicene and substrate interaction [52, 53, 95, 96, 346], or introducing periodic nanoholes on the silicene sheet known as silicene nanomesh [54, 101].

SiNRs are of keen interest for device applications. Highly uniform single nanoribbons with a width of ~ 1.7 nm arranged in an array of parallel nanoribbons have already been demonstrated [128]. Moreover, unlike GNRs, the edges of SiNRs are strongly resistant to oxidation making them more stable than GNRs [347]. There are two types of SiNRs depending on their edge structures: ASiNR and ZSiNR. Theoretically, it has been demonstrated that short ASiNR FETs have a large on-off current ratio of 10^6 and the output characteristic shows a current saturation which cannot be found in GNR FETs [330].

Analogous to graphene and GNRs, silicene sheets and SiNRs can have different types of defects that include vacancies and holes. Although they are defects, they can have beneficial effects on the properties of nanoribbons if controlled and purposely

positioned. A variety of techniques have been developed to produce and control the position of these types of defects, *e.g.*, by using the sharp tips in a STM situated at specific locations to introduce periodic nanoholes [341], nanolithography using scanning near-field optical microscope (SNOM) [348], and by using an extremely focused beam from an aberration-corrected illumination system in a STEM to create vacancies with atomic precision [349]. Recently, theoretical studies have demonstrated that the properties of the pristine silicene sheets [350-355] and SiNRs [356, 357] can be altered significantly in the presence of vacancies.

However, to the best of my knowledge, no study to this point has investigated the effects of periodic nanoholes on electronic properties of SiNRs. Here I used the first-principle method based on DFT to study the electronic properties of ASiNRPNHs. My focus is on the relationship between electronic properties of ASiNRPNHs with repeat periodicities of nanoholes as well as the nanohole's sites relative to both nanoribbon's edges. Mono-hydrogenation and di-hydrogenation effects of the dangling bonds on the electronic structures of ASiNRs and ASiNRPNHs are also studied.

5.2 Computational Details

Calculations employ the first-principle method based on NEGF combined with DFT using ATK [293, 296, 328]. In order to solve Kohn-Sham equation, the PZ parameterized LDA is used for the exchange-correlation functional. A double- ζ polarized basis set is utilized for expanding the electronic density. All the nanoribbon structures are treated using periodic boundary conditions. The density mesh cut-off is chosen to be 150 Rydberg. The electronic temperature of the nanoribbons is kept constant at 300 K and a vacuum space of around 15 Å between neighboring cells avoids interactions between the

nanoribbon and its periodic images. For ASiNRPNHs, first, all atomic positions and lattice constants are relaxed so that the force on each atom is less than 0.05 eV/Å. During structure optimization, a (1×1×51) k-point, where 51 is only for the periodic direction, is used for sampling of the Brillouin zone and increased to (1×1×101) k-point to obtain accurate electronic structures for the nanoribbons.

5.3 Pristine Armchair Silicene Nanoribbons

The nanoribbon structures under investigation were all made of buckled silicene with all of the dangling bonds terminated by hydrogen atoms. ASiNRs are named W-ASiNR:nH where “W”, the nanoribbon width, is the number of Si dimer lines across the ribbon’s width and n is the number of H atoms that are connected to the dangling bonds of Si atoms. Two different configurations of mono-hydrogenation (:H) and di-hydrogenation (:2H) are considered in this study. First, similar to C atoms in graphene, Si atoms are assumed to adopt sp^2 hybridization, so that the dangling bonds of the Si atoms are passivated by forming Si-H bonds. Figure 5.1(a) shows the top view and side view of a 6-ASiNR:H. The cyan and red balls signify Si and H atoms, respectively. Furthermore, the primitive unit cell, which includes 12 Si atoms and 4 H atoms, is marked by a dashed box. The edge diagonal and horizontal Si-Si bond lengths are 2.26 Å and 2.23 Å, respectively, which are less than bond length of inner Si-Si (2.28-2.29 Å). The Si-H bond length is 1.5 Å. The adjacent Si atoms are slightly buckled with a distance of 0.49-0.51 Å. The band structure of 6-ASiNR:H is plotted in Figure 5.1(c). The conduction and valence bands no longer cross at the K-point, but instead, a noticeable direct band gap has emerged at the Γ -point. For 6-ASiNR:H, the calculated energy band gap is around 0.46 eV. Variations of the band gap with a width of the ribbons are plotted in Figure 5.1(d).

All of the examined ribbons with widths of $W = 3 - 20$ (3.93 - 36.55 Å), are semiconducting with a direct band gap at Γ -point. A closer look at the data indicates that the energy gaps of ASiNR:H decrease oscillatory as a function of increasing nanoribbon's width and they, like armchair graphene nanoribbons, can be classified into three families with width $W = 3P - 1$, $3P$, and $3P + 1$, where P is a positive integer, which their energy gap E_G satisfies $E_G(3P - 1) < E_G(3P) < E_G(3P + 1)$. These results are in good agreement with those obtained in previous studies [42, 330, 336]. The oscillatory behavior of energy gap of ASiNRs like Armchair graphene nanoribbons has been explained by quantum confinement effects [358].

As mentioned before, Si atoms prefer to have sp^3 hybridization over sp^2 in silicene. Therefore, it is expected that passivation of dangling bonds with a single H atom would not be enough because a second single dangling bond would remain. For this reason, ASiNRs with doubly hydrogen edge termination (W-ASiNR:2H) are also considered. Figure 5.1(b) and (c) show the top view and side view of a 6-ASiNR:2H and its corresponding band structure, respectively. The primitive unit cell, which includes 12 Si atoms and 8 H atoms, is indicated by a dashed box. The diagonal and horizontal Si-Si bonds are 2.35 Å and 2.34 Å, respectively, while, the bond length of inner Si-Si atoms are 2.27 - 2.28 Å (same as the bond length in the silicene). The buckling distance varies from 0.40 - 0.46 Å for inner adjacent Si atoms to 0.64 - 0.92 Å for adjacent Si atoms in the edges. The Si-H bond length is also 1.5 Å.

Figure 5.1 (a) and (b) The top and side view of pristine 6-ASiNR:H and 6-ASiNR:2H, respectively. The primitive unit cell is marked by a black dashed box, cyan and red balls representing silicon and hydrogen atoms respectively. All bond lengths are embedded in the unit cell. (c) The band structure of 6-ASiNR:H and 6-ASiNR:2H which show a band gap of 0.428 eV and 0.91 eV at the Γ -point, respectively. (d) Pristine ASiNR:H and ASiNR:2H energy band gap dependence on nanoribbon width. The energy band gaps decrease oscillatory as the widths of the nanoribbons increase.

Considering the band structure, the value of band gap energy for 6-ASiNR:2H is 0.91 eV that is 1.97 times greater than that of 6-ASiNR:H. Variations of the band gap of W-ASiNRs:2H with width of the ribbons are also calculated in Figure 5.1(d). Similar to ASiNRs:H, all the nanoribbons with widths in the range of $W = 3 - 20$ are

semiconducting with a direct band gap at Γ -point, and their band gaps can be divided into three distinct families, while their energy gap E_G satisfies $E_G(3P + 1) < E_G(3P - 1) < E_G(3P)$. It can be seen that the band gap for W-ASiNR:H and (W+2)-ASiNR:2H are almost equal. In other words, di-hydrogenation of each armchair edge reduces the effective width of the ribbon by 1. This principle has been confirmed in the literature for graphene [359]. In this way, we can achieve the same band gap of W-ASiNR:H with a wider ribbon of (W+2)-ASiNR:2H which should be easier to fabricate.

The structural stabilities of di-hydrogenated armchair silicene edges are evaluated by the formation energies. The average formation energies are defined as

$$E_f = [E_{\text{ASiNR:2H}} - (E_{\text{ASiNR:H}} + n_H \times E_{\text{H}_2} \times \frac{1}{2})] / n_H \quad (5.1)$$

where, $E_{\text{ASiNR:2H}}$ and $E_{\text{ASiNR:H}}$ are the total energies of ASiNRs with a mono-hydrogen edges termination and ASiNRs with a di-hydrogen edges termination, respectively. E_{H_2} is total energy of an isolated H_2 molecule. Finally, n_H gives the difference of the number of hydrogen atoms between two systems. For 6ASiNR:2H, the formation energy is -0.713 eV/atom. The negative value of the average formation energy indicates that the formation of ASiNR:2H from ASiNR:H is an exothermic reaction. For other ribbons in the widths range of 3 - 20, the values of the average formation energy vary between -0.886 eV/atom and -0.710 eV/atom, suggesting that ASiNR:2H are energetically more favorable and more stable than ASiNR:H regardless of the ribbon width.

5.4 Armchair Silicene Nanoribbons Perforated with Nanoholes

Figure 5.2 shows the superlattice model structures of ASiNRPNHs. Periodic nanoholes are formed by removing a single benzene-like ring of Si atoms, resulting in a hexagonal hole, in a periodic arrangement. All dangling bonds are first passivated by mono-hydrogen and then by di-hydrogen. ASiNRPNHs is defined as W-ASiNRPNHs:nH-r, where “W” is the nanoribbon’s width and “r”, repeat periodicity, is the minimum number of zigzag silicon chains between two opposite edges of two adjacent nanoholes, and n is the number of H atoms connected to the dangling bonds of Si atoms. The structures of 12-ASiNRPNHs:H-2, 12-ASiNRPNHs:2H-3, and 12-ASiNRPNHs:H-4 are shown in Fig. 3a, b, and c, respectively, in which the superlattice’s units are marked by dashed boxes. The smallest unit for the superlattice when “r” is an even number has one hole in the supercell, while it contains two holes in the supercell when “r” is an odd number. This occurs because the centers of the two adjacent nanoholes are unable to align in the same straight line when “r” is an odd number; therefore two nanoholes in the smallest unit are considered. The average distances between two adjacent holes when r is equal to 2, 3, and 4 are 4.48, 6.68, and 11.15 Å, respectively.

Figures 5.3(a), (b), and (c) show band structures of pristine 13-ASiNR:H, 13-ASiNRPNHs:H-4, pristine 13-ASiNR:2H, and 13-ASiNRPNHs:2H-4 and their corresponding Bloch wave functions of the valence band and conduction band at Γ -point, respectively. As one can see, nanoholes with repeat periodicity of 4 increase the band gap of pristine 13-ASiNR:H from 0.315 eV to 0.416 eV and widen the band gap of pristine 13-ASiNR:2H from 0.049 eV to 0.289 eV. There is also a noticeable difference between

the Bloch wave functions of the valence band and conduction band. The occupied valence band states are arranged in the ribbon direction, while unoccupied conduction band states appear more across the ribbon. Comparing wave functions of 13-ASiNRPNHs with pristine 13-ASiNR, the wave functions disappear at the hole edges. The localized states around the nanohole cause flat bands at the Z-point of the valence and conduction band edges of 13-ASiNRPNHs:H-4 and 13-ASiNRPNHs:2H-4 which agrees well with previous work on graphene [360-362].

Figure 5.2 Schematic of superlattice model structures of W-ASiNRPNHs:nH-r for W = 12 and (a) $r = 2$ and $n = 1$, (b) $r = 3$ and $n = 2$, (c) $r = 4$ and $n = 1$ where “r” repeat periodicity is the minimum number of zigzag chains between two opposite edges of two adjacent nanoholes and n is the number of H atoms that are connected to the silicon dangling bonds. The supercell is indicated by a red dashed box.

Furthermore, for pristine 13-ASiNR:2H and 13-ASiNRPNHs:2H-4, the wave functions vanish for Si atoms at the edge of the nanoribbon and edge of the nanoholes that are passivated by two hydrogens which mean that their contributions are almost zero. In order to understand this, the partial density of states (PDOS) of silicon atoms located at the edge of the ribbon and the nanohole and their nearest neighbors are calculated in Figure 5.3(d) and (e). While a Si atom contributes four valence electrons ($Ne\ 2s^2 2p^2$) in the ribbon, the contributions of s orbitals are too small near Fermi level. Therefore, only p_z orbitals are considered. It can be seen that for 13-ASiNRPNHs:H-4, the p_z orbital of Si_1 atom with mono-hydrogen termination is the main contributor to the DOS at the Fermi level, but for 13-ASiNRPNHs:2H-4, the p_z orbital of Si_1 atom vanishes. On the other hand, the p_z orbital of Si_2 atom which lies next to the Si_1 appears at Fermi level and assumes the main role. The reason is that in ASiNR:H, each Si atom at the edge is supposed to bond to two Si atoms and one H by sp^2 hybridization, therefore, p_z orbitals of all the edge and inner Si atoms have contributions in valence band maximum (VBM) and conduction band minimum (CBM) states. While, for ASiNR:2H, Si atoms at the edge are bonded to two Si atoms and two H atoms by sp^3 hybridization. Therefore, p_z orbitals are not available to contribute while the edges are terminated with two H atoms. In the same way, the p_z orbital of the Si_4 in 13-ASiNRPNHs:2H-4 has a larger contribution to the DOS at the Fermi level than that of Si_3 that is located at the hole edge and is terminated by two H atoms. As a result, a W-ASiNR:2H can be modeled as a combination of two edges with sp^3 hybridization that make a large band gap due to strong quantum confinement and an internal ASiNR with sp^2 hybridization with a width of $W-2$ with a

much smaller band gap that is equal to value of band gap of (W-2)-ASiNR:H. The band gap of this combination is defined by the latter.

Figure 5.3 (a) and (b) The band structure of pristine 13-ASiNR:H, 13-ASiNRPNHs:H-4, 13-ASiNR:2H, and 13-ASiNRPNHs:2H-4, which show the bands flat at the Z-point. The value of energy band gap for 13-ASiNR:H and 13-ASiNRPNHs:H-4 are 0.315 eV and 0.416 eV, respectively. The value of energy band gap for 13-ASiNR:2H and 13-ASiNRPNHs:2H-4 are 0.049 eV to 0.289 eV, respectively. (c) Bloch wave function isosurfaces of the conduction band and valence band for pristine 13-ASiNR:H, 13-ASiNRPNHs:H-4, 13-ASiNR:2H, and 13-ASiNRPNHs:2H-4 at Γ -point which show the wave functions disappearing at hole edges. The isosurfaces value is 0.02 a.u. (d) and (e) PDOS for 13-ASiNRPNHs:H-4 and 13-ASiNRPNHs:2H-4, respectively. Insets show schematic models of 13-ASiNRPNHs:H-4 and 13-ASiNRPNHs:2H-4, respectively with selected silicon atoms numbered.

To better understand how the electronic properties of ASiNR can be affected by induced nanoholes, electrostatic difference potential for ASiNR perforated with one hole is modeled and plotted in Figure 5.4(a). In this model, a semiconducting W-ASiNR with

a length of 10 nm is connected to two metallic ZSiNRs with a width of $(W+2)/2$. The electrodes are composed of semi-infinite ZSiNRs. All the periodic nanoholes are assumed to be perforated only in ASiNR region. The number of the nanoholes is defined based on the value of the repeat periodicity. For example, a 12-ASiNR with $L = 6.5$ nm can be perforated by 4 holes (diameter of a hole = 1.02 nm) when $r = 2$ (0.488 nm). One finds that a nanohole at the center of the ASiNR can be considered as perturbative on-site potential in the electronic transmission direction. The reason lies in the fact that since the domain size of a nanohole is small, the electrons are confined by the potential causing Bloch wave functions to vanish into the nanohole [363]. Therefore, the introduction of perturbative on-site potential by nanoholes will result in a quantum confinement effect which modifies the band structure and transmission spectrum of ASiNRPNHs. It should be noted that the effect of quantum confinement depends on two important factors: the repeat periodicity “ r ” and the position of the nanohole relative to the edge of nanoribbon. Figure 5.4 (b) shows the transmission spectra of pristine 12-ASiNR:2H, 12-ASiNR:2H perforated with one hole in the center, and 12-ASiNRPNHs:2H-2 (4 nanoholes with repeat periodicity of 2). A gate voltage ($V_g = -1$ V) is applied to the ASiNR channel that results in a shift of the valence band edges towards the Fermi level. The transmission spectrum of pristine 12-ASiNR:2H has a low value in the energy range of 0 - 0.6 eV, corresponding to the energy the band gap of the armchair nanoribbon. A hole in the center of this ribbon cannot make a big change in the transmission gap of pristine 12-ASiNR:2H, while periodic nanoholes increase it to 0.85 eV.

Figure 5.4 (a) Electrostatic difference potential of 12-ASiNR:2H perforated with one hole in the center. A semiconducting 12-ASiNR:2H as a channel is connected to two metallic 7-ZSiNRs as two electrodes. The yellow and white balls represent Si and H atoms, respectively. (b) Transmission spectra of pristine 12-ASiNR:2H, 12-ASiNR:2H perforated with one hole in the center, and 12-ASiNRPNHs:2H-2 (4 nanoholes with repeat periodicity of 2). Fermi level is set at zero.

In order to consider the effects of periodic nanoholes on the electronic properties of silicene armchair nanoribbons with widths satisfying $W = 3P + 1$, the band structures of 13-ASiNRPNHs:H- r for $r = 2, 3$, and 4, as a representative of this family, are calculated along with the band structure plot of pristine 13-ASiNR:H for comparison in Figure 5.5(a). The largest band gap is seen at $r = 2$ (0.481 eV) and is approximately 1.53 times greater than the 13-ASiNR:H (0.315 eV). It means that the maximum confinement effect is found at $r = 2$ for $W = 13$. However, reducing the linear density of nanoholes with increasing repeat periodicity leads to a decrease in energy band gap as a whole. Therefore, the value of energy band gap at $r = 4$ (0.416 eV) is less than that at $r = 2$. Furthermore, the energy band gap oscillates. The origin of this oscillation can be seen in Figure 5.2. As previously mentioned, unlike when repeat periodicity is an even number, the centers of two adjacent nanoholes are not aligned in a same straight line for an odd number of repeat periodicity. The oscillatory behavior of energy band gap comes from this difference. The effects of electronic transmission for nanoholes as potential barriers

which are positioned in the same straight line are different from the case where the adjacent nanoholes are staggered along the direction of the nanoribbon's width. In other words, when the repeat periodicity is an odd number, the distance from the inner edge of one hole to the outer edge of the ribbon is different from this distance for the adjacent hole, causing different quantum confinement strength through the ribbon. Figure 5.5 presents the partial charge densities of VBM (a-d) and CBM (e-h) for 13-ASiNR, and for 13-ASiNRPNHs:H-r ($r = 2, 3$, and 4). One can observe that the spatial distribution of charges has been changed because of the nanoholes. The inner edge state which has an important impact on the gap size has been increased. While, the charge densities around the nanoholes in the ribbon are the same for the $r = 2$ and 4 cases, the densities of charges for two adjacent nanoholes in the ribbon are different for $r = 3$ due to the different distance of inner edge of one hole to the outer edge of the nanoribbon as seen in Figure 5.5. Hence, the sensitivity of the energy band gap of the nanoribbons to the repeat periodicity and the nanohole's position leads to a smaller or larger energy band gap than that of pristine ASiNR:H depending on the strength of the quantum confinement.

Moreover, the transmission spectra of 13-ASiNRPNHs:H-r ($r = 2, 3$, and 4) are plotted in Figure 5.6(a). One can see both the value of transmission coefficients are zero at the Fermi level and the neighboring energy levels for different values of " r ", which would take a different value for higher energy levels and are in agreement with the band structure. To consolidate the obtained results, the energy band gaps of W-ASiNRPNHs:H-r for $W = 10, 16$, and 19 and $r = 2, 3$, and 4 were calculated and compared with 13-ASiNRPNHs:H-r ($r = 2, 3$, and 4), as shown in Figure 5.6(b). The

pristine ASiNRs correspond to $r \rightarrow \infty$, where the distance between two adjacent nanoholes is infinity. It is obvious that their trends of energy band gap are quite similar.

Figure 5.5 The partial charge density isosurfaces of (a-d) VBM and (e-h) CBM for 13-ASiNR, 13-ASiNRPNHs:H-2, 13-ASiNRPNHs:H-3, and 13-ASiNRPNHs:H-4. Their corresponding band structures are depicted in Fig. 5. The isosurfaces value is 0.01 a.u.

Figure 5.6 (a) Calculated band structure and corresponding transmission spectra of pristine 13-ASiNR:H, 13-ASiNRPNHs:H-2, 13-ASiNRPNHs:H-3, and 13-ASiNRPNHs:H-4 with energy band gaps of 0.315 eV, 0.481 eV, 0.253 eV, and 0.416 eV, respectively. (c) Effect of repeat periodicity on the energy band gap of ASiNRPNHs with widths $W = 3P + 1$ (10, 13, 16, and 19).

In order to determine the stability of ASiNRPNHs, the formation energy of a hole is calculated. The average formation energy of a hole perforated in ASiNRs is expressed as

$$E_{\text{hole}(x)} = \frac{1}{n_{\text{hole}}} [E_{\text{W-ASiNRPNHs-r}} - E_{\text{W-ASiNR}} + 6 \times n_{\text{hole}} \times E_{\text{Si}(x)} - n_{\text{hole}} \times n_{\text{H}} \times E_{\text{H}_2} \times \frac{1}{2}] \quad (5.2)$$

where $E_{\text{W-ASiNRPNHs-r}}$ and $E_{\text{W-ASiNR}}$ are the total energy of W-ASiNR perforated with nanoholes with repeat periodicity of r and the total energy of the pristine W-ASiNR, respectively. $E_{\text{Si}(x)}$ can be defined as the total energy of free Si ($E_{\text{Si}(1)}$), which corresponds to an extreme Si-rich condition and can also be adopted to the total energy of a silicon atom in a perfect silicene sheet ($E_{\text{Si}(2)}$), which correlates with the Si-poor condition. Furthermore, E_{H_2} is the total energy of an isolated H_2 molecule. n_{hole} and n_{H} are the number of the holes in the supercell and the number of H atoms that attach to the dangling bonds at the nanohole edges respectively. In Equation 5.2, 6 represents the number of Si atoms removed to form a nanohole. To assess whether the proposed structures are stable, variations of the average formation energy of a hole from Si-rich ($E_{\text{hole}(1)}$) to Si-poor ($E_{\text{hole}(2)}$) conditions are studied. The negative $E_{\text{hole}(x)}$ values correspond to an exothermic process, indicating that ASiNRPNHs structures are stable. For 13-ASiNRPNHs:H-2, the $E_{\text{hole}(1)}$ is equal to -2.84 eV/hole. The calculated formation energy of a hole is negative and decreases with increasing r ($E_{\text{hole}(1)} = -3.56$ eV/hole for $r = 4$), indicating that 13-ASiNRPNHs:H are energetically favorable in Si-rich condition. As bulk Si is more stable than silicene by 1.56 eV/atom, it is expected that the absolute value of $E_{\text{hole}(2)}$ should be less than $E_{\text{hole}(1)}$. The values of $E_{\text{hole}(2)}$ for 13-ASiNRPNHs:H-2 and

13-ASiNRPNHs:H-4 are 1.35 and 0.626 eV/hole, respectively, suggesting that 13-ASiNRPNHs:H are not stable considering Si-poor condition.

Correspondingly, 12-ASiNRPNHs:H- r for $r = 2, 3$, and 4 are culled from ASiNRPNHs:H with nanoribbons widths $W = 3P$. The band structure of pristine 12-ASiNR:H and 12-ASiNRPNHs:H- r when “ r ” is equal to $2, 3$, and 4 are presented in Figure 5.7(a). As can be seen, the energy band gaps of 12-ASiNRPNHs:H vary similarly to those of nanoribbons with widths satisfying $W = 3P + 1$ that can lead to a resemblance for the electronic properties in both cases. The underlying reason for the oscillatory behavior of the band gap can be explained by the same argument. Regardless of the value of repeat periodicity, the pristine 12-ASiNR:H has a noticeable band gap (0.243 eV). Interestingly enough, the maximum value of the energy band gap (0.459 eV) for 12-ASiNRPNHs:H occurs for $r = 2$ and this value is approximately 1.89 times that of pristine 12-ASiNR:H. Transmission spectra of the 12-ASiNRPNHs:H for $r = 2, 3$, and 4 are plotted in Figure 5.7(a) and correspond well to those in band structures. For 12-ASiNRPNHs:H-2, the $E_{\text{hole}(1)} = -1.57$ eV/hole. The calculated formation energy of a hole is negative and changes slightly with increasing r ($E_{\text{hole}(1)} = -1.54$ eV/hole for $r = 4$), indicating that the Si-rich 12-ASiNRPNHs:H are energetically favorable, but it is less stable than 13-ASiNRPNHs:H. However, the values of $E_{\text{hole}(2)}$ are equal to 2.61 and 2.66 eV/hole for 12-ASiNRPNHs:H-2 and 12-ASiNRPNHs:H-4, respectively. It shows that 12-ASiNRPNHs:H like 13-ASiNRPNHs:H may not be stable for the Si-poor condition.

In order to compare the obtained results with other members of the $W = 3P$ family, the energy band gap changes of the W -ASiNRPNHs:H- r for $W = 9, 12, 15$ and 18 and $r = 2, 3$, and 4 are calculated and plotted in Figure 5.7(b). Obviously, the trend of

band gap variations in 15-ASiNRPNHs:H and 18-ASiNRPNHs:H are almost the same as 12-ASiNRPNHs:H, however, band gap changes for 9-ASiNRPNHs:H are completely different from 12-ASiNRPNHs. For 9-ASiNRPNHs:H, the maximum energy band gap (0.582 eV) occurred at $r = 4$. One possible reason is that perforating a hole in the 9-ASiNR clogged the electronic transmission of the nanoribbon; ergo the electronic properties of 9-ASiNRPNHs are dramatically tailored. One finds that band gap sizes rise monotonically with increasing repeat periodicity for 9-ASiNRPNHs. The difference may result from a stronger confinement effect more so than staggered distance effect of two adjacent nanoholes and more important than reduced density of nanoholes caused by large repeat periodicity for 9-ASiNRPNHs:H. However, it starts to decrease after $r = 4$ and reaches 0.198 eV at $r = 6$. This means that the effects of the smaller density of nanoholes for the repeat periodicities with values larger than 4 play a central role for 9-ASiNRPNHs:H.

Figure 5.7 (a) Calculated band structure and corresponding transmission spectra of pristine 12-ASiNR:H, 12-ASiNRPNHs:H-2, 12-ASiNRPNHs:H-3, and 12-ASiNRPNHs:H-4 with energy band gap of 0.243 eV, 0.459 eV, 0.073 eV, and 0.102 eV, respectively. (b) Effect of repeat periodicity on the energy band gap of ASiNRPNHs:H with widths $W = 3P$ (9, 12, 15, and 18).

In order to investigate the effects of perforating periodic nanoholes on electronic properties of ASiNRs:H with ribbon width fulfilling $W = 3P - 1$, the band structures of 14-ASiNRPNHs:H- r for $r = 2, 3$, and 4 and pristine 14-ASiNR:H are calculated, as shown in Figure 5.8(a). The maximum value of energy band gap (0.341 eV) is found at $r = 2$ and is nearly tenfold compared to pristine 14-ASiNR:H (0.031 eV). Such remarkable increase of energy band gap can be ascribed to strong quantum confinement effect at $r = 2$. Previous observations in other cases including the oscillatory behavior of energy band gap and decreasing maximum value of energy band gap for increasing repeat periodicity as a whole are seen in this case. The transmission spectra of 14-ASiNRPNHs:H- r for $r = 2, 3$, and 4 and pristine 14-ASiNR:H are illustrated in Figure 5.8 (a), which are in good agreement with obtained band structures. For 14-ASiNRPNHs:H-2, the $E_{\text{hole}(1)}$ is equal to -1.61 eV/hole. This negative value does not vary with increasing r ($E_{\text{hole}(1)} = -1.57$ eV/hole for $r = 4$), showing that 14-ASiNRPNHs:H are energetically favorable in Si-rich condition. However, like the two families above, they are not stable in the Si-poor condition. The calculated formation energies of a hole in this condition for 14-ASiNRPNHs:H-2 and ASiNRPNHs:H-4 are 2.57 and 2.61 eV/atom, respectively.

For a deeper insight into the electronic properties of ASiNRPNHs:H of $W = 3P-1$ family, the energy band gap of ASiNRPNHs:H- r for $r = 2, 3$, and 4 and $W = 8, 11$, and 17 are calculated, as seen in Figure 5.8(b). The trend of energy band gap of 17-ASiNRPNHs:H is similar to that of 14-ASiNRPNHs:H. However, for 8-ASiNRPNHs:H and 11-ASiNRPNHs:H, energy band gap sizes roll off almost monotonically after achieving their maximum value at $r = 2$. The reason for the absence of oscillatory behavior can be attributed to a weak staggered distance effect of two adjacent nanoholes.

In other words, effects of decreased density of nanoholes by increasing repeat periodicity determines the trend for these cases.

Figure 5.8 (a) Calculated band structure and corresponding transmission spectra of pristine 14-ASiNR:H, 14-ASiNRPNHs:H-2, 14-ASiNRPNHs:H-3, and 14-ASiNRPNHs:H-4 with energy band gap of 0.031 eV, 0.341 eV, 0.093 eV, and 0.2423 eV, respectively. (b) Effect of repeat periodicity on the energy band gap of ASiNRPNHs with widths $W= 3P - 1$ (8, 11, 14, and 17).

As mentioned before, W -ASiNR:2H can be considered as $(W+2)$ -ASiNR:H because di-hydrogenated Si edge atoms have no contribution to the VBM and CBM states. Figure 5.9 shows the variations of the band gap of W -ASiNRPNHs:2H as a function of repeat periodicity.

Figure 5.9 Effect of repeat periodicity on the energy band gap of ASiNRPNHs:2H with widths of (a) $W= 3P - 1$ (8, 11, 14, and 17), (b) $W= 3P$ (9, 12, 15, and 18), and (c) $W= 3P + 1$ (10, 13, 16, and 19).

As one can see, the trend of band gap variations for the ASiNRs:2H is the same for ASiNRs:H. However, since di-hydrogenation of Si atoms located at the hole edges make their contribution to the band gap almost zero, stronger quantum confinement and higher band gap are expected. Interestingly enough, the value of band gap for 12-ASiNRPNHs:2H when $r = 2$ reaches 0.923 eV, 2.23 times greater than that of pristine 12-ASiNRs:2H and 2 times greater than that of 12-ASiNRPNHs:H. Also, the value of band gap for 18-ASiNRPNHs:2H-2 is 0.635 eV, even greater than that of 10-ASiNRPNHs:H-2 which is 0.601 eV. Thus, di-hydrogenating of the dangling bonds in ASiNRPNHs open a simple way to achieve higher and appreciable band gaps not only with the same geometry of mono-hydrogenated ASiNRPNHs but also with wider ASiNRs which are experimentally favorable. Though, the value of band gaps for 8-ASiNRPNHs:2H and 9-ASiNRPNHs:2H are increased to more than 1.5 eV, they are not reliable because the holes encompass the entire ribbon width. Furthermore, the calculated formation energy of a hole in 12-ASiNRPNHs:2H-2, 13-ASiNRPNHs:2H-2, and 14-ASiNRPNHs:2H-2 in a Si-rich condition are -4.75 , -4.98 , and -4.94 eV/hole, respectively, and they remain approximately constant with increasing repeat periodicity. Interestingly enough, unlike the ASiNRPNHs:H, the value of formation energies of the nanoholes in ASiNRPNHs:2H are negative in the Si-poor condition, so that $E_{\text{hole}(2)}$ for 12-ASiNRPNHs:2H-2, 13-ASiNRPNHs:2H-2, and 14-ASiNRPNHs:2H-2 are -0.563 , -0.797 , and -0.754 eV/hole, respectively, and they reached to -0.409 , -0.468 , and -0.314 eV/hole, respectively, when $r = 4$. These negative values suggest that ASiNRPNHs:2H are much more stable than ASiNRPNHs:H in both poor- and rich-Si conditions. Consequently, perforating a hole with doubly hydrogenated dangling bonds is much more favorable experimentally.

Creating perfect periodic patterns of nanoholes remains a challenging task. However it should be noted that the band gap is underestimated in LDA calculations [364].

Considering that the nanohole's positions relative to the nanoribbon's edges play a critical role in their energy band gap sizes, four inequivalent nanohole sites in pristine 14-ASiNR:2H, 15-ASiNR:2H, 16-ASiNR:2H, and 17-ASiNR:2H are plotted in Figure 5.10(a). Despite 16-ASiNR:2H and 17-ASiNR:2H in which position 2 is a hole at center of the ribbon, for 14-ASiNRs:2H and 15-ASiNR:2H, a hole at the center of the nanoribbon cannot be perforated due to the even number (6) of hexagonal silicon across the ribbon, therefore, positions 2 or 3 can be selected as the semi-central holes. Position 1 specifies a hole at top of position 2, and position 4 is a hole at the edge of the nanoribbon. The repeat periodicity is set at 2. By defining nanoholes as perturbative potentials, sites of nanoholes in nanoribbons cause changes in the strength of quantum confinement that can alter the band structure of nanoribbons. As illustrated in Figure 5.10(b), perforating a nanohole in different positions relative to the edge of nanoribbons can affect the size of their energy band gaps differently depending on the ribbon's width. Position "0" is a pristine W-ASiNRs:2H without a hole. As one can see, for all the nanoribbons, the maximum value of band gap is obtained at position 1 due to the strong confinement effect between the edge of nanoribbons and nanoholes. Also, nanoholes at the edge of nanoribbon decrease the quantum confinement and cause minimum band gaps. Position 2 that contains a central hole for 16-ASiNR:2H and 17-ASiNR:2H, and a semi-central hole for 14-ASiNR:2H, and 15-ASiNR:2H result in the second minimum value of the band gap. Interestingly, a hole at position 3 has a greater band gap than that of position 2 for all the ribbons except 15-ASiNR:2H. The value of energy band gap for nanoholes perforated

in 15-ASiNR:2H at positions 2 and 3 are equal because both of them are located at the same distance relative to the edges, and both edges have an equal shape. Similarly, for 17-ASiNR:2H, nanoholes at position 1 and 3 give rise to an equal band gap. As a result, the energy band gap changes are strongly dependent on the nanoholes sites relative to the edges of nanoribbons. The energy band gap becomes bigger when the holes are perforated near edges because of strong quantum confinement. While the same hole at the center or the edge of nanoholes can decrease the band gap.

Figure 5.10 (a) Schematic of the model structure for 14-ASiNR, 15-ASiNR, 16-ASiNR, and 17-ASiNR. Holes are assumed to be perforated at 4 different positions (numbered 1-4) relative to the nanoribbon's edge when $r = 2$. (b) The variations in energy band gap of 14-ASiNRPNHs:2H-2, 15-ASiNRPNHs:2H-2, 16-ASiNRPNHs:2H-2, and 17-ASiNRPNHs:2H-2 with respect to the position of nanoholes relative to the edge of the nanoribbon. Position 0 indicates a pristine nanoribbon. (c) Variations of energy band gap of 12-ASiNRPNHs:H, 13-ASiNRPNHs:H, 14-ASiNRPNHs:H for large repeat periodicities ($6 < r < 30$).

As previously seen, the band structures of ASiNRs are influenced by perforating periodic nanoholes with small repeat periodicities due to the effect of direct coupling of nanoholes. To develop our understanding of the impact of perforating nanoholes with large periodicities on the band structures of ASiNRs:H, variations of band gap for 12-ASiNRPNHs:H, 13-ASiNRPNHs:H, and 14-ASiNRPNHs:H as a function of repeat periodicity when “r” changes from 6 to 30 are calculated, as shown in Figure 10(c). Despite the substantial modifications in energy band gap for ASiNRPNHs:H with small repeat periodicities, it is clear that the energy band gaps of the nanoribbons tend to slowly approach those of pristine ASiNRs:H for a very large repeat periodicity. It confirms that the effects of nanoholes on the energy near the band gaps lessen with increasing repeat periodicity. In this case, an indirect effect is predominant for the sake of modification in Bloch wave functions of band edges by nanoholes [341]. It should be noted that for ASiNRPNHs:2H, the band gaps start to approach that of pristine nanoribbons for $r > 10$.

5.5 Summary

My results show that periodic nanoholes in ASiNRs modify its energy band gap depending on the armchair nanoribbon’s width, repeat periodicity, and position relative to the edges. Semiconducting pristine ASiNRs can be divided into three distinct families with widths $W = 3P - 1$, $3P$, and $3P + 1$ (P is a positive integer). Their band gaps drop with increasing nanoribbon width. There is a shift of two in the trend of the band gap of ASiNR:H when the edge hydrogenation varies to ASiNR:2H. In the case of ASiNRPNHs with small repeat periodicities, band gaps depend on the nanoribbon’s width as the holes act as perturbative on-site potentials affecting the strength of quantum confinement. For ASiNRPNHs with large repeat periodicities, there is less of an effect because of the

decrease in linear density of nanoholes resulting in band gaps near that of pristine nanoribbons. Perforating periodic nanoholes is an exothermic process, and ASiNRPNHs:2H are more stable than ASiNRPNHs:H. It was found that the value of energy band gap of ASiNRPNHs:2H are larger than ASiNRPNHs:H with the same geometry. The value of energy band gap for 12-ASiNRPNHs:2H-2 is 0.923 eV, approximately two times that of ASiNRPNHs:H-2 and its corresponding pristine nanoribbon. Perforating periodic nanoholes can also produce a noticeable band gap of 0.635 eV in 18-ASiNR. It was also shown that the nanohole position affects the band gap, so that a hole near the edge can increase the band gap much more than the same hole in the center. My findings promote further theoretical and experimental studies on the band gap tuning of silicene, potentially opening a new route to extend the lifetime of silicon electronics.

CHAPTER 6

Emergence of Strong Ferromagnetism in Silicene Nanoflakes via Patterned

Hydrogenation and Its potential Application in Spintronics

Considerably different properties emerge in nanomaterials as a result of quantum confinement and edge effects. In this chapter, the electronic and magnetic properties of quasi-zero-dimensional SiNFs are investigated using first-principles calculations. It has been revealed that the strongly induced spin magnetizations align parallel and demonstrates a collective character by large range ferromagnetic exchange coupling, giving rise to its potential use in spintronic circuit devices. Spin switch models are offered as an example of one of the potential applications of SiNFs in tuning the transport properties by controlling the hydrogen coverage. These results were published in Computational Materials Science.

6.1 Overview

The tendency of silicon atoms to adopt sp^3 and sp^2 hybridization over only sp^2 hybridization [60] makes its honeycomb structure buckled [42, 59], distinguishing it from graphene which is a flat sheet. Hence, silicene is naturally more favorable for atom and molecule adsorption [62, 365-367] than graphene, resulting in a great deal of applications in the area of hydrogen storage [365], thin film solar cell absorbers [368], hydrogen separation membranes [366], and molecular sensors [62, 367]. Hydrogenation was found as a favorable chemical method to modify the electronic and magnetic properties of graphene because of its reversibility [33] and controllability [369, 370]. There has been quite a number of theoretical [45, 87, 127, 306, 371-385] and experimental [123, 125, 126] studies on the hydrogenation

of silicene in the literature. Intriguing properties in hydrogenated silicene have been reported through theoretical calculations, for example, large gap opening [45], and extraordinary FM [372] and optoelectronic properties [127]. A fully hydrogenated derivative of silicene, known as silicane which is the silicon counterpart of graphane, has been expected to have a band gap in the range of 2.9–3.8 eV, depending on the configuration [87]. Ergo, it would be considered a potential material for optoelectronics and FET applications [376]. The hydrogenation process in silicene is uniformly ordered and reversible, making it easier to manipulate the hydrogen coverage [123]. Consequently, the half-hydrogenation can be achieved by hydrogenating of silicene from one side while keeping the other side intact similar to its carbon counterpart graphane. It was found that half-hydrogenated silicene shows FM semiconducting behavior with a band gap of 0.95 eV [372, 385]. Besides, a long-range room temperature FM coupling between Si atoms can be realized in half-hydrogenated silicene [385]. Osborn *et al.* have theoretically shown that H atoms prefer to be adsorbed in pairs to form the most stable configuration of partially hydrogenated silicene [373]. By altering the concentration of hydrogen atoms on silicene, the characteristic of its band structures can be varied from metallic to magnetic semiconducting and then to NM semiconducting [374].

As nanomaterials approach lower dimensions, their properties noticeably change due to the quantum confinement and edge effects. The quasi-one-dimensional nanoribbons show semiconducting or metallic behavior depending on their edge types and the width of the ribbon [297, 320]. Further confinement of

silicene has sparked interest in the study of quasi-zero-dimensional SiNFs since understanding their properties is of great significance in order to continue advancing nanoscale electronic and spintronic device fabrication. Luan *et al.* found that electronic and magnetic properties of SiNFs depend strongly on their size and shape [386]. The hexagonal zigzag SiNF exhibits NM semiconducting behavior, while the triangular zigzag SiNF is a magnetic semiconductor.

Although hydrogenated silicene sheets have been recently discovered, the effects of hydrogen adsorption on SiNFs have not been explored yet. In this chapter, I employed first-principles methods based on DFT to investigate the electronic and magnetic properties of SiNFs with different configurations. The patterned adsorption of hydrogen on SiNFs is systematically explored, and its stability is evaluated by calculating the formation energies. Contrary to bare SiNFs, the hydrogenated SiNFs show unique magnetic properties. I also propose a straightforward and efficient approach to engineering the transport properties of electrons by controlling the coverage of hydrogenation on SiNRs, which may pave a new path to explore spintronics at the nanoscale.

6.2 Computational Details

My first-principles calculations are performed based on DFT combined with NEGF implemented by ATK package [293, 296, 328]. The hybrid B3LYP exchange-correlation functional is utilized as the exchange and correlation functional to solve Kohn-Sham equations. The electronic wave functions are expanded by a double- ζ polarized basis for different atoms, while the cut-off

energies are chosen to be 600 eV. To eliminate the interactions between adjacent nanoflakes, a 30 Å vacuum slab is considered in all directions. The electronic temperature is kept constant at 300 °K during calculations. For geometry optimization, both supercell and the atomic positions are allowed to be fully relaxed until the force and stress are less than 0.0025 eV/Å and 0.005 eV/Å³, respectively.

6.3 The Structure, Electronic, and Magnetic Properties of Silicene Nanoflakes

Four types of hydrogen passivated SiNFs with different shapes (hexagonal and triangular), edges (armchair and zigzag), and sizes are studied. In order to differentiate the various configurations of SiNFs, the abbreviations are used as follows: *AH* stands for armchair-edged hexagonal, *ZH* represents zigzag-edged hexagonal, *AT* implies armchair-edged triangular and *ZT* signifies zigzag-edged triangular. The AT-SiNF and AH-SiNF can be further categorized by the integer number dimer lines across one side of the nanoflake, while the ZT-SiNF and ZH-SiNF are identified by the integer number of edge Si atoms across one side of the nanoflake. The model structures of 3-AH-SiNF, 4-AT-SiNF, 3-ZH-SiNF, and 4-ZT-SiNF, as representatives of the configurations above, are presented in Figure 6.1, in which all structures are made of freestanding silicene and all Si edge atoms are terminated by H atoms. The cyan and red balls signify Si and H atoms, respectively. After structural relaxation, the buckling height between sublattices A and B is ~ 0.50 (0.51) Å in T-SiNFs (H-SiNFs). The distance between Si-H atoms is found to be 1.50 Å, indicating that H atoms are chemically attached to SiNFs' edge. The edge Si-Si bond lengths are 2.23-2.24 Å for T-SiNFs and 2.23-2.25 Å

for Z-SiNFs, which are less than the bond length of inner Si-Si (2.28 Å) (similar to pristine silicene [297, 387]), indicating relatively large atomic distortion at the edges.

Figure 6.1 Schematic structural models of (a) 3-AH-SiNF, (b) 4-AT-SiNF, (c) 3-ZH-SiNF, and (d) 4-ZT-SiNF as representatives of armchair-edged hexagonal SiNF, armchair-edged triangular SiNF, zigzag-edged hexagonal SiNF, and zigzag-edged triangular SiNF, respectively, and their corresponding band structures. The cyan and red balls represent Si and H atoms, respectively. The bond lengths and the buckling distances (in unit of Å) are also given. Black and red lines are spin-up and spin-down channels in (d), respectively.

The band structures of 3-AH-SiNF, 4-AT-SiNF, and 3-ZH-SiNF are also shown in Figure 6.1. My calculations show that N-AH-SiNFs, N-AT-SiNFs, and N-ZH-SiNFs are NM and exhibit semiconducting behavior. Unlike the band structure of a silicene sheet in which the bonding π and antibonding π^* band cross at K points in the Brillouin zone [59, 97], finite gaps of 0.63, 0.89, 0.76 eV are opened between the VBM and the CBM of 3-AH-SiNF, 4-AT-SiNF, and 3-ZH-SiNF, respectively. The energy band gap in SiNF is attributed to the quantum confinement and edge effects caused by the reduced dimensionality of the

structures. As displayed in Figure 6.2, the band gaps decrease gradually by increasing the nanoflakes size. These results are in agreement with previous theoretical findings [386].

Figure 6.2 N-AH-SiNFs, N-AT-SiNFs, N-ZH-SiNFs, and N-ZT-SiNFs energy band gap dependence on nanoflakes size. The energy band gaps decrease as the size of the nanoflakes increase.

Our spin-polarized calculations demonstrate that the ground state of N-ZT-SiNFs have magnetic behaviors. Figure 6.1 shows the band structure of 4-ZT-SiNF as a representative of N-ZT-SiNFs. As can be seen, the E_f lies close to VBM of the spin-up channel, and CBM of the spin-down channel. The value of band gap for the spin-down channel (1.05 eV) is slightly less than that of the spin-up channel (1.07 eV). The isosurfaces of spin density distribution ($\rho_{spin-up} - \rho_{spin-down}$) of 4-ZT-SiNF is plotted in Figure 6.3(a). The system provides a ferrimagnetic spin ordering with opposite spins on Si atoms of sublattices A (Si_A) and B (Si_B) in which the total spin-up is larger than the total spin-down. The energy difference between spin-polarized and spin-unpolarized states of 4-ZT-SiNF is 0.29 eV, in favor of the spin-polarized state. The spin density of the inner Si atoms is less than the edge Si

atoms. Besides, the Si atoms at three corners of nanoflakes, located in sublattice B, have opposite spin direction compared to the outermost Si atoms. This may originate from the charge redistribution of Si-3p states in the region near the edges where the Si-Si bond lengths shrink by 0.05 Å. The total magnetic moment found on our calculations for 3-ZT-SiNF is 2.0 μ_B , and for 4-ZT-SiNF is 3.0 μ_B , showing that the total magnetic moment (M) of N-ZT-SiNF is equal to $N-1$. It indicates that our results are in excellent agreement with Lieb's theorem for bipartite lattices [388].

Figure 6.3 (a) Spin-charge density distribution ($\rho_{spin-up} - \rho_{spin-down}$) and (b) electron difference densities of 4-ZT-SiNF. The cyan and red balls represent Si and H atoms, respectively. The pink and blue regions correspond to the isosurfaces of spin-up and spin-down states. The isosurfaces value is 0.012 a.u.

To visualize the electron redistribution of ZT-SiNFs, the electron difference density of 4-ZT-SiNF is presented in Figure 6.3(b). Electron difference density is the difference between the self-consistent valence charge density and the superposition of atomic valence densities. One could see that electrons

accumulated on H atoms and between neighboring Si atoms. The high electron density between Si-Si shows this fact that electrons are shared by Si atoms, resulting in the formation of a covalent bond between them. Furthermore, since Si is less electronegative than H, the Si-H bond is polarized toward H, resulting in negative charging of H atoms. The results are also similar to the corresponding cases for graphene [389, 390].

6.4 Adsorption of a Single Hydrogen Atom on SiNFs

To understand the effect of hydrogenation on the electronic and magnetic properties of SiNFs, the adsorption of a single H (represented by sH) atom on 4-ZT-SiNF and 3-ZH-SiNF (as representatives of zigzag-edged SiNFs) are analyzed. Although sublattices A and B are equivalent in a free silicene sheet, they are different in ZT-SiNF due to the broken symmetry related to the flakes shape, and in turn to the number of Si_A and Si_B atoms. It is found that Si_B is energetically more favorable than that of Si_A for hydrogen adsorption. The difference of adsorption energies between two sublattices for 4-ZT-SiNF is 0.9 eV in support of Si_B . It should be noted that the difference of adsorption energies between two sublattices for 3-ZH-SiNF can be neglected owing to its structural symmetry. I consider the adsorption of H atom on the Si_B in the following calculations. Figure 6.4(a) shows the geometric structures of sH -4-ZT-SiNF and sH -3-ZH-SiNF in which a single H atom is adsorbed on the Si_B of the nanoflakes. The Si-H bond length is 1.5 Å, indicating a strong Si-H covalent bond. A charge transfer from Si to H atom occurs, as shown in Figure 6.4(b), where electrons are piled up on H (pink area), and the electron density on hydrogenated Si_B (blue area) is slightly

increased. Also, the electron orbital overlap can be observed in the Si_B -H. Such a charge transfer makes the nearest Si_A - Si_B bonds to the H atom longer (weaker) but the second nearest Si_A - Si_B bonds shorter (stronger), where the lengths are 2.35 Å and 2.25 Å, respectively. Furthermore, the buckling height between two sublattices where H atom is adsorbed is 0.71 Å which is much greater than that of bare SiNF (0.50 Å). The bond angle of Si_A - Si_B -H is about 110° which is close to tetrahedral molecule geometry. These values are consistent with earlier research on silicene [381, 382].

Figure 6.4 (a) Optimized geometric structures (b) the corresponding electron difference densities and (c) the corresponding spin-charge density distribution of sH-3-ZH-SiNF and sH-4-ZT-SiNF. The pink and blue regions correspond to the isosurfaces of spin-up and spin-down states. The isosurfaces value is 0.012 a.u.

As explained above, the 4-ZT-SiNF is magnetic, and 3-ZH-SiNF is NM with spin moments of 3.0 and 0.0 μ_B , respectively. It is found that magnetism is

induced in 3-ZH-SiNF which is inherently NM and enhanced in 4-ZT-SiNF upon adsorption of single H atom. Figure 6.4(c) shows the isosurfaces of the spin density distribution of sH-4-ZT-SiNF and sH-3-ZH-SiNF. As can be seen, with adsorption of a single H on Si_B, the spin-down charges on Si_B are faded; interestingly certain spin-up charges appear on H atom, and the spin-up charges on three Si_A neighboring the hydrogenated Si_B are slightly increased. In addition, the spin-up charges on some Si_A sites decrease in the sH-4-ZT-SiNF, as indicated by the green arrows in Figure 6.4(c) bottom. More than that, the strongest spin-up charge appears on edge Si_A site in the sH-3-ZH-SiNF, as indicated by the green arrow in Figure 6.4(c) top. Interestingly, the spin-density of both sH-4-ZT-SiNF and sH-3-ZH-SiNF show some mirror symmetry as shown by the blue dashed lines in Figure 6.4(c). As a result, the total spin moments are augmented, for sH-4-ZT-SiNF increases to 4.0 μ_B , and for sH-3-ZH-SiNF rises to 1.0 μ_B . It means that a single H atom adsorbed on Si_B can increase the total spin moment of the SiNFs by 1.0 μ_B . This phenomenon can be explained as follows. In addition to the strong σ bond between Si_A-Si_B atoms in the bare SiNF, a weak π bond exists between unpaired and localized p_z electrons of the Si_A-Si_B atoms. When a single H atom approaches Si_B, the quasi π bond is destroyed, and true sp^3 hybridization occurs by forming a strong σ bond between Si_B-H and a weaker Si_A-Si_B bond. Furthermore, the p_z electrons of Si_A are left unpaired and delocalized, causing them to move around the Si_A and the H atom. As a result, the spin-up charges accumulate on H atom and Si_A, and the Si_B is depleted from spin-down charges. The contribution of Si_A to magnetism is much larger than that of H atom, as will be explained later. It

is worth mentioning that when the H atom is conversely adsorbed on Si_A, the total spin moment of sH-4-ZT-SiNF and sH-3-ZH-SiNF become 2.0 and $-1.0 \mu_B$, respectively, showing a decrease in the total spin moment by $1.0 \mu_B$.

6.5 Higher Hydrogen Coverage on SiNFs

As previously mentioned, each H atom induces a spin moment of $1.0 \mu_B$ in SiNF. Therefore, higher H concentration is desired to further enhance the magnetism in the SiNFs. To this end, half-hydrogenated (hH) SiNFs, in which all Si_B atoms are hydrogenated, and all Si_A atoms remain unsaturated are considered. Figure 6.5(a) shows the optimized geometries of hH-4-ZT-SiNF and hH-3-ZH-SiNF. The relaxed bond lengths of Si_A-Si_B are ~ 2.33 - $2.35 \text{ \AA}$, and of Si_B-H are $\sim 1.52 \text{ \AA}$. The relaxed bond lengths of Si_A-Si_B are ~ 2.33 - $2.35 \text{ \AA}$, and of Si_B-H are ~ 1.51 - $1.52 \text{ \AA}$. The buckling distance of both structures is found to be $0.71 \text{ \AA}$. These values agree with previous findings for hydrogenated silicene [371, 373, 378, 381, 382, 385]. In order to find the favored coupling of the magnetic moments, three different magnetic types are considered: AFM, FM, and NM states. The spin polarization energy ($\Delta E_{SP} = E_{NM} - E_{FM}$) and the FM energy ($\Delta E_{FM} = E_{AFM} - E_{FM}$) are calculated. It is found that ΔE_{SP} and ΔE_{FM} are 5.86 (8.38) eV and 0.264 (0.427) eV for hH-4-ZT-SiNF (hH-3-ZH-SiNF), respectively, indicating that half hydrogenation of SiNFs leads to a FM state.

The ΔE_{FM} per H atom for hH-4-ZT-SiNF (hH-3-ZH-SiNF) system is 17.6 (15.8) meV. Adopting the mean-field approximation [391], the Curie temperature is estimated to be about 204 and 183 °K for hH-4-ZT-SiNF and hH-3-ZH-SiNF structures, respectively, indicating that the half-hydrogenated SiNFs are predicted

to be FM materials close to the room temperature. My calculated Curie temperatures for half-hydrogenated SiNFs are higher than those reported for half-hydrogenated silicene sheet (111.9-121.6 °K) which could be considered as a nanoflake with infinite size [371, 392], showing a decrease in Curie temperature with increasing the size of nanoflakes. In addition, the net magnetic moment of hH-4-ZT-SiNF is 18.0 μ_B , and hH-3-ZH-SiNF is 27.0 μ_B , which are considerably larger than that of bare 4-ZT-SiNF (3.0 μ_B) and 3-ZH-SiNF (0.0 μ_B).

To visualize spin distributions on half-hydrogenated SiNFs, the spin densities of hH-4-ZT-SiNF and hH-3-ZH-SiNF are plotted in Figure 6.5(b). As can be seen, the systems provide FM spin ordering due to the parallel alignment of spin moments. The magnetic moments for Si_A, Si_B, and H which are marked in Figure 6.5(b) are calculated to be 0.923, -0.011, and 0.088 μ_B , respectively. It is clear that the induced magnetic moments are mainly localized on unsaturated Si_A atoms (92%), while the H atoms above Si_B atoms carry small magnetic moments (8%), showing that the unpaired $3p_z$ electrons in the unsaturated Si_A atoms have the highest contribution to the magnetism. Since the $3p_z$ electrons on Si_A are delocalized to some extent, a long-range FM exchange coupling between the p_z electrons of different Si_A atoms exists due to the extended p - p interactions, giving rise to a significant collective character.

It is worth mentioning that for non-hydrogenated flakes, experimentally, both Si_A and Si_B atoms would be exposed to hydrogen atoms. However, since the adsorption energy is more favorable to Si_B atoms, H atoms would probably bond to Si_B atoms. Once the flake is half-hydrogenated, and the Si_B sites are saturated, Si_A-

H bonds are also formed. Therefore, the $3p_z$ orbitals of the unsaturated Si_A atoms will be saturated by $1s$ orbitals of H atoms, causing the spin states to be suppressed. Similar to silicane [371], fully hydrogenating (fH) of SiNFs where all Si_A and Si_B atoms are saturated by H atoms, quenches the magnetism. It is found that the fH-4-ZT-SiNF and fH-3-ZH-SiNF become NM wide band gap semiconductors with energy gaps of 3.16 and 2.8 eV, respectively.

Figure 6.5 (a) Optimized geometric structures (b) the corresponding spin-charge density distribution of hH-3-ZH-SiNF and hH-4-ZT-SiNF. The pink and blue regions correspond to the isosurfaces of spin-up and spin-down states. The isosurfaces value is 0.012 a.u.

6.6 The Total Spins Moment of Bare and Half-hydrogenated SiNFs

Next, I developed a general rule for the total spin moment of nanoflakes as a function of nanoflakes size. It is found that the total magnetic moment of bare SiNF satisfies $M_{bare} = N_A - N_B$, where N_A and N_B are the numbers of Si_A and Si_B atoms in the nanoflakes. Among the four studied SiNF structures, only ZT-SiNF has a different number of Si atoms in each sublattice ($N_A \neq N_B$), therefore, the magnetic moment of 4-ZT-SiNF, as an example, with $N_A = 18$ and $N_B = 15$ is equal to $M_{bare} = 3.0 \mu_B$. However, the total magnetic moments for the rest of the structures are calculated to be $M_{bare} = 0.0 \mu_B$. For instance, the magnetic moment of 3-HT-SiNF with $N_A = 27$ and $N_B = 27$ is equal to $0.0 \mu_B$. As found before, a single H can boost the SiNF's spin moment by $1.0 \mu_B$. Consequently, the induced spin moments of half-hydrogenated SiNF where all Si_B atoms are saturated and Si_A atoms keep unsaturated is $M_{hH} = M_{bare} + N_B \times 1$. As calculated before, the total spin moment for hH-4-ZT-SiNF is $18.0 \mu_B$, and for hH-3-ZH-SiNF is $27.0 \mu_B$. More careful examination of these values reveals that the total magnetic moment for half-hydrogenated zigzag triangular and hexagonal triangular SiNFs can be expressed as $M_{hH} = (5N + N^2)/2$ and $M_{hH} = 3N^2$, respectively, where N is the nanoflakes size. Figure 6.6(a) represents the variations of the total spin moment of half-hydrogenated zigzag triangular and hexagonal SiNFs as a function of nanoflakes size. The total spin moments of hydrogenated SiNFs are notably larger than that of bare SiNFs and almost increase squarely with the nanoflakes size. Compared to graphene, it is found that the total spin moment of hH-SiNFs is two times larger than that of hH-GNFs [393, 394].

Figure 6.6 (a) The magnetic moment changes *versus* nanoflakes' size for Bare-N-ZT-SiNFs, Bare-N-ZH-SiNFs, hH-N-ZT-SiNFs, and hH-N-ZH-SiNFs (b) the formation energy variations of hH-N-ZT-SiNFs and hH-N-ZH with nanoflakes' size

6.7 The Stability of Half-hydrogenated SiNFs

The stability of hydrogenated nanoflakes is of major importance for practical applications. To address this important factor, the structural stabilities of the hH-N-ZT-SiNF and hH-N-ZH-SiNF configurations with different nanoflakes size (N) are evaluated using formation energy (E_F) which is

$$E_f = [E_{hH-SiNF} - (E_{SiNF} + n_H \times E_{H_2} \times \frac{1}{2})] / n_H \quad (6.1)$$

Here, $E_{hH-SiNF}$ and E_{SiNF} are the total energies of half-hydrogenated and bare SiNF, respectively. E_{H_2} denotes total energy of an isolated H_2 molecule, and n_H represents the difference of the number of hydrogen atoms between two systems and is equal to Si_B atoms. The variations of formation energies of hH-N-ZT-SiNF and hH-N-ZH-SiNF configurations as a function of nanoflakes size are plotted in Fig. 6(b). The calculated formation energies for hH-4-ZT-SiNF and hH-3-ZH-SiNF are found to be -1.7 and -1.58 eV, respectively. Based on the definition, the

more negative value of E_F is, the more stable the nanoflake becomes. As can be seen, all the formation energies are negative, showing that the half-hydrogenated SiNFs are stable. In addition, the formation energies increase monotonically with increasing nanoflakes size, indicating that small size nanoflakes are experimentally more favorable to form.

6.8 DOS and PDOS of Bare and Hydrogenated SiNFs

In order to gain more insight into the origin of magnetic behavior of hydrogenated SiNFs, the PDOS of bare, single-hydrogenated, and half-hydrogenated ZT-SiNF and ZH-SiNF are calculated, as shown in Figure 6.7. In agreement with findings above, the 3-ZH-SiNF is a NM semiconductor with a band gap of 0.76 eV. However, the 4-ZT-SiNF behaves as a magnetic semiconductor with direct HOMO-LUMO energy gaps of 1.07 eV in the spin-up, and 1.05 eV in the spin-down states. Although the silicon atom ($\text{Ne } 3s^2 3p^2$) has four valence electrons in the flake, the contributions of s orbitals are negligible near the Fermi level. It is clear that the magnetic behavior of triangular SiNF originates from the p electrons located near the Fermi level. The value of the prominent peak close to the Fermi level at $E \sim -0.26$ (0.26) eV for spin-up (-down) channel is 15.9 (−16.9) states/eV. The spin-up and spin-down states show the similar distribution in reciprocal space. However, the located energy of the former is slightly lower than that of later in high energy levels. Upon adsorption of a single H atom on Si_B of 4-ZT-SiNF, the p orbital contributions of Si atoms close to the Fermi level in both spin-up and spin down channels are strengthened, confirming a stronger magnetism in the nanoflakes.

Figure 6.7 Spin-polarized PDOS of Bare-3-ZH-SiNF, sH-3-ZH-SiNF, hH-3-ZH-SiNF, Bare-4-ZT-SiNF, sH-4-ZT-SiNF, and hH-4-ZT-SiNF, with the spin-up (spin-down) component on the positive (negative) axis.

Interestingly, the adsorption of a single H atom onto Si_B of 3-ZH-SiNF introduces new spin-up and spin-down states near the Fermi level, mainly

attributed to the $3p$ electrons of Si_A atom. Accordingly, the total magnetic moments of both cases are improved by $1.0 \mu_B$. As stated before, the non-magnetic and ferrimagnetic behavior of bare hexagonal and triangular SiNF are transformed to very strong FM behavior after half-hydrogenation of the SiNFs. For hH-4-ZT-SiNF, the value of the peak close to the Fermi level at $E \sim -0.71$ (0.94) eV for spin-up (-down) channel is increased to 57.5 (-45.6) states/eV which is much greater than of bare 4-ZT-SiNF. The contributions of p and s orbitals in these peaks are 79% and 17% , respectively. A closer look at the PDOS of hH-4-ZT-SiNF indicates that the p orbitals of Si_A atoms have the highest (72%), and the s orbitals of adsorbed H atoms (10%), and the p orbitals of Si_B (7%) have second and third contributions to the magnetism, respectively. It is important to mention that hH-4-ZT-SiNF is a FM semiconductor with direct band gaps of 2.87 eV in the spin-up, and 1.37 eV in the spin-down states. A strong peak of 88.1 (-73.9) states/eV is induced at $E \sim -0.66$ (0.76) eV for spin-up (-down) channel through half-hydrogenation of 3-ZH-SiNF, which is much greater than of hH-4-ZT-SiNF, indicating that the half-hydrogenated hexagonal SiNF can introduce a very large spin. These peaks mainly contribute to the p (74%) and s (14%) orbitals.

6.9 Spin Switch Devices Based on Hydrogenated SiNFs

In order to explore the potential applications of hydrogenated SiNFs in spintronics, simple spin switch devices have been proposed. In these structures, half-hydrogenated and fully hydrogenated 4-ZT-SiNFs are sandwiched between two conducting bare 5-ZSiNRs. Figure 6.8 shows the geometric structures of spin switch devices and the spin density distributions of sandwiched nanoflakes. If all

Si_B atoms of the nanoflake are saturated with H atoms, the spin-up states with similar alignment appear on the half-hydrogenated SiNFs, as shown in Figure 6.8(a). It suggests that this model is an ideal transport channel only for the spin-up electrons even when considering antiparallel spin orientation between two edges of ZSiNFs.

Figure 6.8 Geometric structures of (a) the hH-4-ZT-SiNF with all Si_B atoms covered by H atoms, (b) the hH-4-ZT-SiNF with all Si_A atoms covered by H atoms, and (c) the fH-4-ZT-SiNF with all Si_A and Si_B atoms covered by H atoms, sandwiched between two bare 5-ZSiNRs. The spin density distributions of ZT-SiNFs are only plotted. The pink and blue regions correspond to the isosurfaces of spin-up and spin-down states, with the isosurfaces value of 0.012 a.u.

Despite this, hydrogenation of all Si_A atoms of SiNF makes it a perfect transport channel for only spin-down electrons, as seen in Figure 6.8(b). In this

case, all the spin-down states with same spin configuration appear on the half-hydrogenated SiNFs, which block the transmission of spin-up electrons coming from conducting ZSiNR. As noted earlier, the full hydrogenation of the nanoflakes quenches their magnetism. Therefore, a spin switch device made of the fully hydrogenated SiNFs block the transmission of both spin-up and spin-down electrons, as indicated in Figure 6.8(c). In contrast to a bare ZSiNR with hydrogenation that transports both spin-up and spin-down electrons along the edges [316]. The hydrogenation coverage can be manipulated due to its reversibility [33] and controllability [369, 370]; therefore, it is possible to tune the transport and magnetic properties, opening new gates into novel spintronic circuit devices.

6.10 Summary

In summary, first-principles calculations based on DFT method are employed to study the structural, electronic, and magnetic properties of SiNFs with different configurations. It is found that while both zigzag-edged hexagonal and triangular SiNFs show semiconducting behavior, the former is NM and the latter has ferrimagnetic character. Hydrogenation is accepted as an effective approach to engineering the electronic and magnetic properties of SiNFs owing to its controllability and reversibility. Upon adsorption of a single H atom on a Si atom of a SiNF, the quasi π bond between saturated and unsaturated Si atoms is broken because of a strong σ bond forms between saturated Si and H atoms. It causes the p_z electrons of the unsaturated Si atom to be unpaired and delocalized. As a consequence, the magnetism in SiNFs is augmented by $1.0 \mu_B$. Increasing the

hydrogenation coverage on SiNF to half of the Si atoms gives rise to a very large spin moment that is squarely proportional to the size of the nanoflakes. It is discovered that half-hydrogenated SiNFs present a long-range FM order because of the extended p - p interactions of adjacent Si atoms. Moreover, full hydrogenation of SiNF quenches the magnetism due to the saturation of all the quasi π bonds. Finally, simple switch devices are proposed to show the potential application of silicene to tune the transport properties by harnessing the hydrogenation coverage on SiNFs.

CHAPTER 7

Gas Adsorption on Silicene Nanoribbons and Its Application as an Extremely Sensitive Molecular Sensor

Inspired by the recent successes in the development of two-dimensional based gas sensors capable of single gas molecule detection, I investigate the adsorption of gas molecules (N_2 , NO , NO_2 , NH_3 , CO , CO_2 , CH_4 , SO_2 , and H_2S) on SiNRs using DFT and NEGF methods. The most stable adsorption configurations, adsorption sites, adsorption energies, charge transfer, quantum conductance modulation, and electronic properties of all studied gas molecules on SiNRs are considered. The obtained results suggest that SiNRs show promise in gas molecule sensing applications. These results were published in RSC Advances [[367](#)].

7.1 Overview

Although the global development of the chemical activities in the last century is a consequence of the human demands, it also affects human health and life quality from the associated environmental release of poisonous substances in the forms of solid, liquid and vapour. Therefore, gas detection is vital for managing chemical processes to prevent health hazards such as air pollution, device contamination, and for medical diagnosis.

Today, developing novel gas sensing materials with high sensitivity, even down to the single molecule level, high selectivity, high stability, quick response and recovery, and low power consumption is of considerable importance. Graphene renders outstanding properties such as high surface-volume ratio, low electronic temperature noise, remarkably high carrier mobility, high chemical and

thermal stability, and fast response time, which make it promising in the development of ultrasensitive sensors with high packing density, higher sensitivity, better selectivity, faster recoverability, and less power consumption [181, 249, 254]. The potential application of graphene for gas sensors has been widely studied both experimentally [395, 396] and theoretically [55-57]. However, the physisorption of common gas molecules such as CO₂, CO, CH₄, H₂O, H₂, N₂, NO₂, and NO on pristine graphene [55] restrict its potential for single molecule detection [255, 256]. It was found that sensing ability of graphene can be enhanced by introducing dopants or defects [56-58].

This buckled structure makes it possible for the band gap of silicene to be tuned more intensively with an external electric field [43] and with binding adsorbates [345] as compared to graphene [397]. Furthermore, silicene shows a considerably higher chemical reactivity for atoms [80, 165, 365, 398-400] and molecules [61-63, 366, 401-403] adsorption than graphene due its buckled formation with a great deal of potential applications for silicene-based nanoelectronic devices [26], hydrogen storage [365], thin film solar cell absorbers [368], hydrogen separation membranes [366], and molecule sensors [61-64].

Similar to graphene, silicene is a zero band gap semimetal [59]. It is expected that the effects of gas molecule adsorption on the electronic properties of a material without a band gap are much less than that of a semiconductor with an intrinsic band gap. The intrinsic band gap and small dimension along with free reactive edges make nanoribbons more attractive than sheets for gas nanosensors applications. Several experimental and theoretical studies of GNRs sensing

properties have been already reported [404, 405]. The CO, NO, NO₂, and O₂ molecules are chemisorbed on armchair GNRs (AGNRs), while the adsorption of NH₃ and CO₂ on AGNRs is between weak chemisorption and strong physisorption [252]. It has been found that CO, CO₂, NO, NO₂, and O₂ molecules draw electrons from AGNRs, while NH₃ donates its electrons into AGNRs. Little attention has been focused on molecule adsorption on SiNRs. A recent theoretical work by Osborn and Farajian has proven that ASiNRs can be used for detection of CO molecule due to its weak chemisorption on ASiNRs [406]. They also found that H₂O and O₂ are strongly chemisorbed on ASiNRs, while CO₂ and N₂ barely affect ASiNR's conductance.

It remains an open question as to what is the adsorption behavior of nitrogen-, sulfur-, and other carbon-based gas molecules, including NO, NO₂, NH₃, SO₂, H₂S, and CH₄ which are all of the great practical interest for environmental, medical, and industrial applications, on SiNRs. In this chapter, I employed first-principles methods based on DFT to investigate the adsorption behavior of CO, CO₂, CH₄, N₂, NO, NO₂, NH₃, SO₂, and H₂S molecules on SiNRs. The results promulgate the promising future of SiNR in the development of ultrahigh sensitive sensor platforms.

7.2 Computational Details

All the calculations are carried out based on first-principles DFT implemented in ATK package [293, 296, 328]. The GGA-PBE with a double- ζ polarized basis set is adopted to solve Kohn-Sham equations and to expand electronic density. The density mesh cut off is set to be 150 Rydberg. The Grimme vdW correction (DFT-

D2) [407] is also employed to describe long-range vdW interactions [408]. In order to take into account the vdW interactions, an additional term (E_{vdW}) is added to the DFT total energy (E_{DFT}):

$$E_{DFT-D2} = E_{DFT} + E_{vdw} \quad (7.1)$$

Besides vdW interactions, since our systems have two subsystems: the SiNR (*A*) and the gas molecule (*B*), so-called basis set superposition errors (BSSE) are expected due to the incompleteness of the Linear Combination of Atomic Orbitals (LCAO) basis set. In an isolated *A* system, only the basis orbitals in the *A* system are responsible for describing it. While *A* and *B* are coupled, the basis orbitals in the system *B* will also be used to describe system *A*, resulting in a larger available basis set for system *A*. Consequently, there will be an artificial interaction which increases the total energy. To eradicate BSSE, a counterpoise (cp) correction should be subtracted from the total energy [409]. Therefore, the total energy of the system considering the long-range vdW interactions and artificial attractions between two subsystems is:

$$E_{Total} = E_{DFT-D2} - E^{cp} \quad (7.2)$$

To avoid the mirroring interactions, a vacuum space of 25 Å is considered in *x* and *y* directions in which the structures are not periodic. The electronic temperature is kept constant at 300 °K. All the structures are completely relaxed, prior to the calculations, up until the force and stress are less than 0.01 eV/Å and 0.005 eV/Å³, respectively. 1×1×21 *k*-points in the Brillouin zone are sampled for geometry optimization and 1×1×121 *k*-points for total energy, electronic

properties, charge transfer, and electron transport calculations. To investigate the transport properties, the gas sensing system is divided into three regions: two electrode regions (left and right) and a scattering region (the central region), as illustrated in Figure 7.1. The quantum conductance can be obtained from Equation (3.31).

Figure 7.1 Schematic structural model of SiNR-based gas sensor with two electrodes (black boxes). The cyan and green balls represent Si and H atoms, respectively. Possible adsorption sites of gas molecules on the SiNR are: I (hill), II (valley), III (bridge), and IV (hollow).

7.3 Gas Adsorption on Pristine ASiNRs

All the nanostructures are made of long and non-periodic 7-ASiNRs ($L = 35 \text{ \AA}$). Their edges are passivated by H while their surfaces are kept pristine because the surfaces are less reactive than the edges [302] and silicene lacks complete sp^3 hybridization [373]. It has been reported that 7-ASiNR is a paramagnetic semiconductor with a band gap of $\sim 0.56 \text{ eV}$ [128]. The semiconducting ASiNR is chosen because it is expected that the adsorption of gas molecules has a much smaller effect on the electronic properties of ZSiNRs which are metallic. To evaluate chemical sensing of SiNR-based nanosensors, single gas molecules (N_2 , NO , NO_2 , NH_3 , CO , CO_2 , CH_4 , SO_2 , and H_2S) are initially placed about $3 \text{ \AA}$ from the ASiNRs surface. The adsorption behaviors of molecules on SiNR are

investigated after full relaxation. The structural stability of the molecule's adsorption on SiNR is addressed using adsorption energy (E_{ad}) which is

$$E_{ad} = E_{\text{SiNR+Molecule}} - E_{\text{SiNR}} - E_{\text{Molecule}} \quad (7.3)$$

where $E_{\text{SiNR+Molecule}}$, E_{SiNR} , E_{Molecule} denote the total energies of the SiNR-Molecule system, pristine SiNR, and the isolated gas molecule, respectively. Based on the definition, the more negative E_{ad} is, the stronger adsorption of gas molecules on SiNR would be. By considering different adsorption configurations of gas molecules on SiNR and calculating each configuration's adsorption energy, it is discovered that different gas molecules prefer to be adsorbed with different geometries.

To commence the relaxation, the molecules can be placed at four different positions including valley, hill, bridge sites, and hollow, as shown in Figure 7.1. At these particular positions, different molecular orientations are considered. The structural stabilities of diatomic molecules (N_2 , NO , and CO) are examined when their molecular axis is aligned perpendicular and parallel with respect to the SiNR's surface. Furthermore, for NO and CO molecules, the O atom can point up and down. For the triatomic molecule CO_2 with 180° bond angles, two orientations, parallel and perpendicular to the surface, are tested. For other triatomic (NO_2 , SO_2 , and H_2S), tetratomic (NH_3), and pentatonic (CH_4) molecules, two orientations are considered. In the first orientation, the N atom (in NO_2 and NH_3), S atom (in SO_2 and H_2S), and C atom (in CH_4) point to the SiNR's surface, while, in the second orientation, the H atom (in NH_3 , H_2S , and CH_4), and O atom

(in SO_2 and NO_2) point away from the SiNR's surface. In order to find the most favorable location for gas molecules to be adsorbed, the adsorption energies of gas molecules on the edge site and the interior site are also compared. As an example, the calculated adsorption energy of a CO gas molecule on an edge atom site is 0.35 eV less than that of an interior (center) atom site, concluding that the gas molecules prefer to be adsorbed on the edge sites. This is in agreement with those previously reported for CO adsorption on SiNR [406]. Figure 7.2 presents the most stable adsorption configurations of gas molecules on pristine ASiNRs.

Figure 7.2 The most stable adsorption configurations (top and side view) for N_2 , NO , NO_2 , NH_3 , CO , CO_2 , CH_4 , SO_2 , and H_2S on pristine ASiNR. The cyan, green, blue, red, grey, and yellow balls represent Si, H, N, O, C, and S atoms, respectively. The bond lengths (in unit of Å) of molecule and binding distances between the molecule and the SiNR are also given.

As previously mentioned in section 7.2, the long range vdW interactions which come from non-local dispersion and artificial interactions are important factors to study adsorption behavior of gas molecules on SiNR. In order to find the impacts of vdW and counterpoise corrections on our calculations, the adsorption energy of gas molecules on SiNR and binding distances between gas molecules and SiNR are obtained by DFT-D2+cp (considering vdW dispersion and counterpoise correction) and PBE-GGA approximation and shown in Figure 7.3. The results show that the absolute values of adsorption energy calculated by DFT-D2+cp are significantly more than that of GGA-PBE approximation. In addition, the optimum binding distances between molecules and SiNR obtained by DFT-D2+cp are a little less than calculated distances *via* GGA-PBE approximation.

The calculated adsorption energies and binding distances between the gases and ASiNR which are obtained by the DFT-D2+cp method are also specified in Table 7.1. The results show that CO is chemically adsorbed on SiNR with an adsorption energy of -0.92 eV. In the most stable structure, the CO molecule prefers to be adsorbed in a vertical orientation when the C atom is connected to a Si-edge atom with a covalent bond at a hill position with a binding distance of 1.89 Å. The bond length of the adsorbed CO is 1.16 Å which is little longer than that of an isolated CO molecule (1.14 Å). For CO₂ and CH₄, the results indicate that they are physisorbed on SiNR with a small adsorption energy of -0.31 and -0.18 eV, respectively. Both molecules prefer to be placed at the hollow site after relaxation.

Figure 7.3 (a) Adsorption energies of gas molecules on SiNR obtained by DFT-D2+cp (considering vdW dispersion and counterpoise correction) and PBE-GGA approximation (b) Binding distances between the ribbon and molecules obtained by DFT-D2+cp (considering vdW dispersion and counterpoise correction) and PBE-GGA approximation.

The N₂ molecule is energetically stable when it is horizontally situated at the center of a hexagonal silicon cell near the edge. The low adsorption energy of -0.31 eV shows that N₂ is physically adsorbed on SiNRs. However, SiNR is highly reactive to other N-based gas molecules such as NH₃, NO₂, and NO, whose adsorption energies are -1.12 , -2.53 , -2.68 eV, respectively. NH₃ is chemically adsorbed on top of Si-edge atom at a hill position with the formation of a N-Si

covalent bond (2 Å). The adsorption energy of NO₂ and NO is even less than − 2 eV showing a very strong chemisorption. For the NO₂ molecule, the N-O bond interacts with the Si-Si bond of SiNR at the edge, where the N-Si and O-Si covalent bonds' lengths are 1.91 and 1.77 Å, respectively. The chemisorption of the NO molecule on SiNR is even stronger than that of NO₂ molecule. The N atom is bonded to Si-Si atoms on the edge of the SiNR to form a N-Si-Si triangle with N-Si and Si-Si bond lengths of 1.81 and 2.32 Å, respectively. The O atom is also connected to another Si atom on top of the Si-hexagon with a bond length of 1.73 Å. The adsorption energy of H₂S molecule on top of SiNR is − 0.64 eV, showing that the adsorption of the molecule is a weak chemisorption. Strong chemisorption is also observed for the SO₂ molecule, whose adsorption energy is − 2.63 eV. In this case, the O atoms of SO₂ molecule are bonded to Si-Si bond at the SiNR edge, where the covalent bond lengths are 1.70 Å.

Table 7.1 The calculated adsorption energy (E_{ad}), binding distance which is the shortest atom to atom distance between the molecule and pristine SiNR (D), and the charge transfer from pristine SiNR to a molecule (ρ).

Device	Gas	E_{ad} (eV)	D (Å)	ρ (e)	Device	Gas	E_{ad} (eV)	D (Å)	ρ (e)
P-SiNR	N_2	− 0.30	3.47	− 0.110	P-Silicene ^a	N_2	− 0.08	-	+ 0.005
	NO	− 2.68	1.73	− 0.892		NO	− 0.57	1.99	+ 0.46
	NO_2	− 2.53	1.77	− 0.851		NO_2	− 1.53	1.75	+ 0.82
	NH_3	− 1.12	2.00	− 0.535		NH_3	− 0.60	2.04	+ 0.10
	CO	− 0.92	1.89	− 0.406		CO	− 0.10	3.24	+ 0.03
	CO_2	− 0.31	3.34	− 0.101		CO_2	− 0.04	-	~0.00
	CH_4	− 0.18	3.40	+ 0.025		CH_4	− 0.08	-	+ 0.004
	SO_2	− 2.64	1.74	+ 0.626		SO_2	− 1.08	2.17	+ 0.17
	H_2S	− 0.64	2.45	− 0.342		H_2S	− 0.212	2.28	-

^a From Refs. [[61](#), [62](#), [345](#), [401](#)]

To sum up, the interaction of N_2 , CO_2 , and CH_4 gas molecules with a SiNR is mostly vdW type adsorbing *via* physisorption. A SiNR cannot be an appropriate sensor for detection of NO , NO_2 , and SO_2 gas molecules because of their strong chemisorption on silicene. However, SiNR can be considered as a disposable molecule sensor for detection of NO , NO_2 , and SO_2 . Besides, the strong covalent bonding of these molecules to SiNR makes it possible to tune the electronic properties of SiNR for nanoelectronics applications, as will be discussed later. Finally, the moderate adsorption energies of NH_3 , CO , and H_2S gas molecules make SiNR a promising material for sensitive gas sensors or gas filters because they can be easily desorbed from SiNR by heating. It should also be noted that environmental gas molecules (N_2 , CO_2 , O_2 , and H_2O) can change the NH_3 and CO sensing capability SiNR's. Unlike physisorption of N_2 and CO_2 gas molecules on SiNR, the water and oxygen molecules are strongly chemisorbed on SiNR [406]. Therefore, it is critical that water and oxygen molecules should be removed from the environment to preserve the proper sensing capability of SiNRs.

To investigate the effects of gas molecules on the conductance of SiNR, the quantum conductances of the pristine SiNR before and after adsorption are calculated, as shown in Figure 7.4. Upon adsorption of N-based gas molecules, the band gap of pristine SiNR (0.56 eV) is decreased slightly for N_2 (0.52 eV) and NH_3 (0.48 eV) and is somewhat increased for NO_2 (0.68 eV) and NO (0.68 eV). The conductances of SiNR before and after adsorption of N_2 molecule are similar due to the physisorption of the N_2 gas molecule on SiNR, showing insensitivity of SiNR sensor to the N_2 gas molecule. However, the overall conductances of SiNRs

are detectably dropped after NH_3 , NO_2 , and NO , confirming their chemisorption on SiNRs. The conductance reduction for a NO molecule is more vivid than other N-based gas molecules which are consistent with the calculated adsorption energies. For C-based gas molecules, the band gap of pristine SiNR is preserved for CO_2 (0.56 eV) and slightly decreased for CH_4 (0.52 eV) and CO (0.48 eV). The overall conductance of pristine SiNR is visibly reduced after CO adsorption, while barely changed after CO_2 adsorption, and almost unchanged after CH_4 adsorption which confirms the calculated adsorption energies for C-based gas molecules where the CO adsorption energy is more negative than others. Upon adsorption of S-based gas molecules, the band gap of pristine SiNR is unaltered for SO_2 (0.56 eV) and is diminished for H_2S (0.48 eV) gas molecule. A reduction in the conductance of the SiNR from SO_2 and H_2S adsorption is also observed, confirming the sensing capability of SiNR for SO_2 and H_2S gas molecules.

Figure 7.4 Quantum conductance of pristine SiNR before and after (a) N_2 , NO , NO_2 , NH_3 , (b) CO , CO_2 , CH_4 , (c) SO_2 and H_2S gas molecules adsorption.

The electron charge transfer between gas molecules and SiNR is also investigated using Mulliken population analysis, as shown in Table 7.1. The positive value of charge indicates a charge transfer from SiNR surface to molecule.

N₂, NO, NO₂, NH₃, CO, CO₂, and H₂S are electron-donating gas molecules, while CH₄ and SO₂ have an electron-withdrawing capability. A large amount of charge transfer is observed for NO ($-0.892 e$), NO₂ ($-0.851 e$), NH₃ ($-0.535 e$) and CO ($-0.406 e$) due to their strong electron-donating characteristics. These large charge transfer molecules to SiNR are also correlated to the strong binding energies of the gas molecules chemisorption on SiNR. The calculated adsorption energies of all studied gas molecules on SiNR are distinctly larger than those of GNR [252], showing higher sensitivity of SiNR toward the gas molecules. Furthermore, Comparing these findings with gas molecules adsorption on pristine silicene [61, 62, 345, 401], see Table 1, the value of adsorption energy and charge transfer are much larger in favor of SiNR, presenting a great potential of SiNR for application as a highly sensitive molecule sensor.

The origin of the chemisorption of NO, NO₂, NH₃, CO, SO₂ and H₂S and physisorption of N₂, CO₂, and CH₄ gas molecules on SiNR can be revealed by studying their density of states (DOS). Figure 7.5(a) presents the total DOS of pristine SiNR and the gas molecules. The frontier molecular orbitals, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), of NO, NO₂, and SO₂ are closer to the Fermi level of SiNR than that of NH₃, CO, and H₂S, representing that SiNR shows higher sensitivity for the former molecules. Furthermore, these molecules have higher reactivity to SiNR as compared to N₂, CO₂, and CH₄ which are physisorbed on the SiNR. These results exhibit reasonable agreement with the calculated adsorption energies and are

consistent with earlier research on gas molecule adsorption on silicene sheet [61, 62, 345, 401].

Figure 7.5 (a) DOS of N_2 , NO , NO_2 , NH_3 , b) CO , CO_2 , CH_4 , SO_2 and H_2S gas molecules and SiNR. The positive and negative values represent spin-up and -down states, respectively. (b) PDOS of SiNR (Si-3s and Si-3p) and GNR (C2s and C2p). The inset shows the schematic of a SiNR/GNR, in which a Si/C edge atom is distinguished by a black circle. The cyan and red balls represent Si/C and H atoms, respectively. The Fermi level of SiNR and GNR are set to zero.

As previously mentioned, silicene is more reactive than graphene because of its tendency to adopt $sp^2 + sp^3$ hybridization over sp^2 hybridization. The difference between the chemical reactivity of silicene and graphene can be understood from Figure 7.5(b), where PDOS of silicon/carbon atom located at the edge of SiNR/GNR is calculated. While both silicon ($Ne\ 3s^2\ 3p^2$) and carbon ($1s^2\ 2s^2\ 2p^2$) contributes four valence electrons in the ribbon, the contributions of s orbitals are negligible near Fermi level. Therefore, only p orbitals could be considered. Comparing the p orbital contributions of Si and C atoms near Fermi level, it is clear that the corresponding electronic edge states of 7-ASiNR are closer than that of 7-AGNR to the Fermi level, causing stronger reactivity of SiNR for molecule adsorption.

To gain more insight about chemisorption and physisorption of gas molecules, their electronic total charge densities are calculated, as depicted in Figure 7.6. It can be seen that there is no electron orbital overlap between N_2 , CO_2 , and CH_4 gas molecules and SiNR, confirming this fact that only weak physisorption takes place in these cases. In contrast, a strong orbital overlap is observed between NO , NO_2 , and SO_2 gas molecules and SiNR, resulting in more orbital mixing and a larger charge transfer. It is clear that this strong orbital overlap brought significant changes to the electronic properties of SiNR. Finally, a moderate orbital overlap between NH_3 , CO , and H_2S gas molecules and SiNR is implying the potent applications of SiNR as a reusable gas sensor because the electronic properties of SiNR which are moderately changed can be retrieved by

desorbing gas molecules from SiNR. The results are correspondent with calculated adsorption energies.

In order to find the impact of nanoribbon's width on the adsorption energy, we also considered the CO molecule adsorption on 5-ASiNR, 6-ASiNR, and 8-ASiNR. The values of adsorption energy of CO molecule on 5-ASiNR, 6-ASiNR, 7-ASiNR, and 8-ASiNR are -0.98 , -0.95 , -0.93 , and -0.91 eV, respectively. This overall small decrease in absolute value of adsorption energy with decreasing the surface coverage of the SiNR is in agreement with those previously reported for CO molecule adsorbed on AGNR [373].

Figure 7.6 Electronic total charge densities for the adsorption of N_2 , NO , NO_2 , NH_3 , CO , CO_2 , CH_4 , SO_2 , and H_2S gas molecules on pristine ASiNR.

7.4 Higher Concentration of Molecules on Pristine ASiNRs

Since upon adsorption of individual gas molecules a conduction reduction is observed in the properties of SiNRs, significant alterations in the electronic properties of SiNRs are expected at higher concentrations of gas molecules. To

evaluate this premise, a higher surface coverage with two gas molecules is considered and the impacts of gas molecules adsorption on the conduction of SiNR are investigated. Figure 7.7 presents the most stable configurations of two adsorbed gas molecules on opposite edges of the SiNR.

Figure 7.7 The most stable adsorption configurations for two N_2 , NO , NO_2 , NH_3 , CO , CO_2 , CH_4 , SO_2 , and H_2S on pristine ASiNR.

Based on the calculations, an individual gas molecule can be adsorbed anywhere at the SiNR's edges and its position will not change the quantum conductance. The second gas molecule can also be adsorbed on the same side or the opposite side of the first gas molecule. The results show that the conductance changes are almost the same for two cases, in agreement with the findings of Osborn *et al.* [406]. By calculating adsorption energies, it is found that adding gas molecule to the system doubles the value of adsorption energies of gas molecules on the SiNR, see Table 7.2. It is clear that the NO , NO_2 , NH_3 , CO , SO_2 , and H_2S

sensing capability of SiNR, which is exposed by two gas molecules, is increased due to the significant reduction in the conductance of pristine SiNR and the strong chemisorption of gas molecules to the SiNR (their adsorption energies are less than -1 eV), as shown in Figure 7.8. By performing Mulliken population analysis of the SiNR with one adsorbed molecule and comparing to the SiNR with two adsorbed molecules, it is found that there are no appreciable differences between the amounts of charge transfer, see Table 7.2.

Table 7.2 The calculated adsorption energy (E_{ad}), binding distance which is the shortest atom to atom distance between two gas molecules and pristine SiNR (D), and the charge transfer from pristine SiNR to two gas molecules (ρ).

Device	Gas	E_{ad} (eV)	D (Å)	ρ (e)
P-SiNR	$2N_2$	-0.57	3.36	-0.097
	$2NO$	-5.32	1.72	-0.888
	$2NO_2$	-5.08	1.78	-0.849
	$2NH_3$	-2.18	2.00	-0.493
	$2CO$	-1.78	1.89	-0.386
	$2CO_2$	-0.58	3.38	-0.093
	$2CH_4$	-0.32	3.41	+0.021
	$2SO_2$	-5.11	1.73	+0.620
	$2H_2S$	-1.25	2.45	-0.375

Figure 7.8 Quantum conductance of pristine SiNR before and after a) two- N_2 , - NO , - NO_2 , - NH_3 , b) - CO , - CO_2 , - CH_4 , c) - SO_2 and - H_2S gas molecules adsorption.

It is predicted that the edges of SiNRs are not well controlled similar to GNRs [38, 410]. As a result, it seems difficult to achieve a fully edge hydrogenated SiNR without any dangling bond (DB) defects. It is found that edge DB defects are much more probable than surface DB defects in silicon nanowires [411-414]. Therefore, it is necessary to investigate the sensing capability of a SiNR with an edge DB defect. To this end, a hydrogen atom is removed from one silicone edge atom, and only the gas adsorption above the DB defect is tested. The most stable adsorption configuration of gas molecules on SiNR with an edge DB defect are illustrated in Figure 7.9.

Figure 7.9 The most stable adsorption configurations for N_2 , NO , NO_2 , NH_3 , CO , CO_2 , CH_4 , SO_2 , and H_2S on ASiNR with an edge DB defect. The bond lengths (in unit of Å) of molecule and binding distances between the molecule and the SiNR are also given.

Figure 7.10 shows the conductance modulation of ASiNR with an edge DB defect upon adsorption of gas molecules. As one can see the edge DB defects do not limit the sensing capability of the SiNR. The absolute value of adsorption energies of all gas molecules on SiNR with an edge DB defect, see Table 7.3, are increased, leading to detectable modifications in SiNR's conductance. Based on their adsorption energies, it can be understood that NO (− 3.23 eV), NO₂ (− 2.94 eV), NH₃ (− 1.24 eV), CO (− 1.52 eV), and SO₂ (− 2.72 eV) are strongly chemisorbed on the SiNR with a DB defect, while H₂S (− 0.79 eV) is weakly chemisorbed on the SiNR. However, the N₂ (− 0.32 eV) and CH₄ (− 0.22 eV) molecules are still physisorbed on the SiNR with small adsorption energy. The Mulliken population analysis of the SiNR with an edge DB defect and adsorbed molecule shows that a DB defect slightly decreases the charge transfer between SiNR and gas molecules, see Table 7.3.

Table 7.3 The calculated adsorption energy (E_{ad}), binding distance which is the shortest atom to atom distance between molecule and SiNR with dangling bond defect (D), and the charge transfer from SiNR with dangling bond defect to a molecule (ρ).

Device	Gas	E_{ad} (eV)	D (Å)	ρ (e)
DB-SiNR	N_2	− 0.32	3.28	− 0.090
	NO	− 3.23	1.74	− 0.908
	NO_2	− 2.94	1.92	− 0.848
	NH_3	− 1.24	1.98	− 0.520
	CO	− 1.52	1.83	− 0.395
	CO_2	− 0.35	3.27	− 0.100
	CH_4	− 0.22	3.33	+ 0.020
	SO_2	− 2.72	1.80	− 0.615
	H_2S	− 0.79	2.45	− 0.323

Figure 7.10 Quantum conductance of SiNR with an edge DB defect before and after a) N_2 , NO , NO_2 , NH_3 , b) CO , CO_2 , CH_4 , c) SO_2 and H_2S gas molecules adsorption.

7.5 Gas Molecule Adsorption on Doped ASiNRs

Here, I study the effects of doping on the gas molecules sensing capability of SiNR. To this end, doping effects of SiNRs with N and B impurities have been considered. Based on findings in chapter 3, a single N or B dopant prefers to be substituted with Si edge atoms because the formation energy of N or B impurity at the edge is lower than other positions of the nanoribbon. To focus on the effects of doping on the sensing capability of the SiNR, the gas molecules adsorption above the B and N impurities and their nearest neighbours are studied. It is discovered that the gas molecules energetically tend to be chemisorbed on B atom in B-doped SiNR, and chemisorbed on the Si atoms nearest to the N atom in N-doped SiNR. The adsorption energies of gas molecules on the doped SiNR are larger than that of pristine SiNR, proving that doping improves sensing capabilities of SiNR, see Table 7.4. These findings are in agreement previous studies on gas detection based on doped silicene [62].

Table 7.4 The calculated adsorption energy (E_{ad}), binding distance which is the shortest atom to atom distance between molecule and N-doped and B-doped SiNR (D), and the charge transfer from N-doped and B-doped SiNR to the molecule (ρ).

Device	Gas	E_{ad} (eV)	D (Å)	ρ (e)	Device	Gas	E_{ad} (eV)	D (Å)	ρ (e)
N-SiNR	N_2	-0.35	2.59	-0.151	B-SiNR	N_2	-0.55	1.60	-0.352
	NO	-3.74	1.72	+0.138		NO	-3.82	1.38	-0.233
	NO_2	-3.60	1.75	-0.041		NO_2	-3.53	1.55	-0.162
	NH_3	-1.35	1.98	-0.559		NH_3	-1.14	1.63	-0.663
	CO	-1.89	2.00	-0.274		CO	-1.59	1.50	-0.452
	CO_2	-0.35	2.70	-0.140		CO_2	-0.32	3.28	-0.110
	CH_4	-0.27	3.57	+0.016		CH_4	-0.25	3.39	+0.014
	SO_2	-3.48	1.75	-0.210		SO_2	-2.95	1.57	-0.204
	H_2S	-1.86	2.40	-0.305		H_2S	-0.90	1.98	-0.407

The most stable configuration of adsorbed gas molecules on N-doped and B-doped ASiNR are depicted in Figure 7.11. For CO gas molecule on N-doped SiNR, two covalent bonds are formed between C and two nearest Si atoms to the N atom, while, for B-doped SiNR, C atom and B atom are covalently bonded. The adsorption energies of CO molecule on N- and B-doped SiNR are 2.04 and 1.72, greater than that of pristine SiNR. The NO gas molecule is also strongly chemisorbed on N- and B-doped SiNR. Although three covalent bonds are formed between NO and nearest Si atoms to the N atom in N-doped SiNR, the adsorption of NO on B-doped SiNR totally destroys the configuration of atoms on the edge. The most stable configurations for NO_2 , NH_3 , and SO_2 gas molecules adsorption on N- and B-doped SiNR are quite similar to the pristine SiNR. The only difference is that they prefer to be adsorbed on top of a B atom and the nearest Si atom to the N atom. The CO_2 and CH_4 molecules on the N- and B-doped SiNR and N_2 on the N-doped SiNR are still physisorbed. However, N_2 molecule is chemically adsorbed on B-doped SiNR with

adsorption energies of -0.55 eV which is 1.79 times greater than that of pristine SiNR.

Figure 7.11 The most stable adsorption configurations for N_2 , NO , NO_2 , NH_3 , CO , CO_2 , CH_4 , SO_2 , and H_2S on (a) N-doped and (b) B-doped ASiNR. The cyan, green, blue, red, grey, yellow, and pink balls represent Si, H, N, O, C, S, and B atoms, respectively. The bond lengths (in unit of Å) of molecule and binding distances between the molecule and the SiNR are also given.

Similar to gas adsorption on pristine SiNR, the conductances of N-doped and B-doped SiNR are detectably changed upon adsorption of NO, NO₂, NH₃, CO, SO₂, and H₂S, see Figure 7.12. Furthermore, doping a B atom into the SiNR can improve the N₂ gas sensing capability of SiNR, compared to that of pristine SiNR. Charge transfer analysis shows that N₂, NO₂, NH₃, CO, CO₂, H₂S, and SO₂ act as donors, while NO and CH₄ act as acceptors for N-doped SiNR. However, for B-doped SiNR, all gases have electron donating capability except CH₄, see Table 7.4.

Figure 7.12 Quantum conductance of N-doped SiNR before and after (a) N₂, NO, NO₂, NH₃, (b) CO, CO₂, CH₄, (c) SO₂ and H₂S gas molecules adsorption. Quantum conductance of B-doped SiNR before and after (a) N₂, NO, NO₂, NH₃, (b) CO, CO₂, CH₄, (c) SO₂ and H₂S gas molecules adsorption.

7.6 SiNR-based Gas Sensor

Finally, a design of SiNR-based sensor to detect gas molecules is proposed, as shown in the inset of Figure 7.13 (a). Two semi-infinite 4-ZSiNRs as the leads and

a 98 Å long 7-ASiNR gas sensing zone are the main elements of the device. I have assumed that 5 gas molecules with an average distance of 18 Å are adsorbed on the edge sites of the detection zone. By applying a bias voltage across the leads, conductance can be measured before and after adsorption. To assess the sensing performance of the proposed device for the gas molecules the current *versus* bias voltage is calculated in Figure 7.13 (a). For clarity and brevity, the I - V_{bias} curves for 7-ASiNR before and after adsorption of NO₂ and NO molecules are considered because the currents induced by other molecules are much smaller than that of NO₂ and NO molecules.

As can be seen, the current is always almost zero for pristine 7-ASiNR before adsorption of molecules since 7-ASiNR is a semiconductor with a direct band gap of 0.56 eV, as shown in Figure 7.13 (b). However, upon NO₂ adsorption, the current remarkably increases as a function of increasing voltage bias, the curve is almost linear indicating a metallic behavior. The current can be also increased by NO adsorption; however, the current value is much smaller than that of NO₂. These results can be confirmed by analyzing the band structures of 7-ASiNR after NO and NO₂ adsorption, as shown in Figure 7.13 (b). As mentioned before, the gas molecules are able to tune the electronic properties of SiNRs. The adsorption of NO₂ and NO on 7-ASiNR can transform the system to n-type and p-type semiconductors, respectively, due to the deep defect states induced by gas molecules, as shown in Figure 7.13 (b). These n- and p-type semiconducting SiNRs can be applied in nanoscale electronic devices such as a p-n junction diode and n- or p-type FETs. It is also expected that NO₂ gas molecule adsorption by

SiNR can give rise to a conductance enhancement because of the metallic behavior of SiNR after NO₂ molecule adsorption. However, for NO molecule adsorption, the conductance may be enhanced by some amount since the NO adsorption makes the SiNR a p-type semiconductor.

Figure 7.13 I - V_{bias} curves for the SiNR sensor before and after NO and NO₂ adsorption. The inset shows the schematic of a SiNR-based sensor which consists of a semiconducting 7-ASiNR (detection region) and two metallic 4-ZSiNRs (electrodes). (b) Band structures of pristine 7-ASiNR before and after NO and NO₂ adsorption

7.7 Summary

In summary, we employed first-principle calculations to explore the adsorption geometry, adsorption energy, charge transfer, electronic band structure, and quantum conductance modulation of SiNRs with gas molecules (N₂, NO, NO₂, NH₃, CO, CO₂, CH₄, SO₂, and H₂S) adsorption. Our results reveal that SiNRs are capable of detecting CO, NH₃, and H₂S with high sensitivity because they are

chemically adsorbed on the SiNR and transfer a few electrons to the SiNR. Quantum conductance modulation of SiNRs is clearly detectable upon chemisorption of gas molecules. Furthermore, SiNRs are not appropriate to serve as a sensor for NO, NO₂, and SO₂ due to the fact that they are strongly chemisorbed with covalent bonds to SiNRs and transfer a large amount of electrons to the SiNR. However, the strong bonding of NO and NO₂ molecules is an effective way to tune the electronic properties of SiNRs to fabricate p-type and n-type transistors, respectively. The other gas molecules are physisorbed. We also found that increasing the density of gas molecules will result in more significant changes in quantum conductance. In addition, dangling bond defects which are unavoidable through fabrication process will not hinder the sensing capability of SiNRs. The sensing capability of a SiNR-based sensor can also be increased by either N or B doping. It is found that doping a SiNR with a B atom can enhance the detection capability of N₂ gas molecules. On the basis of our results, SiNRs can be considered as a promising material to detect individual gas molecules.

CHAPTER 8

Adsorption and Dissociation of Toxic Gas Molecules on Graphene-like BC₃: A Search for Highly Sensitive Molecular Sensors and Catalysts

In this chapter, the adsorption of toxic gas molecules (NO, NO₂, NH₃, and CO) on boron carbide (BC₃) sheet is investigated using first-principle DFT. The most stable adsorption configurations, adsorption energies, binding distances, charge transfer, electronic band structures, and quantum conductance are calculated to deeply understand the impacts of molecules above on the electronic and transport properties of the BC₃ monolayer. These results were published on arXiv [[415](#)].

8.1 Overview

The need for miniaturized sensors with high sensitivity, fast response, high selectivity, high reliability, quick recovery, and low cost has motivated developments of new gas sensors based on novel nanomaterials. Graphene has enticed great interest thanks to its extraordinary properties, for instance, high surface-volume ratio, high carrier mobility, high chemical stability, low electronic temperature noise, high thermal stability, and fast response time. As a result, it offers promise in the development of ultrasensitive gas sensors with high selectivity, fast recovery, high packing density, and low power consumption [[181](#), [249](#), [254](#)]. The applicability of graphene in the field of gas sensing has been widely investigated both experimentally [[395](#), [396](#), [416-419](#)] and theoretically [[55-58](#), [255](#), [256](#), [400](#), [420](#), [421](#)]. The pristine graphene shows low sensitivity toward common gas molecules such as CO, CO₂, CH₄, N₂, NO₂, NH₃, H₂, and H₂O [[55-57](#)] which limits its potential for detection of the individual gas molecule [[255](#), [256](#)]. Notably, the sensitivity of graphene-based gas sensors can be significantly improved by

introducing the dopant or defect [56-58, 400, 420-424]. Zhang *et al.* discovered strong interactions between B-doped, N-doped, and defective graphene with small gas molecules such as NO₂, CO, NO, and NH₃ [56]. B-, N-, and Si-doped graphene indicated enhanced interactions with common gases such as N₂, NO, NO₂, NH₃, SO₂, CO, CO₂, O₂, H₂, and H₂O compared to pristine graphene [57]. In another study, graphene doped with transition metals (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt) exhibited high sensitivity toward O₂ adsorption [400]. Borisova *et al.* discovered that the interactions of H₂S with C atoms of defected graphene are much stronger than those of pristine graphene [420]. DFT calculation on Eu decorated single- and double-sided graphene sheets showed that each Eu could firmly bound to six hydrogen molecules [421].

Inspired by the astonishing gas sensing performance of graphene, the sensing capabilities of other 2D structures toward various gases have been investigated. Recently, the graphene-like BC₃ sheet has been epitaxially grown on the NbB₂ (0001) surface [425]. The 2D honeycomb structure of BC₃ and graphene are analogous because of their similar atomic radius. The boron atoms are orderly distributed in the sheet and each boron atom bound to three carbon atoms so that six carbon atoms from a hexagon surrounded by six boron atoms [426, 427]. Unlike the zero-gap semimetal graphene, the BC₃ is a semiconductor with a band gap of 0.46-0.73 eV [426-432]. It was shown that the pristine [433], Li-doped [434], poly-lithiated molecule-doped [435], and transition metal-doped [436-438] BC₃ have a high potential towards H₂ storage. The possibility of BC₃ sheet to be served as a gas sensor has been investigated [439-442]. Beheshtian *et al.* investigated the electronic sensitivity of pristine, Al-, and Si-doped BC₃ sheets to formaldehyde (H₂CO) molecule using DFT [439]. They found that although H₂CO is

weakly adsorbed on the sheet, both Al and Si doping enhance the reactivity of the BC_3 sheet toward H_2CO . Peyghan *et. al.* introduced BC_3 nanotube as a potential gas sensor for CO detection [440].

In this chapter, first-principles methods based on DFT are employed to study the electronic and transport properties of the graphene-like BC_3 sheet upon interaction with toxic gas molecules such as NO, NO_2 , NH_3 , and CO. The sensitivity of the BC_3 -based sensors is evaluated from the variations in their electronic transport properties. The results reveal the promising future of graphene-like BC_3 in the development of ultrahigh sensitive gas sensors.

8.2 Computational details

The results presented in this chapter are obtained using first-principle DFT calculations combined implemented in ATK package [293, 296, 328]. The GGA-PBE exchange-correlation functional with a double- ζ polarized basis is adopted. The Grimme vdW correction (PBE-D2) [407] is also engaged to describe long-range vdW interactions [408]. Furthermore, counterpoise (cp) correction is considered in the binding energy calculations to expunge the BSSE. The energy mesh cut-off and the electronic temperature are set to be 150 Rydberg and 300 °K, respectively. The supercell geometry with periodic boundary condition is accepted, and a large vacuum of 20 Å is considered in x direction (in which the structure is not periodic) to avoid the image-image interaction. All the structures are allowed to fully relax using the conjugate gradient method until the force on each atom is less than 0.01 eV/Å. The first Brillouin zones are sampled using $1 \times 11 \times 11$ and $1 \times 21 \times 21$ k -points for optimization and calculations, respectively.

The adsorption energy of gas molecules on the BC₃ sheet is calculated by:

$$E_{\text{ad}} = E_{\text{BC}_3+\text{Molecule}} - E_{\text{BC}_3} - E_{\text{Molecule}} \quad (8.1)$$

Where $E_{\text{BC}_3+\text{Molecule}}$, E_{BC_3} , and E_{Molecule} are the total energies of the BC₃-Molecule complex, pristine BC₃ sheet, and the isolated gas molecule, respectively. The charge transfer upon adsorption of gas molecules on the BC₃ sheet is studied using Mulliken population analysis from the differences in the charge concentrations before and after adsorption.

To study the transport properties, the gas sensing system is divided into three regions: the central region (scattering region), left, and right electrodes, as shown in Figure 8.1. The conductance of the system is calculated using Equation (3.31).

Figure 8.1 (a) Schematic structural model of BC₃ gas sensor with two electrodes (black boxes). The grey and pink balls represent C and B atoms, respectively. (b) The band structure of a pristine BC₃ sheet. BC₃ is a semiconductor with a band gap of 0.733 eV.

8.3 Adsorption configurations

I first tested the accuracy of my computational method by calculating the band structure of a pristine BC_3 sheet, as shown in Figure 8.1(b), and comparing my results with those reported previously. The calculations show that BC_3 is a semiconductor with a band gap of 0.733 eV. The B-C and C-C bond lengths are 1.57 and 1.43 Å, respectively. These results are in good agreement with literature data [[426-432](#)].

In a BC_3 sheet, each six C atoms form a hexagon, and each B atom is attached to three separate C hexagons. Because the gas molecules tend to be adsorbed in various configurations, a number of input geometries should be taken into account. To this end, a single gas molecule of NO, NO_2 , CO, and NH_3 is placed at a distance of 2 Å above C atom, B atom, C-C bond, B-C bond, the center of C hexagons, and the center of B-C hexagons. At these specific positions, several molecular orientations could be considered. For diatomic molecules (NO and CO), the molecular axis could be aligned in parallel or perpendicular with respect to the surface of the BC_3 sheet. Moreover, the O atom of them can point up or down. On the other hand, two initial orientations for the triatomic (NO_2) and tetratomic (NH_3) molecules are considered. In the first orientation, the N atom of the molecules points toward the BC_3 , while in the second one, the O atom of NO_2 and the H atom of NH_3 points down to the BC_3 sheet. After that, all the structures are allowed to fully relax. The interactions of the molecules with BC_3 sheet can be described regarding their adsorption energies. Based on Equation (8.1), the more negative the value of E_{ad} is, the stronger adsorption of gas molecules on BC_3 would be. The most energetically favorable adsorption configurations are selected for further studies. Figure 8.2 presents the lowest energy configurations among all considered arrangements. The adsorption

energies of aforementioned gas molecules on BC₃ sheet calculated at the PBE-D2 level of DFT, the binding distances, and the net charge transfers using Mulliken population analysis are listed in Table 8.1.

Figure 8.2 The most stable adsorption configurations (top and side view) for NO, CO, NO₂, and NH₃ on the pristine BC₃ sheet. The grey, pink, blue, red, and white balls represent C, B, N, O, and atoms, respectively. The bond lengths (in unit of Å) and the binding distances between the molecules and the BC₃ sheet are also given.

8.4 NO Adsorption on BC₃ Sheet

Upon exposure NO to BC₃ sheet, NO adopts a tilted orientation with respect to the plane of BC₃, as shown in Figure 8.2. The N atom of NO is pointing to B atom of BC₃. The O-N-B angle is 129.51°. The interaction between the electron-deficient B atom and the

electron-donating N atom of the NO leads to moderate adsorption energy of -1.11 eV and the formation of a tight N-B bond (1.66 Å), suggesting that NO is chemically adsorbed on the BC_3 sheet. It should be noted that the B-N distance (1.66 Å) in the NO- BC_3 complex is almost identical to the bond length of B-N in ammonia borane (BH_3NH_3) (1.6576 Å) [443], proving the formation of a covalent bond between BC_3 and NO. The BSSE causes an artificial attraction between the molecule and its adsorbents which lead to a strong binding. To exclude the BSSE, the Bernardi counterpoise correction is considered [409]. The adsorption energies with counterpoise correction for the different systems are tabulated in Table 8.1.

Table 8.1 The calculated adsorption energy (E_{ad}) with and without counterpoise correction, binding distance which is the shortest atom to atom distance between molecule and the BC_3 sheet (D), and the charge transfer (Q), energy band gap (E_g), energy band gap changes (ΔE_g), and recovery time (τ). The negative values of charge indicate a charge transfer from molecule to the BC_3 sheet.

System	E_{ad} (eV)	E_{ad} C.P (eV)	D (Å)	Q (e)	E_g (eV)	ΔE_g (%)	τ (sec)
Pure BC_3	-	-	-	-	0.733	-	-
BC_3 -NO	-1.11	-0.91	1.66	-0.65	0.000	100	0.02
BC_3 -CO	-1.34	-1.12	1.54	$+0.09$	0.767	4.63	11.75
BC_3 -NO ₂	-1.69	-1.41	1.38	-0.77	0.000	100	174662
BC_3 -NH ₃	-1.45	-1.26	1.67	-0.10	0.610	16.7	240.6

The absolute value for NO adsorption on BC_3 is decreased from 1.11 to 0.91 eV, respectively. The obtained adsorption energy for NO on BC_3 is significantly higher compared to those reported for its adsorption on pristine graphene (-0.30 eV) and N-doped graphene (-0.40 eV) [56]. It is also comparable to the reported adsorption energy of NO on B-doped graphene (-1.07 eV) [56].

The BC_3 structure undergoes a structural change upon NO adsorption. The bond angles between N-B-C are 92.42° , 95.20° , and 108.42° . The C-B bond length is elongated from 1.57 Å to 1.59-1.61 Å around the interaction area. Moreover, the B site is transformed from sp^2 hybridization to sp^3 hybridization with an average buckling distance of ~ 0.242 Å. Similar observations have been reported for B-doped graphene [56] and B-doped carbon nanotubes [444]. Furthermore, the N-O bond length is increased from 1.173 Å in an isolated NO molecule to 1.179 Å in the NO- BC_3 complex. The low difference between the bond length values of NO molecule before and after adsorption on BC_3 show that there is no dissociative adsorption of NO on BC_3 . When NO is adsorbed on BC_3 sheet, an apparent charge of 0.65 e is transferred from NO to the BC_3 sheet. The N and O atom experience a decrease of 0.52 and 0.13 e in their charge states, respectively.

8.5 CO Adsorption on BC_3 Sheet

Next, the adsorption mechanism of the CO gas molecule on BC_3 sheet is studied. The most stable adsorption configuration of the CO- BC_3 complex is shown in Figure 8.2. The CO molecule is placed perpendicular to the BC_3 plane with the C atom at B atom and the other way around. The values of adsorption energy without and with counterpoise correction are -1.34 and -1.12 eV, respectively. The minimum atom-atom distance between the CO and BC_3 (C-B bond length) is 1.54 Å which is so close to the C-B dimer bond length (1.56 Å). These results reveal that the CO is chemically adsorbed on the BC_3 sheet. The calculated E_{ad} of CO on BC_3 is significantly higher than values reported for CO adsorption on pristine graphene (-0.12 eV), N-doped graphene (-0.40 eV), and B-doped graphene (-0.14 eV) [56]. The structure of BC_3 is slightly altered in the interaction

area. The B atom protrudes outwards after CO adsorption with an average buckling distance of ~ 0.280 Å. The bond angles between C-B-C are 99.26° , 99.59° , and 101.05° . The C-B bonds in BC_3 got slightly extended to ~ 1.62 Å after CO adsorption in comparison with 1.57 Å in the pristine BC_3 sheet. The bond lengths of CO before and after interaction with BC_3 are 1.14 and 1.15 Å, respectively, indicating that the CO molecule is not dissociated through the adsorption process. Moreover, the interaction between CO and BC_3 results in a charge transfer of $0.09 e$ from BC_3 sheet to CO. The C and O atoms of the CO molecule lose and attain electronic charges of 0.05 and $0.14 e$, respectively.

8.6 NO₂ Adsorption on BC₃ Sheet

The NO₂ adsorption mechanism on BC_3 is more complicated than the other molecules studied above. The BC_3 sheet and NO₂ molecule undergo significant structural changes upon adsorption on BC_3 , as shown in Figure 8.2. The N-O bond lengths in isolated NO₂ (1.21 Å) get extended to 1.79 and 3.11 Å, indicating that the molecule is fully dissociated during the adsorption process into the chemisorbed NO and O species. The N-O-N bond angle of isolated NO₂ decreases from 133.06° to 95.04° after complexation with BC_3 . The O atom of the molecule forms two covalent bonds with C and B atoms of the BC_3 sheet, where the O-C and O-B bond lengths are 1.38 and 1.40 Å, respectively. The C-O-B bond angle is 100.68° . On the other hand, the NO part of the NO₂ molecule binds to another B atom of the same B-C hexagon with a N-B covalent bond. The chemisorption of the dissociated NO on BC_3 is quite similar to that of the NO molecule on the BC_3 sheet. The O-N-B angle is 130.15° , and the N-B bond length is 1.65 Å. The adsorption energy of NO₂ on BC_3 sheet without and with counterpoise correction are -1.69 and -1.41 eV,

respectively. The high adsorption energy and short binding distance confirm the chemisorption/dissociation of NO₂ after interaction with a BC₃ sheet. The value of adsorption energy for NO₂-BC₃ is greater than those calculated for NO and CO molecules. More interestingly, the calculated E_{ad} of NO₂ on BC₃ is greater than those reported for NO₂ adsorption on pristine graphene (−0.48 eV), N-doped graphene (−0.98 eV), and B-doped graphene (−1.37 eV) [56]. Moreover, a significant charge of 0.77 e is transferred from NO₂ molecule to BC₃ sheet after complexation. This large charge transfer correlates to the strong adsorption energies of the NO₂ on BC₃. The first dissociated part of the NO₂ (O atom) loses electronic charge of 0.14 e . The second dissociated part of the NO₂ (NO) loses 0.63 e , which is comparable to the obtained charge transfer for NO-BC₃ complex (0.65 e). The charge states on N and O are reduced by 0.54 and 0.09 e , correspondingly.

8.7 NH₃ Adsorption on BC₃ Sheet

Afterward, the interactions between the NH₃ molecule and BC₃ sheet are investigated. It is found that NH₃ is bound to the B atom with the N atom pointing at the sheet, as shown in Figure 8.2. The N-B binding distance is 1.67 Å which is close to the B-N bond length in BH₃NH₃ (1.6575 Å) [443], indicating the formation of covalent bond between NH₃ and BC₃ sheet. The bond angles between N-B-C are 100.88°, 101.66°, and 101.74°. The NH₃ is chemisorbed on the BC₃ sheet with adsorption energy of −1.45 (−1.26) eV without (with) counterpoise correction. The calculated E_{ad} for NH₃-BC₃ complex is significantly greater than those obtained for NH₃ adsorption on graphene (−0.11 eV), N-doped graphene (−0.12 eV), and B-doped graphene (−0.50 eV) [56].

It should be noted that this relatively high adsorption energy for the NH₃-BC₃ complex is accompanied by a small charge transfer of 0.10 *e* from the molecule to BC₃ sheet which hinders its capability toward NH₃ detection. The N atom of NH₃ donates 0.1 *e* to the BC₃ sheet through the adsorption process, while the charges on H atoms keep constant. The adsorption of NH₃ on BC₃ sheet brings about some structural changes in both the molecule and the BC₃ sheet. The B atom which is bonded to N atom experiences a transformation from sp² to sp³ hybridization where it stands out at an average distance of 0.317 Å above the planar sheet of BC₃. The B-C bonds around the interaction areas get extended to 1.60 Å. The bond lengths of N-H in an isolated NH₃ (1.03 Å) is found to be the same after adsorption on the BC₃ sheet. However, the H-N-H bond angles are increased from 104.58° in an isolated NH₃ to 108.16° in the NH₃-BC₃ complex.

8.8 Electronic and Transport Properties of Gas Molecules-BC₃ Complexes

To gain more insight into the adsorption of gas molecules on the BC₃ sheet, their electronic total charge densities are calculated. As can be seen in Figure 8.3, an orbital overlap can be observed between NO, CO, NO₂, and NH₃ gas molecules and the BC₃ sheet, revealing the occurrence of a strong chemisorption/dissociation. These results are in accordance with obtained adsorption energies and binding distances.

The orbital mixing and the charge transfer are expected to bring significant changes to the electronic structure of the BC₃ sheet which is beneficial for sensing applications. The band gap can determine the electrical conductivity (σ) of materials as follow [445]:

$$\sigma \propto \exp(-E_g / 2kT) \quad (8.2)$$

Figure 8.3 The electronic total charge densities for the adsorption of NO, CO, NO₂, and NH₃ gas molecules on pristine BC₃.

Here, T is the temperature and k_B is the Boltzmann constant. Apparently, a small change in the energy band gap dramatically alters the electrical conductivity. Figure 8.4 presents the band structures of BC₃ after complexation with NO, CO, NO₂, and NH₃. The energy band gap of BC₃ (0.733 eV) increases to 0.767 eV upon interaction with CO and decreases to 0.610 eV after interaction with NH₃. The band gap changes (ΔE_g) for the CO-BC₃ complex is 4.63% and for the NH₃-BC₃ complex is 16.7%. These small variations in the band gap of BC₃ after interaction with CO and NH₃ agree well with the small charge transfer of CO-BC₃ (+0.09 e) and NH₃-BC₃ (−0.10 e) systems. As a result, the electrical conductivity slightly decreases and slightly increases upon interaction with CO and NH₃ gas molecules, respectively. Although the values of adsorption energy of CO (−1.12 eV) and NH₃ (−1.26 eV) on BC₃ are relatively high, the values of ΔE_g implying that BC₃-based gas sensor has low sensitivity to CO and moderate sensitivity to the NH₃ molecule.

In contrast, the influence NO and NO₂ adsorption on the electronic structure of BC₃ is much more pronounced. As can be seen in Figure 8.4, there are almost flat bands on the Fermi levels of NO- and NO₂-BC₃ systems, indicating that the systems are metallic. One possible reason for this phenomena could be the occurrence of significant transfer after adsorption of NO ($-0.65 e$) and NO₂ ($-0.77 e$) molecules on BC₃. It should be noted that the alterations in the electronic structure of BC₃ upon interaction with NO₂ are more noticeable compared to that upon interaction with NO. These results can be confirmed by the obtained adsorption energies. A significant increase (100%) in the electrical conductivity of BC₃-based sensor upon adsorption of NO (NO₂) is expected, confirming its high sensitivity toward NO (NO₂) adsorption (dissociation).

Figure 8.4 Band structures of BC₃ sheet after interaction with NO, CO, NO₂, and NH₃ gas molecules

An important factor for the evaluation of the performance of a gas sensor is the recovery time of the gas sensing material. Novoselov *et al.* have shown that the graphene sensor could be recovered to its initial geometry by annealing at 150°C in a vacuum or ultraviolet (UV) irradiation within 100-200 s [249]. The recovery time τ can be expressed using the conventional transition state theory as follows:

$$\tau \propto \nu_0^{-1} \exp(-E_{\text{ad}} / k_B T) \quad (8.3)$$

Here, ν_0 is the attempt frequency. Based on this equation, a much longer recovery time is expected, if the adsorption energy is considerably increased (more negative). Based on our findings, the NO on BC₃ has the shortest recovery time followed by CO, NH₃, and NO₂. As an example, the recovery time of BC₃-based gas sensor after NO, CO, NH₃, and NO₂ adsorption could be ~ 0.02, 11.75, 174662, and 240.6 s by annealing at 150°C in UV irradiation ($\nu_0 \sim 800$ THz), see Table 8.1.

To further investigate the effects of gas molecules on the conductance of BC₃ sheet, the quantum conductances of the BC₃-based sensor (see Figure 8.1(a)) before and after adsorption of gas molecules are calculated, as shown in Figure 8.5. One can see that the values of the conductance of CO-BC₃ and NH₃-BC₃ complexes slightly decrease and increase at low energies compared to that of pristine BC₃, respectively. However, the alteration of the conductance is more vivid for the later complex which concurs well with our previous results. More excitingly, large picks appear at Fermi levels of NO-BC₃ and NO₂-BC₃ complexes which confirm the metallic behavior of these systems. The variations in the conductance of the BC₃ after NO₂ adsorption are more noticeable in

comparison with that after NO adsorption. All these findings show that the BC₃-based sensor has a great potential for NO detection due to the significant conductance changes, moderate adsorption energy, and short recovery time. Although the sensitivity of BC₃ to CO gas molecule is low, this sensor could detect NH₃ molecule. More interestingly, the BC₃ might be a promising catalyst for dissociation of the NO₂ gas molecule.

Figure 8.5 Quantum conductance of BC₃-based sensor before and after NO, CO, NO₂, and NH₃ gas molecules adsorption.

8.9 Summary

I employed DFT to scrutinize the adsorption geometry, adsorption energy, charge transfer, electronic band structure, and the conductance modulations of graphene-like BC₃ after interaction with toxic gas molecules. While NO, CO, NO₂, and NH₃ gas molecules are weakly physisorbed on the surface of graphene, our results indicated that the presence of active B atoms on BC₃ could strengthen the adsorption of these molecules (with adsorption energies less than -1 eV). Although CO, NO, and NH₃ tend to be

adsorbed in the molecular form, the NO_2 molecule is fully dissociated into chemisorbed NO and O species during the adsorption process. The calculated band structures reveal that the band gap of BC_3 (0.733 eV) is 4.63% increased after CO adsorption and 16.7% decreased after NH_3 adsorption. These variations in the electronic properties of BC_3 correspond to small charge transfers from CO ($-0.1 e$) and NH_3 ($+0.09 e$) to the adsorbent. These findings suggest that the BC_3 -based sensor has low and moderate sensitivities to CO and NH_3 . Significant charge transfers happen upon adsorption of NO ($-0.65 e$) and NO_2 ($-0.77 e$) on BC_3 sheet, resulting in a semiconductor-metal transition in BC_3 . These alternations in the band gap of BC_3 cause a significant increase in its conductance. I demonstrated that the BC_3 -based sensor has a great potential for NO detection due to the significant conductance changes, moderate adsorption energy (-1.11 eV), and short recovery time (0.07 s). Interestingly, the BC_3 might be a promising catalyst for dissociation of the NO_2 gas molecule. On the basis of my theoretical findings, graphene-like BC_3 can be considered as a highly sensitive molecular sensor for NO and NH_3 and a potential catalyst for NO_2 dissociation.

CHAPTER 9

Efficient and Reversible CO₂ Capture by Lithium-functionalized Germanene

Monolayer

In this chapter, first-principles DFT is employed to investigate the interactions of CO₂ gas molecules with pristine and lithium-functionalized germanene. These results were published on arXiv [[446](#)].

9.1 Overview

The development of technology for CO₂, the main man-made greenhouse gas, capture, and storage has garnered huge interest [[447](#), [448](#)]. The current industrial technology which is based on chilled ammonia suffers from toxicity, solvent loss, low energy efficiency, and corrosion issues [[449](#), [450](#)]. To overcome these problems, various materials such as metal-organic frameworks [[451](#)], boron nitride nanotubes [[452](#)], and carbon nanotubes [[453](#)] have been employed as effective sorbents for CO₂ capture. Nevertheless, their large adsorption energies lead to a difficult regeneration step [[452](#)]. Ergo, the selection of adsorbents with both high selectivity and an easy release step is a vital task.

The potential application of graphene for gas sensing has been widely studied [[57](#), [252](#), [454](#), [455](#)]. Although the physisorption of CO₂ on pristine graphene limits its potential for single molecule detection [[454](#)], its sensing capability can be improved by modifying graphene [[57](#), [252](#), [455](#)]. Motivated by the successful detection of individual gas molecules by graphene, the sensing capability of other 2D structures toward different polluting gasses have been explored [[456](#)]. Unlike flat graphene sheet, silicene and germanene have buckled honeycomb structures due to the partial sp³ hybridization of Si

and Ge atoms [42, 59], making them chemically more reactive toward atoms and molecule adsorption compared to graphene [80, 367, 457, 458]. Although N-based molecules are chemisorbed on silicene and germanene *via* strong covalent bonds, CO₂ is weakly physisorbed on silicene and germanene sheets [61, 62, 367, 401, 457, 459]. The electronic structures of silicene and germanene show strong modifications under Li decoration [48, 460-462]. It was also stated that functionalization of Si atoms with Au (Li) improves the interaction between silicene and CO (CO₂) molecules [463, 464]. Yuan *et al.* performed DFT calculations to investigate the stability, structural and electronic properties of saturated and half-saturated germanene with alkali metal atoms and found that the complete lithiated germanene has the highest stability among all the studied structures [465].

9.2 Computational Details

Calculations are performed using first-principle methods based on DFT implemented in ATK package [296]. The exchange-correlation functional is approximated by the GGA-PBE with a double- ζ polarized basis set. To describe long-range vdW interactions, the Grimme vdW correction (DFT-D2) [407] is also considered. The density mesh cut-off for plane-wave expansion is set to be 150 Ry. To avoid adjacent images interactions, a large vacuum space of 25 Å is considered in *z*-direction. Prior to the calculations; all the structures are fully relaxed using the conjugate gradient method up until the force on each atom is less than 0.01 eV/Å. For the germanene unit cell, the first Brillouin zones are sampled using 11×11×1 and 21×21×1 *k*-points for optimization and calculations, respectively. Moreover, first-principles molecular dynamics (MD) calculation are performed under NVT conditions where the number of atoms (N), the volume (V), and

the temperature (T) are conserved. The temperature is controlled by the sampling of the canonical ensembles using algorithm of Nosé Hoover. The MD simulation time is 1.5 ps with a time step of 1.0 fs.

9.3 CO₂ Adsorption on Pristine Germanene

I first discuss the adsorption behavior of CO₂ gas molecules on the pristine germanene sheet. To this end, an individual CO₂ is initially placed on a germanene sheet at four different positions including valley (the Ge atom in the lower sublattice), hill (the Ge atom in the upper sublattice), bridge (the Ge-Ge bond), and hollow (the center of a hexagon ring) sites with two different molecular orientations, parallel and perpendicular to the surface. We use the notation Ge₈(CO₂)_n to distinguish between the various numbers of CO₂ molecules, *n*, in a 2×2 supercell of germanene (adopted from Ref. [464]). The adsorption behavior of molecule on germanene is investigated after full relaxation. The structural stability can be addressed using adsorption energy (*E_{ad}*) which is

$$E_{ad} = [E_{\text{Germanene}+\text{CO}_2} - E_{\text{Germanene}} - n \times E_{\text{CO}_2}] / n \quad (9.1)$$

Here, *E_{Germanene+CO2}*, *E_{Germanene}*, and *E_{CO2}* denote the total energies of the germanene-CO₂ system, pristine germanene, and the isolated CO₂ molecule, respectively. Based on the definition, the negative *E_{ad}* represents the structural stability. Moreover, for a material to be suitable as a medium for CO₂ capture, relatively large amounts of adsorption energy and charge transfer are vital. Comparing the adsorption energies of different adsorption geometries, the horizontal alignment on top of the bridge site is found to be energetically more favorable, as shown in Figure 9.1(a). The distance between CO₂ and the germanene sheet is 3.88 Å, showing weak vdW interactions. A small adsorption energy of −0.11 eV

along with small charge transfer (calculated by Mulliken population analysis) of $0.04\ e$ from the molecule to the germanene confirms this fact that CO_2 molecule is physisorbed on the germanene. Therefore, pristine germanene could not be an appropriate material for CO_2 capture because minimum adsorption energy of $-0.14\ \text{eV}$ is required from an application point of view [466]. These results agree well with previous theoretical [457].

Figure 9.1 The most stable adsorption configurations (top and side view) and their corresponding band structures for (a) and (b) one CO_2 (low coverage) (c) and (d) eight CO_2 (high coverage) on pristine germanene, respectively. The cyan, gray, and red balls represent Ge, C, and O atoms, respectively.

It should be noted that for higher CO_2 coverage, the molecules are inclined with respect to the horizontal direction due to the repulsion between them, as shown in Figure 9.1(c). The distances between CO_2 molecules and germanene are 3.51 to $3.97\ \text{\AA}$. The

average adsorption energy and charge transfer from each CO₂ to germanene are decreased to -0.09 eV and 0.02 *e* for high coverage, respectively. These small values limit the application of germanene as a potential media to capture CO₂. Pristine germanene is a zero-gap semiconductor. It is found that the linear Dirac-like dispersion relation of germanene at K point remains almost unchanged upon physisorption of a single CO₂ gas molecule. A tiny band gap of 3 meV is opened at the Dirac point of germanene, as shown in Figure 9.1(b). The change in the band structure of germanene is a little more pronounced at the high coverage of CO₂ where the band gap is enhanced to 44 meV, as illustrated in Figure 9.1(d).

9.4 Lithium-functionalized Germanene

Lithium functionalization can enhance the stability of CO₂ gas molecules on germanene nanosheet [465]. Similar to fully lithiated silicene [467] and graphene [468], lithium atoms occupy sites on top of the Ge atoms in the lower sublattice, which is in agreement with previous findings [465]. The optimized geometry of Li-functionalized germanene is presented in Figure 9.2(a). The lattice distortion caused by lithium adsorption is noticeable. The buckling distance and Ge-Ge bond length are enlarged from 0.73 and 2.46 Å in pristine germanene to 1.23 and 2.55 Å in lithiated germanene, respectively. Furthermore, the minimum Ge-Li bond length is 2.55 Å. The bond strengths can be assessed on the basis of the adsorption energy of lithium atoms on the surface of germanene using following formula:

$$E_{ad} = [E_{Germanene+Li} - E_{Germanene} - N_{Li} \times E_{Li}] / N_{Li} \quad (9.2)$$

Here, $E_{Germanene+Li}$ and E_{Li} are the total energies of the lithiated germanene system and the single Li atom, respectively. In addition, N_{Li} is the number of adsorbed Li atoms in the

supercell. Adsorption energy of -1.01 eV/atom reflects the stability of fully lithiated germanene (Ge_8Li_8) and suggests the chemisorption of lithium atoms on the surface of germanene. However, the electronic total charge density indicates that there is a small electron orbital overlap between Li and Ge atoms, showing that a weak covalent bonding exists between Li and germanene, see Figure 9.2(c). It is found that each Li atom (electronegativity of 1) donates 0.176 e to the more electronegative Ge atoms (electronegativity of 2); hence, the main character of the bonding between Ge-Li in this system is ionic. Consequently, the ionic interaction induced by large charge transfer between Li and Ge atoms is the reason of high stability of fully lithiated germanene.

Figure 9.2 (a) Relaxed configuration (top and side view) of fully lithiated germanene, its corresponding (b) band structure, and (c) electronic total charge density distributions.

Upon complete lithiation, the band structure is transformed from a zero-gap semiconductor to an indirect semiconductor with 220 meV band gap, as shown in Figure 9.2(b). Unlike pristine germanene, fully lithiated germanene does not have the linear dispersion at the K point. Osborn *et al.* predicted an energy gap of 368 meV in fully lithiated silicene [467]. A Ge atom has a larger atomic radius in comparison with Si atom, giving rise to a decrease in the strength of covalent bonds in Ge-Li compared to Si-Li. Hence, larger energy band gap in fully lithiated silicene than that in germanene can be associated with the stronger covalent nature in the former. Moreover, it has been reported that graphene behaves as a metal upon complete lithiation and keeps its linear dispersion at the K point [468].

9.5 CO₂ Adsorption on Li-functionalized Germanene

Next, I study the adsorption of CO₂ molecules on Li-functionalized germanene (Ge₈Li₈(CO₂)_n). For a single CO₂ molecule adsorption (Ge₈Li₈(CO₂)₁), the most energetically favorable position was found to be on the top of Ge atom in the upper sublattice (hill site) with an adsorption energy of -2.31 eV, showing strong interactions between the molecule and the Li-functionalized germanene, as shown in Figure 9.3(a). The triatomic molecule of CO₂ with 180° bond angles is strongly distorted with the O-C-O bond angle of 123.3°. The C atom points to the germanene sheet, and C-Ge bond length (the distance between the molecule and Li-functionalized germanene sheet) is 2.13 Å which is much smaller than that of pristine germanene sheet (3.88 Å). The CO₂ molecule also interacts with Li atoms by its O atoms, where Li-O bonds are 1.85 and 1.75 Å. Also, the C-O bonds (1.18 Å) in an isolated CO₂ molecule get elongated to 1.28-1.30 Å in Ge₈Li₈(CO₂)₁. The charge redistribution between germanene, Li, and CO₂

(concerning the isolated Li-functionalized germanene and CO₂) are calculated and listed in Table 9.1. Li-functionalized germanene donates 0.338 *e* electrons to CO₂. In comparison with low electrons transfer (−0.04 *e*) in the case of non-functionalized germanene, CO₂ is significantly stabilized on Li-functionalized germanene due to the large charge transfer.

Table 9.1 The adsorption energy E_{ad} (eV) per molecule, energy band gap E_g (eV), and the charge redistribution on germanene, Li atoms, and each CO₂.

	E_{ad} (eV)	E_g (eV)	Q_{MPA} (<i>e</i>) on		
			Germanene	Li	CO ₂
Ge₈(CO₂)₁	−0.11	0.003	0.041	-	−0.04
Ge₈(CO₂)₈	−0.09	0.044	0.176	-	−0.02
Ge₈Li₈	−1.01	0.220	1.408	−1.408	-
Ge₈Li₈(CO₂)₁	−2.31	0.520	−0.564	0.2660	0.338
Ge₈Li₈(CO₂)₂	−2.48	0.620	−0.343	−0.367	0.354
Ge₈Li₈(CO₂)₃	−2.51	0.790	−0.113	−0.848	0.321
Ge₈Li₈(CO₂)₄	−2.60	1.070	0.421	−1.876	0.364
Ge₈Li₈(CO₂)₅	−2.51	0.960	0.337	−2.090	0.350
Ge₈Li₈(CO₂)₆	−1.70	0.640	0.645	−2.701	0.342
Ge₈Li₈(CO₂)₇	−1.54	0.228	0.438	−1.623	0.378
Ge₈Li₈(CO₂)₈	−0.80	0.000	0.700	−1.709	0.047
Ge₈Li₈(CO₂)₉	−0.22	0.000	−0.213	−0.015	−0.02

To better understand the role of Li in the enhancement of the adsorption energy of CO₂ on germanene, the PDOS of Ge₈(CO₂)₁ and Ge₈Li₈(CO₂)₈ are compared, see Figure 9.4. In Ge₈(CO₂)₁, the contributions of p orbitals of C and O are negligible compared to those of Ge atoms. There is no overlapping between orbitals, confirming that the CO₂ is weakly physisorbed on pristine germanene. In Ge₈Li₈(CO₂)₈, the VBM is originated from Ge p orbitals. However, the CBM is due to Li p and Ge p orbitals. The C p and O p orbitals are significantly hybridized with Ge p and Li p orbitals at higher energies in the

valence band and especially in the conduction band, indicating that the CO₂ is chemically adsorbed on the Li-functionalized germanene.

Figure 9.3 The most stable adsorption configurations (top and side view) and their corresponding band structures of (a) and (b) Ge₈Li₈(CO₂)₁ (low coverage) (d) and (e) Ge₈Li₈(CO₂)₈ (high coverage). (e) Ge₈Li₈(CO₂)₈ complex after 1.5 ps of molecular dynamic simulations at 300, 400, and 500 °K.

With increasing the CO₂ molecules in the supercell, the adsorption energy decreases toward a minimum of -2.60 eV (50% CO₂ coverage) and increases again (less stability), see Figure 9.5(a). For high CO₂ coverage (100% coverage), the molecules are positioned on top of Li atoms in an average binding distance of 2 Å which is much

smaller than non-functionalized germanene (3.51-3.97 Å). Only a part of CO₂ molecules (O atom) is firmly bound to the Li-functionalized germanene, and an inclination in the range of 36-48° with respect to the vertical direction of the germanene sheet is found for the CO₂ molecules due to the repulsion between the molecules, as shown in Figure 9.3(c). The moderate adsorption energy of −0.80 eV and a small charge transfer of 0.047 *e* suggests a weak interaction that makes the release step of CO₂ molecules easier, while stabilizes CO₂ on the adsorbent. If another CO₂ molecule is added into the supercell, the adsorption is even further increased to −0.22 eV. The CO₂ capacity is calculated to be 12.57 mol/kg.

Figure 9.4 The projected density of states of $\text{Ge}_8(\text{CO}_2)_1$ and $\text{Ge}_8\text{Li}_8(\text{CO}_2)_1$

Inspired by the method in Ref. [399], the stability of Li-functionalized germanene after desorption of CO₂ molecules are tested. For this purpose, all the CO₂ gas molecules are removed, and the structure is relaxed again. It is found that the Ge₈Li₈(CO₂)_n structure is recovered to its original form after removal of all CO₂ molecules. The stability of Li-functionalized germanene is also investigated using first principles MD calculations. I perform 1.5 ps MD simulations with the step of 1 fs on Ge₈Li₈(CO₂)₈ complex at 300, 400, and 500 °K, as shown in Figure 9.3(e). It is found that the system is stable at room temperature. The results also suggest the stability of the system up to 500 °K.

The band structures of Li-functionalized germanene after CO₂ adsorption with low and high coverage are also shown in Figure 9.3(b) and (d), respectively. The band gap of the Li-functionalized germanene increases from 0.520 eV (12.5% CO₂ coverage) toward a maximum of 1.070 eV (50% CO₂ coverage), and decreases to zero at 100% coverage, see Figure 9.5 (b). Therefore, the CO₂ coverage can be evaluated using the band gap because of the high sensitivity of Li-functionalized germanene toward CO₂ adsorption.

9.6 Summary

Calculations based on DFT method have been performed to explore the capability germanene toward CO₂ adsorption. Our results revealed that the interaction of a CO₂ gas molecule with pristine germanene is very weak due to the small charge transfer. However, the adsorption energy of the Li-functionalized germanene is significantly higher than that of pristine for low CO₂ coverage. At high CO₂ coverage, the interactions of CO₂ molecules with Li-functionalized germanene decrease due to the repulsion

between molecules. Nevertheless, the adsorption energy is enough to stabilize the CO₂ on the adsorbent. Moreover, the structure of Li-functionalized germanene can be recovered to its initial shape after removal of CO₂ molecules. A large CO₂ storage capacity of 12.57 mol/kg is predicted for the system, and the band gap of the system is highly sensitive to the CO₂ coverage.

CHAPTER 10

Conclusions and future direction

10.1 Conclusions

Silicene, the silicon version of graphene, has recently attracted a great deal of interest because of its expected compatibility with current silicon nanoelectronics. Similar to graphene, silicene is a zero band gap semimetal. Therefore, opening a band gap in a silicene sheet is desirable due to the multitude of promising applications of silicene in high-performance electronic devices such as FETs and sensors. One popular approach to open the band gap in 2D nanomaterials is nanostructuring into nanoribbons. This dissertation is mainly dedicated to tuning the electronic and magnetic properties of SiNRs and SiNFs. The main achievements are summarized as follows:

- 1) Halogenated edge SiNRs were found much more stable than those of hydrogenated edge. It was revealed that the asymmetry in edge functionalization of two edges of ZSiNRs induces fantastic SGS and FM metal behaviors into ZSiNRs owing to breaking of the spin degeneracy of two edge states.
- 2) It was observed that several peculiar magnetic states, such as FM metal, AFM metal, half-metal, and SGS, can be obtained in the ribbons depending on dopant atom, edge functional atom, and its density.
- 3) The band gap of pristine ASiNR drops with increasing nanoribbon's width. The results showed that periodic nanoholes in ASiNRs modify its energy band gap depending on the armchair nanoribbon's width, repeat periodicity, and position relative to the edges. Perforating periodic nanoholes could produce a noticeable band gap of 0.635 eV in ASiNR with width of 18 ($\sim 33\text{\AA}$).

- 4) It was found that while both zigzag-edged hexagonal and triangular SiNFs show semiconducting behavior, the former is NM and the latter has ferrimagnetic characteristic. Half-hydrogenated SiNFs present a long-range FM order with a very large spin moment that is squarely proportional to the size of the nanoflakes. However, full hydrogenation of SiNF quenches the magnetism. Simple switch devices were proposed to show the potential application of silicene to tune the transport properties by harnessing the hydrogenation coverage on SiNFs.

Moreover, silicene, germanene, and BC_3 sheets have been studied for gas sensing applications.

- 5) The results revealed that SiNRs are capable of detecting CO , NH_3 , and H_2S with high sensitivity because they are chemically adsorbed on the SiNR and transfer a few electrons to the SiNR. However, SiNRs are not appropriate to serve as a sensor for NO , NO_2 , and SO_2 due to the fact that they are strongly chemisorbed with covalent bonds to SiNRs and transfer a large amount of electrons to the SiNR.
- 6) Dangling bond defects which are unavoidable through fabrication process will not hinder the sensing capability of SiNRs. The sensing capability of a SiNR-based sensor can also be increased by either N or B doping.
- 7) My findings suggested that the BC_3 -based sensor has low and moderate sensitivities to CO and NH_3 . While, BC_3 -based sensor has a great potential for NO detection due to the significant conductance changes, moderate adsorption

energy (-1.11 eV), and short recovery time (0.02 s). Interestingly, the BC_3 might be a promising catalyst for dissociation of the NO_2 gas molecule.

- 8) The interaction of CO_2 gas molecules with pristine germanene is very weak due to the small charge transfer. However, the adsorption energy of the Li-functionalized germanene is significantly higher than that of pristine. The structure of Li-functionalized germanene can be recovered to its initial shape after removal of CO_2 molecules. A large CO_2 storage capacity of 12.57 mol/kg is predicted for the system.

10.2 Future Direction

Despite the predicted tunable band gap in a wide range that makes silicene promising in future electronics applications, one major concern still needs to be addressed. My predicted band gaps from conventional DFT calculations are certainly underestimated. More faithful values of the band gaps can be obtained by adopting the hybrid exchange-correlation functional like HSE06.

My model currently can be used only to quantitatively characterize the adsorption density for the monolayer gas adsorption. Experimentally, it is obvious that the multilayer adsorption can occur beyond a critical target gas concentration. Consequently, several parameters need to be corrected in the future modeling of multilayer adsorption. First, the partial target gas pressure becomes larger and must be determined by establishing the thermodynamics modeling. Second, the binding energies of gas molecules in different layers vary and the binding energy becomes lower for gas molecules further away from the adsorption surface; third, the physical meaning of gas adsorption density might be inappropriate for the multilayer adsorption.

Although I have developed models of gas adsorption density and sensitivity for semiconducting materials, they are still inadequate to characterize the performance of a real gas sensor. Practically, it is intriguing to establish the modeling to characterize the gas adsorption dynamics, namely, the gas adsorption rate and the gas desorption rate. This is significant since both the detection limit and response time/recovery rate are critical in evaluating the performance of a real sensor. Here I propose the following approaches to this end for future studies. First, the adsorption rate is approximated by the classic theory so that it is equal to the gas incoming rate that depends only on the temperature and the mass of the gas molecule, while the desorption rate is dependent on both the temperature and the gas binding energy. Second, the conductance can be predicted by NEGF with respect to the distance between the gas molecule and the adsorption surface. Third, the adsorption/desorption time can be finally determined by adsorption/desorption rate and the conductance change.

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