UNIVERSITI PUTRA MALAYSIA

FIRST PRINCIPLE CALCULATION ON THE STRUCTURAL, ELECTRONIC AND TRANSPORT PROPERTIES OF GRAPHENE, SILICENE AND GERMANENE SUBSTRATE SYSTEM

MOHAMAD AMIN BIN HAMID

FS 2020 42

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By

MOHAMAD AMIN BIN HAMID

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Master of Science

July 2020

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DEDICATION

To my father, Hamid and my mother, Norlia who have always been supportive with my dreams ever since I was born. To my supervisor, Dr. Chan, who patiently guiding me throughout my postgraduate journey. To all my friend and brother, especially Adib who have saved me from countless time of loneliness, heartbroken and boredom. To my lover, Kama for the love and emotional support at times I needed the most. And to you, may this piece of knowledge enlighten you. May you persevere in your journey. I dedicate this thesis to all of you.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Degree of Master of Science

FIRST PRINCIPLE CALCULATION ON THE STRUCTURAL, ELECTRONIC AND TRANSPORT PROPERTIES OF GRAPHENE, SILICENE AND GERMANENE SUBSTRATE SYSTEM

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MOHAMAD AMIN BIN HAMID

July, 2020

Chair : Chan Kar Tim, PhD

Faculty : Faculty of Science

Although graphene, silicene and germanene are an interesting thin nanomaterial with various applications in novel electronic and spintronic devices, the zero-bandgap band structure limits the integration. By stacking different monolayer together, bandgap in graphene, silicene and germanene can be modulated by controlling the stacking configuration and interlayer distance. In this thesis, the structural, stabilities, electronic band, and electronic transport properties of graphene/silicene and graphene/germanene have been studied in three different stacking configurations, which is top, hollow, and bridge configurations using density functional theory and Boltzmann transport equation from first principle calculation. The computation for structural, stabilities and electronic band is performed by using Quantum ESPRESSO. Then, the output is utilized by BoltzTraP package to compute the electronic parts of transport properties for both graphene/silicene and graphene/germanene. This first principle study is motivated to contribute and further enriched the understanding of stacking effects in building two-dimensional superlattice materials. The results in this thesis can be divided into three part which are the structural, electronic and electronic transport properties per unit cell of graphene/silicene and graphene/germanene.

The first part is the structural properties where graphene/silicene and graphene/germanene superlattice are modelled in top, hollow and bridge stacking configurations. Then, the initial structure of graphene/silicene and graphene/germanene is optimized. From the structural optimization, the structural changes experienced by graphene/silicene and graphene/germanene is tabulated in comparisons to pristine graphene, silicene and germanene. The interlayer binding energy and formation energy is computed to find the most stable stacking configurations. For both graphene/silicene and graphene/germanene, it is found that the most stable is top stacking configurations, followed by hollow and bridge stacking. The second part is the electronic properties of graphene/silicene and graphene/germanene. Here, the effect of stacking of the superlattices on the electronic band structure is studied. For both graphene/silicene and graphene/germanene, there is a bandgap opening at K-point with graphene/germanene displaying the self-hole doping characteristics. This study further delved into the effects of stacking configuration on the effective mass of graphene/silicene and graphene/germanene at K-point. Here, the effective mass of electrons is found to increased due to the bandgap opening at K -point. The effects of modulating the interlayer distance of graphene/silicene and graphene/germanene on the bandgap and the effective mass of electrons is also studied and found that decreasing the interlayer distance increased the bandgap and in returns increase the effective mass of electrons for both graphene/silicene and graphene/germanene. The electronic transport properties consist of electrical conductivity, electronic thermal conductivity and Seebeck coefficient of graphene/silicene and graphene/germanene. From the Seebeck coefficient, the majority charge carrier in both graphene/silicene and graphene/germanene is electrons making both of it n-type semiconductors. Generally, electrical conductivity, electronic thermal conductivity and Seebeck coefficient for both graphene/silicene and graphene/germanene is better in n-type doping region. However, an increase in n-type doping concentration induced bipolar transport properties in graphene/germanene which switch the polarity from n-type to p-type semiconductors.

Abstrak thesis ini dikemukan kepada Senat Universiti Putra Malaysia sebagai memenuhi syarat keperluan untuk Ijazah Master Sains

PENGIRAAN PRINSIP PERTAMA TERHADAP SIFAT STRUKTUR, ELEKTRONIK DAN ANGKUTAN UNTUK SISTEM SUBSTRAT GRAFEEN, SILISIN AND GERMANIN

Oleh

MOHAMAD AMIN BIN HAMID

Julai, 2020

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Walaupun grafeen, silisin dan germanin adalah nanobahan yang menarik untuk digunakan dalam peralatan elektonik dan spintronik, penggunaanya tidak meluas kerana ketiadaan jurang jalur di dalam struktur jalur. Dengan menyusun dan mencantumkan lapisan dua dimensi yang berbeza, jurang jalur di dalam struktur jalur boleh dikawal dengan mengawal corak susunan dan jarak antara lapisan. Dalam tesis ini, sifat struktur, elektronik, dan angkutan elektronik dari grafeen / silisin dan grafeen / germanin telah dikaji dalam tiga konfigurasi susunan yang berbeza, iaitu konfigurasi atas, berongga, dan jambatan menggunakan teori fungsi ketumpatan (DFT) dan persamaan angkutan *Boltzmann* dari pengiraan prinsip pertama. Pengiraan untuk struktur, kestabilan dan jalur elektronik dilakukan dengan menggunakan *Quantum ESPRESSO*. Kemudian, hasil pengiraan digunakan oleh pakej *BoltzTraP* untuk mengira bahagian angkutan elektronik bagi kedua-dua grafeen/silisin dan grafeen/germanin. Kajian prinsip pertama ini bermotivasi untuk menyumbang dan memperkaya pemahaman tentang kesan susunan konfigurasi yang berbeza dalam membina bahan superkekisi dua dimensi. Hasil dalam tesis ini dapat dibahagikan kepada tiga bahagian yang merupakan sifat struktur, elektronik dan angkutan elektronik untuk grafeen/silisin dan grafeen/germanin.

Bahagian pertama adalah sifat-sifat struktur di mana struktur grafeen/silisin dan grafeen/germanin superkekisi di konfigurasi atas, berongga dan jambatan dibina. Kemudian, struktur awal grafeen/silisin dan grafeen/germanin dioptimumkan. Dari pengoptimuman struktur, perubahan struktur yang dialami oleh grafeen/silisin dan grafeen/germanin dapat digambarkan dalam perbandingan dengan satu lapisan grafeen, silisin dan germanin. Tenaga mengikat jarak antara lapisan dan tenaga pembentukan dikira untuk mencari konfigurasi susunan yang paling stabil. Didapati untuk kedua-dua grafeen/silisin dan grafeen/germanin, yang paling stabil adalah konfigurasi susunan atas, diikuti oleh konfigurasi berongga dan jambatan. Bahagian kedua adalah sifat elektronik grafeen/silisin dan grafeen/germanin. Di sini, kesan penyusunan superkekisi pada jalur elektronik dikaji. Didapati bahawa bagi kedua-dua grafeen/silisin dan grafeen/germanin, terdapat pembukaan jalur di titik-K, dan grafeen/germanin mempamerkan ciri-ciri doping diri lubang. Seterusnya, kesan kesan susunan konfigurasi pada jisim yang berkesan elektron untuk grafeen/silisin dan grafeen/germanin di titik-K dikaji. Di sini, didapati bahawa jisim yang berkesan elektron meningkat kerana pembukaan jalur di titik-K. Kesan pengubahsuaian jarak antara grafeen/silisin dan grafeen/germanin pada pembukaan jalur dan jisim yang berkesan elektron juga dikaji. Didapati bahawa penurunan jarak antara lapisan meningkatkan pembukaan jalur sekaligus meningkatkan jisim yang berkesan elektron untuk kedua-dua grafeen/silisin dan grafeen/germanin. Ciri-ciri angkutan elektronik terdiri daripada kekonduksian elektrik, kekonduksian terma elektronik dan pekali *Seebeck* untuk grafeen/silisin dan grafeen/germanin. Dari pekali *Seebeck*, pembawa cas majoriti dalam kedua-dua graphene/silicene dan graphene/germanene adalah elektron. Ini menjadikan kedua-duanya semikonduktor jenis-n. Secara umumnya, kekonduksian elektrik, kekonduksian terma elektronik dan pekali *Seebeck* bagi kedua-dua grafeen/silisin dan grafeen/germanin adalah lebih baik dalam rantau pendopan jenis-n. Walau bagaimanapun, peningkatan dalam kepekatan doping jenis-n mendorong sifat pengangkutan dwikutub menyebabkan grafeen/germanin menukar polariti dari semikonduktor jenis-n ke semikonduktor jenis-p.

ACKNOWLEDGEMENTS

I would like to extend my gratitude to my supervisors, Dr. Chan Kar Tim and Dr. Yazid Bin Yaakob for their helpful guidance and support throughout my study. Their professional guidance and vision has kept me on the track in my research work. I have also benefited a lot from various theoretical discussion groups one of which is PWSCF forum. In this regard, many thanks go to the moderator for addressing my problem related to open source package, Quantum ESPRESSO.

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Date:

Declaration by Graduate Student

I hereby confirm that:

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Declaration by Member of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature: _____
Name of Chairman of Supervisory Committee: Chan Kar Tim

Signature: _____
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LIST OF SYMBOLS AND ABBREVIATIONS

Si_2C_6	Graphene/silicene superlattice
Ge_2C_6	Graphene/germanene superlattice
CI	Configuration interaction
PAW	Projected augmented wave method
BTE	Boltzmann transport equation
BO	Born-Oppenheimer method
CVD	Chemical vapour deposition
MBE	Molecular beam epitaxy
vdW	van der Waals
h-BN	Two-dimensional hexagonal boron nitride
LDA	Local density approximation
LSDA	Local spin density approximation
GGA	Generalized gradient approximation
PBE0	Perdew-Burke Ernzerhof-0 pseudopotentials
HSE	Heyd–Scuseria–Ernzerhof pseudopotentials
DFT	Density functional theory
IR	Infrared
UV	Ultraviolet
SCF	Self-consistent field
T	Top
H	Hollow
B	Bridge
NSCF	Non-self-consistent field

DOS	Density of states
VBM	Valence band maxima
CBM	Conduction band minima
BFGS	Broyden-Fletcher-Goldfarb-Shanno algorithm

CHAPTER 1

INTRODUCTION

1.1 Graphene

The physics of graphene has captured the interest of many researchers ever since its discovery in 2004 (Novoselov et al., 2004). Structurally, graphene is a single layer graphitic carbon in honeycomb lattice structure. The in-plane carbon-carbon bond in graphene is composed of sp^2 hybridization. This produces one σ-bond and two π-bond, where the single p_z electrons act as the free electrons in graphene as shown in Figure 1.1. This leads to graphene having semi-metallic properties, where conduction band minima (CBM) and valence band maxima (VBM) at K-point touching each other. The semi-metallic properties are depicted in Figure 1.2.

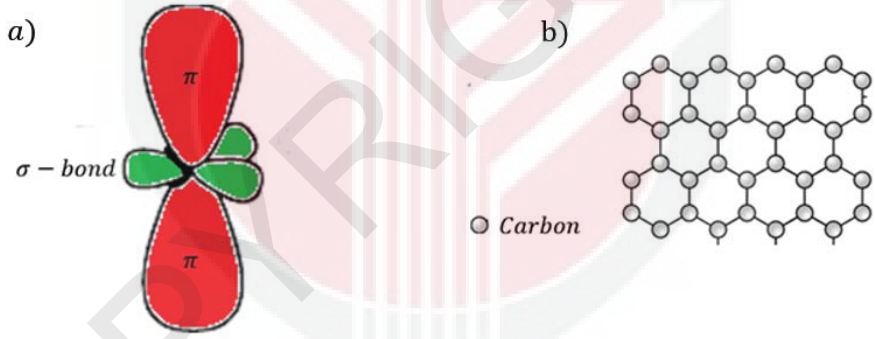

Figure 1.1: The depiction of sp^2 hybridization of carbon in graphene monolayer. a) the bonding analysis of one carbon atom with its three nearest neighbour carbon atoms and b) the structure of free-standing graphene monolayer along (001) (Dimoulas, 2015)**.**

Besides being two-dimensional, graphene has quite interesting mechanical properties. Graphene is one of the strongest materials, with the Young modulus of 1TPa and tensile strength of 130.5 GPa (Lee et al. , 2008). Further study on graphene exhibits unique electronic properties such as high electron mobility transport and electrical conductivity at room temperature (Novoselov et al., 2004). This is attributed to the formation of Dirac cone in its electronic band structure (Novoselov et al., 2005). At these points, electron behaves like Dirac fermions, where the electron mobility is around 15 000 $cm^2\,V^{-1}s^{-1}$ compared to

semiconductor like silicon, which is only 1400 $cm^2\,V^{-1}s^{-1}$ (Novoselov et al., 2004).

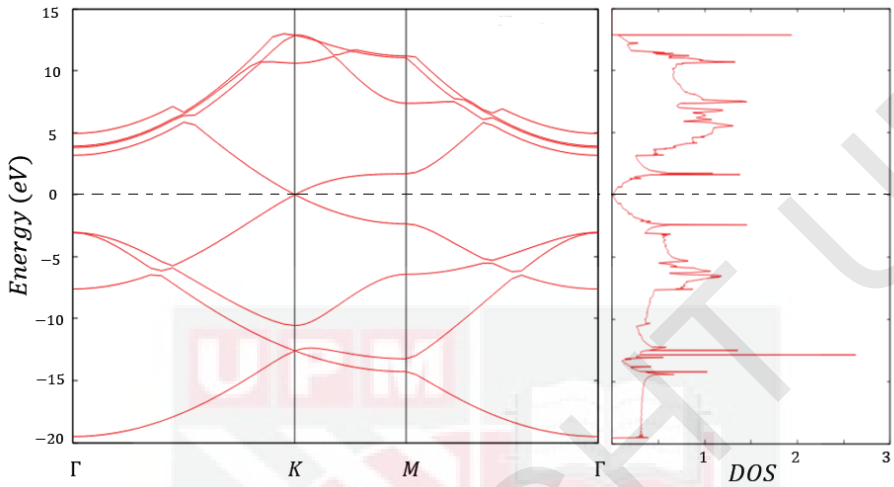

Figure 1.2: The band structure and density of states (DOS) of free-standing monolayer graphene along $\Gamma \rightarrow K \rightarrow M \rightarrow \Gamma$ ($E_f = 0$) (Dimoulas, 2015)**.**

This makes graphene a suitable candidate materials to observe many quantum phenomena such as Klein tunnelling effects and Quantum Hall effect. In a non-relativistic regime, an incident electron propagating towards potential barrier always have transmission coefficient and reflection coefficient. However, Klein tunnelling effects is a relativistic tunnelling effects, where an electron is always transmitted through the step potentials if the potential is of the order of the mass of electrons, m_e (Logemann et al., 2018). This is in contrast to the non-relativistic tunnelling of electron, where the transmission coefficient is less than one and decays exponentially with increasing height and width of the potential barrier. Stander et al. investigated in 2009, the transport properties of graphene through a series of step potential induced by metallic gates coupled to graphene layer. Stander et al. confirmed the Klein tunnelling effect in graphene with potential barrier of different top gate height (60, 100, 220, 540, 860 and 1700 nm) and graphene strip width (1.74 – 4.3 nm). Due to the remarkable properties of graphene, many researchers are interested in using graphene for supercapacitor (Yoo et al., 2011), field-effect transistor (Reddy et al. , 2011), diode (Chen et al. , 2011), solar cell (Miao et al., 2012) and sensor (Yoon et al., 2011). However, due to the Dirac cone formation, graphene is gapless in its electronic band structure which is undesirable for application in electronic devices. Few methods have been proposed to induce and fine tune the bandgap in graphene electronic structure such as surface adsorption (Petrushenko and Petrushenko, 2019),

chemical doping (Wang et al., 2009), structural defect (Raji and Lombardi, 2015) and applied magnetic field (Sahalianov et al., 2018).

1.2 Silicene and Germanene

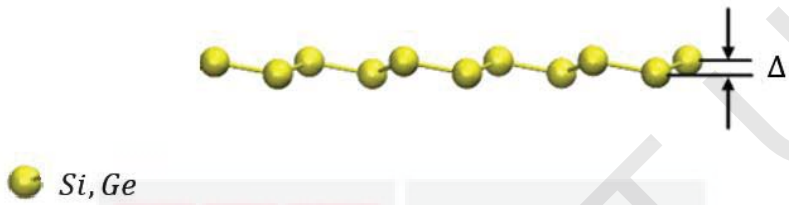

Figure 1.3: The side view of the buckling structure adopted by free-standing silicene and germanene monolayer. Δ is the buckling parameter, Si is the silicon atom and Ge is the germanium atoms (Dimoulas, 2015)**.**

Silicene and germanene are the silicon and germanium equivalents of carbon-based graphene. Silicene and germanene have been predicted to have stable free-standing monolayer forms (Takeda and Shiraishi, 1994). A recent study by using density functional theory (DFT) predicts that silicene (Houssa et al., 2010a) and germanene (Houssa et al., 2010b) to be stable in monolayer forms with corrugated or low buckling surfaces. This is different from the surfaces of graphene which is flat. There is a difference in height, Δ between two lattice sites in silicene and germanene illustrated in Figure 1.3. This is due to the differences in hybridization involved in bonding between silicon-silicon atoms in silicene and germanium-germanium atoms in germanene, which is a combination of sp^2/sp^3 hybridization. The electronic band structure of silicene and germanene are similar with graphene, where the Dirac cone formation is located at the K-point which can be seen from Figure 1.4. This makes silicene and germanene a zero-bandgap semimetal like graphene. The buckling structure of silicene and germanene however, breaks the inversion symmetry which allows the effects of external electric and magnetic field to open the zero-bandgap band structure of silicene and germanene (Ni et al., 2012).

Nonetheless, compared to graphene, the free-standing forms of silicene and germanene have yet to exists in nature. Most of the time, the silicene and germanene are synthesized on a metal substrate using methods such as chemical vapour deposition (CVD). Few experimental studies have shown that silicene can be grown on the surfaces of silver (Vogt et al., 2012), zirconium

diboride (Lee et al. , 2014), zirconium carbide (Aizawa et al., 2014) and iridium (Meng et al., 2013). Study on germanene also shows the possibility to fabricate germanene on the surfaces of gold (Schr et al., 2017) and platinum (Li et al., 2014). This is, however, not suitable for application in electronic devices due to the strong band hybridization induced by metal substrate on the electronic structure of silicene and germanene layers, which often leads to the destruction of Dirac cone (Wang et al., 2016).

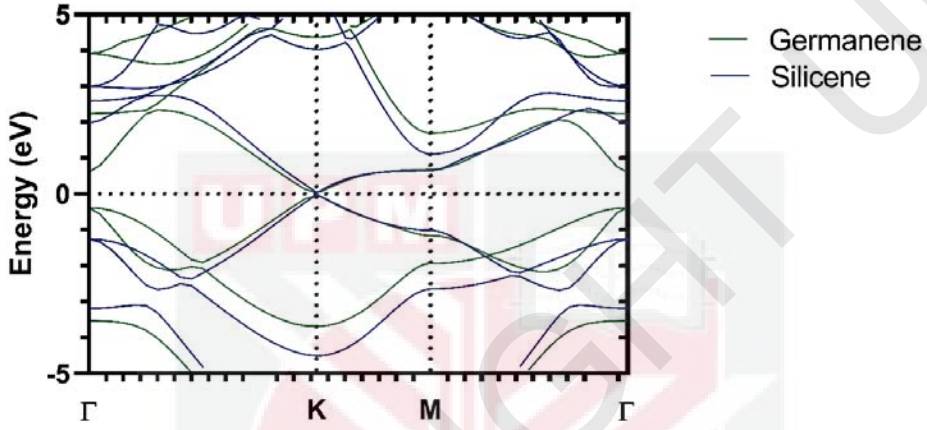

Figure 1.4: The band structure of free-standing monolayer silicene and germanene along high-symmetry point: $\Gamma \rightarrow K \rightarrow M \rightarrow \Gamma$ (Dimoulas, 2015)**.**

1.3 Superlattice

Superlattice is referring to the structures composed of two-different materials stacked together as illustrated in Figure 1.5. Superlattice provides an engineered material with highly desirable properties that is not readily available from nature. In this thesis, the concept of superlattice has been expanded to include stacking monolayer onto monolayer thickness materials in controlled fashion. This is due to the advance in technology such as CVD and molecular beam epitaxy (MBE) which allows for the atomic layer by layer precision assembly of a periodic superlattice structure. The advancement of computing devices and the widespread use of quantum chemistry simulation programme among research communities such as density functional theory and tight-binding model also allow for theoretical prediction on superlattice structure which is still limited for fabrication by current technology.

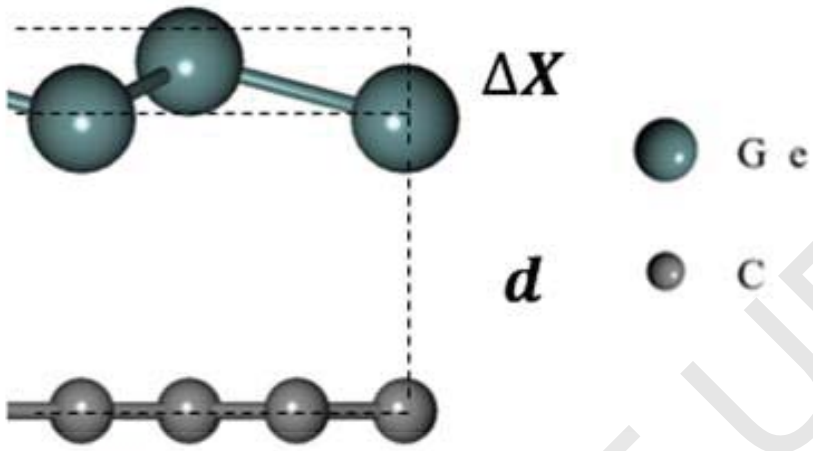

Figure 1.5: The lateral view of vertical stacking of two different monolayers together. The green atom is germanium atom while the grey atom is carbon atom. ΔX **is the buckling parameter, which is the differences between two unequal lattice along the z-axis coordinate.** d **is the interlayer distance, which is the distance between two monolayers in superlattice** (Yu et al., 2014)**.**

The study on the superlattice structure consists of two different two-dimensional materials have become popular recently. Multiple studies have shown that hybrid materials consist of graphene and other two-dimensional materials produced superlattice with different electronics properties than its constituent monolayers. Graphene has been stacked together with insulator such as hexagonal boron nitrene, hexagonal boron nitride (Liu et al., 2011), semi-metal such as silicene (Yu et al., 2014) and germanene (Cai et al. , 2013), semiconductor like two-dimensional molybdenum disulphide, MoS_2 (Roy et al., 2013) and tungsten di-selenide WSe_2 (Kim et al., 2015), and metal like niobium di-selenide, $NbSe_2$ (Efetov et al., 2016).

In many cases, the stacking of graphene with other two-dimensional materials created a superlattice that are held together by weak interaction like van der Waal forces (vdW). Hence, the strong band hybridization due to the interlayer interaction which is a common occurrence in metal substrate is avoided. Added functionality can also be seen in graphene hetero-bilayers, such as bandgap opening in graphene/h-BN superlattice which reported to be 53 meV at K-points (Giovannetti et al., 2007). Even though the graphene layer interacts weakly with monolayer hexagonal boron nitride (h-BN), the inequivalence of the lattice site between graphene and h-BN per unit cell induced the bandgap opening. Considerable bandgap and improved ON/OFF ratio have also been reported in graphene/h-BN/graphene (Meric et al., 2013) which is useful for field effect

transistor. The h-BN layer serves as a dielectric gate and in other literature, promotes quantum tunnelling between graphene electrodes (Britnell et al., 2012). Britnell et al. (2012) reported that graphene/h-BN/graphene field effect transistor has improved ON/OFF switching ratio at ambient temperature, up to 50.

1.4 Problem Statement

Graphene, silicene and germanene are two-dimensional materials with desirable electronic and transport properties. The formation of Dirac cone in the electronic band structure of graphene, silicene and germanene leads to high electron mobility transport, which proves useful for fabrication in many future novel electronic devices such as FET. The composition of silicene and germanene which made up of silicon atoms and germanene atoms, respectively make both of them are highly desirable due to the compatibility with widespread of silicon-based infrastructure in our technology. However, like graphene, silicene and germanene have zero-bandgap band structure which made integration hard. This is due to the facts that materials used in semiconductor devices utilized changes in bandgap to control current flow. Furthermore, the ON/OFF switching ratio in graphene, silicene and germanene are intrinsically small due to the gapless electronic structure compared to standard ON/OFF ratio for logic operation ($< 10^4$) (Avouris et al., 2007).

Hence, many efforts have been done to introduce substantial bandgap in graphene, silicene and germanene. Methods such as chemical doping, surface adsorption and applied magnetics and electric field have been proposed and studied for the past decades. Recently, the idea of superlattice has becomes prominent with the increased of computing powers, availability of open-source quantum chemistry simulation software and the advances of new synthesis methods such as CVD. Previous study by Yu et al. (2014) also suggests by stacking together graphene with other two-dimensional materials, forming new superlattice structure shows preservation of Dirac cone at K-points and improved bandgap in the band structure due to the weak interlayer band hybridization. Thus, a density functional theory study to explore the structural, electronic, and electronic transport properties of graphene, silicene and germanene superlattice structure is proposed. In this study, the effect of stacking between layers with inequivalent lattice site (Graphene/Silicene and Graphene/Germanene) is explored. In addition, a thorough study on the bandgap opening of graphene/silicene and graphene/germanene superlattice by modulating the interlayer distance using perpendicular hydrostatic strain is suggested, which methodology is based on previous study by Khan et al. (2017).

1.5 Objectives

The main objectives of this study are:

i. To determine the structural stability and structural properties of graphene/silicene and graphene/germanene substrate systems under different stacking configuration.
ii. To determine the effects of stacking configurations on the electronic band structure of graphene/silicene and graphene/germanene substrate systems.
iii. To study the effects of interlayer distance variation on the electronic properties and carrier mobility of graphene/silicene and graphene/germanene substrate systems.
iv. To explore the electronic thermoelectric properties and response of graphene/silicene and graphene/germanene substrate systems.

1.6 Thesis Organisation

This thesis is divided into five chapters, where Chapter 1 focussed on the brief overviews on the development of two-dimensional materials study (graphene, silicene and germanene) and prior works, both experimental and computational. Chapter 2 present the in-depth literature reviews on superlattice of two-dimensional materials and brief history of density functional theory approach. Few popular DFT software used widely in the computational condensed matter physics are introduced. Chapter 3 follows with the theoretical principle behinds DFT approach and the methodology involved in this study. Chapter 4 compiled the overall results and analysis of graphene/silicene and graphene/germanene substrate systems in terms of structural, electronic band structure and electronic transport properties. The bandgap tuning of graphene/silicene and graphene/germanene superlattice by modulating the interlayer distance is also included. Finally, the results that are obtained from our study and elaborate further on the future directions of this research is further summarized in Chapter 5.

REFERENCES

Aizawa, T., Suehara, S., & Otani, S. (2014). Silicene on zirconium carbide (111). *Journal of Physical Chemistry C*.

Ambrosi, A., Chua, C. K., Bonanni, A., & Pumera, M. (2014). Electrochemistry of graphene and related materials. *Chemical Reviews*.

Ashcroft, N. W., & Mermin, N. D. (1978). Solid State Physics. *Physik in Unserer Zeit*, *9*(1), 33–33.

Avouris, P., Chen, Z., & Perebeinos, V. (2007). Carbon-based electronics. *Nature Nanotechnology*, *2*(10), 605–615.

Balog, R., Jørgensen, B., Nilsson, L., Andersen, M., Rienks, E., Bianchi, M., Fanerri, M., Lægsgaard, E., Baraldi, M., Lizzit, S., Sljivancanin, Z., Basenbacher, F., Hammer, B., Pedersen, T.G., Hofmann, P., Hornekær, L. (2010). Bandgap opening in graphene induced by patterned hydrogen adsorption. *Nature Materials*.

Becke, A. D. (1988). Density-functional exchange-energy approximation with correct asymptotic behavior. *Physical Review A*.

Behera, H., & Mukhopadhyay, G. (2013). Fermi velocity modulation in graphene by strain engineering. In *AIP Conference Proceedings* (Vol. 1512, pp. 360–361).

Britnell, L., Gorbachev, R. V., Jalil, R., Belle, B. D., Schedin, F., Mishchenko, A., Georgiu, T., Katsnelson, M.I., Eaves, L., Morozov, S.V., Peres, N.M., Leist, J., Geim, A.K., Novoselov, K.S., Ponomarenko, L. A. (2012). Field-effect tunneling transistor based on vertical graphene heterostructures. *Science*.

Cai, Y., Chuu, C. P., Wei, C. M., & Chou, M. Y. (2013). Stability and electronic properties of two-dimensional silicene and germanene on graphene. *Physical Review B - Condensed Matter and Materials Physics*.

Cano-Márquez, A. G., Rodríguez-Macías, F. J., Campos-Delgado, J., Espinosa-González, C. G., Tristán-López, F., Ramírez-González, D., Cullen, D.A., Smith, D.J., Terrones, M., Vega-Cantú, Y. I. (2009). Ex-MWNTs: Graphene sheets and ribbons produced by lithium intercalation and exfoliation of carbon nanotubes. *Nano Letters*.

Chen, C. C., Aykol, M., Chang, C. C., Levi, A. F. J., & Cronin, S. B. (2011). Graphene-silicon Schottky diodes. *Nano Letters*.

Dai, X., Zhang, L., Jiang, Y., & Li, H. (2019a). Electronic transport properties of phosphorene/graphene(silicene/germanene) bilayer heterostructures: A first-principles exploration. *Ceramics International*, *45*(9), 11584–11590.

De Angelis, F., Di Valentin, C., Fantacci, S., Vittadini, A., & Selloni, A. (2014). Theoretical studies on anatase and less common TiO2phases: Bulk, surfaces, and nanomaterials. *Chemical Reviews*.

https://doi.org/10.1021/cr500055q

Dimoulas, A. (2015). Silicene and germanene: Silicon and germanium in the "flatland." *Microelectronic Engineering*, *131*, 68–78.

Efetov, D. K., Wang, L., Handschin, C., Efetov, K. B., Shuang, J., Cava, R., Taniguchi, T., Watanabe, K., Hone, J., Dean, C.R., Kim, P. (2016). Specular interband Andreev reflections at van der Waals interfaces between graphene and NbSe 2. *Nature Physics*.

Ganatra, R., & Zhang, Q. (2014). Few-layer MoS2: A promising layered semiconductor. *ACS Nano*.

Georgiou, T., Jalil, R., Belle, B. D., Britnell, L., Gorbachev, R. V., Morozov, S. V., Kim, Y.J., Gholinia, A., Haigh, S.J., Makarovsky, O., Eaves, L., Ponomarenko, L.A., Geim, A.K., Novoselov, K.S., Mishchenko, A. (2013). Vertical field-effect transistor based on graphene-WS 2 heterostructures for flexible and transparent electronics. *Nature Nanotechnology*.

Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. Fabris, G. Fratesi, S. D. Gironcoli, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, Wentzcovitch, R. M. (2009). QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *Journal of Physics Condensed Matter*.

Giovannetti, G., Khomyakov, P. A., Brocks, G., Kelly, P. J., & Van Den Brink, J. (2007). Substrate-induced band gap in graphene on hexagonal boron nitride: Ab initio density functional calculations. *Physical Review B - Condensed Matter and Materials Physics*.

Grimme, S. (2004). Accurate description of van der Waals complexes by density functional theory including empirical corrections. *Journal of Computational Chemistry*.

Grimme, S. (2006). Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *Journal of Computational Chemistry*.

Grimme, S. (2011). Density functional theory with London dispersion corrections. *Wiley Interdisciplinary Reviews: Computational Molecular Science*.

Grimme, S., Antony, J., Ehrlich, S., & Krieg, H. (2010). A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *Journal of Chemical Physics*.

Guo, J., Liao, X., Lee, M.-H., Hyett, G., Huang, C.-C., Hewak, D. W., Mailis, S., Zhou, W., Jiang, Z. (2019). Experimental and DFT insights of the Zn-doping effects on the visible-light photocatalytic water splitting and dye decomposition over Zn-doped BiOBr photocatalysts. *Applied Catalysis B: Environmental*, *243*, 502–512.

Heyd, J., Scuseria, G. E., & Ernzerhof, M. (2003). Hybrid functionals based on a screened Coulomb potential. *Journal of Chemical Physics*.

Hohenberg, P., & Kohn, W. (1964). Inhomogeneous electron gas. *Physical Review*.

Housecroft, C. E., & Sharpe, A. G. (2004). Inorganic Chemistry (2nd ed.). Prentice Hall. In *Inorganic Chemistry*.

Houssa, M., Pourtois, G., Afanas'Ev, V. V., & Stesmans, A. (2010a). Can silicon behave like graphene? A first-principles study. *Applied Physics Letters*.

Houssa, M., Pourtois, G., Afanas'Ev, V. V., & Stesmans, A. (2010b). Electronic properties of two-dimensional hexagonal germanium. *Applied Physics Letters*, *96*(8), 10–13.

Houssa, M., Scalise, E., Sankaran, K., Pourtois, G., Afanas'Ev, V. V., & Stesmans, A. (2011). Electronic properties of hydrogenated silicene and germanene. *Applied Physics Letters*, *98*(22), 2011–2014.

Jangid, P., Pathan, D., & Kottantharayil, A. (2018). Graphene nanoribbon transistors with high ION/IOFF ratio and mobility. *Carbon*, *132*, 65–70.

Jayaraman, A., Bhat Kademane, A., & Molli, M. (2016). DFT Study on the Carrier Concentration and Temperature-Dependent Thermoelectric Properties of Antimony Selenide. *Indian Journal of Materials Science*, *2016*, 1–7.

Jiang, Q. G., Zhang, J. F., Ao, Z. M., & Wu, Y. P. (2015). First Principles Study on the Electronic Structure and Interface Stability of Hybrid Silicene/Fluorosilicene Nanoribbons. *Scientific Reports*, *5*(June), 1–10.

Khan, A. I., Chakraborty, T., Acharjee, N., & Subrina, S. (2017). Stanene-hexagonal boron nitride heterobilayer: Structure and characterization of electronic property. *Scientific Reports*, *7*(1), 1–10.

Kim, K., Larentis, S., Fallahazad, B., Lee, K., Xue, J., Dillen, D. C., Corbet, C.M., Tutuc, E. (2015). Band Alignment in WSe 2 –Graphene Heterostructures . *ACS Nano*.

Kohn, W., & Sham, L. J. (1965). Self-consistent equations including exchange and correlation effects. *Physical Review*.

Kuroda, K., Reimann, J., Kokh, K. A., Tereshchenko, O. E., Kimura, A., Güdde, J., & Höfer, U. (2017). Ultrafast energy- and momentum-resolved surface Dirac photocurrents in the topological insulator Sb2Te3. *Physical Review B*.

Langreth, D. C., & Mehl, M. J. (1983). Beyond the local-density approximation in calculations of ground-state electronic properties. *Physical Review B*.

Lee, C. C., Fleurence, A., Yamada-Takamura, Y., Ozaki, T., & Friedlein, R. (2014). Band structure of silicene on zirconium diboride (0001) thin-film surface: Convergence of experiment and calculations in the one-Si-atom Brillouin zone. *Physical Review B - Condensed Matter and Materials Physics*.

Lee, C., Wei, X., Kysar, J. W., & Hone, J. (2008). Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*.

Lee, X. J., Hiew, B. Y. Z., Lai, K. C., Lee, L. Y., Gan, S., Thangalazhy-Gopakumar, S., & Rigby, S. (2019). Review on graphene and its derivatives: Synthesis methods and potential industrial implementation. *Journal of the Taiwan Institute of Chemical Engineers*, *98*, 163–180.

Li, G., Zhang, L., Xu, W., Pan, J., Song, S., Zhang, Y., Zhou, H., Wang, Y., Bao, L., Zhang, Y., Du, S. Ouyang, M., Pantelides, S.T., Gao, H. J. (2018). Stable Silicene in Graphene/Silicene Van der Waals Heterostructures. *Advanced Materials*, *30*(49), 1–7. 0

Li, L., Lu, S. Z., Pan, J., Qin, Z., Wang, Y. Q., Wang, Y., Cao, G., Du, S., Gao, H. J. (2014). Buckled germanene formation on Pt(111). *Advanced Materials*.

Li, S. S., Zhang, C. W., & Ji, W. X. (2015). Novel electronic properties in silicene on MoSe2 monolayer: An excellent prediction for FET. *Materials Chemistry and Physics*, *164*, 150–156.

Liu, C. H., Clark, G., Fryett, T., Wu, S., Zheng, J., Hatami, F., Xu, X., Majumdar, A. (2017). Nanocavity integrated van der Waals heterostructure light-emitting tunneling diode. *Nano Letters*.

Liu, H., Neal, A. T., Zhu, Z., Luo, Z., Xu, X., Tománek, D., & Ye, P. D. (2014). Phosphorene: An unexplored 2D semiconductor with a high hole mobility. *ACS Nano*.

Liu, Z., Song, L., Zhao, S., Huang, J., Ma, L., Zhang, J., Lou, J., Ajayan, P. M. (2011). Direct growth of graphene/hexagonal boron nitride stacked layers. *Nano Letters*.

Logemann, R., Reijnders, K. J. A., Tudorovskiy, T., Katsnelson, M. I., & Yuan, S. (2018). Modeling Klein tunneling and caustics of electron waves in graphene, 1–14.

Madsen, G. K. H., & Singh, D. J. (2006). BoltzTraP. A code for calculating band-structure dependent quantities. *Computer Physics Communications*, *175*(1), 67–71.

Mak, K. F., Lee, C., Hone, J., Shan, J., & Heinz, T. F. (2010). Atomically thin MoS2: A new direct-gap semiconductor. *Physical Review Letters*.

Meng, L., Wang, Y., Zhang, L., Du, S., Wu, R., Li, L., Zhan, Y., Li, G., Zhou, H., Hofer, W.A., Gao, H. J. (2013). Buckled silicene formation on Ir(111). *Nano Letters*.

Meric, I., Dean, C. R., Petrone, N., Wang, L., Hone, J., Kim, P., & Shepard, K. L. (2013). Graphene field-effect transistors based on boron-nitride dielectrics. *Proceedings of the IEEE*.

Miao, X., Tongay, S., Petterson, M. K., Berke, K., Rinzler, A. G., Appleton, B. R., & Hebard, A. F. (2012). High efficiency graphene solar cells by chemical

doping. *Nano Letters*.

Mudd, G. W., Svatek, S. A., Hague, L., Makarovsky, O., Kudrynskyi, Z. R., Mellor, C. J., Beton, P.H, Eaves, L., Novoselov, K.S., Kovalyuk, Z.D., Vdovin, E.E., Marsden, A.J., Wilson, N.R., Patanè, A. (2015). High Broad-Band Photoresponsivity of Mechanically Formed InSe-Graphene van der Waals Heterostructures. *Advanced Materials*.

Namhongsa, W., Rittiruam, M., & Singsoog, K. (2018). ScienceDirect Thermoelectric properties of GeTe and Sb 2 Te 3 calculated by density functional theory. *Materials Today: Proceedings*, *5*(6), 14131–14134.

Ni, Z., Liu, Q., Tang, K., Zheng, J., Zhou, J., Qin, R., Gao, Z., Yu, D., Lu, J. (2012). Tunable bandgap in silicene and germanene. *Nano Letters*.

Novoselov, K. S., Fal'Ko, V. I., Colombo, L., Gellert, P. R., Schwab, M. G., & Kim, K. (2012). A roadmap for graphene. *Nature*.

Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Katsnelson, M. I., Grigorieva, I. V., Dubonos, S.V., Firsov, A. A. (2005). Two-dimensional gas of massless Dirac fermions in graphene. *Nature*, *438*(7065), 197–200.

Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I.V.,Firsov, A. A. (2004). Electric field in atomically thin carbon films. *Science*, *306*(5696), 666–669.

Novoselov, K. S., Jiang, D., Schedin, F., Booth, T. J., Khotkevich, V. V., Morozov, S. V., & Geim, A. K. (2005). Two-dimensional atomic crystals. *Proceedings of the National Academy of Sciences*.

Novoselov, K. S., Mishchenko, A., Carvalho, A., & Castro Neto, A. H. (2016). 2D materials and van der Waals heterostructures. *Science*.

Okada, K. N., Ogawa, N., Yoshimi, R., Tsukazaki, A., Takahashi, K. S., Kawasaki, M., & Tokura, Y. (2016). Enhanced photogalvanic current in topological insulators via Fermi energy tuning. *Physical Review B*.

Ooi, N., Rajan, V., Gottlieb, J., Catherine, Y., & Adams, J. B. (2006). Structural properties of hexagonal boron nitride. *Modelling and Simulation in Materials Science and Engineering*.

Perdew, J. P., & Zunger, A. (1981). Self-interaction correction to density-functional approximations for many-electron systems. *Physical Review B*. 8

Perdew, John P., Burke, K., & Ernzerhof, M. (1996). Generalized gradient approximation made simple. *Physical Review Letters*.

Perdew, John P., Ernzerhof, M., & Burke, K. (1996). Rationale for mixing exact exchange with density functional approximations. *Journal of Chemical Physics*.

Petrushenko, I. K., & Petrushenko, K. B. (2019). Adsorption of diatomic molecules on graphene, h-BN and their BNC heterostructures: DFT study. *Diamond and Related Materials*, *100*(August), 107575.

Radaković, J., Batalović, K., Umićević, A., & Miletić, G. I. (2017). Theoretical investigation of interaction of hydrogen and intermetallic compound YCo5. *Journal of Alloys and Compounds*.

Raji, A. T., & Lombardi, E. B. (2015). Stability, magnetic and electronic properties of cobalt-vacancy defect pairs in graphene: A first-principles study. *Physica B: Condensed Matter*, *464*, 28–37.

Reddy, D., Register, L. F., Carpenter, G. D., & Banerjee, S. K. (2011). Graphene field-effect transistors. *Journal of Physics D: Applied Physics*.

Roy, K., Padmanabhan, M., Goswami, S., Sai, T. P., Ramalingam, G., Raghavan, S., & Ghosh, A. (2013). Graphene-MoS 2 hybrid structures for multifunctional photoresponsive memory devices. *Nature Nanotechnology*.

Sahalianov, I. Y., Radchenko, T. M., Tatarenko, V. A., & Prylutskyy, Y. I. (2018). Magnetic field-, strain-, and disorder-induced responses in an energy spectrum of graphene. *Annals of Physics*, *398*, 80–93.

Schr, N. B. M., Watson, M. D., Duffy, L. B., Hoesch, M., Chen, Y., Hesjedal, T., & Kim, T. K. (2017). Emergence of Dirac-like bands in the monolayer limit of epitaxial Ge films on Au(1 1 1). *2D Materials*.

Sengupta, A., Dominguez, A., & Frauenheim, T. (2019). Photo-absorption properties of van der Waals heterostructure of monolayer InSe with silicene, germanene and antimonene. *Applied Surface Science*.

Song, L., Ci, L., Lu, H., Sorokin, P. B., Jin, C., Ni, J., Kvashnin, A.G., Lou, J., Ajayan, P. M. (2010). Large scale growth and characterization of atomic hexagonal boron nitride layers. *Nano Letters*.

Stander, N., Huard, B., & Goldhaber-Gordon, D. (2009). Evidence for Klein tunneling in graphene p-n junctions. *Physical Review Letters*, *102*(2), 1–4.

Su, C. Y., Xu, Y., Zhang, W., Zhao, J., Tang, X., Tsai, C. H., & Li, L. J. (2009). Electrical and spectroscopic characterizations of ultra-large reduced graphene oxide monolayers. *Chemistry of Materials*.

Su, W., Wang, X., Geng, Z., & Liu, Y. (2019). A simple graphene nanoribbon structure-based terahertz all-optical logic gates with fano resonance. *Optical Materials*, *97*(June), 109401.

Takeda, K., & Shiraishi, K. (1994). Theoretical possibility of stage corrugation in Si and Ge analogs of graphite. *Physical Review B*.

Tan, J., Kalantar-zadeh, K., Wlodarski, W., Bhargava, S., Akolekar, D., Holland, A., & Rosengarten, G. (2005). Thermoelectric properties of bismuth telluride thin films deposited by radio frequency magnetron sputtering. *Smart Sensors, Actuators, and MEMS II*, *5836*, 711–718.

Tang, Y., Shen, L., Chen, Z., Sun, L., Liu, W., Liu, J., & Deng, S. (2019). The N-type Pb-doped single crystal SnSe thermoelectric material synthesized by a Sn-flux method. *Physica B: Condensed Matter*, *570*(June), 128–132.

Thomas, L. H. (1927). The calculation of atomic fields. *Mathematical*

Proceedings of the Cambridge Philosophical Society.

Vogt, P., De Padova, P., Quaresima, C., Avila, J., Frantzeskakis, E., Asensio, M. C., Resta, A., Ealet, B., Le Lay, G. (2012). Silicene: Compelling experimental evidence for graphenelike two-dimensional silicon. *Physical Review Letters*, *108*(15), 1–5.

Wang, X., Li, X., Zhang, L., Yoon, Y., Weber, P. K., Wang, H., Guo, J., Dai, H. (2009). N-doping of graphene through electrothermal reactions with ammonia. *Science*.

Wang, Y., Li, J., Xiong, J., Pan, Y., Ye, M., Guo, Y., Zhang, H., Quhe, R., Lu, J. (2016). Does the Dirac cone of germanene exist on metal substrates? *Physical Chemistry Chemical Physics*.

Wu, X., Kang, F., Duan, W., & Li, J. (2019). Density functional theory calculations: A powerful tool to simulate and design high-performance energy storage and conversion materials. *Progress in Natural Science: Materials International*.

Xia, F., Farmer, D. B., Lin, Y. M., & Avouris, P. (2010). Graphene field-effect transistors with high on/off current ratio and large transport band gap at room temperature. *Nano Letters*.

Xia, F., Mueller, T., Lin, Y. M., Valdes-Garcia, A., & Avouris, P. (2009). Ultrafast graphene photodetector. *Nature Nanotechnology*.

Yadav, V. K., Mir, S. H., & Singh, J. K. (2019). A computational study of structural, electronic and carrier mobility of boron and phosphorus/nitrogen co-doped graphene. *Physica B: Condensed Matter*, *571*(July), 291–295.

Yong, Y., Cui, H., Zhou, Q., Su, X., Kuang, Y., & Li, X. (2019). C2N monolayer as NH3 and NO sensors: A DFT study. *Applied Surface Science*, *487*, 488–495.

Yoo, J. J., Balakrishnan, K., Huang, J., Meunier, V., Sumpter, B. G., Srivastava, A., Conway, M., Reddy, A.L.M., Yu, J., Vajtai, R., Ajayan, P. M. (2011). Ultrathin planar graphene supercapacitors. *Nano Letters*.

Yoon, H. J., Jun, D. H., Yang, J. H., Zhou, Z., Yang, S. S., & Cheng, M. M. C. (2011). Carbon dioxide gas sensor using a graphene sheet. *Sensors and Actuators, B: Chemical*.

Yu, S., Li, X. D., Wu, S. Q., Wen, Y. H., Zhou, S., & Zhu, Z. Z. (2014). Novel electronic structures of superlattice composed of graphene and silicene. *Materials Research Bulletin*, *50*, 268–272.

Yu, X., Cheng, J., Liu, Z., Li, Q., Li, W., Yang, X., & Xiao, B. (2015). The band gap modulation of monolayer Ti $_2$ CO $_2$ by strain. *RSC Adv.*

Zakharchenko, K. V., Katsnelson, M. I., & Fasolino, A. (2009). Finite temperature lattice properties of graphene beyond the quasiharmonic approximation. *Physical Review Letters*, *102*(4), 2–5.

Zeng, Z., Yin, Z., Huang, X., Li, H., He, Q., Lu, G., Boey, F., Zhang, H. (2011).

Single-layer semiconducting nanosheets: High-yield preparation and device fabrication. *Angewandte Chemie - International Edition*.

Zhang, T., Liu, J., Wang, C., Leng, X., Xiao, Y., & Fu, L. (2017, March 15). Synthesis of graphene and related two-dimensional materials for bioelectronics devices. *Biosensors and Bioelectronics*. Elsevier.

Zhang, Y., Tang, T. T., Girit, C., Hao, Z., Martin, M. C., Zettl, A., Crommie, M.F., Shen, Y.R., Wang, F. (2009). Direct observation of a widely tunable bandgap in bilayer graphene. *Nature*.