Structural and Electronic Properties of Silicene/*hexagonal*-Boron Nitride/Graphene Hetero-structure

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Abstract: Isolated atomic planes such as graphene, silicene and hexagonal-boron nitride are proven to have novel properties believed to improve the current microelectronic industry. However, their individual limitations make it difficult to functionalize them and be solely applied to the said industry. Combining these atomic planes into layered hetero-structures with specific sequencing is proven to provide further means of functionalizing the electronic structure of the atomic planes. In this study we report the electronic and geometric properties of the hexagonal-boron nitride/graphene (*h*-BN/G) hetero-bilayer and silicene/*h*-boron nitride/graphene (Si/*h*-BN/G) hetero-structure by employing density functional theory-based calculations. The band structure of *h*-BN/G hetero-bilayer shows a small band gap of 0.020eV but with preserved linear dispersion around its Fermi level which is comparable to that of free-standing graphene. On the other hand, the density of states and band structure of Si/*h*-BN/G hetero-structure show that the linear dispersion of graphene and silicene were also preserved with shifted Dirac points and with small band gap opening of 0.03eV and 0.02eV respectively. The electronic characteristics of the h-BN/G hetero-bilayer and Si/h-BN/G hetero-structure suggest that they have great potential for electronic device application. These findings provide insights on the functionalization of hetero-structures of atomic planes that can be used to improve the existing electronic devices like thin film transistors.

Key Words: silicene; graphene; boron nitride; hetero-structure; transistor

1. INTRODUCTION

Guided by Moore's Law, researches are aiming to miniaturize current electronic devices to improve their functionality and efficiency. To do so, nanomaterials that have noble characteristics are in great need. In the past decade, scientist believed that graphene, a monolayer of sp^2-hybridization of carbon atoms, is the noblest two-dimensional material that can advance the electronic world. It is due to its significant characteristics such as massless Dirac fermions, high carrier mobility, very strong/stable lattice structure, high thermal conductivity and half-integer Hall conductance. However, its lack of band gap and low affinity with the existing semiconducting circuits drove scientist to conduct further research for other noble materials.[1, 2]

Theoretically proven, silicene, the silicon analogue of graphene has the same noble characteristics. It also has massless Dirac fermions, high carrier mobility and experimentally accessible quantum spin Hall Effect. Moreover, it has high on/off ratio, electrically tunable band gap and ability to change from topological insulator to a band insulator that can be induced by electric field as well. All these properties and its compatibility with the existing electronic devices make silicene a better material than graphene.[3-6]

So far, silicene was computationally and experimentally proven to form on metallic substrates such as Ag (110), Ag (111), and ZrB$_2$. However, these metallic substrates interact strongly with silicene and create undesirable symmetry breaking resulting to the disappearance of some of its valuable properties such as Dirac fermions. These studies implied that silicene cannot be separated from its substrate due to its strong interaction with them. Thus, silicene is not as stable as graphene and cannot exist in a free-standing state.[3, 5, 7]

There are other atomic planes that were discovered aside from silicene and graphene. Unfortunately, like the above-mentioned atomic planes, these materials have disadvantages that limit their applicability on the electronic industry. Different processes such as doping and adding ad atoms where performed on these atomic planes to provide functionalization and solutions to their limitations. However, these processes provide limited insights in the functionalization of these materials in relation to direct application to electronic devices. Currently, scientists are focusing on the stacking of these atomic planes on top of each other, layer by layer like LEGOS™, as another means of functionalizing their properties while at the same time overcoming their limitations.[8]

Graphene, having a high transparency, high carrier mobility, high flexibility, high stability and high conductivity has a great potential for the conducting gate material of a thin film transistor.[9] On the other hand, silicene, is also flexible, transparent and with high carrier mobility.[5] Moreover, it has a tunable band gap and high on/off ratio, which are properties making it a great candidate for the TFT's semiconducting part. Unfortunately, since silicene interacts strongly with metallic materials such as graphene, a buffer layer in between them is in need. In a previous study, silicene is found to interact weakly with hexagonal-boron nitride (h-BN) such that its intrinsic electronic properties are preserved.[10] This is also true for the interaction of graphene with h-BN.[11] Moreover, h-BN has a honeycomb lattice structure which matches that of graphene and silicene. Furthermore, it was found that h-BN is a high quality and ultrathin two dimensional material with low dielectric constant barrier that has a great potential in application to novel electron tunneling devices and for investigation of strongly coupled and narrowly separated electrodes of different composition.[12] These findings support the suitability of h-BN as the buffer layer and dielectric material between silicene and graphene in the hetero-structure for TFT application.

Thus, by employing density-functional-based calculations, the researcher studied the geometric and electronic structure of hexagonal boron nitride on graphene (h-BN/G) hetero-bilayer and silicene on hexagonal boron nitride on graphene (Si/h-BN/G) hetero-structure for thin film transistor application. In addition, the calculations were performed using local density approximation (LDA), generalized gradient approximation given by Perdew-Burke-Ernzerhof (PBE) and PBE with Tkatchenko-Scheffler van der Waals correction with self-consistent screening (PBE TS+SCS) to provide comparative information.

2. COMPUTATIONAL DETAILS

All calculations performed in this study were based on density functional theory (DFT) using Vienna Ab-initio simulation package (VASP) employed in three exchange correlation functionals namely local density approximation (LDA), generalized gradient approximation given by Perdew-Burke-Ernzerhof (PBE) and PBE with Tkatchenko-Scheffler van der Waals correction with self-consistent screening (PBE TS+SCS).[13] Pseudo-potentials, obtained from projected augmented wave (PAW) method, were used to describe ionic cores. The energy cut-off of at least 800 eV and 16x16x1 *k-point* mesh were utilized to acquire energy and force precision of 10^{-5}eV and 10^{-3}eV/A respectively. For the unit cells, a minimum of 15Å vacuum layer along the direction perpendicular to the atomic planes was implemented in order to minimize to a negligible value the interaction between the adjacent unit cells along the said direction. The geometric structures and charge density distributions were plotted through Visualization for Electronic and Structural Analysis (VESTA).

3. RESULTS AND DISCUSSION

3.1 Hexagonal-Boron Nitride/Graphene (h-BN/G) hetero-bilayer

3.1.1 Structural Properties

In this structure, the super cell has (1x1) *hexagonal*-boron nitride (*h*-BN) placed on (1x1) honeycomb graphene at different stacking arrangements as shown in Fig. 1. The first stacking shows that all the boron and nitrogen atoms are on top of carbon atoms (BNG), second stacking shows that the boron atoms are on top of carbon atoms while nitrogen atoms are on top of the center of graphene hexagonal rings (BG) and third stacking shows that the nitrogen atoms are on top of the carbon atoms while boron atoms are on top of the center of graphene rings.
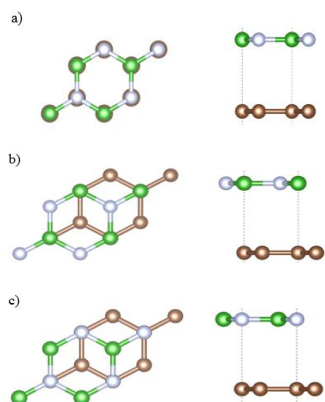

Fig 1: h-BN/G hetero-bilayer stacking: a) BNG Stacking is where all the atoms of boron (green) and nitrogen (grey) are on top of carbon (brown) atoms; b) BG Stacking is where the boron atoms are on top of carbon atoms while the nitrogen atoms are on top of the center of graphene hexagonal ring; c) NG Stacking is where the nitrogen atoms are on top of carbon atoms while the boron atoms are on top of the center of graphene hexagonal ring.

The lattice mismatch (Δ) between these atomic planes is defined as $\Delta = \frac{|a_{BN} - a_G|}{a_G} \times 100\%$, where a_G is the lattice constant of graphene while a_{BN} is the lattice constant of *h*-BN.[14] The values of the lattice mismatch between *h*-BN and graphene using LDA, PBE and PBE TS+SCS are 1.65%, 1.79% and 1.75% respectively. These resulted to the

shortening of the bond length of *h*-BN by at most 1.79%. However, the rest of the geometric parameters of *h*-BN and graphene remain unchanged. Thus, relative to their free-standing states, there is no major distortion in the geometric structures of *h*-BN and graphene due to lattice mismatch.
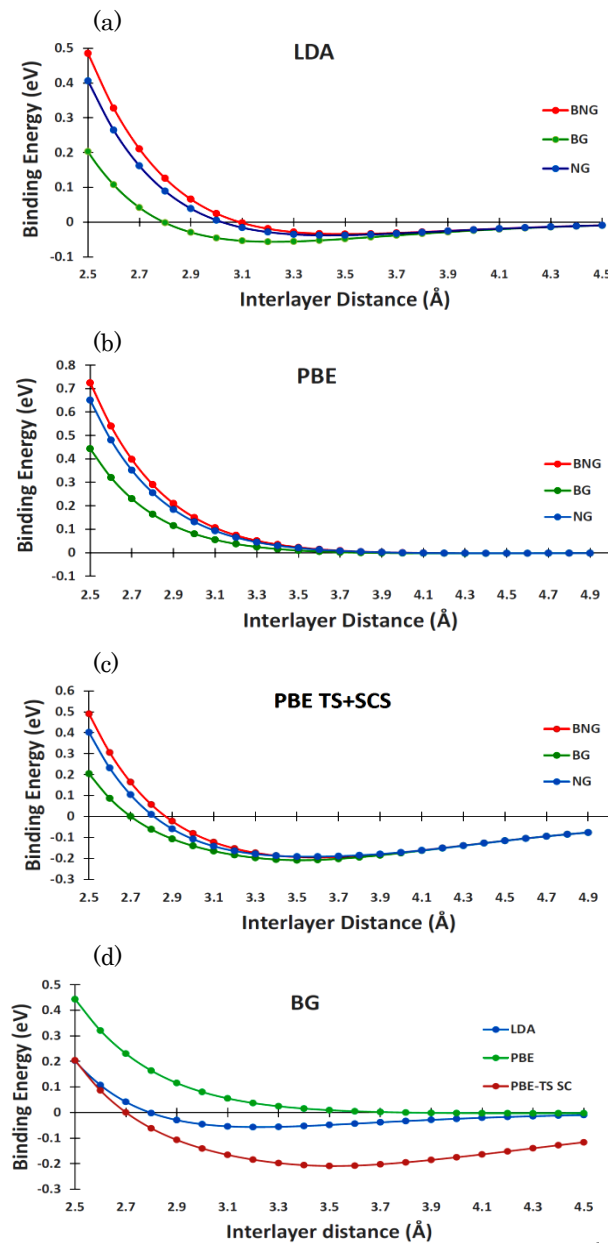

Fig 2: Binding energy versus Interlayer distance of h-BN/G hetero-bilayer with different stacking arrangement and using (a) LDA, (b) PBE and (c)

PBE TS+SCS. The last graph (d) shows calculations done in BG stacking using different exchange-correlation functionals.

Shown in Fig. 2 (a-c), are the graphs of the Binding Energy (BE) versus Interlayer Distance of the hetero-bilayer of *h*-BN on graphene using (a) LDA, (b) PBE and (c) PBE TS+SCS in BNG Stacking (red), NG stacking (blue) and BG stacking (green). It can be seen that for different exchange-correlation functionals, the *h*-BN/G hetero-bilayer always prefers the BN stacking, which is consistent with other studies.[16] As illustrated in Fig. 3, the B cations prefer the location where the electron density is very high, which is on top of carbon atoms. While the N anions prefer the top of the middle of graphene rings since it has the lowest electron density.

Table I: The computed interlayer distance and binding energies of h-BN/G hetero-bilayer in different stacking arrangement obtained by DFT with LDA, PBE, PBE TS+SCS in comparison with experimental data.

Interlayer Distance (Å)				
	LDA	PBE	PBE+TS SCS	Exp
BNG	3.50	4.49	3.59	
BG	3.22	4.30	3.52	3.336 [17]
NG	3.44	4.48	3.56	

Binding Energy (meV/atom)				
	LDA	PBE	PBE+TS SCS	Exp
BNG	-8.637	-0.600	-48.990	
BG	-14.207	-0.733	-52.251	52.00 [18]
NG	-9.5288	-0.604	-48.039	

From Table I, LDA and PBE TS+SCS give an accurate value for the interlayer distance between *h*-BN and graphene relative to the existing experimental data. However, LDA underestimates the binding energy between the atomic planes while PBE TS+SCS gives a very accurate result most especially for the binding energy of the atomic

planes in BG stacking arrangement. The PBE functional underestimation of the binding energy resulted into an overestimation of the interlayer distance between the atomic planes. The accuracy of the calculation with van der Waals correction implies that the van der Waals force is significant in the interaction between *h*-BN and graphene.

3.1.2 Electronic Properties

In Fig.3, the charge density distribution of h-BN/G hetero-structure in BG stacking shows more charge density distribution in the atomic planes and no visible distribution in between them. This implies that strong covalent bonds are present between atoms in same layer only. Such charge density distribution resembles that of a layered structure like bulk graphite.
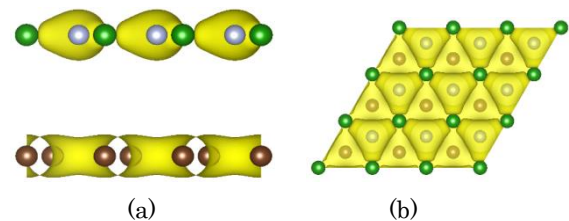

(a)   (b)

Fig 3: Charge density distribution of the h-BN/G structure in BG stacking (a) side view (b) top view.
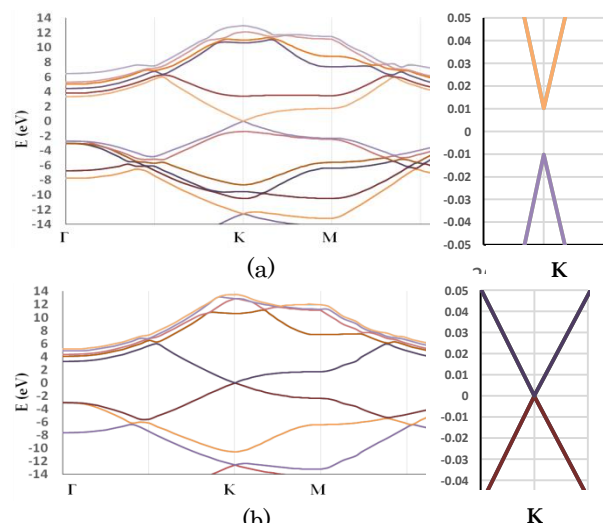

(a)

(b)

Fig 4: Band structures of h-BN/G hetero-bilayer with (a) BG stacking arrangement. The band structure of free-standing graphene (b) is shown for comparison.

In Fig. 4 (a), the band structure of h-BN/G hetero-structure in BG stacking arrangements shows a small band gap of 0.02eV. This is due to the interaction of the boron and nitrogen atoms with the carbon atoms of graphene as mentioned earlier. Comparing the previous band structure to that of free-standing graphene in Figure 4(b), it can be observed that additional bands appear above 3eV and below -1eV. These bands are mainly from the h-BN layer. Despite the very small band gap, h-BN /G hetero-bilayer`s band structure shows preserved linear dispersion near the Dirac Point which are comparable to that of free-standing graphene. This indicates the applicability of the h-BN /G hetero-bilayer to electronic devices that requires finite band gap and high carrier mobility.

3.2 Silicene/hexagonal-Boron Nitride/ Graphene (Si/h-BN/G) hetero-structure
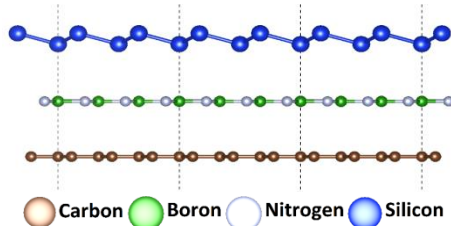
3.2.1 Structural Properties

Fig 5: Optimized geometric structure of Si/h-BN/G hetero-structure

In this structure, silicene is placed on h-BN/G hetero-bilayer in BG stacking arrangement. The super cell is composed of (2x2) honeycomb silicene on (3x3) h-BN (with 9 boron and 9 nitrogen atoms) on (3x3) honeycomb graphene. The lattice mismatch (Δ) between the atomic planes is defined as $\Delta = \frac{|(3 \times a_{BN/G}) - (2 \times a_{Si})|}{(2 \times a_{Si})} \times 100\%$, where $a_{BN/G}$ is the lattice constant of the h-BN /G hetero-bilayer while a_{Si} is the lattice constant of silicene. The values of the lattice mismatch between h-BN /G and silicene using LDA, PBE and PBE TS+SCS are 4.00%, 4.09% and 4.31% respectively. In PBE TS+SCS, graphene`s bond length and buckling remain unchanged. However, due to large lattice mismatch, the bond length of h-BN and silicene shortened by 1.78% and 2.546% respectively. Moreover, the buckling of h-BN and graphene were unchanged however the buckling

of silicene increased by 25% which is believed to have an effect on the electronic properties of the hetero-structures. These percentages are relative to parameters of these atomic planes in free-standing state.

Figure 6 shows the graph of the Binding Energy (BE) versus Interlayer Distance of silicene from the h-BN /G hetero-bilayer using LDA (red), PBE (green) and PBE TS+SCS (blue). It shows that the PBE functional estimates very small binding energy for silicene and h-BN/G hetero-bilayer and thus resulting to a large separation distance between the structures. Table II shows that LDA and PBE TS+SCS calculated interlayer distance, 3.43Å and 3.50Å respectively, are close to one another. However, PBE TS+SCS approximated the binding energy three times than the approximated value of LDA.
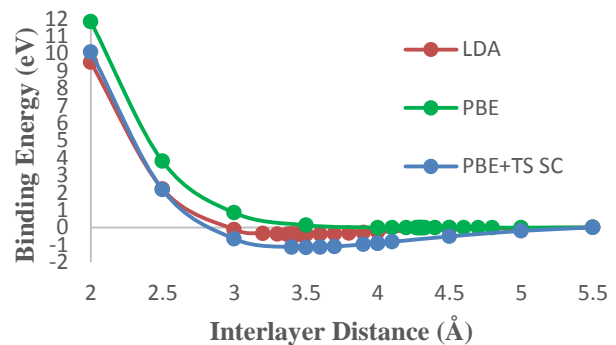
Fig 6: Binding energy versus Interlayer distance of Si/h-BN/G hetero-bilayer using (a) LDA, (b) PBE and (c) PBE+ TS SC.

Table II: The computed interlayer distance and binding energies between silicene and h-BN/G hetero-bilayer obtained by DFT with LDA, PBE, PBE+TS SC.

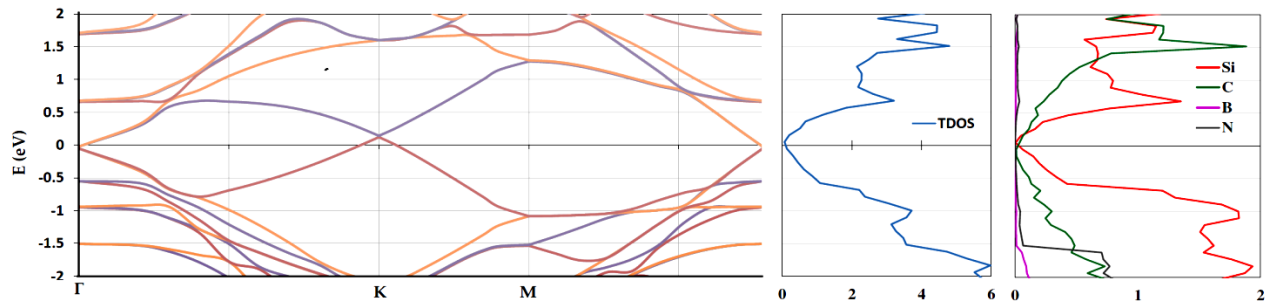|	Interlayer Distance (Å)			Binding Energy (meV/Si atom)		
	LDA	PBE	PBE+TS SCS	LDA	PBE	PBE+TS SCS
Si/h-BN/G	3.43	4.31	3.50	-50.60	-2.29	-143.45

Fig 7: Band structure and density of states of Si/h-BN/G hetero-structure

3.2.2 Electronic Properties

The charge density distributions of Si/h-BN/G hetero-structure as shown in Fig 8 also exhibit characteristics of layered structure. Again, more charge density distributions are visible in the atomic planes and no visible distribution in between them. This implies that strong covalent bonds are present between atoms in same layer only.
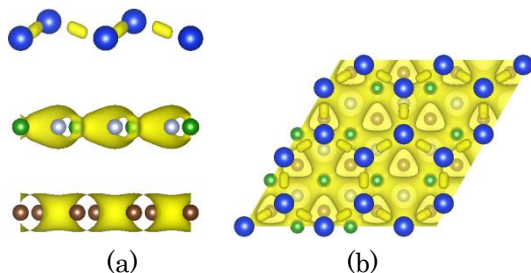

(a)   (b)

Fig 8: Charge density distribution of the Si/h-BN/G hetero-structure from (a) side view and (b) top view

As shown in Fig. 7, the linear dispersions of graphene and silicene are still preserved. However, the Dirac points from graphene and silicene shifted by 0.04eV downwards and 0.13eVupwards respectively. This shows that the charge transfer from silicene to graphene which is enhanced by the overlap in their electronic structure and resulted to p-type doping in silicene and n-type doping in graphene. Consequently, the band gaps of graphene and silicene increased to 0.03eV and 0.02eV respectively. From previous studies, these induced band gaps are usually tunable by external conditions which have great applications for electronic devices like thin film transistors.[15]

4. CONCLUSIONS

In summary, DFT-based calculations is utilized to investigate the geometric and electronic properties of h-BN/G hetero-bilayer and the geometric properties of Si/h-BN/G hetero-structure. It was found that vdW force has a significant role in the interaction of layered hetero-structures. Thus, computations of layered system are encouraged to be done with vdW corrections. Results show that h-BN/G hetero-structure is stable with weak interaction between *h*-BN and graphene. It has a very small band gap of 20meV but with preserved linear dispersion around the Dirac point resembling that of free-standing graphene. Furthermore, it was found that Si/h-BN/G hetero-structure is stable with binding energy of -143.451meV/Si atom. Its band structure shows preserved linear dispersions with shifted Dirac points and small band gap opening. The electronic characteristics of the h-BN/G hetero-bilayer and Si/h-BN/G hetero-structure suggest that they have great potential for electronic device application. Further calculations and investigations can be performed on the effect of additional layers of intercalated h-BN, strain and external electric field on the electronic properties of Si/h-BN/G hetero-structure.

5. ACKNOWLEDGMENTS

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