A Study on Group-IV Two Dimension Element Based Heterobilayers

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Abstract-- The exotic electronic properties of group-IV two dimension (2D) materials including graphene, silicene, germanene and stanene and their potential for nanoelectronic devices have drawn keen interest. But the zero band gap of these materials acts as a barrier for application as FET. Adopting heterobilayers where one layer is one of these material and another one is any other 2D material layer is a good approach to solve this issue. Presently researchers are investigating many of these heterobilayers like graphene-hexagonal boron nitride (h-BN), graphene-BC$_3$, germanene-BeO, silicene-h-BN and so on. This paper reviews the properties of several of these heterobilayer and suggests the potential research gap in the field of heterobilayers.

Keywords: 2D materials, heterobilayers, band gap, electronic properties

1. Introduction:

The mechanical exfoliation of graphene in 2004 commenced a new era of two dimensional (2D) materials in the field of scientific research [1]. The outstanding properties of graphene including high carrier mobility due to the massless Dirac fermions, flexibility [2,3] , strength, high conductivity of heat: all these have drawn keen interest in exploring other 2D materials. Today 2D material family comprises a number of elements including silicene, germanene, stanene, plumbene, hexagonal boron nitride (h-BN), 2D silicon carbide (SiC), transition metal chalcogenides (TMD) and so on. In this family of 2D materials, group-IV 2D elements like graphene, silicene, germanene and stanene are given particular attention due to their outstanding electronic characteristics and high potential for application in nanoelectronic devices. But their zero band gap semi-metallic behavior restricts their application in high performance nanoelectronic devices. To solve this issue, a lot of technique like doping, developing heterostructures are theoretically proposed and experimentally explored. Heterobilayer is also one kind of heterostructure in which two different layers of 2D elements are vertically stacked in a precisely selected arrangements. Adopting heterobilayer is an excellent way to tune the electronic properties and improve the stability. Heterobilayers offer many distinctive properties which were not present in the isolated monolayer. In this review, group-IV 2D materials like graphene, silicene, germanene and stanene based heterobilayers will be discussed along with their different exotic electronic and optical properties.

2. Present Heterobilayers:

2.1 Graphene-Hexagonal Boron Nitride Heterobilayer:

Graphene based heterobilayers were first studied in the literature. Graphene-boron nitride heterobilayers (C/BN HBLs) were studied by Fan *et al.*[5] with the aid of first-principles calculations in the framework of DFT in combination with local density approximation (LDA) functional. Four stacking configuration (I-IV) were taken into consideration in their study as shown in Figure 1. Pattern-I displays AA hexagonal stacking with all C atoms direct above N or B atoms. Together Patterns-II and III possess Bernal *AB* stacking patterns, with the C atoms of one Graphene is located right above B in case of pattern-II; or B in case of pattern-III although those of another sublattice are placed on the top of the centers of BN hexagons. Pattern-IV was obtained by lateral shifting of BN monolayer to a distance of $\sqrt{3}a/6$ along the C–C bond alignment from pattern-I with respect to graphene. Here, *a* is the lattice constant of graphene. By calculating binding energy as a function of interlayer distance, the optimum distance between the two layers were calculated. Pattern II was the most stable one with the highest binding energy and the lowest interlayer spacing (3.2 A^0). The cation-attractive interaction and anion-repulsive interaction between BN and graphene monolayer are the reasons behind it. The N anions desire to stay right below the center of carbon hexagon, where the electron density is very low, whereas the B cations stay right below C atoms to enhance the attractive interaction Their [5] calculations showed that the band gap as well as the mobility of the carriers of C/BN HBLs can be tuned upon varying the interlayer spacing and stacking features. The electron effective mass was a proportionate function of the band gap for most of the situation patterns I-III but the nearly linear dispersion relation was maintained for specific stacking configuration of pattern IV.

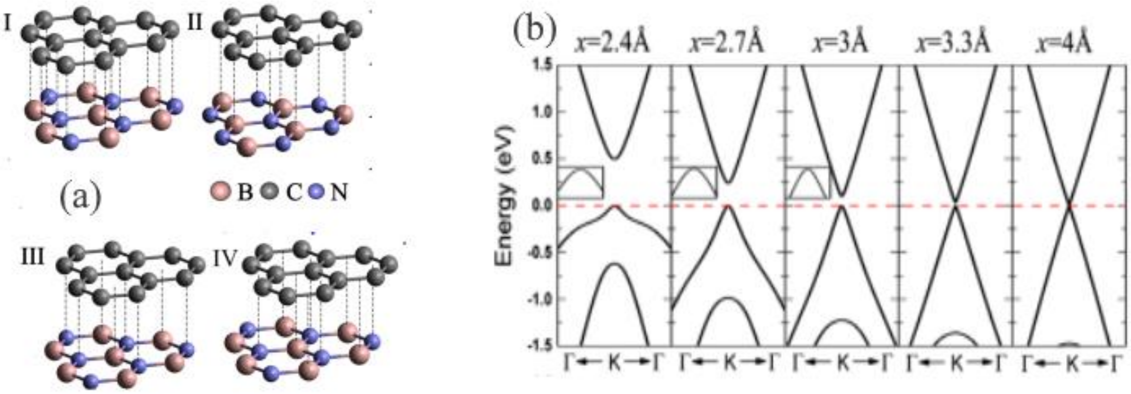


Figure 1. (a) Four inequivalent stacking patterns I–IV of graphene/boron-nitride heterobilayer (b) Band lines near the Fermi level of the heterobilayers with interlayer distances x=5, 3.3, 3, 2.7, and 2.4 Å for the pattern II [5]

2.2 Graphene-BC_3 Heterobilayer:

The energetics, geometric and electronic properties of graphene on BC_3 monolayer were investigated by Li *et al.*[6] . They [6] found that graphene does not interact strongly with monolayer BC_3 rather two different layers are bound through van der Waals interaction. They took three stacking

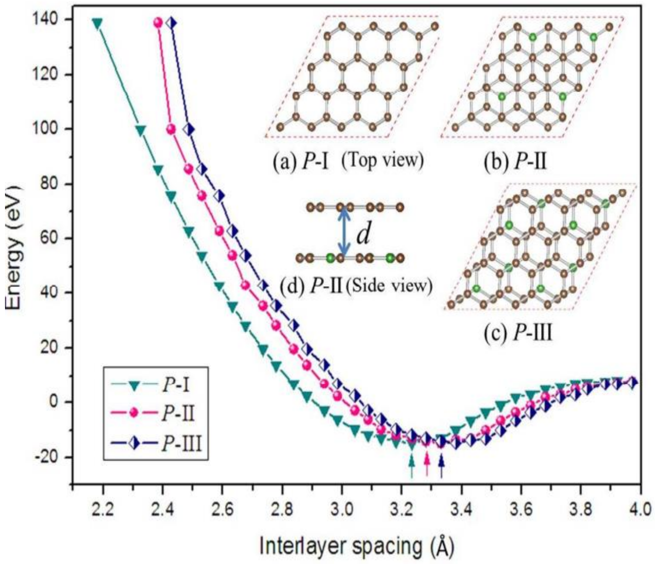


Figure 2. The variation in the binding energy for the three configurations as a function of interlayer spacing. Top views of the relaxed atomic structures of three stacking patterns of G/BC3: (a)P-I, (b)P-II, (c)P-III. The side view of relaxed atomic structure of P-II(d).[6]

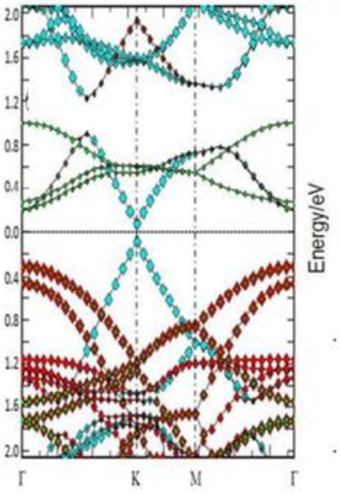
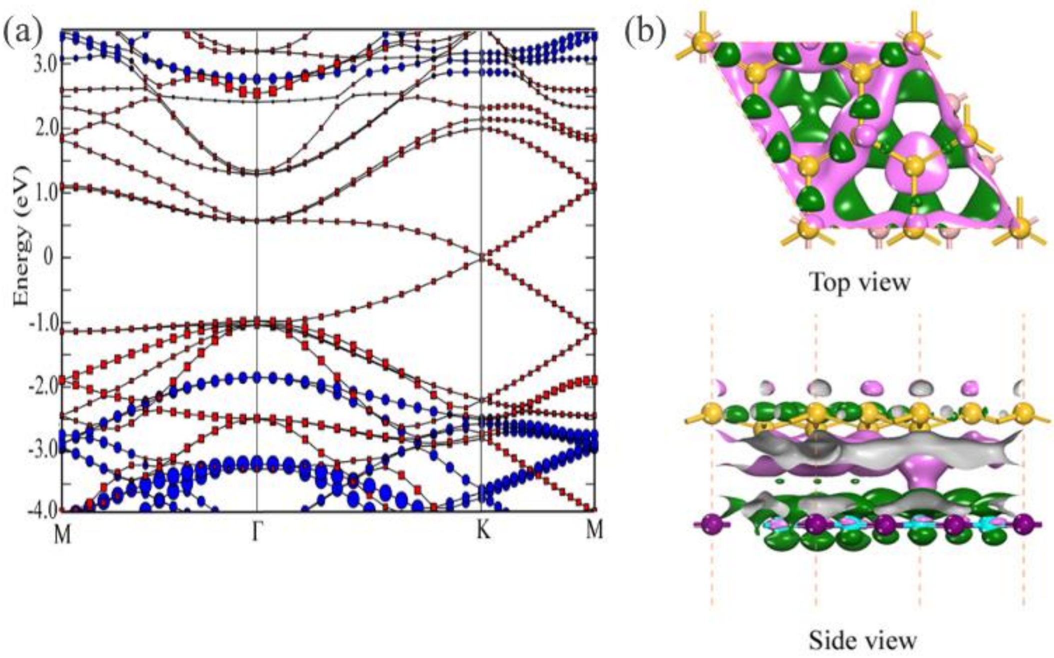


Figure 3. The band structure of Pattern II of G/BC_3 heterobilayer. The cyan, green and red represent the component of graphene, B and C atoms in BC_3 substrate, respectively. [6]

patterns and the equilibrium interlayer spacings were about $3.3A^o$ for all three patterns (P-I,P-II and P-III) as depicted in Figure 2. An energy gap up to ~ 0.162 eV was reported in graphene/BC3 heterobilayers (G/BC3 HBLs). This value is sufficient to open the gap at room temperature. Furthermore, they showed that in-plane strain and the interlayer spacing can modulate the band gap of G/BC3 HBLs effectually. The nearly linear band dispersion relation along with the characteristics of Dirac cone of graphene was preserved, accompanying a small electron effective mass. Therefore, the carriers are expected to show high mobility.

2.3 Silicene-Hexagonal Boron Nitride:

Cai *et al*.[7] investigated interlayer interaction, electronic structure and thermal transport of a bilayer heterostructure comprising silicene and hexagonal boron nitride (h-BN) with the aid of DFT and empirical molecular dynamics calculations. In silicene/h-BN heterostructure, silicene and h-BN show weak interaction between them suggesting the absence of covalent binding. Consequently, the Dirac cone of silicene is well maintained with the point of Dirac cone located just at the Fermi level. The differential charge density shows that not much of electrons are relocated from h-BN to silicene, indicating the electronic transport will be dominated by the silicene. The molecular dynamics simulation indicates thermal transport will be dominated by h-BN because the heat current along the h-BN is six



Top view

Side view

Figure 4. (a) Orbital decomposed band structure of the BN-silicene bilayer. The population of the silicene and h-BN orbitals at each k point scales with the radius of the red and blue circles, respectively. (b) The top and side views of the iso-surface of the Differential Charge Density with the isovalue of $0.005\ A^{\circ-3}$. The violet (green) color denotes an accumulation (loss) of electrons. [7]

times higher than the heat current along silicene. This decoupling between h-BN and silicene regarding thermal and electronic transport indicates that the BN-silicene heterobilayer might be an excellent platform for thermoelectric applications.

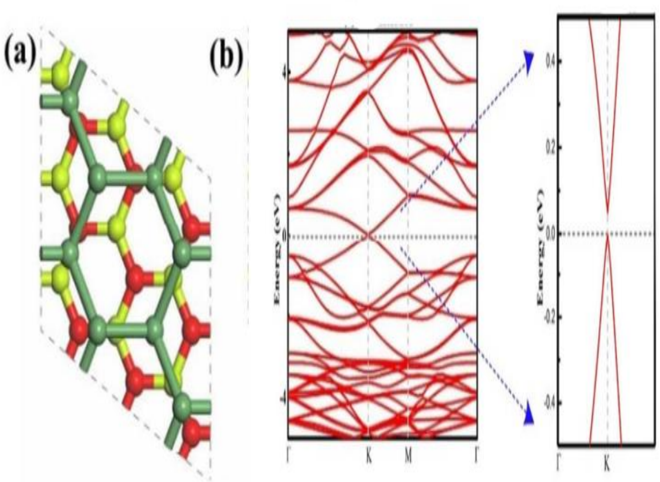


Figure 5. (a) Atomistic model of Ge/BeO heterostructure. Ge, Be, O atoms are presented by green, yellow, and red balls, respectively. (b) Electronic band diagram of Ge/BeO heterostructure [8]

2.4 Germanene-BeO heterobilayer: A systematic first-principles investigation was employed by Chen *et al.*[8] to study the geometry, electrical and optical properties of 2D Germanene/BeO heterostructure. They [8] found that germanene and BeO layer interact weakly with each other through van der Waals force. The absence of site selectivity is also observed. As a result, most of the excellent properties of germanene are maintained, particularly linear band dispersions around the Dirac point. The heterostructure can open a band gap of ~49meV, a sufficiently large value to maintain the gap at room temperature. The band gap shows a tuning property under changing the interlayer distance, applying the external electric field and external strain. The electric field is the most efficient way to tune the energy gap (14 – 382 meV). For all the methods of band gap tuning, the Dirac cone feature is maintained with linear energy dispersion relationship of germanene. Moreover, germanene dominates in the photoabsorption property of heterostructure. The basic optical absorption tendency of germanene is not altered in the the Ge/BeO heterostructure.

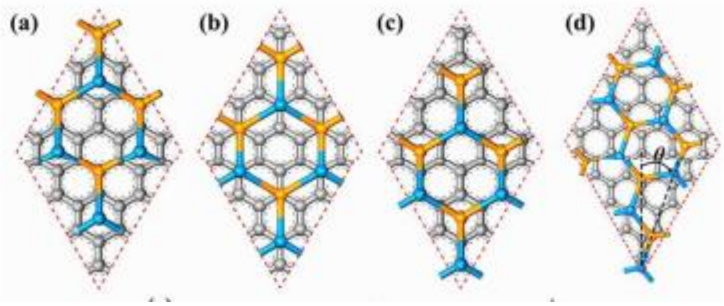


Figure 6. Top view of the atomic model of the graphene/stanene heterobilayer: (a) Pattern i, (b) Pattern ii, (c) Pattern iii of the G(4)/Sn(2) supercell, (d) G(5)/Sn($\sqrt{7}$) supercell, θ is the rotational angle between two layers. The C atom of the graphene, and the Sn atoms in upper/lower level are represented by grey, blue and yellow balls respectively. [6]

2.5 Graphene-Stanene Heterobilayer: Different from others, heterobilayer composed of two group-IV 2D materials, graphene-stanene was investigated by Chen *et al.*[9]. They [9] explored the structural, electronic and optical properties of the graphene-stanene hybrid structure, with the presence of a finite band gap and superior response of visible light. Considering the lattice incompatibility between graphene and stanene, they introduced four stacking configurations to model the bilayer in order to investigate the relevant effects. The interaction between the two layers are comparatively stronger than vdW owing to Stanene's unsaturated P orbital. The Dirac feature of the bilayer system was also reported. Although graphene and stanene both are semi-metals, the bilayer system is electrically neutral along with the opened band gap. The coupling of two important properties: high carrier mobility of graphene and promising QSH effect of stanene will exist simultaneously in the bilayer system. Moreover, they found that the work function of graphene monolayer is relatively higher than that of graphene monolayer and significantly, stanene shows distinct optical adsorption competency compared to graphene. In a nutshell, the graphene/stanene heterobilayer will offer the performance of the stanene-based spintronic devices and will be a good candidate for photoelectronic devices.

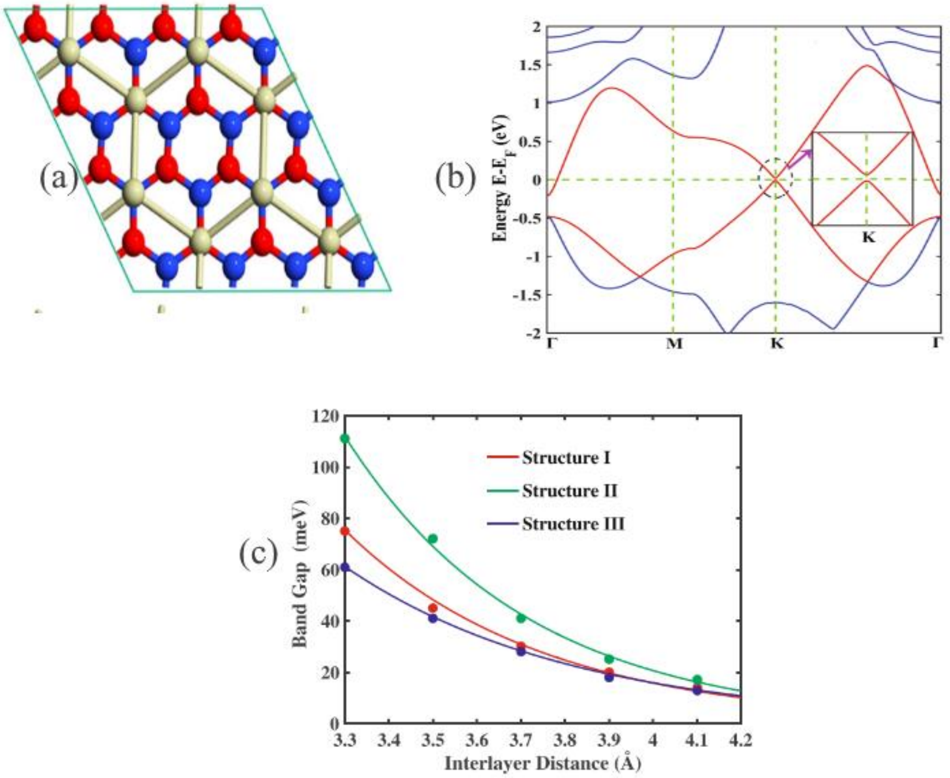


Figure 7. (a) Atom model of stanene/h-BN heterobilayer (b) Band structure for the most stable stanene/h-BN stacking pattern (c) Band gap tuning under the change of inter layer distance for the three structures [7]

2.6 Stanene-Hexagonal Boron Nitride Heterobilayer: Of late, Khan *et al*.[10] studied the structure as well as electronic properties of stanene/hexagonal boron nitride (Sn/h-BN) heterobilayer taking various stacking features by mean of first principle calculations. The heterobilayer showed a direct energy gap of ~30meV locating at the K point and at the Fermi level. A Fermi velocity of ~0.53×10^6 ms^{-1} was reported for the heterostructure accompanied by the linear Dirac dispersion relation and small effective mass on the order $0.05m_o$. These results indicate high mobility for the carriers. They [10] also analyzed the interaction and electronic behavior calculating the density of states and the real space charge distribution of the heterobilayer structure of the conduction and the valence bands. They [10] found the electronic behavior of Sn/h-BN heterobilayer is dominated by the unsaturated π orbitals of stanene. The h-BN layer permits the electrons to move through Sn layer only, thereby making the h-BN layer a good substrate for the heterostructure. They have also examined the tuning of the achieved band gap upon varying the interlayer distance between h-BN and Sn layer and under tensile biaxial strain applied to the heterostructure. A tunable band gap is observed under changing these two properties.

3. Conclusion: In summary, an overview is given on the present research on group-IV 2D elements based heterobilayers. Adopting heterobilayers can be considered an efficient way to open a band gap for the group-IV 2D materials and modulating other electronic properties while preserving their Dirac cone feature. Although in some heterobilayers the band gap was not sufficient, it is expected adopting heterobilayers with newer 2D element might solve this issue which preserving the electronic properties of these group-IV materials. Overall, this review will make one familiar on the recent investigation on graphene, silicene, germanene and stanene based heterobilayers.

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