Ab initio calculation on the Optical Properties of AA-Stacked two dimensional Graphene, Silicene, Germanene, and Stanene

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Abstract: In this study, we have analyzed the electronic band structure and optical properties of AA-stacked bilayer graphene and its 2D analogues and compared the results with single layers. The calculations have been done using Density Functional Theory with Generalized Gradient Approximation as exchange correlation potential as in CASTEP. The study on electronic band structure shows the splitting of valence and conduction bands. A band gap of 0.342eV in graphene and an infinitesimally small gap in other 2D materials are generated. Similar to a single layer, AA-stacked bilayer materials also exhibit excellent optical properties throughout the optical region from infrared to ultraviolet. Optical properties are studied along both parallel (||) and perpendicular (⊥) polarization directions. The complex dielectric function (ε) and the complex refractive index (N) are calculated. The calculated values of ε and N enable us to analyze optical absorption, reflectivity, conductivity, and the electron loss function. Inferences from the study of optical properties are presented. In general the optical properties are found to be enhanced compared to its corresponding single layer. The further study brings out greater inferences towards their direct application in the optical industry through a wide range of the optical spectrum.

Keywords: DFT, GGA, Band structure, graphene, silicene, germanene, stanene, and optical properties

1. Introduction

Graphene, a two dimensional material is well explored in the recent past decades because of its unique electronic properties [1], [2]. Since its band gap is zero and cannot be directly incorporated with the silicon industry, other group IV elements gained attention among the research community. It has been found that the 2D analogues of the single layer graphene also exhibit zero band gap. This instigated us to work on layered structures. Here in this study we try to summarize the properties of AA-stacked bilayer of graphene, silicene, germanene, and stanene.

2. Computational Details

AA-stacked bilayer structures are constructed with 4 atoms in the unit cell. The AA-stacked 3 x 3 supercell lattice of planar (graphene) and buckled (germanene) structures both on and across views is shown in figure 1. In AA-stacked bilayer, the atoms are stacked on top of
each other. The optimized interlayer distance increases from graphene to stanene: 3.35, 4.60, 3.45, and 5.24Å respectively. The increase in the interlayer distance is due to the increase in the size of the atom from graphene to stanene except germanene. The calculations were performed using the Density Functional Theory [3], [4] with Generalized Gradient Approximation (Perdew Burke-Ernzerhof, GGA-PBE) [5] exchange correlation functional as implemented in Cambridge Sequential Total Energy Package (CASTEP) [6].

![Figure 1: AA-stacked bilayer. (a) On view of planar graphene, (b) On view of buckled germanene. (c) Across view of planar graphene: (d) Across view of buckled germanene](image)

3. **Band structure of AA-stacked bilayer**

The electronic band structures of AA-stacked bilayer of all 2D materials resemble the single layer (figure 2). They are in good agreement with the already reported results [7]. In general, the bands are split into two. When the interlayer distance is increased, the band gap increases, while germanene exhibits metallic behaviour with the bands overlapping along the M direction. A band gap of 0.342, 0.012, and 0.038eV are generated in graphene, silicene, and stanene respectively. The π and π* orbitals exhibit degeneracy at K point. The linearity is observed at the Dirac point and is found to decrease in silicene and stanene.

The introduction of the band gap may be accounted for the capping of the electrons in the pₓ orbitals as the atoms are stacked on top of each other. The pₓ unhybridized orbitals form σ bonding along the vertical plane. The formation of σ bond along the c axis reduces the mobility of the Dirac Fermions leading to a band gap. The variation of Eₓ with interlayer distance mainly arises from the overlap of wave function between the two layers [8].

![Figure 2: Electronic band structure with parallel bands (AA stacked) (BLAAG) graphene (BLAASi) silicene (BLAAGe) germanene (BLAASn) stanene.](image)
4. Optical Properties

The optical properties have been calculated from the complex dielectric function and the complex refractive index. The details can be found in our earlier report [9]. The properties are discussed in the following sections.

4.4.1 Dielectric function

The static dielectric function (SDC) in AA-stacked bilayer increases from graphene to stanene along both polarization directions while germanene shows a dip in the series along \( \perp \) polarization direction (figure 3). In AA-stacked bilayer, stanene has the maximum value of SDC. We also find an increase in the SDC of each material from single layer to AA-stacked bilayer. The SDC of silicene and germanene is found to be less than its host materials in the \( \perp \) polarization direction. The oscillatory behaviour of AA-stacked bilayer of all materials is found to exist in all three regions as shown in figure 3. All materials exhibit Plasma Frequency on stacking including graphene and falls in the ultraviolet region in both polarization directions. This thoroughly indicates that AA-stacked bilayer materials behave like metal in the IR and visible regions when light is polarized in either direction (figure 4).

![Figure 3: \( \varepsilon_r(\omega) \): (a) \( \perp \) polarization direction (b) \( || \) polarization direction](image)

![Figure 4: Plasma frequency: (a) \( \perp \) polarization direction (b) \( || \) polarization direction](image)

4.4.2 Refractive index

AA-stacked bilayer materials are anisotropic in nature (figure 5). Graphene is anisotropic throughout the optical region. Silicene, germanene, and stanene are isotropic above: 17.5, 29, and 10eV respectively. Figure 5 also reveals that these materials possess birefringence. The refractive index is greatest when light is polarized \( || \) to the basal plane in all four materials as seen in the case of the single layer. The refractive index of the host material is greater than its 2D analogues when light is polarized along the \( \perp \) direction.
4.4.3 Reflectivity

The value of reflectivity of all materials is less than unity [Figure 6]. They exhibit reflectivity mainly in the UV region along the \( \perp \) polarization direction. \( \parallel \) polarization exhibits reflection from far infrared region with a dip in the visible region. In fact, all materials exhibit reflectivity at zero photon energy. Silicene shows maximum reflectivity exhibiting pure metallic behaviour along \( \perp \) polarization direction while other materials display the semi metallic behaviour. In \( \parallel \) polarization, stanene alone exhibits pure metallic behaviour while germanene and stanene, semi-metallic behaviour. Reflectivity of graphene is less than 0.5 and hence it is proved that even AA-stacked bilayer graphene is transparent.

4.4.4 Electron loss function

The electron loss function \( L(\omega) \) of AA-stacked bilayer is shown in figure 7. The intensity of the peaks is found to be increased compared to the single layer of its counterparts. The peaks due to \( \pi \) Plasmon in all materials are very weak which is attributed to the presence of buckling and the capping of electrons due to stacking. The peaks due to \( \pi^+\sigma \) plasmons are sharper than \( \pi \) Plasmon.
4.4.5 Absorption

The band structure with parallel bands and the absorption peaks are shown in figures 2 and 8. Optical absorption takes place in all three regions (IR, visible, and UV) when light is polarized in either direction. Absorption of all materials are found to be additive on stacking. Stacking increases the absorption almost four times of its single layer. A red shift in absorption has been observed from graphene to stanene due to the increase in the ionic radius. The peaks are mainly due to the parallel bands between bonding and anti-bonding orbitals. Besides the existence of parallel bands which lead to prominent absorption, the other features include; critical points, band extrema at Γ, and Van Hove singularities due to the presence of saddle points along M to K direction. Similar to the single layer all these features are found to be true in AA-stacked bilayer as well.

![Absorption curves](image)

Figure 8: Absorption curves: (BLAA001) ⊥ polarization direction, (BLAA100) || polarization direction

5. Conclusion

In this study, we have analysed the electronic and optical properties of AA-stacked graphene, silicene, germanene, and stanene. The bands are split into two and linearity is maintained at the Dirac point with a small band gap. Optical properties like absorption, reflectivity, and electron loss function are calculated. All the properties are found to be enhanced in AA-stacked bilayer compared to that of the single layer. Hence we conclude that AA-stacked bilayer materials can be widely used in semiconductor and optical industry to a large extent.

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