Electronic properties of aluminium and silicon doped (2, 2) graphyne nanotube

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Abstract. With the help of density functional theory (DFT) approach the electronic properties of Al and Si doped (2, 2) graphyne nanotube (GNT) has been investigated. We have chosen two doping positions. In one situation we have replaced one carbon atom by Al/Si atom in the chain position of the GNT and in other case we have substituted the carbon atom in the hexagonal ring by Al/Si atom. The result of the cohesive energy indicates that pristine graphyne nanotube shows highest stability whereas, Al doped at chain site of the GNT exhibits lowest stability. The density of states above and below the Fermi level for all these system is mainly contributed by carbon atom. Band structure analysis shows that the band gap can be tuned by functionalization of GNT with Al and Si atoms; which makes the possibility of using them in nano-electronic devices.

1. Introduction
A huge amount of research work has been carried out on carbon based nanomaterials such as fullerene [1], carbon nanotube (CNT) [2], graphene [3] etc. by various research groups in the previous decades owing to their unique physical and chemical properties. In 1987 another allotropic form of carbon was proposed by Baughman and co-workers. They termed it as graphyne [4, 5] which become an emerging field for researchers [6-10]. Graphyne has a fascinating structure compare to other carbon based compounds. In graphyne all the carbon atoms are sp\(^2\) hybridized, whereas in case of graphene both sp and sp\(^2\) bonded carbon atoms are present in a crystal lattice. In graphyne there are large numbers of acetylene linkage present between the two nearest hexagonal ring as a result of which it shows enhance performance in optical and electronic applications. Theoretically it was found that graphyne exhibits some outstanding properties such as good electrical conductivity, high mechanical and chemical stability [10] which might be useful for designing optoelectronic and nanoelectronic devices, solar cell application, energy storage, gas sensor [6-9, 12, 13].

The structure of graphyne nanotubes (GNTs) are formed by rolling the graphyne sheet into a cylindrical form. The diameter and chirality of the nanotube influences the electronic property of GNT. The electronic and optical properties of graphyne sheet and tube can also be tuned by substitutional doping by various atoms [5-9]. In our present work we have studied the effect on electronic properties of GNT due to doping by Al and Si atom. We are going to investigate how the conducting nature changes due to the interaction of Al and Si atom with GNT.

On the basis of cohesive energy, the stability of above mentioned systems are determined. We have also calculated the electric and magnetic dipole moment and band gap of the considered systems and find the possible applications of Al and Si doped GNT in nano-electronics.
2. Computational details
We have performed all the calculations using density functional theory (DFT) methodology as suggested in siesta 3.2 package [14]. Perdew–Burke–Ernzerhof (PBE) form has been used to represent the exchange-correlation functional of the generalized gradient approximation (GGA) in the calculation [15]. The Double zeta polarized numerical atomic-orbital and Troullier-Martin type norm-conserving pseudo potentials [16] have been used here. The mesh cut-off value of 300 Ryd has been taken and a mixing rate for self consistent calculations was fixed at 0.05 for the grid integration. Relaxation process continues until the magnitude of the forces acting on each atom is less or equal to 0.01 eV/Å. To avoid the interactions between different layers of graphyne system a vacuum of 20 Å has been kept along X and Y directions. 1×1×18 \( k \) points was used for sampling of Brillouin zone. To study the most stable configuration of these systems, the cohesive energy is calculated using the following relation,

\[
\text{Cohesive energy} = \frac{E(\text{system})-[nE(C)+mE(D)]}{n+m}
\]

where \( E(\text{system}) \), \( E(C) \) and \( E(D) \) are energies of total system, carbon and doped atoms (\( D=\text{Si, Al} \)) and \( n, m \) are number of carbon and doped atoms present in the system respectively.

For the calculation of dipole moment \( (\mu) \) of Al and Si doped GNT we have used the following relation;

\[
\mu = (\mu_X^2 + \mu_Y^2 + \mu_Z^2)^{\frac{1}{2}}
\]

where \( \mu_X, \mu_Y, \) and \( \mu_Z \) are components of dipole moment along X, Y, and Z direction respectively.

3. Results and discussion
Our present work emphasises on the study of electronic properties of \((2, 2)\) GNT due to presence of Al and Si atoms at different doping positions. We have replaced sp and sp\(^2\) hybridized carbon atom by Al and Si atoms. The optimized geometries are presented in figure 1.

![Figure 1](image_url)

(a) (b) (c) (d)

Figure 1. Optimized geometries of (a) Al doped GNT at chain position; (b) Al doped GNT at ring position; (c) Si doped GNT at chain position; (d) Si doped GNT at ring position.

The lattice constant values for all the above mentioned systems are presented in Table 1. The lattice constant of pristine systems is 6.9155 Å, however substitutional doping by Al and Si atom slightly increases it. The increasing trend follows the order GNT < ‘Si doped GNT at chain position’ < ‘Al doped GNT at chain position’ < ‘Si doped GNT at ring position’ < ‘Al doped GNT at ring position’.
Table 1 The lattice constant, cohesive energy, energy gap, electric and magnetic dipole moment of Al and Si doped graphyne nanotube

| System               | Lattice Constant (Å) | Cohesive energy (eV) | Energy gap (eV) | Dipole moment (Debye) | Magnetic moment (μB) |
|----------------------|----------------------|----------------------|----------------|-----------------------|---------------------|
| (2, 2) GNT           | 6.9155               | -9.3071              | 0.7520         | 0.0000                | 0.0000              |
| (2, 2) GNT + Si (ring) | 6.9657               | -9.2025              | 0.4181         | 0.9811                | 0.0000              |
| (2, 2) GNT + Si (chain) | 6.9181               | -9.2015              | 0.2212         | 0.7939                | 0.0000              |
| (2, 2) GNT + Al (ring) | 6.9677               | -9.1641              | ↑0.4558        | ↓0.4969               | 0.6691              |
| (2, 2) GNT + Al (chain) | 6.9270               | -9.1586              | ↑0.3172        | ↓0.1668               | 0.2539              | 1.0018              |

3.1 Cohesive energy
The results of cohesive energy enable us to determine the stable configuration of the system. The more and more negative cohesive energy physically signifies the greater stability of the system. The pristine graphyne nanotube has highest stability. Doping by Si and Al atom decreases the stability of the system. The stability due to doping by Al and Si atoms at two different doping positions is in the order GNT > ‘Si doped GNT at ring position’ > ‘Si doped GNT at chain position’ > ‘Al doped GNT at ring position’ > ‘Al doped GNT at chain position’.

3.2 Electric and magnetic dipole moment
Spin polarized calculation reveals that splitting of spin does not take place in case of (2, 2) pristine GNT and Si doped GNT. Thus these systems do not possess magnetic character. Whereas, Al doped at chain and ring position of GNT initiates the spin splitting. This may occur due to redistribution of charge carriers between Al atom and carbon atom of the GNT. Thus the Al doped GNT systems are showing magnetic characteristics. The magnitudes of magnetic moment are 0.9707 μB and 1.0018 μB for Al doped at ring and chain position respectively. This considerable change in magnetic moment can be measured with the help of a SQUID magnetometer [17] and this may enable us to design a chemical or gas sensor based on Al doped GNT.

There is no induced electric dipole moment in case of intrinsic GNT system but doping by Si and Al atom originates electric dipole moment in the GNT system. The trend of dipole moment of the above mentioned systems follow the order ‘Si doped GNT at ring position’ > ‘Si doped GNT at chain position’ > ‘Al doped GNT at ring position’ > ‘Al doped GNT at chain position’.

3.3 Band structure analysis
The spin polarized band structure is represented in Fig. 2. The result indicates that doping by Al and Si atom at different doping position significantly decreases the band gap of GNT. The pristine GNT has a band gap of 0.752 eV [18] and showing semiconducting behaviour. Al and Si doped at chain and ring position of GNT exhibits same nature of conduction as that of pristine GNT. In case of Al atom at chain position of GNT, the majority spin channel has a band gap of 0.3172 eV whereas minority spin channel possess a band gap of 0.1668 eV and the same atom when placed at ring position of GNT, both the spin channel have a band gap of 0.4558 eV for majority spin and 0.4969 eV for minority spin. When one carbon atom at chain site is substituted by Si atom, the band gap of pristine GNT system decreases to 0.2212 eV and when Si atom replaces the carbon atom at ring position the band gap of the system is 0.4181 eV. We have also noticed that the valence band maximum (VBM) and conduction band minimum (CBM) for the above mentioned systems are located at the X- point of the rectangular Brillouin zone and due to this feature all these systems are direct band gap semiconductors.

The modulation of band gap is possible due to doping by Al and Si atom. The reasonable tuning of band gaps depends not only on dopant atoms but also on doping positions. Adjustment of band gap is one of the major requirements for a system to be used in nano-electronics devices and here we have fulfilled this criterion by doping with Si and Al atom at chain and ring position respectively.
Figure 2. Band structure of (a) Al doped GNT at chain position; (b) Al doped GNT at ring position; (c) Si doped GNT at chain position; (d) Si doped GNT at ring position.

3.4 Density of states

We have presented projected density of states (PDOS) in Figure 3. Positive and negative values of PDOS represent up spin and down spin respectively. We mainly focus on the electronic states near the Fermi level, to study the changes in the electronic properties of GNT due to the presence of dopant atoms. In case of Al doped at chain and ring position of GNT, the contribution of carbon atom both for majority and minority spin channel is predominant in the valence band (VB) compare to that of conduction band (CB) (Fig 3a), whereas Al atom mainly participates in the CB. The contribution of aluminium atom is more significant when Al is situated at ring position of GNT (Fig 3b). PDOS plot for Al at chain and ring position of GNT also reveals that density of states is not symmetrical (upper panel of figure 3a and 3b) for both the spin channels but in case of Si at chain and ring position of GNT, the density of states for up and down spin is symmetrical (upper panel of figure 3c and 3d) in nature as a result no magnetisation is induced when Si is doped at chain and ring site of GNT. In case of Si doped at chain and ring position of GNT, the contribution of carbon atom again dominates in VB compare to CB, whereas in case of Si doped at chain position of GNT (Fig 3c), Si atom mainly participates in VB but when Si is at ring site of GNT (Fig 3d) the same atom mostly contributes in CB.
Figure 3. PDOS plot for (a) Al doped GNT at chain position; (b) Al doped GNT at ring position; (c) Si doped GNT at chain position; (d) Si doped GNT at ring position.

4. Conclusion
We have analysed the effect in electronic properties of GNT due to functionalization by Al and Si atoms using first principle calculations. On the basis of cohesive energy we can infer that stability of the GNT system decreases due to replacement of carbon atom by Al and Si atom. Among all the structures Al doped at chain position of GNT shows lowest stability. Band structure analysis confirms that all the structures are direct band gap semiconductor and doping by Al and Si atom decreases the band gap significantly. This property enables us to use these systems in technological applications where tuning of band gap is required. Al doped GNT exhibits magnetic character. Carbon atom mainly participates in the density of state for all these system. Substitutional doping by Al and Si atom influences the electronic properties of GNT; which makes the possibility of using them in nano-electronic applications.

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