The Defects Effect on Electronic and Structural Properties for Boron – Nitride Sulfide Ribbons as a Gas Sensor Using DFT

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Abstract. In this research study the effect defect on edge of boron – nitride ribbons using first principle study by function B3LYP with large basis set 6-31G. After complete relax replace boron atom by sulfur atom to modify ribbons sensing gas. We using (O₂, NH₃, CO and NO) gases to determine the ability of sensing depending on adsorption energy and total energy. All bond length are agreements with previous study for B-N, C-O, N-H, O₂, N-O and N-S with bond length (1.45 – 1.4338), (1.4090 – 1.3545), (1.012 – 1.0122), (1.4722), (1.3988) and (1.6868) Angstrom. The best position for sensitivity for mixing gases equal (1.75) Angstrom with total energy -1797.434 a.u., this value of energy refer to stability of sensor energy. All sample under study that describe as semiconductor device that using in sensing gas particle depending on energy gap values in electron volt unit varies (0.6 – 1.1). The result from this research is change the insulator state of boron – nitride ribbon to semiconductor state depending on defect on edge of ribbons. Adsorption energy calculation classified that CO gas molecule have high ability of interaction with ribbon resulting from chemical adsorption. Other ribbon have interaction energy is low compared with CO gas molecule. All calculation employed using Gaussian 09 program.

1. Introduction

The discovery of graphene, a single layer of carbon atoms has added a new class of materials to the material family, that of one-atom thick two-dimensional materials [1]. Graphene was discovered in 2004, when Geim and co-workgroup Manchester University isolated single-layer samples from graphite[2]. The electronic, mechanical and thermal properties of graphene are very sensitive to lattice imperfections; therefore study of changing in this material is critically important. Furthermore, the other graphene allotropes such as carbon nanotubes (armchair, zigzag and chiral) and fullerenes have been investigated enormously [3]. Ideal graphene is a semimetal contains a appear density of states at the Fermi energy with remarkably high carrier mobility at room temperature and therefore a single-layer graphene can be considered as a semiconductor with zero energy gap or behave as semi metallic material[4]. Doped graphene received a huge attention from scientists and researchers to understand the properties of their properties (electrical and mechanical), especially doping graphene by Boron and Nitrogen or both and also the possible applications of this doped material[5].

BN nano sheets consist of sp2-conjugated boron and nitrogen atoms that form a honeycomb structure.[6] They contain two different edges: armchair and zig-zag. The armchair edge consists of either boron or nitrogen atoms, while the zig-zag edge consists of alternating boron or nitrogen atoms. These 2D structures can stack on top of each other and are held by Van der Waals forces to form few-layer boron nitride ribbons. In these structures, the boron atoms of one sheet are positioned on top or below the nitrogen atoms due to electron-deficient nature of boron and electron-rich nature of nitrogen [6].

Boron nitride ribbon is a two-dimensional crystalline form of the hexagonal boron nitride (h-BN), which has a thickness of one to few atomic layers. It is similar in geometry to its all-carbon analog graphene, but has very different chemical and electronic properties – contrary to the black and highly conducting graphene, boron - nitride ribbons are electrical insulators with a band gap of ~5.9 eV, and therefore appear white in color[7].
Purified by removing the heterotopic contamination. Brodie first demonstrated the synthesis of GO in 1959 by adding a portion of potassium chlorate to a slurry of graphite in fuming nitric acid [8].

2. Theoretical Background
Density functional theory (DFT) is a widely quantum mechanical method in physics and chemistry used to investigate the electronic structure of many-electron systems. It is today one of the most important tools for calculating the ground state properties of metals, semiconductors and insulators. DFT is among the most popular and useful methods available in computational physics and computational chemistry [9].

The starting point of density theory was the Thomas-Fermi model, in 1927, Thomas and Fermi are calculated the energy of an atom by representing its kinetic energy as a function of the electron density, combining this with the classical expressions for the nuclear-electron and electron-electron interactions, which can both also be represented in terms of the electron density [10]. The DFT focuses on the much simpler electron density \( \rho(\mathbf{r}) \). In general, the electron density is the number of electrons \( N \) per unit volume for a given state. It is dependent only on three coordinates independently of the number of electrons of the system [11].

\[
N = \int \rho(\mathbf{r}) d\mathbf{r}
\]  

(1)

The central concepts of DFT be dependent on the ground state energy and all other ground state electronic properties are uniquely determined by the electron density. Furthermore, the exact ground state of the system corresponds to the electronic density for minimal total energy. Hohenberg and Kohn, in 1964 proved that the ground state of a many electron system can be determined by the ground state electron density \( \rho(\mathbf{r}) \). The two theorems of Hohenberg and Kohn are [11].

**Theorem I:** The ground state energy of a many-electron system is a unique, universal functional of ground state electron density \( \rho(\mathbf{r}) \).

**Theorem II:** The functional of ground state energy is minimized by the ground state electron density \( \rho(\mathbf{r}) \) for a many-electron system.

According to above theorems, any ground state properties of a many electron system can be expressed in terms of the ground state electron density \( \rho(\mathbf{r}) \). The ground state energy functional \( E_V[\rho] \) can be described as [4].

\[
E_V[\rho] = \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + F_{HK}[\rho]
\]

(2)

where \( F_{HK}[\rho] \) is a universal functional of \( \rho(\mathbf{r}) \) to be determined which includes kinetic energy and all the electron-electron interactions, \( F_{HK}[\rho] \) is independent of the external potential \( V_{ext}(\mathbf{r}) \).

Equation for calculation energy gap is [10]:

\[
E_g = E_LUMO - E_HOMO
\]

(3)

Equation used to calculate adsorption energy is [9].

\[
E_{Ad} = (E_T(Boron-Nitride) + E_T(Gas Molecule)) - E_T(Gas Molecule + Boron-Nitride)
\]

(4)

3. Results and discussion

3.1 Structural Properties
The optimization structural of boron-nitride ribbon was employed using density functional theory to obtain relax structural that able to study in ground states. All calculation using hybrid function for three parameters (B3LYP). Calculation of bond length obtained by Gaussian package 09 version, ground state calculation to determine best relaxation system that study. The bond length summary by this data (B-N)
bond varied in value (1.45 – 1.4338) angstrom, (N-H) varies (1.012 – 1.0122) angstrom[11], (C-O) change in (1.4090 – 1.3545) angstrom[11], (O-O) value of bond is (1.4722) angstrom[12], (N-O) bond length is (1.3988) angstrom and (N-S) is equal for all states under study (1.7321) angstrom[11]. Conclude that all bond between atom in ribbon and gas molecule lie in some position in standard measurement of bond length, this change in bond length beyond to accuracy of tool used in calculation, DFT is useful tool using to measure geometry relaxation.

3-2 Total Energy and Energy Gap
First the total energy for pure boron – nitride sheet equal (-1274.2871 a.u.). These values represent energy of stable case, when adding S atom to the ribbon total energy decreased and reached (-1647.2154 a.u.) the change in total energy beyond to the change on electronic distribution, by adding gas molecules the total energy reached maximum value equal (-1797.4341 a.u.), this value of energy represent more stable energy from all sample in other side this value of energy more ability of sensing. Energy gap for ribbons steady in semiconductor region varies (0.4 – 1) electron volt (e.V), important value of energy gap for changing band gap for boron nitride from insulator to semiconductor by making defect in edge of ribbon. Sulfur atom effect is clear on ribbons showed that curvature of edge of ribbons beyond to that electrons between boron and nitrogen are full 3 electrons from boron and 5 electron from nitrogen this refer to equivalent like carbon atom, the electron of sulfur atom play important role to energy rise from ribbons that increasing adsorption process. The energy gap of defect boron-nitride is 1.043 eV and boron-nitride sulfide is 0.4794 eV. Molecular orbitals of boron-nitride ribbon in pure case equal 1.04327 e.V, so after adding the sulfur atom the values of HOMO and LUMO decreased in values energy gap value is reduce until 0.4794 e.V causing by adding sulfur atom that increasing defect in edge of ribbon. First case adsorption of CO gas molecule the molecular orbitals for 1 and 2 ribbon are greater than doped ribbon by sulfur atom that changer in energy gap to value 1.03 and 0.65 e.V mean change in ribbon case to semi metal material. In ribbon 3 adsorption of O₂ molecule gas also the molecular orbital stay bigger than stander ribbon and also bigger than CO molecule gas adsorption value of energy gap 0.98 e.V, ribbon 4 adsorption NO gas molecule molecular orbital also increasing in energy of molecular orbital and energy gaps decreasing from stander ribbon and finally ribbon 5 and 6 adsorption of NH₃ gas molecule molecular orbital stay forward on stander ribbon and energy gap stay in semi metal region with band gap 0.82 and 0.81 e.V. from these result conclude that ribbons under study lie in range of sensor device and ability[6]. Ability of sensitivity can determine it by calculate adsorption energy in next section.
Figure 1. shows geometrical structural for ribbons under study (Blue Nitrogen, white Hydrogen, Yellow Sulfur, Pink White Boron, Black Carbon and Red Oxygen), ribbon 1 and 2 adsorption CO molecule in boron-nitride sulfide ribbon, ribbon 3 O₂ adsorption in ribbon, ribbon 4 NO gas molecule adsorption and ribbon 5 and 6 NH₃ gas molecule adsorption in ribbons.

Table. 1 shows the values of total energy, molecular orbitals and energy gap for ribbon under study that adsorbed with gas molecules (CO, NO, O₂ and NH₃).

| Ribbon | HOMO a.u | LUMO a.u. | Eg eV | Total Energy a.u. | Position Ang. (r) |
|--------|----------|-----------|-------|-------------------|------------------|
| 1      | -0.35388 | -0.31572  | 1.038372 | -1760.4791        | 1.15             |
| 2      | -0.34965 | -0.32551  | 0.656874 | -1760.3124        | 1.18             |
| 3      | -0.39617 | -0.35985  | 0.988304 | -1797.4341        | 1.75             |
| 4      | -0.21552 | -0.1847   | 0.838643 | -1777.3246        | 1.86             |
| 5      | -0.36359 | -0.33355  | 0.817418 | -1703.7479        | 2.14             |
| 6      | -0.3707  | -0.34092  | 0.810344 | -1703.7567        | 3.8              |
| 7      | -0.35494 | -0.3166   | 1.04327  | -1274.2871        |                  |
| 8      | -0.18199 | -0.16437  | 0.479458 | -1647.2154        |                  |
Ribbons 7 and 8 refer to boron–nitride and boron–nitride sulfide

Figure 2. shows total energy for sample under study.

From the Figure 2 conclude that ground state energy for stability sample 3 is -1797.4341 a.u. that reached stability.

Figure 3. shows energy gap for sample for function of position.

From the figure found that varies in energy gap between 0.4 to 1 electron volt all values exact in semiconductor region and for this study abstained these ribbons work as gases sensor.

3.3 Adsorption Energy
The adsorption energy is important concept to determine which gas molecule has high gain to sensitive gases. From the Table (2) conclude the CO gas molecule have high adsorption energy that mean high interaction with boron nitride sulfide ribbons. Other gas molecule have mines energy, other form these gas molecules adsorbed on surface of ribbons. The ribbons 1 and 2 that deal with CO molecule gas adsorbed with ribbon, adsorption energy for process are 16.1892 and 16.3559 a.u. and distance of adsorption is 1.15 and 1.18 angstrom, from the mechanism adsorption nearest gas molecule distance
gave more adsorbed energy rises, the result explain that high interaction between gas molecule and boron-nitride sulfide ribbon, in this process the adsorption is chemical. Adsorption process for O$_2$ molecule in ribbon is weak compared with CO molecule because high distance between molecule and ribbon this clear in ribbon 3 and similar that for ribbon 4 for NO gas molecule, the adsorption distance for O$_2$ and NO molecule are 1.75 and 1.86 respectively. NH$_3$ adsorption on ribbon is very weak infarction and gas molecule are clear from adsorption distance are out of plane from sheet also there are no adsorption process because the molecule go far from the ribbon and very small energy is transfer equal zero approximately that clear from Table (2) so this type of adsorption is physical adsorption the ribbon 5 and 6 show the ammonia adsorption with distance adsorption are 2.14 and 3.8 angstrom on series. The mines sign refer to that interaction between the gas molecule and ribbon is not spontaneous interaction therefore we found ribbon from 3 to 6 have value approximately equal zero, ribbon 1 and 2 are have high adsorption energy and spontaneous interaction we conclude the adsorption between gas molecule and ribbon is very high in this result is important to give reason of sensitivity.

Table 2. shows adsorption energy for ribbons in a.u. unit.

| Ribbons | Adsorption Energy a.u. |
|---------|------------------------|
| 1       | 16.1892                |
| 2       | 16.3559                |
| 3       | -0.4364                |
| 4       | -0.6563                |
| 5       | -0.0007                |
| 6       | -0.0095                |

Figure 4. shows adsorption energy curves for ribbons in a.u. unit
4. Conclusions
1. All ribbons relax with good agreement in bond length with previous study.
2. Ribbon in this study varies between semi-metal and semiconductor.
3. The defect in edge change band gap of boron nitride from insulator to semiconductor.
4. CO gas molecule have high interaction with ribbons depending on adsorption energy.
5. O2 molecules have high stability energy and equilibrium position equal 1.75 Ang.

5. References
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