



The effect of concentration of H₂ physisorption on the current–voltage characteristic of armchair BN nanotubes in CNT–BNNT–CNT set

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Abstract. In this research, we have studied physisorption of hydrogen molecules on armchair boron nitride (BN) nanotube (3,3) using density functional methods and its effect on the current–voltage (I – V) characteristic of the nanotube as a function of concentration using Green’s function techniques. The adsorption geometries and energies, charge transfer and electron transport are calculated. It is found that H₂ physisorption can suppress the I – V characteristic of the BN nanotube, but it has no effect on the band gap of the nanotube. As the H₂ concentration increases, under the same applied bias voltage, the current through the BN nanotube first increases and then begins to decline. The current–voltage characteristic indicates that H₂ molecules can be detected by a BN-based sensor.

Keywords. Hydrogen molecules; physisorption; boron nitride nanotube; transport property; current–voltage characteristic.

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1. Introduction

Nanostructures such as carbon nanotubes (CNT) and boron nitride nanotubes (BNNT), because of their ability to encapsulate hydrogen, have attracted much attention. Dillon and coworkers reported adsorption of hydrogen molecules on carbon single-walled nanotubes [1] and after that many experiments and theoretical studies for understanding adsorption mechanism on nanotube structures have been done. Reaction of hydrogen molecule with nanostructures such as plates of graphene and carbon nanotubes has been investigated more recently [2] and the results show that these materials are suitable for hydrogen encapsulation. Many studies have shown that by inserting heteroatoms in nanostructures, such as boron nitride nanotubes or silicon carbide nanotubes, we can increase the binding energy of adsorption of hydrogen molecules on the substrate [3]. Moreover, understanding the mechanism of adsorption helps us to use precise calculation method for our calculations. Adsorption mechanism

depends on the adsorption of hydrogen in atomic form or molecular form. If hydrogen is adsorbed in atomic form, chemisorption occurs and hydrogen atom shares its electron with the nanostructure [4], but if hydrogen is adsorbed in molecular form, physisorption takes place and hydrogen molecule within Van der Waals force reacts with the nanostructure [5].

Nanostructures such as nanotubes, graphene, etc., due to their unrivalled properties and large surface/volume ratio, are promising nanoscale gas sensors. Understanding the change in electronic properties of nanostructures due to gas adsorption helps us to make gas sensors [6]. Nanostructure gas sensors are interesting subjects of research, because they can be used for identifying leakage of explosive gas such as hydrogen or for detecting toxic gases in such as CO, CO₂, NO and NO₂ in industries. Generally, electronic properties of the sensors, after exposing gas molecules, will change because of charge induction or charge transfer [7–9] between the molecules and the sensor. A molecule can act as a donor or an acceptor of electron

and cause change in Fermi energy system or addition of scattering channels [10].

In this paper, we carry out first-principle calculations for calculating the binding energy of physisorption of hydrogen molecules on boron nitride nanotube (3,3) and present the change in electronic properties and current–voltage characteristics of the nanotube by physisorption of hydrogen molecules in CNT–BNNT–CNT set as a change in H_2 concentrations.

2. Method

The first-principle calculations on the basis of Perdew–Burke–Ernzerhof (PBE) method was applied to forecast the physical interactions of H_2 molecules on CNT–BNNT–CNT set [11,12]. In our calculations, only the behaviour of explicit valence electrons was considered and interaction with ionic nucleus within norm-conserving pseudopotential [13] has been done. The calculations to optimize the system, binding energy and charge transfer were carried out within the Quantum Espresso package [14], through the plane-wave and

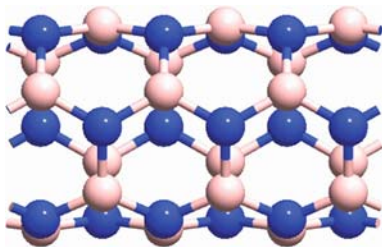


Figure 1. Equilibrium geometries of boron nitride nanotube (3,3). Pink balls represent the boron atoms and blue balls represent the nitrogen atoms.

pseudopotential strategies. To calculate the electron transport, TransSIESTA module in SIESTA package [15] was used through PBE exchange correlation. Orbitals of Kohn–Sham in the form of plan waves up to 90 Ry have been developed. For modelling the detection zone, an armchair boron nitride nanotube (ABNNT) (3,3) consisting of 18 boron atoms and 18 nitrogen atoms has been used. Bond length between the two atoms before relaxation of the structure is 1.45 Å (figure 1) and bond length of a hydrogen molecule is 0.75 Å.

The geometrical set to study the electron transport was composed of semi-infinite armchair carbon nanotubes (ACNT) (3,3) as the left and the right electrodes separated by the detection zone. Figure 2 shows the schematic diagram of the BNNT sensor.

Symmetry cell is hexagonal with parameters $a = b = 25$ Å and $c = 7.36$ Å. We have selected a and b very large to avoid any interaction between periodic replica nanotubes. We have made the structure relaxed in the first Brillouin zone with $1 \times 1 \times 10$ sampling and to calculate the binding energy, sampling in the first Brillouin zone $1 \times 1 \times 100$ has been done. For both cases, method of Monkhorst–Pack [16] has been used. The structure has been completely relaxed according to Hellmann–Feynman theory [17], until the maximum residual force on all the ions was less than 0.001 eV/Å. Total energy has also been calculated with 10^{-8} eV order of accuracy. Binding energy of hydrogen molecule (E_{ad}) is the difference between the total energy of the nanotube plus hydrogen molecule(s) ($E_{BNNT+nH_2}$) and the sum of the total energy of the isolated nanotube (E_{BNNT}) and isolated hydrogen molecule(s) (nE_{H_2}) under identical conditions (cut-off energy, size of the cell and the number of k -points)

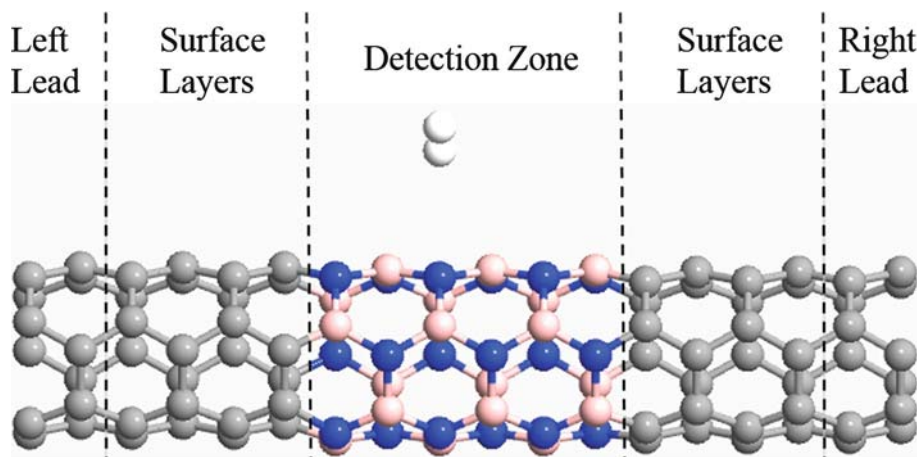


Figure 2. Schematic diagram of the BNNT sensor with the detection zone and CNT leads (white balls represent the hydrogen atoms and grey balls represent the carbon atoms).

(eq. (1)). Here n denotes the number of molecules adsorbed on the BNNT.

$$E_{ad} = E_{BNNT+nH_2} - (E_{BNNT} + nE_{H_2})/n. \quad (1)$$

The concentration of H_2 adsorbed on BNNT is described by varying the number of H_2 molecules in the detection zone, which is determined by the $H_2:N$ ratio based on the number of H_2 molecules and the number of N atoms on the BNNT sidewall.

3. Results and discussion

According to [5,18,19], the most stable state of the H_2 molecule is on top of the hexagonal centre of the nanotubes. Due to this, we have focussed our calculations to this position and considered the hydrogen molecule in two directions, perpendicular to the axis of the nanotube and parallel to the axis of the nanotube (figure 3).

By changing the distance of the hydrogen molecule from the surface of the nanotube in the interval of 2–6 Å, binding energy of the molecule using eq. (1) was obtained. The binding energy vs. distance curves, for both states, perpendicular to the axis of the nanotube and parallel to the axis of the nanotube, are shown in figure 4.

It is seen that the binding energy is more when the molecule is perpendicular to the axis of the nanotube than when it is parallel to the axis of the nanotube and consequently the first state is more stable. This shows that the polarization of hydrogen molecule in the external field due to the nanotube depends on the direction of the molecule and the external field of the BN nanotube. When the molecule is perpendicular to the axis of the nanotube, direction of the external field and the

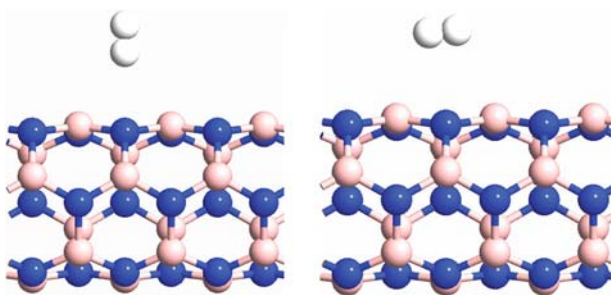


Figure 3. Two different positions for studying hydrogen molecule on boron nitride nanotube.

molecule are parallel, and as a result polarity of the molecule and binding energy are more than in the other case. The minimum of the curve is equal to 2.9 Å, which in fact is the equilibrium distance (ED) of the molecule from the surface of the nanotube.

Binding energy (BE) is approximately equal to 80 meV. By comparing the results with [3], we understand that the binding energy and equilibrium distance are less than the result given in [3] (BE = 110 meV and ED = 3.0 Å). This difference is because in [3] Jhi and Kwon considered a zig-zag boron nitride nanotube (10,0) but in this paper, we have concentrated on the armchair boron nitride nanotube (3,3).

Then, we increase the concentration by adding H_2 molecules uniformly to the symmetric sites on the tube sidewall. Figure 5 shows the representative configurations of the BNNTs with different $H_2:N$ ratios.

Binding energy and charge transfer for each concentration were calculated. Table 1 presents the results. The results reveal that by increasing the concentration of H_2 molecules, binding energy and charge transfer will increase.

In figures 6 and 7, we show the zero-bias transmission spectra for the bare BNNT and BNNT connected to CNT leads with different H_2 concentrations, respectively. The transmission spectrum of the pristine BNNT is also presented as reference. Figure 6 shows that there is a region of zero transmission located around the Fermi level, coinciding with the band gap of bare BNNT (3,3) and is like a semiconductor with 4.2 eV energy gap. The step-like compartment of the spectrum is related to the available conductance channels due to the bands.

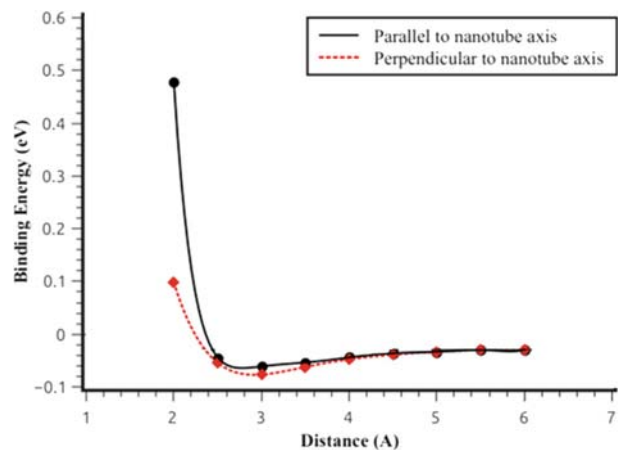


Figure 4. Binding energy vs. distance curve for two states (perpendicular to the axis of the nanotube and parallel to the axis of the nanotube).

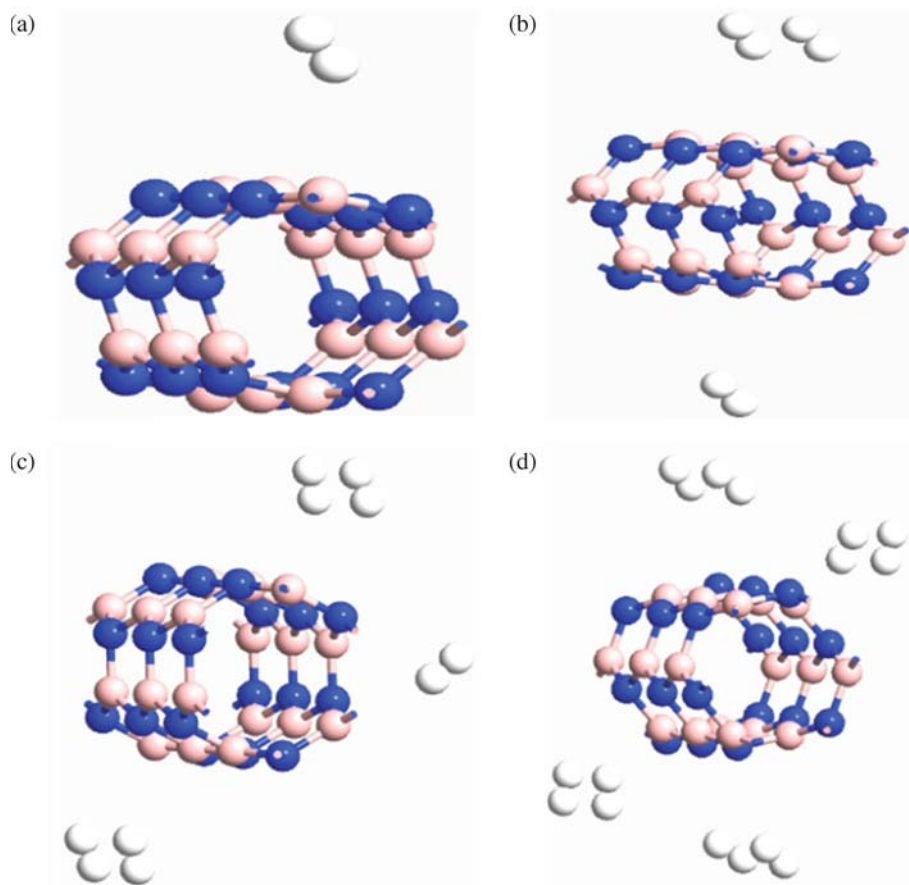


Figure 5. Configurations of the BNNT with $H_2:N$ ratio of (a) 5.55%, (b) 16.66%, (c) 27.77% and (d) 44.44%.

Table 1. Calculated adsorption binding energies (BE) and charge transfer (CT) from the nanotube to the H_2 molecule(s).

$H_2:N$ Ratios (%)	BE (meV)	CT (e)
5.555	80.3	0.002
16.66	82.6	0.006
27.77	84.1	0.015
44.44	85.5	0.033

But, it can be seen from figure 7 that the CNT–BNNT–CNT configuration does not have an energy gap and it has a slight transmission around the Fermi level. When a H_2 molecule is adsorbed on BNNT, the transmission spectrum exhibits a great depression for a wide range of energies.

As the H_2 concentration increases, the transmission for energies greater than 0.55 eV is suppressed as a function of concentration (figure 8a). Figure 8b shows that for energies in the interval of 0–0.55 eV, early transmission of the pristine BNNT is less than BNNTs with H_2 molecules. But for energies greater

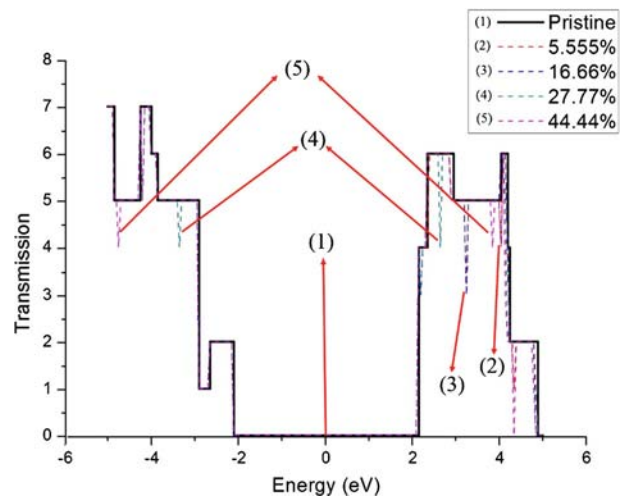


Figure 6. Zero-bias transmission spectra for the bare BNNT with different H_2 concentrations (the Fermi level is set to zero).

than 0.25 eV, transmission of the pristine BNNT starts to increase and takes precedence over BNNTs with H_2 molecules.

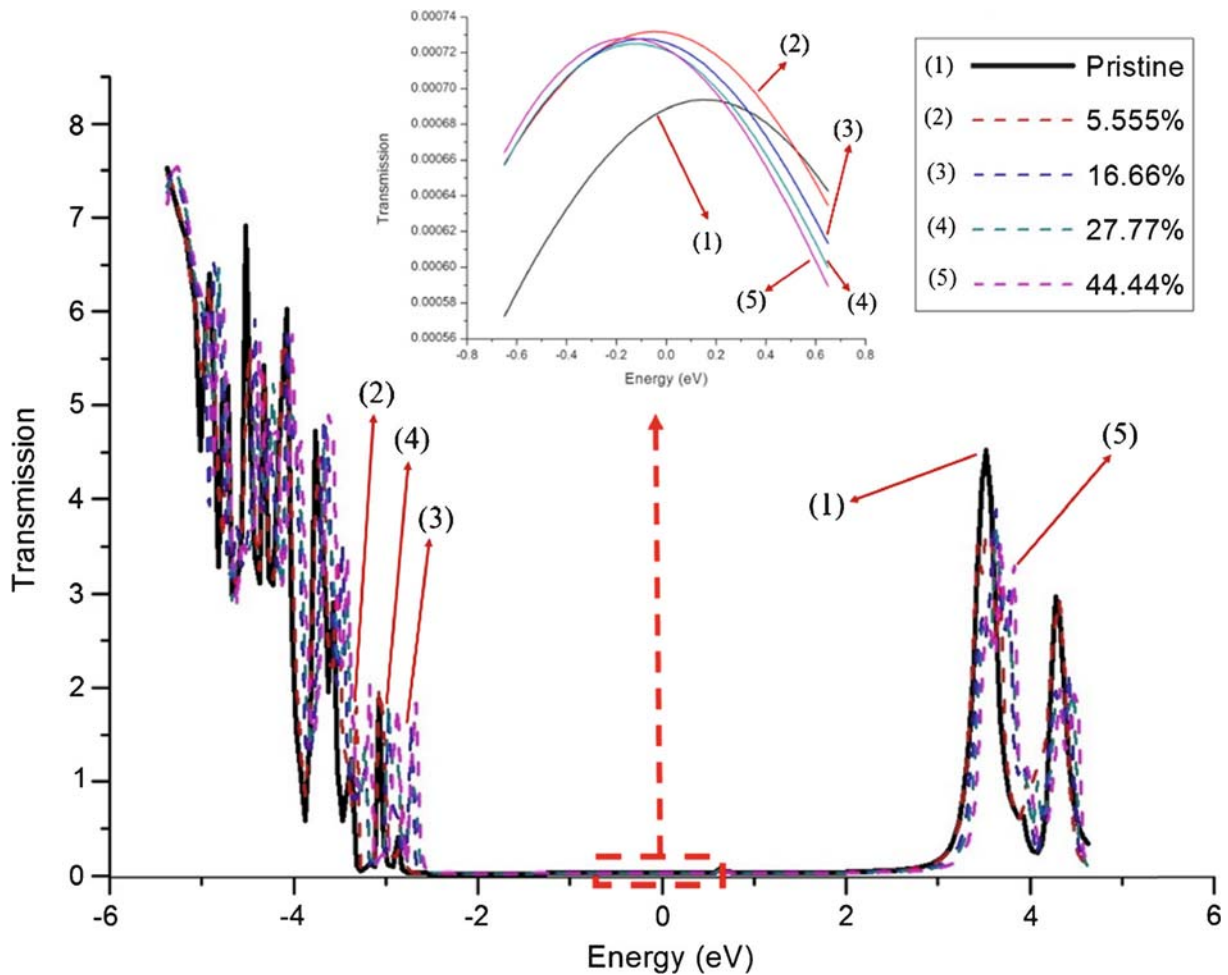


Figure 7. Zero-bias transmission spectra for the CNT-BNNT-CNT configuration with different H₂ concentrations (the Fermi level is set to zero) (at the top of the figure, we have shown the transmission in the interval of $-0.6-0.6$ eV).

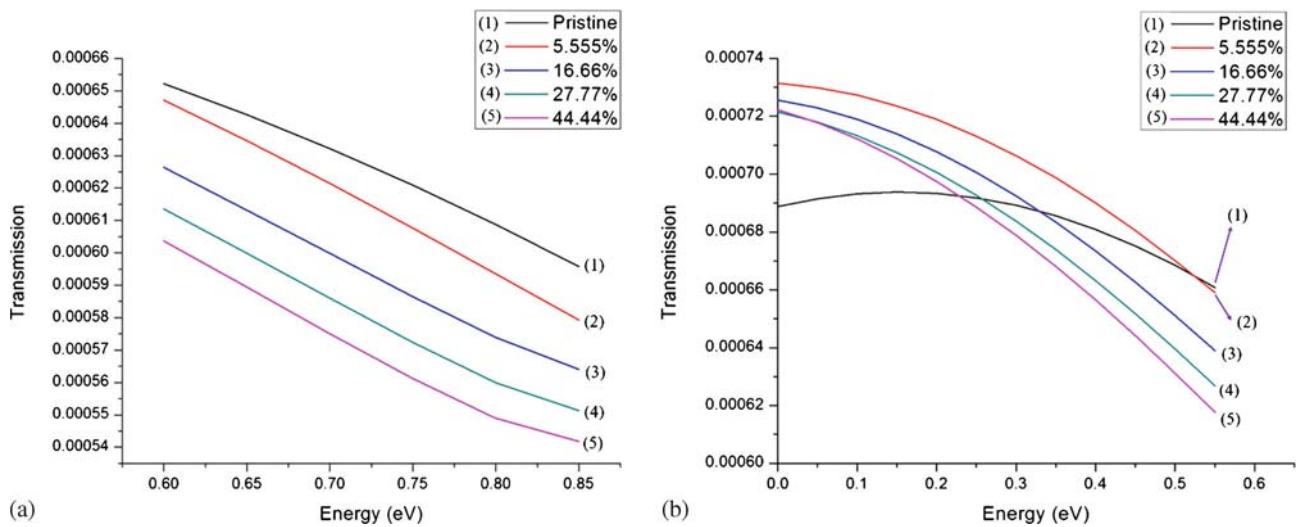


Figure 8. The transmission spectra for the CNT-BNNT-CNT configuration with different H₂ concentrations (a) in the interval of $0.6-0.85$ eV and (b) in the interval of $0.0-0.55$ eV.

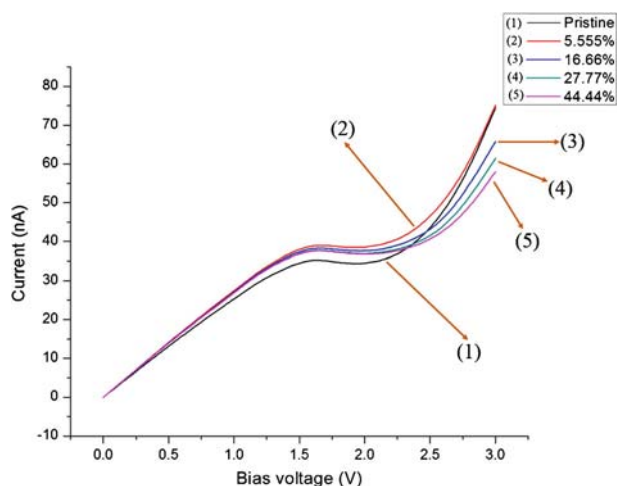


Figure 9. I - V curves of the BNNT with different $H_2:N$ ratios in the CNT-BNNT-CNT set.

In order to study the sensor characteristics, we present the I - V curves of the BNNT in CNT-BNNT-CNT configuration with different H_2 concentrations. As shown in figure 9, due to the metallic nature of H_2 -adsorbed BNNTs in CNT-BNNT-CNT set, current is observed by increasing the bias voltage. After that, the current slightly reduces and negative conductance takes place until the bias voltage reaches 2 V and then it increases rapidly with the increasing bias voltage. Under the same applied bias voltage conditions, the current decreases with the increase of H_2 concentration because the transmission is reduced with the increase of H_2 concentration (figure 8a).

It is important to mention that there is no linearity in the curves for bias voltages below 2.5 V and that all curves are mixed. But, when the proposed sensor is biased at least 2.5 V, linearity can be observed and the device shows the sensor feature. So, to use the proposed sensor, the device should be biased at 2.5 V.

4. Conclusion

In conclusion, binding energy and charge transfer for different H_2 concentrations on boron nitride nanotube (3,3) are found. The results showed that binding energy and charge transfer were increased by increasing H_2 concentration. Also, the effects of H_2 concentration on the transport properties of the bare single-walled

(3,3) BNNT and (3,3) BNNT in CNT-BNNT-CNT set (non-bare BNNT) have been studied using DFT and NGF techniques. It is observed that H_2 adsorption can suppress the transmission of the bare and the non-bare BNNT for a wide range of energies. Although bare BNNT has semiconductive behaviour, non-bare BNNT has metallic behaviour. It is related to that because non-bare BNNT has a small transmission around the Fermi level. When the sensor is biased at least 2.5 V, the current through the BNNT in CNT-BNNT-CNT set decreases by increasing H_2 concentration. So it can be concluded that BNNTs can be good candidate sensors with high sensitivity for H_2 detection.

References

- [1] A C Dillon, K M Jones, T A Bekkedahl, C H Kiang, D S Bethune and M J Heben, *Nature* **386**, 377 (1997)
- [2] D C Elias, R R Nair, T M G Mohiuddin, S V Morozov, P Blake, M P Halsall, A C Ferrari, D W Boukhvalov, M I Katsnelson, A K Geim and K S Novoselov, *Science* **323**, 610 (2009)
- [3] S H Jhi and Y K Kwon, *Phys. Rev. B* **69**, 245407 (2004)
- [4] A H Bayani, N Shahtahmassebi and F D Vahedi, *Physica E* **53**, 168 (2013)
- [5] F Costanzo, P L Silvestrelli and F Ancilotto, *J. Chem. Theory Comput.* **8**, 1288 (2012)
- [6] Y Wang and J T W Yeow, *J. Sens.* 2009 (2009)
- [7] M Dell'Angela *et al.*, *Nano Lett.* **10**, 2470 (2010)
- [8] L Venkataraman, J E Klare, I W Tam, C Nuckolls, M S Hybertsen and M L Steigerwald, *Nano Lett.* **6**, 458 (2006)
- [9] D J Mowbray, G Jones and K S Thygesen, *J. Chem. Phys.* **128**, 111103 (2008)
- [10] J Zhao *et al.*, *Nanotechnol.* **13**, 195 (2002)
- [11] J P Perdew, K Burke and Y Wang, *Phys. Rev. B* **54**, 16533 (1996)
- [12] J P Perdew, J A Chevary, S H Vosko, K A Jackson, M R Pederson, D J Singh and C Fiolhais, *Phys. Rev. B* **46**, 6671 (1992)
- [13] N Troullier and J L Martins, *Phys. Rev. B* **43**, 1993 (1991)
- [14] P Giannozzi *et al.*, *J. Phys.: Condens. Matter* **21**, 395502 (2009)
- [15] J M Soler, E Artacho, J D Gale, A Garcia, J Junquera, P Ordejon and D S Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002)
- [16] H J Monkhorst and J D Pack, *Phys. Rev. B* **13**, 5188 (1976)
- [17] J G Esteve, F Falceto and C G Canal, *Phys. Lett. A* **374**(6), 819 (2010)
- [18] T L Pham, P V Dung, A Sugiyama, N D Duc, T Shimoda, A Fujiwara and D H Chi, *Comput. Mater. Sci.* **49**, S15 (2010)
- [19] X Wu, J Yang, J G Hou and Q Zhu, *J. Chem. Phys.* **121**, 8481 (2004)