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A Comparative Study on In/Ga Doping Effects of Adsorption NH_3 on Surface Electrostatic Potential of (6,0) Boron-nitride Nanotube: A DFT Investigation

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ABSTRACT

Investigations on gas adsorption in nanostructures are important for potential applications such as full cell, gas sensor, hydrogen storage, etc.we examine the possibility of Ga/In doped on BN nanotubes as a potential gas sensors for NH3 detection by first-principal calculations based on density functional theory(DFT). The parameters investigated in this paper involve; binding energies, DOS, Mep, quantum-chemical molecular descriptors were calculated.It is found that NH_3 molecules can be absorbed to Ga, In, B atoms on the wall of Ga/In /BNNTs with binding energies as high as -5762.276 ev. By comparison to nitrogen absorption on BNTs, we infer that molecular NH3 adsorbed on InNNTs can induce significant change in the conductivity of GaNNTs. In view of the high portion of the reactive area, Ga/InNNTs can be potential efficient gas sensors for $_{NH3}$ detection.

Key words: Adsorption, Ga/In doped, Boron-nitride nanotube, Sensors, DFT.

INTRODUCTION

Since its discover by Iijima in 1991, carbon nanotubes (CNT) as a kind of quasi one-dimensional nanomaterial have been a hot subject of physical, chemical and material studies worldwide because of its unique functions in electro-conductivity and mechanics, and its potential applications in molecular devices and composite materials. Carbon nanotubes could be considered as tubular carbon rolled up from planar hexagonal net structural graphite, Boron and nitrogen are the elements nearest to carbon in the Periodic Table. They can form hexa-boron nitride (h-BN) having layer structures similar to graphite and are isoelectronic to graphite. Theoretical studies predicted that h-BN might form a boron-nitride nanotube (BNNT) similar to CNT[1],In fact BNNT was successfully synthesized in a isoionic discharge device by N.G. Chopra *et al*. in 1995.[2] For several years CNT has been theoretically studied extensively and intensively, and the first principle of quantum mechanics was usually used in these studies. However BNNT compared with CNT has

still been much less studied.The performance improvements of gallium nitride (GaN) device applications depend strongly on the features of intrinsic and extrinsic defects in the compound. Bulk GaN has long been viewed as a promising material for lighting device applications. Oxygen is a common contamination in bulk GaN polities. What makes GaN popular is not only it is more robust but it can emit in the short wave-length part of the visible spectrum. For example, there are now GaN-based high-e±ciency blue and green light-emitting diodes[3].

Due to a wide variety of potential applications, carbon nanotubes (CNTs) have been widely studied since their discovery[4]. This superior sensitivity has been theoretically explained in terms of charge transfer between adsorbed molecules and BNNTs, which can dramatically influence the electrical conductivity of the latter(by modifying the electronic structure of BNNTs)[5,6]. Chemical gases such as NH_3 are highly toxic to human beings and animals as they inhibit the consumption of oxygen by body tissues. Therefore, gas sensors with high sensitivity to this gas was highly desired. While BNNTs gas sensors show extreme sensitivity to some gas molecules, they fail to detect the presence of this toxic gas. The reason is due to very weak adsorption of NH_3 molecule on BNNTs and subsequent insufficient charge transfer to affect the electrical conductivity of BNNTs. To overcome the insensitivity of BNNTs to NH_3 molecule, Ga/In-doped BNNTs has been proposed foe NH3 detections. The Indium (In) dopant act as absorption sites for NH3 molecule and induce charge transfer between the nanotube and the adsorbed molecule, making the doped BNNTs capable of sensing NH_3. These two proposals represent significant improvements in detecting NH3 gas using in/Ga doped on BNNTs. However, in both proposed methods, the sensitivity that BNNTs can provide is not fully achieved as only a very small portion of atoms on the BNNTs is reactive to NH_3 molecule since the maximum concentration of In dopants that can be reached in BNNTs is around 5% in the first approach and molecule can only be absorbed to highly deformed regions of the BNNTs in the second method. For practical applications, nanotubes with a large active region are highly desired for detecting NH_3 as far as the sensitivity is concerned. Theoretical studies have shown that In/GaNNTs have better reactivity than BNNTs due to their polar nature. For example, In/GaBNNTs show better nitrogen storage performance than BNNTs in that NH_3 molecules can bind to the side walls of In/GaNNTs with larger binding energies than those of BNNTs.Therefore, the objective of this paper is to examine, by first-principles calculations, the possibility of In/Ga-doped BNNTs gas sensors to detect NH3 gas.

Computational methods

For several years CNT has been theoretically studied extensively and intensively, and the first principle of quantum mechanics was usually used in these studies[7]. However BNNT compared with CNT has still been much less studied. Here from our quantum chemical calculation results of the electronic structure, energy band, density of state and bond order, the conductivity and bonding character of BNNT is discussed and compared with CNT.We first optimized the BN SWNT by allowing all the atoms in the supercell to relax without any symmetry constraint. After the relaxation, the puckered cross section of the initial Ga/In doped on SWBNT in Fig. 1a was transformed into a pseudohexagon (see Fig. 1). It is interesting to note that the tubular morphology of this nanotube is fundamentally deferent from the usual tubular forms of carbon and boron nitride (BN) nanotubes. In the outer shell, the more electronegative atoms (N atoms) are pushed radially outward and the more electropositive atoms (Ga atoms) displaced inward. In the inner shell, the opposite phenomenon occurs and the Ga atoms move outward while the N atoms move inward.

The B3LYP method of Density Functional Theory (DFT) was employed for calculations. Because of more correlation energy being included, the calculated results of energy by B3LYP will be better than that by HF(Hartree-Fock). Calculations were carried out at the 3-21G basis set level, which is reasonable and available for such a big system.

RESULTES AND DISCUSSION

Three absorption sites, that is, atop a B atom, at the In atom, Ga atom on the (8,0) BNNTs, as depicted in fig(1), are considered. The NH3 molecule is placed at the respective site initially

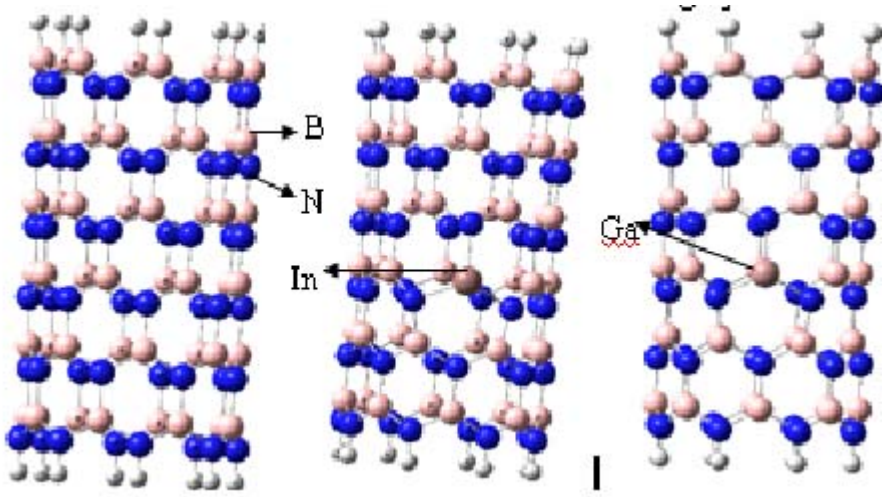

Fig. 1: Absorption sites (B, In, Ga)of NH3 molecule on the (8,0) BNNTs

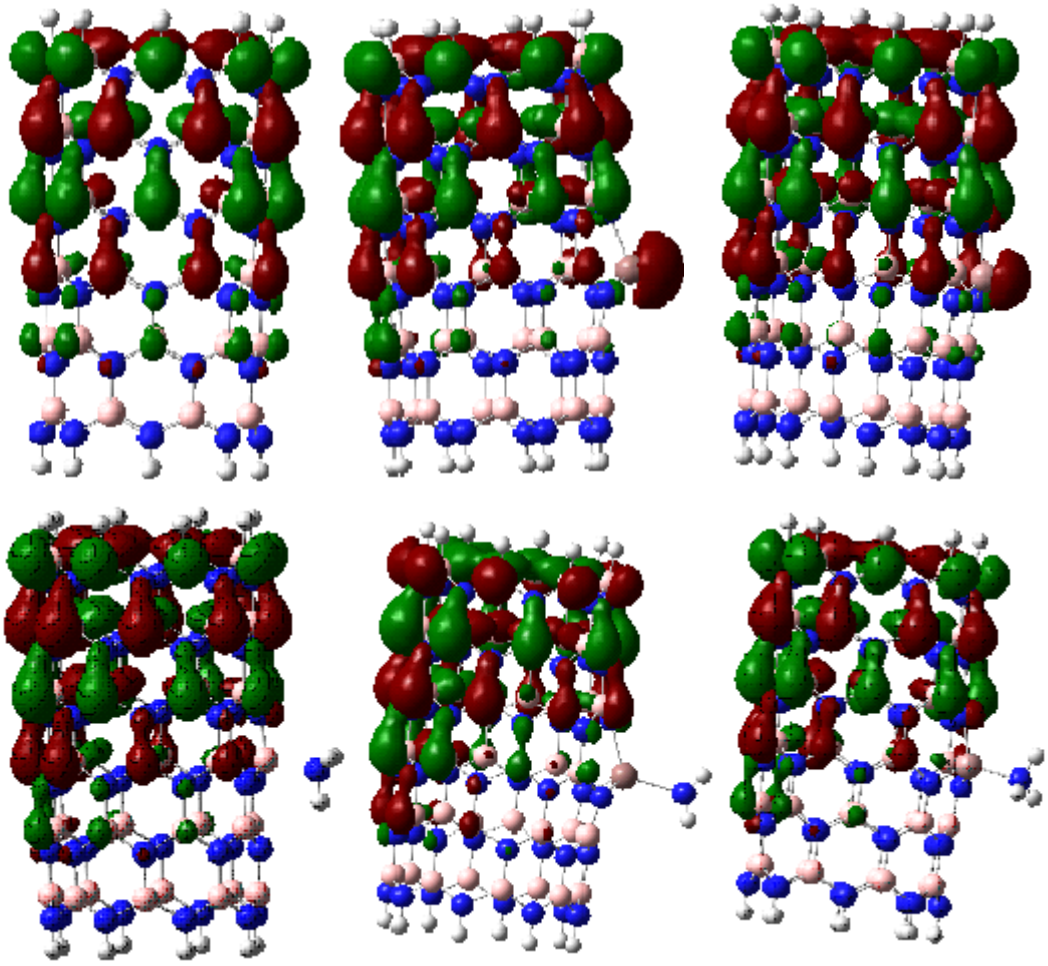

Fig. 2: HOMO and LUMO for different models NH3 adsorption of the Ga/In-doped BNNTs

with its axis norma to one configurations is considered, with either N(referred as the NH3 configuration) closer to the tube wall. All the results are clearly summarized in Table1. The results show that absolute BNNTs cannot detect the NH3 molecule, because it cannot be adsorbed on the pure BN surface. Therefore to solve this problems, we used Ga/In-doped (8,0) BNNTs for the adsorption of the NH3 molecule, because the sensitivity of SWBNNTs can be increased substantially through either doping technology or surface energineering.[8,9,10] The BE of an NH3 on the Ga/In-doped (8,0) BNNTs wall was calculated as follows:

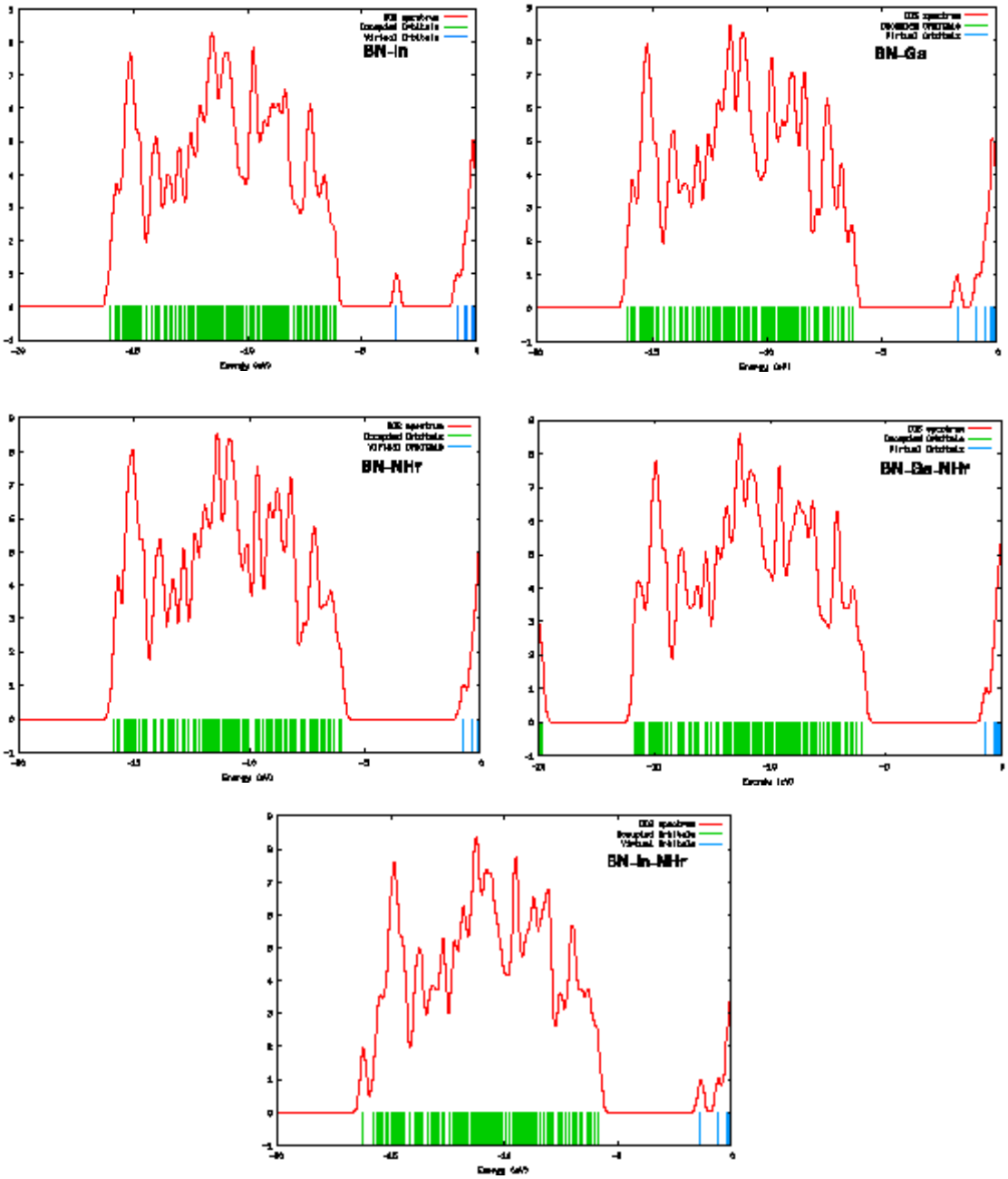

Fig. 3: Total densities states (TDOS) for different models of the adsorption NH_3 on surface In/Ga doped on BNNT

$$BE= E_{BN-NH3}-(E_{BN}+E_{NH3}) \quad ...(1)$$

$$BE= E_{GaBN-NH3}-(E_{GaBN}+E_{NH3}) \quad ...(2)$$

$$BE= E_{InBN-NH3}-(E_{InBN}+E_{NH3}) \quad ...(3)$$

Where E_{BN-NH3} was obtained from the optimization of the potential energy of the BNNT-molecular NH_3 structure, E_{BN} is the energy of the optimized BNNT structure, $E_{GaBN-NH3}$ is the energy of the optimized adsorption NH3 on doped Ga/In on BNNT structure, and E_{NH3} is the energy of an optimized NH3. All the calculations were carried out by ysing the Gaussian 03 suite of programs[11].

Density of state (DOS)

For the first time we investigated the conductivity of Ga/In-doped BNNTs from the viewpoint of DOS distribution. The DOS curves near Fermi energy of Ga/In-doped BNNTs are shown in Fig. 3. It can be seen that the density of state near Fermi energy is very small for BNNT, while it is much bigger for Ga/In-doped on BNNTs. This result means that there are few electrons on highly occupied energy levels of BNN; BNNT is electroconductivity poor. In contrast, for Ga/In-doped BNNTs many electrons occupying high energy levels may easily promote to the conduction band, and makes In/Ga doped display conductivity.

Table 1: Quantum molecular descriptors in representative models NH3 adsorption of the Ga/In-doped (8,0) BNNTs

Parameters	BN	InN	GaN	BN-NH_3	InN-NH_3	GaN-NH_3
BE	-3815.220	-9507.999	-5705.961	0.274	0.234	0.233
EHOMO/ev	-0.229	-0.231	-0.249	-0.205	-0.232	-0.233
ELUMO/ev	-0.010	-0.009	-0.009	-0.006	-0.003	-0.003
[I=-EHOMO]/ev	0.229	0.231	0.249	0.205	0.232	0.233
[A=-ELUMO]/ev	0.010	0.009	0.009	0.006	0.003	0.003
[K=(I-A)/2]/ev	0.109	0.111	0.12	0.099	0.114	0.114
[μ=-(I+A)/2]/ev	-0.119	-0.121	-0.130	-0.152	-0.117	-0.117
[s=1/2K]/ev-1	0.054	0.055	0.06	0.049	0.057	0.057
[w=μ2/2K]ev	0.065	0.067	0.071	0.235	0.123	0.123

I=ionization potential, A=electron affinity, K=Global hardness, ι=chemical potential and w=electrophilicity

CONCLUSIONS

To conclude, we have performed DFT(B3LYP) calculations to study the adsorption of NH3 molecule on Ga/In-doped BNNTs. Our results suggest that NH3can be absorbed on Ga/In-doped BNNTs at In/Ga lattice sites, both with significant binding energies and charge transfer, which could induce significant change in the electrical conductivity of Ga/In-doped BNNTs. Thus, Ga/In-doped on BNNTs are a promising candidate for NH3 detection.

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