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Research Article

PHOSPHINE DETECTION BY ALN NANOTUBE: DFT STUDIES

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ABSTRACT
Electrical sensitivity of an aluminum nitride nanotube (AlNNT) was examined toward Phosphine (PH_3) molecule by using density functional theory (DFT) calculations at the B3LYP/6-31G(d) level of theory, and it was found that the adsorption energy (E_{ad}) of Phosphine on the pristine nanotubes is about -46.3684 kcal/mol. But when nanotube have been doped with Si, S. atoms, the adsorption energy (E_{ad}) and recovery time changed and the sensitivity of the nanotubes as adsorbent of PH_3 molecule was a little decreased but the conductivity of the doped (AlNNT) was increased. Calculations showed that when the nanotube is doping with Si, the adsorption energy will be equal to -12.8574 kcal/mol which leads to a decrease in the recovery time and also, due to doping the nanotube with Si, the amount of HOMO/LUMO energy gap (E_g) reduced significantly. It is seem that nanotube (AlNNT) is a suitable semiconductor after doping, and the doped (AlNNT) in the presence of Phosphine an electrical signal is generating directly and therefore can potentially be used for Phosphine sensors, that nanotube (AlNNT) is suitable adsorbent for PH3 after doping with Si and S atoms

Keywords: *Sensor, Nanotube, DFT, AlNNT, PH_3*

INTRODUCTION
Phosphine is actually a colorless, combustible extremely dangerous gas which has a fishy and also garlic-like odor. Phosphine can be used as being an insecticide for that fumigation of grain, animal feed, and leaf-stored tobacco. Phosphine acts on the central nervous system and lights which leading to pulmonary swelling. Symptoms like faintness, vomiting, headache, Asthma may appear rapidly after exposure. Even a short exposure to a serious volume of Phosphine may cause the chronic neurological problems. It also being recognized that the Phosphine is extremely flammable and even explode when mixed with oxygen. Because of this Reasons phosphine is highly toxic gas and those who work with this material must have safety equipment [U.S. Department of Health and Human Services (1993); U.S. Environmental Protection Agency (1989, 1999); The Merck Index (1989); Amoore and Hautala (1983); and National Institute for Occupational Safety and Health (1997)].
Aluminum nitride is very interesting combination, a mixture of physical, chemical and electro chemical's properties. Properties such as the optical band gap can be large, enhanced field emission, high thermal conductivity also the high thermal conductivity and large electrical resistivity make AlN suitable for advanced nanoscale electronic and optoelectronic device applications, and have motivated sustained efforts to synthesize AlN nanostructures in various morphologies: wires (Haber *et al.*, 1998; Zhang *et al.*, 2001), nanoparticles (Haoa *et al.*, 2002), nanotubes (Tondare *et al.*, 2002), needles (Zhao *et al.*, 2004), and platelets (Tang *et al.*, 2006). While many applications for AlN nanostructures target their use as field emitters in flat panel displays, their superior piezoelectric properties and integration compatibility with silicon substrates make them excellent candidates for sensors, actuators, and nano-electromechanical systems (NEMS) (Cleland *et al.*, 2001; Cimalla *et al.*, 2007). Given the diversity in morphology, cross-section, and size resulting from current synthesis methods (Wu *et al.*, 2003; Yin *et al.*, 2005), the properties of one-dimensional (1D) AlN nanostructures that are important for the fabrication and performance of NEMS, (Stan *et al.*, 2009).
Since the discovery of carbon nanotube (CNT) by Iijima (1991) the properties and applications of this novel material have been investigated extensively (Hummer, 2007; Zhu, *et al.*, 2011; Hung *et al.*, 2004).

CNTs have recently emerged as a promising 2substitute for materials of different properties and various applications in hydrogen storage, gas sensors, textiles and many more (Fam *et al.*, 2011; Cabria, 2006).

MATERIALS AND METHODS

Computational Details

Geometry optimizations, and density of states (DOS) analysis were performed on a (5, 0) zigzag AlNNT (constructed of 30 Al and 30 N atoms), and different PH_3/ AlNNT complexes at B3LYP level of theory with 6-31G (d) basis set as implemented in the GAMESS suite of program (Schmidt *et al.*, 1993). The length and diameter of the optimized pristine AlNNT were computed to be about 21.71 A˚ and 5.28 A˚, respectively. B3LYP is a popular functional that has been commonly used for nanotube structures (Soltani, 2012; Beheshtian *et al.*, 2012; Eid *et al.*, 2012; Eid and Ammar 2011 and Eid and Ammar 2012). Atoms at the open ends of the tube were saturated with hydrogen atoms (10 atoms) to reduce the boundary effects (Figure 1).

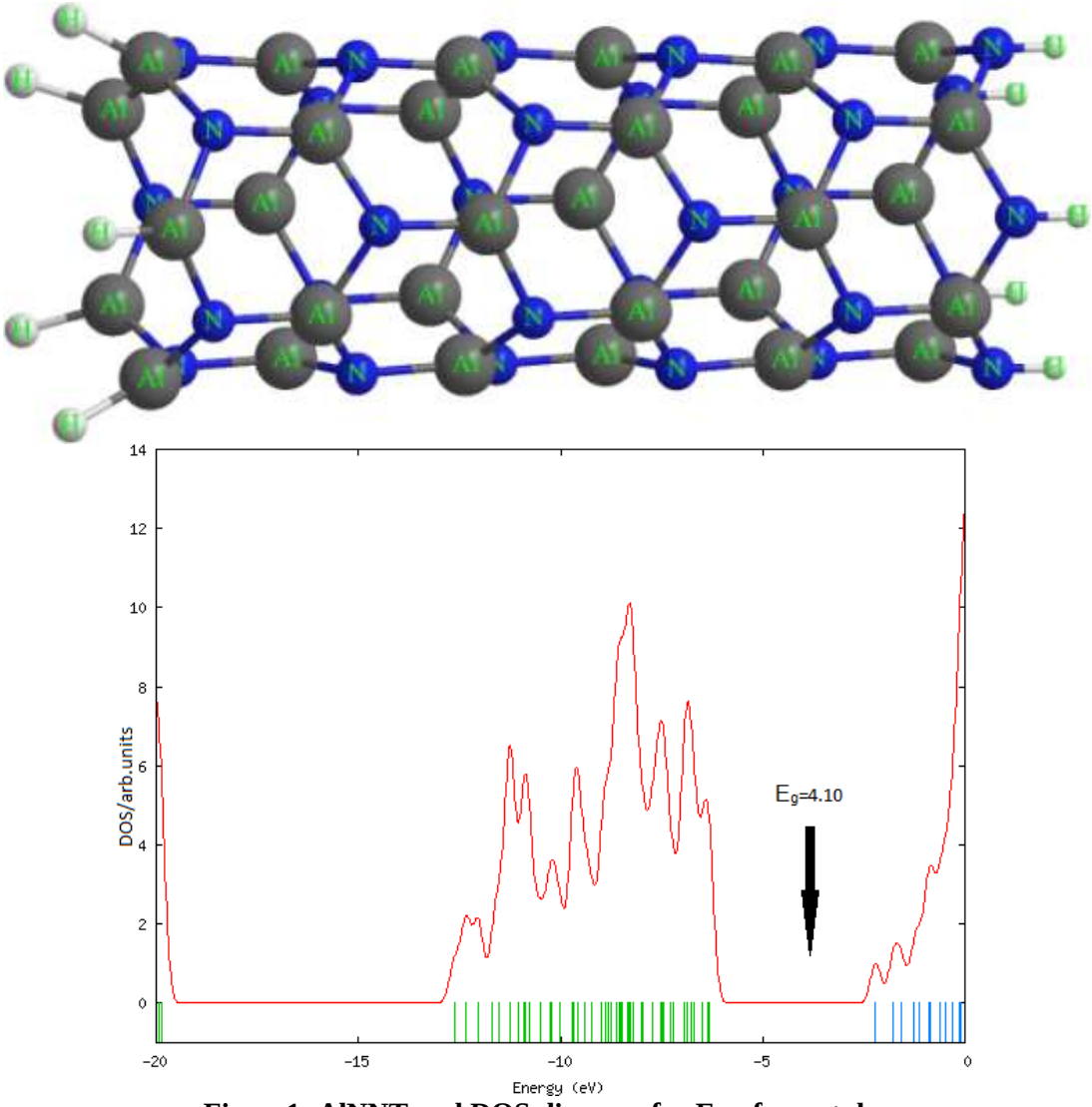

Figure1: AlNNT and DOS diagram for Eg of nanotube

E_{ad} of the PH_3 molecule is defined as follows:

$E_{ad} = E_{PH3 + AlNNT} - [E_{AlNNT} + E_{PH3}] + \delta_{BSSE}$ (1)

Where $E_{PH3 + AlNNT}$ is the total energy of the adsorbed PH_3 molecule on the AlNNT surface, and E_{AlNNT} and E_{PH3} are the total energies of the pristine AlNNT, and the PH3 molecule, respectively. In addition, δ_{BSSE} is representing the basis set super position error. In the following steps Si, S, atoms in the nanotube structure have been doped to examine the Phosphine adsorption on the nanotube and conductivity which is doping with Si, S, atoms.

RESULTS AND DISCUSSION

Figure 1 shows a partial structure of the optimized AlNNT and its DOS plot, indicating that it is considered as a semiconductor with a HOMO/LUMO gap (E_g) of 4.10 eV. It has been already shown that the B3LYP provides an efficient and robust basis for the calculations of semiconductors, capable of reliably predicting both the ground-state energies and the electronic structure. It has been already shown that all zigzag AlNNTs are semiconductors with E_g values ranging from 2.84 to 3.95 eV; it has also shown that E_g slightly increases with increasing the diameter of the tube and saturates at a value corresponding to the gap of an AlN hexagonal sheet. The experimental value of E_g has been reported to be about 6.20 eV, which belongs to bulk AlN. It is noteworthy to mention that DFT underestimates the E_g of semiconductors and molecules, and this aspect must be kept in mind during the following considerations. In order to find energetically stable configurations of a single PH_3 adsorption on the tube, several initial adsorption geometries have been considered, including PH_3 molecule located on an Al or a N atom (perpendicular to the tube surface) and above the center of a hexagonal ring in the tube surface. Interestingly, after optimization, it was found that the molecule becomes parallel to the tube surface.

Adsorption of PH_3 on Si and S Doped AlNNT

To examine the sensitivity of the adsorption of AlNNT of PH_3 as an adsorbent for PH_3 its examining has been done two times, once Al atom doped by Si atom and other time N atom by Si atom has been doped. Doped calculation of Si on AlNNT shows that value of E_g is less than pristine nanotube (Figure 2 & 3).

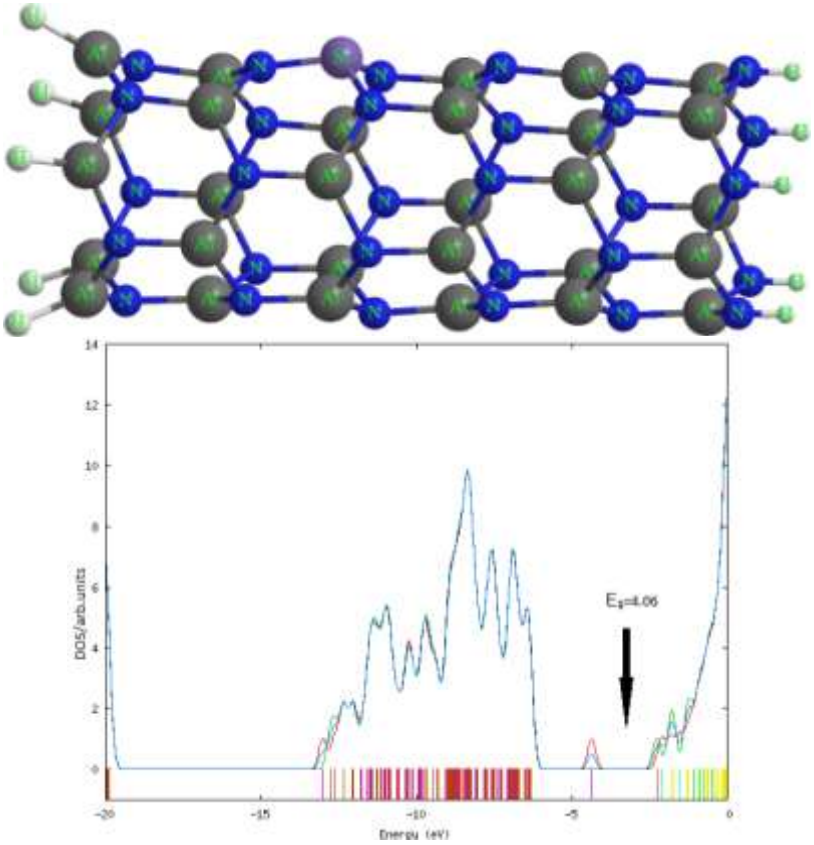

Figure 2: Doped nanotube by Si and DOS diagram for observing Eg nanotube

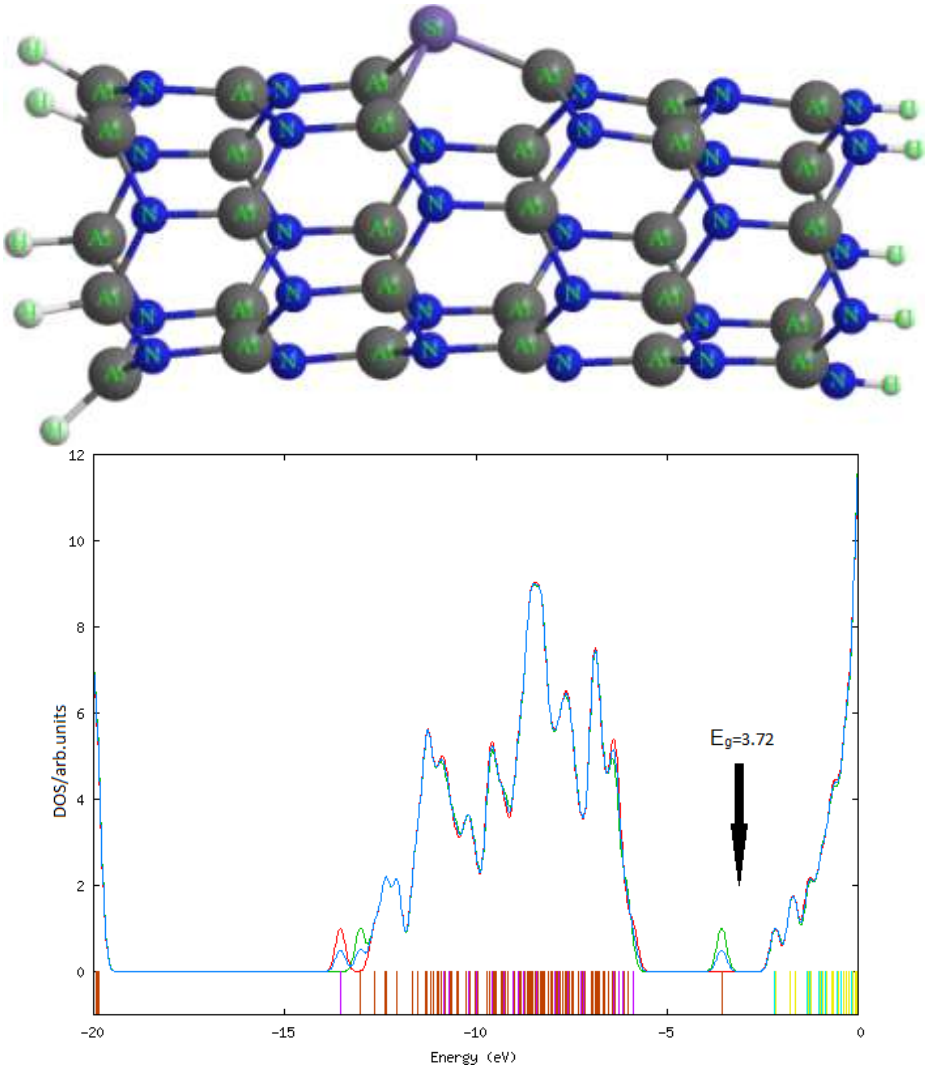

Figure 3: Doped nanotube by Si and DOS diagram for observing Eg nanotube

And the best adsorption energy (E_{ad}) is obtained when Si the usage sitting instead of Al and Phosphine has been adsorbed 49.80 eV. DOS diagram clearly shows that when Si is doped on the AlNNT it will become a semiconductor (E_g=4.06) (Table 1).

Table1: Ead (kcal/mol), eV for the others

System	E_{ad}	E_{HOMO}	E_{LUMO}	E_g	*ΔE_g (%)
AlNNT	**–**	**-6.31**	**-2.21**	**4.10**	**-**
P-AlNNT	-46.40	-6.16	-2.03	4.13	+0.73
S-Al	–	-5.77	-2.37	3.40	-
P-S-Al	-36.50	-5.01	-2.22	2.79	-17.94
S-N	–	-6.26	-2.34	3.92	-
P-S-N	-37.90	-6.29	-2.39	3.90	-0.51
Si-Al	–	-6.33	-2.27	4.06	-
P-Si-Al	-49.80	-6.19	-2.16	4.03	-0.74
Si-N	–	-5.89	-2.17	3.72	-
P-Si-N	-12.90	-5.68	-2.09	3.59	-3.50

When S doping on AlNNT is the presence of phosphine the value of adsorption energy is a according the range of -36.50-37.90 [At this stage to examine the sensitivity of the adsorption of AlNNT of PH_3 as an adsorbent for PH_3 once Al atom by an S atom and other N atom by an S atom is doped.] and the value of HOMO/LUMO energy gap (Eg) … is a according the range of 2.79-3.90 then the AlNNT doped with S is not a suitable adsorbent as pristine Nanotube for ph3 molecule The calculation shows that the amount of the E_g for the doped is less than pristine nanotube (Figure 4 & 5).

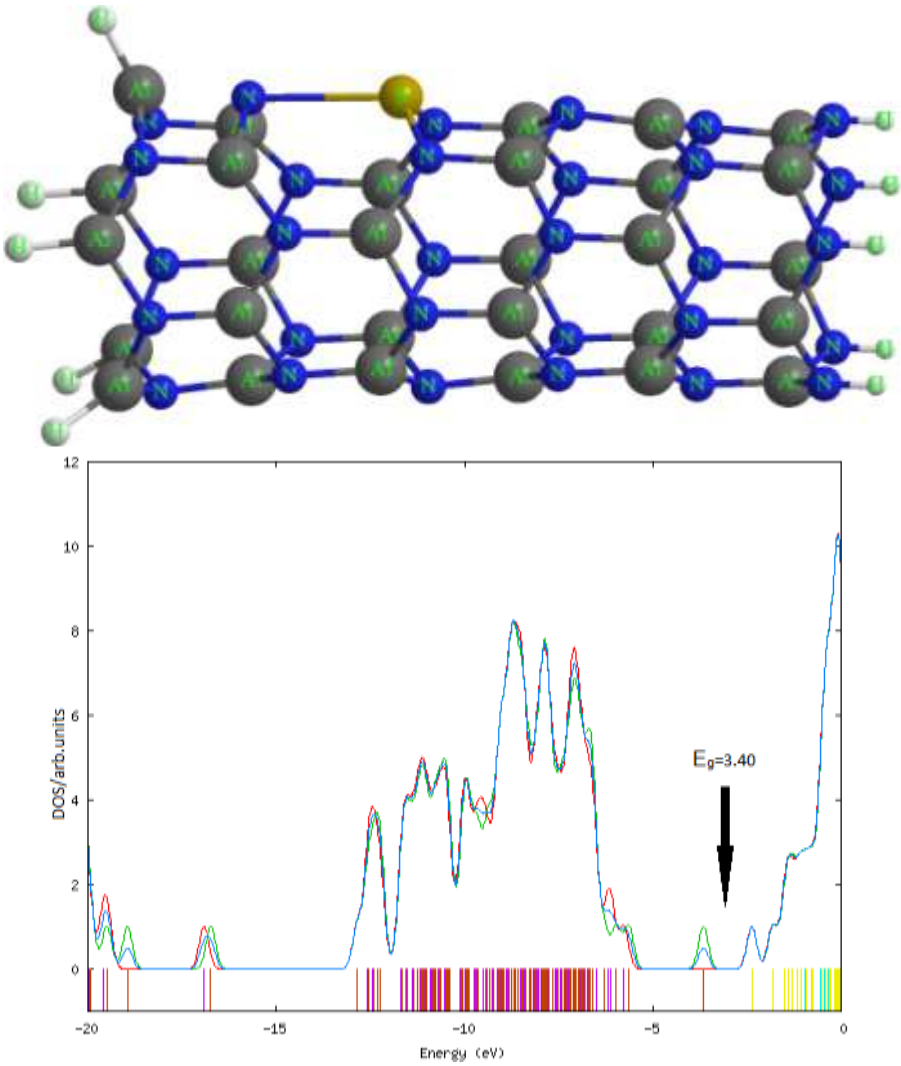

Figure 4: Doped nanotube by S and DOS diagram for observing Eg nanotube

DOS diagram clearly shows that when S doped on the AlNNT is a semiconductor, the doped AlNNT is not as suitable adsorbent as pristine AlNNT for Phosphine molecule (Table 1). If E_g is significantly increased then it is expected that recovery time will be long, meanwhile according to transition state theory and recovery time can be explain as Eq. (2)

$$\tau = \upsilon_0^{-1} \exp(-E_{ad}/kT) \quad (2)$$

Where T is the temperature, k is the Boltzmann's constant, and υ_0 is the attempt frequency. According to this equation as often as adsorption energy (E_{ad}) is increasing the recovery time becomes longer and calculation in Table 1 shows that the recovery time and adsorption energy has suitable level.

Computations showed that when Si is replaced by Al in AlNNT the E_g will become more (Figure 2) when Si is sitting instead of N, and the adsorption energy of Phosphine on nanotube is less than when we just use the pristine nanotube (not doped). After adsorption of PH_3 on the mentioned nanotube that has been doped by Si the HOMO/LUMO energy gap (Eg) will decrease and therefore a substantial increase will occur in conductivity and this phenomenon can be explained by Eq. (3), (Beheshtian *et al.*, 2012)

$$\sigma \propto \exp(-E_g/2kT) \quad (3)$$

Where σ is conductance, T is temperature, k is Boltzmann constant. According to this equation as often as E_g is smaller it leads the conductivity to be more it can be concluded that when S is doping on AlNNT, we think that the AlNNT can be used as semiconductor, and by doping atoms in AlNNT structure in the presence of Phosphine an electrical signal is generating directly and therefore can potentially be used for Phosphine sensors, also the results show AlNNT is a suitable adsorbent for Phosphine

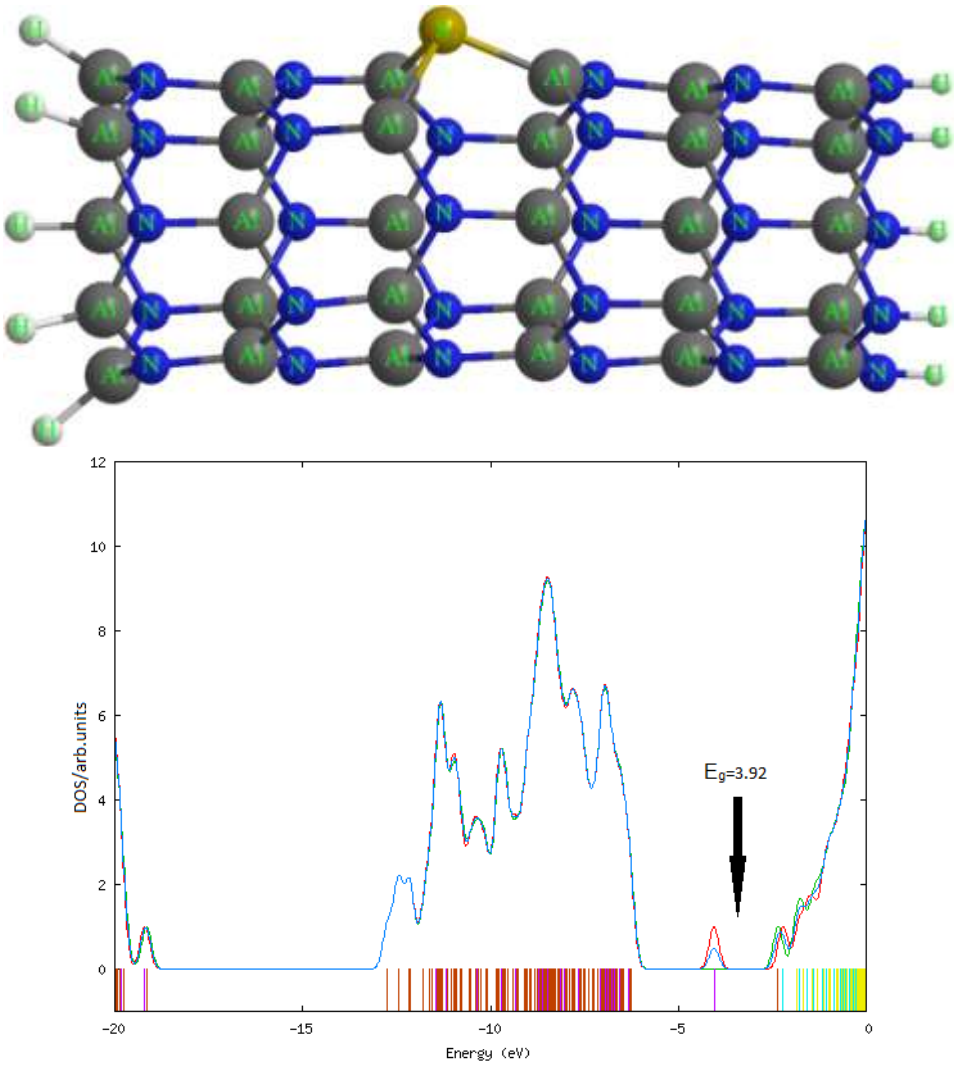

Figure 5: Doped nanotube by S and DOS diagram for observing Eg nanotube

Conclusion

The adsorption of Phosphine (PH_3) molecules on the surface of AlNNT (aluminum nitride nanotube) has been studied by using density functional theory (DFT) and then we doped the Si, S, atoms in the structure

of the nanotube, the results show it is clearly possible to modify nanotubes as a semiconductor and the doped AlNNT in the presence of Phosphine, an electrical signal is generated directly and therefore can potentially be used for Phosphine sensors.

Results show doped AlNNT with Si, atom is as suitable adsorbent as AlNNT for Phosphine. These results maybe open a new gate to chemically modifying the nanotubes in a way to expand the fields of their applications in industry and technology.

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