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Research Article

PROPANOL DETECTION BY AlN NANOTUBE: DFT STUDIES

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ABSTRACT
The adsorption behavior of 1-propanol molecule with external surface of (5, 0), zigzag aluminum nitride nanotube (AlNNT) was studied by using density functional calculation, and it was found that the adsorption energy (E_{ad}) of 1-propanol on the surface of pristine nanotubes is about -27.92 kcal/mol. However when nanotubes have been doped with P,Si atoms, the adsorption energy of 1-propanol (E_{ad}) and recovery time changed and the sensitivity of the nanotubes as adsorbent of 1- propanol molecule was a little decreased. Calculation showed when the nanotube is doped by Si, the adsorption energy range is about -4.09 to -13.94 kcal/mol, and the amount of HOMO/LUMO energy gap (E_g) will reduce significantly. It is seem that nanotube (AlNNT) is a suitable semiconductor after doping, and the doped (AlNNT) in the presence of 1-Propanol electrical signal is generating directly and therefore can potentially be used for 1- Propanol sensors, that nanotube (AlNNT) is not suitable adsorbent for1-propanol after doping with Si and P atoms.

Keywords: *Sensor, Nanotube, DFT, AlNNT, 1-propanol*

INTRODUCTION
1-Propanol is a suitable model system for the study of conformational isomerism with small energy differences (Tobis *et al.*, 2012). 1-Propanol is well known as a common solvent used in chemical, pharmaceutical and cosmetic industry, also as an important compound in basic biochemical research (Michniewicz *et al.*, 2008). Concluded that 1-propanols narcotic effects are stronger than those of ethanol, but that its low volatility would not make it dangerous to humans following inhalation exposures. Occupational exposure standards of 200 ppm (time weighted averages) have been established by the occupational safety and health administration and recommended by the American conference of governmental industrial hygienists (Nelson *et al.*, 1989). 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.*, 1989; 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).

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 $CH_3CH_2CH_2OH$/ 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 *et al.*, 2012; Beheshtian *et al.*, 2012; Eid and Ammar, 2012; Eid and Ammar, 2011; Eid *et al.*, 2012). Atoms at the open ends of the tube were saturated with hydrogen atoms (10 atoms) to reduce the boundary effects (Figure 1).

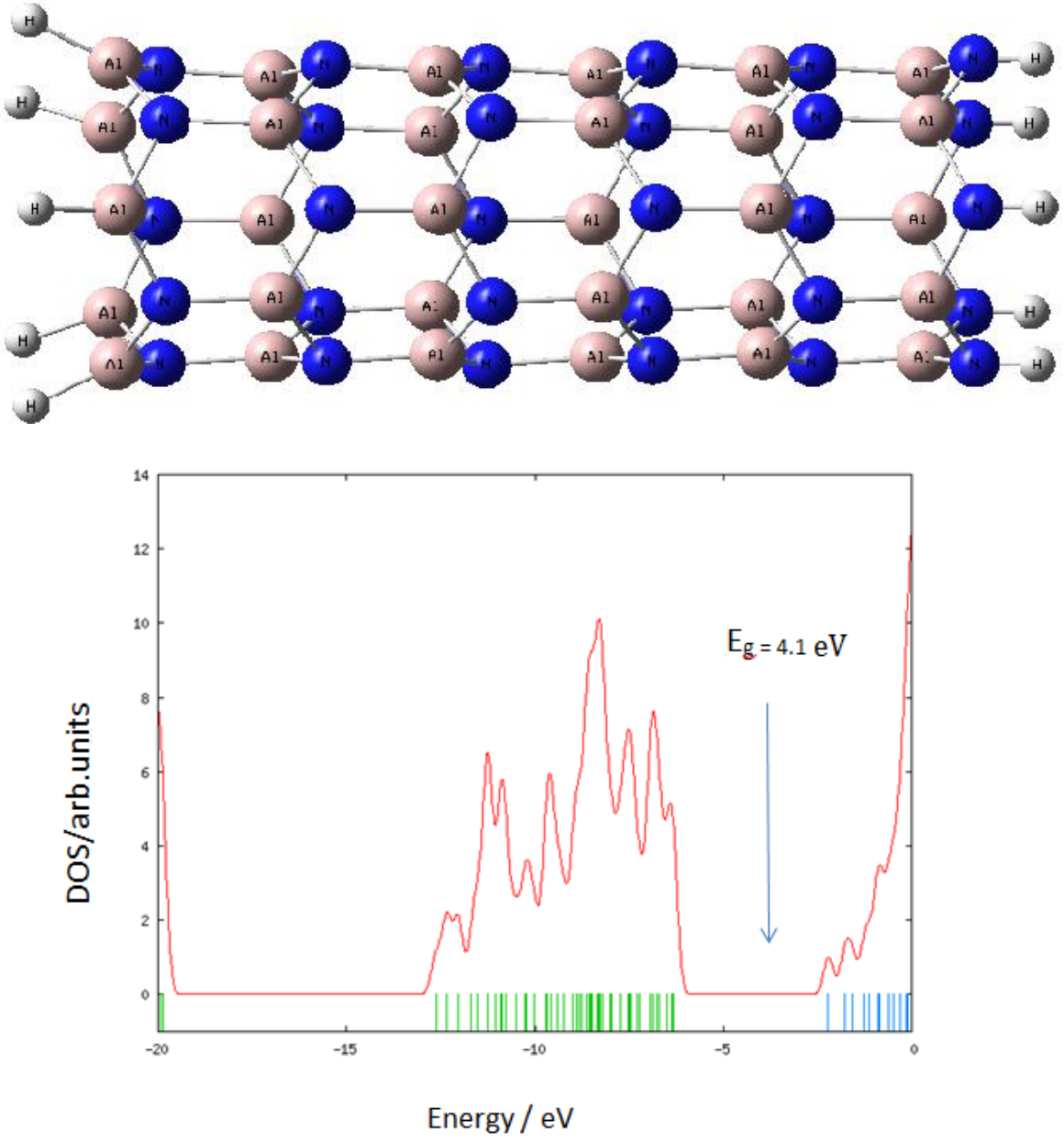

Figure 1: AlNNT and DOS diagram for E_g of nanotube

E_{ad} of the 1-Propanol molecule is defined as follows:

$$E_{ad} = E_{CH3CH2CH2OH + AlNNT} - [E_{AlNNT} + E_{CH3CH2CH2OH}] + \delta_{BSSE} \quad (1)$$

Where $E_{CH3CH2CH2OH + AlNNT}$ is the total energy of the adsorbed $CH_3CH_2CH_2OH$ molecule on the AlNNT surface, and E_{AlNNT} and $E_{CH3CH2CH2OH}$ are the total energies of the pristine AlNNT, and the 1-propanol molecule, respectively. In addition, δ_{BSSE} is representing the basis set super position error. In the following steps Si, P, atoms in the nanotube structure have been doped to examine the 1-Propanol adsorption on the nanotube and conductivity which has been doped with Si, P, atoms.

RESULTS AND DISCUSSION

Figure 1 shows a partial structure of the optimized AlNNT and its DOS diagram, indicating that it is considered as a semiconductor with a HOMO/LUMO gap (E_g) of 4.1 eV.

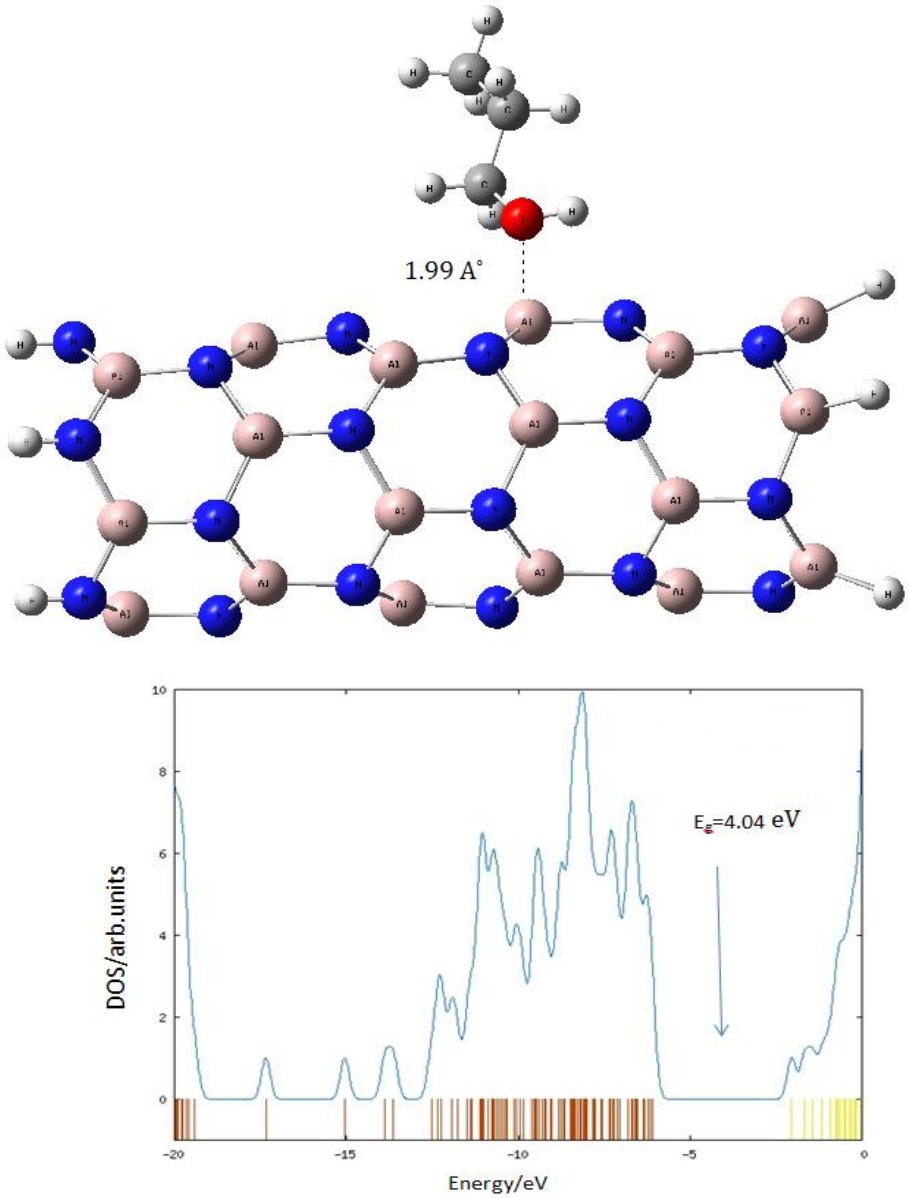

Figure 2: 1- Propanol adsorption on the AlNNT and DOS diagram for observing E_g of nanotube. Distance is in A˚

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 $CH_3CH_2CH_2OH$ adsorption on the tube ,E_{ad} = -27.92kcal/mol and E_g = 4.04eV (Figure 2) several initial adsorption geometries have been considered, including $CH_3CH_2CH_2OH$ 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.

Adsorption of $CH_3CH_2CH_2OH$ on Si and P Doped AlNNT

To sensitivity of the adsorption of 1-propanol on on surface of AlNNT has been examined twice, once with Al atom doped by Si atom and in the other 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 3 & 4).

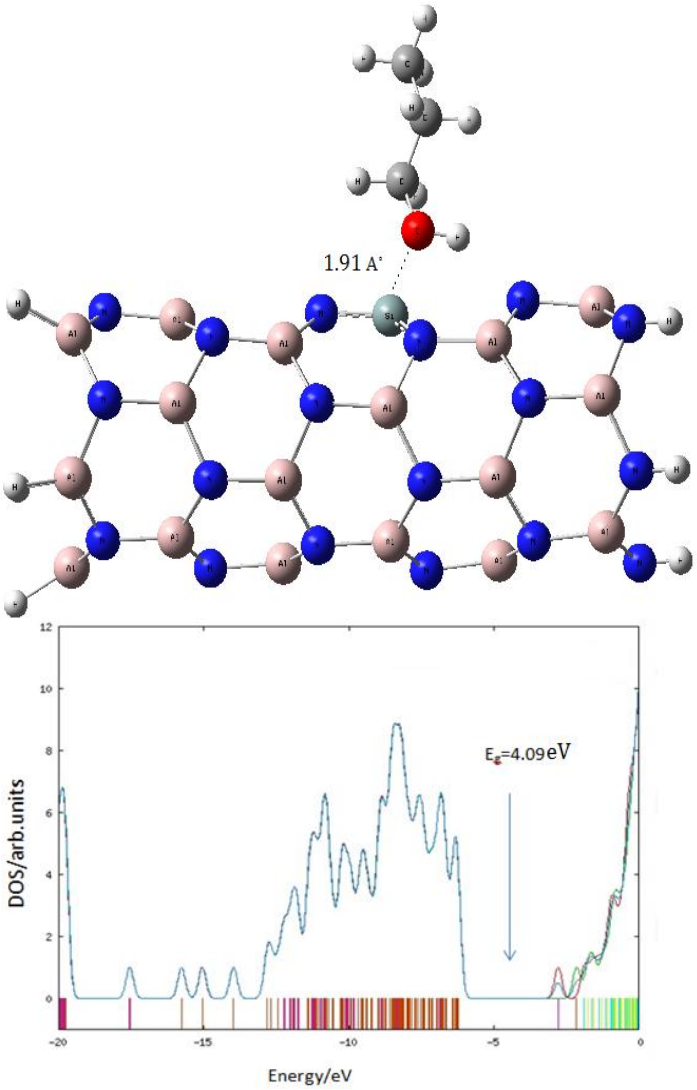

Figure 3: 1-Propanol adsorption on Doped nanotube by Si_{Al} and DOS diagram for observing E_g nanotube. Distance is in A°

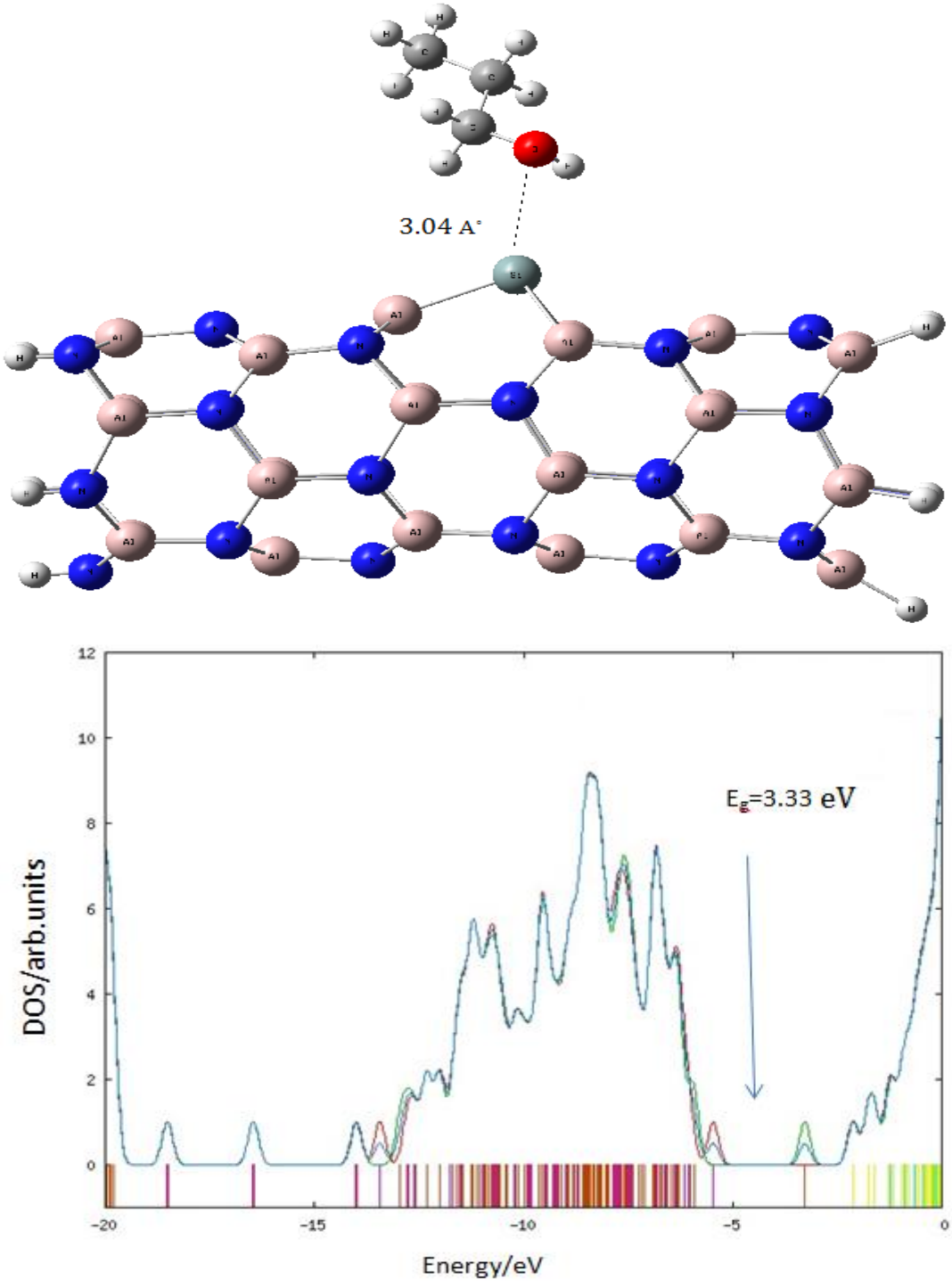

Figure 4: 1-Propanol adsorption on doped nanotube by Si_N and DOS diagram for observing of E_g nanotube. Distance is in A°

The best adsorption energy (E_{ad}) is obtained when Si the usage sitting instead of Al and 1- Propanol has been adsorbed -13.94 kcal/mol.
DOS diagram clearly shows that when Si is doped on the AlNNT it will become a semiconductor E_g=3.33 - 4.09eV (Table 1).

Table 1: E_{ad} (kcal/mol),eV for the others

System	E_{ad}	E_{HOMO}	E_{LUMO}	E_g
AlNNT	-	**-6.31**	**-2.21**	4.10
AlNNT/$CH_3CH_2CH_2OH$	**-27.92**	**-6.90**	**-2.50**	4.04
AlNNT/P_N	-	**-6.33**	**-2.21**	4.12
AlNNT/P_N- $CH_3CH_2CH_2OH$	**-11.78**	**-5.02**	**-1.97**	3.05
AlNNT/P_{Al}	-	**-5.21**	**-2.15**	3.12
AlNNT/P_{Al}- $CH_3CH_2CH_2OH$	**-11.79**	**-6.03**	**-2.04**	3.99
AlNNT/Si_N	-	**-5.89**	**-2.17**	3.72
AlNNT/Si_N- $CH_3CH_2CH_2OH$	**-4.09**	**-5.46**	**-2.14**	3.33
AlNNT/Si_{Al}	-	**-4.35**	**-2.09**	2.26
AlNNT/Si_{Al}- $CH_3CH_2CH_2OH$	**-13.94**	**-6.24**	**-2.14**	4.09

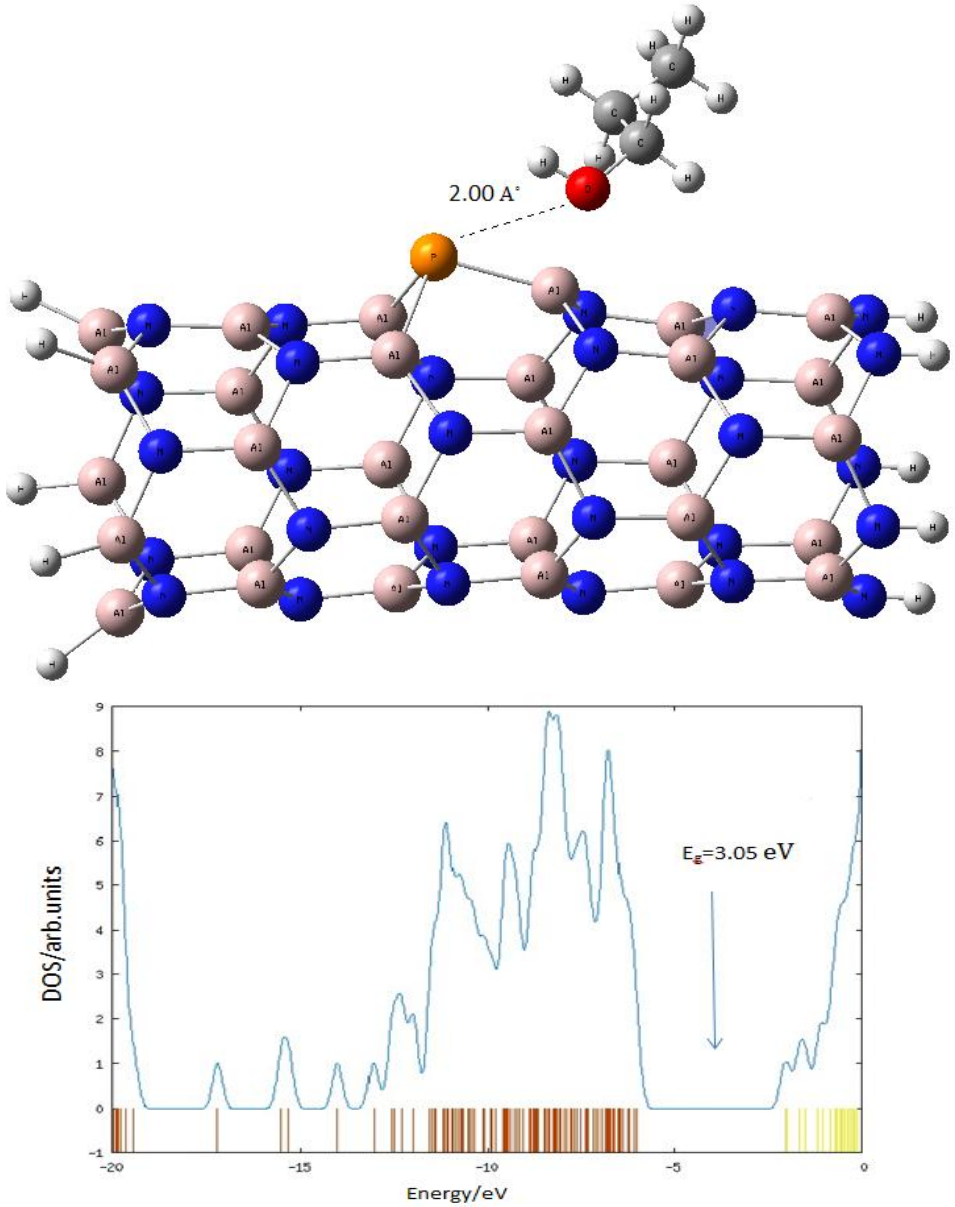

Figure 5: 1-Propanol adsorption on doped nanotube by PN and DOS diagram for observing E_g nanotube. Distance is in A°

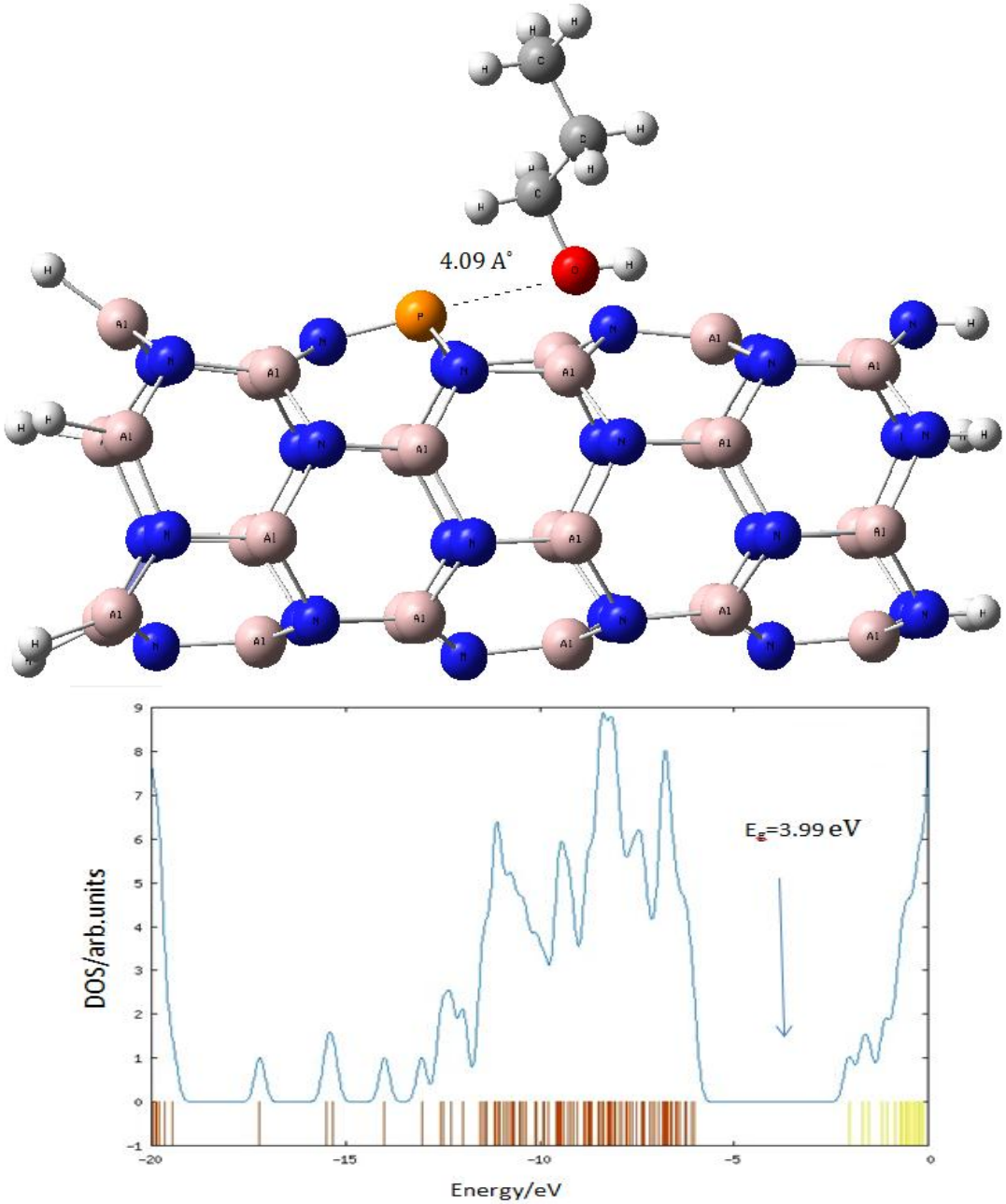

Figure 6: 1-Propanol adsorption on doped nanotube by P_{Al} and DOS diagram for observing E_g nanotube. Distance is in A°

At this stage the sensitivity of the adsorption examine twice, once Al atom doped by P and other N atom by a P is doped. When P doped in AlNNT the adsorption energy range is -11.78-11.79kcal/mol and this range is lower than pristine nanotube so the AlNNT doped by P is not better than pristine AlNNT for adsorption of 1-propanol molecule. The value of HOMO/LUMO energy gap (E_g) is a according the range of 3.05-3.99eV (Figure 5 & 6).

DOS diagram clearly shows that when P doped on the AlNNT is a semiconductor, the doped AlNNT is not as suitable adsorbent as pristine AlNNT for 1-Propanol 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)

$\tau = \upsilon_0^{-1} \exp(-E_{ad}/kT)$ (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=}$4.09ev will become more than (Figure 3) when Si is sitting instead of N, E_g=3.33ev and the adsorption energy of 1- Propanol on nanotube is less than when we just use the pristine nanotube (not doped). After adsorption of 1-propanol on the mentioned nanotube that has been doped by Si the HOMO/LUMO energy gap (E_g) will decrease and therefore a substantial increase will occur in conductivity and this phenomenon can be explained by Eq. (3), (Beheshtian *et al.*, 2012).

$\sigma \exp(-E_g/2kT)$ (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 Si 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 1-Propanol an electrical signal is generating directly and therefore can potentially be used for 1- Propanol sensors, also the results show the AlNNT doped by Si is not a suitable adsorbent for 1-Propanol.

Conclusion

DFT calculations were employed to investigate the adsorption of 1-propanol molecule on the exterior resurface of AlNNT ,when we doped the Si and P, 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 1-propanol, an electrical signal is generated directly and therefore can potentially be used for 1-Propanol sensors. Results show doped AlNNT with Si, P atoms are not as suitable adsorbent for 1- propanol. These results may open new doors to chemically modified nanotubes thereby expanding their applications in industry and technology.

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