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ADSORPTION OF CARBON MONOXIDE GAS MOLECULE ON INDIUM PHOSPHIDE NANOWIRE SURFACE

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Abstract

In this study, the adsorption of a carbon monoxide (CO) gas molecule on the surface of hydrogen passivated indium phosphide nanowire with a diameter of 1.5 nanometers along the [111] direction is investigated using density functional theory. The equilibrium state energies and electronic band structures of the system consisting of nanowire and gas molecule are calculated and the adsorption energy is determined. The results show that the InP nanowires can adsorb the CO gas molecule and they have the potential to be used in small size gas sensors.

Keywords: Nanowires, nanowire sensors, gas adsorption, gas sensors

INTRODUCTION

Nanomaterials are structures with large surface areas and high surface-to-volume ratios that exhibit unique properties due to the effects of quantum phenomena, sized between 1-100 nm [1]. One of these materials is nanowires (NWs), known as one-dimensional materials with diameters of a few nanometers. Nanowires have attracted great interest in recent years from the fields of nanotechnology and materials science, enabling significant applications in many areas such as electronics, optoelectronics, energy storage, and biotechnology [2-6]. Nanowires formed from group III-V, II-VI and IV semiconductor materials are known as semiconductor nanowires. These structures play an extremely important role in electronic applications such as field effect transistörs (FETs), light emitting diodes (LED), photovoltaic cells, logic gates, and sensors.

Recent developments in nanotechnology offer many opportunities for using nanowires as sensors. It stands out with advantages such as having a high surface to volume ratio and low power consumption [7]. Schottky contact nanowire sensors are also used in many applications such as gas sensors, biochemical sensors, strain sensors and photodetectors. These sensors are highly sensitive and have fast response times [8]. Detection of chemical and biological species is important for the recognition of harmful substrances. Progress has been made in chemical and biological sensors with innovations in nanowire production and receptor integration on the nanowire surface [9]. In addition, Silicon nanowire field effect transistor sensors are used to detect viruses, nucleotide sequences and proteins [10]. Polymeric nanowires can also detect NH_3 gas at low concentrations using their sensor properties [11]. Nanowire sensors also stand out with studies in the medical field. It is used in applications such as biomarkers and detection of DNA and the identification of cancer-related analytes [12, 13].

Toxic gases at room temperature are of great concern to public health and safety. Detection of these gases, which are harmful to the environment and humans, is extremely important because they are colourless and odourless. Nanowire sensors can detect the presence of gas molecules thanks to the adsorption properties on their surface. Accordingly, many studies have been carried out on the adsorption of toxic gases and measuring air pollution levels. It has been reported that Si nanowires, a well-

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known semiconductor, can be used as biological and chemical sensors. It has been experimentally shown that Si nanowires have the potential to be used as a gas sensor that can detect NH_3 molecules and cigarette smoke [14]. In another study, the responses of InAs nanowire sensor-based devices to various gas molecules and alcohol vapour have been investigated. It has been observed that gas molecules can change the electron density and electron mobility in nanowires [15]. In the study conducted to investigate the adsorption of H_2O, H_2 and CH_4 gas molecules on wurtzite GaAs nanowires, it has been determined that the GaAs nanowire surface is prone to polar gas molecules. Also, band gap, work function and surface electron affinity increase have been determined [16].

In this study, the capability of a 1.5 nm diameter InP semiconductor nanowire, passivated with hydrogen on its surface, to adsorb CO gas molecules has been investigated using density functional theory.

CALCULATION DETAIL

The calculations have been carried out using the Quantum Espresso Program code packed based on density functional theory [17]. For the exchange-correlation potential, the Generalized Gradient Approximation (GGA) has been used, considering the electron-ion interactions described by Perdew, Burke and Ernzerhof (PBE) [18]. Monkhorst–Pack special k-points, equivalent to the 1 × 1 × 6 mesh, are taken for Brillouin zone integration [19]. The cutoff energy value is 612 eV for the plane wave basis set. All atom positions within the nanowire are relaxed until the forces are less than 0.025 eV/Å, and the optimum nanowire geometry is obtained.

As a first step, a nanowire with a diameter of 1.5 nanometers has been formed along the [111] direction from the optimized Zinc blende (ZB) Indium phosphide (InP) bulk structure. The zinc blende indium phosphide lattice constant a = 6.01 Å has been obtained, and it is seen that this value is consistent with previous studies [20, 21]. The nanowire surface has been passivated with hydrogen atoms to eliminate the bands caused by dangling bonds in the nanowire's band gap and to achieve a cleaner band gap. The unit cell of the InP nanowire passivated with hydrogen atoms is shown in Fig. 1.

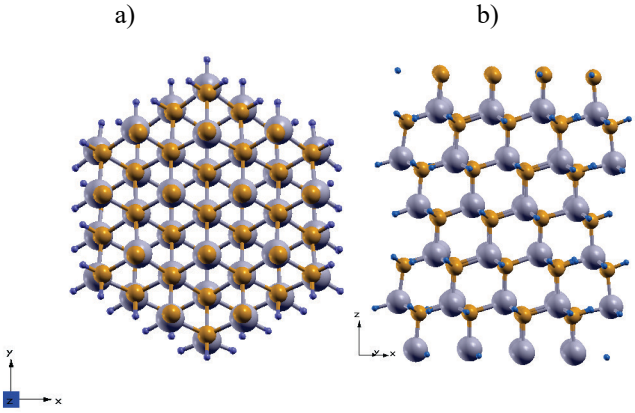

Fig. 1. *H-Passived InP nanowire a) top view, b) side view (grey spheres: Indium atoms, yellow spheres: Phosphide atoms and blue spheres: Hydrogen atoms)*

While the InP nanowire models continue along the z-direction under periodic boundary conditions, 20Å long space has been placed between them in the x and y directions to prevent interaction between neighbouring nanowires.

In order to adsorb CO gas molecule on the surface of H-Passived InP nanowire, a dangling bond is formed by removing a hydrogen atom bonded to the phosphide atom on the surface and this is shown in Fig. 2. Thus, a suitable surface structure has been tried to be prepared for the formation of the adsorption state of a gas molecule close to the nanowire surface.

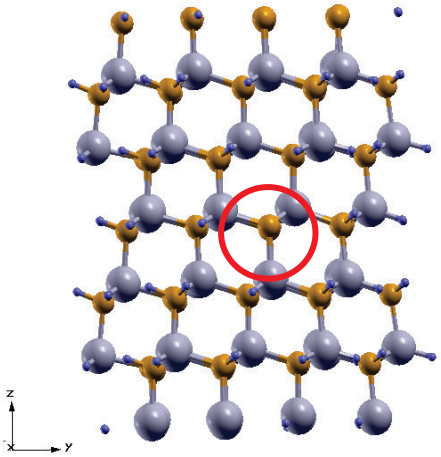

Fig. 2. *H-Passived dangling bonded (one hydrogen atom removed) InP nanowire. (grey spheres: Indium atoms, yellow spheres: Phosphide atoms and blue spheres: Hydrogen atoms)*

Before bringing the carbon monoxide molecule close to the nanowire surface, energy minimization has been performed to obtain the optimized molecular structure shown in Fig. 3. As a result of the optimization, the bond length between the carbon and oxygen atoms has been determined to be 1.14 Å.

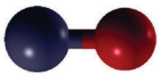

Fig. 3. *CO molecule (Red sphere: Oxygen atom, dark grey: Carbon atom)*

The CO molecule has been got close to the InP nanowire surface in two ways, from the Carbon site, and the Oxygen site. Energy calculations have been made separately for both cases, and the obtained atomic structures of the modelled nanowire-molecule pair are shown in Fig. 4. and Fig. 5.

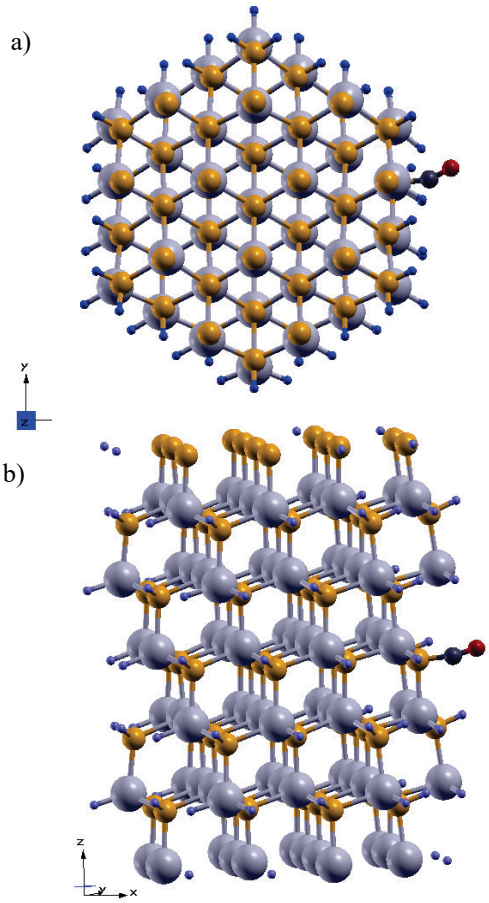

Fig. 4. *CO gas molecule adsorption state of dangling bonded H-passivated InP nanowire (from Carbon site) a) top view, b) side view. (red sphere: Oxygen atom, dark grey: Carbon atom, grey spheres: Indium atoms, yellow spheres: Phosphide atoms and blue spheres: Hydrogen atoms)*

It is easily seen from Fig. 4. that the CO molecule binds with the dangling bonded phosphate atom of the nanowire and is adsorbed on the InP nanowire surface. The bond length between the Carbon atom of the adsorbed CO molecule and the phosphide atom of the nanowire has been found to be 1.739 Å. The adsorption energy of the CO molecule can be easily calculated with the equation (1).

$$E_{ads} = E(NW_{DB}) + E(Mol) - E(NW_{DB} + Mol) \quad (1)$$

Where E(NWDB + Mole) is the total energy of an NW cell containing an adsorbed molecule, E(NWDB) is the total energy of an NW cell with a dangling bond (DB) and E(Mole) is the total energy of the free molecule.

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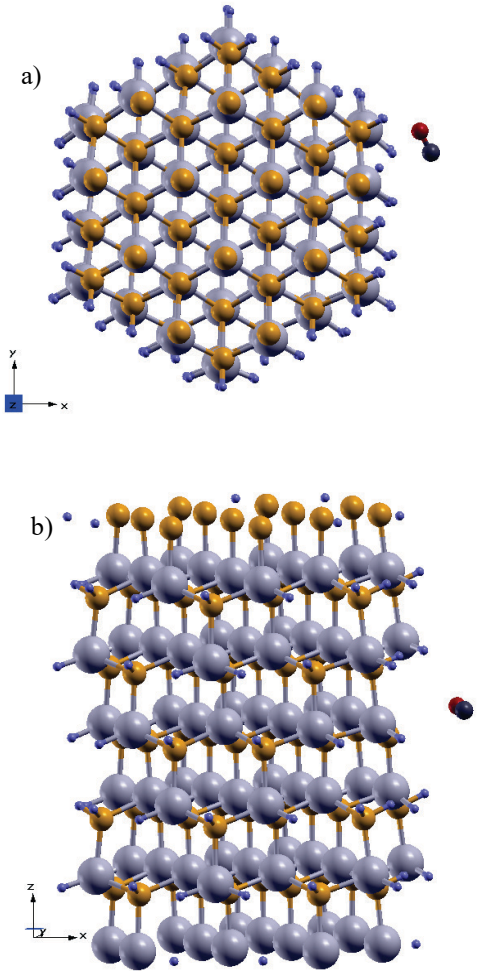

Fig. 5. *CO gas molecule adsorption state of dangling bonded H-passivated InP nanowire (from Oxygen site) a) top view, b) side view. (Red sphere: Oxygen atom, dark grey*: Carbon *atom, (grey spheres: Indium atoms, yellow spheres: Phosphide atoms and blue spheres: Hydrogen atoms)*

In the other case shown in Fig. 5, it is seen that no bond is formed between carbon and phosphite atoms and the CO molecule moves away from the nanowire surface.

RESULTS

As a result of the optimization study of the CO gas molecule considered for adsorption, the bond length between C and O atoms is 1.14 Å. The lattice constant of the Zinc Blende InP bulk structure has been determined as a = 6.01 Å. As a result of the calculations, it has been seen that the InP nanowire can adsorb the CO gas molecule from the Carbon site. Furthermore, the adsorption energy for the CO molecule has been calculated as E_{ads} = 0.269 eV using the expression given in Equation 1. However, when the CO molecule has been brought from the oxygen side of the molecule to the region of the nanowire surface where the dangling bond is located, it has been observed that is not realised adsorption and moves away from the nanowire surface. To see the electronic band structures, energy-band diagrams have been calculated.

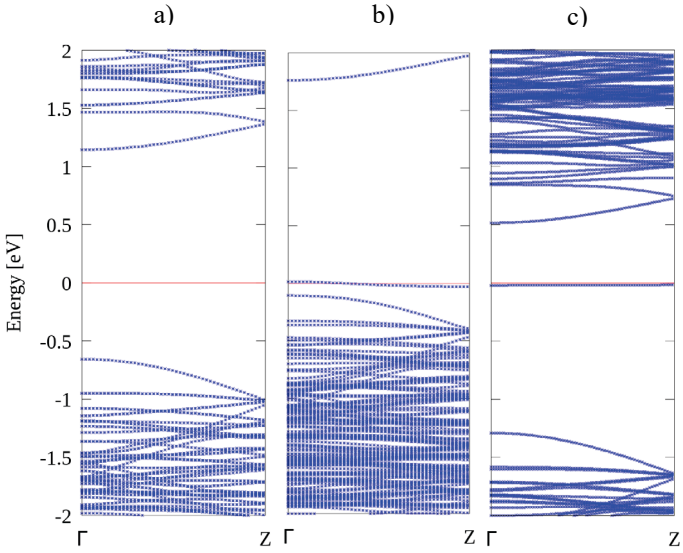

Fig. 6. *Energy band diagrams of a) H-passived b) dangling bonded H-passived and c) CO adsorbed H-passived InP nanowires.*

The electronic band structures of H-passivated, dangling bonded H-passivated and CO-adsorbed H-passivated InP nanowires have been given in Fig. 6.a, b and c, respectively. Here, the Fermi energies for all three cases are set to zero point. In Fig. 6.a, the band gap is very clear and distinct due to the nanowire not having

any dangling bond and, is determined to be approximately 1.9 eV. In Fig. 6.b, the Fermi energy is near the valence band maximum (VBM) and, a band due to the dangling bond localised just above it is observed. In addition, the conduction band minimum (CBM) and the valence band maximum show an upward shift according to Fig. 6.a.. In Fig. 6.c, it can be seen that VBM and CBM have shifted further downwards compared to Fig. 6.a and Fig. 6.b. Besides, the band almost on the Fermi energy level, thought to be the contribution of the CO molecule, is noteworthy. This shows us that the energy band states can be changed with the atomic structures bonded to the nanowire surface. By considering different molecules and nanowire materials, new nanowire structures sensitive to various molecules can be obtained. This can significantly contribute to the development of nanowire-based sensors.

CONCLUSION

A first-principles study of a carbon monoxide gas molecule of adsorption to the surface on a hydrogen passivated InP nanowire along the [111] direction with a diameter of 1.5 nm is reported. Our results show that InP nanowires can adsorb CO gas molecules from the Carbon site. This suggests that InP nanowires may have potential in the fabrication of smaller-sized CO gas sensors.

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