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Full Length Article

Adsorption of gas molecules on graphene-like InN monolayer: A first-principle study

Xiang Sun[a,b,1], Qun Yang[a,b,1], Ruishen Meng[a], Chunjian Tan[b], Qiuhua Liang[a], Junke Jiang[a,b], Huaiyu Ye[b], Xianping Chen[a,b,*]

[a] Faculty of Mechanical and Electrical Engineering, Guilin University of Electronic Technology, 541004 Guilin, China
[b] Key Laboratory of Optoelectronic Technology & Systems, Education Ministry of China, Chongqing University and College of Optoelectronic Engineering, Chongqing University, 400044 Chongqing, China

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ABSTRACT

Using first-principles calculation within density functional theory (DFT), we study the gas (CO, NH_3, H_2S, NO_2, NO, SO_2) adsorption properties on the surface of single-layer indium nitride (InN). Four different adsorption sites (Bridge, In, N, Hollow) are chosen to explore the most sensitive adsorption site. On the basis of the adsorption energy, band gap and charge transfer, we find that the most energetic favourable site is changeable between In site and N site for different gases. Moreover, our results reveal that InN is sensitive to NH_3, SO_2, H_2S and NO_2, by a physisorption or a chemisorption nature. We also perform a perpendicular electric field to the system and find that the applied electric field has a significant effect for the adsorption process. Besides, we also observed the desorption effects on NH_3 adsorbed at the hollow site of InN when the electric field applied. In addition, the optical properties of InN monolayer affected by different gases are also discussed. Most of the gas adsorptions will cause the inhibition of light adsorption while the others can reduce the work function or enhance the adsorption ability in visible region. Our theoretical results indicate that monolayer InN is a promising candidate for gas sensing applications.

1. Introduction

After the discovery of graphene [1], a single layer of sp^2-hybridized two-dimensional (2D) carbon atoms, its subsequent novel applications and superior performance in electronic, mechanical, and chemical have been explored by quite a considerable number of researches [2,3], However, the gapless nature of graphene is a formidable obstacle on the way of using graphene in logic and high-speed switching devices. Thus, it is in great need to search for other two-dimensional materials which not only possess excellent properties similar to graphene but also have a moderate band gap. Group III–V nitrides have long been viewed as a promising system for semiconductor devices applications, especially for AlN and InN [4–6], AlN nanosheets have been studied to the gas sensing [7,8], however, limited by the multilayer structure, it is hard to gain the unique properties like graphene. Recently, remarkable breakthroughs in the growth of Indium nitride (InN) films through molecular beam epitaxy (MBE) have been achieved [9–11]. Various nanostructured InN materials have been synthesized in experiment [12–16]. Furthermore, the InN monolayer has also been theoretically verified to possess excellent thermal stability, high carrier mobility, drift velocity, excellent light adsorption coefficient and sizable band gap [17,18]. The planar structure with three In atoms and three N atoms stagger each other making up a hexatomic ring which not just similar to graphene in the structure but also in their properties. Moreover, unlike graphene, monolayer InN is a direct-bandgap semiconductor with a considerable band gap [19,20]. Therefore, the outstanding properties just like graphene together with the inherently direct-bandgap characteristic make indium nitride monolayer a promising candidate for future electronic devices. To our best knowledge, there are considerable works have been conducted mainly focusing on the optical properties of it. However, a lot of experimental [21,22] and theoretical works [23–25] have greatly demonstrated that 2D atomic-layer semiconductor systems with a direct-bandgap are promising candidate materials for high-performance gas nanosensors. Furthermore, inspired by the large specific surface area, small interactions between materials, and other prominent properties similar to graphene, we are eager to explore better gas sensing per-

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[*] Corresponding author at: Key Laboratory of Optoelectronic Technology & Systems, Education Ministry of China, Chongqing University and College of Optoelectronic Engineering, Chongqing University, 400044 Chongqing, China.
E-mail address: xianpingchen@cqu.edu.cn (X. Chen).

[1] X.S. and Q.Y. contributed equally to this work.

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formance using indium nitride monolayer comparing to that of AlN nanosheets [8,26] and other materials [27]. In this work, we take an attempt to examine the adsorption of several common pollutant gases, CO, NH_3, H_2S, SO_2, NO and NO_2 which are of great importance for industrial and environmental, on indium nitride monolayer using first-principles approach based on density-functional theory (DFT). We systematically calculated the adsorption distances, charges transfer, adsorption energies, charge difference densities, and partial density of states (PDOSs) of InN monolayer upon the adsorption of the gas molecules. Our calculations find out that InN monolayer exhibits better adsorption performance than pristine graphene.

2. Computational methods

Herein, we present a detailed theoretical investigation of the adsorption behaviours of several common pollutant gases (CO, NH_3, H_2S, SO_2, NO and NO_2) adsorbed on InN monolayer by means of DFT calculations. In the present work, all the structural relaxation and electronic calculations were carried out by first-principles calculations based on DFT using the $DMol^3$ code of Materials Studio [25,28]. Density-Burke-Ernzerhof generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [28,29] was chosen to describe the exchange correlation interaction. Taking the van der Waals (vdW) into account, DFT-D (D stands for dispersion) method proposed by Grimme [30,31] was used through all calculations due to the weak interactions are not well described by the standard PBE functional [29,32]. The double numerical atomic orbital plus polarization (DNP) was utilized as the basis set with the global cut-off of 5.0 Å to ensure the high computational quality [33,34]. The k-point was set to $10 \times 10 \times 1$ for structural optimizations and $16 \times 16 \times 1$ for the electronic properties calculations, and the smearing value was 0.005 Ha (1 Ha = 27.2114 eV).

The system consisting of a 3×3 supercell (25 atoms) of InN monolayer with the lattice constant of a = b = 10.722 Å was used, in good agreement with previous reports [18]. A vacuum space of 20 Å is placed to avoid interaction between the adjacent layers in the direction perpendicular to the infinite plane of InN monolayer. To evaluate the stability of the adsorption for different gas molecules on InN monolayer, the adsorption energy (E_{ad}) is defined as

$$E_{ad} = E_{InN+gas} - E_{InN} - E_{gas}$$

where $E_{InN+gas}$ is the total energy of the adsorption of gas on InN monolayer system, E_{InN} and E_{gas} are the total energies of pure substrate and isolated gas molecule, respectively. By definition, negative E_{ad} corresponds to favorable or exothermic adsorption of gaseson InN monolayer.

3. Results and discussion

3.1. Adsorption configurations of gas molecules on InN monolayer

For determining the most energetically stable adsorption configurations, the gas molecule is initially placed at different positions above InN monolayer with different orientations. All possible adsorption sites considered are plotted in Fig. 1, namely, Center (top of the hexagon center), N (top of N atoms), In (top of In atoms), Bridge (top of In—N bonds). For the targeted gas molecules (NH_3, H_2S, SO_2, and NO_2), three initial molecular orientations were then examined at each site, one with molecules plane parallel to the monolayer, and two with molecule plane perpendicular to it, we take SO_2 molecule as an example, with S atom pointing to the surface and S atom pointing away from the surface. The most stable adsorption configurations of the CO, NH_3, H_2S, NO_2, NO, and SO_2 molecules on InN monolayer substrates are summarized in Fig. 1. It is evident that different gases molecule have different preferences for adsorption site and adsorption configuration in the same substrate. In addition, it is noticeable that adsorption of some gas molecules such as NH_3 (Fig. 1(a)), H_2S (Fig. 1(b)), SO_2 (Fig. 1(c)), and NO_2 (Fig. 1(e)) has led to the structural deformation in different level in InN monolayer.

Table 1
The adsorption value of InN monolayer for NH_3, H_2S, SO_2, CO, NO, and NO_2. E_{ad} (eV): the adsorption energy. Q (e): the charge transfer between gas molecule and InN monolayer. D (Å): the shortest distance of the atom in the molecule to the InN surface.

Model	Site	D	E_{ad}	Q
NH_3	Bridge	2.407	−0.837	0.103
	In	2.408	−0.859	0.101
	N	3.450	−0.416	0.056
	Center	2.441	−0.858	0.106
H_2S	Bridge	3.103	−0.416	0.086
	In	2.260	−0.564	0.031
	N	3.561	−0.304	0.039
	Center	3.022	−0.410	0.045
SO_2	Bridge	1.774	−1.747	−0.581
	In	1.889	−1.745	−0.581
	N	1.773	−1.748	−0.583
	Center	1.772	−1.746	−0.583
CO	Bridge	3.200	−0.219	−0.014
	In	3.118	−0.223	0.033
	N	3.764	−0.152	0.015
	Center	3.403	−0.189	−0.007
NO_2	Bridge	2.371	−0.896	−0.464
	In	2.371	−0.900	−0.463
	N	2.376	−0.902	−0.465
	Center	2.375	−0.901	−0.464
NO	Bridge	2.538	−0.361	−0.140
	In	2.577	−0.380	−0.123
	N	2.644	−0.380	−0.130
	Center	2.512	−0.366	−0.141

For a better understanding of the differences above, more detailed information on the different InN–analyte systems, including adsorption energy (E_{ad}), equilibrium InN–analyte distance (D), and charge transfer (i.e. Mulliken charge, Q), are listed in Table 1. In order to find the optimal adsorption configurations, the analyte molecule was initially placed on the various sites of InN with different orientations. Therefore, the effects of the initial adsorption sites (center, N, In, and bridge sites) are considered and also summarized in Table 1. D is defined as the center-to-center distance of nearest atoms between InN and gas molecules; Q is defined as the total Mulliken charge transfer between InN and analyte, and a negative number means charge transfer from InN to gas molecule. For NH_3 on InN, the adsorption energy, InN–NH_3 distance, and charge transfer in the bridge, In, and center sites are found to be very close, and the NH_3 molecule shows tiny different adsorption behaviour. We also note that in the three sites, InN monolayer has a moderate adsorption energy (about −0.8 eV) accompanied by an apparent charge transfer of $\sim 0.1|e|$ from NH_3 to InN monolayer and all their corresponding D is rather large (2.407 Å–2.441 Å), which indicated that only physisorption exists. In sharp contrast, the adsorption energy and charge transfer of NH_3 in N site is much higher as compared with the other three sites. It is reasonable to think of that the bridge, In and center sites are favourable sites for the adsorption of NH_3 on InN monolayer. These results demonstrate that InN monolayer has great potentials for NH_3 separation (or storage) and NH_3 sensing. In the case of H_2S on InN, the most energetic favourable site where the H_2S molecule prefers to reside on the InN monolayer is the In site. After full relaxation, hydrogen atoms are closer to the InN surface as shown in Fig. 1(b). The correspond-