Materials Chemistry and Physics 198 (2017) 49–56

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Effect of external strain on the charge transfer: Adsorption of gas molecules on monolayer GaSe

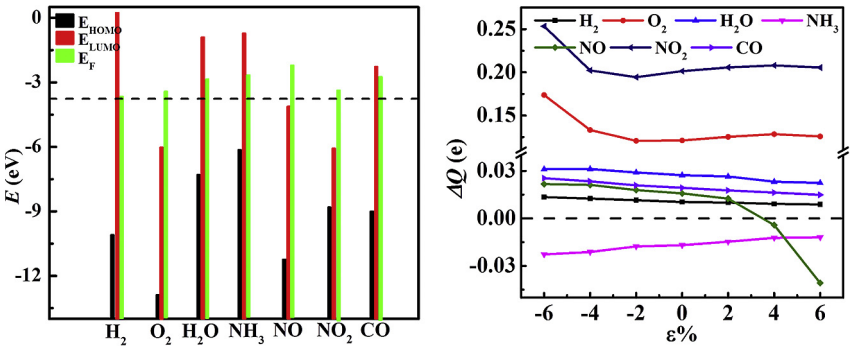
Changjie Zhou [a], Huili Zhu [a, *], Yaping Wu [b], Wei Lin [b], Weihuang Yang [c, **], Linxi Dong [c]

[a] Department of Physics, School of Science, Jimei University, Xiamen 361021, People's Republic of China
[b] Fujian Provincial Key Laboratory of Semiconductors and Applications, Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Department of Physics, Xiamen University, Xiamen 361005, People's Republic of China
[c] Key Laboratory of RF Circuits and System of Ministry of Education, Hangzhou Dianzi University, Hangzhou 310018, People's Republic of China

HIGHLIGHTS

- The preferential configurations of molecules adsorbed systems were investigated.
- Two different kinds of charge transfer mechanisms were demonstrated and confirmed.
- Effect of strain on the charge transfer and the adsorption stability was discussed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 December 2016
Received in revised form
17 April 2017
Accepted 28 May 2017
Available online 29 May 2017

Keywords:
Electronic properties
Biaxial strain
Charge transfer
Monolayer GaSe
First-principles calculations

ABSTRACT

First-principles calculations were performed to investigate the interaction of small gas molecules, including H_2, O_2, H_2O, NH_3, NO, NO_2, and CO, with monolayer GaSe. The energetics, charge transfer and band structures were evaluated by considering the Grimme-D2 correction. Due to the low adsorption energies and the moderate charge transfer, monolayer GaSe could be a promising candidate as a sensor for O_2 and NO_2. The theoretical results for adsorption of O_2 on monolayer GaSe are consistent well with the most recent experimental observation. Diverse projected band structures of these gas molecule-adsorbed systems demonstrate that there exist two kinds of charge transfer mechanisms: traditional and orbital mixing theories. Based on the proposed charge transfer mechanisms, external strain exerted different influences on the charge transfer for gas molecules adsorbed on the GaSe monolayer. The present study provides theoretical insight leading to a better understanding of the novel two-dimensional materials, such as graphene, phosphorene, and transition metal dichalcogenides.

1. Introduction

Layered two-dimensional (2D) nanomaterials [1,2], including graphene [3,4], transition-metal dichalcogenides (MoS_2, $MoSe_2$, WS_2, and WSe_2) [5–11] and phosphorene [12–20], have attracted

* Corresponding author.
** Corresponding author.
E-mail addresses: hlzhu@jmu.edu.cn (H. Zhu), welsong@sina.cn (W. Yang).

http://dx.doi.org/10.1016/j.matchemphys.2017.05.046
0254-0584/

significant attention from the scientific community due to their remarkable physical properties and prospective for technological application in next-generation electronics and optoelectronic devices. Due to their high surface-to-volume ratio and weak electronic screening properties, these atomically-thin 2D nanomaterials can be significantly perturbed even by sub-monolayer adsorption of foreign adatoms and gas molecules [21,22]. The enhanced interaction between external adsorbates and these 2D nanomaterials not only enables modulation of the physical and chemical properties of the latter, but also renders them eligible for sensing applications [22]. To date, the majority of gas sensors fabricated with these 2D nanomaterials are charge transfer based sensing devices [11]. Schedin and coworkers have demonstrated that a micrometer-sized graphene transistor can be used to detect molecules NH_3, CO, and H_2O at concentrations as low as 1 ppb [23]. Similar to graphene, MoS_2-based gas sensor exhibits high sensitivity for NO, NO_2, NH_3, and triethylamine gas [6,7,10,24]. The gas sensitivity of multilayer WS_2 nanoflakes has also been empirically evaluated [25].

Fuelled by interest in these 2D atomically-thin materials, layered group III-VI semiconductors (GaS, GaSe, GaTe, and InSe) have recently received considerable attention and shown promise in the field of nonlinear optics, terahertz (THz) devices, and phototransistors [26–31]. Most recently, photocurrent measurements of GaS nanosheet photodetectors demonstrated respective photoresponsivities of 4.2 and 19.2 A/W at 254 nm, which exceeds that of graphene, MoS_2, or other 2D material-based devices [28]. Furthermore, a photodetector based on few-layer GaS was demonstrated to exhibit variations in the photoresponsivity in different gas environments [32]. A higher photoresponsivity and external quantum efficiency was obtained in ammonia (NH_3) than in air or oxygen (O_2).

Similarly, a photodetector based on few-layer GaSe was demonstrated to have high photoresponsivity (2.8 A/W) and external quantum efficiency (1367%) [33]. A systematic study on the effects of different gas molecules on the photoelectric response of few-layer GaSe phototransistors demonstrated that the performance of the device for adsorption of O_2 is better than in air and vacuum. Introducing defects by thermal annealing increases the photoresponse (18.75 A/W) of the phototransistors significantly, accompanied by high external quantum efficiency (9153%) in an O_2-rich environment [34]. Therefore, these 2D GaSe crystals are potentially useful for field effect transistor (FET), photodetectors, and gas sensors. Although the gas sensitivity and its effect on the photoresponse of the GaSe-FET sensor have been experimentally studied, the mechanism underlying the interaction of gas molecules with the GaSe surface and the effect of external strain on the electronic properties remain undefined. Thus, exploration of the interaction between the adsorbed molecules and the GaSe monolayer and assessment of the distinctive characteristics of the adsorbate-adsorbent system from the theoretical perspective are worthwhile pursuits.

In this study, we evaluate the adsorption of various gas molecules on the GaSe monolayer using first-principles calculations. The preferential binding configurations of these gas molecules are obtained by calculating the adsorption energies. Charge transfer between the adsorbed molecules and the monolayer GaSe is then theoretically quantified to determine the doping behavior of these adsorbates. Two kinds of charge transfer mechanisms, traditional and orbital mixing theories, are then systematically demonstrated to elucidate the diverse band structures upon adsorption of the gas molecules on the GaSe monolayer. In addition, the effects of extra biaxial strain on the charge transfer and the adsorption stability are also discussed.

2. Calculation details

First-principles calculations were performed within the framework of density functional theory (DFT) by using the Vienna ab initio simulation package (VASP) [35,36]. The exchange-correlation energy was described by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional [37]. To evaluate the effect of van der Waals (vdW) interactions on adatom adsorption, we further considered the semi-empirical correction scheme of Grimme (DFT-D2) [38]. It has been demonstrated that the DFT-D2 approach provides good accuracy in the estimation of the geometric configuration and binding energy of the adatom adsorbed system [39]. For comparison, the amount and direction of the charge transfer were further obtained by using the Tkatchenko-Scheffler method [40]. The electron-ion interaction was approximated using the projector-augmented wave potential. The electron wavefunctions were expanded in plane waves with an energy cutoff of 500 eV. The Brillouin-zone integrations were performed with a $5 \times 5 \times 1$ Monkhorst-Pack grid for k-point sampling [41]. The charge transfer between the GaSe monolayer and the adsorbed gas molecules was obtained by using the Bader analysis [42]. The convergence of the calculated Bader charges were further controlled through the NGX, NGY, and NGF variables (NGX = 250, NGY = 250, NGZ = 450). Supercells with 4×4 dimensions (32 Ga and 32 Se atoms) were used to simulate individual monolayer GaSe. The distance between monolayers was set to more than 20 Å to avoid interlayer interactions. The distance between two neighboring gas molecules was larger than 13 Å. The Wigner-Seitz radii of Ga, Se, H, O, N, and C atoms are 1.217 Å, 1.164 Å, 0.370 Å, 0.820 Å, 0.741 Å, and 0.863 Å, respectively. For molecules H_2, O_2, NO, and CO, the H–H, O–O, N–O, and C–O bond lengths are 0.766 Å, 1.221 Å, 1.158 Å, and 1.135 Å, respectively. The H–O bond length and H–O–H angle for the H_2O molecule are 0.974 Å and 105.365°, respectively. The N–H bond length and H–N–H angle for the NH_3 molecule are 1.023 Å and 107.943°, respectively. The N–O bond length and O–N–O angle for the NO_2 molecule are 1.200 Å and 133.918°, respectively. Structural optimizations were carried out by relaxing all the atomic geometries using the conjugate gradient algorithm. The convergence criteria for energy and force were set to be 1×10^{-6} eV and 0.02 eV/Å, respectively.

Based on the above settings, the calculated lattice constant of the pristine GaSe monolayer is 3.74 Å, and the Ga-Ga and Ga-Se band lengths are respectively 2.43 Å and 2.47 Å, which are in agreement with previous calculations and experimental results [43,44]. Moreover, the band structure of pristine monolayer GaSe presents that monolayer GaSe have an indirect bandgap of 2.236 eV, which agrees well with the previous theoretical results [43,45]. According to the geometrical symmetry of monolayer GaSe, four adsorption sites (H site, T_{Ga} site, T_{Se} site and B site), as indicated in Fig. 1(a), were considered to determine the favorable adsorption configuration. The adsorption energy was calculated as: $E_a = [E_{mol/GaSe} - E_{GaSe}]/N - E_{mol}$, where $E_{mol/GaSe}$, E_{GaSe}, and E_{mol} are the total energies of the surface with N adsorbates, the clean surface, and an isolated molecule, respectively. Negative adsorption energy indicates that the adsorption process is exothermic and energetically favored.

3. Results and discussion

3.1. Adsorption of gas molecules on monolayer GaSe

The calculated adsorption energies and equilibrium heights for the adsorption of different gas molecules on monolayer GaSe are listed in Table 1. The equilibrium height is the space between the upper Se-layer and the center of mass of the gas molecule. It is