Effects of gas adsorption on monolayer Si$_2$BN and implications for sensing applications

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Received 16 March 2020
Accepted for publication 27 April 2020
Published 1 June 2020

Abstract

Using density functional theory, we investigate the adsorption behavior of CO, NH$_3$, and NO molecules on monolayer Si$_2$BN. The energetically favorable structural configurations along with their adsorption energies, charge transfers, and electronic properties are discussed. The CO and NH$_3$ molecules show physisorption with moderate adsorption energies, whereas the NO molecule is subject to chemisorption. We further calculate the current–voltage characteristics using the non-equilibrium Green’s function formalism. Significant anisotropy is observed for the armchair and zigzag directions, consistent with the anisotropy of the electronic band structure. Pronounced enhancement of the resistivity upon gas adsorption indicates that monolayer Si$_2$BN is promising as a gas sensing material.

Keywords: density functional theory, non-equilibrium Green’s function formalism, gas sensing

(Some figures may appear in colour only in the online journal)

1. Introduction

Two-dimensional (2D) materials show remarkable chemical, electrical, optical, and thermal properties that are not available in three-dimensional materials. In particular, due to large surface-to-volume ratios and chemical stability, 2D materials are promising candidates for gas sensing applications. In this context, various 2D materials have been studied theoretically [1–7] and experimentally [2, 8–12] during the last couple of years and the search for new materials is still going on with high pace. Monolayer Si$_2$BN, a planar structure of sp$^2$-hybridized Si, B, and N atoms, first has been addressed in the literature in 2016 [13, 14]. Subsequently, it has been characterized with respect to its mechanical [15] and electronic [16] properties. It has been proposed as host material for H storage [17] and as anode for Li and Na ion batteries [18].

Possible applications of monolayer Si$_2$BN as a gas sensing material, however, so far have not been considered. This is remarkable, as the presence of accessible Si atoms makes the 2D material reactive, which is key for gas sensing applications. In the present work, we use ab initio calculations to understand the adsorption behavior of common gaseous pollutants (CO, NH$_3$, and NO) on monolayer Si$_2$BN. We identify the preferential adsorption sites and orientations by determining the adsorption energies. The nature of the gas adsorption is discussed in terms of the charge transfer between molecule and monolayer Si$_2$BN. The current–voltage (I–V) characteristics is determined before and after gas adsorption using the non-equilibrium Green’s function formalism. Due to the anisotropic structure of monolayer Si$_2$BN, we study the transport behavior along the armchair and zigzag directions.

2. Methods

To study gas adsorption we built rectangular (12.72 Å × 11.22 Å) supercells of monolayer Si$_2$BN with 32 atoms, while
the unit cell contains 8 atoms. Each structure model contains a ~20 Å thick vacuum slab to achieve a 2D configuration with periodic boundary conditions. We consider CO, NH3, and NO molecules, studying the hollow (H1, H2, and H3), top (T1, T2, and T3), and bridge (B1, B2, B3, and B4) sites shown in figure 1. The center of mass of the molecule is placed exactly at these sites before the structure is optimized. For each site we consider three orientations of the CO and NO molecules (C/N or O pointing towards the substrate, C/N–O bond aligned parallel to the substrate) and two orientations of the NH3 molecule (N or H pointing towards the substrate).

All calculations are performed within the projector augmented wave method of spin-polarized density functional theory, as implemented in the Vienna ab initio simulation package [19]. For the exchange correlation functional the generalized gradient approximation (Perdew–Burke–Ernzerhof flavor) is employed and long-range dispersion effects are described by the DFT-D3 method with Becke–Johnson damping [20, 21]. We use pseudopotentials with Si 3s23p2, B 2s2p1, C 2s2p2, N 2s2p3, O 2s2p2, and H 1s1 valence states. The energy cutoff is set to 500 eV and the Brillouin zone integrations adopt 3 × 3 × 1 Monkhorst–Pack [22] k-grids. Structure optimizations are performed by the conjugate gradient method without any symmetry constraint. We assume convergence when the total energy changes have declined below 10−6 eV and the atomic forces have declined below 10−3 eV Å−1.

The adsorption energy of a gas molecule on monolayer Si2BN is calculated as

$$E_{\text{ad}} = E_{\text{molecule/Si2BN}} - E_{\text{Si2BN}} - E_{\text{molecule}}$$

(1)

using the total energies of pristine monolayer Si2BN, the isolated gas molecule, and the combined system. A negative value indicates that adsorption results in energy gain. In order to obtain further insight into the interaction, the charge density difference

$$\Delta\rho(r) = \rho_{\text{molecule/Si2BN}}(r) - \rho_{\text{Si2BN}}(r) - \rho_{\text{molecule}}(r)$$

(2)

is calculated from the spatial charge density distributions of pristine monolayer Si2BN, the isolated gas molecule, and the combined system. The amount of charge transfer between the component systems is obtained from Bader charge analysis [23].

3. Results and discussion

We obtain for the unit cell of pristine monolayer Si2BN, see figure 1, optimized lattice constants of a = 6.36 Å and b = 6.45 Å (thus no hexagonal symmetry) as well as bond lengths of 2.24 Å (Si–Si), 1.95 Å (Si–B), 1.76 Å (Si–N), and 1.47 Å (B–N). The electronic band structure in figure 1 shows an anisotropic metallic behavior. The phonon dispersion is calculated from the atomic force constants by a finite displacement method [24]. The result in figure 1 shows no imaginary frequencies, which confirms dynamic stability of the structure. Both the electronic band structure and phonon dispersion agree well with reference [13].

The lowest energy structures of the CO, NH3, and NO molecules on monolayer Si2BN are shown in figure 2. The CO molecule favors site H3 with C pointing to the substrate. The C–O bond is elongated by 3.5% as compared to the pristine molecule and we observe a slight shift of the nearest neighbour Si atom towards the molecule. The C–Si distance of 2.14 Å is much longer than the experimental C–Si bond length of 1.87 Å in allylsilane (C3H8Si), for example [25]. For this reason and because $E_{\text{ad}} = −0.62$ eV, the molecule is physisorbed. The NH3 molecule favors site T1 with N pointing towards the substrate. The N–H bond length is not modified by the adsorption, whereas the H–N–H bond angle increases slightly by 1°. Monolayer Si2BN reveals only small structural modifications. The N–Si distance of 2.00 Å exceeds the experimental N–Si bond length of 1.73 Å in trisilylamine (N(SiH3)3) [26], for example. This fact confirms physisorption, however with an unusually (within the class of 2D materials) high value of $E_{\text{ad}} = −0.73$ eV. The NO molecule favors site H2, being aligned parallel to the substrate. We observe that the N–O bond length increases from 1.17 Å to 1.53 Å, which is close to the length of the single bonds in dinitrogen pentoxide (N2O5; 1.50 Å) [27], and the N–Si distance of 1.88 Å approaches the experimental bond length in trisilylamine. These observations point to N–Si bond formation and reduced N–O bonding. From the energetical point of view, chemisorption is confirmed by a high value of $E_{\text{ad}} = −2.04$ eV. For comparison, we calculate $E_{\text{ad}}$ of the CO, NH3, and NO molecules on graphene, monolayer MoS2, and monolayer WS2, using exactly the same computational methodology as for monolayer Si2BN. The results in table 1 show that the obtained values are significantly higher for monolayer Si2BN.

The effects of gas adsorption on the electronic states of monolayer Si2BN are addressed in figure 3. The band
structures show only minor modifications except for the NO molecule, which induces spin polarization with a total magnetic moment of 0.68 $\mu_B$. For the CO molecule we find contributions of both the C and O atoms to the density of states mainly at $-0.8$ eV and in the energy range from 1 eV to 2 eV, significantly hybridized with the states of monolayer Si$_2$BN despite the fact that the molecule is physisorbed. The NH$_3$ molecule, on the other hand, gives virtually no contributions to the density of states in the energy range shown. Finally, both the N and O atoms of the NO molecule contribute mainly below $-2$ eV and at 0.8 eV.

To better understand the electronic interaction between the molecules and monolayer Si$_2$BN we show charge density difference plots in figure 4. In the case of CO adsorption we observe charge depletion from the two nearest neighbour Si atoms and charge accumulation on the C atom, which demonstrates that the molecule acts as electron acceptor. The amount of transferred charge, calculated by Bader charge analysis, turns out to be 0.69 electrons. NH$_3$ adsorption results in charge depletion from the H atoms and charge accumulation on the N atom of the molecule. In addition, monolayer Si$_2$BN shows some spatial charge redistribution. Effectively, the NH$_3$ molecule donates a small amount of 0.04 electrons to monolayer Si$_2$BN. In the case of NO adsorption the four nearest neighbour Si atoms are subject to charge depletion because of bond formation with the molecule, see the above discussion, and the significantly lower electronegativity of Si as com-

Table 1. Adsorption energies of the CO, NH$_3$, and NO molecules on different 2D materials.

|        | CO  | NH$_3$ | NO    |
|--------|-----|--------|-------|
| Graphene | −0.13 eV | −0.13 eV | −0.16 eV |
| Monolayer MoS$_2$ | −0.09 eV | −0.16 eV | −0.11 eV |
| Monolayer WS$_2$ | −0.11 eV | −0.18 eV | −0.13 eV |
| Monolayer Si$_2$BN | −0.62 eV | −0.73 eV | −2.04 eV |

Figure 2. Top and side views of the lowest energy structures of (a) CO, (b) NH$_3$, and (c) NO molecules adsorbed on monolayer Si$_2$BN.

Figure 3. Electronic band structures (rectangular Brillouin zone) and densities of states (full lines: total; dashed lines: contribution of the molecule) for (a) pristine monolayer Si$_2$BN and (b) CO, (c) NH$_3$, and (d) NO on monolayer Si$_2$BN. In (d) the colors of the bands refer to the spin channels.
Figure 4. Top and side views of the charge density difference for the (a) CO, (b) NH₃, and (c) NO molecules adsorbed on monolayer Si₂BN. Yellow color represents charge accumulation and light blue color charge depletion (isosurface value: $2 \times 10^{-3}$ electrons Å⁻³).

pared to N and O. We find that the molecule accepts a total of 2.12 electrons (1.67/0.45 electrons on N/O). The described charge redistributions and transfers under gas absorption are expected to play a major role for the current–voltage characteristics.

The resistivity change of a material due to charge transfer to/from gas molecules is accessible experimentally and therefore can be exploited in gas sensors. In order to evaluate the potential of monolayer Si₂BN as gas sensor we compare the electronic transport through the material before and after gas adsorption, using the non-equilibrium Green’s function method as implemented in the SMEAGOL package [28, 29]. The electronic wavefunction is expanded in a double-ζ basis with a cutoff energy of 500 Ry. The Brillouin zone is sampled on $1 \times 11 \times 50$ and $1 \times 11 \times 1$ Monkhorst–Pack k-grids in the lead and transport calculations, respectively. Due to the structural anisotropy of monolayer Si₂BN we investigate transport along the armchair and zigzag directions. For both models we set up semi-infinite electrodes (armchair: 12.72 Å × 11.22 Å, zigzag: 11.22 Å × 12.72 Å) of monolayer Si₂BN and connect them to a central scattering region of the same size.

In figure 5 we present the obtained transmission at zero bias and current–voltage characteristics, which confirm structural anisotropy of the armchair and zigzag directions. We find that the adsorption of molecules has virtually no effect on the current in the case of the armchair direction, whereas the current along the zigzag direction is suppressed. Even for a small applied voltage the current is reduced by more than 50%, which shows that monolayer Si₂BN gives rise to a sensitive gas sensor. The origin of the high sensitivity of the zigzag device, in contrast to the armchair device, can be understood in terms of the electronic band structures in figure 3 and transmissions at zero bias in figure 5(a): the adsorption of molecules disturbs mainly states that are more conductive along the zigzag (Γ–X) than along the armchair (Γ–Y) direction, compare the much higher transmission at zero bias obtained for the zigzag than the armchair device in the vicinity of the Fermi energy.

4. Conclusion

In conclusion, we have performed first-principles calculations to investigate the structural and electronic properties of mono-
layer Si$_2$BN as well as the consequences of interaction with CO, NH$_3$, and NO molecules. The interaction is found to be much stronger than in other 2D materials as the Si atoms turn out to be reactive. Our results demonstrate physisorption of the CO and NH$_3$ molecules, however with rather high adsorption energies, whereas chemisorption of the NO molecule prohibits reusability of gas sensors based on monolayer Si$_2$BN in this case. Electronic transport calculations find strong anisotropy of the current–voltage characteristics along the armchair and zigzag directions. Interestingly, we obtain for the zigzag direction pronounced changes in the resistivity for the zigzag direction pronounced changes in the resistivity.

Acknowledgment

The research reported in this publication was supported by funding from King Abdullah University of Science and Technology (KAUST). Computational resources were provided by the Supercomputing Laboratory of KAUST.

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