

## Silicene as a highly sensitive molecule sensor for NH<sub>3</sub>, NO and NO<sub>2</sub>

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On the basis of *first-principles* calculations, we demonstrate the potential application of silicene as a highly sensitive molecule sensor for NH<sub>3</sub>, NO, and NO<sub>2</sub> molecules. NH<sub>3</sub>, NO and NO<sub>2</sub> molecules chemically adsorb on silicene *via* strong chemical bonds. With distinct charge transfer from silicene to molecules, silicene and chemisorbed molecules form charge-transfer complexes. The adsorption energy and charge transfer in NO<sub>2</sub>-adsorbed silicene are larger than those of NH<sub>3</sub>- and NO-adsorbed silicones. Depending on the adsorbate types and concentrations, the silicene-based charge-transfer complexes exhibit versatile electronic properties with tunable band gap opening at the Dirac point of silicene. The calculated charge carrier concentrations of NO<sub>2</sub>-chemisorbed silicene are 3 orders of magnitude larger than intrinsic charge carrier concentration of graphene at room temperature. The results present a great potential of silicene for application as a highly sensitive molecule sensor.

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In recent years, two-dimensional (2D) atomic-thickness sheets have attracted much research attention for their novel properties and wide applications. For example, graphene, a 2D sp<sup>2</sup> hybridized carbon monolayer,<sup>1–3</sup> has received the most interest from both science and industry, partly due to its practical applications in electronics, such as high-performance field effect transistors (FETs). Meanwhile, the adsorption of atoms or molecules on graphene has been widely studied experimentally<sup>4–10</sup> and theoretically<sup>11–15</sup> for the purpose of realizing band-gap engineering<sup>16–19</sup> and charge carrier doping<sup>20–22</sup> for graphene-based FETs, catalysts,<sup>23–26</sup> gas sensors,<sup>27–31</sup> and hydrogen<sup>32–36</sup> and helium<sup>37–42</sup> separation. However, common gas molecules, such as H<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, NH<sub>3</sub>, NO and NO<sub>2</sub>, are all physically adsorbed on graphene with very small adsorption energies,<sup>11</sup> which prevents immediate practical applications, for example as a molecule sensor,<sup>27–31</sup> without introducing dopants or defects.<sup>29</sup>

Silicene, an analog to graphene with buckled honeycomb structures,<sup>43–45</sup> has also attracted increasing attention for its novel chemical and physical properties,<sup>46</sup> such as electric response,<sup>47,48</sup> ferromagnetism,<sup>49,50</sup> half-metallicity,<sup>51,52</sup> quantum Hall effect,<sup>53</sup> giant magnetoresistance<sup>54</sup> and superconductivity.<sup>55</sup> Experimentally, silicene has been successfully fabricated on

Ag,<sup>56–63</sup> Ir<sup>64</sup> and ZrB<sub>2</sub><sup>65</sup> substrates. Semiconducting substrates for silicene have also been proposed theoretically with first-principles calculations, such as h-BN,<sup>48</sup> SiC,<sup>66</sup> Si, diamond<sup>67</sup> and ZnS,<sup>68</sup> for new silicene-based nanoelectronic devices.

Most recently, the adsorption properties of atoms on silicene have been studied theoretically.<sup>69–81</sup> Due to its buckled honeycomb structures, silicene exhibits a much higher chemical reactivity for atom adsorption than graphene<sup>69</sup> with great potential applications for new silicene-based nanoelectronic devices,<sup>46</sup> Li-ion storage batteries,<sup>77</sup> hydrogen storage,<sup>78</sup> catalysts<sup>79</sup> and thin-film solar cell absorbers.<sup>80</sup> However, little attention has been focused on molecule adsorption on silicene. Our recent theoretical works<sup>82,83</sup> have proved that silicene are also chemically inert to most common and noble gas molecules, such as H<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O and CH<sub>4</sub>, as a hydrogen and helium separation membrane superior to graphene. But, it is still an open question as to what is the adsorption behavior of nitrogen-based gas molecules, including NH<sub>3</sub>, NO and NO<sub>2</sub>, which are all of great practical interest for industrial, environmental and medical applications.

In the present work, the adsorption behaviors and electronic properties of NH<sub>3</sub>, NO and NO<sub>2</sub> on silicene are studied *via* first-principles calculations. Our results indicate that NH<sub>3</sub>, NO and NO<sub>2</sub> prefer to chemically adsorb on silicene with high adsorption energies. Charges are transferred from silicene to the molecules, resulting in a p-type doping of silicene with tunable band gap opening at silicene's Dirac point. The calculated adsorption energies indicate that the silicene can be used as a reusable molecule sensor for NH<sub>3</sub> and NO molecules, and a disposable molecule sensor for NO<sub>2</sub> molecules.

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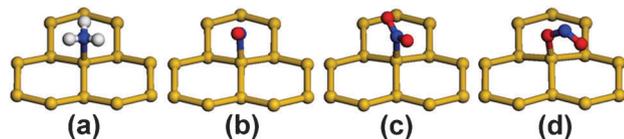


Fig. 1 Atomic structures of (a)  $\text{NH}_3$ , (b)  $\text{NO}$ , (c) and (d)  $\text{NO}_2$  (N–Si and O–Si) chemisorption on silicene. The yellow, white, red and blue balls denote silicon, hydrogen, oxygen and nitrogen atoms, respectively.

The optimized lattice parameter of silicene is  $a = 3.866 \text{ \AA}$ , in agreement with previous theoretical works.<sup>48</sup> To evaluate the concentration effect, a single molecule is adsorbed on silicene with different supercell sizes, containing the  $1 \times 1$ ,  $2 \times 2$ ,  $3 \times 3$ ,  $4 \times 4$ ,  $5 \times 5$  and  $6 \times 6$  supercells of silicene. Different adsorption configurations of gas molecules' adsorption on silicene are considered and the optimized stable adsorption configurations of  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  on silicene are all above the top Si atoms in silicene as shown in Fig. 1. The vacuum space in the  $Z$  direction is about  $15 \text{ \AA}$  to separate the interactions between neighboring slabs.

All the calculations are performed based on density functional theory (DFT) implemented in the VASP package.<sup>84</sup> The generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE)<sup>85</sup> with van der Waals (vdW) correction proposed by Grimme (DFT-D2)<sup>86</sup> is chosen due to its good description of long-range vdW interactions.<sup>87–98</sup> As an benchmark, DFT-D2 calculations give a good bilayer distance of  $3.25 \text{ \AA}$  and binding energy of  $-25 \text{ meV}$  per carbon atom for bilayer graphene, in fully agreement with previous experimental<sup>99,100</sup> and theoretical<sup>101,102</sup> studies. The energy cutoff is set to be  $500 \text{ eV}$ . The surface Brillouin zone is sampled with a  $3 \times 3$  regular mesh and  $240 k$  points are used for calculating the small band gaps at the Dirac points of silicene. All the geometry structures are fully relaxed until energy and forces are converged to  $10^{-5} \text{ eV}$  and  $0.01 \text{ eV \AA}^{-1}$ , respectively. Dipole correction is employed to cancel the errors of electrostatic potential, atomic forces and total energy, caused by periodic boundary condition.<sup>103</sup>

In order to evaluate the stability of  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  adsorption on silicene, the adsorption energy is defined as  $E_a = E_{\text{Gas/Silicene}} - E_{\text{Gas}} - E_{\text{Silicene}}$ , where,  $E_{\text{Gas/Silicene}}$ ,  $E_{\text{Gas}}$  and  $E_{\text{Silicene}}$  represent the total energy with full relaxation for the gas molecule adsorption on silicene, single gas molecule, and pristine silicene, respectively.

We first examine the adsorption behaviors and properties of  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  on silicene with different concentrations (*i.e.* varying the size of the supercells). The DFT-D2 calculated adsorption energy  $E_a$  (eV), adsorbate–Si bond length  $d_{\text{X-Si}}$  ( $\text{\AA}$ ) ( $X = \text{N}$  or  $\text{O}$ ), charge transfer from silicene to gas molecules  $\rho$  ( $e$ ), the Dirac point shift relative to the Fermi level  $\Delta E_D$  (eV) and band gap  $E_g$  (meV) opened at the Dirac points of silicene are summarized in Table 1. Our results show that  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  are chemically adsorbed on silicene with large adsorption energies, compared with their physisorption on graphene.<sup>11</sup> The  $\text{NH}_3$  molecule adsorbs on the uppermost Si atom with the formation of Si–N chemical bonds at low adsorption

Table 1 DFT-D2 calculated adsorption energy  $E_a$  (eV), adsorbate–Si bond length  $d_{\text{X-Si}}$  ( $\text{\AA}$ ) ( $X = \text{N}$  or  $\text{O}$ ), charge transfer from silicene to gas molecules  $\rho$  ( $e$ ), the Dirac point shift relative to the Fermi level  $\Delta E_D$  (eV) and band gap  $E_g$  (meV) opened at the Dirac point for  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  adsorption on silicene in different supercells

DFT-D2	$E_a$ (eV)	$d_{\text{X-Si}}$ ( $\text{\AA}$ )	$\rho$ ( $e$ )	$\Delta E_D$ (eV)	$E_g$ (meV)
$\text{NH}_3$ ( $1 \times 1$ )	−0.24	3.18	0.10	0.00	128
$\text{NH}_3$ ( $2 \times 2$ )	−0.46	2.06	0.08	0.00	471
$\text{NH}_3$ ( $3 \times 3$ )	−0.56	2.05	0.15	0.00/−0.05	429/22
$\text{NH}_3$ ( $4 \times 4$ )	−0.60	2.04	0.14	0.00	117
$\text{NH}_3$ ( $5 \times 5$ )	−0.60	2.04	0.14	0.00	79
$\text{NH}_3$ ( $6 \times 6$ )	−0.59	2.04	0.15	0.00/−0.03	114/11
$\text{NO}$ ( $4 \times 4$ )	−0.57	1.99	0.46	0.00	103
$\text{NO}_2$ (N–Si) ( $4 \times 4$ )	−1.12	1.96	0.69	0.31	168
$\text{NO}_2$ (O–Si) ( $4 \times 4$ )	−1.53	1.75	0.82	0.30	173

concentration (*i.e.* single  $\text{NH}_3$  molecule adsorption in a large supercell). The adsorption energies range from  $-0.46$  to  $-0.60 \text{ eV}$  and the N–Si bond length ranges from  $2.02$  to  $2.06 \text{ \AA}$ , as shown in Fig. 1a. Note, when the concentration of  $\text{NH}_3$  molecules is extremely high (*i.e.* one  $\text{NH}_3$  molecule per  $1 \times 1$  unitcell), the adsorption of  $\text{NH}_3$  on silicene is physisorption and the chemisorption is unstable due to very strong intermolecular interactions. Our results indicate that the chemical adsorption properties of  $\text{NH}_3$  on silicene are similar when the supercell size is not less than  $4 \times 4$ .

Upon the  $\text{NO}$  and  $\text{NO}_2$  adsorption on silicene, only the  $4 \times 4$  supercell is adopted. The  $\text{NO}$  molecule still prefers to adsorb on the top site of Si atom with a moderate adsorption energy of  $-0.57 \text{ eV}$  and a stable chemical N–Si bond length of  $1.99 \text{ \AA}$ , as shown in Fig. 1b. For the  $\text{NO}_2$  molecule, there are two stable adsorption configurations, as shown in Fig. 1c and d. In the first configuration, the  $\text{NO}_2$  molecule adsorbs on the top of the Si atom with the formation of a N–Si covalent bond, whereas it forms an O–Si covalent bond in the second configuration. These configurations are very stable with large adsorption energies of  $-1.12$  and  $-1.53 \text{ eV}$  for the N–Si and O–Si bond lengths of  $1.96$  and  $1.75 \text{ \AA}$ , respectively. Note that the adsorption energies of  $\text{NH}_3$  and  $\text{NO}$  on silicene are moderate, therefore, it is possible to desorb them from silicene by heating at room temperature, implying the potent applications of silicene as a sensitive chemical gas-sensor or gas-filter. Since the chemisorption of  $\text{NO}_2$  molecules on silicene is very strong, the silicene can be used as a disposable molecule sensor for specific  $\text{NO}_2$  detection. However, the strong bonding of the  $\text{NO}_2$  molecule provides an effective method to tune the electronic properties of silicene in the context of electronic applications at the nanoscale.

Electronic band structures of  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  adsorption on silicene are shown in Fig. 2.  $\text{NH}_3$  adsorption on silicene in supercells of different sizes is considered. When the supercell size is  $3N \times 3N$  unit cells (*i.e.*  $3 \times 3$  and  $6 \times 6$ ), negligible energy band gaps are opened at two different kinds of silicene's Dirac points, as shown in Fig. 2c and f. Recent theoretical simulations have also reported similar in atoms doped graphene and silicene,<sup>104–106</sup> in which two kinds of graphene's Dirac points are produced by band folding in the  $3N \times 3N$  or  $\sqrt{3}N \times \sqrt{3}N$

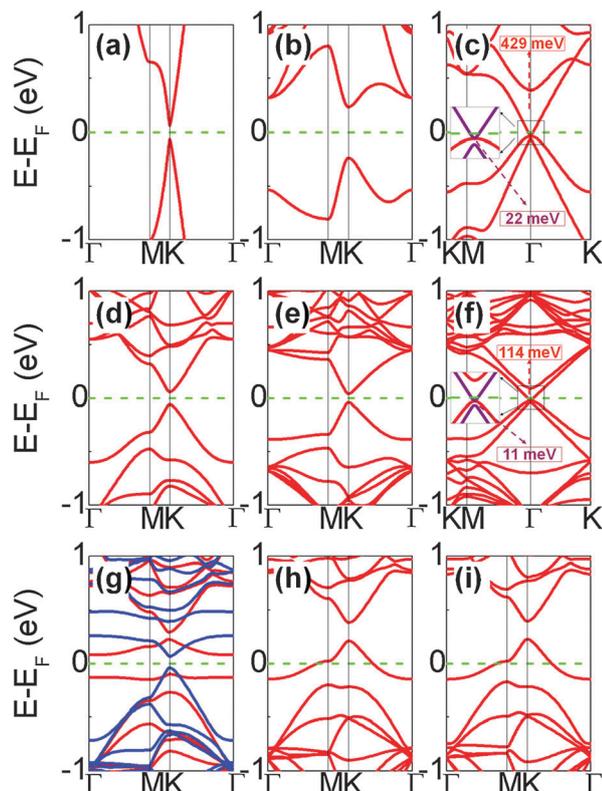


Fig. 2 Electronic band structures of  $\text{NH}_3$ ,  $\text{NO}$ , and  $\text{NO}_2$  adsorption on silicene.  $\text{NH}_3$  adsorption on silicene in the (a)  $1 \times 1$ , (b)  $2 \times 2$ , (c)  $3 \times 3$ , (d)  $4 \times 4$ , (e)  $5 \times 5$  and (f)  $6 \times 6$  supercells, (g)  $\text{NO}$ , (h) and (i)  $\text{NO}_2$  (N-Si and O-Si) adsorption on silicene in the  $4 \times 4$  supercell. The band gaps at two different Dirac points of silicene adsorbed  $\text{NH}_3$  in the  $3 \times 3$  and  $6 \times 6$  supercells are shown in the inset. The red and blue color lines represent spin-up and spin-down states, respectively. The Fermi level is set to zero and marked by green dotted lines.

supercells. In particular, these Dirac points are easily distorted with introducing dopants or defects due to the break of bond symmetry in graphene and silicene.<sup>70,81,104–106</sup>

When  $\text{NH}_3$ ,  $\text{NO}$  or  $\text{NO}_2$  molecules are chemisorbed on silicene with the supercell size of  $4 \times 4$  unit cells, sizable band gaps at the level of hundreds of meV are opened at silicene's Dirac points. These values are significantly larger than that (tens of meV) for common gas molecules physically adsorbed on graphene with similar adsorbate concentrations<sup>11,16,17,21,22</sup> and thermal fluctuation (25 meV) at room temperature. The energy band gap of silicene depends sensitively on the molecules and their adsorption concentrations. The band gap values increase with the increasing molecules' concentrations. Moreover, the band gaps values can be further tuned *via* other external methods, such as electric fields<sup>47</sup> and atom doping,<sup>74</sup> implying the potential applications for silicene-based FETs.

When  $\text{NO}_2$ ,  $\text{NH}_3$  and  $\text{NO}$  molecules adsorb on the silicene, electrons are transferred from silicene to the molecules, resulting in a p-type doping of silicene itself. For the adsorption of the molecule on silicene with a  $4 \times 4$  unit cell-sized supercell, the calculated charge transfer ranges from 0.14–0.82  $e$  for silicene, distinctly larger than those on graphene (−0.027, −0.018 and

0.099  $e$  respectively for  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$ ).<sup>11</sup> For  $\text{NH}_3$ - and  $\text{NO}$ -chemisorbed silicene, the Fermi energy levels remain in their induced gaps at the Dirac points of silicene, showing semiconducting behavior with small amounts of electrons transferring from silicene to the gas molecules ( $\rho(\text{NH}_3) = 0.14 e$  and  $\rho(\text{NO}) = 0.46 e$ ). For  $\text{NO}_2$ -chemisorbed silicene, however, large amount of electrons are transferred from silicene to  $\text{NO}_2$  in two configurations ( $\rho(\text{NO}_2, \text{N-Si}) = 0.69 e$  and  $\rho(\text{NO}_2, \text{O-Si}) = 0.82 e$ ), which move the Dirac points of silicene to 0.31 and 0.30 eV above the Fermi levels. The dominant charge transfer confirms the strong adsorption of  $\text{NO}_2$  molecule on silicene, resulting in heavier p-type doping of silicene than that on graphene with  $\text{NO}_2$  physisorption.<sup>11</sup>

Further, the charge carrier concentrations are calculated for the  $\text{NO}_2$ -chemisorbed silicene. Previously, based on the linear dispersion around the Dirac point of graphene,<sup>3</sup> the charge carrier (hole or electron) concentration of doped graphene can be estimated by the following equation  $N_{h/e} = (\Delta E_D)^2 / \pi(\hbar v_F)^2$ , where  $v_F$  is the Fermi velocity at the Dirac point ( $v_F(\text{Graphene}) = 0.8 \times 10^6 \text{ m s}^{-1}$  and  $v_F(\text{Silicene}) = 0.5 \times 10^6 \text{ m s}^{-1}$ ),<sup>95</sup> and  $\Delta E_D$  is the energy shift of the Dirac point relative to the Fermi level. The gas molecules adsorption on silicene would lower its Fermi velocity. For instance, the calculated  $v_F$  of  $\text{NO}_2$  adsorbed silicene ( $4 \times 4$  supercell in our calculations) is  $v_F(\text{NO}_2/\text{Silicene}) = 0.3 \times 10^6 \text{ m s}^{-1}$ . The estimated charge carrier concentrations are  $N_h(\text{NO}_2/\text{Silicene}) = 8 \times 10^{13} \text{ cm}^{-2}$ . These values are larger than that on graphene with the physisorption of molecules<sup>21</sup> and 3 orders of magnitude larger than intrinsic charge carrier concentration of graphene at room temperature ( $n = \pi(k_B T)^2 / 6\hbar(v_F)^2 = 6 \times 10^{10} \text{ cm}^{-2}$ ).<sup>107</sup> It can therefore be calculated that  $\text{NO}_2$ -chemisorption on silicene with large adsorption energies and charge transfer can effectively enhance the hole conductivity in silicene, opening up new applications for nanoelectronic devices.

Finally, we reveal the origin of chemisorption of nitrogen-based gas molecules ( $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$ ) on silicene, which is different from the physisorption of most gas molecules on graphene<sup>11</sup> or silicene.<sup>81</sup> Fig. 3 shows the total and partial density of states (DOS) of  $\text{NH}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$ , silicene and graphene. From Fig. 3a, the frontier orbitals (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)) of  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  are very close to the Dirac point of silicene compared to other common gas molecules (an example of  $\text{N}_2$  is given in Fig. 3a.). Thus, these nitrogen-based gas molecules have high reactivity to silicene. The differences of chemical reactivity between silicene and graphene can also be found from Fig. 3b and c. Graphene is a carbon  $sp^2$  hybridized monolayer with a stable planar honeycomb structure. However, silicene is a silicon hybrid  $sp^2$  and  $sp^3$  hybridized monolayer with stable buckled honeycomb structures,<sup>45</sup> which possesses chemically rich active electronic states at the top of the silicon atoms. Moreover, the corresponding electronic state peaks are more close to silicene's Fermi level compared to that of graphene. Therefore, silicene exhibits higher reactivity than graphene for atoms' and molecules' adsorption, leading to great potential applications of silicene in gas sensors and nanoelectronic devices.

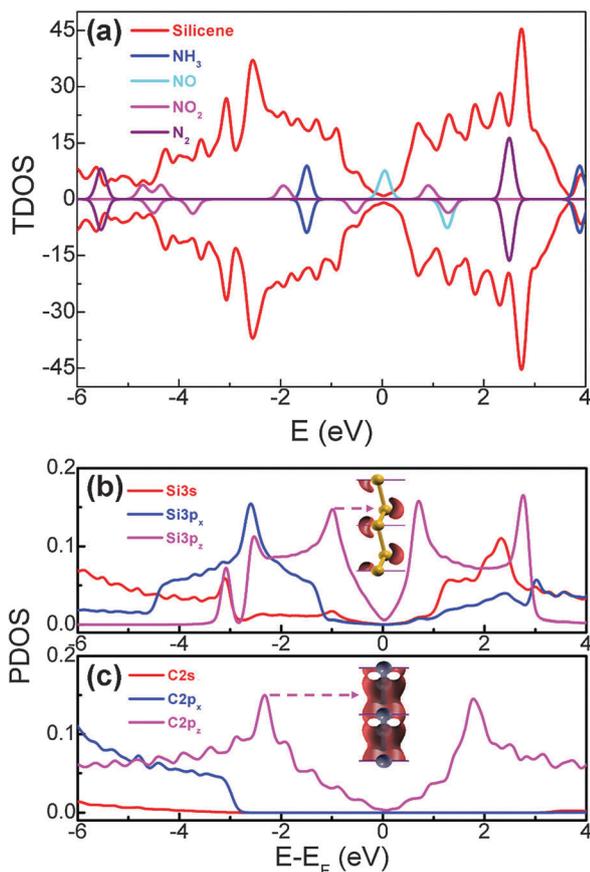


Fig. 3 Total and partial density of states (DOS) of  $\text{NH}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2$ , silicene and graphene. (a) TDOS of  $\text{NH}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2$  and silicene in the  $4 \times 4$  supercell. The positive and negative values represent spin-up and spin-down states, respectively. The Fermi level of silicene is set to zero and all the energy levels are referenced to the vacuum level of silicene. (b) and (c) PDOS of silicene ( $\text{Si}3s$ ,  $\text{Si}3p_x = \text{Si}3p_y$  and  $\text{Si}3p_z$ ) and graphene ( $\text{C}2s$ ,  $\text{C}2p_x = \text{C}2p_y$  and  $\text{C}2p_z$ ) in the unit cell. Partial charge densities with an isosurface value of  $0.1 \text{ e}^{-3}$  of silicene and graphene close to their Fermi levels are shown in the inserts. The yellow and gray balls denote silicon and carbon atoms, respectively. The Fermi levels of silicene and graphene are set to zero.

In summary, we explore the adsorption of  $\text{NH}_3$ ,  $\text{NO}$ , and  $\text{NO}_2$  on silicene on the basis of density functional theory (DFT) calculations. We show that these nitrogen-based molecules chemically adsorb on silicene.  $\text{NO}_2$  has the largest adsorption energy of  $-1.12$  and  $-1.53$  eV per molecule for two adsorption configurations, whereas the adsorption energies of  $\text{NO}$  and  $\text{NH}_3$  range from  $-0.46$  to  $-0.60$  eV per molecule. The high reactivity of silicene to nitrogen-based gas molecules can be understood with the frontier orbitals of molecules and the corresponding electronic states of  $p_z$  electrons in silicene. With the molecular adsorption, an energy band gap can be opened at silicene's Dirac point. Following a simple band folding picture, negligible band gaps are opened at the Dirac point for the  $3N \times 3N$  or  $\sqrt{3}N \times \sqrt{3}N$  supercells of silicene-adsorbed gas molecules, otherwise there are sizable and tunable band gaps opened at silicene's Dirac points. In particular, the calculated charge carrier concentrations of  $\text{NO}_2$ -chemisorbed silicene are

larger than that on graphene with the physisorption of molecules and 3 orders of magnitude larger than intrinsic charge carrier concentration of graphene at room temperature. These findings indicate that silicene is a potential candidate for a molecule sensor with high sensitivity for  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$ .

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