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## A first-principles study of gas adsorption on germanene

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The adsorption of common gas molecules (N<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>, NO, NO<sub>2</sub>, and O<sub>2</sub>) on germanene is studied with density functional theory. The results show that N<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O are physisorbed on germanene via van der Waals interactions, while NH<sub>3</sub>, NO, NO<sub>2</sub>, and O<sub>2</sub> are chemisorbed on germanene via strong covalent (Ge–N or Ge–O) bonds. The chemisorption of gas molecules on germanene opens a band gap at the Dirac point of germanene. NO<sub>2</sub> chemisorption on germanene shows strong hole doping in germanene. O<sub>2</sub> is easily dissociated on germanene at room temperature. Different adsorption behaviors of common gas molecules on germanene provide a feasible way to exploit chemically modified germanene.

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Since the successful identification of graphene from mechanically exfoliated graphite and the subsequent discovery of unusual properties,<sup>1</sup> graphene has attracted enormous experimental and theoretical interest.<sup>2,3</sup> Because of the high surface area, low electrical noise and extremely high electron mobility, graphene is highly sensitive to changes in its chemical environments, making it suitable for applications as a gas sensor.<sup>4</sup> However, the physisorption of common gas molecules on pristine graphene limits its immediate potential.<sup>5</sup> Introducing defect and substitutional doping are effective ways of enhancing the reactivity of gas molecules to graphene.<sup>6–8</sup>

Recently, silicene and germanene, analogues to graphene of silicon and germanium, have also attracted increasing attention. In experiments, silicene was successfully grown on Ag,<sup>9–12</sup> Ir<sup>13</sup> and ZrB<sub>2</sub><sup>14</sup> substrates. Most recently, germanene was also successfully grown on Pt(111).<sup>15</sup> Germanene, multilayer hydrogen-terminated germanene, has also been synthesized and then mechanically exfoliated to a single layer onto SiO<sub>2</sub>/Si surface.<sup>16</sup> Silicene and germanene show the most outstanding properties similar to those of graphene such as high carrier mobility,<sup>17</sup> ferromagnetism,<sup>18</sup> half-metallic,<sup>19</sup> quantum hall effect<sup>20</sup> and a topological insulator.<sup>21</sup> However, silicene on metal substrates does not exhibit these properties, and the properties of silicene on low dimensional materials, e.g. graphene, is considerably closer to pristine silicene.<sup>22</sup>

Interestingly, because of its buckled honeycomb structure,<sup>23</sup> silicene exhibits a significantly higher chemical reactivity than graphene, showing a much stronger adsorption of atoms<sup>24–30</sup>

and molecules<sup>31–35</sup> than graphene with good potential applications on new silicene based nanoelectronic devices,<sup>23</sup> Li-ion storage batteries,<sup>27</sup> hydrogen storage,<sup>28</sup> catalysts,<sup>29</sup> thin-film solar cell absorbers,<sup>30</sup> helium<sup>32</sup> and hydrogen<sup>33</sup> separation membranes, molecule sensor and detection.<sup>34,35</sup> Recently, atom adsorption on germanene is also studied.<sup>36,37</sup> Similar to silicene, atoms bind much stronger to germanene than graphene, which is mainly caused by the sp<sup>2</sup>–sp<sup>3</sup> hybridization of Ge atom. However, little attention has been focused on molecule adsorption on germanene.

In this study, a systematic investigation of common gas molecules' adsorption behavior on germanene is performed with density functional theory calculations. The results show that N<sub>2</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O are physisorbed on germanene but NH<sub>3</sub>, NO, NO<sub>2</sub> and O<sub>2</sub> are chemisorbed on germanene. The moderate adsorption of NH<sub>3</sub> and NO<sub>2</sub> makes germanene a potential material for gas sensing. Strong adsorption of NO<sub>2</sub> and O<sub>2</sub> indicates that they can be used for modifying the electronic structures of germanene.

We perform density functional theory (DFT) calculation implemented in VASP (Vienna ab initio Simulation Package)<sup>38</sup> with the generalized gradient approximation (GGA)<sup>39</sup> of Perdew, Burke, and Ernzerhof (PBE) functional. The van der Waals (vdW) correction proposed by Grimme (DFT-D2)<sup>40</sup> is chosen to describe the long-range interaction.<sup>41–49</sup> As a benchmark, DFT-D2 calculations give a good bilayer distance of 3.25 Å and binding energy of –25 meV per carbon atom for bilayer graphene, which is in complete agreement with the previous experiments<sup>50,51</sup> and theories.<sup>52,53</sup> The energy cutoff is set to 450 eV. The vacuum space in the Z direction is about 15 Å to separate the interactions between the neighboring slabs. For a 4 × 4 supercell, 3 × 3 × 1 *k*-points in Brillouin zone are sampled for geometry optimization and 7 × 7 × 1 *k*-points for static total energy and band structure calculation. The energy and force convergence

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are  $10^{-5}$  eV and  $0.01$  eV  $\text{\AA}^{-1}$ , respectively. Charge transfer is obtained based on Bader analysis.<sup>54</sup> The optimized lattice constant of a unit cell is  $4.058$   $\text{\AA}$ , which agrees with the previous studies.<sup>55,56</sup>

To evaluate the stability of the adsorption of gas molecules on germanene, the adsorption energy is defined as

$$E_a = E_{\text{gas/germanene}} - E_{\text{gas}} - E_{\text{germanene}},$$

where  $E_{\text{gas}}$ ,  $E_{\text{germanene}}$  and  $E_{\text{gas/germanene}}$  are the total energy of the gas molecule, germanene and gas molecule adsorbed on germanene, respectively.

The most stable adsorption configurations for the adsorption of gas molecules on germanene are plotted in Fig. 1, and the corresponding adsorption properties are listed in Table 1. We find that  $\text{N}_2$ , CO,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are physisorbed on germanene *via* van der Waals interactions.  $\text{N}_2$  and CO prefer to adsorb on the hollow site, while  $\text{CO}_2$  is adsorbed on the valley site.  $\text{H}_2\text{O}$  is adsorbed on the top site with two hydrogen atoms pointing toward the surface. The adsorption energies of  $\text{N}_2$ , CO,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are  $-0.13$ ,  $-0.16$ ,  $-0.10$  and  $-0.22$  eV, respectively. Therefore, germanene is also chemically inert to these gas molecules, similar to graphene<sup>5</sup> and silicene.<sup>33</sup> The adsorption energy of water molecule cluster is calculated to find whether germanene is hydrophobic or not. For a cluster with five water molecules, the total adsorption energy is  $-0.11$  eV per  $\text{H}_2\text{O}$  molecule, which is smaller than the binding energy of the water cluster

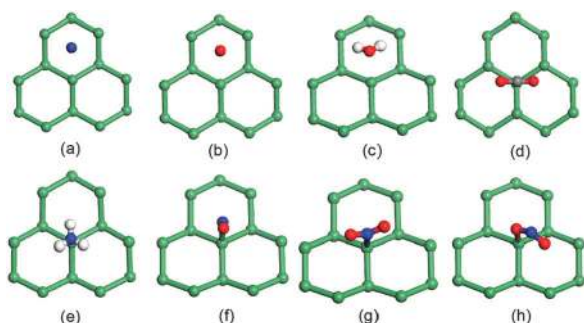


Fig. 1 Atomic structures of the adsorption of gas molecules in the most stable configuration on germanene. (a)  $\text{N}_2$ , (b) CO, (c)  $\text{H}_2\text{O}$ , (d)  $\text{CO}_2$ , (e)  $\text{NH}_3$ , (f) NO, (g)  $\text{NO}_2$  (N-Ge), (h)  $\text{NO}_2$  (O-Ge). The white, blue, gray, red and green balls denote hydrogen, nitrogen, carbon, oxygen and germanium atoms, respectively.

Table 1  $E_a$ : the adsorption energy.  $\rho$ : the charge transfer from germanene to gas molecule.  $d_{\text{Ge-X}}$ : the shortest distance of the atom in the molecule to the germanene surface.  $E_g$ : the band gap opened at the Dirac point of germanene

Model	$E_a/\text{eV}$	$\rho/e$	$d_{\text{Ge-X}}/\text{\AA}$	$E_g/\text{meV}$
$\text{N}_2$	$-0.13$	$0.05$	$3.54$	$4$
CO	$-0.16$	$0.10$	$3.32$	$11$
$\text{CO}_2$	$-0.10$	$0.05$	$3.54$	$3$
$\text{H}_2\text{O}$	$-0.22$	$0.03$	$2.99$	$21$
$\text{NH}_3$	$-0.44$	$-0.12$	$2.33$	$82$
NO	$-0.51$	$0.24$	$2.34$	$95$
$\text{NO}_2$ (N-Ge)	$-0.90$	$0.58$	$2.14$	$161$
$\text{NO}_2$ (O-Ge)	$-1.08$	$0.66$	$2.02$	$170$

( $-0.37$  eV per hydrogen bond). Thus, germanene is hydrophobically similar to graphene.<sup>57</sup>

However,  $\text{NH}_3$ , NO,  $\text{NO}_2$  and  $\text{O}_2$  are chemisorbed on germanene *via* strong covalent (Ge-N or Ge-O) bonds.  $\text{NH}_3$  prefers to adsorb on the top site of germanene with a moderate adsorption energy of  $-0.44$  eV and a Ge-N bond of  $2.33$   $\text{\AA}$ . For NO, spin-polarized calculation is used because it is a molecule with net magnetic moment. NO also prefers to adsorb on the top site and keeps its magnet moment. The adsorption energy is  $-0.51$  eV and the Ge-N bond length is  $2.34$   $\text{\AA}$ . There is little charge transfer between germanene and these two molecules. The electron is transferred from  $\text{NH}_3$  (electron donor) to germanene and then from germanene to NO (electron acceptor). Furthermore, the charge transfer of  $\text{NH}_3$  and NO is distinctly larger than those ( $-0.03$  and  $-0.02$  e) on graphene.<sup>5</sup> Meanwhile, the adsorption energy is moderate, and it is possible to desorb them simply by heating. Therefore, germanene may act as a potential material for the gas sensor of  $\text{NH}_3$  and NO.<sup>34</sup> Although it is paramagnetic,<sup>58</sup> charge transfer in NO adsorption mainly occurs through orbital overlap.

For  $\text{NO}_2$  chemisorption on germanene, we find two stable configurations, namely N-Ge and O-Ge, as shown in Fig. 1g and h with strong adsorption energies of  $-0.90$  and  $-1.08$  eV, and strong covalent Ge-N and Ge-O bonds of  $2.14$  and  $2.02$   $\text{\AA}$ , respectively. The  $\text{NO}_2$  molecule lost its magnet moment in both configurations. A large amount of the charge transfers from germanene to  $\text{NO}_2$ , as listed in Table 1.

The effect of the adsorbed molecules on the electronic structures of germanene is also studied, and the corresponding electronic band structures are plotted in Fig. 2. The linear Dirac-like dispersion relation of germanene  $E_k = \pm \hbar \nu_F |k|$  around the Fermi level, where  $\nu_F$  is the Fermi velocity, remains

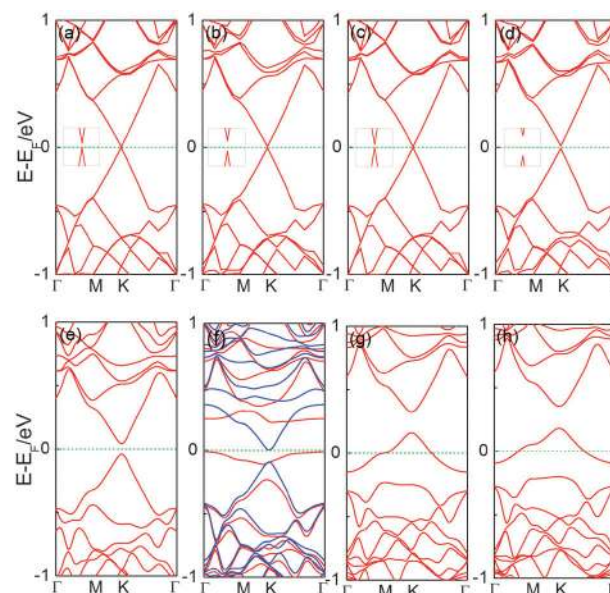


Fig. 2 Electronic band structures of (a)  $\text{N}_2$ , (b) CO, (c)  $\text{CO}_2$ , (d)  $\text{H}_2\text{O}$ , (e)  $\text{NH}_3$ , (f) NO, (g)  $\text{NO}_2$  (N-Ge) and (h)  $\text{NO}_2$  (O-Ge) adsorption on germanene. The red and blue lines represent spin-up and spin-down states, respectively. The Fermi level is set to zero and is marked by the green dotted line.

almost unaffected by the physisorption of  $N_2$ ,  $CO$ ,  $CO_2$  and  $H_2O$  on germanene. Tiny band gaps (3–21 meV) are opened at the Dirac point of silicene, which are lower than thermal fluctuation (about 25 meV) at room temperature, similar to graphene.<sup>5</sup> However, sizable band gaps of (82–170 meV) are opened at the Dirac point of germanene for the chemisorption of  $NH_3$ ,  $NO$ ,  $NO_2$  and  $O_2$  on germanene, which would slightly lower the Fermi velocity of germanene.<sup>34</sup> The large charge transfer from germanene to  $NO_2$  can also be confirmed in their band structures, as shown in Fig. 2g and h, as the Dirac point is moving above Fermi level, resulting in strong p-type doping of germanene.

Recent calculations<sup>31</sup> show that  $O_2$  is very reactive on silicene and can be easily dissociated into two O atoms, which is different from  $O_2$  physisorption on graphene. Here, we study the adsorption behavior of  $O_2$  on germanene. For  $O_2$ , we consider two common initial orientations, namely side-on and end-on mode. The most stable configuration is shown in Fig. 3, and is marked IS. The O–O bond in the  $O_2$  molecule interacts with the Ge–Ge bond, forming a four-membered ring. The O–O bond is parallel to germanene. The adsorption energy is  $-0.90$  eV. The O–O bond is elongated to 1.471 Å, indicating that the  $O_2$  molecule is very reactive. The triplet  $O_2$  molecule lost its magnet moment. To further explore the dissociation process of  $O_2$  on germanene, climbing image nudged elastic band (CI-NEB) is performed. The final state is a state with two O atoms adsorbed on germanene separately, marked as FS in Fig. 3. The adsorption of O atom breaks the Ge–Ge bond. The MEP is shown in Fig. 3. We can see there is a 0.57 eV barrier for  $O_2$  to dissolve into two O atoms. It is quite moderate compared to  $O_2$  dissociation on graphene. Thus, germanene is not very stable in air and chemically modified germanene is possible by  $O_2$  adsorption.

Here, we reveal the origin of the ( $N_2$ ,  $CO$ ,  $CO_2$ ,  $H_2O$ ) physisorption and ( $NH_3$ ,  $NO$ ,  $NO_2$  and  $O_2$ ) chemisorption of gas molecules on germanene. Their densities of states (DOS) are plotted in Fig. 4 and show that the frontier orbitals (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)) of  $NH_3$ ,  $NO$ ,  $NO_2$  and  $O_2$  are close to the Dirac point (or the Fermi level) of germanene. Thus, these gas molecules have higher reactivity to germanene than the

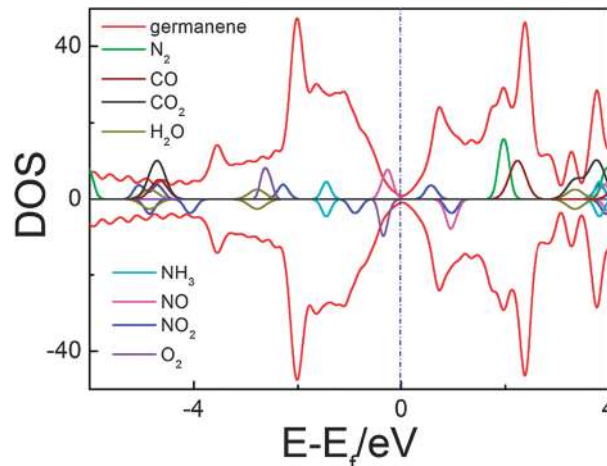


Fig. 4 Density of states (DOS) of  $N_2$ ,  $CO$ ,  $CO_2$ ,  $H_2O$ ,  $NH_3$ ,  $NO$ ,  $NO_2$ ,  $O_2$  and germanene. The positive and negative values represent spin-up and spin-down states, respectively. The Fermi level of germanene is set to zero, and other molecules are referenced to the vacuum level of germanene.

physisorption of other common gas molecules ( $N_2$ ,  $CO$ ,  $CO_2$ ,  $H_2O$ ) on germanene, which is similar to adsorption of these molecules on silicene.<sup>31–35</sup> The adsorption of these molecules is weaker compared to silicene because of the larger radius and electro-negativity of the Ge atom.

In conclusion, we investigate the adsorption of  $N_2$ ,  $CO$ ,  $CO_2$ ,  $H_2O$ ,  $NH_3$ ,  $NO$ ,  $NO_2$ ,  $O_2$  on germanene on the basis of density functional theory calculations. We find that  $N_2$ ,  $CO$ ,  $CO_2$  and  $H_2O$  are physisorbed on germanene, whereas  $O_2$ ,  $NH_3$ ,  $NO$  and  $NO_2$  are chemisorbed on germanene.  $NH_3$  and  $NO$  chemisorption on germanene have moderate adsorption energies and few electrons transfer in different directions, making germanene a candidate for the gas sensing of  $NH_3$  and  $NO$ . For  $NO_2$  chemisorption on germanene, a strong chemical bond is formed, and a large amount of charge is transferred to the molecule, resulting in heavier p-type doping than  $NH_3$  and  $NO$ .  $O_2$  adsorption is very strong, and the molecule is activated and is easily dissociated into two O atoms.

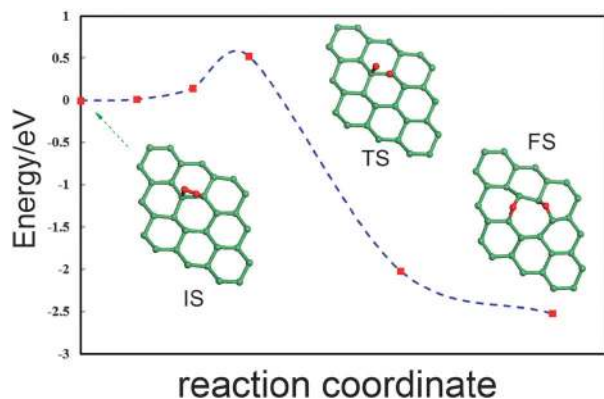


Fig. 3 Minimal energy path (MEP) of  $O_2$  dissociation on germanene. The initial state (IS), transition state (TS) and final state (FS) are shown in the inset. The green and red balls represent Ge and O atom, respectively.

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## Notes and references

- 1 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666.
- 2 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183.
- 3 A. H. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov and A. K. Geim, *Rev. Mod. Phys.*, 2009, **81**, 109.

- 4 F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 652.
- 5 O. Leenaerts, B. Partoens and F. Peeters, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **77**, 125416.
- 6 Y.-H. Zhang, Y.-B. Chen, K.-G. Zhou, C.-H. Liu, J. Zeng, H.-L. Zhang and Y. Peng, *Nanotechnology*, 2009, **20**, 185504.
- 7 J. Dai and J. Yuan, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 165414.
- 8 S. Ni, Z. Li and J. Yang, *Nanoscale*, 2012, **4**, 1184.
- 9 B. Feng, Z. Ding, S. Meng, Y. Yao, X. He, P. Cheng, L. Chen and K. Wu, *Nano Lett.*, 2012, **12**, 3507.
- 10 P. Vogt, P. D. Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet and G. L. Lay, *Phys. Rev. Lett.*, 2012, **108**, 155501.
- 11 L. Chen, C.-C. Liu, B. Feng, X. He, P. Cheng, Z. Ding, S. Meng, Y. Yao and K. Wu, *Phys. Rev. Lett.*, 2012, **109**, 056804.
- 12 L. Chen, H. Li, B. Feng, Z. Ding, J. Qiu, P. Cheng, K. Wu and S. Meng, *Phys. Rev. Lett.*, 2013, **110**, 085504.
- 13 L. Meng, Y. Wang, L. Zhang, S. Du, R. Wu, L. Li, Y. Zhang, G. Li, H. Zhou, W. A. Hofer and H.-J. Gao, *Nano Lett.*, 2013, **13**, 685.
- 14 A. Fleurence, R. Friedlein, T. Ozaki, H. Kawai, Y. Wang and Y. Yamada-Takamura, *Phys. Rev. Lett.*, 2012, **108**, 245501.
- 15 L. Li, S.-Z. Lu, J. Pan, Z. Qin, Y.-Q. Wang, Y. Wang, C.-Y. Cao, S. Du and H.-J. Gao, *Adv. Mater.*, 2014, **26**, 4820.
- 16 E. Bianco, S. Butler, S. Jiang, O. D. Restrepo, W. Windl and J. E. Goldberger, *ACS Nano*, 2013, **7**, 4414.
- 17 F. Bechstedt, L. Matthes, P. Gori and O. Pulci, *Appl. Phys. Lett.*, 2012, **100**, 261906.
- 18 X.-Q. Wang, H.-D. Li and J.-T. Wang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 3031.
- 19 Y. Wang, J. Zheng, Z. Ni, R. Fei, Q. Liu, R. Quhe, C. Xu, J. Zhou, Z. Gao and J. Lu, *NANO*, 2011, **07**, 1250037.
- 20 Y. Ma, Y. Dai, C. Niu and B. Huang, *J. Mater. Chem.*, 2012, **22**, 12587.
- 21 C. Si, J. Liu, Y. Xu, J. Wu, B.-L. Gu and W. Duan, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2014, **89**, 115429.
- 22 G. R. Berdiyrov, M. Neek-Amal, F. M. Peeters and A. C. T. van Duin, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2014, **89**, 024107.
- 23 A. Kara, H. Enriquez, A. P. Seitsonend, L. C. L. Y. Voone, S. Vizzini, B. Aufray and H. Oughaddoub, *Surf. Sci. Rep.*, 2012, **67**, 1.
- 24 X. Lin and J. Ni, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **86**, 075440.
- 25 J. Sivek, H. Sahin, B. Partoens and F. M. Peeters, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2013, **87**, 085444.
- 26 H. Sahin and F. M. Peeters, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2013, **87**, 085423.
- 27 G. A. Tritsarlis, E. Kaxiras, S. Meng and E. Wang, *Nano Lett.*, 2013, **13**, 2258.
- 28 J. Wang, J. Li, S.-S. Li and Y. Liu, *J. Appl. Phys.*, 2013, **114**, 124309.
- 29 C. Li, S. Yang, S.-S. Li, J.-B. Xia and J. Li, *J. Phys. Chem. C*, 2013, **117**, 483.
- 30 B. Huang, H. J. Xiang and S.-H. Wei, *Phys. Rev. Lett.*, 2013, **111**, 145502.
- 31 V. O. Özçelik and S. Ciraci, *J. Phys. Chem. C*, 2013, **117**, 26305.
- 32 W. Hu, X. Wu, Z. Li and J. Yang, *Nanoscale*, 2013, **5**, 9062.
- 33 W. Hu, X. Wu, Z. Li and J. Yang, *Phys. Chem. Chem. Phys.*, 2013, **15**, 5753.
- 34 W. Hu, N. Xia, X. Wu, Z. Li and J. Yang, *Phys. Chem. Chem. Phys.*, 2014, **16**, 6957.
- 35 J.-W. Feng, Y.-J. Liu, H.-X. Wang, J.-X. Zhao, Q.-H. Cai and X.-Z. Wang, *Comput. Mater. Sci.*, 2014, **87**, 218.
- 36 B. van den Broek, M. Houssa, E. Scalise, G. Pourtois, V. V. Afanas'ev and A. Stesmans, *Appl. Surf. Sci.*, 2014, **291**, 104.
- 37 M. Ye, R. Quhe, J. X. Zheng, Z. Y. Ni, Y. Y. Wang, Y. K. Yuan, G. Tse, J. J. Shi, Z. X. Gao and J. Lu, *Physica E*, 2014, **59**, 60.
- 38 G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1993, **47**, 558.
- 39 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 40 S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787.
- 41 S. Grimme, C. Mück-Lichtenfeld and J. Antony, *J. Phys. Chem. C*, 2007, **111**, 11199.
- 42 J. Antony and S. Grimme, *Phys. Chem. Chem. Phys.*, 2008, **10**, 2722.
- 43 N. Kharche and S. K. Nayak, *Nano Lett.*, 2011, **11**, 5274.
- 44 J. Sławińska, P. Dabrowski and I. Zasada, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **83**, 245429.
- 45 R. Kagimura, M. S. C. Mazzoni and H. Chacham, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **85**, 125415.
- 46 Y. Ma, Y. Dai, M. Guo and B. Huang, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **85**, 235448.
- 47 L. Chen, L. Wang, Z. Shuai and D. Beljonne, *J. Phys. Chem. Lett.*, 2013, **4**, 2158.
- 48 W. Hu, Z. Li and J. Yang, *J. Chem. Phys.*, 2013, **138**, 124706.
- 49 W. Hu, Z. Li and J. Yang, *J. Chem. Phys.*, 2013, **139**, 154704.
- 50 Y. Baskin and L. Meyer, *Phys. Rev.*, 1955, **100**, 544.
- 51 R. Zacharia, H. Ulbricht and T. Hertel, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **69**, 155406.
- 52 R. E. Mapasha, A. M. Ukpong and N. Chetty, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **85**, 205402.
- 53 W. Hu, Z. Li and J. Yang, *J. Chem. Phys.*, 2013, **138**, 054701.
- 54 G. Henkelman, A. Arnaldsson and H. Jónsson, *Comput. Mater. Sci.*, 2006, **36**, 354.
- 55 J. C. Garcia, D. B. de Lima, L. V. C. Assali and J. F. Justo, *J. Phys. Chem. C*, 2011, **115**, 13242.
- 56 L. C. Lew Yan Voon, E. Sandberg, R. S. Aga and A. A. Farajian, *Appl. Phys. Lett.*, 2010, **97**, 163114.
- 57 O. Leenaerts, B. Partoens and F. M. Peeters, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **79**, 235440.
- 58 O. Leenaerts, B. Partoens and F. M. Peeters, *Appl. Phys. Lett.*, 2008, **92**, 243125.