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A First-Principles Study of Gas Adsorption on Germanene

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5   The adsorption of common gas molecules (N_2, CO, CO_2, H_2O, NH_3, NO, NO_2, and O_2) on germanene is studied with density functional theory. The results show that N_2, CO, CO_2, and H_2O are physisorbed on germanene via van der Waals interactions, while NH_3, NO, NO_2, and O_2 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_2 chemisorption on germanene shows strong hole doping in
10 germanene. O_2 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.

Since the successful identification of graphene from mechanically exfoliated graphite and subsequent discovery of unusual properties,[1] graphene has attracted enormous
15 experimental and theoretical studies.[2,3] 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 gas sensor.[4] However, the physisorption of common gas molecules on pristine graphene
20 limits its immediate potential.[5] Introducing defect and substitutional doping is an effective way to enhance the reactivity of gas molecules to graphene.[6-8]

Recently, silicene and germanene, analogues to graphene of silicon and germanium have also attracted increasing attentions.
25 In experiments, silicene is successfully grown on Ag, [9-12] Ir[13] and ZrB_2[14] substrates. Most recently, germanene is also successfully grown on Pt(111).[15] Germanane, multilayer hydrogen-terminated germanene has also been synthesized and then mechanically exfoliated to single layer onto SiO_2/Si surface.[16] Silicene and
30 germanene show most outstanding properties similar to graphene, such as high carrier mobility,[17] ferromagnetism,[18] half-metallic,[19] quantum hall effect[20] and topological insulator.[21] However, silicene on metal substrates doesn't exhibit these properties and the properties of silicene on low dimensional materials e.g.
35 graphene is much closer to pristine silicene.[22]

Interestingly, due to its buckled honeycomb structure,[23] silicene exhibits a much higher chemical reactivity than graphene, showing much stronger adsorption of atoms[24-30] and molecules[31-35] than graphene, with great potential applications on
40 new silicene based nanoelectronic devices,[23] Li-ion storage batteries,[27] hydrogen storage,[28] catalyst,[29] thin-film solar cell absorbers,[30] helium[32] and hydrogen[33] separation membrane, molecule sensor and detection,[34,35] superior to graphene. Recently, atom adsorption on germanene is also studied.[36,37]
45 Similar to silicene, atoms bind much stronger to germanene than graphene, mainly caused by the sp^2-sp^3 hybridzation of Ge atom. However, little attention has been focused on molecule adsorption on germanene.

In this study, a systematic investigation of common gas
50 molecules' adsorption behavior on germanene is performed with density functional theory calculations. The results show N_2, CO, CO_2 and H_2O are physisorption on germanene but NH_3, NO, NO_2 and O_2 are chemisorption on germanene. The moderate adsorption of NH_3 and NO_2 makes germanene a potential
55 material for gas sensor. Strong adsorption of NO_2 and O_2 indicates that they can be used to modify germanene's electronic structures.

We perform density functional theory (DFT) calculation implemented in VASP (Vienna ab initio Simulation Package)[38]
60 with the generalized gradient approximation (GGA)[39] of Perdew, Burke, and Ernzerhof (PBE) functional. The van der Waals (vdW) correction proposed by Grimme (DFT-D2)[40] is chosen to describe the long-range interaction.[41-49] As an benchmark, DFT-D2 calculations give a good bilayer distance of 3.25 Å and binding
65 energy of -25 meV per carbon atom for bilayer graphene, fully agreeing with previous experiment[50,51] and theory.[52,53] The energy cutoff is set to 450 eV. The vacuum space in the Z direction is about 15 Å to separate the interactions between neighboring slabs. For a 4×4 supercell, a 3×3×1 k-points in
70 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 are 10^{-5} eV and 0.01 eV/Å. Charge transfer is obtained based on Bader analysis.[54] The optimized lattice constant of a unit cell is 4.058 Å, which agrees with
75 previous study.[55,56]

In order to evaluate the stability of gas molecules adsorption on germanene, the adsorption energy is defined as

$$E_a = E_{gas/germanene} - E_{gas} - E_{germanene}$$

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

The most stable adsorption configurations for gas molecules adsorption on germanene are plotted in Fig 1 and corresponding adsorption properties are listed in Table 1. We find that N_2, CO, CO_2 and H_2O are physisorbed on germanene via van der Waals
85 interactions. N_2 and CO prefer to adsorb on the hollow site while

CO_2 is adsorbed on the valley site. H_2O is adsorbed on the top site with two hydrogen atoms pointing to the surface. The adsorption energies of N_2, CO, CO_2 and H_2O 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[5] and silicene.[32] The adsorption energy of water molecule cluster is calculated to find whether germanene is hydrophobicity or not. For a cluster with five water molecules, the total adsorption energy is -0.11 eV per H_2O molecule, which is smaller than the binding energy of the water cluster (-0.37 eV per hydrogen bond). So germanene is hydrophobic similar to graphene.[57]
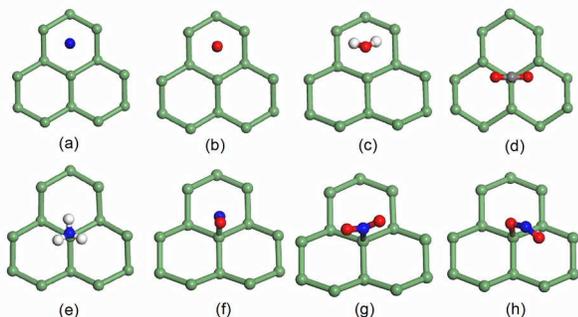

Fig. 1. Atomic structures of gas molecules adsorption in the most stable configuration on germanene. (a) N_2, (b) CO, (c) H_2O, (d) CO_2, (e) NH_3, (f) NO, (g) NO_2 (N-Ge), (h) NO_2 (O-Ge). The white, blue, gray, red and green balls donate hydrogen, nitrogen, carbon, oxygen and germanium atoms, respectively.
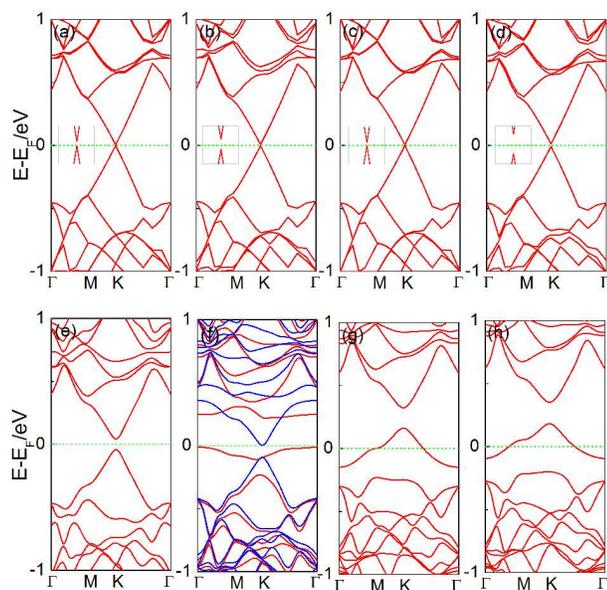

Fig. 2. Electronic band structures of (a) N_2, (b) CO, (c) CO_2, (d) H_2O, (e) NH_3, (f) NO, (g) NO_2 (N-Ge) and (h) NO_2 (O-Ge) adsorption on germanene. The red and blue lines represent spin-up and spin-down states, respectively. The Fermi level is set to zero and marked by green dot line.

Table1: E_a: the adsorption energy. ρ: the charge transfer from germanene to gas molecule. d_{Ge-X}: the shortest distance of the atom in molecule to the germanene surface. E_g: the band gap opened at Dirac point of germanene

model	E_a/eV	ρ/e	d_{Ge-X}/ Å	E_g(meV)
N_2	-0.13	0.05	3.54	4
CO	-0.16	0.10	3.32	11
CO_2	-0.10	0.05	3.54	3
H_2O	-0.22	0.03	2.99	21
NH_3	-0.44	-0.12	2.33	82
NO	-0.51	0.24	2.34	95
NO_2(N-Ge)	-0.90	0.58	2.14	161
NO_2(O-Ge)	-1.08	0.66	2.02	170

However, NH_3, NO, NO_2 and O_2 are chemisorbed on germanene via strong covalent (Ge-N or Ge-O) bonds. 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 2.34 Å. For NO, spin-polarized calculation is used as 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 Å. There is little charge transfer between germanene and these two molecules. Electron transfers from NH_3 (electron donor) to germanene, but from germanene to NO (electron acceptor). Furthermore, the charge transfer of NH_3 and NO is distinctly larger than these (-0.03 and -0.02 e) on graphene.[5]. Meanwhile, the adsorption energy is moderate, it is possible to desorb them simply by heating. Therefore, germanene may act as a potential material for gas sensor of NH_3 and NO.[34] Although it is paramagnetic,[58] charge transfer in NO adsorption is mainly through orbital overlap.

For NO_2 chemisorption on germanene, we find two stable configurations, named N-Ge and O-Ge, as shown in Fig. 1g and Fig. 1h, with strong adsorption energies of -1.08 and -0.90 eV, and strong covalent Ge-N and Ge-O bonds of 2.14 and 2.02 Å, respectively. The NO_2 molecule lost its magnet moment in both two configurations. Large amount of charge transfers from germanene to NO_2, as listed in Table 1.

The effect of adsorbed molecules on germanene's electronic structures is also studied and corresponding electronic band structures are plotted in Fig. 2. Silicene's linear Dirac-like dispersion relation $E_k = \pm \hbar v_F |k|$ around the Fermi level, where v_F is the Fermi velocity, is almost not affected 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.[5] But Sizable band gaps of (82~170 meV) are opened at Dirac point of germanene for the chemisorption of NH_3, NO, NO_2 and O_2 on germanene, which would slightly lower germanene's Fermi velocity.[34] The large charge transfer from germanene to NO_2 also can be confirmed in their band structures as shown in Fig. 2g and Fig. 2h, as the Dirac point is moving above Fermi level, resulting in strong p-type doping of germanene.

Recent calculations[31] show that O_2 is very reactive on silicene and can be easily dissociated into two O atoms, different from compared 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, as marked IS. The O-O bond in O_2 molecule interacts with the Ge-Ge bond, forming a four-remenebered ring. The O-O bond is parallel to the germanene. The adsorption energy is -0.90 eV. The

O-O bond is longed to 1.471 Å, indicating 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, as marked 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 the O_2 dissociation on graphene. Thus, germanene is not very stable in air and chemical modified germanene is possible by O_2 adsorption.
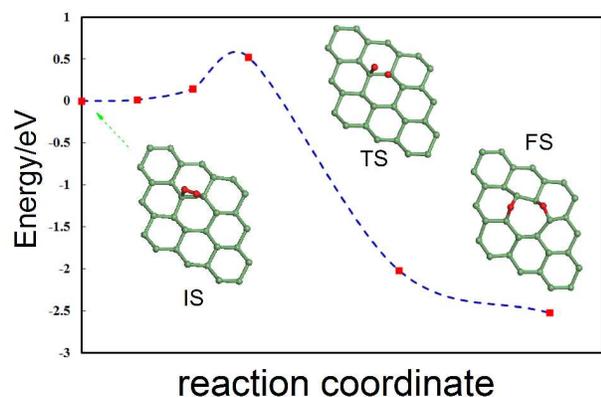

Fig. 3. Minimal energy path (MEP) of O_2 dissociation on germanene. The initial state (IS), transition state (TS) and final state (FS) are shown in the inset. The green and red balls represent Ge and O atom, respectively.

Here, we reveal the origin of gas molecules (N_2, CO, CO_2, H_2O) physisorption and (NH_3, NO, NO_2 and O_2) chemisorption 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 other common gas molecules (N_2, CO, CO_2, H_2O) physisorption on germanene, similar these molecules adsorption on silicene.[31-35] The adsorption of these molecules is weaker compared to silicene because of the larger radius and electronegativity of Ge atom.
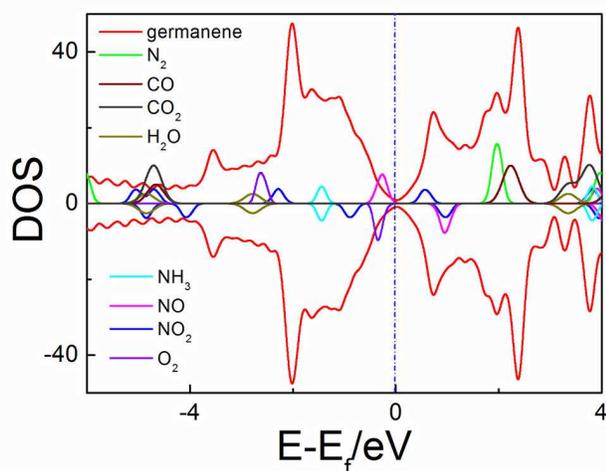

Fig. 4. Density of states (DOS) of N_2, CO, CO_2, H_2O, NH_3, NO, NO_2, O_2 and germanene. The positive and negative values represent spin-up and spin-down states, respectively. The Fermi level of germanene is set to zero and other molecules are referenced to the vacuum level of germanene

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 electron transferring in different directions, making germanene a candidate for gas sensor of NH_3 and NO. For NO_2 chemisorption on germanene, a strong chemical bond is formed and large amount of charge is transferred to the molecule, resulting heavier p-type doping than NH_3 and NO. The O_2 adsorption is very strong and the molecule is activated, thus the molecule is easily dissociated into two O atoms.
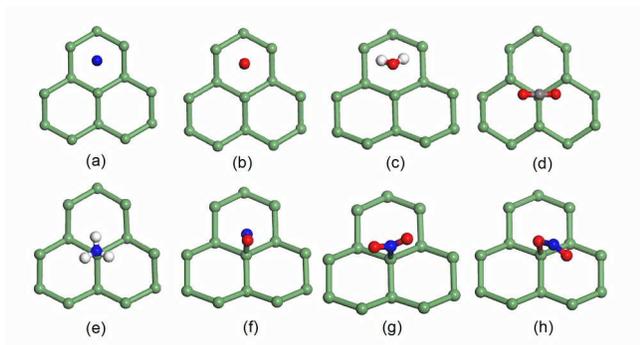.

Notes and references

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1 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Scinece* 2004, **306**, 666.
2 A. K. Geim, and K. S. Novoselov, *Nature 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, *Nature Mater.* 2007, **6**, 652.
5 O. Leenaerts, B. Partoens and F. Peeters, *Phys. Rev. B* 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* 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, 2014, *Adv. Mater.* DOI: 10.1002/adma.201400909

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* 2014, **89**, 115429.

22 G. R. Berdiyorov, M. Neek-Amal, F. M. Peeters, and Adri C. T. van Duin, Phys. Rev. B 2014, **89**, 024107.

23 A. Kara, H. Enriquez, A. P. Seitsonend, L. C. L. Y. Voone, S. Vizzini, B. Aufrayg and H. Oughaddoub, *Surf. Sci. Rep.* 2012, **67**, 1.

24 X. Lin and J. Ni, *Phys. Rev. B* 2012, **86**, 075440.

25 J. Sivek, H. Sahin, B. Partoens and F. M. Peeters, *Phys. Rev. B* 2013, **87**, 085444.

26 H. Sahin and F. M. Peeters, *Phys. Rev. B* 2013, **87**, 085423.

27 G. A. Tritsaris, 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, *Comp. 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* 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* 2011, **83**, 245429.

45 R. Kagimura, M. S. C. Mazzoni and H. Chacham, *Phys. Rev. B*, 2012, **85**, 125415.

46 Y. Ma, Y. Dai, M. Guo and B. Huang, *Phys. Rev. B*, 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* 2004, **69**, 155406.

52 R. E. Mapasha, A. M. Ukpong and N. Chetty, *Phys. Rev. B* 2012, **85**, 205402.

53 W. Hu, Z. Li and J. Yang, *J. Chem. Phys.* 2013, **138**, 054701.

54 G. Henkelman, A. Arnaldsson and H. Jónsso, *Comp. 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* 2009, **79**, 235440.

58 O. Leenaerts, B. Partoens and F. M. Peeters, *Appl. Phys. Lett.* 2008, **92**, 243125.

TOC Figure