Hybrid functional studies on the optical and electronic properties of graphane and silicane

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ABSTRACT

The optical and electronic properties of graphane and silicane are studied by a first-principles method based on density functional theory, employing both the hybrid (HSE06) and the Perdew–Burke–Ernzerhof (PBE) functionals. Our HSE06 results show that graphane has a direct band gap of 4.49 eV, while silicane has an indirect band gap of 2.94 eV. In graphane, the imaginary part of dielectric function $\varepsilon_2(\omega)$ has two peaks at 7.70 and 15.03 eV for $\mathbf{E}\|z$, while for $\mathbf{E}\|x$, there are three peaks lying at 11.56, 13.25 and 14.33 eV. In silicane, $\varepsilon_2(\omega)$ has a main peak at 8.68 eV for $\mathbf{E}\|z$, while there are two peaks at 4.56 and 8.55 eV for $\mathbf{E}\|x$. In graphane, the peaks in $\varepsilon_2(\omega)$ are mainly due to the transitions from C 2p and H 1s states to C 2s and 2p ones; while in silicane, the peaks are primarily originated from the transitions from Si 3p and H 1s states to Si 3s and 3p as well as H 1s states.

1. Introduction

Graphene is a zero band gap semimetal with Dirac cones at the Fermi level. The outstanding optical and electronic properties make it widely used in many areas such as touch screens, ultrafast lasers and transparent coatings [1]. However, the zero band gap restricts its applications in the field of optics and transistor technology [2,3]. Thus, it is crucial to open a band gap for graphene. Recently, Elias et al. [4] have synthesized fully hydrogenated graphene (named as "graphane"), which is a wide band gap semiconductor [5,6]. This change in band gap makes the graphane possible applications in nano-devices, optoelectronics and room temperature field effect transistors [5,7]. Silicon and carbon are in the same column of the periodic table. The optoelectronic applications of semiconductor Si can be improved by nanostructuring, as it is manifested by Si polymers having a strong ultraviolet luminescence [8,9]. Therefore, a lot of attention has been paid to Si-based nanotechnology from both the theoretical and experimental point of view [10–13]. In earlier years, H-saturated Si sheet has been synthesized in the context of polysilane [14]. Recently, silicene, the graphene-like 2-dimensional (2D) silicon material, was synthesized on Ag (110) or (111)

substrates [12,13]. Similar to graphene, silicene is also a zero band gap semimetal with Dirac cones at the Fermi level. For a fully hydrogenated silicene, named as silicane which is the counterpart of graphane, a small indirect band gap is opened. However, its potential application in optoelectronics might be limited by its indirect gap [15]. Although electronic properties of graphane and silicane have been investigated, very little theoretical work has been done for their optical properties. The optical properties of graphane and silicane are crucial to their fundamental applications.

In the present work, we have systematically studied the optical and electronic properties of graphane and silicane. The studies are based on a well-established first-principles method, employing both the hybrid [16–18] and the Perdew–Burke–Ernzerhof (PBE) functionals [19]. The detailed information of optical properties has been obtained by calculating the electronic structures. We have focused on the dielectric functions and absorption coefficients of graphane and silicane. Moreover, the band structures and electronic density of states have also been employed to analyze the interband transitions, which explains the peaks in the dielectric functions.

2. Computational method

The present calculations have been performed by using the Vienna ab initio simulation package (VASP) [20,21], which is based on the density functional theory, the plane-wave basis and the projector augmented wave (PAW) representation [22]. Both the

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generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE) [19] functional, and the Heyd–Scuseria–Ernzerhof hybrid functional (HSE06) [16–18] are used to treat the exchange-correlation energy. Wave functions are expanded by plane waves up to a kinetic energy cutoff of 500 eV. Slab models, which are consisted of repeated 2D atomic layers, are used to treat the two-dimensional materials such as the graphene, graphane, silicene and silicane. To avoid interlayer interactions, we set a vacuum space of 20 Å along the z-direction, when graphane and silicane are in the xy plane. Brillouin-zone integrations are approximated by using special k-point sampling of Monkhorst–Pack scheme [23], with a k-point mesh resolution of $2\pi \times 0.02$ Å^{-1}.

In order to obtain more accurate band structures, the hybrid functional (HSE06) [16–18] calculations are also performed in addition to the PBE results. In the HSE06, the exchange-correlation energy is described as follows:

$$E_{xc}^{HSE06} = \frac{1}{4}E_x^{HF,SR}(\mu) + \frac{3}{4}E_x^{PBE,SR}(\mu) + E_x^{PBE,LR}(\mu) + E_c^{PBE} \qquad (1)$$

where $E_x^{HF,SR}(\mu)$, $E_x^{PBE,SR}(\mu)$, $E_x^{PBE,LR}(\mu)$ and E_c^{PBE} represent the short-range Hartree–Fock (HF) exchange, the short-range PBE exchange, the long-range PBE exchange and the PBE correlation terms, respectively. The screening parameter μ is related to a characteristic distance, $(2/\mu)$, at which the short-range interactions become negligible. Empirically, it was shown that the optimum range-separation parameter μ is between 0.2 and 0.3 [16,17,24]. In this work, the parameter μ is set to be 0.2 Å^{-1}.

3. Results and discussion

Only the chair-like graphane and silicane are considered in this work, since the chair-like configuration is the most preferable and stable structure for graphane and silicane [5,25]. The geometrical parameters of graphene, graphane, silicene and silicane are presented in Table 1 , with both the presently calculated and the previous data. The optimized geometric structures of graphane and silicane are shown in Fig. 1. In 2D graphene, carbon atoms are covalently bonded to three other carbon atoms with planar sp^2 hybridization. For the fully hydrogenated graphene, i.e. graphane, there is a buckling of 0.46 Å for the two carbon sublattices. Compared with graphene, graphane is then mainly sp^3 hybridizations. For the silicene, it is a structure with mixed sp^2–sp^3 hybridization since there is a buckling between two Si sublattices. For the silicane, the buckling is calculated to be as large as 0.72 Å, which is much bigger than that of graphane (showing again sp^3 hybridizations). In Table 1, the calculated lattice constants of graphane and silicene are 2.56 and 3.89 Å, respectively. The C–C and C–H bond lengths in graphane, 1.53 and 1.11 Å respectively,

are smaller than the corresponding ones of Si–Si and Si–H bonds in silicane, 2.36 and 1.50 Å respectively. The angles θ_{C-C-C}, $\theta_{Si-Si-Si}$, θ_{C-C-H} and $\theta_{Si-Si-H}$ are 111.42°, 111.13°, 107.43° and 107.75°, respectively. All these angles are close to the tetrahedral angle of diamond which is 109.47°. The present structural character of graphane and silicane should indicate that the hybridization is sp^3-like in both the materials. As shown in Table 1, our calculated results are in good agreement with those found previously [26–28].

Fig. 2 gives the calculated band structures and density of states (DOS) of graphane and silicane by using both the HSE06 and PBE functionals, respectively. In order to show explicitly the differences between the electronic structures obtained by the two methods, band structures given by the PBE and HSE06 methods are compared in Fig. 3. Band gaps of graphane and silicane are listed in Table 2, which are calculated by employing the LDA, PBE and HSE06 functionals and compared with available data. We found that graphane has a direct band gap of 3.43 eV at Γ point with the PBE functional, while the HSE06 method gives an electronic band gap of 4.49 eV which is closer to experiment data (see Table 2). As for silicane, the PBE method obtains an indirect band gap of 2.19 eV, while the HSE06 gives a band gap of 2.94 eV (again indirect). Both the PBE and HSE06 results show that for graphane both the VBM (valence band maximum) and CBM (conduction
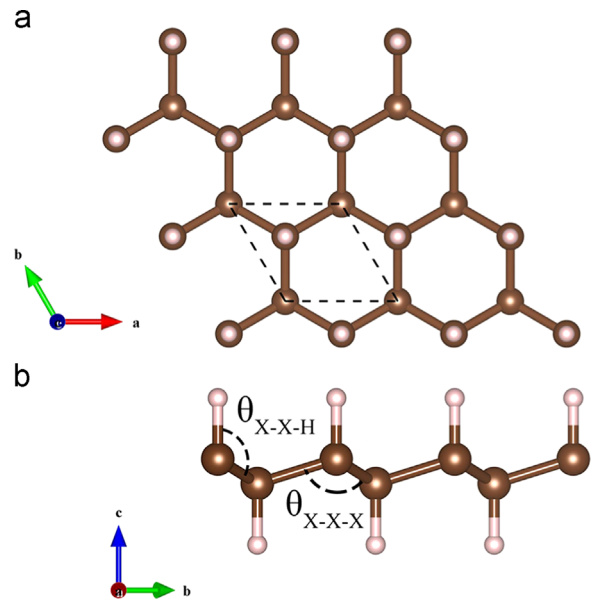

Fig. 1. (Color online) The top and side views of a graphane or silicane sheet. X atoms (X=C, Si) are represented by big brown balls and H atoms by small pink ones, respectively.

Table 1
Geometrical parameters of graphene, graphane, silicene and silicane. Lattice constant a, bond lengths d_{X-X} and d_{X-H} (X=C or Si), buckling distance Δ, angle between adjacent X–X bonds, θ_{X-X-X}, and angle between adjacent H–X and X–X bonds, θ_{X-X-H} are presented.

System		a (Å)	d_{X-X} (Å)	d_{X-H} (Å)	Δ (Å)	θ_{X-X-X} (deg)	θ_{X-X-H} (deg)
Graphene	Present	2.46	1.42	–	0.00	120	–
	Previous	2.46[a]	1.42[a]	–	0.00[a]	120[a]	–
Graphane	Present	2.54	1.53	1.11	0.46	111.42	107.43
	Previous	2.51[a], 2.54[b]	1.52[a], 1.53[b]	1.12[a],1.11[b]	0.45[a],0.46[b]	111.51[a]	107.35[a]
Silicene	Present	3.87	2.28	–	0.45	115.87	–
	Previous	3.86[b], 3.88[c]	2.28[b]	–	0.47[b]	–	–
Silicane	Present	3.89	2.36	1.50	0.72	111.13	107.75
	Previous	3.89[b], 3.88[c]	2.36[b]	1.50[b]	0.71[b]	–	–

[a] Ref. [26].
[b] Ref. [27].
[c] Ref. [28].