

Structural, electronic, and optical properties of hybrid silicene and graphene nanocomposite

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Structural, electronic, and optical properties of hybrid silicene and graphene (S/G) nanocomposite are examined with density functional theory calculations. It turns out that weak van der Waals interactions dominate between silicene and graphene with their intrinsic electronic properties preserved. Interestingly, interlayer interactions in hybrid S/G nanocomposite induce tunable p-type and n-type doping of silicene and graphene, respectively, showing their doping carrier concentrations can be modulated by their interfacial spacing. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4824887>]

I. INTRODUCTION

Silicene, a single silicon monolayer with buckled honeycomb structure,¹ has attracted a considerable attention² owing to its intriguing properties, including ferromagnetism,^{3,4} half-metallicity,⁵ quantum hall effect,⁶ giant magnetoresistance,⁷ and superconductivity.⁸ Interestingly, tunable band gaps can be opened and modulated linearly with external electric field in pristine silicene monolayer⁹ and h-BN-sandwiched silicene.¹⁰ Note that silicene has similar excellent properties to graphene,^{11–15} such as high carrier mobility, with a great potential for high-performance field effect transistors (FETs). Experimentally, silicene can be fabricated by means of depositing silicon on Ag^{16–21} and ZrB₂²² substrates, but which significantly lower its carrier mobility due to strong silicene-substrate interactions, similar to graphene on some substrates, including SiO₂,^{23–26} SiC,^{27–31} and several metal surfaces.^{32–35} Ideal substrates for silicene to preserve its intrinsic properties are still not observed in experiments.

Most recently, atomic and electronic properties of 2D silicon sheet (not silicene) on a graphene substrate^{36,37} have been studied via first-principles calculations. Hybrid silicene/graphene (S/G) monolayer superlattices³⁸ have been proposed theoretically, which may be observed experimentally in graphene layers grown on top of SiC substrates.^{27–31} Moreover, several 2D graphene based nanocomposites have also been predicted theoretically and successfully synthesized in experiments, such as graphene/hexagonal boron nitride (G/h-BN),^{39–41} graphene/MoS₂ nanosheet (G/MoS₂),^{42–44} graphene/MoSe₂ nanosheet (G/MoSe₂),^{45,46} graphene/graphitic carbon nitride (G/g-C₃N₄),^{47,48} and graphene/graphitic ZnO (G/g-ZnO).⁴⁹ These novel nanocomposite systems show new atomic and electronic properties far beyond their simplex components. Here, an interesting question arises: whether silicene and graphene can form a 2D hybrid S/G nanocomposite with new properties?

In the present work, we design new 2D hybrid S/G nanocomposite and study its electronic and optical properties with first-principles calculations. The results show that silicene interacts overall weakly with graphene via van der Waals (vdW) interactions, thus, their intrinsic electronic properties, especially, the high carrier mobility, can be preserved in hybrid S/G nanocomposite. Moreover, interlayer interactions induce tunable p-type and n-type doping of silicene and graphene, respectively.

II. THEORETICAL METHODS AND MODELS

The lattice parameters of graphene and silicene calculated to setup unit cell are $a(G) = 2.47 \text{ \AA}$ and $a(S) = 3.87 \text{ \AA}$.^{3,15} In order to simulate a hybrid S/G nanocomposite, a 2×2 supercell of silicene (8 silicon atoms) is used to match a 3×3 supercell of graphene (18 carbon atoms). The lattice parameter of hybrid S/G nanocomposite is fixed to be $a(S/G) = (2a(S) + 3a(G))/2 = 7.57 \text{ \AA}$ with a small lattice mismatch of about 2% for both silicene and graphene. Different stacking patterns of hybrid S/G nanocomposites are designed, showing similar electronic and optical properties (see Figures S1 and S2 of the supplementary material⁵⁰). The most stable stacking pattern S/G nanocomposite is adopted in this work and its atomic structures are shown in Fig. 1.

First-principles calculations are based on the density functional theory (DFT) implemented in the VASP package.⁵¹ The generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE)⁵² with van der Waals (vdW) correction proposed by Grimme (DFT-D2)⁵³ is chosen due to its good description of long-range vdW interactions.^{54–65} Many recent theoretical studies^{66–68} suggest that DFT-D2 can produce quite close results for many periodic systems comparative with other nonempirical vdW corrections, such as vdW-DF,⁶⁹ which strongly depends on the exchange-correlation functionals.^{70–72} As a benchmark, DFT-D2 calculations give a good bilayer distance of $c = 3.25 \text{ \AA}$ and binding energy of $E_b = -25 \text{ meV}$ per carbon atom for bilayer graphene, which fully agree with previous experimental measurements

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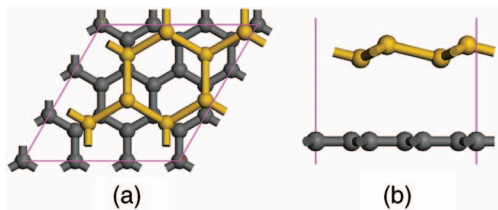


FIG. 1. Atomic structures of hybrid S/G nanocomposite ((a) top and (b) side views). The gray and yellow balls denote carbon and silicon atoms, respectively.

($c = 3.35 \text{ \AA}$ and $E_b = -26 \text{ meV}$)^{73,74} and theoretical studies ($c = 3.34 \text{ \AA}$ and $E_b = -31 \text{ meV}$).^{75,76} The energy cutoff is set to be 500 eV. The surface Brillouin zone is sampled with a 7×7 regular mesh and 300 k points are used for calculating the tiny band gaps at the Dirac points of silicene and graphene in the hybrid S/G nanocomposite supercell. The vacuum space in the Z direction is about 15 \AA to separate the interactions between neighboring slabs. All the geometry structures are fully relaxed until energy and forces are converged to 10^{-5} eV and 0.01 eV/\AA , respectively. Dipole correction is employed to cancel the errors of electrostatic potential, atomic forces, and total energy, caused by periodic boundary condition.⁷⁷

To investigate the optical properties of hybrid S/G nanocomposite, the frequency-dependent dielectric matrix is calculated.⁷⁸ The imaginary part of dielectric matrix is determined by a summation over states as

$$\epsilon''_{\alpha\beta} = \frac{4\pi^2 e^2}{\Omega} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{c,v,\mathbf{k}} 2w_{\mathbf{k}} \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega) \times \langle \mu_{c\mathbf{k}+\mathbf{e}_{\alpha}q} | \mu_{v\mathbf{k}} \rangle \langle \mu_{c\mathbf{k}+\mathbf{e}_{\beta}q} | \mu_{v\mathbf{k}} \rangle^*, \quad (1)$$

where Ω is the volume of the primitive cell, $w_{\mathbf{k}}$ is the \mathbf{k} point weight, c and v are the conduction and valence band states, respectively, $\epsilon_{c\mathbf{k}}$ and $\mu_{c\mathbf{k}}$ are the eigenvalues and wavefunctions at the \mathbf{k} point, respectively, and \mathbf{e}_{α} are the unit vectors for the three Cartesian directions. In order to calculate the optical properties of hybrid S/G nanocomposite, a large 21×21 regular mesh for the surface Brillouin zone, a large number of empty conduction band states (two times more than the number of valence band), and frequency grid points (2000) are adopted. We have crosschecked the optical properties of silicene and graphene and our results are consistent with previous theoretical calculations.^{79,80}

In order to evaluate the stability of hybrid S/G nanocomposite, the interface binding energy is defined as

$$E_b = E(S/G) - E(S) - E(G), \quad (2)$$

where $E(S/G)$, $E(S)$, and $E(G)$ represent the total energy of hybrid S/G nanocomposite, pristine graphene, and silicene, respectively.

III. RESULTS AND DISCUSSION

Electronic properties of pristine silicene and graphene monolayers in the supercells are checked first and their electronic band structures are plotted in Figs. 2(a) and 2(b). Both silicene and graphene are zero-gap semiconductors, showing

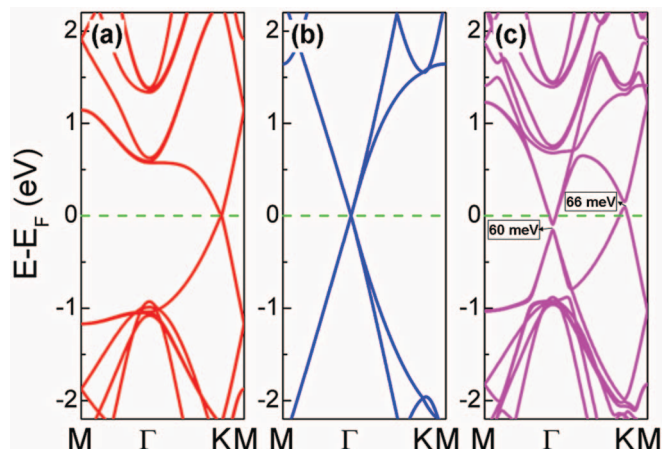


FIG. 2. Electronic band structures of (a) silicene, (b) graphene, and (c) hybrid S/G nanocomposite. The Fermi level is set to zero and marked by green dotted lines. The band gaps at the Dirac points of silicene and graphene are shown in the inset.

a linear Dirac-like dispersion relation $E(k) = \pm \hbar v_F |k|$ around their Fermi levels, where v_F is the Fermi velocity, and $v_F(S) = 0.5 \times 10^6 \text{ m/s}$ and $v_F(G) = 0.8 \times 10^6 \text{ m/s}$ at the Dirac points of silicene and graphene, respectively, agreeing well with previous theoretical studies,⁸¹ although DFT calculations underestimate the Fermi velocity of graphene by 15%–20%.⁸² Moreover, the small lattice mismatch of about 2% for silicene and graphene has little effect on their electronic properties in hybrid S/G nanocomposite.

We then study the atomic and electronic properties of hybrid S/G nanocomposite. Typical vdW equilibrium spacing of about 3.37 \AA with a small binding energy of about -24.7 meV per atom is obtained for hybrid S/G nanocomposite, which is well comparable with recent theoretical calculations in 2D graphene based nanocomposites, such as G/h-BN,^{39,41} G/MoS₂,⁴³ G/MoSe₂,⁴⁶ G/g-C₃N₄,⁴⁸ and G/g-ZnO.⁴⁹ Thus, weak vdW interactions dominate between silicene and graphene, suggesting that silicene and graphene can be used as ideal substrates for each other with their intrinsic electronic structures undisturbed.

Electronic band structure of hybrid S/G nanocomposite is shown in Fig. 2(c). The Dirac points of silicene and graphene are still preserved, and the Fermi velocities at their Dirac points are almost unchanged ($v_F(S) = 0.5 \times 10^6 \text{ m/s}$ and $v_F(G) = 0.8 \times 10^6 \text{ m/s}$) in hybrid S/G nanocomposite compared to free-standing silicene and graphene,⁸¹ though small band gaps (60 meV for silicene and 66 meV for graphene) are opened at their Dirac points. A test calculation with screened hybrid HSE06 functional⁸³ has given wider band gaps⁸⁴ and larger Fermi velocities⁸⁵ at the Dirac points of silicene and graphene in hybrid S/G nanocomposite (see Figure S3 of the supplementary material⁵⁰). Note that induced band gaps at the Dirac points of silicene and graphene are typically sensitive and tunable to other external conditions, such as electric fields^{9,10} and interlayer separation,^{39,41} showing great potential for high-performance FETs.

More interestingly, both silicene and graphene are doped in hybrid S/G nanocomposite, and their Dirac points, respectively, shift 0.12 eV above and below the Fermi levels in

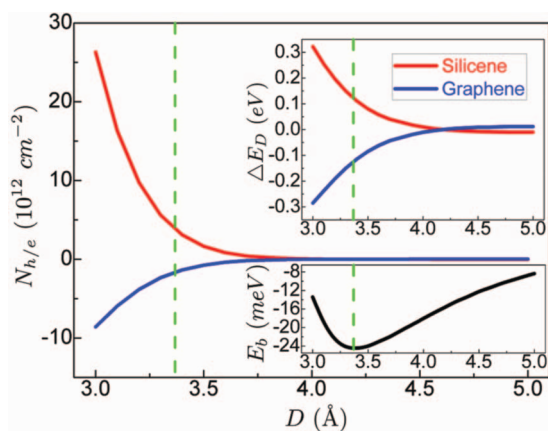


FIG. 3. The doping charge carrier concentrations $N_{h/e}$ (10^{12} cm^{-2}) of silicene and graphene in hybrid S/G nanocomposite as a function of interfacial distance D (\AA). The binding energies E_b (meV) per atom and the Dirac points ΔE_D (eV) of silicene and graphene shift relative to the Fermi level are shown in the inset. The equilibrium spacing is denoted by green dotted lines.

hybrid S/G nanocomposite, showing p-type and n-type doping of silicene and graphene, respectively. Based on the linear dispersion around the Dirac point of graphene,¹⁵ the charge carrier (hole or electron) concentration of doped graphene can be estimated by the following equation:^{86,87}

$$N_{h/e} = \frac{(\Delta E_D)^2}{\pi(\hbar v_F)^2}, \quad (3)$$

where ΔE_D is the shift of graphene's Dirac point (E_D) relative to the Fermi level (E_F), that is $\Delta E_D = E_D - E_F$. The calculated charge carrier concentrations are $N_h(S) = 3.8 \times 10^{12} \text{ cm}^{-2}$ and $N_e(G) = 1.6 \times 10^{12} \text{ cm}^{-2}$ for silicene and graphene in hybrid S/G nanocomposite, respectively. These values are more than 2 orders of magnitude larger than the intrinsic charge carrier concentration of graphene at room temperature ($n = \pi k_B^2 T^2 / 6 \hbar v_F^2 = 6 \times 10^{10} \text{ cm}^{-2}$).³¹ Interestingly, the charge carrier concentrations of silicene and graphene in hybrid S/G nanocomposite can be modulated with their interfacial spacing as shown in Fig. 3. Furthermore, their charge carrier concentrations decrease gradually with their interlayer separation increase and a conversion of doping types of silicene and graphene happens when their interfacial distance artificially increases to above 4.2 \AA . Therefore, selfdoping in hybrid S/G nanocomposite is effective and tunable with a great potential for new p-n junctions.^{88,89} However, notice that increasing interlayer distance is experimentally very challenging.

We reveal the origin of tunable selfdoping in hybrid S/G nanocomposite. When their interfacial distance artificially increases larger than 4.6 \AA , ΔE_D is already unchanged for both silicene and graphene and converges to different values ($\Delta E_D(S) = -0.01 \text{ eV}$ and $\Delta E_D(G) = 0.01 \text{ eV}$). That is because silicene and graphene have different work functions, $W_F(S) = 4.6 \text{ eV}$ and $W_F(G) = 4.4 \text{ eV}$.^{38,90} Based on the Schottky-Mott model,⁹¹ electrons tend to transfer from graphene to silicene, resulting in weak n-type and p-type doping of silicene and graphene, respectively. This is an artificial effect induced by periodic boundary conditions in DFT calculations. But, when their interfacial distance de-

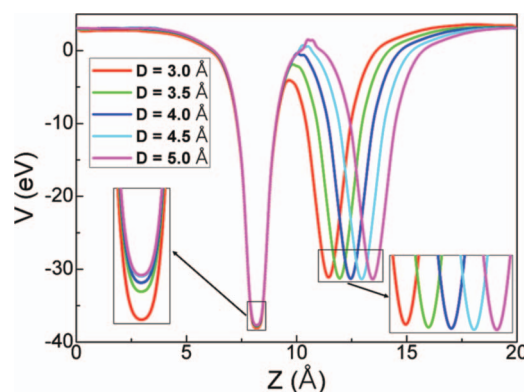


FIG. 4. XY-averaged electrostatic potentials of hybrid S/G nanocomposite at different interfacial distances D (\AA) in the Z direction. Depths of potential wells of silicene and graphene are shown in the inset. Note that the graphene layer is fixed and only the silicene layer is moved away from the graphene layer.

creases, there will be a weak overlap of electronic states between silicene and graphene, which enhances the charge transfer,^{32,34,92} shifting up and down the energy levels of silicene and graphene, respectively, as shown in Fig. 4. Note that there is a tunneling energy barrier for electrons³⁴ at the S/G interface, which is also reduced by their interface interactions. Moreover, silicene and graphene have different electronegativities (silicon 1.90 and carbon 2.55) and graphene has a more deeper potential well than silicene. Thus, when silicene and graphene are close to each other (smaller than 4.2 \AA), electrons are transferred from silicene to graphene, resulting in p-type and n-type doping of silicene and graphene, respectively. That is why a reversion of doping types of silicene and graphene happens when their interfacial distance is 4.2 \AA . Similarly, this feature of tunable doping types and charge carrier concentration of graphene on some metal surfaces³²⁻³⁵ is also observed experimentally and theoretically.

Besides commonly focused electronic structures in 2D graphene based nanocomposites, we also study the optical properties in hybrid S/G nanocomposite. Though pristine silicene and graphene themselves display unique optical properties,^{93,94} interlayer interactions in nanocomposites may induce new optical transitions.^{48,49} In optical property calculations, the imaginary part of dielectric function for silicene and graphene monolayers as well as corresponding hybrid S/G nanocomposite are evaluated, including the light polarized parallel ($\epsilon''_{XX} = \epsilon''_{YY}$) and perpendicular (ϵ''_{ZZ}) to the plane, as shown in Fig. 5. Optical absorption of pristine silicene and graphene monolayers mainly possesses in the frequency range from 0 to 25 PHz due to the transitions from π to π^* states and σ to σ^* states. Their lower frequency spectra in the frequency range from 0 to 3 PHz is mainly dominated by their π electron states close to the Fermi level. Their other broad optical absorption is due to the large band width of their σ electron states. Hybrid S/G nanocomposite exhibits stronger optical absorption, especially in the frequency range from 0 to 15 PHz, compared with simplex silicene and graphene monolayers, because the interlayer coupling in hybrid S/G nanocomposite induces electronic states overlap and

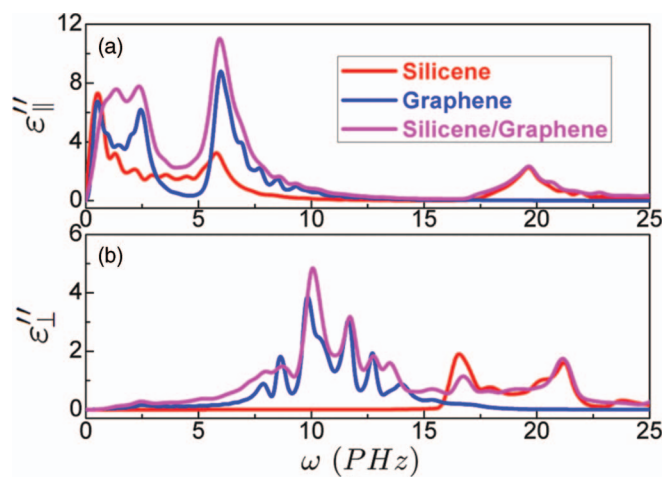


FIG. 5. Imaginary part (ϵ'') of frequency ($E = \hbar\omega$) dependent dielectric function (a) parallel and (b) perpendicular for pristine silicene and graphene monolayers as well as corresponding hybrid S/G nanocomposite.

electrons can now be directly excited between silicene and graphene.

IV. CONCLUSIONS

In summary, we study the electronic structures and optical properties of hybrid S/G nanocomposite with first-principles calculations. Silicene is found to interact weakly with graphene via weak vdW interactions to preserve their intrinsic electronic properties. Electronically, the doping carrier concentrations of silicene and graphene can be modulated by their interfacial spacing, forming tunable p-n junctions in hybrid S/G nanocomposite. Optically, optical adsorption is also enhanced compared with simplex silicene and graphene monolayers. With the excellent electronic and optical properties combined, 2D hybrid S/G nanocomposite system is expected to be of a great potential in new silicene and graphene based devices monolayers.

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