Rich Essential Properties of Si-Doped Graphene

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Abstract

A theoretical framework, which is under the first-principles calculations, is developed to fully explore the dramatic changes of essential properties due to the silicon-atom chemical modifications on monolayer graphenes. For the Si-chemisorption and Si-substituted graphenes, the guest-atom-diversified geometric structures, the Si- and C-dominated energy bands, the magnetic moments, the charge transfers, the spatial charge densities, the spin distribution configurations, and the van Hove singularities in the atom- and orbital-projected density of states are investigated thoroughly by the delicate evaluations and analyses. Such fundamental properties are sufficient in determining the critical physical and chemical pictures, in which the accurate multi-orbital hybridizations are very useful in comprehending the diverse phenomena, e.g., the C- and Si-co-dominated energy bands, the semiconducting or metallic behaviors, and the existence/absence of Dirac-cone band structures. This developing model could be generalized to other emergent layered materials.
I. Introduction

Carbon atoms could form 3D diamond,\(^1\) 3D graphite,\(^2\) 2D layered graphenes,\(^3,4\) 1D graphene nanoribbons,\(^5,6\) 1D carbon nanotubes,\(^7,8\) 0D carbon toroids,\(^9,10\) 0D C\(_{60}\)-related fullerenes,\(^11,12\) and 0D carbon onions.\(^13\) The versatile morphologies directly indicates the peculiar chemical bondings, in which all carbon-created systems possess \(sp^2\)-bonding surfaces except for the \(sp^3\) bondings in diamond. Specifically, the few- and multi-layer graphene systems have been manufactured using the various methods\(^15,16\) since the first experimental observation in 2004 by the mechanical exfoliation. Up to now, they clearly exhibit a plenty of remarkable fundamental properties due to the hexagonal symmetry, the nanoscaled thickness, and the distinct stacking configurations, such as semiconducting and semi-metallic behaviors,\(^17,18\) anomalous quantum Hall effects,\(^19\) diverse magnetic quantizations,\(^20–23\) rich Colomb excitations and decays,\(^24–28\) different magneto-optical selection rules\(^29–31\) the exceedingly high mobility of charge carriers,\(^32,33\) and the largest Young’s modulus of materials ever tested.\(^34\) To induce the novel phenomena and extend the potential applications, the electronic properties could be easily modulated by the layer number,\(^35,36\) stacking configuration,\(^37–39\) mechanical strain,\(^40,41\) sliding,\(^42\) electric and magnetic field,\(^43,44\) chemisorption,\(^45–48\) and direct doping.\(^49–51\) This book chapter focuses on the latter two factors.

How to modulate the fundamental properties becomes one of the main-stream topics in materials chemistry, physics and engineering. The chemical modification is the most effective method. Pristine graphene has a rather strong \(\sigma\) bonding of \((2s, 2p_x, 2p_y)\) orbital in the honeycomb lattice. This system creates a quite active chemical environment, since each carbon contributes one perpendicular \(2p_z\) orbital as a dangling bond. That is to say, the host carbon atoms can bond with the various guest atoms (adatoms),\(^52,53\) molecules\(^54\) and even functional groups.\(^55\) Up to now, there are a lot of theoretical\(^56\) and experimental researches on the surface chemisorptions.\(^57\) The previous results show the adsorption-diversified physical and chemical phenomena, such as, the opening of energy gap,\(^58\) the semiconductor-metal transitions,\(^59\) the absence/the recovery of the Dirac-cone band structure,\(^60\) the spin-split
energy band due to the specific adatoms,\textsuperscript{61} the diverse van Hove singularities in density of states (DOS), the single- or multi-orbital hybridizations in C-adatom bonds shown in the spatial charge density and atom- and orbital-decomposed DOSs,\textsuperscript{62} and the magnetic moments & spin configurations.\textsuperscript{63} It is well known that the graphitic layers, the layered graphene system, are the most efficient anode material in the Li\textsuperscript{+}-ion-based batteries. Maybe, the battery efficiency is deduced to be enhanced by adding some silicon materials, as observed from the experimental measurements.\textsuperscript{64} The Si-atom chemisorption might play an important role in these potential applications. Another chemical modification is the direct doping, the substitution of host carbons by guest adatoms in honeycome lattice. For example, the B\textsubscript{x}C\textsubscript{y}N\textsubscript{z} compounds have been successfullly synthesized in the stable structures of 1D nanotubes\textsuperscript{65} and 2D layers.\textsuperscript{66} Apparently, the essential properties are predicted to present the drastic changes, e.g., electronic structures,\textsuperscript{67} optical absorption spectra,\textsuperscript{68} and transport properties.\textsuperscript{69} The above-mentioned chemical modifications on graphene systems are worthy of a systematic study on the significant fundamental properties, especially for the critical differences in the orbital hybridizations between the weak and strong Si-C bonds.

In this work, a theoretical framework, which is developed within the first-principles calculations, is utilized to fully explore the essential properties of the Si-adsorbed and Si-substituted graphene systems. The concise chemical and physical pictures, the multi-orbital hybridizations without the spin configurations, will be proposed to explain the unusual geometric structures, electronic energy spectra, spatial charge densities, and atom- and orbital-decomposed density of states. That is, all the calculated results are consistent with one another under such mechanisms. Furthermore, they are responsible for the semiconductor-metal transitions after the guest-atom chemisorptions and the creation of energy gaps in the substitution cases. The various experimental characterizations are discussed in detail, and their measurements are required to examine the theoretical predictions, e.g., STM/TEM, ARPES, and STS experiments, respectively, for C-C & Si-C bond lengths, low-lying valence bands & Fermi level, and van Hove singularities in DOSs.
II. Computational methods

The rich geometric structures and electronic properties of the Si-adsorbed and Si-doped graphene systems are thoroughly explored using the density functional theory (DFT) implemented by Vienna ab initio simulation package (VASP). The many-body exchange and correlation energies, which come from the electron-electron Coulomb interactions, are calculated from the Perdew-Burke-Ernzerhof (PBE) functional under the generalized gradient approximation. Furthermore, the projector-augmented wave (PAW) pseudopotentials can characterize the electron-ion intrinsic interactions. As to the complete set of plane waves, the kinetic energy cutoff is set to be $\hbar^2 |k + G|^2 / 2m = 500$ eV, being suitable for evaluating Bloch wave functions and electronic energy spectra. A vacuum space of 10 Å is inserted between periodic images to avoid their significant interactions. The first Brillouin zone is sampled by $9 \times 9 \times 1$ and $100 \times 100 \times 1$ k-point meshes within the Monkhorst-Pack scheme for geometric optimizations and electronic structures, respectively. Such points are sufficient in obtaining the reliable orbital-projected DOSs and spatial charge distributions. The convergence for the ground-state energy is $10^{-5}$ eV between two consecutive steps, and the maximum Hellmann-Feynman force acting on each atom is less than 0.01 eV/Å during the ionic relaxations.

By the delicates VASP calculation on certain physical quantites, the critical physical and chemical pictures, the multi- or single-orbital hybridizations in chemical bonds and the spin configurations due to host and guest atoms, can be achieved under the concise scheme. They will be be useful in fully comprehending the fundamental physical properties. These important concepts are obtained from the absorption- and doping-diversified geometric structures, carbon- and silicon-dominated valence and conduction bands, the total charge distributions and their drastic changes after adatom chemisorption or guest-atom doping, and the atom- and orbital-decomposed density of states through the detailed analyses. Also, such physical quantities could provide the significant differences between the chemical absorptions and dopings, such as, the metallic or semiconducting behaviors, the normal and irregular
electronic energy spectra, and the complicated van Hove singularities, being attributed to the diverse chemical bondings. The developed theoretical framework could be generalized to the emergent two-dimensional materials, e.g., the chemical absorption and dopings in layered silicene,\textsuperscript{[70]} germanene,\textsuperscript{[71]} and tinene systems.\textsuperscript{[72]}

III. Geometric structures of Si-adsorbed and Si-substituted graphene

Monolayer graphene has a planar geometry with a honeycomb lattice, being different from the buckled structures in layered silicene,\textsuperscript{[73]} germanene,\textsuperscript{[74]} and tinene.\textsuperscript{[75]} Apparently, this crystal is formed by the very strong $\sigma$ bonding of $(2s, 2p_x, 2p_y)$ orbitals, and the weak $\pi$ bonding of $2p_z$ orbitals are perpendicular to the graphitic plane. However, the other group-IV systems, with the buckled structures, are stabilized by the optimal competition between the $sp^2$ and $sp^3$ chemical bondings. The bond length remains shortest for the C-C (1.420 Å Table 1) among all the group-IV systems. After the Si-chemisorption on graphene surface, the hexagonal honeycomb of carbon atoms remain planar structure while C-C bond length, $\sim 1.46$-1.49 Å & shown Fig. 1(a), is enhanced under the specific chemical bondings of silicon and carbon atoms. Part of carbon electrons take part in the multi-orbital hybridizations of C-Si bonds, leading to the weakened C-C bondings. As for the Si-substituted cases, the silicon-carbon honeycomb lattices remain planar structures, indicating the sufficiently strong quasi-$\sigma$ bondings due to the $sp^2$-$sp^2$ multi-orbital hybridizations in Si-C bonds [discussed later for the spatial charge densities in Fig. 7, and density of states in Fig. 9]. The Si-C and C-C bond lengths are, respectively, $\sim 1.78$-1.83 Å $\sim 1.47$-1.50 Å under the high-ration substitutions [Fig. 1(b) and Table 1]. The 1:1 substituted system, the pure silicon-carbon compound, has an optimal Si-C bond length (1.78 Å ) much longer than that (1.42 Å ) in a pristine graphene. This will lead to the great decrease of the strength in quasi-$\sigma$ bonding, being further identified the largely reduced charge density between the Si-C bonds.
In addition, the guest-atom distribution configurations could be classified into three kinds under the specific concentrations lower than 50% [Figs. 3(a)-3(c)], namely, the ortho-, para- and meta-substitution cases. However, the former two are degenerate just at 50% [Fig. 3(b)].

Scanning tunneling microscopy (STM) is very powerful in identifying the nano-scaled surface morphology. This tool can characterize the real-space surface structures under the lateral and vertical atomic resolution, such as, the very short bond length, planar or buckled geometries, crystal arrangements, archiral or chiral edges, bridge-, hollow- & top-site adsorptions, local substitutions, and few-atom clusters. Up to now, a lot of high-resolution STM measurements have confirmed the diverse geometric symmetries on the graphene-related systems with the significant $sp^2$ chemical bondings, covering the chiral or archiral hexagons on the hollow and cylindrical carbon nanotubes, the various edge structures in nanoscaled-width graphene nanoribbons, the folded, curved, scrolled & stacked hexagonal lattices, the AAB, ABC & ABA stackings in few-layer graphene systems. The theoretical predictions on the planar graphene after chemisorptions and substitutions, the positions of Si-guest atoms, and Si-C & C-C bond lengths could be verified by the STM experiments, being useful in examining the specific multi-orbital hybridizations in chemical bonds.

Transmission electron microscopy (TEM) is one of most powerful equipments in characterizing the nano-scaled geometric structures, especially for the side-view properties. A high-energy electron beam, with a very narrow distribution width, can penetrate through an ultra thin sample to generate a diffraction spectrum by the interactions of charge carriers and condensed-matter systems. Up to date, the high-resolution TEM measurements can directly identify the side-view crystal structures, being better than other experimental ones. A plenty of previous experimental studies show that they have accurately identified the rich and unique geometric properties arising from the carbon-$sp^2$ bondings in various layered structures, such as, the 1D single- & multi-walled carbon nanotubes, the 2D curved, folded, scrolled and stacked graphene nanoribbons, the 2D AA-, AB-, ABC- and AAB-stacked few-layer graphene systems. The theoretical predictions which cover graphene plane,
adatom height and bridge side under the Si-chemisorptions, could be examined by the TEM measurements, indirectly supporting the $sp^3 - p$ multi-orbital hybridizations in Si-C bonds.

IV. Rich electronic structures

A pristine monolayer graphene, as clearly indicated in Figs. 4(a) and 4(b), exhibits the unusual band structure. The occupied valence bands are asymmetric about the unoccupied ones, mainly owing to the multi-orbital $\sigma$ bondings. The low-lying valence and conduction bands, which are initiated from the K and K' valleys (the corners of the first Brillouin zone), are linearly intersecting there. There exist the isotropic Dirac-cone structures at low energy, in which the Fermi level, $(E_F = 0)$, just crosses the Dirac point. Apparently, this system belongs to a zero-gap semiconductor because of the vanishing density of state at $E_F$. The low-energy band structure mainly comes from the $\pi$ bondings of the perpendicular C-$2p_z$ orbitals. The Dirac-cone structure, being due to the hexagonal symmetry, is predicted to display a lot of unusual phenomena, e.g., the diverse magnetic quantizations, $^9$ Hall effects, $^{91}$ and optical properties, $^{12}$ being consistent with the experimental measurements.$^{93}$

The linear energy dispersions will gradually become the parabolic ones as the state energy of $|E_{c,v}|$ grows, or the wave vector deviates from the K/K' point. Specifically, the middle-energy parabolic valence and conduction bands present the saddle points at M, respectively, corresponding to $\sim -2.4$ eV and 1.81 eV. Such critical points in energy-wave-vector space could be regarded as the significant band-edge states in creating the important van Hove singularities. That is to say, they are thus expected to induce the special structures in the essential physical properties. The $\sigma$ valence bands at the deeper energy come to exist at $E_v \sim -3.02$ eV from the $\Gamma$ point, being regarded as the extreme point of parabolic energy dispersion. Their electronic states are formed by the $(2s, 2p_x, 2p_y)$ orbitals of carbon atoms, or the very strong $\sigma$ bondings on the graphene plane.

Band structure is dramatically changed by the Si-chemisorptions. The band asymmetry
about the Fermi level becomes more obvious. For the double-side full adsorption, the low-lying energy bands, as shown in Fig. 4(c), exhibit the metallic behavior, belonging to the p-type phenomena. There exist some valence and conduction band intersecting with the Fermi level \( (E_F = 0) \). Apparently, the distorted Dirac-cone structure appears near the \( \Gamma \) point. The separation of valence and conduction Dirac points could reach \( \sim 0.51 \) eV. The electronic energy spectrum is highly anisotropic energy spectra along \( \Gamma M \) and \( \Gamma K \). The occupied electronic states come to exits between the Fermi level and the bottom of the conduction-band states. This clearly indicates the creation of free conduction electrons by the effective adatom dopings. On the other hand, the free holes are generated in the unoccupied valence states along \( M \Gamma \) and \( K \Gamma \). As a result, it is difficult to identify Si-adsorbed graphene as a n-type or p-type system. However, this system belongs to a 2D semimetal, since it has a finite density of states at the Fermi level (Fig. 8(c)) arising from the crossing valence and conduction subbands. The above-mentioned unusual band structures are closely related to the very strong competitions/cooperations of orbital hybridizations in Si-C and C-C bonds.

Also, the drastic changes in electronic structures are revealed in the single-side full adsorption case, as clearly indicated from a comparison of Fig. 4(d) with Fig. 4(c). The chemisorption of silicon adatoms induces the free electrons and holes simultaneously, being similar to the double-side case (Fig. 4(c)). The low-lying conduction bands near the \( \Gamma \) point and the vacant valence bands along \( M \Gamma \) and \( K \Gamma \) reduce their number. That is to say, the number of energy bands intersecting with the Fermi level declines in the further decrease of Si-concentration, and the 2D free carrier density behaves so. As to both absorption cases, carbon host atoms and silicon guest ones make significant contributions to the electronic structures of the whole energy range, in which their dominances are obviously displayed by red triangles and blue circles. These important results mean that there exist the non-negligible multi-orbital hybridizations in Si-C, C-C and Si-Si bonds.

The atom- and orbital-dominated energy bands are worthy of a closer examination. Most of energy bands are co-contributed by C-host and Si-guest atoms, and part of them mainly
come from the former or the latter. In general, the low-lying and middle-energy valence and conduction bands are dominated by the Si-guest atoms, compared with C-host atoms. The percentage of atom contribution is about 4 : 1 (2 : 1) under the Si-100% (Si-50%) absorption cases shown in Fig. 4(c) [Fig. 4(d)], being estimated from the $sp^3 - p$ bonding in the Si-C bond [the conclusion from the atom- and orbital-projected density of states; discussed later in Fig. 8(c)]. The four $(3s, 3p_x, 3p_y, 3p_z)$ orbitals of silicon and the single $2p_z$ orbital of carbon make important contributions to such energy bands. Apparently, there are few $\sigma$ valence bands of $(2p_x, 2p_y)$ orbitals near the $\Gamma$ point, and they belong to the concave-downward energy dispersions at $E_v \sim -4.10 \& -4.20$ eV for the full adsorption cases (Figs. 4(d) and 4(c)), as identified from Fig. 8(c). It should be noticed that the pristine $\sigma$ valence bands come to exist at $E_v \sim -3.0$ eV [Figs. 4(b) and 8(b)].

Both silicon and alkali adatoms can create the free carriers, while their band properties are quite different from each other. The alkali-adsorbed graphene systems present the approximately rigid energy bands and few Li-dominated conduction bands, clearly indicating the blue shift of the Fermi level. Their free carriers purely originates from the electron charge transfer from the outmost $s$ orbital of each alkali adatom to carbon host atom. Furthermore, the atom- and orbital-projected densities of states clearly show the weak, but the significant $s - p_z$ orbital hybridization in every alkali-carbon bond. On the other hand, the free electrons and holes in the Si-adsorbed cases are associated with strong overlap of valence and conduction bands, so the shift of $E_F$ is very difficult to characterize its value. There are a lot of extra Si-dominated and (Si, C)-co-dominated energy bands in the whole energy spectrum, especially for those crossing the Fermi level. The complicated chemical bondings are deduced to survive in Si-adsorbed graphene systems, in which they cover the $2p_z-(3s, 3p_x, 3p_y, 3p_z)$, $(3s, 3p_x, 3p_y, 3p_z)$-$(3s, 3p_x, 3p_y, 3p_z)$ and $(2s, 2p_x, 2p_y)$-$(2s, 2p_x, 2p_y)$ multi-orbital hybridizations in the C-Si, Si-Si and C-C bonds. Most important, the above-mentioned differences obviously illustrate the adatom-adsorption-induced diverse phenomena and the critical mechanisms/pictures in determining the fundamental properties.
Electronic properties obviously show the drastic changes in the presence of Si-substitutions, as clearly indicated in Figs. 5(b)-5(d). The asymmetry of valence and conduction bands about \( E_F = 0 \) is greatly enhanced by the high dopings, e.g., 100\% in Fig. 5(b) and 50\% in Figs. 5(c) and 5(d). The substitution and adsorption cases sharply contrast with each other [Figs. 5 and 4]. First, all the latter configurations and concentrations show the semiconducting behaviors, with a finite or a vanishing band gap. For example, the fully Si-substituted graphene is a wide-gap semiconductor with \( E_g^i = 2.56 \) eV. Energy gaps are direct or indirect ones being determined by the highest valence and the lowest conduction state near the \( \Gamma \) point. Their values decline with the decreasing Si-concentration, and they strongly depend on the guest-atom distribution configurations, e.g., \( E_g = 0.56 \) eV for the meta-configuration [Fig. 5(d)] under the 50\% substitution. Also, the zero-gap semi-conducting property is revealed in the ortho-50\% case [Fig. 5(c)], where an anisotropic Dirac-cone structure appears a certain \( \mathbf{k} \)-point in between \( \Gamma \) and \( K \). Only the Dirac point intersects with the Fermi level, so its density of states is vanishing there [Fig. 9(c)]. This is responsible for the zero-gap semiconductor. Second, the pristine Dirac cone at \( \Gamma \) point [Fig. 4(b)] is seriously separated and distorted [Fig. 5(c)], or even thoroughly destroyed [Figs. 5(b) and 5(d)]. Third, the valence and conduction bands near the Fermi level are initiated from the \( \Gamma \) point, but almost independent of the M and K points. Fourth, the number of energy bands keeps identical after the Si-substitutions, compared with those of a pristine graphene. Finally, all the energy bands are co-dominated by the Si-guest and carbon-host atoms under the high substitutions; furthermore, the separated \( \sigma \) bands at deep energies purely due to \( C-(2p_x, 2p_y) \) orbitals are absent. These results suggest the existence of the quasi-\( \sigma \) and quasi-\( \pi \) bondings, respectively, originating from the \( (3s, 3p_x, 3p_y)-(2s, 2p_x, 2p_y) \& 3p_z-2p_z \) orbital hybridizations [supported by the spatial charge distributions in Fig. 7 and the atom- and orbital-projected density of states in Fig. 9]

Angle-resolved photoemission spectroscopy (ARPES) is the only tool in measuring the wave-vector-dependent occupied electronic states, especially for valence and conduction
bands crossing the Fermi level. The details of experimental equipments could be found in the books written by Tran et al. and Lin et al. Up to date, the high-resolution ARPES measurements have identified the rich band structures in graphene-related systems, being greatly diversified by the distinct geometric symmetries, dimensions, stacking configurations, numbers of layers, and absorptions, substitutions & intercalations. For example, the verified electronic structures, which are consistent under the theoretical predictions and the experimental measurements, include parabolic valence bands with an energy gap in the 1D graphene nanoribbons, the linear Dirac-cone structure in monolayer graphene, the blue shift of the Fermi level in alkali-adsorbed graphene systems, two parabolic valence bands near $E_F$ without energy gap in bilayer AB-stacked graphene, the monolayer- and bilayer-like valence bands in trilayer ABA stacking, the partially flat, sombrero-shaped, and linear bands in trilayer ABC stacking, and the parabolic & linear energy dispersions near the K and H points ($k_z = 0$ and $\pi$) in a natural graphite. The similar ARPES measurements are available in thoroughly examining the significant effects on band structures after the chemisorptions and substitutions of Si guest atoms. They are conducted on the finite or vanishing band gap, the numbers of the valence and conduction bands intersecting the Fermi level near the $\Gamma$, K and M points, and the existence/destruction of the carbon-dominated $\sigma$ bands at the $\Gamma$ point initiated from $-4.1 \ eV - -4.2 \ eV$. Such detailed informations are sufficient in determining the critical multi-orbital hybridizations of C-Si bonds, the $p - sp^3$ or $2p^2 - sp^2$ bondings.

V. Spatial charge densities

The multi-orbital hybridizations in chemical bonds, which are responsible for the rich geometric structures, energy bands and density of states, could be delicately identified from the spatial charge densities ($\rho$'s) and their variations ($\Delta \rho$'s) after the various modifications. The latter is obtained from the difference between the Si-chemisorption/Si-substitution and
pristine cases. A pristine graphene, as clearly shown in Fig. 6(a), presents a very high carrier density between two carbon atoms [a red region enclosed by a black rectangle], indicating a rather strong $\sigma$ bonding due to three C-$\left(2s, 2p_x, 2p_y\right)$ orbitals on honeycomb lattice. Such bonding is hardly affected by the Si-adatom adsorptions [Figs. 6(b) and 6(d)]. Also, there exists the $\pi$ bonding near the plane boundary along the $z$-direction [covered by a red rectangle]. The $2p_z$-$2p_z$ orbital hybridizations in C-C bonds might be drastically changed under the Si-chemisorptions. Apparently, the charge distributions related to silicon adatoms and carbon atoms along the $x$-, $y$-, and $z$-directions present the obvious variations. The strong evidences are illustrated by $\Delta \rho$'s in Figs. 6(c) and 6(e). The charge density is enhanced near the carbon atoms on the $(y, z)$- and $(x, z)$-planes [the red-color regions]. This result means some electronic charges transferred from Si to C atoms. In addition to the $z$-direction, the important charge variations along the $x$- and $y$-directions survive between silicon adatoms and carbon atoms/silicon ones, indicating the multi-orbital hybridizations in Si-C and Si-Si bonds. According to the direction- and position-dependent variations of charge densities, there exist the $(3s, 3p_x, 3p_y, 3p_z)$-$2p_z$ and $(3s, 3p_x, 3p_y, 3p_z)$-$\left(3s, 3p_x, 3p_y, 3p_z\right)$ complicated interactions in Si-C and Si-Si bonds, respectively.

The Si-substitution cases exhibit the diversified charge densities, compared with the pristine and Si-chemisorption ones. For the full substitution, the Si-C bonds, which consists of honeycomb lattice [Fig. 3(a)], present the sufficiently high charge densities between two neighboring atoms [Fig. 7(a)]. They are formed by the quasi-$\sigma$ bondings, in which the charge-density-dependent strengths are greatly reduced, compared to the $\sigma$ ones in C-C bonds. This is consistent with the longer Si-C bonds and the shorter C-C bonds. The similar results are revealed in other substitution cases, e.g., the 50% substitutions under the ortho-, and meta-configurations [Figs. 7(c) and 7(e)]. There also exist the quasi-$\pi$ bondings near the boundary. They present the non-well-behaved charge distributions, compared with those of a pristine graphene [Fig. 6(a)]. The obvious variations of charge densities on the $(y, z)$- and $(x, z)$-planes, being clearly show in Figs. 7(b), 7(d) and 7(f), suggest the
significant \((3s, 3p_x, 3p_y)-(2s, 2p_x, 2p_y) \& 3p_z-2p_z\) orbital hybridizations in Si-C bonds. The coexistence of the multi- and single-orbital interactions are further supported by the atom- and orbital-decomposed densities of states [discussed later in Figs. 9(b)-9(d)].

VI. The diverse density of states

The main features of energy dispersions are directly reflected in the diversified density of states. The special structures, the van Hove singularities, mainly originate from the critical points in the energy-wave-vector space, in which the band-edge states might belong to the local minima \& maxima, and the saddle points. In general, there are three kinds of novel structures, the V-shaped structure crossing the Fermi level, logarithmically divergent peaks \([E \sim -2.4 \text{ eV} \& 1.81 \text{ eV}]\) and shoulders \([E \sim -3.02 \text{ eV}]\), as clearly observed in a pristine graphene [Figs. 8(a) and 8(b)]. They are, respectively, due to the linear Dirac cone [the \(\Gamma\) point in Fig. 4(b)], the saddle points [the \(M\) points], and the extreme points of parabolic dispersions [the \(\Gamma\) point]. Specifically, the former two structures are generated by the \(\pi\) bonding of \(2p_z\) orbitals (the dashed red curve), and the initial \(\sigma\) bands are closely related to the \((2p_x, 2p_y)\) orbitals [the dashed green and blue curves]. The \(\pi\)-bonding structures are separated from those of \(\sigma\) bondings.

Apparently, a lot of van Hove singularities in density of states are created by the Si-adatom chemisorption under the double- and single-side cases, being obviously displayed in Figs. 8(c) and 8(d), respectively. The finite density of states at the Fermi level indicates the semi-metallic behavior, while the vanishing value under the pristine case [Fig. 8(b)] correspond to a semiconductor. The strong chemical bonding between Si and C atoms is responsible for the significant overlap of the valence and conduction bands and the creation of new energy bands [Figs. 4(c) and 4(d)]. The significant contributions of carbon-\(2p_z\) orbitals appear in the whole energy range of \(-6 \text{ eV} \leq E \leq 3 \text{ eV}\). Specifically, for that above \(-4 \text{ eV}\), the non-negligible contributions from the four Si-\((3s, 3p_x, 3p_y, 3p_z)\) orbitals come
to exist, respectively, indicated by the solid pink, green, orange and purple curves. The van Hove singularities from these orbitals are merged together. This clearly indicates the $p - sp^3$ chemical bondings in C-Si bonds. The multi-orbital hybridizations, which replaces the $2p_z$-orbital bondings on graphene plane, are also confirmed by the previous charge density distributions [Figs. 6(b)-6(e)]. However, the $\sigma$ of carbon atoms are hardly affected by the Si-chemisorption absorptions, in which they are represented by the isolated shoulder structure below $-4.2$ eV ($-4.1$ eV) in the 100% (50%) case.

Why are valence and conduction bands in Figs. 4(c) and 4(d) dramatically altered by the Si-adsorbed graphene? The diversified band properties are clearly identified from three critical mechanisms. First, the chemical modification belongs to the significant surface adsorption, but not the stronger substitution. This means the existence of $\sigma$ bondings in planar C-C bonds even after the significant Si-chemisorptions. As a result, the $\sigma$ bands of the C-($2p_x, 2p_y$) orbitals exhibit a rigidly red shift of $\sim 1$ eV [the red triangles at $E^v \sim -4.1$ eV in Figs. 4(c) and 4(d)]. The red-shift value is determined by the ionization-energy difference between carbon and silicon atoms. Second, the important $sp^3 - p$ multi-orbital hybridizations are covalently formed by four half-occupied orbitals of $(3s, 3p_x, 3p_y, 3p_z)$ in Si adatoms and one similar orbital of $2p_z$ in C host atoms. For example, a plenty of low-lying valence and conduction bands are dominated by the silicon guest atoms. Furthermore, their contributions to the total density of states are higher than those due to carbon atoms except in the energy range below $-4$ eV, as, respectively, indicated by the solid and dashed curves Figs. 8(c) and 8(d). Finally, from the viewpoint of the separated atomic orbital energies, all the atomic orbitals in silicon adatoms have the larger spatial distributions and the smaller binding energies, compared with those of carbon atoms. These orbitals, which take part in the Si-C bonds, will create many energy bands in the available energy range of the electronic energy spectrum, especially for valence and conduction bands intersecting with the Fermi level. Apparently, the Dirac-cone band structure, without any valence and conduction overlap, is thoroughly replaced by the Si-dominated electronic structures under
the full chemisorptions. The other essential physical properties are expected to behave the diverse phenomena under the Si-chemisorptions, e.g., magnetic quantizations, optical absorption spectra, and transport properties.

The substitution and absorption cases are thoroughly different from each other in the main features of density of states. For the former chemical modifications, the number of electronic states, which is revealed in Figs. 9(b)-9(d), is vanishing within the specific band-gap region centered at the Fermi level. Most of substitution configurations and concentrations correspond to the finite-gap semiconductors, e.g., energy gaps due to the highest occupied valence state and the lowest unoccupied conduction one at the Γ point under the 100% [Fig. 5(b)] and meta-50% substitutions [Fig. 5(d)]. Only part of them belong to the zero-gap semiconductors, with a seriously distorted Dirac-cone structure between the Γ and K points [the ortho-50% case in Fig. 5(c)]. The van Hove singularities can create a plenty of various special structures, namely, the obvious V-shape structure across $E_F$, strong shoulders/asymmetric peaks, and prominent symmetric peaks, as observed in the chemisorption cases. Apparently, the atom- and orbital-projected densities of states show that the contributions coming from the Si-3$p_z$ and C-2$p_z$ orbitals [the solid purple and dashed red curves in Figs. 9(b)-9(d)] appear simultaneously. Furthermore, The merged special structures are also revealed in the other orbitals, e.g., the interactions of Si-(3$s$, 3$p_x$, 3$p_y$) and C-(2$s$, 2$p_x$, 2$p_y$) orbitals. These results clearly illustrate the multi-orbital hybridizations of $sp^2-sp^2 & p - p$ in Si-C bonds. That is to say, the Si-C bonds present the quasi-σ and quasi-π chemical bondings. In addition, it should have the σ and π bondings in C-C bonds. The predicted orbital hybridizations are consistent with the spatial charge distributions in [Figs. 7(a)-7(f)] and can account for the Si-substitution-enriched band structures [Figs. 5(a)-5(d)].

Scanning tunneling spectroscopy (STS) can provide the sufficient informations on the density of states at the Fermi level and the various van Hove singularities due to the valence and conduction bands simultaneously. The high-resolution STS measurements are available in distinguishing the semiconducting, semi-metallic and behaviors. Furthermore,
they are very useful in identifying the close relations between the electronic energy spectra and the orbital hybridizations of the significant chemical bonds. Such experimental studies have been successfully utilized to verify the band properties near the Fermi level and the dimension-diversified van Hove singularities in the graphene-related systems even in the presence of magnetic field, such as, 2D few-layer graphene systems with the AB, ABC, AAB stackings,\textsuperscript{103,104} 1D metallic and semiconducting carbon nanotubes,\textsuperscript{105,106} and 3D Bernal graphite\textsuperscript{107} [the details revealed in Chap. 3]. Apparently, the theoretical predictions on the Si-adsorption- and Si-substitution-diversified density of states in monolayer graphene systems, which could be examined from the STS experiments, cover the finite or vanishing density of states at $E = 0$, the low- and middle-energy van Hove singularities, the presence or absence of a specific shoulder at $E \sim -4.1\text{--}4.2$ eV, and the special structures below $-4.2$ eV. That is, such experimental examinations could provide the critical informations in the multi-orbital hybridizations, the $p$ or $sp^3$ or $sp^2$ chemical bondings.

The essential properties of Si-adsorbed graphene systems might sharply contrast with other adatom-decorated ones. For example, graphene oxides have the bridge-site adsorption position\textsuperscript{93} as observed in the Si-adsorption case. However, the former present the slight buckling and the shorter adatom-C bond lengths. All graphene oxides belong to wide-, narrow- or zero-gap semiconductors, without any band-overlap-induced free electrons and holes. The O-2s orbitals do not take in the low-lying energy bands, while the opposite is true for Si-3s ones. Under the high adatom concentrations ($\geq 50\%$), valence and conduction bands in the range of $-1.5 \leq E_{c,v} \leq 1.5$ eV are absent for graphene oxides, being thoroughly from the frequent crossing over the Fermi level in the current case. Apparently, the $\sigma$ bands purely due to carbon atoms disappear. Moreover, the three ($2p_x, 2p_y, 2p_z$) orbitals of oxygen and carbon atoms would dominate the multi-orbital hybridizations in O-C, O-O and C-C bonds. On the other side, the $2p_z$ and ($2p_x, 2p_y$) orbitals of carbon atoms, respectively, make important contributions to C-C and Si-C bonds; furthermore, the Si-(3s, 3p_x, 3p_y, 3p_z) orbitals participate in the Si-C and Si-Si bonds. The above-mentioned important differences
could be verified by the high-resolution STM, TEM, ARPES and STS measurements.

VII. In summary

The essential properties of Si-modified graphene systems have been explored by the first-principles method in detail. Apparently, the geometric structures, band structures, spatial charge densities, and atom- and orbital-projected density of states exhibit the rich and unique phenomena, being sensitive to the chemisorption & substitution cases, and the concentration & distribution configuration of Si-guest atoms. Furthermore, the magnetic properties arising from the spin configurations are absent in these systems. The complex multi-orbital hybridizations/the significant chemical bondings are proposed to explain the Si-induced chemical modifications on graphene systems. The calculated results clearly show that the free carriers and the energy gap might be created by the chemical adsorptions and substitutions, respectively. The distinct modification ways of silicon guest atoms can modulate the semi-metallic or semiconducting behaviors, being difficult to be observed in other kinds of atoms. For example, there are certain important differences between silicon and alkali atoms in chemisorptions, e.g., the multi-orbital or single-orbital hybridizations, the existence or absence of charge transfer, the blue or undefined shift of the Fermi level, only the conduction electrons or free conduction electrons & holes, and the dramatic or slight changes for the low-lying energy bands. The Si-adsorbed and Si-substituted graphenes could serve as the potential candidates in the nanoscaled-applications. The similar theoretical framework could be generalized the emergent layered materials, such as, chemical adsorptions and substitutions on silicene, germanene, stanene, phosphorene and bismuthene.

The chemisorptions and substitutions of Si-guest atoms on monolayer graphene present the unusual geometric properties, being directly revealed in the spatial charge distributions. The Si-adsorbed graphene is a non-buckled plane, in which the optimal position corresponds to the bridge site. A planar structure clearly indicates a very small variation in the $\sigma$ bonding
of C-(2s, 2px, 2py) orbitals after the Si-chemisorptions; that is, such three orbitals do not take part in Si-C bonds. This adsorption configuration is similar to monolayer graphene oxide, while there is a slight buckling in the latter. The Si-C bond length is $\sim 2.01 - 2.05$ Å, suitable for the significant multi-orbital hybridizations of Si-C bonds. Furthermore, the C-C bond lengths display a minor change. By the detailed analyses on the 3D charge density, its spatial variation, and the atom- and orbital-projected density of states, the $sp^3 - p_z$ multi-orbital hybridizations are deduced to dominate the chemical Si-C bonds. Apparently, three physical quantities are consistent with one another. The theoretical predictions of the bridge site and C-C bond length (the Si height) could be examined from the high-resolution STM (TEM) measurements. Concerning Si-substituted graphene systems, they remain the planar structure, as observed under the chemisorption cases. There exist very strong multi-orbital chemical bondings between Si and C atoms. Si-C bond length is about 1.78 Å-1.83 Å, being shortened than those in Si-adsorbed systems. This means that more C-orbitals are strongly hybridized with the four Si-orbitals. The STM experiments are available in examining the predicted Si-C and C-C bond lengths.

Any chemisorptions and substitutions of Si-guest stoms thoroughly alter the unusual band structure of monolayer graphene, especially for the zero-gap semiconducting behavior and linear Dirac cone due to the $\pi$ bondings of $2p_z$ orbitals. Under the full double- and single-side cases, the Si-adsorbed graphene systems are semi-metals with the free conduction electrons and valence holes simultaneously. The Dirac-cone structure near the $\Gamma$ point are seriously distorted after the Si-chemisorptions. There are more valence and conduction bands, accompanied with the various band-edge states, in the whole electronic energy spectrum, e.g., the emergent low-lying energy bands along the $K\Gamma$ and $M\Gamma$ directions. However, the $\sigma$ bands, which arises from the $(2p_x, 2p_y)$ orbitals of carbon atoms, exhibit a rigid red shift from $-3.02$ eV to $\sim -4.10$ eV $-4.20$ eV. The above-mentioned important results directly reflect the critical mechanisms, namely, the multi-orbital hybridizations of $sp^3$-$p$ in Si-C bonds, $sp^3$-$sp^3$ in Si-Si bonds and $sp^2$-$sp^2$ in C-C bonds. Such chemical bondings consist of four Si-orbitals and
one C-orbital, being closely related to the bridge-site adsorption positions, and the binding energies & charge distributions of the separated orbitals. The high-resolution ARPES measurements are very useful in checking the low-energy valence bands crossing the Fermi level along KΓ and MΓ and the rigid σ bands initiated from the Γ point. On the other hand, all the substituted cases results in the semiconducting behavior with a finite or vanishing band gap. The Dirac-cone structure presents a deviation from the Γ point, a strong distortion, or even a full destruction. The number of valence and conduction bands keeps the same after the chemical substitutions; furthermore, they are co-dominated by the Si-guest and C-host atoms. Apparently, the main features of band structures in Si-substituted graphene systems arise from the \( sp^2-sp^2 \) & \( p-p \) orbital hybridizations in Si-C bonds.

A lot of van Hove singularities in atom- and orbital-decomposed density of states, which mainly come from the band-edge states, are created by the Si-guest-atom chemisorptions and substitutions. A pristine monolayer graphene only presents a V-shaped structure with a vanishing value at the Fermi level, the logarithmically symmetric peaks at \(-2.40\) eV and \(1.8\) eV, and a shoulder structure at \(-3.10\) eV, in which the former two and the last one, respectively, correspond to the π and σ bondings of carbon atoms. The π-bonding strong evidences are totally destroyed by any chemisorption cases except for the very dilute Si-adatoms. They are replaced a finite density of states at \(E = 0\) and many shoulder and peak (or composite) structures. Furthermore, they are co-dominated by the four Si-(3s, 3px, 3py, 3pz) orbitals and the single C-2pz orbital, since their contributions are merged together. Specifically, the σ-band shoulder appears \(-4.2\) eV--\(-4.1\) eV, and \(\sim 1.0\) eV red shift is mainly determined by relative ionization energy of Si and C atoms. The above-mentioned significant features further support and illustrate the \( sp^3-p \) & \( sp^3-sp^3 \) multi-orbital hybridizations in Si-C bonds and C-C bonds, respectively. As for the substitution cases, the density of states is zero within a finite energy range centered at the Fermi level except for few systems with the V-shaped structures at \(E_F\). All the Si-substituted graphene systems are finite- or zero-gap semiconductors. The special structures, which originate from Si-3pz and C-2pz orbitals, ap-
pear simultaneously. Also, the similar behavior is revealed in Si-(3p\textsubscript{x}, 3p\textsubscript{y}) and C-(2p\textsubscript{x}, 2p\textsubscript{y}) orbitals. These clearly indicate the critical single- and multi-orbital hybridizations in Si-C bonds. The above-mentioned theoretical predictions could be verified by the high-resolution STS measurements.
References

(1) Fayos, J. Possible 3D carbon structures as progressive intermediates in graphite to diamond phase transition. *Journal of Solid State Chemistry, 148*, 278-285(1999).

(2) Wang, Y., Panzik, J. E., Kiefer, B. & Lee, K. K. Crystal structure of graphite under room-temperature compression and decompression. *Scientific reports, 2*, 520(2012).

(3) Novoselov, K. S. et al. Electric field effect in atomically thin carbon films. *Science, 306*, 666-669(2004).

(4) Zhang, Y., Tan, Y. W., Stormer, H. L. & Kim, P. Experimental observation of the quantum Hall effect and Berry’s phase in graphene. *Nature, 438*, 201(2005).

(5) Jiao, L., Wang, X., Diankov, G., Wang, H. & Dai, H. Facile synthesis of high-quality graphene nanoribbons. *Nature nanotechnology, 5*, 321(2010).

(6) Kosynkin, D. V. et al. Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons. *Nature, 458*, 872(2009).

(7) Cai, J. et al. Atomically precise bottom-up fabrication of graphene nanoribbons. *Nature, 466*, 470(2010).

(8) Issi, J. P., Langer, L., Heremans, J. & Olk, C. H. Electronic properties of carbon nanotubes: experimental results. *Carbon, 33*, 941-948(1995).

(9) Wilder, J. W., Venema, L. C., Rinzler, A. G., Smalley, R. E. & Dekker, C. Electronic structure of atomically resolved carbon nanotubes. *Nature, 391*, 59(1998).

(10) Odom, T. W., Huang, J. L., Kim, P. & Lieber, C. M. Atomic structure and electronic properties of single-walled carbon nanotubes. *Nature, 391*, 62(1998).

(11) Yang, L., Jiang, J. & Dong, J. Formation mechanism of toroidal carbon nanotubes. *Physica status solidi (b), 238*, 115-119(2003).
(12) Rocha, C. G., Pacheco, M., Barticevic, Z. & Latgé, A. Carbon nanotube tori under external fields. *Physical Review B*, **70**, 233402(2004).

(13) Dresselhaus, M. S., Dresselhaus, G. & Eklund, P. C. *Science of fullerenes and carbon nanotubes: their properties and applications*. Elsevier(1996).

(14) Reinert, L. et al. Dispersion analysis of carbon nanotubes, carbon onions, and nanodiamonds for their application as reinforcement phase in nickel metal matrix composites. *Rsc Advances*, **5**, 95149-95159.(2015).

(15) Park, H. J., Meyer, J., Roth, S. & Skákalová, V. Growth and properties of few-layer graphene prepared by chemical vapor deposition. *Carbon*, **48**, 1088-1094(2010).

(16) Kim, J., Lee, G. & Kim, J. Wafer-scale synthesis of multi-layer graphene by high-temperature carbon ion implantation. *Applied Physics Letters*, **107**, 033104(2015).

(17) Nagashio, K., Nishimura, T., Kita, K. & Toriumi, A. Mobility variations in mono- and multi-layer graphene films. *Applied physics express*, **2**, 025003(2009).

(18) Latil, S. & Henrard, L. Charge carriers in few-layer graphene films. *Physical Review Letters*, **97**, 036803(2006).

(19) Zhang, F. et al. Spontaneous quantum Hall states in chirally stacked few-layer graphene systems. *Physical review letters*, **106**, 156801(2011).

(20) Ho, J. H., Lai, Y. H., Tsai, S. J., Hwang, J., Chang, C. & Lin, M.F Magneto-electronic Properties of a Single-Layer Graphite (Condensed matter: electronic structure and electrical, magnetic, and optical properties). *Journal of the Physical Society of Japan*, **75**, (2006).

(21) Huang, Y. K., Chen, S. C., Ho, Y. H., Lin, C. Y. & Lin, M. F. Feature-rich magnetic quantization in sliding bilayer graphenes. *Scientific reports*, **4**, 7509(2014).
(22) Koshino, M. & McCann, E. Landau level spectra and the quantum Hall effect of multilayer graphene. *Physical Review B*, **83**, 165443(2011).

(23) Wang, Z. F., Liu, F. & Chou, M. Y. Fractal Landau-level spectra in twisted bilayer graphene. *Nano letters*, **12**, 3833-3838(2012).

(24) Ho, J. H., Chang, C. P. & Lin, M. F. Electronic excitations of the multilayered graphite. *Physics Letters A*, **352**, 446-450(2006).

(25) Lin, M. F., Chuang, Y. C. & Wu, J. Y. Electrically tunable plasma excitations in AA-stacked multilayer graphene. *Physical Review B*, **86**, 125434(2012).

(26) Wu, J. Y., Chen, S. C., Roslyak, O., Gumbs, G. & Lin, M. F. Plasma excitations in graphene: Their spectral intensity and temperature dependence in magnetic field. *ACS nano*, **5**, 1026-1032(2011).

(27) Lozovik, Y. E. & Sokolik, A. A. Influence of Landau level mixing on the properties of elementary excitations in graphene in strong magnetic field. *Nanoscale research letters*, **7**, 134(2012).

(28) Ohta, T. et al. Interlayer interaction and electronic screening in multilayer graphene investigated with angle-resolved photoemission spectroscopy. *Physical Review Letters*, **98**, 206802(2007).

(29) Koshino, M. & Ando, T. Magneto-optical properties of multilayer graphene. *Physical Review B*, **77**, 115313(2008).

(30) Mucha-Kruczyński, M., Abergel, D. S. L., McCann, E. & Falko, V. I. On spectral properties of bilayer graphene: the effect of an SiC substrate and infrared magneto-spectroscopy. *Journal of Physics: Condensed Matter*, **21**, 344206(2009).
Mucha-Kruczyński, M., McCann, E. & Falkó, V. I. The influence of interlayer asymmetry on the magnetospectroscopy of bilayer graphene. *Solid State Communications, 149*, 1111-1116(2009).

Novoselov, K. S. et al. Two-dimensional gas of massless Dirac fermions in graphene. *Nature, 438*, 197(2005).

Chen, J. H., Jang, C., Xiao, S., Ishigami, M. & Fuhrer, M. S. Intrinsic and extrinsic performance limits of graphene devices on SiO 2. *Nature nanotechnology, 3*, 206(2008).

Lee, C., Wei, X., Kysar, J. W. & Hone, J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science, 321*, 385-388(2008).

Lee, J. K., et al. The growth of AA graphite on (111) diamond. *The Journal of chemical physics, 129*, 234709(2008).

Jin, C., Lan, H., Peng, L., Suenaga, K. & Iijima, S. Deriving carbon atomic chains from graphene. *Physical review letters, 102*, 205501(2009).

Lui, C. H. et al. Imaging stacking order in few-layer graphene. *Nano letters, 11*, 164-169(2010).

Cancado, L. G. et al. Measuring the degree of stacking order in graphite by Raman spectroscopy. *Carbon, 46*, 272-275(2008).

Lui, C. H. et al. Observation of layer-breathing mode vibrations in few-layer graphene through combination Raman scattering. *Nano letters, 12*, 5539-5544(2012).

Zandiatashbar, A. et al. Effect of defects on the intrinsic strength and stiffness of graphene. *Nature communications, 5*, 3186(2014).

Pereira, V. M. & Neto, A. C. Strain engineering of grapheneâ€™s electronic structure. *Physical Review Letters, 103*, 046801(2009).
(42) Wong, J. H., Wu, B. R. & Lin, M. F. Strain effect on the electronic properties of single layer and bilayer graphene. *The Journal of Physical Chemistry C, 116*, 8271-8277(2012).

(43) Liu, Y., Liu, X., Zhang, Y., Xia, Q. & He, J. Effect of magnetic field on electronic transport in a bilayer graphene nanomesh. *Nanotechnology, 28*, 235303(2017).

(44) Lai, Y. H., Ho, J. H., Chang, C. P. & Lin, M. F. Magnetoelectronic properties of bilayer Bernal graphene. *Physical Review B, 77*, 085426(2008).

(45) Liu, H., Liu, Y. & Zhu, D. Chemical doping of graphene. *Journal of materials chemistry, 21*, 3335-3345(2011).

(46) Chan, K. T., Neaton, J. B. & Cohen, M. L. First-principles study of metal adatom adsorption on graphene. *Physical Review B, 77*, 235430(2008).

(47) Garcia, J. C., de Lima, D. B., Assali, L. V. & Justo, J. F. Group IV graphene- and graphane-like nanosheets. *The Journal of Physical Chemistry C, 115*, 13242-13246(2011).

(48) Liu, H. Y., Hou, Z. F., Hu, C. H., Yang, Y. & Zhu, Z. Z. Electronic and magnetic properties of fluorinated graphene with different coverage of fluorine. *The Journal of Physical Chemistry C, 116*, 18193-18201(2012).

(49) Crook, C. B. et al. Proximity-induced magnetism in transition-metal substituted graphene. *Scientific reports, 5*, 12322(2015).

(50) Wu, J., Rodrigues, M. T. F., Vajtai, R. & Ajayan, P. M. Tuning the Electrochemical Reactivity of Boron-and Nitrogen-Substituted Graphene. *Advanced Materials, 28*, 6239-6246(2016).

(51) Santos, E. J., Ayuela, A. & Sánchez-Portal, D. First-principles study of substitutional metal impurities in graphene: structural, electronic and magnetic properties. *New Journal of Physics, 12*, 053012(2010).
(52) Takahashi, T., Sugawara, K., Noguchi, E., Sato, T. & Takahashi, T. Band-gap tuning of monolayer graphene by oxygen adsorption. *Carbon, 73*, 141-145(2014).

(53) Sun, M. et al. First-principles study of the alkali earth metal atoms adsorption on graphene. *Applied Surface Science, 356*, 668-673(2015).

(54) Gao, H. & Liu, Z. DFT study of NO adsorption on pristine graphene. *RSC Advances, 7*, 13082-13091(2017).

(55) Yan, J. A. & Chou, M. Y. Oxidation functional groups on graphene: Structural and electronic properties. *Physical review B, 82*, 125403(2010).

(56) Cortes-Arriagada, D., Gutierrez-Oliva, S., Herrera, B., Soto, K. & Toro-Labbe, A. The mechanism of chemisorption of hydrogen atom on graphene: Insights from the reaction force and reaction electronic flux. *The Journal of chemical physics, 141*, 134701(2014).

(57) Lee, G., Lee, B., Kim, J. & Cho, K. Ozone adsorption on graphene: ab initio study and experimental validation. *The Journal of Physical Chemistry C, 113*, 14225-14229(2009).

(58) Ivanovskaya, V. V. et al. Hydrogen adsorption on graphene: a first principles study. *The European Physical Journal B, 76*, 481-486(2010).

(59) Yan, H. J., Xu, B., Shi, S. Q. & Ouyang, C. Y. First-principles study of the oxygen adsorption and dissociation on graphene and nitrogen doped graphene for Li-air batteries. *Journal of Applied Physics, 112*, 104316(2012).

(60) Beheshti, E., Nojeh, A. & Servati, P. A first-principles study of calcium-decorated, boron-doped graphene for high capacity hydrogen storage. *Carbon, 49*, 1561-1567(2011).

(61) Wu, M., Liu, E. Z., Ge, M. Y. & Jiang, J. Z. Stability, electronic, and magnetic behaviors of Cu adsorbed graphene: A first-principles study. *Applied Physics Letters, 94*, 102505(2009).
(62) Lin, S. Y., Lin, Y. T., Tran, N. T. T., Su, W. P. & Lin, M. F. Feature-rich electronic properties of aluminum-adsorbed graphenes. Carbon, 120, 209-218(2017).

(63) Tran, N. T. T., Nguyen, D. K., Glukhova, O. E. & Lin, M. F. Coverage-dependent essential properties of halogenated graphene: A DFT study. Scientific reports, 7, 17858(2017).

(64) Hu, C. H. et al. Electronic and magnetic properties of silicon adsorption on graphene. Solid State Communications, 151, 1128-1130(2011).

(65) Yoshioka, T., Suzuura, H. & Ando, T. Electronic states of BCN alloy nanotubes in a simple tight-binding model. Journal of the Physical Society of Japan, 72, 2656-2664(2003).

(66) da Rocha Martins, J. & Chacham, H. Disorder and segregation in B-C-N graphene-type layers and nanotubes: tuning the band gap. ACS Nano, 5, 385-393(2010).

(67) Cortés-Arriagada, D., Miranda-Rojas, S., Ortega, D. E. & Toro-Labbé, A. Oxidized and Si-doped graphene: emerging adsorbents for removal of dioxane. Physical Chemistry Chemical Physics, 19, 17587-17597(2017).

(68) Ain, Q. T., Al-Modlej, A., Alshammari, A. & Anjum, M. N. Effect of solvents on optical band gap of silicon-doped graphene oxide. Materials Research Express, 5, 035017(2018).

(69) Tang, Y. B. et al. Tunable band gaps and p-type transport properties of boron-doped graphenes by controllable ion doping using reactive microwave plasma. ACS Nano, 6, 1970-1978(2012).

(70) Lin, S. Y., Chang, S. L., Tran, N. T. T., Yang, P. H. & Lin, M. F. Si bonding-induced unusual electronic properties of silicene: a method to identify hydrogen concentration. Physical Chemistry Chemical Physics, 17, 26443-26450(2015).
(71) Li, S. S. et al. Tunable electronic and magnetic properties in germanene by alkali, alkaline-earth, group III and 3d transition metal atom adsorption. Physical Chemistry Chemical Physics, 16, 15968-15978(2014).

(72) Chen, R. B., Chen, S. C., Chiu, C. W. & Lin, M. F. Optical properties of monolayer tinene in electric fields. Scientific Reports, 7, 1849(2017).

(73) Sahin, H. & Peeters, F. M. Adsorption of alkali, alkaline-earth, and 3d transition metal atoms on silicene. Physical Review B, 87, 085423(2013).

(74) Dávila, M. E., Xian, L., Cahangirov, S., Rubio, A. & Le Lay, G. Germanene: a novel two-dimensional germanium allotrope akin to graphene and silicene. New Journal of Physics, 16, 095002(2014).

(75) Cai, B. et al. Tinene: a two-dimensional Dirac material with a 72 meV band gap. Physical Chemistry Chemical Physics, 17, 12634-12638(2015).

(76) Nie, S. Scanning tunneling microscopy study of graphene on Au (111): Growth mechanisms and substrate interactions. Physical Review B, 85, 205406(2012).

(77) Biró, L. Scanning tunnelling microscopy (STM) imaging of carbon nanotubes. Carbon, 36, 689-696(1998).

(78) Chen, X., Wan, H., Song, K., Tang, D. & Zhou, G. Scanning tunneling microscopy image modeling for zigzag-edge graphene nanoribbons. Applied Physics Letters, 98, 263103(2011).

(79) Wang, W. X., Scanning tunneling microscopy and spectroscopy of finite-size twisted bilayer graphene. Physical Review B, 96, 115434(2017).

(80) Hattendorf, S., Georgi, A., Liebmann, M. & Morgenstern, M. Networks of ABA and ABC stacked graphene on mica observed by scanning tunneling microscopy. Surface Science, 610, 53-58(2013).
(81) Ortolani, L., Catheline, A., Morandi, V. & Pénicaud, A. Transmission Electron Microscopy Study of Graphene Solutions. Springer, Berlin, Heidelberg, 610, 157-163(2012).

(82) Kasumov, Y. A., Khodos, I. I., Kociak, M. & Kasumov, A. Y. Scanning and transmission electron microscope images of a suspended single-walled carbon nanotube. Applied physics letters, 89, 013120(2006).

(83) Elias, D. C. et al. Control of graphene’s properties by reversible hydrogenation: evidence for graphane. Science, 323, 610-613(2009).

(84) Kim, K. et al. Multiply folded graphene. Physical Review B, 83, 245433(2011).

(85) Xie, X. et al. Controlled fabrication of high-quality carbon nanoscrolls from monolayer graphene. Nano letters, 9, 2565-2570(2009).

(86) Liu, X. H. et al. In situ transmission electron microscopy of electrochemical lithiation, delithiation and deformation of individual graphene nanoribbons. Carbon, 50, 3836-3844(2012).

(87) Warner, J. H., Rümmeli, M. H., Gemming, T., Büchner, B. & Briggs, G. A. D. Direct imaging of rotational stacking faults in few layer graphene. Nano letters, 9, 102-106(2008).

(88) Norimatsu, W. & Kusunoki, M. Selective formation of ABC-stacked graphene layers on SiC (0001). Physical review B, 81, 161410(2010).

(89) Luican, A., Li, G. & Andrei, E. Y. Quantized Landau level spectrum and its density dependence in graphene. Physical Review B, 83, 041405(2011).

(90) Qiao, Z. et al. Quantum anomalous Hall effect in graphene from Rashba and exchange effects. Physical Review B, 82, 161414(2010).
(91) Katsnelson, M. I. Optical properties of graphene: The Fermi-liquid approach. *EPL (Europhysics Letters)*, 84, 37001(2008).

(92) Kralj, M. et al. Graphene on Ir (111) characterized by angle-resolved photoemission. *Physical Review B*, 84, 075427(2011).

(93) Tran, N. T. T., Lin, S. Y., Lin, C. Y. & Lin, M. F. Geometric and electronic properties of graphene-related systems: Chemical bonding schemes. *CRC Press*, book, ISBN:9781138556522(2018).

(94) Lin, C. Y., Chen, R. B., Ho, Y. H. & Lin, M. F. Electronic and optical properties of graphite-related systems. *CRC Press*, book, ISBN 9781138571068(2017).

(95) Son, Y. W., Cohen, M. L. & Louie, S. G. Energy gaps in graphene nanoribbons. *Physical review letters*, 97, 216803(2006).

(96) Ruffieux, P. et al. Electronic structure of atomically precise graphene nanoribbons. *ACS Nano*, 6, 6930-6935(2012).

(97) Senkovskiy, B. V. et al. Finding the hidden valence band of N= 7 armchair graphene nanoribbons with angle-resolved photoemission spectroscopy. *2D Materials*, 5, 035007(2018).

(98) Nigar, S., Zhou, Z., Wang, H. & Imtiaz, M. Modulating the electronic and magnetic properties of graphene. *RSC Advances*, 7, 51546-51580(2017).

(99) Medeiros, P. V., de Brito Mota, F., Mascarenhas, A. J. & de Castilho, C. M. Adsorption of monovalent metal atoms on graphene: a theoretical approach. *Nanotechnology*, 21, 115701(2010).

(100) Lu, C. L., Chang, C. P., Huang, Y. C., Lu, J. M., Hwang, C. C. & Lin, M. F. Low-energy electronic properties of the AB-stacked few-layer graphites. *Journal of Physics: Condensed Matter*, 18, 5849(2006).
(101) L. Lu, C., P. Chang, C., C. Huang, Y., H. Ho, J., C. Hwang, C. & F. Lin, M. Electronic properties of AA-and ABC-stacked few-layer graphites. *Journal of the Physical Society of Japan*, **76**, 024701(2007).

(102) Lin, M. F. Low-frequency π-electronic excitations of simple hexagonal graphite. *Journal of the Physical Society of Japan*, **70**, 897-901(2001).

(103) Choi, J., Lee, H. & Kim, S. Atomic-scale investigation of epitaxial graphene grown on 6H-SiC (0001) using scanning tunneling microscopy and spectroscopy. *The Journal of Physical Chemistry C*, **114**, 13344-13348(2010).

(104) Luican, A., Li, G. & Andrei, E. Y. Scanning tunneling microscopy and spectroscopy of graphene layers on graphite. *Solid State Communications*, **149**, 1151-1156(2009).

(105) LeRoy, B. J., Lemay, S. G., Kong, J. & Dekker, C. Scanning tunneling spectroscopy of suspended single-wall carbon nanotubes. *Applied physics letters*, **84**, 4280-4282(2004).

(106) Odom, T. W., Huang, J. L., Kim, P., Ouyang, M. & Lieber, C. M. Scanning tunneling microscopy and spectroscopy studies of single wall carbon nanotubes. *Journal of materials research*, **13**, 2380-2388(1998).

(107) Niimi, Y. et al. Scanning tunneling microscopy and spectroscopy studies of graphite edges. *Applied surface science*, **241**, 43-48(2005).

(108) Sforzini, J., et al. Structural and electronic properties of nitrogen-doped graphene. *Physical review letters*, **116**, 126805(2016).

(109) Dimakis, N. et al. Density functional theory calculations on alkali and the alkaline Ca atoms adsorbed on graphene monolayers. *Applied surface science*, **413**, 197-208(2017).

(110) Kong, X. Metal-free Si-doped graphene: A new and enhanced anode material for Li ion battery. *Journal of Alloys and Compounds*, **687**, 534-540(2016).
(111) Liu, X., Zhu, X. & Pan, D. Solutions for the problems of silicon-carbon anode materials for lithium-ion batteries. *Royal Society Open Science, 5*, 172370(2018).

(112) Sivek, J., Sahin, H., Partoens, B. & Peeters, F. M. Adsorption and absorption of boron, nitrogen, aluminum, and phosphorus on silicene: Stability and electronic and phonon properties. *Physical Review B, 87*, 085444(2013).

(113) Kaloni, T. P. Tuning the structural, electronic, and magnetic properties of germanene by the adsorption of 3d transition metal atoms. *The Journal of Physical Chemistry C, 118*, 25200-25208(2014).

(114) Zhu, F. F. et al. Epitaxial growth of two-dimensional stanene. *Nature materials, 14*, 1020(2015).

(115) Srivastava, P. et al. Tuning the electronic and magnetic properties of phosphorene by vacancies and adatoms. *The Journal of Physical Chemistry C, 119*, 6530-6538(2015).

(116) Aktürk, E., Aktürk, O. Ü. & Ciraci, S. Single and bilayer bismuthene: Stability at high temperature and mechanical and electronic properties. *Physical Review B, 94*, 014115(2016).

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Figure Captions

Figure 1. The total ground state energy and its dependence on the C-C/Si-C bond length for (a) the fully Si-adsorbed graphene (the double-side 100% case), and (b) the Si-substituted graphene under the 1:1 case.

Figure 2. Geometric structure of the 100% Si-adsorbed graphene: (a) top view and (b) side view.

Figure 3. The optimal geometric structures in Si-substituted graphene systems: (a) 100% case, (b) ortho/para-, and (c) meta-configuration for the 50% case.

Figure 4. The wide-energy-range electronic energy spectra with the dominances of host and guest atoms for Si-adsorbed graphene systems: (a) a pristine case, (b) a similar one under the enlarged unit cell identical to the 100% case, (c) the fully double-side absorption, and (d) the complete single-side adsorption.

Figure 5. The C- and Si-dominated valence and conduction bands in Si-substituted graphene systems: (a) Pristine ($2\sqrt{3} \times 2\sqrt{3}$), (b) 100% configuration, (c) ortho-, and (d) meta-configuration under the 50% case.

Figure 6. The spatial charge density/its variation after chemisorption for (a) a pristine system, (b)/(c) the 100% absorption, and (d)/(e) the 50% case.

Figure 7. Similar plot as Fig. 6, but shown for a Si-doped graphene under (a)/(b) 100% substitution, (c)/(d) ortho-, and (e)/(f) meta-configurations under the 50% case.

Figure 8. The atom- and orbital-projected density of states in Si-adsorbed graphene systems: (a) a pristine configuration, (b) a similar one within the enlarged unit cell the same with the 100% chemisorption, (c) the thorough double-side absorption, and (d) the full
single-side adsorption.

Figure 9. Similar plot as Fig. 8, but displayed for Si-substituted graphene systems: (a) Pristine \((2\sqrt{3} \times 2\sqrt{3})\), (b) 100\% configuration, (c) ortho-, and (d) meta-configuration under the 50\% case.
Table 1: Energy gap/metal; C-C bond length, Si-C bond length, and Si height for Si-substituted/adsorbed graphene.

| Doping type | Ratio of Si and C | percentage | $E_d^{d(i)}$ (eV)/metal | C-C bond (Å) | Si-C bond (Å) | Si height (Å) |
|-------------|------------------|------------|--------------------------|--------------|---------------|--------------|
| Adsorption  | Pristine         | X          | $E_g = 0$               | 1.420        | X             | X            |
|             | Si:C=3:6         | 50% single | M                        | 1.491        | 2.514         | 2.40         |
|             | Si:C=6:6         | 100% double| M                        | 1.492        | 2.535         | 2.422        |
|             | Si:C=6:6         | 100% double| M                        | 1.492        | 2.535         | 2.422        |
| Substitution| Si:C=2:4         | 50% ortho  | $E_g^d = 0.04$           | 1.478        | 1.833         | X            |
|             | Si:C=2:4         | 50% meta   | $E_g^d = 0.56$           | 1.465        | 1.829         | X            |
|             | Si:C=3:3         | 100%       | $E_g^d = 2.56$           | X            | 1.780         | X            |
Figure 1: The total ground state energy and its dependence on the C-C/Si-C bond length for (a) the fully Si-adsorbed graphene (the double-side 100\% case), and (b) the Si-substituted graphene under the 1:1 case.
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