Tailoring of the structural, energetic and electronic properties of silicene-based nanostructures

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Abstract. Silicene-based nanostructures are highly promising for future applications in electronics as silicon is an important element for conventional semiconductor industry. In our recent works, we have studied the effect of external electric filed, strain and metal adatoms on tailoring the structural, energetic and electronic properties of silicene-based nanostructures using first-principles and tight-binding methods. We find that half-metallicity can be realized in zigzag silicene nanoribbons when applying electric field across the nanoribbon width. Under small tensile strain, some armchair silicene nanoribbons are predicted to have linear energy dispersion around the Fermi level. And strain-induced structural phase transitions are observed in silicene bilayers in which strong covalent interlayer bonds form. When metal atoms are adsorbed on silicene, several metal adatoms obtain a larger binding energy than the cohesive energy of the bulk metal and the bonding between the metal atoms and silicene can be ionic or covalent.

1. Introduction
Silicene, the silicon counterpart of graphene, possesses many intriguing properties similar to graphene[1, 2, 3, 4]. The honeycomb $\pi$-orbital network makes silicene show linear energy dispersion near the Fermi level ($E_F$)[1, 2]. Thus the quasiparticles near $E_F$ in silicene show Dirac-type behavior of motion. Since silicon cannot form layered graphite-like material, much efforts have been devoted to grow silicene on the substrates[5, 6, 7, 8, 9, 10, 11]. Recently, silicene has been successfully fabricated on the Ag (111) surfaces[10, 11]. Similar to graphene, Si atoms in silicene form two sublattices. However, the two sublattices in silicene are not in the same plane with a buckled height between the two sublattices of about 0.46 Å[1]. In addition to the structural difference, the Si atoms in silicene have lower electronegativity than C in graphene. Then some silicene-based nanostructures can acquire rather distinct properties from graphene nanostructures. And we have been focusing on exploiting the rich electronic and magnetic properties of silicene-based nanostructures[12, 13]. Besides the pristine silicene nanostructures, the effects of external fields such as electric field[13] and strain[14, 15] as well as functionalization with metal adatoms[16] on tailoring the the structural, energetic and electronic properties of silicene nanostructures have been studied using first-principles and tight-binding methods.

Among the silicene-based nanostructures, silicon nanotubes and silicene nanoribbons are the one-dimensional (1D) structures corresponding to silicene. In experiments, equally spaced silicene nanoribbons have been observed on the Ag (110) surfaces[5, 8]. And silicon nanotubes
with a hollow structure have also been reported to be grown from silicon monoxide[17]. While silicene and graphene are both semimetallic, the 1D structures can be semiconductors as a result of the confinement effect. In both theoretical and experimental studies, graphene nanoribbons are demonstrated to be semiconducting[18, 19]. However, whether a graphene nanotube are metal or semiconductor depends on the chirality for tubes with a large diameter[20]. For silicon nanotubes, our first-principles calculations show that the surfaces of nanotubes are buckled with Si atoms having different distances to the axis of the tube[12]. And this difference in structures makes silicon nanotubes have distinct electronic properties from CNT. In contrast to CNT, the silicon nanotubes with a large diameter are all semiconductors[12]. The external electric field, strain and metal adatoms provide ways of tailoring various properties of silicene structures. For graphene nanoribbons with zigzag edges (ZGNR), it is demonstrated that the transverse electric field can make the ZGNR undergo a transition from semiconductor to half-metal[21]. Half-metallicity can also be realized in zigzag silicene nanoribbons (ZSiNR) under transverse electric field. Since silicene and silicene nanoribbons are obtained through growth on the substrate, the strain may play an important role in the structural and electronic properties of these nanostructure[14]. In addition to the monolayer silicene, silicene bilayers have also been observed in experiments[11]. The structures of silicene bilayers under strain have been studied as the silicene bilayers grown on the substrate tend to be strained compared to the pristine structure[15]. Adsorption of metal atoms is an effective way of functionalizing silicene and graphene nanostructures. Nanostructures adsorbed with metal atoms may be applied for superconductivity[22], hydrogen storage[23, 24, 25, 26], catalyst[27, 28], as well as tuning the electronic and magnetic properties[29]. However, the binding energies of all studied metal adatoms on graphene are smaller than the cohesive energies of the bulk metals[29]. As a result, metal adatoms on graphene with high coverage may tend to form clusters[30]. Silicene has larger hexagons than graphene and the silicene sheet is buckled while the graphene sheet is planar. Moreover, partial $sp^3$ characteristics are present in the Si-Si $\sigma$ bonds in silicene rather than complete $sp^2$ hybridization in graphene. Then silicene with some metal adatoms can exhibit unique structural, energetic, electronic properties compared with graphene[16].

The outline of this paper is as follows: Section II presents the effect of transverse electric field on the electronic structures of ZSiNR. In Sec. III, we show the structural and electronic properties of strained armchair silicene nanoribbons (ASiNR) and silicene bilayers. In Sec. IV, the functionalization of silicene with metal adatoms is discussed. Section V is the summary.

2. Zigzag silicene nanoribbons under transverse electric field
Silicene nanoribbons can be considered to be cut along a specific direction from the silicene sheet. Silicene nanoribbons are also buckled. And the silicene nanoribbons are passivated by hydrogen atoms. For $N_Z$-ZSiNR, $N_Z$ is used to denote the number of zigzag lines across the ribbon width. Using first-principles calculations, the stable magnetic state of ZSiNR and the behavior of ZSiNR under transverse electric field have been investigated[13].

A ZSiNR has an antiferromagnetic (AFM) ground state and is semiconducting[13]. The stabilities of the nonmagnetic (NM) state, ferromagnetic (FM) state, and AFM state of ZSiNR are calculated. It is found that the AFM state has the lowest energy. For example, the energy of the AFM state is 25 meV/unit less than the FM state and the energy of the FM state is 20 meV/unit less than the NM state for 6-ZSiNR. For the antiferromagnetic ZSiNR, the two edges have opposite spin orientations. For 6-ZSiNR, the spin-up and spin-down bands are degenerate with a band gap of 0.17 eV. When applying electric field across the width of the nanoribbon, ZSiNR undergoes a transition from semiconductor to half-metal with the increasing electric field[13]. As an example, for 6-ZSiNR, the band gap of up-spin remain larger than 0.17 eV for electric field in the range of 0 ~ 0.17 V/A. While for the down-spin, the band gap decreases with the increase of E and become closed when E reaches 0.15[13]. From the calculations, it is
found that the critical electric field $E_c$ satisfies a universal behavior as $wE_c=2.6$ V, where $w$ is the width of the ZSiNRs. The value of $wE_c$ is smaller than that of ZGNRs[21], which suggests that it can be easier for a ZSiNR to become half-metals than the ZGNR having the same width as the ZSiNR.

3. Strained armchair silicene nanoribbons and silicene bilayers

3.1. Band gaps of ASiNR tubed by strain

The Dirac type dispersion in silicene and silicon nanoribbons indicates a high mobility of electrons near the Fermi level. It is demonstrated that the silicon nanoribbons with armchair edges (ASiNR) are semiconductors with small gaps[1, 31, 13], recognized as a suitable material. Our first-principles calculations have shown that the structural parameters of 8-ASiNR agree well with the experimental observation [32]. The successful experimental synthesis of the 8-ASiNRs makes this purpose practical. To realize the function of field effect devices, a variation of the conductivity of ASiNRs will be needed, which is traditionally tuned by a gate voltage. However, a quite large gate voltage should be applied to open a small gap in silicene.[33] Other methods such as hydrogenation will open a gap but meanwhile break the linear dispersion near the Fermi level[34]. It is important to find a method to tune the band gaps with the Dirac-type dispersion maintained.

We find that the strain is an effective method to tune the band gap of the SiNRs[14]. Moreover, the Dirac type dispersion is kept near the Fermi level during the modulation. As shown in Fig. 1(a), the linear dispersions still hold except for the $\Gamma$ point when the strain is around the $\varepsilon_0$. The band gap of 11-ASiNR is 39 meV without strain, it becomes 58 meV when $\varepsilon = 3\%$. When applied a strain of $\varepsilon = 1.24\%$, the band gap becomes quite small. The charge densities of the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCO) shows that the strain turn the HOCO state in Fig. 1(a) into LUCO state in Fig. 1(c), and meanwhile turn the HOCO state in Fig. 1(a) into HOCO state in Fig. 1(c). When applied a strain of $\varepsilon = 1.24\%$, the two types of charge density distributions mixed, indicates that the HOCO state and LUCO state are degenerate, and the band gap seem to vanish.

However, the band gaps from DFT calculations can not give an exact zero value because the numerical errors in the computations are inevitable. It is important to judge whether the band gap is exactly equal to zero, which indicates a semiconductor-semimetal-semiconductor phase transition. Therefore, we use the tight-binding model to prove the existence of a zero point in the band gap under certain strain[14]. For the $(3p+2)$-ASiNRs under different strains, the band gap occurs at $k=0$, drawn from the DFT calculations (Fig. 2(a)). The Hamiltonian of the ASiNRs with the the same Si-Si bond lengths is the unperturbed Hamiltonian $H_0$. The perturbation Hamiltonian is $H'$ and thus the total Hamiltonian is $H = H_0 + H'$. The tight-binding model can be represented by a two-leg ladder lattice system, as shown in Fig. 2(b). The unperturbed Hamiltonian $H_0$ can be written as

$$
H_0 = \begin{pmatrix}
T & t_0I \\
t_0I & T
\end{pmatrix}_{2N \times 2N}
$$

where

$$
T = \begin{pmatrix}
0 & t_0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 \\
t_0 & 0 & t_0 & 0 & \cdots & 0 & 0 & 0 & 0 \\
0 & t_0 & 0 & t_0 & \cdots & 0 & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & \cdots & t_0 & 0 & t_0 & 0 \\
0 & 0 & 0 & 0 & \cdots & 0 & t_0 & 0 & t_0 \\
0 & 0 & 0 & 0 & \cdots & 0 & 0 & t_0 & 0 \\
\end{pmatrix}_{N \times N}
$$
Figure 1. (Color online)(top) The detailed band structures of 11-ASiNRs near the $\Gamma$ point with the strain of (a) $\varepsilon = 0\%$, (b) $\varepsilon = 1.24\%$ and (c) $\varepsilon = 3\%$. The highest occupied energies are set to zero. (middle)(bottom) The partial charge densities of the lowest unoccupied crystal orbital (LUCO) and the highest occupied crystal orbital (HOCO) for 11-ASiNR with the strain of (a) $\varepsilon = 0\%$, (b) $\varepsilon = 1.24\%$ and (c) $\varepsilon = 3\%$. The isosurface of partial charge densities is 0.005$e/\AA^3$. With the strain of $\varepsilon = 1.24\%$, the LUCO and HOCO are degenerate.[14]

and $I$ is the $N \times N$ unit matrix. $t_0$ is the hopping integrals between the nearest neighbors. When a strain is applied, the bond are stretched, leading to the variation of the hopping integrals. The perturbation Hamiltonian is

$$H' = \begin{pmatrix} A & B \\ B & A \end{pmatrix}_{2N \times 2N}$$ (3)
where

\[
A = \begin{pmatrix}
0 & \delta t' & 0 & 0 & \cdots & 0 & 0 & 0 & 0 \\
\delta t'_2 & 0 & \delta t_2 & 0 & \cdots & 0 & 0 & 0 & 0 \\
0 & \delta t_2 & 0 & \delta t_2 & \cdots & 0 & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & \cdots & \delta t_2 & 0 & \delta t_2 & 0 \\
0 & 0 & 0 & 0 & \cdots & 0 & \delta t_2 & 0 & \delta t'_2 \\
0 & 0 & 0 & 0 & \cdots & 0 & 0 & \delta t'_2 & 0 \\
\end{pmatrix}_{N \times N}
\]  

(4)

\[
B = \begin{pmatrix}
\delta t_1 \\
\delta t_1 \\
\vdots \\
\delta t_1 \\
\delta t_1 \\
\delta t_1 \\
\delta t_1 \\
\end{pmatrix}_{N \times N}
\]  

(5)

Using perturbation theory, the band gap has been obtained:

\[
E_g = |E'_1 - E'_2| = |-2\delta t_2 + 2\delta t_1 + \frac{2(\delta t'_1 - \delta t_1) - 4(\delta t'_2 - \delta t_2)}{p + 1}|.
\]

(6)

The hopping parameters is assumed to be scaled in Harrison form\[31\] and the bond lengths under various strains are linearly fitted near the strain \( \epsilon = 0 \). As shown in Fig. 2(c), we find the band gaps of 8-ASiNR, 11-ASiNR and 14-ASiNR vanish with small strains and the zero point right shift with the increase of \( N_a \), the same as the results of the ab initio calculations(Fig. 2(a))\[14\].

3.2. Strain-induced Phase Transitions in silicene bilayers

Besides that the monolayer silicene have been grown experimentally\[10, 11\], it is also reported that a bilayer silicene phase coexist and with similar structural and electronic properties with the monolayers\[11\]. However, the first-principle calculations shows that the original low buckled silicene monolayer will become a complete \( sp^3 \) Si(111) sheet. With relaxation, this stacking silicene bilayer turn into the reconstructed silicene bilayer (RSBL), which is the global stable structure\[36, 37\]. This contradiction comes from the substrate effect in the experiments which is not taken into consideration in the calculations. Among these effects strain is an important factor. Thus, it is important to discuss the changes of the silicene bilayer structures under strain\[15\].

We study the reconstructed structures of RSBL under isotropic tensile strains\[15\], as shown in Fig. 3(a) and 3(b). As shown in Fig. 3(c), with the increasing strain, the buckle lengths decrease to 0.08\( \AA \) under the strain of 10.8\%. After that, the RSBL undergoes a phase transition, with decrease of 0.074eV/atom in the total energy. This phase (Fig. 3(b)) is similar as the AA stacking graphene bilayer and thus named as graphene-like silicene bilayer(GSBL). We find that this GSBL phase exists in a wide range of strain. Although the GSBL emerges under the strain over 10\% from the barrierless phase transitions, the GSBL has already become the most stable structure when the strain reaches 6.5\%, as shown in Fig. 3(d). As we gradually decrease the strain from 20\% to 0\% on the GSBL, the total energy decreases to the minimum of -4.96eV/atom at the strain of 8.3\% and increases after that. Before the strain decreases to 6.5\%, the GSBL is always the most stable structure. The SSBL and RSBL will eventually turn into the GSBL when the strain is larger than 6.5\%, but with energy barriers. The extra strain is needed for the RSBL to overcome the barriers and the barrierless phase transitions occur at \( \epsilon = 10.3\% \).
Figure 2. (Color online) (a) The band gaps $E_g$ of (3p+2)-ASiNRs as a function of strain. (b) The two-leg ladder model of ASiNRs at $\Gamma$ point. (c) The band gaps of (3p+2)-ASiNRs as a function of strain in tight-binding calculations.[14]

The silicon atoms in the GSBL are not three-coordinated as silicene, but four-coordinated like the $sp^3$ silicon materials. However, different from the common $sp^3$ silicon materials, the four nearest neighbors of the silicon atoms in the GSBL do not form a regular tetrahedron. It indicates that the hybridization in GSBL are novel and not similar with neither the $sp^2$ hybridization nor the $sp^3$ hybridization. To reveal the hybridization type of the GSBL, we carry on a tight-binding calculation[15].

The model is shown in Fig. 4(a) and the Hamiltonian can be expressed as:

$$H = \begin{pmatrix}
H_{AA} & H_{AB} & H_{AC} & 0 \\
H_{BA} & H_{BB} & 0 & H_{BD} \\
H_{CA} & 0 & H_{CC} & H_{CD} \\
0 & H_{DB} & H_{DC} & H_{DD}
\end{pmatrix},$$

(7)
Figure 3. (Color online) The structures of the (a) RSBL and (b) GSBL. The energies (solid lines) and buckle lengths $h_b$ (dash lines) of (c)RSBL and (d)GSBL with strains. The arrows represent the variations of the strain.[15] 

where $H_{ij} = H_{ji}^\dagger$ is a matrix describing the interaction between atom $i$ and atom $j$. The symmetry demands $H_{AA} = H_{BB} = H_{CC} = H_{DD}$ and $H_{AB} = H_{CD}, H_{AC} = H_{BD}$. There are four atomic orbitals per silicon atom: $s, p_x, p_y$ and $p_z$. Thus in the Slater-Koster scheme[20, 38], $H_{ij}$ is a $4 \times 4$ matrix. $H_{AA}$ and $H_{AB}$ describe the intralayer interactions:

$$H_{AA} = \begin{pmatrix} \varepsilon_s & 0 & 0 & 0 \\ 0 & \varepsilon_p & 0 & 0 \\ 0 & 0 & \varepsilon_p & 0 \\ 0 & 0 & 0 & \varepsilon_p \end{pmatrix}, \quad H_{AB} = \begin{pmatrix} h_{sA}^{A_sB} & h_{sA}^{A_sB} & h_{sA}^{A_sB} & 0 \\ h_{p_xA}^{A_xB} & h_{p_xA}^{A_xB} & h_{p_xA}^{A_xB} & 0 \\ h_{p_yA}^{A_yB} & h_{p_yA}^{A_yB} & h_{p_yA}^{A_yB} & 0 \\ 0 & 0 & 0 & h_{p_zA}^{A_zB} \end{pmatrix}. \quad (8)$$
Figure 4. (Color online) (a) The schematic diagram of the tight-binding model. The left panel shows the top view and the right panel shows the side view. A, B, C, and D represent different sublattices. θ is the direction angle of the vector between the atom A and atom B. (b) and (c) The band structures of the PSML and GSBL. The left panels and the right panels show the first-principles and tight-binding results, respectively.[15]

$H_{AC}$ describes the interlayer interactions in GSBL:

$$H_{AC} = \begin{pmatrix}
h_{p^zA^zC^z} & 0 & 0 & h_{sA^zF^z} \\
0 & h_{p^zA^zF^z} & 0 & 0 \\
0 & 0 & h_{p^zA^zF^z} & 0 \\
h_{p^zA^zC^z} & 0 & 0 & h_{p^zA^zF^z}
\end{pmatrix}, \tag{9}$$

We find that the phase transitions occur under certain tensile strains for SSBL and RSBL, both with no energy barrier[15]. After the transition, the SSBL and RSBL turn into a graphene-like silicene bilayer (GBSL) structure. Different from the AB stacking graphene bilayer with the Van der Waals interlayer interactions, the GBSL is combined in the AA stacking with the strong
covalent bonds. Using the tight-binding model, we demonstrate that the hybridization of the electrons in the GSBL is the $sp^2 - sp^1$ hybridization without any $sp^3$ part.

We use the parameters determined from the first-principles energy band. No extra parameters are introduced when two planar silicene bilayer (PSML) form the GSBL. Therefore, the parameters are fitted with the first-principles band structure of the PSML, as shown in Fig. 4(b). With these parameters, as shown in Fig. 4(c), the band structure of GSBL is achieved. The tight-binding results agree well with the first-principles results, which means that the primary interactions have been included in our tight-binding model[15]. This is totally different from the weak Van der Waals interactions in the graphene bilayer, which can be viewed as a perturbation to the band structure of the graphene monolayer. It concludes that the intralayer $sp^2$ hybridization in the GSBL is the same as that in the PSML, since $H_{AA}$ and $H_{AB}$, which describe the intralayer interaction, are exactly the same. In addition, because of the existence of the interlayer interaction $H_{AC}$, the properties of the GSBL are different from the two isolated PSMLs. We recall that the $H_{AC}$ describe the hybridization just like the $sp^1$ hybridization in the 1D silicon chains. It demonstrates that the hybridization of the silicon atoms in GSBL is $sp^2 - sp^1$ hybridization.

We tailor the GSBL into armchair nanoribbons (Fig. 5(a)) and zigzag nanoribbon (Fig. 5(b)). The band structure of bilayer zigzag silicon nanoribbon (BZSiNR) is similar to the monolayer ZSiNR (Fig. 5(c))[13]. While due to the $sp^3$ edges, the spin-correlation between two edges vanish and the ground state is nonmagnetic. The hydrogen atoms in the passivated edge lies out-plane, which indicates a $sp^3$ hybridization. As shown in Fig. 5(d) and 6(e), the narrower($N_a < 11$) bilayer armchair silicene nanoribbon (BASiNR) is semiconductor, the same as monolayer ASiNR, while the band gaps decrease with the widths increase. The periodicity of band gaps in monolayer ASiNRs is absent. A wider BASiNR($N_a \geq 11$)are metallic.

4. Silicene adsorbed with metal atoms

Adsorption of metal atoms is an effective way of functionalizing nanostructures. Much effort has been devoted to studying the behavior of metal adatoms on graphene[22, 29]. The metal atoms adsorbed on silicene can acquire rather distinct structural, energetic and electronic properties compared with those on graphene. A systematic investigation of the adsorption of 15 different metal atoms on silicene, including alkali and alkali-earth metals Li, Na, K, Ca, group III and IV metals Al, Ga, In, Sn and transition metals Ti, Fe, Co, Ni, Pd, Pt, Au, has been done[16].

Metal atoms have three possible adsorption sites, the hollow (H) site above the center of a Si hexagon, the top (TA) site above a Si atom belonging to sublattice A and the top (TB) site above a Si atom of sublattice B, as shown in Fig. 6(a). This is different from graphene, for which metal atoms can be adsorbed above the midpoint of a C-C bond (bridge site)[29]. Since graphene is planar, the TA and TB sites are equivalent. Li, Na, K, and Ca bind most strongly to the H site of silicene. Al, Ga, In, and Sn prefer the TA site, as shown in Fig. 6(b). For transition metal atoms, the most stable adsorption site is H except for Fe, whose favored site is TA. In the case of Fe at the H site, $E_b$ is a little smaller than the TA site. The Fe adatom at the H site of silicene has a peculiar structure with the six Fe-Si bonds having almost equal length, which is about 2.30 Å, close to the Si-Si bond length 2.39 Å in silicene, as shown in Fig. 6(c)[16].

Compared with graphene, metal atoms have much strong binding to silicene. The binding energy $E_b$ is defined as $E_b(M) = E(M) + E(\text{Silicene}) - E(M-\text{Silicene})$, where $E(M)$, $E(\text{Silicene})$, and $E(M-\text{Silicene})$ are the energies of an isolated metal atom, the silicene supercell and the adatom-silicene system. For silicene, Li, Na, K, Ca, Co, Ni, Pd, and Pt obtain a larger $E_b$ than the cohesive energy of the bulk metal ($E_c$)[16]. However, all the 15 metal atoms considered have smaller $E_b$ than $E_6$ on graphene[29]. Therefore, metal adatoms on silicene are rather stable.

Silicene adsorbed with different metal atoms exhibit various electronic and magnetic
Figure 5. (Color online) (a)(b) The structures of 8-ABSiNR and 5-ZBSiNR. The left panel is the top view and the right panel is the side view. The black and grey balls represent the silicon atoms in different layers. (c) The energy band(left) and density of states(right) of 8-ABSiNR(solid lines) and 12-ABSiNR(dash lines). (d) The energy band(left) and density of states(right) of 5-ZBSiNR(solid lines) and 9-ZBSiNR(dash lines). (e) The energy gaps of ABSiNRs as a function of $N_a$.

When an alkali atom Li, Na or K is adsorbed on silicene, about one electron is transferred from the atom to silicene. $E_F$ is shifted above the Dirac point ($E_D$) for about 0.39 eV, as shown in Fig. 7(b). The K state lies about 1.5 eV above $E_F$. Therefore, the bonding of alkali metal atoms to silicene is approximately ideal ionic. For the adsorption of Ca on silicene, the 3d states of Ca are hybridized with the silicene states around and above $E_F$, as shown in Fig. 8. The Ca adatom on silicene has a magnetic moment of 0.7 $\mu_B$. The hybridization band near $E_F$ of the up-spin is partially occupied, while the down-spin is totally empty. When the group III and IV metals Al, Sn, and transition metal atoms Ti, Fe, Co, and Au are adsorbed on silicene, hybridization between the adatom states and the silicene states occurs around the
Figure 6. (color online) (a) The buckled hexagonal structure of silicene. The three possible adsorption sites are labeled as H, TA, and TB. (b) and (c) The relaxed structure for Al@TA and Fe@H.[16]

Figure 7. (color online) (a) Band structure of the $4 \times 4$ silicene supercell. (b) and (c) Band structures for the K and Pd adatoms on silicene, respectively.
Figure 8. (color online) (a) Band structures of the spin-up states (a) and spin-down states (b) for the Ca adatom on silicene.

Dirac point. In contrast, for silicene with the Ni, Pd, and Pt adatoms, the hybridization states between the adatom d states and the silicene states lie rather far below the $E_F$ with $E_F$ located approximately at $E_D$. Figure 7(c) shows the band structure for Pd on silicene. The interaction between the silicene and Pd d states arise below the energy of -0.88 eV.

5. summary

In summary, we reviewed our recent works on the structural, energetic and electronic properties of silicene-based nanostructures modulated with external electric filed, strain and metal adatoms. We find that under external electric field across the width of the nanoribbon, the ZSiNR which has an antiferromagnetic ground state with the two edges having opposite spin orientations can become half-metallic. The ASiNR are semiconductors with the band gaps showing three series as a function with the width of the ribbon. And the band gap of ASiNR can be tuned by strain and the (3p+2)-ASiNRs are predicted to have linear energy dispersion under some small tensile strain. In addition, the isotropic tensile strain can make silicene bilayers undergo several barrierless structure phase transitions. For silicene bilayers, there exist strong covalent interlayer bonds. When metal atoms are adsorbed on silicene, metal adatoms can have different adsorption configuration on silicene from that on graphene and Li, Na, K, Ca, Co, Ni, Pd, and Pt obtain a larger binding energy than the cohesive energy of the bulk metal. The bonding between metal adatoms and silicene can be ionic or covalent. The alkali atoms bond ionically to silicene. There exits hybridization between the adatoms states and the silicene states for Ca, groups III and IV and transition metal atoms adsorbed on silicene.
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