



Tuneable electronic and magnetic properties of hybrid silicene/silicane nanoribbons induced by nitrogen doping

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ABSTRACT

The geometric, electronic and magnetic properties of N-doped zigzag and armchair silicene/silicane nanoribbons (Z- and A-SSNRs) have been studied by using density functional theory calculations, where silicane is the fully hydrogenated silicene. It is confirmed that the substitution of N for Si atom is preferred at the silicene/silicane interface and silicane edge. The large hydrogen diffusion energy barriers indicate high interface stability of the N-doped SSNRs. When the doping concentration is larger than a critical value, the doped Z-SSNR with N at silicene/silicane interface shows ferromagnetic semiconducting character with a magnetic moment of about 1 μ_B , while the doped Z-SSNR with N at silicane edge shows metallic character and tuneable magnetic moments dependent on the silicane width. For armchair SSNR, the A-SSNR with doping N at silicene/silicane interface is a semiconductor with a local magnetic moment of about 1 μ_B . However, the A-SSNR with doping N at silicane edge shows nonmagnetic metallic state. In addition, the Z- and A-SSNRs with doping N at silicene/silicane interface exhibit decreased band gaps and oscillatory band gaps, respectively, with increasing silicene width. This work provides fundamental insights for the applications of SSNRs in nanoelectronics devices.

1. Introduction

Since its experimental realization [1], graphene has been the subject of intensive research due to the high mobility Dirac fermions with a long elastic scattering length [2,3]. Nevertheless, it is facing many challenges such as incompatibility with current silicon based electronic technology. Silicene, the two-dimensional graphene-like analogue for silicon, has recently been synthesized on Ag [4,5], Ir [6], Au [7] and ZrB₂ [8] substrates and attracted enormous interests to explore its potential applications for electronic devices [9]. Due to the graphene-like lattice structure, the excellent electron transport properties of graphene could be transferred to this innovative material, such as gate-operated field effect transistor at room temperature [9], and massless Dirac fermions [10]. However, unlike graphene, the buckled structure causes silicene to have some different properties, such as controlling its band gap by using an electric field [11] and higher activity [12,13]. However, the active surface makes silicene to be sensitive to the environment. To prevent the unwanted chemical reactions with the ambient, the silicene sheet can be protected by encapsulating between inert layers, such as transition-metal dichalcogenides layers [14].

In actual applications, silicene is usually cut into nanoribbons.

Silicene nanoribbons (SiNRs) offer the possibility to achieve tuneable band structures with changing the width and edge morphology, where armchair and zigzag SiNRs show nonmagnetic (NM) and anti-ferromagnetic (AFM) semiconducting states, respectively [15]. In order to obtain magnetic moment, chemical doping is an attractive option to modulate the electronic properties of SiNRs. Previous studies have reported the electronic and magnetic properties of zigzag SiNRs doped with B [16,17], N [16–19], B/N pair [20], P [19,21,22] and Al [21,22] dopants. However, the magnetic moment of doped silicene nanoribbons cannot be tuned as the dopants are always located at the edge of the pristine silicene. In addition, the defects introduced by dopants scatter the carriers and limit the carrier mobility. The lateral heterostructures of silicene/silicane nanoribbons (SSNRs) provide an opportunity to tune the magnetic moment and reduce dopants scattering for carriers by remotely doping the outer silicane part, which will keep the central silicene part to be pristine as discussed in previous study [23].

Hydrogenation is usually used to tune the electronic properties of silicene [24,25]. The patterned absorption of atomic hydrogen on silicene with Ag(111) substrate was recently found [26], which indicates that the SSNRs can be realized experimentally. Silicene/silicane nanoribbons might be fabricated by selectively hydrogenating silicene by

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using low-damage plasma treatment or exposing to atomic H atmosphere with masking techniques, as proposed in the literatures [27]. Silicene nanoribbons have two edge types, i.e., zigzag and armchair edges [28]. Therefore, the silicane part for silicene/silicane nanoribbons will also has zigzag and armchair edges. Normally, the adsorbates are active at the interface due to the imperfect atomic arrangement. As the energy barrier is proportional to the adsorption energy of adsorbates [29], a large diffusion energy barrier of H atoms at the silicene/silicane interface indicates the high difficulty for H atom mobility and the high stability of the interface. Therefore, the thermal stability of SSNRs can be determined by calculating the diffusion barrier of H atoms at the interface, which is used in determining the interface stability of hybrid graphene/graphane nanoribbons [30,31].

In this work, based on density functional theory (DFT) calculations, combining the effects of both doping N and silicene/silicane interface, we study the electronic and magnetic properties of the N doped silicene/silicane hybrid nanoribbons. All the possible diffusion pathways for hydrogen diffusion at silicene/silicane interface are analysed to search the minimum diffusion barrier, and therefore to provide guidance for designing the viable silicene electronic devices that possess high thermal stability and excellent electronic and magnetic properties.

2. Calculation methods

The spin-unrestricted DFT calculations are carried out by using Dmol³ package [32]. Generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) [33] is taken as the exchange–correlation function. Although the GGA method tends to underestimate the band gap of semiconductors, it can give the corrected band order for the silicon based systems [16–25]. In addition, the advanced theoretical methods, such as hybrid functional, are hardly performed for our systems due to the large number of atoms. Therefore, GGA method is employed in this work. DFT semicore pseudopotentials core treatment is implemented for relativistic effects, which replaces core electrons by a single effective potential. Double numerical plus polarization is employed as the basis set. The convergence tolerance of energy of 10^{-5} Hartree is taken (1 Hartree = 27.21 eV), and the maximal allowed force and displacement are 0.002 Hartree/Å and 0.005 Å, respectively. It was reported that the selection of exchange–correlation functional has evidential effect on the

result of adsorption energies. However, the effect on the calculated reaction energy barriers is much smaller [34]. To investigate the minimum energy pathway for the diffusion of H atoms at the silicene/silicane interface, linear synchronous transit/quadratic synchronous transit [35] and nudged elastic band [36] tools in Dmol³ module are used, which have been well validated to determine the structure of the transition state and the minimum energy reaction pathway. The DFT + D method within the Grimme scheme [37] is used in all calculations to consider the van der Waals forces, which only causes a mean absolute deviation of 3.8 kcal mol^{−1} for the heat of formations [37] and has small effect on our studied system because the hydrogen atoms are chemical adsorbed on the silicene. In the simulation, three-dimensional periodic boundary conditions are taken. The simulation cell for silicene nanoribbon has a vacuum width of 20 Å above the silicene layer to minimize the interlayer interaction, where the *k*-point is set to $1 \times 1 \times 6$ along the periodic direction after careful examinations, and all atoms are allowed to relax according to previous reports. The Phonon dispersions of the SSNRs are calculated by using CASTEP code [38], where the ultrasoft pseudopotentials, finite displacement method, the GGA-PBE functional, and an energy cutoff of 400 eV and $1 \times 1 \times 12$ *k*-point meshes are used.

In order to determine the favourite doping position of N impurity in SSNRs, we considered several different configurations of a single N substitution for the Si site. The formation energy E_f of the N impurity is expressed as [16]

$$E_f = E_{\text{doped}} + E_{\text{Si}} - (E_{\text{pristine}} + E_{\text{N}}) \quad (1)$$

where E_{doped} is the total energy of the doped SSNRs with N impurity, while E_{pristine} is the total energy of the pristine SSNRs. The E_{Si} and E_{N} are the total energies of free Si or N impurity, respectively. According to this definition, a system with smaller E_f value is energetically favourable and thus is more stable.

3. Results and discussions

3.1. Structures and interface stability of pristine SSNRs

Based on the interface morphology, the silicene/silicane nanoribbons can be clarified into zigzag SSNR (Z-SSNR) and armchair SSNR (A-SSNR) as shown in Fig. 1(a) and (b), respectively. The width of the

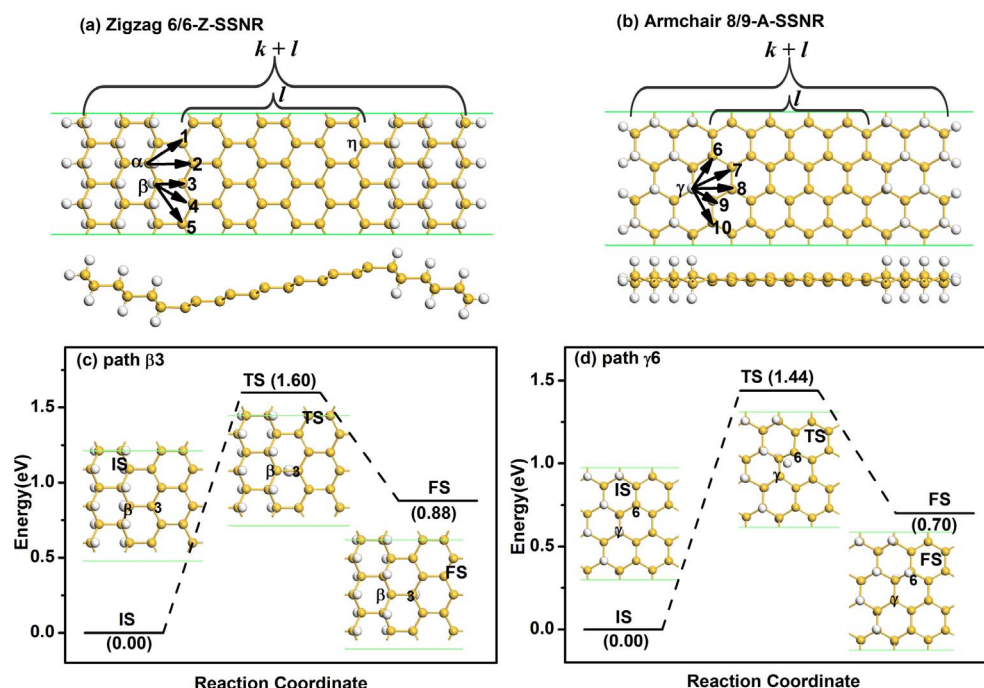


Fig. 1. Atomic structures of pristine 6/6-Z-SSNR (a) and 8/9-A-SSNR (b), where *k* and *l* are the number of zigzag chains (or dimer lines) in silicene and silicane parts, respectively. The white and yellow balls represent H and Si atoms, respectively. The letters and numbers indicate the different atomic positions, and the arrows indicate the hydrogen diffusion pathways at the interfaces. The diffusion pathway β3 of H atom on zigzag 6/6-Z-SSNR (c), and the diffusion pathway γ6 of H atom on armchair 8/9-A-SSNR (d). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

hybrid nanoribbon is defined as $k + l$, where k is the number of zigzag chains (or dimer lines) in silicene nanoribbon and l is the number of zigzag chains (or dimer lines) in centre silicene nanoribbon, and the hybrid system is abbreviated to k/l -Z (or A)-SSNR. The bond lengths of Si–Si between silicene and silicane are different due to the adsorption of hydrogen atoms, which are 2.28 Å and 2.36 Å after fully relaxation, respectively. The lattice mismatch between silicene and silicane is only 3.5%, which is small enough for the formation of lateral hybrid SSNRs. In this work, the representative nanoribbons 6/6-Z-SSNR and 8/9-A-SSNR based on previous report [28] are studied to understand the structure and electronic properties with N doping. The SSNRs with different silicene and silicane widths are also studied for comparison.

The interface stability for SSNRs is analysed by the hydrogen diffusion barriers at the interfaces. For the zigzag interface in Fig. 1(a), there are two types of Si and H atoms (α and β), as well as five possible hydrogen diffusion pathways ($\alpha 1$ – $\alpha 2$ and $\beta 3$ – $\beta 5$). For the armchair interface in Fig. 1(b), there is only one type of Si and H atoms (γ), and thus there are five possible hydrogen diffusion pathways ($\gamma 6$ – $\gamma 10$). The hydrogen diffusion barriers at zigzag and armchair interfaces are summarized in Tables 1 and 2, respectively. The minimum diffusion barriers are 1.60 eV along path $\beta 3$ and 1.44 eV along path $\gamma 6$ for the zigzag and armchair interfaces as shown in Fig. 1(c) and (d), respectively, which are larger than the critical energy barrier $E_{\text{cbar}} = 0.91$ eV [39]. Thus, both interfaces are stable at ambient temperature.

The energy barriers above are considered at zero Kelvin. To take into consideration the effect of temperature, free energy change (ΔG) between IS and TS is considered as the corrected energy barrier and can be determined by $\Delta G = \Delta H - T\Delta S$, where ΔH is the change in enthalpy, T is the room temperature (300 K), and ΔS is the change in entropy. It is known that $\Delta H = (\Delta U + P\Delta V)$, $\Delta U = (\Delta E_{\text{tot}} + \Delta E_{\text{vib}} + \Delta E_{\text{trans}} + \Delta E_{\text{rot}})$ and $\Delta S = \Delta S_{\text{vib}} + \Delta S_{\text{trans}} + \Delta S_{\text{rot}}$, where ΔU is the change of internal energy, ΔE_{tot} is the total electronic energy change obtained from DFT calculations, the subscript vib, trans and rot indicate the components from vibration, translation and rotation, respectively. All the above terms can be calculated with vibrational frequency calculations in Dmol³ code. The corrected energy barriers at 300 K for hydrogen diffusion path at the interfaces of 6/6-Z-SSNR and 8/9-A-SSNR are: $E_{\text{bar-}\alpha 1} = 1.67$, $E_{\text{bar-}\alpha 2} = 1.79$ eV, $E_{\text{bar-}\beta 3} = 1.58$ eV, $E_{\text{bar-}\beta 4} = 1.87$ eV, $E_{\text{bar-}\beta 5} = 2.21$ eV, $E_{\text{bar-}\gamma 6} = 1.43$ eV, $E_{\text{bar-}\gamma 7} = 1.56$ eV, $E_{\text{bar-}\gamma 8} = 1.95$ eV, $E_{\text{bar-}\gamma 9} = 1.58$ eV and $E_{\text{bar-}\gamma 10} = 2.10$ eV, respectively, where the energy barriers are all slightly depressed. Since a surface reaction at room temperature may

Table 1

Energy barrier E_{bar} and diffusion energy E_r for H diffusion paths on pristine and N-doped 6/6-Z-SSNR as indicated in Figs. 1(a), 4(a) and 5(a). The energy barrier E'_{bar} for reversing diffusion of H atom is also shown. α , β and the numbers from 1 to 5 indicate different atomic positions as shown in Figs. 1, 4 and 5. The longline for $\alpha 3$ indicates that the reaction cannot occur based on our calculations.

	Diffusion pathway	E_{bar} (eV)	E_r (eV)	E'_{bar} (eV)
6/6-Z-SSNR	$\alpha 1$	1.68	1.02	0.66
	$\alpha 2$	1.88	1.68	0.20
	$\beta 3$	1.60	0.88	0.72
	$\beta 4$	2.01	0.91	1.1
	$\beta 5$	2.29	0.61	1.68
Doping N at S1	$\alpha 1$	1.71	0.60	1.11
	$\alpha 2$	1.54	0.82	0.72
	$\alpha 3$	–	–	–
	$\beta 3$	2.04	1.45	0.59
	$\beta 4$	2.03	0.93	1.10
Doping N at H6	$\beta 5$	2.04	1.02	1.02
	$\alpha 1$	1.55	0.68	0.87
	$\alpha 2$	1.58	1.33	0.25
	$\beta 3$	1.61	0.70	0.91
	$\beta 4$	1.85	0.92	0.93
	$\beta 5$	2.08	0.46	1.62

The data with bold indicates the lowest energy barrier for the diffusion of H atom at the silicene/silicane interface.

Table 2

Energy barrier E_{bar} and diffusion energy E_r for H diffusion paths on pristine and N-doped 8/9-A-SSNR as indicated in Figs. 1(b), 6(a) and 7(a). The energy barrier E'_{bar} for reversing diffusion of H atom is also shown. γ , η and the numbers from 6 to 10 indicate different atomic positions as shown in Figs. 1, 6 and 7.

	Diffusion pathway	E_{bar} (eV)	E_r (eV)	E'_{bar} (eV)
8/9-A-SSNR	$\gamma 6$	1.44	0.70	0.74
	$\gamma 7$	1.67	1.20	0.47
	$\gamma 8$	2.12	0.78	1.34
	$\gamma 9$	1.63	1.25	0.38
	$\gamma 10$	2.11	0.43	1.68
Doping N at S1	$\gamma 6$	1.72	0.99	0.73
	$\gamma 7$	1.87	1.39	0.48
	$\gamma 8$	1.28	0.81	0.47
	$\gamma 9$	1.83	1.74	0.09
	$\gamma 10$	1.30	0.53	0.77
	$\eta 10'$	1.77	0.39	1.38
	$\eta 6$	1.48	0.47	1.01
	$\eta 7$	1.99	0.74	1.25
	$\eta 8$	1.82	0.42	1.4
	$\eta 9$	2.77	0.87	1.9
Doping N at H4	$\gamma 6$	1.22	0.24	0.98
	$\gamma 7$	1.69	0.63	1.06
	$\gamma 8$	1.79	0.48	1.31
	$\gamma 9$	1.50	0.68	0.82
	$\gamma 10$	1.64	0.20	1.44

The data with bold indicates the lowest energy barrier for the diffusion of H atom at the silicene/silicane interface.

occur only when $E_{\text{bar}} < E_{\text{cbar}} = 0.91$ eV [39], both interfaces are stable at ambient temperature.

To further investigate the stability of the Z-SSNR and A-SSNR, ab initio molecular dynamics (MD) simulations at a constant temperature of $T = 300$ K in the NVT ensemble (i.e., constant particle number, volume and temperature condition) have been carried out for 5 ps with a time step of 1 fs for pristine 6/6-Z-SSNR and 8/9-A-SSNR in Fig. 2(a) and (c), respectively. Three instantaneous structures at 0 ps, 2.5 ps and 5.0 ps from MD calculations are present in Fig. 2(a) and (c), respectively. It is found that the atoms of both SSNRs are roughly located at the original sites after 5000 dynamics steps at 300 K. Thus, the stability of the studied silicene/silicane nanoribbons at room temperature is expected. The phonon dispersions have been calculated by using the CASTEP code to further study the stability of SSNRs as shown in Fig. 2(b) and (d), where no soft modes are found for both 6/6-Z-SSNR and 8/9-A-SSNR, indicating that the studied structures correspond to local energy minimums. This is consistent with the fact that the SSNRs are stable at room temperature when the diffusion energy barrier of H atoms at silicene/silicane interface is larger than the critical barrier of $E_{\text{cbar}} = 0.91$ eV [39] as discussed above and shown in Fig. 1. Therefore, the stability of SSNRs can be evaluated by calculating the hydrogen diffusion energy barriers at the silicene/silicane interface in the following.

3.2. Electronic structures and magnetism of pristine SSNRs

The electronic properties of zigzag and armchair SSNRs are then studied. The 6/6-Z-SSNR has an indirect bandgap of 0.24 eV with the ground AFM state in Fig. 3(a), where the spin states are originated from the hybrid p_z orbitals at the interface. Fig. 3(b) shows the partial density of states (PDOS) for $3p$ orbital of Si atoms at the opposite edges [sites 1 and η in Fig. 1(a)] of silicene part, which have different spin orientations and equivalent values, consistent with the AFM state for 6/6-Z-SSNR. The band gap is mainly determined by the silicene width l , which is confirmed by the fact that the band gaps for 8/6 and 10/6-Z-SSNRs are both 0.23 eV. The l -dependence of band gaps of Z-SSNRs with $k + l = 12$ is shown in Fig. 3(c), where the band gaps decrease linearly with the silicene width increasing, which is similar to the zigzag silicene nanoribbons [15]. For armchair 8/9-A-SSNR, the ground state is

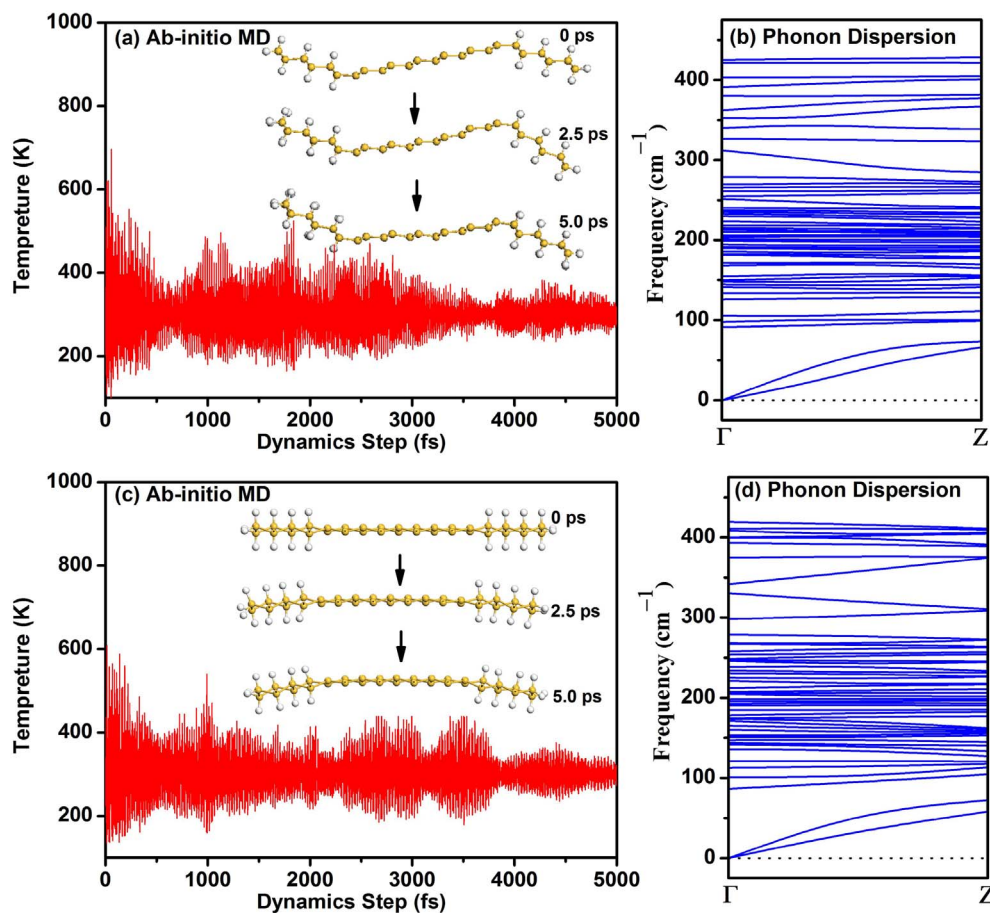


Fig. 2. Panels (a) and (c) show the dynamics process at $T = 300$ K in the NVT ensemble for pristine 6/6-Z-SSNR and 8/9-A-SSNR, respectively. Insets show the three instantaneous structures at 0 ps, 2.5 ps and 5.0 ps, respectively. Panels (b) and (d) show the phonon dispersions for pristine 6/6-Z-SSNR and 8/9-A-SSNR, respectively

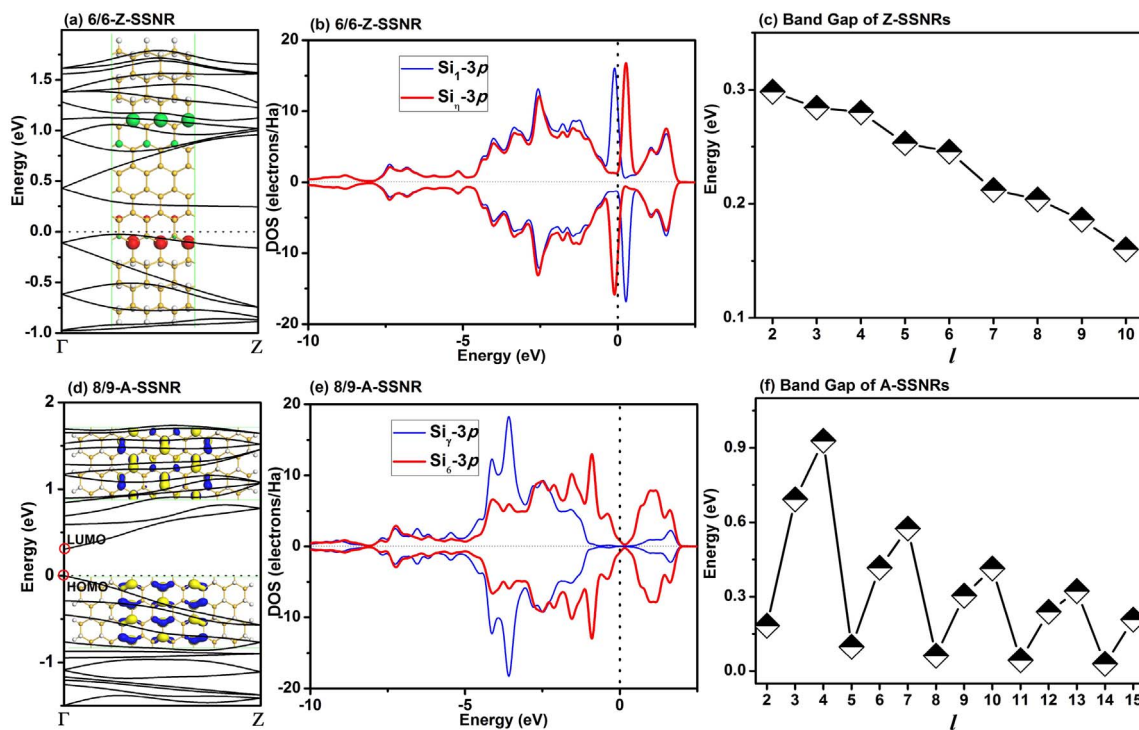


Fig. 3. PDOS of the 3p orbital for different Si atoms in 6/6-Z-SSNR and 8/9-A-SSNR is shown in (a) and (d), respectively. The numbers after the symbol of Si elements denote the atomic positions in the SSNRs in Fig. 1(a) and (b). The band structure of 6/6-Z-SSNR at AFM state is shown in panel (b), inset is the corresponding spin density distribution, where the positive spin density is in red and the negative one is in green. (c) The l -dependence of band gaps of Z-SSNRs with $k + l = 12$. (e) The band structure of 8/9-A-SSNR. (f) The l -dependence of band gaps of A-SSNRs with $k + l = 17$. The charge distributions of LUMO and HOMO states at the Γ point are also given, where the blue and yellow colours indicate different signs of orbital wave function. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

nonmagnetic with direct band gap of 0.30 eV, as shown in Fig. 3(d). The PDOS for 3p orbital of the Si atom [sites γ and 6 in Fig. 1(b)] in the silicene part is shown in Fig. 3(e), where the conductive band minimum (CBM) and valence band maximum (VBM) are mostly contributed by Si-3p states in the silicene part, which is consistent with the charge distributions of highest unoccupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states for 8/9-A-SSNR. Therefore, the band gap of 8/9-A-SSNR is mainly determined by the silicene width l , which is further confirmed by the fact that the band gaps for armchair 10/9 and 12/9-A-SSNRs are 0.30 eV, respectively. As shown in Fig. 3(f), the band gaps of A-SSNRs exhibit oscillatory behaviour classified into three families with $l = 3n$, $3n + 1$ and $3n + 2$ (where n is a positive integer), which is similar to the armchair silicene nanoribbons [15].

3.3. Structures and interface stability of doped SSNRs

To obtain magnetic properties, substitutional doping of N atom is an effective way to tune the electronic and magnetic properties of silicon materials [16–19]. The possible doping positions for a single N atom to substitute for a Si atom in 6/6-Z-SSNR and 8/9-A-SSNR are shown in Fig. 4(a) and (b), respectively. The corresponding formation energies based on Eq. (1) are also compared in Fig. 4(c) and (d). For zigzag SSNR, the most stable doped position, corresponding to the lowest formation energy, is S1 site at the silicene/silicane interface (denoted as 6/6-Z-SSNR-S1). And we also find that there is local minimum in formation energies for the doping position of site H6 at the silicane edge (denoted as 6/6-Z-SSNR-H6), showing that the metastable position is also possible at practical thermodynamical conditions due to the high energy barrier and long distance between sites S1 and H6. For armchair SSNR, the most stable doped position is site H4 at the silicane edge (denoted as 8/9-A-SSNR-H4) and there is also local minimum in formation energies for the doping position of site S1 at the silicene/silicane interface (denoted as 8/9-A-SSNR-S1), indicating that both positions are possible for the substitutional doping of N atoms.

As doping can change the electronic distribution and thus the reactivity of the surrounding atoms near the dopants, the effect of the doped N atom on the diffusion barriers of H atoms at the interface of the doped SSNRs is also investigated. For zigzag 6/6-Z-SSNR-S1 in Fig. 5(a), there are two types of Si and H atoms (α and β), and six possible

diffusion pathways ($\alpha 1$ – $\alpha 3$ and $\beta 3$ – $\beta 5$). For 6/6-Z-SSNR-H6 in Fig. 6(a), similar to the pristine 6/6-Z-SSNR, there are two types of Si and H atoms (α and β), and five diffusion pathways ($\alpha 1$ – $\alpha 2$ and $\beta 3$ – $\beta 5$). The diffusion barriers of H atoms with different pathways are summarized in Table 1. The minimum diffusion barrier at the interface is 1.54 eV along the path $\alpha 2$ and 1.55 eV along path $\alpha 1$ for 6/6-Z-SSNR-S1 and 6/6-Z-SSNR-H6, respectively, which is similar to the minimum diffusion barrier of 1.60 eV on pristine 6/6-Z-SSNR. For armchair 8/9-A-SSNR-S1 in Fig. 7(a), there are two types of Si and H atoms (γ and η) and ten possible diffusion pathways ($\gamma 6$ – $\gamma 10$, $\eta 10'$ and $\eta 6$ – $\eta 9$). For armchair 8/9-A-SSNR-H4 in Fig. 8(a), similar to the pristine 8/9-A-SSNR, there are only one type of Si and H atoms (γ) and five possible diffusion pathways ($\gamma 6$ – $\gamma 10$). The hydrogen diffusion barriers along all pathways are summarized in Table 2, where the minimum diffusion barriers are 1.28 eV along path $\gamma 8$ and 1.22 eV along path $\gamma 7$ for 8/9-A-SSNR-S1 and 8/9-A-SSNR-H4, respectively. Compared with the minimum diffusion barrier of 1.44 eV on pristine 8/9-A-SSNR, doping N slightly depresses the diffusion barrier of hydrogen atom at the interface, but still much larger than the critical value of $E_{\text{cbar}} = 0.91$ eV [39]. Therefore, both types of SSNRs keep high interface stability after N doping.

3.4. Electronic structures and magnetism of doped Z-SSNRs

The electronic structures for the N-doped Z-SSNRs are then investigated and the results are shown in the following. The band structure and spatial spin density distribution of 6/6-Z-SSNR-S1 are shown in Fig. 5(c). It is obviously that the pristine 6/6-Z-SSNR exhibits a negative (positive) magnetic moment at upper (lower) edge and a total zero magnetic moment [see Fig. 3(a)]. Thus, the spin states which originate from the unpaired electrons at the opposite edges of the silicene part have different spin orientations and equivalent values. With one N atom substituting for one Si atom at site S1, the N atom causes hybridization with the unpaired electrons of silicon atoms nearby. Fig. 5b shows the PDOS for Si-3p orbital at the opposite edges [sites 1 and η in Fig. 5(a)] of the silicene part, where the spins on the doped interface are locally suppressed around the N atom, while those on the undoped interface are not influenced. Thus a total magnetic moment of 1.005 μ_B is introduced per supercell. In addition, the band gap for 6/6-Z-SSNR-S1 decreases to 0.12 eV [see Fig. 5(c)]. It is noted that three

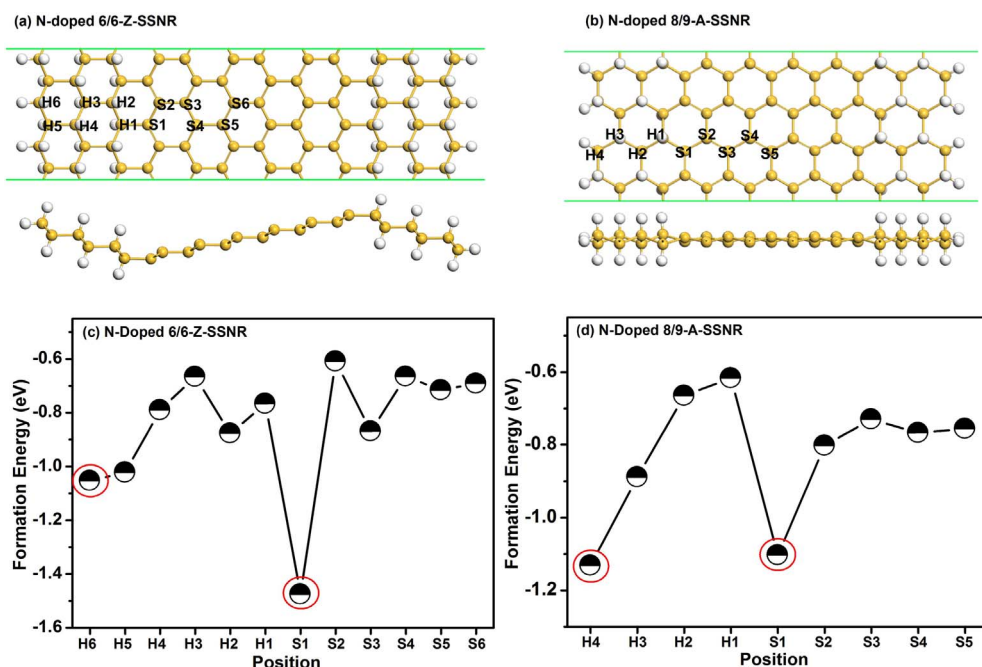


Fig. 4. The different substitutional doping positions for a N atom on 6/6-Z-SSNR (a) and 8/9-A-SSNR (b), where the letters and numbers indicate the doping positions. The formation energy of N dopant at different positions of 6/6-Z-SSNR (c) and 8/9-A-SSNR (d), where the red circles indicate the stable doping positions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

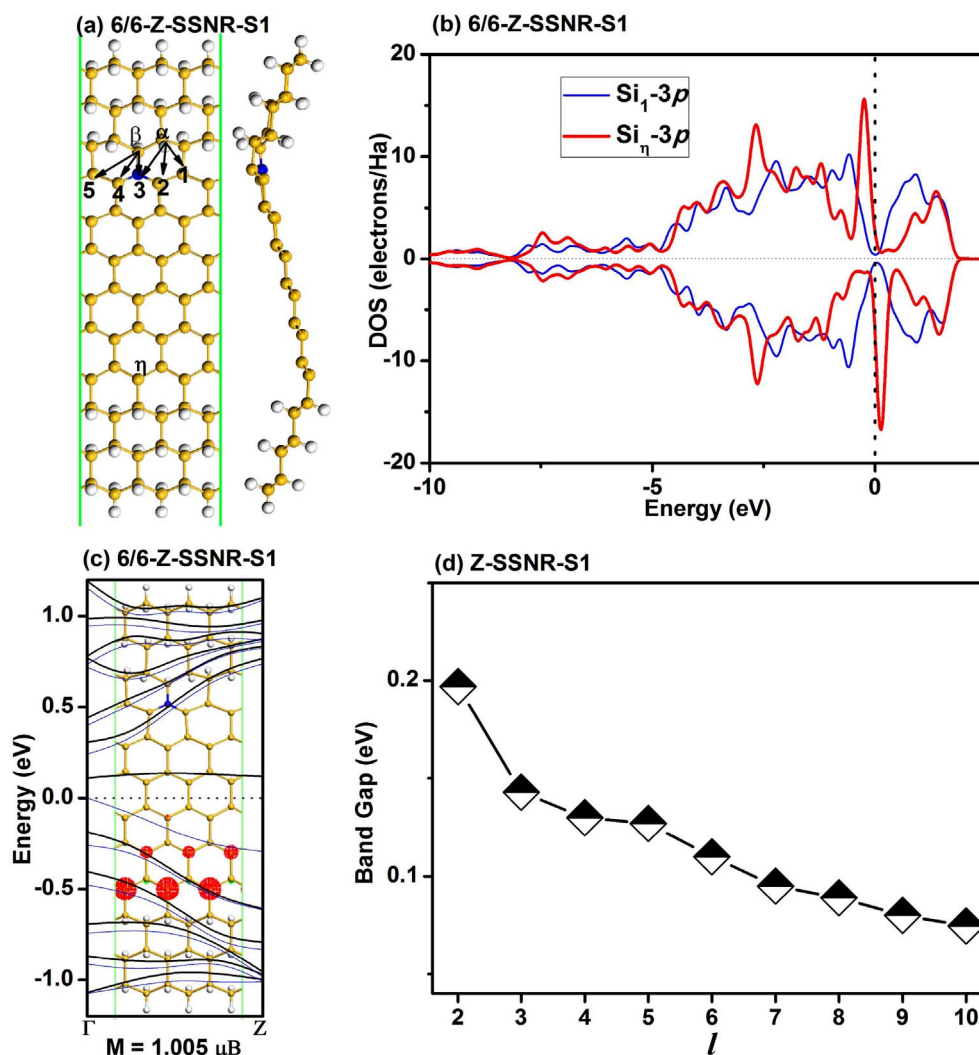


Fig. 5. Atomic structure of N-doped 6/6-Z-SSNR at the substitution positions S1 (a), where the arrows indicate the different diffusion pathways of H atoms at the interfaces. (b) PDOS of the 3p orbital for different Si atoms in 6/6-Z-SSNR-S1. (c) The spin-resolved band structures of N-doped 6/6-Z-SSNR-S1, where the black thick and blue thin lines represent the spin up and spin down states, respectively. (d) The l -dependence of band gaps of Z-SSNR-S1 with $k + l = 12$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

unit cells of zigzag nanoribbon in the periodic direction is employed in Fig. 5(a). When the number of unit cells in the periodic direction increases to five, i.e., if the concentration of nitrogen dopant at one edge of the silicene part is low along the periodic direction, the magnetic moments at that edge still exist, where the FM character for Z-SSNR-S1 is disappeared. However, a total magnetic moment of $0.996 \mu_B$ is still existed for Z-SSNR-S1 with larger size in the periodic direction.

The width effects of silicene and silicane parts on the magnetic moment and band gap of Z-SSNR-S1 are further studied. To consider the effect of silicane width on the magnetic moment, the band structures for Z-SSNR-S1 with changed (k) silicane zigzag chains and six silicene zigzag chains (N/6-Z-SSNR-S1) are calculated, where the magnetic moments for 4/6, 6/6 and 8/6-Z-SSNR-S1 are 1.003 , 1.005 and $0.998 \mu_B$, respectively. When considering the effect of silicene width, the band structure for Z-SSNR-S1 with six silicane zigzag chains and changed (l) silicene zigzag chains (6/M-Z-SSNR-S1) is calculated, where the magnetic moments for 6/4, 6/6 and 6/8-Z-SSNR-S1 are 1.000 , 1.005 and $0.990 \mu_B$, respectively. Therefore, the effect on magnetic moment by the both width of silicene and silicane part with doping N atom at the silicene edge (S1 site) of Z-SSNRs is ignorable. The width effects of silicene and silicane parts on the band gaps are also considered, where the band gaps for 4/6, 6/6 and 8/6-Z-SSNR-S1 are 0.10 ,

0.12 and 0.11 eV, respectively, which indicates that the band gap is independent on the width of silicane part k . The l -dependence of band gaps of Z-SSNR-S1 with $k + l = 12$ is shown in Fig. 5(d), where the band gaps decrease linearly with the increased silicene width.

The band structure and spatial spin density distribution of 6/6-Z-SSNR-H6 is shown in Fig. 6(b). With one N atom substitution of one Si atom at the silicane part, an additional electron is injected and causes n -type doping with the Fermi level crossing the conduction bands, which is confirmed by PDOS of Si-3p orbital at site 1 of silicene part in Fig. 6(c). In addition, as N dopant is relatively far away from the silicene/silicane interface, the spins on the silicene edge near the N dopant are less suppressed compared with that of 6/6-Z-SSNR-S1, which is confirmed by PDOS of Si-3p orbital at site 1 of silicene part in Fig. 6(c). However, the spins on the opposite silicene edge are not influenced by the N dopant confirmed by the PDOS of Si-3p orbital at site η of silicene part in Fig. 6(c), and thus a total magnetic moment of $0.594 \mu_B$ is introduced per supercell.

The width effects of silicene and silicane parts on the electronic structures of Z-SSNR-H6 are then studied. The band structures for Z-SSNR-H6 with changed (k) silicane zigzag chains and six silicene zigzag chains (k /6-Z-SSNR-H6) are first studied, where the magnetic moments for 2/6, 4/6, 6/6, 8/6, 10/6 and 12/6-Z-SSNR-H6 are 0.600 , 0.599 ,

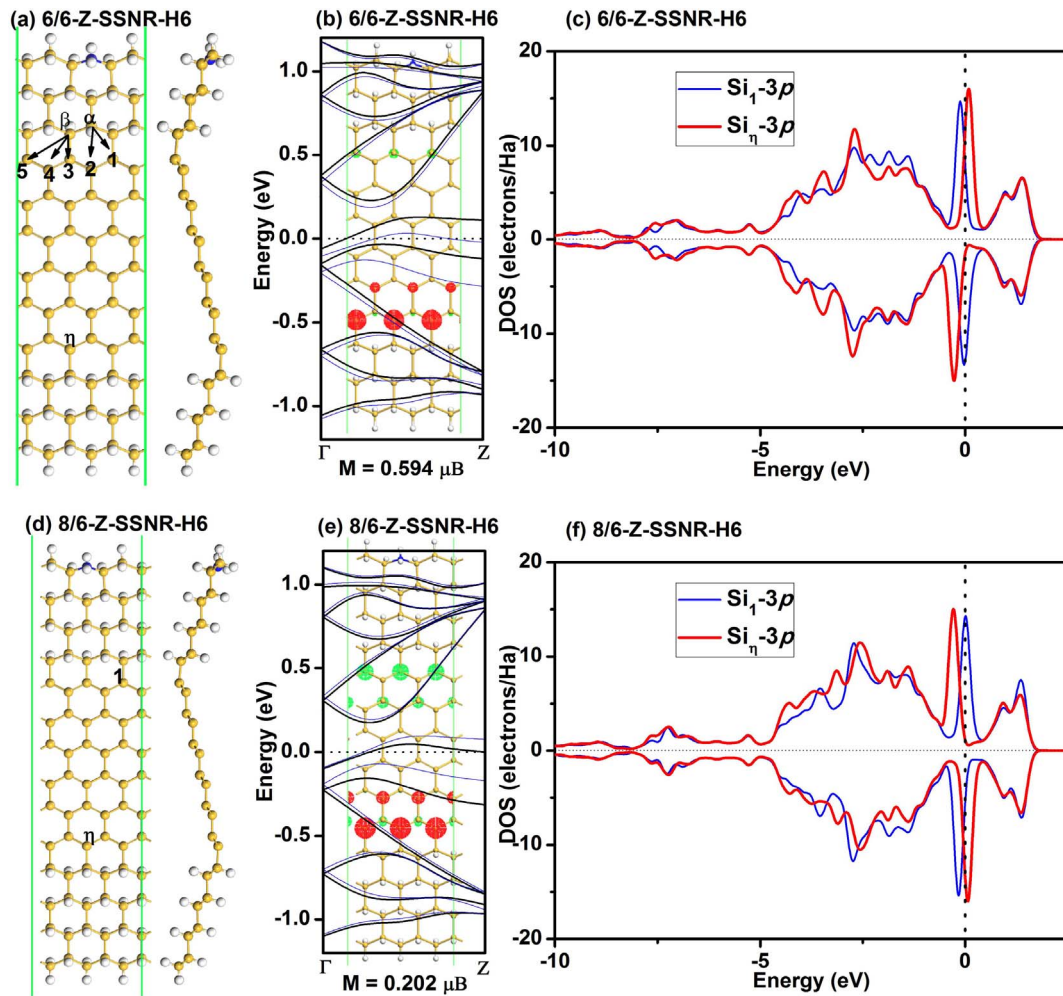


Fig. 6. Atomic structure of N-doped 6/6-Z-SSNR (a) and 8/6-Z-SSNR (d) at the substitution positions H6. The spin-resolved band structures of 6/6-Z-SSNR-H6 (b) and 8/6-Z-SSNR-H6 (e), where the black thick and blue thin lines represent the spin up and spin down states, respectively. Insets are the spin density distributions of different Z-SSNRs, where the positive spin density is in red and the negative one is in green. PDOS of the 3p orbital for different Si atoms in 6/6-Z-SSNR-H6 (c) and 8/6-Z-SSNR-H6 (f), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

0.594, 0.202, 0.201 and 0.084 μB , respectively, and the spin split of energy band is reduced with silicane width increasing. The 8/6-Z-SSNR-H6 is studied as a typical structure as shown in Fig. 6(d), and the band structure and spatial spin density distribution of 8/6-Z-SSNR-H6 is shown in Fig. 6(e). As N dopant is farther away from the silicene/silicane interface, the spins on the silicene edge near the N dopant are less suppressed compared with that of 6/6-Z-SSNR-H6, which is confirmed by PDOS of Si-3p orbital at site 1 of silicene part in Fig. 6(f), thus a smaller total magnetic moment of 0.202 μB is introduced per supercell. When the number of silicane zigzag chains is large than twelve, the magnetic moment for the Z-SSNR-H6 decreases to nearly zero. Therefore, the magnetic moment for Z-SSNR doped at H6 position can be tuned by the width of silicane part. To further study the width effect of silicene part on the magnetic properties, the band structures for Z-SSNR-H6 with six silicane zigzag chains and changed (l) silicene zigzag chains (6/l-Z-SSNR-H6) is calculated, where the magnetic moment is 0.598, 0.594 and 0.596 μB for 6/4, 6/6 and 6/8-Z-SSNR-H6, thus the silicene part has negligible effect on the magnetic properties of Z-SSNR-H6. The Z-SSNR-H6 shows metallic character independent on the width of silicene and silicane parts.

3.5. Electronic structures and magnetism of doped A-SSNRs

The electronic structures for the N-doped A-SSNRs are then investigated in the following. For 8/9-A-SSNR-S1, compared with the

pristine 8/9-A-SSNR with NM state [see Fig. 3(d)], with one N atom substituting for one Si atom at site S1, a total magnetic moment of 1.002 μB is introduced per supercell as shown in Fig. 7(c). Fig. 7(b) shows the PDOS for 3p orbital of Si atoms at site 10 and 2p orbital of N atoms at site 9 of silicene part, which indicates that the spin state of 8/9-A-SSNR-S1 mainly originates from the N atom and Si atoms near the N dopant. The width effects of silicene and silicane parts on the electronic structures of A-SSNR-S1 are also studied. The band structures for A-SSNR-S1 with changed (k) silicane dimer lines and nine silicene dimer lines (k/9-A-SSNR-S1) are first studied, where the magnetic moments are 1.000, 1.005 and 1.002 μB for 6/9, 8/9 and 10/9-A-SSNR-S1, thus the silicane part has negligible effect on the magnetic properties of A-SSNR-S1. To study the width effects of silicene part on the magnetic properties, the band structures for A-SSNR-S1 with eight silicane dimer lines and changed (l) silicene dimer lines (8/l-A-SSNR-S1) is calculated, where the magnetic moment is 1.002, 1.005 and 0.998 μB for 8/8, 8/9 and 8/10-A-SSNR-S1, thus the effect of the width of the silicene part on the magnetic properties of A-SSNR-S1 is also negligible. The band gap for 8/9-A-SSNR-S1 is 0.11 eV [see Fig. 7(c)]. The size effects of silicene and silicane parts on the band gaps are calculated, where the band gaps are 0.11, 0.11 and 0.11 eV for 6/9, 8/9 and 10/9-A-SSNR-S1, respectively, which indicates that the band gap is independent on the width of silicane part k. The l-dependence of band gaps of k/l-A-SSNR-S1 with $k + l = 17$ is shown in Fig. 7(d), where the band gap of the k/l-A-SSNR-S1 also exhibits oscillatory behaviour

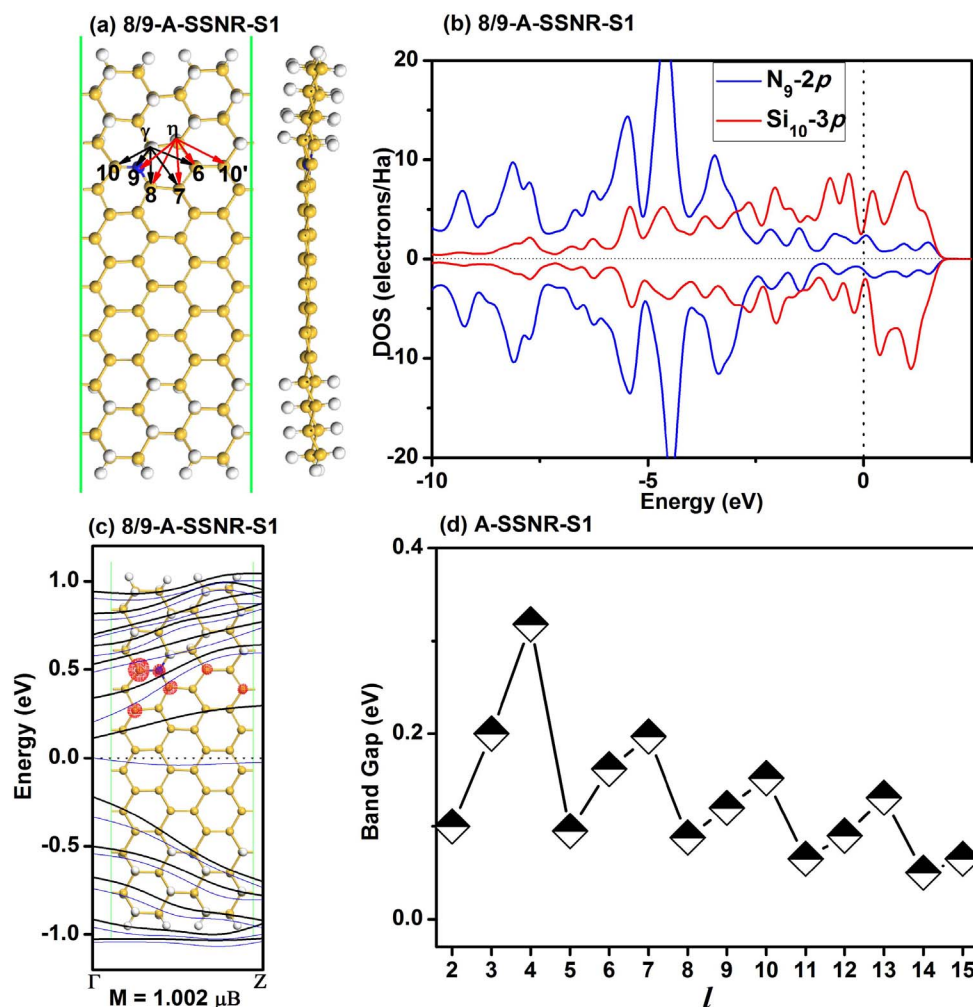


Fig. 7. Atomic structure of N-doped 8/9-A-SSNR at the substitution positions S1 (a), where the arrows indicate the different diffusion pathways of H atoms at the interfaces. (b) PDOS of the 3p orbital for Si and 2p orbital for N atoms in 8/9-A-SSNR-S1. (c) The spin-resolved band structures of 8/9-A-SSNR-S1. Insets are the spin density distributions of different A-SSNRs, where the positive spin density is in red and the negative one is in green. (d) The l -dependence of band gaps of A-SSNR-S1 with $k + l = 17$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

classified into three families with $l = 3n$, $3n + 1$ and $3n + 2$ (where n is a positive integer), which is similar to the pristine A-SSNR in Fig. 3(f).

However, as shown in Fig. 8(b), the ground state for 8/9-A-SSNR-H4 is NM state, an additional electron is injected and causes the 8/9-A-SSNR changing from semiconductor to metallic. This may be caused by the fact that the N atom at S1 site is three-coordinated, while the N atom at H4 site is four-coordinated. Fig. 8(c) shows the PDOS for 3p orbital of Si atoms at sites 9 and 11 as well as 2p orbital of N atoms at site η of silicene part, which indicates that the metallic state of 8/9-A-SSNR-H4 mainly originates from the N atom and Si atoms near the N dopant. The width effects of silicene and silicane parts on the electronic structures of A-SSNR-H4 are also studied. All the band structures for A-SSNR-S1 with fixed nine silicene dimer lines (6/9, 8/9 and 10/9-A-SSNR-S1) and fixed eight silicane dimer lines (8/7, 8/9 and 8/11-A-SSNR-H4) show metallic NM character, indicating that the silicene and silicane parts both have negligible effect on the band structure of SSNRs. Therefore, doing N atom at the silicane edge (H4) changes the A-SSNR from NM semiconductor to NM metallic state.

Based on the above discussions, the effects of N doping in SSNRs are summarized in the following. The pristine Z-SSNR shows AFM

semiconductor state with null magnetic moment, while doping N at silicene/silicane interface shows FM semiconducting state, and doping N at silicane edge shows metallic states with tunable magnetic moments, which is induced by the locally suppressed spins around the N atom. In addition, the magnetic moments of Z-SSNR are tuneable by changing the silicane width when doping N at silicane edge. For A-SSNR, although the pristine A-SSNR shows NM semiconductor state, doping N at silicene/silicane interface changes A-SSNR to semiconductor with a local magnetic moment of about $1 \mu_B$. However, doping N at silicane edge changes A-SSNR to NM metallic state. It is noted that doping N at the silicane part changes the SSNR to metallic state, while doping N at silicene part keeps SSNR to be semiconductor state, which is due to the fact that the N atom at silicene is three-coordinated while the N atom at silicane is four-coordinated.

4. Conclusions

In summary, the substitution of N for Si is preferentially at the silicene/silicane interface and silicane edge for both zigzag and armchair N-doped SSNRs based on first-principles calculations. The larger

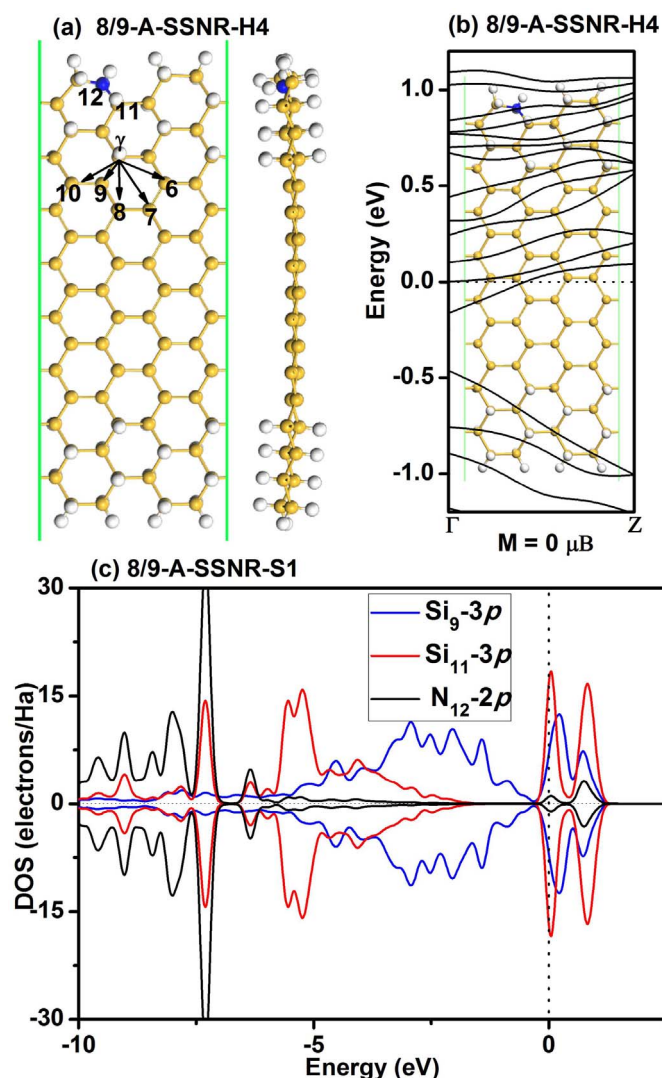


Fig. 8. Atomic structure of N-doped 8/9-A-SSNR at the substitution positions H4 (a), where the arrows indicate the different diffusion pathways of H atoms at the interfaces. (b) The spin-resolved band structures of 8/9-A-SSNR-H4. (c) PDOS of the 3p orbital for Si and 2p orbital for N atoms in 8/9-A-SSNR-H4.

diffusion energy barriers of H atoms at interfaces confirm the thermal stability of N-doped SSNRs. When the N doping concentration is larger enough, the Z-SSNRs with doping N at silicene/silicane interface exhibit permanent magnetic moments and decreased band gaps with increasing silicene width, while those with N doping at the silicane edge show metallic character and tunable magnetic moments when changing the width of silicene part. The magnetic moments of N-doped Z-SSNRs are attributed to the perturbation of p and p^* states localized near the silicene/silicane interface. For armchair SSNR, the N-doped A-SSNRs at silicene/silicane interface show local ferromagnetic semiconducting state and oscillatory band gaps, while those at silicane edge shows nonmagnetic metallic states. Our results provide fundamental insights for the applications of SSNRs in electronic devices of nanoelectronics.

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