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Oxygen- and hydroxyl-edge termination of silicene nanoribbons studied by first-principles calculations

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HIGHLIGHTS

- O- and OH-passivation on silicene edges are energetically favorable over H-passivation.
- Different from the resistence of π-bonds saturation on silicene surface, the oxidation on silicene edges is much easier due to the stronger chemical reactivity of σ-bonds.
- Counting the two new "atom-chains" formed between neighboring OHs on ASiNR-OH edges, the band gaps of O- and OH-functionalized ASiNRs follow the same hierarchy of $\Delta_{3p} > \Delta_{3p-1} > \Delta_{3p-2}$.

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ABSTRACT

The geometrical structures and electronic properties of the armchair- and zigzag-edge silicene nanoribbons (SiNRs), terminated with oxygen and hydroxyl (ZSiNR-O, ZSiNR-OH, ASiNR-O, ASiNR-OH), have been investigated by using the first-principles method. It is found that the silicene edges are rippled upon the oxygen termination. On one edge of ZSiNR-O, the neighboring Si–O bonds move concordantly right (left) from the silicene plane, while on one edge of ASiNR-O, the neighboring Si–O bonds respectively move right and left to result in larger rippled amplitudes. Comparably, the influence of OH-termination on the silicene edge is small, inducing smaller rippled edges. The electronic structure calculations show that the px electrons of oxygen on the rippled edges of ZSiNR-O sp^3 hybridize with the edge Si atoms, forming one more bands. The band gaps of the ASiNR-O and ASiNR-OH also obey the three-family behavior, due to the quantum confinement and the crucial effect of the edges. For ASiNR-OH, by taking account of the new atom chains formed by the hydrogen bonds of the neighboring OHs, the band gaps follow the same hierarchy of $\Delta_{3p} > \Delta_{3p-1} > \Delta_{3p-2}$ with those of ASiNR-Os.

1. Introduction

The graphene-like two-dimensional (2D) silicon sheet, silicene, has been successfully grown on some metal substrates, such as Ag [1–5], Ir [6], and ZrB_2 [7], are expected to be more compatible with the conventional semiconductor industry. Intensive attention has been paid to silicene due to its many similar electronic properties of graphene, e.g., the linear dispersion of electronic band around the Dirac points [8,9]. Most attractively, the easier integration into the current Si-based microelectronic technology makes silicene a promising candidate for nanoelectronic devices. Unlike carbon atoms in graphene, silicon atoms in silicene tend to adopt sp^3 hybridization over sp^2, resulting in a slightly buckled structure of it [10,11], which provides new possibilities for manipulating its electronic structures and so tuning its band gap electrically. For example, a vertical electric field can open a transport gap in silicene, making it possible to fabricate a pure silicon field-effect transistor [12], operating at room temperatures. Moreover, the quantum Hall effect is predicted to occur induced by the much stronger spin-orbit coupling than that in graphene [13–15].

Meanwhile, the nanoribons, a one-dimensional (1D) derivative of the 2D monolayers, are hot topics of experimental and theoretical researches [16–19], since their electronic properties could be tuned by their edge structures, widths, and chiralities, as well as the edge functionalization. The Si nanoribbons (SiNRs) with nanometer-sized widths have been successfully synthesized in experiments [20,21]. These self-organization nanoribbons are demonstrated to be highly metallic, and have straight, atomically perfect, and moreover, massively parallel structures. In addition,

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the electronic structures of SiNRs on Ag surface are also investigated theoretically.

Due to the buckled honeycomb structure of silicene and the weaker Si–Si bonds in it than the C–C ones in graphene, the first principle calculations pointed out that the edge structures of the SiNRs tend to undergo a (2×1) reconstruction [22,23], inducing a non-magnetic ground state. It is known that the dangling bonds on the ribbon's edge hold a great potential for various chemical modifications, and so chemical functionalization might be introduced intentionally in order to tune certain properties. The hydrogen saturation on SiNRs' edges are found to eliminate the edge reconstruction, manifesting the intriguing electronic, magnetic, and half-metallic properties [23–25], just as the case in H-functionalized graphene nanoribbons (GNRs) [26]. Beyond that, other types of edge passivation, such as halogen ones, has been studied to open up enormous number of ways to influence the attributes of SiNRs. The electronic and magnetic properties of SiNRs are demonstrated to be very sensitive to edge modification [27,28].

Experimental and theoretical studies point out that the silicene surface presents a strong resistance toward oxidation though the high chemical activity of Si pz state in it [29–33]. While it is rather interesting to detect the influence of the oxygen σ-functionalization on the silicene edges, since it is a useful method to pattern the silicene grating for future nanometric devices. In this paper, the effects of edge passivation with oxygen atoms and hydroxyl groups on structural and electronic properties of zigzag and armchair-edged SiNRs are investigated by using the first-principle calculations. It is demonstrated that the passivation of the ribbon edge with O and OH are energetically favorable over H passivation. Both of the oxygen- and hydroxyl-termination ripples the silicene edge, comparably, the ripple amplitudes on oxygen-functionalized silicene edges are much larger caused by the stronger electro-negativity of oxygen atoms. The electronic structure calculations show that the sp^3 hybridization are enhanced on the rippled edges, and as a result, the px electrons of oxygen in ZSiNR-O hybridized with the edge Si atoms to form several bands ranging from -0.1 eV to -1.36 eV below the Fermi level. The band gaps of the O- and OH-functionalized ASiNRs oscillate obeying the three-family behaviors and the hierarchies of them follow the same law, as considering the two new ‘atom-chains’ formed by the neighboring hydrogen bonds on ASiNR-OH edges.

The rest of this paper is organized as follows. In Section 2, the computational details and the geometric structures of the oxygen- and hydroxyl-functionalized SiNRs are described. In Section 3, numerical results and related discussions are given. The conclusions are given in Section 4.

2. Model and methods

All edge-functionalized SiNRs in our calculations are defined by the notation of n-Z(A)SiNR-X, in which n refers to the number of Si dimmers per unit cell across the ribbon width. And “Z” and “A” denote the zigzag and armchair orientation of the SiNRs, respectively, and X is the edge terminated oxygen atoms or hydroxyl groups. In our paper, we mainly restricted our studies on 7-ZSiNR-X and 12-ASiNR-X to model a wide enough ribbon, since the related properties are rarely dependent on the ribbon width.

The geometric and electronic properties are calculated by using the density-functional theory in the generalized gradient approximation (GGA), implemented by the VASP code [34,35], in which the projected augmented wave method [36,37] and Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [38] are employed. The $3s^2 3p^2$ orbital of the Si atom and the $2s^2 2p^4$ orbital of the O atom are treated as valence ones. The ribbons are placed along the *x* direction, with a large enough vacuum region in both *y* and *z* direction (>12 Å) in order to make the spurious interactions between neighboring SiNRs negligible. During the geometrical relaxation, the atomic positions as well as the lattice constant in *x* direction are optimized using the conjugated-gradient minimization scheme. A plane-wave basis set with an energy cutoff of 400 eV is used in our numerical calculations, and the energies were converged to 10^{-5} eV/atom. Integration over the Brillouin zone was carried out using the equidistant k-point sampling, in which the k-mesh taken along the ribbon direction is less than 0.01 $Å^{-1}$, as well as the density of states (DOSs) calculated by the tetrahedron integration.

3. Numerical results

3.1. The geometrical structures and electronic bands of 7-ZSiNR-O and 7-ZSiNR-OH

Firstly, the pristine silicene are optimized and in the low-buckle structure, the Si–Si bond lengths are finally relaxed to 2.28 Å. Resulted from the low-buckle structure and the weak Si–Si bonding in silicene, the silicene edges are found to be easily influenced and distorted upon the chemical adsorption of external atoms or groups. Here, taking the O- and OH-functionalized ZSiNRs with seven Si dimers as example, respectively denoted as 7-ZSiNR-O and 7-ZSiNR-OH, the top and side views of the optimized geometrical structures are shown in Fig. 1(a) and (b).

The geometrical structure of 7-ZSiNR-O is firstly investigated, and the bond lengths of O–H, Si–O, Si–Si on the edges of the final optimized structures of 7-ZSiNR-O are given in the top view of Fig. 1(a). The Si–O bond lengths are 1.54 Å and the edge Si–Si bonds are 2.36 Å, which are larger than that in pristine silicene. The important influence of the oxygen-edge termination is that the edge Si-atom chains have an obviously out-of-plane displacement from the silicene plane, consequently resulted in a rippled oxygen-adsorption edge, as seen from the side view of Fig. 1(a). On one edge, the neighboring Si-1 and O atoms move away left (right) concordantly from the ribbon plane, and the corresponding Si–O on the opposite edges respectively move right (left) of the ribbon plane. The same conclusions are also found in a larger (2×1) supercell. Here, to denote the rippled edges, the rippled amplitude *h* is defined as the different distances of the terminated oxygen atoms and Si-2 in *z* direction. For 7-ZSiNR-O, the rippled amplitude *h* is about 1.22 Å. Furthermore, owing to the strong electro-negativity of oxygen, the integral 7-ZSiNR-O are rippled across the ribbon width, with the inner Si atom in it departing from the initial low-buckle structure of pristine silicene, as shown by the guidance of the long dashed line in the side view of Fig. 1(a).

The severe distortion of oxygen-terminated zigzag silicene edges are mainly induced by the much stronger electro-negativity of oxygen than Si, comparably the distortion of the OH-functionalized edges is small, as shown by the guidance of the long dashed lines in the side view of Fig. 1(b), manifesting a small effect of OH-termination on the silicene edges. The top view of Fig. 1 (b) shows that the Si–Si bond length on the 7-ZSiNR-OH edges also has a value of about 2.28 Å, the same with the ones in pristine silicene. The O–H bond lengths are found to be 0.98 Å, equal to the ones of water molecules, while the Si–O bond lengths are enlarged to be 1.73 Å, larger than that in 7-ZSiNR-O. The O–H on silicene edges also have an out-of-plane displacement, and here, the different distances in *z* direction between O and edge Si-1 atoms, denoted by the rippled amplitude *h*, is about 0.83 Å, as shown in the side view of Fig. 1(b).

Now, the non-polarized electronic bands of the O- and OH-