Evolution of the electronic and magnetic properties of zigzag silicene nanoribbon used for hydrogen storage material

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ABSTRACT

Using first-principles calculations, we investigate the evolution of electronic and magnetic properties of zigzag silicene nanoribbon (ZSiNR) along with the concentration of edge adsorbed hydrogen adatoms. Our study shows that the significant covalent bonding helps to stabilize the configurations of hydrogen adsorbed ZSiNRs. The ferro-metallic electronic property of ZSiNR originated from the σ-π mixing effect is suppressed by mono-hydrogenation at the adsorption sites due to the sp^2 bonding. However, bi-hydrogenation at the adsorbed sites will lead to the typical sp^3 bonding, which dominates the electronic property with the increasing of hydrogen adatoms. Under the coexisting situation with mono-hydrogenation and bi-hydrogenation, we find that both the number of adsorption sites and the bonding type of sp^2 or sp^3 have impact on the electronic property of ZSiNR. It is found that symmetry adsorption at the edges changes the stable magnetic state of ZSiNR from ferromagnetic to antiferromagnetic. In contrast, unsymmetrical adsorption along the two edges of ZSiNR keeps its ferromagnetic property.

Introduction

As a typical candidate of two-dimensional material beyond graphene, silicene has attracted much attention in the literature [1–3]. Due to forming chemical hydrides [4] and easily reversible hydrogenation [5], silicene has been proposed as a remarkable material for hydrogen storage. With the help of Na decoration at the two sides of silicene, the maximum density of H_2 adsorption can reach to 9.40 wt% [6]. One side hydrogenation of silicene had been validated in experiments to form half-silicane structure on Ag substrate, which can be looked as another preferable type of hydrogen storage [7,8]. During hydrogen storage, hydrogen concentration can be identified as proposed by Lin et al. [9] using H–Si bonding to

induce the prominent peaks in densities of states (DOS). Hydrogenation of free-standing silicene were previously investigated using first-principles methods by Martinazzo et al. [10]. Their results indicated that sticking of hydrogen atoms on the surface of silicene is barrierless, which will conduct the hydrogen adsorption on silicene randomly under typical laboratory conditions. Density functional theory (DFT) calculations [11] indicated that a single atom vacancy defect or diatom vacancy defect in silicene can facilitate the hydrogenation of silicene. Hussain et al. [12] predicted that functionalization of hydrogenated silicene with alkali and alkaline earth metals can obtain high storage capacities. They also extended their research for an efficient H_2 storage material by functionalizing Mg adatoms on silicene and silicane sheet [13]. DFT calculations [14] also predicted that a perpendicular electric field can reduce the energy barrier of H_2 dissociative adsorption on silicene, which is helpful for the dehydrogenation from silicene. In calcium-decorated single-layer and bilayer silicene, it was found that external electric field can effectively help to complete the hydrogen storage-release cycle [15]. If silicene is patterned into nanoribbons, owing to the quantum confinement with finite ribbon width, one may expect different effect on hydrogen storage.

In experiment, silicene nanoribbons had been successfully grown on epitaxial silver surface [16] or Au(110) surface [17,18]. Based on its shapes at the edges, SiNR can be classified into armchair silicene nanoribbons (ASiNRs) and zigzag silicene nanoribbons (ZSiNRs), respectively. The intrinsic electronic property of ASiNR shows semiconductor character and its band gap oscillates with a period of three with the increasing of the ribbon width [19]. Theoretical calculations [20] showed that hydrogenation at the edges of ASiNRs will induce interesting magnetic behaviors such as the bipolar magnetic semiconductor. For bare ZSiNRs, intriguing properties such as stable antiferromagnetic (AFM) state [21,22], controlled gaps by electric fields [23], symmetry-dependent transport properties [24], and high ZT values for thermoelectric application [25] were found. First-principles study [26] showed that zigzag edges of mono-hydrogen saturated group-IV nanoribbons including ZSiNRs have magnetic edges with a rich variety of electronic and magnetic properties. Fully mono-hydrogenation and bi-hydrogenation at the edges of ZSiNRs could effectively tune the electronic and magnetic properties of ZSiNRs [27]. However, the evolution process of the electronic and magnetic properties of ZSiNR with the variation of hydrogenated concentrations and sites at the edges of ZSiNR are still not explored. For the application of ZSiNR in hydrogen storage, it is critical to know the evolution of its electronic and magnetic properties during the edge hydrogenation. As far as we know, though the saturated hydrogenation along the ZSiNR were investigated before [26,27], the evolution process along with the distribution of hydrogen adatoms at different sites either in mono-hydrogenation or bi-hydrogenation at the edges of ZSiNR are still not clear. In this paper, based on DFT calculations, we investigate the stabilities, electronic and magnetic properties of ZSiNR along with the variation of adsorption sites and concentrations of hydrogen adatoms at its edges.

Computational methods and models

In this paper, we use DFT [28] and plane-wave method as implemented in Vienna ab initio software package (VASP) [29] to perform our simulation. The exchange correlation potential is treated within the general gradient approximation (GGA) as implemented in PAW function [30]. The cut-off energy of 450 eV is sufficient for the convergence in total energy calculations. Monkhorst-Pack grids with $10 \times 1 \times 1$ k-mesh are used in structural relaxation and $30 \times 1 \times 1$ k-mesh is applied for further calculations of electronic states. Spin polarization calculations are taken into account with a criterion of maximum force on each atom to be smaller than 0.01 eV/Å. The DFT-D2 method of Grimme [31] is used in our study. In this DFT method, the van der Waals interactions are described via a simple pair-wise force field, which is able to describe correctly van der Waals interactions resulting from dynamical correlations between fluctuating charge distributions. The detail can be found in Supplementary material.

Normally, the width of ZSiNR is defined by the number of the zigzag Si−Si chains (N_Z) across the ribbon. The pristine edge of ZSiNR is extremely reactive due to the dangling bonds of edge Si atoms and undergoes reconstruction to lower the total energy [32]. Our previous study [33] indicated that with the increasing of the width of ZSiNR from 4 to 8, edge reconstruction will be decreased and exhibits almost same amplitude. In our simulations, pristine 6-ZSiNR without hydrogen saturation is considered as a prototype to storage H adatoms at its edges. The length along with the edge of 6-ZSiNR is 9.655 Å. A vacuum separation of 15 Å is set to eliminate the interactions between the neighbor supercells. Pristine 6-ZSiNR has two unique zigzag edges which can be used for the symmetrical or unsymmetrical adsorption of H adatoms. With the variation of n from 1 to 3, fifteen forms of edge adsorption of H adatoms are considered, i.e. mono-hydrogenation in one single edge (nH-6-ZSiNR), bi-hydrogenation in one single edge (nH$_2$-6-ZSiNR), bi-hydrogenation in one edge and mono-hydrogenation in the other edge (nH$_2$-6-ZSiNR-nH), mono-hydrogenation in both edges (nH-6-ZSiNR-nH), and bi-hydrogenation in both edges (nH$_2$-6-ZSiNR-nH$_2$). n (n = 1, 2 and 3) means the number of adsorption sites on the edges of ZSiNR. With the variation of n, the adsorption concentration of hydrogen adatoms on 6-ZSiNR is in a range between 2.7% and 33.3%. With the full saturation of H_2 decoration at each site of the two sides of 6-ZSiNR, the maximum density of H_2 adsorption can reach to 5.56 wt%.

The structural stability can be reflected by formation energy E_f, which is defined as [34].

$$E_f = \frac{1}{N}(E_{SiNR+H} - n_{Si}E_{Si} - n_H E_H)$$

where E_{SiNR+H}, E_{Si} and E_H are the total energies of H adsorbed 6-ZSiNR, a single Si atom and a single H adatom, respectively. N is the total number of atoms in the supercell. n_{Si} and n_H are the number of the Si atoms and H adatoms, respectively. Spin charge density is defined as

$$\Delta\rho(r) = \rho_{up} - \rho_{dn}$$