



Emergence of strong ferromagnetism in silicene nanoflakes *via* patterned hydrogenation and its potential application in spintronics



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ABSTRACT

Considerably different properties emerge in nanomaterials as a result of quantum confinement and edge effects. In this study, the electronic and magnetic properties of quasi zero-dimensional silicene nanoflakes (SiNFs) are investigated using density functional theory (DFT) calculations. While the zigzag-edged hexagonal SiNFs exhibit non-magnetic semiconducting character, the zigzag-edged triangular SiNFs are magnetic semiconductors. One effective method of harnessing the properties of silicene is hydrogenation owing to its reversibility and controllability. From bare SiNFs to half-hydrogenated and then to fully hydrogenated, a triangular SiNF experiences a change from ferrimagnetic to very strong ferromagnetic, and then to non-magnetic. Nonetheless, a hexagonal SiNF undergoes a transfer from non-magnetic to very strong ferromagnetic, then to non-magnetic. The half-hydrogenated SiNFs produce a large spin moment that is directly proportional to the square of the flake's size. It has been revealed that the strongly induced spin magnetizations align parallel and demonstrates a collective character by large range ferromagnetic exchange coupling, giving rise to its potential use in spintronic circuit devices. Spin switch models are offered as an example of one of the potential applications of SiNFs in tuning the transport properties by controlling the hydrogen coverage.

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1. Introduction

The discovery of graphene in 2004, along with its exotic properties provided new insight in the field of condensed matter science [1]. Toxicity, large area growth, and incompatibility with current silicon-based nanoelectronics are the main challenges for graphene-based device production, inspiring a search for other two-dimensional (2D) nanostructures to produce fast nanoscale electronic devices that do not require retooling. Silicene as a 2D material composed of a group-IV element (silicon) has fascinated the community not only for being easily integrated into Si-based technology [2], but also because of its superlative properties including ferromagnetism [3], half-metallicity [4], quantum Hall effect [5], giant magnetoresistance [6], and superconductivity [7]. In 1994, Takeda and Shiraishi [8] investigated silicene in a theoretical study for the first time, albeit the name silicene was coined by Guzmán-Verri and Lew Yan Voon in 2007 [9]. Experimental synthesis of monolayer silicene with conclusive results was realized by Vogt et al. in 2014 [10]. Silicene has been experimentally synthesized on different substrates such as Ag [7,10–12], Ir [13],

ZrB₂ [14], ZrC [15], and MoS₂ [16], for various phases. Several potential applications of this novel material have been proposed in the area of spintronics [17], field-effect transistors (FETs) [18], and sensing devices [19,20]. Investigation of the electronic structure of silicene through angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling spectroscopy (STS) measurements proved that it is a zero band gap semimetal [10,21]. In order to induce a band gap in a 2D sheet, various procedures have been studied, such as doping [22], substrate effects [23], chemical functionalization [24,25], electric field application [17], nanoribbons [26,27], and introducing nanoholes [28,29].

The tendency of silicon atoms to adopt sp³ and sp² hybridization over only sp² hybridization [10] makes its honeycomb structure buckled [9,30], distinguishing it from graphene which is a flat sheet. Hence, silicene is naturally more favorable for atom and molecule adsorption [31–34] than graphene, resulting in a great deal of applications in the area of hydrogen storage [31], thin film solar cell absorbers [35], hydrogen separation membranes [32], and molecular sensors [33,34]. It has been reported that functionalization, doping, and defects can tune the electronic and magnetic properties of the nanomaterials [36–40]. Hydrogenation was found as a favorable chemical method to modify the electronic and magnetic properties of graphene because of its reversibility [41]

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and controllability [42,43]. There have been quite a number of theoretical [3,4,44–60] and experimental [61–63] studies on the hydrogenation of silicene in the literature. Intriguing properties in hydrogenated silicene have been reported through theoretical calculations, for example, large gap opening [44], extraordinary ferromagnetic (FM) [4], and optoelectronic properties [49]. A fully hydrogenated derivative of silicene, known as silicane which is the silicon counterpart of graphane, has been expected to have a band gap in the range of 2.9–3.8 eV, depending on the configuration [46]. Ergo, it would be considered a potential material for optoelectronics and FET applications [51]. The hydrogenation process in silicene is uniformly ordered and reversible, making it easier to manipulate the hydrogen coverage [61]. Consequently, the half-hydrogenation can be achieved by hydrogenating of silicene from one side while keeping the other side intact similar to its carbon counterpart graphane (half-hydrogenated graphene). It was found that half-hydrogenated silicene shows FM semiconducting behavior with a band gap of 0.95 eV [4,47]. Besides, a long-range room temperature FM coupling between Si atoms can be realized in half-hydrogenated silicene [47]. Osborn et al. have theoretically shown that H atoms prefer to be adsorbed in pairs to form the most stable configuration of partially hydrogenated silicene [45]. By altering the concentration of hydrogen atoms on silicene, the characteristic of its band structures can be varied from metallic to magnetic semiconducting and then to non-magnetic (NM) semiconducting [48].

As nanomaterials approach lower dimensions, their properties noticeably change due to the quantum confinement and edge effects. The quasi-one-dimensional (1D) nanoribbons show semiconducting or metallic behavior depending on their edge types and the width of the ribbon [25,37]. Further confinement of silicene has sparked interest in the study of quasi-zero-dimensional (0D) silicene nanoflakes (SiNFs) since understanding their properties is of great significance in order to continue advancing nanoscale electronic and spintronic device fabrication. Luan et al. found that electronic and magnetic properties of SiNFs depend strongly on their size and shape [64]. The hexagonal zigzag SiNF exhibits NM semiconducting behavior, while the triangular zigzag SiNF is a magnetic semiconductor.

Although hydrogenated silicene sheets have been recently discovered, the effects of hydrogen adsorption on SiNFs have not been explored yet. In this paper, we employed first-principles methods based on density functional theory (DFT) to investigate the electronic and magnetic properties of SiNFs with different configurations. The patterned adsorption of hydrogen on SiNFs is systematically explored, and its stability is evaluated by calculating the formation energies. Contrary to bare SiNFs, the hydrogenated SiNFs show unique magnetic properties. This study also proposes a simple and efficient approach to engineering the transport properties of electrons by controlling the coverage of hydrogenation on SiNFs, which may pave a new path to explore spintronics at the nanoscale.

2. Computational methods

All the DFT calculations in this study are performed using Atomistix ToolKit (ATK) package [65]. The hybrid B3LYP exchange-correlation functional is used, which is a well-known and accurate functional for graphene nanoflakes [66,67]. Geometry optimization, the structural stability, the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states, magnetic moments, spin-charge density distributions, electron difference densities, and density of states (DOS) of pristine and hydrogenated silicene are investigated. To eliminate the interactions between adjacent nanoflakes, a 30 Å

vacuum slab is considered in all directions. For geometry optimization, both supercell and the atomic positions are allowed to be fully relaxed until the force is less than 0.001 eV/Å. Four types of hydrogen passivated SiNFs with different shapes (hexagonal and triangular), edges (armchair and zigzag), and sizes are studied. In order to differentiate the various configurations of SiNFs, the abbreviations are used as follows: AH stands for armchair-edged hexagonal, ZH represents zigzag-edged hexagonal, AT implies armchair-edged triangular and ZT signifies zigzag-edged triangular. The AT-SiNF and AH-SiNF can be further categorized by the integer number dimer lines across one side of the nanoflake, while the ZT-SiNF and ZH-SiNF are identified by the integer number of edge Si atoms across one side of the nanoflake. The accuracy of our method is evaluated using a pristine silicene sheet, and the results are compared with previous findings. The silicene sheet is found to have a buckling distance of about 0.5 Å and lattice constant of 3.86 Å, both in agreement with previous works [68,69].

3. Results and discussions

3.1. The structure, electronic, and magnetic properties of SiNFs

The model structures of 3-AH-SiNF, 4-AT-SiNF, 3-ZH-SiNF, and 4-ZT-SiNF, as representatives of the aforementioned configurations, are presented in Fig. 1, in which all structures are made of freestanding silicene and all Si edge atoms are terminated by H atoms. The cyan and red balls signify Si and H atoms, respectively. After structural relaxation, the buckling height between sublattices A and B is ~ 0.50 (0.51) Å in T-SiNFs (H-SiNFs). The distance between Si-H atoms is found to be 1.50 Å, indicating that H atoms are chemically attached to SiNFs' edge. The edge Si-Si bond lengths are 2.23–2.24 Å for H-SiNFs and 2.23–2.25 Å for T-SiNFs, which are less than the bond length of inner Si-Si (2.28 Å), indicating relatively large atomic distortion at the edges.

The molecular orbital (MO) energy levels, as well as energy gaps between the HOMO and LUMO of 3-AH-SiNF, 4-AT-SiNF, and 3-ZH-SiNF are also shown in Fig. 1. Our calculations show that N-AH-SiNFs, N-AT-SiNFs, and N-ZH-SiNFs are NM and exhibit semiconducting behavior. Unlike the band structure of a silicene sheet in which the bonding π and antibonding π^* cross at K points in the Brillouin zone [9,29], finite gaps of 0.63, 0.89, 0.76 eV are opened between HOMO and LUMO of 3-AH-SiNF, 4-AT-SiNF, and 3-ZH-SiNF, respectively. The HOMO-LUMO energy gap in SiNF is attributed to the quantum confinement and edge effects caused by the reduced dimensionality of the structures. As displayed in Fig. 2, the HOMO-LUMO energy gaps decrease gradually by increasing the nanoflakes size. These results are in agreement with previous theoretical findings [64]. It is also discovered that half-hydrogenated silicene (a nanoflake with infinite size) has an energy band gap of 0.98 eV, which concurs well with those previously achieved [4,47].

Our spin-polarized calculations demonstrate that the ground state of N-ZT-SiNFs has magnetic behaviors. Fig. 1 shows the MO energy levels of 4-ZT-SiNF as a representative of N-ZT-SiNFs. As can be seen, the E_f (is set to the middle of the HOMO-LUMO gap) lies close to HOMO of the spin-up channel, and LUMO of the spin-down channel. The value of HOMO-LUMO energy gap for the spin-down channel (1.05 eV) is slightly less than that of the spin-up channel (1.07 eV). The isosurfaces of spin density distribution ($\rho_{spin-up} - \rho_{spin-down}$) of 4-ZT-SiNF is plotted in Fig. 3(a). The system provides a ferrimagnetic spin ordering with opposite spins on Si atoms of sublattices A (Si_A) and B (Si_B) in which the total spin-up is larger than the total spin-down. The energy difference between spin-polarized and spin-unpolarized states of 4-ZT-SiNF is 0.29 eV, in favor of the spin-polarized state. The spin density of the inner Si

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