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Electronic properties and STM images of vacancy clusters and chains in functionalized silicene and germanene

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HIGHLIGHTS

- Hexagonal & rectangle vacancy clusters retain the semiconducting nature of monolayers.
- Pentagonal and triangle vacancy clusters introduce metallicity and magnetic character.
- Vacancy chain patterns induce small bandgap in O-functionalized monolayers.
- STM images show distinctly different characteristics for various vacancy patterns.
- STM images can be used as electronic fingerprints to identify vacancy patterns created during functionalization.

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ABSTRACT

Electronic properties and STM topographical images of X (=F, H, O) functionalized silicene and germanene have been investigated by introducing various kind of vacancy clusters and chain patterns in monolayers within density functional theory (DFT) framework. The relative ease of formation of vacancy clusters and chain patterns is found to be energetically most favorable in hydrogenated silicene and germanene. F- and H-functionalized silicene and germanene are direct bandgap semiconducting with bandgap ranging between 0.1–1.9 eV, while O-functionalized monolayers are metallic in nature. By introducing various vacancy clusters and chain patterns in both silicene and germanene, the electronic and magnetic properties get modified in significant manner e.g. F- and H-functionalized silicene and germanene with hexagonal and rectangle vacancy clusters are non-magnetic semiconductors with modified bandgap values while pentagonal and triangle vacancy clusters induce metallicity and magnetic character in monolayers; hexagonal vacancy chain patterns induce direct-to-indirect gap transition while zigzag vacancy chain patterns retain direct bandgap nature of monolayers. Calculated STM topographical images show distinctly different characteristics for various type of vacancy clusters and chain patterns which may be used as electronic fingerprints to identify various vacancy patterns in silicene and germanene created during the process of functionalization.

1. Introduction

Silicene and germanene, the silicon and germanium equivalent of atomic layer of Carbon (graphene), have recently attracted a significant attention [1–5] due to their similar electronic properties as exhibited by graphene [6–8]. Theoretical studies [7,8] have predicted the stability of both silicene and germanene in buckled two-dimensional (2D) honeycomb structure. The buckling is due to the mixture of sp^2 and sp^3 hybridization. The realization of freestanding silicene and germanene are still challenging for the experimentalists, however, experiments have shown that silicene and germanene can be grown on metal substrates such as Ag(111) [9–11], Au(111) [12], Ir(111) [13], etc.. The experimental realization of monoatomic layers of Si and Ge in free-standing form may be expected in the near future.

The presence of Dirac cone in atomic layers of group-IV elements including silicene and germanene allows continuous conduction near the Fermi level which limits their direct application in electronic devices. Consequently, alternative techniques such as covalent functionalization have been opted to modify the physical, chemical and electronic properties of 2D monoatomic layers e.g.

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hydrogenated graphene can serve as natural host for graphene quantum dots, cluster of vacancies in hydrogen sublattice [14]; energy gap opens up in SiGe-based 2D layered structures on hydrogenation [15] which can be further modified by external electric field and in-plain strains [15–17]; single hydrogen and hydroxyl vacancies on siloxene (H and OH functionalized silicene) induce spin-polarization in the 2D lattice [18]; hydrogen terminated silicene and germanene nanoribbons show half metallicity which offers their use in spintronics applications [19]; hydrogen passivation of the zigzag edges of hybrid graphene/h-BN nanoribbons provides mechanical strength and stability to 1D superlattice [20] etc.

Not only hydrogenation, but the covalent functionalization of layered structures with halogens and oxygen is also possible. It is well known fact that the hydrogenation and fluorination processes provide structures that are energetically accessible and easy to synthesize in the laboratory [21,22]. Hydrogen and fluorine derivatives of silicene and germanene are known to be semiconducting with a bandgap ranging from 0.2 eV to 2.0 eV [23,24] whereas oxygen derivative of silicene and germanene may be metallic, semiconducting or insulating depending upon the oxidation conditions [25–27].

However, in the process of functionalization and physical or chemical desorption, it is always possible that a small amount of vacancies may get created. Also, it is possible to do full, partial or site specific functionalization of nanomaterials along with the creation of vacancies through lithography technique. The hydrogenation of silicene on Ag(111) substrate at room temperature results into perfectly ordered superstructure, however, dehydrogenation occurs on annealing at moderate temperature [28]. Similarly, partially hydrogenated phase has been found to produced in the process of hydrogenation of silicene [29]. In addition, functionalization and vacancies in nanomaterials induce magnetism [30–32], which has potential applications in the fast emerging field of nanoelectronics and spintronics.

The above possibilities of the occurrence of vacancies in the experiments and their potential applications triggered our interest to explore what role vacancies may play in hydrogenated, fluorinated and oxidized silicene and germanene? In this paper, the electronic and magnetic properties along with the STM topographical images of various vacancy patterns in functionalized silicene and germanene are systematically investigated.

2. Computational method

Calculations have been performed by using SIESTA simulation package [33]. Norm conserving Troullier Martin pseudo-potential in fully separable Kleinman and Bylander form have been used to treat the electron-ion interactions [34]. The exchange and correlation energies have been treated within the General Gradient Approximation (GGA) according to the Perdew–Burke–Ernzerhof (PBE) parameterization. The Kohn Sham orbital's were expanded in a linear combination of numerical pseudo atomic orbital's using a split-valence double zeta basis set with polarization functions (DZP). Throughout geometry optimization confinement energy of numerical pseudo-atomic orbital's are taken as 0.01 Ry. Minimization of energy was carried out using standard conjugate-gradient (CG) technique. Structures were relaxed until the forces on each atom were less than 0.01 eV/Å. A $30 \times 30 \times 1$ Monkhorst pack of k-point was used for sampling the Brillion zone. The spacing of the real space used to calculate the Hartree exchange and correlation contribution of the total energy and Hamiltonian was 250 Ry. A 4×4 supercell with a vacuum of about 20 Å along perpendicular to 2D plane has been used in our calculations.

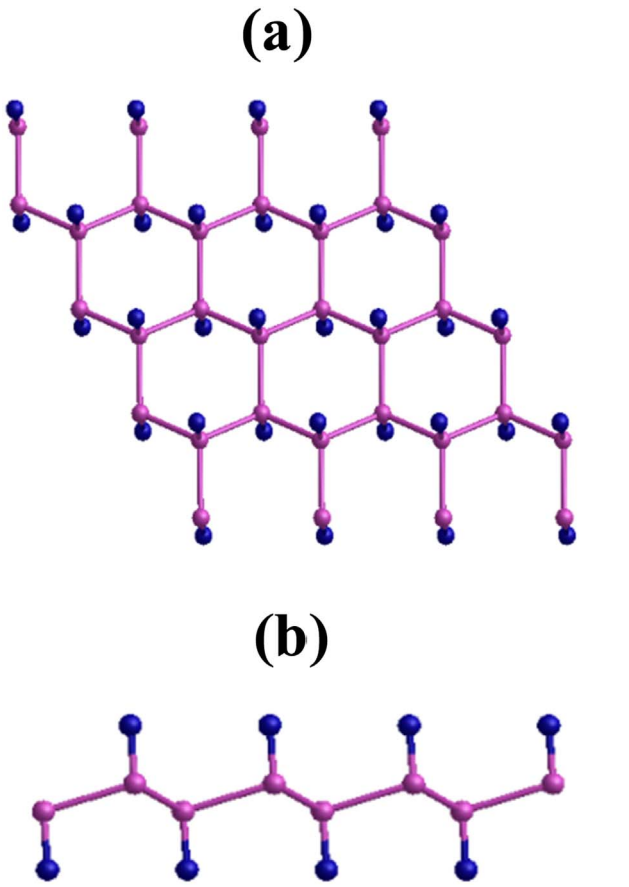

Fig. 1. (a) Top and (b) side view of functionalized silicene or germanene. Violet color balls represents Si or Ge atoms whereas blue color balls represents X atoms, where X=F or H or O. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

3. Results and discussions

Fig. 1(a) and (b) depict the top and side view of X (=F, H, O) functionalized silicene and germanene. Well known mixed sp^2 and sp^3 hybridization in silicene and germanene provides a favorable platform for their functionalization. A fully relaxed 4×4 supercell of 64 atoms of Si or Ge and F or H or O in chair configuration has been taken as a unit cell in the study. Note that chair-configuration of functionalized silicene and germanene is most stable [15] where X atoms on Si or Ge are at alternating above and below positions (Fig. 1(b)). Various vacancy clusters are introduced in functionalized silicene and germanene by removing X (=F, H, O) atoms (Fig. 2). For example, hexagonal vacancy cluster can be created by removing six adjacent X-atoms of functionalized monolayer (Fig. 2 (a)). Similarly, removing of five, four and three atoms results into pentagonal, rectangle and triangle vacancy cluster respectively (Fig. 2(b)–(d)). These different shape vacancies confine 6, 5, 4, and 3 electrons respectively in the vacancy forming region. The various alternating vacancy chains in functionalized silicene and germanene have been created by removing whole row of hexagonal, rectangle and zigzag pattern of periodic supercell (Fig. 3).

Electronic band structure calculations show fluorine and hydrogen functionalized silicene and germanene to be a semiconductor whereas oxygen functionalized silicene and germanene are metallic in nature (Fig. 4). The bandgap values of SiF, SiH, GeF and GeH are found to be as 0.81 eV, 1.92 eV, 0.12 eV and 0.94 eV respectively. It is found that valance band maximum (VBM) and conduction band minimum (CBM) lies on Γ high symmetry point that makes these functionalized monolayers as direct bandgap