



# Tuning the electronic properties of half- and full-hydrogenated germanene by chlorination and hydroxylation: A first-principles study



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## ABSTRACT

The electronic properties of chlorine and hydroxyl-substituted half- and full-hydrogenated germanene were carefully examined based on the first principles calculation. The results reveal that both the concentration and distribution of the substituent greatly affect the electronic properties of germanene. The half-hydrogenated germanene evolves from a magnetic semiconductor to half metal with the increase of chlorine or hydroxyl concentration. The chlorine or hydroxyl decoration on full-hydrogenated germanene does not change the intrinsic electronic structure of direct band gap, but can reduce the band gap with the increase of concentration. Fully hydroxylated and fully chlorinated germanene are semiconductor as fully hydrogenated germanene. Our calculation results demonstrate that the chlorine and hydroxyl can tune the electronic properties of half- and full-hydrogenated germanene differently.

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## 1. Introduction

Due to the unique electronic properties, graphene, a two-dimensional (2D) honeycomb network of carbon atoms, has attracted great attentions from different fields [1–4]. Recently, fully hydrogenated and half-hydrogenated graphene, which are referred as “graphane” and “graphone” have been studied theoretically [5–7] and experimentally [8]. With the coverage of hydrogenation changes on graphene, the system evolves from metallic to semiconducting and from nonmagnetic to magnetic [9]. With rapid growth of the research interests in 2D materials [10,11], group IV elements in the periodic table, such as Si and Ge, have attracted particular attentions. Silicene and germanene, the counterpart of graphene for silicon and germanium, have been widely examined [12–15]. In addition, recent experimental works have demonstrated the synthesis of silicene sheets grown on silver substrates [16–18]. Most recently, Bianco et al. have synthesized millimeter-sized crystallites of fully hydrogen-terminated germanene, and mechanically exfoliated single-layer of full-hydrogenated ger-

manene, named germanane [19,20], which is widely believed to have technologically relevant properties such as a direct band gap and high electron mobility.

Germanane with quite similar structure to graphane [5] is a new exciting 2D functionalized material with much promise, especially with the possibility of using chemical functionalization to modulate its electronic properties. Correspondingly, much effort was devoted to the functionalization of germanene, and lots of interesting results have been reported. Houssa et al. found the adsorption of hydrogen on germanene can open the band gap, and they further predicted that fully hydrogenated germanene is a direct gap material [15]; Wang et al. concluded based on first-principles calculations that germanene change from metallic to magnetic semiconducting and then to nonmagnetic semiconducting with changing the concentration of hydrogen atoms on germanene [21]. For the hydrogenated germanene, the chemical surface can be further modified to adjust the band gap, temperature dependent stability, or other properties of the material. For example, hydrogen group could be replaced by hydroxyl group to form single-layered germoxanene, which has only been studied in form of layered polygermyne [22,23]. Hydroxy group substitution on graphane and silicene has been studied theoretically and experimentally [7,24–26]. The product, half-hydroxylated graphene, is a half metal [7], and the product, siloxene, has a direct energy gap instead of the indirect one in unsubstituted silicene

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[25]. In addition, chlorine is also a frequently-used functionalization group. Gao et al. concluded that the gap of silicene can be opened by functionalized with chlorine [27]. Ma et al. theoretically demonstrated that the gap of fully chlorinated germanene remain crossed at the Fermi level and can be opened at Dirac-like points in the presence of spin–orbit coupling [28]. Previous experiment study has evidenced that hydrogen and chlorine can coexist on germanene, and hypothesized that the lack of observed photoluminescence are consequences of the presence of trace percentages of Ge–Cl bonds in fully hydrogen-terminated germanene [20]. However, the electronic properties of germanene related to the adsorption configuration of functional groups, as well as the role of functional groups have not been discussed, which is very important for practical application of electronic structure properties in the experiment.

In the present work, we performed first-principles calculations on the electronic properties of functionalized 2D half- and full-hydrogenated germanene by substituting the hydrogen atoms with chlorine or hydroxyl. The effects of concentration and distribution of the substituent on the electronic properties were investigated. The results show that chlorination and hydroxylation modify electronic properties significantly. This is very helpful for studying the effect of Ge–Cl bonds on the photoluminescence in full-hydrogenated germanene and for controlling the energy gaps and electronic properties of the 2D half- and full-hydrogenated germanene for future various electronics applications.

## 2. Computational methods

All the calculations were performed by adopting the density functional theory (DFT), as implemented in the Vienna ab initio simulation package (VASP) code [29]. The ion–electron and electron–electron interactions were calculated by the projector augmented plane-wave (PAW) method [30,31], and a plane-wave basis set. The generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof formula [32] has been used to calculate the electronic exchange–correlation potential. A  $2 \times 2$  supercell was adopted for all the configurations in the present calculations. Along z-axis, a vacuum region of 20 Å is applied in order to eliminate the interaction between the adjacent Ge layers. Based on the Monkhorst–Pack scheme [33], Brillouin zone integration was carried out at  $7 \times 7 \times 1$  *k*-points, and  $13 \times 13 \times 1$  *k*-points were used to calculate the density of states (DOS). A cutoff 400 eV was selected for the plane wave basis set. All the atomic positions were fully relaxed until the force on each atom was smaller than 0.02 eV/Å, and the convergence criteria for energy was  $10^{-4}$  eV. The charge populations were calculated using Bader's atom in molecule (AIM) method based on charge density topological analysis [34].

In this work, the formation energies of chlorine and hydroxyl-substituted half- and full-hydrogenated germanene are defined as follows:

$$E_f = E(\text{H}, X : \text{germanene}) - E(\text{H} : \text{germanene}) - n(\mu_X - \mu_{\text{H}}), \quad (X = \text{Cl}, \text{OH})$$

where  $E(\text{H} : \text{germanene})$  and  $E(\text{H}, X : \text{germanene})$  represent the energies of the half and full-hydrogenated germanene before and after Cl or OH-substitution, respectively.  $\mu_{\text{Cl}}$  and  $\mu_{\text{H}}$  are the chemical potential of Cl and H atoms ( $\mu_{\text{Cl}} = 1/2\mu_{\text{Cl}_2}$  and  $\mu_{\text{H}} = 1/2\mu_{\text{H}_2}$ ), and  $\mu_{\text{OH}} = \mu_{\text{H}_2\text{O}} - \mu_{\text{H}}$ . *n* is the numbers of H atoms substituted by Cl atoms. In addition, the adsorption energies of chlorine and hydroxyl-substituted half- and full-hydrogenated germanene with respect to germanene is defined as follows:

$$E_{\text{ads}} = E(\text{H}, X : \text{germanene}) - E(\text{germanene}) - n\mu_X - m\mu_{\text{H}}, \quad (X = \text{Cl}, \text{OH})$$

where  $E(\text{H}, X : \text{germanene})$  and  $E(\text{germanene})$  represent the energies of the half and full-hydrogenated germanene after Cl or

OH-substitution and the pure germanene, respectively.  $\mu_{\text{Cl}}$ ,  $\mu_{\text{H}}$  and  $\mu_{\text{OH}}$  are similar with the statement above. *n* and *m* are the numbers of H and X groups on germanene. According to this definition, a larger negative value of  $E_f$  and  $E_{\text{ads}}$  indicates the easily of H atoms substituted by Cl or OH groups and stronger adsorption of groups on the germanene.

## 3. Results and discussion

### 3.1. Half- and full-hydrogenated germanene

The atomic structures of half- and full-hydrogenated germanene are shown in Fig. 1, which are buckled hexagonal planes of germanium with hydrogen atoms on one side and both sides. In the half-hydrogenated germanene as shown in Fig. 1(a), Ge1 and Ge2 represent the Ge atoms hydrogenated and unhydrogenated, respectively.  $\Delta$  is the buckling parameter denoting the distance between two planes formed by the hydrogenated and unhydrogenated Ge atoms. The optimized Ge–Ge bond length is 2.49 Å, and the Ge–H bond length is 1.58 Å. The value of  $\Delta$  is 0.76 Å which agree with the previous theoretical results [21]. As for fully hydrogenated germanene which is shown in Fig. 1(b), the optimized Ge–Ge and Ge–H bond lengths are 2.47 Å and 1.56 Å, and the value of  $\Delta$  is 0.74 Å which are in agreement with the previous theoretical results [15,19,35,36].

Similar to hydrogen functionalized graphene [7], the Ge atoms have the mixture of  $sp^2$  and  $sp^3$  hybridization in half-hydrogenated germanene and only have  $sp^3$  hybridization in full-hydrogenated germanene. Both half- and full-hydrogenated germanene have unique electronic properties. As shown in Fig. 2, we plot the band gap and partial density of states (PDOS) for half- and full-hydrogenated germanene, and the Fermi level is set to be zero. In Fig. 2(a), the energy bands close to the Fermi level show semiconducting for both spin-down and spin-up channel, but the spin-up energy bands locate lower relative to the corresponding spin-down bands. This indicates that the half-hydrogenated germanene is magnetic semiconducting with a band gap of 0.40 eV, which confirms the previous theoretical results (0.41 eV) [21]. In addition, the half-hydrogenated germanene exhibits ferromagnetic semiconducting behavior which is similar to its congener silicene [37,38]. By examining the electronic states near the Fermi level from our calculated DOS shown in Fig. 2(c), we can see that the magnetism of the half-hydrogenated system mainly originates from the p orbital of

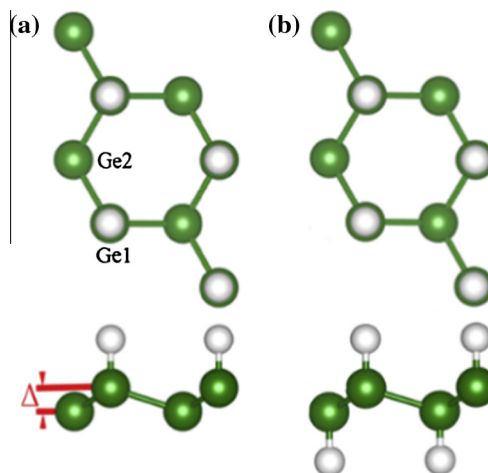


Fig. 1. (a) Top and side view of half-hydrogenated germanene: Ge1 represents for hydrogenated Ge atoms while Ge2 represents for unhydrogenated ones, and  $\Delta$  is the buckled distance. (b) Top and side view of full-hydrogenated germanene. Ge is in green, and H, in white.

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