

Chemically Functionalized Germanene for Spintronic Devices: A First Principles Study[†]

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1 Stability of Functionalized Germanene

To examine the stability of the various functionalized germanene, we make use of the formation energies defined as $E_f = E(\text{con}) - E(\text{ger}) - \sum_i x_i \mu_i$, where $E(\text{con})$ and $E(\text{ger})$ are the total energies of functionalized confirmations and free-standing germanene monolayer, respectively. The x_i ($i = \text{H, O, F}$) is the molar fraction of the corresponding atoms in the attached ligand, and μ_i is the chemical potential of the constituents at a given state. We choose μ_i as the 1/2 total energies of the corresponding diatomic molecules (H_2 , O_2 , F_2)¹. The calculated $\sum_i x_i \mu_i$ is the chemical potential of the attached ligand*. The formation energies of differently functionalized germanene is summarized in Table S1. The formation energy defined above therefore can be regarded as a measure of the stability against molecular desorption from the germanene surface. As a result, the functionalized germanene nanostructures with more negative formation energies are more stable. The two-sided functionalizations are found to be systematically more stable than the one-sided functionalizations. This phenomenon is attributed to the higher symmetry of the fully functionalized nanostructures compared with the semi-functionalized counterparts, and the Ge atoms more approach to the sp^3 hybridization in the former case. The relative stability of the fully functionalized germanenes follows the sequence of F-germanene-F > F-germanene-H > O-germanene-H. For the semi-functionalized germanenes,

Table 1 Formation energies per atom of optimized 2D Ge-based nanomaterials. The energies are given in eV per atom

Conformation	E_f
F-germanene-F	-1.60
F-germanene-H	-0.87
O-germanene-H	-0.07
germanene- CH_3	-0.32
germanene-F	-0.85
germanene-OH	-0.33

the formation energies of the -OH functionalization and - CH_3 are rather similar. More specifically, the functionalized nanostructures are stabilized by fluorination in both fully- and semi-functionalized cases, which is due to the large difference in the dissociation energy between hydrogen (also oxygen) and fluorine molecules. Consequently, the relative stability of the semi-functionalized germanenes decreases in this order: germanene-F > germanene-OH > germanene- CH_3 . It is noted that all the examined functionalized germanenes are exothermic evaluated in terms of their formation energies. The actual conformations of the semi-functionalized germanenes, however, could be more complex than the fully functionalized case, which are associated with the reaction paths during chemical processing³.

References

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* For the methyl functionalization, the chemical potential is obtained by calculating the CH_3 molecule, similar to the previous study of C_2H molecule².