

The Structural, Electronic and Optical Properties of Hydrofluorinated Germanene ($\text{GeH}_{1-x}\text{F}_x$): A First-Principles Study

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The structural, electronic, and optical properties of hydrofluorinated germanene ($\text{GeH}_{1-x}\text{F}_x$): A First-principles study

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Abstract

The structural, electronic, and optical properties of hydrofluorinated germanene have been studied with different occupancy ratios of fluorine and hydrogen. The hybridization of H-1s and Ge-4p orbitals in hydrogenated germanene and F-2p and Ge-4p orbitals in fluorinated germanene plays a significant role in creating an energy bandgap. The binding energy and phonon calculations confirm the stability of hydrofluorinated germanene decreases with the increase of the F to H ratio. The value of the energy bandgap decreased by increasing the ratio of F and H. The optical properties have been studied in the energy range of 0-25 eV. Six essential parameters such as energy bandgap (E_g), binding energy (E_b), dielectric constant $\epsilon(0)$, refractive index $n(0)$, plasmon energy ($\hbar\omega_p$), and heat capacity (C_p) have been calculated for different occupancies of H and F in hydrofluorinated germanene for the first time. The calculated values of structural parameters agree well with the available experimental and reported values.

Keywords hydrogenated germanene · hydrofluorinated germanene · structural properties · electronic properties · optical properties · thermodynamic properties.

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Introduction

In recent years, much attention has been given to the study of graphene, silicene, and germanene due to their exceptional properties such as linear dispersing energy bands, mass-less Dirac Fermions behavior of electrons, quantum Hall-effect, high electron mobility, etc. [1-5]. These three materials show zero bandgaps at Dirac point "K," which restricts their applications in field-effect transistors, logic circuits, and switching devices [6,7]. To open the bandgap, chemical functionalization is one of the main techniques. This leads to adsorption of foreign atoms (H, F, Cl, O, B, and N), several gas molecules (NH₃, NO, NO₂, and O₂), and alkali earth metals on pristine graphene, silicene, and germanene, which converts these materials into insulators, semiconductors, and semi-metals [8-11]. However, graphene may not be compatible with the present silicon-based technology and applications. Besides, silicene and germanene possess high spin-orbit coupling compared to graphene, making promising candidates in spintronic based applications and devices [12].

Some theoretical predictions show that hydrogenated silicene shows indirect bandgap, which is not suitable for optoelectronic devices [13-15]. The direct bandgap of 1.59 eV has been observed in the case of hydrogenated germanene (germanane), which demonstrates the topo-chemical de-intercalation of CaGe₂ in aqueous HCl [16]. Yao et al. [17] synthesized germanane on Ge₂Pt crystal and observed the bandgap of 0.2 eV for half hydrogenated germanene and 0.5 eV for fully hydrogenated germanene on scanning and tunneling spectroscopy (STS). The structural, stability, electronic, magnetic, and ferromagnetic properties of fully and partially hydrogenated germanene nanoribbons have been studied using the Vienna ab-initio simulation package (VASP) and local density approximations (LDA) [18-20]. The effect of spin-orbit

coupling on pristine and functionalized germanene with hydrogen and fluorine has been studied by Singh et al. [21].

Recently, several DFT calculations confirm that hydrogenated germanene shows a large bandgap compared to fluorinated germanene [14, 22-24]. However, in comparison to hydrogen, fluorine has a high electronegativity, large binding, and desorption energies lead to strong bonding between fluorine and germanium compared to hydrogen [25]. Therefore, we thought it would be of great interest to analyze the behavior of electronic and optical properties of hydrofluorinated germanene by increasing the fluorine to hydrogen ratio upon germanene. There are several forms of functionalized germanene such as the chair, boat, tricycle, and stirrup, out of which, chair (C) structure has good stability compared to others [19, 23, 25, 26]. The authors have recently studied several properties of functionalized graphene, silicene, and germanene using first-principle calculations [27-29].

In this paper, the structural parameters such as lattice constants, bond lengths, bond angles, energy bandgap, binding energy and bulk modulus of hydrogenated germanene (GeH), hydrofluorinated germanene (GeH_{0.5}F_{0.5}), and fluorinated germanene (GeF) have been calculated. The optical properties are studied for different occupancy ratios of fluorine and hydrogen upon germanene. The behavior of energy bandgap (E_g), binding energy (E_b), dielectric constant $\epsilon(0)$, refractive index $n(0)$, and plasmon energy ($\hbar\omega_p$) has been calculated for different F:H ratios of hydrofluorinated germanene for the first time. The calculated values of parameters are in good agreement with the available experimental and reported values.

Computational details

The calculations of structural, electronic, optical parameters are performed using the generalized gradient approximation (GGA) parameterized by Perdew Berke Ernjerhof (PBE) scheme in CASTEP code [30, 31]. An ultra-soft Pseudo potential representation is used with a kinetic energy cut-off of 353.70 eV [32]. The DFT-D correction in TS method is used for Vander Walls dispersion correction. The geometry is optimized for 100 iterations using Broyden, Fletcher, Goldfarb, and Shanno (BFGS) algorithm [33]. Throughout the optimization of geometry, maximum tolerance of total energy convergence of 0.2×10^{-4} eV/atom, Fermi energy convergence of 0.27×10^{-13} eV, Hellmann–Feynman ionic force of 0.05 eV/Å, maximum stress component 0.1 GPa, and ionic displacement of 0.2×10^{-2} Å have been used. The pulay density mixing scheme is used with a charge density mixing amplitude of 0.5, charge density mixing g-vector of 1.5 \AA^{-1} , and the maximum length of mixing history is 20. The phonon calculations are performed using density functional perturbation theory (DFPT) in a linear response method and norm-conserving Pseudo potential representation with a kinetic energy cut-off of 500 eV [34]. In the linear response method, the Fourier interpolation is used to calculate phonon dispersion and phonon density of states with a q-vector grid spacing of 0.015 \AA^{-1} and 0.04 \AA^{-1} convergence tolerance for force constants of 1×10^{-5} eV/Å².

Results and discussion

Structural properties

The calculation of structural parameters has been started with the hydrogenated germanene in chair (C) -configuration. The C-conformer belongs to a trigonal lattice structure with the space group of P-3m1. The unit cell of the C-structure has 4 germanium (Ge) and 4

hydrogen (H) atoms. The symmetry constraints of the C-germanane are $\alpha= 90^{\circ}$, $\beta= 90^{\circ}$, and $\gamma= 120^{\circ}$. The optimization has been performed for 100 iterations, and the optimized structural parameters are listed in Table 1. Afterward, it is converted into a 2X2X1 superlattice. Each hydrogen atom is changed to a fluorine atom step by step, for a one-step F: H ratio increased to 12.5%. For every increase of fluorine atoms of 12.5%, the superlattice has been optimized for 100 iterations.

The top view of hydrogenated germanene, hydrofluorinated germanene, and fluorinated germanene are shown in Fig. 1a-c. The calculated values of lattice parameters (a), bond lengths ($d_{\text{Ge-Ge}}$, $d_{\text{Ge-H}}$, and $d_{\text{Ge-F}}$) and bond angles ($\theta_{\text{Ge-Ge-Ge}}$, $\theta_{\text{Ge-Ge-H}}$, and $\theta_{\text{Ge-Ge-F}}$) are listed in Table 1 along with experimental and reported values. A reasonably good agreement has been found between them. The nature of bonding changes with an increase in atomic size. In hydrogenated graphene, the C-H bond is covalent [27], and in fluorinated graphene, the C-F bond is semi-ionic [35, 36]. In the case of functionalized germanene also, the bonding nature changes from hydrogenation to fluorination. The value of bond length (Ge-X, where X=H for germanane and X=F for fluorogermanene) confirms the increase of ionic interaction with the increase of fluorine occupation. The bond length between germanium atoms ($d_{\text{Ge-Ge}}$) is also high in functionalized germanene than pristine germanene due to the depopulation of bonding orbitals between germanium atoms. This depopulation is due to the electronegativity difference between Ge and H, and Ge and F atoms [26]. The optimized total energies (E_{tot}) for germanane and fluorogermanene are -245.845 eV and -1539.236 eV. The bulk modulus (B) is calculated by the equation of state (EOS) using the Birch-Murnaghan equation [37] and listed in Table 1.

Table 1	Fig. 1
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The binding energy (E_b) is calculated using the relation $E_b = (n_1 \times E_T^H + n_2 \times E_T^F + E_T^{Ger} - E_T^{GeH_{1-x}F_x})/n$, where E_T^F , E_T^H , E_T^{Ger} and $E_T^{GeH_{1-x}F_x}$ are the individual total energies of fluorine, hydrogen, germanene, and hydrofluorinated germanene, n_1 and n_2 are the number of hydrogen and fluorine atoms. n is the number of foreign atoms in the unit cell, and X is the fractional ratio of fluorine and hydrogen [38]. The calculated values of E_b for different occupancy ratios are listed in Table 2. The binding energy for germanene is 3.95 eV, which confirms that hydrogenated germanene has good stability. This value is in fair agreement with the reported values [23, 24]. The above statement is also supported by phonon calculations (Fig. 2a) in which phonon dispersion has positive phonon frequencies [39]. Further, Table 2 shows that stability decreases with the increase of fluorine occupation. This is due to an increase in the ionic nature of the material, while for fully fluorinated germanene, the calculated binding energy is -1.076 eV. Figure 2b shows that the phonon dispersion in negative frequencies, the imaginary frequencies ($\omega^2(k, j < 0)$) of phonon spectrum, show negative values, which are called soft modes [40]. The soft modes at K-point lead to an unstable structure [40].

Fig. 2

Electronic properties

The band structure has been calculated along the high symmetry axis in the hexagonal Brillouin zone for different ratios of F and H. The calculated values of energy gaps for GeH, GeH_{0.875}F_{0.125}, GeH_{0.75}F_{0.25}, GeH_{0.625}F_{0.375}, GeH_{0.50}F_{0.50}, GeH_{0.375}F_{0.625}, GeH_{0.25}F_{0.75}, GeH_{0.125}F_{0.875}, and GeF are 1.010 eV, 0.874 eV, 0.835 eV, 0.728 eV, 0.466 eV, 0.415 eV, 0.396 eV, 0.254 eV and 0.159 eV, respectively. The values of E_g for fully hydrogenated and fluorinated germanene are in good agreement with known values. The calculated energy bandgap for fluorination of germanene is very less compared to hydrogenation. This is due to the ionic

bonding between germanium and fluorine. Some of the band structures for 0%, 50%, and 100% occupancies of fluorine upon germanane are shown in Fig. 3a-c. The calculated band structures show that the bandgap of hydrogenated germanene decreases with the increase of fluorine occupancy. The behavior of the bandgap for different occupancies of fluorine is shown in Fig. 4.

Fig. 3 and Fig. 4

The density of states (DOS) shows the orbital character in forming the band structure and energy bandgap between valence and conduction bands. The partial density of states (PDOS) of individual elements and total density of states (TDOS) of hydrogenated and fluorinated germanene are shown in Fig. 5a-b. In fluorogermanene, the valence band is divided into two parts: the first part ranges from -25.77 eV to -22.60 eV, which is due to contributions of 3d orbital of germanium and 2s orbital of fluorine atoms. The second part comes from -9.91 eV to Fermi level (0.00 eV), dominated by 2p orbital of fluorine with minor contributions from Ge-4s and 4p orbitals. The valence band at Fermi energy is due to both the Ge-4p and F-2p states. The conduction band is due to contributions of F-2p, Ge-4s, and Ge-4p states. The small bandgap of 0.15 eV was induced due to the hybridization of F-2p and Ge-4p orbitals. The explanation for DOS of hydrogenated germanene is given in the [earlier](#) publication [26], in which the creation of bandgap is due to the hybridization of H-1s and Ge-4p states. In fluorogermanene, the Ge-3d plays a vital role in forming energy bands in the lower valence band region, whereas, in hydrogenated germanene, it [does](#) not participate in band structure formation.

Fig. 5

The electron localization function (ELF) has been calculated using the relations given by Savin et al. [41]. The isosurface plots of ELF for germanane and fluorogermanene are shown in Fig. 6a and b with an isovalue of 0.5. High is the ELF value; higher is the localization of

electrons. The concept of localized electrons, localized bonds, and delocalized electrons are given elsewhere [42]. Figure 6a shows the electron localization function of hydrogenated germanene in which the Ge-H covalent bond has a highly localized confirmation of electrons due to a strong σ bond. The germanium ring shows less ELF compared to Ge-H due to low bond energy because of bond length elongation. However, in the case of fluorinated germanene, the delocalized electrons around the plane of the Ge-Ge bond, which is due to the germanium has the outer valence of $3d^{10}4s^24p^2$ in which s and p orbitals form bonding with the other germanium and fluorine atoms, and the $3d^{10}$ electrons are roaming around the bonding of atoms.

Fig. 6

Optical properties

The dielectric function is an important parameter of optical properties, which is calculated in perpendicular polarization of the electric field to the plane of hydrofluorinated germanene. The imaginary part of the dielectric function $\epsilon_2(\omega)$ conveys the transitions between occupied valence states to unoccupied conduction states. Transitions are further divided into intra-band and inter-band contributions. The concept of **these transitions is discussed** elsewhere [27]. The momentum matrix elements and $\epsilon_2(\omega)$ are calculated in the range of 0-20 eV using the relations given by Momida et al. [43]. The calculated values of $\epsilon_2(\omega)$ **are** plotted in Fig. 7a for different occupancy ratios of H and F such as 8:0, 7:1, 6:2, 5:3, 4:4, 3:5, 2:6, 1:7 and 0:8. In the first case, i.e., fully hydrogenated germanene, the conduction **starts** after the threshold energy of 2.74 eV and rises rapidly due to the transitions between the occupied upper valence bands (OUVB) to the unoccupied lower conduction bands (ULCB). The $\epsilon_2(\omega)$ reaches a maximum value at 7.25 eV due to the maximum transitions from H-1s to Ge-4p states. Further, Fig.7(a) shows that the conductivity threshold starts shifting towards the higher energy region (blue

shifted) with increased fluorine occupancy. The peak values of $\epsilon_2(\omega)$ are also blue-shifted towards and decrease with the increase of fluorine occupancy. This is due to the ionic bond of fluorine with germanium, which decreases the number of transitions from occupied to unoccupied electronic states.

The real part of dielectric function $\epsilon_1(\omega)$ has been calculated using the Kramer-Kronig relation [44] and plotted in Fig.7b. The calculated value of static dielectric constant $\epsilon(0)$ is listed in Table 2, which shows that $\epsilon(0)$ decreases with fluorine occupancy. The behavior of refractive index $n(\omega)$ in the energy range of 0-25 eV has been shown in Fig.7c. The calculated static refractive index $n(0)$ indicates that the replacement of hydrogen atoms with fluorine increases the mobility of electrons, which is due to the increase of electronegativity of material [45]. The values of two parameters $\epsilon(0)$ and $n(0)$ are of great importance in selecting materials in spintronics, photodetectors, super dielectric capacitors, and various optoelectronic devices. The electron energy loss function $L(\omega)$ for the increase of fluorine occupancy upon hydrogenated germanene is displayed in Fig.7(d). The collective excitations or transitions of electrons between valence and conduction bands are known as plasmon's and cause peaks in $L(\omega)$. The energy associated with these peaks is called plasmon energy ($\hbar\omega_p$). The $\hbar\omega_p$ is red-shifted towards the lower energy region with an increase of fluorine occupancy. The plasmon energy of functionalized germanene is high compared to the pristine germanene. This is due to the change of hybridization from sp^2 to sp^3 causes transitions from lower energy valance band region to higher energy conduction band region which is referred to as σ - σ^* plasmons [46].

Table 2	Fig. 7
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Thermodynamic properties

The thermodynamic properties in phonon spectra are evaluated from the knowledge-based on phonon frequencies across the Brillouin zone [47]. Two approximations are made in this section : (1) the main equilibrium position of each ion in a Bravais lattice site R_i , and (2) the amplitude of atomic displacement is small compared to interatomic distances. The results of phonon calculations have been used to compute the enthalpy (E), entropy (S), free energy (F), heat capacity (C_p), and Debye temperature (Θ_D) using relations given by Baroni et al. [47]. The calculated values of zero-point vibrational energy (ZPE) of germanene, germanane, and fluorinated germanene are 0.042 eV, 0.443 eV, and 0.584 eV, respectively. The heat content in the form of enthalpy is shown in Fig. 8a in the temperature range of 5 K to 1000 K. The change in enthalpy increases in a linear manner with the increase of temperature from 300 K to 1000 K, which should be considered in thermal and industrial applications. The degree of disorderness of the three materials has been studied by calculating entropy shown in Fig. 8b. The change in entropy increases with the increase of temperature, which shows that, at high temperatures, the electronic and optical properties of hydrogenated and fluorinated germanene will be distracted. The free energy $F=E-T*S$ has been demonstrated in Fig. 8d, which goes negative in the high-temperature region due to the disorderness that increases with the increase of internal heat.

The heat capacity has been calculated using the relation

$$C_p(T) = k \int \frac{\left(\frac{\hbar\omega}{kT}\right)^2 \exp\left(\frac{\hbar\omega}{kT}\right)}{\left[\exp\left(\frac{\hbar\omega}{kT}\right) - 1\right]^2} F(\omega) d\omega$$

where $F(\omega)$ is the phonon density of states, k is the Boltzmann's constant, and \hbar the Plank's constant. The calculated heat capacity at room temperature 300 K for germanene, germanane,

and fluorinated germanene are 9.55 cal./cell.K, 13.81 cal./cell.K, and 16.72 cal./cell.K, respectively. The Debye temperature of functionalized germanene and germanane is shown in Fig. 8e, in which Θ_D saturates at 300 K for germanene. In the case of germanene, the Θ_D tries to saturate and has a small slope at high temperatures, while for fluorogermanene, it increases with the increase of temperature up to 1000 K. The calculated thermodynamic properties confirm that thermal sensitivity increases with the increase of adatom mass on pristine germanene. This is due to adatom mass introducing additional modes and causes a downshift in phonon spectra, which is called the isotope effect [48].

Fig. 8

Conclusions

The calculated values of structural parameters of hydrogenated and fluorinated germanene are in good agreement with the experimental and theoretical values. The calculated DOS shows the hybridization of H-1s and Ge-4p orbitals in hydrogenated germanene and F-2p and Ge-4p orbitals in fluorinated germanene play a major role in the formation of energy bandgap between valence and conduction bands. The energy bandgap decreases with the increase of F:H ratio on pristine germanene. The binding energy and phonon calculations confirm the hydrogenated germanene is a stable combination. However, stability decreases with the increase in occupancy of fluorine. The functionalized germanene shows high-temperature sensitivity compared to germanene. The calculated heat capacity at room temperature 300 K for germanene, germanane, and fluorinated germanene are 9.55 cal./cell.K, 13.81 cal./cell.K, and 16.72 cal./cell.K, respectively. The parameters such as E_g , E_b , $\epsilon(0)$, $n(0)$, and $\hbar\omega_p$ have been studied for the different occupancies of hydrogen and fluorine in hydrofluorinated germanene for

the first time, which are **used** in selecting the materials in spintronics, photodetectors, super dielectric capacitors, and various optoelectronic devices.

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Declarations

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Conflict of interest

Authors don't have any conflict to any one while preparing manuscript.

Availability of data and material

Author's can provide data whenever it is required.

Code availability

Not Applicable

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Figures Captions

- Fig. 1.** The top view of hydrofluorinated germanene for different occupancies of hydrogen and fluorine (a) GeH (b) GeH_{0.50}F_{0.50}, and (c) GeF. Where green color circles indicates germanium atoms, white circles indicates hydrogen and blue circles indicates fluorine atoms respectively.
- Fig. 2.** Phonon dispersion of (a) hydrogenated germanene (b) fluorinated germanene.
- Fig. 3.** The calculated band structures of hydrofluorinated germanene for different occupancies of hydrogen and fluorine. (a) GeH, (b) GeH_{0.50}F_{0.50}, and (e) GeF.
- Fig. 4.** The behavior of calculated energy gap and binding energy of hydrofluorinated germanene with increase of fluorine occupancy.
- Fig. 5.** The calculated density of states (a) hydrogenated germanene and (b) fluorinated germanene.
- Fig. 6.** The calculated electron localization function (a) hydrogenated germanene and (b) fluorinated germanene.
- Fig. 7.** The behavior of optical properties of hydrofluorinated germanene with increase of F:H ratio. (a) Imaginary part of dielectric function, (b) real part of dielectric function, (c) refractive index and (d) electron energy loss function.

Fig. 8. The behavior of thermodynamical properties of germanene, hydrogenated germanene and fluorinated germanene in the range of 5K to 1000K. (a) Enthalpy (b) Entropy (c) Free energy (d) heat capacity (e) Debye temperature.

Figures

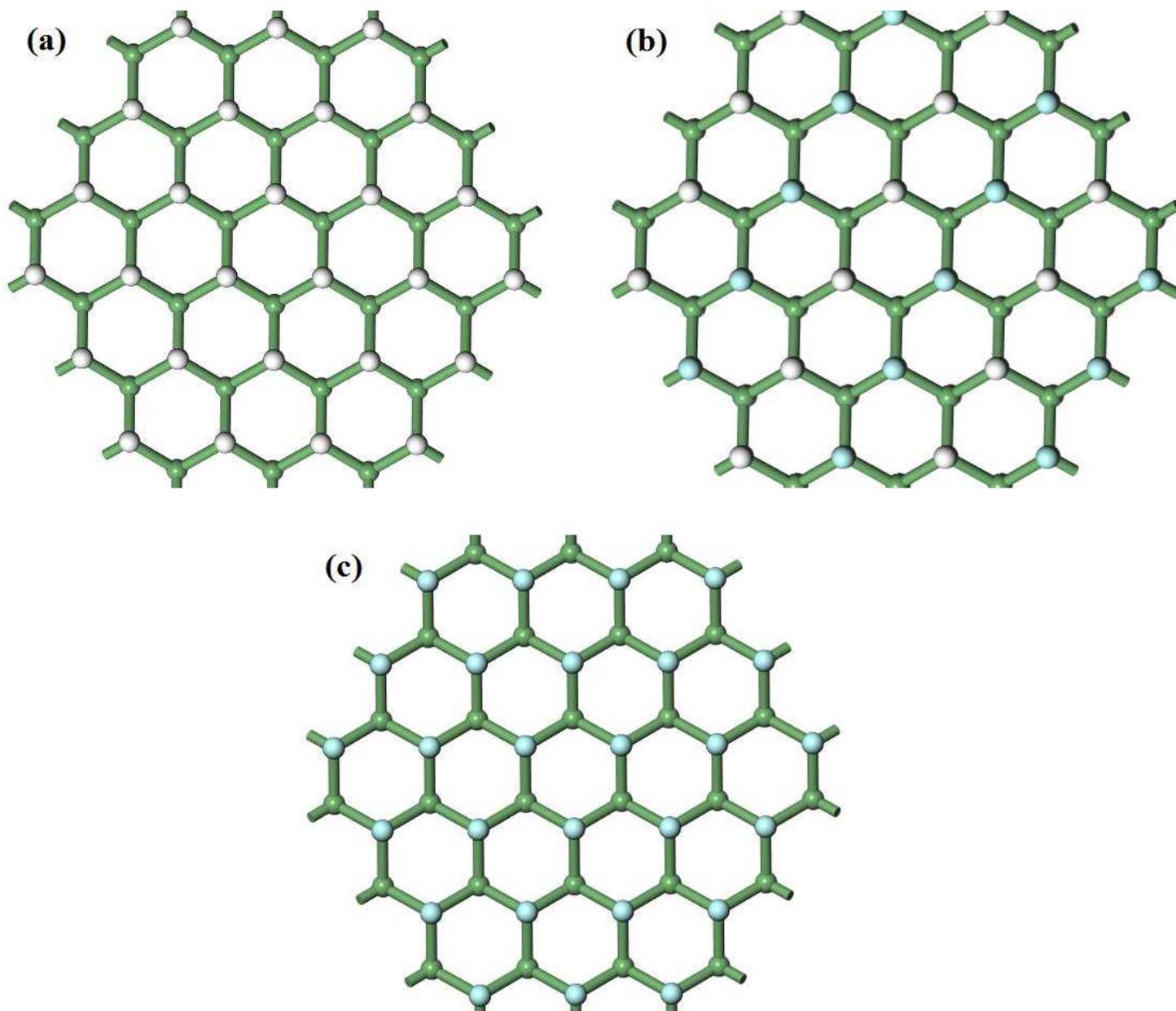


Figure 1

The top view of hydrofluorinated germanene for different occupancies of hydrogen and fluorine (a) GeH (b) GeH_{0.50}F_{0.50}, and (c) GeF. Where green color circles indicates germanium atoms, white circles indicates hydrogen and blue circles indicates fluorine atoms respectively.

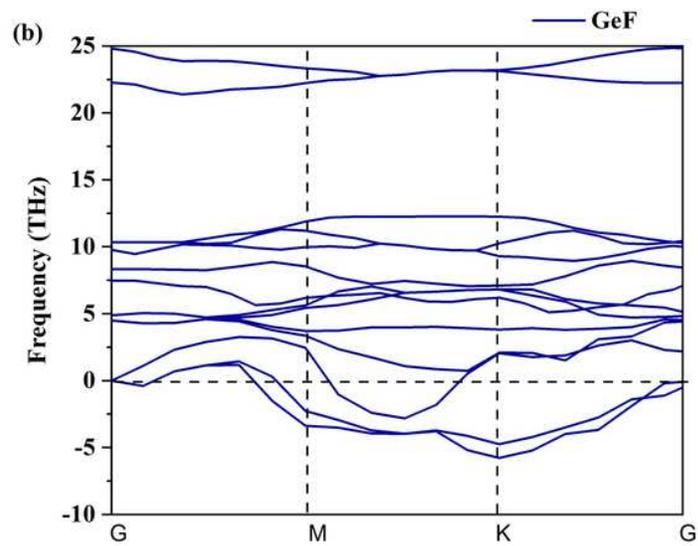
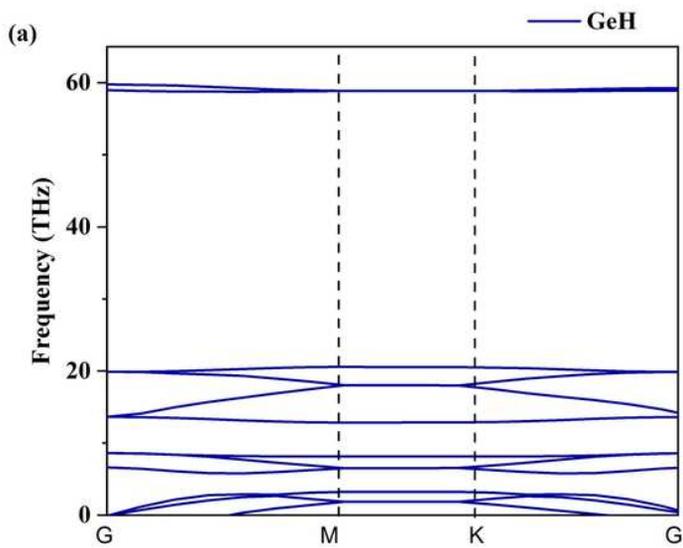


Figure 2

Phonon dispersion of (a) hydrogenated germanene (b) fluorinated germanene.

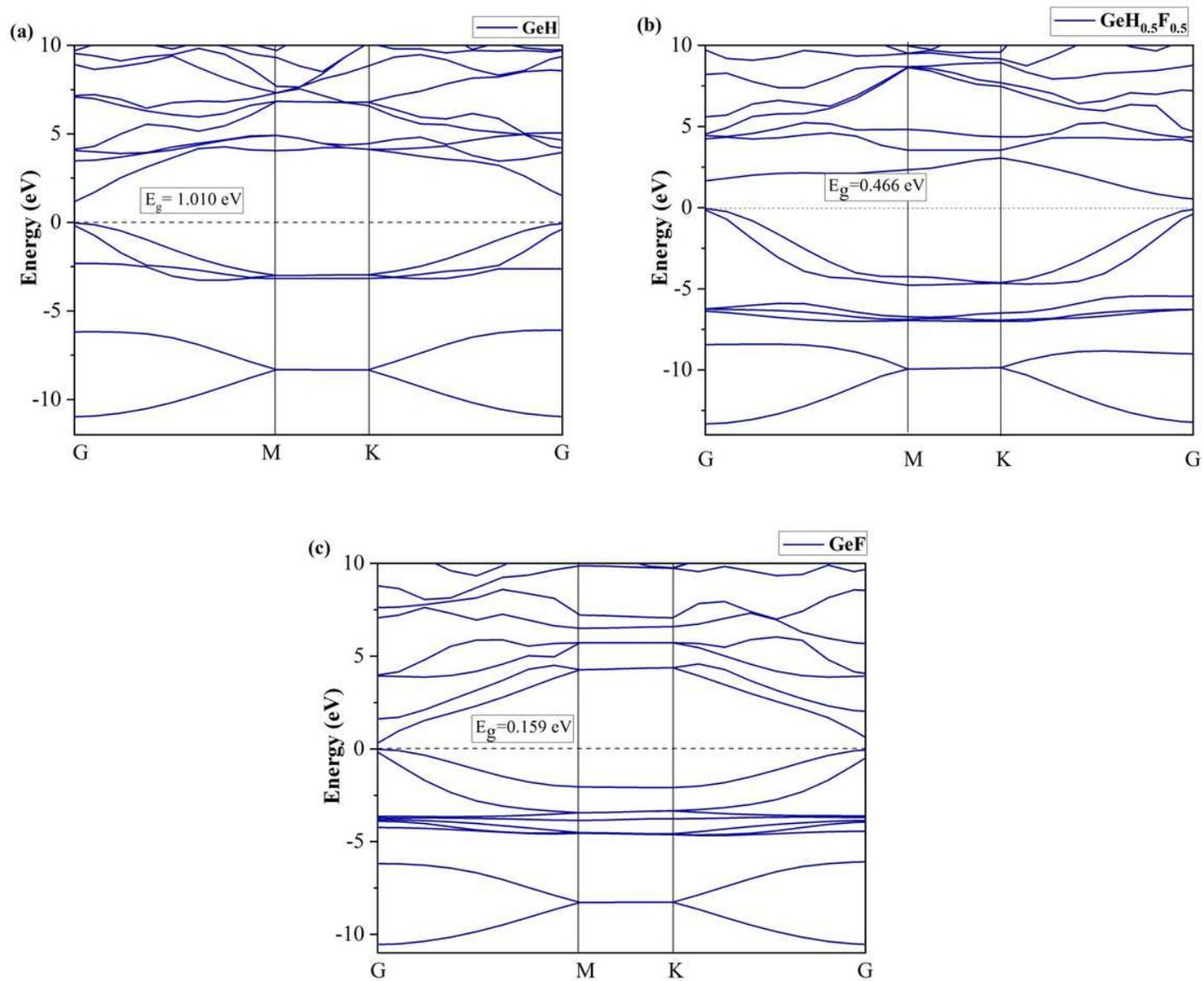


Figure 3

The calculated band structures of hydrofluorinated germanene for different occupancies of hydrogen and fluorine. (a) GeH, (b) GeH_{0.5}F_{0.5}, and (c) GeF.

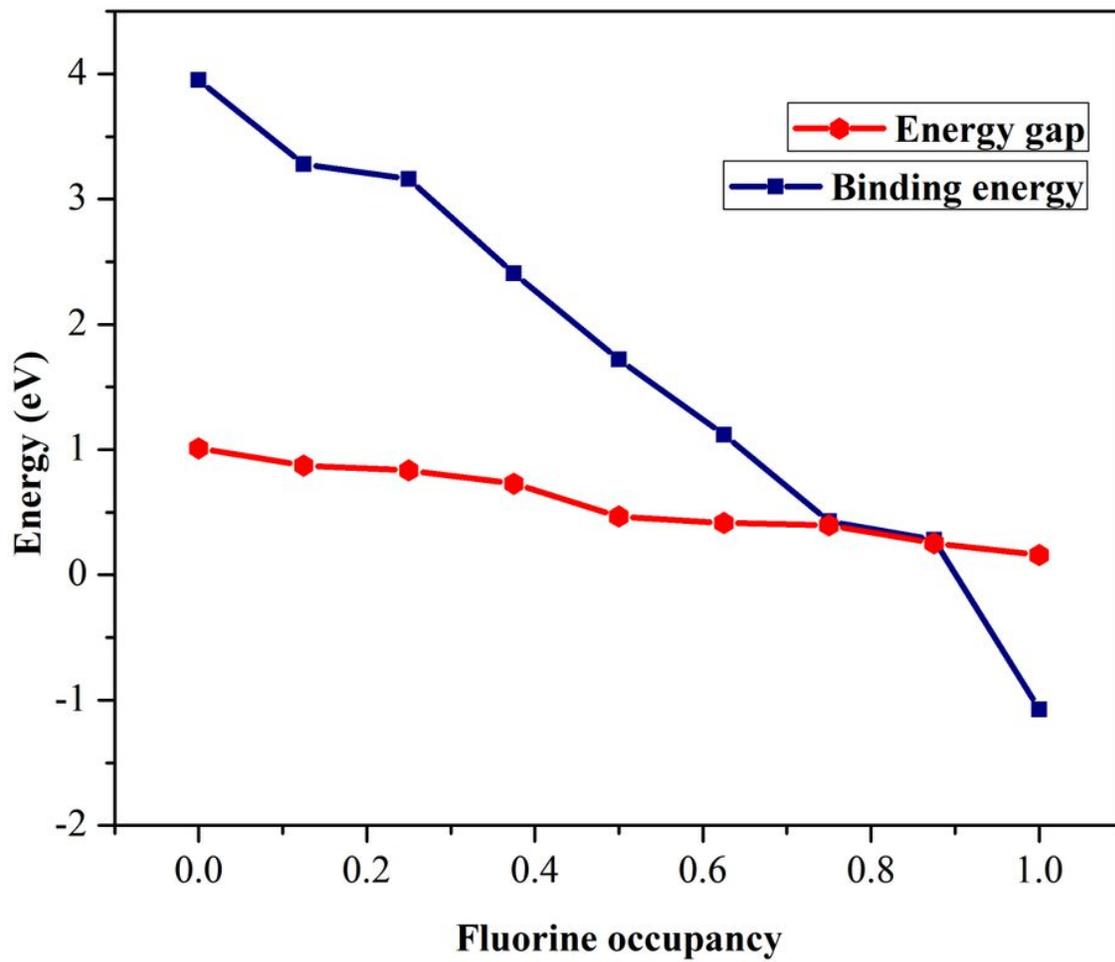


Figure 4

The behavior of calculated energy gap and binding energy of hydrofluorinated germanene with increase of fluorine occupancy.

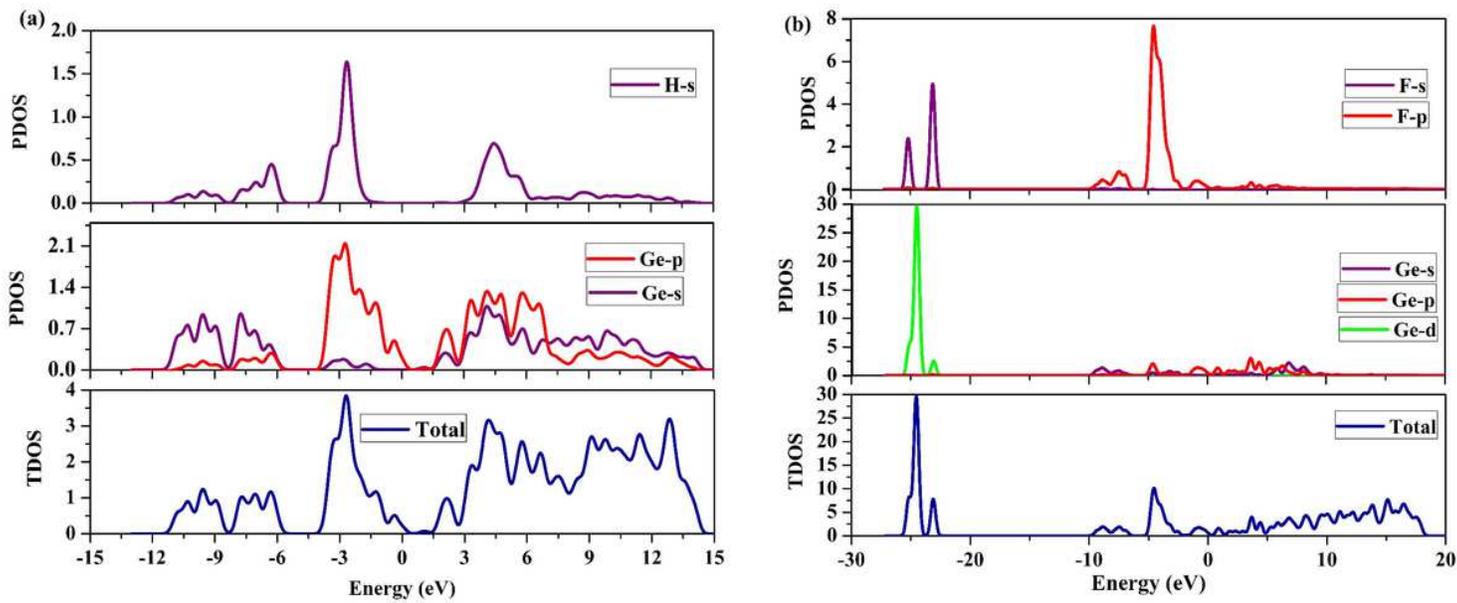


Figure 5

The calculated density of states (a) hydrogenated germanene and (b) fluorinated germanene.

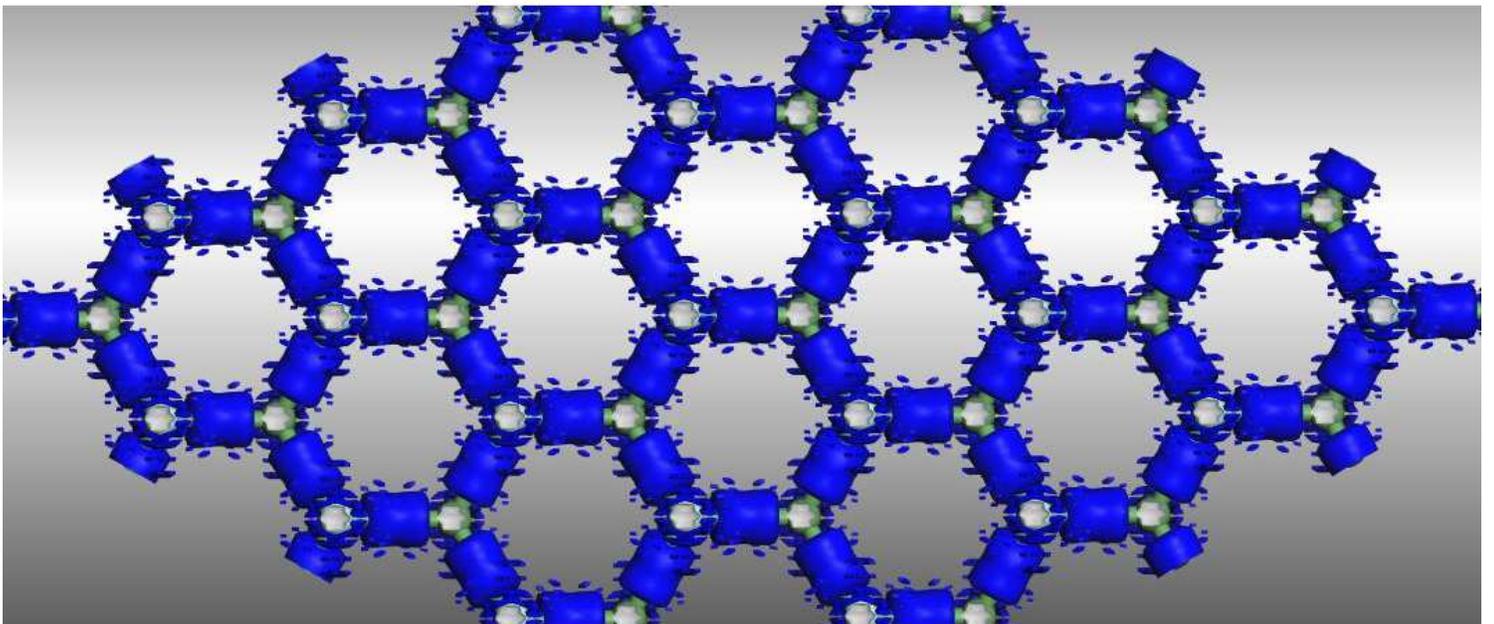
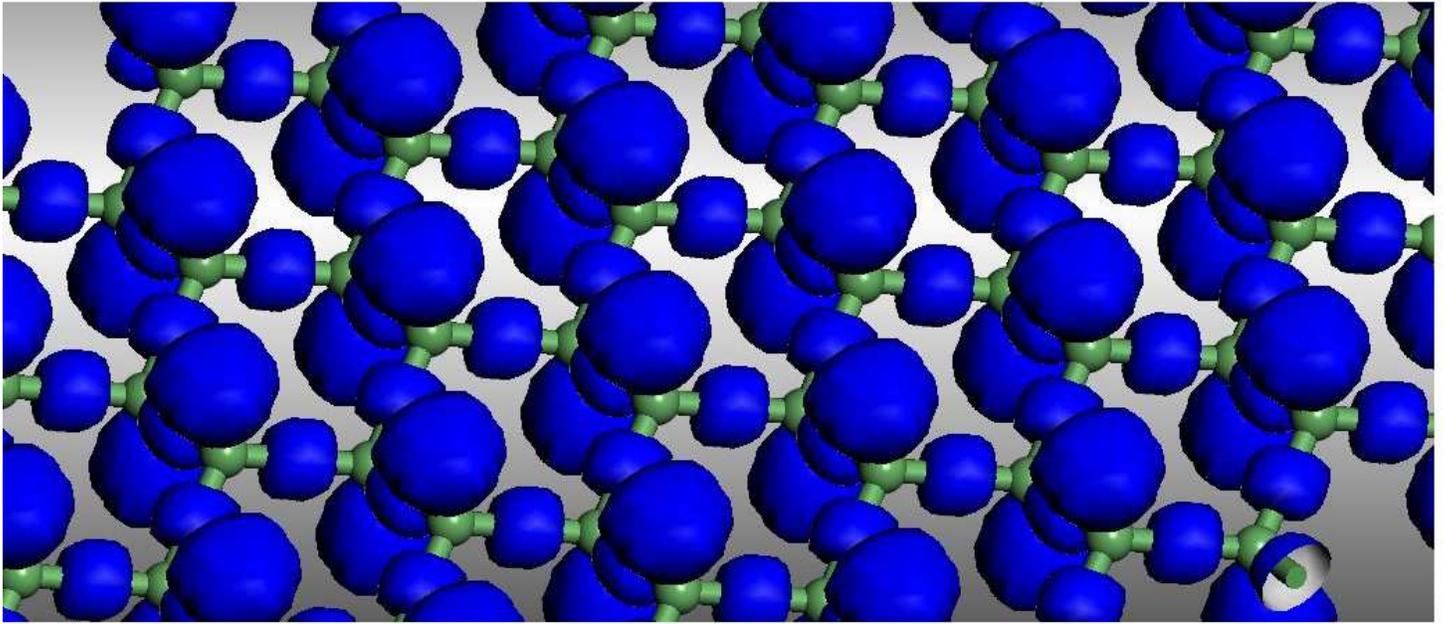


Figure 6

The calculated electron localization function (a) hydrogenated germanene and (b) fluorinated germanene.

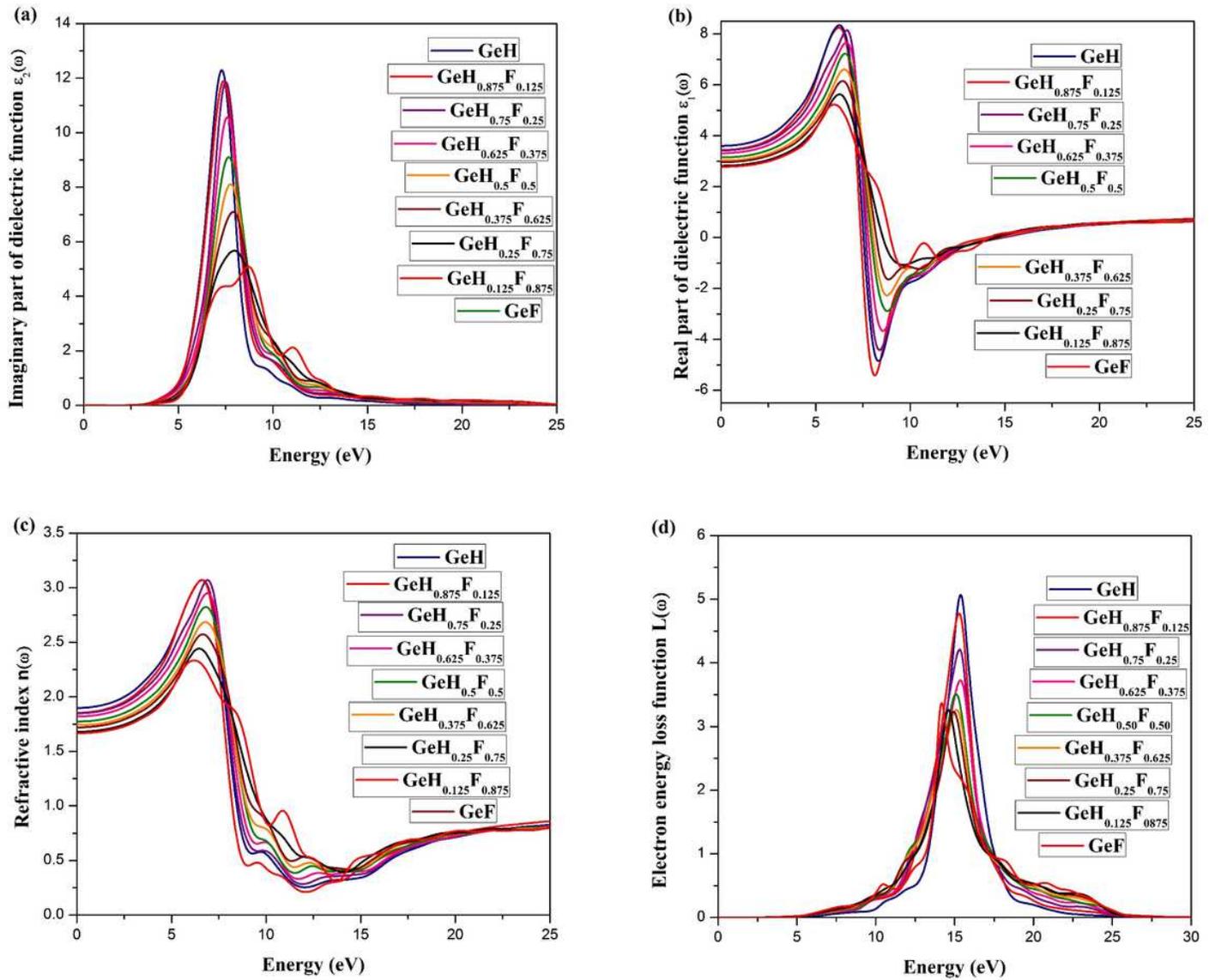


Figure 7

The behavior of optical properties of hydrofluorinated germanene with increase of F:H ratio. (a) Imaginary part of dielectric function, (b) real part of dielectric function, (c) refractive index and (d) electron energy loss function.

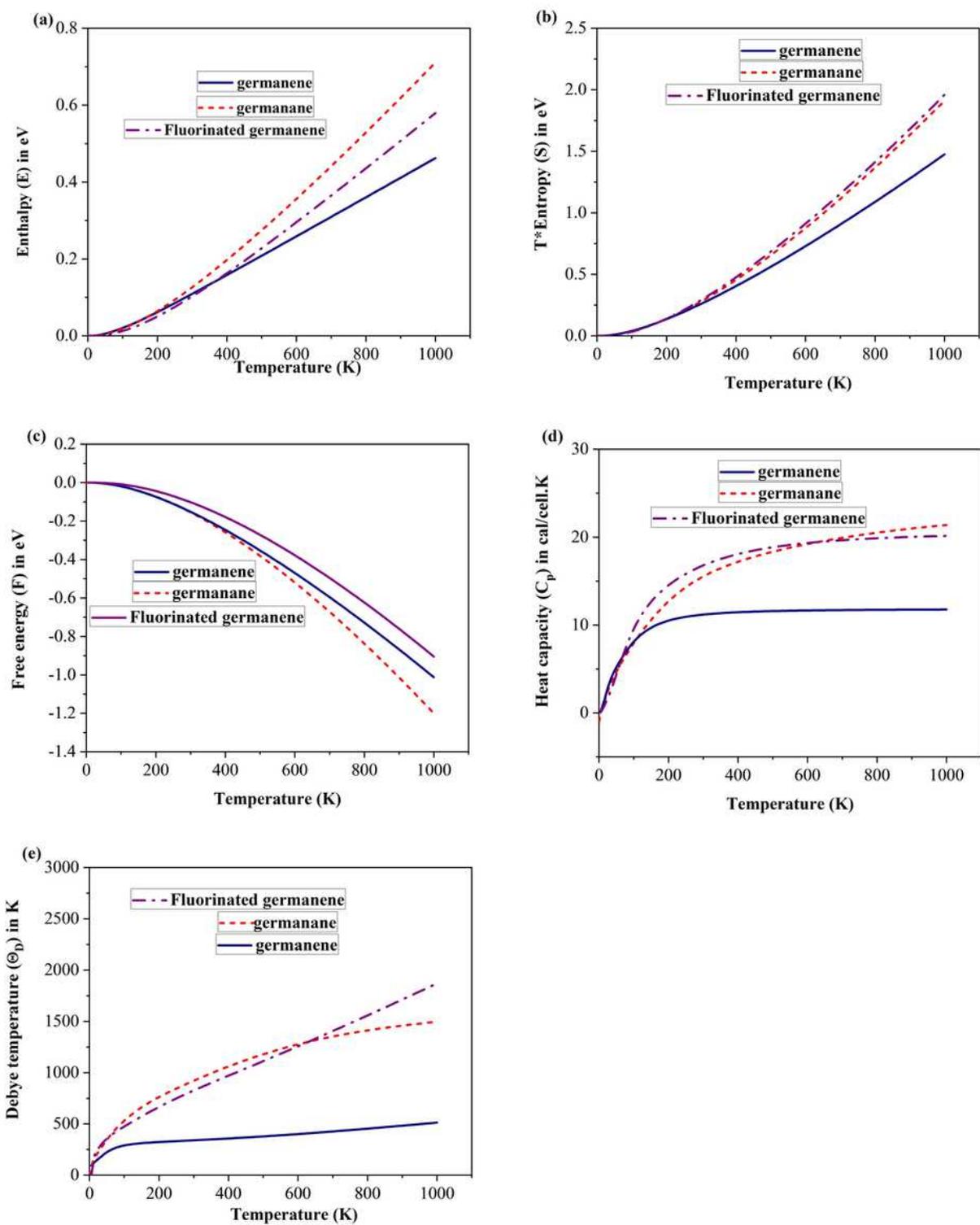


Figure 8

The behavior of thermodynamical properties of germanene, hydrogenated germanene and fluorinated germanene in the range of 5K to 1000K. (a) Enthalpy (b) Entropy (c) Free energy (d) heat capacity (e) Debye temperature.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [RevisedTables.docx](#)