The Structural, Electronic and Optical Properties of Partially Hydrogenated Germanene: A First-Principles Study

Routu Santosh and V. Kumar

Abstract The structural, electronic and optical properties have been studied at different occupancies of hydrogen atoms upon germanene using first-principles density functional theory calculations. The electronic and optical parameters: energy bandgap (E_g), dielectric constant $\varepsilon(0)$, refractive index $n(0)$, absorption coefficient (E_α) and plasmon energy ($\hbar\omega_p$) have been calculated for different occupancy of hydrogen for the first time. The calculated values for 100% occupation of hydrogen are in good agreement with the available experimental and reported values. The above-calculated parameters are essential in the fabrication of several optoelectronic devices and applications.

Keywords Hydrogenated germanene · First-principles · Structural property · Electronic property · Optical property

1 Introduction

In recent years, much attention has been given on graphene-like two-dimensional materials such as silicene and germanene due to their exceptional properties: linear dispersing energy bands, mass-less Dirac fermions behaviour of electrons, high electron mobility, unusual quantum hall effect, spin–orbit coupling, etc. [1–6]. These materials show semi-metallic nature, i.e., zero bandgaps at Dirac point K, which restricts their applications in the field-effect transistors, logic circuits and switching devices [7, 8]. To open bandgap, one of the main techniques used is chemical functionalization. This leads to adsorption of foreign atoms (H, F, Cl, O, B and N), several gas molecules (NH_3, NO, NO_2 and O_2) and alkali earth metals on pristine silicene and germanene and converts into insulators, semiconductors, semi-metals and metals [9–12]. Some theoretical predictions show that hydrogenated silicene shows indirect bandgap, which is not suitable for optoelectronic devices and applications [13–15].

R. Santosh (✉) · V. Kumar
Department of Electronics Engineering, Indian Institute of Technology (Indian School of Mines) Dhanbad, Dhanbad, Jharkhand 826004, India

M. Tiwari et al. (eds.), *Optical and Wireless Technologies*, Lecture Notes in Electrical Engineering 771, https://doi.org/10.1007/978-981-16-2818-4_10

The direct optical band gap of 1.59 eV is observed in the case of hydrogenated germanene (germanane), which is demonstrated from topo-chemical de-intercalation of $CaGe_2$ in aqueous HCl [16]. Yao et al. [17] synthesized germanane on Ge_2Pt crystal and observed the bandgap of 0.2 eV for half-hydrogenated germanene and 0.5 eV for fully hydrogenated germanene on scanning and tunnelling spectroscopy (STS). The structural, stability, electronic, magnetic and ferromagnetic properties of hydrogenated germanene nanoribbons studied by first-principle calculations [18–20]. However, 100% hydrogenation is not possible as some defects may occur while adsorption of hydrogen on germanene. Therefore, authors have taken much interest to calculate several properties of hydrogenated germanene for different occupancies of hydrogen upon germanene. Recently, the authors have studied several properties of hydrogenated, fluorinated and hydrofluorinated graphene using density functional theory (DFT) calculations [21–23].

In this paper, the structural, electronic and optical properties have been studied at different occupancies of hydrogen atoms upon germanene using first-principles density functional theory calculations. The electronic and optical parameters: energy bandgap (E_g), dielectric constant $\varepsilon(0)$, refractive index $n(0)$, absorption coefficient (E_α) and plasmon energy ($\hbar\omega_p$) have been calculated for different occupancy of hydrogen for the first time. The calculated values for 100% occupation of hydrogen are in good agreement with the available experimental and reported values.

2 Methodology

The calculations have performed using first-principle calculations on Cambridge sequential total energy package CASTEP code [24]. The calculations are based on generalized gradient approximation (GGA) parametrized by Perdew-Berke-Ernzerhof scheme [25]. The TS method has been used for DFT-D correction in calculation of structural, electronic and optical properties. The geometry optimization was performed for 100 iterations to obtain minimum total energy using Broyden, Fletcher, Goldfarb and Shanno (BFGS) scheme [26]. An ultra-soft pseudopotential representation has been used with the basis set kinetic energy cut-off of 353.70 eV [27]. The maximum tolerance of geometry minimization parameters: total energy convergence is 2×10^{-5} eV/atom, Hellmann–Feynman ionic force is 0.05 eV/Å, max ionic displacement is 2×10^{-3} Å and maximum stress component is 0.1 GPa, respectively.

3 Results and Discussion

3.1 Structural and Electronic Properties

The adsorption of hydrogen on pristine germanene changes the hybridization of germanium from sp^2 to sp^3, which changes the structural, electronic and optical properties of germanene. The change of hybridization converts structure of germanene from hexagonal (space group = P63/MMC, 196) to trigonal (space group = P-3M1, 164) which has shown in Fig. 1a, b. The corresponding symmetrical constraints are $\alpha = 90°$, $\beta = 90°$ and $\gamma = 120°$, respectively. The optimized lattice parameter (a), bond lengths ($d_{\text{Ge–Ge}}$ and $d_{\text{Ge–H}}$) and bond angles ($\theta_{\text{Ge--Ge--Ge}}$ and $\theta_{\text{Ge--Ge--H}}$) are listed in Table 1, along with the reported values. The calculated bond length of Ge–H shows that the bonding between germanium and hydrogen is covalent or semi-ionic, while the bonding between carbon and hydrogen in hydrogenated graphene is covalent [21]. Table 1 shows that the bond length between germanium atoms of hydrogenated germanene is high compared to germanene. This is due to the electronegativity difference between hydrogen and germanene causes the depopulation of bonding orbitals

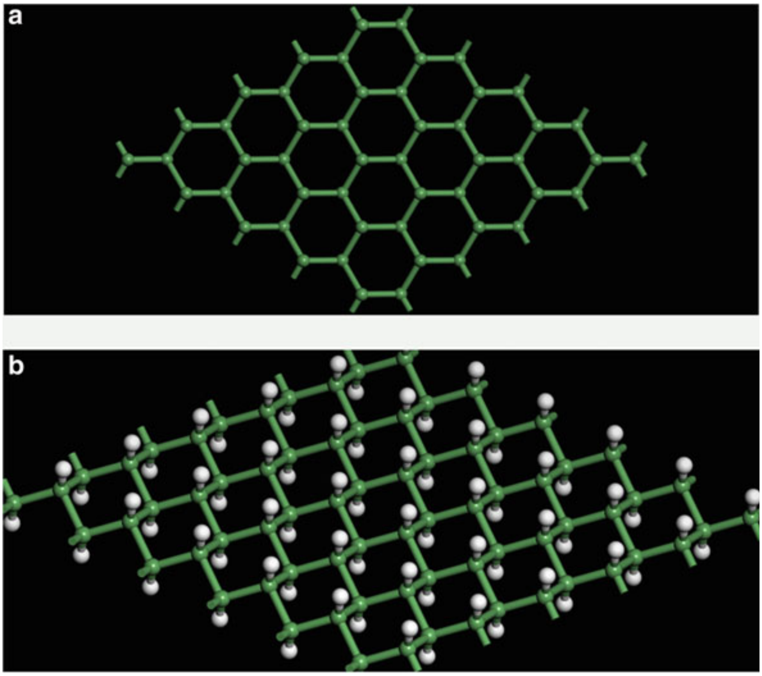

Fig. 1 **a** The top view of pristine germanene. The green circles indicate germanium atoms of sp^2 hybridization with neighbouring atoms. **b** The perspective view of hydrogenated germanene in which white circles indicate hydrogen and green circles are germanium

Table 1 Lattice constant (a), Ge–Ge bond length ($d_{\mathrm{Ge–Ge}}$), Ge-H bond length ($d_{\mathrm{Ge–H}}$), Ge–Ge–Ge bond angle ($\theta_{\mathrm{Ge–Ge–Ge}}$), Ge–Ge–H bond angle ($\theta_{\mathrm{Ge–Ge–H}}$), bandgap energy ($E_g$) and binding energy ($E_b$) of germanane and germanene

Parameters	Germanane		Germanene	
	This work	Reported	This work	Reported
a (Å)	4.059	3.880[a], 3.93[e], 3.908[f], 3.95[d], 4.082[c]	3.694	4.0[j]
$d_{\mathrm{Ge–Ge}}$ (Å)	2.454	2.390[f], 2.401[e], 2.469[c]	2.522	2.382[j]
$d_{\mathrm{Ge–H}}$ (Å)	1.557	1.529[d], 1.56[f], 1.563[c]	–	
$\theta_{\mathrm{Ge--Ge--Ge}}$ (°)	111.487	108.95[f]	94.204	
$\theta_{\mathrm{Ge--Ge--H}}$ (°)	107.372	109.99[f]	–	
E_g (eV)	1.010	1.59[a], 0.5[b], 1.38[e], 3.6[i], 3.5[g], 1.812[f], 1.38[d], 2.81[h]	0.00	0.00[i]
E_b (eV)	3.95	4.069[f], 2.575[d]	–	

Experimental values [a]Ref. [16] and [b]Ref. [17], reported LDA [c]Ref. [18], [d]Ref. [23], [e]Ref. [13] and [j]Ref. [13], reported GGA [f]Ref. [31], reported GW [g]Ref. [13] and [h]Ref. [23], reported HSE [i]Ref. [13]

between germanium atoms. The calculated bond angles of hydrogenated germanene are near to diamond bond angle due to sp^3 hybridization.

The band structure of hydrogenated germanene has been calculated along with high symmetry points (G–M–K–G) with the q-point separation of 0.0151/Å in the Monkhorst pack grid and shown in Fig. 2. Houssa et al. [7] predicts the zero bandgap of germanene at Dirac point 'K' and express the linear Dirac-distribution of energy bands. The direct bandgap has been created for hydrogenated germanene at G-point with bandgap value of 1.0 eV without changing of linear distribution in the band structure. The density of states shows the orbital character in the formation of valence and conduction bands of the band structure. The partial density of states (PDOS) and

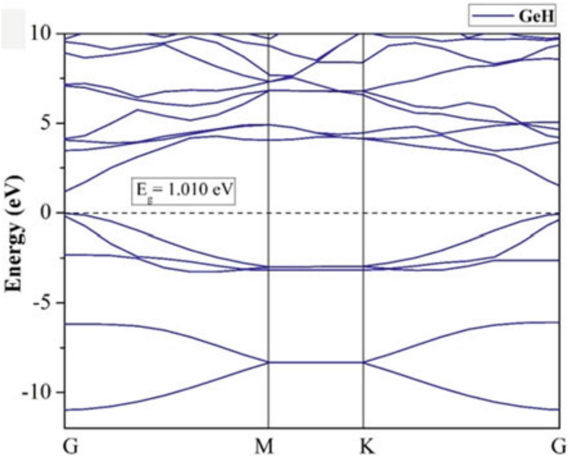

Fig. 2 The calculated band structure of hydrogenated germanene which shows the energy band gap of 1.010 eV at Γ point

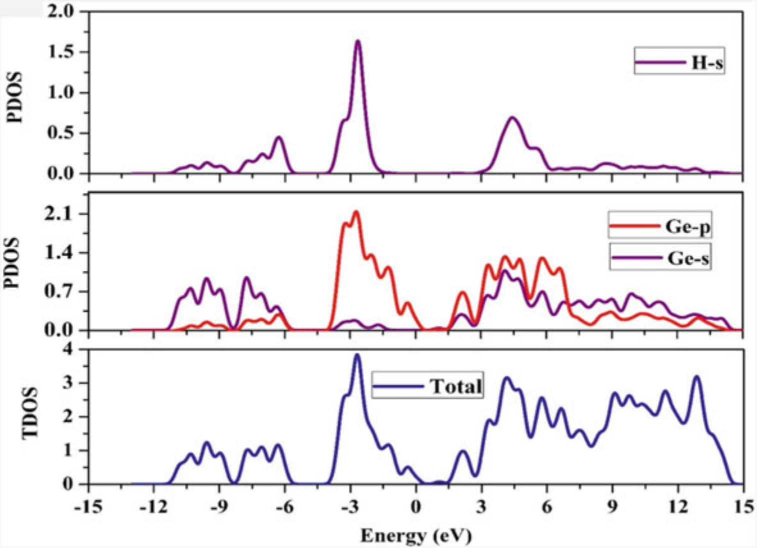

Fig. 3 The calculated partial density of states (PDOS) of individual atoms and the total density of states (TDOS) of hydrogenated germanene

total density of states (TDOS) of hydrogenated germanene have been plotted in Fig. 3. The energy bands in the lower part of valence band are mainly contributed by H-1s and Ge-4s, and the upper valence band is dominated by Ge-3p and H-1s. The conduction band is primarily due to the influence of H-1s, Ge-3p and Ge-4s state, respectively. The Ge-3p and H-1s orbitals play a significant role in the formation of an energy bandgap between the valence and conduction bands.

3.2 *Optical Properties*

The optical properties are calculated in perpendicular polarization of electric field on the plane of hydrogenated germanene. The momentum matrix elements and the imaginary part of dielectric function $\varepsilon_2(\omega)$ have been calculated using the relations given by Momida et al. [28]. The calculated $\varepsilon_2(\omega)$ for different occupancies of hydrogen is shown in Fig. 4a. The conduction in fully hydrogenated germanene started at 2.5 eV and rises rapidly due to the increase of transitions from the upper valence band to lower conduction band. It reaches to a maximum value at 6.8 eV due to the maximum number of transitions from H-1s to Ge-4p states and decreases with the further increase of photon energy. However, as the occupancy of hydrogen decreases, the starting point of conduction also decreases and comes toward the low-energy region (redshift). This may be due to the decrease in optical band gap of the germanane. The low maximum values of $\varepsilon_2(\omega)$ for defective occupancy of hydrogen

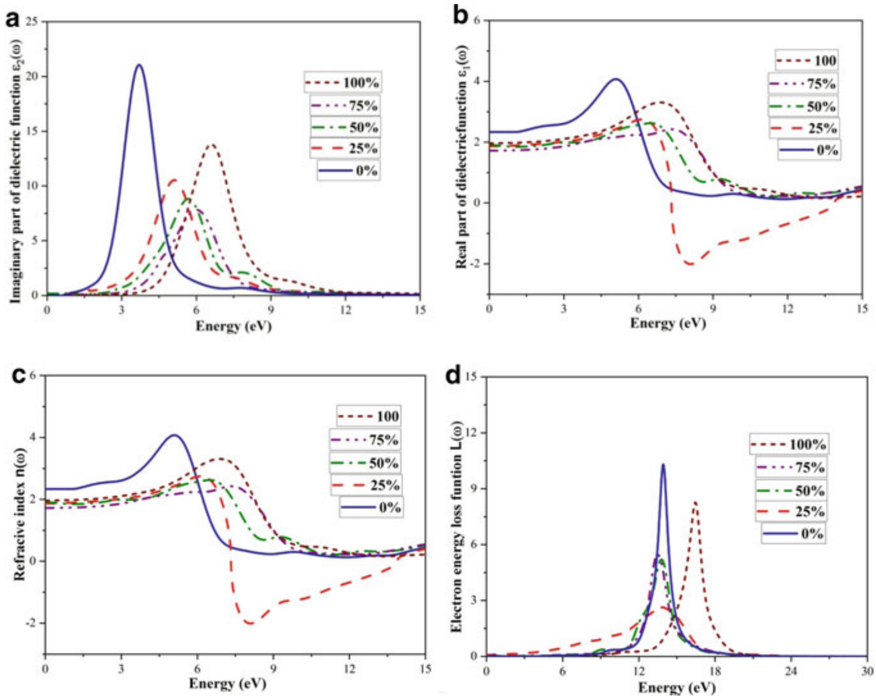

Fig. 4 **a** The imaginary part of dielectric function $\varepsilon_2(\omega)$ for different occupancies of hydrogen upon germanene. **b** The real part of dielectric function $\varepsilon_1(\omega)$ for different occupancies of hydrogen upon germanene. **c** The refractive index $n(\omega)$ for different occupancies of hydrogen upon germanene. *d* The electron energy loss function $L(\omega)$ for different occupancies of hydrogen upon germanene

such as 25, 50 and 75% are due to the lack of symmetry. The pristine germanene has low buckling compared to hydrogenated germanene [14]. Thus, the defect functionalized germanene is the combination of low- and high-buckling structure which is unsymmetrical. While in pristine germanene, the conduction starts nearly from zero point due to semi-metallic nature and reached to a maximum value at 3.5 eV then decreases with the further increase of energy. The real part of dielectric function $\varepsilon_1(\omega)$ is calculated using the Kramer-Kronig relation [29] and shown in Fig. 4b. The calculated dielectric constant $\varepsilon(0)$ for different occupancies of hydrogen is listed in Table 2. The $\varepsilon(0)$ may be decreased after the hydrogenation of germanene due to increase in energy bandgap. The refractive index and electron energy loss function have been calculated using the relation given by Sahin et al. [30] and shown in Fig. 4c, d. The calculated Refractive Index and plasmon energy for different occupancies of hydrogen upon germanene are listed in Table 2.

Table 2 The calculated static dielectric constant $\varepsilon(0)$, refractive index $n(0)$ and plasmon energy ($\hbar\omega_\mathrm{p}$) for different occupancies of hydrogen upon germanene

% occupancy of hydrogen	0%	25%	50%	75%	100%
$\varepsilon(0)$	6.52	3.50	3.56	2.97	3.86
$n(0)$	2.34	1.87	1.94	1.72	1.97
$\hbar\omega_\mathrm{p}$	13.89	13.87	13.83	13.51	16.43

4 Conclusions

The calculated lattice constants, bond lengths and bond angles for germanene and hydrogenated germanene are in good agreement with the earlier reported values. After hydrogenation, H-1s orbital hybridized with Ge-3p state which forms strong σ bond and plays a major role in the formation of energy bandgap between the valence and conduction bands. The dielectric constant $\varepsilon(0)$ may be decreased after the hydrogenation of germanene due to creation of energy bandgap. This may increase the mobility of electrons in the material. The defects in hydrogenation form an unsymmetrical structure which affects the electronic and optical properties of hydrogenated germanene. The optical parameters: dielectric constant $\varepsilon(0)$, refractive index $n(0)$ and plasmon energy ($\hbar\omega_\mathrm{p}$) for different occupancies of hydrogen upon germanene have been calculated for the first time. The above-calculated values are much crucial in the fabrication of linear and non-linear optoelectronic devices and circuits.

References

1. Cahangirov S, Topsakal M, Aktu E, Ciraci S (2009) Two- and one-dimensional honeycomb structures of silicon and germanium. Phys Rev Lett 102:236804, 1–4
2. Zhuo Z, Wu X, Yang J (2018) Two-dimensional silicon crystals with sizable band gaps and ultrahigh carrier mobility. Nanoscale 10:1265–1271
3. Liu CC, Feng W, Yao Y (2011) Quantum spin hall effect in silicene and two-dimensional germanium. Phys Rev Lett 107:076802
4. Liu CC, Jiang H, Yao Y (2011) Low-energy effective Hamiltonian involving spin-orbit coupling in silicene and two-dimensional germanium and tin. Phys Rev B 84:195430
5. Ezawa M (2012) Valley-polarized metals and quantum anomalous hall effect in silicene. Phys Rev Lett 109:055502
6. Wang Y, Zheng J, Ni Z et al (2012) Half-metallic silicene and germanene nanoribbons: towards high-performance spintronics device. Nano Breif Rep Rev 5:1250037
7. Houssa M, Pourtois G, Afanas'ev VV, Stesmans A (2010) Electronic properties of two-dimensional hexagonal germanium. Appl Phys Lett 96:082111
8. Lebègue S, Eriksson O (2009) Electronic structure of two-dimensional crystals from ab initio theory. Phys Rev B 79:115409
9. Pang Q, Zhang C, Li L, Fu Z, Wei X, Song Y (2014) Adsorption of alkali metal atoms on germanene: a first-principles study. Appl Surf Sci 314:15–20
10. Rubio-pereda P, Takeuchi N (2015) Adsorption of organic molecules on the hydrogenated germanene: a DFT study. J Phys Chem C 119:27995–28004

11. Mortazavi B, Dianat A, Cuniberti G, Rabczuk T (2016) Application of silicene, germanene and stanene for Na or Li ion storage. Electrochim Acta 213:865–870
12. Pang Q, Zhang Y, Zhang J, Xu K (2011) Electronic and magnetic properties of pristine and chemically functionalized germanene nanoribbons. Nanoscale 3:4330–4338
13. Houssa M, Scalise E, Sankaran K, Pourtois G, Afanas VV (2011) Electronic properties of hydrogenated silicene and germanene. Appl Phys Lett 98:223107
14. Voon LCLY, Sandberg E, Aga RS, Farajian AA (2010) Hydrogen compounds of group-IV nanosheets. Appl Phys Lett 97:163114, 13–16
15. Takeda K, Shiraishi K (1989) Electronic structure of Si-skeleton materials. Phys Rev B 39:28–37
16. Bianco E, Butler S, Jiang S, Restrepo OD, Wind W, Goldberger JE (2013) Stability and exfoliation of germanane: a germanium graphane analogue. ACS Nano 7:4414–4421
17. Yao Q, Zhang L, Kabanov NS et al (2018) Bandgap opening in hydrogenated germanene. Appl Phys Lett 112:171607
18. Wang XQ, Li HD, Wang JT (2012) Induced ferromagnetism in one-side semihydrogenated silicene and germanene. Phys Chem Chem Phys 14:3031–3036
19. Liu J, Yu G, Shen X et al (2017) The structures, stabilities, electronic and magnetic properties of fully and partially hydrogenated germanene nanoribbons: a first-principles investigation. Phys E 87:27–36
20. Xiao P, Fan X, Liu L (2014) Tuning the electronic properties of half- and full-hydrogenated germanene by chlorination and hydroxylation: a first-principles study. Comput Mater Sci 92:244–252
21. Santosh R, Kumar V (2019) The pressure effect on structural, electronic and optical properties of hydrogenated graphene: a first-principle study. J Electron Mater 18:770–778
22. Kumar V, Santosh R (2019) First-principle calculations of structural, electronic, optical and thermodynamic properties of fluorinated graphene. Mater Sci Eng B 246:127–135
23. Santosh R, Kumar V (2019) First-principle calculations of structural, electronic, optical and thermodynamic properties of hydrofluorinated graphene. Solid State Sci 94:70–76
24. Segall MD, Lindan PJD, Probert MJ et al (2002) First-principles simulation: ideas, illustrations and the CASTEP code. J Phys Condens Matter 14:2717–2744
25. Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. Phys Rev Lett 77:3865
26. Vanderbilt D (1990) Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. Phys Rev B 41:7892
27. Fischer TH, Almlof J (1992) General methods for geometry and wave function optimization. J Phys Chem C 96:9768–9774
28. Momida H, Hamada T, Takagi Y et al (2007) Dielectric constants of amorphous hafnium aluminates: first-principles study. Phys Rev B 75:195105
29. Kronig RL (1926) On the theory of dispersion of X-rays. J Opt Soc Am 12:547–557
30. Sahin S, Ciftci YO, Colakoglu K, Korozlu N (2012) J Alloys Compd 529:1–7
31. Trivedi S, Srivastava A, Kurchania R (2014) J Comput Theor NanoSci 11:1–8