The transformative effects of hydrogenation on the properties of germanene

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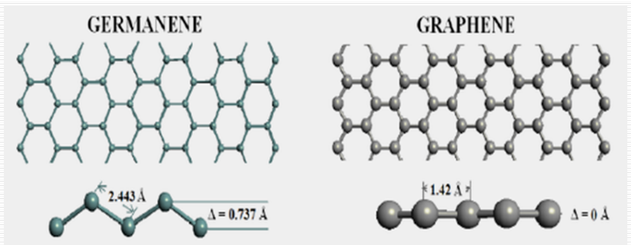
1. INTRODUCTION

• Germanene: 2D material analogous to graphene but with a small band gap (~0.03 eV).

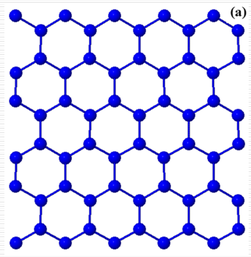


band gap: 0,85 eV

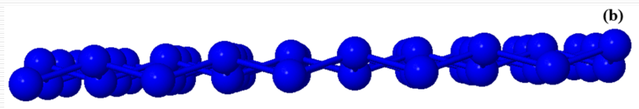
germanium ~ 0,67 eV
Matthes et al, Physical review B, 2013

0,02 eV from Matthes
Matthes et al, J Phys Cond. Mat.,2013

0,033 eV from Safa
Safa et al,Springer handbook, 2016



• Hydrogenation can modify its geometry, electronic, and vibrational properties.

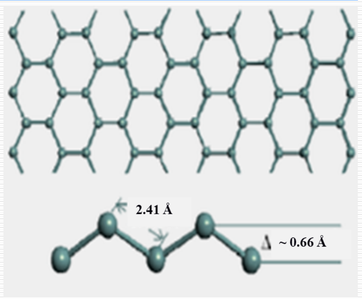


• Aim: Study adsorption, and diffusion of H on germanene via DFT.

2. CALCULATION

❖Simulation methods:

➢*DFT*
➢*The SIESTA*
[J. Phys. Chem. C 111 (2007) 13886]
➢System of (5x4) unit cell
➢k-point: 1 to 221



❖Zero-point energy:

Energy of a harmonic oscillation: $E = \frac{1}{2}kx^2$

Compression frequency: $\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}}$

Zero-point energy: $\varepsilon = \frac{h\nu}{2} = \frac{hc}{2\lambda} = \frac{hc\tilde{\nu}}{2}$

3. RESULTS AND DISCUSSIONS

3.1. Hydrogen adsorption on germanene surfaces

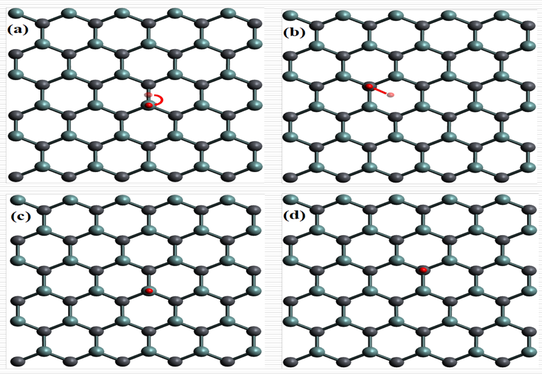


Fig. 3.1. Hydrogen adsorption on different sites.

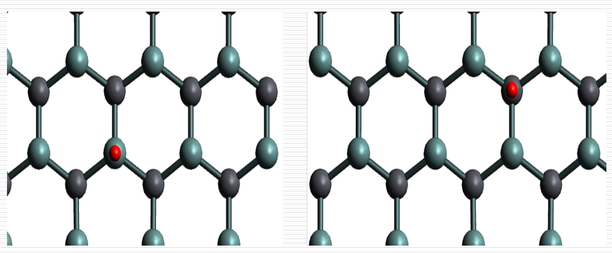


Fig. 3.2. The H atoms are adsorbed only on T_1 and T_2 sites.

[Eur Phys. J. B, 2010, 76, 481–486]

$$E_{ads} = E_{tot}(N_H) - E_{tot}(0) - \frac{N_H}{2}E_{H_2},$$

Site	Fixed germanene				Unfixed germanene			
	d_{Ge-H}	d_{Ge-Ge}	h	E_{ads}	d_{Ge-H}	d_{Ge-Ge}	h	E_{ads}
T_1	1.58	2.49	0.00	-1.83	1.58	2.56	0.00	-1.89
T_2	1.67	2.49	0.00	-1.29	1.59	2.56	1.02	-1.86
							(0.50-0.70)	

Table 3.2. The optimized Ge–H bond length (d_{Ge-H}, Å), the Ge–Ge bond length of the adsorbent Ge atom with its neighbors (d_{Ge-Ge}, Å) the vertical displacement of the adsorbent Ge atom (h, Å) , and the hydrogen adsorption energies (E_{ads}, eV).

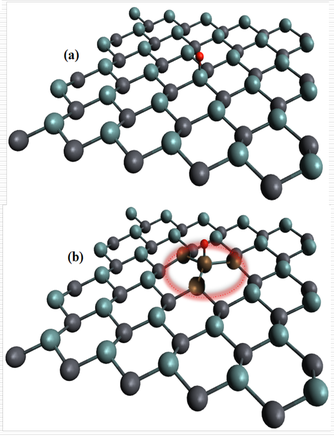


Fig. 3.3. The adsorption of H atoms (red balls) on the T_1 site (a) and T_2 site (b) at the full (5x4) cell relaxation.

(The results obtained from [Science 323 (2009) 610] are parenthesized)

3.2. Vibrational Properties and Zero-Point Energy

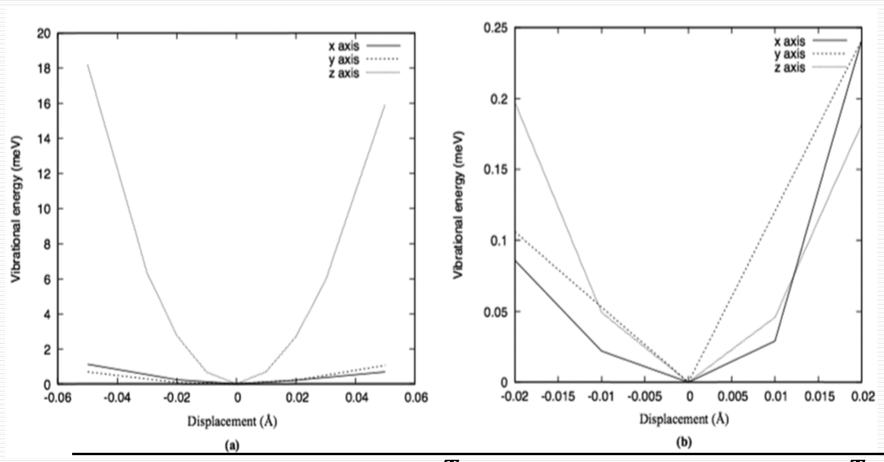


Fig. 3.5. The vibrational energy of the adsorbed hydrogen atom, which is displaced around the equilibrium position along the x, y, and z axes.

	T_1			T_2		
	x	*y*	*z*	*x*	*y*	*z*
k (eV/ Å²)	0.679	0.692	13.656	0.861	0.428	9.521
f (cm⁻¹)	26.907	27.158	120.621	30.295	21.174	100.720
ZPE (meV)	1.668	1.684	7.478	1.878	1.313	6.244
Total ZPE (eV)		0.011			0.009	
Total E_{ads} (eV)		-1.883			-1.849	

Table 3.3. Force constants (k, eV / Å²), vibrational frequencies (f, cm⁻¹), ZPE (eV) and the total adsorption energy (Eads, eV) of H adsorption on the optimized fixed germanene.

3.3. Phonon Spectrum and Structural Stability

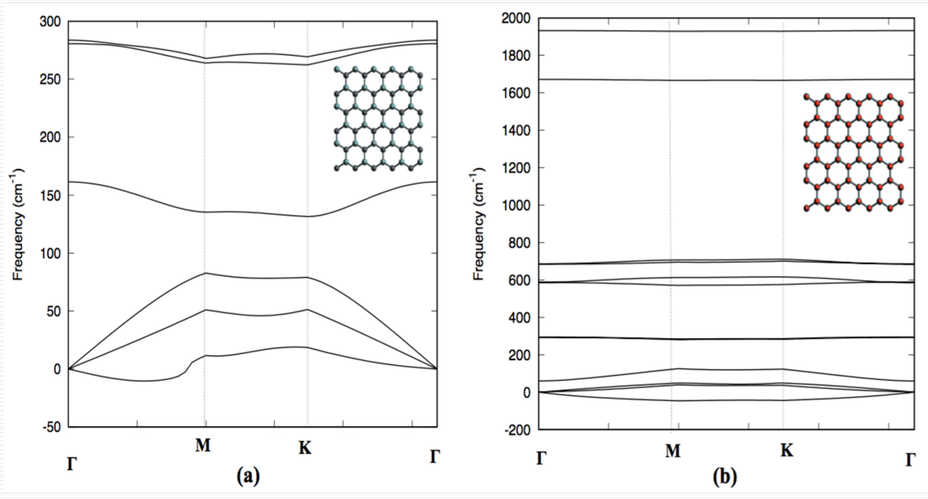


Fig. 3.6. phonon spectrum of (a) germanene, và (b) hydrogenation of germanene

3.4. Hydrogen–Hydrogen Interactions

Interaction pair	E_{int}
$H_{T1} - H_{T1}$	0.093
$H_{T2} - H_{T2}$	0.065
$H_{T1} - H_{T2}$	-0.473

Two adsorbed hydrogen atoms exhibit site-dependent interactions:
• Same-type sites (T_1–T_1 or T_2–T_2): Weak repulsion ($E_{int} > 0$)
• Different-type sites (T_1–T_2): Attractive interaction ($E_{int} = -0.473$ eV)
This suggests the possibility of periodic hydrogenation patterns on germanene surfaces.

Table 3.4. The interaction energies (E_{int}, eV) of the two hydrogen atoms on the germanene surface

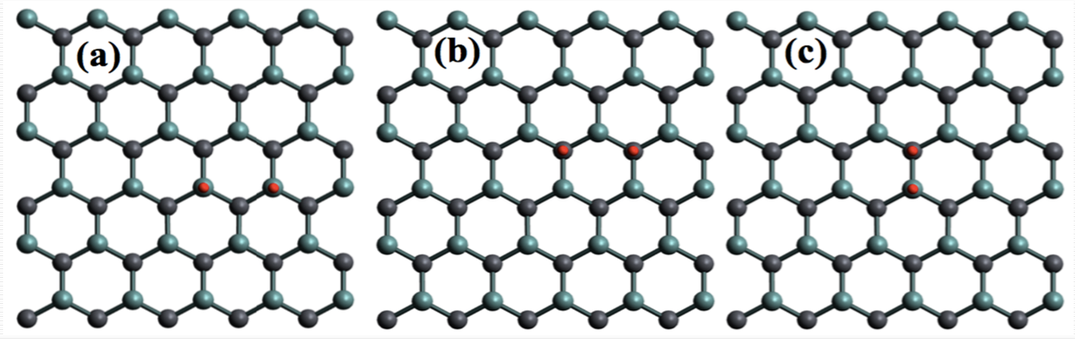


Fig. 3.7. The two adsorbed hydrogen atoms (red ball) on the two T_1 sites (a), two T_2 sites (b), and T_1 and T_2 sites (c).

4. CONCLUSION

❖*Hydrogen adsorption on germanene structures was studied using DFT calculations.*
❖*Adsorption sites: peaks T_1 and T_2.*
❖*Local germanene surface curvature on T_2.*
❖*The fluctuation of H along the z-axis is the largest.*
❖*Two adjacent hydrogen atoms of the same type repel each other, and two hydrogen atoms of different types attract each other.*