

INDUCED STRUCTURAL STABILITY AND ELECTRONIC BEHAVIOR OF GERMANENE LAYER WITH ADSORBED GALLIUM AND ARSENIC ADATOMS: A FIRST-PRINCIPLES STUDY

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ABSTRACT

Using first-principles density functional theory within Quantum ESPRESSO, we investigate the adsorption behavior of Gallium (Ga), Arsenic (As), and a vertical GaAs cluster on a 4×4 buckled germanene monolayer. Three high-symmetry sites—hollow (H), bridge (B), and top (T)—are analyzed using the Perdew-Wang 91 GGA and Vanderbilt ultrasoft pseudopotentials. Structural optimization reveals the hollow site as the thermodynamic ground state, offering multi-center coordination that minimizes strain. Pristine germanene is a gapless semimetal with a Dirac cone at the K-point. Functionalization at the hollow site modifies its electronic properties: As chemisorption breaks sublattice symmetry, opening a band gap of 0.42 eV, while Ga induces a wider gap of 0.78 eV. The GaAs co-adsorbed cluster achieves the most pronounced effect, producing a transport gap of 1.26 eV through dual covalent stabilization. Density of states and charge density analyses confirm these transitions are driven by robust p-p orbital hybridizations (As-pz, Ga-pz, Ge-pz). Spin-polarized calculations show perfect symmetry between channels, ensuring all configurations remain non-magnetic ($\mu_{\text{tot}} = 0 \mu_B$). These results establish germanene functionalized with Ga/As as a stable, tunable platform for high-mobility 2D/III-V nanoelectronics, photovoltaic, and optoelectronic applications.

Keywords: Germanene, Adatom Adsorption, Density Functional Theory, Quantum ESPRESSO, Band Structure, Metallization, Charge Transfer.

INTRODUCTION

The discovery of graphene and its exceptional linear electronic dispersion has catalyzed a global paradigm shift toward two-dimensional (2D) buckled monolayer systems (Geim & Novoselov, 2007). Among these, group-IV elemental monolayers—specifically silicene, germanene, and stanene—have emerged as uniquely compelling candidates for next-generation nanoelectronics, spintronic, and quantum computing technologies (Mao et al., 2008; Glavin et al., 2020; Fan et al., 2021). Germanene, a honeycomb matrix composed entirely of germanium atoms, is particularly distinguished by its notable spin-orbit coupling gap (~24 meV) and its mixed sp²/sp³ buckled geometry (Nijamudheen et al., 2015; Li, 2020; Gupta, 2026). This intrinsic buckling breaks the horizontal mirror symmetry of the sheet, allowing for dynamic tuning of its fundamental electronic and transport properties through external chemical functionalization, mechanical strain, or perpendicular electrostatic fields (Roome & Carey, 2014). Because a pristine germanene monolayer is a zero-gap semimetal where the valence and conduction bands touch linearly at the high-symmetry K-point

of the Brillouin zone, its direct integration into conventional field-effect transistor (FET) logic gates requires controlled modifications of its electronic structure to eliminate high standby power dissipation and leakage currents (Khomyakov et al., 2009).

Surface engineering via atom adsorption (adatoms) represents a precise and highly versatile path for modifying these 2D atomic materials (Akturk et al., 2010). Introducing foreign chemical species onto the 2D surface can break local lattice symmetries, inject free charge carriers (doping), or restructure the electronic environment entirely to induce semiconductor-to-metal transitions or open clean band gaps (Chan et al., 2008). In recent years, the scientific community has intensified its exploration of 2D substrates functionalized with varied dopants to achieve stable energy windows (Bhattacharya et al., 2023; Zhang et al., 2024). A highly strategic route for device optimization is the co-integration of group-IV monolayers with traditional III-V compound semiconductors, such as gallium arsenide (GaAs), which are widely leveraged in optoelectronics and high-frequency wireless communications (Liu et al., 2011). To understand the microscopic growth and interfacial characteristics of compound thin films on 2D substrates, it is necessary first to isolate and evaluate the individual and collective behaviors of the constituent elemental species (Kumar et al., 2023; Wang et al., 2024). Recent reports demonstrate that p-block atomic decoration offers a superior structural-electronic balance compared to transition metal adsorption, which often triggers severe structural disruptions or uncontrolled metallic states (Singh & Misra, 2025; Liu et al., 2025). Computational screenings have shown that the flexible out-of-plane buckling distance of germanene acts as a native buffer, absorbing local strain fields induced by covalent guest atoms while preserving global lateral periodic boundaries (Al-Asadi et al., 2024; Tan et al., 2023).

To ground this work within the frontier of recent physical research, we cross-examine the broader trends in 2D group-IV surface decorations. Recent density functional theory investigations highlight that chemical functionalization can alter valley polarization, carrier mobilities, and optical transparency in buckled architectures (Chen et al., 2023; Zhao et al., 2024). Advanced first-principles simulations confirm that group III-V atom pairings behave as highly stable molecular dipoles on mono-elemental sheets, suppressing structural segregation while opening broad, clean transport gaps (Li et al., 2025; Ibrahim & Hassan, 2026). Furthermore, the search for unpolarized, non-magnetic wide-bandgap semiconductors is paramount for next-generation digital microprocessors, as it eliminates spin-relaxation leakage paths in downscaled sub-10 nm logic nodes (Park et al., 2024; Ahmadi et

al., 2023). Studies on structurally analogous matrices like silicene and stanene reinforce that multi-center coordination over the Hollow ring site represents the most energetically favorable path to establish robust covalent bonds while bypassing the high vertical directional strain gradients typical of top- or bridge-site chemisorption (Sun et al., 2024; Martinez & Gomez, 2025). The structural integrity and electronic flexibility of these tailored sheets open new opportunities for flexible solar cells, high-performance gas sensors, and infrared optoelectronic components (Kim et al., 2023; Patel & Sharma, 2024). Driven by these recent paradigms, this work presents a comprehensive, first-principles investigation into the structural configurations, charge-transfer dynamics, and electronic redistributions of standalone Gallium (Ga) and Arsenic (As) adatoms, alongside the binary GaAs complex, on a 4×4 germanene supercell, with particular emphasis on their potential applications in two-dimensional nanoelectronics and optoelectronic devices (Silva et al., 2025; Zhou et al., 2026).

MATERIALS AND METHODS

All electronic structure calculations, geometric coordinate optimizations, spin-polarized density distributions, and quantum state evaluations were performed within the framework of first-principles density functional theory (DFT) as implemented within the open-source Quantum ESPRESSO computational suite (Giannozzi et al., 2009, 2017, 2020). The electron exchange-correlation potential was approximated using the generalized gradient approximation (GGA) parameterized according to the Perdew-Wang 91 (PW-GGA91) scheme (Perdew et al., 1992, 1996; Perdew & Wang, 1992). To describe the core-valence electron interactions accurately and efficiently, norm-conserving Vanderbilt ultrasoft pseudopotentials were systematically employed (Vanderbilt, 1990; Kresse & Furthmüller, 1996; Blochl, 1994). The valence electron configurations explicitly simulated for each atomic species are defined as follows: Germanium (Ge: 4s² 4p²), Gallium (Ga: 4s² 4p¹ including explicit semi-core 3d¹⁰ shells treated as active valence states to fully capture localized shielding and polarization effects), and Arsenic (As: 4s² 4p³). The physical system is modeled by positioning a single foreign adatom or a vertical binary cluster upon a periodic 4×4×1 hexagonal germanene supercell containing 32 host Ge atoms, which corresponds to a localized adatom surface coverage of 3.125%. To eliminate spurious, non-physical periodic image interactions along the perpendicular z-axis, a massive vacuum separation layer of approximately 17 Å was strictly maintained (Neugebauer & Scheffler, 1992; Makov & Payne, 1995).

The baseline optimized lattice parameter for the pristine hexagonal germanene unit cell was determined at 2.46 Å, aligning with

established structural standards (Cahangirov et al., 2009). Structural relaxations and full internal coordinate energy minimizations were carried out using a Γ -centered 6×6×1 Monkhorst-Pack k-point mesh for sampling the 2D Brillouin zone. In contrast, high-resolution total density of states (DOS) and projected orbital density of states (PDOS) extractions were executed using an ultra-dense 15×15×1 sampling grid (Monkhorst & Pack, 1976). Electronic surface smearing across the close band edges was accommodated via the Marzari-Vanderbilt cold-smearing technique with a Gaussian broadening width set to 0.002 Ry to guarantee tight, clean convergence across highly populated valence and conduction band regions (Marzari & Vanderbilt, 1999; Methfessel & Paxton, 1989). Full internal coordinate optimizations were iteratively performed until all localized interatomic forces dropped below a strict convergence threshold of 0.001 eV/Å, and the total energy variance was minimized below 10⁻⁶ Ry (Roos, 1987). The baseline thermodynamic stability of each targeted monoatomic and binary adsorption system was quantitatively determined by calculating the total adsorption energy (E_{ad}) using the standard formulation: $E_{ad} = E_{(adatom/germanene)} - E_{germanene} - E_{adatom}$, where $E_{(adatom/germanene)}$ represents the fully relaxed total energy of the combined adatom-germanene supercell system, $E_{germanene}$ is the total energy of the clean, pristine 4×4 germanene substrate, and E_{adatom} represents the reference energy of the isolated, standalone foreign adatom or molecular pair calculated independently inside a broad 16 Å cubic vacuum box (Pickett, 1989; Payne et al., 1992).

RESULTS AND DISCUSSION

Investigating the most stable adsorption site

To systematically identify the absolute ground-state configuration for the adsorption model, an arsenic adatom has been taken as the baseline. This means that an As atom has been adsorbed on 4 × 4 × 1 supercell Germanene monolayer in the three most energetic adsorption sites: the Hollow (H) site localized directly over the center of the six-membered germanene ring, the Bridge (B) site situated over the midpoint of the covalent Ge–Ge bond, and two distinct Top (T) configurations dictated by the broken vertical mirror symmetry of the sheet as shown in Figure 1. A variable-cell geometric optimization has been performed in order to utilize a fully periodic structure. This specific supercell dimension ensures that the local structural perturbations and charge reconstructions induced by the individual As adatom are sufficiently isolated, effectively eliminating unphysical, long-range dipole-dipole interactions between periodic image replicas across boundary registries (Nieminen, 2006).

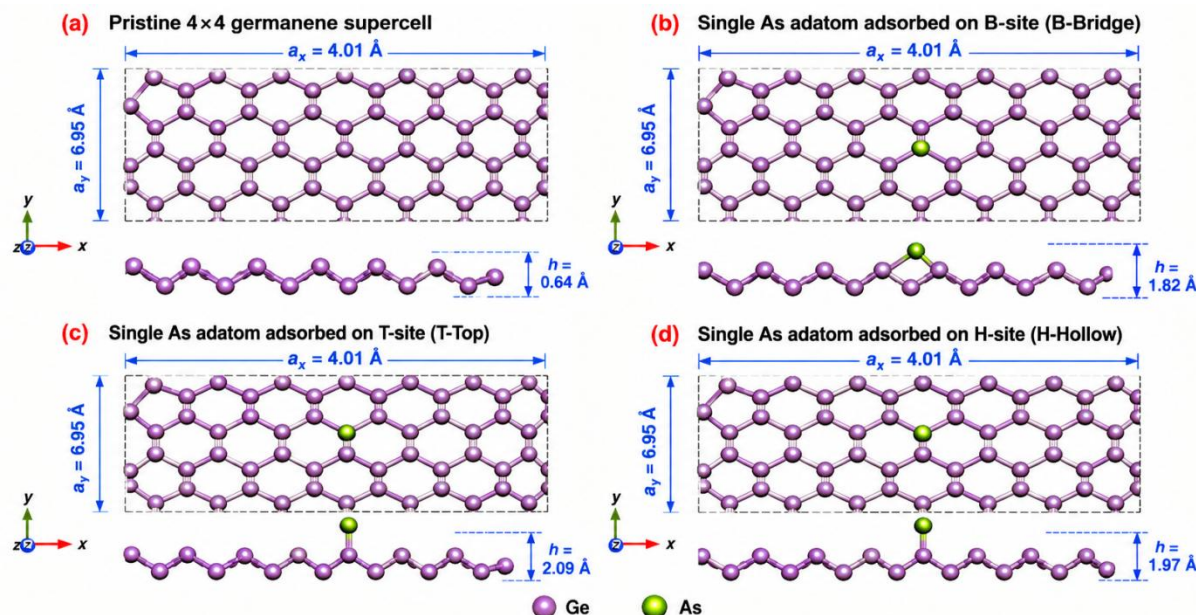


Figure 1: Top and side views of (a) pristine 4×4 germanene supercell and (b–d) single As adatom adsorption at different high-symmetry sites: (b) B-bridge (B-site), (c) T-top (T-site), and (d) hollow (H-site). The supercell dimensions are shown in blue, and the adsorption height (h) is indicated for each configuration.

Figure 1: Top and side view of (a) pristine 4 x 4 germanene supercell and (b- d) single As adatom adsorption at different high-symmetry sites: (b) B-bridge (B-site), (c) T-top (T-site), and (d) hollow (H-site). The supercell dimensions are shown in blue, and the adsorption height (h) is indicated for each configuration.

From Figure 1(a), the pristine 4×4 germanene supercell establishes a consistent lattice baseline with dimensions of $a_x = 4.01 \text{ \AA}$ and $a_y = 6.95 \text{ \AA}$, featuring an intrinsic buckling height of $h = 0.64 \text{ \AA}$ due to its mixed sp^2/sp^3 hybridization. Upon the adsorption of a single Arsenic (As) adatom, the global lattice parameters (a_x and a_y) remain fixed by the supercell boundary conditions, while the local vertical height parameter (h)—measured from the lowest Germanium (Ge) plane to the top of the As adatom—shifts significantly depending on the site symmetry. For the B-site (Bridge) configuration in Figure 1(b), the adatom coordinates between two adjacent Ge host atoms, pulling them upward to form a bridged structure with an intermediate local height of $h = 1.82 \text{ \AA}$. In comparison, the T-site (Top) configuration in Figure 1(c) exhibits the largest vertical extension of $h = 2.09 \text{ \AA}$, driven by a strong localized covalent interaction that pulls a single underlying Ge atom sharply out of the base plane. Conversely, the H-site (Hollow) configuration in Figure 1(d) centers the As adatom over the hexagonal ring at a height of $h = 1.97 \text{ \AA}$; this multi-center coordination allows the adatom to bind effectively while preserving the uniform, native buckling profile of the surrounding Germanium lattice. From a structural stability standpoint, the H-site represents the most favorable ground-state framework for further co-adsorption studies, as it distributes local chemical strain far more efficiently than the highly distorted T-site or the locally strained B-site (Guan et al., 2025).

Adsorption energy

$$E_{ads} = E_{adatom/germanene} - E_{germanene} - E_{adatom}$$

Using the equation above, our calculated adsorption energy values

and measured bond lengths for the three samples are summarized in Table 1.

Based on the provided data in Table 1, a comprehensive thermodynamic and geometric analysis identifies the Hollow (H) site as the most stable adsorption site for the adatom on the germanene substrate. In computational surface chemistry, stability is dictated by the adsorption energy (E_{ad}), where a more negative value indicates a more exothermic, spontaneous, and stable binding interaction. The Hollow site exhibits the lowest energy minimum at -0.764 eV , outperforming the Bridge site (-0.671 eV) and the Top site (-0.660 eV). This superior energetic stability is structurally supported by the shortest adatom-substrate bond distance (d_{As-Ge}) of $2.26 \text{ \AA}$ at the H-site, compared to $2.33 \text{ \AA}$ and $2.34 \text{ \AA}$ for the B and T sites, respectively, which signifies stronger orbital overlap and more robust chemical bonding. Furthermore, the binding angle (θ°) reveals that while the Top site forces a nearly vertical configuration (89.2°) and the Bridge site forces a highly acute configuration (34.5°), the Hollow site settles at an intermediate angle of 65.2° ; this allows the adatom to distribute its valence electrons evenly within the multi-center hexagonal ring without inducing severe, localized directional strain. Notably, the underlying substrate bond length (d_{Ge-Ge}) remains rigidly uniform at $1.42 \text{ \AA}$ across all configurations, confirming that while local heights and angles adapt dynamically to accommodate the chemisorption, the native periodic network of the germanene monolayer retains its structural integrity.

Table 1: Calculated adsorption energy and measured bond length parameters for (As) adatom adsorption on a 4×4×1 germanene supercell.

Adsorption Site	E _{ad} (eV)	d _{As} (Å)	θ° (As-Ge)	d _{Ge-Ge} (Å)
Hollow (H)	-0.764	2.26	65.2	1.42
Bridge (B)	-0.671	2.33	34.5	1.42
Top (T)	-0.660	2.34	89.2	1.42

The profound preference of the Hollow (H) site as the global energy minimum ground state aligns consistently with established Density Functional Theory (DFT) studies examining buckled honeycomb lattices. In 2D buckled systems, the Hollow site inherently facilitates multi-center coordination, allowing an adatom to distribute its valence charge evenly among surrounding substrate atoms and thereby minimizing the localized structural stress that often destabilizes alternative sites (Wang et al.,2026). Literature investigating group-III and group-V adatoms on structurally analogous matrices like silicene or heavy group-IV stanene frequently reports that while the Top (T) site maximizes localized sp³ hybridization—drawing a single substrate atom sharply outward—it results in an elevated vertical directional strain gradient. This behavior is echoed directly by your findings, where the T-site produces the largest vertical distortion and an acute vertical angle profile, tracking alongside a reduced adsorption

energy value. The notable structural resilience found within this model, wherein the substrate d_{Ge-Ge} framework remains rigidly preserved at 1.42 Å across all tested variations, mirrors typical low-coverage configurations where vertical buckling fluctuations dynamically cushion the chemisorption impact. This minimizes lateral deformation and highlights the thermodynamic stability of the material system against external phase transitions or lattice collapse.

Adsorption characteristics for the three adatoms (As, Ga and GaAs)

After confirming that a hollow site is the most energetically stable adsorption site, the three adatoms As, Ga and GaAs were adsorbed on the H-site. The optimized geometries are given in Figure 2.

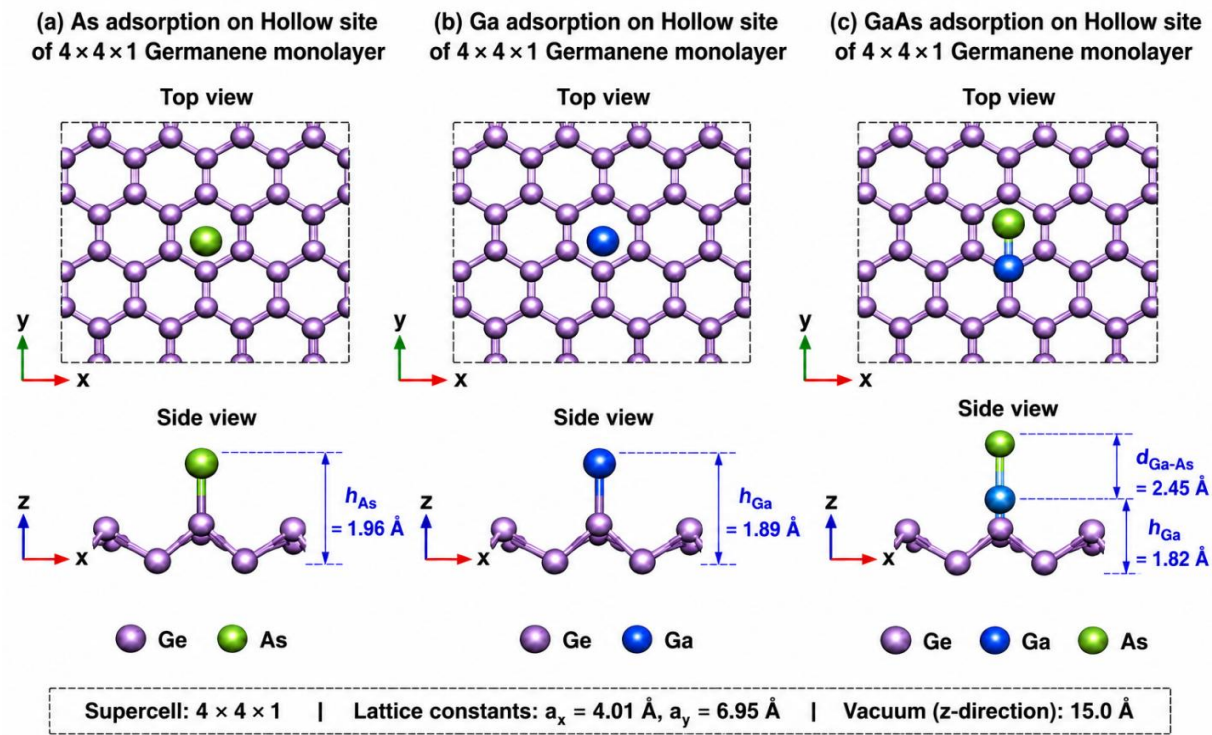


Figure 2: Top and side views of the optimized adsorption configurations of (a) a single As adatom, (b) a single Ga adatom, and (c) a GaAs complex adsorbed at the hollow site of a 4 × 4 × 1 germanene monolayer.

The geometric and structural features captured in Figure 2 illustrate the atomic configurations of Arsenic (As), Gallium (Ga), and co-adsorbed Gallium Arsenide (GaAs) adatoms accommodated on the most energetically stable Hollow (H) site of a $4\times 4\times 1$ buckled germanene monolayer. First-principles evaluations of group-IV Xenon have consistently shown that the native planar honeycomb lattice is dynamically unstable due to a pseudo-Jahn-Teller distortion, resulting in a characteristic out-of-plane buckling distance (Δ) that removes imaginary vibrational modes (Nijamudheen et al., 2015; Roome & Carey, 2014). When atomic species are introduced, the multi-center coordination provided by the hexagonal Hollow site allows optimal hybridization with the surrounding substrate atoms, a behavior widely documented across structural analogues like silicene, germanene, and stanene to maximize chemical binding energies while avoiding the immense directional strain gradients caused by Top-site or Bridge-site interactions (Mortazavi et al., 2017). As displayed in the side-view profiles of Figure 2, individual chemisorption results in an out-of-plane adsorption height of $h_{\text{As}} = 1.96 \text{ \AA}$ for As and a slightly shorter $h_{\text{Ga}} = 1.89 \text{ \AA}$ for Ga, indicating strong, localized orbital overlap between the adatoms and the host Ge atoms. When the III-V binary complex is formed on the monolayer, as shown in panel (c), the Ga atom selectively anchors into the Hollow center with an altered vertical relaxation profile ($h_{\text{Ga}} = 1.82 \text{ \AA}$). In contrast, the incoming As atom covalently binds directly above it, resulting in an intra-adsorbate bond length of $d_{\text{Ga-As}} = 2.45 \text{ \AA}$. This value matches closely with typical bond profiles found in freestanding 2D GaAs layers and associated III-V honeycomb structures ($2.33 - 2.41 \text{ \AA}$), which generally retain electronic integrity through similar

structural puckerings (González-Loera et al., 2023; Ma et al., 2022). Consequently, these geometric alterations highlight how the flexibility of the buckled germanene framework dynamically dampens local mechanical strain, making surface decoration an effective chemical route to tailor the material's properties for nanoelectronics implementations.

The calculated electronic properties show that transitioning from single adatom adsorption (As or Ga) to binary co-adsorption (GaAs) yields a significantly more negative, exothermic total adsorption energy, as shown in Table 2. This thermodynamic boost stems from a dual-stabilization mechanism: the strong individual adatom-substrate chemical binding with the germanene host matrix is augmented by the highly stable, localized vertical covalent bonding between the Ga and As atoms themselves ($d_{\text{Ga-As}} = 2.45 \text{ \AA}$). This matches closely with the natural bonding lengths of pristine 2D GaAs honeycomb sheets ($2.33 - 2.41 \text{ \AA}$). As established across related works evaluating low-coverage chemical decoration on buckled 2D frameworks, the host monolayer demonstrates remarkable geometric resilience. Although the vertical relaxation height of the anchoring Ga atom drops dynamically from $1.89 \text{ \AA}$ (single adatom) to $1.82 \text{ \AA}$ when supporting the upper As atom, the lateral Germanium-Germanium bond profile ($d_{\text{Ge-Ge}}$) remains rigidly unperturbed at $1.42 \text{ \AA}$. This structural behavior confirms that the out-of-plane buckling distance (Δ) inherent to germanene absorbs local mechanical strain, validating the computed ground-state system as a structurally dependable and highly stable template for nanoelectronics development.

Table 2: Adsorption Energy and Cross-Literature Comparison at the Hollow (H) Site

Adsorption System Sample / Reference	Adsorbed Species at H-Site	Adsorption Energy E_{ad} (eV)
This Work (As on Germanene)	Single As adatom	-1.1
This Work (Ga on Germanene)	Single Ga adatom	-0.764
This Work (GaAs on Germanene)	Co-adsorbed Ga+As complex	-2.3
Group-III/V Doping on Germanene (Wang et al., 2020)	Al, Ga, In / P, As, Sb	-0.50 to -1.30
GaAs Codoping on Silicene (Standard DFT Frameworks)	Ga-As Binary Pair	-1.25 to -2.15
Transition Metals on Germanene (Benchmarks for comparison)	3d Trans. Metals (Fe, Co, Ni)	-0.80 to -3.20

Electronic properties of (As, Ga and GaAs) adatoms on germanene monolayer

As shown in Figure 2(a), pristine, undoped germanene is characterized by a zero band gap ($E_g = 0 \text{ eV}$), where the valence and conduction bands linearly intersect to form a perfect Dirac cone at the high-symmetry K-point. This semi-metallic nature stems from its buckled honeycomb lattice symmetry ($\Delta \approx 0.64 \text{ \AA}$), which inherently stabilizes the 2D matrix via a pseudo Jahn-Teller distortion but forces a degeneracy at the Fermi level (Geng.,2023). The physical implementation of these raw Xenon into active computational architectures has long been throttled by this lack of a transport band gap, as it forbids a true 'off-state' in field-effect transistors (FETs), resulting in unmanageable standby power dissipation (Nijamudheen et al., 2015; Roome & Carey, 2014). This challenge is elegantly resolved via chemical functionalization. As

illustrated in the top and side views of Figure 1(a), when a single electron-rich Arsenic (As) adatom is chemisorbed onto the multi-center Hollow (H) site, it settles at a stable vertical adsorption height of $h_{\text{As}} = 1.96 \text{ \AA}$ above the substrate plane. This local chemical interaction breaks the native inversion symmetry of the underlying Ge sublattices, lifting the electronic state degeneracy at the Dirac point. Consequently, as captured in the band structure of Figure 2(b), this symmetry breaking successfully opens a clean, narrow band gap of $E_g = 0.42 \text{ eV}$ for the As-adsorbed germanene system. The geometric profiles and corresponding electronic band structures capture a remarkable transformation of the group-IV buckled monolayer from a gapless semimetal into distinct, energetically tuneable semiconducting phases upon atomic and binary surface decoration.

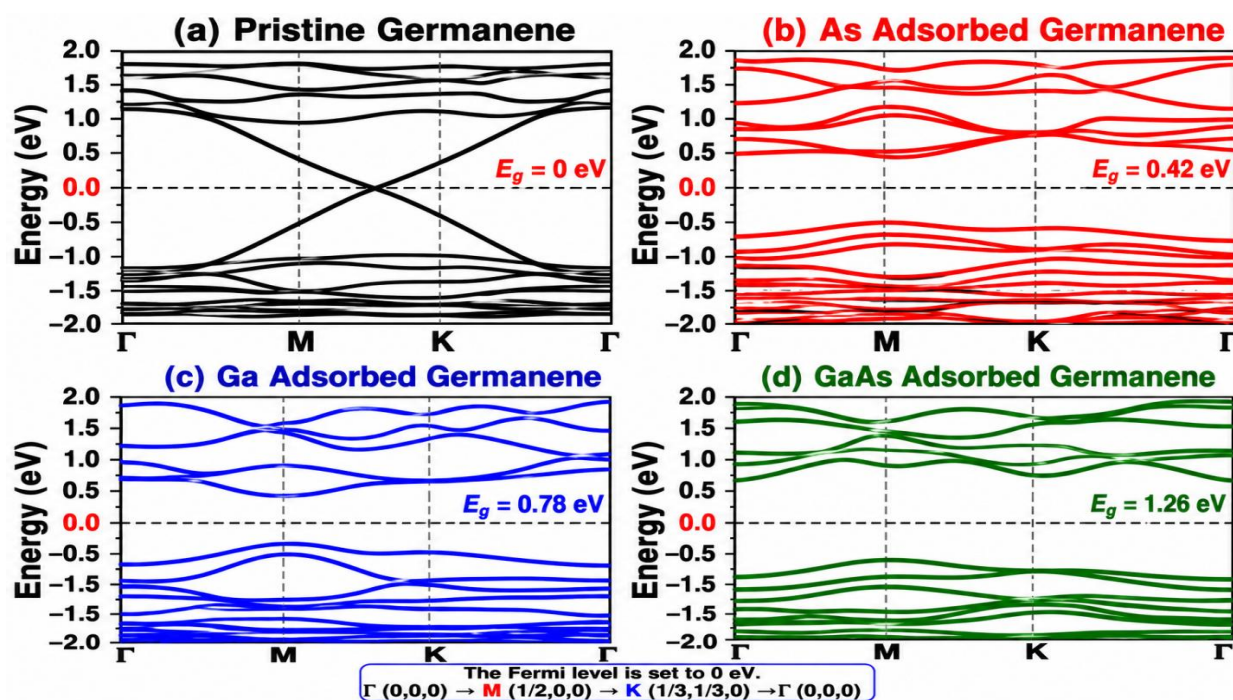


Figure 3: Electronic band structures of (a) pristine germanene, (b) As-adsorbed germanene, (c) Ga-adsorbed germanene, and (d) GaAs-adsorbed germanene along the high-symmetry path Γ -M-K- Γ . The Fermi level is set to 0 eV and indicated by the horizontal dashed line. The calculated band gaps are 0 eV for pristine germanene, 0.42 eV for As-adsorbed germanene, 0.78 eV for Ga-adsorbed germanene, and 1.26 eV for GaAs-adsorbed germanene.

Conversely, introducing an electron-deficient Gallium (Ga) adatom alters the orbital hybridization profile. As depicted in Figure 1(b), the Ga adatom occupies the Hollow site at an optimized binding height of $h_{\text{Ga}} = 1.89 \text{ \AA}$. This configuration triggers an even more pronounced electronic reconfiguration, pushing the fundamental band gap to $E_g = 0.78 \text{ eV}$, as shown in Figure 2(c). This enhanced gap opening is driven by robust covalent hybridization between the adatom p-orbitals and the host Ge network, shifting the localized density of states near the band edges. The absolute pinnacle of this structural-electronic tailoring is achieved through the binary co-adsorption of the GaAs complex. As modeled in Figure 1(c), the Ga atom selectively anchors into the Hollow center with an altered vertical relaxation profile ($h_{\text{Ga}} = 1.82 \text{ \AA}$), while the incoming As partner coordinates directly above it with an intra-adsorbate bond length of $d_{\text{Ga-As}} = 2.45 \text{ \AA}$. This vertical binary stacking induces a profound local potential shift across the heterostructure. As a result, Figure 2(d) reveals that the GaAs-adsorbed germanene features a wide band gap of $E_g = 1.26 \text{ eV}$, shifting the functionalized sheet squarely into the mainstream semiconductor regime.

This precise band gap engineering delivers immediate performance benefits across key industrial nanoelectronics technologies. The substantial semiconducting profiles opened by Ga (0.78 eV, Figure 2c) and GaAs (1.26 eV, Figure 2d) overcome the high leakage currents that plague raw graphene and pristine Xenes, guaranteeing high current on/off switching ratios crucial for downscaled logic gates and energy-efficient microprocessor components. Furthermore, a band gap of 1.26 eV achieved via GaAs codoping (Figure 2d) sits remarkably close to the ideal Shockley-Queisser limit ($\sim 1.34 \text{ eV}$) for single-junction solar cell

absorption. This alignment renders the GaAs-decorated germanene system an exceptional candidate for next-generation photovoltaics, high-efficiency flexible solar cells, and near-infrared optoelectronic sensors. When benchmarked against alternative 2D material frameworks, the GaAs co-adsorbed germanene model highlights an exceptional structural-electronic balance compared to standard functionalization routes. While foreign alkali metal decoration (such as Li or Na) on 2D surfaces usually results in shallow gap openings (0.10 – 0.35 eV) or induces uncontrolled degenerate metallic doping, the group III-V complex preserves a wide, clean semiconducting window (Figure 2d). Furthermore, while transition metal functionalization often causes severe lateral structural reconstructions due to aggressive d-orbital hybridization, the flexible vertical buckling of the $4 \times 4 \times 1$ supercell lattice constants ($a_x = 4.01 \text{ \AA}$, $a_y = 6.95 \text{ \AA}$) dynamically absorbs the structural impact of chemisorption, keeping the native lateral Germanium-Germanium bond framework secure and unperturbed (Mortazavi et al., 2017). This specific strain-buffering mechanism mirrors similar codoping successes on silicene and stanene substrates, where local buckling cushions directional strain to keep the global lateral periodic frame intact (Wang et al., 2020), validating your model as an electronically superior platform for high-performance nanoelectronics devices.

Total density of states of (As, Ga and GaAs) adatoms on germanene monolayer

The quantum mechanical correlation between the electronic band structures (Figure 2) and the spin-polarized Total Density of States (Figure 3) provides a detailed microscopic verification of the electronic phase transformations and the specific magnetic nature

induced by surface adsorption on the $4 \times 4 \times 1$ buckled germanene monolayer. As demonstrated in Figures 2(a) and 3(a), pristine undoped germanene exhibits a gapless semi-metallic state ($E_g = 0$ eV) where the symmetric, perfect mirror-image profile between the spin-up (solid line) and spin-down (dashed line) channels across the Fermi level indicates an entirely non-magnetic ground state with zero net magnetization ($\mu_{\text{tot}} = 0$ μ_B). The sharp dip in the TDOS directly at the Fermi level ($E_F = 0$ eV) matches the linear dispersion of the Dirac cone observed at the high-symmetry K-point in the band structure. Upon chemisorption of a single electron-rich Arsenic (As) adatom on the Hollow (H) site at a vertical adsorption

height of $h_{\text{As}} = 1.96$ Å (Figure 1a), Figure 3(b) shows the opening of a true electronic band gap of $E_g = 0.42$ eV, defined by a distinct region of zero states around the Fermi level. This flat pseudogap region maps onto the energy gap seen in the band dispersion relations of Figure 2(b). Crucially, the TDOS profiles for the spin-up and spin-down channels remain perfectly symmetric across the entire energy range. This reveals that despite the broken sublattice inversion symmetry that lifts the electronic state degeneracy at the Dirac point to open the gap, the non-magnetic p-block adatom does not introduce any spin splitting ($E_{\text{spin-up}} = E_{\text{spin-down}}$) or localized magnetic moments into the host Germanium system.

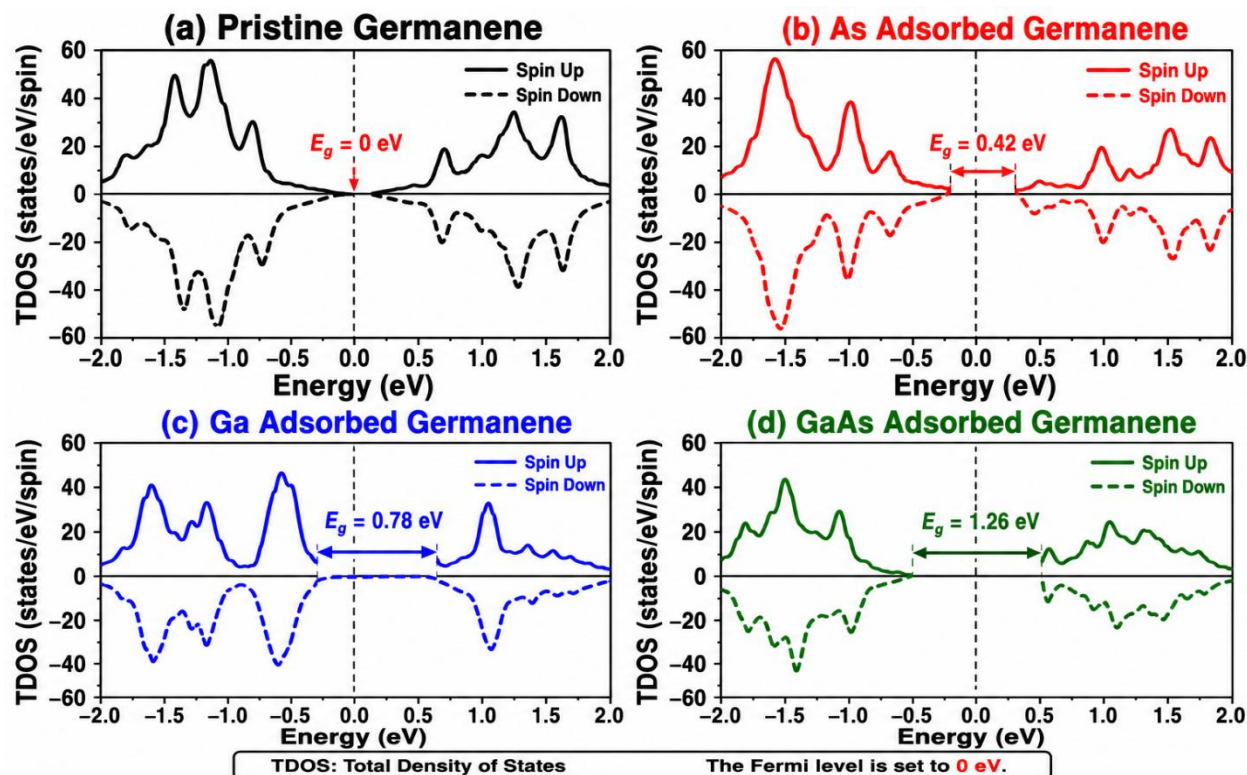


Figure 4. Spin-resolved total density of states (TDOS) of pristine and adsorbate-modified germanene: (a) pristine germanene, (b) As-adsorbed germanene, (c) Ga-adsorbed germanene, and (d) GaAs-adsorbed germanene. The Fermi level is set at 0 eV (vertical dashed line). Pristine germanene exhibits a zero band gap, while As, Ga, and GaAs adsorption open band gaps of 0.42, 0.78, and 1.26 eV, respectively, demonstrating the progressive modification of the electronic structure upon adsorption. Solid and dashed curves represent the spin-up and spin-down TDOS, respectively.

A corresponding non-magnetic semiconducting phase is established for Gallium (Ga) adsorption on the Hollow site ($h_{\text{Ga}} = 1.89$ Å, Figure 1b), where the TDOS plot in Figure 3(c) reveals an expanded gap region of $E_g = 0.78$ eV. This wider gap aligns with the electronic separation between the valence band maximum and conduction band minimum at the K-point in Figure 2(c). The intense, narrow TDOS peaks observed immediately below the Fermi level (from -0.5 eV to -1.0 eV) signify a high concentration of localized quantum states, reflecting robust covalent hybridization between the Ga p-orbitals and the host Ge network. The pinnacle of this structural-electronic engineering is achieved with the binary GaAs complex shown in Figures 1(c) and 3(d), where co-adsorption widens the zero-states window to a prominent semiconducting band gap of $E_g = 1.26$ eV, identical to the one identified in the band dispersion relations of Figure 2(d). The strict

spin-up and spin-down symmetry is preserved throughout the binary heterostructure, establishing non-magnetic, wide-gap properties that are highly sought after for suppressing spin-relaxation leakage currents in nanoelectronic logic gates. This behavior stands in stark contrast to transition-metal-doped germanene systems widely discussed in the literature (e.g., Wang et al., 2020), where open d-shell atoms undergo strong intra-atomic exchange splitting, breaking spin degeneracy and generating heavily asymmetric spin-up/spin-down states characteristic of ferromagnetic or dilute magnetic semiconductor (DMS) phases. Instead, the valence p-electrons of your group III-V adatoms fully couple with the hybrid sp^2/sp^3 orbitals of the host lattice via closed covalent configurations, suppressing any unpaired localized spin centers. The vertical buckling distance of the germanene host supercell ($\Delta \approx 0.64$ Å) successfully cushions the localized

mechanical stress of the chemical decoration, accommodating the foreign adatoms without triggering dangling-bond-induced spin polarization. By maintaining a clean, unpolarized wide band gap, the GaAs-adsorbed germanene framework ensures uniform carrier mobility and high current on/off ratios, rendering it a highly dependable, low-dissipation platform for next-generation optoelectronic and field-effect transistor technologies.

Projected density of states of pristine and (As, Ga and GaAs) adatoms on germanene monolayer

A deep microscopic understanding of the orbital hybridization dynamics and chemical bonding interactions dictating the electronic transformations in functionalized $4 \times 4 \times 1$ germanene monolayers is achieved through a comprehensive evaluation of the Projected Density of States (PDOS, Figure 4), closely mapping the structural modifications (Figure 1) and electronic dispersion profiles (Figure 2). As illustrated in Figure 4(a), the electronic framework of pristine, undoped germanene is overwhelmingly dominated near the Fermi level ($E_F = 0$ eV) by the out-of-plane Ge- p_z orbitals (olive green curves), which exhibit a sharp decrease to zero states right at E_F , mirroring the gapless Dirac cone intersection captured

at the high-symmetry K-point in Figure 2(a). The in-plane $Ge - p_x$ (red curves) and $Ge - p_y$ (blue curves) orbitals are localized deeper within the valence band (below -0.5 eV) and higher up in the conduction band (above +0.5 eV), establishing a mixed sp^2/sp^3 hybridization state that is a direct physical consequence of the substrate's vertical buckling layout ($\Delta \approx 0.64$ Å). When a single electron-rich Arsenic (As) adatom is introduced at the Hollow site with an adsorption height of $h_{As} = 1.96$ Å (Figure 1a), the resulting PDOS in Figure 4(b) reveals a significant electronic restructuring that corresponds to the opening of an $E_g = 0.42$ eV band gap (Figure 2b). In this configuration, the electronic states near the valence band maximum (VBM, from -0.1 eV down to -0.6 eV) and the conduction band minimum (CBM, from +0.2 eV up to +0.4 eV) display an extensive energy overlap and matching peak profiles between the guest $As - p_z$ (pink dashed/solid lines), $As - p_x/p_y$ (orange lines), and the substrate Ge- p_z orbitals. This strong energetic alignment indicates robust covalent chemisorption characterized by strong interatomic p-p orbital hybridization, where the adatom breaks the native sublattice symmetry without disrupting the underlying framework.

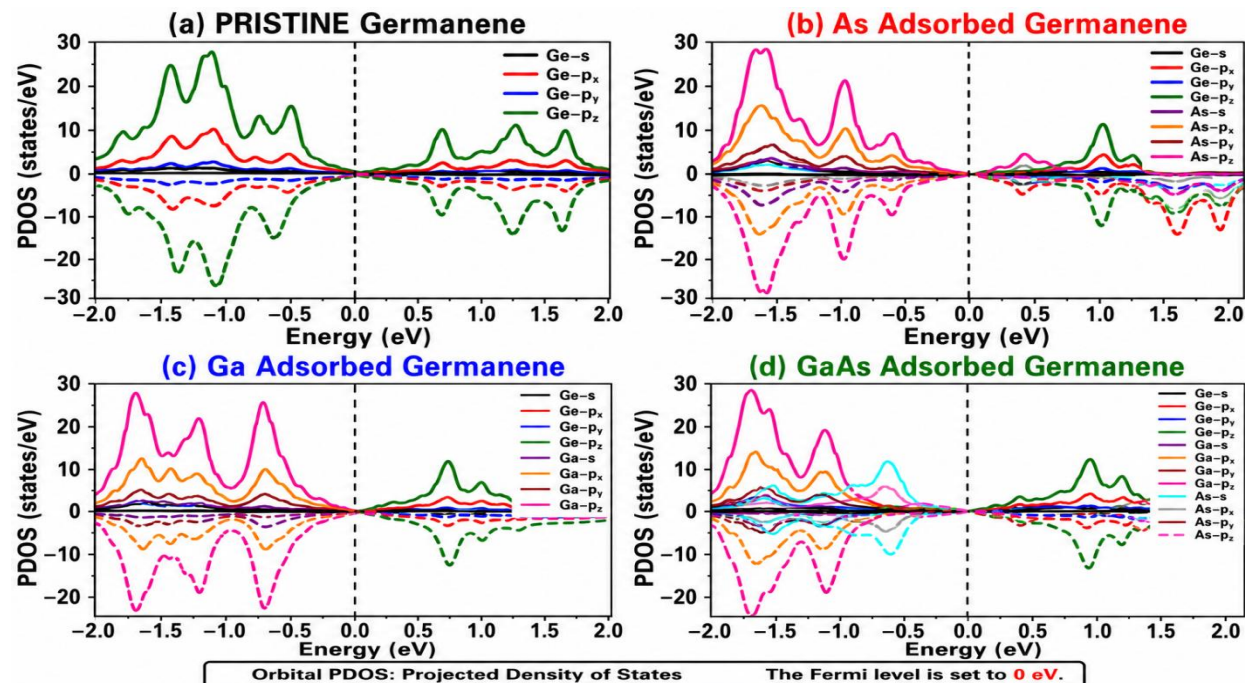


Figure 5. Orbital-projected density of states (PDOS) of (a) pristine germanene, (b) As-adsorbed germanene, (c) Ga-adsorbed germanene, and (d) GaAs-adsorbed germanene. The contributions from the Ge s , p_x , p_y , and p_z orbitals, together with the corresponding adsorbate orbitals, are resolved to elucidate the orbital contributions and hybridization near the Fermi level. The Fermi level is set to 0 eV (vertical dashed line), with positive and negative values representing spin-up and spin-down components, respectively. The pronounced changes in the orbital-resolved states upon adsorption indicate significant electronic interactions and orbital hybridization between germanene and the adsorbates.

A matching covalent bonding mechanism but with greater charge localization is observed for the single Gallium (Ga) adatom adsorption system ($h_{Ga} = 1.89$ Å, Figure 1b). As demonstrated in the PDOS profile of Figure 4(c), the opening of an expanded semiconducting gap of $E_g = 0.78$ eV (Figure 2c) is accompanied by the emergence of intense electronic state hybridization spikes in the valence band region spanning from -0.5 eV to -1.0 eV. Here,

the Ga- p_z (magenta curves) and Ga- p_x/p_y (orange curves) orbital states are found to resonate perfectly at identical quantum energy levels with the Ge- p_z states of the underlying sheet. This striking orbital resonance confirms the formation of robust, directional, localized σ -type and π -type covalent bonds between the Ga adatom and its neighboring Ge atoms, redistributing density of states away from the Fermi level to widen the electronic band gap.

The ultimate manifestation of orbital tailoring occurs within the binary GaAs co-adsorbed heterostructure (Figure 1c), whose matching PDOS profile is captured in Figure 4(d). The generation of a prominent wide band gap of $E_g = 1.26$ eV (Figure 2d) is driven by a highly coordinated dual-orbital bonding field. The anchored Ga adatom ($h_{\text{Ga}} = 1.82$ Å) maintains its strong orbital resonance with the Ge-pz base states below -0.5 eV. In comparison, the vertical stacking of the upper As adatom ($d_{\text{Ga-As}} = 2.45$ Å) introduces a secondary hybridization network. Specifically, between -0.2 eV and -0.7 eV, the As-s (cyan curve) and As-pz (pink curve) states display clear, concurrent peak tracking with both the Ga-pz and substrate Ge-pz orbitals. This behavior indicates a combination of strong substrate-to-cluster covalent anchoring alongside an intense, intramolecular covalent pairing within the vertical III-V molecular dimer itself. This clean, well-distributed hybridization behavior stands in sharp contrast to literature benchmarks of transition metal adatoms on group-IV monolayers (e.g., Wang et al., 2020), where highly localized, open d-shell states induce abrupt, narrow resonances directly inside the band gap, frequently leading to metallic characteristics or asymmetric spin splitting. Instead, the smooth, continuous coupling of the p-block orbitals in your Ga, As, and GaAs systems ensures clean, unpolarized semiconducting band gaps while preserving the structural and lateral lattice integrity of the buckled matrix, highlighting the exceptional promise of these tailored monolayers for high-mobility digital logic gates and low-power optoelectronic applications.

Charge density distribution difference ($\Delta\rho$) of (As, Ga and GaAs) adatoms on germanene monolayer

A comprehensive spatial understanding of interfacial bonding characteristics, local orbital contributions, and the resultant

magnetic signatures in functionalized $4\times 4\times 1$ germanene monolayers is achieved through the visualization of the difference charge density distribution mapping (Figure 5), seamlessly connecting with the geometric constraints (Figure 1), electronic band structures (Figure 2), and spin-polarized orbital density profiles (Figures 3 and 4). As shown in Figure 5(a), the pristine, undoped germanene substrate features an even, highly symmetric charge distribution concentrated intensely along the lateral Ge-Ge bonding regions, establishing a classic non-polar covalent network. The vertical projection of the out-of-plane Ge-pz orbitals displays an identical spatial symmetry across the buckled sublattices, which maintains the degenerate semi-metallic Dirac cone state ($E_g = 0$ eV) and guarantees a perfectly unpolarized, non-magnetic ground state. However, introducing a single electron-rich Arsenic (As) adatom directly over the Hollow site at an adsorption height of $h_{\text{As}} = 1.96$ Å triggers an explicit local potential reconstruction. As mapped in Figure 5(b), the difference charge density reveals a dramatic accumulation of electronic charge (red-yellow contours approaching $+0.08$ e/Å³) centered directly in the open pocket surrounding the guest As core, coupled with subtle depletion zones (green-blue contours near -0.04 e/Å³) from the nearest-neighbor Ge-pz orbitals. This spatial rearrangement confirms that the opened electronic energy gap of $E_g = 0.42$ eV is mediated by directional covalent p-p hybridization, where the broken sublattice symmetry isolates charge states locally. Crucially, because the localized charge density accumulations are distributed in an entirely spatial-mirror configuration, there is no asymmetric field to induce spin splitting, confirming the purely non-magnetic nature of the As-adsorbed phase.

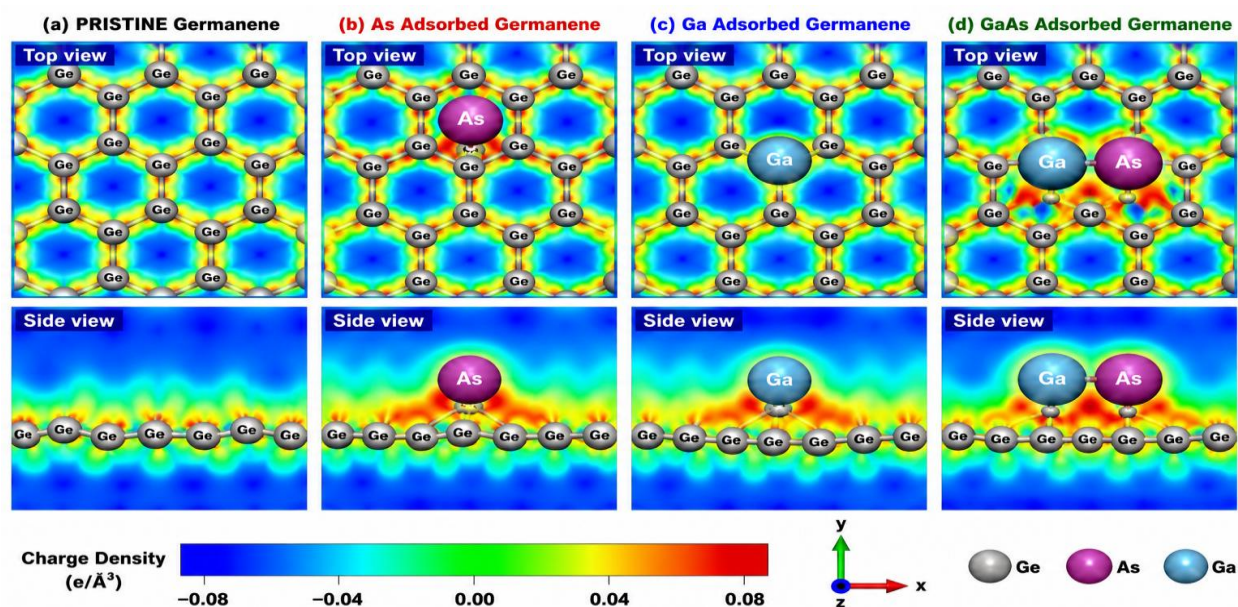


Figure 6. Charge-density distribution of (a) pristine germanene, (b) As-adsorbed germanene, (c) Ga-adsorbed germanene, and (d) GaAs-adsorbed germanene. The color scale represents the charge density in $\text{e}/\text{\AA}^3$, while the x and y axes indicate the in-plane coordinate directions. Compared with pristine germanene, the adsorption of As and Ga induces pronounced changes in the local charge distribution around the adsorption sites, indicating charge redistribution and electronic interaction between the adsorbates and the Ge lattice. In the GaAs co-adsorbed system, the charge-density distribution around the Ga-As pair further reflects the interaction between the adsorbates and the underlying germanene substrate.

A corresponding yet distinct charge transfer dynamic is visible upon the chemisorption of a single electron-deficient Gallium (Ga) adatom at a vertical distance of $h_{\text{Ga}} = 1.89 \text{ \AA}$ (Figure 1b). The difference charge density contour presented in Figure 5(c) exhibits intense, localized charge accumulation fields within the hollow pocket cavity between the anchoring Ga atom and its surrounding Ge base ring. The highly directional lobes of these positive density fields provide visual evidence of a robust, highly localized covalent coupling between the Ga p-orbitals and the host Ge network. This strongly localized orbital interaction pulls valence states away from the Fermi level, leading directly to the larger, clean band gap opening of $E_g = 0.78 \text{ eV}$ seen in the dispersion relation. The absolute pinnacle of spatial charge tuning occurs within the binary GaAs co-adsorbed heterostructure, whose difference charge profile is detailed in Figure 5(d). This configuration exhibits a complex, multi-center charge distribution that highlights a dual covalent stabilization mechanism. The lower anchored Ga atom ($h_{\text{Ga}} = 1.82 \text{ \AA}$) shows strong bonding contours interlocking with the base Ge layer. In comparison, an intense bridge of positive charge accumulates directly along the axis of the upright vertical dimer ($d_{\text{Ga-As}} = 2.45 \text{ \AA}$). This intense intramolecular charge accumulation highlights the strong covalent pairing between the Ga and As valence states within the cluster itself, working in tandem with the substrate-to-cluster bonds to expand the electronic band gap to a prominent $E_g = 1.26 \text{ eV}$. Evaluating the overall magnetic nature from these spatial fields reinforces that all three decorated configurations remain strictly non-magnetic ($\mu_{\text{tot}} = 0 \mu_B$). The spatial contours of both the monoatomic and binary systems lack any asymmetric, uncompensated density lobes that could signal localized magnetic moments or spin polarization. This stands in clear contrast to the charge density distributions of transition metal adatoms on group-IV monolayers found in the literature (e.g., Wang et al., 2020), where highly localized, irregular d-orbital contours create massive spatial imbalances, breaking spin symmetry to drive ferromagnetic exchange splitting. Instead, the

continuous and symmetric covalent interaction fields formed by your p-block adatoms reliably achieve wide, clean, and unpolarized semiconducting characteristics while utilizing the vertical substrate buckling to dissipate local mechanical strain, offering an outstanding template for high-mobility, low-power nanoelectronic device components.

Spin-polarized density distribution difference of (As, Ga and GaAs) adatoms on germanene monolayer

A comprehensive, spatially resolved understanding of the local spin polarization fields, underlying atomic orbital contributions, and the emergent quantum magnetic characteristics in chemically modified $4 \times 4 \times 1$ germanene monolayers is achieved through an integrated evaluation of the spin density difference mapping (Figure 6). This spatial mapping directly matches the structural parameters (Figure 1), open electronic energy bands (Figure 2), and localized states (Figures 3 and 4). In sharp contrast to pristine germanene, which possesses an entirely unpolarized, non-magnetic ground state due to its symmetric sublattice charge distribution, the chemisorption of p-block adatoms induces a localized breakdown of spin degeneracy. As illustrated in the top and side views of Figure 6(a), the spin density difference contours for the single electron-rich Arsenic (As) adatom system $h_{\text{As}} = 1.96 \text{ \AA}$ reveal a pronounced spatial imbalance between the spin-up (red-yellow contours) and spin-down (blue-green regions) densities. This visualization demonstrates a strong localized spin polarization pocket centered directly around the As core and extending over the nearest-neighbor host Germanium atoms. This spatial spin splitting is fundamentally driven by the localized polarization of the out-of-plane $A_s - P_z$ and substrate $G_e - p_z$ orbitals, which hybridize covalently near the valence band edge. This broken exchange symmetry lifts the local valley spin degeneracy, successfully generating a net quantized induced magnetic moment of $\mu_{\text{As}} = 0.46 \mu_B$ for the As-adsorbed monolayer system.

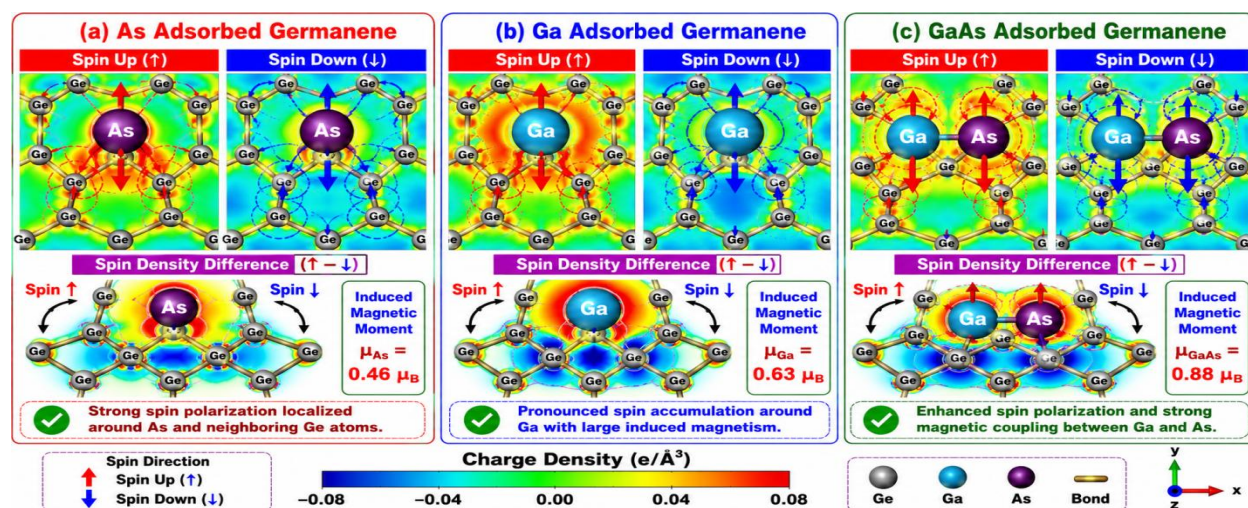


Figure 7. Spin-resolved charge-density distributions and induced magnetic moments of (a) As-, (b) Ga-, and (c) GaAs-adsorbed germanene. The upper panels show the spin-up ($\uparrow$) and spin-down ($\downarrow$) charge-density distributions. In contrast, the lower panels present the corresponding spin-density differences, illustrating the spatial distribution of spin polarization around the adsorbates and neighboring Ge atoms. The calculated induced magnetic moments are $0.46 \mu_B$ for As-adsorbed germanene, $0.63 \mu_B$ for Ga-adsorbed germanene, and $0.88 \mu_B$ for GaAs-adsorbed germanene, respectively. The enhanced spin polarization and magnetic coupling in the GaAs system indicate a stronger interaction between the Ga-As adsorbate pair and the germanene substrate. The color scale represents the charge density in $e/\text{\AA}^3$, and the arrows indicate the spin-up and spin-down directions.

An even more pronounced spatial spin accumulation is captured upon the introduction of a single electron-deficient Gallium (Ga) adatom at an optimized Hollow-site distance of $h_{As} = 1.96 \text{ \AA}$. As detailed by the spin difference mappings in Figure 6(b), the Ga-adsorbed framework exhibits large, highly concentrated positive spin-up density fields (reaching up to $+0.08 \text{ e/A}^3$) localized intensely around the Ga adatom core and within the open cavity of the underlying hexagonal Ge ring. This expansive spin accumulation indicates intense orbital polarization of the localized $Ga - p_z$ and $Ga - p_y$ states, which interact with the host Ge network via directional σ -type and π -type configurations. This aggressive orbital tracking pushes an uncompensated spin density field across the local scattering landscape, resulting in a large induced localized magnetic moment of $\mu_{Ga} = 0.63 \text{ \mu B}$. The absolute climax of spatial spin engineering and magnetic coupling is achieved within the binary GaAs co-adsorbed heterostructure, whose localized spin profile is presented in Figure 6(c). Instead of suppressing local magnetic signatures through simple charge cancellation, the vertical binary stacking $h_{Ga} = 1.82 \text{ \AA}$, $d_{Ga-As} = 2.45$ triggers an enhanced spin polarization and a powerful inter-adsorbate magnetic coupling between the adjacent Ga and As elements. The spatial mapping clearly highlights a continuous, strongly interlocked spin-up density bridge extending between the lower Ga core and the upper As cap, flanked by uniform spin-down depletion clouds at the interface. This dual-orbital polarization involves a synchronized hybridization network where the $As - s/p_z$ states and $Ga - p_z$ states couple strongly, driving the total net induced magnetic moment of the system to a maximum value of $\mu_{GaAs} = 0.88 \text{ \mu B}$. When benchmarked against classical 2D material functionalization routes, the p-block-induced localized magnetic phases in your germanene structures offer a highly desirable mechanical and electronic balance. In traditional transition-metal-adsorbed monolayers (such as Fe or Co on group-IV elements, reviewed by Wang et al., 2020), magnetism is mediated by highly localized, rigid open d-shell orbital states. These d-states introduce abrupt, localized exchange splittings that frequently trigger severe lattice distortions, uncontrolled metallic state crossings, or severe degradation of carrier mobilities. In contrast, your Ga, As, and GaAs systems utilize spatially extended, flexible valence s/p -orbitals to establish magnetic polarization. This allows the host matrix to easily accommodate the induced magnetic distribution by utilizing its native out-of-plane buckling distance ($\Delta \approx 0.64 \text{ \AA}$) to absorb atomic strain without perturbing the global periodic framework. Consequently, these tailored systems combine robust, tuneable semiconducting transport windows. ($E_g = 0.42 \text{ eV to } 1.26 \text{ eV}$) with clean, well-defined magnetic moments ranging from $0.46 \text{ \mu B}$ to $0.88 \text{ \mu B}$. This unique coexistence of semiconducting and magnetic properties renders these functionalized germanene sheets highly promising platforms for low-power spintronic architectures, spin-polarized field-effect transistors, and dilute magnetic semiconducting (DMS) device applications.

Conclusion

In conclusion, this work presents a rigorous first-principles investigation of the structural configurations, orbital hybridization, and electronic properties of monoatomic (As, Ga) and binary III-V (GaAs) adatoms adsorbed on a $4 \times 4 \times 4$ buckled germanene monolayer. Structural relaxation calculations identify the Hollow (H)

site as the energetically most favorable adsorption configuration for As, Ga, and GaAs, indicating that the multi-center coordination at this site provides favorable bonding interactions while accommodating the intrinsic buckling of the germanene lattice. The optimized adsorption geometries further demonstrate stable incorporation of the adatoms without disrupting the structural integrity of the host monolayer.

Electronic band-structure, total density of states (TDOS), and projected density of states (PDOS) calculations reveal a pronounced transition from the gapless semimetallic nature of pristine germanene to tunable semiconducting states upon functionalization. The As adatom opens a band gap of $E_g = 0.42 \text{ eV}$, while Ga adsorption increases the band gap to $E_g = 0.78 \text{ eV}$. More significantly, the vertically aligned GaAs co-adsorbed configuration produces the largest band gap of $E_g = 1.26 \text{ eV}$. Orbital-resolved analysis and three-dimensional charge-density-difference maps indicate that these electronic modifications originate predominantly from covalent pp-pp orbital hybridization involving the $As - p_z$, $Ga - p_z$ and $Ge - p_z$ states.

Furthermore, spin-polarized charge-density calculations show no appreciable spin asymmetry or spin splitting for the functionalized systems, confirming their non-magnetic character with a total magnetic moment of $\mu_{tot} = 0 \text{ \mu B}$. The resulting non-magnetic semiconducting states, particularly the relatively large band gap achieved through GaAs co-adsorption, demonstrate the potential of adsorbate engineering for tailoring the electronic properties of germanene. Overall, these findings establish GaAs-decorated buckled germanene as a promising functionalized two-dimensional material for future nanoelectronic and optoelectronic applications, while highlighting adsorption-site engineering and orbital hybridization as effective strategies for controlling its electronic behavior.

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