



# GeAs and SiAs monolayers: Novel 2D semiconductors with suitable band structures

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## ABSTRACT

Two dimensional (2D) materials provide a versatile platform for nanoelectronics, optoelectronics and clean energy conversion. Based on first-principles calculations, we propose a novel kind of 2D materials – GeAs and SiAs monolayers and investigate their atomic structure, thermodynamic stability, and electronic properties. The calculations show that monolayer GeAs and SiAs sheets are energetically and dynamically stable. Their small interlayer cohesion energies (0.191 eV/atom for GeAs and 0.178 eV/atom for SiAs) suggest easy exfoliation from the bulk solids that exist in nature. As 2D semiconductors, GeAs and SiAs monolayers possess band gap of 2.06 eV and 2.50 eV from HSE06 calculations, respectively, while their band gap can be further engineered by the number of layers. The relatively small and anisotropic carrier effective masses imply fast electric transport in these 2D semiconductors. In particular, monolayer SiAs is a direct gap semiconductor and a potential photocatalyst for water splitting. These theoretical results shine light on utilization of monolayer or few-layer GeAs and SiAs materials for the next-generation 2D electronics and optoelectronics with high performance and satisfactory stability.

## 1. Introduction

The boom of graphene has stimulated the interest in many other two-dimensional (2D) materials of atomic thickness, such as transition metal dichalcogenides (TMDs) [1–3], group-IV monochalcogenides [4], group-III monochalcogenides [5,6], silicene, and germanene [7], which are candidate materials for future nanoelectronics, optoelectronics, and photocatalysts due to their suitable amplitude of band gap and fast carrier transport [8–11]. For instance, MoS<sub>2</sub> monolayer, a famous example of the 2D TMD family, is a semiconductor with direct band gap of 1.80 eV and carrier mobility of  $\sim 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , rendering it rather promising candidate optoelectronic devices and field effect transistors [9,12].

Binary compounds of Ge (Si) and As are also known to form layered structures, in which 2D covalently bonded layers are stacked on each other through weak van der Waals interaction, similar to TMDs [13]. Bulk GeAs and SiAs crystallize in a layered structure with C2/m space group (No. 12) [14]. In experiments, GeAs and SiAs solids have been synthesized by vapor-growth and chemical vapor transport growth methods [15,16]. Both crystals are semiconductors with measured band gap of 0.65 eV for GeAs and 1.45 eV for SiAs, respectively [17,18]. The electrical resistivity of these two materials follows a 2D variable range hopping conduction mechanism at low temperature

[15]. The anisotropic structure of GeAs crystal leads to highly anisotropic transport properties with mobilities up to  $60 \text{ cm}^2/\text{V}$  and high-temperature thermoelectric character with a remarkable ZT value of 0.35 at 660 K by Sn doping [17,19].

On the theoretical aspect, the structure, mechanical and electronic properties of bulk GeAs and SiAs crystals have been extensively investigated by density functional theory (DFT) calculations. The theoretical band gap of 0.41 eV for bulk GeAs is smaller than 0.93 eV for SiAs, which is resulted from the lower ionicity of the Ge-As bonds in germanium arsenide [20]. The DFT studies further support the result from the vibrational spectroscopy, that is, the monoclinic crystal structure will be more stable than the orthorhombic structure at all pressures [21]. However, GeAs and SiAs monolayers with bulk-like structure have not been investigated so far.

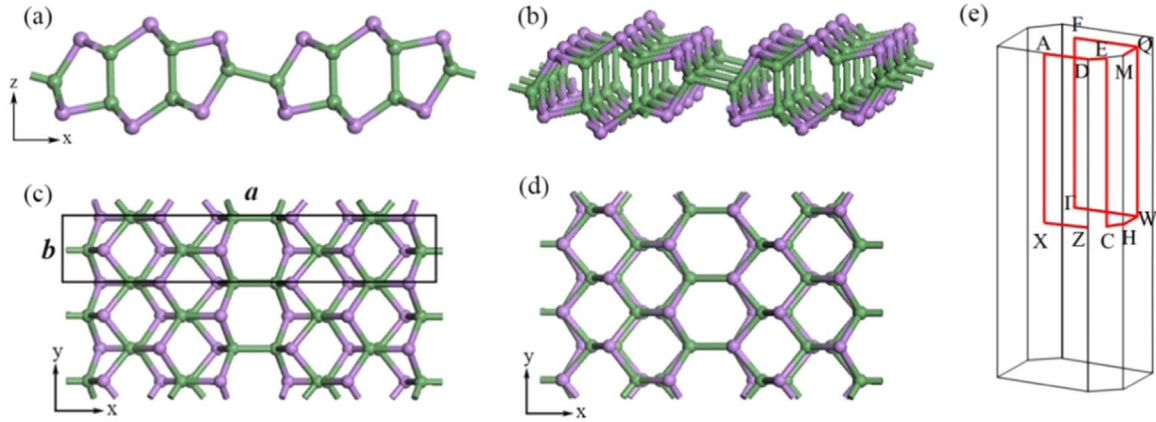
Motivated by the GeAs and SiAs crystals with layered structure, here we explore the structures and electronic properties of GeAs and SiAs monolayers using first-principles calculations. According to the computed interlayer cohesive energies, monolayer sheets of GeAs and SiAs should be easily fabricated by mechanical exfoliation of the bulk materials, like graphene and phosphorene. From HSE06 calculations, SiAs (GeAs) monolayer is a direct (indirect) semiconductor with a band gap of 2.50 (2.06) eV, while the band edge positions of SiAs monolayer fulfill the requirement of photocatalyst for water splitting. Thus, these

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**Fig. 1.** The lattice structure of monolayer GeAs from (a) top and (c) side view. (b) The structure of monolayer GeAs extends by four times along the  $y$  direction. (d) Top view of monolayer GeAs with a little angle rotation. The Brillouin zone is shown in (e), with high-symmetry points labeled. The Purple and green balls represent the As atoms and Ge atoms, respectively.

GeAs and SiAs monolayers expand the family of 2D materials and hold promise in future nanoelectronics, optoelectronics and clean energy conversion

## 2. Computational methods

First-principles computations were performed using density functional theory combined with the norm conserving pseudopotentials, as implemented in the Cambridge Sequential Total Energy Package (CASTEP) [22]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [23] and the energy cutoff value of 600 eV for planewave basis were adopted for all DFT computations. The D2 dispersion correction scheme [24] was used to properly take into account the long-range van der Waals interactions. As shown in Fig. 1, monolayer structures of GeAs and SiAs were directly taken from their crystal structures and then fully optimized in terms of both in-plane lattice parameters and internal coordinates. The supercell size perpendicular to the basal plane of monolayer sheet was chosen as  $30 \text{ \AA}$  to avoid the interaction between periodic images. During the geometry optimization, the  $\mathbf{k}$  spaces was sampled by  $2 \times 9 \times 1$  Monkhorst-Pack grids with a uniform separation of  $0.03 \text{ \AA}$ , and the convergence thresholds were set as  $5.0 \times 10^{-6}$  eV/atom in energy and  $10^{-2}$  eV/ $\text{\AA}$  in force, respectively. A fine separation of  $0.001 \text{ /\AA}$  for  $\mathbf{k}$  points was chosen for band structure calculations. To achieve more accurate band gaps, we used a hybrid HSE06 functional [25] to calculate the conduction band minimum (CBM) and the valence band maximum (VBM) of these two monolayers based on the PBE optimized geometries.

Using the above computational scheme with PBE functional, we first optimize the crystal structures of bulk GeAs and SiAs without constraints; but there's a small change in angle  $\beta$  by about  $6^\circ$  probably due to limitation of computational method. Therefore, angle  $\beta$  has been fixed entirely to mimic the experimental structure of bulk crystal as well as the exfoliated 2D layers. With fixed cell angle parameter ( $\beta = 101.03^\circ$  for GeAs,  $\beta = 106.00^\circ$  for SiAs) of the monoclinic lattice, the optimized lattice parameters ( $a = 15.99 \text{ \AA}$ ,  $b = 3.82 \text{ \AA}$ ,  $c = 9.64 \text{ \AA}$ ) for GeAs crystal agree reasonably with the experimental values of  $a = 15.52 \text{ \AA}$ ,  $b = 3.78 \text{ \AA}$ ,  $c = 9.46 \text{ \AA}$ , [18] and the theoretical lattice parameters ( $a = 16.32 \text{ \AA}$ ,  $b = 3.67 \text{ \AA}$ ,  $c = 9.64 \text{ \AA}$ ) for SiAs crystal are also consistent with the experimental data of  $a = 15.98 \text{ \AA}$ ,  $b = 3.67 \text{ \AA}$ ,  $c = 9.53 \text{ \AA}$ . For simplicity, the lattice angle  $\beta$  is also fixed for the study of monolayer or bilayer sheets.

## 3. Results and discussion

As shown in Fig. 1, monolayer GeAs and SiAs possess monoclinic

structure consisting of 12 Ga (Si) and 12 As atoms in the primitive unit cell. From side view, these monolayers comprise pairs of pentagon and hexagonal rings. Compared to most other 2D binary compound materials, the lattices of monolayer GeAs and SiAs are distorted and have lower symmetry. To assess the stability of monolayer GeAs and monolayer SiAs, the formation energy  $E_{\text{form}}$  is defined as:

$$E_{\text{form}} = (E_{\text{total}} - n_1 \times E_1 - n_2 \times E_2) / (n_1 + n_2) \quad (1)$$

where  $E_{\text{total}}$  is the total energy of monolayer, bilayer and bulk GeAs and SiAs;  $E_1$  and  $E_2$  are the energy of a group-IV and group-V atom in their solid phases, respectively;  $n_1$  and  $n_2$  are the number of group-IV and group-V atoms in the primitive cell, respectively. By definition, a negative formation energy means an exothermic formation process. As listed in Table 1, monolayer GeAs and SiAs possess negative formation energy of  $-0.075$  eV/atom and  $-0.145$  eV/atom, respectively. Previously, a hexagonal phase of GeAs monolayer analogous to the monolayer structure of group-III monochalcogenides [6] has been considered by Shojaei and Kang [26], whose formation energy from our present PBE calculation is  $-0.021$  eV/atom. Similar result is found for SiAs monolayer (formation energy of  $-0.069$  eV/atom for the hexagonal phase). In other words, monolayer GeAs and SiAs with monoclinic structure is more energetically favorable than the hexagonal phase. In addition, the dynamic stability of both monolayer structures is confirmed by their phonon dispersions shown in Fig. 2, where no imaginary band is found.

Since the 2D monolayer or few-layer materials are usually fabricated by mechanical exfoliation of their bulk solid, we calculate the interlayer cohesion energy to assess the possible exfoliation from bulk counterparts. We define the interlayer cohesive energy  $E_c$  as follows:

$$E_c = (E_{\text{bulk}} - 2 \times E_{\text{ML}}) / n \quad (2)$$

where  $E_{\text{bulk}}$  and  $E_{\text{ML}}$  are the total energy of bulk and monolayer GeAs or SiAs in the unit cell, respectively;  $n$  is the total number of atoms in the unit cell for bulk GeAs or SiAs. The calculated cohesive energies of monolayer GeAs and SiAs are  $-0.191$  and  $-0.178$  eV/atom, which are higher than but still comparable to the values of phosphorene ( $-0.055$  eV/atom) [27], graphite and h-BN (both are around

**Table 1**

The lattice parameters, formation energy ( $E_{\text{form}}$ ) and band gap ( $E_g$ ) of monolayer (ML) and bilayer (BL) GeAs and SiAs.

	$a$ ( $\text{\AA}$ )	$b$ ( $\text{\AA}$ )	$\beta$ ( $^\circ$ )	$E_{\text{form}}$ (eV)	$E_g$ (eV)
ML GeAs	22.07	3.78	101.03	-1.80	1.66
BL GeAs	22.07	3.79	101.03	-1.77	1.08
ML SiAs	21.19	3.66	106.00	-3.49	1.84
BL SiAs	21.19	3.66	106.00	-3.40	1.42

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