Two-Dimensional Tetrahex-GeC₂: A Material with Tunable Electronic and Optical Properties Combined with Ultrahigh Carrier Mobility

Wei Zhang,* Changchun Chai, Qingshun Fan, Minglei Sun, Yanxing Song, Yintang Yang, and Udo Schwingenschlögl*  

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ABSTRACT: Based on first-principles calculations, we propose a novel two-dimensional (2D) germanium carbide, tetrahex-GeC₂, and determine its electronic and optical properties. Each Ge atom binds to four C atoms, in contrast to the known 2D hexagonal germanium carbides. Monolayer tetrahex-GeC₂ possesses a narrow direct band gap of 0.89 eV, which can be effectively tuned by applying strain and increasing the thickness. Its electron mobility is extraordinarily high (9.5 × 10⁴ cm²/(V s)), about 80 times that of monolayer black phosphorus. The optical absorption coefficient is ~10⁶ cm⁻¹ in a wide spectral range from near-infrared to near-ultraviolet, comparable to perovskite solar cell materials. We obtain high cohesive energy (5.50 eV/atom), excellent stability, and small electron/hole effective masses. 

KEYWORDS: two-dimensional material, germanium carbide, narrow direct band gap semiconductor, band gap engineering, nanoelectronic, optoelectronic, and photovoltaic applications.

1. INTRODUCTION

Since the first experimental realization of graphene,¹ two-dimensional (2D) materials have attracted attention due to exotic structural and electronic properties.²⁻⁵ Belonging also to the class of group 14 2D materials, silicene and germanene show low buckled honeycomb structures and Dirac dispersions similar to graphene. Epitaxial growth has been achieved experimentally for both silicene and germanene.⁶⁻¹¹ Many studies have demonstrated that group 14 2D materials are promising for next-generation nanoelectronic devices due to intriguing features such as high carrier mobility (massless Dirac fermions),¹² significant spin–orbit coupling (which can induce band gaps of tens of meV),¹³ and extraordinary stiffness.¹⁴ However, the lack of adequate band gaps limits the applicability of graphene, silicene, and germanene in high-performance integrated logic circuits and optoelectronics, motivating the search for new 2D materials that combine a sizable band gap with high stability and good charge transport properties.

The fabrication of layered g-SiC with a thickness down to 0.5–1.5 nm has stimulated interest in binary 2D group 14 materials,¹⁵⁻¹⁸ as band gap opening has been predicted for this class of materials.¹⁹ Unlike silicene and germanene, the honeycomb structures of g-SiC and g-GeC are not buckled. Despite this structural similarity to graphene, g-SiC and g-GeC realize no massless Dirac fermions but sizeable band gaps. Monolayer g-SiC shows an indirect band gap of 2.56 eV,¹⁹,²⁰ high exciton binding energies of up to 2.0 eV,²¹ and pronounced photoluminescence.²² Monolayer g-GeC exhibits a direct band gap of 2.19 eV and strong optical absorption in a wide spectral range.²² It has been demonstrated that the electronic and optical features of g-SiC and g-GeC nanosheets can be effectively tuned by introducing defects or adatoms, modifying the stacking sequence, adjusting the thickness, and applying strain or an external electric field.²³⁻²⁶ Numerous experimental and theoretical investigations have addressed the functionalization of g-SiC and g-GeC nanosheets for optoelectronic devices,²⁷ integrated nanodevices,²⁸ and metal-free electrocatalysts.²⁹ Since photovoltaic applications are hindered by wide and indirect band gaps, extensive research efforts have been made toward predicting new 2D silicon carbides.³⁰⁻³⁷ For example, based on the density functional theory, Li et al.³⁰ and Zhou et al.³¹ have reported metallic siligraphene and semi-conducting siligraphene (g-SiC₂) with a direct band gap of 1.09 eV, respectively. Li et al.,³⁰ Shi et al.,³² and Borlido et al.³³ have comprehensively studied the stabilities and electronic properties of monolayer Si₅C₄ for different stoichiometric compositions. On the other hand, so far no additional stable structures of 2D germanium carbides have been identified.

In this work, we predict a 2D germanium carbide (tetrahex-GeC₂) that consists of tetra- and hexa-rings. The material...
exhibits excellent stability, an effectively tunable narrow direct band gap, ultrahigh electron mobility, and strong optical absorption in a wide spectral range, pointing to excellent potential in nanoelectronic, optoelectronic, and photovoltaic applications.

2. THEORETICAL METHODS

First-principles calculations are performed using the Vienna ab initio simulation package (VASP),36,37 with the electron–ion interactions represented by projector-augmented wave pseudopotentials and the exchange-correlation potential described by the Perdew–Burke–Ernzerhof functional in the structure optimizations. The electronic band structure (including carrier effective mass and mobility) is obtained by the hybrid Heyd–Scuseria–Ernzerhof functional. The G3W0 approach41 is applied together with the Bethe–Salpeter equation42,43 for calculating accurate optical absorption spectra. The energy cutoff of the wave function expansion is set to 500 eV and a 9 × 9 × 1 Monkhorst–Pack mesh is used to sample the Brillouin zone. In calculations for multilayer tetrahex-GeC2, the DFT-D3 correction is implemented in VASP. The Phonopy code44 is used to calculate second-order force constants and phonon frequencies. Ab initio molecular dynamics (AIMD) simulations are carried out for 5 ps with a time step of 1 fs using a canonical ensemble.35

3. RESULTS AND DISCUSSION

The optimized atomic structure of monolayer tetrahex-GeC2 is depicted in Figure 1a, with the Ge and C atoms represented by blue and gray spheres, respectively. The lattice is orthorhombic with the space group Cmna (No. 67) and the structure consists of a network of tetra- and hexa-rings. The conventional cell contains four Ge atoms and eight C atoms, with optimized lattice parameters of a = 5.89 Å and b = 7.29 Å. Each Ge atom bonds covalently to four C atoms with a bond length of 2.00 Å, which is 0.13 Å longer than the bond length of g-GeC.46 Each C atom bonds covalently with two Ge atoms and one C atom. A C–C bond length of 1.34 Å falls between the bond lengths of acetylenic linkage (1.20 Å) and graphene (1.42 Å). As the Ge atoms aim for their standard tetrahedral configuration, the structure is buckled with a total layer thickness of 1.41 Å. C–Ge–C bond angles of 85.1° and 109.4° demonstrate distortions as compared to bulk c–Ge (a bond angle of 109.5°). The Ge–C–Ge and Ge–C–bond angles are 94.9° and 125.3°, respectively. Figure S1 summarizes the structural details of monolayer tetrahex-GeC2. While the structure is hardly affected by H2O in air, it turns out that monolayer tetrahex-GeC2 is susceptible to oxidation by breaking of C–Ge bonds and formation of C–O and Ge–O bonds (Figure S2). To analyze the chemical bonding, the electron localization function (ELF) is addressed in Figure 1b. High values at the bond centers suggest strong covalent C–C bonding, while asymmetric shapes suggest polar covalent Ge–C bonding (Bader charge imbalance of ~0.65 electrons) in agreement with the smaller electronegativity of Ge than C.

To verify the structural stability, we analyze the cohesive energy

\[ E_{coh} = \frac{[E(\text{Ge}) + 2E(\text{C}) - E(\text{tetrahex - GeC}_2)]}{3} \] (1)

where \( E(\text{Ge}) \) and \( E(\text{C}) \) are the total energies of isolated Ge and C atoms, respectively. With an obtained value of 5.50 eV/atom, monolayer tetrahex-GeC2 falls short of graphene (7.85 eV/atom) and h-BN (7.07 eV/atom) but outperforms 2D MoS2 (5.02 eV/atom), g-GeC (4.90 eV/atom), and Cu2Si (3.46 eV/atom),47 verifying high stability and great promise for future synthesis. More specifically, the lattice parameters of tetrahex-GeC2 (\( a = 5.89 \) Å and \( b = 7.29 \) Å) are close to those of a 2 × 2 supercell of the CuAu (110) surface (\( a = 5.60 \) Å and \( b = 7.34 \) Å).48 This fact enables synthesis by the strategy illustrated in Figure 2 since we find the strain experienced by tetrahex-GeC2 during this process to increase its cohesive energy by only 20 meV per atom. Deposition of Ge on the CuAu (110) surface is possible using a Ge evaporator by Ar+ ion bombardment and annealing, analogous with the synthesis of germanene on the Au(111) surface and silicene on the Ag(111) surface, with the C provided by ethylene or CaC2.49,50

The phonon band structure and partial densities of states given in Figure 3a demonstrate the absence of imaginary phonon modes and, thus, dynamical stability of monolayer tetrahex-GeC2. The two highest optical branches fall in a frequency range...
The in-plane elastic constants $C_{11}$, $C_{22}$, $C_{12}$, and $C_{44}$ of a 2D material are given by the second partial derivatives of the elastic energy:

$$U(e) = \frac{1}{2}C_{11}e_{xx}^2 + \frac{1}{2}C_{22}e_{yy}^2 + C_{12}e_{xx}e_{yy} + 2C_{44}e_{xy}^2$$

(2)

and see the results in Figure 4a. We obtain $C_{11} = 124$, $C_{22} = 114$, $C_{12} = 15$, and $C_{44} = 49 \text{ N/m}$, which satisfy the mechanical stability criteria $C_{44} > 0$ and $C_{11}C_{22} - (C_{12})^2 > 0$. The in-plane Young’s modulus ($E$) and Poisson’s ratio ($\nu$) of a 2D material along an arbitrary direction $\theta$ (angle relative to the $x$-direction) are defined as

$$E(\theta) = \frac{C_{11}C_{22} - C_{12}^2}{C_{11}\alpha^4 + C_{22}\beta^4 + \left(\frac{C_{11}C_{22} - C_{12}^2}{C_{44}} - 2C_{12}\right)\alpha^2\beta^2}$$

(3)

and

$$\nu(\theta) = \frac{\left(C_{11} + C_{22} - \frac{C_{11}C_{22} - C_{12}^2}{C_{44}}\right)\alpha^2\beta^2 - C_{12}(\alpha^4 + \beta^4)}{C_{11}\alpha^4 + C_{22}\beta^4 + \left(\frac{C_{11}C_{22} - C_{12}^2}{C_{44}} - 2C_{12}\right)\alpha^2\beta^2}$$

(4)

where $\alpha = \sin \theta$ and $\beta = \cos \theta$. The results in Figure 4b,c evidence mechanical anisotropy due to the orthorhombic lattice. The maximum of Young’s modulus appears in the $x$-direction (122 N/m) and the minimum in the $y$-direction (112 N/m). Poisson’s ratios of $\nu_x = 0.13$ and $\nu_y = 0.12$ suggest that under tensile strain, the material expands less along the $x$ than the $y$-direction.

To analyze the electronic characteristics, we study the band structure and partial densities of states in Figure 5a. Monolayer tetrahex-GeC$_2$ turns out to be a direct band gap semiconductor with a band gap of 0.89 eV. The conduction band minimum (CBM) and the valence band maximum (VBM) are located at $(0,0)$ and $(\pi/2,0)$, respectively. While the hole effective mass is minimal in the $x$-direction (122 N/m), the in-plane Young’s modulus appears in the $y$-direction (112 N/m).

The results in Figure 5c show strong anisotropy with the electron/hole effective mass being minimal in the $x$-direction (0.19/0.10 $m_0$) and maximal in the $y$-direction (0.37/0.70 $m_0$). The effective masses vary by factors of 2 (electrons) and 7 (holes), respectively. While the hole effective mass is smaller than the electron effective mass in the $x$-direction, the opposite applies to the $y$-direction. The obtained values are comparable with those of monolayer black phosphorus.

The low carrier effective masses point to high carrier mobilities

$$\mu_d = \frac{e^2C_{22D}}{k_B T m_{2D}^* m_d^* E_1^*}$$

(6)

of 43–46 THz and originate entirely from the vibrations of the sp$^2$-hybridized C atoms. The final atomic structures after AIMD simulations at 300, 600, and 1000 K (4 x 4 supercell of the conventional cell) are presented in Figure 3b-d together with the fluctuations of the total energy. Neither C–C nor Ge–C bonds break during the simulations, nor are phase transitions observed. We find no significant structural distortions at 300 and 600 K. While monolayer tetrahex-GeC$_2$ loses its planarity at 1000 K, the atomic skeleton is well preserved, indicating excellent thermal stability at least up to 1000 K.
where $C_{2D}$ is the in-plane elastic constant, $m^{*}_{2D} = \sqrt{m^{*}_x m^{*}_y}$, and the deformation potential constant $E_1$ is given by the shift of the band edge under strain. The band edge positions $E_{VBM}$ and $E_{CBM}$ relative to the vacuum energy $E_{vacuum}$ are shown in Figure 6a−d as functions of strain and the obtained parameters at room temperature are summarized in Table 1. Both the deformation potential constants and carrier mobilities show significant anisotropy. We find that the electron mobility in the $x$-direction is almost 700 times that in the $y$-direction, which is a consequence of the very low effective mass and deformation potential constant (weak electron−phonon scattering). The hole mobility is also larger in the $x$ than in the $y$-direction, by a factor of $\sim 2$, due to the lower effective mass. The fact that the predicted electron mobility of monolayer tetrahex-GeC$_2$ is more than 80 times that of monolayer black phosphorus (1100−1140 cm$^2$/V s)$^{52}$ and the predicted hole mobility clearly exceeds that of monolayer MoS$_2$ (200−270 cm$^2$/V s)$^{53,54}$ suggests potential in high-performance electronic devices.

We next investigate the effect of biaxial tensile strain on monolayer tetrahex-GeC$_2$. The stress−strain relationship in Figure 7a shows a maximal stress of 5.10 N/m at the 12% strain. According to Figure 7b, imaginary phonon modes are absent at 7.5% but not at 7.6% biaxial tensile strain, indicating that the lattice of monolayer tetrahex-GeC$_2$ becomes unstable in this range. The effects of biaxial tensile strain on the band structure are addressed in Figure 8a, and for the band gap, the results are summarized in Figure 8b. Up to 6% biaxial tensile strain, the direct band gap decreases from 0.89 to 0.36 eV. This tunability of the band gap enables band gap engineering as required for optoelectronic applications. At 7% biaxial tensile strain, the band gap becomes indirect with the VBM now located at the $\Gamma$ point.
energetically favorable, we study only AA stacking in the following. The ELF in Figure 9d agrees with the notion that the interlayer interaction is due to van der Waals forces and the phonon band structure in Figure 9e shows dynamic stability of bilayer tetrahex-GeC\textsubscript{2} due to the absence of imaginary phonon modes. The results of AIMD simulations at 300 K (3 \times 3 supercell of the conventional cell) in Figure 9f give no indication of bond breaking or phase transitions, indicating the thermal stability of bilayer tetrahex-GeC\textsubscript{2}.

Figure 10 shows the electronic band structures of monolayer, bilayer, three-layer, four-layer, five-layer, six-layer, and bulk tetrahex-GeC\textsubscript{2} with AA stacking. The band gaps can be tuned from 0.89 eV in the case of monolayer tetrahex-GeC\textsubscript{2} to 0.06 eV in the case of six-layer tetrahex-GeC\textsubscript{2} without affecting the locations of the CBM and the VBM, i.e., the direct band gap is maintained. The band gap varies strongly from monolayer tetrahex-GeC\textsubscript{2} to three-layer tetrahex-GeC\textsubscript{2} and much less at higher thicknesses, which is explained by the fact that starting from three-layer tetrahex-GeC\textsubscript{2}, the structure contains bulk-like coordinated layers. Bulk tetrahex-GeC\textsubscript{2} turns out to be metallic.

The fact that semiconductors with a narrow direct band gap can absorb light in the near-infrared and visible regions is key for applications in optoelectronics and photovoltaics. Figure 11 shows the optical absorption spectra of monolayer tetrahex-GeC\textsubscript{2} under 0, 2, 4, and 6% biaxial tensile strain. For the x-direction, we find substantial absorption throughout the near-infrared, visible, and near-ultraviolet regions. For the y-direction, the absorption coefficient even reaches values of \(\sim 10^6 \text{ cm}^{-1}\) in the near-ultraviolet region, comparable to perovskite solar cells.\cite{55} Mainly due to the shrinking band gap, biaxial tensile strain results in red shifts of the optical absorption spectra and promising enhancement of the absorption in the visible region.

Table 1. Carrier Effective Mass, Deformation Potential Constant, In-Plane Elastic Constant, and Carrier Mobility at 300 K

| Carrier type | \(d\) (Å) | \(m^*\) (m_e) | \(E_f\) (eV) | \(C_{44}\) (N/m) | \(\mu_x\) (cm\(^2\)/(V s)) |
|-------------|------------|--------------|-------------|-----------------|-------------------------|
| electron x  | 0.19       | 0.74         | 124         | 9.53 \times 10^4 |                         |
| electron y  | 0.37       | 13.71        | 114         | 132             |                         |
| hole x      | 0.10       | 10.35        | 124         | 934             |                         |
| hole y      | 0.70       | 5.31         | 114         | 466             |                         |

4. CONCLUSIONS

We discover a novel 2D material, tetrahex-GeC\textsubscript{2}, and predict its mechanical, electronic, and optical properties. Great promise for future synthesis is demonstrated in terms of cohesive energy, phonon spectrum, thermal stability, stress-strain relationship, and elastic constants. Most notably, monolayer tetrahex-GeC\textsubscript{2} shows extraordinarily high-room-temperature electron mobility as required for next-generation nanoelectronic devices. Its optical absorption coefficient in excess of \(10^5 \text{ cm}^{-1}\) in the visible and near-ultraviolet regions is comparable to that of the...
Perovskites currently employed in solar cells. Additionally, we find that biaxial tensile strain is able to substantially enhance the absorption of visible light, calling for the consideration of monolayer tetrahex-GeC₂ in photovoltaics and optoelectronics.

It turns out that the narrow direct band gap (0.89 eV) and small electron/hole effective mass (0.19/0.10 m₀) of monolayer tetrahex-GeC₂ can be effectively tuned by applying strain and/or by increasing the thickness to multilayer geometries. Our results thus offer a new strategy for achieving 2D germanium carbides with desirable material properties.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c23017.

Structural details of tetrahex-GeC₂ and coordinates and conventional cell of tetrahex-GeC₂ (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

Wei Zhang — School of Microelectronics, Xidian University, Xi'an 710071, China; orcid.org/0000-0001-5802-9488; Email: wzhang.1993@stu.xidian.edu.cn

Udo Schwingenschlogl — Physical Science and Engineering Division (PSE), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia; orcid.org/0000-0003-4179-7231; Email: udo.schwingenschlogl@kaust.edu.sa

**Authors**

Changchun Chai — School of Microelectronics, Xidian University, Xi’an 710071, China

Qingyang Fan — College of Information and Control Engineering, Xi’an University of Architecture and Technology, Xi’an 710055, China; Shaanxi Key Laboratory of Nano Materials and Technology, Xi’an 710055, China; orcid.org/0000-0002-6130-1312
Minglei Sun — Physical Science and Engineering Division (PSE), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia; orcid.org/0000-0001-5105-0065
Yanxing Song — School of Microelectronics, Xidian University, Xi'an 710071, China; orcid.org/0000-0002-5026-1431
Yintang Yang — School of Microelectronics, Xidian University, Xi'an 710071, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.0c23017

Author Contributions
W.Z. and U.S. conceived the study; W.Z., C.C., and M.S. formulated the theoretical approach; W.Z., Y.S., and M.S. performed the calculations and analyzed the data; W.Z. and Q.F. wrote the manuscript guided by C.C., M.S., and U.S.; and C.C. and Y.Y. provided equipment support.

Notes
The authors declare no competing financial interest.

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ABBREVIATIONS
2D, two-dimensional
AIDM, all-inclusive molecular dynamics
CBM, conduction band minimum
ELF, electron localization function
VASP, Vienna ab initio simulation package
VBM, valence band maximum

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