Novel graphene-like two-dimensional bilayer germanene dioxide: electronic structure and optical properties

Yan-Mei Dou, Chang-Wen Zhang, Ping Li and Pei-Ji Wang

Using ab initio calculations, we present a two-dimensional (2D) \(\alpha\)-2D-germanene dioxide material with an ideal sp\(^3\) bonding network which possesses a large band gap up to 2.50 eV. The phonon dispersion curves and molecular dynamics (MD) simulation under the chosen parameters suggest that the novel 2D structure is stable. The dielectric function and absorption spectrum also show the consistent band gap within the electronic structure diagram, suggesting possible application as an ultraviolet light optical detector. The calculated carrier mobility of \(4.09 \times 10^3\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) can be observed along the \(x\) direction, which is much higher than that of \(\text{MoS}_2\) (~3.0 cm\(^2\) V\(^{-1}\) s\(^{-1}\)). Finally, we found that \(\alpha\)-2D-germanene dioxide could potentially act as an ideal monolayer insulator in so-called van der Waals (vdW) heterostructure devices. These findings expand the potential applications of the emerging field of 2D \(\alpha\)-2D-germanene dioxide materials in nanoelectronics.

Other 2D materials also have a high carrier mobility of up to \(10^5\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) (ref. 19 and 20) and novel in-plane negative Poisson’s ratio,\(^{21}\) while the excellent bandgap is also beneficial to applications in optoelectronics.\(^{22}\) The germanene monolayer has been found to be an insulator with a large bandgap, as well as high carrier mobility (of the order of \(10^5\) cm\(^2\) V\(^{-1}\) s\(^{-1}\)) due to its linear band dispersion near the Fermi level (\(E_F\)) at the \(K\) point. It has a low-buckled (0.84 Å) structure compared with silicene due to the weak p-p interactions and distinct coupling of s and p bonds between Ge atoms,\(^{23-26}\) giving rise to new characteristics beyond silica, such as detectable quantum spin Hall (QSH) and valley-polarized quantum anomalous Hall (QAH) states, for example.\(^{27-28}\) In addition, Gao \textit{et al.}\(^{29}\) showed that it can be used for infrared materials, precision instruments and catalysts. Several remarkable features of germanene have been reported.\(^{26,30,31}\)

Despite the extensive efforts of 2D germanene dioxide monolayers,\(^{32}\) we investigate the electronic structure, dynamic mechanical stabilities and carrier mobilities of germanene dioxide bilayer as a noninteracting dielectric in van der Waals (vdW) electronics employing density functional theory (DFT) in this work. A number of low-energy structures had been investigated based on the of DFT optimization combined with the particle-swarm optimization (PSO) algorithm, and only the bilayer structure with space groups of \(P6/mmm\) of the most stable several 2D structures were obtained in our computations.\(^{33-36}\) The supercell in the \(\alpha\)-2D-germanene dioxide structure is shown in Fig. 1. The optimized lattice constant \(a\) is 4.00 Å for \(\alpha\)-2D-germanene dioxide in a hexagonal unit cell, as enclosed in the gray dashed lines in Fig. 1a. \(\alpha\)-2D-germanene dioxide has an ideal sp\(^3\) bonding network, which means that
all O atoms are connected to Ge atoms with same solid angles 109°28'; i.e., Ge is in a perfect O tetrahedron. The new α-2D-germanene dioxide structure is dynamic and mechanical stabilities. Meanwhile, α-2D-germanene dioxide has good stability, and can be stable up to 300 K. These fantastic properties make α-2D-germanene dioxide more attractive for electric and optical applications.

Methods

In the framework of DFT, the Vienna Ab initio Simulation Package (VASP) was used to optimize the initial structure using the method of projector augmented wave (PAW). In the general gradient approximation (GGA) around the optimization process, the exchange–correlation function for selecting Perdew–Burke–Ernzerhof (PBE) was used to relax the force of atoms in the system, until the force of each atom in the system was less than 0.1 eV nm−1. The cut-off kinetic energy is set to 360 eV. At the time of calculation, the doped systems were modeled with periodic geometry, growing along the Y-axis. Respectively, the Brillouin zone (BZ) was sampled using a 9 × 9 × 1 gamma-centered Monkhorst-Pack grid, and the vacuum space was set to 30 Å to minimize artificial interactions between neighboring slabs. All structures were fully optimized, including cell parameters and atomic coordinates. Phonon dispersion curves were obtained using the Phonopy package.

Results and discussion

Intrinsic structural and electronic properties

We first present the geometric and electronic structures of the α-2D-germanene dioxide, as shown in Fig. 1. The α-2D-germanene dioxide has a hexagonal honeycomb structure, and the relaxed lattice parameter is found to be a = 5.75 Å. The band structure is plotted in Fig. 1d. In the top view, α-2D-germanene, like graphene, has a hexagonal crystal structure and an electronic performance like indirect-gap semiconductors. The α-2D-germanene dioxide monolayer exhibits (quasi) direct-gap semiconducting character with a PBE- energy gap of 2.50 eV (see Fig. 1d). It has a larger band gap than MoS 2 (bandgap = 1.9 eV), and is more easily used as short-wavelength light-emitting devices, ultraviolet detection and high-temperature, and high-power electronic devices. The valence band maximum (VBM) is based on the hybridized O 2p orbitals, while the conduction band minimum (CBM) derives from the hybridized Ge 4s orbitals.

Stability

First, α-2D-germanene dioxide was considered to determine its energetic stabilities. Fig. 2 shows the formation energy with area per Ge atom for germanene dioxide (α-2D-germanene dioxide). The formation energy of the α-2D-germanene dioxide configuration with respect to its constituent atoms is calculated as:

$$E_{\text{form}} = (E_{\text{total}} - N_{\text{Ge}}E_{\text{Ge}} - N_{\text{O}}E_{\text{O}})(N_{\text{Ge}} + N_{\text{O}})$$

where $E_{\text{total}}$ is the total energy of the system. $E_{\text{Ge}}$ and $E_{\text{O}}$ are the energies of single Ge and O in bulk Ge and O₂ molecules, which are calculated to be −0.765 and −1.842 eV, respectively. $N_{\text{Si}}$ and $N_{\text{O}}$ are the numbers of Si and O atoms in the unit cell. A negative formation energy suggests that the configuration is stable. Note that the energy minimum in each curve of Fig. 2c represents the equilibrium configuration of the given structure. The calculated formation energies of α-2D-germanene dioxide are
−4.80 eV per atom (Fig. 2b). These results suggest that the α-2D-germanene configuration is either stable or metastable.

Next, the thermal stabilities of the germanene dioxide configurations are calculated by ab initio molecular dynamics (AIMD) simulations in Fig. 2a. The MD simulations selected the supercell of $4 \times 4 \times 1$ based on the Nose thermostat at 500 K. The phonon dispersion (based on Vibra of SIESTA utility) curves show the dynamic stability of α-2D-germanene dioxide (Fig. 2c). The deformation charge density shown in Fig. 2d suggests the charge transfer from Ge to O yielding the charge of Si to be 3.52 e by Bader analysis. The same structure of the silica sheet in Russia (0001) (i.e. double silicon layer) was recently synthesized. This indicates that our material is likely to be prepared.

**Carrier mobility**

The carrier mobility ($\mu$) of α-2D-germanene dioxide is calculated based on the deformation potential (DP) theory as proposed by Bardeen and Shockley, which has been proven to be reasonable in estimating $\mu$ of 2D materials. Thus, the carrier mobility ($\mu$) of α-2D-germanene dioxide, as predicted using the DP theory, is calculated as:

$$\mu_{2D} = \frac{2e\hbar C_{2D}}{3k_B T|m^*|^2E_1^2}$$

where $e$ is the electron charge, $\hbar$ is reduced Planck, $k_B$ is Boltzmann’s constant and $T$ is the temperature which set to 300 K, while $m^*$, $E_1$, and $C_{2D}$ are the effective mass, deformation potential constant, and in-plane stiffness, which will appear in the next calculation. The effective masses ($m^* = h^2(\partial^2 E/\partial k^2)^{-1}$) of electrons and holes associated with the direct semiconducting α-2D-germanene dioxide are computed. Interestingly, the effective mass of electrons in the $k_a$ direction (0.05 $m_e$) is much smaller than that in the $k_b$ direction (0.07 $m_e$), indicating the easy drift of electrons in the $k_a$ direction. However, the holes entail an effective mass of ~0.41/0.05 $m_e$ ($k_a/k_b$), suggesting the easy drift of holes in the $k_b$ direction. In addition, the small effective mass in a direction could promise high carrier mobility for α-2D-germanene dioxide in this direction. By fitting the change of total energy ($E$) versus the uniaxial strain ($\varepsilon$), as shown in Fig. 3a, the in-plane stiffness $C_{2D} = [\partial^2 E/\partial \varepsilon^2]S_0$. $S_0$, the area of α-2D-germanene dioxide along $a$ and $b$ directions, are evaluated to be 96.73 and 99.21 N m⁻¹, respectively, as shown in Table 1. The absolute DP constant $E_1 (= dE_{edge}/d\tilde{\varepsilon})$ for electrons along $a$ and $b$ directions is calculated to be 16.11 and 14.53 eV, respectively, as shown in Table 1. According to the calculated effective mass $m^*$, $C_{2D}$ and $E_1$, the electron mobility can be evaluated based on Table 1. Interestingly, the holes mobility in the $k_a$ direction can be as high as 4.09 $\times$ 10³ cm² V⁻¹ s⁻¹, which is much higher than that of MoS₂ (~3.0 cm² V⁻¹ s⁻¹) at room temperature. Therefore, the high carrier mobility found in the study is of great significance to the study of electron transport.

**Optical properties**

The optical properties are tied closely to the dielectric function which can be calculated by:
\[ \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \]

where the \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) are the real and imaginary part of the function, and \( \varepsilon_1(\omega) \) can be derived from the imaginary part, \( \varepsilon_2(\omega) \), the dielectric function by Kramer-Kronig, can be expressed as:

\[
\varepsilon_2(\omega) = \frac{4\pi^2}{m^*\omega^2} \sum_{\text{VZ}} \int d^3k \frac{2}{2\pi} |eM_{\text{CV}}(K)|^2 \times \delta[E_C(k) - E_V(k) - \hbar\omega]
\]

In addition, the absorption coefficient \( I(\omega) \) was obtained by:

\[
I(\omega) = \sqrt{2}\omega \left[ \sqrt{\varepsilon_1^2(\omega) - \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2}
\]

where the \( C \) is the conduction band, \( V \) is valence band states, \( \Omega \) is the unit-cell volume, \( m \) is the mass of free electrons, \( e \) is the charge of free electrons, and \( \omega \) is the frequency of incident photons.

The properties of materials are also directly reflected in the optical properties. The wide bandgap of \( \alpha \)-2D-germanene dioxide means that it can more easily be used in short-wavelength light-emitting devices and ultraviolet detection compared with MoS\(_2\). Attracted by the proper band gap and excellent electronic properties of \( \alpha \)-2D-germanene dioxide, we further explored the light absorption of \( \alpha \)-2D-germanene dioxide. As shown in Fig. 4b, \( \alpha \)-2D-germanene dioxide shows absorption starting at \( \approx 2.5 \) eV, with two main absorption peaks from \( \approx 5.5 \) to \( \approx 7.5 \) eV, corresponding to significant light absorption in the ultraviolet region of the solar spectrum.
incident light can be effectively absorbed in three directions, with the adsorption coefficients increasing up to the order of 4.5 a.u., as shown in Fig. 4a. As shown in Fig. 4b, the plot of dielectric functions versus energy shows the same trend. Therefore, \( \alpha \)-2D-germanene dioxide seems rather attractive for efficient light harvesting and may have promising applications in optoelectronics.

Conclusions

In conclusion, based on first-principles calculations, we show that \( \alpha \)-2D-germanene dioxide has an appropriate band gap and excellent electronic and optical properties, attracting great attention as a possible candidate for electronic devices. \( \alpha \)-2D-germanene dioxide shows semiconductor properties, with a gap reaching up to 2.50 eV. To our delight, \( \alpha \)-2D-germanene dioxide is fairly stable according to calculations of formation energy, MD simulation and phonon dispersion curves. \( \alpha \)-2D-germanene dioxide possesses a very high electron mobility of \( 4.09 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) along the \( k_x \) direction, which is much higher than that of MoS\(_2\) (\( \approx 3.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \)). Furthermore, the excellent optical properties makes \( \alpha \)-2D-germanene dioxide an excellent optical device. Prominent stability, appropriate band gap, high carrier mobility and remarkable light absorption render the studied materials highly suitable for applications in electronics and optoelectronics.

Conflicts of interest

There are no conflicts to declare.

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