Atomically thin mononitrides SiN and GeN: New two-dimensional wide band gap semiconductors

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Abstract – To match well with the Si-based electronics and satisfy the demand of miniaturization in modern industry, low-dimensional Si-based semiconductors maybe are the best candidates. Owing to the lack of such materials, in this work, we predicted two-dimensional atomically thin mononitrides SiN and GeN via a swarm structure search method and density functional theory. By the employment of HSE functional, both SiN and GeN are calculated as indirect wide band gap semiconductors with the gaps of $\sim 2.75$ and $\sim 2.25$ eV, respectively. Ab initio molecular-dynamics calculation displays that both mononitrides can exist stably even at an extremely high temperature of $\sim 2000$ K. Notably, phonon limited electron mobilities are evaluated as $\sim 0.888 \times 10^3$ and $\sim 0.413 \times 10^3$ cm$^2$V$^{-1}$s$^{-1}$ for SiN and GeN, respectively. We hope this work could expand the family of low-dimensional Si-based and wide band gap semiconductor.

Introduction. – With the development of modern industry, devices with low power consumption and small scale are desirable, which attracts a lot of research focused on searching for corresponding materials. Two-dimensional (2D) materials are the potential ones that could be utilized in the future components [1–3]. Subsequently, motivated by the exfoliation of graphene [4,5], researchers put a great deal of their work into designing new 2D materials or tuning properties of the existing 2D materials via theoretical or experimental methods [6,7]. For instance, hexagonal boron nitride (h-BN) sheet, borophene, phosphorene, germanene, silicene, 2D transition metal dichalcogenides, and 2D transition metal dinitride are reported in succession [8–16]. A lot of methods such as strain, vacancy, electric field and so on are employed to regulate the properties of 2D materials [17–20]. On the other hand, some properties of low-dimensional materials are usually very different from the bulk counterparts. For example, graphite behaves with a common metallic nature, while graphene shows a zero-gap semiconductor with Dirac points [4,5]. Such amazing properties also garner researchers’ tremendous interest to design new functionalized components.

It is well known that semiconductors are the key materials for the modern industry, such as in integrated circuits, power components, light-emitting diode (LED) fields, etc. Associated with the demand of miniaturization of components, searching for 2D semiconducting materials shows urgent need. Benefitting from the extensive study on 2D materials, some works have been reported on 2D semiconducting materials. For example, h-BN behaves as a semiconductor with a gap of 5.8 eV [21], monolayered MoS$_2$ exhibits semiconducting nature with a direct gap of $\sim 1.80$ eV [22], few-layer black phosphorus was also reported as a direct-gap semiconductor and the gap could increase up to 2.0 eV
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due to the
in air, which is caused by the existence of a dangling bond
with a buckling graphene-like structure, but it is unstable
character. It is well known that silicene is a semimetal
pounds without unpaired electrons exhibit semiconducting
means, is desired and maybe a suitable way. Usually, com-
conducting nature, instead of tuning silicene by different
of 0.026 eV.

However, although many 2D semiconductors have been
reported by theoretical or experimental methods, few
works were reported on applications of these 2D semi-
conductors, especially in integrated circuit. We think the
reason is that, in the previous integrated circuit, semi-
conducting materials are usually grown on Si or SiC sub-
strates, while so far reported 2D semiconductors cannot
match well with these substrates.

The above fact motivates researchers to search for 2D
silicon-based semiconductors. Silicene, as a 2D silicon
material with a buckling hexagonal honeycomb structure,
was theoretically designed in 2009 [10]. The electronic
calculation told it appears as a gapless semimetal, instead
of a semiconductor like its bulk counterpart, and its charge
carriers behave as a massless Dirac fermion due to the lin-
ear band crossing at the Fermi energy level (\(E_F\)). Fol-
lowing this report, some work was focused on tuning the
band gap of silicene. For example, Du et al. regulated silicene
from semimetal to semiconductor by chemically
adsorbing oxygen atoms, and the band gap could range
from 0.11 to 0.30 eV through the adsorption configura-
tions and amount of adsorbed oxygen atoms [36]. But
whether silicene with the oxygen atoms adsorbed on the
surface could match well with other silicon-based devices
is an open question, because the adsorbed atoms would
destroy the structure at the atomic level. Additionally,
chemical modification is still hard to achieve by experi-
ment now. Besides, Ni et al. theoretically predicted that
silicene also could be tuned to a semiconductor via a ver-
tical electric field [37]. However, the electric field applied
to open an effective gap is too high to achieve in exper-
iment, especially in practical applications, for example,
an electric field of 0.16 V/Å is required to open a gap
of 0.026 eV.

Therefore, searching for 2D silicides with intrinsic semi-
conducting nature, instead of tuning silicene by different
means, is desired and maybe a suitable way. Usually, com-
ounds without unpaired electrons exhibit semiconducting
character. It is well known that silicene is a semimetal
with a buckling graphene-like structure, but it is unstable
in air, which is caused by the existence of a dangling bond
due to the \(sp^3\) hybridization of Si atom. Based on this fact,
making monolayered SiN by substituting N for Si atoms
in one Si sublattice of silicene and then combining two SiN
monolayers via forming a Si-Si bond could just eliminate
the Si dangling bonds. Following this idea, we theoretically
design a new 2D layered silicide SiN. Since Ge is the
same group of Si, GeN with a similar structure is studied
as well. As expected, the results demonstrate that 2D
layered SiN and GeN both behave as semiconductors, with
wide band gaps of \(\sim 2.75\) and \(\sim 2.25\) eV, respectively.

Computational methods. – In order to confirm the
possibility of the experimental synthesis of 2D SiN and
GeN we hypothesized, the CALYPSO code is employed
to search for structures of these two compounds firstly.
The code is developed to search for the stable struc-
tures of compounds by using the swarm-intelligence–based
structural prediction calculations [38,39]. The underly-
ing \textit{ab initio} structural relaxations and electronic band
structure calculations are carried out in the framework
of DFT within generalized-gradient approximations using
the Perdew-Burke-Ernzerhof (PBE) exchange-correlation
functional and projector augmented-wave (PAW) poten-
tials [40,41] as implemented in the VASP code [42]. The
structural relaxations are performed until the Hellmann-
Feynman force on each atom is less than 0.001 eV/Å. To
ensure high accuracy, the \(k\)-point density and the plane-
waves cutoff energy are increased until the change of the
total energy is less than \(10^{-5}\) eV, and the Brillouin-zone
(BZ) integration is carried out using \(15 \times 15 \times 1\) Monkhorst-
Pack grid in the first BZ, the plane waves with the kinetic
energy up to 600 eV are employed. In addition, the sim-
ulations are performed using a 2 \(\times 2 \times 1\) supercell based
on unit cell, and the layered geometry is repeated with a
thick vacuum region of 20 Å. The phonon calculations are
performed using a supercell approach implemented in the
PHONOPY code [43,44].

Results and discussions. – The structures of SiN
and GeN found by CALYPSO, just as we hypothetically
designed, are pictured in fig. 1. Both 2D mononitrides ex-
hibit the space group \(P6_3m2\), and, moreover, some struc-
tural parameters are listed as well. The bond length of
Si-N is \(\sim 1.76\) Å, this value is consistent with \(\sim 1.72\) or
\(\sim 1.73\) Å in the bulk \(Si_3N_4\) given by the experiment [45]
or our calculation. The Si-Si bond length (i.e., the dis-
tance between two SiN atomic planes) is \(\sim 2.43\) Å, which
is somewhat larger than \(\sim 2.34\) and \(\sim 2.25\) Å in single-crystal
Si and silicene [10]. This slight difference of bond length is
originated from the different electronegativity between N
and Si atoms. The electronegativity of N is stronger than
that of Si atoms, leading to the fact that there would be
more electrons to form a Si-N bond and less electrons to
form a Si-Si bond compared with the corresponding bonds
in two pure Si isomers. The lessening of electrons would
weaken the Coulomb attractive force between Si atoms, re-
sulting in the lengthening of the bond. This is opposite to
the case with the amount of electrons increasing. Due to
the \(sp^3\) hybridization of Si atoms, the buckling charac-
teristic is present in SiN, and the buckling \(\Delta Z\) is \(\sim 0.56\) Å, a
bit larger than \(\sim 0.45\) Å in pure silicene [10]. This could be
explained by the following mechanism. When substituting
N for Si atoms in one Si sublattice, the Si-N bond length
is much shorter than that of the Si-Si bond in silicene, i.e.,
the 2D atomic plane is heavily compressed and such plane
compression pushes the N and Si sublayers outwards from
the plane and leads to the enhancement of buckling. For
the layered GeN plotted in figs. 1(b) and (d), it has a sim-

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Fig. 1: (Color online) The optimized structures of ground-state 2D layered mononitrides SiN and GeN. (a) and (b) are for the top views, and (c) and (d) are for the side views.

Fig. 2: (Color online) The isosurfaces of the electron localization function (ELF) for 2D layered mononitrides SiN and GeN. (a) and (b) are for the top views, and (c) and (d) are for the side views.

Similar structural configuration to that of the layered SiN. In detail, the Ge-N and Ge-Ge bond lengths are $\sim$1.91 and $\sim$2.57 Å, respectively, and the buckling $\Delta Z$ is $\sim$0.67 Å. These lengths of the bonds are both larger than those of the corresponding bonds in 2D layered SiN, arisen from the larger radius of Ge than that of Si atoms.

Based on the comparison of 2D mononitrides and some relative materials in bond length, this suggests that there are strong covalent bonds between the nearest-neighboring atoms in 2D layered SiN and GeN, and this is clearly confirmed by the isosurfaces of the electron localization function (ELF) plotted in fig. 2. The figure obviously shows that the electrons are distributed in the regions around the two nearest-neighboring atoms link, indicating the robust interaction between the two atoms. Besides, all the bonds show a $\sigma$ characteristic.

To investigate the possibility of experimental synthesis of these two layered mononitrides, the thermodynamic stability of 2D SiN and GeN is discussed through the cohesive energy. The cohesive energy is expressed as follows:

$$\Delta E_{\text{SiN}} = (E_{\text{Si}} + E_{\text{N}} - E_{\text{SiN}})/2,$$

$$\Delta E_{\text{GeN}} = (E_{\text{Ge}} + E_{\text{N}} - E_{\text{GeN}})/2,$$

where $E_{\text{SiN}}$ and $E_{\text{GeN}}$ are the total energies of one chemical formula SiN and GeN, $E_{\text{Si}}$, $E_{\text{Ge}}$, and $E_{\text{N}}$ are the total energies of the isolated single Si, Ge, and N atoms, respectively. The calculated $\Delta E_{\text{SiN}}$ and $\Delta E_{\text{GeN}}$ are 5.59 and 4.27 eV, respectively. These values are larger than 3.98 and 3.26 eV of silicene and germanene calculated in this work. The relatively large cohesive energies of 2D SiN and GeN layers indicate that their phases could exist stably.

Next, the dynamical properties of 2D layered SiN and GeN are studied by calculating the phonon dispersion, and the phonon dispersion curves are plotted in fig. 3. If the curve shows no imaginary frequency, it indicates that the structure is dynamically stable. Otherwise, the structure is dynamically unstable. The figure clearly shows that there is no imaginary frequency for the structures of two mononitrides, indicating the dynamical stability for both of them. Additionally, the highest frequencies of 2D SiN and GeN are around 900 and 700 cm$^{-1}$, respectively, much higher than those of silicene ($\sim$600 cm$^{-1}$) and germanene ($\sim$350 cm$^{-1}$) reported previously [10]. High frequencies suggest that there are strong bonds formed between the two nearest-neighboring atoms in SiN and GeN. Besides, the highest frequency of SiN is higher than that of GeN, corresponding to the fact that the Si-N bond length is much shorter.

To further evaluate the thermal stability of SiN and GeN, the ab initio molecular-dynamics (AIMD) simulations are performed. During the calculations, a large $4 \times 4 \times 1$ supercell based on the primitive cell is employed, AIMD simulations are calculated using the $NVT$ ensembles, the temperature controlled by the Nosé-Hoover method ranges from 300 K to 2000 K, and the simulations last for 10 ps with a time step of 2.0 fs. Simulation snapshots of the last step for the two mononitrides at different temperature are described in fig. 4. For SiN, there is no breaking of the bonds and the original configuration is well kept even at a high temperature of 2000 K, while the warp in the atomic plane enhances with increasing temperature from the side view. For GeN, the performance is similar to that of SiN, except that the warp is much stronger than that in SiN at the same temperature. When the temperature reaches 2000 K, some Ge atoms approach to breaking away from the atomic plane, but the original configuration still mainly remains. These facts tell us that the thermal stability of SiN is much stronger than that of GeN,
Fig. 4: (Color online) Snapshots of 2D layered mononitrides SiN (left column) and GeN (right column) equilibrium structures at (a) 300 K, (b) 500 K, (c) 1000 K, (d) 1500 K, and (e) 2000 K at the last step of 10 ps AIMD simulations.

originated from the higher cohesive energy of SiN than that of GeN. As a result, the above performance means that both layered SiN and GeN possess high thermal stability, indicating their potential applications even at an extremely high temperature.

Based on the stability of SiN and GeN, the investigation of their electronic properties is encouraged. The density of electronic states (DOS) and partial density of electronic states (PDOS) are calculated and described in fig. 5. The total DOS in figs. 5(a) and (c) display that the two layered mononitrides SiN and GeN both show semiconducting nature, and the energy gaps are $\sim 1.75$ and $\sim 1.20$ eV, respectively. Since the binding energy of valence electrons in Si is much stronger than that in Ge, the energy gap of SiN is larger than that of GeN. In detail, the PDOS further reveals that there are many peaks of the Si/Ge and N states located at the same energy levels, indicating the strong interaction between two types of atoms. This can be confirmed by ELF in fig. 2 which exhibit strong covalence bonds. Furthermore, the band structures are also explored, as plotted in figs. 5(b) and (d). It presents that SiN and GeN both behave as indirect band gap semiconductors, since the conduction band minimum (CBM) and the valence band maximum (VBM) are situated at $\Gamma$ and $K$ reciprocal points, respectively. It is well known that the PBE functional would usually underestimate the band gap, thus the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE), which can usually give more accurate band gaps than that of the PBE functional, is employed additionally. The calculated band gaps pictured in fig. 5 are $\sim 2.75$ and $\sim 2.25$ eV for 2D SiN and GeN, respectively, indicating that both mononitrides are wide band gap semiconductors. Figures 5(e)–(h) show the projected density of electronic states of each atom, and they unveil that VBM is mainly composed of Si/Ge $p_z$ and N $p_z$ orbitals, and CBM is mainly composed of Si/Ge $s$ and N $p_z$ orbitals. Figure 6 plots the partial (band decomposed) charge density of valence and conduction band edges, telling that both CBM and VBM of the two layered compounds SiN and GeN are originated from the orbitals of both types of atoms. The charge at VBM is localized around the N atom and along the Si-Si (Ge-Ge) bond, forming a $\sigma$ bond, and the charge at CBM is localized along Si-Si (Ge-Ge) with the $\pi$ bond characteristic and some is around the N atom.
is the partial (band decomposed) charge density of valence band edges for 2D layered mononitrides SiN and GeN, respectively. (c) and (d) are the partial (band decomposed) charge density of valence band edges for 2D layered mononitrides SiN and GeN, respectively.

Notably, the charge carrier transport property is so important for practical applications, thus the phonon limited carrier mobility in 2D materials is explored quantitatively as well. It can be calculated by the expression \[ \mu_{2D} = \frac{\hbar^3 C_{2D}}{k_B T m^* m_a (E_i^*)^2}, \] where \( e \) is the electron charge and \( h \) is Planck’s constant divided by \( 2 \pi \), \( k_B \) is Boltzmann’s constant, and \( T \) is the temperature with 300K employed here. \( m^* \) is the effective mass at CBM and VBM in the transport direction and defined as \( m^* = \frac{\hbar^2}{2E_i} \), and \( m_a \) is the average effective mass determined by \( m_a = (m_{3K+M}^* m_{K+\Gamma}^*)^{1/2} \). \( C_{2D} \) is the elastic modulus of the longitudinal strain in the propagation directions of the longitudinal acoustic wave and expressed by \( (E - E_0)/S_0 = C_{2D} (\Delta l/l_0)^2/2 \); here \( E \) is the total energy and \( S_0 \) is the lattice volume at equilibrium for a 2D system. \( E_i \) with the expression \( E_i = \Delta V_i / (\Delta l/l_0) \) represents the deformation potential constant of VBM for hole or CBM for electron along the transport direction. Here \( \Delta V_i \) is the energy change of the \( i \)-th band under proper cell compression and dilatation, \( l_0 \) and \( \Delta l \) are the lattice constant in the transport direction and the deformation of \( l_0 \), respectively. According to this equation, the evaluated electron mobility is \( \sim 0.888 \times 10^3 \) and \( \sim 0.413 \times 10^3 \) cm\(^2\)V\(^{-1}\)s\(^{-1}\) for SiN and GeN, respectively. The hole mobility in SiN is calculated as \( \sim 0.191 \times 10^3 \) and \( \sim 0.060 \times 10^3 \) cm\(^2\)V\(^{-1}\)s\(^{-1}\) along the \( K-\Gamma \) and \( K-M \) directions, respectively, and it is \( \sim 0.296 \times 10^2 \) and \( \sim 0.069 \times 10^2 \) cm\(^2\)V\(^{-1}\)s\(^{-1}\) for GeN along the same two directions, respectively. This carrier mobility anisotropy can be explained by partial charge density of valence and conduction band edges in fig. 6. For VBM, the figure indicates that the charge spreads along the \( K-\Gamma \) direction rather than the \( K-M \) direction, illustrating that the carrier transporting along the \( K-\Gamma \) direction is relatively easily than along the \( K-M \) direction, since the carrier must cross the hexagonal hole along the \( K-M \) direction. While for CBM, the charge fills the whole hexagonal hole, leading to the same electron mobility along different directions. Interestingly, these mobilities of the two 2D mononitrides are much higher than those of boron nitride nanoribbons (\( \sim 58.80 \) cm\(^2\)V\(^{-1}\)s\(^{-1}\)) \cite{51} [51] and MoS\(_2\) (\( \sim 3.5 \) cm\(^2\)V\(^{-1}\)s\(^{-1}\)) \cite{52}, and have the same order of magnitude of \( \sim 10^3 \) cm\(^2\)V\(^{-1}\)s\(^{-1}\) in atomically thin InSe \cite{35} at room temperature. Such high carrier mobility demonstrates that 2D mononitrides SiN and GeN could be potential materials for power components and so on.

**Conclusions.**—In conclusion, via first-principles calculations in combination with a swarm structure search method, 2D atomically thin mononitrides SiN and GeN are designed. Both layered mononitrides are constructed by two hexagonal single-atom–thick structures which are linked by strong Si-Si or Ge-Ge bonds between two sublayers. The atomic configuration can be kept even at an extremely high temperature up to 2000K. The electronic calculation reveals that 2D layered SiN and GeN both exhibit semiconducting nature with the wide band gaps of \( \sim 2.75 \) and \( \sim 2.25 \) eV, respectively. Excitingly, their carrier mobilities have a magnitude of \( \sim 10^3 \) cm\(^2\)V\(^{-1}\)s\(^{-1}\). This work opens a promising way for developing 2D atomically thin wide band gap semiconducting materials.

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