Theoretical prediction of a graphene-like structure of indium nitride: A promising excellent material for optoelectronics

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1. Introduction

Group III-nitride (BN, AlN, GaN, InN, TIN) semiconductors have been intensively studied for a long time because of their application in semiconductor devices, such as blue/UV light emitting diodes (LEDs), laser diodes and high-frequency transistors [1–5]. Among them, InN exhibits unique electronic and optical properties and thus has been a key material for optical and high temperature device applications. In most of the reports InN has been grown on sapphire (0001) substrates and it is an n-type semiconductor [6,7]. Wurtzite InN possesses a direct band gap of about 0.7 eV [8,9]. The band gaps of hexagonal InN are weakly dependent on the electron concentrations and close to 0.65 eV [10]. Alloysed with large

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Single-crystal Wurtzite type Indium nitride nano-wires and nanotubes have been fabricated [21–24] and similar to BN nano wires, a semiconductor-to-metal transition is observed at 80 K [21]. This transition is attributed to a donor level below conduction band minimum (CBM). Other nano-structure of InN is also successfully made, strong aligned InN nano- and micro-scale rods were produced with chemical vapor deposition (CVD) [25], and branched InN nano-structures were grown with hydride vapor phase epitaxy [26].

Despite the extensive efforts, the fabrication of mono-atomic-layer graphene-like hexagonal InN monolayers (g-InN) has not yet been reported to the authors’ best knowledge, though the atomistic structure of g-InN as depicted in Fig. 1 were proposed using first-principles calculations [4,5]. Motivated by the success of graphene but non-successful fabrication of g-InN, We carry out computationally investigation on the mechanical stabilities to ensure its existence, and the structural, electronic, thermal, and mechanical properties of g-InN monolayers. We focus on the planar structure of g-InN in this study because it is more interesting in applications as buckled structure can be suppressed under constraints such as substrate, sandwiching, or heterogeneous multi-layers [27–29].

Mechanical forces are much more tangible, reliable, and widely applicable than other stimuli to materials. Macroscopic mechanical stimuli are used for control of molecular systems and molecular machines, in addition to micro-device fabrication [30]. The knowledge of mechanical properties of a material [31,32] is the base for development of mechanically responsive nanomaterials which will make a significant contribution to improvements in our lifestyles and our society [30,33,34]. It is desirable to know the mechanical properties of g-InN monolayers as it will be different from its bulk counterpart [35]. We use density functional theory (DFT) calculations to model their responses under various mechanical loadings. The strain energy potential profile, the stress–strain relationships, the high order elastic constants, and the pressure dependent properties are studied.

Combining the first-principles calculations with elastic theory, we make a link between continuum formulation and atomistic modeling. Therefore, our results could also be useful in finite element modeling of the multi-scale calculations for mechanical properties of g-InN monolayers. As a part of the effort searching for flexible electronics, we have previously examined other graphene-like compounds, such as g-BN, g-GaN, g-TiN, g-ZnO, g-ZnS, g-GeC, g-MoS2, g-C3O, g-Boron, etc. [36–48]. Using the same method, we examine the mechanical stability and mechanical properties including high-order elastic constants up to fifth orders. Our results are compared to that of graphene and graphene-like boron nitride monolayer (g-BN). The results of graphene [38] and g-BN [49] were reported previously. They serve as references to g-InN monolayers because they have similar structures. Another goal of this report is the propose the existence of g-InN, though it has not been fabricated yet. To that end, we systematically studied the dynamical stabilities and thermal stabilities in addition to the mechanical stabilities, which is prominent in the similar work. Furthermore, we studied the electronic properties and thermal properties besides mechanical properties. Our results shows that the g-InN is quite stable with a direct band gap of 0.57 eV, indicating that it is very promising to fabricate it in the near future for optoelectronics. The organization of this paper is as follows. Section 2 presents the computational details of DFT calculations. The results and analysis are in Section 3, followed by conclusions in Section 4.

2. Computation method

We perform the first-principles calculations with density-functional theory (DFT) for the total energies of the system, forces on each atom, and stresses of the simulation box under the desired deformation configurations. The stress–strain relationship of g-InN monolayers then are obtained. The first-principles calculations are appropriate and required to capture the quantum confinement in the third dimension in the atom-thick 2D materials, especially under extremely large mechanical loading. DFT calculations were carried out with the Vienna Ab-initio Simulation Package (VASP) [50] which is based on Kohn–Sham Density Functional Theory [51] with the generalized gradient approximations as parameterized by Perdew, Burke, and Ernzerhof for exchange-correlation functions [52]. The electrons explicitly included in the calculations are the \(4d^{10}5s^25p^1\) electrons for indium atoms and \((2s^22p^3)\) electrons for nitrogen atoms. The core electrons are replaced by the projector augmented wave and pseudo-potential approach [53]. A plane-wave cutoff of 600 eV is used in all the calculations. The convergence of the total energy and forces is \(10^{-5}\) eV and \(10^{-3}\) eV/A, respectively. The calculations are performed at zero Kelvin within the frame of DFT. The irreducible Brillouin Zone was sampled with a Gamma-centered \(24 \times 24 \times 1\) k-mesh. There was a 15 Å thick vacuum region to reduce the inter-layer interaction to model the single layer system. The van der Waals interactions are described by the DFT-D3 method [54] throughout this study.

The atomic structures of all the deformed and undeformed configurations were obtained by fully relaxing 6-atom-unit cell where all atoms were placed on one plane. The simulation invokes periodic boundary conditions for the two in-plane directions. The phonon dispersion curves and thermal properties are calculated using the finite displacement method implemented in the phonopy package [55]. A super cell containing \(3 \times 3 \times 1\) unit cell \((54\ \text{atoms in total})\) are used to avoid significant artificial image interactions due to finite displacement for the force constants calculations. A \(31 \times 31 \times 1\) \(q\)-mesh are used for phonon calculations.

To eliminate the artificial effect of the out-of-plane thickness of the simulation box on the stress, we used the second Piola–Kirchhoff stress [49] to express the 2D forces per length with

![Fig. 1. Geometry of g-InN monolayers. The proposed graphene-like planar structure of g-InN are displayed in (a) overview, (b) armchair-side-view, and (c) zigzag-side-view. The In and N atoms are depicted by the large and small balls, respectively.](image-url)
units of N/m. The Lagrangian strain [56] was used in this study, defined as \( \eta = \epsilon + 1/2\epsilon^2 \), where \( \epsilon \) is the engineering strain [49].

For high order elastic constants up to fifth order in this graphene-like structure, there are only 14 independent elastic constants that need to be explicitly considered due to the symmetries of the atomic lattice point group \( \Gamma \) which consists of a sixfold rotational axis and six mirror planes [49]. The 14 independent elastic constants of g-InN monolayers are determined by least-squares fit to the stress–strain results from DFT calculations in two steps, detailed in our previous work [49], which have been well used to explore the mechanical properties of 2D materials [36,37,57,38,59,40,59,41–48].

*Ab initio* molecular dynamics (AIMD) simulations are carried out with Canonical ensemble (or NVT ensemble) where the volume \( V \) is fixed. A super cell is built with \( 5 \times 5 \times 1 \) 6-atom-unitcells, of which the total atom number is \( N = 150 \). The Nose–Hoover thermostat is used to control the frequency of the temperature oscillations during the simulations. The time step is 1 fs and the total simulation time is 2 ps.

3. Results and analysis

3.1. Atomic structure

We consider a conventional unit cell as shown in Fig. 2 which contains three nitrogen atoms and three indium atoms forming a coplanar hexagonal ring with periodic boundary conditions in plane directions only. The *armchair* direction is the direction of an atom to one of its nearest neighbors in the planar honeycomb network and was set to be parallel to the \( x \) axis, which is denoted “1” in superscript of strains and stresses, as shown in Fig. 2. The *zigzag* direction is perpendicular to the armchair direction and was set as \( y \)-axis, which is denoted “2” in superscript of strains and stresses.

We first optimize the atomistic structures for g-InN monolayers. The initial configuration is generated by placing 3 indium atoms and 3 nitrogen atoms alternatively on the same plane, forming the 6-atom-unit cell. The relaxed structure shows that the six atoms are still coplanar, as shown in Fig. 2.

The most energetically favorable structure is set as the strain-free structure, whose In–N bond length is 2.074 Å (Fig. 2), much larger than the corresponding B–N bonds in g-BN (1.52 Å). The N–In–N and In–N–In bond angles are 120°. The lattice constant or the second nearest neighbor distance is 3.585 Å. Our result agree with a previous DFT study [4]. It is worth noting the that the lattice constants of Wurtzite structure of bulk InN is \( a = 3.540 \) and \( c = 5.704 \) Å in experimental measurement [60]. This strain-free structure is then set as the reference when mechanical strain is loaded.

3.2. Electronic band structure and density of state

We study the electronic band structure of unstrained monolayer g-InN. All the bands are shifted so that the Fermi energy are set to be zero. We only illustrate those bands within 4 eV around the Fermi energy, as in Fig. 3. The first Brillouin zone and high symmetrical \( k \) points of \( \Gamma \), \( X \), and \( M \) are shown in Fig. 2. We observed a direct band gap of 0.57 eV at \( \Gamma \) point. The total density of states (DOS) is also plotted in Fig. 3 aligned with the band structure for better view. As a comparison, the band gap of bulk InN is 0.65–0.8 eV by experiments [9,10] and 0.4–0.8 eV [4,61–64] by first-principles calculations. It is worth noting that the indium atoms have heavy 5d electrons which contribute the spin orbit coupling (SOC). However, the contribution should be smaller than 0.089 eV which is the SOC in g-TiN with 6d electrons [65]. Therefore, the contribution of SOC to the total band gap could be ignored. It is well known that the GGA-PBE underestimates the electronic band gap. Therefore, our result 0.57 eV gives a lower boundary of the band gap of g-InN and the direct band gap is still valid.

To gain a better insight of how the electrons of individual elements contribute to the band structures, we have studied their projected DOS (namely PDOS). The contribution from the two elements are compared in Fig. 4(a). It is clear that the valence electrons are mainly from nitrogen atoms. The local DOS plot in Fig. 4(b) implies that the \( p \) electrons are the majority of valence electrons. \( s \) and \( p \) electrons have the same population in conduction bands just

![Fig. 3. Electronic structure](image-url) The electronic band structure (left) and the corresponding total electronic density of states (right) of a g-InN monolayer predicted from GGA-PBE with vdW-D3 calculations. The Fermi energy are set to be zero.
above the band gap. The analysis of the DOS of nitrogen in Fig. 4(c) shows that p electrons of nitrogen are outweighed than s electrons. This means that the s electrons in low part of conduction bands are mainly from Indium atoms. Further study of the components of the p electrons of nitrogen reveals that the p\_2\_2 electrons are responsible for the upper part of the valence bands. From these analysis, we can conclude that the N 2p\_2 electrons and In 5s electrons are critical in forming band gap.

3.3. Phonon modes

The lattice vibrations play important role in the crystals properties. The dynamics instability of a crystal structure is marked by the imaginary frequencies of phonon modes. A crystal is dynamically stable if its potential energy always increases against any combinations of atomic displacements. In the harmonic approximation, this is equivalent to the condition that all phonons have real and positive frequencies. Therefore, a imaginary frequency indicates dynamical instability of a system, which means that the corrective atomic displacements could reduce the potential energy in the vicinity of the equilibrium atomic positions. Imaginary mode provides useful information to study displacive phase transition, as a given structure having imaginary phonon modes can be led to alternative structures through continuous atomic displacements and lattice deformations.

To investigate the dynamics instability of the g-InN monolayers, we calculate its phonon dispersion curves. The results of the phonon band structure and its corresponding density of states are shown in Fig. 5 for an strain-free monolayer of g-InN. First of all, there is no imaginary frequencies of all phonon modes, which indicates that the monolayer g-InN is dynamically stable. It is worth noting that there is a negligible amount of imaginary frequencies (<50 Hz) around gamma point which is numerical artifact due to relatively small simulation box in this super-cell method limited by the computing resources. That all phonon modes are positive confirms that the atomic structures are in an energy-minimum position in a configurational space. The phonon band structure is a direct evidence that the g-InN monolayer are stable in finite temperature, and it should be fabricated experimentally.

The frequencies of all the phonon modes are no more than 21.8 THz. The three acoustic phonon bands with lowest frequencies around \Gamma points reflect the long-wave phase motions. They are longitudinal acoustic (LA), transverse acoustic (TA), and flexural acoustic (ZA) modes. These three bands show a linear dependence on the wave vectors around the zone center. There is 15 optical phonon modes with much higher frequencies. There is a large phonon band gap of 9.3 THz lies between 7.6 and 16.9 THz. Our results agree with a previous DFT prediction [4]. The corresponding total density of states of these phonon modes confirm such an observation, as illustrated by the gray line and area in right panel of Fig. 5. We further analyze the projected phonon density of states.
on each atom. It is interesting that the upper branches of optic phonon modes that are above the phonon band gap (or those with a frequency larger than 16.9 THz) are contributed more by the Nitrogen atoms. On the contrary, the lower branch of optic phonon that are below the phonon band gap (or those with a frequency less than 7.6 THz) depends mainly on the Indium atoms. This could be understood by the fact that an Indium atom has a mass 8.2 times larger than that of a Nitrogen atom. We could predict that the phonon band gap will be smaller in BN, AlN, and GaN, but larger in InN monolayers. This could be useful in designing phononic materials with 2D materials.

3.4. Thermal properties

Once phonon frequencies over Brillouin zone are known, from the canonical distribution in statistical mechanics for phonons under the harmonic approximation, the energy of phonon system can be obtained [55]. The thermal properties of solids at constant volume can be calculated from their phonon density of states as a function of frequencies. The phonon contribution to the Helmholtz free energy $F_A$ is given by [55]:

$$F_A = \frac{1}{2} \sum_{q,v} \hbar \omega_{q,v} + k_B T \sum_{q,v} \ln \left[ 1 - \exp \left( -\frac{\hbar \omega_{q,v}}{k_B T} \right) \right],$$

(1)

where $k_B$ and $\hbar$ are the Boltzmann constant and the reduced Planck constant, respectively, $q$ and $v$ are the wave vector and band index, respectively, $\omega_{q,v}$ is the phonon frequency at $q$ and $v$, and $T$ is the temperature. The heat capacity $C_V$ at constant volume is given by

$$C_V = \sum_{q,v} \left( \frac{\hbar \omega_{q,v}}{k_B T} \right)^2 \exp \left( -\frac{\hbar \omega_{q,v}}{k_B T} \right) \left[ \exp \left( -\frac{\hbar \omega_{q,v}}{k_B T} \right) - 1 \right]^2,$$

(2)

The entropy $S$ is calculated as the relationship of

$$S = -k_B \sum_{q,v} \ln \left[ 1 - \exp \left( -\frac{\hbar \omega_{q,v}}{k_B T} \right) \right] - \frac{1}{T} \exp \left( -\frac{\hbar \omega_{q,v}}{k_B T} \right) - 1.$$

(3)

With the phonon density of states plotted in Fig. 5, we calculated the Helmholtz free energy $F_A$, entropy $S$, and heat capacity $C_V$ at constant volume of g-InN monolayers as a function of temperature, as shown in Fig. 6. It is known that the melting temperature of a bulk InN is 1320 K. The quasi-harmonic approximation is valid in general up to 2/3 of melting temperature. Therefore, we only plot their thermal properties up to 600 K within the quasi-harmonic approximation. We notice that the Helmholtz free energy decreases monotonically with respect to temperature, opposed to trends of entropy and heat capacity. These normal thermal behaviors imply the validity of our calculations. At a room temperature of 300 K, the Helmholtz free energy, entropy, and heat capacity are $-2.977$ kJ/mol, $197.17$ J/Kmol, and $120.57$ J/Kmol, respectively. According to the Debye approximation, the Debye frequency can be obtained from the specific heat capacity. The Debye frequency of a g-InN monolayer is 6.06 THz and the corresponding Debye temperature is 290.92 K.

3.5. Thermal stability

Molecular dynamics simulations are a common approach to examine the thermal stabilities of a material. Limited by the availability of the reliable empirical force field of InN, we investigate the thermal stabilities using the accurate and computing demanding AIMD simulations [66]. We study the thermo-dynamical behaviors of g-InN monolayers at finite temperature $T = 600$ K. The snapshot of the structure of g-InN after 2.0 ps equilibrium at 600 K are displayed in Fig. 7. There are small wiggles due to the out-of-plane vibration modes at finite temperatures. However, no broken bonds are observed, which implies that this g-InN structure is thermodynamically stable under finite temperatures, up to 600 K.

3.6. Strain energy profile

To obtain the strain–energy profile, we need to have mechanical loading on the system, both elongation or compression. When strain is applied, the system will be disturbed away from the equilibrium state. All the atoms of the system are allowed full freedom of motion. A quasi-Newton algorithm is used to relax all atoms into equilibrium positions within the deformed unit cell that yields the minimum total energy for the imposed strain state of the supercell. Since the configuration energy of the strain–free configuration is the minima of the potential well, any strain will increase the system's energy. By applying different amounts of strain along different directions, the potential well can be explored.

In this study, Lagrangian strains ranging from $-0.1$ to 0.3 are considered with an increment of 0.01 in each step for all three deformation modes. It is important to include the compressive strains since they are believed to be the cause of the rippling of the free standing atomic sheet [67]. Because it was reported that a graphene sheet experiences biaxial compression after thermal annealing [68], which could also happen with g-InN monolayers. We selected such an asymmetrical strain range ($-0.1 \leq \eta \leq 0.3$) owing to the non-symmetric mechanical responses of material. The lower and upper boundary of the strain are consequent upon its mechanical instability to the compressive and tensile strains.

The strain energy is defined as $E_s = (E_{tot} - E_0)/n$, where $E_{tot}$ is the total energy of the strained system, $E_0$ is the total energy of the strain-free system, and $n = 6$ is the number of atoms in the unit cell. The results of $E_s$ of the g-InN monolayer are plotted in Fig. 8a as a function of strain in three modes of uniaxial armchair, uniaxial zigzag, and biaxial deformation. We have also compared the potential profile of g-InN with that of g-BN (Fig. 8b). It is clear that $E_s$ is anisotropic with strain direction. $E_s$ is non-symmetrical for compression ($\eta < 0$) and tension ($\eta > 0$) for all three modes. This non-symmetry indicates the anharmonicity of the g-InN monolayer structures, and it is common in large deformation of condensed matters. It is worth noting that for small strain, there is a harmonic
region, where the $E_s$ is a quadratic function of applied strain. As a consequence, the stresses as the derivatives of the strain energies are linearly increasing with the increase of the applied strains in the harmonic region. From the plots of the strain energy profile, one can tell that the harmonic region can be taken between $-0.02 < \eta < 0.02$ in the g-InN monolayers.

When the strain is larger, the linear stress–strain relationship is invalid. The range of these strain is anharmonic region. The main feature of the anharmonic region is that the higher order terms are not negligible. With even larger loading of strains, the system will undergo irreversible structural changes. Then the system enters a plastic region where it may fall into parts. The maximum strain in the anharmonic region is the ultimate strain. The summation of the critical tensile strain and critical compressive strain is the stable region of that deformation. The width of the stable region defines the opening width of the potential energy well (Fig. 8). In general, the opening width and depth of the potential energy well $\eta_0$ reflects the flexibility and strength of a nano structure, respectively. The average width of the stable regions of the three deformation modes (i.e., the opening width of the potential energy wells) is a reasonably good scale for the mechanical stabilities of the nano structures. As a result, from the point view of potential energy, we conclude that g-InN is mechanically stable. However, it is less stable than g-BN, because both the depth and width of the potential energy well are smaller than that of g-BN. Besides the scale for mechanical stabilities, strain energy profile can be used to estimate the range of lattice mismatch feasible for epitaxial growth of the 2D materials on the substrates [5].

### 3.7. Stress–strain curves

The stresses are the derivatives of the total energies with respect to the strains. We plot the stress–strain relationship in Fig. 9 along the three modes of uniaxial strains along the armchair direction (mode $a$), uniaxial strains along the zigzag direction (mode $z$), and biaxial strains (mode $b$). The material behaves in an asymmetric manner with respect to compressive and tensile strains. With increasing strains, the In–N bonds are stretched and eventually rupture. When strain is applied in the mode $a$, the bonds of those parallel in this direction are more severely stretched than those in other directions. Under the deformation mode $z$, in which the strain is applied perpendicularly to the armchair direction, there is no bond parallel to this direction. The two In–N bonds at an incline to the zigzag direction with an angle of about 30° are more severely

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**Fig. 7. Thermal stability.** *ab initio* molecular dynamics simulations show that g-InN monolayers are stable at $T=600$ K. The snapshot of the structure of g-InN after 2.0 ps are displayed in (a) overview, (b) armchair-side-view, and (c) zigzag-side-view. The In and N atoms are depicted by the large and small balls, respectively.

**Fig. 8. Strain energy.** Energy-strain responses for armchair, zigzag, and biaxial strains of g-InN (top), compared with g-BN (bottom) [49].
stretched than those in the armchair direction. Under the ultimate strain in mode $z$, which is 0.26, the two In–N bonds that are at an incline to the armchair direction are observed to rupture. Under the ultimate strain in mode $b$, $\nu_{yz} = 0.18$, the two In–N bonds that are at an incline to the zigzag direction with an angle of about 30° are observed to rupture.

3.8. Elastic constants

The elastic constants are essential parameters to describe the elasticity of materials. The 14 independent elastic constants of g-InN are determined by a least-square fit to the stress–strain results from DFT calculations [49]. The second order elastic constants model the linear elastic response. The higher (>2) order elastic constants are important to characterize the nonlinear elastic response of g-InN using a continuum description. These can be obtained using a least square fit of the DFT data and are reported in Table 1. Corresponding values for graphene are also shown.

Our results of in-plane stiffness of g-InN is $Y_s = 62.0 \text{ N/m}$, much smaller than that of g-BN and graphene. In order to interpolate our results in terms of standard units of GPa, we need the size of the out-of-plane dimension, which however is not well defined in 2D material. Taking the interlayer vdW distance of 5.7 Å from its 3D layered Wurtzite-type structure [60], our result of the in-plane stiffness is 109 GPa, less than the bulk modulus (125 GPa) of its bulk counterpart [60]. This could be a consequence of the stretch of its lattice constants. The Poisson’s ratio of g-InN is $\nu = 0.586$, about 2.6 and 3.3 times that of g-BN and graphene, respectively.

Higher order (>2) elastic constants are important quantities [69] in studying the nonlinear elasticity, harmonic generation, lattice defects, phase transitions, strain softening, temperature dependence of elastic constants, phonon–phonon interactions, photon–phonon interactions, thermal expansion (through the Gruneisen parameter), echo phenomena, and so on [38]. Experimentally the higher order elastic constants can be determined by measuring the changes of sound velocities under the application of hydrostatic and uniaxial stresses [70]. As it is more convenient to apply pressure in experiment, the full stress–strain relationship described by the higher order elastic constants are critical. Explicitly, when pressure is applied, the pressure dependent second-order elastic moduli can be obtained from the higher order elastic continuum description [49]. The third-order elastic constants are important in understanding the nonlinear elasticity of materials, such as changes in acoustic velocities due to finite strain. As a consequence, nano devices (such as nano surface acoustic wave sensors and nano waveguides) could be synthesized by introducing local strain [71,72].

Table 1

<table>
<thead>
<tr>
<th>Elastic constants</th>
<th>g-InN (GPa)</th>
<th>g-BN (GPa)</th>
<th>Graphene (GPa)</th>
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<tr>
<td>$\alpha$ (Å)</td>
<td>3.585</td>
<td>2.512</td>
<td>2.468</td>
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<td>$Y_s$ (N/m)</td>
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<td>$\nu$</td>
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\[Fig. 9. \textbf{Stress–strain relationship.} \textit{Stress–strain responses of g-InN (left) under armchair (top), zigzag (middle), and biaxial (bottom) strains, compared with that of g-BN (right). $\Sigma_1$ ($\Sigma_2$) denotes the x (y) component of stress. “Cont” stands for the fitting of DFT calculations (“DFT”) to continuum elastic theory.}\]
C_{11}, C_{22}, C_{111}, C_{222}, and so on. The other is shear terms, which are C_{12}, C_{112}, C_{1112}, and so on. The normal terms are in charge of the strength of the material, and the shear terms reflect more about the flexibility. The comparison of the data in Table 1 reveals that the normal terms of g-InN monolayers are smaller in magnitude than those of g-BN and graphene, consistent with the conclusion that the g-InN is “softer”. However, the shear terms do not show a clear trend. The g-InN monolayers exhibit instability under large tension. Stress–strain curves in the previous section show that they might soften when the strain is larger than the ultimate strain. From the view of electron bonding, this is due to the bond weakening and breaking. This softening behavior is determined by the TOECs and FFOECs in the continuum aspect. The negative values of TOECs and FFOECs ensure the softening of g-InN monolayer under large strain. It should be pointed out that the tensile strength could be an overestimate of the onset of the instability due to the limitation of the model [73].

The importance of the high order elastic constants can be perceived when we consider their contribution to the nonlinear elasticity. When we only consider the second order elasticity, the stress varies with strain linearly. Take the biaxial deformation as an example. As illustrated in Fig. 10, the linear behaviors are only valid within a small strain range, about 0.02, \( \eta = 0.02 \). With the knowledge of the elastic constants up to the third order, the stress–strain curve can be accurately predicted within the range of \( \eta \leq 0.06 \). Using the elastic constants up to the fourth order, the mechanical behaviors can be well treated up to a strain as large as 0.1. For the strains beyond 0.1, the fifth order elastic are required for accurate modeling. The analysis of the uniaxial deformations provides similar results.

### 3.9. Pressure effect on the elastic moduli

As a demonstration of the usage of the high order elastic constants, we predicted the pressure effect on the elastic moduli from these elastic constants (Table 1). The pressure effect on the photoluminescence and emission energies of the InN/GaN super lattices has been reported [74]. The nonlinear elasticity and the pressure dependence of elastic constants have been investigated in bulk III-N compounds [75]. However, the pressure effect on the elastic moduli is still unknown in g-InN monolayers. We calculate the effect of the second-order elastic moduli on the pressure \( p \) acting in the plane of g-InN from the third-order elastic moduli. Explicitly, when pressure is applied, the pressure dependent second-order elastic moduli \( \tilde{C}_{11}, \tilde{C}_{12}, \tilde{C}_{22} \) can be obtained from \( C_{11}, C_{12}, C_{22}, C_{111}, C_{222}, Y_s, v, \) as detailed in Ref. [71].

The second-order elastic moduli of g-InN are seen to increase linearly with the applied pressure (Fig. 11). Poisson’s ratio also increases monotonically with increasing pressure. \( C_{111} \) is not symmetrical to \( C_{222} \) any more; only when \( P = 0, C_{11} = C_{22} = C_{111} \). This anisotropy could be the outcome of anharmonicity.

#### 3.10. Mechanical instabilities

The mechanical instabilities are the most important in the real applications and material or system designs. The ultimate strains are determined as the corresponding strain of the ultimate stress, which is the maxima of the stress–strain curve. The ultimate strengths and strains corresponding to the different strain conditions are summarized in Table 2, compared with that of g-BN and graphene, since they have similar structure and they are close to each other in the periodic table. The g-InN sheet behaves in an asymmetric manner with respect to compressive and tensile strains. With increasing strains, the B–B bonds are stretched and eventually rupture. The positive slopes of the stress–strain curves and the positive ultimate tensile stresses indicate that this structure is mechanical stable.

The g-InN sheet behaves in an asymmetric manner with respect to compressive and tensile strains. With increasing strains, the In–N bonds are stretched and eventually rupture. The positive slope of the stress–strain curves and the positive ultimate tensile stresses indicate that this structure is mechanical stable. Our results show that the g-InN monolayers are stable under various strains.

### Table 2

**Elastic limits.** Ultimate strengths \( \left( \Sigma_{y}, \Sigma_{x}, \Sigma_{z} \right) \) in units of N/m and ultimate strains \( (\eta_{y}, \eta_{x}, \eta_{z}) \) under uniaxial strain (armchair and zigzag) and biaxial from DFT calculations, compared with g-BN and graphene.

<table>
<thead>
<tr>
<th></th>
<th>g-InN</th>
<th>g-BN*</th>
<th>Grapheneb</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Sigma_{y} )</td>
<td>8.0</td>
<td>23.6</td>
<td>28.6</td>
</tr>
<tr>
<td>( \eta_{y} )</td>
<td>0.18</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td>( \Sigma_{x} )</td>
<td>8.0</td>
<td>26.3</td>
<td>30.4</td>
</tr>
<tr>
<td>( \eta_{x} )</td>
<td>0.21</td>
<td>0.26</td>
<td>0.23</td>
</tr>
<tr>
<td>( \Sigma_{z} )</td>
<td>8.0</td>
<td>27.8</td>
<td>32.1</td>
</tr>
<tr>
<td>( \eta_{z} )</td>
<td>0.15</td>
<td>0.24</td>
<td>0.23</td>
</tr>
</tbody>
</table>

* Ref. [38].

b Ref. [49].
From the view of energy, the mechanical instabilities are related to the energy barriers, over which the material fails. In our ideal model, this energy barrier is the binding energy. Therefore, we can estimate the binding energy of 1.3 eV from the strain-energy plot (Fig. 8) with $\psi_0^{\text{vac}} = 0.15$.

Note that the softening of the g-InN monolayers under strains beyond the ultimate strain only occurs for ideal conditions. The systems under this circumstance are in a meta-stable state, which can be easily destroyed by long wavelength perturbations and vacancy defects, as well as high temperature effects, and enter a plastic state [76]. Thus only the data within the ultimate strain has physical meaning.

4. Conclusions

In summary, our first-principles calculations based on density functional theory shed light on the stabilities and properties of the proposed g-InN. For stabilities, the main concern is the mechanical, dynamical, and thermal stabilities, which could be theoretically examined by the mechanical loading, phonon band structure, and molecular dynamics simulations, respectively. The imaginary frequencies are absent from the phonon band structure of g-InN, indicating that the planar structure of g-InN is dynamically stable.

From the phonon density of states, we obtained the Helmholtz free energy, entropy, and heat capacity at constant volume of g-InN monolayers as a function of temperature up to 600 K using lattice dynamics within quasi-harmonic approximation. At a room temperature of 300 K, the Helmholtz free energy, entropy, and heat capacity are $-2.977$ kJ/mol, 197.17 J/Kmol, and $120.57$ J/K/mol, respectively. The Debye temperature is 290 $\pm$ 2 K.

By applying various mechanical strains, we examined the elastic and mechanical properties of g-InN. We find that a low in-plane stiffness, about 18% of that of graphene, and a high Poisson ratio of 0.586, 3.3 times that of graphene. The potential profiles and the stress–strain curves indicate that the free standing g-InN monolayers can sustain large tensile strains, up to 0.13, 0.21, and 0.15 for armchair, zigzag, and biaxial deformations, respectively. However, both the strength and flexibility are reduced compared to graphene-like boron nitride monolayers. The third, fourth, and fifth order elastic constants are indispensable for accurate modeling of the mechanical properties under strains larger than 0.02, 0.06, and 0.10 respectively. The second order elastic constants, including in-plane stiffness, are predicted to monotonically increase with pressure, while the trend in the Poisson ratio is reversed.

Our results imply that g-InN monolayers are mechanically stable under various large strains, in addition to dynamical and thermal stability, suggesting the existence of such a planar structure at temperatures up to 600 K. The elastic limits provide a safe-guide for strain-engineering the g-InN based electronics.

Competing financial interests

The authors declare no competing financial interests.

Authors’ contributions

Q.P., S.L., and S.D. designated the research topic. Q.P. and X.S. carried out the calculations. Q.P., H.W., Y.Y., C.H., and X.W. did the analysis. Q.P. wrote the main manuscript text and designed the figures. All authors discussed the results and commented on the manuscript.

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