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Versatile $GaInO_3$-sheet with strain-tunable electronic structure, excellent mechanical flexibility, and an ideal gap for photovoltaics*

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Due to many remarkable physical and chemical properties, two-dimensional (2D) nanomaterials have become a hot spot in the field of condensed matter physics. In this paper, we have studied the structural, mechanical, and electronic properties of the 2D $GaInO_3$ system by first-principles method. We find that 2D $GaInO_3$ can exist stably at ambient condition. Molecular dynamic simulations show that $GaInO_3$-sheet has excellent thermal stability and is stable up to 1100 K. Electronic structural calculations show that $GaInO_3$-sheet has a band gap of 1.56 eV, which is close to the ideal band gap of solar cell materials, demonstrating great potential in future photovoltaic application. In addition, strain effect studies show that the $GaInO_3$-sheet structure always exhibits a direct band gap under biaxial compressive strain, and as the biaxial compressive strain increases, the band gap gradually decreases until it is converted into metal. While biaxial tensile strain can cause the 2D material to transform from a direct band gap semiconductor into an indirect band gap semiconductor, and even to metal. Our research expands the application of the $GaInO_3$ system, which may have potential application value in electronic devices and solar energy.

Keywords: two-dimensional (2D) material, $GaInO_3$-sheet, first-principles method, strain effect

PACS: 61.46.–w, 61.50.Ah, 61.82.Fk, 62.23.Kn **DOI:** 10.1088/1674-1056/28/1/016105

1. Introduction

Due to the size effect, two-dimensional (2D) materials have many remarkable physical and chemical properties, making them the frontier of current materials science research.[1–11] Generally, 2D materials refer to thin film materials with only one or several atomic layers, in which electrons can move freely only in two dimensions at non-nanoscale. In 2004, breakthroughs were made in the study of 2D materials: Novoselov *et al.* successfully synthesized single-layer graphene under ambient conditions.[12] Graphene has a Dirac point band structure and has excellent physical and chemical properties, such as a large specific surface area, an extremely high carrier mobility, and a very good mechanical property, which makes graphene show great application prospects in nanoelectronic devices, energy storage, sensors, supercapacitors, and so on. However, graphene is a semi-metallic material with a band gap of 0 eV,[13] which cannot be used as a logic circuit switch, which limits its application in electronic devices.

$GaInO_3$ is a typical transparent conductive oxide material (TCO).[14,15] TCO is a unique material that combines electrical conductivity and optical transparency in one material[16–18] Thus, $GaInO_3$ currently plays an important role in a wide range of optoelectronic devices including transistors, transparent electrodes, solar cells, flat panel displays, light emitting diodes, and so on.[19] The excellent performance of $GaInO_3$ has inspired unremitting research and a series of novel properties, such as optical properties and electronic properties,[20–22] have been discovered. At the same time, the phase transition of $GaInO_3$ under high pressure and high temperature has been studied, and a new $GaInO_3$ II phase was synthesized under high pressure.[23] Although there has been so much research on $GaInO_3$, previous studies were limited to the three-dimensional (3D) material, and the exploration of the 2D $GaInO_3$ is still to be done. Therefore, whether there is a stable 2D structure in the $GaInO_3$ system with excellent electronic and mechanical properties is a meaningful topic.

Here, we systematically study the 2D system of $GaInO_3$, and find a new stable 2D layered structure. The calculation results show that the structure has a direct band gap of 1.56 eV,

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which is very close to the optimal band gap of solar cell materials, thus it can be used as a potential solar material. It is the first time for the discovery of the existence of 2D $GaInO_3$ system.

2. Methods

All calculations are performed based on density functional theory by using the VASP[24] software package. The projection conjugate wave method (PAW) is used to describe the ion potential, and the valence electrons of gallium, indium, and oxygen are $3d^{10}4s^24p^1$, $4d^{10}5s^25p^1$, and $2s^22p^4$, respectively. The generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE)[25] exchange and correlation of the electrons are used in the total energy calculations and geometrical optimization. The hybrid Heyd–Scuseria–Ernzerhof functional (HSE)[26] is used to get highly accurate band structure. A vacuum distance of 15 Å is placed in the z-direction of the unit cell so that the interaction between adjacent layers is negligible. The Monkhorst–Pack method is used to generate a $9\times9\times2$ mesh to sample the Brillouin zone. The energy cutoff of the plane wave is taken as 800 eV. The phonon spectrum of the $GaInO_3$ sheet is calculated by using the phonopy code.[27]

3. Results and discussion

It has been reported that the $GaInO_3$ crystal can undergo a structural phase transition to $GaInO_3$ II phase under high pressure, and the $GaInO_3$ II phase has a layered structure.[23] As shown in Fig. 1(a), the structure is composed of a GaO layer and an InO_2 layer, of which the GaO layer has a graphene-like planar structure and the InO_2 layer has a pleated layered structure, and all In atoms have a six-coordinated structure. By carefully observing the structure, it can be found that the Ga–O bond has two lengths: the slightly longer interlayer Ga–O bond (1.96 Å) and the ultra-short intra-layer Ga–O bond (1.91 Å). In fact, with the current level of technology, a single layer can be obtained by a layered structure or a non-layered structure. For van der Waals coupling layers like graphite, mechanical stripping[12] is efficient to obtain a single layer sheet (graphene). While for a chemically bonded bulk phase like MAX (a family of transition metal carbides or nitrides), a single layer also has been extracted using the stripping technique (like MXene).[28] As shown in Fig. 1(b), a $GaInO_3$-sheet is obtained by peeling off from the $P6_3/mmc$-$GaInO_3$ structure. The $GaInO_3$-sheet has a hexagonal crystal system, the space group is P_3M_1 (No. 56), and the lattice constants are $a=b=3.28$ Å. In addition, we have constructed simple GaO and InO_2 monolayers, unfortunately, both cannot be stable.

It is well known that kinetic stability is an essential condition for a material to be stable. Under normal conditions, the phonon spectrum is a powerful method for detecting the stability of a structural dynamic. As shown in Fig. 2, we calculated the phonon spectrum of the structure under ambient conditions. The results show that the structure has no imaginary frequency, indicating that the structure has dynamic stability.

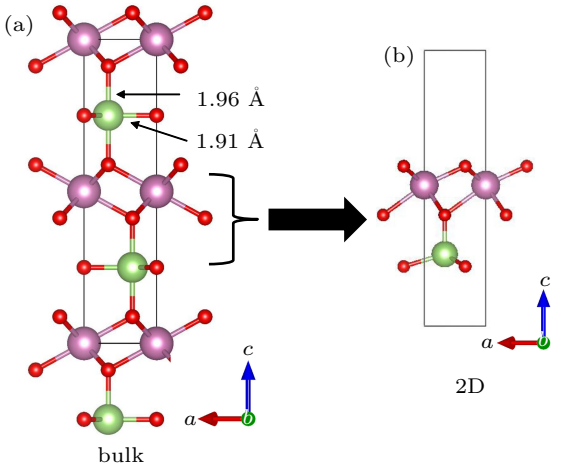


Fig. 1. (a) Crystal structure of $P6_3/mmc$-$GaInO_3$ viewed from the [101] directions. (b) Top and side views of the atomic configuration of $GaInO_3$-sheet.

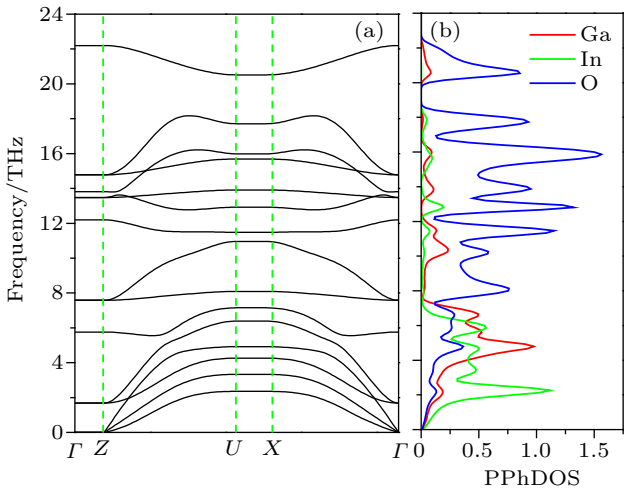


Fig. 2. (a) Phonon band structures and (b) partial phonon density of state (PPhDOS) of $GaInO_3$-sheet.

To further examine the thermodynamic stability of the structure, we calculated the thermal stability of the thin layer structure by molecular dynamics simulation (MD) of the canonical ensemble (NVT). In order to reduce the constraints of periodic boundary conditions, before doing MD, we selected a $8\times8\times1$ supercell for simulation, and the calculation results are shown in Fig. 3. First, we performed the MD calculation for the $GaInO_3$-sheet at room temperature (300 K) for 20 ps. There was no structural change in the $GaInO_3$-sheet monolayer during the entire simulation, but there were some minor changes in the bond length. Further increasing the simulated temperature, we found that the structure did not undergo structural reconstruction until the high temperature of 1100 K, but structural deformation occurred. When the temperature was higher than 1100 K, the system tended to decompose. The above results show that the structure can be stabilized to a high temperature of 1100 K, which also indicates that the structure has excellent thermal stability.

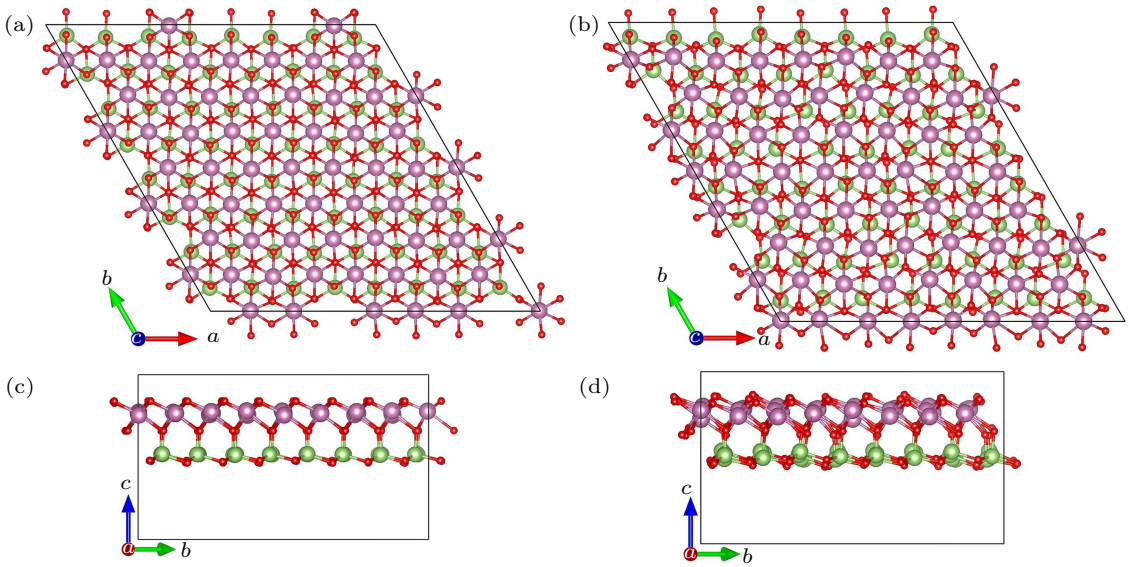


Fig. 3. Snapshots of the final frame of each MD simulation at (a), (c) 300 K and (b), (d) 1100 K (top and side views).

We calculated the energies of the $GaInO_3$-sheet and the bulk $GaInO_3$. The results show that the energies of the $GaInO_3$-sheet and the bulk $GaInO_3$ are -5.598 eV/atom and -5.770 eV/atom, respectively. It can be seen that the energy of the $GaInO_3$-sheet is higher than that of bulk $GaInO_3$. The thermodynamic calculation results combined with phonon spectrum and MD simulation data show that the $GaInO_3$-sheet structure has metastable properties. In fact, this phenomenon is very common in two-dimensional materials, such as the famous penta-graphene structure.[29] For comparison, we also calculated the energies of the penta-graphene and its bulk phase (T12 structure). The energies of the penta-graphene structure and the T12 structure are -8.33 eV/atom and -8.99 eV/atom, respectively. It is obvious that the energy of the penta-graphene structure is also higher than the energy of the T12 structure.

For a stable 2D material, mechanical stability is also an indispensable requirement. By calculation, the elastic constants are $C_{11} = 214.2$ GPa, $C_{22} = 215.0$ GPa, $C_{66} = 61.2$ GPa, and $C_{12} = C_{21} = 90.6$ GPa. For a mechanically stable 2D structure, the elastic constants must satisfy $C_{11}C_{22} - C_{12}^2 > 0$ and $C_{66} > 0$.[29] It is clear that this stability condition can be met for the structure, which also indicates that the structure is mechanically stable.

It is well known that the PBE method significantly underestimates the bandgap value of semiconductor materials compared to experimental values. The HSE hybrid functional can get an accurate band gap value. Therefore, we also applied the PBE and HSE functions to calculate the electronic structures of bulk $GaInO_3$ material and 2D material. The calculation results show that the bulk $GaInO_3$ material is a semiconductor with an indirect band gap. Its band gap is 1.61 eV at the PBE level and the HSE band gap is 3.32 eV. The $GaInO_3$-sheet is a semiconductor with a direct band gap at the Γ point, and its band structure is shown in Fig. 4(b). The similar transition from indirect band gap to direct band gap has also been observed in other systems like transition metal chalcogenides.[30] As shown in Fig. 4(b), the $GaInO_3$-sheet has a HSE band gap value of 1.56 eV and a PBE band gap value of 0.83 eV. The HSE method mainly corrects the conduction band of the PBE band structure. Compared to the PBE method, the HSE method increases the conduction band minimum (CBM) by 0.73 eV. At the same time, we calculated the projected state density (PDOS) of the $GaInO_3$-sheet, as shown in Fig. 4(b). It can be seen that the PDOS near the valence band maximum (VBM) and CBM are mainly composed of 2p orbitals of O, and the difference of PDOS between Ga and In atoms is small.

Stress effects caused by radial dimensional changes have important applications for nanomaterials. Previous studies have also shown that the introduction of stress can significantly change the electronic structure of nanomaterials, thus providing an effective way to tune the band gap of nanostructures.[31,32] Therefore, we investigated the strain effect of the electronic structure of the $GaInO_3$-sheet structure. First, we defined the isotropic strain as $(a - a_0)/a_0$, where a and a_0 are the lattice parameters of the $GaInO_3$-sheet with and without strain, respectively. Then, by calculating the stress–strain curve of the $GaInO_3$-sheet, we found that it can be stable up to 22%, which is comparable to the famous graphene and MoS_2. Next, we calculated the change curve of the band gap of the material by using the PBE method within the stable range of strain. As shown in Fig. 5, the band gap curve of the $GaInO_3$-sheet with strain is given. The results show that the compressive strain in the range of 0% to -22% is applied to the structure, and the structure keeps a direct band gap. As the compressive strain increases, the band gap value of the 2D structure monotonically decreases until it becomes 0 eV when the compressive strain is -22%. When a small tensile stress

is applied to the structure, the structure begins to transform from a direct bandgap semiconductor to an indirect bandgap semiconductor. Therefore, we can obtain a new material with continuous and controllable bandgap by applying an external mechanical stress. This feature has great application prospects in the fields of electronic devices and photocatalysis.

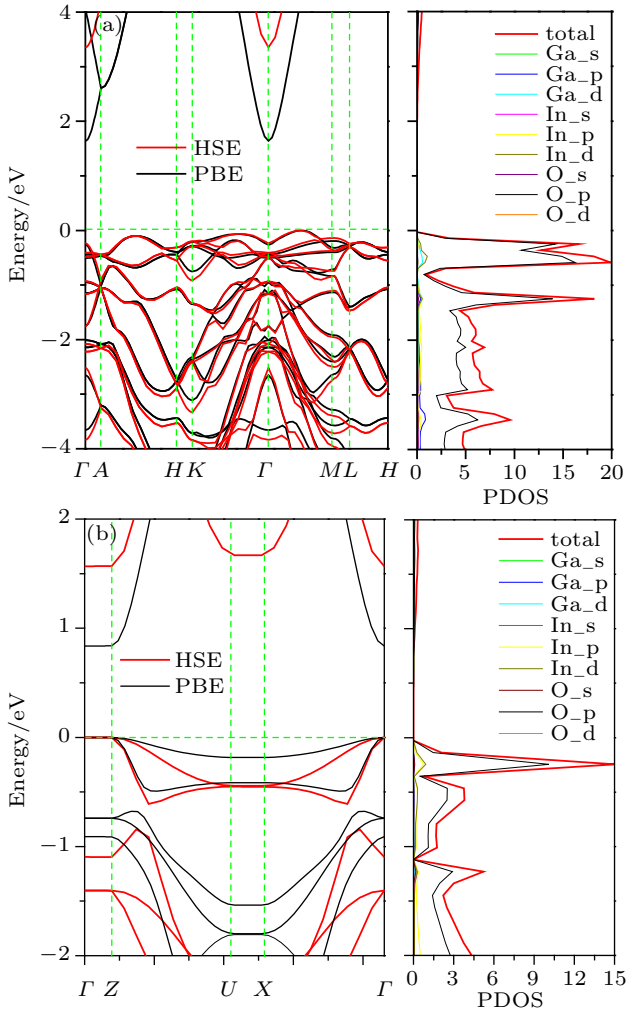


Fig. 4. The calculated band structures and DOS of (a) bulk $GaInO_3$ and (b) $GaInO_3$-sheet by PBE and HSE methods.

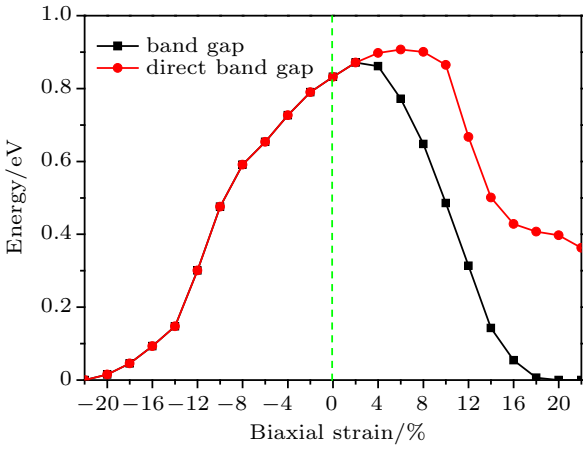


Fig. 5. Band gaps of the $GaInO_3$-sheet as a function of biaxial strain based on the PBE calculations.

To gain a deeper understanding of the transitions, we analyzed the band structure of the $GaInO_3$-sheet with and without strain by using the PBE method. As shown in Fig. 6, the calculations reveal the intrinsic mechanism of direct–indirect bandgap and semiconductor-to-metal transitions: the energy competitions in several near-band edge states. When 0% strain is applied, the structure is a direct band gap semiconductor at the Γ point with a band gap of 0.83 eV. When the compressive strain is applied to the structure, the VBM and CBM are always at the Γ point, and the energy of CBM gradually reduces until the CBM overlaps with the VBM at -22%. Therefore, the change of the CBM mainly determines the band gap value under compressive strain: the $GaInO_3$-sheet maintains a direct band gap and the band gap gradually decreases until -22%, then it begins to transform into metal. When the tensile strain is applied to the $GaInO_3$-sheet, the valence band energies of the U and X points gradually increase, while the CBM is always at the Γ point. Therefore, the electronic properties of the structure are mainly affected by the valence band. At 2%, although the energies of the U and X have increased, however, they are still lower than the energy of the Γ point. Therefore, the structure still exhibits a direct band gap. At 4%, the energies of the U and X are considerably higher than that of point G, indicating a direct-to-indirect gap transition. With the tensile strain increasing, the energy of CBM gradually decreases, until 20% strain the downward shift of the CBM and upward shift of the VBM trigger the semiconductor-to-metal transition. In summary, the structure can exhibit direct band gap, indirect band gap, and metal properties under strain. Such rich electronic properties indicate that the $GaInO_3$-sheet has a promising potential on the applications in flexible electronic and photonics devices.

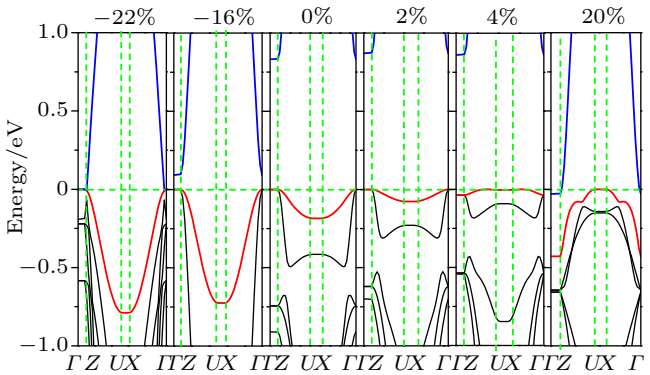


Fig. 6. Band structure of $GaInO_3$-sheet under selected different strains of -22%, -16%, 0%, 2%, 4%, and 20%, respectively. Positive and negative strains represent tensile and compression, respectively. The Fermi energy was set to 0 eV.

4. Conclusion and perspectives

In this paper, we found a new stable 2D $GaInO_3$ structure, and studied its structural, mechanical, electronic properties by first-principles method. MD simulations show that

the $GaInO_3$-sheet has excellent thermal stability and is stable up to 1100 K. Electronic structural calculations show that the $GaInO_3$-sheet has a bandgap of 1.56 eV, which is close to the ideal band gap of solar cell materials, demonstrating great potential for future photovoltaic application. In addition, strain effect studies show that the $GaInO_3$-sheet structure always exhibits a direct band gap under biaxial compressive strain, and as the biaxial compressive strain increases, the band gap gradually decreases until it is converted into a metal. Biaxial tensile strain can cause the 2D material to transform from a direct band gap semiconductor into an indirect band gap semiconductor, and even to metal. Our research expands the application of the $GaInO_3$ system and may have potential application value in electronic devices and solar energy.

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