Tunable Properties of Novel Ga\textsubscript{2}O\textsubscript{3} Monolayer for Electronic and Optoelectronic Applications

Yikai Liao, Zhaofu Zhang, Zhibin Gao, Qingkai Qian, and Mengyuan Hua

ABSTRACT: A novel two-dimensional (2D) Ga\textsubscript{2}O\textsubscript{3} monolayer was constructed and systematically investigated by first-principles calculations. The 2D Ga\textsubscript{2}O\textsubscript{3} has an asymmetric configuration with a quintuple-layer atomic structure, the same as the well-studied α-In\textsubscript{2}Se\textsubscript{3}, and is expected to be experimentally synthesized. The dynamic and thermodynamic calculations show excellent stability properties of this monolayer material. The relaxed Ga\textsubscript{2}O\textsubscript{3} monolayer has an indirect band gap of 3.16 eV, smaller than that of β-Ga\textsubscript{2}O\textsubscript{3} bulk, and shows tunable electronic and optoelectronic properties with biaxial strain engineering. An attractive feature is that the asymmetric configuration spontaneously introduces an intrinsic dipole and thus the electrostatic potential difference between the top and bottom surfaces of the Ga\textsubscript{2}O\textsubscript{3} monolayer, which helps to separate photon-generated electrons and holes within the quintuple-layer structure. By applying compressive strain, the Ga\textsubscript{2}O\textsubscript{3} monolayer can be converted to a direct band gap semiconductor with a wider gap reaching 3.5 eV. Also, enhancement of hybridization between orbitals leads to an increase of electron mobility, from the initial 5000 to 7000 cm\textsuperscript{2}V\textsuperscript{−1}s\textsuperscript{−1}. Excellent optical absorption ability is confirmed, which can be effectively tuned by strain engineering. With superior stability, as well as strain-tunable electronic properties, carrier mobility, and optical absorption, the studied novel Ga\textsubscript{2}O\textsubscript{3} monolayer sheds light on low-dimensional electronic and optoelectronic device applications.

KEYWORDS: Ga\textsubscript{2}O\textsubscript{3} monolayer, intrinsic dipole, carrier mobility, strain engineering, first-principles calculations

1. INTRODUCTION

Wide-band-gap semiconductors such as ZnO, GaN, AlN, and Ga\textsubscript{2}O\textsubscript{3} have attracted increasing attention for optoelectronic and power electronic applications.\textsuperscript{1} Among them, Ga\textsubscript{2}O\textsubscript{3}, especially in the form of single-crystal bulk or thin films, has been investigated extensively for its attractive material properties, such as an ultrawide band gap (~4.8 eV),\textsuperscript{2} outstanding breakdown field (8 MV/cm),\textsuperscript{3} and good chemical stability. In addition, common methods of crystal growth including the Czochralski method (CZ) and edge-defined film fed (EFG) are feasible for bulk Ga\textsubscript{2}O\textsubscript{3}, promoting the wide investigations of β-Ga\textsubscript{2}O\textsubscript{3}.\textsuperscript{2}

Ever since the graphene monolayer was successfully synthesized, two-dimensional (2D) materials such as transition-metal dichalcogenides (TMDs) and hexagonal boron nitride have become the up-to-date focal point and the mainstream of scientific research. In contrast to the three-dimensional (3D) materials with a very long history of study, 2D materials still need to be explored. To expedite the process, theoretical calculations by tools such as density functional theory (DFT) have been widely employed to study certain structures or material applications. The high-throughput method has been used as an efficient access to screen materials with certain desired properties for potential applications.\textsuperscript{3,4}

However, the cost to cover an enormous number of potential materials could be huge. An alternative method is obtaining the material structure from a known one by atomic replacement, which has been widely used to create and compare compounds in the same element groups with the same or similar structure and serves as a guide for experimental chemists to explore new materials and applications.\textsuperscript{5,6} Compared with their 3D counterparts, 2D materials exhibit interesting and outstanding properties such as tunable band gap by strain and high surface-area-to-volume ratio, benefitting to their wider application ranges over the bulk counterparts. Since the properties of 2D materials can be tuned by strain-induced lattice distortion, one widely studied application is flexible electronic devices, by changing the performance of devices via applying external strain, i.e., bending, stretching, or compressing the substrates.\textsuperscript{7}

For example, a 2D material-based photodetector is able to possess strain-tunable wavelength selectivity of photodetec-
For 2D material-based power transistors, strain-induced tunable properties such as effective mass and Schottky barrier height are significant for device performance. Thus, to delve into the uncharted territory of wide-band-gap semiconductors, DFT research studies on their 2D structures are proceeding rapidly and productively. For example, Claeyssens et al. theoretically predicted the existence of stable graphene-like ZnO (g-ZnO) by density functional theory and Tusche et al. successfully observed the unreconstructed planar sheet of g-ZnO monolayers. Zhuang et al. predicted and investigated the energetic and dynamic stability of 2D GaN by DFT, which was later experimentally synthesized via migration-enhanced encapsulated growth (MEEG). Compared with ZnO and GaN monolayers, the study on 2D Ga$_2$O$_3$ still remains the very infant step. Theoretically, as a start, Van de Walle et al. tried to model the monolayer Ga$_2$O$_3$ structure by reducing the thickness of the monoclinic $\beta$-Ga$_2$O$_3$ unit cell (12 Å) along the $[100]$ direction down to half (6 Å). Until now, some progress has been made based on Van de Walle’s model. Su et al. studied its hydrogen-passivated structure and demonstrated its surprisingly high electron mobility (≈25 000 cm$^2$/V$^{-1}$s$^{-1}$) and optoelectronic properties. Wei et al. revealed the influence of surface vacancies on its electrical and optical properties. Experimentally, even though mechanical exfoliation from bulk $\beta$-Ga$_2$O$_3$ is a feasible way to obtain Ga$_2$O$_3$ nanomembranes with a thickness less than 100 nm, which can to some extent be regarded as quasi-2D materials, their physical properties are still close to the bulk $\beta$-Ga$_2$O$_3$ because their thicknesses are far away from the angstrom scale. What is more, despite the fact that exfoliation energy along the $[100]$ direction is much lower than others, the covalent bond is still so strong that it is difficult to slice monoclinic $\beta$-Ga$_2$O$_3$ down into nanoscale and obtain the authentic 2D monolayer in experiments. Besides, it should be noted that once scaled down to monolayer thickness, the structure of the monolayer does not always maintain the same as its bulk counterpart. More importantly, it still remains to be experimentally verified whether the hydrogen-passivated 2D $\beta$-Ga$_2$O$_3$ monolayer can be synthesized. Thus, the feasibility of a 2D Ga$_2$O$_3$ monolayer based on monoclinic $\beta$-Ga$_2$O$_3$ remains controversial and the existence of monolayer Ga$_2$O$_3$ in other crystal forms is still worth investigating.

In spite of the very limited investigations on the 2D Ga$_2$O$_3$ monolayer, researchers have focused on its 2D III–VI van der Waals (vdW) family members for their attractive properties and outstanding application potentials such as optoelectronics and ferroelectrics. Some of them have been successfully synthesized by experiments. Among those, 2D $\alpha$-In$_2$Se$_3$ with the crystal structure of ferroelectric-zinc blende (FE-ZB$'$) phase is theoretically proven stable and has been successfully fabricated by experiments through mechanical exfoliation or van der Waals epitaxy. Interestingly, its asymmetric atomic configuration leads to the existence of unusual polarization, broadening its application ranges to water splitting, gas sensing, and piezoelectricity, indicating that this In$_2$Se$_3$ atomic configuration is of great importance in research and development. Thus, it is of technological interest to study the properties of the Ga$_2$O$_3$ monolayer with the same configuration as $\alpha$-In$_2$Se$_3$.

It is noted that, despite the relatively stronger ionic bond, the exfoliation of metal oxide is not that hard. One typical example is that $\beta$-Ga$_2$O$_3$ can be exfoliated, benefiting from weak Ga–O bonds along the [100] direction. Apart from the 2D Ga$_2$O$_3$ monolayer, a considerable amount of 2D metal oxides has already been experimentally synthesized, such as 2D WO$_3$, 2D MoO$_2$, and 2D TiO$_2$. Theoretically, some researchers have proved that 2D metal oxides, such as Ga$_2$O$_3$, InO, and Mo$_2$O$_9$ will have the same structure as metal selenides. Experimentally, significant progress on the oxidation of 2D vdW semiconductor materials such as HfS$_2$ and TaSe$_2$ has been made to synthesize their monolayer oxides. In fact, some researchers have successfully converted non-van der Waals (non-vdW) solids to 2D vdW chalcogenides in experiments. Since Ga$_2$O$_3$ shares the same element groups as In$_2$Se$_3$, it is reasonable to infer that the Ga$_2$O$_3$ monolayer with the lattice structure of 2D $\alpha$-In$_2$Se$_3$ can be experimentally synthesized by similar methods such as epitaxial growth or controlled oxidation.

In this work, we conducted a pioneering investigation on the properties of the novel Ga$_2$O$_3$ monolayer, which has 2D $\alpha$-In$_2$Se$_3$ geometry, by first-principles calculation. This novel Ga$_2$O$_3$ monolayer shows excellent dynamic and thermodynamic stability. The Ga$_2$O$_3$ monolayer is identified to be an indirect band gap semiconductor with a band gap of 3.16 eV and an electron mobility of ~5000 cm$^2$/V$^{-1}$s$^{-1}$. While with biaxial strain engineering, the tunable band gap, intrinsic dipole, carrier transport ability, and optical properties were studied. The direct–indirect transition of band gap has been observed with different lattice distortions. The compressed Ga$_2$O$_3$ monolayer (~4% lattice distortion) is found to be a direct band gap semiconductor with a wide band gap (~3.5 eV) and outstanding electron mobility (~7000 cm$^2$/V$^{-1}$s$^{-1}$), while the stretched Ga$_2$O$_3$ monolayer has a good solar radiation absorption capability. The considerable electrostatic potential difference between the top and bottom surfaces, which is induced by the intrinsic dipole in the asymmetric structure, is able to boost the separation of photon-generated holes and electrons. These tunable properties suggest that the Ga$_2$O$_3$ monolayer has great application potentials for flexible nanoscale electronic devices and solar energy conversion.

2. COMPUTATIONAL METHODS

The calculations were conducted based on density functional theory, as implemented in the Vienna ab initio simulation package (VASP). The projector augmented wave (PAW) pseudopotential was used. The PAW potential is capable of precisely handling the difficult and complex cases such as strong magnetic moments and large electronegativity differences, whose reliability is better than ultrasoft pseudopotential and precision is comparable with norm-conserving. The use of the PAW pseudopotentials addresses the problem of inadequate description of the wavefunctions in the core region common to other pseudopotential approaches. A plane wave cutoff energy of 450 eV was used. This cutoff energy was tested effective for convergence by comparing the calculated band gap with a much higher cutoff energy of 700 eV, and a negligible difference of 1 meV was found. The total energy difference is within 1 meV/at.

Even though the Perdew–Burke–Ernzerhof (PBE) version of generalized gradient approximation (GGA-PBE) is widely used for calculations, it suffers from the slightly overestimated lattice constant and unavoidable band gap narrowing problems. To guarantee the precise property descriptions of this novel material, the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional was employed (with a default mixing fraction) throughout this work, including the lattice structure optimization and electronic and optical properties. The convergence criteria were set to be 1 × 10$^{-5}$ eV/atom for self-consistent electronic loop and 0.02 eV/Å for the residual forces on each atom. A 9 × 9 × 1 k-mesh grid was used. The vdW correction
well-known conclusion that GGA-PBE produces the slightly 
energies are shown in Figure 1. Similar to In$_2$Se$_3$, Ga$_2$O$_3$ with 
the FE-ZB (001) and (001$'$) surfaces are de
The calculated band gap of the Ga$_2$O$_3$ monolayer is 3.16 eV 
by the HSE functional, as demonstrated in Figure 2a. The Ga$_2$O$_3$ monolayer is an indirect band gap semiconductor with the conduction band minimum (CBM) at Γ point and the valence band maximum (VBM) at K point. Oxygen, especially the O p orbital, contributes most to the valence band regions near VBM, while gallium contributes more to the conduction band. Also, hybridization between different orbitals can be seen in both CBM and VBM. The CBM is composed of Ga s and O s with little Ga p$_z$ and O p$_z$ orbitals, VBM at K point is mainly composed of O p$_z$ with little O p$_x$ and O p$_y$ and negligible Ga p and Ga d orbitals, and VBM at Γ point is mainly composed of 
known monoclinic β-Ga$_2$O$_3$ in Figure S1 with the same 
functional and calculation settings. The Ga–O bond lengths of the Ga$_2$O$_3$ monolayer here are comparable with those of the monoclinic β-Ga$_2$O$_3$, which can stably exist in nature, indicating the stable Ga–O connection in the Ga$_2$O$_3$ monolayer.

Figure 1. (a) Atomic structures of different In$_2$Se$_3$ and Ga$_2$O$_3$ phases. (b) Total energy comparison, with the total energy of the most stable FE-ZB phase set to be 0 eV.

Figure 2. (a) Band structure (left) and DOS (right) of the Ga$_2$O$_3$ monolayer with the FE-ZB' phase by HSE. In the left panel, the green and red dots represent the contribution strength from gallium and oxygen orbitals, respectively. The purple arrow shows the indirect band gap from VBM (K) to CBM (Γ). In the right panel, the purple dashed parallelogram indicates the primitive cell. (b) Electrostatic potential of the relaxed Ga$_2$O$_3$ monolayer along the z direction. The direction of spontaneous polarization is indicated by the black arrow. Band alignment of the Ga$_2$O$_3$ monolayer with (c) different vacuum levels and (d) aligned vacuum levels. Insets show the spatial charge distributions of CBM (yellow) and VBM (blue), respectively. The (001) and (001$'$) surfaces are defined in the insets in (a) and (b).

3. RESULTS AND DISCUSSION

3.1. Structural and Electronic Properties. To demonstrate the feasibility of the proposed Ga$_2$O$_3$ monolayer, based on several In$_2$Se$_3$ structures, including zinc blende (ZB), wurtzite (WZ), FCC, FE-ZB', and FE–WZ' phases discussed in Ding's work, we modeled various Ga$_2$O$_3$ structures with these phases for comparison. The structures and relative energies are shown in Figure 1. Similar to In$_2$Se$_3$, Ga$_2$O$_3$ with the FE-ZB' structure has the lowest total energy among all of the structures, as shown in Figure 1b, proving that this Ga$_2$O$_3$ phase is the thermodynamic ground state and is promising to be synthesized without other-phase byproducts. Thus, this work will focus on the discussion of the Ga$_2$O$_3$ monolayer with the FE-ZB' configuration. The optimized lattice parameters are $a = b = 3.08$ Å by GGA-PBE and $a = b = 3.04$ Å by the HSE functional, with $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, agreeing with the well-known conclusion that GGA-PBE produces the slightly overestimated lattice constant. The lattice constant of Ga$_2$O$_3$ is much smaller than that of α-In$_2$Se$_3$ (4.11 Å), owing to the smaller atomic radii of gallium and oxygen. Since HSE offers a better prediction of semiconducting behavior than the local or semilocal functionals, the optimized structure obtained by the HSE functional is employed for further electronic and optical discussions.

The geometries of Ga$_2$O$_3$ monolayer are shown as insets of the right panel in Figure 2a. The same as α-In$_2$Se$_3$ and other 2D M$_x$X$_y$ (M = Al, Ga, In; X = S, Se, Te) family members, the Ga$_2$O$_3$ monolayer is stacked in the atomic layer sequence of O–Ga–O–Ga–O, forming the quintuple layer consisted of covalently bonded gallium and oxygen triangular lattices. We also compared geometries of the Ga$_2$O$_3$ monolayer with...
shift of CBM and VBM at two surfaces. As a result, CBM and VBM wavefunctions spatially localize at the opposite sides of the Ga2O3 surfaces, as shown in the insets of Figure 2c,d and later Figure 6. The energy difference between CBM of (001) and VBM of (001) is contributed from two parts: band gap energy and electrostatic potential difference (ΔΦ), as shown in Figure 2d.

The structural stability of the Ga2O3 monolayer is of great importance not only for the theoretical prediction of properties but also for synthesizing this novel structure and thus further practical applications. The lattice dynamic stability of the Ga2O3 monolayer is evaluated by the phonon dispersion spectrum, as shown in Figure 3a. No imaginary-frequency phonon mode is observed in the phonon dispersion spectrum, indicating a dynamic stable structure. An AIMD simulation at 500 K was conducted for a (3 × 3) supercell to verify its thermostability. After 10 ps high-temperature annealing, no structural corruption was observed (Figure 3c). The temperature and total energy of systems during AIMD calculations fluctuate stably with small ups and downs (Figure 3b), indicating excellent thermostability. An AIMD calculation at 300 K was also evaluated, as shown in Figure S3. After 10 ps high-temperature AIMD simulation, the distorted structure further went through an extra structural relaxation. Interestingly, it turned out that the distorted structure can return to its original well-symmetrical structure after final relaxation, as shown in Figures 3d and S3b. The AIMD results indicate that the Ga2O3 monolayer shows excellent thermostability at high temperatures, guaranteeing the possible applications in high-temperature ambient such as nanoscale power devices and sensors.

### 3.2. Strain-Engineered Band Structures

Since the Ga2O3 monolayer has a large band gap of ~3.2 eV, in the UV light region, it is attractive to investigate its application potentials in flexible UV detectors and other possible fields. In flexible devices, strain-induced lattice distortion would modulate the electronic band structure, carrier transport, and optical properties. Biaxial strain engineering with a series of lattice distortions from −6 to 6% was applied to the Ga2O3 monolayer, with the strained energy tendency shown in Figure S4a. The relaxed system (no strain condition) has the lowest total energy, which means it is the most stable status. When strain is applied to the lattice, distances between atoms in different layers with the quintuple-layer structure change

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**Figure 3.** (a) Phonon dispersion spectrum of the Ga2O3 monolayer. (b) Evolution of temperature (red, left axis) and total energy (blue, right axis) with time during AIMD simulations. Atomic structures of the Ga2O3 (3 × 3) supercell after (c) 10 ps AIMD simulation at 500 K and further (d) geometry relaxation.
correspondingly. Thus, the change of wavefunction overlapping in different layers occurs accordingly, causing the change of total system energy. Besides, it requires more energy to compress the lattice to the distortion of $-6\%$ (0.66 eV) than stretch to $6\%$ (0.44 eV), which means it is easier to stretch the Ga$_2$O$_3$ monolayer than to compress it. To release the applied strain, the quintuple-layer thickness of Ga$_2$O$_3$ elongates and shrinks linearly along the $z$ direction when compressive or tensile strains are applied, indicated by the variation of thicknesses in Figure S4b.

The stability of the Ga$_2$O$_3$ monolayer with extreme lattice distortion was also tested using phonon dispersion and AIMD, as shown in Figure S5. There is no imaginary-frequency phonon mode and structural corruption after AIMD in the Ga$_2$O$_3$ monolayer with distortion from $-4\%$ to $+6\%$, indicating that the monolayer can maintain its dynamic and thermodynamic stability within this strain range. The compressed Ga$_2$O$_3$ monolayer shows poorer stability than the stretched one, similar to the previous reports.$^{56}$ Under $-6\%$ compressive strain, the model shows unstable characteristics from both AIMD and phonon dispersion calculations. As a result, we only focus on from $-4\%$ to $6\%$ lattice distortion in the following discussions. Since a large strain of $\sim 6\%$ in the 2D material is already obtained in the experiment,$^{57}$ our work is referable in future applications. Despite the tunable properties by strain engineering are desirable for future applications in flexible devices, the main claim in this work is still the availability and the basic properties of this novel Ga$_2$O$_3$ monolayer.

Figure 4 presents the strain-dependent band structure of the Ga$_2$O$_3$ monolayer. The direct−indirect transition of band gap is observed from compressive strain to tensile strain. CBM remains at $\Gamma$ point, while VBM changes from $\Gamma$ to K point with decreasing compressive strain and increasing tensile strain. Since there exist two vacuum levels at opposite surfaces of the Ga$_2$O$_3$ monolayer, we plotted the shift of band gap and band edges versus two vacuum levels, respectively, in Figure S6. However, due to polarization, CBM tends to locate closer to the (001) surface, while VBM to the (001) surface. Thus, the energy change of CBM with respect to the vacuum level of the (001) surface and the energy change of VBM to that of the (001) surface are summarized in Figure 5 to precisely study the shift of band edges. With decreasing compressive strain (from $-4\%$ lattice distortion to zero strain) and increasing tensile strain (from zero strain to $+6\%$ lattice distortion), energy positions of both VBM at $\Gamma$ and K points keep increasing, with a variation of VBM (K) being more rapid than VBM ($\Gamma$). As a consequence, the energy position of VBM at K point surpasses that of VBM at $\Gamma$ point at about $-2.5\%$ lattice distortion, leading to the transition from the direct band gap to the indirect one. What is more, the band gap value reaches a maximum at a lattice distortion of $-4\%$ (Figure 5) and then keeps narrowing down due to the opposite trends of a shift of CBM ($\Gamma$) and VBM (K). We also calculated the strain-dependent band gap values by PBE and GW$_0$ functions for comparison (Figure S7). All three functionals show the same variation of band gap versus lattice distortion. Clearly, the PBE functional results in underestimated band gap values. Taking excited state into consideration, GW$_0$ results in higher band gap values than the HSE case, similar to the In$_2$Se$_3$ case.$^5$ Considering the computational consumption, we only adopt the HSE hybrid functional in this work.

To better investigate the origins of the variation trend of CBM and VBM with lattice distortion changing, we studied the wavefunction distributions of CBM and VBM, as shown in Figure S8. CBM at $\Gamma$ point (Figure S8a,d,g), labeled as a, d, and g in Figure S5, respectively, is mainly composed of in-plane antibonding of top Ga−O layers between Ga $s$, O $s$, Ga $p_x$ and
O p₆ orbitals, indicated by orbital-projected band structure in Figure S2. This orbital hybridization characteristic of CBM (Γ) is similar to the monoclinic β-Ga₂O₃ monolayer. As the compressive strain keeps decreasing (more positive) and finally undergoes a transition into tensile strain, the in-plane bond lengths increase. According to the Heitler–London exchange energy model, increasing atomic distance leads to a decrease of antibonding energy. However, the in-plane bonding characteristic (the blue beltlike areas in Figure S8a,d,g) weakens, leading to higher CBM edge. Thus, because of the competition of in-plane bonding and antibonding, the energy position of CBM (Γ) increases first until reaching −2% distortion and then decreases with strain changing from compressive to tensile. Similar competition of bonding and antibonding and the variation of CBM can also be seen in other 2D materials. With strain becoming more positive, the VBM (Γ) edge is pushed upward because of the decreasing in-plane bonding characteristic (more clearly demonstrated by the in-plane connected areas in Figure S9) in top O vicinity shown in Figure S8b,e,h (labeled as b, e, and h in Figure 5, respectively).

As for VBM (K) (Figure S8c,f,i, labeled as c, f, and i in Figure 5, respectively), the increasing energy position of VBM (K) can be indicated by the absence of two minor hybridization orbitals near the top oxygen atomic layers. Increasing in-plane atomic distance leads to the weakening of orbital hybridization, further resulting in a less stable and higher-energy status. Thus, the energy position of VBM (K) shows a similar variation trend to VBM (Γ). Since the spatial distribution of VBM (K) is wider than that of VBM (Γ), if we compare Figure S8e,f, VBM (K) is more sensitive to strain, which explains the more rapid variation of VBM (K) than VBM (Γ) in Figure 5.

Figure 6a shows the electrostatic potential curves of relaxed and strained Ga₂O₃ monolayers along the z direction. The variation of ΔΦ versus lattice distortion is shown in Figure 5. At the relaxed status, ΔΦ reaches 3.47 eV by the HSE functional calculation, much larger than that of the other 2D Ga₂X₃ family members (Ga₂S₃, 1.65 eV; Ga₂Se₃, 1.30 eV; Ga₂Te₃, 0.88 eV) and also larger than α-In₂Se₃ (1.38 eV), even though they share the same structural configuration. The largest ΔΦ of Ga₂O₃ among the 2D Ga₂X₃ monolayers could originate from the largest electronegativity of oxygen in the group VI. Figure 6b shows the variation of the dipole moment of the Ga₂O₃ monolayer with lattice distortion. With decreasing compressive strain and increasing tensile strain, the dipole moment keeps increasing. A similar variation of the dipole moment versus in-plane strain can also be seen in α-In₂Se₃. Since the dipole moment is introduced from the asymmetric configuration between top and bottom O–Ga–O trilayers, we studied the relative thickness between these two trilayers (T_top and T_bottom in Figure 6b, respectively) as shown in Figure 6b. Interestingly, with decreasing compressive strain and increasing tensile strain, the ratio of T_top and T_bottom (T_top/T_bottom) keeps decreasing. Since top and bottom O–Ga–O trilayers act as negative and positive charge centers, respectively, the spatial separation of positive and negative charge centers becomes more intense, leading to larger dipole moment.

Since the Ga₂O₃ monolayer changes from direct band gap to indirect band gap with VBM changing from Γ to K point when decreasing compressive strain and increasing tensile strain, we compared the charge distribution of Ga₂O₃ with direct and indirect band gap characteristics under the corresponding distortion, as shown in Figure 6c,d. It can be seen that despite the difference in band gap characteristics, due to the asymmetric configuration, CBM and VBM tend to locate on opposite sides of the monolayer. Spatial charge distributions of the Ga₂O₃ monolayer from −4 to 6% are presented in Figure S10. When Ga₂O₃ is a direct band gap semiconductor, the spatial separation of CBM and VBM is more intense (Figure 6c) than when it is an indirect band gap material (Figures 6d

**Figure 6.** (a) Electrostatic potential of the Ga₂O₃ monolayer along the z direction. (b) Variation of the dipole moment (black, left axis) and relative thickness of the top O–Ga–O trilayer (T_top) and bottom O–Ga–O trilayer (T_bottom) (red, right axis) versus lattice distortions. Charge distribution of the Ga₂O₃ monolayer at lattice distortion of (c) −4% and (d) 6% along the z direction. In (c) and (d), the inset figures in blue and red rectangles show spatial charge distribution of CBM and VBM, respectively, with the same isosurface level.
In general, larger effective masses are more than 20 times higher than the electron masses. As shown in Figure S12a, b, the calculated effective masses are 0.356 \( m_0 \) along all directions (i.e., isotropic), while the calculated hole effective masses are more than 20 times higher than the electron effective masses, as shown in Figure S12c, d. Besides, the isotropic feature of electrons at CBM (Γ) and anisotropic feature of holes at CBM (K) can also be indicated by the 3D band diagram (Figure S12). In general, larger effective mass results in lower carrier mobility, so hole mobility is far much lower than electron mobility. Thus, detailed discussions of electron mobility are presented herein.

The electron mobility (\( \mu_{2D} \)) of 2D semiconductor materials can be calculated based on the deformation potential theory as follows:\(^{62,63}\)

\[
\mu_{2D} = \frac{e^2 \hbar C_{2D}}{k_B T m^* m^*_T E_1^T}
\]  

(1)

where \( e \) is the electron charge, \( \hbar \) is the reduced Planck constant, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature, which is set to be 300 K to represent room temperature ambient. \( m_0 \) is the average effective mass, which can be calculated by \( m_k = \sqrt{m_x m_y} \). \( C_{2D} \) is the elastic modulus and can be calculated by

\[
C_{2D} = \frac{1}{S_0} \frac{\partial^2 E}{\partial l^2}
\]

(2)

where \( E \) is the total energy of the system, \( l_0 \) is the lattice constant, \( \Delta l \) is its lattice deformation, and \( S_0 \) is the area of the optimized lattice. \( m^* \) is the electron effective mass calculated along the \( x \) and \( y \) directions, respectively. \( E_1 \) is the deformation potential constant, calculated by \( E_1 = E_1 = \frac{\Delta V}{\Delta l/l_0} \), where \( \Delta V \) is the energy difference of CBM (Γ) induced by lattice distortion. In principle, calculating the practical electron–phonon matrix is more rigorous and accurate than the deformation potential theory, but it is highly time-consuming. The deformation potential theory is a more efficient method, which has been widely used in calculating the intrinsic mobility.\(^{62,63}\)

The details on the calculation of elastic constants, deformation potentials, as well as the estimated errors are summarized in Table 1 and Figure S13. It is noted that the estimated error of \( \mu_1 \) is smaller than 12\%, so the obtained results are well acceptable.\(^{62,63}\) Table 1. Calculated Electron Mobility \( \mu \) (cm\(^2\) V\(^{-1}\) s\(^{-1}\)) of the Ga\(_2\)O\(_3\) Monolayer along the \( x \) and \( y \) Directions\(^{62}\)

<table>
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<tr>
<th>lattice distortion</th>
<th>( m_0^* / m_0^* ) (( m_0 ))</th>
<th>( E_{1x} ) (eV)</th>
<th>( E_{1y} ) (eV)</th>
<th>( C_{2D-x} ) (J/m(^2))</th>
<th>( C_{2D-y} ) (J/m(^2))</th>
<th>( \mu_x ) (cm(^2) V(^{-1}) s(^{-1}))</th>
<th>( \mu_y ) (cm(^2) V(^{-1}) s(^{-1}))</th>
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<td>−6%</td>
<td>0.426</td>
<td>2.294</td>
<td>2.315</td>
<td>187.193</td>
<td>184.832</td>
<td>4182</td>
<td>4421</td>
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<tr>
<td>−4%</td>
<td>0.397</td>
<td>1.919</td>
<td>1.837</td>
<td>6880</td>
<td>7414</td>
<td>6901</td>
<td>7429</td>
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<td>−1.948</td>
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<td>9774</td>
<td>3134</td>
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<tr>
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<td>1537</td>
<td>1609</td>
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<tr>
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<td>0.326</td>
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<tr>
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<td>0.312</td>
<td>−5.166</td>
<td>−5.018</td>
<td></td>
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</tr>
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</table>

\(^{62}\)Effective electron mass is labeled as \( m^* \) (\( m_0 \)), \( E_{1x} \) represents the deformation potential constant (eV), and \( C_{2D} \) represents the elastic coefficient (J/m\(^2\)). Note that all of the calculations here use the HSE hybrid functional.
noted that the calculated electron effective masses along Γ–K and Γ–M are almost the same (i.e., isotropic) even with different biaxial strain engineering, together with the electron mobility along the x and y directions, which indicates a weak electronic anisotropy of the 2D Ga2O3 monolayer, similar to the α-InS3Te3 case.70 The calculated values of C2D along the x and y directions are similar, resulting from the same values of lattice constants of the in-plane a and b directions.15 Interestingly, this electronic and mechanical isotropy can be also seen in other 2D M2X3 family members with the same atomic configuration, such as Ga2S3, Ga2Se3, In2S3, and In2Te3.71 The common feature of these 2D M2X3 materials is that their CBM always locates on low absolute values of the deformation potential constant (decreasing tensile strain and increasing compressive strain, strains). What is more, from +6 to −6% lattice distortion, with decreasing tensile strain and increasing compressive strain, electron mobility keeps increasing, which originates from the low absolute values of the deformation potential constant (Efi) in the region of compressive strain, as shown in Table 1. As a result, the electron mobility of the Ga2O3 monolayer reaches ∼7000 cm2 V−1 s−1 with a lattice distortion of −4%. The decrease in mobility at −6% is likely to be from the corruption of stability at the extreme compressive status. Even at the extremely stretched status, the electron mobility is still larger than 1000 cm2 V−1 s−1, which exceeds those of the monolayers of MoS2 (∼200 cm2 V−1 s−1)65 and GaN (∼300 cm2 V−1 s−1)66 and is comparable to those of α-InS3Te3 (1.04 × 104 cm2 V−1 s−1) and β-In2Se3 (1.39 × 104 cm2 V−1 s−1).69 Owing to its outstanding electron mobility, the Ga2O3 monolayer is well qualified in applications of nanoscale electronic devices. The hole mobility is also calculated, which is obviously smaller compared with the electron mobility, as shown in Table S1.

To have a deeper insight into the influence of lattice distortion on electron mobility and to explain the extremely high electron mobility with −4% compressive strain, we investigated the spatial charge distribution at CBM (Γ) of the Ga2O3 monolayer with different lattice distortions, as shown in Figure 7c−e. With decreasing distances between the neighboring gallium and oxygen atoms, overlapping of wavefunctions and the bonding characteristics are strongly enhanced, as shown by the yellow triangular cross-linking regions in Figure 7c,d. This can explain the increasing electron mobility when increasing compressive strain. Similarly, low deformation potential constant (absolute value) and high mobility under extreme compressive strain condition are also seen in the monoclinic β-Ga2O3 monolayer.60

3.4. Strain-Engineered Optical Properties. To evaluate the light absorption ability, we studied the absorption spectra of the Ga2O3 monolayer with different lattice distortions, as shown in Figure 8a. The absorption spectra are calculated from the imaginary part of the complex dielectric function ε(ω) = ε₁(ω) + iε₂(ω), and the absorption coefficient could be obtained from calculating α(E) = (\sqrt{2α/ε})\left(\left|\left[(ε₁ + ε₂) \right]^{1/2} − ε₁\right|\right)^{1/2}$ as described in ref 43. In energy regions near the absorption edge from 2 eV to 3 eV, as shown in Figure 8b, with decreasing compressive strain and increasing tensile strain, absorption edge exhibits blueshift first and then redshift, in good accordance with the band gap variation. The absorption tail below the band gap is owing to the smearing effect in the calculation, which determines how the partial occupancies are set for each wavefunction, and can be considered as the temperature effect in experiments. The absorption tail is also observed in previous reports.6,65 As shown in Figure 8a, when tensile strain is applied to the Ga2O3 monolayer, much-enhanced light absorption can be observed in energy regions below 4 eV, where the solar radiation is strong (red areas in Figure 8a). This is owing to the gap narrowing by strain engineering. What is more, if an extreme tensile strain of +6% lattice distortion is applied, the absorption ability is several times higher, which can be used as excellent photoabsorber. The strong solar radiation absorption of the Ga2O3 monolayer makes it promising in photocatalytic applications.3,50,43 For many 2D materials, the large exciton binding energy will prevent the separation of electrons and holes. However, in this novel Ga2O3 monolayer, the intrinsic electric field is introduced by the intrinsic polarization because of its asymmetric atomic configuration. Such an intrinsic polarization may bring benefits to the separation of photogenerated electrons and holes, which has been theoretically studied in many novel asymmetric 2D materials.5,6,30,52 It should also be noted that the intrinsic polarization correlated with photocatalyst activity, such as water splitting, has been widely studied theoretically and verified experimentally in ferroelectric materials, which also feature an intrinsic electric field.33,54 The presence of the internal field provides a driving force for electrons and holes to move in the opposite directions, thus separating the carriers. As a result, the CBM and VBM wavefunctions spatially localize at the opposite sides, as shown in Figures 2c,d and 6. From this aspect of view, the novel Ga2O3 monolayer with similar characteristics shows advantages and potentials in energy conversion such as photocatalytic water splitting and photodetection. The squared dipole transition matrix elements ($P^2$) were calculated to reveal the transition probability of electrons between VBM and CBM at different k points,69 which...
evaluates whether the incident light can be absorbed by the semiconductor, shown in Figure 8c. It is obvious that transition at Γ point is always allowed at different lattice distortions. Besides, decreasing compressive strain and increasing tensile strain lead to higher $P^2$ at Γ point. This originates from the increasing orbital overlapping of the electrons and holes, as illustrated in Figure S10 with CBM (Γ) and VBM (Γ) wavefunctions. As a result, the allowed optical transition of electrons from VBM to CBM guarantees excellent optoelectronic applications.

4. CONCLUSIONS

In conclusion, we systematically study the electronic, carrier transport, and optical properties of the novel Ga$_2$O$_3$ monolayer with the FE-ZB$^l$ configuration using first-principles calculations. Excellent dynamic and thermodynamic stability of the studied Ga$_2$O$_3$ is demonstrated by phonon dispersion and AIMD verifications. Indirect-to-direct transition and enhanced electron mobility can be realized by biaxial strain engineering. The intrinsic dipole induced in the asymmetric Ga$_2$O$_3$ monolayer guarantees its strong ability to boost the separation of holes and electrons within the quintuple-layer structure. As a result, CBM and VBM locate on opposite sides of the Ga$_2$O$_3$ monolayer. The tunable properties of the Ga$_2$O$_3$ monolayer indicate that when compressive strain is applied to the Ga$_2$O$_3$ monolayer, it still has suitable band gap values and outstanding carrier transport ability, promising for the flexible power devices. When tensile strain is applied, the stretched Ga$_2$O$_3$ monolayer exhibits enhanced optical absorption, extending the range from the UV to visible light region, guaranteeing its potential applications in optoelectronic devices and energy conversion such as photocatalytic water splitting. These tunable properties certify the wide application ranges of our studied novel Ga$_2$O$_3$ monolayer.

ASSOCIATED CONTENT

Supporting Information

Comparison of the Ga$_2$O$_3$ monolayer with β-Ga$_2$O$_3$ projected band structures; demonstration of room-temperature stability; variation of deformation energy and monolayer thickness under different strains; phonon dispersion spectra and AIMD simulations of the extremely strained Ga$_2$O$_3$ monolayer; shift of band edge and band gap with respect to different vacuum levels; band gap values calculated by different functionals; CBM and VBM wavefunctions of the Ga$_2$O$_3$ monolayer under different strains; partial charge distributions of different lattice distortions; angular-dependent effective mass and 3D band diagram of the relaxed Ga$_2$O$_3$ monolayer; mobility calculation process and error estimation; and hole mobility calculation (PDF).

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Notes

The authors declare no competing financial interest.

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