Article

The Possibility of Layered Non-Van Der Waals Boron Group Oxides: A First-Principles Perspective

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Abstract: Two-dimensional (2D) metal oxides have broad prospective applications in the fields of catalysis, electronic devices, sensors, and detectors. However, non-van der Waals 2D metal oxides have rarely been studied because they are hard to peel off or synthesize. In this work, taking alumina (Al_2O_3) as a typical representative of 2D boron group oxides, the structural stability and electrical properties of 2D Al_2O_3 are investigated through first-principles calculations. The thinnest Al_2O_3 structure is a bilayer, and the band gap of Al_2O_3 is found to decrease with decreasing layer thickness because of the giant surface reconstruction. The band gap of bilayer X_2O_3 (X = Al, Ga, and In) decreases with increasing atomic radius. Our findings provide theoretical support for the preparation of non-van der Waals 2D boron group oxide semiconductors.

Keywords: boron group oxides; non-van der Waals material; first-principles calculation

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1. Introduction

Since the discovery of graphene in 2004 [1], two-dimensional (2D) materials have been receiving increasing attention because of their excellent thermal, mechanical, optical, and electrical properties. Besides graphene, other 2D materials, such as black phosphorus, covalent organic frameworks, hexagonal boron nitride, layered double hydroxides, metals, metal oxides, metal–organic frameworks, transition metal carbides/nitrides (MXenes), and transition metal dichalcogenides [2–4], have been discovered and investigated extensively. Because metal oxides are abundant in nature, 2D metal oxides are expected to integrate with other 2D materials for electronic, spintronic, and optoelectronic applications [5–11]. Although some van der Waals (vdW) layered metal oxides, such as SnO and PbO [12,13], have been predicted, the corresponding experimental realization of vdW layered metal oxides is sparse [14]. Therefore, many attempts have recently been made to prepare non-vdW layered metal oxides, such as WO_3 and MoO_3 [15–19]. Non-vdW metal oxides are difficult to exfoliate into a few layers due to their strong chemical bonds in three dimensions, and the bottom-up synthesis method also poses significant difficulties and challenges [20]. As a result, less has been reported on 2D non-vdW metal oxides, and their corresponding properties have not been fully explored.

Binary non-vdW boron group oxides, such as Al_2O_3, Ga_2O_3, and In_2O_3, are wide-band-gap semiconductors and have been applied in electronic devices and photodetectors [21,22]. Because of its ultra-wide band gap and good thermal conductivity, Al_2O_3 is often used in ceramic applications [23–25]. A bottom-up method to synthesize graphene-like γ-Al_2O_3 nanosheets has been reported [26]. Using graphene oxide (GO) as template, a homogeneous aluminum sulfate layer was firstly deposited on the GO sheets. Then, the prepared GO–,Al composite sheets were calcined to remove GO and convert basic aluminum sulfate into γ-Al_2O_3 nanosheets [26]. The γ-Al_2O_3 nanosheets exhibit faster adsorption kinetics

and larger adsorption capacity, which suggests broad applications in catalysis and environmental science. However, the metastable γ-Al_2O_3 will transform into stable α-Al_2O_3 under higher temperature. Theoretically, various different monolayer aluminum oxide have been predicted [27–29], for example, hexagonal Al_2O_3 [29] and rectangle AlO_2 [27]. Therefore, exploring the stability of 2D α-Al_2O_3 is highly essential. Ga_2O_3 is a transparent semiconductor with wide band gap and high critical electric field, and therefore holds the promising applications in power electronics and solar blind photodetectors [30–34]. In_2O_3 doped by Sn has been widely used for electronic and optoelectronic devices, such as solar cell [35], optical window [36], film transistor [37], and Schottky contact [38]. Because of its ultra-flat surface, Al_2O_3 (0001) substrate is considered a promising substrate for 2D materials, such as graphene and transition metal dichalcogenides obtained by chemical vapor deposition [39–42]. Recently, Ga_2O_3 is also applied as a substrate to grow transition metal dichalcogenides nanoribbons. Because of their similar structures, 2D Al_2O_3, Ga_2O_3, and In_2O_3 are promising when coupled with 2D electronic devices. It has been reported that 2D Fe_2O_3 was successfully synthesized via the liquid-phase exfoliation of hematite ore in an organic solvent N,N-dimethylformamide (DMF) [43]. Because bulk Fe_2O_3 has a similar structure to boron group oxides, the synthesis of other non-van der Waals 2D metal oxide materials should thus also be achievable.

In this work, taking 2D Al_2O_3 as a representative, we design a series of stable 2D boron group oxides using first-principles calculations and investigate their crystal structures, stability, and electronic structures. Two-dimensional Al_2O_3 is stable down to the bilayer limit and the band gap of few-layer Al_2O_3 increases with increasing layer thickness. This is the opposite of the band gap thickness trend of vdW layered materials, such as black phosphorus and transition metal dichalcogenides. In addition, we investigate the stability and electronic properties of bilayer Ga_2O_3 and In_2O_3, assuming both bilayers are thermally stable. Our work predicts promising stability for 2D non-vdW boron group oxides and provides theoretical support for the future experimental preparation of 2D boron group oxides.

2. Methods

All first-principles calculations in this work, such as structural optimization, phonon dispersion, and electronic properties of Al_2O_3 with different number of layers, were performed using the QUANTUM ESPRESSO package based on density functional theory (DFT) [44,45]. The Perdew–Burke–Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) was adopted for electron exchange and correlation interactions [46]. Ultrasoft pseudopotentials were selected to describe the interaction between electrons and ions. A vacuum spacing of 20 Å was used to minimize the interaction between neighboring slabs. The cut-off energy of 680 eV and the Brillouin zone sampling of a $10 \times 10 \times 1$ Monkhorst–Pack k-point grid [47] were applied for all layered structures. The convergence threshold for self-consistency was set as 10^{-11} eV. To ensure the accuracy of the calculation, the structural optimization was continued until the residual forces converged to less than 1.4×10^{-3} eV/Å and the total energy to less than 1.4×10^{-4} eV. The phonon dispersions and Raman spectra were calculated using Phonon code within density-functional perturbation theory [48]. We used norm-conserving pseudopotentials (NCPPs) within the local density approximation (LDA) with a plane-wave cutoff energy of 816 eV to describe the interaction between electrons and ions. A $16 \times 16 \times 1$ Monkhorst−Pack k-mesh and a $8 \times 8 \times 1$ Monkhorst−Pack q-mesh were applied for the phonon dispersion calculations. For the Raman spectra calculations, a $10 \times 10 \times 1$ Monkhorst−Pack k-mesh was used. The threshold for self-consistency was set at 1.36×10^{-13} eV.

3. Results and Discussions

Pristine bulk Al_2O_3 is trigonal with the space group $R\bar{3}c$ (Figure 1a). O^{2-} ions are arranged in a hexagonal close packing and Al^{3+} ions are filled into the octahedral voids. The calculated band gap of bulk Al_2O_3 is 5.83 eV, which is close to the previously calculated

value (6.05 eV) [49]. To model the Al_2O_3 (0001) surface, we consider the two common surface structures shown in Table 1. The thermodynamic stability of different surface structures can be evaluated based on the surface formation energy, which is defined by the following equation: $E_f = E_{surface} - E_{bulk}$, where $E_{surface}$ is the energy of an optimized surface structure and E_{bulk} is the energy of optimized bulk Al_2O_3. The calculated surface formation energies of type I and II surfaces are listed in Table 1. The calculated surface formation energy of the type I surface is about 3.78 eV, which is a quarter of that of the type II surface. Therefore, the type I surface structure is more stable than the type II surface. In the following, all calculations are performed based on the type I surface structure.

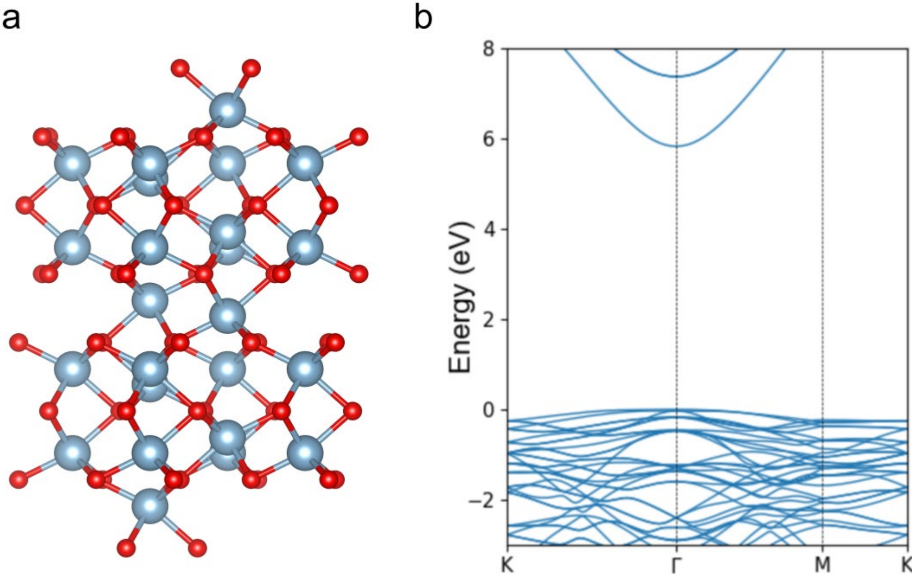

Figure 1. (**a**) Side view of the structure and (**b**) calculated electronic band structure for bulk Al_2O_3. The Fermi level is set at valence band maximum (VBM).

Table 1. The side views and E_f (eV) for type I and II Al_2O_3(0001) surface before and after optimization.

	Before Optimization	After Optimization	E_f (eV)
Type I			3.78
Type II			15.12

The energetically stable structures of the monolayer, bilayer, trilayer, four-layer, and five-layer Al_2O_3 are shown in Figure 2a–e. There are five atoms (two Al atoms and three O atoms) in the unit cell of monolayer Al_2O_3. By analogy, the bilayer, trilayer, four-layer, and five-layer Al_2O_3 have 10, 15, 20, and 25 atoms, respectively. During the structural optimization, the Al atoms on the upper and lower surfaces gradually move inward, inducing a flat surface structure. The reconstruction of the surface may further enhance the stability of 2D Al_2O_3. Figure 2f shows the in-plane lattice constants of few-layer and

bulk Al_2O_3. The in-plane lattice constant for monolayer Al_2O_3 is 5.84 Å, which is 21% larger than that of bulk Al_2O_3 (4.81 Å). The large change in the lattice constants suggests that the monolayer Al_2O_3 may be unstable. In addition, the lattices of the bilayer, trilayer, four-layer, and five-layer Al_2O_3 are similar to that of bulk Al_2O_3, indicating that bilayer Al_2O_3 is the thinnest Al_2O_3 structure that can be fabricated experimentally.

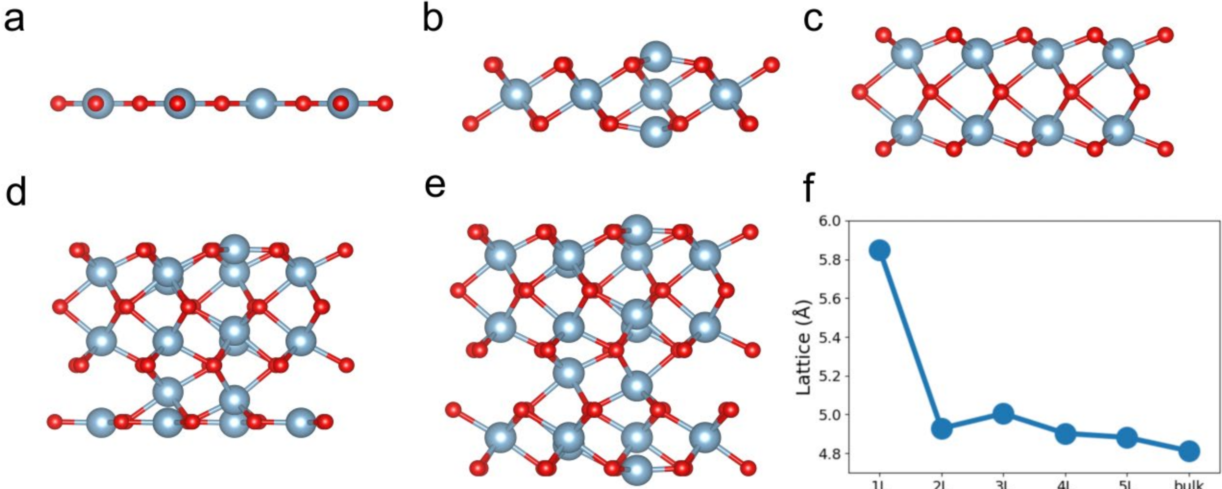

Figure 2. A side view of the optimized structures for the (**a**) monolayer, (**b**) bilayer, (**c**) trilayer, (**d**) four-layer, and (**e**) five-layer Al_2O_3. The gray and red balls represent Al and O atoms, respectively. (**f**) The optimized in-plane lattices of the few-layer and bulk Al_2O_3.

The dynamic stability of few-layer Al_2O_3 can be examined from the phonon dispersions. The absence of negative frequencies in Figure 3a,b indicates that the monolayer and bilayer Al_2O_3 are dynamically stable and can exist as free-standing 2D structures. Although monolayer Al_2O_3 is dynamically stable, the giant lattice difference between monolayer and bulk Al_2O_3 indicates the difficulty of synthesis monolayer Al_2O_3 by top-down strategy. Considering the small lattice constant change and high dynamic stability of bilayer Al_2O_3, it can be inferred that the synthesis of bilayer Al_2O_3 is quite possible by top-down or bottom-up method. Because of the large number of atoms in the cell of trilayer, four-layer, and five-layer Al_2O_3, the phonon calculation for these structures are extremely heavy. Here, the phonon dispersions of trilayer, four-layer, and five-layer Al_2O_3 are not present. The in-plane lattice constants of trilayer, four-layer, and five-layer Al_2O_3 are close to that of bilayer Al_2O_3, and we claim that the trilayer, four-layer, and five-layer Al_2O_3 are likely synthesized experimentally.

Figure 4a–e show the electronic band structures of few-layer Al_2O_3 calculated via the GGA scheme. The band gaps of the monolayer and five-layer Al_2O_3 are direct, with the conduction band minimum (CBM) and the valence band maximum (VBM) located at the Γ point. The band gaps of bilayer, trilayer, and four-layer Al_2O_3 are indirect, with the CBM located at the Γ point and the VBM located at a general point along the $\Gamma-$M line. In addition, with the increase in the number of layers, the band structure of Al_2O_3 gradually shows the characteristics of a flat band in the VBM, which implies a large intensity of the density of states. Moreover, such a flat band in the VBM also indicates the large mass of hole carrier, which limits the mobility of holes.

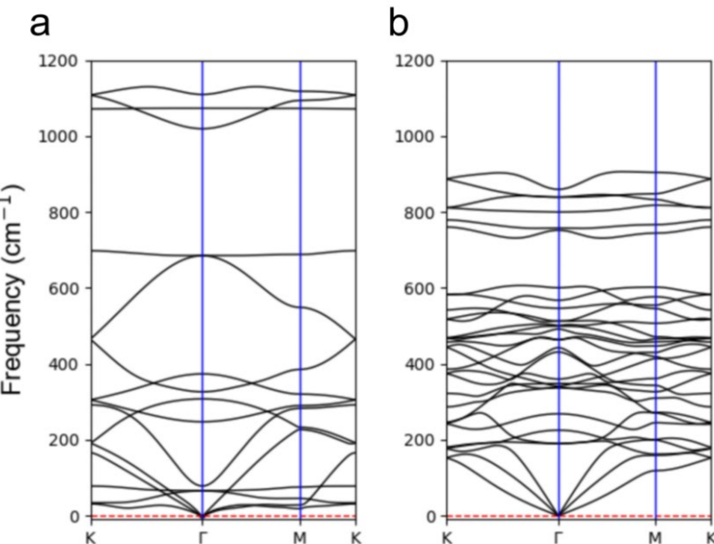

Figure 3. Phonon dispersions of (**a**) monolayer and (**b**) bilayer Al_2O_3.

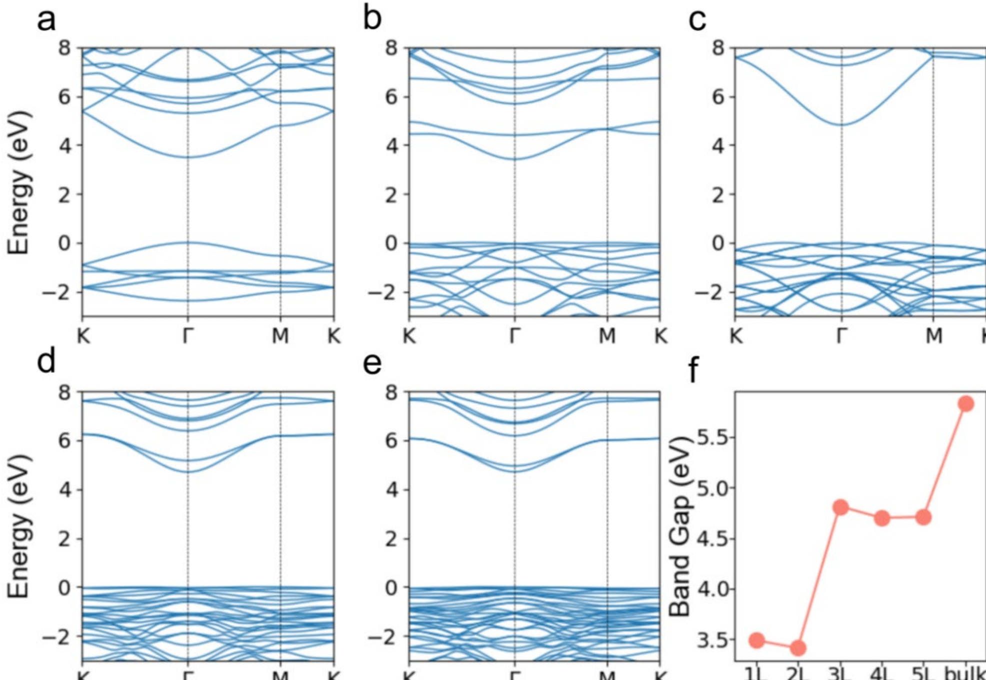

Figure 4. Band structures of (**a**) monolayer, (**b**) bilayer, (**c**) trilayer, (**d**) four-layer, and (**e**) five-layer Al_2O_3, respectively. The Fermi level is set at the valence band maximum (VBM). (**f**) The bandgap of few-layer and bulk Al_2O_3.

Figure 4f shows that the band gap of Al_2O_3 increases with an increase in the number of layers. For comparison, the band structure of bulk Al_2O_3 is presented in Figure 1b and shows a direct band gap of 5.83 eV. The values of the band gap for monolayer and bilayer Al_2O_3 are similar (~3.5 eV), and those for the trilayer, four-layer, and five-layer Al_2O_3 are also similar (~4.7 eV). It is well known that the band gap is always underestimated and lattice constants are overestimated when using GGA calculation due to the lack of Fock exchange. The hybrid functional will improve band gap and lattice constants because of including the exact exchange correction, but will induce a rise in computational costs [50,51]. In order to obtain the more reliable band gaps, we used the HSE06 hybrid functionals to calculate the band structures of monolayer and bilayer Al_2O_3, as shown in Figure 5. The band gaps are 5.08 and 4.95 eV for monolayer and bilayer Al_2O_3, respectively. The band

gap calculated through using HSE06 hybrid functional is about 1.5 eV larger than that through GGA. However, the band gap of bilayer Al_2O_3 is also slightly smaller than that of monolayer Al_2O_3 through using HSE06 hybrid functional, which is consistent with the results through GGA calculation. In addition, the band gap of monolayer Al_2O_3 is direct, and that of bilayer Al_2O_3 is indirect when using HSE06 functional, which is also consistent with the result obtained via GGA calculation. Therefore, the band gap calculated using the HSE06 hybrid functional is 1.5 eV larger than that through GGA, but the band gap nature and band gap variation on layer thickness are independent on the functional used. The band gaps of few-layer Al_2O_3 are wider than 3.0 eV, corresponding to the ultraviolet spectral range. Therefore, the few-layer Al_2O_3 is suitable for ultraviolet optoelectronic applications. The quantum confinement effect for most semiconductors means that the band gap increases as the thickness decreases. However, for Al_2O_3, the band gap narrows as the thickness decreases, indicating that the band gap variation with thickness cannot be explained by the quantum confinement effect. From the partial density of the states of on-surface and interior Al atoms for bilayer Al_2O_3 (Figure 6), we can find that band edge states, which determine the band gap, mainly originate from on-surface Al atoms. Due to the surface states, the band gap of few-layer Al_2O_3 is smaller than that of bulk Al_2O_3 (Figure 4f). Because the surface reconstruction of few-layer Al_2O_3 varies with thickness (Figure 2a–e), the band gap changes with thickness accordingly. Therefore, we attribute the band gap variation with the thickness to the different giant surface reconstruction of the few-layer Al_2O_3.

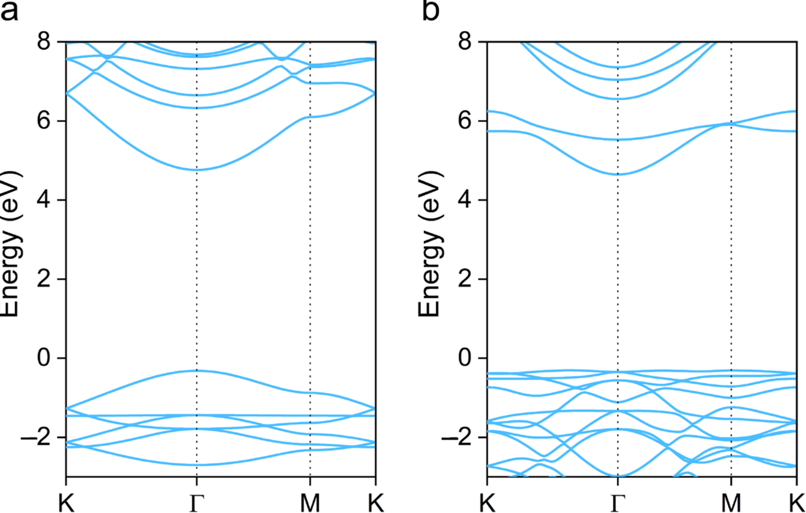

Figure 5. Band structures of (**a**) monolayer and (**b**) bilayer Al_2O_3 using HSE06 hybrid functional.

Raman spectrum is an effective method with which to identify different materials and structures. In order to facilitate future experimental efforts on few-layer Al_2O_3, the Raman spectra of monolayer and bilayer Al_2O_3 were calculated (see Figure 7). Monolayer Al_2O_3 belongs to the space group P$\bar{6}$2m with 1 f.u. in the primitive cell (five atoms). The zone-center optical phonons can be classified as the following irreducible representations: Γ_{opt} = E″ + 3E′ + A″1 + A'_1 + A″2 + A'_2, where E″, E′, and A'_1 are Raman active. For monolayer Al_2O_3, the peaks are centered at 387, 754, and 1043 cm^{-1}, corresponding to the A'_1, $E'^{(1)}$, and $E'^{(2)}$ modes, respectively. The corresponding vibration for A'_1, $E'^{(1)}$, and $E'^{(2)}$ modes are listed in Table 2. In addition, in Figure 7a, the intensity of A'_1 at 387 cm^{-1} is significantly higher than the other two peaks. Therefore, the A'_1 mode can be used as a Raman signature of monolayer Al_2O_3. Bilayer Al_2O_3 belongs to the space group P$\bar{3}$1m with 2 f.u. (10 atoms) in the primitive cell. Therefore, bilayer Al_2O_3 has 30 vibrational modes. Among these modes, five E_g and three A_{1g} modes are Raman active. For bilayer Al_2O_3, there are five dominant modes at 367, 521, 554, 797, and 881 cm^{-1} (Figure 7b) corresponding to the ${A_{1g}}^{(1)}$, ${A_{1g}}^{(2)}$, ${E_g}^{(1)}$, ${A_{1g}}^{(3)}$, and ${E_g}^{(2)}$ modes with apparent intensity, respectively.

The corresponding vibrations for $A_{1g}^{(1)}$, $A_{1g}^{(2)}$, $E_g^{(1)}$, $A_{1g}^{(3)}$, and $E_g^{(2)}$ modes are shown in Table 3. Furthermore, among these peaks, $A_{1g}^{(3)}$ at 797 cm^{-1} has the highest intensity and can be considered as the Raman signature of bilayer Al_2O_3.

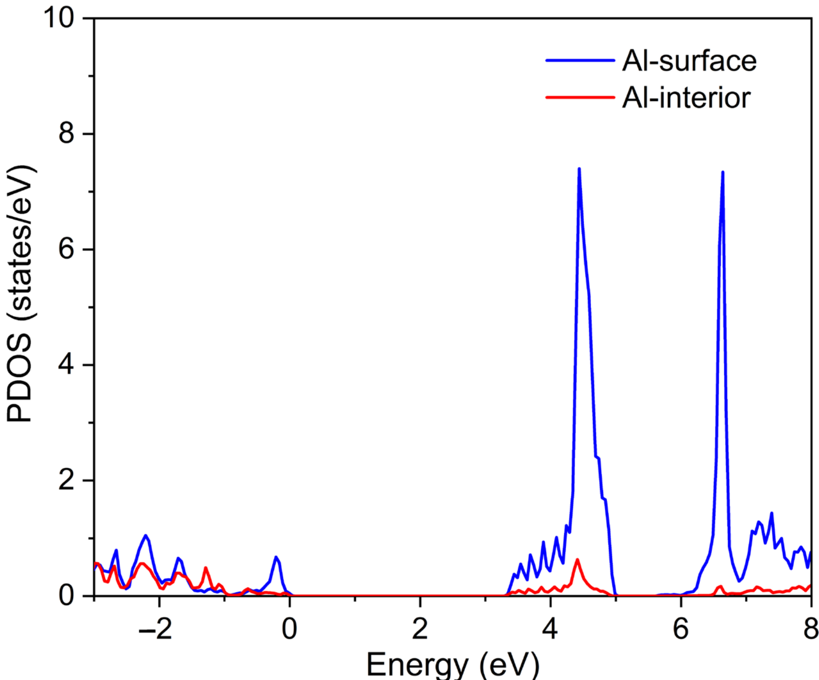

Figure 6. The partial density of states (PDOS) of Al atoms for bilayer Al_2O_3.

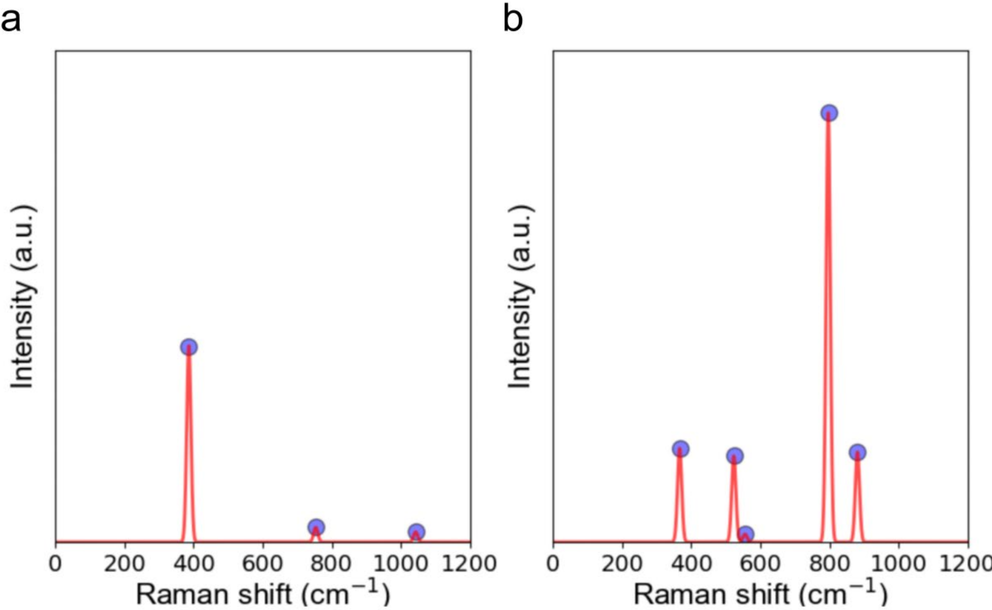

Figure 7. The calculated Raman spectra of (**a**) monolayer and (**b**) bilayer Al_2O_3.

Table 2. Vibrational modes for monolayer Al_2O_3.

Mode	Frequency (cm^{-1})	Top View
A'_1	387	
$E'^{(1)}$	754	
$E'^{(2)}$	1043	

Based on the above results, which provide evidence of the stability of bilayer Al_2O_3, we can assume that the bilayer Ga_2O_3 and In_2O_3 are also stable because Al, Ga, and In are in the same group. The absence of negative frequencies in phonon dispersions (Figure 8a,c) demonstrates the stability of bilayer Ga_2O_3 and In_2O_3. Bilayer Ga_2O_3 and In_2O_3 are indirect semiconductors (Figure 8b,d) with band gaps of 2.01 and 1.17 eV, respectively, which are smaller than that of bilayer Al_2O_3. The CBM of either bilayer Ga_2O_3 or In_2O_3 is located at the Γ point and the VBM at a general point along the K−Γ line. To obtain a variation of band structure on layer thickness, Figures 9 and 10 show the band structures of few-layer Ga_2O_3 and In_2O_3, which show a similar band gap variation to that of few-layer Al_2O_3.

Table 3. Vibrational modes for bilayer Al_2O_3.

Mode	Frequency (cm^{-1})	Side View
$A_{1g}^{(1)}$	367	
$A_{1g}^{(2)}$	521	
$E_g^{(1)}$	554	
$A_{1g}^{(3)}$	797	
$E_g^{(2)}$	881	

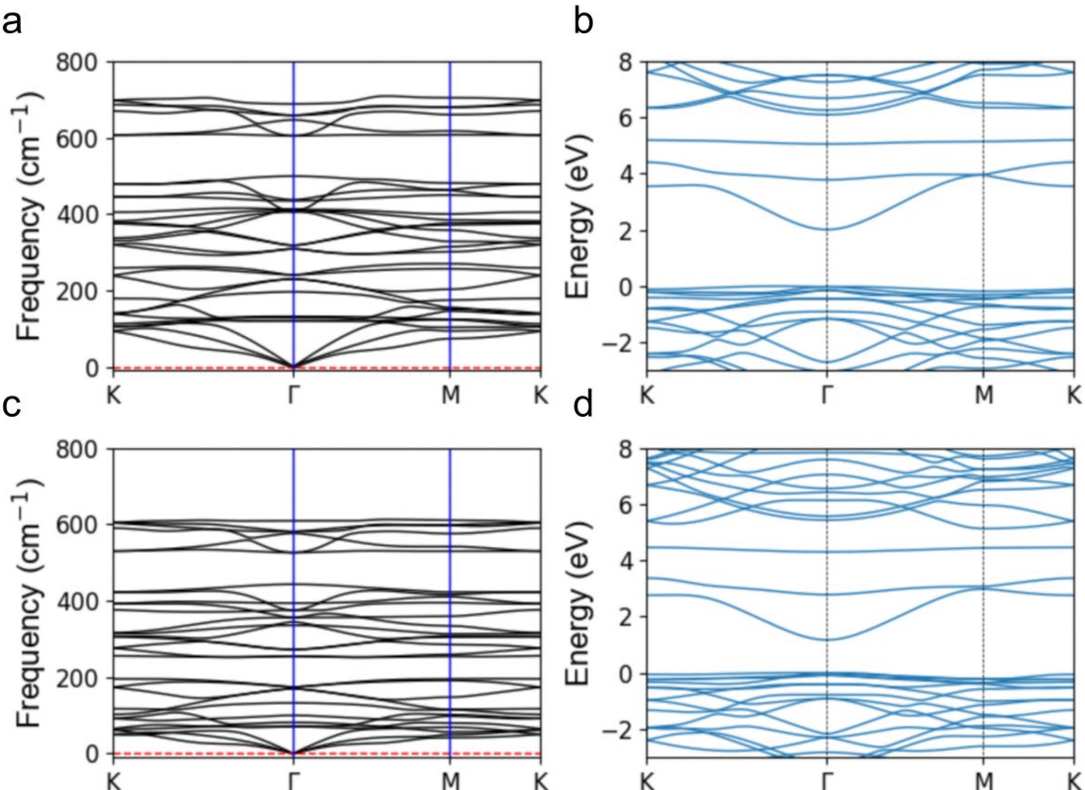

Figure 8. Phonon dispersions of bilayer (**a**) Ga_2O_3 and (**c**) In_2O_3. Calculated electronic band structures of bilayer (**b**) Ga_2O_3 and (**d**) In_2O_3. The Fermi level is set at the valence band maximum (VBM).

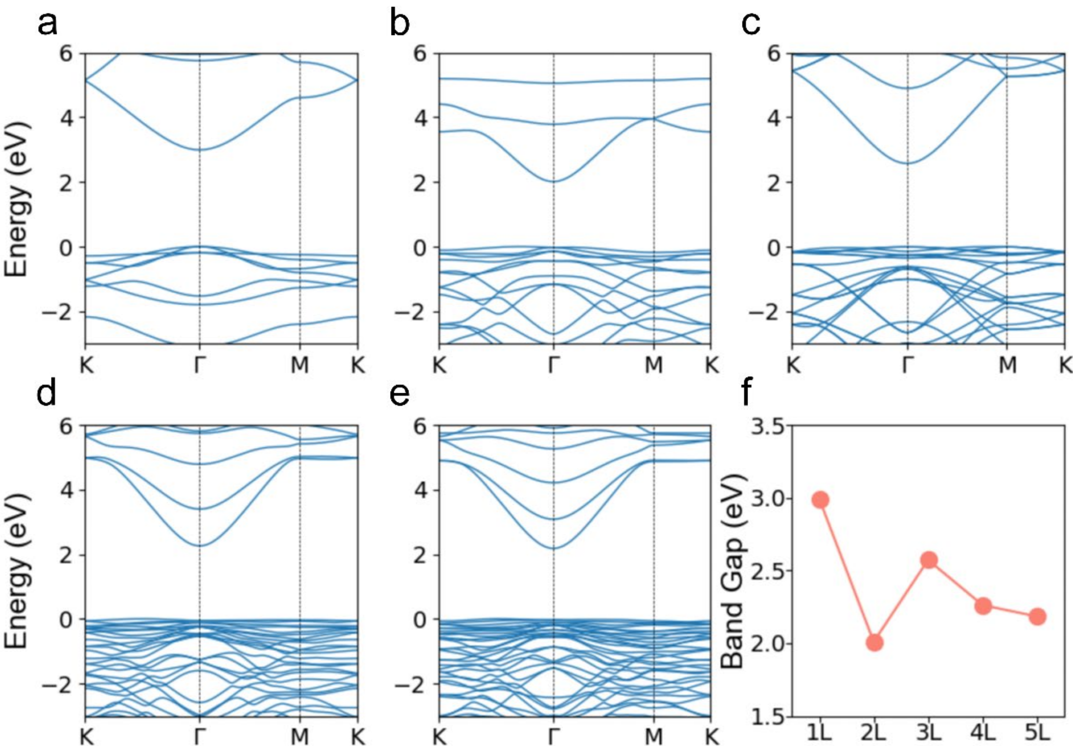

Figure 9. Band structures of (**a**) monolayer, (**b**) bilayer, (**c**) trilayer, (**d**) four-layer, and (**e**) five-layer Ga_2O_3, respectively. (**f**) The bandgap of few-layer Ga_2O_3.

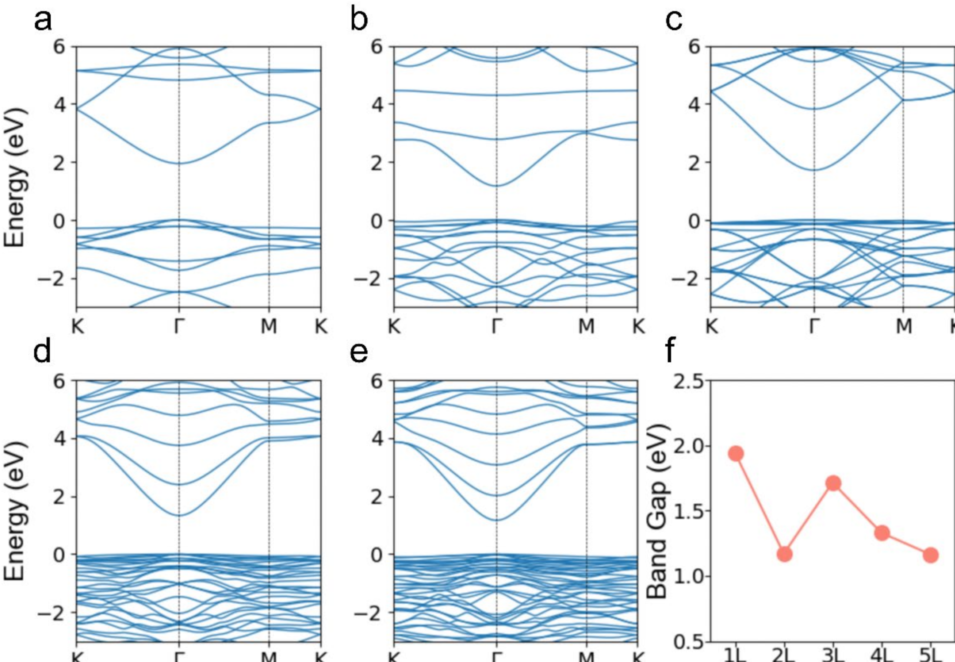

Figure 10. Band structures of (**a**) monolayer, (**b**) bilayer, (**c**) trilayer, (**d**) four-layer, and (**e**) five-layer In_2O_3, respectively. (**f**) The bandgap of few-layer In_2O_3.

It is also necessary to provide the Raman signature for bilayer Ga_2O_3 and In_2O_3. As shown in Figure 11, the Raman spectra of bilayer Ga_2O_3 and In_2O_3 were calculated, which were similar to that of bilayer Al_2O_3. Bilayer Ga_2O_3 and In_2O_3 belong to the space group $P\bar{3}1m$ with 2 f.u. (10 atoms) in the primitive cell. For bilayer Ga_2O_3, the peaks are centered at 196, 320, 410, 664, and 689 cm^{-1} corresponding to the $A_{1g}{}^{(1)}$, $E_g{}^{(1)}$, $A_{1g}{}^{(2)}$, $E_g{}^{(2)}$, and $A_{1g}{}^{(3)}$ modes, respectively (Figure 11a). The corresponding vibration for $A_{1g}{}^{(1)}$, $E_g{}^{(1)}$, $A_{1g}{}^{(2)}$, $E_g{}^{(2)}$, and $A_{1g}{}^{(3)}$ modes are listed in Table 4. The peak centered at 689 cm^{-1} ($A'_{1g}{}^{(3)}$) with strong intensity should be considered as the Raman signature of bilayer Ga_2O_3. As for bilayer In_2O_3, Figure 11b shows that there are four major peaks and two minor peaks in the Raman spectra. Six peaks centered at 133, 269, 333, 357, 580, and 607 cm^{-1} correspond to the $A_{1g}{}^{(1)}$, $E_g{}^{(1)}$, $A_{1g}{}^{(2)}$, $E_g{}^{(2)}$, $E_g{}^{(3)}$, and $A_{1g}{}^{(3)}$ modes, respectively. All the Raman active vibrational modes for bilayer In_2O_3 can be found in Table 5. Similarly, the Raman signature of bilayer In_2O_3 should be the $A_{1g}{}^{(3)}$ peak, which has a pronounced intensity.

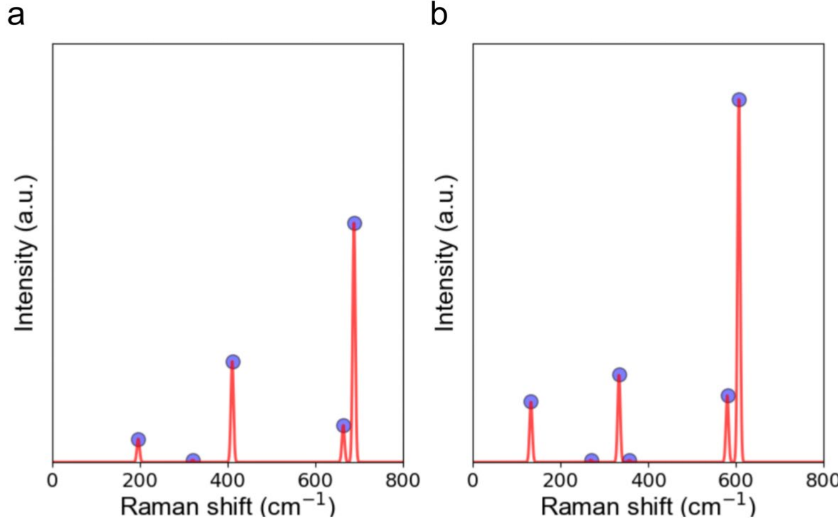

Figure 11. The calculated Raman spectra of bilayer (**a**) Ga_2O_3 and (**b**) In_2O_3.

Table 4. Vibrational modes for bilayer Ga_2O_3.

Mode	Frequency (cm^{-1})	Side View
$A_{1g}^{(1)}$	196	
$E_g^{(1)}$	320	
$A_{1g}^{(2)}$	410	
$E_g^{(2)}$	664	
$A_{1g}^{(3)}$	689	

Table 5. Vibrational modes for bilayer In_2O_3.

Mode	Frequency (cm^{-1})	Side View
$A_{1g}^{(1)}$	133	
$E_g^{(1)}$	269	
$A_{1g}^{(2)}$	333	
$E_g^{(2)}$	357	

Table 5. *Cont.*

Mode	Frequency (cm^{-1})	Side View
$E_g^{(3)}$	580	
$A_{1g}^{(3)}$	607	

4. Conclusions

In summary, using first-principles calculations based on DFT, we have investigated the structural stability and electronic properties of 2D boron group oxides. The thinnest stable Al_2O_3 structure is a bilayer with an indirect band gap of 3.41 eV. Interestingly, we find that the band gap of Al_2O_3 decreases with decreasing layer thickness, which is opposite to the trend seen in vdW 2D materials, such as MoS_2. We attribute this to the giant surface reconstruction of Al_2O_3. In addition, the phonon dispersion curves and band structures show that both bilayer Ga_2O_3 and In_2O_3 are also stable, with band structures similar to that of bilayer Al_2O_3. From bilayer Al_2O_3 to bilayer Ga_2O_3 and In_2O_3, the band gap decreases with the increasing atomic radius. It is expected to synthesize few layer boron group oxides by top-down strategy, such as liquid exfoliation method. This work provides theoretical support for the discovery of non-vdW 2D boron group oxides. Because of their large band gap, non-vdW 2D boron group oxides hold potential applications in ultraviolet optoelectronics and high-power electronics.

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Conflicts of Interest: The authors declare no conflict of interest.

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