# First-Principle Electronic Properties of Monoclinic $(Al_xIn_yGa_{1-x-y})_2O_3$ Alloys

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***Abstract*-First-Principle DFT calculations are carried out to investigate the electronic properties of β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys with x ranging from 0~12.5% and y ranging from 0~ 18.75%. The electronic properties of monoclinic gallium oxide alloy with added aluminium and indium atoms are explored. The incorporation of both aluminium and indium results in the reduction of energy bandgap of β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys. Additionally, indium of higher content than aluminium in the quaternary alloy promotes the indirect bandgap transferring to direct bandgap. This work provides new findings on the flexible band property modification of monoclinic gallium oxide-based material and indicates their potential in deep ultraviolet photodetector.**

As a transparent semiconductor material with ultrawide bandgap of 4.6~4.9 eV [1], monoclinic gallium oxide (β-$Ga_2O_3$) is drawing humungous interests in various technological applications such as high-power field effect transistors, ultraviolet (UV) photodetectors and advanced micro/nanoelectromechanical systems. β-$Ga_2O_3$ material possesses excellent properties such as large critical breakdown field voltage and high electrical conductivity [2]. However, the application of β-$Ga_2O_3$ materials is still in the early stage due to the limitation including the p-type doping difficulty and low thermal conductivity.

Considering the requirement of material design flexibility for device applications, the materials from the same class are often implemented in the purpose of forming heterostructures for carrier confinement to enable optoelectronics with specific spectrum region for various technological applications including transistors, light emitting didoes, and photodetectors. Recent studies suggest emerging interests in applying β-$Ga_2O_3$-based compound alloys for various device technologies. Specifically, it is considered to incorporate aluminium (Al) or indium (In) to design ternary alloys, in a relatively similar fashion to the III-Nitride-based materials in the form of InGaN and AlGaN alloys [3]. Extensive research work on III-oxide binary alloys ($Al_2O_3$, $Ga_2O_3$ and $In_2O_3$) has been reported [4-9], but the understanding on the properties of β-$Ga_2O_3$-based ternary materials is still limited by far [5] comparing to that of other wide-established materials such as GaN and GaAs. More importantly, there has been no literature on the β-$Ga_2O_3$-based quaternary material. Thus, investigating the optoelectronic properties of the β-$Ga_2O_3$-based quaternary materials is critical to gauge their potential use in device applications.

In this work, the electronic band structures of β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys with Al-content (x) up to 12.5% and In-content (y) up to 18.75% are investigated using Density function theory (DFT) calculations. The effect of aluminium and indium atoms on the electronic properties of β-$Ga_2O_3$ quaternary alloys are then analyzed.

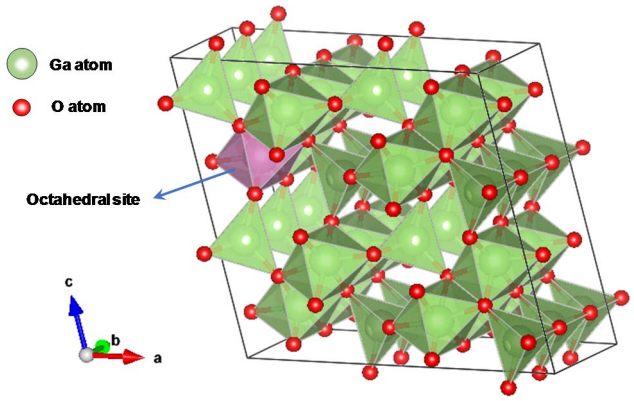


Fig. 1 supercell structure -$Ga_2O_3$ crystal.

### *A. Simulation method*

Fig. 1. illustrates an appropriate crystal model constructed for the band structure calculations using the supercell approach implemented in atomistic simulation package MedeA-VASP software [10,11]. The β-$Ga_2O_3$ crystal structure with 1×2×2 supercell consists 32 gallium atoms and 48 oxygen atoms in total. In the 80-atom supercell, one Ga atom is replaced by one aluminium or indium atom corresponds to a dilute concentration of 3.125%. Note that all the substituted gallium atoms are located at the octahedral sites of the β-$Ga_2O_3$ crystal structure, since the formation energy required to substitute Ga atom at tetrahedral site is higher compared to octahedral site [7]. Similar approach was implemented in creating β-$(Al_xIn_yGa_{1-x})_2O_3$ alloys with Al/In-content up to 12.5%, in which the supercell size is kept unchanged. It is important to point out that the β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys with higher content are not considered in this study, due to the known phase separation issue in the β-$Ga_2O_3$ alloys [5]. First-Principle DFT calculations are then carried out using GGA-PBE exchange correlation functional for β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys.

### *B. Results and discussions*

Fig. 2. presents the band structure of β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys with x and y equal to 6.25%. The scissor operation has been applied to correct the error resulted from the GGA exchange correlation functional in the calculations [12]. According to the band structures of -$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys

with different Al/In-contents obtained through DFT clculations, the alloys exhibit indirect band gaps.

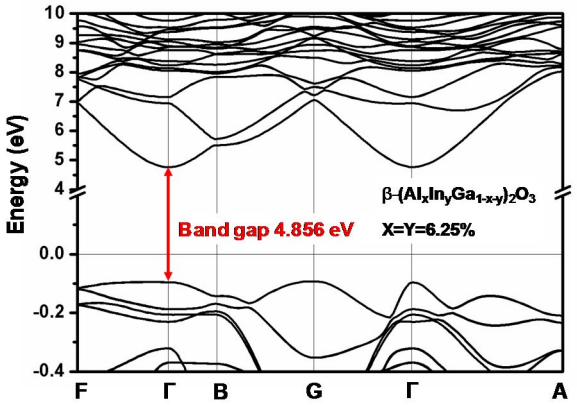


Fig. 2 First principle calculated band structure of -$(Al_xIn_yGa_{1-x-y})_2O_3$ alloy with x and y equal to 6.25%.

The conduction band minimum of the alloys is always located at the point in the Brillouin Zone, while the valance band maximum location is off the point. Further analysis revealed that when the content of indium is equal or higher than that of aluminium, the valance band maximum tends to move from Γ-Z direction to Γ-Y direction, which implies the addition of impurity has effect on not only the conduction band, but also the valance band dispersion.

Fig. 3. presents the energy band gap as a function of Al and In-contents for β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys with x up to 12.5% and y up to 18.75%. The solid line and dotted line in Fig. 3. represent direct and indirect energy band gap property of the oxide alloys respectively. As shown in Fig. 3., the β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys exhibit indirect bandgap property, which is consistent with the property of β-$Ga_2O_3$. As shown by the solid lines, the direct bandgap increases from 4.835eV to 5.086eV when the Al-content increases from 0% to 12.5% in β-$(Al_xGa_{1-x})_2O_3$, while it decreases from 4.835eV to 4.432eV in the β-$(In_xGa_{1-x})_2O_3$ alloys. This can be explained by the band property of $Al_2O_3$ and $In_2O_3$, which possess bandgaps of ~7.5 eV and ~3 eV [8,9], respectively. The incorporation of aluminium content tends to enlarge the bandgap and the indium contrarily promotes bandgap to shrink. In addition, our analysis found that the quaternary alloy system can be designed to be lattice-matching with β-$Ga_2O_3$ alloy, implying the possibility of adjusting the band properties of β-$Ga_2O_3$-based material without creating compressive or tensile strain within the material systems.

Our analysis shows that there is a possibility to have a direct-indirect band gap property switching by introducing

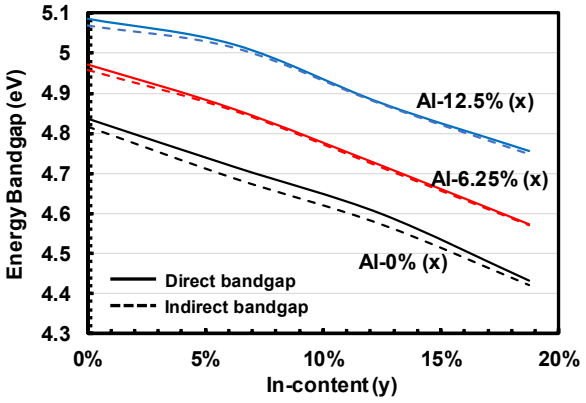


Fig. 3 Energy bandgap of -$(Al_xIn_yGa_{1-x-y})_2O_3$ alloy with Al-content up to 12.5% and In-content up to 18.75%.

additional Indium or aluminium content in the β-$Ga_2O_3$-based materials. As shown in figure 3, there is an overlapping of the solid and break lines for Al-6.25% and Al-12.5% β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys, indicating the tendency of bandgap type transferring from indirect to direct in the quaternary alloy. The difference between the direct and indirect bandgap for these alloys reduces from 0.0277 eV(β-$(In_{0.0625}Ga_{0.9375})_2O_3$ to 0.0016 eV (β-$(Al_{x0.125}In_{0.1875}Ga_{0.6875})_2O_3$), which is small.

The ultrawide bandgap gallium oxide-based material is expected to be applicable in the ultraviolet (UV) photodetector devices. The transition wavelength of β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys covers a range of 240 nm to 280 nm, which implies that the β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys can be applied for device applications operating in the deep UV regime.

### *C. Conclusions*

In summary, First-Principle DFT calculations are carried out using GGA-PBE exchange correlation functional to investigate the electronic properties of β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys. With Al-content and In-content changing from 0%~12.5% and 0%~18.75% respectively, the band structures of β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys are found to exhibit indirect bandgap property with the bandgap energy ranging from 5.086 eV to 4.432 eV. Higher Al-content promotes the bandgap transferring from indirect to direct. The electronic properties of β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys has yet been studied, and the relationship between the Al/In content and the bandgap of the quaternary alloy is presented for the first time. Our results are essential for device modeling and simulations involving the oxide materials. The wavelength corresponding to the bandgap energy is extracted which covers a region of 240~280nm, indicating the potential use of β-$(Al_xIn_yGa_{1-x-y})_2O_3$ alloys for deep UV photodetector.

### Acknowledgement

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### REFERENCES

[1] M. Razeghi, et al., "A review of the growth, doping, and applications of β-$Ga_2O_3$ thin films," In oxide-based materials and devices IX, 10533, 2018.
[2] S. I. Stepanov, et al., "Gallium oxide: properties and applications-a review," Rev. Adv. Mater. Sci, 44, 63-86, 2016.
[3] S. Nakamura, et al., "Candela□class high□brightness InGaN/AlGaN double□heterostructure blue□light□emitting diodes," Applied Physics Letters, 64(13), 1687-1689, 1994
[4] D. Shinohara, et al., "Heteroepitaxy of corundum-structured α-$Ga_2O_3$ thin films on α-$Al_2O_3$ substrates by ultrasonic mist chemical vapor deposition," Japanese Journal of Applied Physics, 47(9R), 7311, 2008.
[5] M. B.Maccioni, et al., "Phase diagram and polarization of stable phases of $(Ga_{1-x}In_x)_2O_3$," Applied Physics Express, 9(4), 041102, 2016.
[6] K. Yamaguchi, "First principles study on electronic structure of β-$Ga_2O_3$," Solid State Communications, 131(12), 739, 2004.
[7] H. Peelaers, et al., "$(In_xGa_{1-x})_2O_3$ alloys for transparent electronics," Physical Review B, 92(8), 085206, 2015.
[8] H. Peelaers, et al., "Structural and electronic properties of $Ga_2O_3$-$Al_2O_3$ alloys," Applied Physics Letters, 112(24), 242101, 2018.
[9] P. D. C. King, et al., "Band gap, electronic structure, and surface electron accumulation of cubic and rhombohedral $In_2O_3$," Physical Review B, 79(20), 205211, 2009.
[10] G. Kresse, et al., "Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set," Computational materials science, 6(1), 15, 1996.
[11] J. P. Perdew, et al., "Generalized gradient approximation made simple," Physical review letters, 77(18), 3865, 1996.
[12] V. Fiorentini, et al., "Dielectric scaling of the self-energy scissor operator in semiconductors and insulators," Physical Review B, 51(23), 17196, 1995.