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Recent progress on the electronic structure, defect, and doping properties of \( \text{Ga}_2\text{O}_3 \)

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ABSTRACT

Gallium oxide (\( \text{Ga}_2\text{O}_3 \)) is an emerging wide bandgap semiconductor that has attracted a large amount of interest due to its ultra-large bandgap of 4.8 eV, high thermal stability, and availability of large-scale native substrates for mass production. Despite the tremendous progress achieved in material development and devices based on wide bandgap (WBG) semiconductors represented by SiC and GaN, \( \text{Ga}_2\text{O}_3 \) is becoming a competitive candidate because of its unique applications such as high power electronic devices and solar-blind ultraviolet (UV) photodetectors. The most prominent feature of \( \text{Ga}_2\text{O}_3 \) is its ultra-large bandgap, which enables great potential for high electric breakdown field strength \( (\varepsilon_c) \) due to an exponential relationship between the breakdown field and bandgap value \( (E_g) \), \( \varepsilon_c = a(E_g)^n \), \( (n = 2–2.5) \). \( \text{Ga}_2\text{O}_3 \) has a theoretical breakdown field of up to 8 MV/cm, which is attracting attention from the ultrahigh-power device market (>1 MW) beyond SiC and GaN based electronics, with specific applications in electrical power transmission, hybrid propulsion, etc., as shown in Fig. 1. Figure 2 shows Baliga’s figure of merit (BFOM) of WBG and UWBG semiconductors. Drawn on a log-log specific on-resistance vs breakdown voltage plot, Baliga’s figure of merit (BFOM) plots the log-log specific on-resistance vs breakdown voltage and is a type FOM of interest for low-frequency unipolar vertical power switches. As shown in the chart, the BFOM of \( \text{Ga}_2\text{O}_3 \) is significantly larger than SiC and GaN.

I. INTRODUCTION TO \( \text{Ga}_2\text{O}_3 \) AND APPLICATIONS

Gallium oxide (\( \text{Ga}_2\text{O}_3 \)) is an emerging ultra-wide bandgap (UWBG) semiconductor that has attracted a large amount of interest due to its ultra-large bandgap of 4.8 eV, high thermal stability, and availability of large-scale native substrates for mass production. Despite the tremendous progress achieved in material development and devices based on wide bandgap (WBG) semiconductors represented by SiC and GaN, \( \text{Ga}_2\text{O}_3 \) is becoming a competitive candidate because of its unique applications such as high power electronic devices and solar-blind ultraviolet (UV) photodetectors. The most prominent feature of \( \text{Ga}_2\text{O}_3 \) is its ultra-large bandgap, which enables great potential for high electric breakdown field strength \( (\varepsilon_c) \) due to an exponential relationship between the breakdown field and bandgap value \( (E_g) \), \( \varepsilon_c = a(E_g)^n \), \( (n = 2–2.5) \). \( \text{Ga}_2\text{O}_3 \) has a theoretical breakdown field of up to 8 MV/cm, which is attracting attention from the ultrahigh-power device market (>1 MW) beyond SiC and GaN based electronics, with specific applications in electrical power transmission, hybrid propulsion, etc., as shown in Fig. 1. Figure 2 shows Baliga’s figure of merit (BFOM) of WBG and UWBG semiconductors. Drawn on a log-log specific on-resistance vs breakdown voltage plot, Baliga’s figure of merit (BFOM) plots the log-log specific on-resistance vs breakdown voltage and is a type FOM of interest for low-frequency unipolar vertical power switches. As shown in the chart, the BFOM of \( \text{Ga}_2\text{O}_3 \) is significantly larger than SiC and GaN.
Ga$_2$O$_3$ is also deemed as a rising star in the field of solar-blind photodetectors, again due to its wide bandgap. The solar-blind ultraviolet photodetectors have been broadly investigated with the goal of acquiring precise and accurate information of weak signal by night and day through the absence of solar-blind region irradiation (200–280 nm) at the Earth’s surface.

From a more practical point of view, the ease of fabrication of large area native substrates, control of carrier concentration, and inherent thermal stability also motivate the development of Ga$_2$O$_3$-based devices. $N$-type doping of Ga$_2$O$_3$ with Si or Sn has shown good controllability with a broad range from $10^{15}$ cm$^{-3}$ to $10^{20}$ cm$^{-3}$. Although some UWBG semiconductors (such as AlN, c-BN, and diamond) beat Ga$_2$O$_3$ in the BFOM chart, their wide utilization is strongly constrained by practical limits: AlN, c-BN, and diamond still suffer from a lack of proper substrates for high quality epitaxial growth.

Although Ga$_2$O$_3$ based devices have become the focus of research only in recent years, the explorations of Ga$_2$O$_3$ may date back to several decades ago (as shown in Fig. 3). The first report was on the optical properties of Ga$_2$O$_3$ in early nineteenth century, when the French scientist Lecoq de Boisbaudran found that “gallium oxide which contains chromium shows a red fluorescence in a vacuum” right after his discovery of the new element gallium.

Most of the early publications mainly focused on the basic physical properties and chemical synthesis of Ga$_2$O$_3$. In 1955, five different polymorphs of Ga$_2$O$_3$, their crystal structure, and phase stability have been explicitly illustrated by Roy et al. The investigations of Ga$_2$O$_3$ in the period of 1960s–1980s were mostly based on materials with poor crystallinity or even in amorphous forms, though some attempts for making Ga$_2$O$_3$ single crystals started to appear.

For example, small flasks of single crystals grown by Chase revealed the optical properties of $\beta$-phase Ga$_2$O$_3$, which established a bandgap value of 4.7 eV based on the observation of a band-to-band transition at 270 nm. The bandgap values were in consistency with values measured from bulk crystals and epitaxial thin films with much better quality. Because a native layer of Ga$_2$O$_3$ naturally forms on the surfaces of GaAs and GaN compound semiconductors, Ga$_2$O$_3$ thin films, mostly in amorphous or $\alpha$-phase polycrystalline forms, were also used as passivating layers for GaAs based complementary metal-oxide-semiconductor (CMOS) devices or as anti-reflective coating on GaAs light emitting diodes and as dielectric layers on GaN for MOS devices (native Ga$_2$O$_3$ on the GaN structure was chemically stable and supposed to be correlated with the low density of interface states) or Ga$_2$O$_3$/GaN dielectrics. Ga$_2$O$_3$ bulk crystals have also been used as substrates for the growth of GaN. Nevertheless, no significant progress has been made in this attempt because of poor control over the interface, film quality, and device performance. In fact, it is generally believed that Ga$_2$O$_3$ plays a negative role in GaAs and GaN technology, in which the naturally occurred Ga$_2$O$_3$ must be carefully removed before device processes.
From the 1990s to 2010s, significant breakthroughs have been made in successful growth of a bulk single crystal of high quality and large size. For example, a large Ga$_2$O$_3$ single crystal with size up to 70 mm $\times$ 50 mm $\times$ 3 mm was realized by the edge-defined film-fed growth (EFG) method, making EFG one of the most promising methods for large-scale production.\textsuperscript{44,45} Commercially available large $\beta$-phase Ga$_2$O$_3$ bulk crystals and wafers with a size up to 2 in. and 4 in. have been achieved by the Czochralski method\textsuperscript{46} and EFG method\textsuperscript{47,48} respectively. Figure 4 shows the picture of a 4-in. single crystal grown by the EFG technique. The availability of large area substrates has in-turn motivated the homoepitaxial growth of high quality Ga$_2$O$_3$ thin films with more sophisticated controlling of doping, defects, modulation doping, superlattice, etc.\textsuperscript{13,49-51}

Triggered by the growth of large-size bulk crystals, Ga$_2$O$_3$-based device research, including Ga$_2$O$_3$ based field-effect transistors (FETs),\textsuperscript{3,48} Schottky barrier diodes (SBDs),\textsuperscript{3,52-57} and solar-blind ultraviolet detectors,\textsuperscript{11,12,58,59} has been experiencing a rapid rise in the past few years. Some representative device structures are shown in Fig. 5. In 2012, Higashwaki et al.\textsuperscript{60} from the Novel Crystal Technology, Inc. reported the metal-semiconductor field-effect transistors (MESFETs) based on the Ga$_2$O$_3$ epitaxial layer grown on the $\beta$-Ga$_2$O$_3$ (010) substrate, which raised a boom in developing Ga$_2$O$_3$-based transistors with a variety of architectures. Ga$_2$O$_3$ MOSFETs with undoped or $n$-type channels utilizing dielectrics such as SiO$_2$\textsuperscript{61} or Al$_2$O$_3$\textsuperscript{62} as well as normally off Ga$_2$O$_3$ MOSFETs\textsuperscript{63} have all been extensively investigated.\textsuperscript{64} Breakthroughs are also achieved in transistor architectures, including heterostructure field-effect transistors (HFETs),\textsuperscript{65} current aperture vertical electron transistors (CAVETs),\textsuperscript{66} and fin-based vertical junction field-effect transistors (JFETs).\textsuperscript{67} Lateral FET with a breakdown voltage of 775 V and channel current of 100 mA/mm has been demonstrated in 2016.\textsuperscript{68} It is worth mentioning that two-dimensional electron gas (2DEG) was achieved in the ternary HFETs with the modulation-doped $\beta$-(Al,Ga)$_{2-x}$O$_3$/Ga$_2$O$_3$ interface by Zhang et al.\textsuperscript{69}

SBDs based on epitaxial layers of $\beta$-Ga$_2$O$_3$ have exhibited power figure-of-merits (V$_B^2$/R$_{ON}$) with great promises, in terms of a high reverse breakdown field (V$_B$) together with a low on-resistance (R$_{ON}$) value.\textsuperscript{70} Benefiting from the recent development of homoepitaxial growth techniques such as halide vapor phase epitaxy (HVPE) and low-pressure chemical vapor deposition (LPCVD), capable of growing thick (>1 mm) and high-quality layers, Ga$_2$O$_3$ SBDs had developed rapidly in the last four years.\textsuperscript{71-75} The breakdown strength of SBDs based on $\beta$-Ga$_2$O$_3$ has reached up to 4.2 MV/cm with an extrinsic R$_{ON}$ of 3.9 m$\Omega$ cm$^2$,\textsuperscript{76} exceeding the theoretical limits of 4H-SiC (2.2 MV/cm) and GaN (3.3 MV/cm).\textsuperscript{77}

Solar-blind UV photodetectors based on Ga$_2$O$_3$ single crystal substrates were initially developed by Oshima et al.\textsuperscript{78} and Suzuki et al.\textsuperscript{79} in 2008. Their pioneering works paved the way for the increase of investigations in this field. Ga$_2$O$_3$ solar-blind UV photodetectors have been broadly studied in the types of metal-semiconductor-metal (MSM) photodetectors, Schottky barrier photodetectors, and $p$-$n$ or $n$-$n$ junction photodiodes using Ga$_2$O$_3$ bulk crystals,\textsuperscript{80,81,72,73} films,\textsuperscript{82,83} and micro/nanostructures.\textsuperscript{84} Compared with the widely used Al$_2$Ga$_{1-x}$O$_3$\textsuperscript{74,75} and Mg$_2$Zn$_{1-x}$O$_x$\textsuperscript{86} whose detectivity is limited due to their serious alloying composition fluctuation or even phase segregation, a Ga$_2$O$_3$-based photodetector is highly suitable for practical applications of solar-blind photodetection with improved photoresponsivity and response speed.\textsuperscript{12}
Despite the great progress achieved in multiple technological fronts of Ga$_2$O$_3$, several challenges still require efforts from both the academic community and industrial community. There is still no solid experimental evidence showing the achievement of $p$-type doped Ga$_2$O$_3$, which makes it impossible to fabricate a $p$-$n$ homojunction and, thus, strongly limits its potential in optoelectronic application. Attempts to make ultra-high breakdown devices with low turn on voltages still lack valid strategy. Issues with the device fabrication process including contact, dielectrics, and surface passivation require further optimization. Although great improvements have been made in the growth of bulk crystals and epitaxial layers, more precise control over defects and impurities, and origin of unintentional defects as well as deeper understanding on the origin of unintentional defects, deep level trap states, carrier transport mechanism, and trapping effects. This review aims to provide an updated account of the semiconductor physics of Ga$_2$O$_3$ in terms of electronic structures, optical properties, chemistry of defects and dopants, and bandgap engineering. Recent progress and fundamental understanding on synthesis of bulk single crystals, epitaxial thin film growth, chemical and physical properties, chemistry of defects and impurities, and origin of unintentional n-type doping, $p$-type doping, and ternary alloys with In$_2$O$_3$ and Al$_2$O$_3$ were also discussed.

II. SEMICONDUCTOR PHYSICS OF Ga$_2$O$_3$

A. Polymorphism and crystal structure

There are at least five different polymorphs possible for Ga$_2$O$_3$, including monoclinic phase ($\beta$-Ga$_2$O$_3$), rhombohedral phase ($\alpha$-Ga$_2$O$_3$), defective spinel phase ($\gamma$-Ga$_2$O$_3$), cubic phase ($\delta$-Ga$_2$O$_3$), and hexagonal phase ($\epsilon$-Ga$_2$O$_3$). Among these polymorphs, $\beta$-Ga$_2$O$_3$ is the most stable at ambient environments and, hence, the most extensively studied phase. The thermodynamic stability of the five polymorphs was ranked as $\beta < \epsilon < \alpha < \delta < \gamma$. For details on the polymorphs and transition temperature, see, e.g., Ref. 23.

$\beta$-Ga$_2$O$_3$ has a monoclinic crystal structure with a space group C2/m, as shown in Fig. 6(b). The lattice parameters are $a = 12.21$ Å, $b = 3.04$ Å, $c = 5.80$ Å, and $\beta = 103.8^\circ$, and the unit cell volume is 208.85 Å$^3$. A detailed crystal structure of $\beta$-Ga$_2$O$_3$ has been reported by Åhman et al. Briefly, the unit cell of $\beta$-Ga$_2$O$_3$ [Fig. 6(b)] contains two crystallographically different Ga cations and three O anions. Half of the Ga cations are in distorted tetrahedral coordination (Ga1), and the other half are in distorted octahedral coordination (Ga2). O anions are packed in a distorted cubic structure with two threefold coordinated types (O1 and O2) and one fourfold coordinated type (O3). Therefore, different bonding environments could be found in $\beta$-Ga$_2$O$_3$: the tetrahedrally (T$_d$) coordinated Ga1 shares bonds with one O1 ion with a bond length of 1.835 Å, one O3 ion with a bond length of 1.833 Å, and two O2 ions with a bond length of 1.863 Å. The octahedrally (O$_h$) coordinated Ga2 ions share bonds with two O1 ions with a bond length of 1.937 Å, one O2 ions (1.937 Å), and three O3 ions (one with 2.005 Å and two within the $k$-plane with 2.074 Å). The low crystallographic symmetry of the monoclinic phase leads to anisotropy of the physical, optical, and electrical properties, as both predicted theoretically and observed experimentally. The (010) and (201) planes are the most commonly used crystal surfaces for device application and thin film growth.

Polymorphs other than the $\beta$-phase are metastable phases and cannot be grown as bulk crystals from the melt. However, they could be epitaxially grown as thin films stabilized on substrates. For example, $\alpha$-Ga$_2$O$_3$ [Fig. 6(a)] has the same corundum structure as Al$_2$O$_3$, containing only O$_h$ coordinated Ga sites, with lattice parameters of $a = 4.98$ Å and $c = 13.43$ Å and a space group of R3c. This structure is based on a hexagonally close packed array of O ions with the Ga cations filling up 2/3 of the central O$_h$ sites. High quality epitaxial layers of $\alpha$-phase Ga$_2$O$_3$ have

![Fig. 6](https://example.com/fig6.png)

**FIG. 6.** (a) Rhombohedral crystal structure of corundum-like $\alpha$-Ga$_2$O$_3$ with only O$_h$ (blue) coordination Ga. (b) Monoclinic $\beta$-Ga$_2$O$_3$ crystal structure: Ga cations located at T$_d$ (Ga1, green) and O$_h$ (Ga2, blue) coordination. O anions are packed in a distorted cubic structure with two threefold coordinated types (O1 and O2) and one fourfold coordinated type (O3). (c) Cubic defective spinel lattice structure of $\gamma$-phase Ga$_2$O$_3$ consists of T$_d$ (Ga1, green) and O$_h$ (Ga2, blue) coordinated Ga with a ratio of 1.2. (d) Orthorhombic $\epsilon$-Ga$_2$O$_3$ structure.
been obtained on Al₂O₃(0001) substrates by mist chemical vapor deposition (mist-CVD), 83–85 HVPE, 86 and pulsed laser deposition (PLD). 87 Remarkably, FLOSIA Inc. has succeeded in the growth of a high-quality α-Ga₂O₃ epitaxial thin film on 4-in. Al₂O₃ (0001) substrates by mist-CVD, which makes α-Ga₂O₃ a promising phase for mass production. 88

γ-phase Ga₂O₃ [Fig. 6(c)] consists of O₆ and T₄ coordinated Ga with a ratio of 2:1, with a space group of Fd3m, and lattice parameters of 8.22 Å. 89 It is analogous to the spinel Al₂O₃ framework. γ-phase Ga₂O₃ thin films have been obtained on Al₂O₃ and MgAl₂O₄ substrates by mist-CVD at a growth temperature of 390 °C–400 °C, 86 PLD, 118 and molecular beam epitaxy (MBE). 119

α-Ga₂O₃ is the most elusive Ga₂O₃ polymorph. α-Ga₂O₃ was first reported by Roy et al. 3 through heating β-Ga₂O₃ above 500 °C, and they assigned it to the hexagonal space group. α-Ga₂O₃ is now accepted with an orthorhombic structure [Fig. 6(d)] with lattice parameters of a = 5.0–5.1 Å, b = 8.7–8.8 Å, and c = 9.2–9.4 Å. Since 2015, single-phase α-Ga₂O₃ thin films have been obtained on Al₂O₃, AlN, or pseudo-hexagonal substrates by HVPE, 86 MOCVD, 118 PLD, 119 MBE, 120 and mist-CVD. 121 Difficulties in growing phase-pure crystals as well as the disordering nature of the Ga atoms in the α phase lead to difficulty in determination of the structure and properties of α-Ga₂O₃.

B. Electronic band structure and optical properties

The fundamental electronic structure of β-Ga₂O₃ and optical properties have been studied by numerous first principle calculation and a few photoemission spectroscopic experiments. 107–110 There is general consensus that β-Ga₂O₃ has a direct bandgap of ~4.87 eV (though with a slightly smaller indirect bandgap of 4.83 eV). The conduction band (CB) is mainly composed of delocalized Ga 4s derived states, giving rise to a dispersive band with a low electron effective mass, while the valence band (VB) is mainly formed by occupied O 2p derived states with minor hybridization with Ga 3d, 4p, and 4s orbitals.

The band structure of β-Ga₂O₃ has been calculated by density functional theory (DFT), 108–110 hybrid HF-DFT, 110 and GW methods. 103–106 Standard DFT results in an underestimate bandgap because of the approximations in the calculation of electron exchange correlation (XC) energy. 108–110 Hybrid B3LYP or GW methods were proven to provide results with better agreement with the experimental bandgap and lattice parameters. Figure 7(a) shows the calculated band structure of β-Ga₂O₃ by Varley et al. 117 hybrid B3LYP. It can be seen that the bottom of CB, of mainly the Ga 4s character, shows a highly dispersive feature at the Γ point.

On the other hand, the top of VB is mainly composed of localized O 2p orbitals, exhibiting very low dispersion. This results in a large hole effective mass, in agreement with other calculations for Ga₂O₃ and the situations for other post-transition metal oxide semiconductors. 122 An indirect bandgap of 4.83 eV was found for Ga₂O₃, with the VB maximum (VBM) located just off the M point, slightly smaller than the direct bandgap of 4.87 eV at Γ. 122 Vertical transitions at the Γ point and VB maximum (VBM) are both dipole-allowed, but indirect transition probability at VBM are around one tenth of the strength of direct transition at the Γ point, as revealed by the dipole matrix analysis. The relatively weak indirect transitions as well as the slight difference between indirect and direct bandgaps make β-Ga₂O₃ a “pseudo-indirect” semiconductor, as shown experimentally in a sharp absorption edge at roughly 4.9 eV. 117

The electronic structure of β-Ga₂O₃ was also investigated experimentally by angle resolved photoemission spectroscopy (ARPES), showing the VB dispersion along the Γ-A and A-M direction of the Brillouin zone, as shown in Fig. 8. 112 The experimental VB band structures also exhibit weak dispersion, which fits well with the calculated band structure. The position of conduction-band minimum (CBM) was also measured to be at the Γ-point. The experimental direct and indirect bandgaps are Eg₂^n = 4.9 eV and Eg₂^d = 4.85 eV, respectively.

The VB spectra have been measured by photoemission spectroscopy excited with photon energies ranging from 27 eV to 39 eV by Varley et al. 107, 112 80 eV to 130 eV by Lovejoy et al., 113, 114 526 eV to 556 eV, and 150 eV and 1300 eV by Michling and Schmeisser, 115 soft x ray (Al Kα at 1486.6 eV) by Navarro-Quezada et al. 116 and Swallow et al., 117 and hard x ray (at 8000 eV) by Li et al. 118

![FIG. 7.](image)

(a) Band structure of β-Ga₂O₃ calculated by Varley et al. 117 The conduction band minimum is located at the Γ point, while the valence band maximum is at the M point. The inset shows the hybridization of Ga 4s orbital and O 2p orbital. (b) Band structure of α-Ga₂O₃ calculated by Kobayashi et al. 125 The conduction minimum band is located at the Γ point, while the valence band maximum is at a point between the Γ and S0 points.

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FIG. 8. Valence band structure along the A-M (left) and Γ-Z (right) direction of the Brillouin zone for β-Ga2O3 measured by angular resolved photoemission spectroscopy (ARPES). The experimental bands are shown by black dots. Calculated band structures based on hybrid DFT calculation are shown as blue lines. The red marked areas highlight the regions of the direct and indirect gaps.

Figure 9 shows the comparison of the experimentally measured VB spectra excited with photon energies of 150 eV and 8000 eV, with VB density of states (DOS) calculated by DFT. The measured VB spectra in conjunction with calculated total and partial DOSs weighted by photoionization cross sections reached the conclusion that the VB spectra of β-Ga2O3 mainly consist of O 2p with a band-width of 7.7 eV. The VB of β-Ga2O3 shows three main regions: region I at 0–2 eV below the VBM, region II at 2–6 eV below the VBM, and region III at 6–8 eV, corresponding to the occupied O 2p states slightly hybridized with Ga 3d, 4p, and 4s states, respectively.

The optical properties of β-Ga2O3 show notable anisotropy due to the asymmetry of the crystal structures, as mentioned earlier. This optical anisotropy has come into the view of physicists for a long time. Optical absorption measurement of β-Ga2O3 by Tippins in 1965,26 though all conducted with light in the same polarization, still recognized the occurrence of the absorption shoulder which was assigned to different transition energies between Td coordinated Ga1 and O1/O2 [Fig. 10(a)]. A more systematic study on the pleochroism of vapor phase reaction grown Ga2O3 single-crystalline platelets was conducted by Matsumoto et al. using incident light polarized in six different orientations, in which they observed the highest absorption edge at room temperature to be 4.90 eV for E//b shown in Fig. 10(b).119 The absorption edge in other geometries at room temperature was also measured for E//c and E⊥b⊥c with the value of 4.54 eV and 4.56 eV, respectively. Moreover, larger energies were found at 77 K for both E//b and E//c with the corresponding magnitude of 40 meV and 220 meV.

Optical floating zone (OFZ) grown single crystals were also investigated for pleochroism by Ueda et al.27 Smaller absorption edges measured for light polarized E//b and E//c were found to be 4.90 eV (253 nm) and 4.59 eV (270 nm), as shown in Fig. 10(c). Moreover, increasing the angle φ between E and c could result in the appearance of a shoulder at a shorter wavelength in optical transmission spectra. The shoulder transmittances also become stronger with an increase in φ.

Conditions for material synthesis, defects, and doping also show a great influence on optical properties of β-Ga2O3. Ueda et al. studied the influence of O2 annealing on Ga2O3 crystals grown by the OFZ method and found that the transmittance of Ga2O3 increased with the elongation of annealing time.120 Galazka et al.46 reported that Ga2O3 crystals with lower concentration of free electrons (controlled with different growth atmospheres and dopants by the Czochralski method) showed better transmittance.

There are fewer studies on the electronic structure for other metastable phases of Ga2O3, mostly based on theoretical works. A few experimental121,122 and theoretical123–125 results are reported for α-Ga2O3 because it has already been grown by epitaxial
The bandgap of α-Ga₂O₃ has been measured to be in the range of 4.9–5.6 eV, and 5.15 eV, respectively.

The band structure of α-Ga₂O₃ has been calculated to be 4.26 eV by Mulazzi et al. using the HSE functional and 4.62 eV by Pavesi et al. using the B3LYP functional. The ARPES results suggest a lower bandgap value of 4.41 eV, while optical absorption and photoconductivity measurements suggest a bandgap value of 4.6 eV.

The band structure of γ-Ga₂O₃ was calculated by Gake et al. The calculated direct and indirect bandgaps were 5.30 eV and 5.15 eV, respectively.

II. MATERIALS SYNTHESIS

High quality bulk crystals and thin films are the starting point for the fundamental study of the structural, electrical, and optical properties and for further device fabrication. In the last decade, achievement in growing large scale and high-quality bulk crystals has triggered enormous research efforts in the use of Ga₂O₃ for high power electronics and solar-blind photodetectors. Recently, 4-in. high quality β-Ga₂O₃ (201) wafers, with the full width at half maximum (FWHM) for the rocking-curve (402) diffraction below 17 arcsec and etch pit density (EPD) as low as 10³ cm⁻², were achieved using the EFG-growth method and also commercially available from Novel Crystal Technology, Inc. Furthermore, high-purity, 1.25 µm-thick (010) β-Ga₂O₃ homoepitaxial thin films, with record-high carrier electronic mobilities of 184 cm²/V s and low carrier concentrations of 2.5 × 10¹⁶ cm⁻³ at room temperature, have been achieved by MOCVD. Using Si, Sn, or Ge as dopants, a controllable n-type doping with free carrier concentration ranging from 10¹⁶ to 10²⁰ cm⁻³ and mobility decreasing from 140 to 40 cm²/V s has been achieved for MBE grown homoepitaxial films. Recently, using modulation doped β-(AlₓGa₁₋ₓ)₃O₃/Ga₂O₃ heterostructures to form two-dimensional electron gas (2DEG) at the interface, a record room-temperature channel mobility of 180 cm²/V s and low temperature peak mobility of 2790 cm²/V s have been demonstrated.

Clearly, the availability of large volume and high structural quality substrates with high electrical and optical parameters at reasonable costs will accelerate the development of devices and circuits, in the case of SiC and GaN.

This section will briefly introduce the progress on the growth technique for bulk single crystals and homo- and hetero-epitaxial thin films.

A. Bulk single crystals

For the growth of β-Ga₂O₃ bulk single crystals, a variety of techniques have been used, including the Verneuil method, OFZ method, Czochralski method, Vertical Bridgman (VB) method, and EFG method. Earlier trials of growing Ga₂O₃ bulk crystals were performed by Chase et al. and Lorenz et al. using the Verneuil method. The largest dimension achieved by the Verneuil method was 20 × 8 × 2 mm² with a Hall mobility of about 100 cm²/V s at room temperature. The Verneuil growth of β-Ga₂O₃ was merely used in these days due to the high mechanical stresses caused by the growth.
processes and limited size obtained. The use of the OFZ method in growing $\beta$-Ga$_2$O$_3$ crystals was initially introduced by Villora et al.,$^{36}$ achieving the growth of substrate-level crystals (~1 in.) in 2004. The OFZ growth of $\beta$-Ga$_2$O$_3$ has shown great controllability in both crystal quality and doping level. A wide range of conductivity ($<10^{-12}$ S cm$^{-1}$ to 38 S cm$^{-1}$) could be reached through the change in growth atmosphere and doping concentration.$^{206}$ However, the achievement of a large crystal via the OFZ method is limited by optical heating.$^{207}$ The Czochralski growth of $\beta$-Ga$_2$O$_3$ single crystals was first reported by Tomm et al.$^{138}$ and the growth of 2-in. in diameter $\beta$-Ga$_2$O$_3$ single crystals was already achieved by Galazka et al.$^{139}$ in 2014. However, the growth of larger crystals was impeded by their higher oxygen content during growth.$^{140}$ Among those methods, EFG is one of the leading candidates to produce large-size wafers beyond 2-in. with low defect density and high crystal quality. This method has also been widely used for mass production of sapphire wafers.$^{141}$ Recently, Kuramata et al.$^{142}$ reported EFG-grown $\beta$-Ga$_2$O$_3$ bulk crystals with dimensions of 50 $\times$ 55 $\times$ 18 mm$^3$ and 110 $\times$ 110 $\times$ 6 mm$^3$. The crystals could be processed into (010), (001), and (201)-oriented 10 $\times$ 15 mm$^2$ substrates, as well as (201)-oriented 2- and 4-in. in diameter wafers. 4-in. diameter (001) oriented and 25 $\times$ 25 mm$^2$ (010) oriented single-crystal substrates are currently commercially available from Novel Crystal Technology, Inc. The substrates can be undoped and Sn- or Fe-doped with different conductivities. The undoped substrates have carrier concentration below $9 \times 10^{17}$ cm$^{-3}$. The background $n$-type carrier concentration can be compensated by addition of an Fe acceptor to produce semi-insulating substrates; Sn doping, on the other hand, increases the carrier concentration up to $9 \times 10^{18}$ cm$^{-3}$ to make highly conductive substrates. Images of bulk $\beta$-Ga$_2$O$_3$ crystals grown by OFZ, Czochralski, and EFG methods are displayed in Fig. 11.

B. Epitaxial thin film growth

In order to realize high-performance Ga$_2$O$_3$-based devices, it is essential to grow high-quality Ga$_2$O$_3$ thin films with controlled density of carriers, defects, and interfaces. From this perspective, homoepitaxial growth on available native Ga$_2$O$_3$ substrates is ideal. The commercial availability of large area Ga$_2$O$_3$ substrates is one of the advantages of Ga$_2$O$_3$ in many potential electrical and optical device applications, compared with a large mismatch for heteroepitaxial growth of GaN and AlN on Al$_2$O$_3$. Undoped and intentionally doped Ga$_2$O$_3$ thin films have been grown by MBE,$^{13,49,51,141–155}$ MOCVD,$^{134,156–170}$ mist-CVD,$^{13,55,83,127,128,171,172}$ PLD,$^{11,173–179}$ HVPE,$^{186,83,134,140}$ and other techniques such as magnetron sputtering,$^{197–212}$ atomic layer deposition (ALD),$^{213–217}$ spin-coating,$^{218–222}$ and so on. In this section, we will provide a brief overview of the properties, progress, and technical challenges of homoepitaxial and heteroepitaxial growth techniques.

1. MBE

MBE has the potential for generating exceedingly pure and defect-free films by virtue of the high purity levels available in commercially available metals and O$_2$, as well as the low energy (~1 eV) of the incident species. MBE has a typical growth rate ranging from 12 nm h$^{-1}$ to 700 nm h$^{-1}$ and a growth temperature of 700°C–900°C. The system also houses a reflection high-energy electron diffraction (RHEED) system, allowing the monitoring of surface structure and morphology in real time during growth with atomic layer precision.$^{223}$ MBE is one of the two predominant growth methods used in GaAs and GaN semiconductor technology and also the commonly used technique for the epitaxial growth of oxide semiconductors, such as In$_2$O$_3$,$^{223,224}$ MZ$_2$O$_3$,$^{225}$ and Ga$_2$O$_3$.$^{13,49,50,230–234}$

Due to its ultrahigh vacuum (UHV) environment and high purity source materials, electrically insulating 0.7 μm-thick undoped films with a smooth surface morphology have been achieved on (010) Ga$_2$O$_3$ substrates by MBE.$^{143}$ It has a low residual carrier concentration of $<2.5 \times 10^{16}$ cm$^{-3}$ and carrier mobility of $>140$ cm$^2$/V s. Intentional Sn or Ge doping can induce the $n$-type electrical conductivity. For example, by increasing Sn dopant flux, the free electron concentration can be accurately controlled in a wide range from $\sim 10^{16}$ cm$^{-3}$ up to $1 \times 10^{20}$ cm$^{-3}$ with mobility decreasing from 120 to 40 cm$^2$/V s.$^{13,49}$ At present, (010) $\beta$-Ga$_2$O$_3$ homoepitaxial wafers with a 0.5 μm thick unintentional doping or Si doped Ga$_2$O$_3$ layer or 60 nm-thick (Al$_x$Ga$_{1-x}$)$_2$O$_3$ (x < 0.23) layer grown by MBE are commercially available.

Because of the controllability over the growth at atomic precision, MBE is a promising method to fabricate modulation doping $\beta$-(Al$_x$Ga$_{1-x}$)$_2$O$_3$/ $\beta$-Ga$_2$O$_3$ heterojunction or superlattice for an abrupt band discontinuity and confinement of high mobility two-dimensional electron carrier at the interface. It has been demonstrated that $\beta$-(Al$_x$Ga$_{1-x}$)$_2$O$_3$ solid solution with x as high as 0.20 at 650°C$^{231}$ and 0.61 at 800°C$^{232,233}$ or higher can be grown by MBE. However, the MBE growth temperature is usually limited to less than 700°C, in order to avoid the decomposition of Ga$_2$O$_3$ in vacuum.$^{225}$ Therefore, the Al composition is limited at x = 0.20. Most interestingly, $\beta$-(Al$_x$Ga$_{1-x}$)$_2$O$_3$/ $\beta$-Ga$_2$O$_3$ (x = 0.18) modulation doped FETs (MODFETs) have recently been fabricated by

![FIG. 11. Bulk $\beta$-Ga$_2$O$_3$ crystals obtained from the following growth methods: (a) OFZ, (b) Czochralski, and (c) EFG.](image-url)
2. MOCVD

MOCVD is in essence a CVD system that uses metal-organic compounds as some of or all its precursors. It is highly scalable with a large deposition area, suitable for large scale production. At present, MOCVD is a mature technique for mass production of GaN based semiconductors and GaN can be epitaxially grown on an 8-in. Si wafer with reasonably high growth rate.

Recently, benefiting from the low background charge and compensation concentration by optimizing the growth pressure, high quality 1.25 μm thick β-Ga2O3 films with record-high electron mobility values of 184 cm²/V s at room temperature and 4984 cm²/V s at 45 K were achieved on (010) Fe-doped Ga2O3 substrates using MOCVD.130 The room temperature mobility approaches the predicted theoretical limit of 220 cm²/V s.222,235 Using Si and Sn as dopants, a controllable carrier concentration ranging from 1 × 10¹⁷ cm⁻³ to 8 × 10¹⁹ cm⁻³ with a decrease in mobility from ~130 cm²/V s to ~50 cm²/V s was achieved.236 The feasibility of achieving low background impurity concentration and high electron mobility will inspire more extensive studies on MOCVD for the fabrication of high-performance power electronics.

Furthermore, due to its higher growth temperature (>800 °C) than that of MBE and smooth surface morphology compared to that of MBE, MOCVD can grow β-(Al,Ga₁₋ₓ)O₃/β-Ga₂O₃ heterojunction or superlattice with abrupt heterointerfaces and a higher Al content (x > 0.4).237 These features in combination with its high growth rates (0.8 μm/h, much higher than typical 0.2 μm/h by MBE) make MOCVD very promising for mass production of β-(Al,Ga₁₋ₓ)O₃/β-Ga₂O₃ MODFETs.

Although encouraging results were obtained on (010) substrates, their preparation in large scale remains challenging because of the limited availability of large size (010) wafers. Because the (010) substrates must be sliced perpendicularly to both easy cleavage planes, its largest scale commercially available from the EFG method (Novel Crystal Technology, Inc.) is 4-in. in diameter.

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4. PLD

PLD is a versatile technique for the deposition of complex oxide thin films, heterostructures, and interfaces.238,239 The composition of targets is preserved in the film, enabling impurity doping or alloying by varying the composition of targets. However, ions from targets can be of very high (~100 eV) energy and, thus, can create point defects, giving rise to unwanted electrical properties in the epilayer film. Similar to MBE, RHEED can also be used here to monitor surface structure and morphology.240,241

Recently, a record-high conductivity of 798 S cm⁻¹ with a carrier concentration of 1.74 × 10²⁰ cm⁻³ was achieved by PLD on a (010) Ga₂O₃ substrate from a 1 wt. % SiO₂-Ga₂O₃ target.242 Its high conductivities are critical to address a known problem of Ohmic contact formation including in β-Ga₂O₃ and have extensive implications on forming low on-resistance for both power switching and radio frequency (RF) applications. However, the highest mobility (27 cm²/V s)243 achieved until now in PLD-grown films is still much lower than those grown by MOCVD (184 cm²/V s),244 MBE (120 cm²/V s),25,26 and HVPE (149 cm²/V s) and bulk single crystals grown by EFG-grown (123 cm²/V s),27 which is likely due to the ionized impurity scattering of the high density of Si dopants (≥3 × 10¹⁸ cm⁻³).28 Therefore, steady efforts are required in future to optimize target compositional control and deposition parameters to achieve a higher mobility.
to $x = 0.8$ at a relatively low temperature of 400 °C, which is comparable to $x = 0.8$ in bulk polycrystals prepared by solid state synthesis in the 850–1950 °C temperature range and much higher than $x = 0.18$ in thin films prepared by MBE at a typical temperature of 650 °C. Therefore, with the characteristics of the higher solubility of Al at a low growth temperature, it seems reasonable to push the CB bottom higher by increasing the Al content in the $\beta$-(Al,Ga$_{1-x}$)$_2$O$_3$ barrier by PLD, enabling the enhancement of 2DEG channel mobility and realization of high-performance modulation-doped $\beta$-(Al,Ga$_{1-x}$)$_2$O$_3$/β-Ga$_2$O$_3$ FETs. However, the fabrication of such FETs by PLD is still in its infancy, and much effort is needed to optimize deposition parameters and conditions.

5. HVPE

HVPE is an old epitaxy growth method that was previously used for the growth of III-V and GaN compound semiconductors. HVPE has the highest growth rate (250 μm/h) for growth of $\beta$-Ga$_2$O$_3$ and is promising for growing thick layers with high productivity. However, it typically results in rough surface morphology containing a high density of defects and pits, even when grown on native substrates. Therefore, chemical and mechanical polishing processes need to be applied prior to device fabrication.

Recently, 5 μm-thick high quality $\beta$-Ga$_2$O$_3$ layers, with a low effective donor concentration below $10^{15}$ cm$^{-3}$, have been homoepitaxially grown on (001) $\beta$-Ga$_2$O$_3$ substrates by HVPE with a high growth rate of 5 μm/h. Controllable $n$-type concentration in the range of $10^{15}$ cm$^{-3}$ to $10^{18}$ cm$^{-3}$ with the carrier mobility decreasing from 149 to 88 cm$^2$/V s has been obtained by intentional Si doping. The mobility is almost equal to those of bulk crystals. At present, (001) $\beta$-Ga$_2$O$_3$ homoepitaxial wafers with a 10 μm-thick Si-doped layer grown by HVPE are commercially available from Novel Crystal Technology, Inc. HVPE can also be utilized to grow high purity $\alpha$-Ga$_2$O$_3$ on Al$_2$O$_3$ substrates typically at 500–600 °C. The structural quality of HVPE-grown $\alpha$-Ga$_2$O$_3$ is similar to that of mist-CVD grown films, with the dislocation density measured by plan-view TEM of typically ~$10^{10}$ cm$^{-2}$. Using the epitaxial lateral overgrowth (ELO) technique, the dislocation density in laterally grown wing regions can also be reduced down to less than 5 × 10$^6$ cm$^{-2}$. The Ge doped $\alpha$-Ga$_2$O$_3$ films show a Hall mobility of 28 cm$^2$/V s and carrier concentration of $3 \times 10^{15}$ cm$^{-3}$, which are comparable to those of Sn doped films grown by mist-CVD (24 cm$^2$/V s and $10^{16}$ cm$^{-3}$).

Moreover, as achieved in mist-CVD grown $\alpha$-Ga$_2$O$_3$ and III-V compound semiconductors, inserting a buffer layer can confine misfit dislocations within the buffer layers and significantly improve the crystalline quality of the films grown after. Inserting a buffer layer seems a promising strategy to overcome the lattice mismatch between $\alpha$-Ga$_2$O$_3$ and Al$_2$O$_3$ and to reduce the dislocations in HVPE-grown $\alpha$-Ga$_2$O$_3$. The realization of free-standing $\alpha$-Ga$_2$O$_3$ wafers by HVPE can also be expected as it happened in GaN industry and $\alpha$-Ga$_2$O$_3$ by mist-CVD.

To summarize this section, as described above, different epitaxial techniques have been applied to grow Ga$_2$O$_3$ thick layers or thin films. Heteroepitaxial $\beta$-Ga$_2$O$_3$ layers are often polycrystalline, containing a high density of defects and show low conductivity <10 S cm$^{-1}$ and low mobility <1 cm$^2$/V s. Although such heteroepitaxial layers might be good enough for some applications, such as gas sensing and a solar-blind UV detector, high crystal quality layers are still demanded for high-power electronic and optoelectronic applications. Homoeopitaxial growth on native substrates is needed to reduce the epitaxial dislocations, defects, and impurities, and to optimize electrical and optical properties of the materials. One of the major advantages of the Ga$_2$O$_3$ technology is that high quality single-crystal substrates can be grown by melt methods, as reviewed above. High quality homoeopitaxial $\beta$-Ga$_2$O$_3$ layers, with a low residual carrier concentration below $5 \times 10^{15}$ cm$^{-3}$ and mobility higher than 150 cm$^2$/V s, have been grown by MBE, MOCVD, and HVPE. Their growth kinetics and thermodynamics have been well understood, which are important to achieve the required structural quality and controllable electrical properties, with a reasonable growth rate. Among them, MOCVD and HVPE with a typically high growth rate >0.8 μm/h can be used to grow thick layers for vertical devices including SBDs, while MBE, with a control over the growth at atomic precision and a typical growth rate of 200 nm/h, has promising potential to grow thin films for lateral devices, such as $\beta$-(Al,Ga$_{1-x}$)$_2$O$_3$/β-Ga$_2$O$_3$ modulation doped FETs.

The mist-CVD system is relatively new, and its growth kinetics and thermodynamics are not well understood. However, this growth system and HVPE are both suitable for growth of highly crystalline $\alpha$-Ga$_2$O$_3$ thick films on an inexpensive sapphire. Both methods can be or are expected to realize free-standing $\alpha$-Ga$_2$O$_3$ wafers (>4 in. in diameter) by lift-off technology, providing an alternative platform to realize high performance power devices at low cost and solve the problem of poor thermal conductivity of Ga$_2$O$_3$ on native substrates, as it happened in GaN industry. However, the highest reported mobilities for $\alpha$-Ga$_2$O$_3$ films grown by mist-CVD and HVPE are still below 30 cm$^2$/V s. Thus, much effort is needed to optimize the growth condition or use a buffer layer at the interface to reduce the dislocation. Based largely on its relative ease of use and higher solubility of Al at a low growth temperature, PLD has potential to enhance the 2DEG channel mobility in modulation-doped $\beta$-(Al,Ga$_{1-x}$)$_2$O$_3$/β-Ga$_2$O$_3$ FETs.

IV. DEFECT AND DOPING (ELECTRONIC STRUCTURE, OPTICAL, MOBILITY, AND TRANSPORT)

In the undoped stoichiometric state, Ga$_2$O$_3$ should be a transparent insulator because of its ultra-large bandgap of 4.87 eV. However, Ga$_2$O$_3$ exhibits an unintentional $n$-type conductivity and the origin of the unintentional doping is still under debate. Defects such as oxygen vacancies (V$_O$), hydrogen interstitials (H), and substitutions (HO), Ga interstitials (Gai), and other impurities have been proposed. Recently, $n$-type doping with Si, Sn, Ge, Nb, Ta, and so on. The free electron concentration could be controlled by growth conditions, post-growth treatment, or intentional doping, in the range of $10^{15}$–$10^{19}$ cm$^{-3}$ for bulk crystals and in the range of $10^{15}$–$10^{28}$ cm$^{-3}$ for epitaxial thin films with a corresponding Hall mobility of up to about 140 and 184 cm$^2$/V s, respectively. On the other hand, as discussed earlier, $p$-type doping in Ga$_2$O$_3$ would be fundamentally difficult because of the very flat VBM of O 2p in nature and self-compensation. Understanding the physical properties of defects and impurities in Ga$_2$O$_3$...
and in turn controlling them are crucial for increasing device performance since defects and impurities affect material properties critical to device operation, output power, breakdown voltage, carrier mobility by scattering and trapping effects, luminescence and charge-trapping, and a prerequisite for p-type doping. For instance, Neal et al. have carried out a critical assessment of the specific on-resistance ($R_{on}$) and breakdown voltage of Schottky diodes containing defect states at 110 meV below the CBM, as shown in Fig. 12; to achieve 20 kV breakdown voltage in Ga₂O₃ (comparable to SiC devices), the concentration of these defects must be below $5 \times 10^{15}$ cm$^{-3}$, while at present, only a 1.1 kV device has been demonstrated with a defect concentration of $1 \times 10^{16}$ cm$^{-3}$.

In this section, we will review the defects and doping chemistry in Ga₂O₃ and its impact on electrical conductivity, mobility, and optical properties. We will begin with a brief introduction on the fundamental semiconductor physics for doping and defects in oxide materials.

### A. Fundamental semiconductor physics of doping and defects in Ga₂O₃

The fundamentals of doping and defects can be understood by the physics of semiconductors. The electrical conductivity ($\sigma$) of a semiconductor is directly related to its carrier concentration ($n$) and carrier mobility ($\mu$), according to the relation $\sigma = ne\mu$, where $e$ is the elementary charge. These parameters are fundamentally related to the electronic structure of oxides. $n$ is determined by the intrinsic ease of generation of mobile carriers (electrons for n-type and holes for p-type) by defects or dopants. The carrier mobility $\mu$ is directly proportional to the free carrier scattering time, $\tau$, and is inversely proportional to the carrier effective mass, $m^*$, via $\mu = e\tau/m^*$. $\tau$ largely depends on extrinsic factors such as ionized dopants, defects, and grain boundaries determined by film preparation procedures. $m^*$ is an intrinsic property of the materials, a tensor whose components are obtained from the electronic band structure by analyzing the variation of energy ($E$) with momentum ($k$). Thus, a highly dispersive VBM or CBM gives rise to small $m^*$ and hence potentially a high $\mu$.

#### 1. Effective mass and doping

For Ga₂O₃, the top of VB is primarily formed by fully filled O $2p^5$ states and the CBM mainly by the unoccupied Ga $4s^0$ orbitals. The Ga $4s^0$ derived CBM is the key for achieving a high n-type conductivity and mobility in Ga₂O₃ for the following two reasons.

First of all, the 4s orbital normally has large spatial distributions and their wavefunctions overlap with each other [inset in Fig. 7(a)], leading to a facile pathway for the conduction of electrons. In the view of band structure [Fig. 7(a)], the s orbitals form a highly dispersive CBM at the Γ point, giving rise to a small $m^*$. $m^*$ for β-Ga₂O₃ have been theoretically predicted to be 0.227–0.242 $m_e$ ($m_e$ is the rest mass of an electron), 0.342 $m_e$, 0.26–0.27 $m_e$, 0.28 $m_e$, 0.27–0.28 $m_e$, and 0.22–0.23 $m_e$ depending on the calculation methods. Experimental results revealed the $m^*$ values of 0.28 $m_e$, 0.283–0.288 $m_e$ for the (010) surface, and 0.276–0.311 $m_e$ for the (201) surface. A small $m^*$ is also true for other wide bandgap oxide semiconductors, including In₂O₃, SnO₂, ZnO, and SnO₂, which typically have small electron effective masses of 0.20–0.35 $m_e$. On the other hand, the effective masses for holes are as large as 10 $m_e$, suggesting the fundamental limitation to obtaining highly mobile holes at the VBM. This is reflected in part by numerous attempts at p-type doping of ZnO$^{35,36,286,288}$ and In₂O₃$^{287,288,289,290}$, but no encouraging results have been achieved so far, and there are still problems concerning the reproducibility of the results.

Second, owing to the Ga 3d contraction, the energy of Ga 4s is relatively lower than those of pre-transition metals (e.g., MgO). This gives rise to a relatively high electron affinity that facilitates n-type doping. Ga₂O₃ has an electron affinity of 4.0 eV, compared to 1.4 eV for MgO. For Ga₂O₃, substitution of Ga$^{3+}$ by Si$^{4+}$, Ge$^{4+}$, and Sn$^{4+}$ introduces dopant energy levels with ionization energy less than ~50 meV below the CBM. The extra electrons can be easily activated into the CBM as free carriers, inducing a significant increase in conductivity. The activation energy ($E_a$) for donors depend on the doping concentration ($N_d$), i.e., $E_a$ decreases with an increase in $N_d$, resulting from a combined effect of screening of the dopant’s Coulomb potential by free carriers and charged impurities and of spatial fluctuations of the CB edge induced by the potentials of randomly distributed charged impurities. Generally, $\Delta E_a$ decreases according to

$$\Delta E_a = \Delta E_0 - \beta N_d^{1/3},$$

where $\Delta E_0$ is the activation energy for isolated donors and $\beta$ is a constant. For example, Irmscher et al.$^{299}$ measured $E_a$ for Si doped Ga₂O₃ bulk crystals grown by the Czochralski method with $N_d$ from 1.25 × 10¹⁷ cm$^{-3}$ to 9 × 10¹⁷ cm$^{-3}$; $E_a$ decreases from 25 meV to 16 meV, as shown in Fig. 13. The extrapolation of this dependence to zero concentration $N_d$ yielded for the ionization energy $E_a$ of isolated donors a value of about 36.3 meV.

With more doping, the Fermi level ($E_F$) moves up into the CB and the materials ultimately become a degenerate semiconductor.
with metallic transport behavior [Fig. 14(a)]. The critical carrier concentration $n_c$ for the transition from an insulating state to metallic state is defined by the Mott criterion, $(n_c)^{3/2}/n_0 > 0.26$, where $a_0^* = \hbar^2/(2m^*$) is the Bohr radius. Taking Sn doped Ga$_2$O$_3$, for example, the literature suggests that the static dielectric constant is $\varepsilon(0) = 10.2^{100}$ and an electron effective mass is $m^* = 0.28\ m_e^{12,256}$ giving an effective Bohr radius of $a_0^* = a_0\sqrt{\varepsilon(0)/(m^*/m_e)} = 1.92$ nm. Thus, $n_c$ is calculated to be $2.48 \times 10^{18}$ cm$^{-3}$. For example, a carrier concentration of $1.74 \times 10^{20}$ cm$^{-3}$ can be achieved, together with a typically electron mobility of 26.5 cm$^2$/V s, yielding a high conductivity of 732 S cm$^{-1}$.\cite{12,256} It should be noted that dopants and other defects such as vacancies or interstitials in the lattice behave as point scatters of electrons and such scattering events limits electron mobility.

The free electrons in the CB can oscillate with an external electromagnetic field, such as the free electrons in metals (plasma oscillations). Below the plasma energy, any material exhibits a high reflectivity. The plasma frequency, $\omega_p$, is given by

$$\omega_p^2 = \frac{n e^2}{m^* (\varepsilon(0) \varepsilon_0)},$$

where $n$ is the free carrier density, $m^*$ is the electron effective mass, and $\varepsilon_0$ is the permittivity of free space. The plasma frequency depends on the carrier concentration.\cite{301,302} For a carrier concentration of $10^{18}$ cm$^{-3}$, the plasma energy is typically in the near-infrared (NIR) region at around 0.4–0.7 eV. Bluish coloration due to reflectivity in the NIR has typically been observed for electrically conductive specimens.\cite{303} Insulating specimens were colorless and, therefore, transparent in the UV, visible, and IR regions, as shown in Fig. 14(b). Therefore, the “optical window” for doped Ga$_2$O$_3$ is set at short wavelengths by its optical bandgap and at longer wavelengths by its reflectivity plasma edge ($\hbar\omega_p$).

2. Intrinsic mobility limits in Ga$_2$O$_3$

We now turn back to discuss the electron mobility in Ga$_2$O$_3$. As mentioned above, $\beta$-Ga$_2$O$_3$ has a small $m^*$ of 0.28–0.33 $m_e$ because the CBM derives mostly from the dispersive Ga 4s states. The $m^*$ of $\beta$-Ga$_2$O$_3$ and its character are quite similar to those of GaN.\cite{303} One may initially expect that the electron mobility of Ga$_2$O$_3$ is similar to that of GaN of 1500 cm$^2$/V s.\cite{304,305} However, so far, the best room temperature mobility in $\beta$-Ga$_2$O$_3$ is in the range of 150–184 cm$^2$/V s,\cite{237,112,280} nearly an order of magnitude lower than GaN. One critical question is whether the reported lower mobilities in $\beta$-Ga$_2$O$_3$ are intrinsic or extrinsic which can be improved by eliminating defects/impurities. Ma et al.\cite{112} performed experimental and theoretical analyses on temperature dependent transport properties of Ga$_2$O$_3$. They found a strong electron–phonon interaction in Ga$_2$O$_3$ because of the high ionic Ga–O bonds. For pure $\beta$-Ga$_2$O$_3$ with low density of defects and impurities ($<10^{17}$ cm$^{-3}$), the electron mobility in $\beta$-Ga$_2$O$_3$ is limited by the polar optical phonon (POP) scattering with a maximum of 220 cm$^2$/V s at room temperature; for doped...
β-Ga2O3 with a higher density of defects and impurities, the electron mobility is limited by scattering at ionized impurities. POP scattering was also reported by Ghosh and Singisetti and Parisini and Forneri.

3. Deep level states

Several deep level states in β-Ga2O3 bulk crystals and thin films have been identified using deep level transient spectroscopy (DLTS), deep level optical spectroscopy (DLOS), and other techniques and DFT calculations. Using DLTS, Irmscher et al.79 found three deep trap states in undoped β-Ga2O3 crystals grown by the CZochralski method, including E1 with energy level located at 0.54 eV below CB (E(level states), Irmscher et al. 80 detected the presence of Fe3+ in their samples. However, more work is needed to verify these interesting but speculative results. The proposed electron donors include oxygen vacancies (V_O) and Co2+ in their samples.

Zhang et al. 81 performed DLTS and DLOS to probe the deep level states in bulk β-Ga2O3 single crystals grown by EFG, in which five distinct deep states have been detected. Their energy levels and concentrations are shown in Fig. 15. Three states, E1 (Ec-0.62 eV), E2 (Ec-0.82 eV), and E3 (Ec-1.00 eV), detected by DLTS are very similar to those found in the work by Irmscher et al. 80 Moreover, DLOS allowed to identify another two deeper states than DLTS, including E4 (Ec-2.16 eV) and E5 (Ec-4.40 eV), i.e., 0.43 eV above VB). E2 and E3 are the dominant ones, with a concentration of ~10^16 cm^-3. The authors also speculated that E2 may be associated with either SnGa or V_Ga point defects, and E4 may be with Ga vacancies (V_Ga). However, more work is needed to verify these interesting but speculative assignments.

Ingebrigtsen et al. 82 combined DLTS, proton radiation, secondary ion mass spectrometry (SIMS), and hybrid DFT calculations to study the deep level states in β-Ga2O3 synthesized by different methods, including EFG single crystals and homoepitaxial film grown by MBE and HVPE. For the EFG single crystals, they found similar trap distribution to those measured by Irmscher et al. 80 and Zhang et al. 80 with E2 dominating. However, for the epitaxial films by MBE and HVPE, E1 has 2 orders of magnitude lower concentration. As further confirmed by SIMS measurements, they concluded that E1 is an extrinsic origin, associated with residual Fe3+ impurities occupying Ga sites. More interestingly, their results also revealed another deep state, E2*, at 0.72 eV below CB (Ec-0.72 eV). E2* was identified as having an intrinsic origin, perhaps from Ga vacancies or its complexes. Similar results were also reported by Polyakov et al. 83 based on HVPE-grown β-Ga2O3 epitaxial films which exhibit E1, E2, and E3 deep states near Ec-0.6 eV, Ec-0.75 eV, and Ec-1.05 eV, but the concentration of these traps in the HVPE film is 1-2 orders of magnitude lower than that in bulk crystals. However, proton irradiation increases the concentrations of E2 and E4 states, suggesting that these states are associated with intrinsic defects, different from the conclusion by Irmscher et al. 80 and Ingebrigtsen et al.

To summarize this part, although several deep level states in bulk crystals and thin films of β-Ga2O3 have been identified, their physical origin remains elusive. More works such as high-resolution photoemission spectroscopy, photoluminescence, and DFT calculations should be performed to clarify their origins. Knowledge of the natures of these types of deep levels is critical for further developing Ga2O3-based optoelectronic devices.

B. Unintentional doping and intrinsic defects (oxygen V_O and hydrogen H, H_3)

It is often observed that β-Ga2O3 bulk crystals and thin films exhibit an intrinsic n-type conductivity (with a background free electron concentration), despite the absence of intentional doping. 84 Such unintentional n-type conductivity is also commonly observed for other wide bandgap oxide semiconductors (ZnO, 85 In2O3, 86,87,88 SnO2, 89,90,91). Table I summarizes unintentional doping electron concentration and mobility for Ga2O3 single crystals (bulk and epitaxial thin films) grown by different methods and at different conditions. The resulting electron concentrations between 10^16 cm^-3 and 10^19 cm^-3 would correspond to a donor concentration of 0.000 01%–0.01%. Despite intense research in the last few years, the origin of the unintentional doping is still not settled. The proposed electron donors include oxygen vacancies (V_Ga), hydrogen (H), and other impurities from the material synthesis process, but no conclusive agreement has been reached yet.

1. Oxygen vacancies (V_Ga)

It is often experimentally observed that the growth of Ga2O3 or post-growth annealing in high oxidizing environments reduces the free electron density whereas in reducing conditions (nitrogen, hydrogen, or ultra-high vacuum) leads to an increase in n-type conductivity. Table I summarizes the basic electrical properties of β-Ga2O3 bulk crystals grown by different methods in different environments. For example, as further shown in Fig. 16(a), Ueda et al. 92 synthesized β-Ga2O3 bulk crystals by the floating zone method and showed that the conductivity strongly depends on the...
O$_2$ flow in the growth atmosphere: the conductivity is lower than $10^{-9}$ S/cm when grown in pure O$_2$ atmosphere, increases with a decrease in the O$_2$ content, and reaches a large conductivity of 38 S/cm with $n = 5 \times 10^{18}$ cm$^{-3}$ at an N$_2$/O$_2$ ratio of 0.4/0.6. On the other hand, the conductive crystals became insulating after annealing in O$_2$. Furthermore, the dependence of conductivity on oxygen partial pressure ($P_{O_2}$) was investigated by Cojocaru and Alecu and Fleischer and Meixner using Ga$_2$O$_3$ polycrystalline thin films: Ga$_2$O$_3$ shows a characteristic ($P_{O_2}$)$^{-1/4}$ dependence of conductivity with a relation of $\sigma \sim (P_{O_2})^{-1/4}$. Because of the inverse correlation between conductivity and oxygen partial pressure, the $n$-type conductivity in Ga$_2$O$_3$ was commonly attributed to the presence of Vo$^-$.

In order to preserve the charge neutrality, a Vo captures two electrons and is denoted as a neutral vacancy Vo$^5$. Free carriers can be generated, by single or double ionization of Vo$^5$, resulting in Vo$^+$ or Vo$^{**}$, respectively. The donor state energy levels were experimentally determined to be located only $\sim 0.02–0.03$ eV below the CBM. Aubay and Gourier synthesized β-Ga$_2$O$_3$ single crystals using the Verneuil method. The samples showed a very high conductivity of 200 S/cm and slightly blue color, when synthesized under reducing conditions (H$_2$/O$_2$ flow rate of 2:3). In normal conditions, the sample was insulating with a conductivity of $10^{-8}$ S cm$^{-1}$ and transparent. They also performed a detailed EPR study on the magnetic bistability and Overhauser shift of conduction electrons and concluded that Vo forms a partially occupied shallow impurity donor and is responsible for the low-temperature conductivity. Using EPR, Yamaga et al. provided further microscopic evidence that among the three oxygen sites, the one in fourfold coordination acts as a shallow donor, trapping a single unpaired electron (Vo$^+$), i.e., each Vo donates one delocalized electron responsible for conductivity, while the other is localized.

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**TABLE I. A summary for unintentional doping electron concentration and mobility for basic electrical properties of β-Ga$_2$O$_3$ single crystals (bulk and epitaxial thin films) grown by different methods and at different conditions.**

| Sample type | Substrate | Growth method | Growth (T/C) | $O_2$ pressure/flow | Electron conc. (cm$^{-3}$) | Electron mobility (cm$^2$/V s) | Conductivity (S/cm) | References |
|-------------|-----------|---------------|-------------|---------------------|--------------------------|-------------------------------|---------------------|------------|
| Bulk        | ...       | Verneuil      | ...         | ...                 | $10^{18}$                | 80                            | 30                  |            |
| Bulk        | ...       | OFZ           | ...         | 0.12 m$^3$ h$^{-1}$ | $5 \times 10^{18}$       | ...                          | 38                  |            |
| Bulk        | ...       | OFZ           | ...         | $6 \times 10^{-3}$ m$^3$ h$^{-1}$ | $1.4 \pm 0.5 \times 10^{17}$ | $60 \pm 20$ | 12          | 446        |
| Bulk        | ...       | OFZ           | ...         | $2 \times 10^5$ Pa  | $5 \times 10^{17}$       | 88                            | 7                   |            |
| Bulk        | ...       | OFZ           | ...         | ...                 | $7.7 \times 10^{16}$     | 172                           | 2                   | 447        |
| Bulk        | ...       | EFG           | ...         | ...                 | $2 \times 10^{17}$       | ...                          | ...                 |            |
| Bulk        | ...       | EFG           | ...         | 0                   | $3.9 \times 10^{18}$     | 107                           | 0.67                | 47         |
| Bulk        | ...       | CZ            | ...         | 0                   | $5.2 \times 10^{17}$     | 126                           | 10.5               | 448        |
| Bulk        | ...       | CZ            | ...         | $2 \times 10^4$ Pa  | $3.5 \times 10^{17}$     | 121                           | 6.7                 | 448        |
| Bulk        | ...       | CZ            | ...         | $1 \times 10^6$ Pa  | $1 \times 10^{18}$       | 86                            | 14                  | 46         |
| Bulk        | ...       | CZ            | ...         | $8 \times 10^2$ Pa  | 0.4–4.8 $\times 10^{17}$ | 100–144                       | 0.9–8               | 46         |
| Bulk        | ...       | CZ            | ...         | $1.2 \times 10^5$ Pa | 0.98–22 $\times 10^{17}$ | 80–152                        | 5–11                | 46         |
| Bulk        | ...       | CZ            | ...         | $4.4 \times 10^4$ Pa | 2.8–6 $\times 10^{17}$   | 114–127                       | 17–100              | 46         |
| Bulk        | ...       | CZ            | ...         | 0.8–3.5 $\times 10^5$ Pa | 0.5–6 $\times 10^{17}$    | 80–90                        | 2–6                | 240        |
| Thin films  | Ga$_2$O$_3$(010) | MBE      | 600         | ...                 | $<2.5 \times 10^{16}$    | $>140$                       | ...                 | 49         |

**FIG. 16.** (a) The electrical conductivity of the β-Ga$_2$O$_3$ single crystals along the b axis as a function of the O$_2$ flow rate. The total gas flow rate (N$_2$+O$_2$) was 0.2 m$^3$ h$^{-1}$. The closed circles and the open square refer to samples grown from undoped and Sn-doped Ga$_2$O$_3$ rods, respectively. (b) Hall free carrier concentration vs the dopant concentration of Si and Sn doped β-Ga$_2$O$_3$ single crystalline epitaxial layers obtained by secondary-ion mass spectrometry (SIMS).
However, this assumption was questioned by Varley et al.\textsuperscript{298} and others\textsuperscript{18} who performed first-principle calculations based on hybrid DFT of various impurities and Vo in β-Ga\textsubscript{2}O\textsubscript{3}. According to these calculations, Vo acts as a deep donor with an ionization energy of more than 1 eV and, thus, cannot be the source of \textit{n}-type conductivity. This would be similar to the case of other oxide semiconductors (In\textsubscript{2}O\textsubscript{3},\textsuperscript{314} SnO\textsubscript{2},\textsuperscript{311,312} and ZnO\textsuperscript{323,324}), where the energy level of Vo is too deep to be ionized for \textit{n}-type conductivity.\textsuperscript{315} The deep level states of Vo in Ga\textsubscript{2}O\textsubscript{3} may also be associated with the observations of blue luminescence emissions arising from the recombination of a localized donor state (attributed to Vo) with trapped hole states.\textsuperscript{274,321} A high concentration trap state at 0.82 eV (likely related to the deep level state, e.g., Vo) below the CBM of Ga\textsubscript{2}O\textsubscript{3} detected by DLTS,\textsuperscript{316} and depth-resolved cathodoluminescence spectroscopy and surface photovoltaic spectroscopy.\textsuperscript{22}

2. Hydrogen interstitials (\textit{H}\textsubscript{i}) and substitution (\textit{H}O\textsubscript{2})

Alternatively, hydrogen impurities were proposed to act as shallow donors in Ga\textsubscript{2}O\textsubscript{3} and can be present both as an interstitial species (\textit{H}\textsubscript{i}) and as a substitutional donor at the oxygen vacancy site (\textit{H}O\textsubscript{2}).\textsuperscript{324} \textit{H}\textsubscript{i} has low formation energy under both O-rich and O-poor conditions, indicating that it will easily be incorporated as an unintentional impurity, when hydrogen is present in the growth or annealing environment. However, \textit{H}O\textsubscript{2} has a lower formation energy only under O-poor conditions. There is also experimental evidence that hydrogen may be a shallow donor in Ga\textsubscript{2}O\textsubscript{3}\textsuperscript{299} based on its implanted muonium counterpart whose properties mimic those of hydrogen form shallow donors and EPR of single-crystal samples. Hydrogen impurities are suggested as shallow donors, in general, in many wide bandgap oxide semiconductors such as ZnO,\textsuperscript{326} In\textsubscript{2}O\textsubscript{3},\textsuperscript{328} and SnO\textsubscript{2}.\textsuperscript{329} It was theoretically predicted that \textit{H}i and \textit{H}O\textsubscript{2} were shallow donors in In\textsubscript{2}O\textsubscript{3} and further proved by King et al.\textsuperscript{325} based on muon-spin-resonance experiments.

However, the hydrogen shallow donor model has been questioned by Polyakov et al.\textsuperscript{324} based on hydrogen plasma treatment of β-Ga\textsubscript{2}O\textsubscript{3}, after which they observed a pronounced decrease in the concentration of shallow donors that provide free electrons, which did not corroborate the theoretical prediction that hydrogen in β-Ga\textsubscript{2}O\textsubscript{3} should be an efficient shallow donor. There is a possibility that hydrogen forms electrically active complexes with deep native defects, such as V\textsubscript{Ga}, and gives rise to donor compensation.

3. Ga interstitials (Ga\textsubscript{i})

Ga\textsubscript{i} are shallow donors and could act as an alternative source of \textit{n}-type conductivity, but the recent calculation suggests that Ga\textsubscript{i} is highly mobile and it has a large formation energy (>2.5 eV) at extreme oxygen-poor growth conditions, which make them less likely to be present.\textsuperscript{321,315}

4. Other impurities

In addition to Vo, hydrogen, and Ga\textsubscript{i}, residual impurities (Si, C, F, etc.) are present in bulk crystals, typically at a concentration of a few ppm by weight.\textsuperscript{1} The sources of the residual impurities may come from starting precursors used for synthesis (all growth methods), containers and crucibles for growth, flux composition (solution methods), and thermal insulation and furnaces (all growth methods). Some of the residual impurities could be electrically active, e.g., Si, F, and others not, but they may affect the electrical properties (e.g., mobility) indirectly through structural quality. For example, it has been shown that Si is the main impurity present in high-purity Ga\textsubscript{2}O\textsubscript{3} powders\textsuperscript{33} and single crystals.\textsuperscript{275} The Si impurity concentrations are determined at 10–20 ppm (weight) for 4N (99.999%) purity Ga\textsubscript{2}O\textsubscript{3} and 0.05–1.8 ppm for 6N (99.99999%), which corresponds to a Si concentration of 1–3 × 10\textsuperscript{18} cm\textsuperscript{−3} and 10\textsuperscript{16}–10\textsuperscript{17} cm\textsuperscript{−3}. These values would give comparable electron density observed in unintentional doped Ga\textsubscript{2}O\textsubscript{3}.

C. Intentional \textit{n}-type doping

Controllable \textit{n}-type conductivity can be realized by intentional doping with group IV elements (e.g., Si, Ge, and Sn)\textsuperscript{10–14,208} and transition metals (e.g., Nb, Zr, and Ta)\textsuperscript{9–27} as shallow donors, or by Mg and Fe compensating the \textit{n}-type conductivity. Si and Sn are the most extensively studied dopants because of their low activation energy (7.4–60 meV for Sn,\textsuperscript{331} 16–50 meV for Si,\textsuperscript{332} and 17.5–30 meV for Ge\textsuperscript{9,135}) and compatibility with epitaxial growth processes. Using Si, Sn, and Ge as dopants, a wide range of free carrier concentration (\textit{n}) from 10\textsuperscript{16} up to 10\textsuperscript{19} cm\textsuperscript{−3} and a peak mobility of 152 cm\textsuperscript{2}/V s have been achieved for bulk crystals, and \textit{n} from 10\textsuperscript{15} cm\textsuperscript{−3} to 10\textsuperscript{20} cm\textsuperscript{−3} and a peak mobility of 184 cm\textsuperscript{2}/V s have been achieved for epitaxial thin films. Table II provides an overview for the basic electrical properties (conductivity, carrier concentration, and mobility) of doped Ga\textsubscript{2}O\textsubscript{3} bulk crystals and epitaxial thin films grown by different methods and dopants. Varley et al.\textsuperscript{298} have performed hybrid DFT calculations and showed that Si, Sn, and Ge form shallow donor states close to the bottom of the CB of Ga\textsubscript{2}O\textsubscript{3}; all three dopants have lower formation energy under oxygen-poor conditions, whereas secondary phases of SiO\textsubscript{2}, GeO\textsubscript{2}, and SnO\textsubscript{2} preferentially form under oxygen rich conditions.

Si and Ge preferentially substitute the \textit{T}\textsubscript{d} coordinated Ga\textsubscript{i} site, while Sn prefers the \textit{O}\textsubscript{h} coordinated Ga\textsubscript{2} site because of its large cation size. Sn at Ga\textsubscript{2} sites has been confirmed by x-ray absorption spectroscopy (XAS).\textsuperscript{336} However, scanning tunneling microscopy/spectroscopy (STM/STS) on Si-doped EFG single crystals suggested an even distribution of Si between the Ga\textsubscript{i} and Ga\textsubscript{2} sites.\textsuperscript{337} Si at different coordination may have different activation energies. Some authors suggest that Si at Ga\textsubscript{2} sites may not be electrically active\textsuperscript{338} or with an activation energy of 120 meV.\textsuperscript{134}

Figure 16(b) shows the total doped concentration determined by SIMS and carrier density determined by Hall effect measurements in van der Pauw geometry at room temperature.\textsuperscript{334} It showed that free electron density systematically increases with dopants for dopants <10\textsuperscript{19} cm\textsuperscript{−3}, indicating that most of the dopants are activated to give free carriers. At higher dopant concentration, the actual carrier concentration is limited by the solubility of the dopants, either through the formation of secondary phases of oxides (e.g., SiO\textsubscript{2} and GeO\textsubscript{2}) or through low incorporation of Sn due to their high vapor pressure. On the other hand, it should be noted that the carrier concentration is also strongly influenced by other
Table II. A summary for the basic electrical properties of doped β-Ga2O3 single crystals (bulk and epitaxial thin films) grown by different methods and at different conditions.

| Sample type | Substrate | Growth method | Dopant | Electron conc. (cm⁻³) | Electron mobility (cm² V⁻¹ s⁻¹) | Conductivity (S cm⁻¹) | Reference |
|-------------|-----------|---------------|--------|----------------------|--------------------------------|----------------------|-----------|
| Bulk        | OFZ       | 10⁻⁵–10⁻¹ mol. % Si | 5 × 10¹⁶−5 × 10¹⁸ | ~100 | 0.9–40 | 449 |
| Bulk        | OFZ       | 2 mol. % SnO₂ | 2.26 × 10¹⁷ | 65 | 23 | 263 |
| Bulk        | OFZ       | 5 mol. % SnO₂ | 7.12 × 10¹⁷ | 49 | 56 | 263 |
| Bulk        | OFZ       | SnO₂ | 1 × 10¹⁸ | 80 | 13 | 340 |
| Bulk        | OFZ       | Mg | ... | ... | 1.7 × 10⁻¹² | 447 |
| Bulk        | EFG       | SiO₂ | 4.9 × 10¹⁸ | 93 | 7.1 | 450 |
| Bulk        | EFG       | SiO₂ | 1 × 10¹⁹ | ... | ... | 47 |
| Bulk        | CZ        | 800 wt ppm Sn⁴⁺ | 3–10 × 10¹⁸ | 35–52 | 17–100 | 46 |
| Bulk        | CZ        | 6–28 wt ppm Mg²⁺ | ... | ... | ... | 46 |
| Bulk        | Bridgman  | 150–400 wt ppm Sn⁴⁺ | 5–10 × 10¹⁸ | 30–40 | ... | 240 |
| Thin films  | Ga₂O₃(001) | MBE | Ge | 5 × 10¹⁶–10²⁰ | 120–40 | ~0.952–635 | 13 |
| Thin films  | Ga₂O₃(001) | MBE | Sn | 10¹⁶–7.5 × 10¹⁹ | 97–39 | ~0.154–464.3 | 13 |
| Thin films  | Ga₂O₃(001) | MBE | Sn | 10¹⁶–10¹⁹ | 140–33 | ~0.22–532.8 | 49 |
| Thin films  | Ga₂O₃(001) | MOCVD | Si | 10⁷–8 × 10¹⁹ | 130–50 | ~2.06–634 | 238 |
| Thin films  | Ga₂O₃(001) | MOCVD | Si | 2.5 × 10¹⁶ | 184 | ~0.73 | 344 |
| Thin films  | Ga₂O₃(001) | PlD | SiO₂ | 3.25 × 10⁻¹⁹–1.75 × 10²⁰ | 20–30 | ~732 | 345 |
| Thin films  | Ga₂O₃(001) | HVPE | Si | 10⁻¹⁵–10⁻¹⁸ | 149–88 | ~0.076–16.67 | 194 |
| Thin films  | Ga₂O₃(001) | HVPE | Si | 3 × 10⁻¹⁵–10⁻²⁰ | 124–50 | ~4.76 × 10⁻¹⁸–800 | 347 |

The growth of highly conductive doped Ga2O3 layers has important implications for device application. In particular, Ohmic contact formation to wide semiconductors has been a known problem in Ga2O3. The highly conductive Ga2O3 layers can be used as electrodes to form Ohmic contacts with a low contact resistance. Furthermore, because of the large bandgap, the doped Ga2O3 is also highly transparent in the visible region, of particular interest as an alternative to Sn doped In2O3 (ITO) transparent electrodes in optoelectronic applications.

1. Activation energies (Ea) of the shallow donors

Temperature dependent transport measurements, EPR, and theoretical calculation have also been performed to examine energy levels of the shallow donors in Ga2O3. These results, in general, revealed a low activation energy (Ea) of less than 70 meV. However, some discrepancies still remain regarding the values of Ea and the exact activation mechanisms.349,64,173 Ea for Sn ranges from 7.4 meV to 60 meV331,332 for Si ranges from 16 meV to 50 meV337,378,299,303,335 and for Ge ranges from 17.5 meV to 30 meV334,335. The variation in Ea may be associated with differences in doping concentrations, other impurities and defects, growth methods, accuracy in the measurements, etc. Recent EPR studies by Son et al.35 reported that Si may also behave as a negative-U center (often called a DX center) with the negative charge state DX⁻, similar to the Si donor in Al(Ga)N with a high Al content.35 For DX⁻ the variation in Ea is in the range of 44 meV–49 meV. After annealing at 1150 °C in nitrogen, the DX⁻ donors are fully activated and become partly delocalized, forming impurity bands, which reduces the donor activation energy to Ea = 17 meV. The DX properties and the formation of impurity bands explain the large variation of the donor activation energies.
reported in the literature. However, other groups have reported no evidence supporting the DX state. Recently, Neal et al. performed temperature dependent carrier density and mobility of n-type β-Ga2O3, as determined by Hall effect measurements in van der Pauw geometry. They accurately determined the donor energy by reliable estimation of the compensating acceptor concentration through fitting of the low temperature ionized impurity limited mobility. Their results indicate that Si and Ge act as typical shallow donors in β-Ga2O3 with an ionization energy of 30 meV, as opposed to shallow DX centers.

Other studies reported relatively deeper donor states. For example, Neal et al. found that the energy level for unintentional donors with a concentration of ~10^{18} cm^{-3} in commercial Ga2O3 (001) substrates was measured to be 110 meV using temperature dependent Hall effect measurements and 131 meV using admittance spectroscopy. Feng et al. grew Si doped (010) β-Ga2O3 homoepitaxial films using MOCVD with a record room temperature mobility of 184 cm^2/V s; in their film, in addition to the primary shallow donor state with an activation energy of 34.9 meV and a concentration of 5 x 10^{15} cm^{-3}, a secondary deep donor state with an activation energy of 120 meV and a concentration of 5 x 10^{15} cm^{-3} was also found. Possible origins of the deep donor state at 120 meV could include antisites, interstitials, and impurities such as hydrogen or Si on the Ö coordinated Ga2 site. The presence of such relatively deep donors and their ionization percentage at device operating temperatures could have an effect on the on-state resistance and breakdown voltage of rectifiers.

While the achievement of highly conductive doped Ga2O3 is interesting on the one hand, the achievement of Ga2O3 bulk crystals and particularly thin films with high carrier mobility and low defect density, on the other hand, is more crucial for FETs and RF rectifiers. As reported by Ma et al., the mobility in Ga2O3 is limited at 220 cm^2/V s by polar optical phonon (POP) scattering when the electron concentration is lower than 1 x 10^{18} cm^{-3} and by ionized impurity scattering at high electron concentrations. Great efforts have been made to grow high crystalline quality and high mobility Ga2O3 by minimizing the defect, dopant, and carrier concentration.

Table II shows a summary of the room-temperature mobility vs carrier concentration for the state-of-the-art doped β-Ga2O3 bulk single crystals and epitaxial thin films reported in the literature. It can be seen that the room temperature mobility for epitaxial thin films with lowest carrier concentration is close to the predicted theoretical limit of approximately 220 cm^2/V s. Remarkably, Feng et al. have recently grown high purity and high quality (010) β-Ga2O3 homoepitaxial thin films with controllable...
Si doping as low as $10^{16}$ cm$^{-3}$ using MOCVD. The films were found to exhibit record-high carrier mobilities of 184 cm$^2$/V s at room temperature and 4984 cm$^2$/V s at 45 K. The extracted compensation concentration was as low as $9.4 \times 10^{14}$ cm$^{-3}$, which is critical for controllable tuning of the doping concentration lower than mid-$10^2$ cm$^{-2}$. The $Ga_2O_3$ films grown with high mobility and low compensation concentration are critical for developing high-performance lateral and vertical power devices with high critical fields. Another strategy to achieve high mobility is to use modulation doped $\beta-(Al,Ga_{1-x})O_3/\beta-Ga_2O_3$ heterostructures to form a 2DEG at the interface. This is attributed to the spatial separation between ionized impurities and the 2DEG. The high mobility values allowed for the observations of the Shubnikov–de Haas (SdH) effect oscillations at cryogenic temperatures. A record-high room-temperature channel mobility of 180 cm$^2$/V s and a low temperature peak mobility of 2790 cm$^2$/V s have recently been demonstrated. Both the mobilities exceeded the highest experimental mobility values for bulk $\beta$-$Ga_2O_3$.

Doping of $Ga_2O_3$ with transition metals (Nb, Ta, W, Mo, Fe, Co, and Cr) or rare-earth metals (Eu and Er) has also received much interest. This is because, on the one hand, transition metals (e.g., Nb$^{5+}$, Ta$^{5+}$, W$^{6+}$, and Mo$^{6+}$) have higher ionization states and, in principle, each dopant donates more electrons than Si and Sn, minimizing the effect of ionized impurities in doped devices. This research also showed that Ga, Sn, and Re act as deep level trap states with high localization energies, which, in principle, limits the use of these dopants for carrier concentration tuning. This has been demonstrated by the achievement of high mobility and conductivity of W$^{5+}$-doped $Ga_2O_3$ and Mo$^{5+}$-doped In$_2O_3$ and Ta$^{5+}$-doped SnO$_2$. However, another transistor metal doping (e.g., Co) may be more likely to achieve dilute magnetic semiconductors/oxides, and rare-earth metals (Eu) could improve the luminescence and electroluminescence properties.

Peelea and Van De Walle$^{352}$ have performed DFT calculations on the viability of W, Mo, Re, and Nb as n-type dopants in $Ga_2O_3$. Their results show that Nb is the best candidate because it has a low formation energy (1.19 eV for $Ta_x Ga_{1-x}$ at the CBM and 0.31 eV for $O_x Ga_2$) and a small ionization energy (0.03 eV for $Ta_x Ga_{1-x}$ at the CBM and 0.31 eV for $O_x Ga_2$ below the CBM), whereas W, Mo, and Re act as deep donors. Zhou et al.$^{355}$ have grown high quality $\beta$-$Ga_2O_3$ bulk crystals with controllable Nb doping concentration by the OFZ method. It was proved that Nb is an effective n-type dopant for $Ga_2O_3$, and the carrier concentration can be controlled from 9.55 to $10^{16}$ cm$^{-3}$ by tuning Nb doping concentration. Moderate electrical conductivity and mobility have also been achieved for Zr$^{2+}$ and Ta$^{5+}$ doping in $Ga_2O_3$ bulk crystals. More experimental works should be done to explore the possibility of other transition metal dopants.

D. P-type doping in $Ga_2O_3$

As mentioned earlier, p-type doping in wide bandgap oxide semiconductors including $Ga_2O_3$ remains an outstanding challenge. The challenge is due to the intrinsic electronic structure of oxide semiconductors; (i) the top of VB of most oxides mainly consists of strongly localized O 2p-derived orbitals, resulting in a large hole effective mass and, thus, low hole mobility; this means that most of the doped holes tend to be trapped by local lattices as small polarons, as opposed to the free holes that are delocalized in the valence band as in conventional semiconductors; (ii) the valence bands are deep in energy, and holes are easily compensated by defects such as $Vo$, leading to the low p-type dopability, and therefore, a shallow acceptor that can contribute to significant hole concentrations is still lacking. In simple chemical terms, p-type doping involves the introduction of holes into the O 2p states at VBM (i.e., oxidation of O anions), resulting in strongly localized, deep lying holes centered on single oxygen sites.

There are limited experimental works on the p-type doping of $Ga_2O_3$. Inspired by the success in GaN, Mg doping has received much attention, but the results are not conclusive. Chikiozide et al.$^{356}$ claimed the success of p-type conduction in Mg doped $Ga_2O_3$, as proved by combined Hall and Seebeck measurements, and photoemission and cathodoluminescence spectroscopy, but the ionization energy of the acceptor level was measured to be 1.1 eV above the VBM. Another study claimed p-type conductivity in Mg doped $Ga_2O_3$, but the as-grown materials were highly resistive, without hole carrier concentration and acceptor ionization energy being determined. Other studies have found that Mg doping leads to semi-insulating $Ga_2O_3$ and gave rise to sub-bandgap blue luminescence near 2.9 eV. Zn is also a potential candidate for p-type doping in $Ga_2O_3$. Feng et al.$^{357}$ reported the fabrication of p-type $Ga_2O_3$ nanowires doped with Zn, and the homojunction consisting of p-type doped nanowires and n-type $Ga_2O_3$ substrates exhibited rectifying behavior. The cathodoluminescence spectra study suggests that the ionization energies for Zn doped $Ga_2O_3$ are 0.25–0.5 eV which is relatively shallow and promising, but the films remained highly resistive. Overall, achieving efficient p-type doping remains elusive. On the other hand, doping of acceptor impurities (e.g., Fe or Mg) has been used to reduce the background electron density in $Ga_2O_3$, e.g., to create insulating material. Semi-insulating Fe doped $Ga_2O_3$ substrates are available commercially and are widely used for epitaxial thin film growth and device fabrication.

Extensive theoretical studies have also been done to understand the microscopic mechanism of p-type doping in $Ga_2O_3$. Early studies based on standard DFT calculations reported that Zn could lead to p-type conductivity. However, it should be noted that DFT seriously underestimates the bandgaps and the extent of charge localization at defects, leading to difficulties in determining acceptor ionization energies. A later study by Kyrtsos et al.$^{358}$ using hybrid functional DFT (which provides a better bandgap description) suggested that Zn and other acceptors (Li and Mg) incorporated at the Ga sites have ionization energies in excess of 1 eV. The calculation by Varley et al.$^{359}$ also predicted that holes in $Ga_2O_3$ can self-trap with a trapping energy of 0.53 eV, indicating that free holes are unstable and are spontaneously localized as small polarons. The localized hole states are consistent with the ultraviolet luminescence observed in undoped $Ga_2O_3$ crystals. EPR studies have also observed that the holes are trapped at nearest-neighbor oxygen sites of the Mg acceptors.

Nitrogen (N) has a similar atomic size as oxygen but has one less valence electron and a higher 2p orbital than oxygen. N has been explored as a dopant for other oxides such as ZnO but was theoretically found to have a large formation energy and ionization energies in excess of 2 eV$^{360,361}$ and cannot be an effective p-type dopant in $Ga_2O_3$. The deep energies of N acceptors are caused by their defect states. It is found that N can form a variety of complexes with native defects, including $Vo$ and Ga, whose presence in
N doped Ga$_2$O$_3$ could compensate any p-type conduction.\textsuperscript{372} This result suggests that the observed red-light emission originates from the recombination of an electron trapped on a donor due to Vo and a hole trapped on an acceptor due to N doping.\textsuperscript{75}

Very recently, Lyons\textsuperscript{75} using hybrid DFT examined a large series of potential elements as acceptors in Ga$_2$O$_3$, including N, group 2 (Be, Mg, Ca, and Sr), and group 12 (Zn and Cd), as shown in Fig. 18. All the elements are found to exhibit acceptor transition levels above 1.3 eV. After examining formation energies as a function of chemical potential, Mg is determined to be the most stable acceptor species, followed closely by Be.

For summary, so far, there is no solid experimental evidence showing the achievement of high p-type doping in Ga$_2$O$_3$; theoretical studies reach the consensus that the conventional acceptor doping approach gives rise to strongly localized hole states with larger ionization energies, prohibiting p-type conductivity. This is inherently caused by the localized nature of the O 2p-derived VB that leads to difficulty in introducing shallow acceptors and large hole effective mass. Learning from the design of p-type oxides,\textsuperscript{380} a way to mitigate this problem is to use the hybridization of O 2p orbitals with closed-shell Cu 3d\textsuperscript{10} orbitals and post-transition metal cations with filled lone pair states (ns\textsuperscript{2}), such as Sn\textsuperscript{2+} (5s\textsuperscript{2}) and Bi\textsuperscript{3+} (6s\textsuperscript{2}).\textsuperscript{383,380,381} For example, because the s orbitals are generally spatially extended, it is, therefore, expected that their hybridization with O 2p states can result in lower effective mass. Sn in SnO\textsuperscript{382,383} and Bi in Ba$_2$BiTaO\textsubscript{6}\textsuperscript{378} have been proved to lead to a relatively high p-type mobility. Similarly, Sabino et al.\textsuperscript{385} proposed based on hybrid DFT calculation that Bi doped Ga$_2$O$_3$, i.e., (Ga$_{1-x}$Bi$_x$)$_2$O$_3$ solid solution, introduces a fully occupied intermediate VB that is significantly higher in energy than the original VB. This intermediate VB is composed mainly of Bi 6s and O 2p orbitals, providing the opportunity to achieve p-type doping in this system. It would be interesting to carry out experiments to prove this concept based on high-quality bulk crystal or thin films. Alternatively, Islam et al.\textsuperscript{386} recently claimed that a remarkable hole density of 10\textsuperscript{20} cm\textsuperscript{-3} can be achieved by incorporation of hydrogen at Ga vacancy position in the Ga$_2$O$_3$ lattice. The hydrogen induced acceptor ionization energy is as low as 42 meV.

Very recently, Chikoidze et al.\textsuperscript{387} reported an exciting result of the achievement of a hole mobility of 10 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} and free hole concentrations of 10\textsuperscript{17} cm\textsuperscript{-3} by annealing Ga$_2$O$_3$ in oxygen atmosphere. The authors claimed that although p-type doping in Ga$_2$O$_3$ has been considered impossible due to the flat VB resulting in a high hole effective mass, it has been also recently reported that the hole effective mass in Ga$_2$O$_3$ is, indeed, fairly anisotropic and can be as low as 0.4 m$_e$ for certain crystal orientations. It is particularly exciting to the research community that p-type Ga$_2$O$_3$ is possible at least along some crystal directions. However, more research must be conducted to verify and determine its prospects for Ga$_2$O$_3$ solar blind bipolar optoelectronics and high-power electronics based on p-n homojunctions.

On the other hand, as long as p-type Ga$_2$O$_3$ remains elusive, combining n-type Ga$_2$O$_3$ with existing wide bandgap p-type semiconductors such as p-GaN, SnO, NiO, Cu$_2$O, Ir$_2$O$_3$, and SiC, and diamond to form p-n heterojunctions would also be a compromising solution for vertical devices. Combining n-type GaN with existing p-type GaN is promising for enabling next-generation high-performance transistors and optoelectronic devices. Attempts have been made to grow Ga$_2$O$_3$ on GaN epitaxial layers\textsuperscript{388,389} and directly grow GaN epitaxially on a Ga$_2$O$_3$ single crystal substrate\textsuperscript{390,391,392} for the fabrication of a high-responsivity UV photodetector. However, efforts need to be done to control the interface because of the incompatible growth of oxides and nitrides.\textsuperscript{391,392} Diamond is also a particularly attractive candidate due to its range of highly desirable properties for power electronics including an ultra-wide bandgap of 5.5 eV, highest thermal conductivity, high electron and hole mobilities, and a high electric breakdown field.\textsuperscript{393} P-type doping in diamond can be achieved either through conventional substitutional doping with boron (hole mobility of 2000 cm$^2$/V s)\textsuperscript{394} or by inducing on its surface through the so-called surface doping process (hole mobility of 100–300 cm$^2$/V s).\textsuperscript{395} However, the growth of Ga$_2$O$_3$ on diamond or vice versa poses a challenge. Integrating Ga$_2$O$_3$ with p-type wide bandgap oxides would ease the growth, but p-type oxides are also limited by their low mobilities, with reported values of 5–10 cm$^2$/V s for SnO (optical bandgap of 2.7 eV),\textsuperscript{381,396–399} divergent values of 0.1–30 cm$^2$/V s for NiO (optical bandgap of 3.75 eV),\textsuperscript{390–393} and a reported value of 1 cm$^2$/V s for Ir$_2$O$_3$ (optical bandgap of 2.6 eV).\textsuperscript{394,395}

V. ALLOYING AND BANDGAP ENGINEERING WITH Al$_2$O$_3$ AND In$_2$O$_3$

Over the past decades, tremendous progress has been made in the engineering of the bandgaps of semiconductors over a wide range by tuning the composition of semiconductor alloys that have the same crystal structure and similar lattice constants, as shown in Fig. 19. For example, the bandgaps of In$_x$Ga$_{1-x}$N and Al$_x$Ga$_{1-x}$N can be systematically tuned from 1.9 eV to 3.5 eV by varying the x value.
and from 3.5 eV to 6.28 eV by varying the y value, respectively. Extensive understanding of material properties and continued pursuit of high-quality thin film growth lead to various optimized heterostructures and superlattices and, consequently, the rapid establishment of high performance III-nitride-based optoelectronics. In a similar fashion, there is also possibility to use Al2O3 (Eg = 8.8 eV), Ga2O3 (Eg ~ 4.8 eV), and In2O3 (Eg = 2.9 eV) to design ternary or quaternary alloys. Alloying Ga2O3 with Al2O3 and In2O3 would offer an opportunity to tailor the bandgaps and other properties and to form heterojunctions, enabling electronic modulation and confinement. However, a major problem is that Al2O3, Ga2O3, and In2O3 have quite different crystal structures. It is, therefore, interesting to understand which crystal structure the alloys would adopt and how their structures affect the optical and electronic properties. In the following, we first provide a brief introduction on the structures and properties of each oxide.

A. Crystal structures

Al2O3 crystallizes in a corundum structure (space group R3c) with lattice constants of a = 4.76 Å and c = 12.99 Å, as shown in Fig. 20(a). This structure is based on a hexagonally close packed array of O ions with the Al cations filling up 2/3 of the central O6 sites. Al2O3 is the commonly used substrate for the growth of GaN and Ga2O3. The bandgap of Al2O3 is 8.8 eV. Al2O3 also has a metastable monoclinic structure, same as β-phase of Ga2O3.

The thermodynamically stable phase of In2O3 adopts a body-centered cubic (bcc) bixbyite structure, with a lattice parameter of a = 10.117 Å. The structure may be regarded as a 2 × 2 × 2 superstructure of fluorite with ordered removal of O from 1/4 of the anion sites, as shown in Fig. 20(b). In3+ cations are O6 coordinated by six O anions but with slightly different bonding lengths. The bixbyite In2O3 has a fundamental bandgap of 2.9 eV but is optically forbidden; the optical bandgap with a strong absorption occurs at 3.75 eV. In2O3 is also a metastable polymorph of hexagonal corundum structure, with a lattice constant of a = 5.478 Å and c = 14.51 Å. The corundum phase In2O3 has a direct bandgap of 3.0 eV. Although the corundum In2O3 is a metastable phase, it has been shown that it can be stabilized at the interface during the epitaxial growth of In2O3 on Al2O3 substrates.

As mentioned earlier, Ga2O3 adopts five polymorphs. The monoclinic β-Ga2O3 is the most stable one. In β-Ga2O3, Ga has a T4 coordinated Ga1 site and O6 coordinated Ga2 site. α-Ga2O3 is equivalent to the corundum structure with lattice constants of a = 4.76 Å and c = 12.99 Å. In the corundum phase, only O6 coordinated sites are present. γ-Ga2O3 is equivalent to the bixbyite structure with a = 8.22 Å.

B. (AlxGa1-x)2O3

Al2O3 alloyed with Ga2O3, i.e., (AlxGa1-x)2O3, in principle, can increase the bandgap from 4.85 eV to 8.8 eV. However, as mentioned above, different crystal structures and coordination bring frustration as for what is the preferred crystal structure as a function of x. For the bulk polycrystallines prepared by solid state synthesis and thin films grown by PLD, it was reported that (AlxGa1-x)2O3 keep the monoclinic β-phase with Al contents up to x = 0.80. With more Al content, the corundum structure is preferred. However, it should be noted that for the epitaxial thin films using MBE, the solubility of Al in (AlxGa1-x)2O3 is restricted to x = 0.20. The limited Al contents were attributed to the low growth temperature (<800°C) during MBE growth, while incorporation of Al in Ga2O3 lattice requires a temperature higher than 800°C. The lattice constants decrease linearly with an increase in the Al-content, consistent with the smaller atomic radius of Al compared to Ga. The linear decrease in lattice constant is in agreement with Vegard’s law. The recent DFT calculations by Peelaers et al. revealed more insights into the phase stabilities, lattice parameters, and electronic properties of (AlxGa1-x)2O3 alloys. They found that the monoclinic phase remains energetically preferable for Al.
concentrations up to \( x = 0.71 \); for a higher Al content, a corundum structure is preferred, in close agreement with experimental phase diagrams.\(^{25,29,234}\) More interestingly, it was found that the energetics strongly correlate with the preferred coordination environment of Al and Ga: Al atoms favor \( O \) sites, which are the only coordination environments in corundum; in the monoclinic structure, half of the sites are \( O \) coordinated and half of the sites are \( T_d \) coordinated. Therefore, the \( x = 0.5 \) alloy (GaAlO\(_3\)) has a high stability with all Al atoms at the \( O \) sites and all Ga atoms at \( T_d \) sites.

As expected, the bandgaps of (Al\(_x\)Ga\(_{1-x}\))O\(_3\) alloys can be tuned from the bandgap of \( \beta\)-Ga\(_2\)O\(_3\) (4.8 eV) to 6 eV with an increase in Al contents. Figure 21(b) shows the experimentally measured and DFT calculated bandgaps for the monoclinic and corundum (Al\(_x\)Ga\(_{1-x}\))O\(_3\) as a function of Al contents, adapted from Ref. 411. Good agreement is found between the calculated and experimental values.\(^{111}\) The increased bandgaps would enable the realization of new applications in many devices such as FET, modulation-doped electron channels, and solar-blind photodetectors responsive to deeper UV bands. For example, the larger bandgap of \( \beta\)-(Al\(_x\)Ga\(_{1-x}\))O\(_3\) would lead to an even higher BFOM than that of Ga\(_2\)O\(_3\), which makes \( \beta\)-(Al\(_x\)Ga\(_{1-x}\))O\(_3\) a potential candidate for even higher power and higher frequency electronic devices. Kaun et al.\(^{425}\) have grown (Al\(_x\)Ga\(_{1-x}\))O\(_3\) epitaxial thin films using MBE with composition up to \( x = 0.2 \). A preliminary report on \( \beta\)-(Al\(_x\)Ga\(_{1-x}\))O\(_3\) MESFETs shows a higher critical breakdown field than \( \beta\)-Ga\(_2\)O\(_3\).\(^{412}\) However, a low mobility of 4 cm\(^2\)/Vs in the grown \( \beta\)-(Al\(_x\)Ga\(_{1-x}\))O\(_3\) film results in a lower on-current in the device. Further work needs to be done to improve the crystal quality and mobility. Another very interesting use of \( \beta\)-(Al\(_x\)Ga\(_{1-x}\))O\(_3\) is as a barrier layer for \( \beta\)-(Al\(_x\)Ga\(_{1-x}\))O\(_3\)/Ga\(_2\)O\(_3\) high electron mobility transistors (HEMTs). \( \beta\)-Ga\(_2\)O\(_3\) suffers from POP scattering which limits its maximum mobility to 220 cm\(^2\)/Vs.\(^{23} \) Because of the larger bandgap of \( \beta\)-(Al\(_x\)Ga\(_{1-x}\))O\(_3\), i.e., higher CBM, it is expected that electrons in (Al\(_x\)Ga\(_{1-x}\))O\(_3\) doped by Si would be transferred to the adjacent Ga\(_2\)O\(_3\) to form a 2DEG at the interface. The enhanced 2DEG sheet charge is predicted to screen out certain phonon modes, resulting in reduced scattering in the 2DEG channel. Theoretical studies predict that the 2DEG at the \( \beta\)-(Al\(_x\)Ga\(_{1-x}\))O\(_3\)/\( \beta\)-Ga\(_2\)O\(_3\) interface has a mobility of about 500 cm\(^2\)/Vs\(^{434}\) much higher than that of bulk \( \beta\)-Ga\(_2\)O\(_3\). Recently, modulation-doped \( \beta\)-(Al\(_x\)Ga\(_{1-x}\))O\(_3\)/\( \beta\)-Ga\(_2\)O\(_3\) HEMTs with a sheet charge of \( 2 \times 10^{12} \) cm\(^{-2}\) and Hall mobility of 180 cm\(^2\)/Vs have been demonstrated.\(^{435}\)

C. \( (\text{In}_x\text{Ga}_{1-x})_2\text{O}_3 \)

While there is extensive research work in (Al\(_x\)Ga\(_{1-x}\))O\(_3\) alloys, the literature on (In\(_x\)Ga\(_{1-x}\))O\(_3\) ternary alloys is limited. In\(_2\)O\(_3\) (doped with 6% Sn, known as ITO) has been extensively investigated as a transparent electrode for flat panel displays, touch screens, and solar cells. The bandgap of In\(_2\)O\(_3\) has been widely quoted to be 3.75 eV,\(^{413,414}\) which marks the onset of strong optical absorption. A weaker absorption onset at 2.62 eV has either been ignored or attributed to indirect optical transitions.\(^{417}\) In 2008, it was established based on XPS and DFT that In\(_2\)O\(_3\) has a direct but optically forbidden bandgap of around 2.9 eV.\(^{434}\) The establishment of fundamental bandgap in turn leads to the identification of the surface electronic structure of In\(_2\)O\(_3\), e.g., strong downward band bending and 2DEG at the surface of In\(_2\)O\(_3\).\(^{418,421}\) Alloying Ga\(_2\)O\(_3\) with In\(_2\)O\(_3\) offers the opportunity to tune the bandgaps from 4.8 eV to a lower value (2.9 eV) and also other material properties. However, similar to the (Al\(_x\)Ga\(_{1-x}\))O\(_3\) system, because Ga\(_2\)O\(_3\) and In\(_2\)O\(_3\) have quite different crystal structures, phase separation is expected. Shannon and Prewitt investigated the structural properties of (In\(_x\)Ga\(_{1-x}\))O\(_3\) powder and single crystalline samples for \( 0 < x < 0.5 \)\(^{422}\) and found that a monoclinic \( \beta \)-phase structure was maintained. A complete phase diagram of (In\(_x\)Ga\(_{1-x}\))O\(_3\) alloys was established by Edwards et al.\(^{423}\) using powder samples prepared by conventional solid state synthesis; they showed that the solubility of In\(_2\)O\(_3\) in Ga\(_2\)O\(_3\) maintaining a monoclinic structure is limited at \( x = 0.44 \), while on the In\(_2\)O\(_3\) side, the solubility limit for Ga in

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FIG. 21. Lattice parameter and bandgap evolutions as a function of Al contents in (Al\(_x\)Ga\(_{1-x}\))O\(_3\) alloy contents. (a) Pseudocubic lattice parameter as a function of alloy composition \( x \) for the corundum and monoclinic structures. Experimental values for monoclinic are shown as solid black triangles, open triangles, and solid downward triangles. The top inset shows the monoclinic unit cell, and the bottom inset shows the corundum unit cell. Octahedrally coordinated sites are indicated in blue, and tetrahedrally coordinated sites are indicated in green. Small red spheres depict O atoms. (b) Direct (solid symbols) and indirect (open symbols) bandgaps for the monoclinic and corundum structures as a function of the alloy composition. The solid (dashed) lines are quadratic fits to the indirect (direct) bandgaps, as described in the text. The computed values are shown in color, and the experimental values are shown in black.\(^{411}\)
the cubic bixbyite phase is only at \((1-x) = 0.1\). In the composition range between the two doping limits, bulk samples are biphasic, consisting of a mixture of cubic Ga doped In\(_2\)O\(_3\) and monoclinic In doped \(\beta\)-Ga\(_2\)O\(_3\). Most of the works also found that the lattice constants of \((\text{In}_{1-x}\text{Ga}_x)\text{O}_3\) increase linearly with an increase in the In content, \(^{24,28}\) as expected from the larger cation size of In\(^{3+}\) (0.79 Å) as compared to Ga\(^{3+}\) (0.62 Å). As shown in Fig. 22(a), the increase in lattice parameters \((a, b, c)\) is in agreement with Vegard’s law.

Epitaxial \((\text{In}_{1-x}\text{Ga}_x)\text{O}_3\) thin films have been prepared by a wide range of techniques including MBE,\(^{159,170,194,249}\) MOCVD,\(^{212,247}\) PLD,\(^{347}\) and so on, but the reported solubility values are quite scattered depending on the growth techniques and growth conditions. Oshima and Fujita\(^{159}\) grew \(\beta\)-(In\(_{1-x}\text{Ga}_x)\text{O}_3\) thin films on \(\beta\)-Ga\(_2\)O\(_3\) buffer layers on Al\(_2\)O\(_3\)(0001). The thin films had a monoclinic structure up to \(x = 0.35\); the crystalline quality degraded with an increase in the In content such that films with \(x = 0.35\) were nearly amorphous. MOCVD thin films on Al\(_2\)O\(_3\)(0001) crystallize in the monoclinic structure for \(x \leq 0.22\). For \(x \geq 0.51\), only the cubic structure of In\(_2\)O\(_3\) is observed. Kokubun \textit{et al.}\(^{200}\) prepared \((\text{In}_{1-x}\text{Ga}_x)\text{O}_3\) thin films on Al\(_2\)O\(_3\)(0001) by a sol-gel method. For \(x < 0.4\), the monoclinic structure was observed, while for \(x > 0.8\), the bixbyite structure was observed. For intermediate \(x\) values, the monoclinic and the cubic phase coexist. Baldini \textit{et al.}\(^{228}\) grew monoclinic \((\text{In}_{1-x}\text{Ga}_x)\text{O}_3\) thin films by MOVPE for \(x \leq 0.25\), while for higher \(x\), in admixture, phase separation occurred. UV and deep-UV selective photodiodes from Baldini\(^{159}\) were fabricated using a Si-doped \((\text{In}_{1-x}\text{Ga}_x)\text{O}_3\) thin film with a monotonic lateral variation of 0.0035 < \(x < 0.83\).\(^{231}\)

First-principle calculations were also performed to reveal more insights into the formation enthalpies, structural parameters, and electronic properties of the alloys. Maccioni and Fiorentini\(^{32}\) showed that the solubility limit of In in Ga\(_2\)O\(_3\) was \(x = 0.1\), significantly lower than the experimentally derived values of 0.43. Recently, Peelaers \textit{et al.}\(^{33}\) showed that a monoclinic phase is energetically favorable for \(x < 0.5\). All In cations prefer occupying the \(O_h\) sites because of their much larger size than that of Ga. In incorporation increases the local strain around the In cations, resulting in phase instability at higher In contents. A lower In content results in a partial occupation of the \(O_h\) sites by Ga atoms. This effect may explain why the cation ordered Ga\(_2\)O\(_3\) with all In at the \(O_h\) sites and all Ga at \(T_d\) sites similar to the case of Ga\(_2\)O\(_3\) were rarely synthesized and perhaps can only be synthesized at high pressures.

The incorporation of In in Ga\(_2\)O\(_3\) allows us to tailor the optical bandgap from 4.86 eV down to 4.1 eV in the range of \(x = 0–0.44\). Thin films grown by the MBE,\(^{212,247}\) MOCVD,\(^{212,247}\) PLD,\(^{347}\) and sol-gel method\(^{259}\) have been measured using optical absorption spectroscopy. Figure 22(b) presents a few typical results from Refs. 159, 161, 170, 194, 238, 347, and 434. The bandgaps systematically decrease with an increase in the In content.\(^{161}\) For \(x \leq 0.3\), the absorption edge depends linearly on \(x\) and can be fitted by 
\[E_g(x) = 4.90 \text{ eV} - (2.42 \times x) \text{ eV}\]
Although the bandgaps have been deduced from optical absorption edges for higher \(x\) values (\(x > 0.44\)), bandgap bowing can be observed and can be fitted by 
\[E_g(x) = 4.87 \text{ eV} - (1.26 \times x) \text{ eV} + (1 \times x^2) \text{ eV}\]
for \(0 < x < 1\). However, it should be noted compositions for \(0.44 < x < 0.90\) produce mixed phases of \(\beta\)-Ga\(_2\)O\(_3\) and bixbyite In\(_2\)O\(_3\). Furthermore, In\(_2\)O\(_3\) actually has a much smaller fundamental bandgap (2.9 eV) than the optical bandgap (3.7 eV).\(^{161}\)

Finally, it is interesting to note that the \(\alpha\)-phase Ga\(_2\)O\(_3\) has the same corundum structure as Al\(_2\)O\(_3\). All Ga cations are \(O_h\) surrounded by six oxygen ions. The lattice parameters are \(a = 4.9825\) Å and \(c = 13.433\) Å.\(^{161}\) Epitaxial thin films of \(\alpha\)-Ga\(_2\)O\(_3\) can be stabilized by growing on \(\alpha\)-Al\(_2\)O\(_3\) by mist-CVD at 430–470 °C.\(^{203,204,238}\) The stabilization of the \(\alpha\)-phase was attributed to the unique reaction path of this growth technique. The incorporation of Al contents up to 0.81 was reported by Ito \textit{et al.}\(^{171}\) The bandgap was increased from 5.3 eV to 7.8 eV. The thermal stability of the \(\alpha\) phase is strongly enhanced due to alloying with \(\alpha\)-Al\(_2\)O\(_3\).

Moreover, the metastable corundum phase In\(_2\)O\(_3\) has the same corundum structure as \(\alpha\)-phase Ga\(_2\)O\(_3\). It has been shown that corundum In\(_2\)O\(_3\) could be stabilized by the Al\(_2\)O\(_3\)\(^{409}\) or Fe\(_2\)O\(_3\) buffer layer on Al\(_2\)O\(_3\).\(^{436}\) In the \(\alpha\)-(In\(_{1-x}\text{Ga}_x)\text{O}_3\) alloy system, a phase separation occurs for intermediate In admixtures. In Fig. 23, the bandgap energy of the experimentally realized solid solutions of

FIG. 22. (a) Lattice parameters for \((\text{In}_{1-x}\text{Ga}_x)\text{O}_3\) samples as a function of In concentration. Data from bulk powders, thin film samples, and ceramic samples are shown in black squares, blue squares, and red triangles, respectively.\(^{259}\) (b) Bandgap energy of \((\text{Ga}, \text{In})\text{O}_2\) bulk crystals and thin films determined from absorption measurements. The dotted black line and the dashed black line are calculated values. The rest of the results are obtained experimentally. The black line is a fit to the experimental data excluding results for \(\text{Elb}\) and that of Fujita \textit{et al.} See Ref. 458 for more details.
α-(Ga,In)2O3 and α-(Ga,Al)2O3 is shown to depend on the average bond length and α-lattice constant. The dependence of the bandgap energy on the composition can be fitted by $E_g(x) = xE_{Ga_2O_3} + (1 - x)E_{Ga_2O_3} - bx(1 - x)$, with $E_{Ga_2O_3}$ being the bandgap of α-Al2O3 or α-In2O3 with the respective bowing parameters of $b = 0.1$ eV or $b = 1.1$ eV. Furthermore, there are a variety of rhombohedral corundum-structured M2O3 oxides, including M = Al, Ga, In, Cr, Fe, and V. Owing to the same crystal structure, alloying and the formation of heterostructures with α-Ga2O3 and α-In2O3 are essentially expected, leading to novel multi-functionality, such as a wide range tunability in the bandgap and ferromagnetic semiconducting properties (e.g., weak ferromagnetic FeO2 with a bandgap of 2.2 eV).

Motivated by the successful epitaxial growth of ε-Ga2O3 as well as κ-Ga2O3, Al and In alloying of these two unstable phases begins to come into the view of researchers. Tahara et al. first reported the Al2O3 alloying in ε-Ga2O3 using mist-CVD, with the Al content of ε-(AlGa1−x)2O3 reaching up to the value of $x = 0.395$ and bandgap tuned from 5.0 eV to 5.9 eV. In2O3 alloying with ε-Ga2O3 was also achieved by mist-CVD, and its bandgap could be controlled from 4.5 eV to 5.0 eV without phase separation. Recently, alloying in κ-Ga2O3 was reported by the researchers from Universität Leipzig. A specially designed continuous composition spread (CCS)-PLD method was utilized to grow κ phase (Al(Ga1−x)2O3 and (In(Ga1−x)2O3). For Al alloying, the Al content could be achieved to a remarkable value of $x = 0.65$ with a tunable bandgap value from 4.9 eV to 5.8 eV. The In alloying was reported with a maximum content of $x = 0.35$ and the bandgap value varied from 4.3 eV to 4.9 eV.

VI. SUMMARY AND REMARKS

In this article, we provided a timely review on the semiconductor physics of Ga2O3 in terms of electronic structures, optical properties, chemistry of defects and dopants, and bandgap engineering. Recent progress and fundamental understanding on the synthesis of bulk single crystals, epitaxial growth of thin films, chemical and physical properties of defects and impurities, deep level states, and origin of unintentional n-type doping, p-type doping, and ternary alloys with In2O3 and Al2O3 were reviewed.

In the past decade, a significant process has been made for the growth of high-quality bulk crystals and thin films of Ga2O3. 4-in: high quality β-Ga2O3 (201) wafers grown by EFG with EPD on the order of 10⁴ cm⁻² were commercially available from Novel Crystal Technology, Inc. High quality β-Ga2O3 homoepitaxial thin films, with record-high carrier mobilities of 184 cm²/V s and low carrier concentrations of $2.5 \times 10^{16}$ cm⁻³, have been achieved by MOCVD. This enables further scaling-up for mass production. Using Si, Sn, or Ge as dopants, electron carrier concentrations ranging from $10^{16}$ up to $10^{19}$ cm⁻³ can be controllably obtained.

Through modulation doped β-(AlGa1−x)2O3/Ga2O3 heterostructures to form a two-dimensional electron gas at the interface, a record-high room-temperature channel mobility of 180 cm²/V s and peak mobility of 2790 cm²/V s at 50 K have also been demonstrated.

The achievement in growing high quality bulk crystals and thin films has accelerated research progress in the fundamental understanding of semiconductor physics of Ga2O3 and device optimizations. Similar to other oxide semiconductors such as ZnO, In2O3, and SnO2, Ga2O3 exhibits unintentional n-type conductivity. The origin of the unintentional doping is still not clear. Vo, H2, H3O, Ga3, and impurities from the synthesis/growth processes have been proposed as possible sources. Based on more advanced hybrid DFT calculations and evidence from experiments, it appears that Vo is a deep level donor, unlikely contributing free electrons at room temperature, and Ga3 has a high formation energy. Hydrogen and unintentional impurities such as Si are most likely the origins of unintentional n-type conductivity. Several studies reported the detection of Si residual (with ppm wt) even in 6N purity Ga2O3. Such a trace amount of Si can lead to a free electron density of $10^{16}$ cm⁻³. Furthermore, a trace amount of Fe impurity has also been detected in bulk crystals likely from the containers used for material growth. It is interesting to obtain Ga2O3 precursors with an even higher purity, thus eliminating possible contaminations during the synthesis process to further reduce the background electron carriers. Several deep level states, including $E_1$ ($E_C - 0.62$ eV), $E_2$ ($E_C - 0.82$ eV), $E_3$ ($E_C - 1.00$ eV), $E_4$ ($E_C - 2.16$ eV), and $E_5$ ($E_C - 4.4$ eV), have been detected in bulk single crystals and epitaxial thin films. These deep level states may be associated with the above-mentioned unintentional impurities (e.g., Fe) or defects (e.g., Vo and VGa) or may be the intrinsic properties of Ga2O3. The identification of their physical origins is an important task because these deep level states are associated with the breakdown voltage, specific on-resistance, and leakage in power electronic devices and may also be associated with the long delay times and persistent photoconductivity often observed in solar-blind photodetectors. It has been proved that Si, Sn, Ge, and Nb act as shallow dopants with activation energy in the range of 10–60 meV. The doping behaviors (conductivity, carrier
concentration, mobility, activation, Fermi level, optical properties, etc.) can be understood by classic semiconductor physics. There are certain discrepancies regarding the electronic structure and substitution sites of the dopants, e.g., Si substitution at the Ga1 site may act as deep donors. More experiments based on temperature dependent transport measurement, EPR, photoluminescence, photoemission, x-ray absorption, and so on should be performed to clarify this point. It is a challenging task to achieve p-type doping in Ga2O3, which is inherently caused by the localized nature of the O 2p-derived VBM that leads to difficulty in introducing shallow acceptors but the ease of formation of localized polaron states. So far, there is a lack of strong experimental evidence proving the achievement of p-type doping in Ga2O3. Some new strategies have been proposed but remain to be further proved, such as to form a band using elements such as Bi3+ and Sn4+ containing ns2 lone pair states or hydrogen substitution at the Ga position. One the other hand, integrating Ga2O3 with other p-type semiconductors (p-GaN, SiC, and diamond) or oxides (NiO, Ga2O3, and Ir2O3) to form p-n heterojunctions would be a convenient solution. In particular, integration of Ga2O3 with p-type diamond could open up new opportunities to develop high-performance and robust power devices. Being the best thermal conductor (thermal conductivity of diamond of 22 W cm−1 K−1), diamond can additionally help mitigate the low thermal conductivity of Ga2O3 by dissipating heat from it, in a similar fashion as GaN-on-diamond power electronics in which diamond acts as a heat spreader.43,223 However, there remain significant challenges in the direct growth of one on the other due to lattice mismatch and different crystal symmetries. Transfer of mechanically exfoliated Ga2O3 nanomembranes on a diamond substrate provides an alternative approach to forming van der Waals-type heterojunctions,224 but this procedure clearly poses limitation to practical applications.

Despite Ga2O3 having a small electron effective mass, the Hall mobility of Ga2O3 is limited to 220 cm2/V s due to POP scattering and decreases with an increase in doping and defects due to ionized impurity scattering.225 Besides the continuous efforts to further increase the quality of material growth, modulation doping using the β-(Al,Ga1−x)2O3/β-Ga2O3 interface has been proved as a promising strategy to enhance the mobility. It is predicted that 2DEG at the interface can screen out certain phonon modes and a mobility of ~500 cm2/V s can be achieved.412

Bandgap engineering by alloying with Al and In results in an increase or reduction in the bandgap and offers new properties for the realization of enhanced device performance, such as increased bandgap for higher power electronic devices, forming heterostructures for high electron mobility devices and the design of wavelength selective photodetectors. However, because Al2O3, Ga2O3, and In2O3 have quite different crystal structures, their ternary alloys adopt a variety of crystal structures with different solubility limits, which also leads to different optical and electronic properties. For bulk crystals, (Al,Ga1−x)2O3 keeps the monoclinic phase with x up to x = 0.80; a corundum structure is preferred with x > 0.80. The bandgap of (Al,Ga1−x)2O3 can be tuned from 4.8 eV to 6 eV. However, in the epitaxial thin films using MBE, the solubility of Al in (Al,Ga1−x)2O3 is restricted to x = 0.20 because the incorporation of Al in Ga2O3 requires a higher temperature (>800°C) than that required for the MBE growth. It was predicted that to avoid unwanted parallel conduction channels in MODFETs based on β-(Al,Ga1−x)2O3/β-Ga2O3 heterostructures and achieve a high performance modulation doping, a large CB offset of at least 0.47 eV is preferred, which requires a bandgap of 5.15 eV with an Al concentration of x > 0.2.122 Increasing Al contents using other growth techniques (e.g., MOCVD and PLD) and demonstration of modulation doped devices remain to be explored. Furthermore, the as-grown β-(Al,Ga1−x)2O3 films still showed a low mobility of 4 cm2/V s, which results in a lower on-current in devices. Further work needs to be done to improve the crystal quality and carrier mobility. Alloying Ga2O3 with Ir2O3 has been less explored. Ir2O3 in Ga2O3 maintaining a monoclinic structure is limited at x = 0.44, which allows us to tailor the optical bandgap from 4.86 eV down to 4.1 eV. This would offer opportunity to realize selective optoelectronic devices from UV to deep-UV. Overall, the fundamental research on the alloys is still in its infancy and the realization of heterostructures and devices still awaits demonstration.

Finally, it is important to point out that although β-Ga2O3 has been extensively studied, α-Ga2O3 has the potential as the dark horse in Ga2O3 research. Although it is a metastable phase, it can be stabilized by Al2O3 substrates because of the same crystal structures and the small lattice mismatch. As a matter of fact, the only commercial Ga2O3 device at present is the SBD fabricated using α-Ga2O3 grown by mist-CVD and commercialized by FLOSPIA, Inc. In view of the material structure, α-Ga2O3 with only O3 coated Ga provides a more symmetric structure to achieve low defect density and possible higher mobility (300 cm2/V s). The corundum structure is more compatible with many other oxides and III-V semiconductors, α-Ga2O3 can form solid solutions with Al2O3 and corundum Ir2O3, FLOSPIA, Inc. and a group from Kyoto University recently reported that α-Ga2O3 can form epitaxial p-n heterojunctions with corundum Ir2O3 as an inversion layer.122 Certainly, more attention should be paid to α-Ga2O3.415

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