Gallium oxide (β-Ga2O3) is an emerging semiconductor with relevant properties for power electronics, solar-blind photodetectors, and some sensor applications due to its ultra-wide bandgap and developing technology base for high quality, melt-based substrate growth and thick, low-doped homoepitaxial layers. Of critical importance for the commercialization of this potentially important material is understanding of doping mechanisms in the monoclinic lattice, where two types of Ga sites and three types of O sites have been identified. A critical literature review of doping and defects of the monoclinic β-phase of gallium oxide is provided in this work. Theoretical fundamentals of both donor and acceptor doping in Ga2O3 are reviewed. Advances in doping of epitaxial Ga2O3 with a focus on molecular beam epitaxy and ion implantation are critically examined. As doping is fundamentally related to defects, particularly in this material, a review of defect characterization by optical and electrical spectroscopic methods is provided as well. P-type doping, one of the fundamental challenges for Ga2O3, is discussed in terms of first-principles calculations and ion implantation of known acceptors such as Mg and N.

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optical properties of

tions have reported these species are highly mobile,\textsuperscript{28} in addition to donors and could act as a source of conductivity.\textsuperscript{32} Although carbon could incorporate on the oxygen site (H\textsubscript{O}) is most stable under O-rich conditions, as the hydrogen interstitial (H\textsubscript{i}), though its formation energy is moderate even under O-poor conditions. H\textsubscript{i} can also be trapped at and form stable complexes with acceptors such as gallium vacancies.\textsuperscript{29} Since the hydrogen-vacancy complex has a lower formation energy than the hydrogen substitutional (HO) is most stable under O-rich conditions, as also as a substitutional donor on the oxygen site. The acceptor will be even higher than 530 meV).

Figure 1. The conventional unit cell of monoclinic β-Ga\textsubscript{2}O\textsubscript{3}. The two inequivalent Ga sites (large spheres) and the three inequivalent O sites (smaller spheres) are indicated. The Ga sites are labeled as tetrahedral (Ga\textsubscript{tetra}), corresponding to a Ga(I) site, and octahedral (Ga\textsubscript{octa}), corresponding to a Ga(II) site. Reprinted from H. Peelaers and C.G. Van de Walle, Phys. Rev. B 94, 195203 (2016). Copyright 2016 by the American Physical Society.

e.g., by acting as compensating centers). Although Ga\textsubscript{i} are shallow donors and could act as a source of n-type conductivity, recent calculations have reported these species are highly mobile,\textsuperscript{28} in addition to having large formation energies under n-type conditions. A number of different impurities have been predicted to be efficient n-type dopants in β-Ga\textsubscript{2}O\textsubscript{3}.\textsuperscript{24} Hydrogen impurities were found to act as donors in gallium oxide, and can be present both as an interstitial species (H\textsubscript{i}) and also as a substitutional donor on the oxygen site. The hydrogen substitutional (H\textsubscript{O}) is most stable under O-rich conditions, as is the hydrogen interstitial (H\textsubscript{i}), though its formation energy is moderate even under O-poor conditions. H\textsubscript{i} can also be trapped at and form stable complexes with acceptors such as gallium vacancies.\textsuperscript{29} Since the hydrogen-vacancy complex has a lower formation energy than the bare vacancy, H\textsubscript{i} can stabilize the presence of negatively charged cation vacancies, but also lowers their charge state through passivation.

Silicon, germanium, tin, chlorine and fluorine have also been investigated as potential donor dopants in β-Ga\textsubscript{2}O\textsubscript{3}.\textsuperscript{25} Both fluorine and chlorine were found to be shallow donors when substituting on the oxygen site (F\textsubscript{O} and Cl\textsubscript{O}), whereas silicon, germanium and tin were found to be shallow donors when incorporating on the gallium site.\textsuperscript{24,30} Under both O-rich and Ga-rich conditions, F\textsubscript{O} had the lowest formation energy among all donors, indicating it should incorporate most easily into gallium oxide. Incorporation of cation-site impurities was found to be most favorable in Ga-rich conditions, and among those dopants considered the Si\textsubscript{Ga} donor had the lowest formation energy.\textsuperscript{24} Transition metal impurities have also been explored as n-type dopants;\textsuperscript{31} although W, Mo, and Re were found to be deep donors, Nb was found to be a promising shallow donor candidate.

Carbon impurities have also been predicted to be a source of n-type conductivity.\textsuperscript{32} Although carbon could incorporate on the oxygen site and act as a deep acceptor, under more likely growth conditions the C\textsubscript{Ga} shallow donor was found to be most favorable. A subsequent study\textsuperscript{33} disputed this finding, and found that C\textsubscript{Ga} was a deep donor that exhibited DX-like behavior.\textsuperscript{34} However, it should be noted that in Ref. \textsuperscript{33} a post hoc band-edge correction was employed, in contrast to the self-consistent hybrid functional approach employed in Ref. \textsuperscript{32}

First-principles calculations have also explored the vibrational and optical properties of n-type β-Ga\textsubscript{2}O\textsubscript{3}. Kang et al. have investigated electron-phonon scattering in donor-doped material, and reported that intrinsic anisotropic carrier mobility was small, and suggested that experimentally measured anisotropy\textsuperscript{35} was due to other factors.\textsuperscript{36} Furthermore, mobility reduction and high doping levels were attributed to compensating defects (such as gallium vacancies). Peelaers et al. also explored sub-band-gap absorption by free electrons in n-type doped β-Ga\textsubscript{2}O\textsubscript{3}.\textsuperscript{37} Strong, polarized sub-band-gap free carrier absorption was reported, even for carrier concentrations as low as 10\textsuperscript{18} cm\textsuperscript{-3}, which could lead to decreased transparency in heavily donor-doped gallium oxide.

\textbf{p-type doping.—}Holes have been predicted to self-trap in β-Ga\textsubscript{2}O\textsubscript{3},\textsuperscript{38} behavior that is well documented in wide-band-gap oxide semiconductors.\textsuperscript{39} This means that holes are more stable localized as small polarons at a single O site, as opposed to being a free hole delocalized over a much larger region as in conventional semiconductors. The self-trapped hole was predicted to be 530 meV more stable than the free hole (the largest trapping energy among all oxides considered in Ref. \textsuperscript{21}), even in the absence of any defect or impurity. Negatively charged acceptors will bind strongly with positively charged free holes, and this result implies that no shallow acceptors will exist in gallium oxide (since with the added binding energy, the ionization energy of the acceptor will be even higher than 530 meV).

Recent calculations have explored the properties of a range of substitutional acceptor impurities in β-Ga\textsubscript{2}O\textsubscript{3}.\textsuperscript{28,39–47} Early studies reported that cation substitutional acceptors such as Zn could lead to p-type conductivity,\textsuperscript{45–47} however these studies employed standard DFT that is known to underestimate charge localization at defects (and hence, acceptor ionization energies). Despite employing such methods, these calculations already found that impurities such as Cu and N lead to deep levels.\textsuperscript{40,45,46} Kyrtsos et al. demonstrated that acceptor ionization energies increase significantly when employing a hybrid functional, and found that Li, Mg and Zn acceptors incorporating on the Ga site have ionization energies in excess of 1 eV.\textsuperscript{41} Later work found that group-II cation-site acceptors had ionization energies larger than Mg (and all above 1.3 eV), and that they trapped localized holes at nearest-neighbor oxygen sites.\textsuperscript{43} Very similar behavior for the Mg\textsubscript{Ga} acceptor has been observed in experiment.\textsuperscript{48} Nitrogen impurities incorporating on the oxygen site (N\textsubscript{O}) were calculated to have ionization energies in excess of 2 eV. The deeper nature of N\textsubscript{O} acceptors is caused by their defect states being derived from N 2p\textsubscript{z}–like orbitals, as opposed to the cation-site acceptors whose properties derive from the polaronic O 2p\textsubscript{z}–like orbitals.\textsuperscript{43}

The consensus among recent theoretical studies is that conventional doping approaches will not lead to p-type conductivity, since all acceptors are too deep to give rise to free holes. However, incorporating acceptor impurities can still be useful for controlling electrical conductivity (e.g., to create semi-insulating material). Varley et al. explored the properties of iron impurities, which are used explicitly for this purpose and are common impurities in Ga\textsubscript{2}O\textsubscript{3}.\textsuperscript{39} They reported that iron incorporates readily on the gallium site, where it acts as an exceedingly deep acceptor with a level only 0.6 eV from the conduction band minimum. Moreover, Fe\textsubscript{Ga} has very low formation energy, especially under O-rich conditions. Peelaers et al. also considered deep acceptor doping, and considered N\textsubscript{O} (most stable under Ga-rich conditions) and Mg\textsubscript{Ga} (most stable under O-rich conditions).\textsuperscript{39} Exploring diffusion mechanisms, Peelaers et al. found distinct migration behavior for N\textsubscript{O} and Mg\textsubscript{Ga} acceptors. Whereas Mg\textsubscript{Ga} diffuses easily via an interstitial mechanism, N\textsubscript{O} migrates via a N\textsubscript{O}–V\textsubscript{O} complex with a much larger migration barrier, making N\textsubscript{O} more immobile.\textsuperscript{28} These results agree well with depth-resolved diffusion studies of Mg- and N-doped material.\textsuperscript{49} Recent work has also demonstrated that Mg–H complexes are likely to form in Mg-doped gallium oxide containing hydrogen.\textsuperscript{50}

\textbf{Doping in Epitaxial Gallium Oxide}

As discussed in previous sections, β-Ga\textsubscript{2}O\textsubscript{3} has the distinct advantage being one of the few UWBGs that can compete with wide bandgap semiconductors such as GaN and SiC for power and radio frequency devices. For almost all applications, control of carrier concentration via doping with foreign impurities is essential. Either group
14 elements on Ga site or 17 elements on O site can be used as donor doping for n-type conductivity. N, Mg, or Zn do form acceptor levels, but they are too deep to give rise to p-type conductivity in $\beta$-Ga$_2$O$_3$.

In this section, we focus on n-type doping of Ga$_2$O$_3$ using molecular beam epitaxy (MBE) and also the prospects of acceptor doping.

**Donor doping.**—As discussed earlier, group 14 elements such as C, Si, Ge, and Sn on Ga site and Group 17 elements such as F and Cl on O site forms shallow donor level in Ga$_2$O$_3$. Their calculation shows that Si and Ge prefer tetrahedral site (Ga(I)) while Sn prefers octahedral site of Ga (Ga(II)). While Si$_{Ga(I)}$ has lower formation energy than Sn$_{Ga(I)}$ for Ga-rich growth, they have almost same formation energy for O-rich growth. Among the previously mentioned discussed transition metals, Nb$_{Ga(II)}$ has low formation energy and Nb doping control is demonstrated using optical floating zone. Among different shallow donor impurities Si, Ge and Sn are most common n-type dopant in Ga$_2$O$_3$. Among then Si is predicted to be shallowest donor. Table I summarizes most shallow common foreign impurity donors, their levels and MBE growth figure of merits. Gas phase oxidation in chemical vapor deposition growth and Si source oxidation in molecular beam epitaxy growth are the practical challenges for Si. Krishnamoorthy et al. demonstrated Si-delta doping by shutting the Si source and controlled higher carrier concentration ($6.8 \times 10^{19}$ to $1.7 \times 10^{20}$ cm$^{-3}$). Each donor dopant impurity has its own practical challenges. Recently, much research has been carried out on controlling electron concentration in the Ga$_2$O$_3$ using these dopants. Sasaki et al. showed growth rate dependence on substrate orientation with maximum MBE growth rate along (010) directions. Higashiwaki et al. demonstrated the first field effect transistors on (010) $\beta$-Ga$_2$O$_3$ using Sn-doped epitaxial films. Following these reports, most of the previous research on n-type doping were focused on (010) $\beta$-Ga$_2$O$_3$.

Han et al. investigated and compared Ge and Sn on $(001)$ via MBE for the fixed Ga beam equivalent pressure (BEP) of $3 \times 10^{-4}$ Torr and Sn and Ge cell temperatures of 800 and 560°C, respectively. It was shown that the Ge concentration decreases with increasing growth temperature above 675°C, however Sn concentration remains constant up to 800°C. This is important for the Al$_{Ga(II)}$Al$_{Ga(I)}$ on $\beta$-Ga$_2$O$_3$ heterostructures design for device applications as alloys of $\beta$-Ga$_2$O$_3$ with Al$_2$O$_3$ are generally grown at higher temperatures. It is also found that Ge incorporation saturates at Ge cell temperature over 700°C, however Sn doped layer can be grown at higher temperature (800°C) and was independent to the growth temperature. At higher temperature formation of volatile Ge suboxides dominate and limits the incorporation into the film however it was not the case for Sn up to 800°C.

Defect free as grown $\beta$-Ga$_2$O$_3$ is usually n-type, due to the presence of impurities. Thus, the insulating compensator doping of $\beta$-Ga$_2$O$_3$ has been carried out using deep acceptor such as iron (Fe). Fe-doped semi-insulating substrates are available commercially. Fe-derived levels are about 0.86 eV below the conduction band minimum. Therefore, exploring potential effective acceptors and the possibility of hole conductivity is very important. All probable acceptor dopants are at least 1.1–1.3 eV above conduction band maximum (CBM). Furthermore, the almost flat VBM results in high hole effective masses. Also, the formation of compensating donor oxygen vacancies and hole self-trapping are will impede p-type doping of $\beta$-Ga$_2$O$_3$. Although claims of p-type conductivity on $\beta$-Ga$_2$O$_3$ nano-wires by Zn doping, undoped and Mg-doped $\beta$-Ga$_2$O$_3$ layers have been made, p-type conduction appears to be very difficult.

In summary, n-type doping control in $\beta$-Ga$_2$O$_3$ was carried out using impurities such as Sn, Si and Ge has been studied most extensively to date. The choice of impurity dopant depends on the film growth system and device requirements. On the other hand, acceptor doping to get p-type carrier is very challenging, and it remains unclear whether it will be possible to demonstrate, either theoretically or experimentally. Rather, innovative heterostructure design appears to be a more fruitful approach for demonstrating $\beta$-Ga$_2$O$_3$-based bipolar devices.

**Diffusion and Ion Implantation Doping in Gallium Oxide**

Electronic device architectures depend on selective semiconductor doping. Early silicon technology at Bell Labs showed that diffusion-driven impurities can be used for emitter and base formation in bipolar transistors. Ion implantation, on the other hand, relies on a high energy ion beam of a specified fluence, as opposed to the usual thermal diffusion kinetics of impurities in a material. This fundamental difference allows for much more precise control of impurity profiles, which in turn translates to smaller device footprint. Therefore, ion implantation has for decades been the standard method of selective doping control in semiconductor devices. In contrast, ion implantation in Ga$_2$O$_3$ has been explored by a few groups primarily for the purpose of implanting Si to produce highly doped source and drain regions for low-contact-resistance ohmic contacts. To the authors’ best knowledge, the first report of electrically active impurities in Ga$_2$O$_3$ was by Peter and Schawlow in 1960, who showed Cr$^{3+}$ ions substituting Ga$^{3+}$ at the octahedral sites in the $\beta$-Ga$_2$O$_3$ crystal. In addition to the doping technology discussed in the previous section, here we review the progress made to-date in Ga$_2$O$_3$ diffusion and ion implantation technology.

**Donor diffusion and ion implantation: Si and Sn.**—Doping by diffusion has been demonstrated by Zeng et al. using a spin-on-glass with Sn concentration of $4 \times 10^{21}$ cm$^{-3}$ and a 1200°C, 5 minute drive-in anneal. The simulated and SIMS-measured profile of Sn were described by a simple exponential function $D(T) = D_0 \exp \left( -\frac{E_a}{kT} \right)$ used to model interstitial diffusion of a single positively charged particle, where $D(T)$ is the diffusion coefficient, $D_0$ is the activation energy, $D_0$ is a constant and $k$ is Boltzmann’s constant. The authors extracted an activation energy of 4.2 eV for the diffusion of Sn in what was most likely (010) oriented Ga$_2$O$_3$/Fe.

Sasaki et al. performed the first ion implantation in $\beta$-Ga$_2$O$_3$ using Si in the 10–175 keV range and total concentrations of $10^{14}$–$10^{16}$ cm$^{-3}$. Annealing temperatures ranged from 700–1100°C in N$_2$ atmosphere, achieving activation efficiency (defined as the ratio of $N_0$–$N_a$ measured by capacitance-voltage method near the Ga$_2$O$_3$ surface to the total Si implantation dose) as high as 80 percent for the lowest implantation dose ($10^{14}$ cm$^{-2}$) annealed at 1000°C. The implanted Ga$_2$O$_3$ substrates were all of the (010) orientation and grown by the float-zone (FZ) method, with some samples having an additional 150 nm thick epitaxial layer grown by molecular beam epitaxy. This early success in measuring low contact resistance using Ti/Al electrodes (4.6 × 10$^{-6}$ Ω⋅cm$^{-2}$) resulted in a number of successful device demonstrations from the same group.

An important consideration for the viability of ion implantation in Ga$_2$O$_3$ is the rate of diffusion of the different impurities, which can be

| Impurity | $E_D$ (meV) | ~n (cm$^{-3}$) | $T_C$ (°C) | $T_f$ (°C) | $\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$) | Reference |
|----------|-------------|---------------|------------|-----------|-----------------|------------|
| Si       | 16–50       | $6.8 \times 10^{19}$–$1.7 \times 10^{20}$ | 850–950    | 700       | 83              | 11,13,56   |
| Sn       | 7.4–60      | $2.0 \times 10^{16}$–$1.0 \times 10^{20}$ | 470–650    | 750       | 21–25           | 13,52,54,57,58 |
| Ge       | 17.5        | $1.0 \times 10^{17}$–$1.4 \times 10^{19}$ | <800       | 675       | 21–97           | 13,54,59,60 |
| Nb       | 30–150      | $9.6 \times 10^{16}$–$1.8 \times 10^{19}$ | –          | 40–80     | 31,51           |            |

*Note: *The table represents the donor level, carrier concentration, cell and growth temperatures and electron mobility ($\mu$) for grown layer on (010) $\beta$-Ga$_2$O$_3$. Nb was doped using optical floating zone method.
Acceptor implantation: Mg and N.—M.H. Wong et al. have studied activation of implanted acceptors using Mg and N with the objective of demonstrating current-aperture vertical transistors (CAVET). Figure 3 compares the SIMS profiles of implanted Mg and N, showing that significant redistribution of Mg occurs even at 800°C, whereas N was relatively stable after 1100°C anneal and could even be annealed at 1200°C. The significant thermal diffusivity of Mg required the use of N for the selective implantation required for a CAVET.\textsuperscript{73,74} However, as pointed out previously, Mg is still a useful acceptor for achieving uniformly-doped semi-insulating Ga₂O₃.

It has also been observed that post-annealing treatments result in effective crystal lattice recovery caused by Mg and/or N ion implantation damage.\textsuperscript{49,75} The availability of samples with intrinsically low free-electron concentrations and the development of ion implantation technology could therefore potentially create a unique opportunity to accomplish effective acceptor doping of Ga₂O₃. Figure 4 shows the low temperature CL spectra of (001) EFG β-Ga₂O₃ samples implanted with 10\textsuperscript{18} and 10\textsuperscript{19} N/cm\textsuperscript{2} dosages, and annealed at 900°C in oxygen atmosphere for 30 minutes. Note that the intensity of the CL spectrum of the sample implanted at lower dosage recovers quite well with the annealing procedure, consistent with considerable reduction of the implantation-induced defect concentration. A detailed study, including XRD and electrical characterization will be reported elsewhere. Despite the increase in resistivity and reduction of leakage current observed by Wong, no evidence of acceptor related emission bands were observed in the CL spectra of our samples.\textsuperscript{39,75} These preliminary results are important for the potential high field management using guard rings or edge termination strategies. However, detailed research of various potential acceptors, as well as implantation and thermal annealing schedules must be investigated to find out if acceptor doping of Ga₂O₃ can be achieved in practice.

**Luminescence Studies of Gallium Oxide**

Point defects (intrinsic, impurity related, and their complexes) and extended structural defects (dislocations, stacking faults, etc.) have long been associated with poor device performance. They are responsible for excess of dark current, noise, and reduced responsibility of detectors, and for reduced efficiency and operation lifetime in optical devices. Point defects and impurity complexes introduce parasitic current paths, decrease device gain, increase noise in electronic devices. At the same time they can increase threshold current, slope efficiency, and operation lifetime of laser diodes, and introduce instabilities in charge control in high-electrical-field devices. Therefore, to realize high performance devices, these defects must be detected and identified, and those correlated to specific poor device performance must be eliminated or reduced to the lowest possible concentrations. The effects related to extended defects are considerably reduced in bulk and...
homoeopitaxial films. Despite that, a handful of point defects have been
detected in bulk β-Ga₂O₃ by deep level spectroscopies. Therefore, to
achieve full control of the optical and electronic properties of homo-
and hetero-epitaxial device layers, these defects must be thoroughly
investigated by employing various defect-sensitive techniques which
can identify the defects responsible for device failure.

Luminescence is a well-established, highly-sensitive, non-
invasive, and non-destructive technique to detect and identify native and
impurity related point defects and their complexes in semiconduc-
tors. Characterization by luminescence involves the measurement and
interpretation of the spectral distribution of recombination radiation
emitted by the samples. Generated electrons and holes usually become
localized or bound to an impurity or intrinsic defect before recombin-
ing. The identity of the localized center that they were bound can often
be determined from the luminescence spectrum. Qualitative informa-
tion about crystal quality can be inferred from the efficiency and line
width of near-band-edge emission spectra, and impurities can some-
times be identified based on the binding energies inferred from the
spectral positions and free-to-bound transitions. In general, due to the
presence of various radiative and/or non-radiative recombination pro-
cesses competing for the generated electron-hole pairs, luminescence
processes alone cannot be conveniently used as a reliable quantitative
technique.

If electrons and holes are generated by the absorption of photons,
the process is called photoluminescence (PL). But, if these carriers are
created by kinetic energy transfer from an electron-beam to the semi-
conductor lattice, the process is named cathodoluminescence (CL).
While one absorbed photon creates one electron-hole pair, one im-
pinging electron-beam (E-beam) energy. CL depth-profiling is ex-
trmely useful in the study of activation of implanted dopants, thermal
annealing lattice recovery, and multi-layered structured materials.

Low temperature (4-6K) CL spectra of high crystalline quality bulk
β-Ga₂O₃ grown by edge-defined film-fed (EFG) method are depicted
in Fig. 5. These spectra were excited with a beam accelerating voltage
and current of 3 keV and 3 μA, respectively. The light emitted by
the samples, mounted on a continuous liquid-helium flow cold-finger
cryostat placed in a UHV chamber, collected by a combination of
f-number matching mirror and lens, was analyzed by a compact fiber-
optical CCD spectrometer.

The spectra of as grown β-Ga₂O₃ shown consistently lack of near
band-edge emissions, but they show frequently a broad emission band
made of three major emission bands, in the spectral range between
2.3 and 4.5 eV. Similar spectral intensity distributions are also ob-
served in homoeopitaxial films deposited by metal-organic chemical
vapor deposition and hydride vapor phase epitaxial. In nominally
undoped EFG samples, similar to those discussed in this work,
Onuma et al. reported that the UV emission bands at 3.2, 3.4 and
3.6 eV dominate at low temperatures, while at room temperature the
blue (2.8 and 3.0 eV) and green (2.4 eV) bands were more promi-
nent. Si-doped EFG samples showed only the UV bands. Yamaga et
al. suggested that the blue emission occurs through recombination of
self-trapped holes and electrons trapped at single oxygen vacan-
cies. More recently, CL studies performed on neutron-irradiated or
remote oxygen plasma treated bulk EFG samples and epitaxial Ga₂O₃
films grown by various methods suggested that this broad band may
be fit with four Gaussian lines with peaks around 2.5, 3.0, 3.5, and
3.8 eV. In this study, the 2.5 and 3.0 eV emission bands were ten-
vatively attributed to V_(Ga-related defects, while the 3.5 eV emission
band was assigned to V_o-related defects. The unambiguous identifi-
cation of these defects are critical for achieving full material control,
but this will require an extensive and detailed research work carried out on control sets of samples.

Luminescence studies of Mg- and Zn-doped β-Ga2O3 leads to semi-insulating samples with sub-bandgap emission bands near 2.9 eV, and 2.4 and 2.8 eV, respectively. Both Mg and Zn were reported to contribute to the blue luminescence intensity consistent with deep acceptor levels (2.8–2.9 eV), whereas the ultraviolet emission intensity was independent of dopant concentration.\(^{80,83,84}\) Finally, luminescence studies of rare earth ions (Er, Eu, Gd) implanted into nanowires and single crystals of Ga2O3 have been performed in order to study the optical response of these materials for potential applications as optical devices in the ultraviolet regime.\(^{85–87}\) Luminescence effects of optical response of these materials for potential applications as optical devices need to be employed. The use of deep level transient spectroscopy (DLTS) and deep level optical spectroscopy (DLOS), which can interrogate deep levels all the way to the valence band of Ga2O3,\(^{76}\) must be employed.

The ultra-wide bandgap, complex monoclinic structure, and the relatively immature material growth technology of Ga2O3 translate to a large number of defect states that can potentially exist. Defects have been shown to degrade the performance of Ga2O3 devices, and can be observed as threshold voltage instability and dynamic on-resistance in field effect transistors.\(^{91,92}\) To measure defect states deeper inside the bandgap, optical techniques, such deep level optical spectroscopy (DLOS), which can interrogate deep levels all the way to the valence band of Ga2O3,\(^{76}\) must be employed.

Deep Levels in Gallium Oxide

To characterize defect states within the entire ultra-wide bandgap of Ga2O3, a combination of both thermal and optical-based measurement techniques need to be employed. The use of deep level transient spectroscopy (DLTS), which relies on thermal emission rates of trapped charge, provides sensitivity only within ~1 eV of the majority carrier band edge.\(^{93}\) To measure defect states deeper inside the bandgap, optical techniques such deep level optical spectroscopy (DLOS), which can interrogate deep levels all the way to the valence band of Ga2O3,\(^{76}\) must be employed.

The ultra-wide bandgap, complex monoclinic structure, and the relatively immature material growth technology of Ga2O3 translate to a large number of defect states that can potentially exist. Defects have been shown to degrade the performance of Ga2O3 devices, and can be observed as threshold voltage instability and dynamic on-resistance in field effect transistors.\(^{91,92}\) It is critical to understand the origin of these defect states that adversely affect device performance. Also, some defects are intentional dopants, and are incorporated into the crystal to serve a specific role, such as Si for low contact resistance\(^{69}\) or Fe for forming semi-insulating material.\(^{95}\) Deep level optical characterization can aid in understanding the effectiveness of dopant incorporation and activation. It is important to understand which defects depend on material growth method and crystal orientation and which defects are intrinsic or extrinsic, and so on.

An example of where DLOS and DLTS were performed on EFG UID (010) Ga2O3 substrates resulted in five distinct defect states illustrated in Fig. 6 (left).\(^{76}\) These five states states detected were located at EC – 0.62 eV, 0.82 eV, 1.00 eV, 2.16 eV, and 4.40 eV, with the EC – 0.82 eV and Ec – 4.40 eV states having the highest concentration. According to Zhang et al., the state located near Ec–0.82 eV is assumed to be attributed to SnGa.\(^{84}\) However, it is also possible that the Ec – 0.8 eV level is due to FeGa.\(^{39}\)

Another EFG UID (010) Ga2O3 sample showed similar defect signature as grown, but was then exposed to neutron irradiation.\(^{59}\) Figure 6 (right) shows the EC–0.8 eV and EC–4.4 eV levels were not impacted by the irradiation, whereas there was an increase in the EC–1.03 eV and Ec–2.00 eV states, as well as an introduction to a new state at Ec–1.29 eV. Capacitance-voltage measurements showed that the irradiation created a reduction in carrier concentration, indicating the radiation induced defects contributed as compensation centers.

As discussed earlier, compensating defects formed by dopant incorporation were demonstrated by co-doping with Si and N in halide vapor phase epitaxy (HVPE) grown Ga2O.\(^{70}\) The N acceptors were determined to compensate Si donors, which resulted in low carrier concentration films. Photoionization spectroscopy is a technique useful in characterizing traps in semi-insulating materials shows an acceptor-like state located at Ec–0.23 eV (Fig. 7b) in the Si and N co-doped sample, which is not observed from measuring a reverse-biased Schottky diode with an unintentionally Si-doped HVPE drift layer (Fig. 7a).

Summary

In this review, we have summarized advances in the theory and growth of doped monoclinic β-Ga2O3 structures. Special attention was paid to focus on doping-related issues, as published reviews of this rapidly re-emerging material so far have not fully encompassed this critically important topic. The theoretical portion of this review considered donor and acceptor impurities, including commonly found impurities such as hydrogen and carbon. Defects such as the oxygen vacancy are not expected to contribute to conductivity even if present as deep energy levels in luminescence studies. Acceptors, even if not expected to produce room-temperature p-type Ga2O3, are still useful for producing semi-insulating material. Ion implantation of Ga2O3 is still in early stages of development. Both donor (Si and Sn) and acceptor (Mg and N) implantation studies have been published. The large diffusion coefficients implanted species (Si and Sn) as well as Fe introduced in EFG Ga2O3 substrates during growth, have been documented. Several studies of deep levels in Ga2O3 have been performed. Photo and catodoluminescence studies, as well as deep level transient and optical methods, reveal a number of deep levels in Ga2O3. Even though the controllable doping range of Ga2O3 already is remarkably wide (10¹⁵–10²⁰ cm⁻³), much more exploratory work remains to be done, particularly as material quality improves and new doping techniques are discovered. Of the possible applications for this material, photodetectors and high power devices are most sensitive to the quality of substrate and epitaxial material used in device fabrication. Thus, doping and defect science are indelibly linked for the
foreseeable future, particularly in the emerging field of ultra-wide bandgap semiconductors.

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