Diffusion of dopants and impurities in β -Ga₂O₃ 🕑

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ABSTRACT

The understanding and availability of quantitative measurements of the diffusion of dopants and impurities in Ga₂O₃ are currently at an early stage. In this work, we summarize what is known about the diffusivity of the common donor dopants, Sn, Ge, and Si, as well as some of the deep acceptors, N, Fe, and Mg, and donors, Ir. Two commonly encountered interstitial impurities are H and F, the former through growth and processing ambients and the latter through its use in plasmas used for stripping dielectrics from Ga₂O₃. Both are found to have high diffusion coefficients and an effect on electrical conductivity, and H shows anisotropy in its diffusion behavior. Si, Ge, and Sn implanted into bulk β -Ga₂O₃ at total doses from 2×10^{13} to 2×10^{15} cm⁻² and annealed at 1100 °C for 10–120 s in either O₂ or N₂ ambients showed a significant effect of the annealing ambient on the donor's diffusivity. In the case of O₂ annealing, there was extensive redistribution of the Si, Sn, and Ge across the entire dose range, while, in sharp contrast, the use of N₂ annealing suppressed this diffusion. The N₂ ambient also suppressed loss of dopants to the surface, with >90% of the initial dose retained after annealing at 1100 °C for 120 s, compared to 66%–77% with O₂ anneals under the same conditions.

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I. INTRODUCTION

Ga₂O₃ is attracting much recent interest for next generation power devices due to its superior materials parameters and availability of high quality, large area substrates grown by scalable melt growth techniques.^{1–2,3} The bandgap of the most stable β polytype is in the range 4.6–4.8 eV depending on orientation, and the theoretical breakdown field is ~8 MV cm⁻¹. β -Ga₂O₃ is characterized by flat valence bands that lead to deep ionization energies for acceptors (typically, >1 eV) and the formation of self-trapped hole polarons.^{24–30} This flat valence band results in a large hole effective mass of ~40m₀, which also gives rise to the trapped hole polarons with trapping energy of 0.53 eV.^{28,29,31–33} Hole conduction, therefore, has been achieved only at high temperatures (>600 K).^{13,14}

The impetus for the development of Ga_2O_3 is the increasing electrification of vehicles and the need to integrate renewable energy sources such as wind and solar into the existing power grid.^{22,34-40} Wider bandgap semiconductor devices provide more

efficient power switching than Si, leading to significant energy savings. A clear need is the development of efficient manufacturing and the reduction of size and cost for power electronic systems.^{22,38,41-43} The development of the newer generation of ultrawide bandgap (UWBG) semiconductors has pushed the boundary of power semiconductor devices.^{22,25} The commercialization of SiC and GaN device technologies has resulted in power electronics well-suited to smart grid and renewable energy applications.^{9,20,21} SiC is still the leading material for future improvements in power-handling capabilities. SiC Schottky rectifiers and hybrid junction FET (with Si MOSFETs) are already commercialized with the cost decreasing and performance increasing. The possibility of UWBG semiconductors with bandgaps exceeding SiC and GaN replacing traditional Si power devices has grown, and Ga₂O₃ is perhaps the leading option at this time.^{1,9,22,25}

The understanding of doping and diffusion in UWBG materials is still at an early stage, and it is the purpose of this review to summarize the current state of the art of this knowledge in Ga_2O_3 .



II. PROPERTIES AND APPLICATIONS OF Ga₂O₃

While Ga was well known by 1857,44 gallium oxide was first studied in detail in 1952 when its polymorphism of Ga2O3 was established during an investigative study of gallia gel (Al₂O₃-Ga₂O₃-H₂O system) using x ray and electron diffraction.⁴⁵ The study explored the formation of five polymorphs of Ga_2O_3 , namely, α -, β -, γ -, δ -, and ε -Ga₂O₃ upon subjecting the gallia gel to different conditions, while also identifying the most stable polymorph, i.e., β-Ga₂O₃.These polymorphs have been studied in detail,⁴⁶⁻⁵¹ but overwhelmingly most work has been performed on the β -polymorph due to its stability, attractive electronic properties, and potential in the UWBG semiconductor device market.^{22,51} The interest in this material arose initially during the 1950s and 1960s, but then this interest died till the 1990s when the semiconducting properties were truly recognized.^{3,40,46,51} There has followed a period where the material quality and purity have improved to the accepted standards of established semiconductors like Si, Ge, and GaAs. This work has focused predominantly on the power electronic applications of the β - phase polymorph,¹⁻ although there is also much interest in its use in solar-blind UV photodetectors.23,38

Ga₂O₃ is the most recent entry into the field of UWBG materials⁵² ⁵⁴ that includes more established materials like SiC and GaN and also the lesser established materials like diamond, AlN, and c-BN. The past few decades have seen an immense rise in the number of publications on all these materials, including growth techniques, electronic structure, thermal and mechanical properties, power devices, solar-blind UV detectors, gas sensors, nanostructures, and dopant behavior. Ga2O3 is also a part of the family of transparent conducting oxides (TCOs) or transparent semiconducting oxides, although it has also been as an insulating barrier, in the form of nanoribbons or nanowires, in nanoelectronics and molecular electronics.⁴⁶ Overall, Ga₂O₃ shows great potential as an UWBG material; however, there are still a few discrepancies between the experimental and theoretical results. Figure 1 shows a spider diagram comparing the properties of β -Ga₂O₃ with those of Si, SiC, and GaN in terms of their suitability for high power electronics capable of operating at high temperatures. Figure 2 shows how the critical electric breakdown field scales with the bandgap of the semiconductor and emphasizes why larger bandgaps are desirable.⁵ The lack of commercially available Ga₂O₃ products and the availability of numerous Technology Computer-Aided Design (TCAD) tools have led to a large number of simulation-based studies.

In addition to the five commonly observed polymorphs mentioned above, Playford *et al.*⁴⁸ fabricated a transient intermediate phase before the formation of β -Ga₂O₃, which was analogous to orthorhombic κ -Al₂O₃ and was labeled as κ -Ga₂O₃. The authors also noted the difficulty in isolating this polymorph in a pure form and had the formation of a mixture of β -Ga₂O₃ and κ -Ga₂O₃.⁴⁸ This re-iterates the difficulty in isolating the different phases of Ga₂O₃ in pure crystalline form and initially led to an emphasis on the calculation of structural parameters and band structures by atomistic modeling, using density functional theory (DFT).^{4,24,26} The most commonly occurring phases are α and β phases, with β -Ga₂O₃ formed by heat treatment in the air of any of other polymorphs at suitably high temperatures.^{1,3,40} The structure of ε -Ga₂O₃ has been inconsistently reported with early DFT studies stating that it belonged



FIG. 1. Spider diagram of different parameters of wide and ultrawide bandgap semiconductors and relative capabilities under different operating conditions of interest.

to the Pna21 group,⁴⁷ while experimental results suggest that the ε phase belongs to the P63mc group of symmetry. Furthermore, it is also reported that the δ -phase is a nanocrystalline form of the ε -phase.⁴⁸ The unit cell of β -Ga₂O₃ with a monoclinic structure in the space group c2/m consists of a total of four Ga₂O₃ molecules, i.e., 20 atoms in one unit cell, and the complicated structure comprises two inequivalent crystallographic gallium sites, one has tetrahedral geometry while the other has octahedral coordination geometry.



FIG. 2. Breakdown electric field as a function of the bandgap for different semiconductors. This critical field for breakdown scales with bandgap to a power of roughly 2.7. Reprinted with permission from Higashiwaki *et al.*, Appl. Phys. Lett. **100**, 013504 (2012). Copyright 2012, AIP Publishing LLC.





FIG. 3. Ball-and-stick model of the conventional β -Ga₂O₃ unit cell, where Ga/O atoms are represented by the green/red balls. Lattice parameters and angles are shown. Right: Polyhedra showing the local symmetry of the five different lattice sites with bond lengths and sites indicated. Reprinted with permission from Frodason *et al.*, Phys. Rev. Mater. **5**, 025402 (2021). Copyright 2021, American Physical Society.

Inequivalence is also reflected in the oxygen atoms, of the three oxygen atoms two of them have threefold coordination (but paired to different atoms) and the other has fourfolded coordination. This results in the anisotropy of the physical, optical, and electrical properties. Figure 3 shows the unit cell of β -Ga₂O₃ and the inequivalent O and Ga sites within the crystal structure.⁷

In wide-bandgap oxides like β -Ga₂O₃, compensating anion vacancies form easily under p-type doping conditions, resulting in degradation of doping efficiency. The issues with the doping of β -Ga₂O₃ include the deep acceptor levels (>1 eV), which arises from the relatively low-lying valence bands; the formation of compensating defects (e.g., V_O and V_{Ga}) that are unavoidable under p-type doping conditions; and dislocations or unintentional

impurities that are incorporated during synthesis and serve as carrier-trapping centers.⁵⁵⁻⁶⁵ The electronic band structure of β -Ga₂O₃ has the conduction band minima at the zone center, i.e., at Γ , while the valence band is predominantly flat in the momentum space.^{3–5} This leads to a large effective mass for holes, which then results in holes forming localized polarons (localized hole trapped by lattice distortions), resulting in lack of freedom for the holes to move.^{16,24,28} This and the large ionization of acceptors makes it difficult to achieve p-type doping in the material. Figure 4 shows the hydrogenic nature of the shallow donor Si, while substitutional nitrogen creates a deep acceptor state.⁸

The effective mass for electrons in β -Ga₂O₃ is calculated to be 0.34m₀ for the β -phase, where m₀ is the free-electron mass. Other



FIG. 4. Schematic of shallow vs deep defects. Si_{Ga} is a shallow donor, where the donor electron (yellow isosurface) occupies a delocalized hostlike state close to the CBM (yellow dotted line) in the sketched band structure. N_O introduces an empty acceptor level deep within the bandgap (blue line), and the hole (blue isosurface) is localized mostly at the N impurity itself. Reprinted with permission from Zimmermann *et al.*, Phys. Rev. Mater. **4**, 074605 (2020). Copyright 2020, American Physical Society.

TABLE I. Properties of β -Ga₂O₃.

Parameter	Valuea
Density $(g^2 cm^{-3})$	5.95-6.66
Dielectric constant	9.9-10.2
Bandgap (eV)	4.6-4.85
Melting point (°C)	1740-1820
Specific heat (J/g K)	0.56
Thermal conductivity (W/m K)	10.9-13
[100]	13.3 ± 1.0
[-201]	14.7 ± 1.5
[001]	21-29
Refractive index (@532 nm)	1.92-1.95

studies report the electron effective mass values between 0.27 and 0.28m₀,^{66,67} which match with experimentally observed values of 0.28m₀.⁶⁸ However, the DFT-based calculation has been known to underestimate the bandgap, which can be rectified by using a semi-empirical self-energy expression.⁶⁹ The bandgap has been estimated to be 4.6–4.9 eV,^{66,67} with a direct bandgap of 4.69 and an indirect bandgap of 4.66 eV. Peelaers *et al.*⁶⁶ reported that the primary bandgap of β -Ga₂O₃ is 4.84 (indirect), while Varley *et al.*⁶⁷ reported similar values of 4.83 (indirect) and 4.87 (direct) at Γ in the momentum space. The large bandgap translates into high critical field strength with theoretical values up to 8 MV/cm.

Another issue for Ga₂O₃ is its poor thermal conductivity. The physical properties of the material are listed in Table I, while Table II compares these properties and device figures of merit with the common semiconductors in the industry today.^{1,3,21,22,25,70} The typical thermal conductivity (κ) values are about an order of magnitude lower than of both SiC and GaN while also about half of that of sapphire. A focus in the research of Ga₂O₃ devices has been on ways to circumvent this problem by employing diamond or sapphire substrates, top side active cooling, and structural variations to maximize the device performance. β -Ga₂O₃ has an excellent Young's modulus ($E_Y = 230-280$ GPa),^{38,41-43} which is better than or comparable to those of the conventional materials for micro/

nanoelectromechanical systems' (M/NEMS) Young's modulus in the (100) plane, $E_{Y_{5}(100)} = 261.4 \pm 20.6$ GPa, for β -Ga₂O₃ nanoflakes synthesized by low-pressure chemical vapor deposition (LPCVD), and in the [010] direction, $E_{Y_{5}[010]} = 245.8 \pm 9.2$ GPa, for β -Ga₂O₃ nanobelts mechanically cleaved from bulk β -Ga₂O₃ crystal grown by the edge-defined film-fed growth (EFG) method.^{38,41-43}

Ultraviolet (UV) detection has been one of the major application spaces for β -Ga₂O₃ since the bandgap of 4.4–4.9 eV corresponds to absorption in the range 258-280 nm.^{1,3,23} The UV spectral ranges are classified into three regions: ultraviolet A (UVA from 315-400 nm), ultraviolet B (UVB from 280-315 nm), and ultraviolet C (UVC from 100-280 nm), and Ga₂O₃ together with bandgap engineering is a promising candidate for UVC or deep UV applications. The β phase in its pure form is colorless and extremely transparent, till the UVC region where its solar-blind applications are developed, in the form of photodetectors.³ The absorption spectrum shows a cut-off absorption edge at around 255-260 nm attributed to transitions from the valence band to the conduction band.³ The UV band (3.2–3.6 eV) is attributed to the recombination of free electrons and the self-trapped holes, the blue band (2.8-3.0 eV) attributed to oxygen vacancies, and the green band (2.4 eV) was attributed to specific dopants like Be, Sn, Ge, and Li.3 The photodetectors have applications ranging from military surveillance to photolithography and satellite communication. The different device structures include metal-semiconductor-metal (MSM), metal-intrinsic-semiconductor-metal photodetectors, avalanche photodiodes, and Schottky barrier photodiodes.²

Si still accounts for over 95% of power electronics products. The suitability of semiconductors as electronic power switches is evaluated by calculating various figure-of-merits (FOMs), and several FOMs of some common semiconductor materials have been listed in Table II. The large bandgap of β -Ga₂O₃ leads to high-temperature operability and large critical field strengths for high voltage applications.⁷⁰ Compared to other power electronic material candidates such as GaN and SiC. As shown in Table II, β -Ga₂O₃ demonstrates superior power switching metrics represented by Baliga's figure of merit (BFOM) and better power switching capabilities represented by Johnson's figure of merit (JFOM). The Huang chip area manufacturing figure of merit (HCAFOM) is used

TABL	E II.	Properties	of dif	ferent	semicond	luctors	and	various	figures	of mer	it norma	ized	to	Si	•
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Parameter	Si	GaAs	4H-SiC	GaN	Diamond	β-Ga ₂ O ₃
Bandgap (eV)	1.1	1.43	3.25	3.4	5.5	4.85
Dielectric constant	11.8	12.9	9.7	9	5.5	10
Breakdown field (MV cm ⁻¹)	0.3	0.4	2.5	3.3	10	8
Electron mobility $(cm^2/V s)$	1480	8400	1000	1250	2 000	200
Saturation velocity (10^7 cm/s)	1	1.2	2	2.5	1	1.8
Thermal conductivity (W/mK)	150	50	490	230	2 000	10.9-13
Johnson FOM (power-frequency capability)	1	1.8	278	1089	1 1 1 0	2844
Baliga FOM (R _{ON} in drift region)	1	14.7	317	846	24 660	3214
Combined FOM	1	3.7	249	354	9 331	37
Baliga high frequency (switching losses)	1	10.1	46.3	101	1 500	142
Keyes FOM (thermal capacity for power density/speed)	1	0.3	3.6	1.8	41.5	0.2
Huang chip area manufacturing FOM	1	5	48	85	619	279

to compute the manufacturability and the expense is reported to be superior; however, the actual manufacturing cost of β -Ga₂O₃ substrates is only marginally comparable to SiC and GaN and will improve as more research is performed.

The space environment consists of various forms of radiations that can cause electronics on satellites to fail or degrade, while other harsh environments that exist on the earth require radiation-hard electronic devices. Ga₂O₃ exhibits extremely strong bonds between the gallium and oxygen atoms and hence makes the material radiation-hard. β -Ga₂O₃ devices have been subjected to particle irradiation in the form of electrons, protons, alpha particle, neutron, and gamma-ray and the device degradation measured.^{71–76}

A. Doping in Ga₂O₃

Electronics oxides, such as ZnO, In2O3, and Ga2O3 have always presented difficulty in doping due to self-compensation, solubility, and defects issues, while they also exhibit asymmetry in conductivity, where only one conductivity (usually n-type) is favored over the other.^{77–112} Generally, it is the case that insulators cannot achieve high doping concentrations without developing structural changes that cause carrier compensation, a reason why the coexistence of transparency and conductivity is rare.^{113,11} Theoretical studies on dopant impurities and native defects in Ga₂O₃ have all been based on DFT; however, DFT has been known to underestimate bandgaps.¹¹⁵ In an attempt to solve this problem, hybrid density functional theories like the Heyd-Scuseria-Ernzerhof (HSE)¹¹⁶ have been used which efficiently predicts a quantitative value for semiconductor bandgaps.¹¹⁵ HSE has been shown to predict an accurate band structure and also been able to predict stable self-trapped holes for Ga_2O_3 , which has been verified by experiments.^{113,114} Incorporation of dopants depends on the chemical potentials of the host and dopant species, and the dopant formation energy is not a material constant but depends on the Fermi level, chemical potential, and charge state.¹

B. N-type dopants

Early theoretical studies suggested the unintentional n-type doping in Ga_2O_3 could be attributed to oxygen vacancies (V_O); however, Varley *et al.* used hybrid DFT (HSE)⁶⁷ to conclude that

TABLE III. Ionization energies and lattice locations of donor impurities in Ga₂O₃.

V_O is deep donors and would not contribute to the n-type background conductivity. Similarly, more studies have also demonstrated that most of the native defect species will not have an effect on the electrical conductivity.^{117,118} However, the native defects could indirectly cause compensation to the conductivity while the gallium interstitial (Gi) is considered to be a shallow donor and hence could contribute to the n-type conductivity.¹¹⁹ Hydrogen impurities have also been seen to act as donors in Ga2O3. Other impurities like silicon, germanium, tin, chlorine, and fluorine have also been investigated to be potential donors in Ga2O3,67 all of which are predicted to be shallow donors. The group 4 elements, i.e., Si, Ge, and Sn, are substituted on the Ga site, whereas group 7 elements such as Cl and F are on the O site. However, Ga₂O₃ has a complex structure involving two inequivalent gallium sites [Ga(I) and Ga(II)] and three inequivalent oxygen sites [O(I), O(II), O (III)], which causes the Si and Ge to favor the tetrahedral [Ga(I)] site, while Sn favors the octahedral [Ga(II)] site. Similarly, Cl and F are seen to favor the threefold coordination of the O(I) site. The donor states mentioned above are incorporated with ease because they have low formation energies.

Between the different shallow donors, Si, Sn, and Ge are the most commonly used for n-type doping in Ga₂O₃, while studies have shown Si to have the shallowest donor, as Tadjer *et al.*¹²⁰ reviews the donor levels, carrier concentration, and electron mobility achieved for the (010) β -Ga₂O₃ layer. The type of dopant is chosen depending on the availability of that dopant on the type of growth technique used. The limits of the electron mobility (μ_n) for β -Ga₂O₃ have been examined,¹²¹ and experimental results for Ahmadi *et al.*¹²² have demonstrated μ_n of 39 cm²V⁻¹s⁻¹ for Sn doped (n = 10²⁰ cm⁻³) β -Ga₂O₃ grown by MBE, while Baldini *et al.*^{123,124} have demonstrated μ_n of 50 cm²V⁻¹s⁻¹ for Si doped (n = 8 × 10¹⁹ cm⁻³) β -Ga₂O₃ grown by MOVPE. Usually, β -Ga₂O₃ layers are grown they are unintentionally n-type due to the presence of impurities like hydrogen and silicon, while gallium vacancies provide compensation in n-type Ga₂O₃ thin films.¹²⁵

Controllable n-type doping has been achieved using group IV elements. As shown in Table III, Si, Sn, and Ge have hydrogenic donor energies. Sn doping can be quite well controlled using Sn or SnO_2 source material and covers the widest range of electron concentrations but the mobilities are consistently below the empirical

Dopant or impurity	Nature	Ionization level (meV)	Lattice location
Sn	Hydrogenic donor	7-60	Ga
Ge	Hydrogenic donor	18-29	Ga
Si	Hydrogenic donor	15-31	Ga
Fe	Deep acceptor	$E_{\rm C} = 0.8 \rm eV$	Ga(II)
Mg	Deep acceptor (could be donor on O site)	Not measured	Ga(II)
Zn	Deep acceptor	Not measured	Ga(II)
Ν	Deep acceptor	$E_{C} = 0.25 \text{ eV}$	O-inequivalent sites have different ionization energies
Ir	Deep donor	Unknown	Ga(II)
Н	Shallow donor and passivant of defects, dopants	Not measured	Interstitial and bound to vacancy as substitutional
F	Passivant of donors	Unknown	Interstitial

mobility limit, partially related to the large donor activation energy and the presence of compensating defects and impurities.¹ Dopant segregation, in agreement with the metal-exchange catalyzing effect of Sn, compromises the controllability under standard MBE conditions but can be avoided using Sn-doping during In-catalyzed MOCATAXY at elevated growth temperature which results in similar electron mobilities to that of standard MBE.¹² In comparison, Ge doping seems to produce higher electron mobilities but the incorporation of the dopant was found to be strongly depending on the MBE growth conditions, compromising the controllability. The highest reported electron mobilities were realized by Si-doped, MOCVD/MOVPE-grown films. The control of Si-doping in oxide MBE, however, is challenged by source oxidation resulting in the drift of the Si flux, which is why only delta-doped layers have been reported historically. Their electron mobilities exceed those of homogeneously doped films since the electron wavefunction spreads out into donor-free film regions, resulting in significantly decreased ionized impurity scattering. Si doping has been found to be mediated by the formation and evaporation of the suboxide SiO instead of elemental Si from the source, resulting in a dopant flux that depends on the background oxygen pressure rather than the cell temperature.

Unintentional doping by a variety of sources has been reported for MBE-grown films.^{141,142} In particular, unintentional Si-doping has been identified to limit the lowest achievable donor concentration in MBE-growth films. In MOCVD, silicon has shown promising performance as a donor and the other candidates such as Ge, Sn, Zr, and Hf are less explored in the context of the MOVPE growth. The effect of growth conditions and precursors (metal-organic precursors versus gas sources) on dopant incorporation, segregation, and dopant substitution in crystallographically distinct sites remains to be studied in detail.

C. P-type dopants-deep acceptors

Even early on, it was obvious that Zn, Cu, and N were deep acceptor levels.^{151–154} Kyrtsos *et al.*¹¹⁸ reported a feasibility study of p-type Ga₂O₃ and found the acceptor ionization energies for Li, Mg, and Zn, were more than 1 eV. A survey was done by Lyons *et al.*^{4,136} on acceptor doping also showed high (1.3 eV) ionization energies for group-II acceptors on the cation sites, and an even higher (2 eV) ionization energy for nitrogen impurities on the oxygen sites. Furthermore, Fe impurities are explicitly used as means to control the electrical conductivity because these impurities are too deep to give rise to free holes.^{87–94} Due to the low formation energy of Fe_{Ga}, this defect is readily available especially in O-rich conditions and has a deep acceptor level ~0.8 eV from the conduction band minimum.

Even though p-type doping is particularly difficult, acceptor dopants are important for applications in bipolar Ga₂O₃ devices and for edge termination regions. The p-type doping is further hampered by the formation compensating donor oxygen vacancies and the self-trapped holes, while the hole effective mass is high due to an almost flat valence band maximum. However, there have been reports which claim to have shown p-type (Mg) doped β -Ga₂O₃ thin layers,¹⁵⁵ and β -Ga₂O₃ nanowires using Zn as the acceptor.¹⁵⁶ Chikoidze *et al.*^{13,14} have seen p-type conductivity at high temperatures, possibly due to ionized V_{Ga} . The absence of shallow acceptor doping to get p-type carriers in Ga₂O₃ opens up doors for innovative heterostructure designs to demonstrate bipolar Ga₂O₃ devices using NiO, Cu₂O, or CuI.

In terms of deep acceptor diffusion, it was reported that Mg diffusion is assisted by interstitials and N diffusion by vacancies, with predicted diffusion activation energies of 2.8 and 3.7 eV, respectively.⁶⁶ These activation energies agree quantitatively with the temperatures at which diffusion has been experimentally observed.¹³⁹

While achieving appreciable hole concentration and hole conduction is an open challenge, the detailed study of Mg-, Fe-, or N-doped epitaxial layers can enable controlled energy barriers in device structures for electric field management and current blocking capabilities Fe, Mg, and N are deep acceptors,⁸³⁻¹⁰¹ which form semi-insulating substrates or current blocking layers. Iron is an important impurity in β -Ga₂O₃ crystals. It is present at trace levels $(10^{16}-10^{17} \text{ cm}^{-3})$ in nearly all bulk-grown crystals because of impure starting materials Fe acts as an electron trap, and acts as a compensating acceptor, producing semi-insulating material that can be used in device fabrication. The FeGa trap level causes threshold voltage instabilities in transistors grown on Fe-doped substrates.^{82–96} The Fe³⁺/²⁺ acceptor level or (0/-) level in conventional semiconductor notation, is approximately 0.8 eV below the conduction band minimum, allowing Fe to provide compensation for the unintentional shallow donors that are typically present, such as Si, Ge, and Sn.^{82–96} The ε (0/–) transition was calculated to fall 0.61 (0.59) eV below the CBM for the FeG_{aII} (FeG_{aI}), in good agreement with experimentally reported levels of ~0.78 to 0.86 eV below the CBM. $^{97-99}$ The Fe⁴⁺/³⁺ donor level, or (+/0) level, is expected to be in the lower half of the bandgap, with recent computational results predicting it to be 0.51 eV above the valence band maximum.¹⁰¹ Thus, Fe is both a donor and an acceptor in β -Ga₂O₃, i.e., an amphoteric impurity.



FIG. 5. Model of the neutral magnesium acceptor (Mg_{Ga}^0) in a β -Ga₂O₃ crystal. The unpaired spin (the hole shown in blue) is localized in a nonbonding *p* orbital on a threefold oxygen ion, O(I), adjacent to the Mg ion at a sixfold Ga(II) site. The primary hyperfine interactions are with the Ga(I) and Ga(II) ions adjacent to the hole. Reprinted with permission from Kananen *et al.*, Appl. Phys. Lett. **111**, 072102 (2017). Copyright 2017, AIP Publishing LLC.





FIG. 6. Estimated energy levels for selected impurities in Ga_2O_3 (Eg = 4.8 eV). The hydrogenic (shallow) donor level is Ed = 30 meV, and the calculated Mg acceptor level is Ea = 1.0–1.5 eV. Theory and experiment place the Ir deep donor level 2.2–2.3 eV below the CBM. DLTS experiments indicate that the Fe acceptor level lies 0.8 eV below the CBM. Reprinted with permission from M. D. McCluskey, J. Appl. Phys. **127**, 101101 (2020). Copyright 2020, AIP Publishing LLC.

Electron paramagnetic resonance (EPR) determined the (0/-) level of the Mg acceptor at $\sim 0.65 \,\text{eV}$ above the valence band, closer to the valence band than predictions.^{92,93,101,103-107} Mg sits on a Ga(II) site (MgGa) and since Mg has two valence electrons, it acts as an acceptor. The model for the neutral magnesium acceptor (Mg_{Ga}^{0}) is shown in Fig. 5.¹⁰¹ As expected for an acceptor-bound small polaron in the partially ionic $\hat{\beta}\text{-}\text{Ga}_2\text{O}_3$ crystal, the Mg^{2+} ion on the Ga³⁺ site attracts a hole, with the hole residing on an adjacent oxygen ion instead of forming an Mg^{3+} ion or having the hole delocalized and centered on the Mg ion.¹⁰¹ The EPR data show a resolved hyperfine structure with two Ga neighbors.¹⁰¹ This requires the hole to be on a threefold-coordinated oxygen ion with the Mg ion at one of the three nearest-neighbor Ga positions. This oxygen must be an O(I) ion because the two Ga hyperfine interactions are not equivalent. The Mg ion at the sixfold-coordinated gallium site, in agreement with computational studies that suggest that Mg ions occupy the sixfold-coordinated Ga(II) sites in β-Ga₂O₃. The energy levels of various dopants and impurities in the bandgap of Ga_2O_3 are shown in Fig. 6.¹

III. HYDROGEN AND FLUORINE

A. Hydrogen

The behavior of hydrogen is of interest in semiconductors due to the significant changes it causes in the electronic and structural properties of these materials.^{150,151,157–184} In crystalline semiconductors, hydrogen tends to passivate the impurities and in conducting oxides it tends to form defect complexes with deep gap states

or behaves like a shallow donor.^{150,151} The hydrogen diffusion process in B-doped Si for temperatures T in the range from 60 to 140 °C is entirely trap-limited and shows no dependence on the diffusivity of the free hydrogen.¹⁶³ The behavior of hydrogen in oxides is of importance because of the undesirable donor activity that results in uncontrollable conduction.^{157,173} A study on the behavior of hydrogen in wide bandgap oxides reveals that hydrogen behaves in two different ways, either as an amphoteric defect leading to deep gap states (positive, negative, or neutral) or as a shallow donor near the conduction band edge.^{158,162} Figure 7 shows the relaxed structures of H⁻ (left) and H⁺ (right) in β -Ga₂O₃.¹²⁶ In the negative charge-state, the H forms a bond with the Ga2 atom associated with the O vacancy, and two electrons are trapped in a deep defect state (blue isosurface).

Theoretical and experimental studies on TCOs like ZnO, SnO₂, $\mathrm{In_2O_3},$ and $\mathrm{Ga_2O_3}$ have suggested the importance of hydrogen in TCOs.^{159,162} The behavior of hydrogen has been comprehensively studied in ZnO, showing rapid diffusion of ion-implanted or plasma incorporated hydrogen¹⁷¹ and its shallow donor behavior.¹⁶⁸ Similarly, experimental and theoretical works on In₂O₃ showed the importance of hydrogen as a shallow donor;¹⁶⁹ however, other studies argue that oxygen vacancies would be the cause for the n-type conductivity. Annealing of TCOs like In2O3 in H2 or D2 ambients have resulted in thin conducting layers near the surface with a high carrier concentration of 1.6×10^{19} cm⁻³, and a similar rise in the bulk n-type conductivity is seen when SnO₂ was annealed in a hydrogen-containing ambient producing many hydrogen centers.¹⁷⁰ The diffusion of hydrogen has been studied in ZnO where incorporation depths of $30\,\mu m$ were observed for a 0.5 h exposure to a ²H plasma; however, a similar process produces incorporation depths of only $1 \,\mu m$ in GaN.¹⁷

When In₂O₃ crystals were annealed in an H₂ or D₂ ambient, an OH vibrational line at 3306 cm^{-1} corresponding to the Hi shallow donor center was observed. This is responsible for the hydrogen-related conductivity while the corresponding Di center had an OD line at 2464 cm⁻¹. This is relevant to the case of Ga_2O_3 since alloys of (In_xGa_{1-x})₂O₃ will play a role in future heterostructure device technologies. In Ga₂O₃, it has been observed by density function theory (DFT) and total energy calculations that hydrogen acts like a shallow donor,^{172,173} in both interstitial and substitutional forms. Under certain conditions, cation vacancies form hydrogenated complexes that give rise to distinct O-H vibrational modes. King et al.¹⁸² performed muon-spin rotation and relaxation spectroscopy to understand the electrical nature of muonium (a hydrogen counterpart) and demonstrated hydrogen to be a shallow donor in Ga₂O₃ and an important source of n-type conductivity. Furthermore, Wei et al.¹⁸³ used a computational approach to understand the stability of various $H-V_{Ga}$ vacancies in β -Ga₂O₃. Up to four hydrogen atoms can bind to a gallium vacancy, and calculations show that the higher number of hydrogens bound to a gallium vacancy, the more stable the vacancy complex. This is due to low formation energies and the gradual disappearance of transformation levels as the number of hydrogen atoms is increased in the vacancy complex. This suggests that interstitial H₂ would be harder to separate from the complex vacancy than interstitial H, while the gallium vacancy complex with four hydrogen atoms bound to it will have the largest concentration among all kinds of vacancies.



FIG. 7. Relaxed structures of H⁻ (left) and H⁺ (right) in β -Ga₂O₃. In the negative charge-state, the H forms a bond with the Ga₂ atom associated with the O vacancy, and two electrons are trapped in a deep defect state (blue isosurface). Reprinted with permission from Zimmermann *et al.*, Appl. Phys. Lett. **116**, 072101 (2020). Copyright 2020, AIP Publishing LLC.

Theory predicts that interstitial H (Hi) and H substituting at an oxygen site (HO) will behave as shallow donors, but H can also form complexes with other defects of both extrinsic and intrinsic type, passivating their electrical activity.^{162,172,173,185–191} Infrared spectroscopy measurements of gas-hydrogenated or ion-implanted β -Ga₂O₃ showed localized vibrational modes of O–H stretches originating from different H-related point defects, the most dominant one being a shifted gallium vacancy (V^{ib}_{Ga}) containing two H atoms (V^{ib}_{Ga}-2H), as shown schematically in Fig. 8.¹⁷⁷ Recent investigations using deep-level transient spectroscopy show that the concentration of the deep-level E2 defect associated with an intrinsic defect can be increased considerably by heat treatments in the presence of H under n-type conditions. This is important since E2 was shown to be the main defect limiting the performance of Ga₂O₃ metal-semiconductor field-effect transistors.^{126,127}

Islam *et al.*¹⁸¹ reported the observation of p-type conductivity, which could expand the application space of β -Ga₂O₃, and that was claimed to originate from H-related point defects created by specific sample treatments. Islam *et al.*¹⁸¹ reported changes in



FIG. 8. Illustration of the hydrogenated gallium vacancy. Missing Ga(I) atoms are indicated by dashed circles. Reprinted with permission from M. D. McCluskey, J. Appl. Phys. 127, 101101 (2020). Copyright 2020, AIP Publishing LLC.

electronic properties of β -Ga₂O₃ associated with hydrogen incorporation by particular chemical and heat treatments of the material. Their results have led them to conclude that the trapping of two H atoms at a Ga(1) vacancy leads to p-type behavior, while subsequent n-type behavior is the result of the trapping of four H atoms at Ga(1) vacancy. They support these conclusions by using DFT to calculate the binding energies of one, two, three, and four H atoms at Ga(1) vacancy. Polyakov *et al.*^{187,188} reported that the electrical properties of plasma-hydrogenated n-type β -Ga₂O₃ single crystals are radically different depending on the crystal surface orientation. One potential explanation is differences in the fundamental diffusion properties of H along the different crystallographic directions.

Nickel and Gellert¹⁷⁸ reported a study of hydrogen diffusion in β -Ga₂O₃ and from the concentration-depth profiles obtained from SIMS measurements, the diffusion coefficients for H and D were estimated to be 2.6×10^{13} and 2.0×10^{13} cm² s⁻¹, respectively. Gas effusion measurements revealed that the effusion rates for H₂, HD, and D₂ were comparable, with maximum values of dN/dt = 2.9×10^{13} , 2.0×10^{13} , and 5.1×10^{13} cm⁻² s⁻¹, respectively. In combination with the concentration-depth profiles, the data provide clear evidence for monatomic H and D diffusion in β -Ga₂O₃.

Fowler *et al.*¹⁷⁷ reported that the absence of experimental evidence for H centers with multiple H atoms trapped at an unshifted Ga(1) vacancy could mean there were no defects with three or four H atoms, although there is evidence for their existence in the Varley configuration. Despite their energetic favorability, three- and four-H defects may not occur in the unshifted configuration.¹⁷⁷ The experimental evidence for the absence of two-H defects in the unshifted configuration and the corresponding robustness of the Varley and Kyrtsos structures for two-H defects suggests that subsequent H trapping will continue to decorate these shifted configurational H atoms to reach their lowest-energy configurations within an unshifted Ga(1) vacancy.

Reinertsen *et al.*¹²⁷ and Weiser *et al.*¹⁷⁹ found that hydrogen diffusion was both anisotropic and trap-limited in bulk crystals.



Concentration-depth profiles of ²H-implanted single crystals show that 2H can diffuse along the direction perpendicular to the (010) surface at temperatures as low as 300 °C, whereas diffusion along the direction perpendicular to the (-201) surface occurs only around 500 °C. For both directions, the evolution of the 2H concentration-depth profiles after heat treatments can be modeled by trap-limited diffusion (TLD).^{127,179} The traps were found to be present in the as-received crystals or created during ion implantation. Comparison of the experimentally obtained binding energy for 2H to the trap (2.3 eV) with the calculated binding energies suggests that intrinsic point defects (e.g., V_{iGa}) or defect complexes (e.g., V_{Ga}, and V_{O2}) are likely candidates for the trap.^{127,179}

Ahn *et al.*¹⁷⁵ reported on the diffusion properties of hydrogen in β-Ga₂O₃. Deuterium (²H) was used to provide high detection sensitivity during SIMS profiling to determine the thermal stability and migration of both ion implanted $(100 \text{ keV}, 10^{15} \text{ cm}^{-2})$ or plasma diffused (100-270 °C for 0.5 h) 2H in single-crystal β -Ga₂O₃, as a function of post-annealing temperatures. Annealing at 650 °C removed 90% of the implanted deuterium, while the incorporation via plasma exposure at 270 °C occurred to a depth of 0.68 μ m with a diffusion coefficient of 6.4×10^{-13} cm²/V s.¹⁸⁰ The plasma did not create damage at the depths where the 2H is incorporated, in contrast to the case of ion implantation and thus it was possible to isolate the role of implant damage in the redistribution of hydrogen. Outdiffusion in the case of ion implanted deuterium in Ga₂O₃ is controlled by trapping at residual damage, whereas in the case of deuterium incorporated by plasma exposure, the outdiffusion is dominated by the formation of deuterium molecules.¹

B. Fluorine

Fluorine has an important role in compound semiconductors because of the reduction in carrier concentration in InAlAs/InGaAs heterojunction FETs and High Electron Mobility Transistors (HEMTs).^{192–199} Wakejima *et al.*¹⁹⁴ noted partial recovery of the two-dimensional electron gas concentration (Ns) during the annealing and donor compensation in heterojunction FETs with modulation-doped structures. The compensation effect is due to the thermally activated diffusion of fluorine into the Si-doped InAlAs layer. To overcome this degradation, annealing in ultrahigh vacuum conditions while purging the fluorine is performed and has become a frequently used method in AlInAs/GaInAs device fabrication.^{192–199}

Experiments on step-doped InAlAs layers found that the fluorine moves through the intrinsic InAlAs layer and collects in the following n-InAlAs layers, and that this accumulation depends upon the Si doping concentration. Wakejima *et al.*¹⁹⁴ developed a model for the Si-doping dependent accumulation of F atoms by considering fractions of F as free and bound, similar to that in other semiconductors.^{200–203} The thermally activated fluorine diffusion and the high electronegativity of fluorine atoms have been used to control the threshold voltage in both AlInAs and AlGaN/ GaN HEMTs.^{192–199} Fluorine plasma treatment incorporates the negatively charged fluorine ions into the AlGaN barrier which results in a positive threshold voltage shift. CF₄ plasma exposure is used to insert the F.

Konishi *et al.*⁷⁹ fabricated field-plated β -Ga₂O₃ Schottky barrier diodes (FP-SBD) with a high breakdown voltage while also

achieving a higher than normal barrier height of 1.46 eV. This was attributed to the fluorine incorporation via hydrofluoric acid treatment prior to metal deposition. The fluorine atoms tend to bind to the semiconductor surface during an HF solution process, while the fluorine atoms also tend to diffuse into the material during the subsequent annealing. Similar to the behavior of fluorine in AlInAs and AlGaN/GaN HEMTs, the highly reactive F tends to react with the ionized donor species (Si) forming neutral complexes or acts as a negative ion to compensate the n-type doping, and further causes surface depletion.

C. Simulation framework

FLOOPS has been successful in modeling the diffusion and impurity migration in traditional silicon technologies.²⁰⁴ For deuterium incorporation, previous studies have reported that only 12% of the implanted deuterium remains in the samples after annealing at 650 °C, while the diffusivity of plasma incorporated deuterium at 270 °C was 6.4×10^{-13} cm⁻². The model used to simulate the 2H diffusion during post-implant annealing is based on the motion of free deuterium and trapping of some of those species at residual implant-induced damage (trapped deuterium) and also the association of atomic deuterium into molecular deuterium. The trapping on the damage sites can be represented by the following equation for the recombination rate R, which relates the atomic deuterium concentration, implant damage sites, and the deuterium trapped at these sites,

$$R = (K_T^2 HV) - (K_R T),$$
 (1)

where ²H is the mobile deuterium concentration, V is the vacancy concentration associated with the residual implant damage, K_T is the capture/trap rate of deuterium on these damage sites, K_R is the release rate of hydrogen from damage sites, and T is the concentration of trapped deuterium on vacancy sites.

The associated damage equations, which assume mobile vacancies and mobile interstitials, are

$$\left(\frac{dVac}{dt} - D_{Vac}\frac{d}{dx}\frac{dVac}{dx} + R + K_{DA}(V - Ev)(I - Ev) = 0\right), \quad (2)$$

$$\left(\frac{dInt}{dt} - D_{Int}\frac{d}{dx}\frac{dInt}{dx} + K_{DA}(V - Ev)(I - Ev) = 0\right), \qquad (3)$$

where D_{Vac} is the vacancy diffusivity, D_{Int} is the interstitial diffusivity, K_{DA} is the rate of damage annealing, I is the interstitial concentration, and Ev is the equilibrium damage concentration after implantation as evaluated by the software Stopping and Range of Ions in Matter (SRIM).²⁰⁵ SRIM predicts the damage (vacancy and interstitial concentrations) after ion implantation, i.e., the concentration of damage sites (vacancies) (and/or interstitials) at an equilibrium stage in the reaction. The damage concentration is the final temperature dependent value – after all Frenkel pair recombination occurs, then we have the equilibrium. Therefore, the initial condition of damage is computed by SRIM.

The time rate of change of concentration of the mobile deuterium which can diffuse, be trapped, and subsequently released or



outgas immediately at the surface, is given by

$$\frac{d^2H}{dt} - D_D \frac{d}{dx} \frac{d^2H}{dx} + R = 0, \qquad (4)$$

where D_D is the deuterium diffusivity.

The boundary conditions at the Ga_2O_3 surface, where the reaction rate is assumed to be large (10^6 s^{-1}) , based on previous results for semiconductor surface-dominated reactions) are

$$H_2$$
 gas boundary condition: $K_S^2 H$, (5)

Vac gas equation:
$$1.0 \times 10^6 (Vac - Ev) = 0$$
, (6)

where K_S is the surface outgas rate of ²H.

Finally, the change in trapped deuterium concentration as a function of time (which increases when mobile atoms are captured and decreased when these are released) is given by

$$\frac{\mathrm{dT}}{\mathrm{dt}} - \mathbf{R} = \mathbf{0}. \tag{7}$$

The model used to simulate the outdiffusion of the species incorporated by plasma exposure involves the possibility of the formation of a dimer of the species.^{170,173} For both the deuterium and fluorine incorporated samples there is a high-concentration nearsurface population, which may be due to molecular deuterium or fluorine. Some of the equations used to simulate the plasma incorporated ²H diffusion are similar to the case of ion-implanted deuterium diffusion (surface outgassing via Neumann boundary condition); however, in the absence of lattice damage and associated point defects, the outdiffusion is mediated through (deuterium or fluorine) molecule formation. Due to the absence of this damage layer, the damage equations and the trapped species equations were omitted from this model. We also note the plasma exposure itself created defects that alter the barrier height, but these are restricted to the very near-surface region $(\ll 0.1 \,\mu\text{m})^{206,207}$ and they do not affect the motion of hydrogen at much deeper depths. The dominant reaction is now

$$S + S \rightleftharpoons S_2$$
, (8)

where S is the diffusing species concentration and S_2 is the dimer molecule concentration.

The overall reaction rate is given by

$$Rc = K_{for}[S^2] - K_{rev}[S_2], \qquad (9)$$

where $K_{\rm for}$ is the forward reaction rate and $K_{\rm rev}$ is the reverse reaction rate.

The species rate equations are given by

$$\frac{\mathrm{dS}}{\mathrm{dt}} - \mathrm{D}_{\mathrm{D}}\frac{\mathrm{d}}{\mathrm{dx}}\frac{\mathrm{dS}}{\mathrm{dx}} + \mathrm{R} + \mathrm{Rc} = 0, \tag{10}$$

$$\frac{\mathrm{dS}_2}{\mathrm{dt}} - \mathrm{Rc} = 0. \tag{11}$$

IV. FITTING TO EXPERIMENTAL DATA

A. Ion implanted deuterium

Figure 9 shows the experimental SIMS profile of the ionimplanted deuterium before and after the subsequent annealing at 450–650 °C. The as-implanted ²H profile has a peak concentration at 0.85 μ m. As the samples are annealed, the deuterium starts migrating towards the surface, with both an increasing loss of ²H through the surface and trapping of deuterium atoms on residual implant damage. This mechanism is similar to that observed in deuterium implanted GaN.²⁰³ The simulations using the trapped deuterium model give fits that accurately reproduce the experimental data. The rapid outdiffusion behavior suggests that stable, slowdiffusing H₂ molecules or larger clusters do not form in Ga₂O₃ during the annealing of implanted deuterium. The results are



FIG. 9. (a) SIMS profiles of ²H-implanted into Ga_2O_3 (100 keV, 10¹⁵ cm⁻²) before and after annealing at different temperatures (5 min anneals). (b) Experimental and fitted data from these implanted samples after annealing at 450,550, or 650 °C.

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consistent with an implant-damaged trap-controlled release of ${}^{2}\text{H}$ from the Ga₂O₃ lattice at 650 °C. All the parameters show an Arrhenius behavior. The following equations are used to complete the parameter extraction:

$$k = A e^{\frac{k_A}{-RT}},$$
 (12)

where k is the rate constant (or diffusion coefficient), A is the preexponential factor, E_A is the activation energy, R is the universal gas constant, and T is temperature.

Another useful form of the Arrhenius equation is used to relate the rate constants at two different temperatures

$$\ln\frac{k_1}{k_2} = -\frac{E_A}{R} \left(\frac{1}{T_2} - \frac{1}{T_2}\right),$$
(13)

where k_1 and k_2 are the rate constants at temperatures T_1 and T_2 , respectively. The above equation can further be transformed to eliminate the activation energy and gas constant and to achieve the correlation between three rate constants at three different temperatures,

$$\frac{T_3(T_1 - T_2)}{T_3(T_1 - T_2)} = \frac{\ln \frac{k_1}{k_2}}{\ln \frac{k_1}{k_3}},$$
(14)

where k_1 , k_2 , and k_3 are the respective rate constants at temperatures T_1 , T_2 , and T_3 . The Arrhenius plots of all the parameters were also produced from this model, with the parameters derived from Arrhenius-relationship-based calculations. Deuterium, vacancy, and interstitial diffusivities show respective activation energies of 1.22, 4.97, and 1.73 eV, respectively, and the figure shows the Arrhenius plots of these diffusivities.

Detailed fits to the diffusion of implanted ²H are shown in Figs. 10 and 11.¹²⁷ The former shows data for a (-201)-oriented β -Ga₂O₃ sample implanted with ²H after 30-min heat treatments between 350 and 600 °C. The solid curves are fits to the data using the TLD model. The activation energy for diffusion is found to be 1.9 eV. Figure 11 shows the data for a (010)-oriented sample implanted with ²H after 30-min heat treatments between 300 and 575 °C and also the ²H profiles for the same (010) sample shown in (a) after a second ²H implantation (energy = 1.1 MeV, fluence = 2×10^{15} cm⁻²) and subsequent heat treatments between 300 and 355 °C. Fits for each temperature using the TLD model are shown as solid curves. The concentration of V_{Ga} generated by the ²H implantation was simulated using SRIM (dashed blue curve) and assumes that 2% of the vacancies do not annihilate.

B. Plasma incorporated deuterium

Indiffusion is done without the formation of the deuterium molecule as the temperature is low and the formation of deuterium molecules $(^{2}H_{2})$ is negligible. We assumed $^{2}H_{2}$ has a high formation rate at 400 °C, which affects the deuterium diffusion through the sample. Figure 12 shows the experimental data of SIMS profiles of deuterium incorporated into Ga₂O₃ by plasma exposure at three different temperatures. An earlier study has been done to fit the



FIG. 10. ₂H concentration-depth profiles (unfilled points) for a (-201)-oriented β -Ga₂O₃ sample implanted with ²H (energy = 200 keV, fluence = 4 × 10¹⁵ cm⁻²) after 30-min heat treatments at selected temperatures between 350 and 600 °C. The solid curves are fits to the data using the TLD model. Inset: Arrhenius plots of the ²H diffusivity (left axis) and trap dissociation rate (right axis) determined from TLD fits at each temperature. Linear fits (solid lines) were used to determine the thermal activation energies and prefactors for ²H diffusion and trap dissociation, respectively. Reprinted with permission from Reinertsen *et al.*, Appl. Phys. Lett. **117**, 232106 (2020). Copyright 2020, AIP Publishing LLC.

indiffusion of the deuterium in Ga_2O_3 based on a conventional Fickian approach by using the FLOOPS code and an activation energy for the diffusion of ~0.3 eV is found. The outdiffusion is modeled using the molecule formation mechanism. Figure 12 shows the SIMS profiles for the plasma diffused deuterium for indiffusion at 200 °C (a) and outdiffusion after annealing at 400 °C (b), along with the respective simulations for these conditions shown by the fitted lines to the data curves.

C. Plasma incorporated fluorine

Figure 13 shows the experimental SIMS profiles of F in Ga₂O₃ exposed to a CF₄ plasma, and also the profiles after subsequent annealing for temperatures ranging from 300 to 500 °C. Compared to fluorine diffusion in AlInAs it is observed fluorine behaves differently in Ga₂O₃. In the former case, the F diffuses further into the AlInAs.¹⁸⁸ In the case of Ga₂O₃, there is a high-concentration near-surface population, which may be due to molecular fluorine, F₂, since there is no indication that such a high concentration of this impurity is charged. Similar to the plasma incorporated deuterium model, the fluorine outdiffusion is mediated through F₂ formation. Even though the plasma exposure itself created defects that altered the barrier height, these are annealed out before the bulk of the fluorine begins to out-diffuse.

Figure 13 shows the fitted simulated profiles to the experimental SIMS profiles for samples annealed at 300, 400, and 500 °C. The activation energy for diffusion was obtained by fitting the



FIG. 11. (a) ²H concentration-depth profiles (unfilled points) for a (010)-oriented β -Ga₂O₃ sample implanted with ²H (energy = 200 keV, fluence = 5 × 10¹⁴ cm⁻²) after 30-min heat treatments at selected temperatures between 300 and 575 °C. (b) ²H concentration-depth profiles (unfilled points) for the same (010)-oriented sample shown in (a) after a second ²H implantation (energy = 1.1 MeV, fluence = 2 × 10¹⁵ cm⁻²) and subsequent heat treatments between 300 and 355 °C. Fits for each temperature using the TLD model are shown as solid curves. The concentration of V_{Ga}s generated by the ²H implantation was simulated using SRIM (dashed blue curve) and assumes that 2% of the vacancies do not annihilate. Reprinted with permission from Reinertsen *et al.*, Appl. Phys. Lett. **117**, 232106 (2020). Copyright 2020, AIP Publishing LLC.

experimental data at the different annealing temperatures, as shown in the figure, with a value of 1.23 eV. The forward and reverse reaction rates, K_{for} and K_{rev} , were also fitted to the data and followed Arrhenius dependence with temperature, as shown in Fig. 14 with values of 1.24 and 0.34 eV, respectively.

The simulation results of the amount of fluorine remaining at each annealing temperature showed a slightly skewed fit to the F retention data at each annealing temperature due to the likely presence of retrapping; however, the fit provides a good estimate of the activation energy needed for outgassing of the high near-surface fluorine, 1.24 eV. The activation energy for outgassing of fluorine is quite similar to the value reported for outgassing of deuterium (~1 eV), The activation energy of fluorine diffusion and the thermal activation energy of the surface outgas rate are in principle the same. It is possible that the latter is smaller than the diffusion activation energy and that the outgas rate is determined by the diffusion process.

D. N-type dopant diffusion

1. Diffusion during ion implantation doping

The preferred method of selective doping in semiconductor devices has for decades been ion implantation, because of the accurate control of the impurity profiles which results in small device footprint. Ion implantation in Ga_2O_3 has been used primarily to produce heavily doped source and drain regions using Si.^{208–210} However, the earliest study done on electrically active impurities in a Ga_2O_3 crystal was performed by Peter and Schawlow,²¹¹ who showed the substitution of Cr^{3+} ions on the G_a^{3+} octahedral sites.



FIG. 12. (a) SIMS depth profile of the experimental deuterium concentration in plasma diffused deuterium for indiffusion at 100, 200, or 270 °C. (b) SIMS and FLOOPS simulator fits for indiffusion at 200 °C and subsequent outdiffusion at 400 °C.

A lot of the initial work focused on Si and Sn diffusion in Ga_2O_3 after incorporation via ion implantation. Another approach has been used by Zeng *et al.*²¹² with a spin-on-glass doping process (Sn) on Ga_2O_3 power MOSFET. A Sn concentration of 4×10^{21} cm⁻³ was achieved after a 5-min drive-in anneal at 1200 °C. The diffusion was modeled based on the diffusion of metals in silicon dioxide,²¹³ which involves a simple exponential function and an interstitial diffusion model. Zeng *et al.*²¹² used this diffusion model to fit profiles to the experimental SIMS profile and extracted activation energy of 4.2 eV for the diffusion of Sn.

Sasaki *et al.*²⁰⁸ performed the first Si ion implantation on β -Ga₂O₃ substrates, using a 10–175 keV energy range and achieving Si concentrations of 10^{19} – 10^{20} cm⁻³. After the implantation, annealing at temperatures (700–1100 °C) was performed in an N₂ atmosphere. The activation efficiency was 80%, i.e., 80% of the

FIG. 13. SIMS profiles of F in Ga_2O_3 exposed to CF_4 plasmas for 20 min and then subsequently annealed in the range 300–500 °C. Reprinted with permission from Yang *et al.*, J. Appl. Phys. **123**, 165706 (2018). Copyright 2018, AIP Publishing, LLC.

implantation dose was subsequently activated as a n-type charge carrier (as revealed by CV measurements to obtain N_D-N_A). A discrepancy is observed in the rate of diffusion of various impurities highlighted by Sasaki *et al.*²⁰⁸ where the authors observe no significant Si diffusion in a UID Ga₂O₃ substrate annealed up to 1100 °C, and also highlighted by Wong *et al.*²⁰⁹ where a significantly high diffusion of Fe from the Ga₂O₃:Fe substrates into the MBE grown epilayer.

Wong *et al.*²⁰⁹ confirmed the above discrepancy by performing Mg and N (acceptors) implantation to realize the possibility of current aperture vertical transistors. The authors reported significantly higher Mg diffusivity as seen in Fig. 15(a), compared to the diffusivity of nitrogen. Figure 15(b) shows that even at a low annealing temperature of 800 °C there is substantial redistribution of Mg whereas at annealing temperatures of above 1100 °C the implanted N is very stable, demonstrating the high activation efficiency of implanted N.

The success in implantation doping can be used to realize acceptor doping in Ga_2O_3 samples with intrinsically low freeelectron concentrations. Both nitrogen and magnesium are very useful acceptors in Ga_2O_3 to achieve highly resistive regions for the purpose of guard rings and edge termination.

2. Simulation framework

The model used to simulate the diffusion of various impurities implanted into Ga_2O_3 is based on Fickian diffusion, the influence of vacancies and interstitials, and the trapping and releasing of dopant atoms on damage sites created by the implantation.²¹⁰

The differential equations in the model are the same as in the model described earlier for deuterium/fluorine atom diffusion. The experimental SIMS profiles also suggest the possibility

FIG. 14. Arrhenius plots of diffusivity (a) and forward and reverse reaction rates (b) for F in Ga₂O₃. Reprinted with permission from Yang *et al.*, J. Appl. Phys. **123**, 165706 (2018). Copyright 2018, AIP Publishing.

of concentration-dependent diffusion, which is reflected by the box-type profiles and has been incorporated into our model by the following equation:

$$D_o = [D + (D_D.C)],$$
 (15)

where D is the diffusing species diffusivity, D_D is the concentration-dependent diffusion coefficient, C is the species concentration, and Do is the concentration-dependent diffusivity.

Tadjer *et al.*^{214,215} reported on the effect on the conductivity of $(-201) \beta$ -Ga₂O₃ single-crystal substrates when the samples were

FIG. 15. Mg in Mg⁺-implanted Ga₂O₃ (a) and N and Si in N⁺-implanted Ga₂O₃ (b). At temperatures of ~900 °C, substantial Mg diffusion was observed, whereas no N diffusion at temperatures >1100 °C. Reprinted with permission from Wong *et al.*, Appl. Phys. Lett. **113**, 102103 (2018). Copyright 2018, AIP Publishing LLC.

annealed in an O_2 or an N_2 ambient. In Raman spectroscopy, only the N_2 annealed samples exhibited a carrier concentrationdependent vibrational mode at 254 cm⁻¹, and the main defect contributing to this vibrational mode is possibly the gallium vacancy (V_{Ga}), a deep acceptor. Other possible defects that could contribute to the Raman phonon mode are N-related deep donor defects like N_{Ga} , N_O-V_O complex, Ni, as well as oxygen vacancy (V_O).

The effect of the annealing ambient has also been observed in earlier studies where a much greater redistribution is observed with samples annealed in an O_2 ambient compared to annealing in a N_2 ambient. In the N_2 ambient anneals, more Ga vacancies may be created, enabling interstitial dopant species to migrate onto a substitutional Ga site where it has a low diffusivity. From the experimental SIMS profile, it is seen that the N_2 ambient also suppresses the loss of the diffusing species to the surface. This has been represented by the equation

Vac gas equation:
$$K_{Vout}(V - E_V) - K_{Vin} = 0$$
, (16)

where K_{Vin} is the surface influx rate for the vacancies and K_{Vout} is the surface outgas rate for the vacancies. The simulations are done considering the vacancy/defect concentration as the important factor for the difference in the O₂ and N₂ annealing ambients.²¹⁶

3. Simulated fits to experimental profiles

All the samples were unintentionally doped EFG Ga₂O₃ substrates with no epitaxial layer grown, and a room temperature carrier concentration of $1-2 \times 10^{17}$ cm⁻³ and (-201) orientation.^{210,217} The samples were implanted with Si, Sn, or Ge nominally at room temperature with a 7° tilt with respect to the beam normal, while the specific implantation conditions with Si to get the 10^{20} cm⁻³ average doping concentrations were 3×10^{14} cm⁻²/30 keV + 7×10^{14} cm⁻²/60 keV + 10^{15} cm⁻²/120 keV. The doses were reduced by 1 or 2 orders of magnitude, respectively, to get 10^{18} or 10^{19} cm⁻³ doping profiles, while the annealing was performed at 1150 °C for 60 s.

The fits achieved by the FLOOPS simulator to the experimental profiles of Si implantation, fits achieved were accurate. The extracted diffusion coefficients at 1150 °C are given in Table IV.

a. Effect of annealing ambient. The Si implanted were subsequently annealed for 10–120 s in either O_2 or N_2 ambients. There was a clear difference in the redistribution of the Si as a result of these different ambients, which emphasize the effect of the point defect population present in the near-surface area. Figure 16 shows a summary of the experimental profiles for the three different dose conditions and two different annealing ambients.²¹⁰ The experimental results clearly show that the samples annealed in O2 display much greater redistribution than those annealed in N2, although the box shape profile developed for the highest dose sample annealed in N2 is an indicator of concentration-dependent diffusion. There is a greater loss of Si to the surface when annealed in O2, and the diffusion distance is well beyond the range of the implanted Si ions and therefore the defects assisting Si transport are highly mobile at 1100 °C, as shown in Fig. 17. In the simulations, the highest dose ($\sim 10^{15}$ cm⁻³) has been ignored due to the inconsistency in the diffusion mechanism and the possible presence of an interface between two phases of Ga₂O₃.

Figures 18–21 show the same type of simulation results compared with the experimental profiles for Ge and Sn, for annealing in O_2 or N_2 for two dose conditions, i.e., 10^{13} cm⁻² and 10^{14} cm⁻², respectively. Note there is diffusion into the bulk of the sample and significant loss of the dopant from the surface. The diffusion simulations were done considering the vacancy/defect concentration as the important factor for the difference in the O_2 versus N_2 annealing ambients. As the total vacancy influx rate is increased, we see a rise in the total vacancy population. Since the mobile dopants are

TABLE IV. Summary of fitting parameters obtained from FLOOPS for annealing of Sn, Ge, and Si in O₂ ambients at 1150 °C.

Parameters/rates	Sn	Ge	Si
Diffusivity $(cm^2 s^{-1})$	2.7×10^{-13}	1.1×10^{-11}	9.5×10^{-13}
Trap rate on damage sites (s^{-1})	8.0×10^{-16}	8.0×10^{-16}	8×10^{-16}
Release rate (s^{-1})	1.2	1	1
Vacancy diffusivity $(cm^2 s^{-1})$	2.0×10^{-8}	$7.0 imes 10^{-8}$	10^{-8}
Surface outgas rate (s^{-1})	1.3×10^{-7}	7.0×10^{-7}	8×10^{-8}
Concentration-dependent diffusion $(cm^2 s^{-1})$	3.5×10^{-30}	2.0×10^{-30}	8.0×10^{-31}
Vacancy inflow rates $(cm^2 s^{-1})$			
O ₂ ambient	10^{10}	4×10^{10}	2×10^{10}
N ₂ ambient	2×10^{15}	7×10^{15}	5×10^{15}

experimentally observed to be trapped at these vacancies for N_2 anneals, they are presumably V_{Ga} . Use of the N_2 annealing ambient should supply more V_O into the Ga_2O_3 , but the high migration energy of V_O means they are less effective than V_{Ga} in determining the site occupation of the Si and the reduced migration of the Si results in higher retained concentrations.^{210,217} The O_2 ambient does not supply as many of these defects into the sample, hence causing the Si to diffuse out without getting trapped. Naively, one would expect O_2 anneals to favor more V_{Ga} relative to V_O and hence less diffusion of the potential energy surface and hence migration paths of V_O and V_{Ga} in monoclinic Ga_2O_3 , which enables them to use alternative routes even at low temperatures and that

some paths are redundant for defect migration towards a certain direction. At this stage, we cannot differentiate the charge state of the V_O (neutral or 2+) or V_{Ga} (neutral, 1–, 2–, or 3–) species that control the migration and site occupation of the Si, but it is more likely that V_{Ga} are the defects assisting migration since their concentration rises with O₂ annealing and they have lower migration energies than oxygen vacancies.^{125,216}

The vacancy concentration for the N₂ annealed samples is found from simulations to be higher than for O₂ annealing. The Si diffusivity stays constant at ~4.5 × 10⁻¹² cm² s⁻¹ for both doses while the Si outgas rate shows a slight increase from 10⁻⁷ cm⁻² s⁻¹ for 10¹³ cm² dose to 3×10^{-7} cm⁻² s⁻¹ for 10¹⁴ cm⁻². Furthermore, while modeling the vacancy inflow and outflow, K_{Vout} is set to be a constant and the vacancy outflow rate has a concentration dependence while the influx rate K_{Vin} varies for the two ambients. For the N₂ ambient,

FIG. 16. Compilation of SIMS profiles of Si implants in Ga_2O_3 annealed at 1100 °C for 120 s, as a function of dose and annealing ambient. Reprinted with permission from Sharma *et al.*, AIP Advances **9**, 085111 (2019). Copyright 2019 Author(s), licensed under a Creative Commons License.

FIG. 17. Experimental and simulated percentages of Si remaining after 1100 °C anneals in either O₂ or N₂ for ~10¹⁴ cm⁻² Si-implanted Ga₂O₃. Reprinted with permission from Sharma *et al.*, AIP Advances **9**, 085111 (2019). Copyright 2019 Author(s), licensed under a Creative Commons License.

FIG. 18. SIMS profiles of implanted Ge (10^{13}) as a function of the anneal time at 1100 °C.

high values for the K_{Vin} are observed $\sim 10^{15}$ cm⁻² s⁻¹, while for the O_2 ambient low values below 10^{10} cm⁻² s⁻¹ are observed. In previous simulations, we assumed that the Si diffusivity and outgas rate would have a dose dependency; however, after incorporating the vacancy dependence, the diffusivity loses the dose dependency and stays constant but the Si outgas rate is seen to have a slight dose dependence based on the new simulations.

Figure 17 shows the experimental and simulated retained fractions relative to the as-implanted value for the 10^{14} cm⁻² dose. Similar data for the lower dose has been obtained. The samples annealed for 120 s in the O₂ ambient result in a 23.1% loss of Si for the 10^{13} cm⁻² dose and 34% loss of Si for the 10^{14} cm⁻² dose. By sharp contrast, annealing for 120 s in the N₂ ambient result in a 5% loss of Si for the 10^{13} cm⁻² dose and 8.2% loss of Si for the 10^{14} cm⁻² dose.

The Sn implantation conditions were the same as for the Si implantation, i.e., a 7° tilt for the implantation, and specific conditions

FIG. 19. SIMS profiles of implanted Ge (10^{13}) as a function of anneal ambient at 1100 °C.

FIG. 20. SIMS profiles of implanted Sn (10^{13}) as a function of the anneal time at 1100 °C.

of 3×10^{12} cm⁻²/30 keV + 7×10^{12} cm⁻²/60 keV + 10^{13} cm⁻²/120 keV for average doping concentrations of 10^{18} cm⁻³, while the doses were increased by 1 or 2 orders of magnitude to achieve 10^{19} and 10^{20} cm⁻³ average concentrations. The samples were annealed for 60 s at 1150 °C. The temperature of the anneals is decided by the 2/3 rule for implant activation annealing, as the melting temperature for Ga₂O₃ is 1790–1820 °C, annealing temperatures in the range 1150–1250 °C are considered to achieve significant activation percentages.

Figure 18 shows the fit to the experimental SIMS profiles of the Ge implantation, showing the as-implanted curves, with the experimental and fitted profiles after annealing. The fits achieved are accurate for the Ge profile, and clearly display a box-type diffused profile after the annealing. The mechanism behind the diffusion has been discussed earlier, where a concentration-dependent diffusivity has been considered. The parameters have been listed in Table IV.

FIG. 21. SIMS profiles of implanted Sn (10¹³) as a function of anneal ambient at 1100 °C.

As discussed earlier for Si diffusion, a high redistribution of Ge was found for samples annealed in the O_2 ambient and a low redistribution when annealed in the N_2 ambient. Figure 19 shows the experimental profiles as well as the simulated fits of as-implanted Sn, and when the samples annealed for 10, 30, and 120 s at 1100 °C. Utilizing the diffusion model for ion implanted samples annealed in an O_2 ambient, accurate fits have been achieved using the FLOOPS simulator.

The simulated fits of the Sn profiles are shown in Fig. 20 where a diffusivity of 2.7×10^{-13} cm s⁻¹ is assumed based on the previous simulation and then iterated to achieve the best fit to the experimental profile. The difference in diffusivity values are primarily because of different implantation conditions and slightly different annealing temperatures. Other important fitting parameters are summarized in Table IV, like the vacancy diffusivity, trap, and release rates at the damage sites and surface outgas rates. The difference between the ion-implanted pre-anneal damage concentration and trapped Sn concentration is considered the equilibrium vacancy concentration and was obtained from the incorporation of SRIM data.

The contrast for the results obtained with annealing of Sn implants in an N₂ ambient is shown in Fig. 21 for the case of annealing at 1100 °C for 120 s. The figure shows the simulated fit to the experimental Sn profiles for annealing in N₂, as well as the total concentration of vacancies after annealing. The total vacancy concentration for annealing in N₂ is higher than for O₂ annealing, according to the simulations involving a vacancy inflow and outflow from the surface and an example is shown in the figure. The suppression of the Sn diffusion in N₂ is controlled by V_{Ga} .^{210,216,217} The results here emphasize the effect of the point defect population present in the near-surface region on the diffusion of the implanted dopants.

The results and trends for implanted Ge are similar to Sn, while the redistribution is even more pronounced than for Sn, as evidenced by the higher diffusivity of 1.1×10^{-11} cm s⁻¹ at 1100 °C. While Ge is a smaller atom than Sn and might be expected to diffuse faster, it is noted that the diffusivity is even faster than for Si under the same conditions $(4.5 \times 10^{12} \text{ cm s}^{-1})$, and that the size is not the only determining factor. The fit to the experimental data was not as accurate in this case, which may be due to a more pronounced concentration dependence of the diffusivity in the case of Ge. There is a higher concentration of vacancies present according to the simulations, and this may cause compensation on the end-of-range region profile.^{218–224}

V. SUMMARY AND CONCLUSIONS

The diffusion of two unintentionally incorporated impurities in Ga_2O_3 , namely, hydrogen and fluorine, has been studied for ion implanted and plasma exposed samples. Both of these impurities affect the near-surface conductivity and can act as a shallow donor (hydrogen) or cause compensation to n-type Si-doped samples (fluorine). The thermal stability of implanted or plasma diffused hydrogen (in the form of ²H isotope) in Ga_2O_3 has been examined. Annealing at 650 °C completely evolved hydrogen from the material in the case where it has been introduced by the ion implantation, and the release kinetics are dominated by trapping onto the damage sites. The activation energies of the various parameters used in the model have also been extracted. In the case of the introduction of deuterium or fluorine by exposure to plasma, the release kinetics are dominated by self-trapping to form molecules. The experimental data for fluorine were accurately fit by FLOOPS for three temperatures allowing the extraction of activation energies for diffusion, outgassing, and forward and reverse fluorine molecule rates.

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The ion implantation and the diffusion mechanisms during the subsequent annealing of Si, Ge, and Sn in Ga_2O_3 showed a concentration-dependent diffusion, with a dramatic effect of the annealing ambient on the diffusivity of the implanted species. All of these dopants display significant redistribution during the O_2 annealing and their atomic profiles could be accurately fitted to a concentration-dependent diffusion model and concentrationdependent diffusion.

There was significantly less diffusion for annealing in a nitrogen ambient as compared to an oxygen ambient. At this stage, electrical profiling experiments have not been performed to confirm the compensation effect of the gallium vacancies on the end-of-range region of the profiles. This is mainly because the control of impurities and defects in the starting material needs optimization, and spatial measurements of activation would likely not be reproducible. There was more rapid diffusion of Ge relative to Sn, and further studies are needed to explain the mechanism behind the Sn redistribution and the faster diffusion of Ge. The experimental profiles can be accurately fit with a model involving Fickian diffusion of mobile Si, Sn, or Ge, with trapping at vacancies, and loss to the surface. The model currently cannot differentiate between Ga and O vacancies in determining the diffusion enhancement, but since the donor species, i.e., Si, Sn, or Ge occupy Ga substitutional sites, we can assume that V_{Ga} is the controlling factor during N₂ anneal since the dopants are less mobile and are trapped at these vacancies.

There are still numerous areas that require further study, including the following:

- (i) The effect of strain from dielectrics and other patterned layers on the diffusivity of dopants and impurities.
- (ii) Is the diffusion of implanted dopants faster due to the presence of implant damage compared to dopants incorporated during epitaxial growth?²²⁵⁻²³⁴
- Quantification of the density of point defects injected under oxidizing anneal ambients and the mechanism for substitutional diffusion of dopants and also more accurate data for effective mass of carriers.²³⁵
- (iv) What are the optimum dopants for both n-type and semiinsulating regions based on solubility and diffusivity data and their effect on compensating point defects?^{236–242}
- (v) The effect of total dose and single event radiation on the diffusivities, especially under electrical bias, and how this affects the drift and diffusion of defects.^{243–249}
- (vi) What is the solid solubility of the dopants and is it anisotropic? Initial data on Sn show it occupying a substitutional Ga octahedral site in the 4+ charge state but also a significant fraction in the 2+ charge state.²³⁶
- (vii) Is transient-enhanced diffusion present in Ga2O3?
- (viii) Is there pairing between doubly charged vacancies and dopant atoms? In Si, the resulting mobile negatively charged

V-dopant complexes readily react with the positive substitutional donors due to the Coulomb attraction, causing an enhanced clustering.

- (ix) The stability of molecular forms of hydrogen and fluorine and their role in the effective diffusivity of the atomic species.
- (x) Does clustering of dopants occur at high concentrations, and, in general, what is the electrically active fraction of these dopants at different concentrations.
- (xi) What is the nature of the interaction between point and line defects, and how do the latter affect diffusivity?
- (xii) What models are needed to explain dopant profile shapes; enhanced dopant diffusion; and nonequilibrium effects caused by chemical reactions, immobilization, and reduced electrical activation of dopants via the formation of impurity phases and complexes with other impurities and the pileup of dopants at interfaces and surfaces?
- (xiii) How does diffusion phenomenon in β-Ga₂O₃ compare to that in the major polytype, α -Ga₂O₃?

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DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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