

Point defects in Ga_2O_3

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ABSTRACT

In the field of high-power electronics, gallium oxide (Ga_2O_3) is attracting attention due to its wide band gap and ability to be doped *n*-type. Point defects, including vacancies, impurities, and dopants, play important roles in optimizing device performance. This tutorial discusses the fundamental properties of point defects in monoclinic β - Ga_2O_3 and the methods employed to study them. Oxygen vacancies are deep donors that do not cause *n*-type conductivity but may compensate acceptors. Gallium vacancies are deep acceptors that can be partially passivated by hydrogen. Substitutional magnesium is a promising acceptor that produces semi-insulating material and also forms a complex with hydrogen. Calcium and iron also have deep acceptor levels. Iridium deep donors are introduced into crystals grown from a melt in an Ir crucible. Other defects are introduced by irradiation with energetic particles such as neutrons or protons. In addition to altering the electronic properties, defects give rise to UV/visible emission bands in photoluminescence and cathodoluminescence spectra.

I. INTRODUCTION

Gallium oxide (Ga_2O_3) is emerging as an important wide-band-gap semiconductor for power electronics. To develop Ga_2O_3 -based devices, dopants and defects must be understood and controlled. This tutorial gives an overview of point defects in this material and the methods used to investigate them. Ga_2O_3 has several crystal structures, the most stable of which is the monoclinic β phase. All discussions in this tutorial refer to $\beta\text{-Ga}_2\text{O}_3$ unless stated otherwise.

There is a growing body of literature in this area and only a representative sample is presented here. Interested readers are encouraged to consult review articles on materials and device issues by Higashiwaki et al.,¹ Stepanov et al.,² Pearton et al.,^{3,4} and Galazka,⁵ and a volume edited by Pearton, Ren, and Mastro.⁶ A review of “ultrawide” band gap semiconductors including Ga_2O_3 is given by Tsao et al.⁷ Focused reviews are available on Ga_2O_3 bulk growth,⁸ thin-film growth by sputtering,⁹ defects,^{10,11} and solar-blind photodetectors.¹² General information about semiconductor defects, growth, and characterization of semiconductors can be found in Ref. 13, and more details about defect characterization are in a volume edited by Tuomisto.¹⁴

A. Historical background

The once-separate topics of gallium oxide and semiconductor devices can trace their origins to the same decade. The existence of Ga_2O_3 was predicted by Mendeleev in 1871 and the element Ga was discovered a few years later.¹⁵ Around the same time, rectifying metal-semiconductor junctions were reported by Ferdinand Braun, a German high school teacher.¹⁶ Braun found that the current-voltage relationship was nonlinear, violating Ohm's “law.” The ability to pass current more freely in one direction than the other was important for radios.

However, “crystal radios” were unreliable because defects in crystals were not well understood or controlled. In the 1920s, vacuum tubes became the preferred option, while semiconductors such as germanium were the subject of basic research.

Work on germanium proceeded through the 1940s, culminating with the revolutionary Bell Labs inventions of the point-contact transistor and bipolar transistor.¹⁷ Silicon was developed seriously beginning in the 1950s. Its intrinsic advantages over germanium included its larger band gap (1.1 versus 0.7 eV) and ease of forming an insulating native oxide layer (SiO_2). This latter property was important for metal oxide semiconductor field effect transistors (MOSFETs) and integrated circuits.¹⁸

For widespread applications like computing, silicon is hard to beat. However, other applications require different levels of electrical power and voltage.¹⁹ Low-power / low-voltage (< 1 kW, <400 V) devices are common in consumer electronics. Mid-power / mid-voltage (1 – 100 kW, 400 V – 1.2 kV) applications include photovoltaic inverters and uninterruptable power supplies. High-power / high-voltage (>1 MW, >1.2 kV) systems are found in wind turbines and smart power grids. It is in the mid- to high-power space that Ga_2O_3 could make a major contribution. In particular, improving the efficiency of power devices is an important component of energy conservation.

B. Power electronics

An example of a Ga_2O_3 metal-semiconductor field effect transistor (MESFET) is shown in Fig. 1.²⁰ For this device, an *n*-type thin film was grown on a semi-insulating substrate. Free electrons travel from the source to the drain. When the gate is negatively biased (relative to the source), electrons are repelled and the depletion region under the gate widens. For sufficiently

negative gate voltage, the depletion width equals the thin-film width and current is effectively zero. The gate thus acts as an “on/off” switch that allows or prohibits current to flow. Consider the “off” mode, where current is blocked. For a large source-drain voltage, the electric field in the depletion region can get very high. If the maximum electric field exceeds a critical value, E_c , *electrical breakdown* will occur and current will flow.

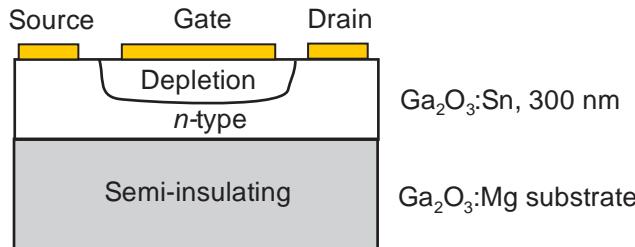


Fig. 1. Schematic diagram of a Ga_2O_3 MESFET.²⁰

For a power transistor, it is important to have a large critical breakdown field. One mechanism for breakdown is *tunneling*. At high electric fields, the conduction band (CB) and valence band (VB) tilt steeply, and it is possible for an electron to tunnel from the VB straight into the CB.²¹ In this way, current will flow even in a pure semiconductor. A second mechanism is *impact ionization*, where a carrier collides with an atom, generating an electron and hole. These free carriers then cause additional impact ionization events, leading to avalanche breakdown.

C. Benefits of a wide band gap

A large band gap E_g has a strong tendency to reduce the generation of free carriers and hence raise the critical field E_c . Ga_2O_3 , with its wide direct gap of 4.8 eV, has a distinct advantage in this regard. Empirically, for direct-gap semiconductors,²²

$$E_c = 1.73 \times 10^5 E_g^{2.5} \quad (1)$$

where E_c is in V/cm and E_g is in eV. Inserting $E_g = 4.8$ eV for Ga_2O_3 , Eq. (1) yields a predicted breakdown field of 8.7 MV/cm. This value is significantly higher than competitors such as GaN (3.5 MV/cm) and 4H-SiC (3.2 MV/cm). Experimentally, breakdown field strengths near 3.8 MV/cm in Ga_2O_3 MOSFETs were reported by Green et al.²³

Along with the critical field, an important design consideration is the power dissipated by the device. In the “on” state, the transistor should have low resistance R_{ON} . Baliga²⁴ proposed comparing devices with a fixed breakdown voltage. Given this constraint, a device made from a high- E_c material can be designed with a thin depletion region, which lowers R_{ON} . The Baliga figure of merit (BFOM) is defined²⁵

$$\text{BFOM} = \epsilon \mu E_g^3 \quad (2)$$

where ϵ is the relative dielectric constant and μ is the carrier mobility. This metric points toward a large-gap semiconductor with good carrier mobility. Ga_2O_3 satisfies both of these criteria, with a band gap of 4.8 eV and free-electron mobility of ~ 100 cm²/Vs at room temperature.²⁶

II. BASIC PROPERTIES

A. Crystal structure

$\beta\text{-Ga}_2\text{O}_3$ has a monoclinic crystal structure, denoted $C2/m$.²⁷ The unit cell is shown in Fig. 2, where $\mathbf{a} \perp \mathbf{c}$, $\mathbf{b} \perp \mathbf{c}$, and the angle between the \mathbf{a} and \mathbf{c} axes is 104° .²⁸ The lattice parameters are $a = 12.2$ Å, $b = 3.04$ Å, and $c = 5.80$ Å. There are two distinct Ga sites, labeled Ga(I) and Ga(II). The Ga(I) atoms are bonded to four neighboring O atoms in a (roughly) tetrahedral arrangement. The Ga(II) atoms are in an octahedral environment and bind to six neighboring O atoms. (Some of the bonds, which extend to atoms in neighboring unit cells, are not shown in Fig. 2). The O atoms have three distinct sites: O(I) and O(II) bind to three Ga atoms while O(III) binds to four

Ga atoms. There are four atoms of each type, for a total of $4 \times 5 = 20$ atoms in the unit cell (Fig. 2). The Ga–O bond lengths range from 1.8 to 2.1 Å.

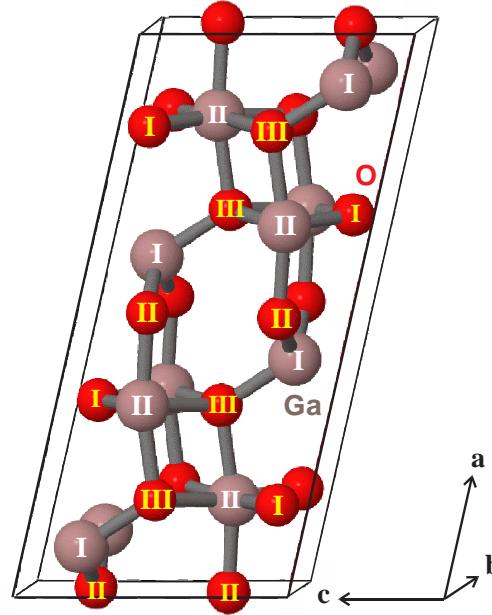


Fig. 2. Crystal structure of monoclinic β - Ga_2O_3 . Some of the bonds, which extend to atoms in neighboring unit cells, are not shown. Figure made using a #3Dview at <https://doi.org/10.1107/S0108270195016404> @ActaCrystC @IUCr.

B. Band structure

First-principles calculations show the conduction-band minimum (CBM) at the Brillouin zone center and a fairly flat VB (Fig. 3).^{29,30} Quasiparticle (GW) calculations indicate a direct band gap of 4.8 eV and indirect gap ~0.1 eV lower.³¹ This wide gap is key to its potential as a material for power electronics and has also been exploited for solar-blind detectors.³² The band gap can be estimated by measuring the transmission of light through the sample. Photon energies above the gap are able to excite an electron from the VB to the CB, leading to strong absorption. Optical transmission experiments show a room temperature band-gap absorption threshold near 4.8 eV (260 nm) or 4.5 eV (275 nm) for light polarized along the **b** or **c** axis respectively.^{33,34} This anisotropy has been explained in terms of selection rules for the VB-to-CB transition.^{35,36} A

detailed model of the absorption features is given in Ref. 37. In this paper, the band gap is taken to be 4.8 eV.

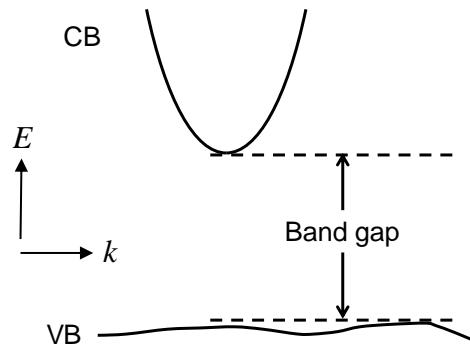


Fig. 3. Simplified band structure of Ga₂O₃. The minimum in the CB occurs at the zone center ($k = 0$). The indirect band gap is shown. After Ref. 31.

C. Free carriers

Electronic transport has been investigated with *Hall effect* and other electrical characterization methods.³⁸ For the Hall effect in the Van der Pauw geometry, four electrical contacts are placed on the sample on the corners of a square (Fig. 4). Current is sent through one pair of contacts while voltage is measured across the other pair. A magnetic field is applied perpendicular to the square. By measuring different contact-pair combinations, with and without magnetic field, one can obtain the free-carrier mobility, density, and type (electrons or holes). Unintentionally doped Ga₂O₃ is generally *n*-type with electron mobilities around 100 cm²/Vs.³⁹ First-principles calculations^{40,41} indicate that phonon scattering is the primary limiting factor for room-temperature electron mobility (<200 cm²/Vs).

Free electrons lead to *IR absorption* and a *Burstein-Moss shift* of the optical band gap. IR absorption is due to the electric field of the IR radiation accelerating electrons; i.e., Drude absorption. The Burstein-Moss shift occurs when there is a high density of electrons such that the

Fermi level lies within the CB. For Ga_2O_3 with a high free-electron density of 10^{20} cm^{-3} , the Fermi level is 0.2 eV above the CBM.⁴² Because the states are filled up to the Fermi level, the VB-to-CB transition shifts to higher energy. The electron effective mass, calculated from the curvature of the CB, is $0.28m$ for low doping and $0.36m$ at high electron density, where m is the fundamental electron mass.

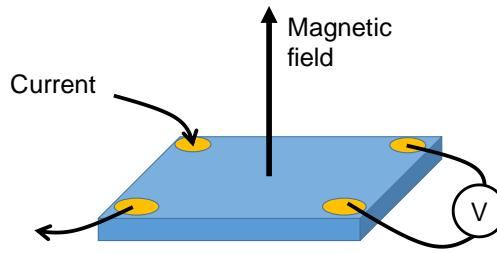


Fig. 4. Hall-effect experiment in the Van der Pauw geometry. Current flows through two contacts and the voltage is measured across the other two. A magnetic field is applied perpendicular to the sample.

D. Growth

In contrast to nitride semiconductors, β - Ga_2O_3 bulk single crystals can be grown from the melt without the need for extreme pressures. With the *Czochralski* (CZ) method, Ga_2O_3 powder is melted in a heated iridium (Ir) crucible.⁴³ A seed crystal is dipped into the melt and raised slowly, drawing up the melt, which cools and crystallizes (Fig. 5). The seed and/or crucible are rotated to promote the growth of a symmetric, cylindrical ingot. Growth occurs in a mixture of CO_2 and O_2 in order to provide an optimal oxygen partial pressure that prevents decomposition. CZ-grown Ga_2O_3 typically contains Ir, Fe, and Si impurities, and Ga vacancies. A related technique, *edge-defined film-fed growth* (EFG), uses a die with a slit.⁴⁴ When the die is dipped into the melt, a liquid Ga_2O_3 film is drawn up through the slit by capillary action, where it cools and crystallizes. The ingot's shape is defined by the shape of the slit.

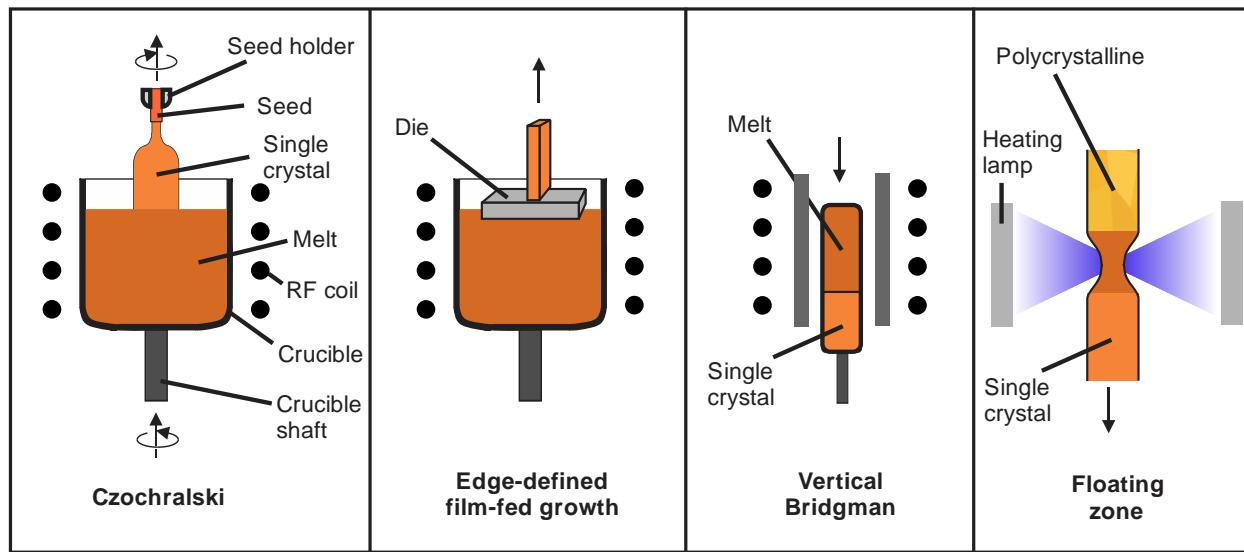


Fig. 5. Bulk crystal growth techniques.

In *vertical Bridgman* growth, the crucible and starting powder are in a thermal gradient where temperature increases as a function of height. The crucible is lowered such that the solid-liquid interface moves upward slowly, resulting in crystal growth. Ga_2O_3 grown in a Pt-Rh crucible in the ambient air contained Si, Pt, and Rh impurities at the 1-10 ppm level.⁴⁵ The *floating zone* technique starts with a polycrystalline rod, which is melted by halogen heating lamps. The rod is translated vertically so that the molten zone moves through the length of the rod, leaving behind single-crystal Ga_2O_3 .⁴⁶ Crystals grown this way have free-electron densities of $\sim 10^{17} \text{ cm}^{-3}$, likely due to Si impurities, similar to CZ-grown crystals.

Ga_2O_3 thin films have been grown using a variety of methods. *Sputtering* is a relatively inexpensive technique that uses an Ar^+ plasma to dislodge, or sputter, atoms from a Ga_2O_3 target.⁹ The plasma (Ar^+ ions and electrons) is created by a radio frequency (RF) power source. A magnetic field is typically applied in order to bend electrons into helical paths, which confines the electrons and makes them ionize many Ar atoms. The sputtered Ga and O atoms coat the

substrate, forming a thin film. *Pulsed laser deposition* (PLD), which uses a high-intensity laser to ablate target atoms, has also been used.⁴⁷

Sputtering and PLD generally do not yield *epitaxial* growth. Epitaxy is defined as the growth of a crystalline film on a crystalline substrate with well-defined atomic bonds between the film and substrate.⁴⁸ Because single-crystal substrates can be grown, it is straightforward to grow Ga_2O_3 on Ga_2O_3 substrates. This is referred to as *homoepitaxy*. The growth of Ga_2O_3 on a different substrate, such as sapphire (Al_2O_3), is an example of *heteroepitaxy*.

Metalorganic chemical vapor deposition (MOCVD) is a preferred epitaxial growth technique. Typical starting molecules, or precursors, are trimethyl gallium (TMGa) and oxygen gas. The precursors are transported to the substrate by a carrier gas such as Ar, adsorb on the surface, and dissociate. The Ga and O atoms go to the proper sites by surface diffusion. During growth, the substrate is maintained at a temperature around 500-850°C.⁴⁹ A similar technique, *halide vapor phase epitaxy* (HVPE), uses GaCl and oxygen as the precursors.⁵⁰ SiCl_4 or SnCl_4 can be used to dope with Si or Sn donors. HVPE has a fast growth rate, over 100 $\mu\text{m}/\text{hr}$, making it attractive from an industrial point of view.

Finally, *molecular beam epitaxy* (MBE) is an ultrahigh-vacuum technique that enables atomic layer control. Thanks to the vacuum, atoms travel from the source to the substrate without colliding with each other. For Ga_2O_3 MBE growth, the gallium source is Ga evaporated from an oven (Knudson cell), and either oxygen plasma⁵¹ or ozone⁵² is used as the oxygen source. As the sources are turned “on” and “off,” the film is grown layer by layer.

E. Point defects

A *point defect* is an imperfection that occurs at a specific location, or point, in a crystal. This is in contrast to an *extended defect*, which is not localized at a specific lattice site. A *dislocation*, for example, is a one-dimensional “line” defect. When there is an extra plane of atoms in the lattice, the edge of that plane is a line and is referred to as an edge dislocation. A *stacking fault*, where a plane of atoms is in the wrong sequence, is an example of a two-dimensional defect.

Dislocations, stacking faults, and hollow nanopipes have been observed in Ga_2O_3 .^{53,54,55}

Point defects in crystals fall into two categories: (1) *native* defects, which involve only the atoms of the host crystal, and (2) *extrinsic* defects, which involve impurity atoms. When an impurity is deliberately introduced into a semiconductor, it is referred to as a *dopant*. A *vacancy*, or missing atom, is a type of native defect. Oxygen and gallium vacancies are denoted V_O and V_Ga respectively. If an oxygen or gallium atom is not in its proper site, then it is a *self-interstitial* (O_i and Ga_i). Self-interstitials may be created when an energetic particle such as a proton knocks the atom out of its lattice site. However, there is limited experimental evidence for Ga or O interstitials under normal conditions.

A very important quantity is the defect *formation energy* (E^f). If the formation energy is low, then the sample may contain many defects. The concentration of such defects is given by

$$N = N_{\text{sites}} \exp(-E^f/k_B T) \quad (3)$$

where N_{sites} is the concentration of available sites for the defect, k_B is Boltzmann's constant, and T is temperature in Kelvin.

Group IV elements such as Si or Sn substitute for a host Ga atom. These *donors* have one more valence electron than the group-III Ga. This extra electron can be thermally excited to the CB, making the crystal *n*-type. The energy required to excite the electron to the CB is the *donor*

binding energy. Because the donor binding energy is only tens of meV, Si and Sn are referred to as *shallow donors*. The group-II elements Mg and Ca also substitute for a host Ga. Because they have one fewer valence electron than Ga, they are *acceptors*. The energy required to excite an electron from the VB to the acceptor level is quite large; because of this, Mg and Ca are *deep acceptors*.

III. NATIVE DEFECTS

A. Oxygen vacancies

In oxide semiconductors, a missing oxygen atom, or oxygen vacancy (V_O), is hard to detect. Perhaps because of this elusiveness, oxygen vacancies often get blamed for unintentional *n*-type conductivity. Most of the information we have for V_O in Ga_2O_3 comes from density functional theory (DFT). This “first principles” technique calculates quantities based on the electron density distribution and positions of the nuclei. Recently, *hybrid functionals* have been employed to obtain reasonably accurate energy levels and band gaps.⁵⁶

Let's look at the example of V_O . First, the total electron energy (potential plus kinetic) is calculated for the intrinsic semiconductor. All the bond lengths are allowed to vary, or *relax*, to minimize the energy. Then, an oxygen atom is removed and placed into a reservoir. In this reservoir, the oxygen's energy is given by the chemical potential μ_O . The formation energy is the energy difference between the material with one defect and material that is pure (intrinsic).

An additional factor to consider is the charge state q of the defect. If $q = 1$, the defect has given one electron to the electron reservoir, where the electron's energy is the Fermi energy E_F . If $q = 2$, then the defect donated two electrons. In general, the contribution to the formation energy due to charge state is qE_F . Taking everything into account, the formation energy is

$$E^f = E(\text{Ga}_2\text{O}_3:\text{V}_0) - E(\text{Ga}_2\text{O}_3) + \mu_0 + qE_F \quad (4)$$

where $E(\text{Ga}_2\text{O}_3:\text{V}_0)$ and $E(\text{Ga}_2\text{O}_3)$ are the calculated energies for the defective and pure semiconductor, respectively. Energies are relative to the valence-band maximum (VBM).

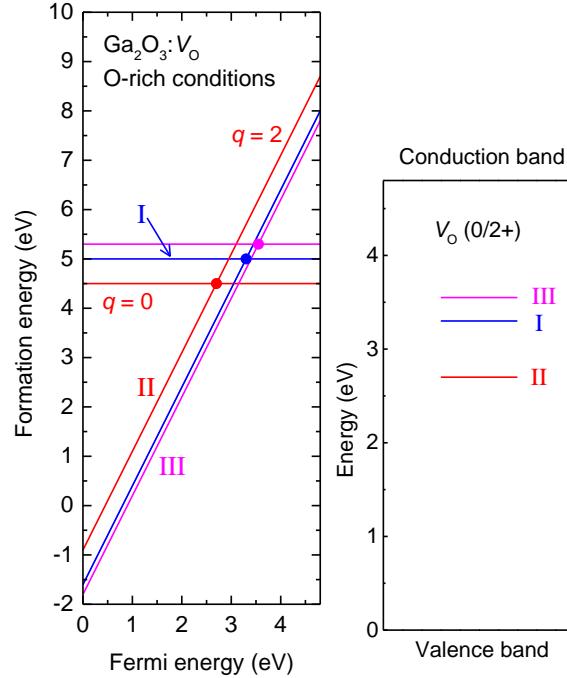


Fig. 6. Left: Formation energy for oxygen vacancy at the O(I), O(II), and O(III) sites.⁵⁷ Right: Energy level diagram showing the (0/2+) donor levels in the band gap.

The results of calculations by Varley et al.⁵⁷ are shown in Fig. 6 for the oxygen vacancy at the three different sites (I, II, and III). From Eq. (4), the slope of E^f versus E_F equals the charge state q . When looking at a formation energy plot, one can infer the charge state from the slope of a line. The oxygen vacancy is an example of a *negative-U* defect, where the +1 charge state is unstable. When the Fermi energy is low, the energetically preferred charge state is $q = 2$. When the Fermi energy is high, the charge state is neutral ($q = 0$). In the literature, it is common to show only the charge state that has the lowest formation energy for a given Fermi energy.

The point where the lowest-energy state goes from $q = 2$ to 0 is shown as a horizontal line in an energy-level diagram (Fig. 6). Because this (0/2+) level is far from the CB, the defect is a *deep donor*. The amount of thermal energy required to promote an electron from the defect level to the CB is much greater than room temperature. Therefore, oxygen vacancies cannot be responsible for *n*-type conductivity in Ga_2O_3 . They can, however, *compensate* acceptors by donating their electrons. As acceptor doping increases, the Fermi level is pushed down toward the VB. This reduces the formation energy for oxygen vacancies. At some point, the formation energy gets small such that the Fermi level is prevented from going any lower.

Finally, note that the formation energy plotted in Fig. 6 is for O-rich conditions. This environment exists when the sample is in contact with O_2 gas. A sample in vacuum, hydrogen, or in contact with Ga would be in an O-poor (Ga-rich) environment. In that case, the chemical potential μ_0 , and hence E^f , is lowered by ~ 3.5 eV.⁵⁷ The lower formation energy results in a higher V_O concentration [Eq. (3)].

B. Gallium vacancies

Gallium vacancies (V_{Ga}) are common defects in Ga_2O_3 . Because Ga has three valence electrons, a missing Ga atom leaves behind three O dangling bonds that can accept electrons. V_{Ga} therefore acts as a triple acceptor. This is important because V_{Ga} can compensate donors, reducing free-electron concentration. Calculations show that the Ga(I) vacancy has a lower formation energy than Ga(II).^{58,59}

The structure of V_{Ga} is unusual. Figure 7 shows a piece of the crystal structure (the middle portion of Fig. 2) with one Ga(I) removed. It is energetically favorable for a neighboring Ga(I) atom to leave its site and reside in the middle of the six-oxygen cage. This *relaxation* process

results in two “half vacancies” with a Ga atom in-between. In the figure, the displaced Ga atom is bonded to four O(II) and two O(III) atoms. It is also possible to have a vacancy where the displaced Ga atom binds to four O(II) and two O(I). A recent study used scanning transmission electron microscopy (STEM) to produce high-resolution images of a Ga_2O_3 sample.⁶⁰ The images showed a structure quite similar to Fig. 7 (V_{Ga} relaxed).

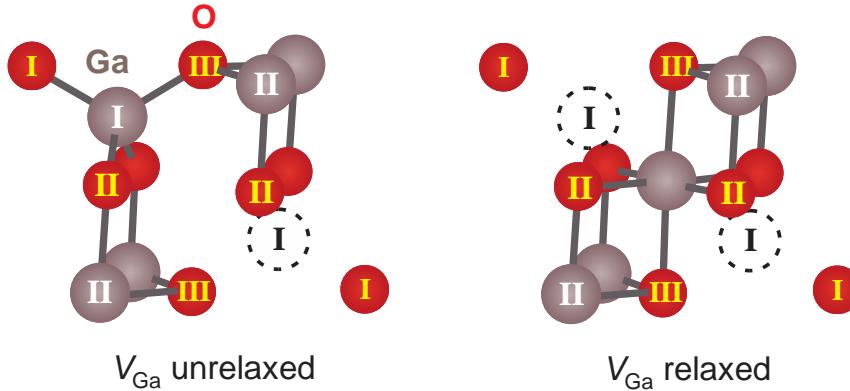


Fig. 7. Illustration of the gallium vacancy, where the relaxed model is the lowest-energy one. Missing Ga(I) atoms are indicated by dashed circles.

Electron paramagnetic resonance (EPR) is an excellent technique for characterizing defects that have unpaired spins. When a magnetic field is applied, the energies of spin-up and spin-down electrons split. A microwave source can excite a transition from down to up. In practice, the magnetic field is varied while the microwave frequency is fixed, and the derivative of the absorption spectrum is plotted (Fig. 8). For a spin-1/2 electron, the microwave excites a transition when

$$h\nu = \mu_B g B \quad (5)$$

where $h\nu$ is the microwave photon energy, g is the Lande factor (~ 2 for a free electron), μ_B is the Bohr magneton, and B is the applied magnetic field. The exact value of g depends on the particular defect and the orientation of the field with respect to the crystal.

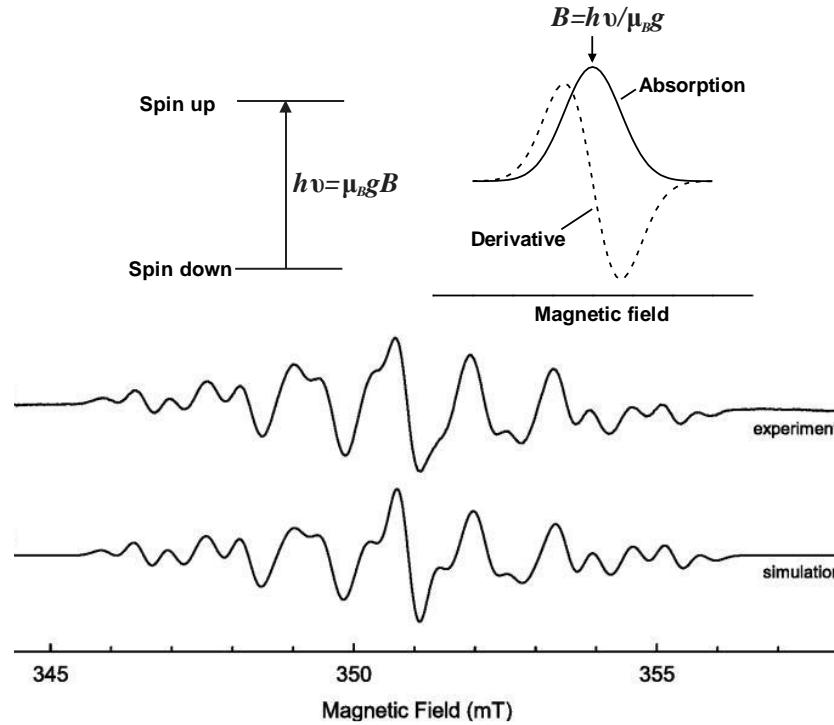


Fig. 8. Top: Illustration of an EPR transition and spectra. Bottom: Experimental and simulated EPR derivative spectra of gallium vacancies (V_{Ga}^{2-}). Splittings occur due to hyperfine interactions between the electron spin, localized on an O atom, and two neighboring Ga nuclear spins. Spectra reprinted from B.E. Kananen, L.E. Halliburton, K.T. Stevens, G.K. Foundos, and N.C. Giles, Appl. Phys. Lett. **110**, 202104 (2017).

In an n -type sample, the gallium vacancy is fully occupied and has a charge $q = -3$, denoted V_{Ga}^{3-} . The electrons are paired, so there is no EPR signal. Kananen et al.⁶¹ irradiated a sample with high-energy neutrons, creating vacancies and lowering the Fermi energy below the (2-/3-) level. This resulted in the V_{Ga}^{2-} defect, which has one unpaired spin ($S = 1/2$) located on one of the O(I) atoms near the vacancy. In a perfect crystal, O(I) has three Ga neighbors, but because of the vacancy it has only two. The EPR spectrum showed hyperfine splitting due to neighboring

^{69}Ga and ^{71}Ga nuclei, both of which have spins of $I = 3/2$ (Fig. 8). The authors also found evidence for V_{Ga}^- , which has two unpaired spins for a total spin of $S = 1$.⁶¹

Another method for detecting gallium vacancies is *positron annihilation*.⁶² A positron, or anti-electron, is positively charged. When it annihilates an electron, two gamma rays are emitted. If a positron becomes trapped in a gallium vacancy, its lifetime increases because the electron density is low in the open volume of the vacancy. This increased lifetime allows one to estimate the concentration and type of vacancies. Also, the momenta of the electrons in the vacancy are different than those in the pure crystal, which leads to subtle changes in the gamma-ray spectrum. Positron annihilation experiments have confirmed that V_{Ga} is a compensating acceptor in *n*-type Ga_2O_3 .⁶³

C. Hydrogenated gallium vacancies

As noted in Sec. III.B, the gallium vacancy is a triple acceptor; i.e., it has three dangling bonds. A hydrogen atom can passivate an acceptor such as V_{Ga} by providing an electron and forming an O–H bond. The O–H bond-stretching vibrational mode is detected by *IR spectroscopy*.

In order to be “IR-active,” a dipole moment must be induced by the vibrational motion. An IR-active mode results in a peak in the IR absorption spectrum. Classically, the absorption of light comes about because the electric field pushes and pulls the impurity atom. The electromagnetic energy goes into driving mechanical motion, resulting in a dip in the transmitted light intensity I at the vibrational frequency ν . Frequency is usually expressed as wavenumbers (cm^{-1}), defined as

$$\text{Wavenumber} \equiv 1/\lambda = \nu/c \quad (6)$$

where λ is the wavelength of IR light and $c = 3.0 \times 10^{10} \text{ cm/s}$. IR spectra are typically plotted in absorbance units:

$$\text{Absorbance} = \log_{10}(I_0/I) \quad (7)$$

where I_0 is a reference spectrum that does not contain the defect. In this paper, IR spectra are for samples at low temperatures (5–12 K) unless stated otherwise.

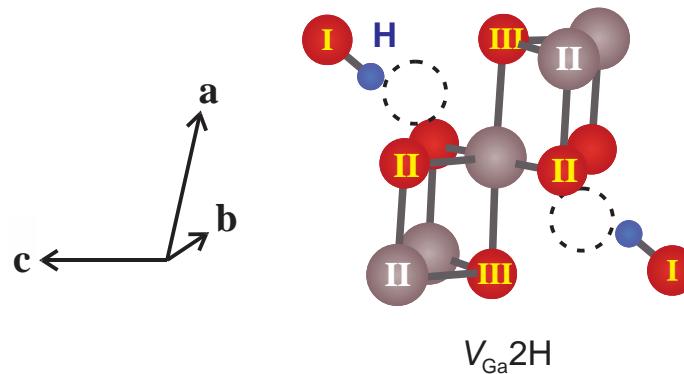


Fig. 9. Illustration of the hydrogenated gallium vacancy. Missing Ga(I) atoms are indicated by dashed circles.

When Ga_2O_3 is annealed in H_2 gas at temperatures above 800°C, hydrogen forms a complex with V_{Ga} .⁶⁴ This complex, denoted $V_{\text{Ga}}2\text{H}$, has two hydrogen atoms that form O–H bonds (Fig. 9). A simplified mass-spring model is shown in Fig. 10. When the H atoms oscillate together, a dipole moment is induced. This *asymmetric* vibrational mode absorbs IR light at a vibrational frequency of 3437 cm^{-1} . The *symmetric* mode, on the other hand, does not induce a net dipole moment, resulting in no IR absorption peak. The 3437 cm^{-1} peak has polarization dependence. Light polarized along the **b** axis, [010], is perpendicular to the O–H bonds and therefore does not excite the vibrational mode (Fig. 10).

When hydrogen is replaced by deuterium, the heavier isotope results in a lower vibrational frequency. Deuterated samples form $V_{\text{Ga}}2\text{D}$ with a corresponding O–D line at 2546 cm^{-1} .

Samples annealed in a H₂/D₂ mixture form V_{Ga}2H, V_{Ga}2D, and V_{Ga}HD complexes. The latter complex gives rise to two new peaks corresponding to its O–H and O–D vibrations [Fig. 10(c,d)]. The appearance of these new peaks provides strong evidence that the defect has two hydrogen atoms.

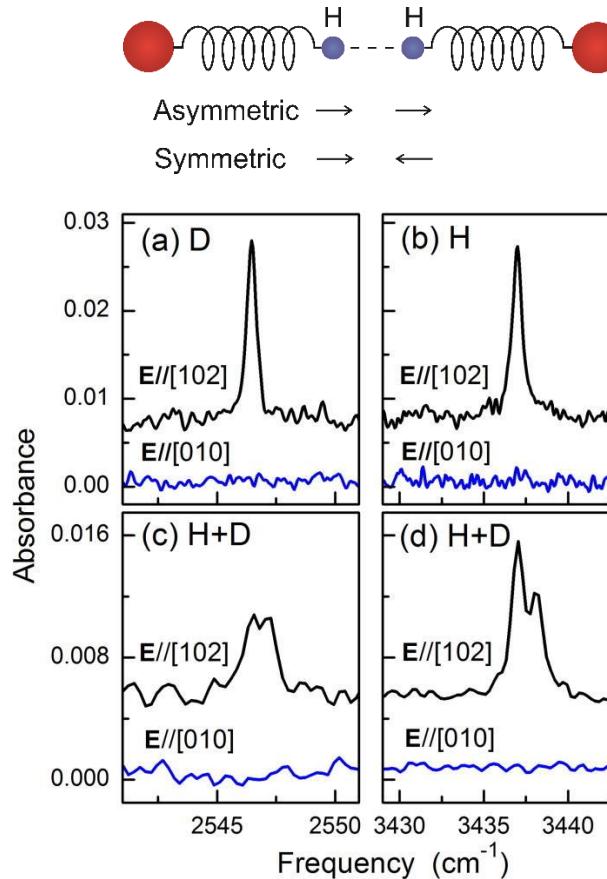


Fig. 10. IR transmission spectra of V_{Ga}2H complexes. Samples with a mixture of H and D show new peaks that correspond to V_{Ga}HD centers. IR light polarization along [010] is perpendicular to the O–H bonds and is not absorbed. Spectra reprinted from P. Weiser, M. Stavola, W.B. Fowler, Y. Qin, and S. Pearton, Appl. Phys. Lett. **112**, 232104 (2018).

As the sample is warmed from 5 K to room temperature, the V_{Ga}2H shifts to lower frequency by -8 cm^{-1} .⁶⁵ This shift is due to interactions between O–H and neighboring atoms, which jiggle as the temperature increases. Along with a shift, the peak broadens. The broadening occurs

because the random motion of the neighboring atoms interrupts the O–H oscillation, effectively reducing the vibrational lifetime.

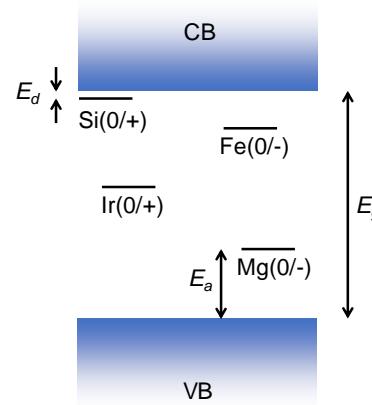


Fig. 11. Estimated energy levels for selected impurities in Ga_2O_3 ($E_g = 4.8$ eV). The hydrogenic (shallow) donor level is $E_d = 30$ meV and the calculated Mg acceptor level is $E_a = 1.0\text{--}1.5$ eV. Theory and experiment place the Ir deep donor level 2.2–2.3 eV below the CBM. DLTS experiments indicate the Fe acceptor level lies 0.8 eV below the CBM.

IV. EXTRINSIC DEFECTS

A. Shallow donors

A substitutional single donor has one more valence electron than the atom it replaces. An example is silicon (Si_{Ga}), which has four valence electrons and substitutes for trivalent gallium. The extra electron orbits the positively charged Si_{Ga} impurity, analogous to the hydrogen atom. The amount of energy required to liberate the electron is called the *donor binding energy* and is estimated by the Bohr model:

$$E_d = (13.6 \text{ eV})(m^*/m)(1/\epsilon^2), \quad (8)$$

where $m^*/m \approx 0.28$ and the relative dielectric constant is $\epsilon \approx 11$.⁶⁶ Inserting those values into Eq. (8) yields $E_d \approx 30$ meV. On an energy-level diagram, the (0/+) donor level is depicted as a

horizontal line E_d below the CBM (Fig. 11). Because the level is close to the CBM, it is referred to as a *shallow donor*. Shallow donors give rise to an EPR transition with $g \approx 1.96$.⁶⁷

In addition to being a source of unintentional *n*-type conductivity in bulk Ga₂O₃,⁶⁸ deliberate Si doping can yield free-electron concentrations in the $10^{16} - 10^{18} \text{ cm}^{-3}$ range.⁶⁹ Silicon doping has also been achieved during thin-film deposition⁷⁰ and by ion implantation.⁷¹ The group-IV elements Ge and Sn have also been used to obtain *n*-type thin films.^{72,73} Calculations indicate that Si and Ge prefer the Ga(I) site while Sn occupies the Ga(II) site.⁵⁷ Zirconium, a transition metal, acts as a shallow donor in bulk Ga₂O₃.⁷⁴ The neutral charge state (0) is typically denoted Zr³⁺ because Zr³⁺ is neutral with respect to the trivalent Ga³⁺ atom that it replaces. The positive charge state (+) is labeled Zr⁴⁺.

Hydrogen has two forms that are predicted to act as shallow donors, *interstitial* and *substitutional*.⁵⁷ Interstitial hydrogen (H_i) forms a bond with a host oxygen atom. Substitutional hydrogen (H_o) is essentially a proton inside an oxygen vacancy. While H_i should give rise to an O–H peak in the IR spectrum, H_o has a low vibrational frequency that lies in the two-phonon absorption spectrum, making it hard to detect. Evidence for hydrogen shallow donors was obtained indirectly by measuring an increase in free-carrier absorption after annealing in hydrogen.⁷⁵ The measurements further indicated that there is a reservoir of “hidden hydrogen” that releases hydrogen donors upon annealing in an inert gas.

B. Deep acceptors

A promising dopant for semi-insulating Ga₂O₃ is magnesium (Mg_{Ga}),^{76,77} which sits on a Ga(II) site. Because Mg has two valence electrons, one fewer than Ga, it acts as an acceptor. The acceptor level is calculated to be deep, 1.0–1.5 eV above the VBM.^{78,79} For neutral Mg, the hole

is very localized, residing on an O(I) atom adjacent to the Mg.⁸⁰ Ritter *et al.*⁷⁹ found that high concentrations of Mg (10^{18} – 10^{19} cm⁻³) can be incorporated in bulk crystals, enough to overwhelm compensating donors. This is great for semi-insulating material but *p*-type conductivity is not practical with such a deep acceptor. Indeed, substitutional acceptor dopants are all calculated to be deep.⁸¹

Hydrogen passivates Mg, forming a neutral MgH complex in samples annealed in hydrogen at 800°C.⁷⁹ This center consists of an O–H bond oriented primarily along the **a** axis. IR absorption spectroscopy indicates a bond-stretching vibrational frequency of 3492 cm⁻¹ (Fig. 12). The corresponding O–D mode is 2586 cm⁻¹. Samples annealed in hydrogen-deuterium mixtures show the O–H and O–D peaks but no new peaks that might indicate multiple hydrogen atoms. Therefore, the MgH complex contains only one hydrogen. IR spectra taken with a polarizing filter show that the peak is strongest when **E**//**c** and zero when **E**//**b**. Hence the O–H dipole is oriented in the *a*-*c* plane, consistent with calculations.

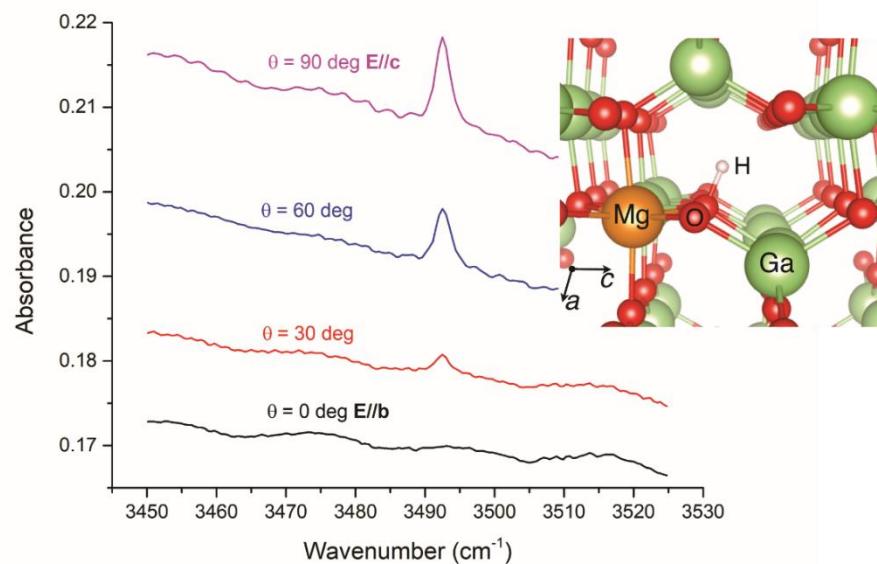


Fig. 12. Polarized IR transmission spectra of the MgH complex. The structure of the complex obtained from first-principles calculations is shown in the inset. Reprinted from J.R. Ritter, J. Huso, P.T. Dickens, J.B. Varley, K.G. Lynn, and M.D. McCluskey, Appl. Phys. Lett. **113**, 052101 (2018).

Resistance measurements with pressed indium contacts give a rough estimate of how acceptors affect the electrical properties. While nominally undoped Ga_2O_3 has a resistance of $\sim 10\text{k}\Omega$, Mg-doped samples have very high resistance ($> 100\text{ G}\Omega$). $\text{Ga}_2\text{O}_3:\text{Ca}$ is *n*-type but has a higher resistance than undoped material, $\sim 10\text{ M}\Omega$, indicating that Ca acceptors partially compensate the donor impurities. $\text{Ga}_2\text{O}_3:\text{Ca}$ annealed in hydrogen gives rise to an IR peak at 3441 cm^{-1} , attributed to an O–H bond-stretching mode of a CaH complex.⁸² The corresponding O–D line has a frequency of 2558 cm^{-1} .

Deep-level transient spectroscopy (DLTS) has been used to study deep levels introduced by defects such as Fe, a common contaminant. DLTS is a technique that measures the rate at which a defect captures and releases free carriers. Consider a junction between metal and *n*-type Ga_2O_3 . Assume that the donors are shallow such that they all give their electrons to the CB. In addition to shallow donors, the sample contains *electron traps*, which have deep levels in the upper portion of the band gap. An applied reverse bias has swept electrons out of the depletion region, resulting in positive donors and unoccupied traps [Fig. 13(a)]. Suddenly, the reverse bias is increased, sweeping out more electrons and widening the depletion region [Fig. 13(b)]. The electron traps hold on to their electrons. As time goes on, electron traps release the electrons. This causes the positive space charge density to increase, which shrinks the depletion region. After a while, the depletion width reaches a steady-state value [Fig. 13(c)].

The depletion region plays the role of an insulating dielectric in a planar capacitor. Its width is inversely proportional to the capacitance. Therefore, the capacitance provides a convenient measure of the depletion width. By measuring the capacitive transient as a function of temperature, one can estimate the position of the deep level relative to the CBM. The deeper the level, the slower the defect will release its carrier.

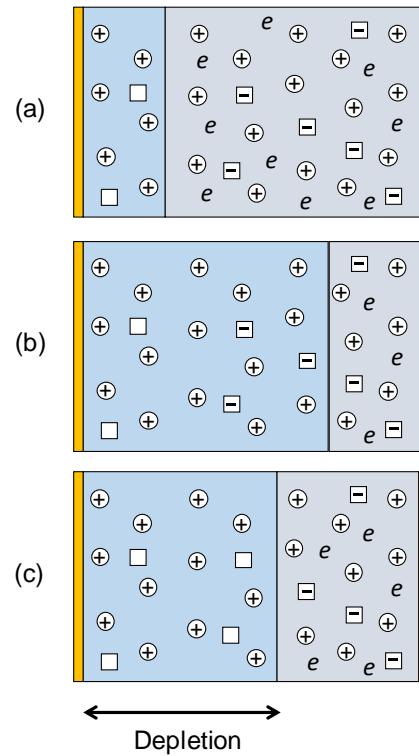


Fig. 13. Illustration of the DLTS process. Circle = shallow donor, square = electron trap, and e = free electron. (a) An applied reverse bias results in a depletion region with no free electrons. (b) The reverse bias is increased, causing the depletion region to widen. The electron traps hold on to their electrons. (c) After some time, the electron traps have released their electrons. This results in a decrease in depletion width.

DLTS and hybrid calculations indicated that Fe prefers the Ga(II) site and has a deep acceptor level 0.8 eV below the CBM.⁸³ This acceptor (0/−) level is also denoted $\text{Fe}^{3+}/\text{Fe}^{2+}$, since Fe^{3+} is neutral relative to the Ga^{3+} host whereas Fe^{2+} is negative. EPR measurements can detect the Fe^{3+} signal. Bhandari et al.⁸⁴ used EPR to observe the photoexcitation of an electron from Fe^{2+} to the CB, leaving behind Fe^{3+} .

C. Iridium impurities

Bulk Ga_2O_3 crystals are commonly grown in an iridium crucible, which leads to Ir impurity incorporation in the 10^{17} - 10^{18} cm^{-3} range.^{79,85} Ir sits preferentially on the Ga(II) site and acts as a deep donor. In *n*-type material, the donor is neutral. Following the convention for transition metals, this charge state is denoted Ir^{3+} . In Mg-doped samples, Ir gives its electron to compensate the Mg acceptor, becoming positively charged (Ir^{4+}). The Ir^{4+} impurity has an IR absorption peak at 5148 cm^{-1} due to the transition of an electron from its ground state to an excited *d* orbital (Fig. 14).⁷⁹ When a sample was annealed in hydrogen, Mg acceptors became passivated (Sec. IV.B) and could not accept electrons from Ir^{3+} . This led to a decrease in the 5148 cm^{-1} peak. The peak shows strong anisotropy, being weakest when the IR light is polarized along the **c** axis.^{85,86}

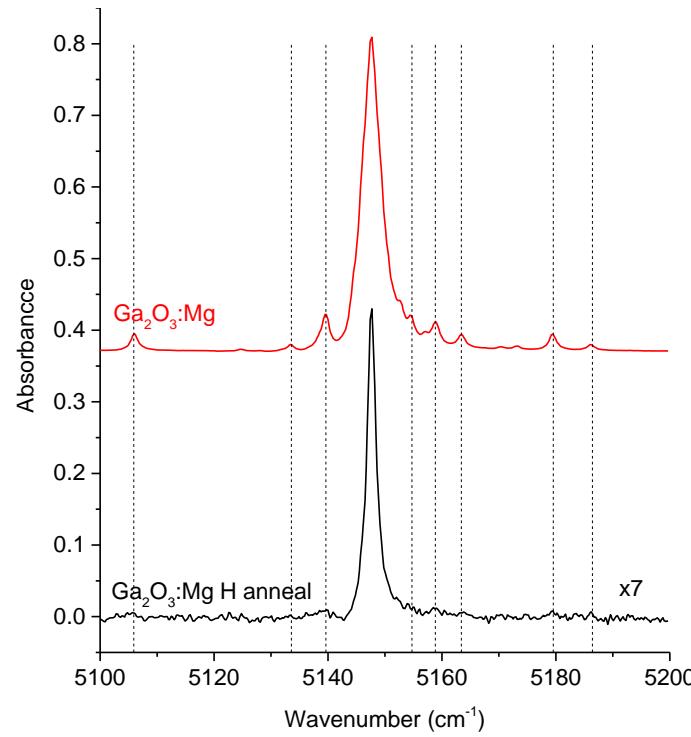


Fig 14. IR spectra of Mg-doped gallium oxide, as-grown and hydrogen-annealed. The peak at 5148 cm^{-1} is due to Ir^{4+} and the sidebands are attributed to IrMg pairs. The hydrogen-annealed sample is scaled for comparison. Spectra are offset for clarity. Reprinted from J.R. Ritter, K.G. Lynn, and M.D. McCluskey, *J. Appl. Phys.* **126**, 225705 (2019).

Ir^{3+} does not have a spectral signature in the IR. When a lightly *n*-type sample was illuminated with photon energies above 2.2–2.3 eV, electrons were excited from Ir^{3+} into the CB, resulting in Ir^{4+} . This caused the 5148 cm^{-1} peak to appear.⁸⁶ The threshold for this process suggests that the donor level is ~ 2.25 eV below the CBM, in agreement with hybrid functional calculations.

In addition to the main Ir^{4+} peak at 5148 cm^{-1} , Ritter et al.⁸⁶ observed numerous smaller sideband peaks in the spectral neighborhood. Because they only were observed in Mg-doped material, these small peaks were attributed to IrMg pairs. The IrMg peaks decreased in intensity when illuminated by photons > 2.2 eV. The authors suggested that this effect may be due to a photo-induced electron transfer from the Mg to Ir ($\text{Ir}^{4+}\text{Mg}^- \rightarrow \text{Ir}^{3+}\text{Mg}^0$).

N-type, bulk Ga_2O_3 samples that were annealed in hydrogen show IR absorption peaks at 3313, 3437, 3450, and 3500 cm^{-1} .⁷⁹ Annealing in deuterium yields peaks that have the appropriate frequency shift. As noted in Sec. III.C, the 3437 cm^{-1} peak is due to a $V_{\text{Ga}2\text{H}}$ complex. The other three peaks, however, have not been identified. Ritter et al.⁸⁶ suggested that they could arise from IrH complexes. However, this assignment is tentative.

V. LUMINESCENCE

Photoluminescence (PL) spectroscopy is a sensitive technique for detecting optically active defects. In a PL experiment, an excitation light source shines on the sample. The source is often a laser but can also be light from a lamp that passes through a filter or monochromator. If the photons are above the band gap, then electrons can be excited into the CB, leaving holes in the VB. Another way to generate electrons and holes is through electron irradiation; this is called *cathodoluminescence* (CL). In Ga_2O_3 , holes form *self-trapped hole* (STH) states, which means

that the hole is localized on an oxygen atom.^{87,56,88} This is in contrast to electrons in the CB, which are delocalized and are free to roam. The system can return to the ground state by radiative or nonradiative paths; the radiative ones give rise to luminescence.

PL and CL spectra of Ga_2O_3 generally show broad peaks that fall into rough categories: UV, UV', blue, and green (Fig. 15).⁸⁹ The UV band (photon energy 3.4 eV, wavelength 360 nm) is due to the recombination of an electron with a STH. This is an intrinsic feature and is not due to defects. The UV' (3.1 eV, 400 nm) and blue bands (2.9 eV, 430 nm) have been attributed to *donor-acceptor pair* (DAP) transitions.^{90,91} A DAP transition occurs when a photoexcited electron is captured by a donor and a hole is captured by an acceptor. Then, the electron tunnels from the donor to the acceptor, emitting a photon to conserve energy. Because the blue band seems to correlate with oxygen-vacancy concentration, the donor in this process was tentatively assigned to V_O .^{92,93} The green band (2.4 eV, 520 nm) has also been assigned to a DAP, although there is no donor assignment. Villora et al.⁹⁴ noted that high O_2 pressure during growth increases the green PL intensity.

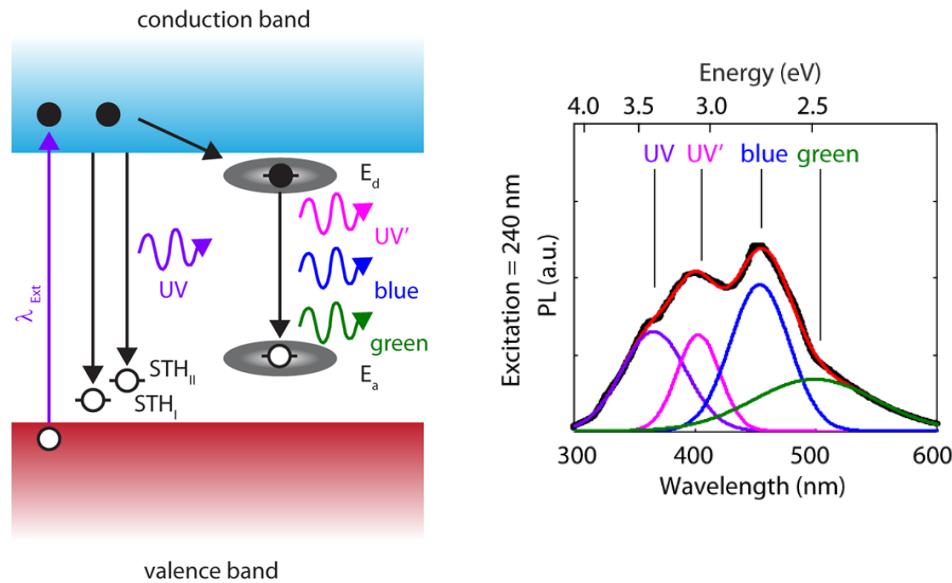


Fig 15. Left: Energy level diagram, where λ_{Ext} is the excitation photon, STH_I and STH_{II} are self-trapped hole states localized on O(I) and O(II), and a DAP transition is indicated. Right: PL spectrum showing the UV, UV', blue, and green bands. Reprinted from Y.S. Wang, P. T. Dickens, J. B. Varley, X. Ni, E. Lotubai, S. Sprawls, F. Liu, V. Lordi, S. Krishnamoorthy, S. Blair, K. G. Lynn, M. Scarpulla, and B. Sensale-Rodriguez, *Scientific Reports* **8**, 18075 (2018).

CL peaks were observed at 2.5 and 3.0 eV (500 nm and 410 nm), which are similar to the aforementioned green and blue bands. These peaks increase after neutron irradiation, suggesting that they involve V_{Ga} .⁹⁵ Chromium (Cr^{3+}) has absorption and emission spectra similar to ruby, with R_1 and R_2 lines near 1.8 eV (700 nm).⁹⁶ PL in a similar deep-red spectral range has been attributed to a transition from the CB (or shallow donor level) to the nitrogen acceptor level.⁹⁷

VI. DAMAGE

Experiments by Ernest Rutherford's research group established the existence of the atomic nucleus when some helium ions travelling through gold foil were observed to undergo large-angle scattering. The elastic collisions between helium and gold nuclei are analogous to collisions between billiard balls. If the kinetic energy of an energetic particle is large enough, it can knock the host atom out of its substitutional site. The rate at which defects are created is given by

$$N = \eta\phi \quad (9)$$

where N is the defect density (cm^{-3}), η is the defect production rate (cm^{-1}), and ϕ is the particle dose (cm^{-2}).

In Ga_2O_3 , gallium vacancies are deep acceptors while oxygen vacancies are deep donors. The creation of gallium vacancies in n -type material causes electrical compensation that decreases the

free-carrier density. Often it is the free-electron removal rate that is measured in Eq. (9), which is proportional to the number of acceptor defects that are produced. Wide-gap materials such as Ga_2O_3 tend to be “radiation hard,” meaning the defect production rate is low.⁹⁸ This is a useful property for applications in harsh environments such as space.

One way to determine the effect of energetic particles is to place the sample in a nuclear reactor, which have fast neutrons in the 1 eV – 20 MeV energy range. Such an experiment was performed on EFG-grown Ga_2O_3 . The fast neutrons created deep electron traps with levels 1.3 and 2.0 eV below the CBM (determined by DLTS) with defect production rates of $8\text{--}10 \text{ cm}^{-1}$.⁹⁹ The generation of these traps results in a decrease of the free-electron concentration; i.e., the traps are compensating acceptor defects. Irradiation with 1.5 MeV electrons also leads to the creation of defects and reduction of carriers, with a carrier removal rate of 5 cm^{-1} .¹⁰⁰ Pearton et al.¹⁰¹ compared carrier removal rates in GaN and Ga_2O_3 and found them to be roughly similar. Implantation with 0.6 and 1.9 MeV protons results in a strong decrease in free-electron concentration for doses above $6 \times 10^{12} \text{ cm}^{-2}$.¹⁰² The free carriers are basically gone for doses above $2 \times 10^{13} \text{ cm}^{-2}$. The authors attributed this to the creation of native defects such as vacancies (V_{Ga}) that compensate the donors. Thermally annealing the sample leads to a recovery of carriers, which may involve passivation by the implanted protons. EPR results combined with calculations¹⁰³ indicate that a center created by proton implantation is consistent with V_{Ga} (Sec. III.B); a second center was unidentified.

VII. CONCLUSIONS

The development of Ga_2O_3 for power electronic applications requires knowledge of, and control over, point defects. Oxygen vacancies, once thought to be responsible for unintentional

n-type conductivity, are actually deep donors. Gallium vacancies are deep acceptors that can form complexes with hydrogen. Group IV elements (Si, Ge, Sn) and hydrogen are shallow donors, while Mg and Ca are deep acceptors with levels 1.0–1.5 eV above the VBM. The fact that acceptors are deep – along with the formation of self-trapped holes – implies that *p*-type conductivity is out of reach. However, devices utilizing semi-insulating substrates are viable.

Irradiation with energetic particles results in deep levels that have only been partially characterized. Future research may provide assignments for “unknown” defects and elucidate the role of omnipresent impurities such as C, H, and Fe. In particular, the identity of the specific donors and acceptors involved in DAP transitions has yet to be determined. Deep acceptors such as Zn have not been investigated thoroughly and may provide better characteristics than Mg or Ca. Understanding the isoelectronic center Al will be crucial for developing $(\text{Ga}_{1-x}\text{Al}_x)_2\text{O}_3$ alloys. Transition metals and other impurities introduced during growth need to be characterized.

Thus far, the majority of characterization studies on Ga_2O_3 have obtained spatially averaged quantities. Optical techniques such as CL and micro-PL have the potential to reveal inhomogeneous defect distributions with micron spatial resolution, while STEM can provide atomic-scale detail. For example, luminescence centers may localize at defects such as dislocations or stacking faults. High-resolution imaging of such defects will provide feedback to crystal growers and potentially identify defects that limit the critical breakdown field.

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zero. The gate thus acts as an “on/off” switch that allows or prohibits current to flow. Consider the “off” mode, where current is blocked. For a large source-drain voltage, the electric field in the depletion region can get very high. If the maximum electric field exceeds a critical value, E_c , *electrical breakdown* will occur and current will flow.

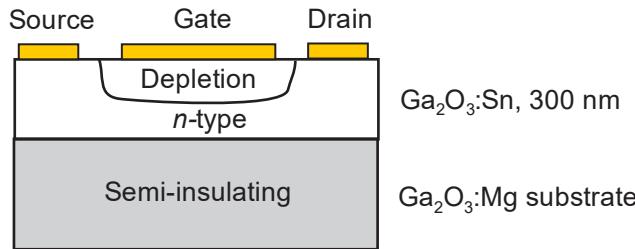


Fig. 1. Schematic diagram of a Ga_2O_3 MESFET.²⁰

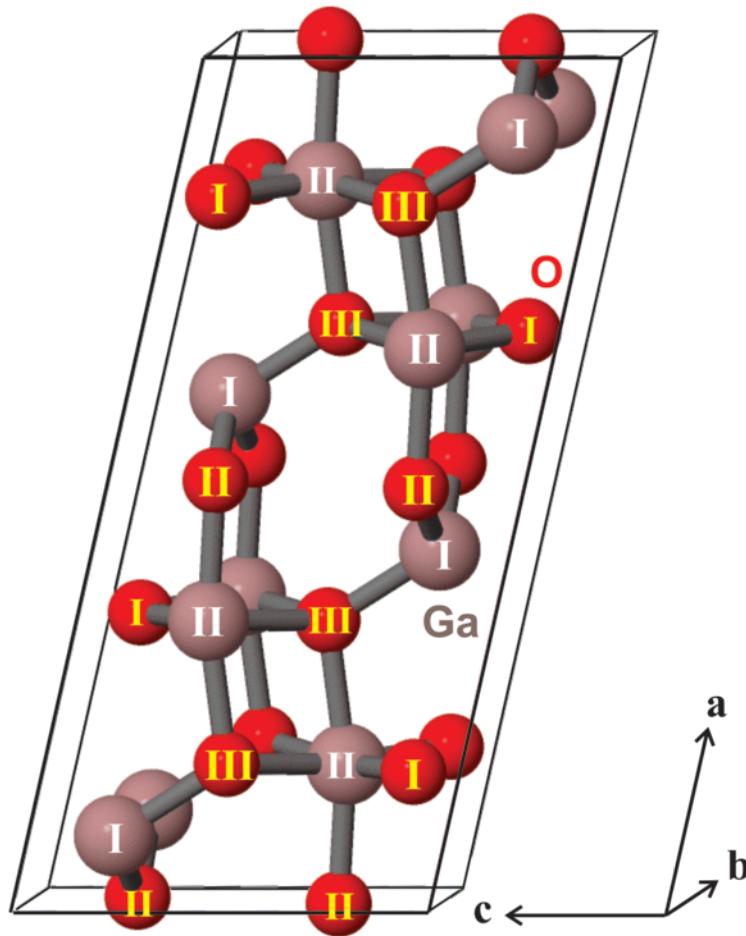
For a power transistor, it is important to have a large critical breakdown field. One mechanism for breakdown is *tunneling*. At high electric fields, the conduction band (CB) and valence band (VB) tilt steeply, and it is possible for an electron to tunnel from the VB straight into the CB.²¹ In this way, current will flow even in a pure semiconductor. A second mechanism is *impact ionization*, where a carrier collides with an atom, generating an electron and hole. These free carriers then cause additional impact ionization events, leading to avalanche breakdown.

C. Benefits of a wide band gap

A large band gap E_g has a strong tendency to reduce the generation of free carriers and hence raise the value of E_c . Ga_2O_3 , with its wide direct gap of 4.8 eV, has a distinct advantage in this regard. Empirically, for direct-gap semiconductors,²²

$$E_c = 1.73 \times 10^5 E_g^{2.5} \quad (1)$$

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This anisotropy has been explained in terms of selection rules for the VB-to-CB transition.^{35,36} A detailed model of the absorption features is given in Ref. 37. In this paper, the band gap is taken to be 4.8 eV.

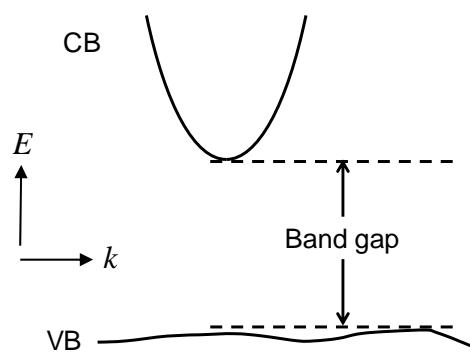


Fig. 3. Simplified band structure of Ga_2O_3 . The minimum in the CB occurs at the zone center ($k = 0$). After Ref. 31.

C. Free carriers

Electronic transport has been investigated with *Hall effect* and other electrical characterization methods.³⁸ For the Hall effect in the Van der Pauw geometry, four electrical contacts are placed on the sample on the corners of a square (Fig. 4). Current is sent through one pair of contacts while voltage is measured across the other pair. A magnetic field is applied perpendicular to the square. By measuring different contact-pair combinations, with and without magnetic field, one can obtain the free-carrier mobility, density, and type (electrons or holes). Unintentionally doped Ga_2O_3 is generally *n*-type with electron mobilities around $100 \text{ cm}^2/\text{Vs}$.³⁹ First-principles calculations^{40,41} indicate that phonon scattering is the primary limiting factor for room-temperature electron mobility ($<200 \text{ cm}^2/\text{Vs}$).

Free electrons lead to *IR absorption* and a *Burstein-Moss shift* of the optical band gap. IR absorption is due to the electric field of the IR radiation accelerating electrons; i.e., Drude absorption. The Burstein-Moss shift occurs when there is a high density of electrons such that the

Fermi level lies within the CB. For Ga_2O_3 with a high free-electron density of 10^{20} cm^{-3} , the Fermi level is 0.2 eV above the CBM.⁴² Because the states are filled up to the Fermi level, the VB-to-CB transition shifts to higher energy. The electron effective mass, calculated from the curvature of the CB, is $0.28m$ for low doping and $0.36m$ at high electron density, where m is the fundamental electron mass.

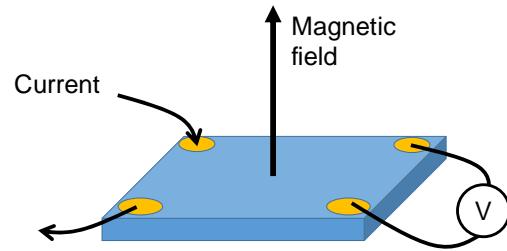
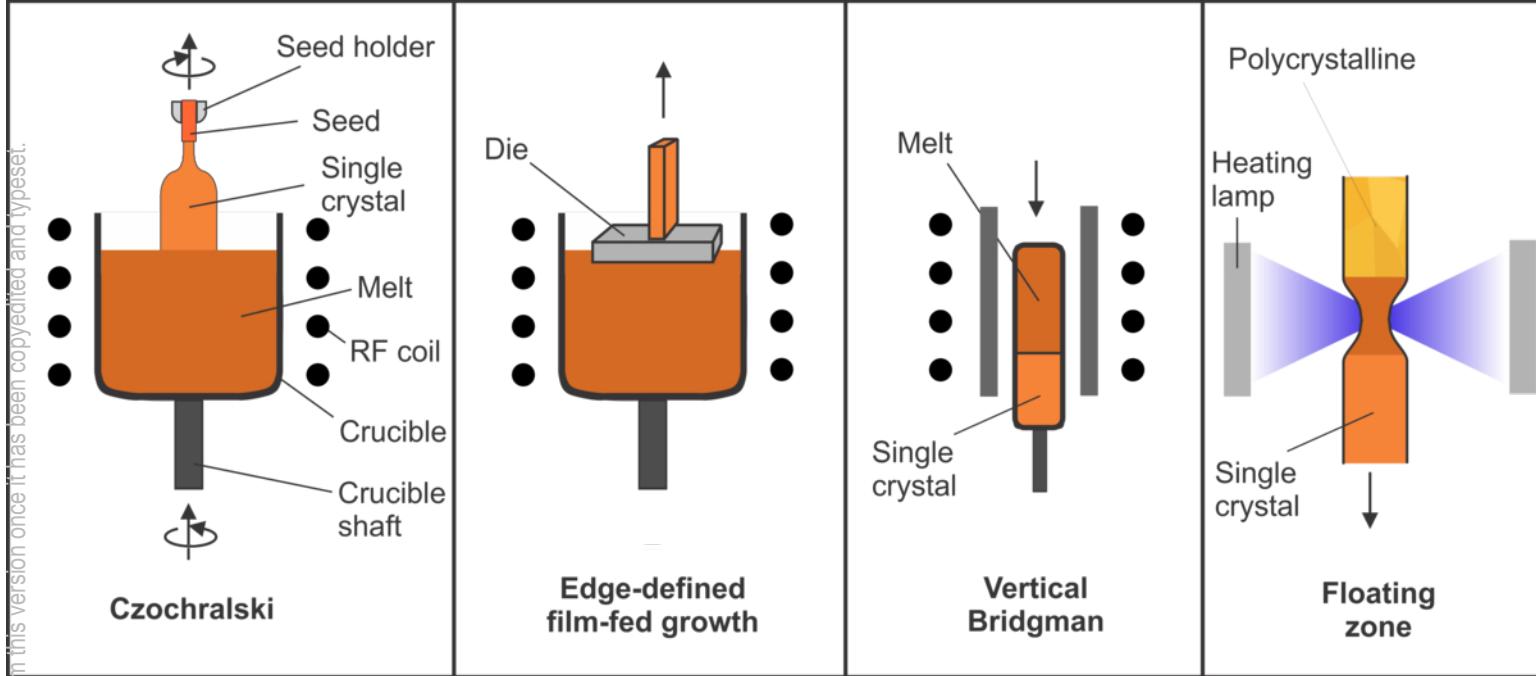


Fig. 4. Hall-effect experiment in the Van der Pauw geometry. Current flows through two contacts and the voltage is measured across the other two. A magnetic field is applied perpendicular to the sample.

D. Growth

In contrast to nitride semiconductors, $\beta\text{-Ga}_2\text{O}_3$ bulk single crystals can be grown from the melt without the need for extreme pressures. With the *Czochralski* (CZ) method, Ga_2O_3 powder is melted in a heated iridium (Ir) crucible.⁴³ A seed crystal is dipped into the melt and raised slowly, drawing up the melt, which cools and crystallizes (Fig. 5). The seed and/or crucible are rotated to promote the growth of a symmetric, cylindrical ingot. Growth occurs in a mixture of CO_2 and O_2 in order to provide an optimal oxygen partial pressure that prevents decomposition. A related technique, *edge-defined film-fed growth* (EFG), uses a die with a slit.⁴⁴ When the die is dipped into the melt, a liquid Ga_2O_3 film is drawn up through the slit by capillary action, where it cools and crystallizes. The ingot's shape is defined by the shape of the slit.

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An additional factor to consider is the charge state q of the defect. If $q = 1$, the defect has given one electron to the electron reservoir, where the electron's energy is the Fermi energy E_F . If $q = 2$, then the defect donated two electrons. In general, the contribution to the energy due to charge state is qE_F . Taking everything into account, the formation energy is

$$E^f = E(\text{Ga}_2\text{O}_3:V_O) - E(\text{Ga}_2\text{O}_3) + \mu_0 + qE_F \quad (4)$$

where $E(\text{Ga}_2\text{O}_3:V_O)$ and $E(\text{Ga}_2\text{O}_3)$ are the calculated energies for the defective and pure semiconductor, respectively. Energies are relative to the valence-band maximum (VBM).

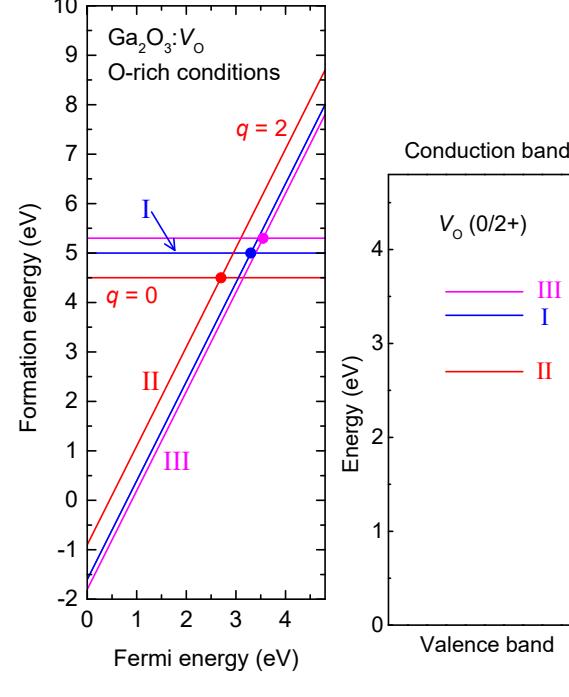
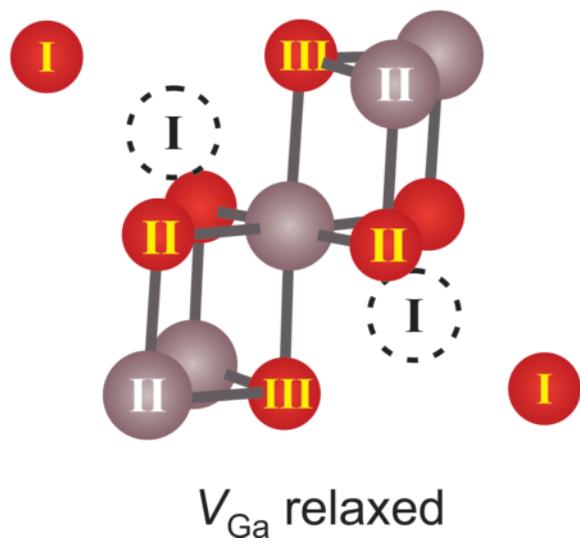
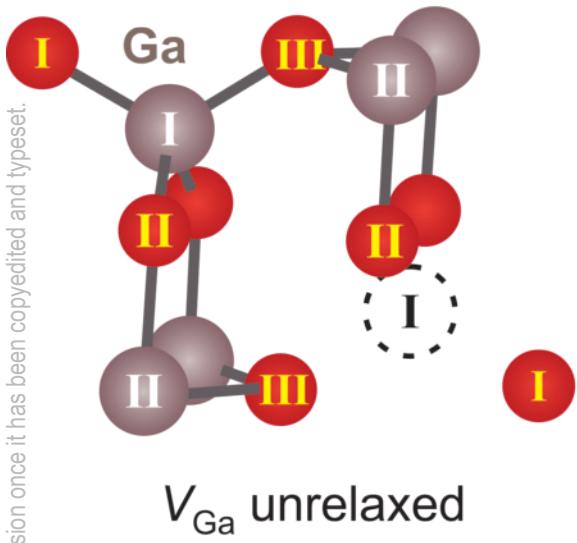


Fig. 4. Left: Formation energy for oxygen vacancy at the O(I), O(II), and O(III) sites.⁵⁸ Right: Energy level diagram showing the (0/2+) donor levels in the band gap.

The results of calculations by Varley et al.⁵⁸ are shown in Fig. 4 for the oxygen vacancy at the three different sites (I, II, and III). From Eq. (4), the slope of E^f versus E_F equals the charge state q . When looking at a formation energy plot, one can infer the charge state from the slope of a line. The oxygen vacancy is an example of a *negative-U* defect, where the +1 charge state is

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$$h\nu = \mu_B g B \quad (5)$$

where $h\nu$ is the microwave photon energy, g is the Lande factor (~ 2 for a free electron), μ_B is the Bohr magneton, and B is the applied magnetic field. The exact value of g depends on the particular defect and the orientation of the field with respect to the crystal.

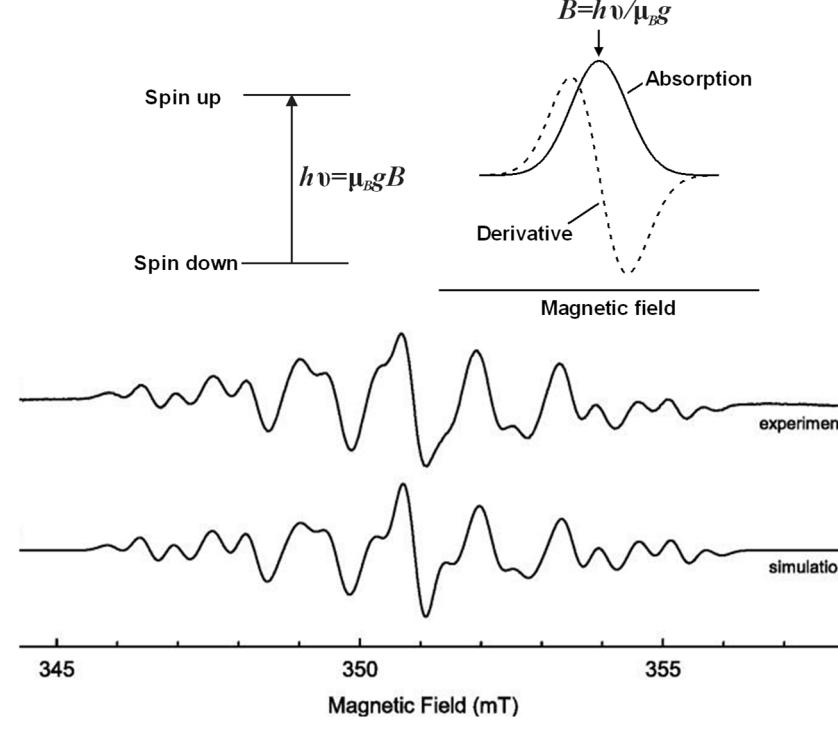
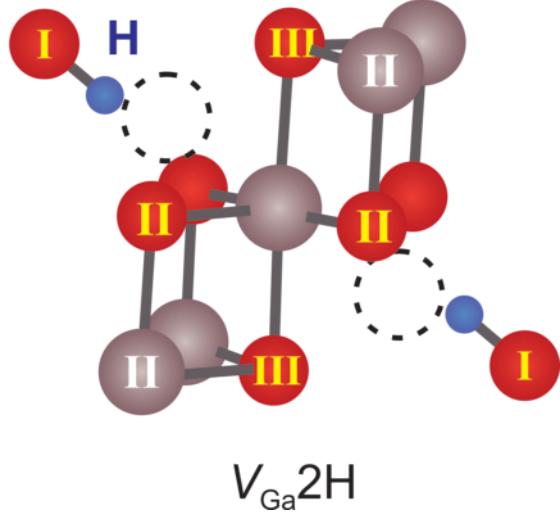
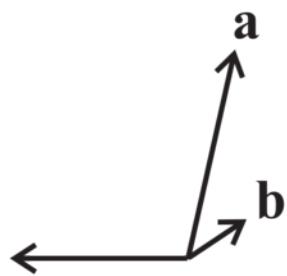


Fig. 6. Top: Illustration of an EPR transition and spectra. Bottom: Experimental and simulated EPR spectra of gallium vacancies (V_{Ga}^{2-}). Splittings occur due to hyperfine interactions between the electron spin, localized on an O atom, and two neighboring Ga nuclear spins. Spectra reprinted from B.E. Kananen, L.E. Halliburton, K.T. Stevens, G.K. Foundos, and N.C. Giles, Appl. Phys. Lett. **110**, 202104 (2017).

In an n -type sample, the gallium vacancy is fully occupied and has a charge $q = -3$, denoted V_{Ga}^{3-} . The electrons are paired, so there is no EPR signal. Kananen et al.⁶² irradiated a sample with high-energy neutrons, creating vacancies and lowering the Fermi energy below the $(2-3-)$ level. This resulted in the V_{Ga}^{2-} defect, which has one unpaired spin ($S = 1/2$) located on one of the O(I) atoms near the vacancy. In a perfect crystal, O(I) has three Ga neighbors, but because of

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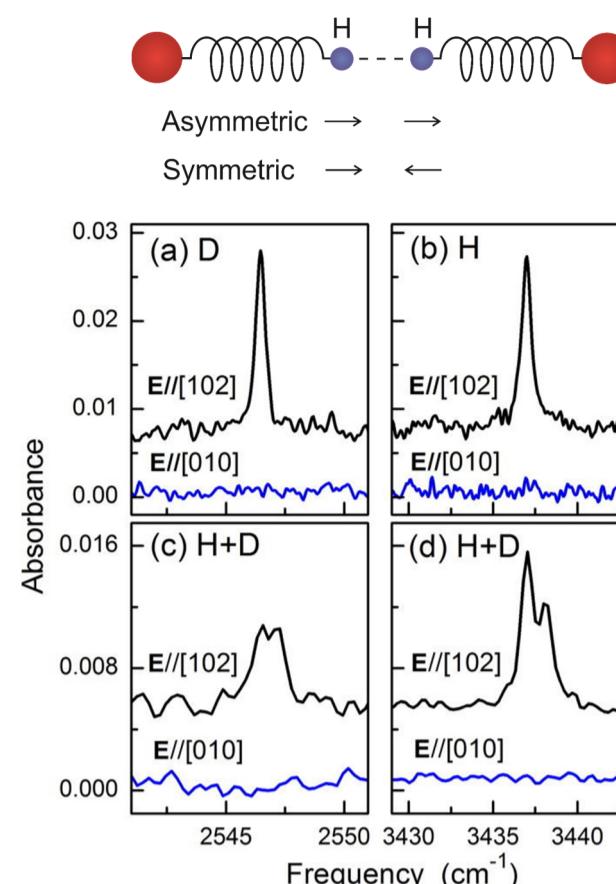


Fig. 8. IR transmission spectra of $V_{\text{Ga}}2\text{H}$ complexes. Samples with a mixture of H and D show new peaks that correspond to $V_{\text{Ga}}\text{HD}$ centers. IR light polarization along [010] is perpendicular to the O–H bonds and is not absorbed. Spectra reprinted from P. Weiser, M. Stavola, W.B. Fowler, Y. Qin, and S. Pearton, Appl. Phys. Lett. **112**, 232104 (2018).

When hydrogen is replaced by deuterium, the heavier isotope results in a lower vibrational frequency. Deuterated samples form $V_{\text{Ga}}2\text{D}$ with a corresponding O–D line at 2546 cm^{-1} . Samples annealed in a H_2/D_2 mixture form $V_{\text{Ga}}2\text{H}$, $V_{\text{Ga}}2\text{D}$, and $V_{\text{Ga}}\text{HD}$ complexes. The latter complex gives rise to two new peaks corresponding to its O–H and O–D vibrations (Fig. 8). The appearance of these new peaks provides strong evidence that the defect has two hydrogen atoms.

As the sample is warmed from 5 K to room temperature, the $V_{\text{Ga}}2\text{H}$ shifts to lower frequency by -8 cm^{-1} .⁶⁶ This shift is due to interactions between O–H and neighboring atoms, which jiggle

as the temperature increases. Along with a shift, the peak broadens. The broadening occurs because the random motion of the neighboring atoms interrupts the O–H oscillation, effectively reducing the vibrational lifetime.

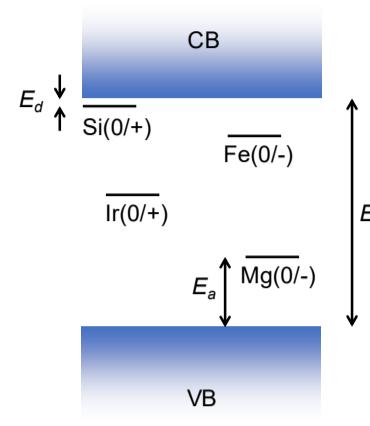


Fig. 9. Estimated energy levels for selected impurities in Ga_2O_3 ($E_g = 4.8$ eV). The hydrogenic (shallow) donor level is $E_d = 30$ meV and the calculated Mg acceptor level is $E_a = 1.0\text{--}1.5$ eV. Theory and experiment place the Ir deep donor level 2.2–2.3 eV below the CBM. DLTS experiments indicate the Fe acceptor level lies 0.8 eV below the CBM.

IV. EXTRINSIC DEFECTS

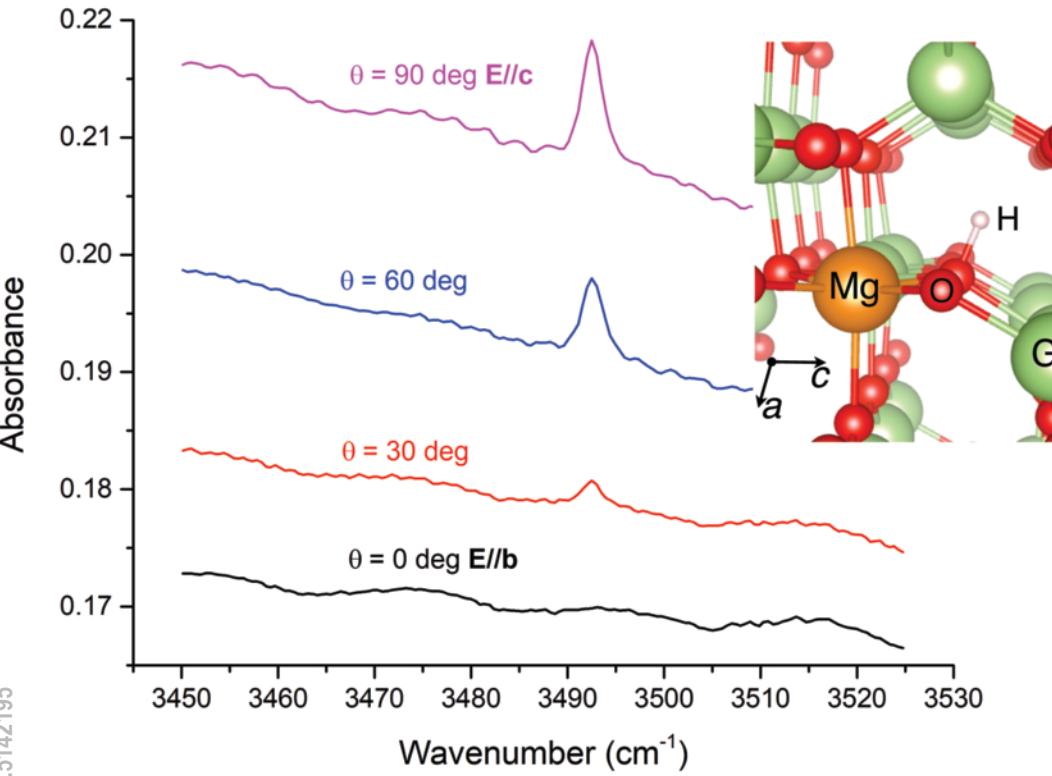
A. Shallow donors

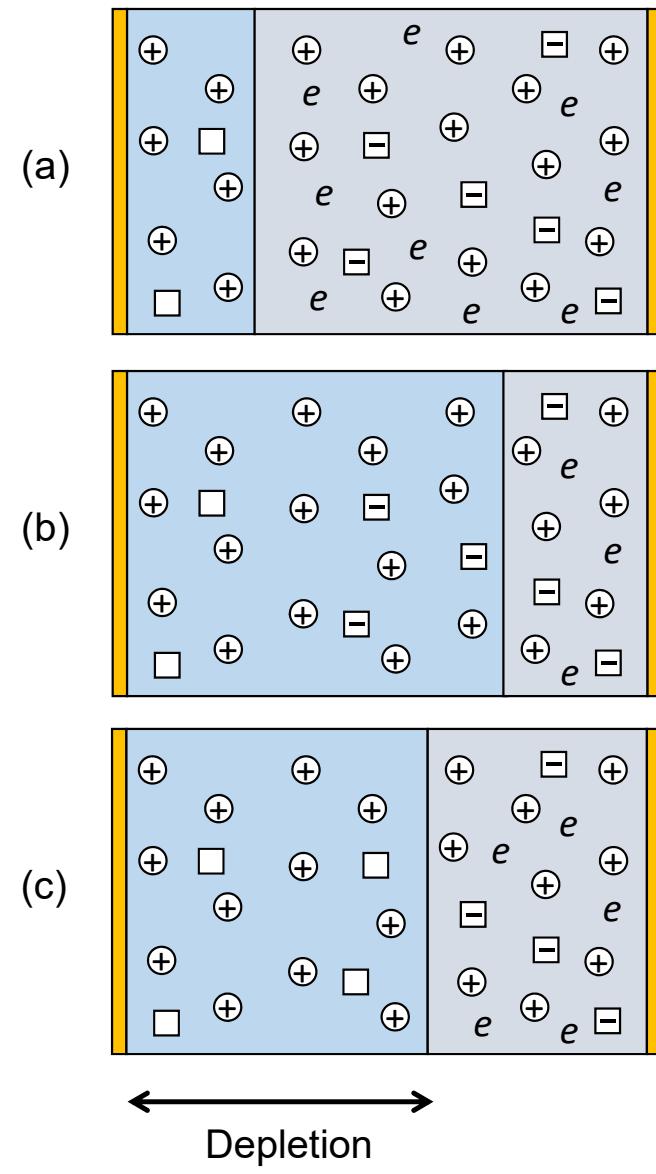
A substitutional single donor has one more valence electron than the atom it replaces. An example is silicon (Si_{Ga}), which has four valence electrons and substitutes for trivalent gallium. The extra electron orbits the positively charged Si_{Ga} impurity, analogous to the hydrogen atom. The amount of energy required to liberate the electron is called the *donor binding energy* and is estimated by the Bohr model:

$$E_d = (13.6 \text{ eV})(m^*/m)(1/\varepsilon^2), \quad (8)$$

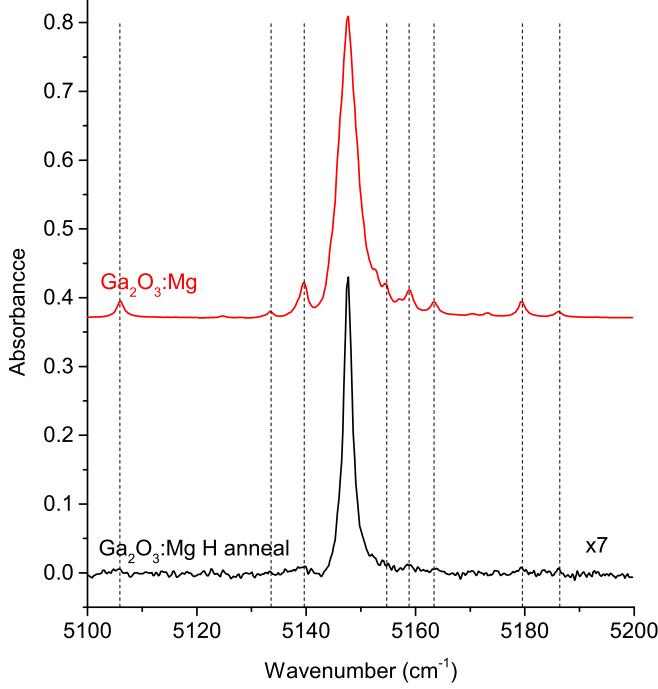
where $m^*/m \approx 0.28$ and the relative dielectric constant is $\varepsilon \approx 11$.⁶⁷ Inserting those values into Eq. (8) yields $E_d \approx 30$ meV. On an energy-level diagram, the (0/+) donor level is depicted as a

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calculations⁹³ indicate that a center created by proton implantation is consistent with V_{Ga} (Sec. III.B); a second center was unidentified.

VI. LUMINESCENCE

Photoluminescence (PL) spectroscopy is a sensitive technique for detecting optically active defects. In a PL experiment, an excitation light source shines on the sample. The source is often a laser but can also be light from a lamp that passes through a filter or monochromator. If the photons are above the band gap, then electrons can be excited into the CB, leaving holes in the VB. Another way to generate electrons and holes is through electron irradiation; this is called *cathodoluminescence* (CL). In Ga_2O_3 , holes form *self-trapped hole* (STH) states, which means that the hole is localized on an oxygen atom.^{94,57,95} This is in contrast to electrons in the CB, which are delocalized and are free to roam. The system can return to the ground state by radiative or nonradiative paths; the radiative ones give rise to luminescence.

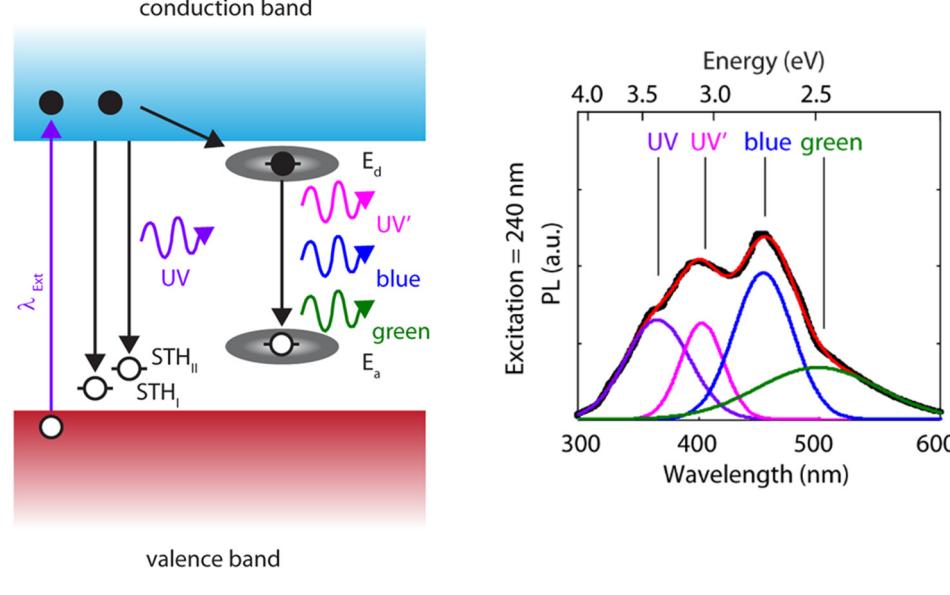


Fig 12. Left: Energy level diagram, where λ_{Ext} is the excitation photon, STH_I and STH_{II} are self-trapped hole states localized on O(I) and O(II), and a DAP transition is indicated. Right: PL spectrum showing the UV, UV', blue, and