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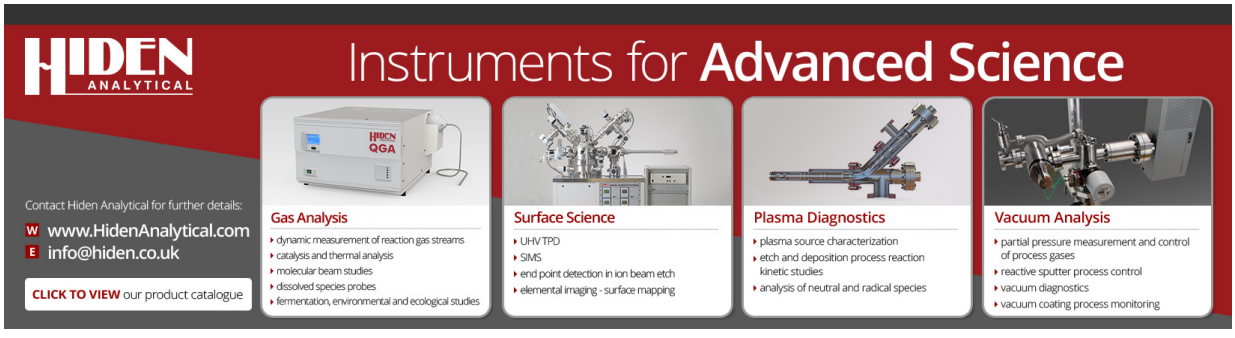

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ABSTRACT

The dual nature of the magnesium acceptor in gallium nitride results in dynamic defect complexes. Europium spectator ions reveal switching between two spectrally unique metastable centers, each corresponding to a particular acceptor state. By ion co-implantation of europium and oxygen into GaN(Mg), we produce, in addition, an anchored state system. In doing so, we create an abundance of previously unidentified stable centers, which we denote as "Eu0(Ox)." We introduce a microscopic model for these centers with oxygen substituting for nitrogen in the bridging site.

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The magnesium (Mg) acceptor is the most common commercially employed dopant for creating effective p-type III-nitrides for optoelectronics. Despite its widespread use, the true nature of the magnesium acceptor is much debated and its interplay with other atomic species within the GaN lattice remains mysterious. During the growth of GaN, many unintentional dopants will be incorporated, such as oxygen, hydrogen, and carbon,[1] rendering the interaction of magnesium with many other atomic species inevitable. These dopant species can cause numerous negative effects on the electrical and optical properties of the crystal, but may also be beneficial.

The rare-earth element europium (Eu) is incorporated into GaN in an attempt to create efficient optoelectronic devices that emit in the red.[2] In GaN, trivalent rare earth (RE^{3+}) ions present sharp intra-4*f* transition lines. Small changes in the ion's local environment will induce Stark splitting in the RE spectrum. This allows for these ions to be used as spectator ions to examine defect complexes within the crystal.

Together, within a GaN host, europium and magnesium form defect complexes displaying a curious behavior.[3] At room temperature, high quality GaN codoped with Eu and Mg displays luminescence spectra dominated by a single defect center (named "Eu0"[4]). Upon cooling (≈20 K) a sample under excitation, one observes a switch in optical dominance, from Eu0 to a more symmetric Eu1(Mg) center. This increase in symmetry is most clearly seen in the $^5D_0 \rightarrow {}^7F_1$ transition with the narrowing of the doublet, attributed to a photo-induced migration of the magnesium acceptor. To understand why this migration occurs, one must recognize the true character of the magnesium acceptor.

Using photoluminescence spectroscopy, Monemar *et al.*[5] found experimental evidence for two distinct acceptor states. Following this, Lany and Zunger introduced the concept of metastable shallow transient and deep ground states.[6] The shallow transient state (STS) exists when the acceptor's hole is delocalized, resulting in equal bond lengths to nearest nitrogen neighbors (2.05 Å). The STS produces a Eu0 center when present in a complex with a europium ion.[7] When the hole becomes localized at one specific bond, a deep ground state (DGS) is formed, elongating one bond length to 2.23 Å. It has been debated as to which particular bond the hole is localized to, with Lany and Zunger's original model suggesting a basal bond and latterly works by Callsen, Lyons, and Davies suggesting an axial bond localization.[8–10] The particular model by Singh *et al.*, which we extend in this work, favors an axial localization, driving the acceptor away from the interlinking nitrogen ion.[7] This effectively increases the Eu–Mg separation and is the root cause of the symmetry increase observed in the Eu0 → Eu1(Mg) transition.

Switchback from Eu1(Mg) to Eu0 upon warming occurs at higher temperatures (≈100 K) giving a hysteretic defect switching

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cycle. The behavior of this metastable system is therefore described as hysteretic photochromic switching (HPS).

Oxygen incorporated during the growth of GaN is known to influence carrier concentrations, implying that oxygen acts as a shallow donor and likely lies on a nitrogen site.[11] This substitutional oxygen is shown to be singly positively charged and have a very low formation energy, lower than that of a nitrogen vacancy; this gives an explanation as to why oxygen is likely the cause of the unintentional *n*-type conductivity of GaN. Other oxygen sites such as interstitials and gallium substitutions are possible, although these alternative oxygen placements would not be energetically favorable. Calculations have shown that oxygen ions may form complexes with gallium vacancies to reduce Coulomb energy.[12] It is expected that these defects may contribute to broad band yellow luminescence (YL), via shallow donor to deep acceptor transitions.[13,14] This case is supported further by positron annihilation spectroscopy measurements that show a relation between the negatively charged gallium vacancy concentration and YL intensity.[15] When forming complexes with magnesium, the most energetically favorable configuration would be neighboring substitutional sites with the oxygen sitting on the nitrogen site and magnesium on a gallium site. When in this configuration, ions lie almost directly substitutional with a minimal influence on the neighboring atoms in the crystal.[16]

Only recently has the role of oxygen in europium doped GaN been investigated. Experimentally, oxygen was found to play a critical role in facilitating europium incorporation during MOVPE growth.[17] Rutherford backscattering spectrometry measurements showed that with oxygen free growth only 70% of Eu ions sat on the desired substitutional Eu_{Ga} sites, with the rest incorporated as interstitials. From this, it is apparent that an oxygen presence is beneficial for the growth (although for electroluminescent technologies, the quantity must be limited, as a portion of these ions will be electrically active). Unfortunately, this work was not extended to p-type GaN.

Theoretical works by Massago *et al.* have predicted that co-doping GaN with europium, magnesium, and oxygen may be advantageous for optoelectronic devices.[18,19] They predict stable and efficient light-emitting europium centers thanks to acceptor and donor levels improving excitation pathways. Until now, no experimental work has been able to test this prediction. Here, we experimentally examine GaN:Eu,Mg,O using temperature dependent photoluminescence spectroscopy and relate our results to previous work, producing a model of the defect complexes in the system and describing their properties.

For temperature dependent photoluminescence (TDPL) measurements, excitation was preformed using a 355 nm CW laser (Cobolt Zouk) with a maximum power of 20mW passed through a neutral density filter to reduce power down to 2mW over a 1.5 mm spot. The light emitted from the sample was collected into a 0.67m spectrometer (McPherson 207) and dispersed over a cooled CCD (Andor Technology). For room temperature measurements, excitation was preformed by a 1000 W xenon arc lamp fed through a monochromator to obtain a 355 nm beam. The collection system remains the same as for the temperature dependent measurements.

GaN:Mg was grown on sapphire by MOVPE and then ion implanted with Eu (300 keV) and either N (40 keV) or O (37 keV). This resulted in a maximum overlap of doping profiles 60 nm below the surface. For samples implanted with nitrogen and oxygen using fluences ranging from 1×10^{13}cm^{-2} to 1×10^{14} cm^{-2}, europium was implanted with 3×10^{13} cm^{-2}. This results in peak concentrations of nitrogen and oxygen $\approx 1.4 \times 10^{18}$ cm^{-3} to 1.4×10^{19} cm^{-3} and a europium concentration of 6×10^{18} cm^{-3} to match the mean magnesium concentration. Samples implanted with more extreme oxygen fluences of 3×10^{14} cm^{-2} (4.2×10^{19} cm^{-3}) and 1×10^{15} cm^{-2} (1.4×10^{20} cm^{-3}) were also prepared, but with higher levels of europium—1×10^{14}cm^{-2} (2×10^{19}cm^{-3})—and magnesium which decreases some broad band luminescence. To repair damage caused by ion implantation, high temperature high pressure (HTHP) annealing was performed at 1400 °C under 1 GPa of N_2 for 30 minutes. This corresponds to the optimum annealing conditions for the optical activation of Eu.[20]

Room temperature photoluminescence spectra taken from oxygen implanted samples and a nitrogen implanted sample are compared in Figs. 1(a) and 1(b). The nitrogen implanted sample displays a classic Eu0 emission spectrum, which can be confirmed by the wavenumber table in Ref. 21. The oxygen implanted samples show a superficially similar, but nonetheless distinct emission spectrum. The majority of spectral lines appear only to be slightly shifted, by around ±0.01 nm on average. The largest disparity occurs in the $^5D_0 \rightarrow {}^7F_2$

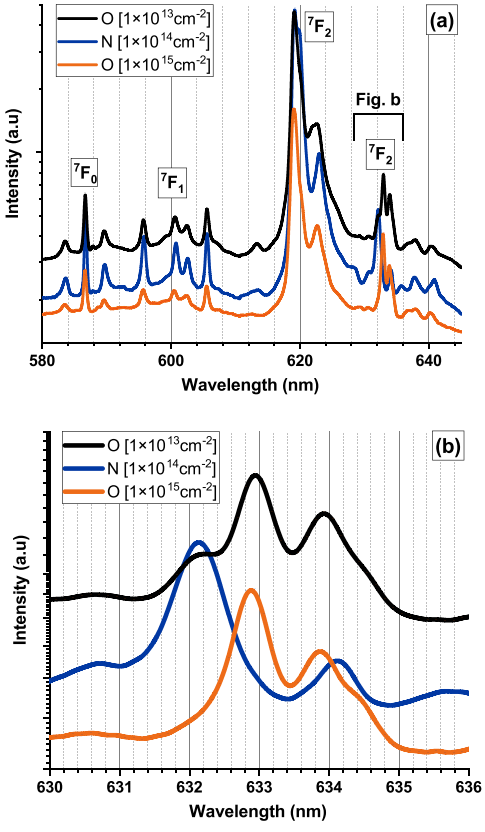

FIG. 1. Room temperature PL spectra for three samples. Spectral region (a) includes the entirety of $^5D_0$ to $^7F_{0,1,2}$ transitions and some $^5D_0$ to $^7F_3$ transitions. (b) Highlights of a $^5D_0$ to $^7F_2$ doublet which exhibits the largest spectral disparity of nearly 1 nm.

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doublet near 630 nm, where the shift is closer to 1 nm [Fig. 1(b)]. This minimal but measurable perturbation of the spectral landscape explains why the existence of these centers has gone hitherto unrecognized. These centers will henceforth be referred to as Eu0(Ox) due to their spectral similarities with "real" Eu0 sites.

Although not shown here, the presence of substantial populations of Eu0(Ox) is accompanied by an increase in competing broad band (peaks at 405 nm and 570 nm) and near band edge (365 nm) luminescence, resulting in a decrease in europium luminescence. This is not unexpected, with excess oxygen shallow donors potentially pairing with deep acceptor gallium vacancies allowing for the shallow-deep transitions required for YL. It should be mentioned that the broad band behavior of these samples is non-trivial, being affected by dopants, implantation defects, and annealing and so will not be discussed in detail here. The presence of these additional broad bands would be detrimental to creating an efficient light emitting device in the red.

The existence of oxygen induced centers is further evidenced by TDPL measurements. The luminescence from each defect center species should have a characteristic dependence on temperature. The expected TDPL behavior in the $^5D_0 \rightarrow {}^7F_0$ region in oxygen free samples is shown in Fig. 2(a). The Eu0 singlet transmission rapidly decreases at low temperatures, as the population evolves and acceptors migrate forming Eu1(Mg) centers. This particular sample has been implanted with nitrogen to explore the possibility that the ballistic ion implantation may be causing the formation of additional defect centers. As can be seen in the spectra, there is no obvious indication that this is the case. The nitrogen implanted samples, regardless of implantation fluence, all display Eu0 and Eu1(Mg) emissions. This is likely thanks to the post implantation HTHP annealing acting as a quasi-regrowth step and repairing any damage.

An example of the TDPL of a highly oxygen implanted sample is shown in Fig. 2(b). Here, we observe the coexistence of Eu0 and Eu0(Ox). During cooling under excitation, the real Eu0 population will begin migrating into Eu1(Mg) through HPS as expected, while the Eu0(Ox) acceptor state remains anchored.

The highly oxygen implanted samples also display two unidentified emission lines in this region. By virtue of the singlet nature of the $^5D_0 \rightarrow {}^7F_0$ transition, we expect each center to display one line or no line regardless of the symmetry. This implies that these extra lines correspond to the emission from another two centers. Note, however, that the intensities of the lines here do not directly reflect the populations of their source centers. This is because this forbidden transition can only occur as a result of J-mixing or Wybourne-Downer mechanisms.[22] Both of these favor low symmetry sites, requiring a relaxation of the selection rules. A small population of low symmetry centers could therefore "outshine" a large population of highly symmetric centers in this spectral region, meaning these extra lines may be from small populations of low symmetry centers.

Although the fluences used to produce the samples examined in Figs. 2(a) and 2(b) differ, similar behaviors occur in samples implanted to a greater and lesser degree.

The temperature dependence of each center is plotted in Fig. 3 to allow for easy comparison. The data here stresses the stability of Eu0(Ox) and its anchored states over prolonged excitation times and various temperature ranges. Even at a temperature of 10 K, the population remains non labile and emission intensity stable.

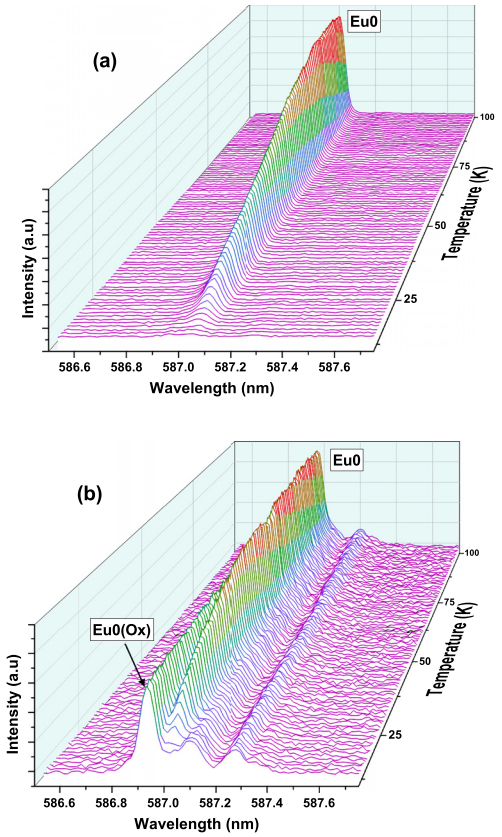

FIG. 2. TDPL measurements acquired during cooling from 295 K to 10 K. (a) Shows the spectra from a nitrogen implanted (10^{13} cm^{-2}) sample displaying the familiar decrease in Eu0 as population transfer occurs. (b) Shows the spectra from an oxygen implanted (10^{15} cm^{-2}) sample displaying multiple spectral lines and dependencies in addition to the expected decrease in Eu(0). The strongest among these lines following the decay of Eu0 is the closely lying Eu0(Ox).

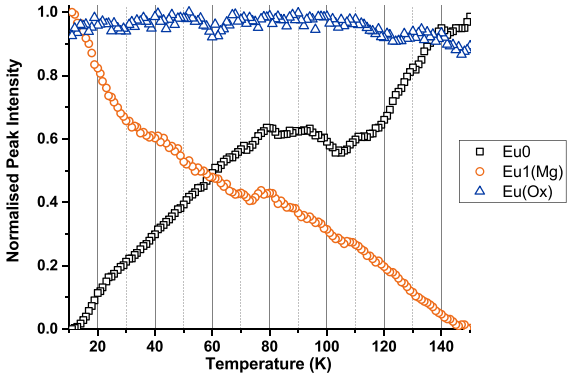

FIG. 3. Temperature dependences of normalized peak intensities for the three dominant centers. The data for Eu0 and Eu1(Mg) were extracted from a TDPL cooling run of a nitrogen implanted sample. The Eu0(Ox) signal was traced from an oxygen implanted sample.

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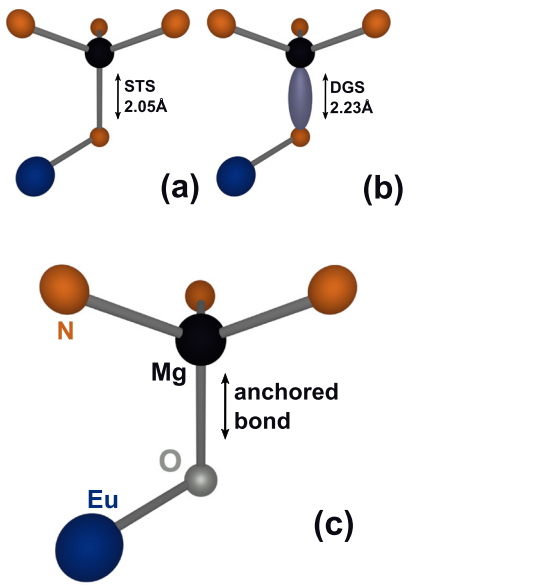

FIG. 4. Microscopic models displaying (a) Eu0, (b) Eu1(Mg), and (c) Eu0(Ox): nitrogen in orange, europium in blue, magnesium in black, and oxygen in gray. An extended axial magnesium bond length is shown in Eu1(Mg), and a strong anchoring bond between magnesium and oxygen is shown in Eu0(Ox).

In proposing a coherent configuration for these defects, we extend a previous model describing the Eu0 and Eu1(Mg) centers. This model, based on dynamic acceptor states and mobile ions, is modified to include the implanted oxygen and the formation of the Eu0(Ox) center. The accepted structure for the Eu0 and Eu1(Mg) defects as described by Singh *et al.*[7] consists of both centers having similar Eu_{Ga}–N–Mg_{Ga} compositions but unique magnesium axial bond lengths. This is due to the transformation in acceptor states from STS to DGS; these centers can be seen in Figs. 4(a) and 4(b), respectively.

From energetic considerations, the oxygen will likely lie at a nitrogen substitutional site. When neighboring a magnesium acceptor, these form the closest donor–acceptor pair possible, existing as an isoelectronic complex. For single europium centers containing oxygen and magnesium in GaN, the most favorable configuration is Eu_{Ga}–O_N–Mg_{Ga}, seen in Fig. 4(c).[18]

From this system, we can form an explanation as to why Eu0(Ox) is state anchored and does not undergo HPS despite its spectral resemblance to Eu0. In the Eu0(Ox) complex, out of the four bonds the magnesium acceptor will make, the Mg–O bond will be the strongest. This is caused by a significant increase in ionicity (Pauling contrast + 0.4) and will force an anisotropic hole distribution. Despite the unusual state, large disturbances of the spectator ion's local crystal environment will be avoided thanks to the acceptor remaining close to the ideal substitutional site and causing minimal external relaxation. A minimal change in the electric field would induce a stark splitting congruent with what we observe spectroscopically.

To conclude, we have unveiled a europium magnesium defect with a previously unseen acceptor state, responsible for anchored acceptor states resistant to hysteretic photochromic switching. This defect is formed when an oxygen ion substitutes for the bridging nitrogen between the europium spectator and the magnesium acceptor. The stability of these centers is attributed to the increase in bond strength between the axial acceptor and the bridging ion, causing an anisotropic hole distribution preventing the conventional shallow transient and deep ground states of the acceptor from forming.

DATA AVAILABILITY

The data presented in this paper are available at https://doi.org/10.15129/0fcb3dc2-582f-489a-ab88-2d141f7c2611.

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