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Abstract

Although *p*-type activation of GaN by Mg underpins a mature commercial technology, the nature of the Mg acceptor in GaN is still controversial. Here, we use implanted Eu as a 'spectator ion' to probe the lattice location of Mg in doubly doped GaN(Mg):Eu. Photoluminescence spectroscopy of this material exemplifies hysteretic photochromic switching (HPS) between two configurations, Eu0 and Eu1(Mg), of the same

Eu-Mg defect, with a hyperbolic time dependence on 'switchdown' from Eu0 to Eu1(Mg). The sample temperature and the incident light intensity at 355 nm tune the characteristic switching time over several orders of magnitude, from less than a second at 12.5 K, ~ 100 mW/cm² to (an estimated) several hours at 50 K, 1 mW/cm². Linking the distinct Eu-Mg defect configurations with the shallow transient and deep

ground states of the Mg acceptor in the Lany-Zunger model, we determine the energy barrier between the states to be 27.7(4) meV, in good agreement with the predictions of theory. The experimental results further suggest that at low temperatures holes in deep ground states are localized on N atoms axially bonded to Mg acceptors. [1]

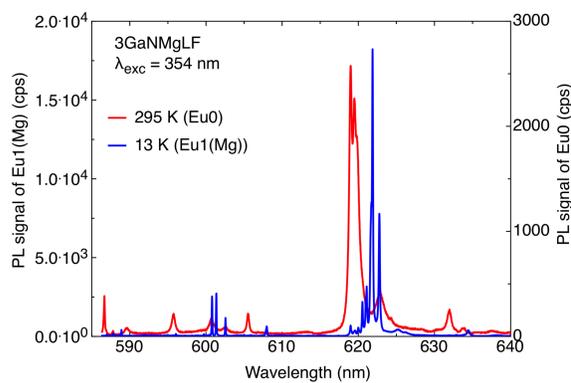


Link to paper

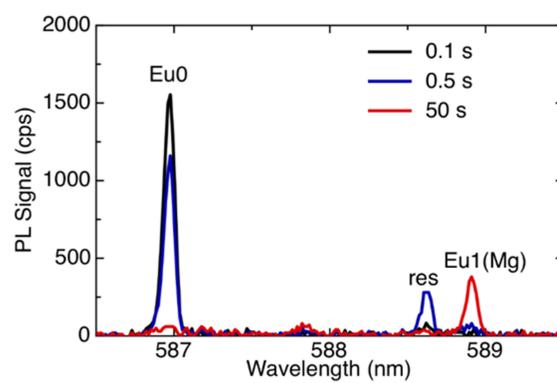
Sample fabrication

1. **MOCVD growth** of 2 μ m GaN on sapphire, doped with Mg to $1.1\text{--}1.2 \times 10^{19}$ cm³ (Cambridge)
2. **Implantation** of Eu ions at multiple energies (70–380 keV) to approximately match the Mg concentration (Lisbon)
3. **Annealing** in N₂ atmosphere at 1400 °C and 1 GPa to repair implantation damage (Warsaw)

Photoluminescence spectroscopy

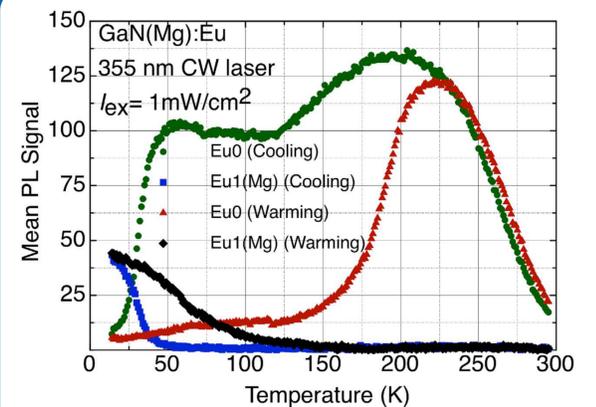


- Sharp PL lines due to intra-4*f* transitions
- Each transition (⁵D₀–⁷F₁ triplet, ⁵D₀–⁷F₂ multiplet etc.) shows **two distinct centres**



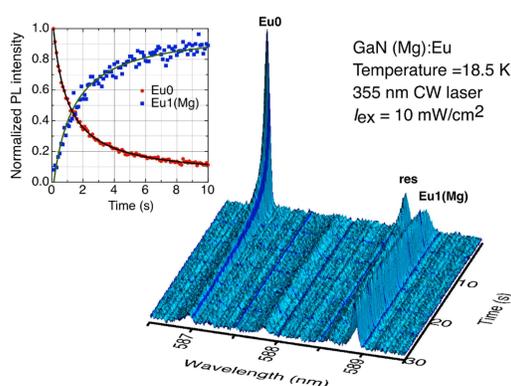
- '**Eu1(Mg)**' dominates at low T, '**Eu0**' at high T
- We focus here on the simplest transition, the ⁵D₀–⁷F₀ singlet (no Stark line splitting)

Luminescence hysteresis

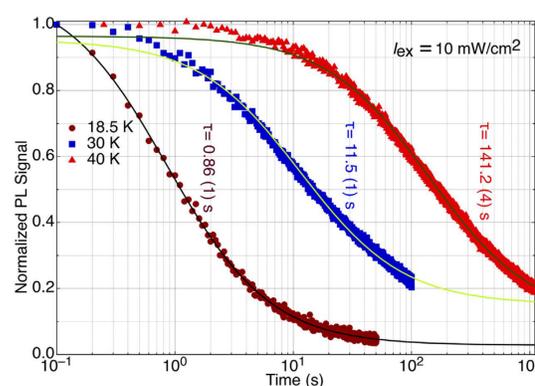


- Switching is reversible but **hysteretic** with temperature

Photochromic switching

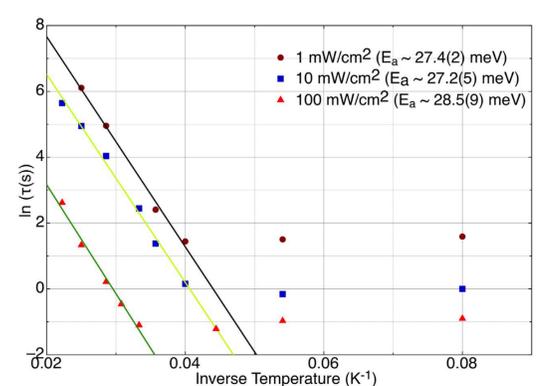


- Sample **cooled in dark**—out of equilibrium
- Excitation source turned on, simultaneously **causing** and **monitoring** the switch from Eu0 to Eu1(Mg)



- Switching occurs with **hyperbolic** time dependence:

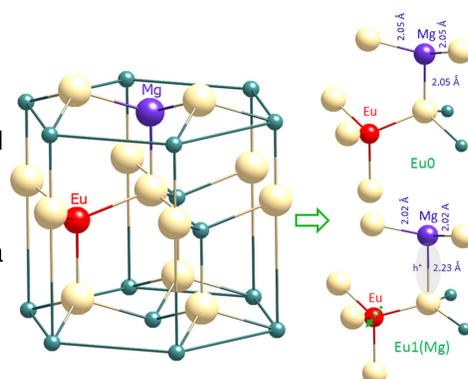
$$I(t) = I(\infty) + \frac{I(0) - I(\infty)}{1 + t/\tau}$$



- Time constant is temperature and power dependent
- Arrhenius plot gives activation energy of $\sim 27.7(4)$ meV

Proposed model

- Eu and Mg impurities prefer Ga substitutional sites
- Eu0/Eu1(Mg) defect comprises single Mg atom associated with substitutional Eu
- Eu0 to Eu1(Mg) switching related to structural instability of Mg acceptor in GaN
- crystal field theory, applied to the ⁷F₁ multiplet of Eu0, suggests a strong non-axial distortion [2]: Mg might be linked through non-axial nitrogen to spectator Eu³⁺ ion
- emission lines very sharp: definite sites rather than a distribution.
- activation energy of ~ 27.7 meV is close to the ~ 20 meV energy barrier between a *shallow acceptor state* and *deep ground state* predicted by Lany and Zunger [3]
- **Eu0: shallow acceptor state**
- **Eu1(Mg): deep ground state**—hole localised on N atom



References

- [1] A. K. Singh, K. P. O'Donnell, P. R. Edwards, K. Lorenz, M. J. Kappers & M. Boćkowski (2017) *Sci. Rep.* **7**, 41982.
- [2] K. P. O'Donnell, P. R. Edwards, M. Yamaga, K. Lorenz, M. J. Kappers & M. Boćkowski (2016) *Appl. Phys. Lett.* **108**, 022102.
- [3] S. Lany & A. Zunger (2010) *Appl. Phys. Lett.* **96**, 142114.

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