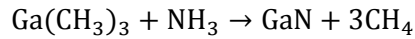
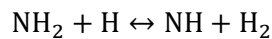
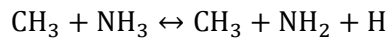


Hydrogen in Mg-doped GaN

- Sources of hydrogen for MOCVD-grown Mg-doped GaN include the MO sources such as trimethylgallium (TMGa) as well as ammonia (NH₃) and the H₂ carrier gas. Below is a typical reaction that occurs when TMGa and NH₃ are formed during GaN growth:



Many reactions occur during MOCVD growth¹ and reactions that produce hydrogen include:



- The group III and V precursors and the H₂ carrier gas can passivate GaN:Mg.
- Diatomic hydrogen is electrically and optically inactive whose diffusivity is small inside a semiconductor.
- Atomic hydrogen whose diffusivity is large form neutral complexes with dopant atoms or combine with dangling bonds.
- Neutral complexes increase carrier mobility and resistivity of GaN:Mg.
- Residual hydrogen present during growth leads to highly resistive GaN:Mg.

Thermal annealing

Annealing of semiconductor materials or devices is performed for dopant activation, dopant diffusion, junction formation, oxide formation, reduction of defect densities, and other purposes.

- Annealing is required for activating Mg_{Ga} acceptor that has an activation energy of 170 meV.
- After dissociation of neutral dopant-hydrogen complexes during annealing, hydrogen diffuses to extended defects or surface.
- Annealing above 850 °C can create defects and lead to nitrogen desorption.
- MBE-grown GaN:Mg has p-type conductivity after growth, even without annealing.
- MOCVD-grown GaN:Mg using N₂ as a carrier gas can be p-type conductive without annealing
- Methods other than thermal annealing can activate Mg acceptors in GaN:Mg such as low-energy electron-beam irradiation (LEEBI)².

Below are two thermal annealing methods:

Furnace thermal anneal: Typically a high temperature diffusion furnace used to anneal a sample for long periods of time (~30 min to a few hours).

- Heats sample through conduction
- High temperature uniformity over wafer

- Minimal thermal stress (long transients)
- Batch process

Rapid thermal annealing (RTA): The process by which a sample or substrate is heated rapidly (~20-200 °C/sec.) to a particular temperature, remains at that temperature for a brief amount of time (1-10 min.), and then is quickly (1-5 min.) cooled back to room temperature.

- Radiates sample typically through the use of high-intensity lamps
- Minimal transient times
- Minimizes dopant diffusion
- Single-wafer process

Activation of Mg-doped GaN

Experiments have been performed using N₂, NH₃, H₂: N₂ (5:95 or 7:93), O₂, and air as the ambient during post-growth annealing typically using an RTA system and are described as follows:

Nitrogen (N₂) ambient: Most common ambient used for Mg-doped GaN activation (see, for example, ref. 3)

- Annealing above 600 °C GaN:Mg exhibits p-type conductivity due to the dissociation of neutral dopant-hydrogen complex.
- Annealing between 700 °C and 1000 °C p-type conductivity remains relatively the same.

Oxygen (O₂) ambient: Commonly used to produce transparent ohmic contacts such as ITO, but is also performed for activation of GaN:Mg (see, for example, ref. 4)

- Removal of hydrogen from neutral dopant-hydrogen complex occurs at lower annealing temperatures (500 °C or higher) compared to N₂ ambient annealing.
- O₂ annealing of GaN:Mg typically shows a higher hole concentration value compared to N₂ ambient
- Ga-oxide islands form on GaN:Mg surface and enhance the electrical conductivity.

Air ambient: Commonly used to produce transparent ohmic contacts such as Ni/Au but is also studied for activation of GaN:Mg (see, for example, ref. 5)

- Annealing 500 °C for 30 min can produce GaN:Mg of high hole concentration = 10^{18} cm^{-3} with a Mg doping of 10^{19} cm^{-3} .
- Peak PL intensity of air annealed sample compared to N₂ annealed sample at 500 °C for 30 min are identical.
- Yellow luminescence (YL) band occurs for samples annealed in air.
- Ga vacancies are assumed to assist in the activation of Mg.

Passivation of Mg-doped GaN

Ammonia (NH₃) ambient: NH₃ begins to dissociate into N₂ + H₂ above 200 °C and will *passivate* Mg in GaN:Mg rather than *activate* Mg (see, for example, ref. 2)

- The diatomic hydrogen molecules minimize the activation of Mg-doped GaN due to the reincorporation of atomic hydrogen that form neutral dopant-hydrogen complexes.
- Annealing above 400 °C increases resistivity of GaN:Mg while blue luminescence (BL) band intensity decreases.

Forming gas H₂:N₂ (5:95 or 7:93) ambient: Used to study the effect of forming gas on the passivation of GaN:Mg (see, for example, ref. 6)

- Annealing between 700 °C to 800 °C passivated GaN:Mg using H₂:N₂ (7:93) forming gas.
- Ultra-violet luminescence (UVL) band of GaN:Mg increases when annealed in H₂:N₂ (5:95) ambient.

References

1. A. Hirako, K. Kusakabe, and K. Ohkawa, "Modeling of reaction pathways of GaN growth by metalorganic vapor-phase epitaxy using TMGa/NH₃/H₂ system: a computational fluid dynamics simulation study", *Jpn. J. Appl. Phys.* **44**, 874 (2005)
2. S. Nakamura, M. Senoh, and T. Mukai, "Highly p-typed Mg-doped GaN films grown with GaN buffer layers", *Jpn. J. Appl. Phys.* **30**, L1708 (1991)
3. S. Nakamura, N. Iwasa, M. Senoh, T. Mukai, "Hole compensation mechanism of p-type GaN films", *Jpn. J. Appl. Phys.* **31**, 1258 (1992)
4. Y. Nakano, O. Fujishima, T. Kachi, "Effect of p-type activation ambient on acceptor levels in Mg-doped GaN", *J. Appl. Phys.* **96**, 415 (2004)
5. Y-J Lin, "Activation mechanism of annealed Mg-doped GaN in air", *Appl. Phys. Lett.* **84**, 2760 (2004)
6. M. A. Reshchikov and H. Morkoc, "Luminescence properties of defects in GaN", *J. Appl. Phys.* **97**, 061301 (2005)