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 (NH_3) and the H_2 carrier gas. Below is a typical reaction that occurs when TMGa and NH_3 are formed during GaN growth:

  $$\mathrm{Ga(CH_3)_3 + NH_3 \rightarrow GaN + 3CH_4}$$

  Many reactions occur during MOCVD growth[1] and reactions that produce hydrogen include:

  $$\mathrm{CH_3 + NH_3 \leftrightarrow CH_3 + NH_2 + H}$$

  $$\mathrm{NH_2 + H \leftrightarrow NH + H_2}$$

- The group III and V precursors and the H_2 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 N_2 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 N_2, NH_3, $H_2 : N_2$ (5:95 or 7:93), O_2, and air as the ambient during post-growth annealing typically using an RTA system and are described as follows:

Nitrogen (N_2) 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 (O_2) 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 N_2 ambient annealing.
- O_2 annealing of GaN:Mg typically shows a higher hole concentration value compared to N_2 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 N_2 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 (NH_3) ambient: NH_3 begins to dissociate into N_2 + H_2 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 H_2:N_2 (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 H_2:N_2 (7:93) forming gas.
- Ultra-violet luminescence (UVL) band of GaN:Mg increases when annealed in H_2:N_2 (5:95) ambient.

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