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“Ultra High p-doping Material Research for GaN Based Light Emitters”

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Project Summary

The main goal of the Project is to investigate doping mechanisms in p-type GaN and AlGaN and controllably fabricate ultra high doped p-GaN materials and epitaxial structures. Highly doped p-type GaN-based materials with low electrical resistivity and abrupt doping profiles are of great importance for efficient light emitters for solid state lighting (SSL) applications. Cost-effective hydride vapor phase epitaxial (HVPE) technology was proposed to investigate and develop p-GaN materials for SSL.

High p-type doping is required to improve (i) carrier injection efficiency in light emitting p-n junctions that will result in increasing of light emitting efficiency, (ii) current spreading in light emitting structures that will improve external quantum efficiency, and (iii) parameters of Ohmic contacts to reduce operating voltage and tolerate higher forward currents needed for the high output power operation of light emitters. Highly doped p-type GaN layers and AlGaN/GaN heterostructures with low electrical resistivity will lead to novel device and contact metallization designs for high-power high efficiency GaN-based light emitters. Overall, highly doped p-GaN is a key element to develop light emitting devices for the DOE SSL program. The project was focused on material research for highly doped p-type GaN materials and device structures for applications in high performance light emitters for general illumination.

P-GaN and p-AlGaN layers and multi-layer structures were grown by HVPE and investigated in terms of surface morphology and structure, doping concentrations and profiles, optical, electrical, and structural properties. Tasks of the project were successfully accomplished. Highly doped GaN materials with p-type conductivity were fabricated. As-grown GaN layers had concentration $N_a-N_d$ as high as $3 \times 10^{19}$ cm$^{-3}$. 
Mechanisms of doping were investigated and results of material studies were reported at several International conferences providing better understanding of p-type GaN formation for Solid State Lighting community. Grown p-type GaN layers were used as substrates for blue and green InGaN-based LEDs made by HVPE technology at TDI.

These results proved proposed technical approach and facilitate fabrication of highly conductive p-GaN materials by low-cost HVPE technology for solid state lighting applications. TDI has started the commercialization of p-GaN epitaxial materials.
1. **Introduction**

In this project, TDI developed a novel technology of ultra highly doped p-type GaN layers and AlGaN/GaN heterostructures for lighting applications. Highly doped p-type GaN-based materials with low electrical resistivity and abrupt doping profiles are of great importance for efficient light emitters for SSL applications. High p-type doping is required to improve (i) carrier injection efficiency in light emitting pn junctions, (ii) current spreading in light emitting structures, and (iii) parameters of Ohmic contacts to reduce operating voltage and tolerate higher forward currents needed for the high output power operation of light emitters. The project is focused on material research for highly doped p-type GaN materials and device structures for applications in high-efficient light emitters for general illumination. The project goal is to investigate novel technological approaches and doping mechanisms for p-type GaN layers and AlGaN/GaN heterostructures.

2. **Project Objectives**

1. Investigation of doping mechanisms in p-type GaN.

2. Study of an influence of background impurities (oxygen, carbon, hydrogen, and others) and crystal defects on doping efficiency, hole concentration and mobility in highly-doped GaN materials.

3. Determination of growth conditions resulting in a maximum doping efficiency and lowest electrical resistivity in highly-doped p-type GaN and AlGaN materials.

3. Technical Approach

The proposed technology to grow highly-doped p-type GaN materials and AlGaN/GaN structures is based on hydride vapor phase epitaxy (HVPE). The HVPE is known as a low cost technique to produce low-defect n-type GaN layers with high electron mobility and low background carrier concentrations.

N-type GaN and AlGaN grown by HVPE are known to have a record-high electron mobility, probably due to low defect density in HVPE materials and self-cleaning effect provided by HCl gas. TDI has demonstrated precise Si doping for n-type HVPE grown GaN. Due to ability to deposit GaN materials with high deposition rate, it is possible to grow thick GaN layers on low cost sapphire substrates with defect density below $10^7$ cm$^{-2}$. These features of the HVPE technique open an opportunity to grow and investigate p-type GaN layers on low-defect GaN foundation layer fabricated in the same epitaxial run.

4. Project Results

P-GaN and p-AlGaN layers and multi-layer structures were grown by HVPE and investigated in terms of surface morphology and structure, doping concentrations and profiles, optical, electrical, and structural properties. Tasks of the project were successfully accomplished. The main results are summarized below and illustrated by figures given in Section 6 of the report.

- 2-10 µm thick p-GaN layers were grown by HVPE on sapphire substrates. Mg and Zn impurities were used for doping.
• Mg doping can be precisely controlled providing both uniform doping and abrupt doping profiles with low memory effect. Depending on growth conditions, Mg atomic concentration may be controlled in the range from \(10^{16}\) to \(10^{20}\) cm\(^{-3}\).

• Investigation of background impurities in p-GaN and p-AlGaN was performed by secondary ion mass spectrometry (SIMS). Hydrogen atomic background concentration is up to one order of magnitude less than that of Mg in a wide range of Mg doping for p-type GaN layers.

• As-grown Mg-doped GaN layers grown by HVPE showed p-type conductivity without any activation.

• Concentration \(N_A-N_D\) up to \(3 \times 10^{19}\) cm\(^{-3}\) was obtained for as-grown Mg-doped GaN layers.

• Abrupt Zn-doping profiles were demonstrated. Concentration \(N_A-N_D\) up to \(8 \times 10^{17}\) cm\(^{-3}\) was obtained for as-grown Zn-doped p-GaN layers. Two-dimensional hole gas (2DHG) in p-GaN/AlGaN structures was studied.

• Process for precise Zn concentration control was developed resulting in n-, i-, and p-type GaN layers.

• First HVPE grown p-GaN/p-AlGaN superlattices were demonstrated.

• P-GaN layers were used as substrate materials for HVPE grown InGaN-based LED structures. First blue (450-480 nm) and green (490-510 nm) n-InGaN/p-GaN inverted LED structures were grown.

• Novel process to form Ohmic contacts to p-type GaN layers has been developed at NIST based on p-GaN materials produced by TDI.
Unique features of HVPE technology related to p-type GaN are the following:

- P-type GaN layers having thickness up to 15 microns were grown, for the first time.
- Low background impurity concentrations in HVPE grown Zn- and Mg-doped GaN layers leads to high hole mobility and low electrical resistivity.
- As-grown Mg-doped GaN layers have p-type conductivity with concentration \( N_A - N_D \) up to \( 3 \times 10^{19} \text{ cm}^{-3} \).
- As-grown Zn-doped GaN layers have p-type conductivity with concentration \( N_A - N_D \) up to \( 1 \times 10^{17} \text{ cm}^{-3} \). P-type GaN doped with Zn has not been reported by MOCVD so far.
- Hydrogen atomic concentration in HVPE grown GaN is substantially less than both Mg and Zn atomic concentrations. This low background hydrogen atomic concentration in may explain high values of \( N_A - N_D \) concentration in as-grown GaN layers.

TDI has started commercialization of Mg-doped p-GaN materials grown by HVPE. P-Ga(Al)N/sapphire wafers produced by TDI have been sold to more than 20 customers worldwide including industrial and academia customers. Future commercialization plan includes three main goals:

- Fabrication and sale of low defect p-GaN-on-sapphire templates.
- Development and commercialization of bulk p-GaN materials.
- Development and commercialization of novel LED structures employing p-GaN substrate materials.
Additional information on p-GaN templates developed at TDI can be found on the website at [http://www.tdii.com](http://www.tdii.com)

5. Experimental

GaN and AlGaN layers were grown using multi-wafer proprietary HVPE growth machine designed and assembled at TDI. The HVPE growth machine was equipped with an atmospheric-pressure horizontal hot-wall quartz reactor and resistively heated furnaces. Figure 1 shows a schematic view of the HVPE process. Ammonia and hydrogen chloride (HCl) served as the active incoming gases and Ar served as a carrier gas. Ga and Al metals were used as group III material sources. The HCl was passed over Al and (or) Ga metallic sources located in the separate gas channels to form aluminum and gallium chlorides, respectively. The chlorides were transferred to the growth zone with flowing argon where they reacted with ammonia to form GaN, AlGaN or AlN layers on the substrate depending on the chloride flows. Mg and Zn were used for doping. Growth temperature was about 1050°C. Epitaxial layers and structures were grown on 2-inch single side polished (0001) sapphire substrates. In more details, the HVPE growth procedure was described elsewhere [1,2].

The grown structures were characterized by X-ray diffraction (XRD), reflection high-energy electron diffraction (RHEED), optical and scanning electron microscopy (SEM), capacitance-voltage (C-V) mercury probe measurements at 1 MHz, Hall-effect measurements, photoluminescence (PL), and micro-cathodoluminescence (CL). Doping profiles in the structures were measured by SIMS. The micro-CL experiments were done at Boston University using Gatan MonoCL2 system attached to JSM6100 JEOL SEM.
and containing PMT and grating blazed at 250 nm. Both CL spectra and images were recorded from cross-sections using a 10 kV electron beam with 0.2-1 nA beam currents. The beam raster size was varied from 5.2×8 µm² to collect luminescence from larger areas to 2.1×1.1 µm² to collect local luminescence spectra. The recorded spectra were corrected for the system response. Monochromatic CL images were obtained by collecting luminescence at the wavelengths selected by the grating.

Cross-sectional image of Mg-doped GaN layers grown on sapphire substrate is given in Fig. 2. In this project, thickness of p-type GaN layers was varied from 2 to 15 µm. Atomic Mg concentration in grown layers was varied from 10¹⁶ to 10²⁰ cm⁻³.

As-grown p-GaN layers had smooth surface (Fig. 3). Crystalline structure of the surface was studied by RHEED. Figures 4 and 5 show RHEED patterns obtained for p-GaN as-grown surface. The RHEED patterns indicate high crystalline quality of the near-surface region of the material. Concentration N_A-N_D for this as-grown sample was about 3×10¹⁸ cm⁻³.

As-grown Mg-doped GaN layers had p-type conductivity with concentration N_A-N_D ranging from 2×10¹⁶ to 3×10¹⁹ cm⁻³ depending on the doping level and growth conditions. As-grown Zn-doped GaN layers had p-type conductivity with concentration N_A-N_D ranging from 2×10¹⁵ to 8×10¹⁷ cm⁻³.

As-grown Mg-doped GaN layers showed p-type conductivity without any activation. Concentration N_A-N_D as high as 3×10¹⁹ cm⁻³ was measured for as-grown Mg-doped GaN layers. It was detected that Mg atomic concentration (C_Mg) and N_A-N_D concentration depends on GaN growth rate. Under other growth and doping conditions
being equal, lower growth rate resulted in higher Mg atomic concentration. A similar tendency was observed for Si-doped GaN layers.

Results of SIMS analysis showed that hydrogen background atomic concentration is substantially less than Mg atomic concentration. Figure 6 shows relationship between Mg and H atomic concentrations in Mg-doped p-type GaN within a wide range of Mg concentrations from $3 \times 10^{17}$ cm$^{-3}$ to $1.6 \times 10^{20}$ cm$^{-3}$. The hydrogen background concentration remained lower than that for Mg in HVPE grown p-type GaN layers for the whole doping range. Hydrogen is known to form H:Mg complexes in GaN and post-growth activation is required to obtain p-type conductivity for MOCVD grown materials. Note that hydrogen is typically used as a carrier gas in MOCVD process. As-grown Mg-doped GaN layers grown by HVPE showed p-type conductivity without any activation of the grown layers. It was also observed for Mg-doped p-GaN layers that lower hydrogen concentration resulted in higher concentration $N_A - N_D$ values for materials having the same $C_{Mg}$ values (Table 1). This is another indication of an important role, which hydrogen plays in p-type GaN. It is suggested that doping efficiency may be substantially increased in MOCVD process by reduction of hydrogen content in the growth environment.

Although as-grown samples had p-type conductivity, we performed a post-growth thermal treatment (annealing) of the grown layers to study an influence of the activation on the net acceptor concentration $N_A - N_D$. Figure 7 shows comparison results of the $N_A - N_D$ concentration for as-grown samples and for the same samples after annealing procedure. The annealing was performed at about 750°C in argon ambient during 25 min.
It is seen that for p-type GaN with high as-grown \( N_A - N_D \) concentration activation of Mg is not needed.

X-ray diffraction measurements proved high crystalline quality of grown highly-doped GaN layers. For 3-5 \( \mu \text{m} \) thick p-type GaN layers, the FWHM values of x-ray \( \omega \)-scan rocking curves measured for the (00.2) symmetric and the (10.2) asymmetric reflections ranged from 350 to 500 arc sec and from 400 to 600 arc sec, respectively (Figs. 8-9). No clear dependence was observed for the FWHM values of X-ray rocking curves on doping concentrations in the range from \( 1 \times 10^{17} \text{ cm}^{-3} \) to \( 1 \times 10^{19} \text{ cm}^{-3} \). Noticeable increasing of the rocking curves width for the (10.2) reflection measured for Mg-doped GaN layers grown on AlN/sapphire templates may be due to an additional strain in the GaN/AlN/sapphire structures.

Hall-effect measurements at 300 K for as grown 4.5 \( \mu \text{m} \) thick Mg-doped p-GaN layer revealed hole mobility and carrier concentration of 15-65 cm\(^2\)V\(^{-1}\)s\(^{-1}\) and \( 4 \times 10^{17} - 8 \times 10^{18} \text{ cm}^{-3} \), respectively. The measured conductivity was as high as 37 \( \Omega^{-1} \text{ cm}^{-1} \) at room temperature (corresponding resistivity is about \( 2.7 \times 10^{-2} \Omega \text{ cm.} \) (Fig. 10).

Figure 11 shows SIMS depth profiles measured for multi-layer GaN structure comprising three Zn-doped GaN layers with various doping level. Sample surface is on the left side. Hydrogen background concentration is lower than Zn doping concentration at a doping level higher than \( 1 \times 10^{18} \text{ cm}^{-3} \). Concentration \( N_A - N_D \) up to \( 8 \times 10^{17} \text{ cm}^{-3} \) was measured for as-grown Zn-doped p-GaN layers. The grown structures had abrupt Zn-doping interfaces and demonstrated low level of Zn impurity memory in undoped layers. Turn-on slope of Zn profile (the right side slope in Fig. 11a) had a width of 100 nm. Turn-off slope of Zn profile (the left side slope in Fig. 11b) had a width less than
30 nm that was beyond the depth resolution of the SIMS analysis. No evidence of back Zn (or Mg) diffusion was observed. The data demonstrated the precise control of Zn atomic concentration by HVPE technology.

P-type Mg-doped AlGaN layers and p-AlGaN/p-GaN heterostructures (10 – 25 mol.% of AlN) were also grown and investigated. Hole mobility of 120 cm$^2$V$^{-1}$s$^{-1}$ at hole concentration of (3-6)×10$^{18}$ cm$^{-3}$ was measured in p-AlGaN/p-GaN heterostructure at room temperature for annealed sample. We believe this result indicates two-dimensional hole gas (2DHG) formation at the p-AlGaN/p-GaN interface.

Cathodoluminescence spectra acquired from the surface of heavily doped p-type GaN layer having concentration $N_A-N_D$ of about 1×10$^{19}$ cm$^{-3}$ consisted of dominated peak at 430 nm and a weak peak at 363 nm. To clarify the origin of the peaks, micro-CL measurements were performed on the sample cleaved edge. The sample was a 5.4 µm thick GaN layer doped with Mg-grown on sapphire. Fig. 12 shows micro-CL spectrum acquired by rastering 10 kV 0.4 nA e-beam over the area of 4×6 µm$^2$. Micro-CL measurements showed the same emission peaks at 362 nm and at 430 nm. Micro-CL studies performed on cleaved edge of the sample revealed a columnar-like structure of the GaN material with a non-uniform distribution of material regions having dominant 360 nm or 430 nm luminescence as shown in Fig. 13. SIMS data and micro-CL study confirm that thick Mg-doped GaN layers possesses p-type conductivity through the whole layer.

AlGaN based multi-layer structures consisting of 6 pairs p-GaN/p-AlGaN layers (11 nm/11 nm) were grown on GaN/sapphire templates. The surface morphology of the grown structures was featureless (Fig 14). High-resolution X-ray diffraction
measurements at $2\theta/\omega$ scan reveals satellite peaks confirming the existence of a superlattice (SL) structure.

Novel process to form Ohmic contacts to p-type GaN layers has been developed at NIST based on p-GaN materials produced by TDI.

To fabricate p-n light emitting structures, a set of n-InGaN layers having different InN content were grown by HVPE on GaN/sapphire templates. Depending on composition of InGaN layers, the structures exhibit EL emission covering blue-green (450 nm-510 nm) spectral region. Simple up side down LED based on HVPE grown at TDI p-GaN/n-InGaN structures were processed and tested at TDI, PARC and ARL demonstrating the first ever all-HVPE made InGaN-based blue and blue-green emitting devices.

References

6. Deliverables

Grown p-type samples were delivered to NIST for Ohmic contact development and material testing.

Grown p-type samples were delivered to Boston University for optical investigations.

Grown LED structures based on p-GaN template substrates were delivered to Palo Alto Research Center (PARC) for LED processing and testing.

Project results have been reported at numerous scientific conferences and meetings including:

1. Two poster and two oral presentations acknowledged DOE support at the International Workshop on Nitride Semiconductors held on October 22-27, Kyoto, Japan.


9. “Electrical and optical properties of thick highly doped p-type GaN layers grown by HVPE” A. Usikov, O. Kovalenkov, V. Soukhoveev, V. Ivantsov, A. Syrkin,
V. Dmitriev, A.Yu. Nikiforov, S.G. Sundaresan, S.J. Jeliazkov, and A.V. Davydov, poster presentation (with DOE project support acknowledgements) at the 7-th International Conference of Nitride Semiconductors (ICNS7), September 17-21, Las-Vegas, NV, 2007.


7. Tables.

Table 1. Atomic Mg doping concentration and atomic hydrogen background concentrations measured by SIMS in GaN samples showing different net acceptor concentration $N_A-N_D$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mg (cm$^{-3}$)</th>
<th>H (cm$^{-3}$)</th>
<th>$N_A-N_D$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$3.3 \times 10^{19}$</td>
<td>$1.3 \times 10^{18}$</td>
<td>$1.2 \times 10^{18}$</td>
</tr>
<tr>
<td>B</td>
<td>$1.3 \times 10^{19}$</td>
<td>$4 \times 10^{17}$</td>
<td>$1.2 \times 10^{19}$</td>
</tr>
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</table>
Figure 1. Schematic view of HVPE reactor used in the project. Typical growth conditions were the following:

- Growth temperature ~ 1050°C;
- Reactor pressure 1 atm;
- Growth rate 0.002 - 3.0 µm/min;
- Carrier gas argon;
- Doping Mg, Zn;
Figure 2. Cross-sectional SEM image of GaN p-n structure grown by HVPE on c-plane sapphire substrate. P-type GaN layer was doped with Mg. N-type and p-type layers were grown in the same epitaxial run.
Figure 3. Optical micro-photograph of p-type GaN layer having $N_A - N_D$ concentration of $3 \times 10^{19}$ cm$^{-3}$. 
Figure 4. RHEED pattern measured for p-GaN as-grown surface. Beam azimuth is along the [1120]. Survey angle is about 0.5°.
Figure 5. RHEED pattern measured for p-GaN as-grown surface. Beam azimuth is along the [1100] with rotation of ~10°. Survey angle is about 0°.
Figure 6. Relationship between Mg doping concentration and H background concentration in Mg-doped p-type GaN layers grown by HVPE on sapphire substrates. The data are taken form the SIMS analysis. Dashed line corresponds to equal atomic concentration of Mg and H.
Figure 7. Concentration $N_A - N_D$ measured for p-type GaN samples before and after thermal treatment (annealing). The annealing procedure was performed at about 750°C in argon ambient during 25 min.
Figure 8. The FWHM of (00.2) X-ray rocking curves vs. $N_A-N_D$ concentrations in as grown samples.
Figure 9. The FWHM of (10.2) X-ray rocking curves vs. $N_A - N_D$ concentrations in as grown samples.
Figure 10. Temperature dependence of electrical conductivity measured for p-GaN layer doped with Mg. The measured conductivity was as high as 37 $\Omega^{-1}\text{cm}^{-1}$ at room temperature (corresponding resistivity is about $2.7\times10^{-2} \Omega\text{cm}$.).
Figure 11. SIMS depth profiles measured for multi-layer GaN structure comprising three Zn-doped GaN layers with various doping level. Sample surface is on the left side. The data demonstrate an ability of the HVPE technology to form abrupt Zn doping profiles.
(a) The whole structure;
(b) Part of the structure in enlarged scale.
Figure 12. CL spectrum detected on cleaved edge of 5.4 µm thick p-GaN sample. The peak at 363 nm is coming from p-GaN/sapphire interface as seen in Fig.13 (left image). The peak at 430 nm is observed across the whole thickness of the p-GaN layer as shown in Fig.13 (right image).

Figure 13. Monochromatic cathodoluminescence micrographs of 5.4 µm thick Mg-doped GaN layer taken for a wavelength of 360 nm (left image) and 430 nm (right image). It is known that for p-type GaN doped with Mg either blue luminescent band at 2.7-2.9 eV (430-460 nm) or ultraviolet luminescence band at 3.0-3.2 eV (370-380 nm) dominate the PL spectrum. The micro-CL studies were performed on a cleaved edge of the sample. Columnar-like structure of the GaN material with a non-uniform distribution of material regions having dominant 360 nm or 430 nm luminescence was revealed.
6 pairs of GaN/AlGaN layers

Sketch of Mg-doped GaN/AlGaN superlattice (SL) structure grown by HVPE

GaN undoped layer:
- Thickness: 3 microns
- Growth rate: 1 µm/min

AlGaN barrier layers:
- AlN content (13%, 16%, and 119%)
- AlGaN growth rate: 0.8 nm/sec (~0.05 µm/min)
- AlGaN thickness: 11 nm

GaN well layers:
- GaN growth rate: 0.7 nm/sec (~0.04 µm/min)
- GaN thickness: 11 nm.

Optical micrograph of the SL surface morphology. The image width is about 300 µm.

HRXRD 2θ/ω scan for HVPE grown GaN/AlGaN multi-layer structure. Higher-order diffraction peaks are clearly seen indicating good periodicity.

**Figure 14.** Parameters of the first AlGaN<sup>Mg</sup>/GaN<sup>Mg</sup> superlattice grown by HVPE.