

Fermi Level Control of Point Defects During Growth of Mg-Doped GaN

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In this study, Fermi level control of point defects during metalorganic chemical vapor deposition (MOCVD) of Mg-doped GaN has been demonstrated by above-bandgap illumination. Resistivity and photoluminescence (PL) measurements are used to investigate the Mg dopant activation of samples with Mg concentration of $2 \times 10^{19} \text{ cm}^{-3}$ grown with and without exposure to ultraviolet (UV) illumination. Samples grown under UV illumination have five orders of magnitude lower resistivity values compared with typical unannealed GaN:Mg samples. The PL spectra of samples grown with UV exposure are similar to the spectra of those grown without UV exposure that were subsequently annealed, indicating a different incorporation of compensating defects during growth. Based on PL and resistivity measurements we show that Fermi level control of point defects during growth of III-nitrides is feasible.

Key words: Mg, GaN, UV excitation, Photoluminescence, Metal-organic chemical vapor deposition (MOCVD)

INTRODUCTION

Mg is utilized as a *p*-type dopant for GaN because its relatively low thermal ionization energy, estimated at 250 meV, and relatively high solubility have enabled the achievement of technologically useful hole concentrations.¹ In the past 20 years, GaN-based light-emitting diodes, laser diodes, and photodetectors have been developed, but the optical transitions in GaN:Mg are still not well understood.² Mg doping of GaN is complicated by compensation of Mg ions by H through the formation of a neutral Mg-H complex during growth.³ A post-growth thermal anneal is typically employed to dissociate the Mg-H complex and obtain *p*-type conductivity.^{3–5} It has been shown that, in GaN:Mg grown by metalorganic chemical vapor deposition

(MOCVD), a maximum hole concentration of mid 10^{17} cm^{-3} can be achieved, at room temperature, with Mg concentrations of $2 \times 10^{19} \text{ cm}^{-3}$ to $3 \times 10^{19} \text{ cm}^{-3}$.⁶ At higher Mg concentrations, there is overcompensation, which means there is an increase in the concentration of compensating donors different from H.⁷ Ideally, point defect control during growth would allow for a reduction of this overcompensation.

Illumination by UV lamps or lasers during MOCVD growth of II-VI compounds such as ZnO, ZnSe, ZnS, and CdTe has led to lower growth temperatures, enhancement of the growth rate, reduction of compensating defects, and an increase in *p*-type conductivity.^{8–12} Photoassisted MOCVD growth of GaAs has also been explored; illumination during growth enhanced the incorporation of Si at low growth temperatures and increased the growth rate of the material.¹³ These results gathered from II-VI and III-V compounds indicated that UV

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irradiation during growth affected the material, but the nature of the effect was not well understood. Only a few attempts at using UV illumination during growth of GaN and its ternary alloys have been reported, and the results have led to mixed conclusions.¹⁴

In this study we demonstrate point defect control in Mg-doped GaN, by UV irradiation during growth. First, details of the illumination process and experimental setup are explained. Then, we use photoluminescence (PL) spectroscopy as a tool to confirm Mg dopant activation by comparing the resistivity and PL spectra of the same samples. Finally, PL spectra and resistivity measurements of samples grown with and without exposure to above-bandgap UV light during growth are used to demonstrate that the samples exposed to UV light have a different incorporation of point defects.

EXPERIMENTAL PROCEDURES

GaN:Mg films were grown to thickness of about $0.7 \mu\text{m}$ by low-pressure MOCVD on top of $1.2 \mu\text{m}$ of nominally undoped Ga-polar GaN templates grown on (0001) *c*-plane sapphire. Trimethylgallium (TEG), ammonia (NH_3), and bis-cyclopentadienyl magnesium (Cp_2Mg) were used as sources for Ga, N, and Mg, respectively. The GaN:Mg films were grown at 1040°C using V/III ratio of 200. This V/III ratio was achieved by flowing $67 \mu\text{mol}/\text{min}$ of TEG and 0.3 slm of NH_3 under a total flow rate of 7.4 slm and reactor pressure of 20 Torr. The Cp_2Mg molar flow rate was $0.2 \mu\text{mol}/\text{min}$. Other details of the growth process can be found elsewhere.¹⁵ High-resolution x-ray diffraction (HRXRD) was used to characterize the crystalline quality of the samples. HRXRD was performed using a Philips XPert materials research diffractometer with a Cu anode. On- and off-axis rocking curves were obtained using a four-bounce Ge [220] crystal monochromator on the incident beam side and an open detector.

For this study, GaN films with nominal Mg concentration of $2 \times 10^{19} \text{ cm}^{-3}$ were grown with and without above-bandgap UV illumination. Secondary-ion mass spectroscopy (SIMS) measurements were performed to verify the Mg concentration. For samples grown with UV illumination, UV light from a 1-kW mercury arc lamp was directed onto the sample through a 2-inch UV-transparent window as shown in Fig. 1. This window was also used to monitor the growth temperature with a pyrometer. The focal point of the lens was positioned so that the UV light uniformly illuminated the entire sample. The power density of above-bandgap light incident on the samples was determined to be $\sim 1 \text{ W}/\text{cm}^2$ by using an Ophir PD300 photodetector. An unintentionally doped GaN wafer was used as a filter to measure the power density of below-bandgap light. The power density of above-bandgap light was determined by subtracting this power density from the total measured power density. Samples were

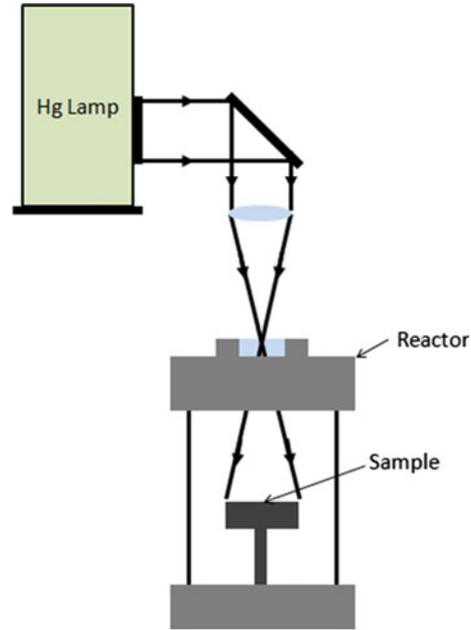


Fig. 1. Schematic of the UV illumination setup, which includes a 1-kW Hg lamp, mirror fixed at 45° , focusing lens, and MOCVD reactor. Not shown is a shutter, used to block the light when desired.

exposed to the UV light only during the growth of the $0.7 \mu\text{m}$ Mg-doped layer.

Multiple $1 \text{ cm} \times 1 \text{ cm}$ samples were cut from each 2-inch wafer. Samples grown without UV light exposure were annealed in a tube furnace at temperatures ranging from 450°C to 650°C . Annealing was performed under N_2 atmosphere for 2 h. Room-temperature resistivity measurements were performed before and after annealing, using the van der Pauw method with soldered In contacts. PL measurements were also acquired on the samples before and after annealing. A continuous-wave He-Cd laser (325 nm) was used to excite the samples, and the luminescence was detected with a 1-m double monochromator with spectral resolution better than $50 \mu\text{eV}$ around 350 nm . Low-temperature PL was measured at $\sim 2 \text{ K}$ using a helium bath cryostat.

RESULTS AND DISCUSSION

Point defects in semiconductors are critical to the performance of electronic and optoelectronic devices. While intentional point defects are incorporated to act as dopants, unintentional point defects can act as compensators, reducing free carrier concentration. They can also contribute to impurity scattering, affecting the mobility of carriers. Fermi level control of point defects by using above-bandgap illumination is realized by the use of photo-generated charge carriers to modify the point defect formation energy and, as a consequence, their concentration. This modification occurs by controlling the electrochemical potential of the system and the

formation energies of electrically charged point defects. In general, control of point defect formation can be achieved by modifying their formation energy.

The formation energy of a particular charge state is dependent on the position of the Fermi level. Density functional theory (DFT) calculations by Walle and Neugebauer¹⁶ have shown that, if the Fermi level is increased in the Mg-doped GaN system, then the formation energy of Mg_{Ga} , an acceptor, decreases, while the formation energy of donors such as H and V_{N} increases. In general, the formation energy of a positively charged defect increases, while the formation energy of a negatively charged defect decreases, with an increase of the Fermi level. We propose an extension to the analogy between the Fermi level and the electrochemical potential such that the electrochemical potential of a charged defect in a material with steady-state populations of free charge carriers may be expressed in terms of the quasi-Fermi levels, which incorporates contributions from both the majority and minority carriers. This quasi-Fermi level approach can be used to explain how the formation energy of charged defects will change when minority carriers are generated in a steady state.

By subjecting the material to above-bandgap illumination during growth, a nonequilibrium process is created in which there is continuous generation of charge carriers. In our case, a photon flux density of $\sim 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$ is estimated by dividing the power density of above-bandgap light by 3.4 eV, the approximate bandgap of GaN at room temperature. Note that the bandgap decreases to around 3 eV at 1040°C, but using this bandgap in this approximation does not change the order of magnitude of the photon flux density. The Hg lamp used in this experiment had multiple emission peaks above the bandgap of GaN, but the most intense peaks were around 3.4 eV. If every photon creates an electron-hole pair, we can estimate that a maximum of $\sim 10^{18}$ free carriers $\text{cm}^{-2} \text{ s}^{-1}$ are generated. Thus, photogeneration will not significantly change the majority carrier concentration, but we expect a significant change in the minority carrier concentration, which will lead to a shift of the quasi-Fermi level of the minority carriers and a significant change of the formation energies of the compensating defects such as H and possibly V_{N} .

HRXRD rocking-curve measurements show that the samples grown with and without exposure to UV light, with Mg concentration of $2 \times 10^{19} \text{ cm}^{-3}$, have dislocation density of less than 10^{10} cm^{-2} .¹⁷ PL and resistivity measurements were performed on the samples grown without UV exposure to investigate the Mg dopant activation. Low-temperature PL spectra of samples annealed at 450°C, 550°C, and 650°C are shown in Fig. 2. The intensities were normalized to the highest donor-acceptor pair (DAP) peak intensity. The samples exhibit strong DAP transitions in the 3.25 eV to 3.27 eV range and

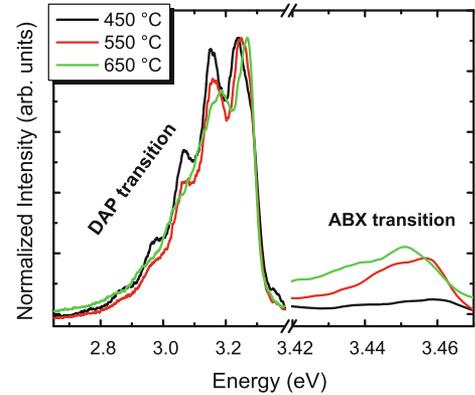


Fig. 2. Low-temperature (2 K) PL spectra of Mg-doped GaN films annealed at different temperatures. The intensities were normalized to the highest DAP peak to show the increase of the ABX intensity with an increase in annealing temperature for a given annealing time. The ABX intensity has been scaled by two for clarity.

near-band-edge luminescence around 3.4 eV. The near-band-edge luminescence contains multiple acceptor-bound-exciton (ABX) transitions between 3.44 eV and 3.47 eV.¹⁸ By using temperature-dependent PL and PL excitation (PLE) measurements, Callsen et al.¹⁸ identified the DAP2 at 3.27 eV as a transition based on ABX2 at 3.458 eV and ABX3 at 3.445 eV, which are both Mg-related acceptor levels. In the samples grown without UV illumination, ABX2 and ABX3 transitions dominated the spectra after annealing. More specifically, the ABX2 transition dominated the spectra of the sample annealed at 450°C, the sample annealed at 550°C showed strong ABX2 and ABX3 emissions, whereas the ABX region of the sample annealed at 650°C was dominated by ABX3. With an increase in the annealing temperature for a given annealing time, there was a decrease of the DAP intensity and an increase of the ABX intensity. The instability of the DAP at annealing temperatures above 500°C and the appearance of ABX2 after annealing were also observed by Monemar et al.¹⁹

Figure 3 shows the DAP to ABX intensity ratio and the resistivity values for each given annealing temperature. The DAP and ABX intensities were determined by peak fitting the DAP region, 2.65 eV to 3.39 eV, and the ABX region, 3.42 eV to 3.47 eV. The DAP to ABX intensity ratio and resistivity both decrease with an increase in annealing temperature for a given annealing time. We have observed that the lowest resistivity was achieved by annealing around 650°C. Annealing at temperatures greater than 650°C, under these same conditions, will cause a slight increase in the resistivity values. Therefore, resistivity measurements on samples annealed at temperatures higher than 650°C are not shown. Similar resistivity versus annealing temperature dependence was obtained by Nakamura et al.⁵ There is a direct correlation between the DAP to ABX intensity ratio and the activation of the Mg acceptor. Electrically, a reduction in compensation

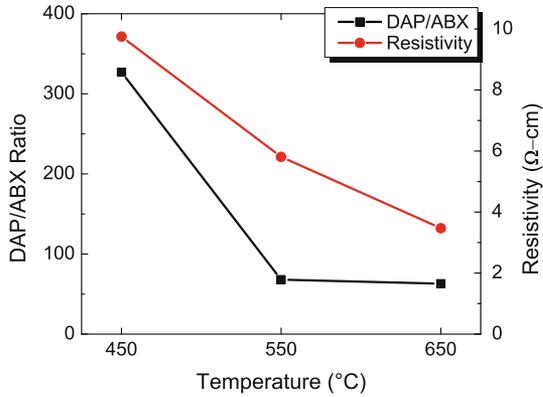


Fig. 3. DAP to ABX intensity ratio obtained from PL spectra and resistivity of Mg-doped GaN films annealed at different temperatures.

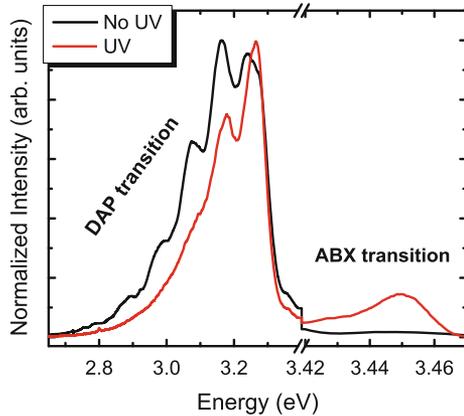


Fig. 4. Low-temperature (2 K) PL spectra of two unannealed GaN:Mg samples, one grown without UV light exposure (“No UV”) and one grown with UV light exposure (“UV”). The intensities were normalized to the highest DAP peak intensity.

due to H and/or other compensating defects is shown with a decrease in resistivity. Optically, the decrease in compensation can be seen in the reduction of DAP intensity and an increase in ABX intensity. Figure 3 shows that both the resistivity and DAP to ABX intensity ratio can be used to characterize the activation of GaN:Mg samples.

PL spectra of samples grown with and without exposure to UV light are shown in Fig. 4. The spectra labeled “UV” and “No UV” were taken before any annealing was performed. The intensities were normalized to the highest peak intensity of the DAP luminescence to show the difference in the ABX intensity with respect to the DAP intensity. The ABX region of the “UV” sample is dominated by an ABX3 transition, and the DAP to ABX intensity ratio is similar to activated samples grown without UV exposure, indicating that the “UV” sample is activated. The “UV” spectrum gives a clear indication that UV illumination influenced the incorporation of defects during growth.

Hall measurements confirmed that the “UV” sample had resistivity lower than 9 Ω-cm, showing that the sample was activated before any annealing was performed. Normally, GaN:Mg samples taken right out of the reactor are strongly compensated and typically have resistivities on the order of 10^6 Ω-cm before annealing. The PL of the “No UV” sample had an intense DAP and no ABX transitions, which also points to strong compensation. Optical and electrical data suggest that there was less incorporation of compensating defects, such as H and possibly V_N , in the “UV” sample.

CONCLUSIONS

Control of point defect incorporation during growth of GaN:Mg thin films by MOCVD using above-bandgap illumination was demonstrated. PL and resistivity measurements on samples with 2×10^{19} cm⁻³ Mg concentration indicated that UV illumination during growth influenced the incorporation of compensating defects. PL spectra show that the “UV” sample and activated samples have similar DAP to ABX intensity ratios, indicating activation during growth. The resistivity of the “UV” sample was five orders of magnitude lower than that of typical unannealed GaN:Mg samples. UV illumination during growth significantly changes the concentration of unintentional point defects, such as H and possibly V_N , and the resulting compensation by changing their formation energy. This study has shown that there is significant potential for control of point defects in III-nitrides by controlling the Fermi level during growth. With the understanding gained from this model system, similar point defect control schemes could be implemented in wider-bandgap systems such as AlN and AlGaIn alloys in which doping is more challenging.

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