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This paper describes a detailed analysis of the effects of high temperatures on the optical performance and structural characteristics of GaN-based LED structures with a high threading dislocation density. Results show that, as a consequence of storage at 900 °C in N₂ atmosphere, the samples exhibit: (i) an increase in the efficiency of GaN and quantum-well luminescence, well correlated to an increase in carrier lifetime; (ii) a decrease in the parasitic luminescence peaks related to Mg acceptors, which is correlated to the reduction in the concentration of Mg in the p-type region, detected by Secondary Ion Mass Spectroscopy (SIMS); (iii) a diffusion of acceptor (Mg) atoms to the quantum well region; (iv) a reduction in the yield of Rutherford Backscattering Spectrometry (RBS)-channeling measurements, possibly due to a partial re-arrangement of the dislocations, which is supposed to be correlated to the increase in radiative efficiency (see (i)). © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4934491]

The high temperature levels reached during the growth and processing of GaN-based LEDs can significantly influence the electrical and optical performance of these devices. Early studies demonstrated that exposure to high temperatures (in the range 750 °C – 1150 °C) can significantly change the spectral properties and/or the efficiency of InGaN-based structures, possibly due to the modifications in the concentration of defects within the active layer. The exposure to high temperature can also induce modifications in the Mg profile, due to the diffusion of the acceptor atoms within the device structure. For a careful optimization of the growth and processing conditions of GaN-based LEDs, it is important to understand how high temperatures can modify the internal structure of the devices, and in particular the distribution of structural defects such as dislocations, and the profile of the acceptor doping. Although relevant results have been described by the studies quoted above, no extensive analysis of the impact of high temperatures on the crystalline quality and on the Mg profile has been presented up to now.

The aim of this paper is to give a contribution in this field, by presenting a study of the effect of high temperature storage on the optical efficiency of LEDs with a high density of threading dislocations. More specifically, the photoluminescence spectra, the crystalline quality of the LEDs, and the doping profiles were studied in detail, with the aim of understanding how the device structure and Mg distribution can be modified by the high temperature treatment.

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The study was carried out on wafers containing InGaN/GaN LED structures grown on a sapphire substrate; the threading dislocation density (TDD) of the analyzed samples is \(8 \times 10^9\) cm\(^{-2}\). The device structure consists of a Si-doped GaN layer (2.6 µm), a five-fold In\(_{0.15}\)Ga\(_{0.85}\)N Multi Quantum Well (MQW) with GaN barriers, and a Mg-doped p-type GaN layer (130 nm). The Mg concentration in the p-side is \(3\times10^{19}\) cm\(^{-3}\), as estimated based on the growth conditions; the Hole concentration – estimated by Hall measurements – is \(2\times10^{17}\) cm\(^{-3}\). Devices were subjected to high temperature storage for 2 hours at 900 °C in an N\(_2\) atmosphere. The optical characteristics of the samples were analyzed by means of photoluminescence (PL) measurements (both integrated and time-resolved, TR-PL, excitation wavelength = 303 nm, pulse duration = 3 ps, repetition rate = 76 MHz, \(T=15\) K, 10 W/cm\(^2\)). Secondary ion mass spectrometry (SIMS) measurements were carried out to characterize the modifications in the doping profile induced by annealing. Rutherford Backscattering Spectroscopy (RBS) measurements, both in random and channeling configurations, were used to characterize the crystalline quality of the materials before and after the thermal treatment. The samples under investigation have a higher TDD than that of typical commercial GaN LEDs; they were grown to study the effects of a high TDD on the light output.

Figure 1 shows the PL spectra of a reference and a treated sample. The treated sample shows an increased radiative efficiency: after the thermal treatment, both the QW-related blue luminescence (Figure 1(a)) and the GaN near-band edge (NBE, Figure 1(b)) emission peaks show a higher emission intensity. This effect is strongly correlated with an increase in carrier lifetime (\(\tau\)) measured – on the QW peak - by TR-PL measurements (Figure 2): The TRPL traces in Fig. 2 show a single exponential trend until a \(1/\text{e} (~36\%\) decay. For this reason, the TRPL lifetimes can be reliably extrapolated from these data: \(\tau\) increased from 900 ps, before annealing, to 4 ns, after annealing. This result (combined with the RBS data described in the following) supports the hypothesis that the thermal treatment induces a decrease in non-radiative recombination rate within the active region of the devices. It is worth noticing that it is not possible to extrapolate the first-order ABC coefficients starting from the TR-PL data reported within this paper; previous evidence on similar samples (see for instance Ref. 6) indicate that the PL signal originates from strongly localized states: a reliable estimation of carrier density (necessary for the extrapolation of the ABC coefficient) is therefore not possible starting from these data. We refer to Ref. 6 for further details on TRPL results on the investigated samples. Figure 1(b) shows another interesting feature: annealed samples show a decrease in the emission intensity in the spectral region around 3.2 eV. Previous reports indicated

![Figure 1](image_url)

**FIG. 1.** (a) photoluminescence spectra measured on a reference and on a treated sample. (b) enlarged plot of the same graph, showing the changes in the region between 3 eV and 3.6 eV. Results indicate that the thermal treatment induces an increase in the radiative efficiency, both for the QW-related blue peak, and the GaN-related luminescence. A decrease in the luminescence is observed for the acceptor-related peaks around 3.2 eV.
FIG. 2. TR-PL transients collected on a reference and a treated sample (measurements were taken at 430 nm). The treatment was found to induce an increase in carrier lifetime, possibly due to a decrease in non-radiative recombination rate. The signal measured on the treated sample is higher than zero for $t<0$; this is due to the fact that – after treatment – carrier lifetime has become significantly longer than the period of the excitation signal.

that parasitic emission at 3.2 eV may originate from radiative transitions from a shallow donor, or from the conduction band, to the acceptor level (Mg). For this reason, the measured reduction of PL signal around 3.2 eV suggests that annealing induced a change in the concentration or distribution of Mg in the p-type material.

This hypothesis was verified by SIMS investigation: results (Figure 3) indicate that the thermal treatment induces a decrease in the concentration of Mg at the boundary between the active region and the p-side of the diode; this is consistent with the reduction in the Mg-related emission bands around 3.2 eV (Figure 1(b)). Furthermore, SIMS analysis indicates a significant diffusion of acceptor atoms towards the quantum well region of the LEDs. This latter result is consistent with previous studies on the stability of Mg doping in GaN layers; the diffusion of magnesium in GaN has been extensively studied - both theoretically and experimentally - over the last decade. The results of the molecular dynamics (MD) simulations reported in Ref. 8 strongly suggest that

FIG. 3. SIMS profiles measured on a reference and a treated sample. A reduction of the Mg concentration at the p-side of the diodes, and a diffusion of Mg towards the active layer of the devices are detected after treatment.
the diffusivity of interstitial Mg can be significantly higher for the atoms located inside the core of dislocations, with respect to the atoms located outside the dislocations. The enhanced diffusion is due to the fact that along the dislocations there are smaller interactive atomic forces between the Mg and the surrounding atoms. Since the analyzed samples have a relatively high threading dislocation density ($8 \times 10^9$ cm$^{-2}$), the changes of Mg profile described in Figure 3 are supposed to be due to the diffusion of interstitial Mg atoms along dislocations.

A moderate presence of Mg in quantum wells can improve the optical properties of InGaN-based samples, due to an increased overlapping between electron and hole wavefunctions induced by the partial screening of the internal fields (see for instance Ref. 13). However, the intensity increase detected on the annealed samples (Figure 1(a)) cannot be simply explained by the diffusion of Mg towards the quantum well/barrier system, since - if this were the case - the intensity increase should be accompanied by a blue-shift of the emission peak, as explained in Ref. 13, and this is not observed (see Figure 1(a)). A further confirmation of this hypothesis is given by the fact that the efficiency increase does not involve only the active layer, but also the GaN near band edge emission (Figure 1), which is likely to originate from the top p-GaN layer, rather than from the barriers. A different mechanism may therefore be responsible for the enhanced emission intensity detected after annealing.

To clarify the origin of the intensity increase measured after stress, we have carried out RBS measurements, both in channeling and in random configurations. In this way we were able to evaluate the modification in the crystalline quality of the samples induced by the annealing.$^{14,15}$ Dislocations are not easily resolved by means of RBS-channeling measurements carried out in the [0001] direction, since they are usually aligned along the c-axis. For this reason RBS-channeling measurements were carried out in the [1-101] direction. Results (Figure 4) revealed a decrease in the dechanneling rate after annealing, thus suggesting that the annealing induced a partial improvement of the crystalline quality of the samples, possibly due to a re-arrangement of the dislocations.

![RBS-channeling spectra](image)

**FIG. 4.** RBS-channeling spectra measured on as-grown and treated samples. A 2.2 MeV $^4$He$^+$ beam was used, detecting backscattered ions at a 170° angle. Measurements were taken in a [1-101] crystal direction. The "GaN aligned" spectrum represents a measurement taken on a reference sample with low threading dislocation density ($10^6$ cm$^{-2}$). The "Random" spectrum represents the RBS-channeling yield measured in a random direction.
This is in agreement with previous papers on GaN and GaAs, reporting on the rearrangement and modifications in dislocations after high temperature treatment.\textsuperscript{15–21} This mechanism may be responsible for the increase in carrier lifetime (Figure 2(a)) and for the improved efficiency (Figure 1) detected after annealing. It is worth noticing that the RBS-channeling curves of the annealed samples are considerably higher than those of a reference sample with lower threading dislocation density (TDD=10^{6} cm\(^{-2}\)). This supports the hypothesis that the thermal annealing at 900 °C is not sufficient for a complete recovery of the crystalline quality of the samples. Important modifications of the optical and structural properties of the devices were observed mostly on devices with high densities of dislocations; devices with lower TDD values showed smaller modifications as a consequence of high temperature annealing (not reported here for sake of brevity). This confirms that the changes in the efficiency and the instabilities of dopant are strongly related to the presence of high densities of dislocations.

In summary, we have reported a detailed study of the effects of high temperature treatment on the performance and structural characteristics of GaN-based LED samples having a high density of threading dislocations. The high temperature treatment was found to induce an efficiency increase, which was ascribed to an improvement in the crystalline quality of the devices. Furthermore, we described the changes in the Mg profile induced by the annealing.

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