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Correlation of doping, structure, and carrier dynamics in a single GaN nanorod

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We report the nanoscale optical investigation of a single GaN p-n junction nanorod by cathodoluminescence (CL) in a scanning transmission electron microscope. CL emission characteristic of dopant-related transitions was correlated to doping and structural defect in the nanorod, and used to determine p-n junction position and minority carrier diffusion lengths of 650 nm and 165 nm for electrons and holes, respectively. Temperature-dependent CL study reveals an activation energy of 19 meV for non-radiative recombination in Mg-doped GaN nanorods. These results directly correlate doping, structure, carrier dynamics, and optical properties of GaN nanostructure, and provide insights for device design and fabrication. © 2013 AIP Publishing LLC.

GaN-based nanostructures are promising materials systems for optoelectronic applications such as high efficiency light emitting diodes (LEDs), and low lasing threshold lasers. These nanowires and nanorods are synthesized by either vapor-liquid-solid mechanism using metal seeds or by catalyst-free approach using plasma assisted molecular beam epitaxy (PAMBE). Nanoscale correlation of heterostructure properties with the structure, doping, and alloying is essential for improving device design and fabrication. While chemical analyses using energy dispersive x-ray spectroscopy or electron energy loss spectroscopy can precisely determine the position of an alloy junction such as GaN/InGaN, these techniques cannot determine the position of a p-n junction as their sensitivities (0.1–1 at. %) are insufficient to detect dopant concentrations (0.001 at. %). Secondary ion mass spectroscopy (SIMS) typically used to obtain doping profiles in thin films is usually performed on a wafer scale and can only give compositional profile on an ensemble of nanowires of different heights. Other techniques, such as atom probe tomography, electron-beam induced current, or Kelvin probe force microscopy suffer from shortcomings such as challenging sample preparation, requirements for pristine surface conditions, or suitable contacts. Cathodoluminescence in scanning transmission electron microscope (CL-STEM) collects light signal excited by nanometer-sized electron probe, making it suitable to studying optical properties of nanowires, and axial nanowire alloy heterostructures with nanoscale resolution. In addition, physical insights into the correlation of doping, structure, and carrier diffusion can be extracted from CL-STEM optical mapping, particularly in one-dimensional nanostructures. These parameters are critical for future development of nanorod-based devices. For example, shorter minority carrier diffusion lengths have been reported in nanowires compared to bulk in certain materials systems (e.g., GaAs), and increased carrier diffusion through in-situ surface passivation has led to improved performance in GaAs and GaAsb nanowire based solar cells. In this letter, we report on the CL-STEM characterization of a single axial GaN p-n junction nanorod at both room and cryogenic temperatures. Through this method, we not only determine the position of the metallurgical junction but also probe optical transitions associated with dopant energy levels and minority carrier diffusion in a non-destructive and simple manner.

Vertically aligned, catalyst-free GaN p-n junction nanorods were grown using PAMBE on a 3 in., n-type silicon (111) substrate, as reported previously. During the growth, Si was first introduced as n-type dopant, after which Mg was introduced for p-type doping. Wafer-scale SIMS result suggests Mg concentration on the order of 1020 cm−3. Single nanorod device exhibits rectifying characteristics in current-voltage measurement at room temperature, confirming the presence of p-n junction. For TEM and CL-STEM studies, GaN nanorods were mechanically removed from the growth substrate and placed on a carbon film TEM grid. CL-STEM studies on these nanorods were performed using a JEOL 2011 TEM fitted with a Gatan MonoCL3 system using 80 kV electrons with 5 nm, 300 pA probe current. A high sensitivity photomultiplier tube and a CCD camera fitted with 300 line/mm grating were used to detect the CL signal. Besides room temperature (RT) measurements, the sample was cooled by liquid nitrogen for low temperature measurements.

SEM micrograph (Figure 1(a)) shows that GaN nanorods grow perpendicularly to the Si substrate. An inverse tapering is observed in all nanorods, whereas the contrast along nanowire length is indicative of the doping contrast in secondary electron images. TEM and selected area electron diffraction results (Figures 1(b) and 1(c)) confirm that the nanorods grow along the (0001) direction of the wurtzite structure and are approximately 2 µm long. Figure 1(d) shows TEM Moiré fringes at the base of the nanorod, indicating that coalescence of thinner nanorods occurs during the growth to eventually form bigger nanorods. The top part of the nanorod is single...

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crystalline without visible defects, as exemplified by the high resolution TEM image in Figure 1(e).

Figures 2(a) and 2(b) show STEM and corresponding panchromatic RT CL images of the same nanorod shown in Figure 1(b). Strong CL emission was observed only in the base portion of the nanorod (nominally Si-doped), whereas the corresponding CL spectrum (Figure 2(d)) reveals the base portion of the nanorod consists mainly of a relatively sharp peak centered at 3.59 eV (345 nm). In contrast, the CL emission from the top portion is dominated by an asymmetrical broad emission with the peak intensity at 3.35 eV (350 nm), with a long tail comprising of phonon replicas spaced out by 92 meV LO phonons (see supplemental information for individual spectra). The pair of monochromatic images taken at 3.59 eV and 3.35 eV (Figures 2(f) and 2(g), respectively) confirms that the two portions of the nanorods exhibit different, well-defined CL emission at 93 K.

The observed spatial distribution and spectral response of the CL signal from the two parts of the nanorod are indicative of its doping. For the base portion of the nanorod, CL peak at 93 K is only slightly blue shifted (0.05 eV) with respect to the peak at RT implying they have the same origin. The positions and relatively narrow widths of the peak suggest that it originates from either a near band edge transition or a shallow donor level. The 3.35 eV peak produced by the top part of the nanowire is typical of an optical transition associated with unionized Mg acceptor.27–31 The spectral analysis and the mapping results indicate that the top portion of the nanorod is p-doped by Mg, conversely the base portion is n-doped by Si. Furthermore, by comparing the energy level of the near band edge emission and conduction band to Mg level transition, we can estimate that the acceptor level in the Mg-doped GaN is located about 0.24 eV above the valence band, a value consistent with the reported values of the Mg-doped GaN thin films.

The observation that the p-type GaN section has much higher CL intensity at 93 K than at RT can be quantitatively explained considering Mg acceptor ionization. With an acceptor level of 0.24 eV, Mg concentration of 1020 cm⁻³, and average effective mass of 1.4 m₀, the number of thermally activated acceptors can be estimated using Fermi-Dirac statistics. Our calculations show a near five order of magnitude decrease in the number of ionized acceptors from 300 K to 93 K, and conversely, a significant increase in the concentration of unionized Mg acceptor levels leading to a sharp increase in intensity of acceptor-related optical transition at low temperatures.

GaN nanorods with incorporated p-n junctions could be made into photodetectors, LEDs, and lasers. Knowing the RT (3.4 eV) is likely due to the Burstein-Moss effect,23,24 as a high density of carriers is generated in a small volume of the TEM sample. (Based on the experimental conditions, we estimate that the primary electron beam generates 2.9 × 10²⁸ cm⁻³ s⁻¹ carrier pairs within the excited volume (see supplemental information)). A monochromatic image (Figure 2(c)) taken at 3.54 eV confirms that this CL emission comes only from the base portion of the nanorod.

Interestingly, the intensity, energy, and spatial distribution of the CL emission change drastically as temperature is lowered to 93 K. Figure 2(e) shows the panchromatic CL map of the same nanorod shown in Figure 2(a). Clearly, the brightest CL emission at 93 K comes from the top portion of the nanorod, while the base portion, which is bright at RT, exhibits a drastically reduced CL luminescence compared to the top portion. Moreover, a CL line scan spectrum image (Figure 2(h)) along the nanorod length reveals distinct emission in different nanowire parts. The CL spectrum from the base portion of the nanorod consists mainly of a relatively sharp peak centered at 3.59 eV (345 nm). In contrast, the CL emission from the top portion is dominated by an asymmetrical broad emission with the peak intensity at 3.35 eV (350 nm), with a long tail comprising of phonon replicas spaced out by 92 meV LO phonons (see supplemental information for individual spectra). The pair of monochromatic images taken at 3.59 eV and 3.35 eV (Figures 2(f) and 2(g), respectively) confirms that the two portions of the nanorods exhibit different, well-defined CL emission at 93 K.

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position of the metallurgical junction during the nanorod growth is crucial for device design and fabrication to improve the device performance. From the CL line scan spectrum mapping with 16 nm steps, we can further infer the position of the metallurgical p-n junction by closely analyzing the integrated intensity profile (Figure 3) of the near band edge luminescence (3.59 eV) and acceptor level related luminescence (3.35 eV). We observe that the intensity of the 3.59 eV peak from n-type GaN begins to rise from the base of the nanorod, reaches a maximum at 0.95 μm and drops down to zero at approximately 1.2 μm. The intensity of the 3.35 eV p-type CL emission shows a sharp rise at approximately 0.8 μm, reaches a maximum at 1.09 μm, and begins a more gradual decline until the top of the nanorod. Based on the intensity profile, we can deduce that the doping switches from n-type to p-type in a 140 nm section between 0.95 μm and 1.09 μm from the base of the nanorod. Here, we note that the observed 140 nm overlap is not due to the beam broadening as the Monte-Carlo simulation of electron-matter interaction using Wincasino software shows that 95% of energy transfer from the incident electron beam occurs within 5 nm radius of the incidence of the sample. We cannot rule out the possibility of limited Si and Mg interdiffusion, which has been reported in p-GaN growth using metalorganic chemical vapor deposition performed at temperatures above 1000 °C. However, p-n junction nanorods investigated here were grown at 800 °C so dopant diffusivity is much lower in our case. Studies on Mg diffusion in PAMBE-grown GaN thin films also shows insignificant Mg diffusion compared to the observed 140 nm overlap of the CL intensities.

Since the effects of electron-matter interaction volume and dopant diffusion are small, we attribute the overlap of the CL intensities to carrier diffusion, thus be purely due to doping and carrier diffusion, with minimal effect from build-in potential and carrier drift inside the junction.

Besides the CL intensity variation due to doping in the middle of the nanorod, decrease in the CL intensity near the base and the top of the nanorod are also observed in Figure 3. For the n-GaN section, the quenching of CL emission could be related to the structural defects during nanorod coalescence. In Figure 1(c), we show that the base of the nanorod consists of several thin rods that coalesce at about 450 nm into the nanorod. This length scale is consistent with the length of the n-GaN section with low CL emission. Indeed, detailed TEM studies on MBE grown GaN nanorods have shown the presence of defects such as small angle grain boundaries, dislocations, and stacking faults when thinner GaN nanorods coalesce. These defects have been observed in epitaxial lateral overgrown GaN thin films and are known to be non-radiative recombination centers that quench CL emission. Charge carriers generated by the electron beam within the diffusion length from the defects can recombine non-radiatively, resulting in quenching of the CL signal. Carriers generated far away from the base are less likely to diffuse into the defect region, thus, the CL signal increases when the electron beam is scanned toward the middle of the nanorod (away from the defects). Since the intensity of the CL emission is mostly governed by the concentration of minority carriers, we can then fit decay of the CL intensity towards the base of the nanorod as an exponential decay function: \[ I = a \exp(\pm(x-b)/L_{e,h}) + I_0, \]
where \( I \) is the CL intensity, \( L_e \) and \( L_h \) are electron and hole diffusion lengths as minority carriers, respectively, \( a, b, \) and \( I_0 \) are fitting constants. In this way, we estimated the minority diffusion length of holes in n-GaN at 93 K to be \( L_h = 165 \pm 10 \) nm, which is comparable to the values reported in n-GaN thin films and nanowires measured by different techniques. The intensity of p-GaN emission (3.35 eV) also decreases towards the tip of the nanorod, which suggests the presence of other non-radiative recombination centers near the tip of the nanorod not revealed by TEM studies. By applying the similar approach, we extract the electron diffusion length in p-GaN.

![FIG. 3. Normalized integrated intensities of the 3.59 eV and 3.35 eV CL luminescence along the length of the nanorod shown in Figure 2(h). The positions of the nanorod coalescence in the n-GaN section and metallurgical junction are indicated. The squares and circles are experimental data, and the dashed lines are fits based on an exponential decay model.](image-url)
to be $L_c = 650 \pm 70 \text{ nm}$ at 93 K. The minority carrier diffusion length, while important for optoelectronic device design, is also an indicator of material quality. In GaN thin films, minority carrier diffusion lengths are limited by the density of dislocations.\textsuperscript{45,48} For the nanorod investigated, minority carrier diffusion length in n-GaN is limited by defects caused by thinner nanorod coalescence. In the p-GaN nanorod portion, while no visible defects were observed, the electron diffusion is likely to be limited by surface recombination. These results provide an important insight for the design and fabrication of optoelectronic devices using nanowires and nanorods as building blocks. For example, minority carrier diffusion length is one of the key factors in the figure of merit of photodetectors to optimize sensitivity and speed.

Finally, we also measured the intensity of the GaN CL emission as a function of temperature to further investigate the phenomenon of thermally activated CL quenching. Panchromatic images of a single GaN p-n junction nanorod were taken in the 93–182 K temperature range, and the CL intensity from the p-GaN region was measured (Figure 4). Following the treatment of Leroux et al.\textsuperscript{27} the quenching of the CL intensity $I$ with respect to temperature is caused by thermally activated non-radiative recombination centers: \( I = I_0/(1 + \exp(-E_a/kT)) \), where $I_0$ is total number of carrier pairs excited, \( \exp \) is proportional to the non-radiative recombination time, and $E_a$ is the activation energy for non-radiative recombination. By fitting the experimentally obtained results shown in Figure 4, the activation energy of $E_a = 19 \pm 5 \text{ meV}$ was extracted. For the n-GaN region, the CL intensity remains low throughout the temperature range and a reliable temperature-dependent study is not achievable. Given that no visible defects are observed in the p-GaN section, the non-radiative recombination centers likely originate from surface states, which also limit minority carrier diffusion lengths discussed previously. Proper surface passivation for both bulk and nanostructured GaN can reduce surface states density and improve minority carrier diffusion\textsuperscript{44} and light emission.\textsuperscript{49,50}

In conclusion, using CL-STEM, we identified the position of a p-n junction with high spatial resolution inside a single GaN nanorod. The overlap of the CL signals from n- and p-doped GaN was shown to be limited only by carrier diffusion. Si doped n-GaN exhibits near band edge CL emission at both room and cryogenic temperature, while Mg-doped p-GaN emits light strongly only at cryogenic temperatures due to temperature-dependent dopant ionization. We confirmed that the Mg acceptor level is 240 meV above the valence band by comparing the CL spectra of n- and p-type GaN sections. In addition, CL quenching along the length of the nanorod was attributed to structural defects through a combination of TEM and CL-STEM investigations. The minority carrier diffusion lengths were determined to be 165 $\pm$ 10 nm and 650 $\pm$ 70 nm for n- and p-type GaN, respectively. Temperature-dependent studies on CL intensity further revealed a thermally activated non-radiative recombination center with the activation energy of 19 meV in p-GaN. The measured optical emission, dopant level, and estimated carrier diffusion lengths from this study focusing on GaN nanorods are consistent with the previous thin film studies. The defect induced CL quenching highlights the importance of controlling nanorod coalescence during MBE growths and surface passivation for nanostructures to further improve the performance of devices made from these nanostructures.

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See supplementary material at http://dx.doi.org/10.1063/1.3812241 for estimation of electron induced carrier density in the nanorod, and detailed CL spectra of n- and p-GaN nanorod portions at 93 K.


