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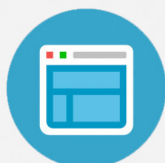

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Fabrication of magnesium-doped gallium nitride nanorods and microphotoluminescence characteristics

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High density magnesium (Mg)-doped gallium nitride (GaN) nanorods were fabricated by inductively coupled plasma reactive ion etching technique from the epitaxial film. Under the fixed Cl_2/Ar flow rate of 10/25 SCCM (SCCM denotes cubic centimeter per minute at STP) and inductively coupled plasma/bias power of 200/200 W, the nanorods were fabricated with a density of 10^8-10^{10} cm^2 and dimension of 20–100 nm by varying the chamber pressure from 10 to 30 mTorr. A large blueshift was observed in the photoluminescence (PL) peak energy of Mg-doped GaN nanorods under HeCd laser (325 nm) excitation. The PL spectra of nanorods show a typical donor-acceptor-pair emission around 3.0 eV with a large blueshift compared to the Mg-doped GaN film. The blueshift energy increases from 8 to 67 meV as the excitation intensity varies from 12 to 56 kW/cm^2. Possible reasons causing the power dependence of spectral shift in the PL emission energy are discussed. © *2006 American Vacuum Society.*
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I. INTRODUCTION

Nanostructures such as quantum dots or quantum wires can exhibit different optical and electrical properties different from those in the bulk material due to the quantum confinement effects. The gallium nitride (GaN) nanostructures including quantum dots and wires have attracted considerable interest in recent years for potential application in light emitting devices such as lasers and light emitting diodes. Recently, Johnson *et al.*[1] demonstrated optical pumped single nanowire laser emission from the synthesized GaN nanowires, and Tanaka *et al.*[2] reported stimulated emission from self-assembled GaN quantum dots. In addition, there are several investigations on the emission properties of GaN nanostructures and quantum dots. The photoluminescence (PL) emission wavelengths of these nanorods were shown to either have the same band-gap energy as the bulk GaN (Refs. 3–5) or spectral blueshift depending on the size of nanorod with the latter attributed to the quantum confined effect.[6] On the other hand, redshift of the PL spectrum from the synthesized GaN nanowires had also been observed and was attributed to the biaxial compressive strain effect.[7] As for the self-assembled GaN quantum dots, study of the PL emission spectra indicated that the peak energy generally depends on the balance between quantum confinement and strain related effects such as strain induced piezoelectric field.[8–10] However, most of the GaN nanostructures reported to date were undoped and fabricated by either self-assembled growth or physical/chemical synthesis methods.[1–10] In this article we report the fabrication and μ-PL characterization of Mg-doped GaN nanorods fabricated from GaN epitaxial film using inductively coupled plasma reactive ion etching (ICP-RIE). The technique offers a one-step, relatively straightforward method for the fabrication of vertically aligned GaN based nanorods with controllable size and density. We also observed a large spectral blueshift in the PL peak from the Mg-doped GaN nanorods with respect to the Mg-doped GaN film and discussed the possible mechanisms.

II. EXPERIMENTAL PROCEDURE

The GaN epitaxial film used in this study was grown by using metal-organic chemical vapor deposition facility (Emcore D75). The sample structure consisted of a 30-nm-thick GaN buffer layer first grown on the *c* plane of sapphire substrate, followed by a 3.0-μm-thick undoped GaN layer, and finally a 1-μm-thick Mg-doped GaN layer with Mg concentration of about $(5-10)\times10^{19}$ cm^{-3} measured from secondary ion mass spectroscopy (SIMS). The nanorods were fabricated from the Mg-doped GaN film by ICP-RIE etching technique.[11] A nickel thin film was used as the etch mask for ICP-RIE etching system. A non-nanorod region covered by nickel serves as a reference to compare the PL emission spectrum with respect to the nanorod region. The ICP power and bias power source with rf frequency were set at 13.56 MHz. The etchant gases were Cl_2 and Ar. Both Cl_2 and

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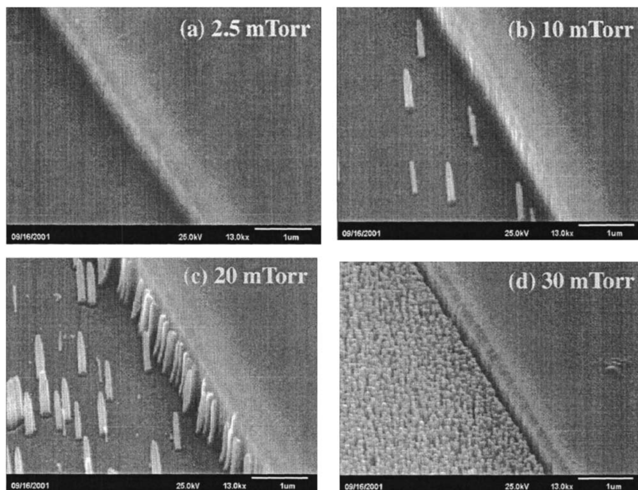
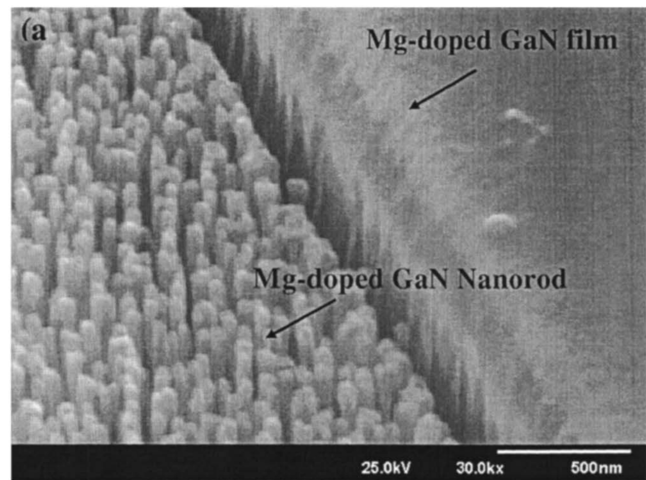


FIG. 1. SEM image of the etched GaN sample surface morphology with different chamber pressures of (a) 2.5 mTorr, (b) 10 mTorr, (c) 20 mTorr, and (d) 30 mTorr at the same Cl_2/Ar flow rate of 10/25 SCCM, and ICP/bias power of 200/200 W for a 2 min etching time.

Ar gases were introduced into the reactor chamber through independent electronic mass flow controllers (MFCs) that can control the flow rate of each gas with an accuracy of about 1 SCCM (SCCM denotes cubic centimeter per minute at STP). An automatic pressure controller (APC) was placed near the exhaust end of the chamber to control the chamber pressure. The etching was conducted under a gas mixture condition of $Cl_2/Ar=10/25$ SCCM with the ICP source power and bias power at 200 W for a 2 min etching time. GaN nanorods of various dimensions and densities were obtained by controlling the chamber pressure from 2.5 to 30 mTorr. After the etching process, the etching depth was measured by stylus profilometry. Atomic force microscopy (AFM) was used to investigate the surface morphology. The dimensions of the nanorods were estimated by a scanning electron microscope (SEM).

III. RESULTS AND DISCUSSION

As shown in the SEM image of Fig. 1(a), a uniform etched surface with no nanorod formation was observed at and below the chamber pressure of 2.5 mTorr, and the surface roughness was about 1.5 nm. As the chamber pressure was increased to 10 mTorr, the GaN nanorods began to form and the density of nanorods increased as the chamber pressure was further increased to 20 and 30 mTorr. The nanorods have a near hexagonal structure with a height of about 1 μm as estimated from the SEM image of Figs. 1(b) and 1(c) and about 0.4 μm at 30 mTorr from Fig. 1(d). The variation in the height of the nanorods seems to be related to the etching rate. In our experiment, the etching rate is about 3000 Å/min at 2.5 mTorr, increases to about 5000 Å/min at 10 and 20 mTorr, and then decreases to 1450 Å/min at 30 mTorr. This seems to correspond to the variation in height of the nanorods. At 30 mTorr as shown in Fig. 1(d), the nanorods form a two-dimensional array of uniform density. Figure 2 shows the high resolution SEM images of the high density



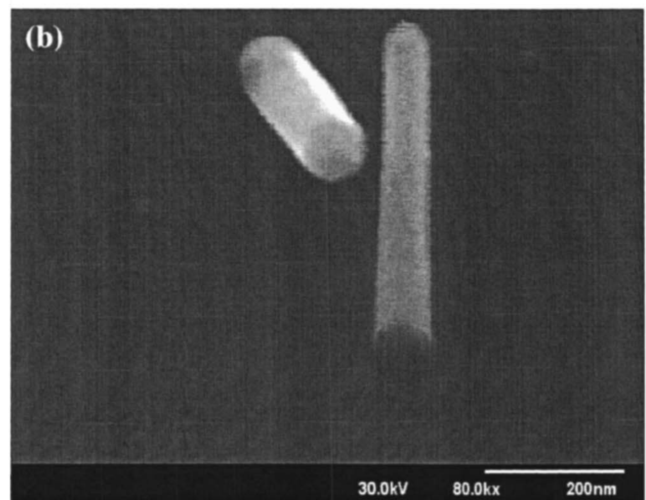


FIG. 2. (a) Top view SEM image of the Mg-doped GaN nanorod. (b) High resolution SEM image of Mg-doped GaN nanorod.

Mg-doped GaN nanorods. Figure 2(a) is the top view image of the Mg-doped GaN nanorods, and the density of the nanorods was estimated to be about 3×10^{10} cm^{-2}. Figure 2(b) is a high resolution SEM image of the nanorods showing a nanorod diameter of about 50 nm. From the SEM shown in Fig. 1, the mean dimension and density of the nanorods as a function of the chamber pressure were plotted in Fig. 3. The nanorod density increases from 1×10^{8} to 1×10^{9} cm^{2} and then to 3×10^{10} cm^{2} as the pressure increases from 10 to 20 and then to 30 mTorr, respectively. The dimension of the nanorods decreases from about 100 nm to the 20–50 nm range as the chamber pressure increases from 10 to 30 mTorr. The result indicates that the chamber pressure plays an important role in the nanorod formation and can be utilized to control the dimension and density of the nanorods.

For optical investigation, micro-PL was chosen to avoid the spatial variation. The micro-PL system consists of a commercial microscope combined with a scanning near-field optical microscope (SNOM) and a confocal microscope. The sample was placed on a piezoelectric transducer (PZT) con-

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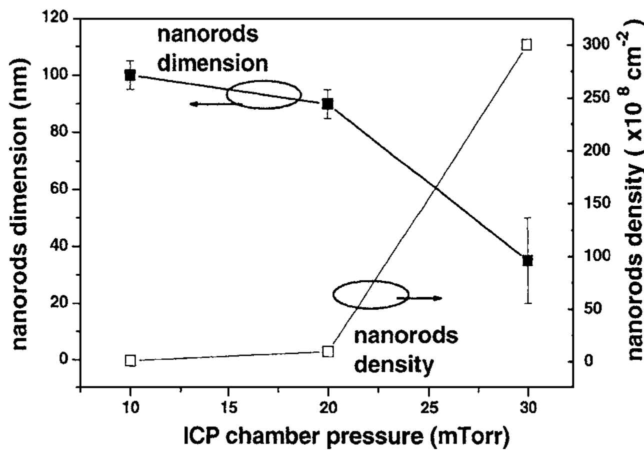

FIG. 3. Mean dimension and density of GaN nanostructure as a function of the chamber pressure which is varied from 10 to 30 mTorr.

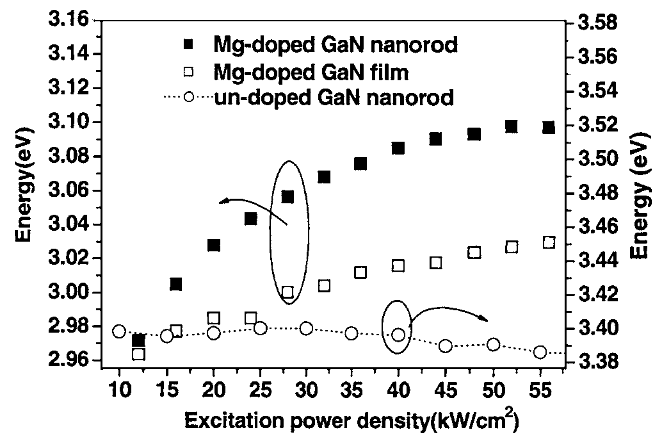

FIG. 5. PL peak energy as a function of the excitation power density. Filled (open) square represents Mg-doped GaN nanorod (film) while the open circle indicates the undoped GaN nanorod.

trolled stage with a resolution of 2 nm and excited by a 325 nm HeCd laser through a 100× objective. The focused spot size on the sample was about 1 μm in diameter which corresponds to about 300 illuminated nanorods. By moving the PZT stage, the PL spectra of both the non-nanorod and nanorod regions can be measured under the same excitation density and spot size. The PL emission from the sample was collected by the same 100× objective and fed to a 0.32 m spectrometer with a spectral resolution of 0.1 nm and a cooled UV-enhanced charge-coupled device (CCD).

Figure 4 shows the typical micro-PL spectra obtained from the nanorod region and the non-nanorod region under laser excitation intensity of about 32 kW/cm^2. The PL spectra from both regions show a typical donor-acceptor-pair emission of Mg-doped GaN with an emission at 3.0 eV similar to those reported by others[12–19] and emission peak energy of the nanorod region shows a large blueshift of 64 meV from that of the non-nanorod region. The periodic fluctuation in the PL spectrum of the non-nanorod region is caused by Fabry-Perot interference of the epitaxial Mg-doped GaN film. In addition, the emission peak at 3.4 eV might originate from the underlying undoped GaN layer. This can be firmly believed from the wavelength invariance and enhanced emission intensity of 3.4 eV due to the removal of the 1-μm-thick Mg-doped GaN film. For comparison, undoped GaN nanorods fabricated from the same method were also investigated. These undoped GaN nanorods showed strong band edge emission at 3.4 eV, the same as as-grown GaN thin film. However, no spectral blueshift was observed at the band edge emission. Figure 5 plots the PL emission peak energy as a function of excitation power density for Mg-doped nanorod, Mg-doped GaN film, and undoped GaN nanorod, respectively. The PL peak energy increases were 125 and 67 meV for Mg-doped nanorod and Mg-doped GaN film as the excitation intensity varies from 12 to 56 kW/cm^2. The corresponding spectral shift between nanorod peak and the non-nanorod peak ranging from 8 to 67 meV within the excitation intensity range indicates stronger power dependence of the Mg-doped GaN nanorod emission. Our data for the non-nanorod region show that the emission peak energy increase is 99 meV per decade power which is comparable to the 90 meV per decade power increase, as reported for the films.[18] In contrast, the PL emission peak of undoped GaN nanorod appeared the same in the same excitation range.

One of the possible explanation of the large spectral blueshift in the Mg-doped GaN nanorod emission peak could be due to the strained related effects such as strain induced piezoelectric effect and strained relief. However, the micro-Raman measurement of our samples showed no observable Raman shift between the nanorods and the non-nanorod region indicating that strain related effects are not the dominating factor. Other possible contributing factor is the quantum confined effect of nanorod which has been reported in single GaN nanorod with diameter of 80–120 nm.[6] However, for a two-dimensional (2D) confined nanostructure with size in 50 nm, the ground state energy shift was estimated to be less than 5 meV based on the published effective mass data of GaN.[20] Therefore the quantum confined effect is not the

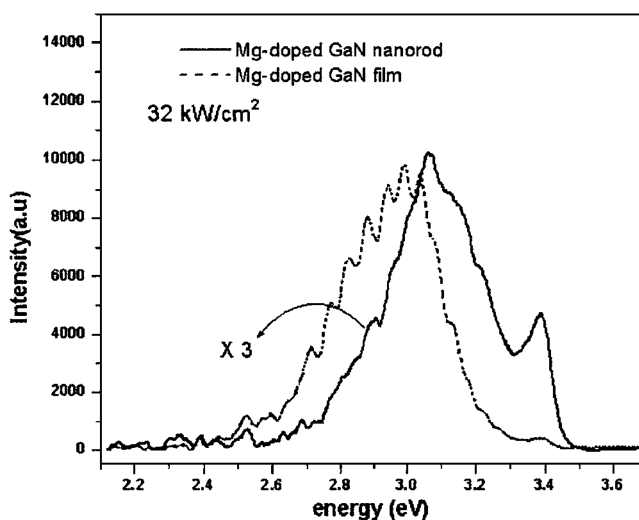

FIG. 4. Micro-PL spectra of Mg-doped GaN nanorods (solid line) and Mg-doped GaN film (dash line) at excitation power density of 32 kW/cm^2.

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dominating factor for the large blueshift. Previously the PL spectra of Mg-doped GaN films were reported with the blueshift dependent on the excitation intensity,[18,19] and the blueshift was attributed to the Coulomb interaction of distant donor-acceptor-pair transition. The effect of a distant donor-acceptor-pair (DAP) Coulomb interaction on the DAP transition energy can be expressed by the following equation:[21]

$$h\nu = E_g - (E_A + E_D) + \frac{e^2}{4\pi\varepsilon R_{\mathrm{DA}}} - mh\nu_{\mathrm{LO}},$$

where E_g is the band gap of GaN, E_D and E_A are the donor and acceptor binding energies, respectively, ε is the dielectric constant, R_{DA} is the mean distance between the involved donor and acceptor, the third term is the Coulomb interaction term which depends on R_{DA}, and the last term describes the LO phonon replica. From the equation we could expect an increase in the transition energy when the average distance R_{DA} of the Coulomb interaction decreases. This condition could occur as the excitation intensity increases causing an increase in the occupied donor and acceptor centers and results in the shortening of the average distance R_{DA}. At high excitation intensity, the emission energy of nanorod is 125 meV higher than that at low excitation intensity, and the averaging R_{DA} estimated from the Coulomb interaction of 125 meV is 1.18 nm. Since the average distance is of concern, it is nature to investigate the Mg concentration in the sample. From the SIMS profile, the Mg concentration was found to be $\sim 8 \times 10^{19}$ cm^{-3}. Consider the doped Mg concentration of about $(5-10) \times 10^{19}$ cm^{-3}, the mean separation between the acceptor sites estimated from $(2\pi N_{\mathrm{Mg}})^{-1/3}$ is $1.47-1.16$ nm, which is in agreement with the R_{DA} estimated from Coulomb interaction. The nanorod region was fabricated right beside the bulk region as shown in Fig. 2(a) and all regions show similar blueshift after measuring a lot of region for both bulk and nanorods. Nonuniform distribution of Mg was thus excluded to occur the further blueshift in nanorods and we suggest that the further blueshift was due to the smaller R_{DA} in the nanorods. Although the detail mechanisms responsible for larger spectral blueshift of nanorods are not fully understood yet, the Coulomb interaction should be the contributing factor. This implies that the blueshift is the intrinsic phenomenon for the PL emission of nanostructure which involved DAP emission and more investigation is needed to clarify the mechanisms.

IV. CONCLUSION

In summary, we demonstrate a straightforward method to fabricate GaN-based nanorods of controllable dimension and density from epitaxial film using ICP-RIE. Under the fixed Cl_2/Ar flow rate of 10/25 SCCM and ICP/bias power of 200/200 W, the nanorods were fabricated with a density of 10^8-10^{10} cm^2 and dimension of $20-100$ nm by varying the chamber pressure from 10 to 30 mTorr. A large spectral blueshift of the PL peak energy was observed in Mg-doped GaN nanorods using micro-PL under 325 nm HeCd laser excitation. The PL emission spectra of the Mg-doped GaN nanorods show a typical DAP transition of about 3.0 eV with a large blueshift compared to the Mg-doped GaN film. The blueshift energy increases from 8 to 67 meV as the excitation intensity varies from 12 to 56 kW/cm^2. Possible mechanisms for the occurrence of the large spectral shift were discussed. This fabrication method should be applicable for the future nitride nanodevices including *p-n* junctions, heterojunctions, and laser devices.

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