Surface States Effect on the Large Photoluminescence Redshift in GaN Nanostructures

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Abstract: We report on the large photoluminescence redshift observed in nanostructures fabricated using n-type GaN by ultraviolet (UV) metal-assisted electroless chemical-etching method. The scanning electron microscopy (SEM) characterization showed nanostructures with size dispersion ranging from 10 to 100 nm. We observed the crystalline structure using high resolution transmission electron microscopy (HRTEM) and electron energy loss (EELS) techniques. In contrast to 362 nm UV emission from the GaN epitaxy, the nanostructures emitted violet visible-light in photoluminescence (PL) characterization with increasing optical excitation. An energy band model was presented to shed light on the large PL redshift under the influence of surface states, which resulted in two competing photoluminescence mechanisms depending on excitation conditions.

OCIS codes: (160.4236) Nanomaterials; (160.6000) Semiconductor materials; (250.5230) Photoluminescence; (300.6490) Spectroscopy, surface

1. Introduction

III-Nitride materials are of great interest for solid state lighting applications because of their wide band-gap tunability from UV to visible range [1, 2]. The emission of the bulk GaN usually occur at the ultra violet (UV) photon energy of $\sim 3.42\text{eV}$ [3]. Blue luminescence was reported in some studies due to defects and impurities [4], and the power dependent photoluminescence (PL) of these peaks usually blue shift with increasing power [5]. Although such defects can be destructive in a device, well engineered nanostructure may offer many advantages [6]. Moreover, the smaller the nanostructure, the larger surface-volume ratio and the stronger the surface effects. Combining surface effects and defect engineering will help filling many research gaps. One such research gap is the existing light-emitting diode (LED) phosphor that suffers optical degradation and poor material compatibility. In recent years, much research has been devoted to the development of rare earth doped III-V compound semiconductor based phosphors including GaN-based semiconductors [7, 8]. The GaN and InGaN nanoparticle based phosphors have advantages over other types of phosphors in terms of high quantum efficiency, excitation spectrum well matched to LED emission wavelengths and linewidths, large tunability of excitation and emission wavelength, and high thermal stability.

In this paper, we report on the light emission mechanism of GaN nanostructures, which showed controllable redshift of $\sim 40\text{ nm}$ ($\sim 250\text{meV}$) with increasing optical excitation power. These group-III nitride-based nanostructures were fabricated using UV-assisted electroless chemical etching method. The resultant GaN nanostructures offer good material compatibility with III-V LEDs, high chemical stability, large excitation range, and a life-time compatible to that of the GaN-based LEDs. The nanostructures are simple in fabrication, easy to integrate, and, most importantly, offer tunable broadband emission rendering them a good candidate for tunable color-temperature white LEDs.

2. Experimental

The substrate used in this study consisted of a $30\text{ }\mu\text{m}$ thick Si-doped GaN epitaxy grown on c-axis (0001) sapphire substrate with a measured resistivity of less than $0.03\text{ }\Omega\cdot\text{cm}$. The estimated dislocation density and measured carrier concentration of the film are $1\times 10^8\text{ cm}^{-2}$ and $2\times 10^{18}\text{ cm}^{-3}$, respectively. Prior to etching in a $\text{HF}:\text{CH}_3\text{OH}:\text{H}_2\text{O}_2$ (2:1:2) solution under UV illumination, 10 nm thin stripes of platinum (Pt) were sputtered onto the GaN samples [9]. The nanostructure layers were later transferred onto a Si wafer for subsequent room temperature micro-photoluminescence ($\mu\text{-PL}$) measurements using Jobin Yvon's LabRAM ARAMIS micro-photoluminescence (μPL) spectroscopy system. The optical excitation was produced using a Helium-Cadmium (HeCd) laser emitting at 325 nm with a $<10\text{ }\mu\text{m}$ spot-size. The scanning and transmission electron microscopy (SEM and TEM) investigations were performed using FEI Quanta 600 and FEI Titan G² 80-300 electron microscopes, respectively.

3. Results and discussion

Figure 1 (a) shows the SEM image of the GaN nanostructures sonicated and dispersed on a Si substrate. The nanostructures have the grain-like form with sizes ranging from 10nm to 100nm. Along with these nanostructures we formed nanowires with diameters ~30nm and lengths from 1-4 μ m. Using high resolution TEM (HRTEM), we observed adjoining single-crystal GaN nanostructures with each particle surrounded by an amorphous-like boundary (Fig. 1(b)). Electron energy loss spectroscopy (EELS) analysis revealed the 20 atomic percentage of oxygen (Fig. 1(c)). The presence of oxygen can be explained by the oxidation of GaN in contact with HF solution producing Ga₂O₃.

Figure 1. (a) SEM image of the nanostructures prepared using UV metal-assisted electroless etching technique, and (b) TEM image of GaN nanostructure, with the amorphous like boundary (red line) (c) EELS analysis on the GaN nanostructures.

Figure 2 shows the typical room temperature μ -PL emission spectrum of the as-grown GaN excited at 0.08 kW/cm² together with the excitation power dependent μ -PL emission spectra of the GaN nanostructures. For the room temperature PL of the as-grown GaN epitaxy we observe a dominant peak at 3.42 eV (~362 nm) attributed to the free-exciton to valence band recombination. Most importantly, room temperature PL of GaN nanostructures excited at 0.08 kW/cm² exhibits a peak centered at 3.376 eV (367nm) which is red-shifted by 34 meV (5 nm) compared to the as-grown sample. As the excitation power increases from 0.08 kW/cm² to 8 kW/cm², we observe an almost linear decrease of the peak PL photon energy by 246 meV. This was not observed in the as-grown GaN epitaxy with increasing excitation power. Besides the redshift, the measured FWHM increases with the excitation power from 99 meV (~10 nm) at 0.08 kW/cm² to 191 meV (~24nm) at 8 kW/cm². Such a wide FWHM is twice as large compared to that of the peak from the as-grown GaN, where the line width broadening at the same power density is 42 meV (~4.5 nm). This FWHM widening indicates a contribution of inhomogeneous broadening in the clusters of nanostructures.

Figure 2. Normalized room temperature μ PL emission spectra of as-grown GaN epitaxy (dash line), and GaN nanostructures (solid line) cluster excited with increasing laser power (0.08, 0.8, 2, 4, 8 kW/cm²).

In the following discussion, we investigate the large redshift in PL emission in the nanostructures with increasing power density. Due to the extremely high surface to volume ratio of the produced nanostructures, surface states effect is expected to dominate the emission mechanism. The n-type GaN nanostructures have surface defects such as Ga vacancies [10, 11], and sidewall oxide formation as evident in the EELS measurement in Fig. 1(c), thus we have band bending in these regions. The creation of surface depletion will change the emission in the GaN nanostructures. The calculated width of the depletion region in our case is $d \sim 24$ nm, given by $d = \sqrt{2\epsilon_{\text{GaN}} V_{\text{bi}} / q N_d}$ [12]. Where ϵ_{GaN} is the static dielectric constant of GaN, V_{bi} the potential at the boundary, q the electronic charge, and N_d the

donor density. For nanostructures with a size, $W < 2d$, the nanostructure will be totally depleted. Ga vacancy centers acting like acceptor sites will be depleted from holes, and we then have the free-excitonic (FX) transitions dominating. If $W > 2d$, both depleted region and non-depleted region co-existing. As verified in the excitation power, holes are expected to populate the acceptor-like states in the depletion region and electrons populating the donor-like states, leading to an increase in donor-acceptor pair (DAP) and donor-to-valence band transitions, as the optical and thermal energy excited more carriers to reduce the depletion region, and eventually, visible-emission at a higher excitation power.

4. Summary

In summary, we have studied the PL spectrum of GaN nanostructures with size dispersion between 10 nm to 100 nm fabricated using the ultraviolet (UV) metal-assisted electroless etching method. A large emission wavelength tunability of ~250 meV has been observed from the nanoparticles. We demonstrated that surface effects are responsible for the redshift dependence of the PL peak with increasing optical power injection. The method used to synthesize these GaN nanoparticles emitting in the visible is promising for producing III-V semiconductor nanoparticle phosphor.

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