Yellow luminescence depth profiling on GaN epifilms using reactive ion etching

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Depth profiling measurements of photoluminescence on GaN epitaxial films grown on *c*-plane sapphire with metalorganic chemical vapor deposition have been performed. Dry etching technique of reactive ion etching is used with reactive gas of $CCl_2F_2/H_2/Ar$ under an operation power of 200 W. Before and after each etching, reflectivity and photoluminescence spectra are measured. Film thickness is determined from both the scanning electron microscopy and the interference oscillations of the reflectivity spectra. An excellent steady etching rate of 19.2 nm/min is established. The photoluminescence measurements show that both the near-band-edge and the yellow luminescence remain fairly constant until the film thickness of about 700 nm, and a large drop is obtained in the ratio of near-band-edge to yellow emission intensity under about 300 nm. Analysis shows that the yellow luminescence emitters are mostly confined within the near interface region, and supports the origin of yellow luminescence to be due to native defects instead of impurities. © *1998 American Institute of Physics.* [S0003-6951(98)02845-9]

The studies of GaN begin more than thirty years ago. Good results like smooth epitaxial growth and blue light emitting with metal–insulator–semiconductor (MIS) structures have been obtained.[1,2] Yet, major breakthrough did not come until the low temperature AlN buffer layer growth on the sapphire substrate and *p*-type dopant activation by low-energy electron beam irradiation (LEEBI) are achieved.[3] Shortly, low temperature GaN buffer layer growth, two-flow growth, and thermal annealing of *p*-type dopant advance the progress further.[4] At present, several candle light blue light emitting diode (LED) is manufactured with tremendous growth in the capacity. Defects density is greatly reduced using epitaxial lateral overgrowth (ELOG) technique, and commercial blue laser diode (LD) with room temperature, continuous wave (cw) performance is around the corner.[5,6]

Although commercial products of N-based/sapphire are available on the market already for several years, the mechanism of light emission is under vigorous research. One of the interesting and puzzling phenomena observed on the photoluminescence (PL) spectra of GaN films is the broad luminescence peak around 2.3 eV.[7] Many theories and various experimental results can be found in the literature.[8,9] Among them, deep level models have been proposed by many groups. The physical origins of the deep levels can be ascribed to two kinds, one is due to impurities, and one is due to native defects. Siegle *et al.* used spatially resolved PL and Raman techniques to examine very thick (400 μm) sample grown by hydride vapor phase epitaxy (HVPE).[10] Their observation suggests that the yellow luminescence is primarily due to structural defects. The resolution of their technique is limited to about 1 μm. In this work, metalorganic chemical vapor deposition (MOCVD)-grown GaN thin films ($\sim$2 μm) are dry etched through reactive ion etching (RIE).[11–15] PL and reflectivity measurements are performed before and after each etching. Much finer spatial resolution is achieved. Detailed analysis on the data shows that the yellow light emitters are confined mainly in the vicinity of the interface of GaN and the sapphire substrate. This result supports the physical origin of the yellow luminescence to be due to native defects.

The GaN epitaxial layers are grown by MOCVD. Substrates are (0001) 2 in. sapphire wafers. The GaN epifilms are Si doped with a doping concentration of 1×10^{18} cm^{-3}. Cross-sectional view of the sample is examined with scanning electron microscopy (SEM) before the etching. Film thickness is determined with reflectivity measurements before and after each etching. A 50 W white light source is used as the incident light beam, the reflected light is fed into an optical spectrum analyzer that covers a wavelength range from 350 to 1750 nm. In the PL measurements, excitation source is a 325 nm He–Cd laser. The luminescence emission is collected with lenses and fed into a SPEX spectrometer. After dispersed by the grating plate, the light is detected by a photomultiplier tube (PMT, Hamamatsu). RIE (Plasma-Therm 790) is done using the reactive gas $CCl_2F_2/H_2/Ar$. All measurements are performed at room temperature.

GaN sample is scratched from the substrate side with a diamond scriber, and then broken with pressure applied along the scratched line from the sapphire side. Figure 1 is an SEM photo showing the cross-sectional view of the sample. The GaN film is in the middle and the sapphire substrate is on the left. From the SEM photo, the interface is clearly shown, and the thickness of the GaN film is measured as 1.7 μm. This thickness is determined with another method utilizing reflectivity measurement. A calibration run is done

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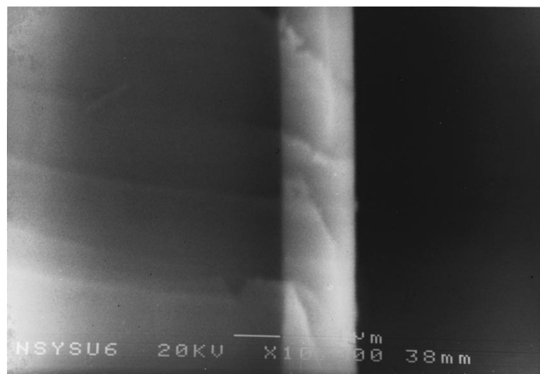

FIG. 1. SEM cross-sectional view of GaN/sapphire sample. Scale bar shown is 1 μm.

first to serve as the reference signal having the white light emit into the spectrometer directly. After divided by the reference, the reflectivity spectrum of the GaN/sapphire sample is shown as in Fig. 2. From the interference maxima/minima points, the GaN film thickness can be calculated as 1.74 μm that is identical with the SEM result. Established with this noncontacting, nondestructive, and fairly simple thickness measurement method, reflectivity measurements are performed after each etching to determine the film thickness.

Chemical gas used in the RIE process is a mixture of 22.5 sccm CCl_2F_2, 2 sccm H_2, and 5 sccm Ar. The pressure is 12 mTorr and the operation power is 200 W. Figure 3 is the result showing the relation of the GaN film thickness with the RIE etching time. The good linear fit indicates a steady etching process and the slope yields an etching rate of 19.2 nm/min. Figure 4 shows a PL spectrum with near-band-gap UV peak at 364 nm, and a low broad yellow peak centered around 547 nm. After each 10 min etching, PL is measured as well as reflectivity. The result is shown as in Fig. 5. Both the UV and the yellow emission intensities keep fairly constant with little decease until the thickness of about 700 nm, and drop much faster after that. In the same figure, UV to yellow PL intensity ratio is shown, too, which remains fairly constant until the thickness of about 300 nm. The faster decrease of UV and yellow signal below the thickness of about 700 nm is believed due to the finite thickness effect, i.e., the film thickness is smaller than the penetration depth of the laser beam. On the following, analysis on the UV to

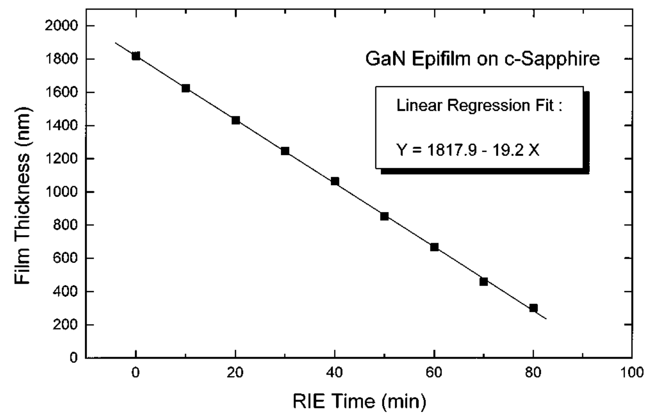

FIG. 3. GaN film thickness vs RIE etching time. An excellent linear fit, where *Y* stands for the film thickness and *X* the RIE time, indicates a steady etching rate. The slope yields an etching rate of 19.2 nm/min.

yellow luminescence intensity ratio is done and shows that more yellow emitters is located near the interface.

Applying the exponential form for the light intensity absorption in the medium and treating the problem as in one dimension, the incident laser beam intensity at a depth of x into the GaN film is

$$I(x)=I_0 \exp(-\alpha_0 x), \tag{1}$$

where α_0 is the absorption coefficient of the incident 325 nm laser beam within the GaN film, and I_0 is the incident laser beam intensity. Assuming that the generation efficiency of UV luminescence is η_1, and η_2 for yellow, then, the luminescence intensity emitted from a depth of x into the GaN film surface is

$$I_{\mathrm{UV}}(x)=I_0 \exp(-\alpha_0 x)\eta_1 \exp(-\alpha_1 x) \tag{2}$$

and

$$I_{\mathrm{Yel}}(x)=I_0 \exp(-\alpha_0 x)\eta_2 \exp(-\alpha_2 x), \tag{3}$$

where α_1 and α_2 are the absorption coefficients for the UV and yellow emission, respectively. So that, the total luminescence emission emitted from the GaN film is, assuming η_1 and η_2 are constant,

$$I_{\mathrm{UV}}=I_0\eta_1\int_0^d \exp[-(\alpha_0+\alpha_1)x]dx \tag{4}$$

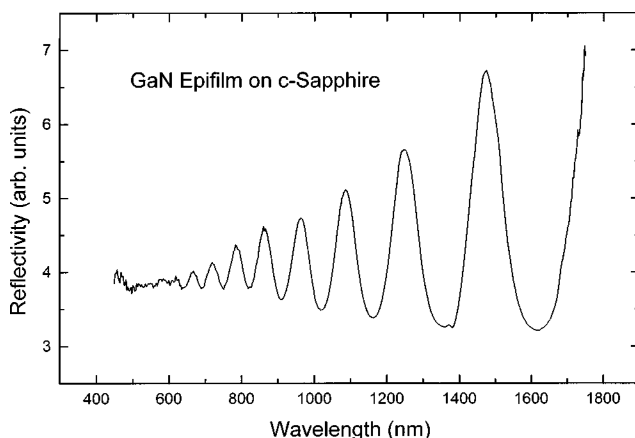

FIG. 2. Reflectivity spectrum of GaN epifilm on sapphire substrate. Oscillation maxima/minima are due to interference.

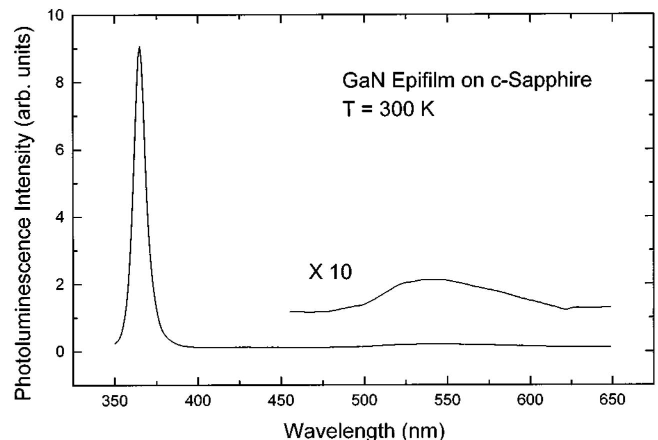

FIG. 4. Room temperature PL spectrum of as-grown GaN epifilm. A large near-band-gap UV peak is at 364 nm. A low, broad yellow peak centered around 547 nm is magnified ten times.

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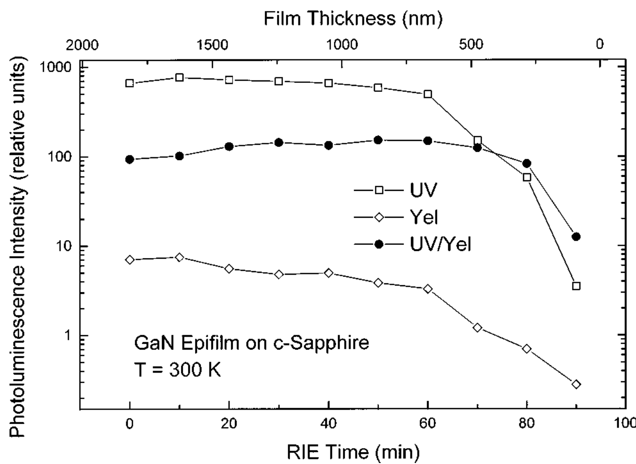

FIG. 5. UV, yellow, and UV-to-yellow PL intensities are shown with respect to RIE etching time.

and

$$I_{\mathrm{Yel}}=I_0\eta_2\int_0^d \exp[-(\alpha_0+\alpha_2)x]dx, \tag{5}$$

where d is the GaN film thickness. Therefore, knowing that $\alpha_0>\alpha_1>\alpha_2$, the ratio of UV to yellow emission, $I_{\mathrm{UV}}/I_{\mathrm{Yel}}$, will be decreasing with increasing thickness d, i.e., the ratio will be increasing with increasing RIE etching time, and this is in contradiction to the experimental results of Fig. 5. Figure 5 shows a fairly constant $I_{\mathrm{UV}}/I_{\mathrm{Yel}}$ ratio until a film thickness of about 300 nm, and a large drop after that. For a constant η_1 situation, Fig. 5 shows that η_2 is a function of depth and increases with increasing depth into the GaN film. Based on this analysis, yellow emitter distribution along the film depth is not uniform, and impurities inclusion during the growth should not be the origin for the yellow luminescence. Most yellow emission is from the region near the interface of GaN and sapphire. This is believed to be due to the higher density of defects near the interface region because of the large mismatch of the lattice constant between GaN and the sapphire substrate. This is consistent with the observation of Siegle *et al.*[10] Although the possibility that the structural defects could lower η_1 as well near the interface cannot be ruled out. In addition, PL measurement on the back substrate side is done, and a strong yellow signal as compared to UV signal is obtained. This eliminates the possibility of an RIE induced effect.

In conclusion, depth profiling of GaN on sapphire has been done using RIE. A steady etching rate of 19.2 nm/min is established using $CCl_2F_2/H_2/Ar$ under 200 W. On each stage of the etching, PL measurement is performed on the sample. UV and yellow luminescence peaks are compared at different depth of the GaN film. Analysis shows that yellow emitters are denser near the interface under a constant UV efficiency. This rules out the possibility of the inclusion of impurities during the growth process as the origin of yellow luminescence, since they are most likely uniformly distributed. Because there is a large mismatch in the lattice constant between the GaN and the sapphire, defects are denser near the interface, and these are believed to be the origin of the yellow emitters. Heavy yellow emitters due to native defects are located within 300 nm near the GaN/sapphire interface.

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