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Spatially resolved cathodoluminescence of GaN nanostructures fabricated by photoelectrochemical etching

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The emission properties of GaN nanostructures created by photoelectrochemical etching have been investigated by cathodoluminescence (CL) in the scanning electron microscope. Columnar structures with diameters of 150–250 nm formed near the surface of the as-grown GaN layers branch into nanowires with diameters of 20–60 nm, while islands with coral-like relief were observed at the bottom of the etched areas. CL emission of the observed nanostructures is dominated by free electron to acceptor transitions. Local CL spectra provide direct evidence of the existence of either compressive or tensile stress in different nanostructures. No free exciton luminescence was observed in GaN nanowires, supporting their relation to threading dislocations. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1940734]

Over the last decade, GaN became one of the most intensively investigated semiconductors due to its potential applications in optoelectronics and high-frequency/high-power electronics. A serious obstacle to the realization of many device structures is the high content of threading dislocations in GaN epilayers, which are grown on lattice mismatched substrates due to the limited availability of GaN substrates. The impact of dislocations upon emission properties of GaN epilayers has been previously assessed by cathodoluminescence (CL).[1,2] Nonradiative recombination of free carriers at threading dislocations is thought to cause a deficiency of minority carriers and results in dark regions of the epilayer.[1] However, regions of enhanced emission have also been observed by cross-sectional CL and attributed to decorated dislocations.[2] Previous investigations[3–5] indicate that threading dislocations in *n*-GaN can be visualized by the formation of whiskers during photoelectrochemical (PEC) etching. The high resistance of whiskers to PEC attack was attributed to the negative charge inherent to threading dislocations in *n*-GaN.[4] Indeed, the photogenerated holes will not contribute to the etching process in case they exhibit fast recombination via defect states at dislocations. An alternative explanation is that dislocations represent regions of decreased potential and the photogenerated holes are repelled from them and confined in the surrounding areas stimulating their dissolution. In this work, CL microscopy and spectroscopy have been applied to correlate the local optical and structural properties of different GaN nanostructures created by PEC.

The GaN layers used were grown by low-pressure metalorganic chemical vapor deposition on sapphire substrates. A buffer layer of 25-nm-thick GaN was first grown at 510 °C. Subsequently, a 0.5-μm-thick *n*-GaN film followed by a Si-doped n^+-GaN film and a top *n*-GaN layer with 2.0 μm thickness each were grown at 1100 °C. The concentration of free electrons in the top *n*-GaN layer was 1.7×10^{17} cm^{-3}. PEC etching was carried out in a stirred 0.1 M aqueous solution of KOH for 10–30 min under *in situ* ultraviolet illumination provided by focusing the radiation of a 200 W Xe lamp on the GaN surface exposed to the electrolyte. No bias was applied to the sample during etching. The morphology of the etched layers was studied using a Jeol JSM-6335F field emission scanning electron microscope (SEM) and a Leica 440 Stereoscan SEM. The latter instrument was also used for CL investigations, carried out at 90 K using accelerating voltages of 5–15 kV and beam currents between 0.2 and 5 nA. CL spectra were recorded either using a charge coupled device camera with a built-in spectrograph (Hamamatsu PMA-111) or a Hamamatsu R928P photomultiplier working in the photon counting mode and a computer controlled Oriel 74100 monochromator.

Figure 1 shows high-resolution SEM images taken in

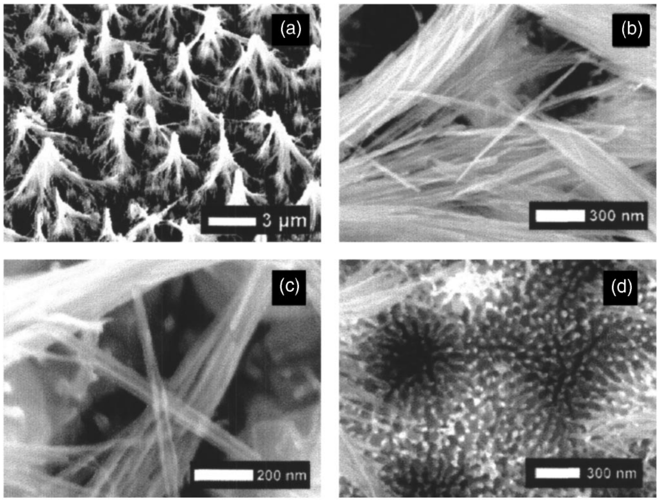

FIG. 1. SEM images taken in different areas of an etched GaN layer showing columnar structures (a), branches of nanowires stemming from the bottom of the columns (b,c) and islands with coral-like relief (d).

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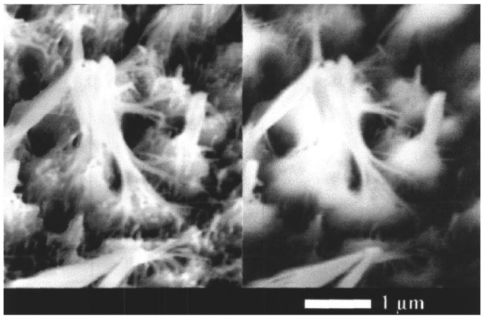

FIG. 2. SE image (left) and corresponding panchromatic CL micrograph (right) of a PEC etched GaN film.

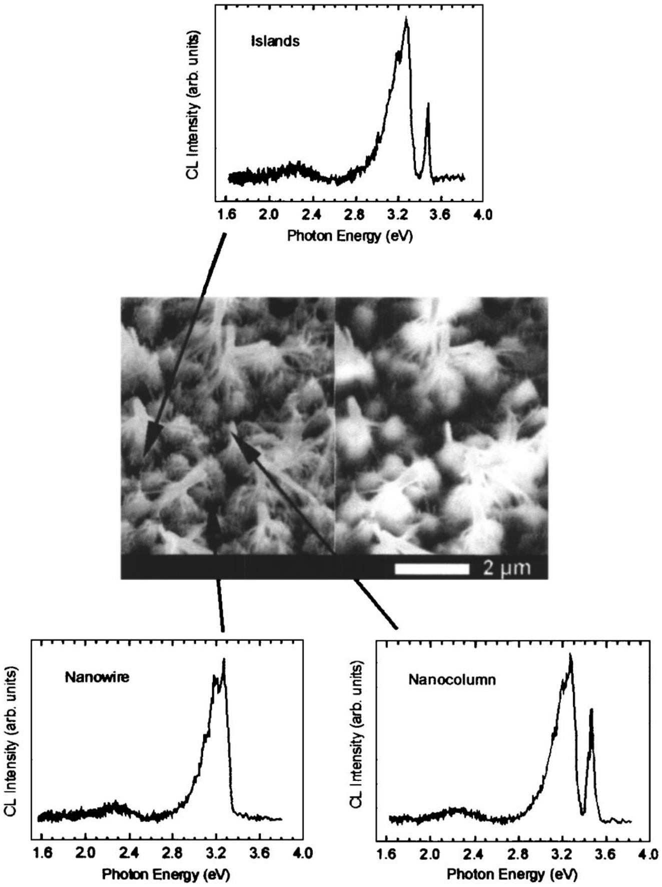

FIG. 4. SE (left) and corresponding CL image (right) of a PEC etched GaN layer. CL spectra recorded in particular luminescent nanostructures marked in the image are displayed around the micrographs.

different areas of an etched layer. Columnar structures with diameters of 150 to about 250 nm and lengths up to 2 μm can be observed in Fig. 1(a). Each columnar structure branches into a bundle of nanowires [Figs. 1(b) and 1(c)]. The length of the nanowires varies from 1 to 4 μm, while the diameters vary between 20 and 60 nm. As observed in Fig. 1(d), the bottom of the etched area exhibits a coral-like relief, the nanowires being distributed nonuniformly along the sample surface. These features reflect the columnar or domain structure of the GaN layer merging the sapphire substrate.[6] In order to ascertain the potential role of dopant segregation in the formation of these nanostructures, x-ray microanalysis were carried out in the columns and nanowires formed by PEC etching. No differences were found between the composition measured in the nanostructures and that measured in the as-grown material. Figure 2 shows a secondary electron (SE) image and the corresponding CL micrograph taken from a PEC etched GaN sample. The CL micrograph shows a rather uniform emission that sometimes appears enhanced in areas containing a high density of nanowires. CL spectra were recorded in both as-grown and PEC etched GaN layers. Figure 3 shows results obtained at low magnification in the SEM (scanned area $\sim 400 \times 400\ \mu\text{m}^2$), representative of the samples at macroscopic level. The integrated luminescence intensity is about one order of magnitude higher in the PEC etched samples. The spectral distribution of the CL emission exhibits, in both cases, peaks in the visible and the UV spectral ranges. In the low energy region, the so-called yellow band is observed centered at about 2.25 eV. According to recent studies, the emissions contributing at 90 K to this complex band can be attributed to radiative transitions from the conduction band to deep acceptor levels.[7] The narrow emission centered at 1.791 eV arises from the sapphire substrate.

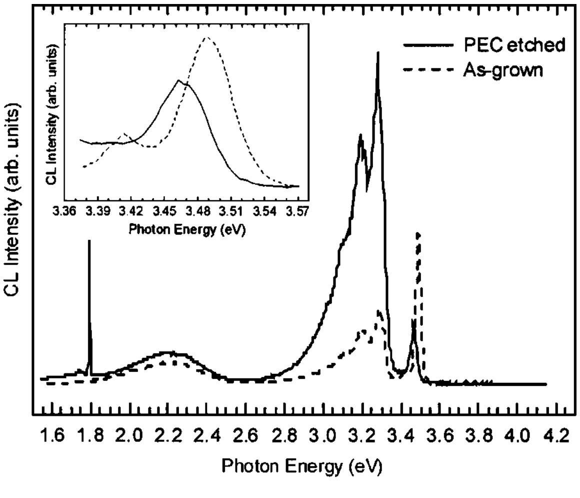

FIG. 3. Low magnification CL spectra, recorded using an accelerating voltage of 7 kV, from a PEC etched GaN layer (solid line) and an as-grown epilayer (dashed line). The inset shows a detail of the near-band gap CL emission from both samples.

The second group of peaks is dominated by an intense CL band centered at 3.287 eV. This emission is related to electron transitions from the conduction band to shallow acceptors (eA^0 transitions)[8,9] and appears as the dominant emission in CL spectra recorded from PEC etched samples. The peaks centered at 3.200 and 3.108 eV correspond respectively to the first and second LO phonon replicas of the eA^0 transition. The peaks at higher energies, shown in detail in the inset of Fig. 3, correspond to GaN near band gap transitions. Irrespective of the growth method, shallow donor ionization in GaN is complete at 90 K and the near band gap luminescence is dominated by the *A* free exciton (FXA) transition.[8,10,11] In strain-free samples, the FXA transition is peaked at 3.471 eV for $T = 90$ K.[8,10] However, the thermal expansion mismatch between GaN and the sapphire substrate strains the GaN layer. This biaxial compressive strain decreases as the layer thickness increases.[12] The compressive strain blueshifts the free exciton peak position, while the tensile stress, as that inherent to thin GaN layers grown on SiC substrates, redshifts the free exciton peak. The free exciton emission in our as-grown GaN epilayers is peaked at 3.488 eV. This evidences the occurrence of an average biaxial stress of about 0.5 GPa.[13] On the contrary, CL spectra recorded on PEC etched samples shows a FXA peak at 3.462 eV, indicating the existence of a tensile stress of about 0.33 GPa.[13] In addition, CL spectra of the as-grown samples (Fig. 3) also exhibit a peak at 3.413 eV that is absent in the spectra of PEC etched samples. A very recent combined CL and transmission electron microscopy (TEM) study reveals that stacking faults in the basal plane are responsible for this emission.[14]

Information about the luminescence properties of the observed features of the etched samples, columnar structures [Fig. 1(a)], nanowires [Fig. 1(c)], and islands with coral-like relief [Fig. 1(d)] was obtained by recording local CL spectra from specific nanostructures observed in high-magnification SEM micrographs. Figure 4 shows a SE image and the corresponding CL micrograph of an etched layer, as well as spectra recorded at particular luminescent nanostructures. Our spatially resolved CL spectral measurements show that regardless of their size, the eA^0 band, centered between 3.268 and 3.275 eV depending on the spot considered, always dominates the nanowires CL emission. No excitonic luminescence was observed in the nanowires under consideration. These observations support previous correlation[15] established by TEM between GaN whiskers and threading dislocations. The free electron to acceptor transition also dominates spectra from islands with coral-like relief. However, the excitonic luminescence is peaked at about 3.485 eV in this case, revealing the occurrence of compressive stress in these particular regions. On the contrary, CL spectra from nanocolumns show excitonic luminescence peaked between 3.355 and 3.464 eV, evidencing the existence of tensile stress in such structures. No peak shift due to quantum confinement effects is observed. This can be explained by the fact that the excitonic Bohr radius of GaN (11 nm) is smaller than the size of the nanowires found in the sample (20–60 nm). The obtained results agree with those reported for other GaN nanostructures, as nanocolumns grown by molecular beam epitaxy on sapphire, where the existence of strain at the nanocolumn bottom interface was revealed by CL spectroscopy.[16] Moreover, uniaxial tensile stress in the growth direction was recently observed in GaN nanowires grown by chemical vapor deposition.[17]

In summary, a direct correlation between structural and optical properties of GaN nanostructures formed by PEC etching has been achieved using spatially resolved CL microscopy and spectroscopy. CL emission of the observed nanostructures is dominated by free electron to acceptor transitions. Local CL spectra evidence the existence of compressive stress in islands with coral appearance while tensile stress is detected in columnar nanostructures. No free exciton luminescence was detected in GaN nanowires, supporting their relation to threading dislocations.

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