# Luminescence of GaN nanocolumns obtained by photon-assisted anodic etching

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GaN nanocolumns with transverse dimensions of about 50 nm were obtained by illumination-assisted anodic etching of epilayers grown by metalorganic chemical vapor deposition on sapphire substrates. The photoluminescence spectroscopy characterization shows that the as-grown bulk GaN layers suffer from compressive biaxial strain of 0.5 GPa. The majority of nanocolumns are fully relaxed from strain, and the room-temperature luminescence is free excitonic. The high quality of the columnar nanostructures evidenced by the enhanced intensity of the exciton luminescence and by the decrease of the yellow luminescence is explained by the peculiarities of the anodic etching processing. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1605231]

GaN and related nitrides became recently the most intensively investigated semiconductor materials due to their applications for high-efficiency light-emitting devices in the ultraviolet and blue energy regions[1,2] and electronic devices capable to operate at high temperature/power and in harsh environments.[3,4] Due to the lack of suitable nitride substrate material, heteroepitaxial growth on sapphire or 6H–SiC substrates is actually common practice. The large lattice parameter and thermal expansion coefficient mismatches between GaN and these materials result in residual strain in heterostructures that can seriously influence the device quality. The common practice to reduce the strain in GaN layers is the growth of a buffer layer. In spite of that, in many cases the remaining amount of strain is considerable. It is important to understand the impact of strains on excitons in photoluminescence (PL) of GaN since the nature of the band-edge radiative recombination processes was shown to be excitonic up to room temperature.[5] The influence of biaxial strain on the exciton resonance energies and the band structure of wurtzite GaN was extensively studied (see Ref. 6, and references therein). The accumulated experimental data allow one to reliably characterize strains in GaN layers by analyzing exciton lines in optical spectra.

Unique possibilities to fabricate strain-relaxed structures and to further extend the area of practical applications of nitrides are provided by material nanostructuring. In particular, wurtzite GaN nanowire arrays are an important focus of current research, cf. Refs. 7 and 8. Nanotexturization is expected to induce a strongly enhanced nonlinear optical response that may lead to the development of fully integrated light source and frequency converter subsystems.[9] Nanostructuring is also a powerful tool for phonon engineering.[10,11]

The GaN nanowires synthesized by chemical vapor deposition on silicon substrates proved to experience significant stresses,[8] while x-ray investigation showed that porous GaN structures suffer from less residual stresses than the as-grown GaN epilayers.[12] Wurtzite GaN nanocolumns fully relaxed from strain were grown recently by molecular beam epitaxy on Si and sapphire substrates.[13]

In this work, we present the results of PL spectroscopy characterization of GaN nanocolumns obtained by illumination-assisted anodic etching of bulk epilayers. The investigated columnar nanostructures are shown to be relaxed from strain, their room-temperature luminescence being free excitonic.

The GaN layers were grown by low-pressure MOCVD techniques on (0001) $c$-plane sapphire. A buffer layer of 25-nm-thick GaN was grown at 510 °C. Subsequently, a 0.5-$\mu$m-thick $n$-GaN followed by a Si-doped $n^+$-GaN film and a top $n$-GaN layer with 2.0 $\mu$m thickness each were grown at 1100 °C. The concentration of free electrons in the top layer was $1.7\times10^{17}$ cm$^{-3}$. Anodic etching was carried out at current density 5 mA/cm$^{-2}$ in 0.1 mol aqueous solution of KOH under *in situ* UV illumination provided by focusing the radiation of a 250 W Hg lamp on the GaN surface exposed to electrolyte.

The PL was excited by the 334 nm line of an $Ar^+$ SpectraPhysics laser and analyzed through a double spectrometer. The resolution was better than 0.5 meV. The samples were mounted on the cold station of a LTS-22-C-330 cryogenic system.

A scanning electron microscope (SEM) image taken from the etched GaN sample is shown in Fig. 1. GaN columns with transverse dimensions of 50 nm or less prove to be oriented perpendicular to the initial surface. In some re-

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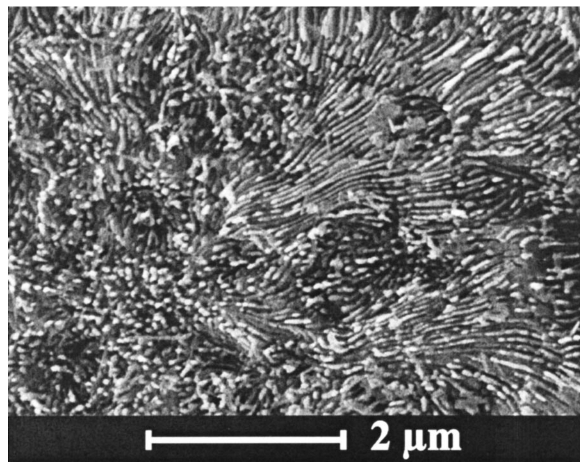


FIG. 1. SEM image taken from GaN sample subjected to anodic etching.

gions of the sample, the columns were bent parallel to the surface to facilitate the analysis of transverse dimensions.[14]

Figure 2 illustrates the PL spectra of the initial GaN layer (curve 1) and of the columnar nanostructures (curve 2). The evolution of the PL spectra with the temperature increase is shown in Figs. 3 and 4 for the bulk and nanostructured layers, respectively. The luminescence spectra are predominated by the $D^0X$ bound exciton, $X_A^{n=1}$ and $X_B^{n=1}$ excitonic emission. The positions of the $D^0X$ (1.481 eV), $X_A^{n=1}$ (1.487 eV), and $X_B^{n=1}$ (1.495 eV) peaks in the luminescence spectrum of the as-grown GaN layer are shifted by $\sim 10$ meV towards high energies in comparison with the positions of respective excitons in nonstressed GaN layers.[5,6,15] It means that considerable strain remains in the GaN layer in spite of the existence of an intermediate 25-nm-thick GaN buffer film. According to Refs. 6 and 16, the $D^0X$ luminescence peak is shifted by about 20 meV toward high energies for a GaN layer of similar thickness grown on sapphire substrate without any buffer film. Comparing the mentioned shifts for the $D^0X$ peak, one can deduce that the GaN buffer film twice reduces the strains. The remaining strain of 0.5 GPa can be estimated using the previously reported rates of the exciton line shifts with the biaxial stress.[6,17]

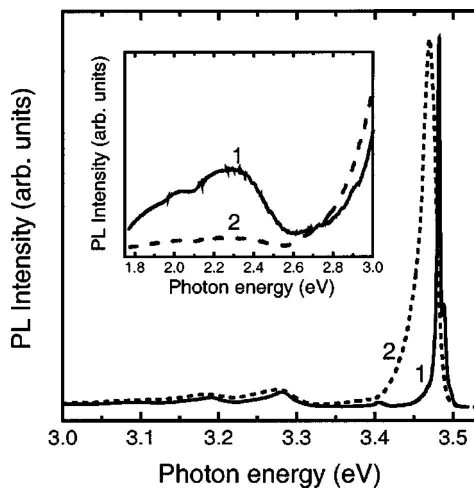


FIG. 2. Normalized PL spectra of GaN bulk layer (curve 1) and sample subjected to anodic etching (curve 2) measured at $T=10$ K. The insert shows the PL spectra in the visible region.

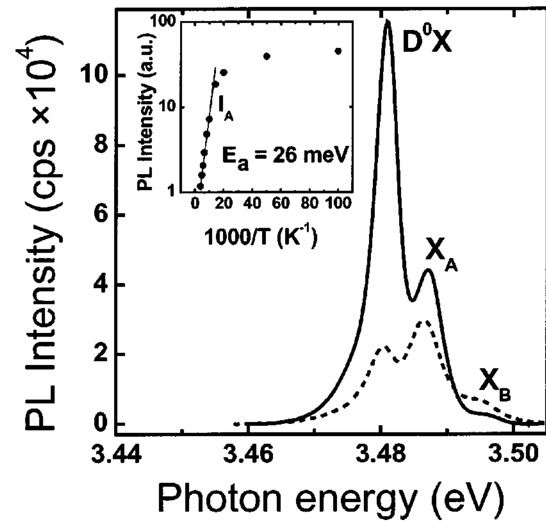


FIG. 3. PL spectra of GaN bulk layer measured at $T=10$ K (solid line) and 50 K (dashed line). The insert illustrates the temperature dependence of the $A$-exciton line intensity.

With increasing temperature the PL intensity is redistributed in favor of free-exciton emission against the bound exciton, and in favor of $B$ exciton against $A$ exciton (see Fig. 3). The first is explained by the difference in the binding energies of the bound and free excitons. The second is consistent with the previous observations explained by the long lifetime in "bottleneck" states.[15,18] The binding energy of the donors responsible for the $D^0X$ line in GaN is estimated to be around 35 meV.[5] According to the Haynes rule,[19] the binding energy of the donor-bound exciton should be a factor of five lower than this value. The activation energy of the donor-bound exciton in GaN was estimated to be $\sim 7$ meV.[20] From the slope of the straight line in the inset of Fig. 3, the activation energy of the $A$ exciton is estimated as 26 meV and coincides with the free exciton binding energy.[5,6,15]

The position of the PL line in nanocolumns at low temperature (3.470 eV) proves to be shifted towards low energies by $\sim 10$ meV relative to the position of the $D^0X$ exciton

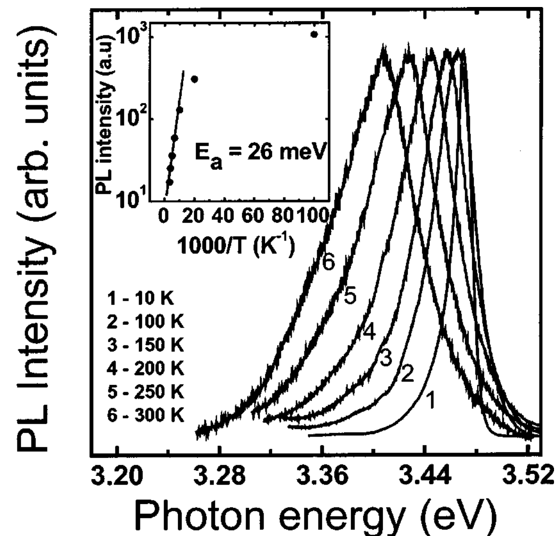


FIG. 4. Evolution of the normalized PL spectrum of GaN columnar nanostructures with the temperature increase. Inset shows the temperature dependence of the PL intensity.

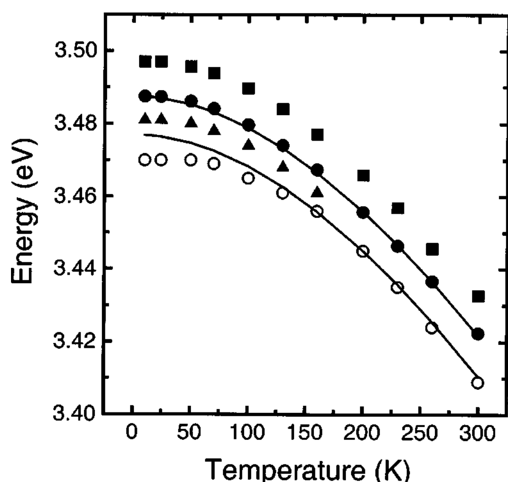


FIG. 5. Temperature dependence of the exciton line energies in bulk GaN layer (full symbols) and columnar nanostructures (open symbols): triangles correspond to the donor-bound exciton; circles and squares correspond to the *A* and *B* free excitons, respectively. Lines represent the fit of the experimental data according to the Varshni formula.

in the as-grown GaN layer (see Fig. 2), and corresponds to the position of the $D^0X$ line in nonstressed GaN layers.[5,6,15] The PL band in nanocolumns represents obviously a superposition of PL lines related to the bound and free excitons. With increasing temperature, the $D^0X$ exciton PL is thermally quenched and at $T>100$ K the luminescence is expected to be free excitonic. Indeed, the activation energy of the PL band in nanocolumns determined from the high-temperature region in the inset of Fig. 4 equals 26 meV and coincides with the binding energy of the free excitons in bulk GaN.

The assumption about the redistribution of radiative recombination channels from bound to free exciton recombination with increasing temperature in GaN nanocolumns is supported by the analysis of the temperature dependence of the position of PL lines presented in Fig. 5. The temperature dependence of the *A* exciton in the bulk layer is well fitted with the phenomenological Varshni formula[21]

$$E(T)=E_0-\alpha T^2/(T+\beta),$$

with the parameters $E_0=3.487$ eV, $\alpha=9.5\times10^{-4}$ eV K$^{-1}$, and $\beta=1000$ K. At $T>100$ K, the temperature dependence of the PL line position in nanocolumns is very well fitted by the Varshni formula with the $E_0=3.477$ eV corresponding to the *A*-exciton line position in nonstressed GaN and the same $\alpha$ and $\beta$ parameters as in the bulk layer.

It is interesting to note that the intensity of excitonic luminescence in nanostructured layers is one order of magnitude higher than that of the bulk layer. Apart from that, the yellow luminescence in nanocolumns is essentially reduced in comparison with that inherent to as-grown bulk layer (see the inset in Fig. 2). These observations may be explained taking into account that local dissolution under anodic etching conditions is initiated by surface defects.[22] According to Mynbaeva *et al.*,[12] anodic etching of GaN layers occurs preferentially along the boundary of columnar structures of the as-grown GaN films. The yellow luminescence was shown previously[23] to come from the boundary regions of GaN columns or grains. The anodization removes preferentially these defect regions, leaving GaN nanocolumns with high crystalline quality. The enhanced linewidth of the PL bands in nanocolumns may be attributed to the peculiarities of strain relaxation. A certain fraction of the nanocolumns exhibits probably only partial strain-relaxation although most of them are fully relaxed from strain.

Thus, the blueshift of the exciton lines in bulk GaN layers indicates to the presence of strain as high as 0.5 GPa. After processing, the majority of the GaN nanocolumns proves to be fully relaxed from strain. The luminescence of nanostructures is shown to be excitonic up to 300 K.

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