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Improvement of the optical properties of metalorganic chemical vapor deposition grown GaN on sapphire by an *in situ* SiN treatment

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We have studied the effect of an *in situ* SiN treatment of sapphire substrates on the optical properties of GaN films grown by metalorganic chemical vapor deposition. The SiN deposition, partially covering the substrate, forms a mask for the formation of nanoscale auto-organized GaN islands. These islands formed upon an increase of the temperature after deposition of a GaN buffer layer on this mask. A photoluminescence study of the GaN epilayers obtained by lateral overgrowth of these islands shows significant enhancement of the luminescence emission intensity of the near band edge peaks and a reduction of the full width at half maximum of the donor bound exciton (D^0X) peak by 32% down to 4 meV compared to in our standard process. The GaN films grown using SiN treatment are highly stressed as evidenced by a blueshift of 10 meV in the D^0X peak energies. Photoelectrochemical etching in aqueous solution of KOH was applied to reveal the dislocation density. The density of ''whisker-like'' etch features, which form due to the presence of dislocations, was reduced from 6×10^9 cm^{-2} in standard GaN films to 8×10^8 cm^{-2} in the GaN layers grown with the optimized SiN treatment. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1409277]

The recent spectacular progress in research on III-N materials evidenced by the realization of high performance optoelectronic and microwave devices is related to improvement of the growth of epitaxial material either by metalorganic chemical vapor deposition (MOCVD) or molecular beam epitaxy techniques. Due to the large difference in the lattice parameters and in the thermal expansion coefficient between GaN and sapphire, the growth of GaN epilayers on this substrate usually takes place in two steps.[1,2] The standard way of growing GaN on sapphire includes a nitridation step[3–6] and formation of a GaN or AlN buffer layer at low temperature. This buffer layer consists of a high density of small crystallites, which act as nucleation centers for the GaN epilayer. Replacing the high density of small nuclei by a smaller number of bigger islands constitutes an alternative approach to the buffer layer concept. The islands' buffer layer promotes a kind of epitaxial lateral overgrowth, reducing thereby the dislocation density. In order to achieve the formation of such auto-organized islands, recently a growth process[7–9] based on the insertion of an *in situ* SiN treatment at high temperature of a sapphire substrate was developed. In this letter, we demonstrate that the optical properties of GaN epilayers studied by the photoluminescence (PL) technique are considerably improved by SiN treatment and we carry out photoelectrochemical etching in order to reveal the dislocation density.

The PL measurements were performed at low temperature (4 K) using a HeCd laser (325 nm) as the excitation source with power densities up to 50 W/cm^2. The light emitted was dispersed by a 0.6 m monochromator and detected by a cooled GaAs photomultiplier. The spectral resolution of the measurements was 0.4 meV in the region from 3.2 to 3.55 eV.[10]

Photoelectrochemical etching was performed in a stirred KOH solution (0.004 molar) at room temperature. UV illumination was provided by a 450 W Xe lamp. A 100 nm thick Ti layer was used to assure photocurrent conduction.[11]

The GaN films studied in this letter were grown in a low-pressure MOCVD (AIX200) machine equipped with a horizontal reactor. A 2 in. rotating susceptor ensured good homogeneity of the material deposition. Before loading, *c*-plane sapphire substrates were chemically cleaned. The growing process started by annealing the substrate at high temperature (1000 °C) under H_2 atmosphere for 5 min, then a short nitridation (NH_3 treatment) was carried out at 1170 °C using 2.5 slm of NH_3. This flow was kept constant in the reactor during the growth process. After that, a SiN treatment was introduced using silane (SiH_4) flow of 100 sscm diluted to 50 ppm with H_2. The duration of this step was varied from 15 to 120 s. The GaN buffer layer was deposited at 525 °C, immediately after temperature stabilization. The flow of the gallium precursor (trimethylgallium) was 13.5 μmole/min and the V/III ratio was about 8230. The thickness of this buffer layer was 30 nm. Finally, a 3 μm thick GaN layer was deposited at 1170 °C using a 64 μmol/min flow of trimethylgallium. Hydrogen was used as the carrier gas, resulting in a growth rate of about 1.70 μm/h.

Scanning electron microscopy (SEM) shows that, for a fixed thickness of the buffer layer (30 nm), the size and the density of GaN islands formed upon increasing the temperature to 1170 °C were controlled by the SiN treatment previously reported.[7] The size of these islands increases when their density decreases and vice versa.

Figure 1 shows the evolution of the near-band edge PL spectra of GaN films with the SiN treatment time (0–120 s). The nontreated sapphire substrate corresponds to the standard growth process. Each PL spectrum consists of the near-band edge emission attributed to the exciton related lumines-

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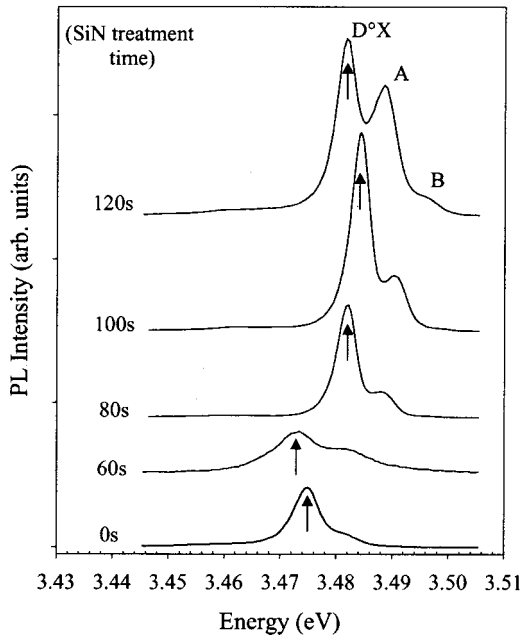

FIG. 1. Evolution of the near-band edge PL spectra at low temperature (4 K) of GaN films with the SiN treatment time (0–120 s).

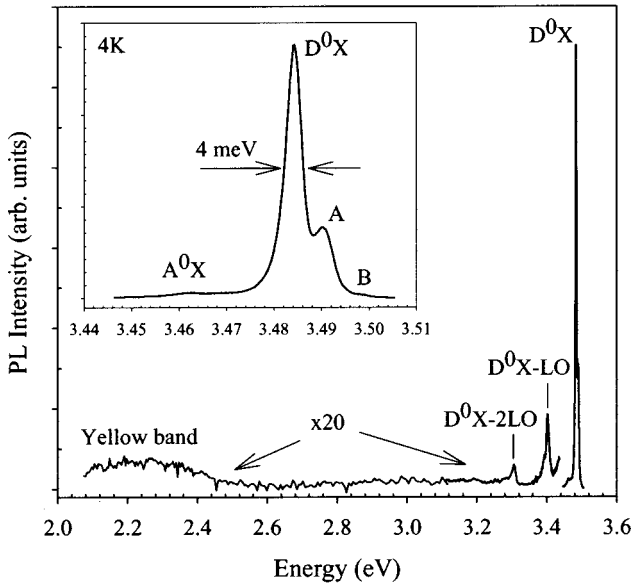

FIG. 3. PL spectra of the GaN sample grown with the optimum SiN time (100 s) in the range of 3.55–1.8 eV recorded at 4 K.

cence. Temperature dependence measurements (4–120 K) combined with reflectivity measurements showed evidence that the dominant line emission in these spectra was related to recombination of donor bound excitons (D^0X) at an energy position between 3.474 and 3.484 eV, depending on the SiN treatment time. Only for long SiN treatment times (100 or 120 s), can A and B free exciton transitions be observed at the higher energy side of the D^0X peak, indicating improvement of the optical quality of these materials.

The full width at half maximum (FWHM) and the energy position of D^0X, *A* and *B* free excitons' transition vary with the SiN treatment time. In order to clearly illustrate the changes in optical properties we plotted in Fig. 2 the dependence of the FWHM of D^0X, the energy position of D^0X, and the *A* free exciton on the SiN treatment time. Using the standard process, the FWHM of the D^0X peak was 5.9 meV but this width rapidly increases to 11 meV for a SiN treatment time of 60 s and then decreases to 4 meV for 100 s. This decrease of about 32% of the FWHM of D^0X compared to in the standard process indicates that the SiN treatment considerably improved the optical properties of GaN.

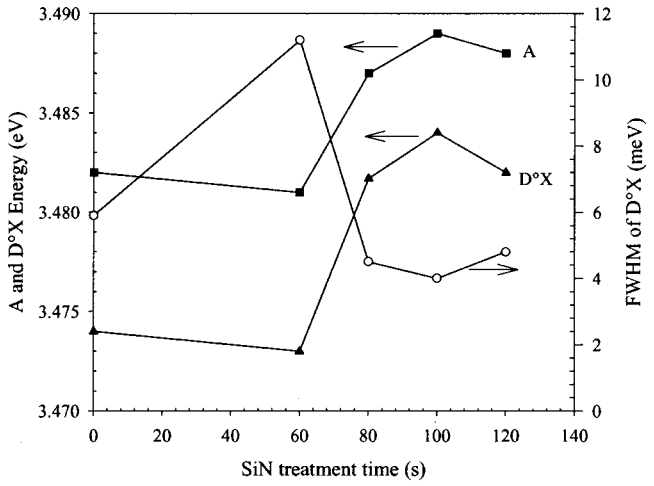

FIG. 2. Variation of the energy position of D^0X, free *A* excitons (left scale) and full width at half maximum of D^0X (right scale) as a function of the SiN treatment time. The measurements were performed at low temperature (4 K).

On other hand, the near band edge peak positions (D^0X and the *A* free exciton) were strongly modified by SiN treatment. In fact, the D^0X and *A* free exciton transitions are found at 3.474 and 3.482 eV, respectively, for GaN films grown with the standard process and 3.484 and 3.490 eV for GaN layers treated for 100 s by SiN. The blueshift of about 10 and 8 meV, respectively, of D^0X and *A* peaks for the GaN layer grown with SiN treatment is related to the increase of residual stress.[12–17] Compared to the low temperature unstrained GaN value of the free *A* exciton in homoepitaxial GaN around 3.477 eV,[18] all GaN epilayers grown in present work are under biaxial compressive strain at low temperature (4 K). By using the figure showing the stress dependence of the free *A* exciton transition reported by Gil *et al.*,[12,13] the biaxial strain is evaluated to be about 0.7 and 1.2 GPa in GaN grown with the standard process and with SiN treatment for 100 s, respectively.

The luminescence intensity of the near-band edge was also affected by the SiN treatment: the GaN grown with a 100 s SiN treatment time has PL intensity about six times higher than the GaN grown by the standard process. This improvement can be explained by a decrease of the dislocation density, which is known to act as a nonradiative recombinations center.[19,20]

Therefore, from PL measurements it can be concluded that 100 s is the optimum SiN treatment time because it results in the lowest FWHM of peak transitions and the highest luminescence intensity. Figure 3 shows PL spectra of the GaN sample grown with this optimum SiN time in the range of 3.55–1.8 eV recorded at 4 K. The D^0X peak, which is located at 3.484 eV, was accompanied by two longitudinal optical (LO) phonon replicas at 3.4 and 3.31 eV. The sharp line at energy of 3.46 eV is attributed to an acceptor bound exciton transition (labeled A^0X). The donor–acceptor pair

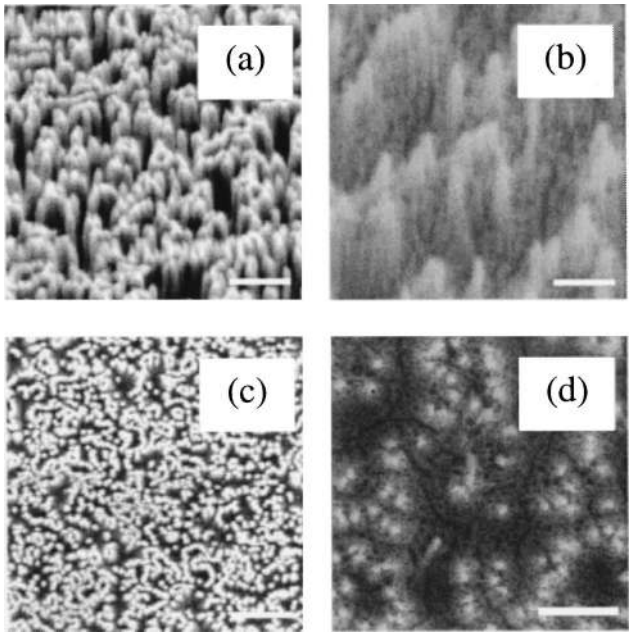

FIG. 4. SEM images of photoelectrochemical etched GaN grown with a standard buffer layer (a), (c) and with the optimized SiN treatment time (b), (d). All markers represent 0.5 μm.

(DAP) recombination, usually reported at 3.27–3.29 eV is absent which is indicative of the high optical quality of GaN grown by this process. It is important to note that the yellow luminescence (YL) located at 2.24 eV is almost negligible compared to the near-band edge transitions (more than two magnitudes of order lower in intensity).

In order to prove the hypothesis that the dislocation density is lower in the layers grown on this new buffer layer, photoelectrochemical (PEC) etching was performed. Figure 4 shows SEM images of PEC etched GaN films grown with the standard process [Figs. 4(a) and 4(c)] and those with the optimum SiN treatment time [Figs. 4(b) and 4(d)]. The density of filamentary etch features (whiskers) calculated from the images in Figs. 4(c) and 4(d) is 6×10^{9} and $8\times10^{8}\,\mathrm{cm}^{-2}$, respectively. This density is a direct measure of the density of dislocations in GaN epitaxial layers as was demonstrated by calibration of PEC etch features with cross-sectional and plan-view transmission electron microscopy (TEM).[21,22] Detailed TEM analysis of PEC etched samples reported in this letter has confirmed a one-to-one correlation between whiskers and dislocations (both edge and mixed type),[23] which allows one to conclude that the density of dislocations is remarkably lower in GaN layers grown after SiN treatment compared with the density in layers obtained using the standard process.

In conclusion, we studied the effect of an *in situ* SiN treatment of a sapphire substrate on the optical properties of GaN epilayers. For the optimized SiN treatment time (100 s), the FWHM of the D^0X transition is 32% lower and the luminescence intensity of the near band edge is considerably higher compared to in the standard process. PEC etching confirmed that the improvement of the optical properties was accompanied by a reduction in the dislocation density.

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