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# Molecular beam epitaxial growth of high-quality GaN nanocolumns

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**Abstract**

Vertically oriented gallium nitride (GaN) nanocolumns (NCs) approximately 90 ± 10 nm wide and 0.75 μm tall were grown by plasma-assisted molecular beam epitaxy on $Al_2O_3$(0 0 0 1) and Si(1 1 1). The dense packing of the NCs gives them the appearance of a continuous film in surface view, but cross-sectional analysis shows them to be isolated nanostructures. Low-temperature photoluminescence measurements of NCs show excitonic emission with a dominant, narrow peak centered at 3.472 eV and FWHM of 1.26 meV. This peak is identified as the ground state of the A free exciton as confirmed by reflection measurements. Cross-sectional transmission electron microscopy identifies the NC microstructure as wurtzite GaN and that the NCs are largely free of defects. The GaN NCs are subsequentiy utilized as a defect-free vehicle for optical studies of Si-doped GaN; and the donor state was identified through low-temperature photoluminescence experiments.


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## 1. Introduction

Wide bandgap, wurtzite semiconductors such as gallium nitride (GaN), AlN, and their alloys are employed for high-power transistors, optoelectronic applications, and are attractive for use in caustic environments. Despite technological advances in group III-nitride device development, the effects of defects in these materials, mainly due to a lack of native GaN substrates, is an ongoing concern. Recently, however, many epitaxial nanostructures have been reported that are composed of relatively defect-free $Ga_xAl_{1-x}N$ crystals with nanometer widths, and lengths on the order microns [1–10]. While these nanocolumns (NCs) take on a variety of aerial densities and the results span a range of growth parameters and epitaxial techniques, a key condition is that NC formation requires epitaxial growth under nitrogen-rich conditions—resulting in reduced Ga surface diffusion.

This communication discusses the growth and characterization of tightly spaced, high-quality GaN NCs. The NCs were grown by self-assembly on both $Al_2O_3$(0 0 0 1) and Si(1 1 1) substrates by molecular beam epitaxy (MBE). Cross-sectional transmission electron microscopy (XTEM) and X-ray diffraction (XRD) studies revealed the nanostructures to be wurtzite single crystals with no visible dislocations or extended defects within the NCs. Low-temperature photoluminescence (PL) emission from these NCs was observed, with intense and spectrally narrow excitonic emission. These properties have been related to the morphology and the microstructure, measured by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively.

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## 2. Experimental procedure

GaN columnar structures were grown by MBE on both $Al_2O_3(0\,0\,0\,1)$ and Si(1 1 1). The sapphire substrates were prepared by etching in 1:1 $H_2SO_4$:$H_3PO_4$ at 200 °C for 20 min, followed by a rinse in deionized water. A 5000 Å thick layer of titanium was deposited on the backside of the sapphire substrates for thermal absorption. The Si(1 1 1) preparation consisted of a dip in 20% aqueous HF solution, followed by rinsing in deionized water, before blowing dry under a liquid nitrogen boil off. The substrates were heated to 725 °C under an active nitrogen flux provided by an EPI Unibulb plasma source operated at 330 W and 0.65 sccm nitrogen flow. Substrate temperatures were measured using an optical pyrometer. An AlN nucleation layer was grown prior to the initiation of the GaN NC growth at a rate of 0.4 Å $s^{-1}$. After the AlN buffer layer was deposited, the substrate temperature was raised to 810 °C, and the GaN NC layer was deposited at a growth rate of 0.7 Å $s^{-1}$.

PL spectroscopy was used to analyze the GaN NCs. Measurements were performed using a He–Cd laser, with the sample immersed in liquid helium. The spectra were analyzed using a SPEX 1.26 m high-resolution spectrometer equipped with an RCA C31034 photomultiplier tube for detection. XSEM measurements were performed using an FEI Strata DB 235 scanning electron microscope. The sample was scored using a diamond scribe, and cleaved for a cross-sectional measurement. Specimens for cross-sectional TEM studies were glued face to face and then cut perpendicular to the substrate orientation. These cross-section slices were then thinned by mechanical grinding, polishing, and dimpling followed by Ar-ion milling to electron transperancy using a Gatan Precision Ion Polishing System with a 5 kV beam at an angle of 6°. Electron diffraction patterns and bright field images were then obtained from these thinned foils using a Philips CM-200 field emission gun TEM operated at 200 kV.

## 3. Results and discussion

Columnar morphologies are found in many different heteroepitaxial material systems with highly mismatched lattice constants [11]. One of the first reports of columnar properties for GaN was given by Gaskill et al. [12] who used metal-organic vapor phase epitaxy with hydrazine as the nitrogen source. While this was achieved under apparently Ga-rich conditions, the increased substrate temperatures extended the Ga adatom diffusion length, and hence enhance the probability of a Ga adatom encountering a N adatom before being desorbed. This is similar to increasing the V/III flux ratio and, as a consequence, one can enhance GaN column formation [1]. The growth kinetics of GaN NC formation is controlled primarily by means of the V/III ratio and substrate temperature. The columnar GaN structures shown in Fig. 1 are synthesized under N-rich conditions.

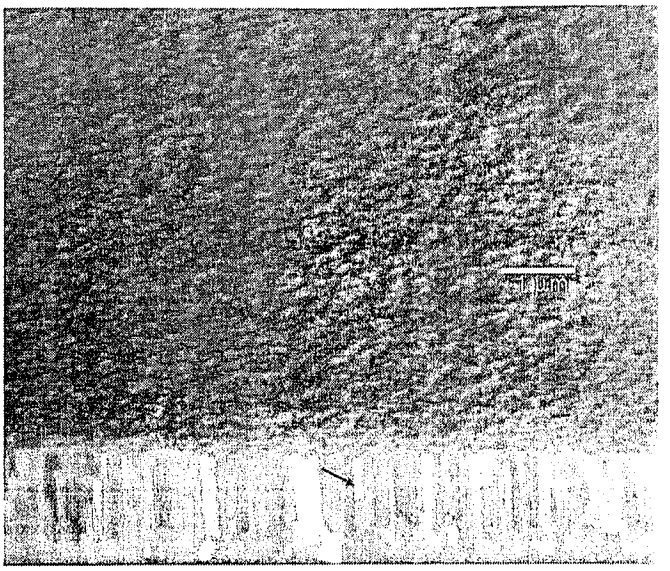

Fig. 1. SEM image of GaN NCs. The arrow identifies a NC which has cracked in the cleave process and exhibits charging on the upper portion of the column.

Similar behavior for nanocolumn formation was observed using either silicon or sapphire as the substrate. The GaN NCs, in this work, are oriented along the (0 0 0 1) direction, and have an average diameter of $90 \pm 10$ nm. We have found that limiting the Ga flux towards a GaN growth rate of 0.7 Å $s^{-1}$ allowed a significant substrate temperature range (±20 °C) over which a reproducible, dense growth of uniform GaN NCs could be produced.

The SEM micrograph in Fig. 1 is a GaN NC sample which shows densely packed columns extending along the growth direction. These NCs give the appearance of a nearly continuous film in surface view, but are clearly isolated when viewed in cross-section. The wafer cleaving process caused some columns to crack laterally, and electron charging above the break resulted in increased brightness of the top portion of the damaged column (see arrow in Fig. 1). This suggests that vertical conduction occurs along the NC, but that charge does not dissipate laterally to adjacent columns. Therefore, a significant level of electrical isolation between columns must exist which limits conduction in the lateral plane.

An XTEM image of the GaN NCs is shown in Fig. 2. The microstructure is found to be wurtzite, and is generally free from extended structural defects along the length of the column. Fig. 2 shows a column with strain fields (far left) extending from the surface along the [0 0 0 $\bar{1}$]. We suspect this is damage to the NC during the XTEM sample preparation process. The strain fields of the damaged NC are in contrast to the defect free columns present in the same image. Otherwise, the NCs are free from defects, and no evidence of threading dislocations are found within the columns.

XRD measurements on undoped GaN NCs were performed to quantify the degree of strain present within

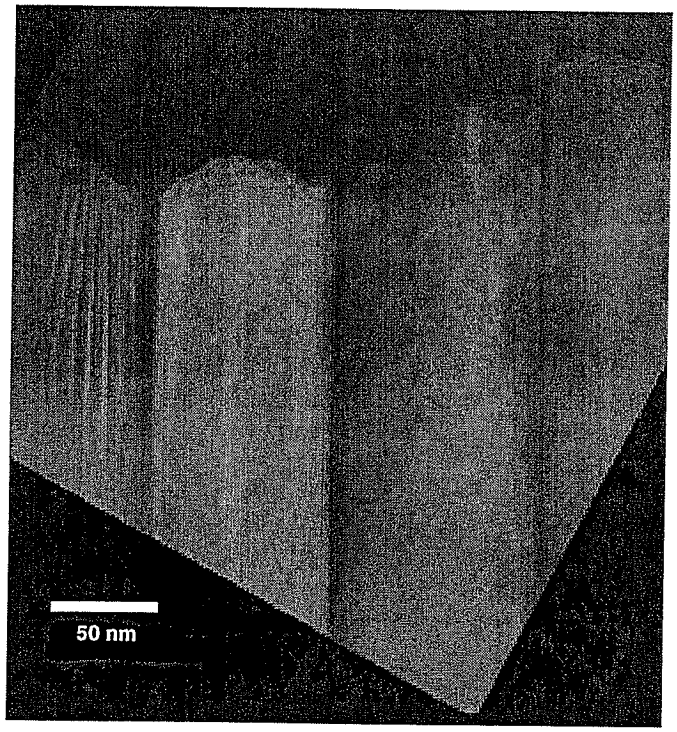


Fig. 2. XTEM images in (1 1 $\bar{2}$ 0) of GaN NCs. The far left shows strain fields from TEM preparation methods, while other NCs are defect free.

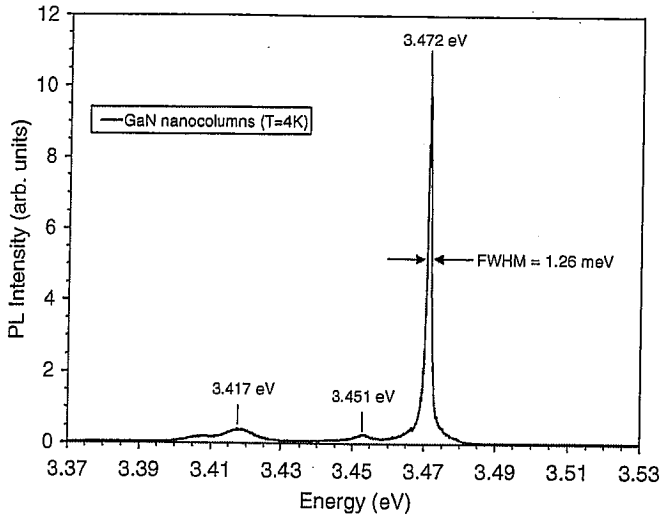


Fig. 3. PL spectrum of GaN NC material at $T = 4$ K. A Gaussian fit to the peak gives a FWHM = 1.26 meV centered at 3.472 eV. The secondary peaks at 3.451 and 3.417 eV are identified as a donor peak and nanocolumn/buffer layer interface peak, respectively.

the columns. Averaging over the (0 0 0 2), (0 0 0 4), and (0 0 0 6) symmetric planes gives an out of plane lattice constant value of $c = 5.1897 \pm 1.8 \times 10^{-4}$ Å. The in-plane lattice constant, obtained by averaging over the asymmetric planes (1 0 $\bar{1}$ 4), (1 0 $\bar{1}$ 5), and (2 $\bar{2}$ 0 4) gives a value of $a = 3.1835 \pm 2.5 \times 10^{-3}$ Å. In comparison to the lattice constants for bulk GaN [13], our value for the in-plane lattice constant is compressively strained at ~0.4%. The in-plane lattice constant for bulk GaN is ~2.7% larger than that of AlN. The AlN nucleation layer, which is fully relaxed during the growth, will cause the epitaxial GaN layer to experience a large compressive stress at the initiation of the GaN NC growth. This compressive stress may be a critical factor in the kinetics of NC formation. A second possible source of the residual strain in the NCs is from the difference in coefficients of thermal expansion between the epi-material and the substrate.

In general, epitaxial growth of III-nitride semiconducting material on highly mismatched substrates has resulted in emission with broad peaks from donor–acceptor pair transitions well within the bandgap [14]. Quasi-substrates of GaN by high growth rate techniques such as hydride vapor phase epitaxy have reduced the "yellow-band" emission [15], resulting in significant improvements in the film properties of GaN. However, it is costly and not amenable to device layer growth due to the rapid deposition rate required.

Fig. 3 represents a low-temperature PL emission spectra of GaN NCs. The dominant PL emission is centered at 3.472 eV, with a full-width at half-maximum (FWHM) of 1.26 meV. This is a remarkably narrow FWHM for a GaN epitaxial material, and is illustrative of what can be achieved using NCs in highly mismatched systems. There is also a small shoulder on the high-energy side of the A exciton at 3.479 eV that we attributed to the B exciton. A very weak, broad peak centered at 3.451 eV can also be observed in Fig. 3. Its origin is as of yet unidentified, but is thought to be related to the oxygen donor. Additionally, Fig. 3 shows a low-intensity doublet at 3.417 and 3.416 eV, respectively. Similar to the results of Calleja et al. [1], we believe this emission to be associated with defects near the nanocolumn/buffer layer interface. Finally, PL of GaN NCs show no "yellow-band" emission.

PL reflection spectroscopy was used to determine the nature of the exciton in the low-temperature PL measurement. Band-to-band absorption peaks can often be observed for the A, B, and sometimes C excitons. In comparing the locations of the excitonic emission with the corresponding absorption peaks (from reflection measurements), PL reflection data confirms that the exciton at the energy level of 3.472 eV is associated with the ground state ($n = 1$) of the A free exciton. The domination of the PL spectra by the A free exciton tells us that the NC material is generally free from defects, and that the walls of the NC represent an energy barrier which confine the exciton to a single nanocolumn.

The effect of silicon doping on the NC PL is shown in Fig. 4, which shows the low-temperature PL emission spectra of Si-doped GaN NCs. As shown in Fig. 4, high silicon doping levels result in a broadening of the PL emission peaks. The emission spectra can be fit to two Gaussian functions (not shown). The first peak, fit at 3.473 eV, is similar in origin to the undoped GaN NC, but at a slightly higher energy. We believe this energy shift is due to strain fields in the heavily doped NCs. The second

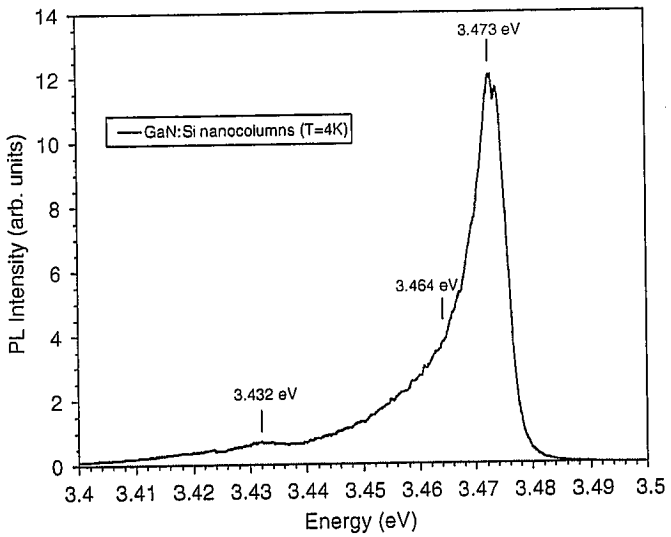


Fig. 4. PL of Si-doped GaN NC material at $T = 4$ K. A Gaussian fit gives a FWHM = 5.24 meV centered at 3.473 eV, with a silicon donor level 8.9 meV below the main peak. The peak at 3.432 eV is attributed to the nanocolumn/buffer layer interface.

peak at 3.464 eV is attributed to the Si donor state. The separation of 9 meV between the first and second peaks suggests the second peak is a neutral donor-bound exciton. A third peak centered at 3.432 eV is similar to that seen in Fig. 3 and was described earlier.

## 4. Conclusions

We have reported the growth details for synthesis of tightly spaced GaN NCs by molecular beam epitaxy on both sapphire and silicon. The NCs have a diameter of $90 \pm 10$ nm, and a length of the film thickness. Detailed analysis using XTEM and XRD on the GaN NC films identifies the microstructure as wurtzite GaN and reveals a surprisingly low defect density within the NCs. Low-temperature PL of the undoped NCs produces intense, narrow excitonic emission centered at 3.472 eV with a FWHM of 1.26 meV. This peak is determined to be the ground state energy of the A free exciton by photoluminesence reflection spectroscopy. The GaN NCs are electrically isolated from one another, as seen in XSEM. In addition, the GaN NCs have been used to study the Si donor state. Doped NCs show a PL signature consistent with a donor-bound exciton in addition to the strong A exciton emission, with a donor level 9 meV below the A free exciton peak.

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