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The Controlled Growth of GaN Nanowires

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ABSTRACT

This paper reports a scalable process for the growth of high-quality GaN nanowires and uniform nanowire arrays in which the position and diameter of each nanowire is precisely controlled. The approach is based on conventional metalorganic chemical vapor deposition using regular precursors and requires no additional metal catalyst. The location, orientation, and diameter of each GaN nanowire are controlled using a thin, selective growth mask that is patterned by interferometric lithography. It was found that use of a pulsed MOCVD process allowed the nanowire diameter to remain constant after the nanowires had emerged from the selective growth mask. Vertical GaN nanowire growth rates in excess of 2 μm/h were measured, while remarkably the diameter of each nanowire remained constant over the entire (micrometer) length of the nanowires. The paper reports transmission electron microscopy and photoluminescence data.

Nanowires composed of GaN and related group III−N alloys have a huge potential for revolutionary, semiconductor-device configurations. If this potential is to be fully realized, a scalable process is required that as well as forming high-quality GaN nanowires also allows precise control of the geometry and position of each nanowire.

GaN nanowire preparation is typically based on the vapor−liquid−solid (VLS) growth mechanism and involves the use of catalysts such as Au, Ni, Fe, or In.[1−3] The catalyst creates a highly selective growth environment with growth occurring only at the catalyst location. These approaches include the reaction of Ga/Ga_2O_3 mixtures with NH_3 in anodized alumina templates,[4] direct reaction of Ga with NH_3 in a tube furnace,[5] and the reaction of Ga-containing precursors and NH_3 on catalyst-coated substrates.[6] Processes in which the catalyst is self-assembled (i.e., where the catalytic nanoscale particles are randomly located) produce nanowires that are randomly positioned and also exhibit a significant range of diameters. A further problem with catalytic processes is that the metal catalyst will inevitably incorporate into the nanowire, which may be prohibitive for many semiconductor applications. GaN and InGaN nanowire structures have been fabricated without additional catalysts using hydride vapor phase epitaxy (HVPE),[7−9] molecular beam epitaxy (MBE),[10] and metalorganic chemical vapor deposition (MOCVD).[11] In the latter,[11] it was demonstrated that nanowires could be positioned and shaped using a silicon dioxide growth mask. The nanowires were grown to a length of approximately 80 nm, which was approximately equal to the mask thickness. While these approaches represent important milestones, they are limited in either their scalability or their ability to fabricate uniform arrays of GaN-based nanowires with well-defined locations and diameters.

This paper reports a scalable process for the growth of high-quality GaN nanowires and uniform nanowire arrays in which the position and diameter of each nanowire is precisely controlled. The approach is based on conventional metalorganic chemical vapor deposition (MOCVD) using trimethygallium (TMGa) and ammonia (NH_3) and requires no additional metal catalyst. The location, orientation, and diameter of each GaN nanowire are controlled using a thin, selective-growth mask that is patterned by interferometric lithography.[12] An important and novel feature of this process is that the nanowire diameter remains constant after the nanowires have emerged from the selective growth mask. Thus nanowires of arbitrary length can be fabricated even though the growth mask is only 30 nm thick.

A 30 nm silicon nitride growth-mask layer was deposited by low-pressure chemical vapor deposition (LPCVD) onto 600 nm GaN films that had been previously grown by MOCVD on sapphire, silicon carbide, and silicon (111) substrates. The LPCVD silicon nitride film was patterned by interferometric lithography and dry etching, to form a hexagonal array of apertures on a 500 nm pitch. The apertures were approximately circular and had an average diameter of 221 ± 7 nm. This patterned silicon nitride film then served as an MOCVD growth mask which defined the position each GaN nanowire.

GaN growth was begun at 1050 °C, at a pressure of 100 Torr and in a hydrogen/nitrogen carrier gas mixture in a model P75 (Veeco TurboDisk) MOCVD reactor. During the

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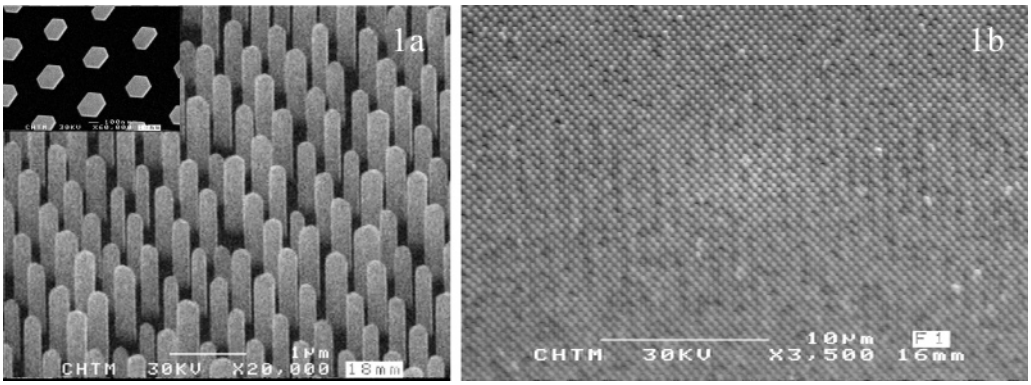

Figure 1. (a) Scanning electron micrograph of a GaN nanowire array consisting of 1 μm GaN nanowires (inset shows plan view and reveals the hexagonal symmetry of the nanowires). (b) A lower magnification SEM image reveals the long-range order of the GaN nanowire arrays.

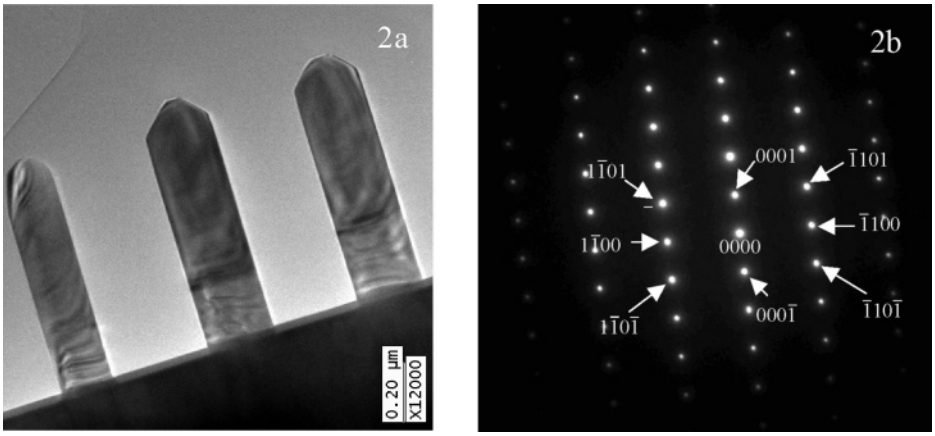

Figure 2. (a) XTEM image showing the vertical sidewall and top crystallographic facets of the nanowires. (b) Electron diffraction pattern confirming the single-crystal nature of the GaN nanowires.

first growth phase the precursors were introduced simultaneously and the group V/group III ratio was maintained at 1500. This condition provided growth selectivity and allowed excellent "filling" of all available growth apertures. If these growth conditions were maintained, then as soon as the nanowires emerged from the growth mask lateral growth occurred and the nanowire geometry was lost. If however, the growth conditions were changed to a pulsed MOCVD growth mode (defined below) before the nanowires emerged from the growth mask, then the GaN nanowires maintained their geometry **after they had emerged from the growth mask**. Vertical GaN nanowire growth rates in excess of 2 μm/h were measured, while remarkably the diameter of each nanowire remained constant, apparently to within a few monatomic layers, over the entire (micrometer) length of the nanowires. During the pulsed growth mode the group III and group V precursors were introduced alternately in the sequence: TMGa, 10 sccm, 20 s; NH_3, 500 sccm, 30 s. The timing of the changeover from regular MOCVD growth to pulsed MOCVD growth was found to be critical and was effected after 10 nm of GaN had been deposited. The duration of the steps within the pulse sequence was also found to be critical, and the optimum timing given above will undoubtedly need reoptimizing for different reactor geometries. During pulsed MOCVD growth the temperature and reactor pressure were maintained at the same values as for the initial growth step.

Figure 1a shows a scanning electron micrograph of part of a GaN nanowire array. A plan view of the nanowires (inset) shows the hexagonal symmetry of the sidewall facets. The diameter of the nanowires (measured in the $\langle 11\bar{2}0\rangle$ directions) was 227 $\pm$ 13 nm. This agrees well with the average diameter (221 $\pm$ 7 nm) previously measured for the apertures in the growth mask and indicates that the diameter of the nanowires was controlled by the diameter of the growth mask aperture. The small variation of nanowire diameter that is observable in Figure 1a reflects the actual variation in patterned aperture size in the growth mask. Massive GaN nanowire arrays with excellent long-range order have been fabricated using this approach (Figure 1b).

Cross-sectional, transmission electron microscopy (XTEM) (Figure 2a) reveals that the nanowires were orientated along the [0001] direction, and each nanowire was bounded by six, vertical sidewall facets, which are of the $\{1\bar{1}00\}$ family. At the top of each nanowire there is a small, central (0001) facet that is bounded by inclined $\{1\bar{1}02\}$ facets. The single-crystal nature of these GaN nanowires was confirmed by electron diffraction analysis, and an example of this analysis, with the beam orientation along the $[11\bar{2}0]$ zone axis, is shown in Figure 2b. The assignment of Miller indices to the

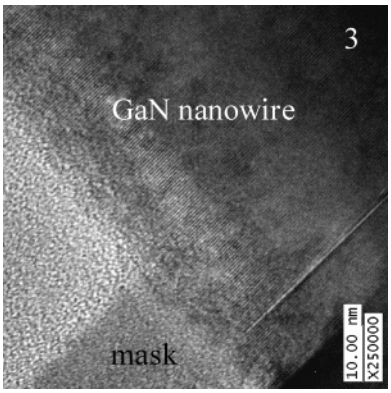

Figure 3. XTEM image showing one side of a single GaN nanowire as it emerges (bottom-right to upper-left) from the growth mask. The growth mask is at the lower left of the image.

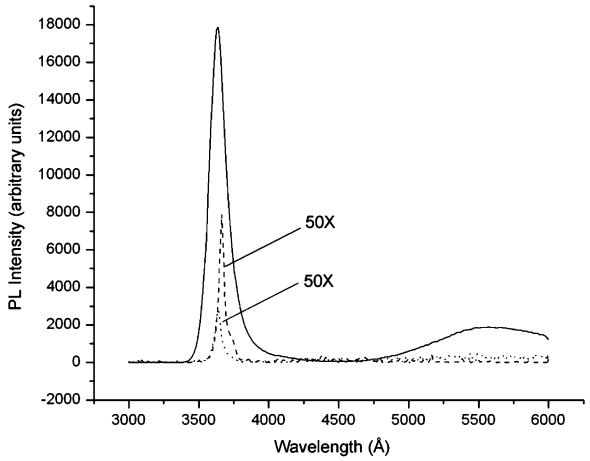

Figure 4. Room-temperature photoluminescence spectra of GaN nanowire array (solid line), 5 μm planar GaN film (dashed line), and 0.6 μm planar GaN film (dotted line). Spectral intensity for the planar GaN films has been magnified by 50×.

nanowire facets is unambiguous and is deduced using the following rationale. During IL patterning the rows of apertures in the silicon nitride growth mask are intentionally oriented along the GaN $\langle 1\bar{1}00 \rangle$ directions, which are known from the facets on the original substrate wafers. Here it must be remembered that for GaN growth on sapphire substrates there is a 30° rotation about the *c* axis between the GaN and sapphire unit cells.[13] The plan view of the nanowires (inset in Figure 1a) shows that the nanowire sidewall facets are perpendicular to the direction of the pattern rows meaning that the sidewall facets are of the $\{1\bar{1}00\}$ family. From the continuity of faceting, it is clear that the inclined facets observed at the nanowire tips must also be of the $\{1\bar{1}0n\}$ family, where *n* is an integer. To determine the value of *n*, we measured the angle between opposing inclined facets on TEM images of the nanowires, such as shown in Figure 2a. This angle was within the range 92° ± 2° indicating that the inclined facets are of the $\{1\bar{1}02\}$ family, where the angle of intersection between opposite facets is 93.62°. This facet assignment also agrees with previous work where it was ascertained[14] that the inclined facets bounding GaN pyramidal features were also of the $\{1\bar{1}0n\}$ family.

The XTEM images show no threading dislocations (TDs) in the GaN nanowires, even though TDs were observed in the planar GaN film beneath the growth mask. This was found to be the case for GaN nanowire growth on all substrates, including growth on silicon (111). The high-resolution XTEM image (Figure 3) shows one side of a GaN nanowire emerging (lower-right to upper-left) from an aperture in the Si_3N_4 growth mask (lower left). The diameter of the nanowire remains constant as it emerges from the growth mask confirming our assertion that the nanowire diameter is indeed controlled by the diameter of the growth mask aperture.

A typical room-temperature photoluminescence (PL) spectrum of the GaN nanowire samples is shown in Figure 4 and compared to the PL spectrum for 5 and 0.6 μm planar GaN films. The PL pump laser was a frequency-doubled, Ar^+ laser that produced a continuous wave power of 30 mW at a wavelength of 244 nm. The room temperature PL spectrum of the nanowire array is dominated by band-edge emission at 363.5 nm, although we consistently observe an increased relative intensity of yellow emission in the nanowire samples compared to that observed in planar GaN films. The band-edge PL peak intensity for the nanowire sample was 100× greater than that measured for a 5 μm planar GaN film and more than 200× greater than that measured for a 0.6 μm planar GaN film. Much of this intensity increase is undoubtedly due to the geometry of a nonplanar nanowire sample, where the input coupling of the PL pump beam and the out-coupling of the resulting PL will both be increased significantly.

During pulsed-MOCVD the ratio of vertical to lateral growth rate (i.e., the ratio of growth rate on the top (0001) and $\{1\bar{1}02\}$ facets, to growth rate on the sidewall $\{1\bar{1}00\}$ facets) was in excess of 1000. This occurred despite the larger area of the $\{1\bar{1}00\}$ facets. While it has been shown previously that the MOCVD growth rate is orientation dependent,[15] the extreme orientation dependence observed here indicates that this pulsed-MOCVD regime has created a close-to-equilibrium growth process. While more work is required to understand this growth process, we speculate that the low effective group V/group III ratio that occurs during pulsed growth may be preferentially destabilizing the less-stable facets at the tip of each nanowire. It is possible then that a VLS type of growth may be occurring, and if this is the case, we suggest that liquid gallium would serve the role of the catalyst.

In conclusion, we report a scalable process for the fabrication of high-quality, GaN nanowires and nanowire arrays. The process uses selective MOCVD growth through an IL-patterned growth mask and allows the position and diameter of each nanowire to be precisely controlled. Pulsed MOCVD growth was found to provide a remarkable growth selectivity (in excess of 1000) that allowed the nanowire diameter to be maintained after it had emerged from the growth mask. The results shown above were for GaN nanowires grown on SiC substrates, but similar results have also been obtained for GaN nanowire growth on sapphire and silicon (111) substrates. Preliminary experiments, which will be reported later, indicate that AlGaN/GaN and InGaN/GaN heterostructures, and n- and p-type doping can also be incorporated into these nanowires. The minimum nanowire diameter and array pitch achievable by this approach are

limited by ability of IL to pattern at nanoscale. Using short wavelength lasers and immersion lithography,[12] it is expected that GaN nanowire arrays with diameters in the 10−100 nm range, with a pitch in the 100−200 nm range, will soon be fabricated.

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