Fabrication of GaN nanowire arrays by confined epitaxy

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The authors report the fabrication of GaN nanowire arrays inside a thick SiN_x, selective growth mask that was patterned by interferometric lithography and dry etching. The GaN nanowires are molded by the apertures in the selective growth mask and the growth is epitaxial with respect to the underlying GaN layer. The precise location and diameter of each nanowire in the array are controlled by the growth mask patterning, and the resulting array has a long-range order that is compatible with photonic crystal applications. This process uses conventional metal organic precursors and does not require any additional metal catalysts. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2402893]

Ordered arrays of GaN nanowires can be used as photonic crystals[1] that have broad application in manipulating light. Recently Deb *et al.*[2] reported the catalyst-free, metal organic chemical vapor deposition (MOCVD) growth of vertically aligned GaN nanowires by forming them within a SiO_2 selective growth mask that was patterned using an anodic-aluminum-oxide (AAO) template. The SiO_2 mask thickness was approximately 80 nm and nanowires were grown to a length equal to the mask thickness. The nanowire size and position were not uniform because of the lack of long-range order in the initial AAO template and because of incomplete filling of the available mask apertures. A previous example of ordered GaN nanowires was demonstrated on *c*-plane sapphire substrates via metal-catalyzed chemical vapor deposition.[3]

This letter reports the selective growth of uniform arrays of GaN nanowires inside a silicon nitride selective-growth-mask that was patterned using interferometric lithography[4] (IL) and dry etching. Arrays of GaN nanowires with uniform size and long-range positional order were grown by MOCVD using conventional precursors (trimethylgallium and ammonia) with no additional catalyst. Under regular MOCVD growth conditions once the nanowire emerged from the growth mask, lateral growth occurred and the nanowire geometry was lost.[5–7] Longer nanowires could be fabricated using a thicker growth mask; however, due to the limitations of reactive ion etching the minimum achievable diameter also increased with the growth mask thickness. Using this approach we estimate that it is possible to fabricate GaN nanowires of length equal to the growth mask thickness and with a minimum diameter that is approximately 30% of the growth mask thickness. These limitations can be eliminated, however, using a pulsed MOCVD approach that is described elsewhere.[8]

The sample structure [Fig. 1(a)] consisted of an 850 nm thick SiN_x growth-mask layer that was deposited by plasma-enhanced chemical vapor deposition on a 600 nm thick, planar MOCVD GaN film that had been grown on a 6*H*-SiC substrate. The thickness of the SiN_x film was measured using spectrometer. For lithography, an antireflection coating (ARC) layer (Brewer Science, XHRiC-16) and a 500 nm layer of positive photoresist (Shipley, 505A photoresist) were employed. The resist was patterned using IL to form a hexagonal array of circular apertures, where the rows of apertures were oriented in the $\langle 1\bar{1}00\rangle$ directions. After the photoresist had been patterned a 150 nm thick Ni layer was e-beam deposited, and the photoresist was removed using a spray, lift-off process. The pattern was transferred from the Ni film into the ARC and silicon nitride layers using reactive ion etching (RIE). The RIE conditions for the ARC layer were an O_2 flow of 10 SCCM (SCCM denotes cubic centimeter per minute at STP) and a chamber pressure of 15 mTorr. For RIE of the underlying SiN_x an O_2 flow of 2 SCCM, a CHF_3 flow of 45 SCCM, and a chamber pressure of 50 mTorr were used. Following patterning and just prior to growth, the samples were cleaned in piranha solution ($4H_2SO_4:1H_2O$) for 3 min followed by a rinse in de-ionized water for 5 min. This process produced a hexagonal array of approximately circular apertures with a diameter of 300 nm, on a 500 nm pitch in the SiN_x layer. Figure 1(b) shows an angle view, scanning electron micrograph (SEM) of the patterned SiN_x sample.

GaN was grown in a high-speed, rotating-disk MOCVD reactor (Veeco Turbodisk, model P75) at a temperature of 1060 °C and at a reactor pressure of 100 Torr. To ensure nucleation of GaN growth in all of the available growth mask apertures, a high V/III ratio of 1500 was used for the first 5 min of growth. The V/III ratio was then reduced to 500 for the remainder of the nanowire growth. The vertical growth rate of the GaN nanowires was approximately 2 μm/h. A four quantum-well (QW) GaN/InGaN heterostructure was included in some nanowires, and in this case the 15 nm GaN barrier layers were grown at 900 °C and the 10 nm InGaN quantum wells were grown at 820 °C.

Growth duration for the nanowires was adjusted to allow the nanowire length to grow to the full thickness of the growth mask. In some longer growths, the nanowires were allowed to extend to beyond the growth mask to investigate coalescence above the mask. For detailed examination of the GaN nanowires after growth the SiN_x growth mask was completely removed in some samples by etching in HF.

Figures 1(c) and 1(d) show GaN nanowire array after removal of the silicon nitride growth mask. Under optimized

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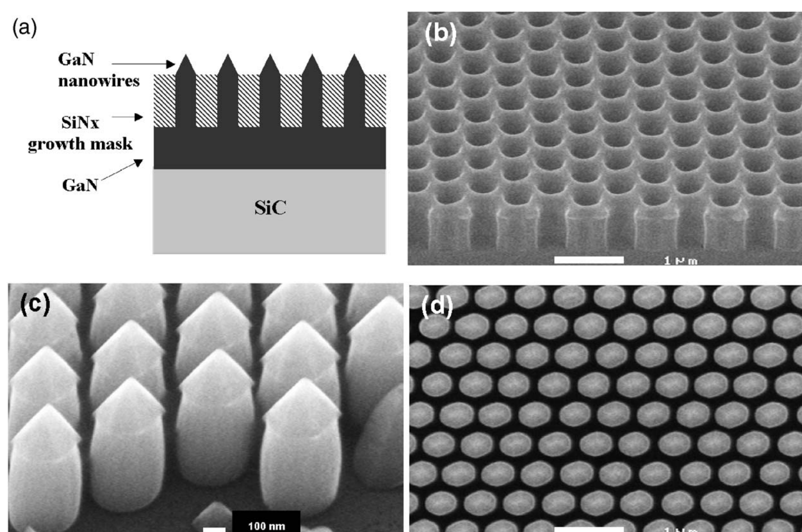
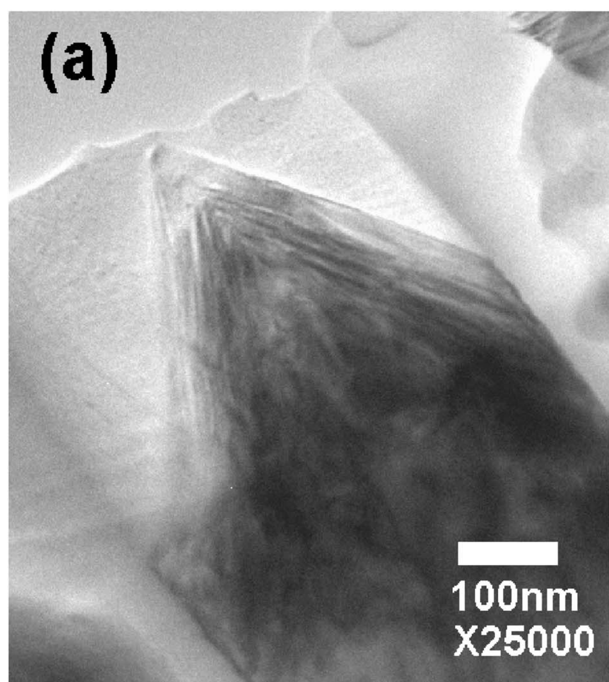
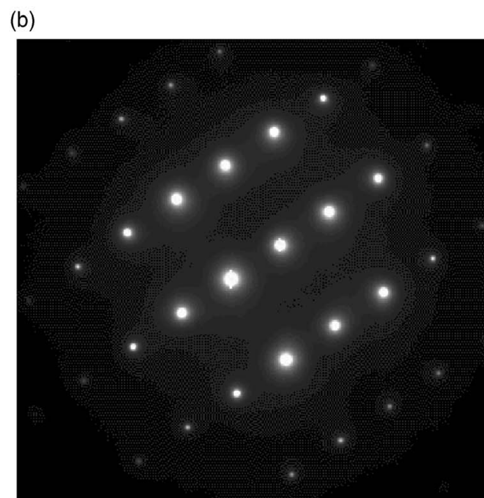


FIG. 1. (a) Selective epitaxial growth of GaN nanowires inside SiN_x growth mask, (b) SEM micrograph of the patterned SiN_x growth mask, (c) SEM 45° angle view of GaN nanowire array after etch removal of growth mask, and (d) SEM plan view at lower magnification shows uniformity of nanowire array.





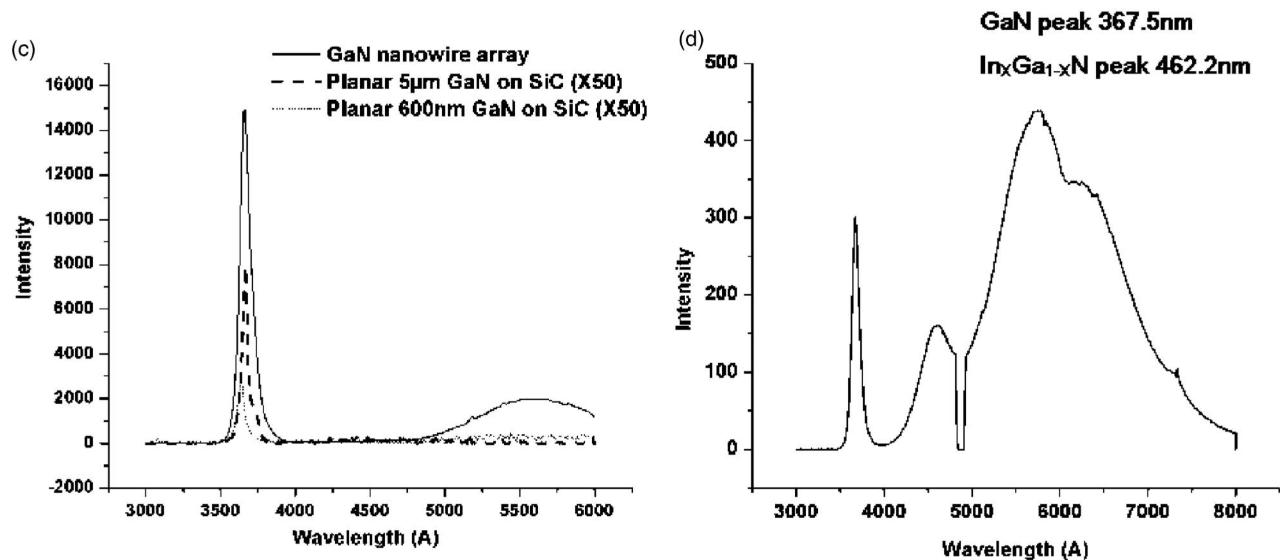


FIG. 2. (a) XTEM of nanowire within SiN_x growth mask showing evidence of multiple QW structure on inclined facets, (b) electron diffraction pattern from GaN region of one nanowire, and (c) comparison of PL spectra for a typical GaN nanowire array and planar GaN films. The spectral intensity for the planar GaN films has been magnified 50× to allow comparison, (d) room-temperature PL spectrum of nanowire array containing $GaN/In_xGa_{1-x}N$ heterostructures.

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growth conditions, ⩾80% of the available growth apertures were filled and a uniform array of GaN nanowires was grown. The tip of each nanowire exhibited six pyramidal $\{1\bar{1}01\}$ facets, and this facet, structure was apparent on the nanowire tip while the tip was inside the growth mask. Interestingly, the nanowire sidewalls were smoothly curved and unfaceted, which we attribute to MOCVD growth within the confined volume formed by the aperture in the thick growth mask. It was previously shown[9] that growth inside a confined volume can create close-to-equilibrium MOCVD growth conditions, and under such conditions nonplanar III-V crystalline surfaces can exhibit smooth curvature rather than faceting.

Figure 2(a) is a bright-field, cross-sectional transmission electron microscopy (XTEM) image of one GaN nanowire. This nanowire is composed mainly of GaN; however, the last ~100 nm of growth on the inclined nanowire facets, contains a four-quantum well, $GaN/In_xGa_{1-x}N$ heterostructure that was discussed above. Some of the $GaN/In_xGa_{1-x}N$ heterostructure features can be identified, however, there appears to be significant variation in quantum-well and barrier layer thickness across the nanowire facets. In spite of this variation these images confirm that the inclined hexagonal $\{1\bar{1}00\}$ facets were present while the nanowire was confined within the growth mask. An electron diffraction pattern taken from a pure GaN region with the zone axis in the $\langle 11\bar{2}0\rangle$ direction [Fig. 2(b)] indicates that the nanowires are single crystal GaN.

A typical room-temperature photoluminescence (PL) spectrum for a pure GaN nanowire array is shown in Fig. 2(c). Also included are PL spectra for a 600 nm planar GaN film and a 5 μm planar GaN film. (The spectral intensity for the planar GaN films has been magnified 50× to allow comparison.) All PL spectra were obtained using a frequency-doubled, Ar^+ pump laser emitting at a wavelength of 244 nm and with a continuous-wave power of 10 mW. Each PL spectrum shows a band-edge peak and a broad "yellow" peak at approximately 560 nm. The PL intensity of the band-edge peak for the nanowire sample was 94× greater than for the planar of 5 μm GaN sample and 267× greater than for the planar of 600 nm GaN sample. The band-edge peak wavelengths for the nanowire and 5 μm planar GaN film were 366.8 nm, while the band-edge peak wavelength for the 600 nm planar GaN film was 363.8 nm. This difference of band-edge wavelength indicates an increased biaxial stress (approximately 1 GPa higher) in the nanowire and 5 μm planar GaN film compared to that in the 600 nm planar GaN film.[10]

Figure 2(d) shows the PL spectrum for a GaN nanowire array containing the four QW $GaN/In_xGa_{1-x}N$ heterostructure. The highest energy peak for the $GaN/In_xGa_{1-x}N$ quantum wells is centered at 462 nm indicating an InN molar fraction (x) within the well of approximately 18%. As expected from the XTEM observation of quantum well and barrier width variation across the nanowire, the $In_xGa_{1-x}N$ peak is significantly broader than the peak for GaN. Interestingly, PL characterization of the $GaN/In_xGa_{1-x}N$ heterostructures grown on planar GaN samples during the nanowire growth, indicated a lower InN molar fraction of approximately 14.5%.

In conclusion, this letter reports the "molding" or confined MOCVD growth of GaN-based nanowires inside apertures that were patterned within a thick SiN_x growth mask. Uniform arrays of epitaxial GaN nanowires were grown and the uniformity appears to be compatible with photonic crystal applications. The preliminary growth of $GaN/In_xGa_{1-x}N$ multi-quantum-well heterostructures was described, and it appears that the uptake of In on the inclined $\{1\bar{1}01\}$ facets that define the nanowire tip may be higher than on planar (0001) surfaces.

In this approach the maximum length of the nanowire is fixed by the thickness of the growth mask, thus if very long nanowires are required a very thick growth mask must be used. Unfortunately the RIE etching of vertical-walled apertures inside a thick silicon nitride layer is not trivial and this will practically limit either the maximum length or minimum diameter of nanowires that can be achieved by this approach. We estimate that if the RIE etching is carefully controlled it will be possible to achieve a minimum nanowire diameter that is approximately 30% of the mask thickness. In a recent report,[8] we demonstrate that by using a modified MOCVD growth regime this limitation can be avoided and nanowires of arbitrary length can be grown with a constant diameter using a thin (35 nm) growth mask.

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