Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Highly ordered GaN-based nanowire arrays grown on patterned (100) silicon and their optical properties

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Supplementary Methods

Fabrication of patterned Si (100): This procedure started from depositing a 100-nm-thick SiO_2 film on Si (100) substrates by plasma-enhanced chemical vapor deposition. The SiO_2 periodic stripes (2 μm spacing/2 μm width) along the $<11\bar{2}0>$ direction of GaN were formed by photolithography and wet chemical etching. The substrates then underwent anisotropic etching in a KOH solution (30 wt %) at 40 ℃ solution to fabricate 400-nm-deep trapezoidal grooves with two opposed Si (111) facets separated by a bottom Si (100) facet. After that, the periodical lateral ditches with spacing of 3000 μm, width of 10 μm and depth of 30 μm, perpendicular to the $<\bar{1}10>$ direction of Si, was fabricated by inductive coupled plasma-reactive ion etching. The trapezoidal grooves along the $<11\bar{2}0>$ direction are perpendicular to the lateral ditches and severed periodically by them. Prior to growth, the substrates were immersed in HF (7 %) to yield an oxide-free hydrogen-passivated Si surface. Thereafter, the substrates were cleaned with deionized water and loaded into a metal-organic chemical vapor deposition reactor for epitaxial growth.

Nanowires synthesis: MqwNW nanowire structures were synthesized on a patterned Si (100) substrate in a metal–organic chemical vapor deposition reactor (Thomas Swan Scientific Equipment Ltd) using trimethylgallium (TMG), trimethylAluminium (TMAl), trimethylindium (TMIn) and ammonia (NH_3) as Ga, Al, In and N sources, respectively. GaN cores were selectively grown on the two opposite Si (111) facets in hydrogen at 1050 ℃ and 400 mbar for 800 s using TMG (50 standard-state cubic centimeter per minute (sccm)) and NH_3 (5000 sccm). Under this condition, the diameters of most GaN cores were of 700–800 nm. Subsequently, the growth conditions were altered to favor homogeneous MQW shell deposition onto the nanowire surface. MQW shell growth was carried out in constant NH_3 flow (5000 sccm) in nitrogen at 400 mbar. An InGaN quantum well was deposited at 700–800℃ for 110s using TMG (1 sccm) and trimethylindium (150 sccm). A GaN quantum barrier was grown at 830 ℃ for 180 s using TMG (5 sccm). A purge time of 60 s was applied between layer depositions. This quantum well/quantum barrier growth unit was alternated for 10 cycles to achieve 10 MQW nanowire structures. On the other hand, for DsNW nanowire heterostructure, we grew six-period MQWs, then a p-type AlGaN electronics barrier layer was grown on MQWs for 80 s using TMAl (80 sccm)， followed by Mg doped p-GaN deposited at 920 ℃ for 500 s using TMG (10 sccm) and Cp_2Mg (360 sccm).

Lifting off the as grown nanowires: The nanowires/patterned silicon substrate was immersed in BOE solution to eliminate SiO_2 mask layer. Afterward, it was ultrasonicated in ethanol for 30 min after etching in KOH (30 wt %) at 40 ℃ solution for 20 min to separate the nanowires from the patterned silicon substrate. The residue was then separated by centrifuging the solution at 1000 rpm for 30 s and decanting, thereby eliminating most of the Si particles from the solution. For the structure and optical analysis, nanowires were transferred by dropping a small droplet of nanowire suspension on an oxidized Si (600 nm thermal SiO_2) substrate allowed to dry.

Figures S1-S4 and related discussion

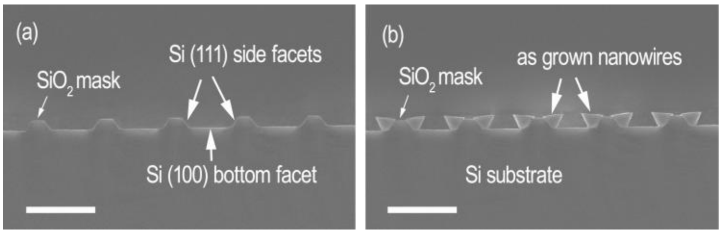

Figure S1. (a) Cross-sectional SEM images of the patterned Si substrate; Scale bar is 4 μm; (b) Cross-sectional SEM images of the as grown nanowire on the patterned silicon; scale bar is 4 μm.

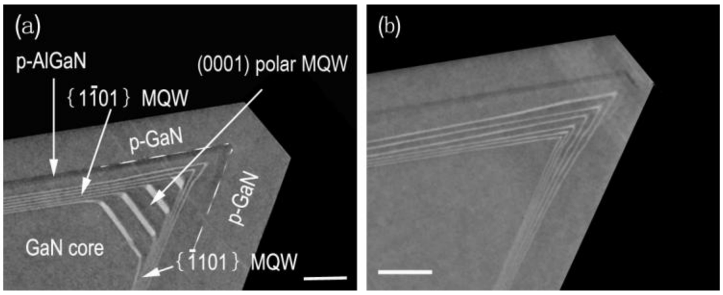

Figure S2. (a) The dark-field STEM image of DsNW sample with (0001) polar MQW, which recorded the corner between the $\{1\bar{1}01\}$ semipolar facet and $\{\bar{1}101\}$ semipolar facet. The dashed line outlines the interface between p-GaN and p-AlGaN. Scale bar is 50 nm. (b) Dark-field cross-sectional STEM images of DsNW without polar MQWs recorded the corner between $\{1\bar{1}01\}$ facet and $\{\bar{1}101\}$ facet; scale bar is 50 nm.

The TEM results (see the main text) confirm that we can prepare low-dislocation MQW nanowire heterostructures with InGaN quantum-well thicknesses similar to or smaller than the Bohr radius, ~3 nm, for InGaN. And it has been reported that nanostructures will show enhanced excitonic effects (leading to lower lasing threshold) if the size of the structure approaches the exciton Bohr radius[1]. The dark-field STEM image of DsNW sample with (0001) polar MQWs is exhibited in Fig. S2a. Considering the growth of polar (0001) crystallographic plane can be adjusted by varying the depth of the trapezoidal groove or the duration of the n-GaN core growth, we have prepared another type of DsNW sample in which the polar (0001) plane was eliminated. The dark-field STEM image of this kind of DsNW sample that recorded the corner between the two semipolar facets is also exhibited in Fig. S2b. No (0001) polar facets can be seen in this region because the growth time of the GaN core is long enough to make the two semipolar planes intersected. The difference in the component of facet types result in different photoluminescence properties. Figure S3 shows the room-temperature Micro-PL spectrum recorded the DsNW sample with

(0001) polar plane. It implies that we have great flexibility in controlling the optical properties of our nanowires heterostructures, which may be used for the generation of white-light sources without luminescence converters.

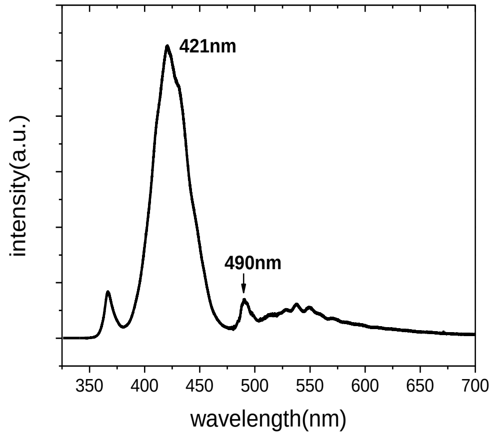

Figure S3. Room-temperature Micro-PL spectra recorded the DsNW sample with (0001) polar plane.

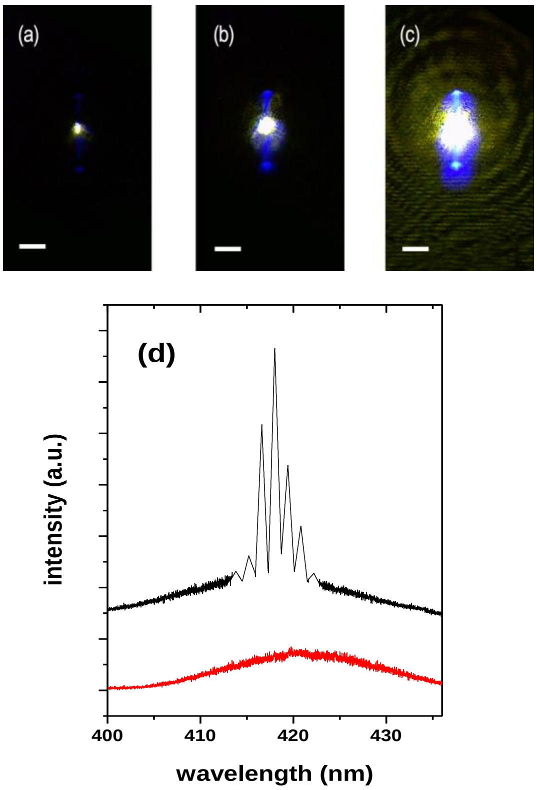

Figure S4. Power-dependent optically pumped studies of DsNW nanowire cavity properties. Images of a single 20 μm long DsNW sample excited with: (a) 160 kW cm^{-2}, (b) 1000 kW cm^{-2}, and (c) 1600 kW cm^{-2}. Scale bars are 3 μm. (d) PL spectra recorded at the end of 20 μm long DsNW nanowire sample for 300 kW cm^{-2} and 1500 kWcm^{-2} power densities.

The optically pumped properties of DsNW samples were investigated. Figure S4a-c exhibit that lasing action was observed during the evolution of the emission spectra with increasing pump power. In Figure S4d, the mode spacing was calculated to be about 1.3 nm, which also agrees with our experimental result. Measurements made on a number of DsNW samples showed that the threshold power densities for the DsNW lasers are all above 900 kW cm^{-2}. These DsNW lasers have lasing thresholds higher than the MqwNW counterpart because of the decreased number of quantum wells in DsNW sample, which is in good agreement with the previous report[2]. In addition, the absorption of laser by the p-GaN shell in DsNW structure may be another factor leading to higher laser threshold.

REFERENCES:

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