Supplementary information

Long-range ordered and Si-integrated vertical III-nitride nano-cylinder arrays via plasma-assisted atomic layer deposition

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Experimental

AAO foils preparation
The free standing AAO molds were fabricated by using voltage reduction method. Firstly nanoporous AAO molds were synthesized on both sides of the high purity Al foil by a two-step anodization method. Briefly, Al foil (99.998%, Alfa Aesar, Germany) was polished with sand paper and cleaned by using a standard electrochemical process. During this process, Al foil was electropolished in a chemical mixture of 95 wt% H3PO4 (Sigma, USA), 5 wt% H2SO4 (Sigma, USA) and 20 g/l of CrO3 (Prolabo, Belgium) at 15 V. The first anodization step was then carried out at 50 V at 7 ºC in 0.3 M oxalic acid solution for 18 h. A thick and non-uniform AAO layer was removed from Al foil by using 0.2 M chromic acid (Prolabo, Belgium) solution at 75 ºC and second anodization step was completed under the same conditions for 20 min. At the end of these steps, anodization voltage was gradually reduced to 14 V by a 5% voltage reduction every 2 min. To obtained free standing AAO mold, this material was immersed in v/v %10 H3PO4 solution until bubble layer was formed on AAO molds. The thin molds (5 cm2) were then collected from Al foil using a thin parafilm backing paper.
Results and Discussion:

Figure S1. SEM image of (a) top side of AAO membrane with partially blocked pores, (b) bottom side of AAO membrane with dominantly open nanopores, (c) cross-section of AAO membrane after substrate attachment showing the total height of AAO membrane and the rough top portion, (d) porous Si surface with AAO membrane on top, (e) nanoporous Si revealing pore-widening effect and uniformly aligned hexagonal pores, and (f) angled-view image of nanoporous Si indicating the depth of etched pores.

Prior to the attachment of AAO hard-mask to the Si substrate, SEM inspection of a free standing AAO membrane revealed that two sides of the membrane have different morphology; one with symmetrical open pores, other with partially open asymmetrical pores with higher surface roughness. Top-view SEM image of the open pores side is shown in Fig. S1b which clearly indicates the high density arrays of uniform and aligned nanopores in a honeycomb-like geometry. Average pore diameter of the as-grown AAO membrane was about 70-80 nm while the average interpore distance was measured as ~130-135 nm. Angled-view SEM image of the AAO membrane (Fig. S1c) depicted the height of AAO membrane to be ~2.85 μm, out of which top ~350 nm portion consists of rough and partially blocked pores. Rest of the membrane is composed of relatively uniform pore diameter which extends throughout the entire AAO membrane thickness. AAO membrane is attached to Si with the side having open pores facing Si. In this strategy, RIE etch gases will initially etch the exposed semi-blocked pores of the membrane and hence the rest of etching will proceed smoothly through the open pores. A thickness decrease in the AAO membrane (Fig. S1d) is observed from ~2.85 μm to ~1.67 μm after 70 minutes of RIE process, which implies that AAO membrane itself is also being etched simultaneously with the formation of nanopores.
Figure S2. (a) Top view and (b) cross-sectional view SEM images obtained after 2 minutes of Ar plasma exposure successfully removed GaN from top of nano-pores leaving GaN integrated inside Si(100).
Figure S3. (a) Top view and (b) cross-sectional view SEM images obtained after 3 minutes of Ar plasma exposure successfully removed AlN from top of nano-pores leaving AlN integrated inside Si(100).
Figure S4. (a) Top view SEM image obtained from HCPA-ALD (500-cycle) grown AlN on nanoporous Si substrates, (b) Angled-view SEM image of the same sample, (c) Top-view SEM image of AlN HNCs revealing their morphology and dimensions, (d) angled-view SEM image of AlN HNCs depicting the total height of nanocylinders.
Figure S5. (a) Top view SEM image of AlN HNCs obtained after 5 sec of SF$_6$ based Si(100) etching revealing their morphology and dimensions, (b) cross-sectional image of same AlN HNCs showing the total height of nano-cylinders.
Figure S6. GIXRD pattern obtained from (a) ~173 nm long AlN HNCs, (b) ~50 nm thick AlN deposited on Si via HCPA-ALD.

The structural properties of AlN HNCs were also examined by GIXRD (Fig. S6(a)). Measurement was performed on ~173 nm long AlN HNCs integrated in Si substrate. For comparison, the GIXRD data was also gathered from ~50 nm thick AlN thin film deposited on Si and shown in Fig. S6(b). Various reflections were observed from GIXRD spectrum of both thin film and HNCs which correspond to polycrystalline wurtzite structure of AlN. The exhibited patterns were indexed by hexagonal crystal system (ICDD reference code: 00-025-1133). The reflections detected from hexagonal wurtzite crystal system in both these spectra are well supported by SAED diffraction patterns revealed in Fig. 5f and table II.
XPS was used to examine the chemical composition and bonding states of AlN HNCs. XPS survey scan collected from top of ~172 nm long AlN HNCs revealed the presence of aluminum, nitrogen, carbon, fluorine, and oxygen elements. Atomic percentages of elements detected were as follows: 19.45 at. % Al, 14.05 at. % N, 24.42 at. % C, 24.97 at. % F, and 17.12 at. % O. AlN thin film deposited with the same recipe had zero carbon content and 2 at. % O in bulk of the films.

The high-resolution XPS (HR-XPS) scans of Al 2p and N 1s are collected to investigate the bonding schemes of AlN HNCs and are presented in Figs. S7(a) and (b), respectively. Based on asymmetry and
FWHM of peaks, more than one type of bonding scheme was observed for both Al and N. Al 2p HR-XPS spectrum was fitted using two subpeaks located at 73.15 eV (subpeak#1) and 74.72 eV (subpeak#2) which were attributed to the Al-N and Al-O bonds, respectively.\textsuperscript{3-5} N 1s HR-XPS spectrum (Fig. S7 (b)) was fitted by two subpeaks located at 396.28 eV (subpeak#1) and 398.54 eV (subpeak#2) which were assigned to presence of N-Al and oxynitrides bonding species.\textsuperscript{3-5}

Figure S8. (a) Top view and (b) cross-sectional view SEM images obtained after 3 minutes of Ar plasma exposure successfully removed InN from top of nano-pores leaving InN integrated inside Si(100).
Figure S9. (a) Top view SEM image of InN HNCs obtained after 6 sec of SF$_6$ based Si(100) etching revealing their morphology and dimensions, (b) cross-sectional image of same InN HNCs showing the total height of nano-cylinders.
The structural properties of InN HNCs were further investigated by GIXRD (Fig. S10). Measurement was performed on ~210 nm long InN HNCs integrated in Si substrate. For comparison, the GIXRD measurement obtained from ~47 nm thick InN thin film deposited on Si is also provided. Various reflections of polycrystalline wurtzite structure of InN are visible in the recorded GIXRD spectrum for both thin film and HNCs. The exhibited patterns were indexed by hexagonal crystal system (ICDD reference code: 00-050-1239). The reflections detected from hexagonal wurtzite crystal system in both these spectrum are well supported by SAED diffraction patterns.
XPS was conducted to analyze the elemental composition and chemical bonding states of the InN HNCs. Atomic percentages of elements detected from InN HNCs were as following: 11.08 at. % In, 9.34 at. % N, 33.65 at. % C, 10.51 at. % F, and 35.41 at. % O. From the bulk of InN thin film grown with HCPA-ALD using the same growth parameters used in this study, 2.1 % O and 3.05 % C were detected. Figure S11 (a) and (b) shows HR-XPS scans of In 3d and N 1s, respectively, both of which were obtained from ~210 nm long InN HNCs. In 3d spectrum reveals In 3d\(^{5/2}\) and In 3d\(^{3/2}\) spin orbit doublet and considering their unsymmetrical nature, both these peaks have been deconvoluted into two Gaussians. The first subpeak of In 3d\(^{5/2}\) spin orbit located at 443.50 eV belongs to In-N bond while the second subpeak originating at 445.04 eV corresponds to In-O bond.\(^8\) In 3d\(^{3/2}\) spin orbit was deconvoluted into two subpeaks detected at 451.09 and 452.68 eV which are associated with In-N and In-O bonds, respectively. In both these spin orbits, the subpeak having larger area among the two belongs to In-O species. In a previous report, In 3d HR-XPS spectrum obtained from bulk of HCPA-ALD grown InN thin film showed the same In 3d\(^{5/2}\) and In 3d\(^{3/2}\) spin orbit doublet which have been deconvoluted in two subpeaks each.\(^8\) In that case, the larger subpeak of these

Figure S11. HR-XPS scans of (a) In 3d and (b) N 1s obtained from ~210 nm long InN HNCs revealing presence of different bonding schemes.
spin orbits belonged to In-N bonding species which showed that In-O bonding content is significantly less than In-N bonding species in the bulk of the InN film. In the present case, In 3d spectrum obtained from surface of InN HNCs reveals that In-O bonding content is greater than In-N in the first few lateral nm of HNCs. N1s HR-XPS spectra obtained from InN HNCs is deconvoluted into two sub-peaks as shown in the Fig. S11(b). Based on the reported literature, we conclude that first subpeak in N1s spectra detected at 395.93 eV is attributed to the N-In while shoulder peak located at 397.96 eV is attributed to the presence of oxynitrides.\textsuperscript{6-8}

References: