Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

S1) Detailed explanation of NW-MOVPE

In this section, information about substrate preparation and MOVPE NW growth processes are given. First, the process for self-catalyzed dominant N-polar NW growth is presented, followed by the polarity- and site-controlled (PSCG) growth of Ga-polar NWs. For both types of NWs, As-doped n-type Si(111)-substrates ($\rho_{Si} = 1\ x\ 10^{-3}\ \Omega cm$) are used.

Self-catalyzed growth of GaN NWs (N-polar)

Without any surface preparation, the Si substrates are loaded inside the close-coupled showerhead MOVPE reactor. Under constant H_2 flow, the temperature is ramped to T_S = 910°C, determined by *in-situ* pyrometry on the substrate surface. The reactor conditions are kept constant for the next 600 s to remove the native oxide from the substrate surface. All parameters for this step and the following nitride growth are listed in Table 1.

Table 1. Growth procedure for self-catalyzed dominant N-polar NWs.

self-catalyzed NWs	T_S $[°C]$	t $[s]$	p $[mbar]$	$Q_{TMGa/Al}$ $\left[\frac{\mu mol}{\min}\right]$	Q_{NH_3} $\left[\frac{mmol}{\min}\right]$	Q_{SiH_4} $\left[\frac{nmol}{\min}\right]$	Q_{N_2} $[sccm]$	Q_{H_2} $[sccm]$
native Oxide removal by H_2 bake	910	600	100	--	--	--	--	8000
AlN interlayer	1060	150	100	10	67	--	--	8000
GaN nucleation	1000	30	100	137	2.9	--	7873	--
three steps GaN NW growth	1030	300 1100/300 50	800	137	4.9	202 5.6 0	1662	166

Next, a 20 nm thin AlN interlayer is grown by injecting TMAl and NH_3 at a V/III ratio of 6700 to avoid Ga melt-back etching during the following GaN growth. Randomly distributed and mixed polar GaN seeds are established by changing the reactor conditions to the "GaN nucleation" conditions (Table 1) and injecting TMGa and NH_3 (V/III ratio ≈ 21). After this nucleation step, the metalorganic supply is stopped, and reactor pressure and total gas flow are adjusted for NW growth. Next, the NW growth is initiated by injection of TMGa and SiH_4. The Si and N atoms form silicon nitride (SiN_x), which passivates the *m*-planar shell, suppresses the lateral growth and thereby promotes the vertical NW growth.[55,86] During the initial 300 s of NW growth, a high SiH_4 flow is necessary to additionally passivate small parasitic nucleation sites, thereby localizing the growth on the thicker NW seeds. Next, the SiH_4 flow is decreased, since NWs with smoother shells are attained at this flow. The duration of the last step has been changed to obtain different total NW core lengths of 4 µm or 7.6 µm. Finally, the NW upper part (< 300 nm) is grown without any silane to circumvent the SiN_x passivation on the NW top, which may otherwise affect the subsequent shell growth. NWs grown under these conditions are highly n-doped, as was shown in reference [39].

The surface passivation by H is critical to attain NW growth. H-atoms passivate N-terminated surfaces and, thus, strongly influence the growth kinetics, which leads to different observable crystal facets, growth rates and growth directions. *c*-facet surface termination of Ga- and N-polar wurtzite crystal planes are inverted, which leads to a strong influence of H, strongly influenced by the x_{H_2}. In the here used mixed polar approach, a x_{H_2} of 9 % is used to promote the N-polar growth.

Polarity- and Site-controlled growth of GaN NWs (Ga-polar)

The basic conditions to achieve PSCG are, i) realizing separated growth locations of each polarity, and ii) the different growth rates of Ga- and N-polar GaN. We have shown in references [54,72] that a distinct *ex-situ* oxidation of a structured Si-substrate, followed by an *in-situ* H_2-bake inside the MOVPE system leads to Al- or N-polar AlN nucleation on specific

Si crystal planes. To use this effect for selective area epitaxy, a Si-substrate was structured by NanoImprint lithography and dry etching. Thereby, hexagonally arranged Si pillars were manufactured (100 nm high, diameter of 500 nm, pitch of 2.5 µm), which exhibit crystal facets at their sides, leading to Me-polar growth. Everywhere else, N-polar growth is initiated. This leads to PSCG of AlN, and thus condition i) is achieved. On top of the Al-polar AlN sites, first Ga-polar GaN islands and then Ga-polar NWs are attained by choosing adequate growth conditions for each step. The NW growth is separated in two steps indicated by an increase of NH_3 flow after the first 10 s. The two-step NH_3 flow is crucial to suppress multi-pod growth and to realize homogeneous epitaxy of NWs on all GaN islands. A detailed explanation and discussion of the sample preparation, the surface termination and the growth process can be found in references [54,72]. The parameters for each step carried out in the MOVPE system are summarized in Table 2.

Table 2. Procedure for Ga-polar NWs on polarity- and site-controlled AlN/Si-templates.

polarity- and site-controlled Ga-polar NWs	T_S $[°C]$	t $[s]$	p $[mbar]$	$Q_\mathrm{TMGa/Al}$ $\left[\frac{\mu mol}{\min}\right]$	$Q_{\mathrm{NH_3}}$ $\left[\frac{mmol}{\min}\right]$	$Q_{\mathrm{SiH_4}}$ $\left[\frac{nmol}{\min}\right]$	$Q_{\mathrm{N_2}}$ $[sccm]$	$Q_{\mathrm{H_2}}$ $[sccm]$
ex-situ fabricated SiO_x removal by H_2 bake	930	420	100	--	--	--	--	8000
AlN interlayer	930	150	100	7.5	18.5	--	--	8000
PSCG: GaN islands	870	70	800	72.8	0.3	107	1670	323
two steps NW growth	830	10	800	55	0.7	288	1920	64.5
	830	1800		55	1.5			

S2) N-polar CS-NW: additional SEM images

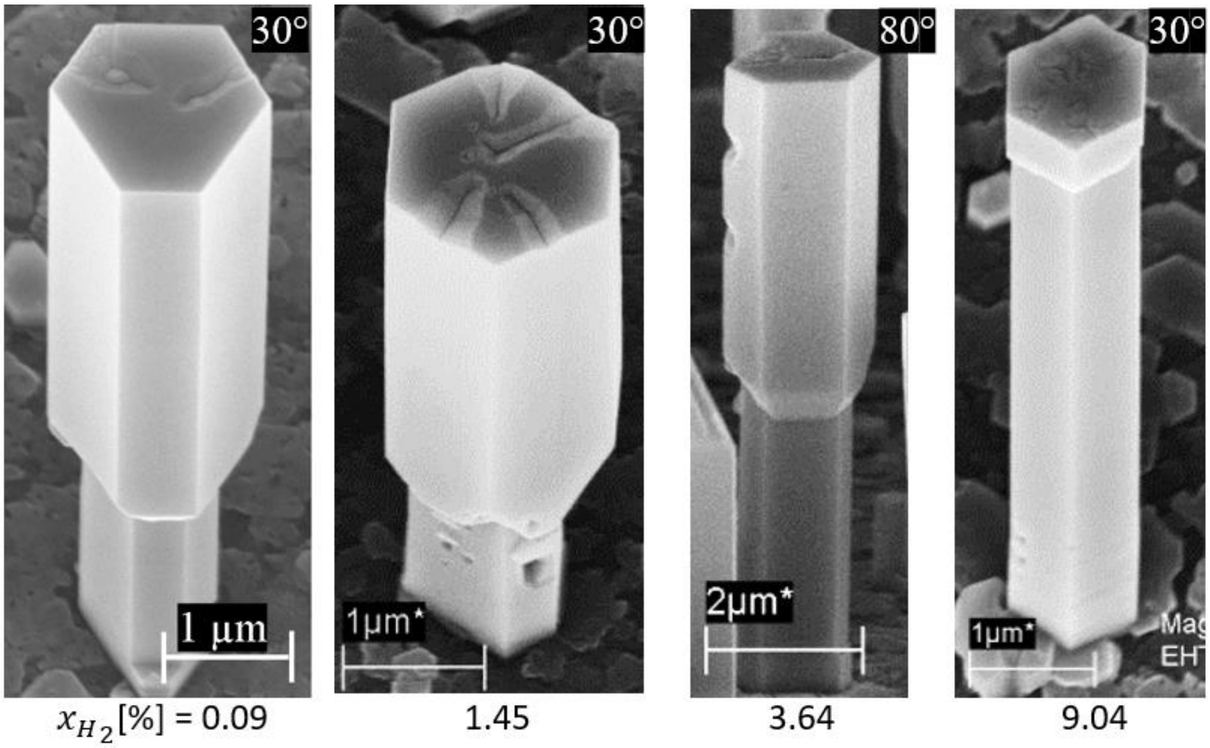

Figure SI 1. Shell growth on self-catalyzed NWs for different carrier gas ratios x_{H_2}.

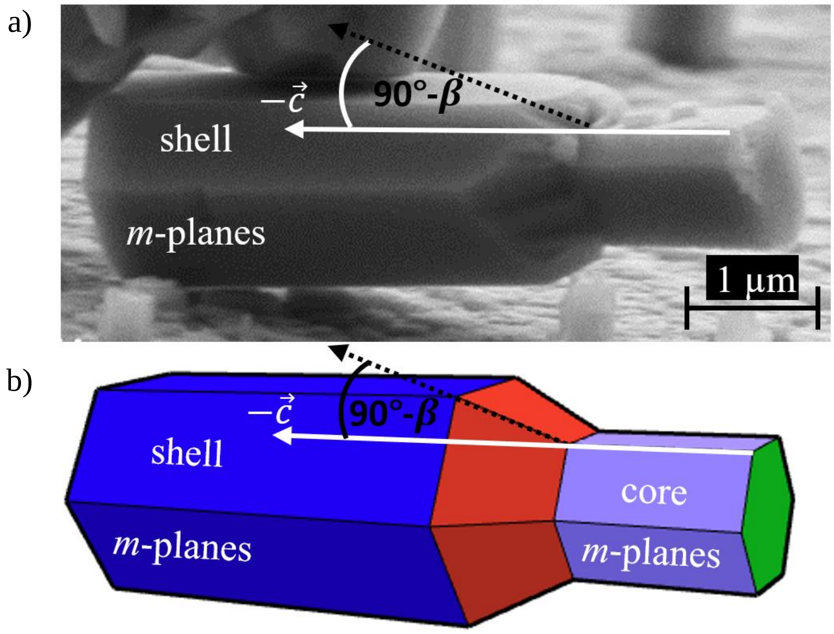

Figure SI 2. SEM image (a) and sketch (b) of a detached N-polar CS NW. All m-planes are blue (bright blue for core), the c-facet is green and the determined tilted facets are red colored.

S3) Ga-polar CS-NW: additional SEM images

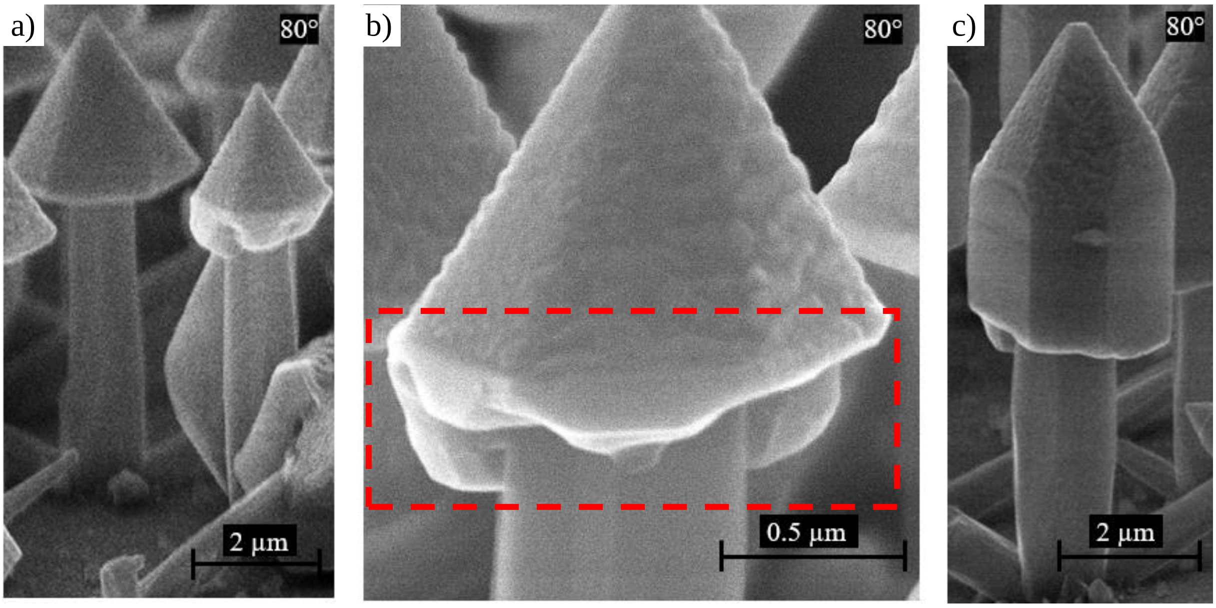

Figure SI 3. Shells grown on Ga polar NWs at x_{H_2} of 9 % (a and b) and 50 % (c). An initial m-planar growth is highlighted by a red box in b.