A route for the top-down fabrication of ordered ultrathin GaN nanowires

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Abstract
We introduce a facile route for the top-down fabrication of ordered arrays of GaN nanowires with aspect ratios exceeding 10 and diameters below 20 nm. Highly uniform thin GaN nanowires are first obtained by lithographic patterning a bilayer Ni/SiNx hard mask, followed by a combination of dry and wet etching in KOH. The SiNx is found to work as an etch stop during wet etching, which eases reproducibility. Arrays with nanowire diameters down to (33 ± 5) nm can be achieved with a uniformity suitable for photonic applications. Next, a scheme for digital etching is demonstrated to further reduce the nanowire diameter down to 5 nm. However, nanowire breaking or bundling is observed for diameters below ≈20 nm, an effect that is associated to capillary forces acting on the nanowires during sample drying in air. Explicit calculations of the nanowire buckling states under capillary forces indicate that nanowire breaking is favored by the incomplete wetting of water on the substrate surface during drying. The observation of intense nanowire photoluminescence at room-temperature indicates good compatibility of the fabrication route with optoelectronic applications. The process can be principally applied to any GaN/SiNx nanostructures and allows regrowth after removal of the SiNx mask.

Keywords: Nanowires, GaN, top-down, ordered, digital etching, capillary force, collapsing

(Some figures may appear in colour only in the online journal)

1. Introduction

Downscaling of Si-based devices was shown to be decisive to increase performance, expand functionalities and decrease production costs [1]. Along the same line, miniaturization of GaN three-dimensional structures like wires and fins has today become relevant for both electronic and photonic applications in order to profit from the wide-bandgap, the high electron mobility and the excellent thermal stability of the nitride semiconductors in nanoscale devices [2–7]. Specifically, ultrathin GaN nanowires (NWs) with diameters ≤20 nm are beneficial for achieving ultrafast switching in field-effect transistors [8, 9], they can elastically relax large amounts of epitaxial strain [10–13], and they host dielectrically confined excitons up to room temperature [14]. If arranged deterministically on the substrate surface, such NW arrays can principally form photonic cavities [15] and they ease the parallel contacting of many single NWs [16]. Yet, the fabrication of such ordered arrays of ultrathin NWs remains to date an open challenge.

Using self-assembled processes, randomly placed NWs with ultrathin diameters can readily be obtained in a top-down or bottom-up fashion, with a minimum diameter of 8 [17, 18] and 15 nm [19], respectively. However, if the substrate surface is deterministically patterned—e.g. using electron beam lithography (EBL)—to gain control over the NW position and dimensions, diameters larger than 25 nm are systematically obtained if neglecting tapering [13, 20]. Ordered arrays of thinner GaN NWs could still be achieved through additional processing steps. Thermal sublimation in vacuum or NH₃...
environment allows reducing the NW diameter down to a few nanometers [14, 21]. Yet, the thinning rate depends exponentially on temperature, a parameter that is in practice difficult to change abruptly in vacuum chambers. Direct wet etching in solutions of tetramethylammonium hydroxide or KOH can reduce NW diameter, but the etching rate must be slow in order to control the final NW diameter [3, 16, 22–24]. More attractive for a nanometer-scale etching is the use of digital etching or atomic layer etching for which the etching depth is controlled by the number of applied etching cycles [25–35]. So far, most of these processes have been developed on polar GaN and (Al,Ga)N surfaces for recess etching of III-nitride transistors. Only one recent work deals with semipolar facets [35] but little is known about digital etching of nonpolar facets corresponding to the sidewalls of GaN NWs.

Here, we demonstrate a facile route for top-down fabrication of ordered arrays of vertical GaN NWs with the smallest possible diameter. Highly uniform arrays of GaN NWs with a minimum diameter of (33 ± 5) nm are first obtained by lithographic patterning of a bilayer Ni/SiN, hard mask followed by a combination of dry and wet etching. The SiN layer is found to act as an etch stop during wet etching in KOH, which provides an enhanced control on the final NW diameter. Next, a controlled decrease of the NW diameter down to 5 nm is obtained by establishing a digital etching approach based on plasma oxidation and KOH etching. The observation of intense NW photoluminescence indicates that the various etching steps do not introduce strong nonradiative centers. However, below 20 nm in diameter, NWs with large aspect ratio are seen to collapse as a result of capillary forces acting during sample drying. The early collapsing of the NWs cannot be accounted for by models developed so far for macroscopic elastic rods. Instead, our explicit calculations of the NW bent states under capillary forces show that a critical parameter governing the NW mechanical instability is the inclination angle of the water surface with respect to the NW axis.

2. Experiments

2.1. Top-down NW fabrication

To produce the initial GaN NW array with high uniformity, we follow a conventional top-down fabrication scheme comprising mask patterning, plasma etching and wet etching in concentrated KOH [36]. This approach schematically depicted in figure 1(a) was shown effective for synthesizing micrometer long GaN NWs with a minimum diameter of ≈100 nm. To achieve smaller NW diameters, we rely here on EBL for mask patterning.

The substrates are commercial GaN layers grown epitaxially on sapphire with estimated donor concentrations of $10^{16}$ cm$^{-3}$ [non intentionally doped (n-d)GaN] and $10^{19}$ cm$^{-3}$ (n-GaN). The chosen mask consists in a vertical stack of SiN$_x$ and Ni. A 20 nm thick SiN$_x$ layer is first deposited by magnetron radio-frequency (RF) sputtering (PRO line PVD75 from Kurt J. Lesker Company) at a power of 160 W, a pressure of 1.9 mTorr and an Ar:N ratio of 1. The layer is further treated by rapid thermal annealing at 600°C for 10 min. Next, an adhesion layer AR300-80 is spin-coated and baked for 2 min at 180°C. It is covered by an 80 nm thick CSAR 62 positive resist (Allresist GmbH) deposited by spin-coating, baked for 1 min at 180°C and eventually exposed by EBL (RAITH150 Two EBL). The printed pattern is made of circular patches arranged in a hexagonal symmetry within a 50 × 50 μm$^2$ quadratic microfield. Various microfields are printed with pitches ranging from 0.2 to 15 μm (nearest-neighbour center-to-center distance), and patch diameters ranging from 30 to 120 nm. The electron dose is varied from 30 μC cm$^{-2}$ for the smaller features to 140 μC cm$^{-2}$ for the bigger ones. The pattern is developed by successive baths in developer AR600-546 and stopper AR600-60 solutions for 70 and 60 s, respectively, leaving holes in the resist layer. The sample is then coated with a 25 nm thick Ni layer by metal evaporation (Pfeiffer classic 500) and mask lift-off is
eventually performed with the remover AR600-71 for 60 min. The obtained Ni pattern will be used as a hard mask for the subsequent chlorine-based plasma etching [37–43]. The non-protected part of the SiN$_x$ layer is first reactively etched in CF$_4$/O$_2$ at a plasma power of 50 W and pressure of 4 Pa (Sentech SI 500). Next, GaN is anisotropically etched via inductively coupled plasma reactive ion etching (ICP) at a pressure of 1.3 Pa with a BCl$_3$/Cl$_2$ gas ratio of 20:5, an RF power of 25 W and an ICP power of 100 W (SAMCO RIE-140iP). Ni is then removed in a ferric chloride solution for 1 min at 40 °C–60 °C (Ni etchant type I from Transene). Finally, the formed GaN NWs are dipped for 70 s at 40 °C in a 6.9 M KOH aqueous solution or in the AZ400K developer which also contains KOH. The temperature of the KOH solution ranges between 40 °C and 80 °C, as measured by a thermometer placed in the beaker. Dislocations in the GaN substrate are not etched at this moderate temperature [44].

2.2. Digital etching

The digital etching examined here consists in two steps per cycle and is applied on GaN NWs with their top facet still capped by SiN$_x$. The NWs are first oxidized in an O$_2$ plasma for 15 min (SAMCO RIE-140iP). The O$_2$ plasma is at a pressure of 7 Pa (10 sccm of O$_2$) with an ICP power of 100 W and an RF power of 20–50 W. A supplementary NW sample was treated with an ICP power of 50 W and an RF power of 15 W. The oxidized NWs are eventually dipped in a 6.9 M KOH aqueous solution at 60 °C for up to 5 min.

3. Results

3.1. NW array morphology

Exemplary arrays of vertical GaN NWs produced here can be seen in the representative secondary electron micrographs of figure 1(b). For these NWs, ICP etching was carried out for 3 min and KOH treatment was 130 s long at 60 °C in aqueous solution. The 0.6 μm long NWs are all vertical and exhibit excellent uniformity. The analysis of 10$^4$ NWs from such sample provides a total yield of 99% due to missing NWs in some microfields. The magnified views of single NWs shown in figures 1(c) and (d) reveal a constant diameter along the NW length and the presence of smooth sidewalls resulting from the final KOH treatment, which is reported to remove defects induced by the ICP etching [40, 45, 46].

Cross-sectional secondary electron micrographs views of randomly dispersed NWs [figure 1(d)] allow visualization of the SiN$_x$ top patch. It has a comparable thickness as the initial sputtered SiN$_x$ layer and features a tapered morphology, likely resulting from the ICP etching. Importantly, the base of the SiN$_x$ patch has a similar diameter as the GaN NW underneath, suggesting that both are correlated.

Figure 1(e) shows the average length of NWs obtained for different ICP etching times. Regardless of the donor concentration in the GaN template and the type of KOH solution, the graph evidences a linear relationship up to etching times of 6 min. For longer etching time, the NW length saturates at about 1.1 μm and the yield is drastically reduced, which is associated with a complete consumption of the 45 nm thick Ni/SiN$_x$ hard mask. The ratio between the GaN and the Ni/SiN$_x$ etching rates indicates an etching selectivity of ≈24, a value that compares favorably with prior reports [47–49]. In the absence of Ni, NWs only 0.1 μm long are obtained, which translates in an etching selectivity between GaN and SiN$_x$ of 5, similar to [48]. The best reported selectivity between GaN and Ni amounts to ≈20 [49]. By taking the selectivity of individual SiN$_x$ and Ni layers, our hard mask should thus provide a maximum NW length of only 0.6 μm. Our enhanced selectivity compared to [49] may be due to an improved adhesion of the mask provided by the underlying SiN$_x$ layer and/or to less aggressive etching conditions. Figure 1(e) also evidences that the final NW length has no marked dependence on the temperature of the KOH bath, on the nature of the KOH solutions and on the doping level of the initial GaN layer. Similar conclusions are drawn concerning the NW diameter. Interestingly, straight NW sidewalls are already obtained after 130 s, whereas etching times of several hours were required in [36, 46]. We associate the faster etching observed in this work ($>20$ nm min$^{-1}$) to the smaller volume of material to be etched and to the higher temperature of the KOH bath.

To assess the uniformity of the fabricated GaN NW arrays, we use ImageJ to analyse the top-facet morphology and position of 10$^3$ NWs per microfield which are pictured top-view by scanning electron microscopy (SEM). The resulting distribution of NW equivalent disk diameter$^2$, circularity$^2$, and (center-to-center) nearest-neighbour distance are shown in figures 2(a)–(i). The distributions of NW diameter peak close to the nominal values and exhibit standard deviations of 3–5 nm. Independently of the NW diameter, the circularity of the NW top facet amounts to 0.88–0.89, which is close to that of a regular hexagon (0.91). Likewise, the nearest-neighbor distance approaches the nominal pitch value with a standard deviation of 2–7 nm. Thus, the uniformity of the arrays is very high and very well suited for inducing photonic crystal effects [50, 51]. The thinnest NWs that could be achieved with high yield are characterized by an average diameter of (33 ± 5) nm.

Next, we examine the photoluminescence (PL) of the fabricated NW arrays to check for possible damages induced by the processing steps [52]. PL spectra acquired for different NW microfields and for an unprocessed GaN substrate are shown in figure 2(j). We benefit from the different strain states between the NWs (strain free) and the underlying GaN layer (in compressive strain on sapphire) to differentiate the PL contributions of both [53]. Hence, for arrays with the largest NW fill factor, the measured PL mostly stems from the NWs as the signal shows higher intensity (up to a factor 10) and a pronounced redshift (up to 13 meV) compared to spectra acquired away from the NW microfields. The redshift

$^1 d = \sqrt{A_A}$, with $A$ the NW top facet area

$^2 c = 4\pi AP^{-2}$, with $P$ the NW top facet perimeter.
is due to the reduced strain and the largest PL intensity relates to the enhanced light extraction \[50, 51, 54\]. In contrast, for microfields with thinner NWs, the PL signal corresponds essentially to the underlying GaN substrate, which results from the small NW volume and to the inefficient laser light coupling for diameters lower than \(\approx 70\) nm \[55\].

Compared to the unprocessed GaN substrate, the etched GaN layer measured away from the NW microfields shows a 5 times lower PL intensity. This results from the introduction of nonradiative centers during the anisotropic dry etching \[52, 56–58\]. Yet, the Ni mask at the NW tip should prevent the introduction of such defects in the NWs, which is in agreement with the fact that the NWs show intense PL. The enhanced light extraction in the NW microfields also contributes at increasing the NW intensity compared to layers. For comparison, similar GaN substrates nanostructured without the use of dry etching leads to a PL enhancement on the order of 2–3 \[54\], which compares well with the maximum enhancement observed here for the microfield with a pitch and diameter of 500 and 90nm, respectively. A two fold increase is also observed in \[52\] when using mild dry etching conditions for top-down fabrication of \(\approx 1\) \(\mu\)m thick GaN NWs. We would thus conclude that the etching sequence proposed here does not introduce strong nonradiative centers in the NWs, which makes it compatible for optoelectronic applications.

To address the benefits of the SiN\(_x\) patch in the fabrication process, we further examine GaN NW arrays produced with a hard mask made of Ni only. Figure 3(a) depicts that, upon ICP etching for 3 min, tapered GaN NWs exhibiting rough sidewalls and an hexagonal base are obtained, which compares well with the case where a Ni/SiN\(_x\) mask is used (not shown here). This morphology is also consistent with previous studies \[40, 41, 59\]. Straight NW sidewalls are eventually obtained during KOH etching (figure 3(b)), in agreement with previous reports \[36, 45\]. However, the roughness of the sidewalls is larger than in the presence of SiN\(_x\). Remarkably, if the KOH etching is performed after removal of the Ni, the GaN NWs remain tapered and are eventually etched away, as seen in figure 3(c). The NWs first
disappear at the edge of the microfields, suggesting that the etching rate is kinetically limited by mass transport in the KOH solution. The GaN (0001) facet at the NW tip is known to be resistant against KOH, whereas nonpolar and semipolar facets can be attacked by KOH [60]. Here, our observations indicate that etching of thin GaN NWs in KOH can be mitigated by the presence of a SiN_x cap or, to some extent, by a Ni cap placed at the NW tip. This finding is in agreement with the fact that the GaN NWs feature the same diameter as the SiN_x cap (figure 1(d)) and that the final NW diameter is found to be independent of the KOH etching conditions. As a result, it can be deduced that SiN_x and Ni caps act as an etch stop by protecting the edge of the GaN (0001) top facet where the KOH attack otherwise proceeds. Such an etch stop is of high practical relevance since the final NW diameter is now solely determined by the size of the top patch written by EBL, hence providing higher reproducibility. The discovery that Ga-polar GaN NWs can be etched out by KOH is also of relevance if using KOH etching as a mean to determine the polarity of GaN NWs [61].

3.2. Digital etching of the NWs

The minimum NW diameter achieved here by direct selective area etching amounts to $(33 \pm 5) \text{ nm}$, a value that is likely limited by the precision of the EBL patterning of the Ni/SiN_x hard mask. We thus explore digital etching to further decrease the NW diameter. The digital etching approach consists in plasma oxidation of the NWs followed by etching in KOH. This process is shown to be effective in figure 4(a), where NWs initially 120 nm thick are substantially reduced in diameter by repeating three times the etching process with a RF power of 20, 35, and 50 W, respectively. The etching rate appears to be uniform along the NW length and similar for all NWs of the same sample.

The etching rate as a function of the RF power is quantified by analysing SEM images of 20–50 NWs before and after treatment, and the results are shown in figure 4(b). First, the O_2 plasma exposure actually increases the NW radius by an amount $\Delta r_1$ that scales linearly with the RF power. As seen in figure 4(c), only the GaN NW expands whereas the SiN_x cap remains visually unaffected. A similar increase in the NW radius was reported in [62] for GaN NWs annealed in O_2 atmosphere and is associated to the formation of a GaO_x shell with a width equal to $\approx 2\Delta r_1$. The size increase relates to the 18% larger specific volume of $\beta$-Ga_2O_3 compared to GaN (for an equal number of Ga atoms), to the epitaxial strain at the GaO_x/GaN interface, and to the abundance of defects.

After exposure to both O_2 plasma and KOH, the NW radius experiences a net decrease $|\Delta r_2|$, that scales linearly with the RF power. The linearity is lost when processing the NWs for the third time. Since $|\Delta r_2| > \Delta r_1$, we conclude that the NW thinning during KOH treatment is not limited to the removal of the GaO_x shell formed during O_2 plasma. Instead, we propose that the NW thinning is limited by the radial etching of the SiN_x cap. This is substantiated by figure 4(d), where the SiN_x cap is seen to undergo a major change in morphology after etching and keeps sharing the same diameter as the underlying GaN stem. SiN_x etching is further confirmed by treating SiN_x layers deposited on GaN. X-ray
As can be seen in Figure 5, the nanotechnology field micrographs of ultrathin GaN NWs grown on TiN that were dipped in water and ethanol, respectively, and dried in air. The histogram in Figure 5(d) shows the diameter distribution of 0.55 μm long NWs taken from the same field that remained either vertical, suffered from bundling or broke during the thinning process. It evidences the existence of two critical diameters amounting to (22 ± 2) and (17 ± 2) nm, below which NWs bundle and break, respectively.

We associate this mechanical instability to capillary forces acting on the NWs during the drying step. These forces become non-negligible for nano- and microstructures with increasingly high aspect ratio, having a major impact on their mechanical stability [65–72]. To test for this hypothesis, we subsequently wet and dry in air ensembles of thin GaN NWs obtained bottom-up by self-assembly on a TiN substrate. Such ensembles feature a broad NW length distribution, which allows determining the critical NW dimensions possibly leading to failure. The micrographs in Figures 5(e) and (f) confirm that the sole wetting and drying is indeed sufficient to break some NWs, with a more pronounced effect when using water as solvent compared to ethanol. This difference can be explained by the 3.5 times larger surface tension of water compared to ethanol. The plot clearly reveals two regions: the longer and thinner NWs break, while the shorter and thicker ones remain vertical.

Neukirch et al. [70] have described the various buckling configurations that can be reached for a vertical elastic rod piercing a horizontal liquid surface. The NW buckling limit deduced from this work and plotted in Figure 5(g) as a dashed line labelled $\alpha = 0^\circ$ is seen not to match our experimental observations. As detailed below, an excellent agreement is found instead when considering an inclined liquid surface ($\alpha \neq 0^\circ$), as can be expected when the solvent has a finite wettability on the substrate surface and forms droplets.

Let us consider a vertical NW of length $L$ placed in water, under the horizontal liquid surface. By lowering the water level, the liquid surface comes in contact with the NW and exhibits very strong bending leading to NW breaking is only expected below which NWs bundle and break, respectively.

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arrows depict two different bending paths occurring during water wetting angle at the NW sidewalls. According to the Euler criterion \[ \frac{L_m}{L_b} = \frac{\pi^2}{2} \frac{EI}{F^2}, \]
with \( E \) the NW Young modulus, and \( I = \pi r^4 / 4 \) the geometrical moment of inertia of the NW cross section. Taking the water surface tension \( \gamma = 72 \) mN m\(^{-1}\), the water wetting angle on GaN \( \Theta = 40^\circ \) [74], and the GaN Young modulus \( E = 300 \) GPa [75], we obtain \( L_b \approx 40 \times 10^{3} \), with \( L_b \) and \( r \) expressed in nanometers. It is this buckling limit for a horizontal liquid surface \( (\alpha = 0^\circ) \) that is plotted in figure 5(g) as a dashed line. This limit is seen to largely overestimate the threshold at which NW breaking is experimentally observed. A lower threshold would require either a reduced mechanical strength of the NWs, or a higher surface tension of the solvent, both of which are not physically reasonable assumptions.

Compared to the case described in [70], we deal here with much shorter wires, which can make the assumption of a horizontal liquid surface not valid anymore. Since water does not wet either TiN or GaN substrate surfaces [74, 76], it is reasonable to assume that water has already assembled in droplets when the liquid surface comes in contact with the NW tip [see figure 6(b)]. The inclination angle \( \alpha \) of the liquid surface at the NW tip may thus take any value between \( 0^\circ \) and \( \Theta \), with \( \Theta \) the water wetting angle on the NW substrate surface. The direction of the capillary force is normal to the liquid surface and is thus misaligned with the NW axis for \( \alpha > 0^\circ \), which will always result in some bending of the NWs. The capillary force is proportional to the perimeter of the NW cross-section in the plane of the liquid surface [70]. Compared to the case \( \alpha = 0^\circ \), the amplitude of the capillary force thus increases by a factor 1/\( \cos \theta_0 \), with \( \theta_0 \) the angle between the NW axis at its tip and the normal to the liquid surface [see figure 6(c)].

During drying, once the liquid surface touches the NW tip and goes lower, the NW starts bending \( (\theta_0 \) increases), which raises in turn the strength of the capillary force \( F / \cos \theta_0 \) eventually resulting in some more bending. In this process, \( \theta_0 \) evolves from \( 0 \) (no deflection) possibly up to \( 90^\circ \) (NW tip axis parallel to the liquid surface). In the course of bending, however, the strength of elastic restoring force may exceed the capillary force, which will result in the NW piercing the liquid surface and getting back to its vertical configuration \( (\theta_0 = \alpha) \).

Calculations of stable NW bending configurations as function of \( \alpha \) are detailed in the appendix and the results are presented in figure 6(d) for \( \alpha = 20^\circ \). NW lengths are given in units of the buckling length \( L_b \) and \( \theta_0 \) ranges from \( \alpha \) to \( 90^\circ \). For bending states falling in the grey area, the elastic restoring force is larger than the capillary force, making these states unstable. The maximum NW length within the unstable region is denoted by \( L_{um} \). During sample drying, NWs follow two different paths, depending on their length exceeding \( L_{um} \) or not. These paths are exemplified by the two blue dotted arrows in the stability diagram. For path 1 \( (L < L_{um}) \), \( \theta_0 \) reaches its maximum value at the boundary of the unstable area. If the water level further decreases, the NW will pierce the water surface and straighten up, as shown in the inset of figure 6(e). In contrast, for path 2 \( (L > L_{um}) \), \( \theta_0 \) can reach the maximum value of \( 90^\circ \). As detailed in the appendix, we have checked that the bending states that can be achieved for \( L < L_{um} \) do not build a sufficient stress for inducing NW breaking. In contrast, we propose that once \( \theta_0 \) reaches \( 90^\circ \) the NW will not be released from the droplet as it shrinks in size and the NW will thereby enter complex bending configurations resulting in breaking. The breaking condition thus becomes \( L > L_{mr} \). Figure 6(e) shows that \( L_{mr} \) monotonously decreases from \( L_b \) to 0 when \( \alpha \) increases from 0 to \( 90^\circ \).

As can be seen in figure 5(g), an excellent agreement between calculations and the experimental threshold at which GaN NWs on TiN are breaking can be obtained by taking \( \alpha = 45^\circ \) \( (L_{mr}/L_b = 0.37) \). Similarly, \( \alpha = 25^\circ \) \( (L_{mr}/L_b = 0.55) \) can account for the observed breaking of GaN NWs on GaN (figure 5(d)). These values are reasonably close to reported wetting angles on TiN (32° [76]) and GaN (40° [74]), taking into account the fact that the droplet itself is likely deformed in the presence of many NWs. We thus conclude that NW breaking is initiated in the vicinity of droplet edges.
However, the bent NWs may escape their fate if their tip ends up touching neighbouring NWs in the droplet, eventually forming tripod structures as can be seen in figure 5(b). These bundled NWs are mechanically more robust than single NWs and may not break.

Several options can be used to prevent the collapsing of ultrathin NWs occurring during drying. One can either work with shorter NWs \((L < L_{mg})\), use a critical point dryer as typically used during fabrication of microelectromechanical systems, or perform dedicated surface treatments as described in [77].

### 4. Conclusions

We have introduced a facile route for the top-down fabrication of ordered arrays of GaN NWs with aspect ratios exceeding 10 and diameters below 20 nm. Thin NWs are first obtained top-down by EBL patterning of a Ni/SiN\(_x\) hard mask followed by dry etching and wet etching in KOH. SiN\(_x\) in the hard mask is found to work as an etch stop during wet forming tripod structures as can be seen in [52]. After all, the ultrathin nanostructures produced here can be used as template for epitaxy of highly mismatched materials [79], as host for single photon emitters, or as channel in ballistic deflection transistors [8].

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### Data availability statement

The data cannot be made publicly available upon publication because they are not available in a format that is sufficiently accessible or reusable by other researchers. The data that support the findings of this study are available upon reasonable request from the authors.

### Appendix. NW bending under an inclined liquid surface

We consider here a thin elastic rod with circular cross-section that is referred to as a NW. The NW is placed in a liquid having a surface inclined by an angle \(\alpha\) with respect to the horizontal. The height of the meniscus that forms once the NW pierces the liquid surface is on the order of the NW radius \([80, 81]\) and is thus further neglected. We emphasize that for macroscopic rods as described by Neukirch et al [70], the meniscus height scales instead with the capillary length \(L_c = \sqrt{\gamma/(\rho g)}\), with \(\gamma\) the surface tension, \(\rho\) the liquid density, and \(g\) the gravitational acceleration \((L_c \approx 2 \text{ mm for water})\).

When the NW comes in contact with the liquid surface, a capillary force \(f\) acting on the NW tip builds up and points in a direction normal to the liquid surface (see figure 6(c)). Its component tangential to the liquid surface is zero since a displacement along the liquid surface does not cost energy. The amplitude of \(f\) is proportional to the perimeter of the NW cross-section in the plane of the liquid surface. We denote by \(\theta_0\) the angle between the NW axis at its tip and the normal to the liquid surface (see figure 6(c)). For fixed \(\theta_0\), \(f\) reaches its maximum value \(F/\cos \theta_0\), with \(F\) given by equation (1), once the NW completely pierces the liquid surface [70]. After piercing, the elastic restoring force becomes larger than the capillary force which makes the bent state unstable and leads to a straightening of the NW [70].

Our aim is to find the stability diagram of the NW bent states under the action of capillary forces. To this end, we calculate the NW equilibrium state assuming the maximum capillary force \(F/\cos \theta_0\), which corresponds to the border of the stable region. The NW bending configuration can be described using the general solution of Problem 1 to section
19 in [73]. Let us take the plane of bending as the $xy$ plane and direct the $y$ axis antiparallel to the capillary force acting at the NW tip (see figure 6(c)). The $x$ axis is parallel to the liquid surface and makes an angle $\alpha$ to the substrate. Let $\theta(t)$ be an angle between the $y$ axis and the NW axis at a distance $l$ along the NW length ($l = 0$ at the NW anchor point on the substrate). Then, the NW shape is described by the equation [73]

$$l(\theta) = \frac{EF}{2} \int_{0}^{\theta} \frac{d\theta}{\sqrt{\cos \theta - \cos \theta_0}}.$$

(4)

Substituting $f = F/\cos \theta_0$ and using the definition of the buckling length $L_b$ in equation (2) results in a bent state

$$L \frac{L_b}{L_b} = \frac{\sqrt{2 \cos \theta_0}}{\pi} \int_{0}^{\theta_0} \frac{d\theta}{\sqrt{\cos \theta - \cos \theta_0}}.$$

(5)

The line defined by equation (5) is plotted in figure 6(d) in the case of a GaN NW placed in water with $\alpha = 20^\circ$. The bending configurations below the line are unstable since one would need a capillary force exceeding $F/\cos \theta_0$ to reach such states. During drying, $\theta_0$ increases, following the paths exemplified by blue arrows in figure 6(d). For $L < L_m$, the bending path enters the unstable region, meaning that the NW will eventually pierce the water surface. In contrast, for $L > L_m$, the NW will always remain below the water surface, likely reaching complex bending configurations as the droplet shrinks in size. Their calculation is beyond of the theoretical framework presented here. The bent states located on the right side of the unstable area cannot be reached during drying.

It remains to check, if the elastic stress building up in bent NWs with $L \leq L_m$ is sufficient to induce NW breaking during drying. During bending, there is a critical surface stress $\sigma_c$ above which NWs will crack. The longitudinal stress at the NW surface depends on the local radius of curvature $R$ and can be expressed as $\sigma = ER/R$. Hence, the breaking criterion can be written as

$$\sigma < E \frac{R}{R}.$$

(6)

For a fragile material, a critical stress $\sigma_c = 2\gamma/a$ can be estimated as a force needed to break chemical bonds and separate from each others the two newly formed surfaces by a distance equal to the bond length $a$ (see, e.g. [82]). For a GaN surface energy $\gamma_{\text{GaN}}$ of approximately 100 meV/Å$^2 = 1.6$ N m$^{-2}$ [83–85] and $a = 3.2$ Å, we get $\sigma_c = 10$ GPa, fairly close to values reported for CuO and ZnO NWs broken by AFM tips [86].

Figure 7. Maximum curvature accessible for NW length $L = L_m$ during drying as function of the liquid surface angle $\alpha$.

The NW curvature along its length $d\theta/dl$ is maximum at the NW bottom and can be obtained from equation (3). Using again the definition of $L_b$ from equation (2), we find for

$$\frac{L_b}{R} = \pi \left( \frac{\cos \alpha - \cos \theta_0}{2 \cos \theta_0} \right)^{1/2}.$$

(7)

The right-hand side of equation (7) is monotonically increasing with $\theta_0$. Hence, for $L \leq L_m$ and for bent states accessible during drying, the minimum bending radius $R_m$ is obtained at the boundary of the unstable region for $L = L_m$. Figure 7 shows the dependence of $L_b/R_m$ on the liquid surface angle $\alpha$. In the range $\alpha < 45^\circ$ that is of interest here, we have $L_b/R_m < 2$. Substituting this maximum curvature in equation (6) and using a buckling length of $L_b = 40r^3/3$ as mentioned in the main text for GaN NWs in water, we obtain that only NWs with $r < 2$ nm would crack. Such small radius is out of the experimental range, meaning that NW breaking for $L \leq L_m$ can be neglected. The main breaking condition thus remains $L > L_m$ as used in the main text.

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