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Morphology controlled growth of arrays of GaN nanopillars and randomly distributed GaN nanowires on sapphire using $(N_3)_2Ga[(CH_2)_3NMe_2]$ as a single molecule precursor†

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Controlled growth of oriented GaN nanopillars and randomly distributed nanowires is accomplished by MOCVD using $(N_3)_2Ga[(CH_2)_3NMe_2]$ as a single molecule precursor.

Free standing nanowires of semiconducting materials hold much promise for quite unique applications as nanolasers (ZnO), nano-LEDs (InP) and nano-FETs (GaN).[1] The oriented, size and shape selected crystal growth of such low dimensional structures is a major challenge and many physical and chemical strategies are pursued including laser ablation, MBE, template, electrochemical routes, as well as chemical vapour deposition methodologies.[2] The group-III nitrides are especially interesting targets because of their attractive properties for nano-sized UV or blue emitters, detectors, sensors and high-speed field effect transistors.[3] GaN nanowires are typically synthesised by metal-catalysed CVD from Ga vapour and NH_3 around 900–1000 °C and taking advantage of the so-called vapour–liquid–solid (VLS) growth mode.[4] Recently, we demonstrated the growth of InN whiskers by MOCVD using the single molecule precursor $(N_3)In[(CH_2)_3NMe_2]_2$ where the compound delivers traces of indium metal besides InN upon thermal decomposition, thus initiating an autocatalytic VLS growth mechanism.[5] Following this strategy we now achieved an unique oriented and self organised growth of size selected GaN nanopillars forming a homogeneous, nanoporous layer on (0001)-Al_2O_3.

Dense, smooth, epitaxial GaN thin films can routinely be grown by MOVPE using bis(azido)(dimethylaminopropyl)gallium {$(N_3)_2Ga[(CH_2)_3NMe_2]$ **1**} as a single molecule precursor even in the absence of NH_3 as an additional nitrogen source.[6] However, by employing a distinct set of CVD process parameters an unusual morphology comprising of ordered, self aligned GaN nanopillars was consistently achieved.‡ Contrasting this, the formation of long and randomly distributed GaN nanowires resulted when H_2 was used as a component of the carrier gas mixture. For comparison, we also deposited GaN nanowires by the direct reaction of Ga with NH_3 observing the very same morphology of randomly distributed GaN nanowires as reported in the literature.[7] The arrays of highly oriented GaN nanopillars were obtained only when the single molecule precursor **1** was used in the presence of pure N_2 as carrier gas at high flow rates of 100 sccm at 950 °C and 8.000 mbar at a growth rate of 900 nm h^{-1}. As revealed by SEM, the size and shape of the hexagonal shaped nanopillars is uniform over a wide range and averages approximately 50(±10) nm in diameter and around 500(±50) nm in length with the distance between the nanopillars ranging up to 50 nm which leads to a surface density of about 10^{14} cm^{-2} (Fig. 1). The surface of the nanopillars is flat and clear hexagonal pyramid facets are not observed by SEM and TEM. Presence of large (~ 50 nm in diameter) and small (~5–15 nm in diameter) droplets were detected on the tip and at the upper end of the single nanopillars, respectively (Fig. 2a). From the *d*-spacings obtained by HRTEM analyses, the droplets are identified as Ga which indicates the VLS growth mode of these nanopillars being catalysed by metallic Ga. The gas-phase decomposition of **1** as a function of temperature was studied previously and species like $[GaN_3]$ were identified as important intermediates for the GaN growth.[8] However, at temperatures above 920 °C the formation of Ga atoms increases rapidly. This intrinsic formation of traces of metallic Ga is most likely the reason for the Ga droplet formation besides the thermal decomposition of GaN itself which starts above 850–900 °C. Dipping the coated sapphire substrate in a 15% aqueous HCl etch for 3 min at 25 °C, enabled the complete removal of the Ga droplets without changing the morphology of the GaN nanopillars (Fig. 2b). From SAED patterns the hexagonal α-GaN phase was confirmed and the corresponding lattice parameters were found (a = 3.174 Å, c = 5.156 Å). Further crystalline properties investigated by XRD again revealed the hexagonal symmetry as well as the preferred orientation of the nanopillars perpendicular to the substrate by θ–2θ-scans. The out-of-plane mosaicity analysed by rocking curve measurements revealed a very small tilt spread of the nanopillars resulting in a full width at half maximum (FWHM) of 90 arc-sec. The in-plane

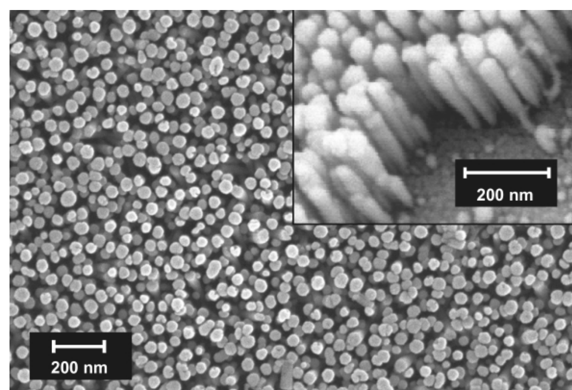

Fig. 1 Scanning electron micrograph of the ordered GaN nanopillars. Inset: Side view of the nanopillars.

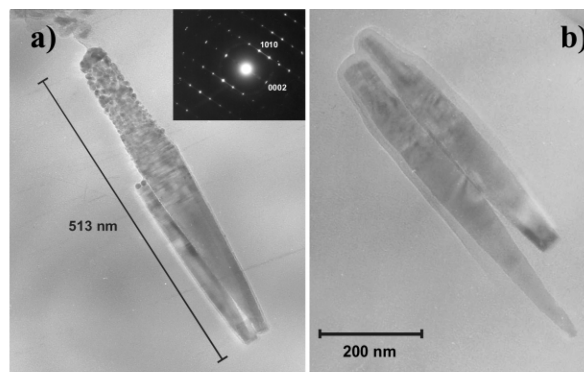

Fig. 2 Transmission electron micrographs: a) GaN nanopillars with Ga droplets on the top, inset: SAED pattern, b) GaN nanopillars 3 min etched in 15% aqueous HCl etch without Ga droplets.

† Electronic supplementary information (ESI) available: characterisation data. See http://www.rsc.org/suppdata/cc/b2/b201858f/

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orientation was determined by pole figure measurements showing an orientation of 30° between the GaN structure relative to the Al_2O_3 structure parallel (0001). This value is the corresponding tilt angle for the epitaxial relationship $(0001)_{GaN} \| (0001)_{Al_2O_3}$, $[0\bar{1}10]_{GaN} \| [11\bar{2}0]_{Al_2O_3}$ which is well known from conventional MOVPE of GaN.[9] The GaN nanopillars could be easily removed from the substrate by ultrasonic treatment and were dispersed in triglyme. The room temperature PL of this suspension showed a strong broad emission peak around 430 nm (Fig. 3) the nature of which is unknown so far but may be attributed to defects and surface states.

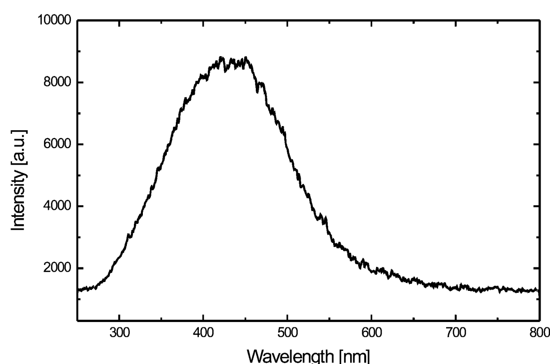

Fig. 3 Room temperature PL spectrum of the GaN nanopillars.

In sharp contrast to these arrays of rather perfectly oriented GaN nanopillars, a disordered growth of long GaN nanowires, randomly distributed over the substrate and measuring up to 10 µm in length and approximately 50 nm in diameter were obtained when adding H_2 (15 sccm) to the carrier gas N_2 (100 sccm) at 920 °C and 5.000 mbar (Fig. 4). The SAED and XRD patterns again confirmed the hexagonal α-GaN phase (a = 3.229 Å, c = 5.196 Å). Interestingly, Ga droplets on the tip of the nanowires or elsewhere were not detected by TEM in this case. The morphology of these nanowires is similar to the GaN nanowires deposited by direct reaction of Ga vapour and NH_3 on (0001)-Al_2O_3 as well as (100)-Si substrates which we obtained using literature procedures.[7] Those nanowires grown on the (0001)-Al_2O_3 substrates were 250–300 nm in diameter and up to 25 µm in length. Using (100)-Si substrates, the nanowires showed nearly the same diameter but were distinctly longer measuring up to 75 µm. However, no matter what we tried, we failed to achieve an oriented VLS–CVD growth of GaN nanopillars on (0001)-Al_2O_3 using separate sources for Ga and N. The nanostructure growth is a complex kinetic phenomenon depending on the substrate, the surface chemistry, certain metal catalysts and the hydrodynamics of the reactor. From GaN MOVPE it is known that the surface morphology and the growth mode is determined by the relative fluxes of Ga and N species to the surface.[10] Even H_2 and NH_3 itself seem to have an influence by stabilising the growing GaN surface.[11] One should note, that H_2 is the by-product of the chemical reaction of Ga metal with NH_3 to yield GaN. However, the single molecule source **1** allows the deposition of the GaN material in the absence of both, excess of NH_3 as well as H_2. Under these conditions an unusual growth mode leading to a special morphology is possible.‡

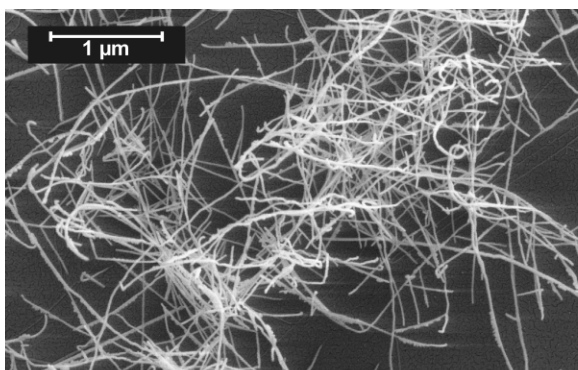

Fig. 4 Scanning electron micrograph of the disordered GaN nanowires.

In summary we have demonstrated that the concept of single molecule precursors for MOVPE of GaN thin films can be extended for the growth of nano-GaN materials. The precursor chemistry plays a significant role in the growth of these nanostructures, wherein the particular precursor discussed here decomposes in such a manner so as to facilitate or exploit the VLS mechanism of growth. We believe that the ability to tailor such molecular precursors opens up a route to grow nanostructures with varying morphologies that may be interesting for functional nanodevices.

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Notes and references

‡ *Experimental:* for all depositions (0001)-Al_2O_3 substrates were used. Ordered GaN nanopillars were deposited using a horizontal cold wall CVD reactor (base pressure (p_b): 10^{-5} mbar, carrier gas (g_c): N_2 (99.9999%, 100 sccm), substrate temperature (T_s): 950 °C, reactor pressure (p_r): 8.000 mbar, deposition time (t): 35 min). Disordered GaN nanowires were deposited using either the cold-wall reactor or a vertical stainless steel reactor (p_b: 10^{-6} mbar, g_c: N_2 (99.9999%, 100 sccm), reactive gas (g_r): H_2 (99.9999%, 15 sccm), T_s: 920 °C, p_r: 5.000 mbar, t: 1 h). For nanowires repeating the literature procedure, a hot wall CVD reactor was used (p_b: 10^{-4} mbar, reactive g_c: NH_3 (99.999%, 90 sccm), T_s: 915 °C, p_r: 10^{-1} mbar, t: 2 h). For these depositions also (100)-Si substrates were used. *Characterisation:* The morphology was analysed by scanning electron microscopy (SEM) [LEO 1530 Gemini SEM] and transmission electron microscopy (TEM) [Hitachi H-8100, operated at 200 kV]. The crystalline properties were analysed by selected area electron diffraction (SAED) in the TEM and by X-ray diffraction (XRD) [Bruker AXS D8 Advance and D8 Discover] methods using CuKα-radiation. The optical properties were investigated by room temperature photoluminescence (PL) [S.A. Instruments Fluoromax-2] measurements using a Xe-lamp (excitation wavelength: 230 nm). The nanopillars were removed by ultrasonic treatment and dispersed in triglyme. The PL-spectrum of the pure triglyme was considered and subtracted from the spectrum of the dispersed GaN nanopillars.

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