

Catalytic hydride vapour phase epitaxy growth of GaN nanowires

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Abstract

Catalytic growth of GaN nanowires by hydride vapour phase epitaxy is demonstrated. Nickel–gold was used as a catalyst. Nanowire growth was limited to areas patterned with catalyst. Characterization of the nanowires with transmission electron microscopy, x-ray diffraction, and low temperature photoluminescence shows that the nanowires are stoichiometric 2H-GaN single crystals growing in the [0001] orientation when grown on sapphire, with occasional stacking faults along the *c*-axis as the only defect type observed in most of the wires. A red shift observed in the photoluminescence was too large to be explained by the minor strain observed alone, and was only marginally affected by temperature, suggesting a superposition of several factors.

1. Introduction

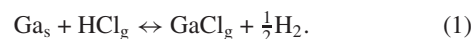
GaN nanowires combine the advantages of GaN, a promising wide band gap semiconductor material for visible optoelectronics applications, with the advantage of the quasi-one-dimensional nanowire structure that offers maximum size confinement while maintaining electrical conduction. Control of size and position of nanowires has so far been achieved only in the catalytic growth mode, also known as the vapour–liquid–solid (VLS) growth mode [1]. In this mode, the position and size of the resulting wire are defined through the placement and size of a metallic nanoparticle serving as a catalyst. In principle, any vapour phase delivery of the ingredients could be combined with VLS to grow nanowires. VLS growth of GaN nanostructures by various methods has been reported by several groups [2–8]. However, the only reported work on hydride vapour phase epitaxy (HVPE) growth of GaN nanowires did not employ a catalyst [9]. HVPE is of particular interest due to its high growth rates and simplicity of basic reactor design. HVPE also provides a better process control than the commonly used chemical vapour deposition techniques. A potential drawback of the method is the HCl released in the chemical reaction of gallium chloride and ammonia, as it may corrode the metal catalyst required for

the wire growth. Hence, it has been unclear whether HVPE may be useful for growing GaN nanowires *catalytically*.

In this paper, we report on a successful catalytic HVPE growth of GaN nanowires. We show the GaN wires grow only where the catalyst metal was deposited. However, dissolution of the catalyst remains a limiting factor. During extended growth periods the catalyst is eventually consumed and the VLS growth mode self-terminates.

2. Experimental details

Growth of GaN nanowires was carried out in a custom designed HVPE reactor. The reactor consists of 75 mm quartz tube, placed in a three-zone Mellen horizontal furnace. A quartz insert with a rectangular cross-section is employed to produce laminar flow in the growth zone and to suppress turbulence (figure 1). Two of the heating zones are used for hydride reactions of column-III metals with HCl gas. In this work, only gallium was used as the source metal and the GaCl was formed in a direct reaction between molten Ga and HCl gas diluted with nitrogen (equation (1)):



Gallium chloride is formed in an internal quartz tube (10 mm cross-section) at 800–850 °C and is carried in that tube into the rectangular part. The third zone is the growth zone that was

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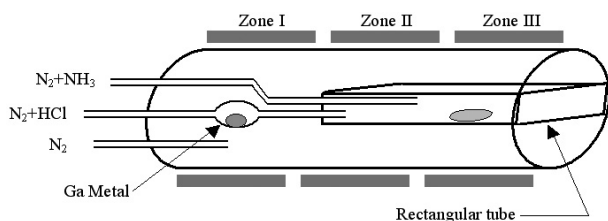


Figure 1. Horizontal HVPE system for GaN nanowire growth.

kept at 650–750 °C during the process. Ammonia is delivered to the growth zone via a separate 10 mm diameter quartz tube. In the HVPE process GaCl gas reacts with ammonia to form GaN (equation (2)):



Process gases are exhausted through a Lab Guard wet scrubbing system. The growth was carried out at atmospheric pressure. Ultrahigh purity nitrogen was used as a carrier gas. The typical carrier flow was 3000 sccm; the HCl and NH₃ flows were 1–10 and 50–200 sccm, respectively. Fast growth rates were achieved (in excess of a micron per minute) and the growth process lasted between 1 and 5 min.

Silicon (111) and *c*-plane sapphire substrates were used. The HVPE environment and source materials determined the choice of the catalyst. Gold is a commonly used catalyst in VLS growth of silicon and germanium nanowires. However, gold is unsuitable for the growth of nitrides due to the very low solubility of nitrogen in it [10]. Nickel was used in this work, as nickel, iron, and cobalt have been reported to produce VLS nanowires of GaN [4, 8]. To protect nickel from corrosion by the HCl gas, a thin layer of gold was deposited over the Ni layer. Thermal evaporation was employed to deposit 1–10 nm thick Ni and Au layers. The films were patterned either lithographically or using a ‘shadow’ mask.

Scanning and transmission electron microscopy (SEM and TEM), energy dispersive spectroscopy (EDS), x-ray diffraction (XRD), and room temperature and low temperature photoluminescence (PL) were used to characterize the nanowires. Scanning electron microscopy was carried out in a LEO (Zeiss) 982 FEG-SEM field emission gun scanning electron microscope with a Noran thin-window EDS detector. TEM was performed using a JEOL 2010-FEG-TEM/STEM with an attached EDAX thin-window detector. Photoluminescence was excited using a HeCd laser (325 nm, 8 mW). The emitted luminescence was monochromatized, filtered, and sensed using a Si CCD camera.

3. Results and discussion

Growth of GaN nanowires took place only on areas covered with catalyst. The nanowires obtained were 20–400 nm thick with typical lengths of several microns. The left panel of figure 2 shows an array of photolithographically defined circular pads of catalyst particles on a Si(111) substrate, and its right panel shows that the resulting wire growth is restricted to the pads, whereas between the pads, where the catalyst was absent, no growth took place. Due to the large lattice mismatch

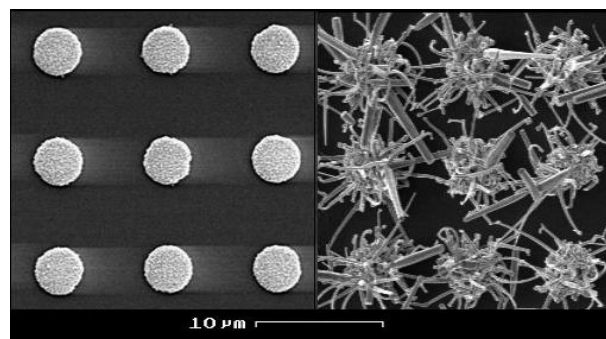


Figure 2. GaN nanowires grown catalytically by HVPE on patterned Si (right panel). The left panel shows the catalyst pattern before growth.

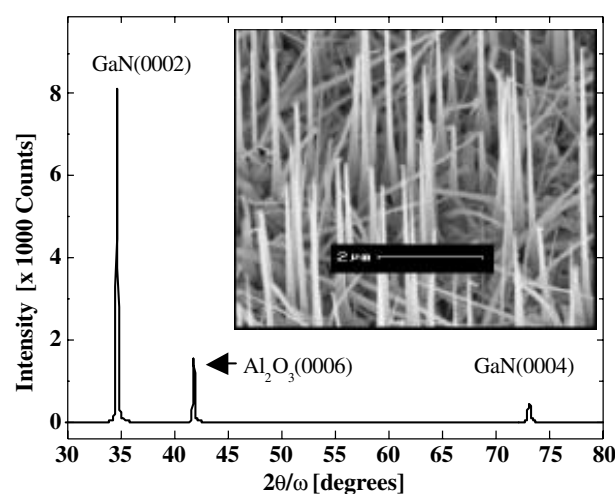


Figure 3. Symmetric 2θ – ω x-ray diffraction of oriented GaN nanowires grown on sapphire (shown in the inset).

of GaN and Si the wires do not assume a preferred orientation. Relative to other methods, HVPE growth of nanowires is fast (up to ten microns per minute), and takes place at relatively low temperatures (630–780 °C). The catalytic growth mode enables control over the growth site which can be defined to submicron patterns. Growth on lattice-matched substrates, such as sapphire, can control the growth well along the GaN *c*-axis (see the inset of figure 3).

Well-oriented nanowires grown on sapphire substrates were characterized by high resolution XRD. The wire thickness varied between 200 and 400 nm at the base with a slight tapering toward the tip of the wire (as determined by SEM). Figure 3 shows a typical 2θ – ω symmetric XRD scan obtained over a wide angular range. Diffraction peaks from (0002) and (0004) planes of hexagonal GaN indicate good alignment between the *c*-axes of the sapphire and nanowires. Lattice constants of $a = 3.1907 \text{ \AA}$ and $c = 5.1869 \text{ \AA}$ were calculated from separate measurements of asymmetric (11 $\bar{2}$) and symmetric (0002) reflections, for which the measured 2θ angles were 99.90° and 34.55°, respectively. The calculated hydrostatic and biaxial strain ranged from –0.13 to –0.24 GPa and from –0.01 to 0.07 GPa respectively. According to Perlin [11] and Zhao [12], this observed strain should

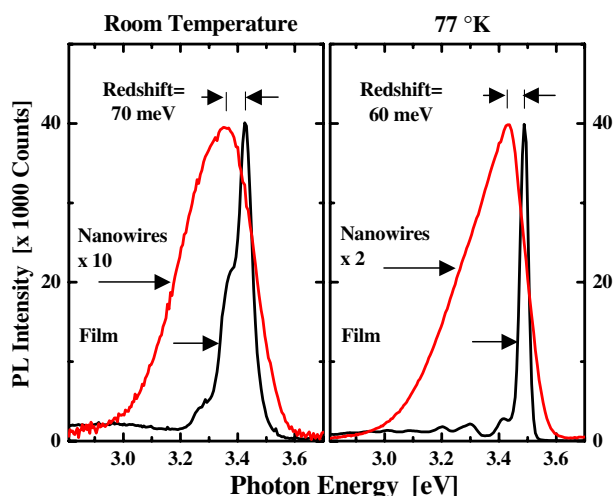


Figure 4. Comparison of PL from *film* to that from *nanowires* (both HVPE grown on sapphire) at room temperature (right panel) and at low temperature (left panel).

(This figure is in colour only in the electronic version)

narrow the energy gap by 30–40 meV. Room temperature PL measurements of our sample indeed show a red shift of the band edge emission from 3.42 eV in a reference GaN film (TDI Inc.) to 3.35 eV (70 meV; see figure 4, left panel). However, this shift is too large to be accounted for by the strain alone. Photoluminescence at a range of two orders of magnitude of laser beam power (0.08–8 mW) was used to assess the effect of local heating. However, no change in peak position with the beam intensity was observed. A slight decrease of the shift was observed at 77 K (60 meV; see figure 4, right panel). Even if this difference were totally related to a heating effect, it would still be too small to account for the entire shift. We therefore consider the red shift likely to be a superposition of several effects, possibly involving other band gap lowering mechanisms, such as a Stokes shift and defect or impurity states. Further investigation is needed to fully understand the observed red shift in nanowires grown by HVPE.

Figure 5 shows low magnification bright field and high resolution TEM images as well as a selected area diffraction (SAD) pattern. The stacking of hexagonal basal planes along the growth orientation of the wire, the [0001] direction, can be seen in the high resolution mode. The GaN nanowire exhibits a 2H hexagonal structure. The high resolution image was taken along the $[0\bar{1}10]$ direction, and the projected edge of the wire was roughly parallel to the $(\bar{2}110)$ plane. The observed broad horizontal fringes are thickness fringes, caused by natural thickening of the wire toward the middle. The presence of these fringes near the thin edge suggests that $(\bar{2}110)$ is not a strong faceting plane of the wire side. This corroborates SEM imaging of nanowires end-on which shows that the wires have a hexagonal cross-section (and all/most facets are $(1\bar{1}00)$ planes). In the lower magnification bright field image we also see thickness fringes near the wire edges. Also the wire tapers near the end. Electron diffraction from a larger selected area diffraction aperture confirms that the wires are single crystals. The diffraction pattern is of the $[0\bar{1}10]$ zone axis, and provides further confirmation of the [0001] growth orientation.

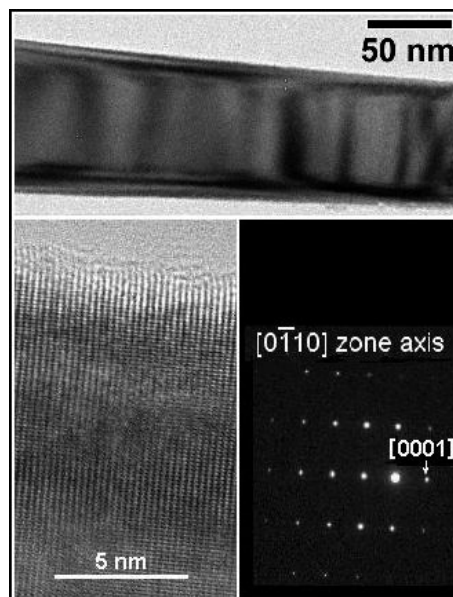


Figure 5. Top—low magnification TEM image of the middle part of a single GaN nanowire. Bottom left—high resolution TEM image of the side of the wire near the surface. Bottom right—selected area diffraction pattern (SAD).

The bright field image exhibits diffraction contrast within the wire. Most of these particular contrast features are thickness fringes due to thickness variations of the wire. However, such bright field contrast is very sensitive to defects within the wires. The only internal defects that we observed were stacking faults in the growth direction, while negligible twinning has been observed (no defects are visible in the wire imaged in figure 5). Stacking faults are common in GaN in general, and in nanowires in particular [13]. The observed tapering involves surface steps as the wire tapers. Occasionally, these surface defects become apparent when a step is larger than usual.

STEM/EDS was used to monitor Ni. Ni is detected as residual catalyst at the tips of wires grown for short growth periods of up to 2 min; however Ni is absent at the tips of wires grown for 10 min. This suggests that Ni is eventually consumed in the HVPE reaction, but the time window is probably well above the short growth period defined by the typically high growth rate of HVPE. The Ni EDS signal within the wires was negligible (<0.5 at.%).

4. Conclusion

This work demonstrates that VLS growth of quality GaN nanowires can be achieved with HVPE. While catalyst etching does pose a timing limitation, it is compensated by the typical high growth rate inherent to HVPE. These results also suggest that other compound material nanowires may be grown by HVPE.

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