porosity between grains and at the grain boundaries, where continued sintering will likely result in further crystal growth until a fully dense polycrystalline body is formed.

In contrast to MEEA-A and MEA-A, A-A has a small particle size with a high surface area/volume ratio and small organic substituent groups [CH₃CO₂]⁻ on the surface of the nanoparticles. The small size of the organic substituents results in a significantly smaller inter-particle distance between individual alumoxanes nanoparticles. Upon thermolysis, the organic surface of the A-alumoxane nanoparticle is pyrolyzed, leaving discrete alumina particles with a small inter-particle separation. As previously discussed, the high surface energy inherent in these alumoxanes allows for rapid crystallization; when combined with the small inter-particle distance, crystal growth within one particle results in crystallization of the adjacent particle. This “knock-on” or “domino” effect is somewhat akin to an epitaxial growth. The rapid sintering results in the crystallization of large groups of adjacent particles within a single body, such that the resulting crystals are macroscopic (i.e., ≤ 2 μm) in diameter. It may be expected that crystallization (and crystal growth) is sufficiently rapid so that defects or channels created by the outgassing of the pyrolysis products (e.g., primarily, CO₂, H₂O, and acetone in the case of A-alumoxane), will result in the creation of pores, and that these defects are retained in the resulting ceramic. The resulting ceramic is highly crystalline with porosity contained inside the individual crystal grains. The alumina formed from MA-alumoxane is intermediate between that formed from MEA-alumoxane and A-alumoxane. There exists both a high number of seed crystals distributed throughout a polycrystalline matrix, as well as large single crystals that are independent of the primary matrix material. It is likely that the seed crystals will form larger crystal domains upon further sintering.

Carboxylate-alumoxanes are novel, environmentally benign precursors for developing alumina bodies and films with controlled porosity. The pore size and pore size distribution is influenced by the selection of the organic substituent on the nanoparticle surface, while the average pore sizes may be altered through either physical or chemical mixtures of two (or more) carboxylate-alumoxanes. This has applications especially in advanced ceramic materials in that pores located between crystal grains, and especially at the grain boundaries, encourage crack propagation which increases the opportunity for catastrophic failure. However, pores isolated inside crystal grains provide less opportunity for detrimental pore/boundary/crack interactions to occur, and may therefore provide a mechanism to increase fracture toughness.

**Experimental**

MEEA-, MEA-, MA-, and A-alumoxanes were prepared as described previously [9]. Transmission electron microscopy was conducted at 200 kV on a JEOL 2010 TEM or a JEOL2010 field emission transmission electron microscope (FETEM). Thin specimens were produced for TEM analysis using the following preparation method: embed in epoxy (EpoTek, 10 resin:1 hardener) and cure on aluminum foil on a laboratory hot plate at 70 °C. Remove from foil and attach to a glass slide using thermoplastic wax (m.p. ≥ 130 °C). Mechanically thin both sides of the using sandpaper with successively finer grit until specimen thickness is determined < 100 μm with a micrometer. Remove from slide by melting the wax, and rinse excess wax from the sample using acetone. Sindle to remove grit. Attach to metal stub with wax and dimple grind (Gatan Precision Dimple Grinder model 658) to < 20 μm using 2–6 mm diamond paste. For final thinning and polishing, a felt wheel and fine grit diamond paste and/or alumina slurry is used. Remove specimen from stub and rim with acetone. Attach to TEM grid using epoxy (EpoTek) and ion mill (Gatan DuoMill, 12 kV) to electron transparency.

In order for a comparison of the effects of chemical substitution, all processing was consistent for all experiments. The carboxylate-alumoxane (5.0 g) was heated from 25 °C to 225 °C at the rate of 2 °C/min⁻¹, soaked for 30 min at 225 °C, followed by a temperature ramp up to 300 °C at the rate of 2 °C/min⁻¹, and soaked for 30 min, with a final ramp to the maximum temperature of 1100 °C at the rate of 10 °C/min⁻¹, which was then maintained for 6 h. The one exception is for MA-alumoxane, where the final sintering time was 3 h instead of 6 h.

Received: December 22, 1999


**Large-Scale Catalytic Synthesis of Crystalline Gallium Nitride Nanowires**

By Chia-Chun Chen* and Chun-Chia Yeh

Nanometer-scale gallium nitride one-dimensional structures (GaN nanowires or nanorods) are known to have great prospects in fundamental physical science and novel...
nano-technological applications.\[1\] Because of the large bandgap and structural confinement of GaN nanowires, for example, the fabrication of visible and UV optoelectronic devices with relatively low power consumption is potentially feasible.\[2\] Although GaN nanorods have been prepared on a small scale using carbon nanotubes as a template,\[3\] to our knowledge, no report of large-scale preparation of GaN nanowires has been made so far. Here, we describe a simple method for large-scale production of GaN nanowires, by reacting gallium and ammonia using polycrystalline indium powder as a catalyst. This new synthetic technique opens up possible applications of the nanowires for high-efficiency optoelectronic devices.

The vapor–liquid–solid (VLS) crystal growth mechanism has been widely used for the syntheses of fiber-like semiconductors of InP, InAs, GaAs, and silicon.\[4\] The main feature of this mechanism is the presence of intermediates that serve as catalysts between the vapor feed and the solid growth at elevated temperatures under chemical-vapor-deposition conditions. VLS growth should be a practical route for the syntheses of one-dimensional nanometer-sized structures (i.e., nanowires and nanorods) provided that the diameters of the resulting fiber-like structures can be controlled within the nanometer range. The most important parameter in VLS growth is the catalyst added in the reaction. Gold metal has been commonly used as a catalyst for the syntheses of micrometer-scale II-VI and III-V semiconductor fibers in the VLS process.\[5\] Recently, In or Ga/In flux has also been found to serve as an intermediate for the syntheses of InP, InAs, or GaAs fibers or whiskers with widths of 10–150 nm, via solution–liquid–solid crystal growth.\[6\] In our work, we found that elemental indium, but not gold,\[7\] was an ideal catalyst in the reaction of gallium and ammonia to form GaN nanowires. Although the detailed mechanism on ternary phase diagrams of In–Ga–N is still not fully understood, we suggest that very small miscible droplets of In–Ga–N may be generated rapidly during the heating process of the reaction and hence act as nucleation sites in the VLS growth of GaN nanowires (as reported in this work).

A typical scanning electron microscopy (SEM) image (Fig. 1) showed that the material resulting from the reaction of Ga and NH\(_3\) in the presence of In powder, produced a high yield of nanometer wire-like structures (nanowires). These nanowires were distributed over a certain area of the substrate and had uniform diameters. The diameters of the nanowires ranged from 20 to 50 nm and the lengths between two entanglement points were up to several micrometers. The yield of the nanowires (with respect to the total amount of solid material observed in SEM images) was estimated to be greater than 95 %. The residual material on the substrate was almost all nanoparticles.

The X-ray diffraction (XRD) pattern (Fig. 2) revealed the overall crystal structure and phase purity of the nanowires. The sharp diffraction peaks in the pattern can be indexed to a hexagonal wurtzite structure with lattice constants of \(a = 3.188\) \(\text{Å}\) and \(c = 5.180\) \(\text{Å}\), which agree well with the reported values of GaN bulk crystals.\[8\] The strong intensities of the GaN diffraction peaks relative to the background signal indicated that the resulting product had high purity of the GaN wurtzite phase. In comparison with the (002) and (101) peaks, the stronger intensity of the (100) peak suggested that the [100] direction was aligned along the wire axis. This was further confirmed by high-resolution transmission electron microscopy (HRTEM) data, as described below. In addition, the stronger (100) peak also suggested that the crystal growth direction of nanowires was mostly perpendicular to the substrate in the initial growth period, as observed in the SEM images (not shown).

The TEM images of a single GaN nanowire provided further structural information about this material. The bright-field TEM image showed that a linear segment was
crystalline with a uniform diameter of 40 nm (Fig. 3a). The HRTEM image (Fig. 3b) was recorded along the \( \langle 001 \rangle \) zone axis. The clear lattice fringes in this image indicated a single crystal structure of the nanowire. In this image, the \([100]\) direction was parallel to the long axis of the wire, indicating that the \([100]\) direction is a common growth direction in GaN nanowires. Selected-area electron diffraction patterns of the same nanowire recorded from \([001]\) and \([100]\) directions confirmed that it was a single crystal, and that the electron diffraction patterns (Fig. 3c and 3d) were indexed to the reflection of hexagonal GaN crystals, which was consistent with the XRD measurement.

A typical small-scale SEM image (Fig. 4) of a single nanowire provided further details of VLS growth in GaN nanowires. This image showed a long nanowire terminating in a nanoparticle at the tip. The energy dispersive X-ray spectroscopy (EDX) analyses indicated that the nanoparticle on the tip mainly consisted of In, Ga, and N, but that the nanowire was only composed of Ga and N. The molecular ratio of Ga/N of the nanowire calculated from the EDX data was close to that of a bulk GaN crystal. In addition, faceted structures of nanoparticles were observed in the TEM images. These data from SEM, EDX, and TEM analyses altogether were consistent with the proposed mechanism of VLS growth similar to that of other systems \([4]\) indicating that indium only functioned as a catalyst in GaN nanowire growth.

Figure 5 shows the photoluminescence spectrum of bulk GaN nanowires. With a He–Cd laser excitation at 325 nm, a band-edge emission at 380 nm, and a defect band emission at 630 nm were observed. The band-edge emission was in agreement with that of the bulk GaN crystals \([9]\).
which further confirmed the formation of GaN nanowires in our experiment. Several reports have indicated that the defect band emission of bulk GaN crystals may be attributed to the Ga or N vacancies or a related complex.[10]

We describe a method for obtaining large quantities of high-purity crystalline GaN nanowires via VLS growth using indium metal as a catalyst. The resulting nanowires have a preferred [100] growth direction. The strong photoluminescence of the nanowires in the UV region suggests possible applications in nanotechnological optoelectronic devices. Further studies on optimization of the synthetic parameters, such as heating rates and heating times to control the diameter of the nanowires and highly oriented selective area growth, are underway.

Experimental

A silicon wafer or a quartz plate was used as a substrate for the growth of gallium nitride nanowires. The substrates were cleaned by a standard treatment (concentrated NH₃ solution (90%), H₂O, 70% H₂SO₄) and rinsed with deionized water before use. Molten gallium (0.5 mL, 99.9999 %, Stream Chemicals) was placed on the substrates. A suspension (0.15 mL) was prepared by adding powdered indium (20 mg, 99.9999 %, 60 mesh, Stream Chemicals) to toluene (2 mL). This mixture was sonicated and then immediately dispersed onto the substrate. After toluene was evaporated, the substrate was transferred into a quartz tube placed in a furnace. The quartz tube was degassed under vacuum and purged with ammonia. The temperature of the furnace was increased to 910 °C from room temperature at a rate of 50–100 °C/min and kept at 910 °C for 12 h under a constant flow (18 scem) of ammonia. After the furnace was cooled to room temperature, gray-black material was found on the surface of the substrate. The morphologies and crystal structures of the resulting materials were characterized using SEM (Hitachi, S2400 instrument) and XRD (Toshiba, A-40-Cu). Further structural and elemental analyses of a single nanowire were performed using TEM (Hitachi, S2400 instrument) and XRD (Toshiba, A-40-Cu). Further structural and elemental analyses of a single nanowire were performed using TEM (Hitachi, S2400 instrument) and XRD (Toshiba, A-40-Cu).

[7] No nanowires were observed on the substrate according to SEM analyses when gold nanoparticles were used. This may be because of the poor solubility between gold and nitrogen (T. B. Massalski, Binary Al-loy Phase Diagrams, Vol. 1 (Ed: W. W. Scott Jr.) ASM, Metals Park, OH 1986, p. 283).


Photonresponsive Dendritic Monolayers**

By Jan-Willem Weener and E. W. Meijer*

A number of papers have appeared in the last few years in which the molecular organization in Langmuir–Blodgett (LB) mono- and multilayers has been exploited to obtain photoresponsive surfaces.[1–3] Azobenzene derivatives are candidate materials for application in the areas of optical information storage and optical switching systems, due to their facile and reversible photoisomerization characteristics.[4–6] However, in LB films the azobenzene chromophores are usually aggregated, a phenomenon that suppresses the photoinduced cis–trans isomerization.[7–9] Different molecular engineering approaches have recently been put forward to circumvent this difficulty. All of these approaches can broadly be divided into two main categories: low molecular mass amphiphiles[8,10–15] and polymeric materials.[16–19] Polymers are attractive due to the fact that the polymer backbone prevents film damage in subsequent isomerization cycles through self-healing of the monolayer.[20] A major drawback of photoactive polymer systems is, however, that their composition is not well defined, due to the polydispersity of the macromolecules.

Dendritic macromolecules are considered promising as uniform building blocks in the construction of functionalized interfaces.[21] Recently, we reported on the synthesis of poly(propylene imine) dendrimers modified with apolar alkyl chains (Fig. 1), which were found to form stable LB monolayers.[22] These amphiphilic dendrimers are, with a dispersity of 1.002 and a branched architecture, highly defined.[23] In this communication, we present a novel photoresponsive LB film based on the fifth generation