Highly Aligned Arrays of GaN Nanowires Achieved via Selection of Substrate Orientation, Catalyst Concentration, and Growth Temperature

by **George T. Wang, J. Randall Creighton, A. Alec Talin, and Don Werder**

Motivation—A lack of understanding of vapor-liquid-solid (VLS) based nanowire growth has frustrated rational approaches for controlling size, optical and electrical properties, and morphology. In particular, the ordered growth of vertical nanowire arrays with controlled density, uniformity, anisotropy, and coupled interactions is of interest for potential novel device applications.

Accomplishment—We have demonstrated the growth of dense, highly aligned arrays of single crystalline GaN nanowires on untemplated, unpatterned r-plane (1-102) sapphire substrates via VLS catalyzed metal-organic chemical vapor deposition (MOCVD). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis indicate that the nanowires share a common [11-20] growth direction and have aligned facets. This growth direction is the same as the observed (11-20) GaN film growth on r-plane sapphire, with a relatively low in-plane lattice mismatch of 1.15% in the [0001] GaN direction, leading to ordered, vertical growth. In contrast, nanowires grown on c-plane (0001) sapphire also most commonly exhibit a [11-20] growth direction, rather than the [0001] growth direction observed for film growth, and do not exhibit a high degree of ordering.

Interestingly, we find that the degree of alignment and size uniformity is highly dependent on the catalyst concentration applied to the substrate. Optimal density, alignment, and size uniformity occurs when the $Ni(NO_3)_2$ concentration is ~20 times more dilute than typically used for VLS-based nanowire and carbon nanotube growth, as shown in Fig. 1. Additional experiments show that the average catalyst nanocluster size decreases and size uniformity increases with decreasing catalyst concentration, suggesting orientation is dependent on particle size. Surprisingly, analysis shows that the majority of the aligned nanowires grown on r- plane sapphire do not have a catalyst droplet at the tip (Figs. 1 and 2), in contrast to GaN nanowires grown on c-plane sapphire and SiO_2, even though the presence of catalyst is necessary for nanowire growth. Further investigation of this observation is underway.

The effect of growth temperature on nanowire properties was also studied. Characterization using a Sandia-developed platform reveals that nanowires grown at 900 °C show a greater than 50 times increase in the absolute band edge peak intensity (Fig. 3) and approximately three orders of magnitude lower resistivity versus those grown at 800 °C. We propose that these effects are caused by increased carbon incorporation as the nanowire growth temperature is decreased.

Significance—The ability to use inexpensive, large area, and process compatible sapphire wafers for the growth of aligned, vertical arrays of GaN nanowires by MOCVD and without the use of templates or patterning represents an important step towards realizing devices based on vertically integrated III-nitride nanowires. Our results suggest that the alignment of VLS-grown nanowires may be influenced not only by substrate orientation, but also by catalyst particle size. Additionally, we find that the growth temperature is a critical factor for controlling the nanowire properties, due most likely to its effect on impurity incorporation.

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Contact: George T. Wang, Advanced Materials Sciences, Dept. 1126
Phone: (505) 284-9212, Fax: (505) 844-3211, E-mail: gtwang@sandia.gov

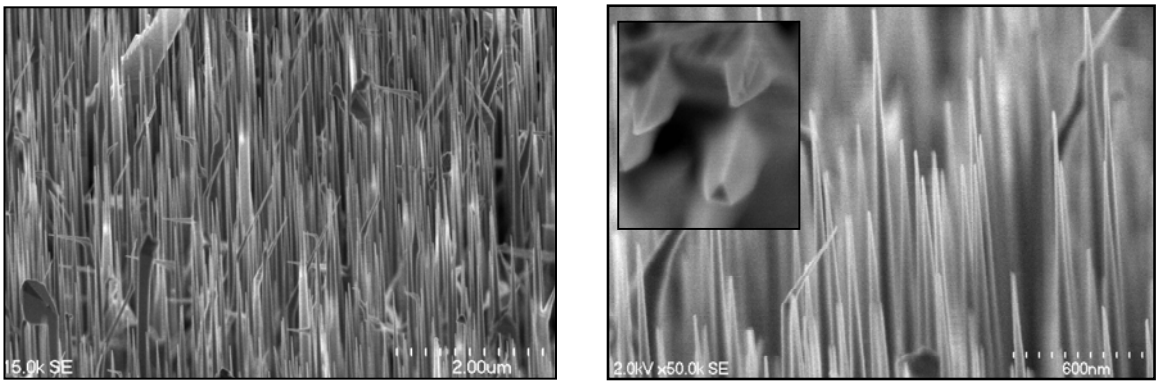

Figure 1. SEM images of highly aligned GaN nanowires grown on r-plane sapphire at 800 °C using 0.0005 M nickel nitrate solution. Inset shows that facets of different wires are aligned.

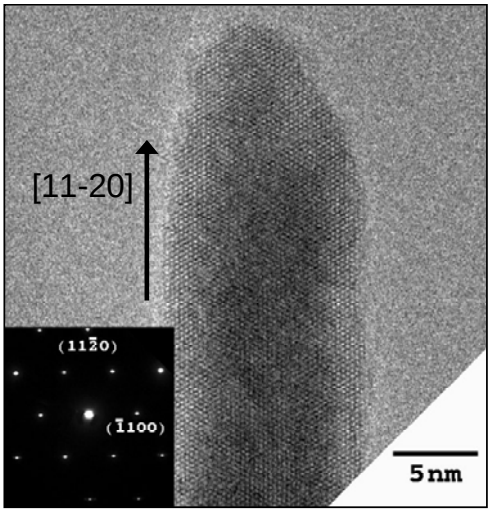

Figure 2. High resolution TEM image and selected area electron diffraction (SAED) patterns (inset) of single crystalline GaN nanowire grown at 800 °C. Note lack of catalyst nanocluster at tip.

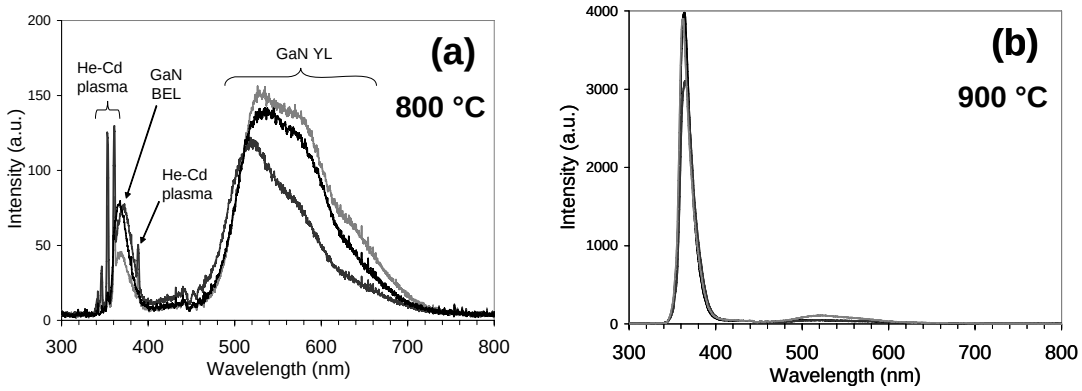

Figure 3. Representative photoluminescence (PL) spectra of GaN nanowires grown on r-plane sapphire at (a) 800 °C and (b) 900 °C.