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Comparison of GaN nanowires grown on *c*-, *r*- and *m*-plane sapphire substrates

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ABSTRACT

Gallium nitride nanowires were grown on *c*-plane, *r*-plane and *m*-plane sapphire substrates in a showerhead metalorganic chemical vapor deposition system using nickel catalyst with trimethylgallium and ammonia as precursors. We studied the influence of carrier gas, growth temperature, reactor pressure, reactant flow rates and substrate orientation in order to obtain thin nanowires. The nanowires grew along the $\langle 10\bar{1}1\rangle$ and $\langle 10\bar{1}0\rangle$ axes depending on the substrate orientation. These nanowires were further characterized using x-ray diffraction, electron microscopy, photoluminescence and Raman spectroscopy.

1. Introduction

Gallium nitride (GaN) nanowires (NWs) have been of interest for nanoscale photonic [1–8] and electronic [9–12] applications. The growth of GaN NWs by catalyst mediated [9,10,13–16] as well as catalyst free [6,17–19] methods have been reported. Unlike InAs, where $\langle 111\rangle$ oriented wires are usually obtained [20–22], III-nitride NW growth has been observed along different crystal directions and is strongly dependent on growth conditions, the substrate and its orientation.

In most of the reports of GaN NW growth, the axis along the nanowire length (or the growth direction) is along either the polar $\langle 0001\rangle$ direction (i.e. *c*-axis) or the non-polar directions $\langle 11\bar{2}0\rangle$ (*a*-axis) and $\langle 1\bar{1}00\rangle$ (*m*-axis). The most common substrates used for GaN NW growth are (0001) *c*-plane sapphire, $(1\bar{1}02)$ *r*-plane sapphire, (111) silicon and (100) silicon. On *c*-plane sapphire by metalorganic chemical vapor deposition (MOCVD), Gottschalch et al. [13] reported the growth of vertical wires growing along *c*-axis using gold as catalyst, while Ji et al. [23] obtained wires growing along the *a*-axis with nickel catalyst. On *r*-plane sapphire using nickel-catalysed MOCVD, Zhou et al. obtained wires tilted on the substrate and growing along *m*-axis [14]. On the other hand, Wang et al. [15] and Qian et al. [4] reported the growth of NWs along the *a*-axis on *r*-plane sapphire with nickel catalysed MOCVD. Kuykendall et al. obtained *a*-axis oriented wires on *r*-plane sapphire via MOCVD. They also showed that the orientation of the NWs can be controlled using the composition of Au-Ni as catalyst. Ni-rich catalyst gave *a*-axis wires while gold rich catalyst resulted in *m*-axis wires [24]. Compared to growth of GaN NWs on *c*-plane and *r*-plane sapphire there are lesser reports about growth on *m*-plane sapphire, and hardly any on Ni-catalysed GaN NW growth. The growth of inclined GaN nanorods on *m*-plane $(1\bar{1}00)$ sapphire as substrate without any foreign catalyst by MOCVD was reported recently along the *c*-axis [19,25,26].

There are very few reports on the growth of GaN NWs along semipolar directions. On sapphire substrates using MOCVD Kuykendall et al. obtained, along with a majority of wires growing along nonpolar directions, a few wires along $\langle 10\bar{1}4\rangle$ and $\langle 11\bar{2}2\rangle$ when using gold catalyst and $\langle 11\bar{2}2\rangle$ while using nickel or iron [27]. The growth along the semi-polar $\langle 10\bar{1}1\rangle$ direction has been reported on *c*-plane sapphire by Park et al. by reaction of metallic Ga and gaseous NH_3 using nickel as catalyst [28].

There are hardly any reports that compare the growth axis on different planes of sapphire at similar reactor conditions. Tessarek et al. obtained thick GaN wires (>200 nm) oriented along the *c*-axis via a self-catalysed method by MOCVD on different planes of sapphire substrates [25]. We report the growth of thin, nickel-catalysed, GaN NWs on *c*-, *r*- and *m*-plane sapphire substrates under identical conditions. We studied the dependence of growth direction on the substrate orientation with other growth conditions kept similar, and characterized the samples using electron microscopy, x-ray diffraction, photoluminescence and Raman spectroscopy.

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2. Growth of nanowires

GaN NWs were grown in a Thomas Swan 3 × 2 in. closed-coupled showerhead MOVPE system with nickel catalyst and trimethylgallium (TMGa) and ammonia (NH_3) as precursors. The substrates were cleaned, drop-coated with nickel nitrate hexahydrate solution (~ 0.01 M), blow-dried with N_2 gas and annealed in hydrogen to form metallic nickel nanoparticles which subsequently served as the catalyst particle [15,29]. This method to form the catalyst particles is more convenient than techniques involving evaporation of nickel or gold. The size of the catalyst particle can be controlled by the annealing time and temperature (see Supplementary Information Section 1 for details). Since the exact composition and phase (solid/liquid) of the nickel-gallium alloy that serves as the catalyst during growth is unknown, the NW growth mechanism could be either vapour–liquid–solid (VLS) or vapour–solid–solid (VSS). However, from a post-growth compositional analysis of the catalyst particle (not presented here), we believe that at the growth temperatures used in our experiments (~ 840 °C) GaN NW growth happens via a VSS process. We also tried to grow GaN NWs using gold nanoparticles as catalyst. Gold catalysed wires grew slower than their nickel assisted counterparts under similar growth conditions, similar to Zhou et al. [14].

After annealing the nickel nitrate hexahydrate coated sapphire substrates in a hydrogen environment to produce nickel nanoparticles, we could grow GaN NWs in a pure nitrogen ambient. The scanning electron micrograph (SEM) of the NWs is shown in Fig. 1(a). The wires typically had a triangular cross section (Fig. 1(b)). However, under similar reactor conditions in an H_2 ambient or in a mixture of equal volumes of N_2 and H_2, we did not obtain any wires. Instead, we obtained just hemispherical gallium droplets (Fig. 1(c) and (d)), unlike earlier reports [11].

We varied the reactor pressure, temperature and rate of flow of precursors in order to obtain thin and non-tapering NWs. The growth of NWs was sensitive to the reactor conditions. Experiments carried out at different reactor pressures between 50 torr and 200 torr (Fig. 2) showed that long thin NWs were obtained at 150 torr. At a relatively low pressure of 100 torr icecream-cone shaped structures were formed. On the other hand, a lot of wires grown at 175 torr had kinks or had a zig-zag morphology. At 200 torr there were very little NW growth, and the few that grew were highly tapered and short. Our preliminary experiments showed that NWs grow only in a small temperature window around 840 °C (thermocouple temperature).

Very low flow of precursors (7.8–9.7 μmol/min of TMGa and ~45 μmol/min of NH_3) and small V/III ratio (~ 5) was used to facilitate anisotropic growth. At large V/III ratio the growth is slower, while at low V/III ratio the NWs obtained are more tapered. (For SEM images refer Supplementary Information Section 2.) We found that a pressure of 150 torr in N_2 environment, ~ 840 °C and a low V/III ratio (~ 5) was optimum for obtaining thin non-tapering wires.

NWs were grown in the same run on different orientations of sapphire—*c*-plane, *r*-plane and *m*-plane—using these optimized conditions (Fig. 3). We find that the optimized conditions are same for all substrate orientations. Hence we believe that the NW growth itself is primarily determined by processes occurring at the catalyst tip, which depend on the reactor conditions of temperature, pressure, V/III ratio, precursor supply, etc., and is not strongly influenced by the substrate orientation. On these substrates we obtained NWs as thin as ~ 20 nm diameter with a triangular cross section. A comparison is given in Table 1. The NWs obtained on *c*-plane sapphire are narrower than the NWs on *r*-plane. On *m*-plane sapphire we see two distinct set of NWs—one which is narrow (thickness ~ 30 nm) and one which is thicker (thickness ~ 90 nm). The length of the NWs were determined by imaging cross sectional samples. Since the NWs on *m*-plane sapphire are not erect, it is difficult to measure their exact length, but they are longer than NWs grown on *c*- and *r*-plane sapphire substrates.

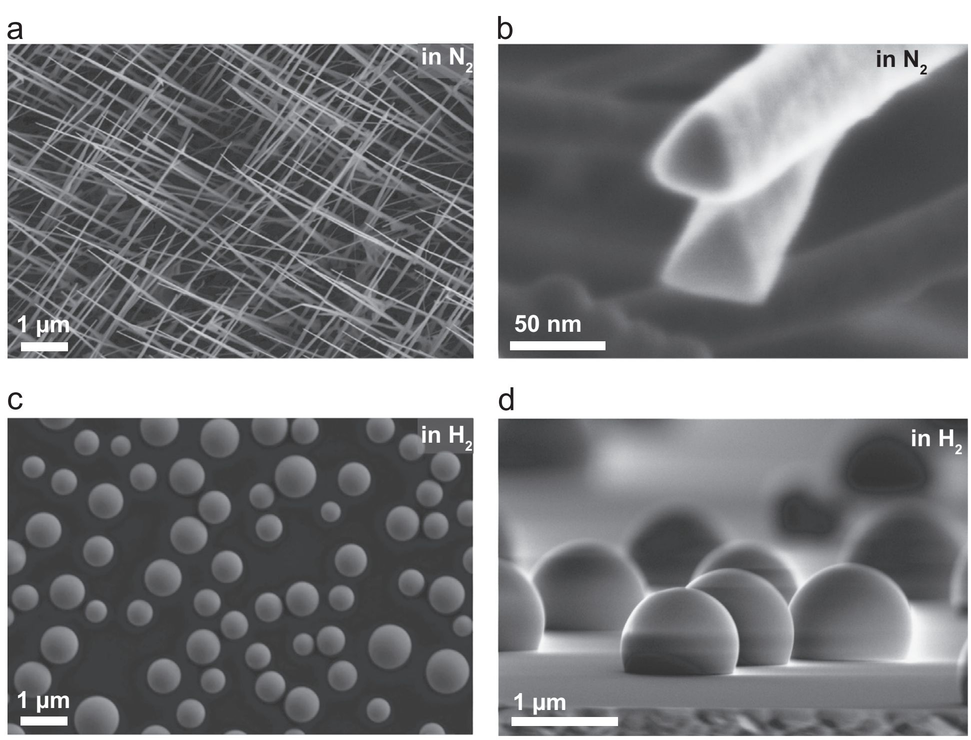

Fig. 1. *Growth of GaN NWs*: (a) GaN NWs obtained by growing in N_2 environment (840 °C and 150 torr with ~45 μmol/min NH_3 flow and 9.7 μmol/min TMGa flow, on *r*-plane sapphire). (b) Image showing that the cross section of the NWs grown in N_2 is triangular. (c) Gallium droplets obtained at similar growth conditions but under H_2 ambient. (d) Cross sectional image of the sample shown in (c). Images were taken by a Zeiss ULTRA plus microscope with a field emission gun.