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Growth of GaN nanotubes by halide vapour phase epitaxy

Carl Hemmingsson, Galia Pozina, Sergey Khromov, and Bo Monemar
*Department of Physics, Chemistry and Biology (IFM), Linköping University, S-581 83
Linköping, Sweden*

Corresponding author: Carl Hemmingsson

Phone: +46 13 282627

Mobile: +46 73 0651264

Fax: +46 13 142337

Email: cah@ifm.liu.se

Abstract

We have investigated low temperature growth of GaN nanostructures using halide vapour phase epitaxy on c-oriented Al_2O_3 and Au-coated Al_2O_3 substrates. Depending on the III/V ratio and the growth temperature, the shape and density of the structures could be controlled. By increasing the GaCl partial pressure, the structure changed from dot like to nanotubes. The nanotubes, which could be open or closed, were about 1 μm long with a diameter of typically 200 nm. In addition, it was observed that the nanostructures were spontaneously nucleated at droplets of Ga or, when using Au coated Al_2O_3 , on droplets of Au/Ga alloy. By varying the growth temperature, the inner diameter of the nanotubes could be controlled. The experimental results suggest that this approach with pre-patterned Au-coated Al_2O_3 substrates has the potential for fabrication of well-organized nanotubes with a high density.

PACS classification codes: 61.46.Fg, 78.47.Jd, 78.67.Ch, 81.05.Ea, 78.60.Hk, 81.16.Hc

Keywords : Nanotubes ;Gallium Nitride; Halide vapour phase epitaxy; Time-resolved photoluminescence; Time-resolved photoluminescence spectroscopy; Nanostructures; Nanotechnology

1. INTRODUCTION

GaN and related group III–V nitride semiconductors are getting considerable attention during the last decade due to their applications for solid lighting and optoelectronics [1-3]. GaN nanostructures, such as quantum dots, nanorods, nanowires and nanotubes have also become interesting subjects because of the wide range of potential applications in short-wavelength optoelectronic devices. One important aspect of nanostructures is that they are as small as several tens to hundreds of nanometers. For that reason it is expected that crystal strain arising from the growth on a foreign substrate will relax during growth, resulting in a reduction in dislocation density. Thus, this type of nanostructures may be used for low power optoelectronics applications on foreign substrates, or as seed crystals for producing low density templates for growth of thick crack-free GaN, which is highly desired for fabrication of GaN substrates. In addition, due to the large surface-to-volume ratio, nanostructures are interesting for various types of sensor and photocatalytic [4] applications. However, crucial to the development of GaN based nanotechnology is the creation of nanoscale building blocks of various sizes and shapes [5]. GaN nanotubes are one of the building blocks which are of high interest. In addition to fundamental interest in understanding how the size, geometry and dimensionality influences the physical properties of nanostructures, there are several interesting applications based on GaN nanotubes. One of them is nanofluidic applications [6]. By flowing a fluid or molecular species through the tube, a charge transfer between the inner walls of the tube and the flowing media can lead to a dramatic changes in the electrical conductance of the nanotube. This property could be used for applications such as solution-based transistors or highly sensitive nanotube molecular sensors. By ab-initio calculations there have also been shown that the conduction of GaN nanotubes can be modulated by an external transverse electric field [7]. These possibilities may open up new exciting applications within areas such as biochemical sensing, nanofluidics, and optoelectronics.

However, in order to realize these types of new applications, techniques for synthesis of high quality nanotubes has to be further developed.

For the synthesis of GaN based nanostructures several techniques have been used, for example, metal-organic chemical vapor deposition [8], laser ablation [9], molecular beam epitaxy [10], the sol-gel method [11], template-induced growth [12], sublimation method [13], halide vapor phase epitaxy (HVPE) [14] and conversion of amorphous gallium oxide nanotubes [15]. Among the various kinds of fabrication methods, HVPE is an attractive technique since it has the advantages of high growth rate and relatively low cost. Although the synthesis of GaN based nanostructures like nanowires has been reported the detailed growth mechanism for such structures has not been clearly understood. Control of size and position of nanowires can be achieved using a catalytic growth mode, also known as the vapor-liquid-solid (VLS) growth [16]. In this mode, the position and size of the resulting wire are defined and controlled through the placement and size of a metallic nanoparticle serving as a catalyst. VLS growth of GaN nanostructures by HVPE using an alloy of Au and Ni [17] or pure Ni [18] as a catalytic metal has been reported, but also non-catalytic growth [14] has been successfully demonstrated.

In this paper, we present results of HVPE growth of nanostructures using bare Al_2O_3 substrates or substrates coated with Au films. The nanostructures size, shape, density and the selectivity of growth have been studied depending on process parameters and substrate material. It is observed that the shape and density of the nanostructures is dependent on the partial pressure of GaCl, the choice of substrate material and the growth temperature, respectively. By varying the partial pressure of GaCl, the shape of the nanostructures could be controlled from dots to tubes with a typical diameter in the range 50-500 nm; however, smaller structures with diameters down to 15 nm have been observed. It is also found that the inner diameter of the nanotubes can be controlled by growing at different temperatures. The grown nanostructures have been characterized using scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), high resolution electron microscopy (HRTEM), scanning-transmission electron microscopy with energy dispersive spectroscopy (STEM/EDS),

cathodoluminescence (CL), X-ray diffraction spectroscopy (XRD) and low temperature time-resolved photoluminescence (TRPL).

2. EXPERIMENTAL

In the experiments, Al₂O₃ (0 0 0 1) and Au-coated Al₂O₃ (0 0 0 1) substrates were used. The Au film with a thickness of 5 nm was thermally evaporated on a sapphire wafer. The GaN growth was performed in a vertical HVPE reactor at atmospheric pressure. In this reactor, the process gases are delivered from the bottom. For additional details about the reactor geometry, see Ref. 19. The growth process of GaN can be described as a two-step process where the GaCl, which is the Ga precursor, is synthesized within the reactor by reacting HCl with liquid Ga at 725 °C. This process is very efficient and it has been estimated that about 98% of the HCl is converted to GaCl in this growth equipment [19]. The GaCl is transported to the substrate where it reacts with NH₃ according to the reaction:

The temperature of the substrate was varied in the range 480-520 °C. As a carrier gas for the precursor, we have used N₂. The NH₃ and HCl flow rate was varied in the range 0.5-2 l/min and 5-20 ml/min, respectively, and the total carrier flow including precursor carrier gases was 13 l/min. In order to estimate partial pressure of process gases at the substrate surface and assure laminar flow conditions, numerical simulations using the commercial software CFD-ACE, was done. For additional details about the simulations, see Ref. 20. Using a GaCl flow of 20 ml/min and a NH₃ flow of 1 l/min gave a V/III ratio about 0.2 at the at the substrate surface. Prior to growth, the substrate was cleaned in H₂ atmosphere during 10 min at 500 °C.

For TRPL, the optical excitation has been done with the third harmonics ($\lambda_e=266$ nm) from a Ti:sapphire femtosecond pulsed laser with a frequency of 75 MHz. TRPL measurements were performed with a Hamamatsu syncroscan streak camera with a temporal resolution of ~20 ps. The SEM and CL images were obtained with a Leo 1500 Gemini scanning electron microscope equipped with a MonoCL system from Oxford Instruments using a 1200 lines/mm grating blazed at 500 nm and

detected by a Peltier-cooled photomultiplier. This analytical microscope also has an Oxford Inca EDS to provide chemical information of the layer. Structural characterization was carried out with a Philips MRD XRD system with a $K_{\alpha 1}$ ($\lambda=1.54\text{\AA}$) radiation source operating at 45 kV and 40 mA. A $1\times 1\text{ mm}^2$ point source and a parallel plate collimator were used to analyze the diffracted radiation. Specimens for cross-section TEM were prepared by ion milling. The transmission electron microscopy images were obtained in a Phillips FEI Tecnai G2 FEG instrument operating at 200 kV.

3. RESULTS AND DISCUSSION

Figure 1 shows four SEM images of 2 samples with GaN nanostructures grown on Al_2O_3 (0 0 0 1) at 500 °C during 90 min. Using a V/III ratio of 12 [figure 1 (a), (b)], we obtain a high and uniform density of dot-like nanostructures with a typical diameter of 50-400 nm. By reducing the partial pressure of ammonia, i.e. decreasing the V/III ratio to 0.2 at the substrate surface as determined by the simulation, the density of nanostructures drops and becomes less uniform. However, what is most striking is the change of geometrical shape from a dot-like structure to tube-like. The diameter of the nanotubes in the base is typically 200 nm and is increasing at the top. The top of the tubes can terminate in two different ways, i.e. either closed or as a bowl like structure with an opening about 50 nm in radius. The length of the nanotubes is typically about 1-2 μm and they are oriented randomly without any preferential order or direction. The chemical composition of the nanotubes was studied by EDS measurements and it confirmed a stoichiometric composition of the GaN nanotubes.

In order to study the temperature dependence of the growth, runs at different temperatures were done. Figure 2(a)-(c) shows nanotubes grown with a V/III ratio of 0.2 at temperatures 480 °C, 500 °C and 520 °C, respectively. It is interesting to see how the shape is changing with the growth temperature. Synthesis at 480°C results in nanotubes with a wall thickness about 50 nm. By increasing the temperature to 500 °C, the wall becomes thicker (~100 nm) and many of the tubes are closed. At a temperature of 520 °C, no growth is observed. Thus, the temperature window for growth of nanotubes on Al_2O_3 is narrow. The outer diameter of the tubes is almost constant while the inner diameter varies. Judging from the spiral like appearance of the top of the structures, as can be seen in figure 2 (d) and

(e), it is suggested that the nanostructures formation obeys a spiral-like growth mode with a hollow core and the radius of the hollow core was found to reduce by increasing the growth temperature.

By growing on Au-coated Al_2O_3 substrates, the density of nanostructures becomes higher. Figure 3 (a-b) shows the result of 90 min growth of nanostructures at 500 °C on an Al_2O_3 substrate with a 5 nm thick Au film. The V/III ratio at the surface was 0.2. While the density of nanostructures has increased, the nanotubes turn out to be shorter, typically between 750 nm to 1 μm . However, the diameter, about 100-200 nm, is similar to the diameter obtained without Au coated substrates. In areas where the Au was absent, practically no growth of nanostructures took place as shown in Fig 3. (a) where the black contrast in the SEM image corresponds to an area without Au. By studying broken nanostructures it was revealed that the core of the structure is open. Figure 3 (c) shows a broken nanostructure grown at 480 °C. From this image, we observe that the nanostructures are nanotubes with a closed top. The wall thickness of the tubes were estimated from SEM images to be about 35 nm. For tubes grown at higher temperatures (500 °C), the wall thickness was increased to about 75 nm. Thus, the tube wall thickness increases with increasing temperature. This is a similar behavior as we observed for nanotubes grown without Au.

In order to further investigate the nucleation mechanism using Au, a 5 nm-thick Au-coated Al_2O_3 substrates were annealed at 500 °C and pre-treated in the same way as before growth of nanotubes. The SEM image in figure 3 (d) shows the result of such treatment. The Au forms droplets with a density similar to the density of nanotubes. Thus, this result suggests that Au droplets work as an initiator to growth. In the VLS mechanism, the growth is promoted by a metallic particle serving as a catalyst and after growth the structures normally end with a metallic tip. In our case, no Au droplet was observed in SEM, and after the growth time exceeding 30 min no Au could be detected by EDS measurements using SEM. However, from cross-sectional STEM/EDS measurements of the tubes, we have observed traces of Au in the walls of the nanotubes. Thus, it means that the Au is practically completely consumed during the growth process and is essentially important for the initial nucleation process of the nanotubes.

Figure 4(a) and 4(b) shows cross sectional low magnification TEM and high resolution TEM (HRTEM) images of a nanotube section, respectively, grown at 480 °C with a V/III ratio of 0.2 on a Au coated sapphire substrate. From fig. 4(a), the hollow core of the structure is revealed. The outer and inner diameter of the studied section is varying in the range 105-90 nm and 60-40 nm, respectively. Figure 4(b) shows HRTEM micrograph of the wall. From the Fourier transform of the micrograph (FFT), shown as an inset of fig.4 (b), we observe several peaks in the pattern which indicates that the nanotubes consists of different nanocrystalline phases.

Figure 5 demonstrates a possible growth mechanism of GaN nanostructures. The starting layer is a 5 nm-thick Au film on a sapphire substrate (figure 5 (a)). Upon heating to the growth temperature, nanodroplets of Au are formed as depicted in figure 5(b). After the GaCl is introduced (figure 5(c)), the Au droplets converts to an alloy of Au and Ga and nanotubes are grown assisted by the droplets which are acting as catalysts. As the growth continues, the Au in the droplet gets depleted, and finally, only Ga is left (figure 5(d)). Despite that the STEM/EDS measurements have revealed traces of Au in the nanotubes, we can not rule out that some of the Au is transported away as volatile AuCl_x due to a reaction with the HCl which is released in the growth process according to reaction (1). To prevent solidification of the droplet, a very Ga-rich growth condition is required. In case of growth on Al_2O_3 substrate with no Au film, Ga droplets are formed spontaneously on the substrate.

The tube like shape may be explained, as a first approximation, by a simple model based on diffusion-limited growth, see fig 5 (e). The driving force for growth of the nanotube is supersaturation within the droplet, which is established by catalytic absorption of the gaseous reactants from the surroundings. If the growth rate at the liquid-solid interface is larger than the rate of diffusion of N atoms in the droplet, the concentration of nitrogen depletes with decreasing distance to the core of the nanotube. As a result of this, a ring-shaped growth front at the solid-liquid interface is formed which will result in a hollow core. At increasing growth temperatures, the diffusion rate of nitrogen in the droplet and the decomposition rate of NH_3 increases. This will result in a higher concentration of N in the surrounding and in the droplet, and consequently, supersaturation of N can be maintained closer to the center of the tube which give rise to thicker walls, as was experimentally observed in Fig. 2.

Similar growth models for nanotubes have previously been suggested for other materials such as GeO₂ [21], InP [22] and MgO [23].

In order to investigate the optical properties of the nanotubes, low temperature TRPL studies were performed on samples grown on a 5 nm thick Au film on sapphire grown at 480 °C (wall thickness ~35 nm) and for comparison on nanotubes grown at 500 °C with thicker walls (~75 nm). The TRPL measured at 5 K [figure 6 (a)] shows for these samples a broad emission band in the range of 320-360 nm with contributions both from a fast and a slow recombination process. Detailed analysis of the PL decay curve is presented in figure 6 (b). By fitting the experimental decay curves assuming a bi-exponential decay law, the fast and the slow recombination times were determined. The fast component was about 30 ps and 45 ps for samples with wall thickness ~35 nm and ~75 nm, respectively, while the slow component was 2 ns in both cases.

To clarify the origin of the observed two recombination processes, the time-resolved PL spectra are plotted in figure 7 for a sample with wall thickness ~35 nm at three different delay times, corresponding to the maximum PL intensity (0 s), after the fast decay (30 ps) and after 1.4 ns delay time. The PL emission peak is rapidly shifted to the higher energy from 3.47 eV to 3.75 eV within a very short time of 30 ps. We can conclude from this observation that the fast decay process is associated with photoluminescence peaking at 3.47 eV, which corresponds to the near band gap luminescence in GaN [24]. Due to a very short lifetime it is a very small contribution of the GaN-related emission to the time-integrated PL spectrum, which is dominated by the slow 3.75 eV emission band. The observed dependence of the fast PL decay time related to the recombination in GaN on the wall thicknesses can be explained by non-radiative surface recombination processes. Since nanotubes possess a large surface with respect to their volume the influence of surface recombination can be significant for the carrier lifetime in nanoparticles [25]. By reducing the wall thickness, the surface to volume ratio increases, and consequently, the carrier lifetime drops in correlation with experimental observations. The PL decay time for the GaN-related transition is also in agreement with TRPL studies by Tackeuchi *et. al.* [26] for GaN nanorods grown with HVPE on Si substrate, where, however, the only emission related to the donor-bound excitons in GaN at 3.46 eV was observed. This

PL band demonstrated contributions of both a fast and a slow decay mechanism. The fast decay with a lifetime of ~ 9 ps corresponds well to our observations and was attributed to non-radiative surface recombination.

The origin of 3.75 eV in the sample is rather intriguing and should be discussed. Note here that the underlying Al_2O_3 substrate does not give any luminescence in the measured range as was controlled by separate luminescence measurements. To investigate the 3.75 eV emission in more detail, low temperature spatially-resolved CL analysis were performed on the sample with nanotubes. Figure 8(a) shows a SEM image of the sample having regions with and without nanotubes. Areas without nanotubes are formed where the Au film is absent before growth, i.e. in this case a scratch. The monochromatic CL image (figure 8 (b)) measured at a photon energy ~ 3.75 eV shows exactly the same region of the sample. The CL spectrum in figure 8 (c) is dominated by a broad fluorescence with a maximum at ~ 3.75 eV, which is the same luminescence band observed in the time-integrated PL spectrum presented in the insert of figure 6 (b). As it can be clearly seen from comparison of SEM and CL images, we observe a strong luminescence signal in areas without nanotubes (corresponds to the brighter contrast in the CL image). Thus, the 3.75 eV emission with a relatively slow PL decay time is not related to the GaN nanotubes, but to the interface underlayer which is formed on the substrate during the growth.

Figure 9 shows a (ω -2 θ) XRD scan from a sample grown with a V/III ratio of 0.12 on a Au coated $\text{Al}_2\text{O}_3(0001)$ substrate. The spectrum is dominated by the strong (0006) sapphire line originating from the substrate. However, we also observe a weak and broad peak at $\sim 34.7^\circ$. This feature could be associated to the (002) peak of strained GaN, but we can not rule out that the peak originates from other materials.

It is well known that sapphire which is exposed to ammonia at elevated temperatures forms a thin layer of AlN since the oxygen atoms in the sapphire can be exchanged by nitrogen atoms from the ammonia [27]. Thus, one may expect formation of a thin film containing Al and N during growth. Assuming that the 3.75 eV luminescence observed in PL and CL corresponds to near bandgap luminescence from an AlGaN layer, which have been spontaneously grown at the interface to

substrate. The peak emission energy corresponds to the AlGaN alloy with an Al content about 8 %. With that Al content the (002) AlGaN reflection peak in the XRD spectrum should be at $\sim 34.7^\circ$ which is in good agreement with our observation. However, we can not exclude other possible explanations of the 3.75 eV peak, for example such as a formation of gallium oxynitride which has a XRD peak position for the symmetric (006) reflection at 34.63° [28]. The optical properties of gallium oxynitride are poorly known; however, from theoretical calculations it has been shown that the band gap depends on composition and phase. For the spinel- $\text{Ga}_3\text{O}_3\text{N}$ phase, the energy gap may be very similar to GaN [29] and density-functional calculations of the γ -phase of the Ga-O-N system as a function of GaN content has predicted a variation of the band gap from 2.9 eV for $\gamma\text{-Ga}_3\text{O}_3\text{N}$ to 3.5 eV for $\gamma\text{-Ga}_2\text{O}_3$ [30]. Density-functional calculations typically underestimates the band gap with 20-50%, thus, the measured photoluminescence peak energy of 3.75 eV might be expected for near bandgap transitions in oxynitrides.

4. SUMMARY

We have successfully synthesized GaN nanotubes using HVPE. It was shown that nanotubes growth could be performed both on Al_2O_3 substrates coated with and without Au films. Using Au coated Al_2O_3 , the density of nanotubes was increased. From EDS measurements it was concluded that the nanotubes consisted of stoichiometric GaN and by TEM measurements, it was revealed that the nanotubes are polycrystalline. A growth model has been suggested, and in this model the nanotubes are nucleated at droplets of Ga or an Au/Ga alloy. The growth is governed by diffusion-limited growth in the droplet which will give rise to a ring-shaped growth front at the solid-liquid interface. By changing the growth temperature, it was found that the radius of the inner diameter could be controlled. From TRPL measurements, we observe two broad recombination bands having different peak positions at ~ 3.47 and ~ 3.75 eV, respectively. These two emissions demonstrate different recombination rates. The PL line at 3.47 eV with a fast decay time is associated with excitonic recombination in GaN nanotubes while the PL at 3.75 eV having a slow decay time is related to the underlayer spontaneously formed at the interface to the substrate during the growth. The fast PL decay

time is dependent on the nanotube wall thickness and it was suggested that the lifetime is governed by non-radiative surface recombination processes. Considering results from XRD and CL, the luminescence at ~3.75 eV is likely related to the near bandgap transitions in the thin $\text{Al}_{0.08}\text{Ga}_{0.92}\text{N}$ layer unintentionally synthesized at the Al_2O_3 interface; however, the possibility of the gallium oxynitride layer formation or strained GaN can not be excluded.

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Figure captions

Figure 1. SEM images of GaN nanostructures grown at 500 °C on sapphire using (a,b) a V/III ratio of 12 and (c,d) a V/III ratio of 0.2.

Figure 2. SEM images of GaN nanostructures grown with a V/III ratio of 0.2 on Al₂O₃ substrates with a 5 nm thick Au film at (a) 480 °C, (b) 500 °C and (c) 520 °C. (d) and (e) are magnified images of nanotubes grown at 480 °C and 500 °C, respectively.

Figure 3. (a-c) SEM images of GaN nanotubes grown at 500 °C with a V/III ratio of 0.2 on Al₂O₃ substrates with a 5 nm thick Au film. (d) SEM image of Au coated Al₂O₃ substrates after annealing at 500 °C in a similar atmosphere as before growth of nanotubes.

Figure 4. (a) Cross sectional TEM micrographs of a GaN nanotube grown at 480 °C and (b) HRTEM images of the nanotube wall. The fourier transform (FFT) of the HRTEM micrograph is shown as an insert.

Figure 5. A schematic illustration of the formation process of GaN nanotubes: a) substrate before growth; b) formation of Au droplets upon heating to growth temperature; c) initial growth of GaN nanotubes using an Au/Ga alloy as catalyst; d) continuous growth of nanotubes using Ga droplets as catalyst; e) Cross sectional image of a nanotube illustrating the diffusion limited growth process. The N concentration in the Ga droplet is schematically depicted with the grey scale (darker indicates higher N concentration).

Figure 6. (a) TRPL image measured at 5 K and (b) PL decay curves of nanotubes with 35 nm thick wall ($\tau_f \sim 30$ ps) and with 75 nm wall ($\tau_f \sim 45$ ps). The insert in (b) shows the time integrated PL spectrum.

Figure 7. Low temperature time-resolved PL spectrum measured at the delay time 0 s, 30 ps and 1.4 ns after the end of the excitation pulse.

Figure 8. (a) SEM image of nanotubes grown on a Au coated Al_2O_3 substrate with a V/III ratio of 0.2; (b) low temperature monochromatic CL image at 340 nm and (c) low temperature CL spectrum of the same region as in (a).

Figure 9. ω - 2θ scan of nanotubes grown on Au(5nm) coated sapphire with a V/III ratio of 0.2 at $T = 500^\circ\text{C}$.

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