

Growth of One-dimensional Gallium Nitride Nano- and Microstructures in an Alumina Matrix Containing Gallium Oxide

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Nanostructures of gallium nitride (GaN) with a direct bandgap of 3.4 eV are of interest because of their great prospects in fundamental physical science, novel nanotechnology applications, and significant potential in optoelectronics.¹ One-dimensional nanostructures such as nanowires and nanorods have been grown by various methods. Most of them are based on the chemical vapor deposition (CVD) of GaN on the substrate. The substrate is coated with transition metals such as Ni,^{2,3} Fe,^{4,5} Co,⁵ In,⁶ and Au,⁷ which inevitably results in undesired contamination within GaN nanostructures. One of the useful synthetic methods to avoid the contamination is to employ the so-called confined reactor such as the carbon nanotube⁸ or the anodic alumina membrane.⁹ GaN nanowires were obtained by placing the confined reactor on a mixture of Ga and Ga₂O₃ and calcining it under a flow of ammonia at temperatures ≥ 900 °C.^{8,9} Their growth mechanism in the reactor remains unknown.

In this report we prepare one-dimensional GaN nano- and microstructures by using a confined reactor made of alumina containing a Ga source and propose their growth mechanism.

Experimental Section

A homogeneous mixture of aluminum oxyhydroxide and gallium oxyhydroxide (mole ratio = 1 : 0.05) was prepared by mixing Al(III) and Ga(III) hydrolysis gels, filtering, and then drying the mixture in an oven. Each hydrolysis gel was obtained by refluxing a mixture of metal nitrate salt and urea (mole ratio = 1 : 4) in aqueous solution. The mixture was calcined at 500 °C for 2 h under a flow of nitrogen and ground in mortar with a pestle. The resulting precursor powder was pressurized into a pellet. The precursor powder and its pellet were placed in an alumina crucible and then heated at a rate of 5 °C min⁻¹ to the reaction temperature (700-950 °C) under a flow of ammonia (Showadenko Co., 99.999%). The flow rate was, if not stated otherwise, 50 mL min⁻¹. The duration time was 5 h. The products were taken from the furnace after they were cooled to the room temperature under a flow of ammonia. A homogeneous mixture of NaF and gallium oxyhydroxide (weight ratio = 1 : 0.1) was pressurized into a pellet and nitrided in order to investigate the effect of the confined reactor material on growth of GaN nanostructure.

The products were characterized by XRD (Rigaku

DMX-2500 diffractometer with Cu-K α radiation operating at 40 kV and 100 mA). The morphology of GaN products was investigated by scanning electron microscopy (SEM, Hitachi S-4100).

Results and Discussion

The hydrolysis of Ga(III) salt by decomposition of urea in aqueous solution gives a gel precipitation of gallium oxyhydroxide (GaOOH).¹⁰ The precipitate turns into α -Ga₂O₃ and then GaN by the reaction of NH₃ above 800 °C without the phase transformation from α - to β -Ga₂O₃.¹⁰ On the other hand, the gel obtained by hydrolysis of Al(III) salt transforms into Al₂O₃ on its calcination at 500 °C. As a consequence, the precursor powder in which Ga₂O₃ is dispersed in an Al₂O₃ matrix was obtained by calcining the homogeneous mixture of Al(III) and Ga(III) gels at 500 °C. The precursor powder and its pressurized pellet were nitrided at different reaction temperatures under a flow of ammonia. Figure 1 shows the X-ray diffraction pattern of the product obtained by the nitridation of the precursor powder at 850 °C, indicating that the product consists of both GaN and γ -Al₂O₃. It is evident, therefore, that NH₃ gas diffused into the alumina matrix enough to react with Ga₂O₃ in a small space. Product powders obtained between 800 and 950

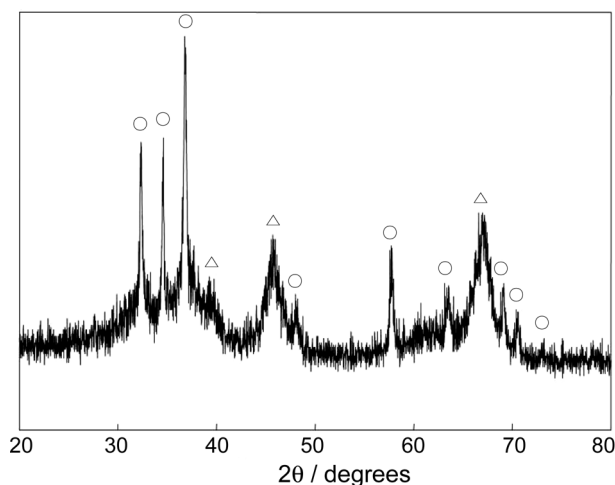


Figure 1. XRD pattern of powder obtained by calcining of a mixture of GaOOH and AlOOH at 850 °C for 5 h under a flow of ammonia. ○, GaN; △, γ -Al₂O₃.

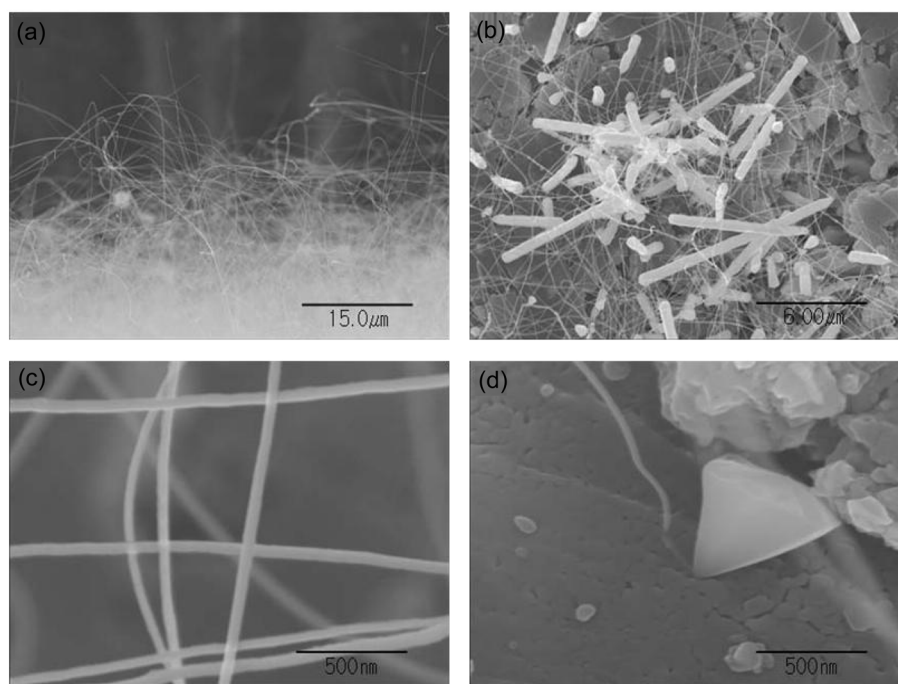


Figure 2. SEM micrographs of nano- and microstructured GaN obtained by calcining the pellet containing a mixture of GaOOH and AlOOH at 950 °C for 5 h under a flow of ammonia.

°C had a small amount of GaN nanorods or nanowires, showing the confinement effect.^{10,11} That is to say, GaN vapor is confined and easily supersaturated in a very small space. It is noted that no GaN nanowires were obtained by nitridation of GaOOH powder under the same reaction condition.¹⁰

The pressurized pellet of the precursor powder was more favorable for formation of GaN nano- and microstructures than the precursor powder. Both nanowires and microstructures such as microcones, stacked microcones, and hexagonal prismatic microcrystals were found on the surface of the pellets which were nitrided between 700 and 950 °C. The relative yield of microstructures to nanowires and their total yield increased with the reaction temperature. At 700 °C very few nanowires were obtained, while both at temperatures above 750 °C nanowires and microstructures were obtained. Figure 2(a)-2(d) show GaN morphology of the sample obtained at 950 °C for 5 h. Figure 2(a) shows lots of very long nanowires at the edge of the pellet. As shown in Figure 2(b), there were many nanowires and corrugated hexagonal prismatic microcrystals with one end being tapered. The nanowires were relatively homogeneous in diameter, which is as thick as 50 nm (Figure 2(c)). Figure 2(d) shows that the nanowires and microcones grew up out of the inner side of the pellet.

The confinement of GaN vapor in voids derived by pressurization of the precursor powder might be responsible for the growth of GaN nanowires and microstructures. The voids act as a confined reactor like carbon nanotube⁸ and anodic alumina membrane.⁹ We propose that nano- and microstructured GaN might grow by the vapor-solid (VS) mechanism. According to the VS mechanism, GaN vapor is

supersaturated in a confined reactor made of alumina, condensed, and then nucleated at the alumina wall. Continuous diffusion of GaN vapor into the reactor makes one-dimensional GaN nano- and microstructures grow out of the inner side of the pellet. On the basis of the following experimental results we rule out the possibility of the vapor-liquid-solid (VLS) mechanism in which the Ga droplet derived from decomposition of GaN plays a role of catalyst. Ga droplets, if they are formed during the reaction, will be supersaturated with GaN vapor and the nanostructures will grow. First, no GaN nanostructures were found using the pure GaOOH powder as a precursor.¹⁰ If the VLS mechanism operates, the nanostructures should be found in the reaction system. Second, GaOOH powder in a NaF matrix transformed into GaN powder at 900 °C under a flow of NH₃, but no GaN nanostructures were observed. If the VLS mechanism operates in a confined reactor, GaN nanostructures will grow in the reactor irrespective of its material. Therefore, this leads to the conclusion that the GaN nano- and microstructures grew out of the inner of an alumina matrix by the VS mechanism.

We observed the growth of GaN nano- and microstructures on the c-plane of sapphire which was placed on the pellet. The GaN structures are also thought to grow via the VS mechanism because there was no Ga droplet on the sapphire. Stach *et al.* observed the growth of GaN nanowires on the sapphire *via* the self-catalytic VLS mechanism, in which the catalyst is nanoscale Ga liquid droplets evolved by thermal decomposition of GaN.¹² However, they did not exclude the possibility of GaN nanowire growth via the VS mechanism.

As shown in Figure 3, we also obtained GaN microstructures such as hexagonal microcones, stacked microcones,

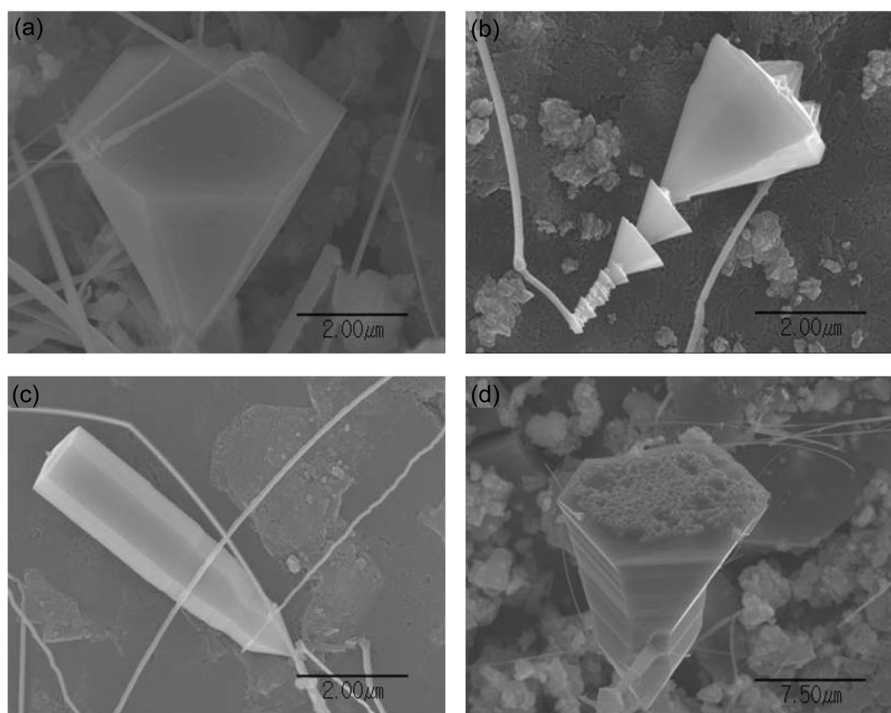


Figure 3. Various morphology of microstructured GaN obtained by calcining the pellet containing a mixture of GaOOH and AlOOH under a flow of ammonia: (a) hexagonal microcone, (b) stacked microcone, (c) hexagonal prismatic microcrystal, and (d) immature hexagonal prismatic microcrystal.

and hexagonal prisms, which were not prepared using other confined reactors.^{8,9} The yield of microstructures increased with the reaction temperature. It is inferred from Figure 3 that the hexagonal microcone grows to either the stacked microcone or hexagonal prismatic microcrystal and the latter microstructure grows via the structure as shown in Figure 3(d). To our knowledge, such microstructures produced by the nitridation of Ga₂O₃ have not been reported in the literature. Stacked-cones have been grown by the CVD method recently.^{2,4,13} Cai *et al.* prepared a mixture of stacked-cone and smooth-surface GaN nanowires on Ni-coated Si substrates by evaporation of Ga in NH₃/Ar gas flow and found that the yield of the two types of nanowires depend on the NH₃ flow rate.² They suggested that the more N-rich condition favors the stacked-cone morphology.² But in this study the relative yield of GaN nanostructures did not depend on the NH₃ flow rate but depended on the reaction temperature. It seems, therefore, that the diffusion rate of GaN vapor into the confined reactor has an effect on the morphology. It is well known that the degree of supersaturation determines the prevailing growth morphology. A low supersaturation is required for one-dimensional nanostructure (such as whisker, nanorod and nanowire) growth, whereas a medium supersaturation support bulk crystal growth.¹⁴ The low diffusion rate at relatively low reaction temperatures causes a low degree of supersaturation in the confined reactor that favors the formation of smooth nanowires, while the high diffusion rate at higher reaction temperatures causes a medium degree of supersaturation that favors the formation of microstructures. The stacked

microcones may be attributed to the oscillation of supersaturation because of discontinuous diffusion rate of GaN vapor.²

Han *et al.*⁸ and Cheng *et al.*⁹ reported that only GaN nanowires were synthesized using nanometer confined reactors such as carbon nanotubes and anodic alumina membranes which were placed on a mixture of Ga and Ga₂O₃. They assumed that Ga₂O vapor would evolve by the reaction between Ga and Ga₂O₃. The reason why no other nanostructures than the nanowire were formed might be explained in terms of the degree of supersaturation in the confined reactor. It may be difficult for the Ga₂O vapor to diffuse into the nanometer confined reactor and then react with NH₃, and thereby for the reactor to be saturated with GaN vapor at a low degree of supersaturation. As mentioned, the low degree of supersaturation causes the formation of GaN nanowires. On the other hand, the confined reactor employed in this study is easily supersaturated with GaN vapor because it contains a Ga source whereby GaN vapor easily diffuses into the reactor, resulting in the low and medium degree of supersaturation. If the reaction temperature increases, a medium degree of supersaturation will be reached more easily.

To conclude, we synthesized two main types of GaN nanowires and microstructures by calcining a confined reactor made of alumina containing Ga₂O₃ at temperatures above 700 °C under a flow of ammonia, and suggested that they grow by the VS mechanism in the reactor. It was found that the material of the reactor has an effect on their growth and the relative yield of the two types depends on the reaction temperature.

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