Synthesis of gallium nitride nano-wires on nickel–alumina composites from gallium oxide powder under a low partial pressure of ammonia

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GaN nanowires were synthesized on silicon, nickel nitrate [Ni(NO₃)₂]-dispersed silicon, and a nickel-dispersed alumina (Ni/Al₂O₃) composite under an argon atmosphere containing a low partial pressure of ammonia (P_NH₃ = 10 kPa). GaN nanowires were formed on the Ni(NO₃)₂-dispersed silicon and Ni/Al₂O₃ composite substrates. Two kinds of nanowires with different morphologies were observed. Initially, the formation of rough-surfaced nanowires occurred, which was followed by the formation of smooth-surfaced nanowires. In the case of the Ni/Al₂O₃ composite, GaN nanowires with rough surfaces were formed after 15 min at 1000°C, and the number of nanowires increased with the holding time. TEM observations showed that the nanowires grew in the [100] direction, which supported the proposed vapor–liquid–solid growth mechanism.

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Key-words : Gallium nitride, Gallium oxide, Nano-wires, Nickel, Alumina, Catalyst, Ammonia

1. Introduction

Gallium nitride (GaN) is a wide band gap (3.4 eV) semiconductor with a large breakdown field strength used in blue light emitting diodes (LEDs) and power electronic devices. GaN nanowires, which are 5–70 nm in diameter and several tens of micrometers in length, have also attracted much attention because of their size, electronic characteristics, and potential applicability in nano-electronic devices. Nanowires have been synthesized using metal–organic chemical vapor deposition (MOCVD), hydride vapor phase epitaxy (HVPE), molecular beam epitaxy (MBE), and laser-assisted catalytic growth methods. These methods have the advantages of the availability of high-purity raw materials and the precise control of raw material supplies. The disadvantage of these methods, however, is the required handling of toxic and reactive raw materials.

Nanowires have been grown using vapor–solid (VS) and vapor–liquid–solid (VLS) mechanisms. In the VLS-based growth mechanism, nickel or gold is used as a catalyst for the synthesis of GaN nanowires. First, gallium oxide (β-Ga₂O₃) was used as a raw material. The nitridation reaction was

\[ β-Ga₂O₃ + 2NH₃ \rightarrow 2GaN + 3H₂O \]  

Reaction (1), which was investigated in a previous study, proceeds at temperatures higher than 650°C and becomes remarkable at temperatures above 1100°C. It was also suggested that the nitridation proceeded via a gas phase species such as Ga₂O₃(g). The synthesis of GaN nanowires from β-Ga₂O₃ through nitridation with ammonia has been reported.

The second condition was the use of a Ni-dispersed α-Al₂O₃ (Ni/Al₂O₃) composite as a substrate. In this substrate, nano- to micrometer-sized nickel particles are homogeneously dispersed in a sintered α-Al₂O₃ matrix. Thirdly, the synthesis was carried out under low P_NH₃ (≈10 kPa) conditions. NH₃ is widely used as a nitrogen source for GaN nanowires, but it is corrosive. Low P_NH₃ conditions make it possible to synthesize nanowires without special gas feeding and removal equipment.

2. Experimental procedure

β-Ga₂O₃ powder (99.9% purity; Koujyundo Kagaku Co.) was used as a starting material. Three kinds of substrates were used for the growth of the nanowires: (i) silicon (Si), (ii) Ni(NO₃)₂-dispersed Si, and (iii) Ni/Al₂O₃ composites. The Si substrate (i) was commercially available silicon single crystal (111) wafers with mirror-polished surfaces. The wafers were cut into 7 × 3 × 1 mm³ pieces and washed with HF (0.5%)/H₂O₂ (0.1%) solution. The Ni(NO₃)₂-dispersed Si (111) substrate (ii) was prepared by dip-coating the silicon in an ethanolic solution of Ni(NO₃)₂ (0.1 M). The Ni/Al₂O₃ composites (iii) were fabricated by hot-pressing Ni and Al₂O₃ powders; the details of this method have been previously described. The substrate was cut into 10 × 4 × 1 mm³ pieces and the surfaces were polished using silicon carbide abrasives of 30 and 15 µm.

Nanowire growth was performed using a horizontal tube furnace. β-Ga₂O₃ powder (about 0.1 g) was placed on an alumina boat. The polished substrate was placed about 2 mm above the β-Ga₂O₃ powder. The nanowires were formed on the lower surface, which was toward the β-Ga₂O₃ powder. The samples
were heated to 900–1100°C for 0–1 h. An NH₃/Ar (P_{NH₃} = 10 kPa) atmosphere with a flow rate of 50 mL/min was used. Samples were characterized using X-ray powder diffraction (XRD, RINT TTRIII, Rigaku), scanning electron microscopy (SEM, JSM-7400F, JEOL) with energy dispersive X-ray spectroscopy (EDX, EDAX), and transmission electron microscopy (TEM, JEM-2010, JEOL).

3. Results and discussion

No GaN deposition was observed on the substrate surface in the case of growth experiments using Si substrates (i) at the temperature of 1000°C. These results show that the Si substrate is not suitable for the growth of GaN nanowires. In the case of the experiment using Ni(NO₃)₂-dispersed Si substrates (ii), the Si plate was wetted using an ethanolic Ni(NO₃)₂ solution, and Ni(NO₃)₂ was dispersed inhomogeneously over the surface like rain drops. Figure 1(a) shows the sample after growth experiments at 1000°C, showing that yellow-colored deposits were observed only at these regions. The XRD results showed that GaN was present in the samples. Figure 1(b) shows SEM photographs of the deposits. Nanowires 50–100 nm in diameter and a few micrometers in length were observed in the deposits. The XRD results suggest that the nanowire was GaN and the formation of the GaN nanowires was assisted by Ni(NO₃)₂.

In the case of the growth experiments using Ni/Al₂O₃ substrates (iii), yellow-colored deposits covered the surface homogeneously at 1000°C. At 900 and 1100°C, trace amount of yellow-colored deposits were also observed. Figure 2 shows the XRD patterns at the surface of the substrate. In the sample prepared at 900°C, small peaks assigned to GaN were observed [Fig. 2(a)]. In the sample prepared at 1000°C, larger peaks corresponding to GaN were observed [Fig. 2(b)]. In the sample prepared at 1100°C, peaks corresponding to GaN were not found [Fig. 2(c)].

Figure 3 shows a photographs of the substrate after the experiment at 1000°C for 1 h, the microstructure of the surface before experiments and the same samples investigated in Fig. 2. As described above, the deposits covered the surface homogeneously at 1000°C except for the both ends, which were hidden by support of the substrate [Fig. 3(a)]. SEM image of the surface showed the homogenous distribution of Ni particles shown by white-contrasted particles [Fig. 3(b)]. In the sample prepared at 900°C [Fig. 3(c)], particles about 1 μm in diameter, together with elongated particles, were observed. In the sample prepared at 1000°C [Fig. 3(d)], nanowires 30–50 nm in diameter and a few micrometers in length were observed. In the sample prepared at 1100°C [Fig. 3(e)], particles about 1 μm in diameter, which were similar to those in the sample prepared at 900°C, were observed. The XRD results of the sample prepared at 1000°C, which show the presence of peaks corresponding to GaN (Fig. 2), suggested that the crystalline phases of the nanowires in the sample prepared at 1000°C were GaN. The substrate was placed about 2 mm above the β-Ga₂O₃ powder, so the nanowires were formed from some gaseous species containing Ga, generated from the β-Ga₂O₃ powder by a reaction with NH₃ gas. The majority of the particles formed at 1100°C were similar to those formed at 900°C. Because no crystalline phase was observed in the sample prepared at 1100°C except for the substrate phase, the phase of the particles present on the surface were not identified. Small peaks corresponding to GaN were observed in the XRD pattern [Fig. 2(a)], indicating that the crystalline phase of the elongated particles was GaN.

Figure 4 shows the XRD patterns of the surface of the Ni/Al₂O₃ substrate for holding times between 0 and 60 min at 1000°C. No peaks corresponding to GaN were observed in the pattern of the sample held for 0 min [Fig. 4(a)]. In the patterns of the samples held for 5–60 min [Figs. 4(b)–4(g)], peaks corresponding to GaN were observed, and the intensities of the peaks increased with longer holding times. Figure 5 shows SEM photographs of the samples described in Fig. 4. In the sample
held for 0 min [Fig. 5(a)], particles about 1 μm in size were observed on the substrates. In the sample held for 5 min [Fig. 5(b)], the particles became slightly larger, about 2 μm in size. Based on the XRD results [Fig. 4(b)], the particles observed in the 5 min sample [Fig. 5(b)] were assumed to be composed of GaN. The particles observed in the sample held for 0 min were also assumed to be GaN based on the similarity of the particle shapes. As a result of the small number of particles, peaks resulting from GaN were not found in the XRD pattern of the sample held for 0 min. In the sample held for 10 min [Fig. 5(c)], elongated particles about 3 μm in length were observed. The XRD pattern of this sample [Fig. 4(c)] showed small GaN peaks, thus the elongated particles were GaN. In the sample held for 15 min [Fig. 5(d)], wires 100 nm in diameter and a few micrometers in length with a rough surface were observed. In the sample held for 30 min [Figs. 5(e) and 5(f)], smooth-surfaced nanowires were formed. In some wires, no particle was observed at the tips but in the others, particles about 100 nm in diameter were observed. The smooth-surfaced wires were formed on the rough-surfaced wires [indicated by arrow in Fig. 5(g)].

Figure 6 shows SEM photographs and EDX spectra of the samples held for 0 and 10 min. In the sample held for 0 min...
[Figs. 6(a) and 6(b)], peaks corresponding to both Ni and Ga were observed for a white particle about 1 μm in size. From the EDX results, the particle as thought to be a Ga–Ni alloy. In the sample held for 10 min [Figs. 6(c) and 6(d)], peaks corresponding to Ni and Ga were observed from an elongated particle thought to be GaN. In both EDX spectra, the observed Pt peaks resulted from sputter coating prior to SEM observation.

Figure 7 shows TEM photographs and EDX spectra of the smooth-surfaced nanowires in the sample held for 60 min. In the EDX spectrum of the particle formed at the tip, large peaks due to Ga with a small peak due to Ni were observed [Fig. 7(b)]. The spectrum of the wire showed no obvious peak due to Ni [Fig. 7(c)]. Similar results were also observed in the other nanowires, but in some cases, obvious peak due to Ni were not observed in the spectrum at the particle. The EDX analysis showed that the particles with various compositions of Ga and Ni were present. In the EDX spectra, the C and O peaks were due to the coatings and the contamination on the sample, and the Cu peaks due to a sample supporting grid. In the TEM photograph of the nanowire, no boundary was observed [Fig. 7(d)], showing that the nanowires were single crystals.

The high-resolution photographs [Fig. 7(e)] showed layered images with an interplaner spacing of 0.23 nm. This value is in relatively good agreement with the spacing of GaN (101) planes (0.244 nm), which is observed to be about 60° relative to the grown direction of the nanowires. Based on the crystal structure of GaN, the angle between the (101) and (001) planes is formed to be about 61° from the view point parallel to (101) planes. Therefore, the GaN nanowires were expected to grow in the [100] direction. This growth direction corresponded with that previously reported directions ([110] or [100]).

From the above results, we propose a growth mechanism, which is shown in Fig. 8. Immediately after heating, the reaction of Ga2O (g) with Ni in the substrate started, resulting in the formation of Ga–Ni alloy particles [Fig. 8(b)]. The intensity of the Ni L line in the EDX spectrum of this sample was significantly greater than that of the Ga L line, suggesting that the particles should be in the solid state considered from the phase diagram of a Ga–Ni system, which shows that the liquid phase appears at above 58 wt % Ga in the system at 1000°C. Over the next 10 min, Ga2O (g) continued to react with the particles and some of the alloy become liquid [Fig. 8(c)]. Following this, rough-surfaced nanowires grow from the GaN particles [Fig. 8(d)]. 15 and 60 min, nanowires with smooth surfaces grown on the rough-surfaced nanowires [Fig. 8(e)]. The SEM observations showed some nanowires that had particles at the tips and others that did not. It was not determined whether a VLS or VS process dominated the growth mechanism of the smooth-surfaced GaN.
nanowires; however, it was suggested that the formation of low melting-point Ga-rich Ga–Ni particles assisted the growth of the smooth-surfaced nanowires by a VLS mechanism. In the formation of Ga–Ni particles, Ga metal are able to be supplied by the disproportionation reaction of Ga2O21)

\[ 3\text{Ga}_2\text{O}(g) \rightarrow \text{Ga}_2\text{O}_3(s) + 4\text{Ga}(l). \]  

4. Conclusions

GaN nanowires were grown on substrates composed of Ni(NO3)2 dispersed on silicon, and a Ni/Al2O3 composite. The nanowires were fabricated from β-Ga2O3 powder under 10% NH3/Ar at 1000°C. Ni(NO3)2 was not homogeneously dispersed on the silicon surface, and nanowires were only observed in areas coated with Ni(NO3)2. In the case of the Ni/Al2O3 composite, GaN nanowires were grown all over the substrate; nanowires with a rough surface were formed over the course of 15 min, followed by smooth-surfaced nanowires. From TEM observations, nanowire growth occurred in the [100] direction.

Acknowledgment

This study was partly supported by the Environment Research and Technology Development Fund (ERTDF 3K15301) of the Ministry of the Environment, Japan.

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