Declarations of interest: none

Effects of nitrogen flow rate on the morphology and composition of AlGa_N nanowires grown by plasma-assisted molecular beam epitaxy

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Abstract

Nitrogen flow rate is one of the important growth parameters for the growth of group-III nitride nanowires in plasma-assisted molecular beam epitaxy. However, nitrogen flow rate has received less attention compared to the group-III metal fluxes since its effects are not as prominent as that of the metal fluxes. In this study, we investigated the effects of nitrogen flow rate on the morphology and composition of AlGa_N nanowires. It was confirmed that reducing the nitrogen flow rate improved the structural uniformity and increased the Al composition. We present a composition change model and show that excess nitrogen suppresses Ga desorption by recombining the Ga atoms, thereby causing a change in the composition of

AlGa_{1-x}N_x. It was also confirmed that the influence of the nitrogen flow rate on the Al composition varied with the growth temperature. These results provide insights into the role of nitrogen flow rate on the growth of AlGa_{1-x}N_x nanowires and suggest that more sophisticated growth control is possible by considering the nitrogen flow rate.

Keywords: A1. Nanostructures, A1. Growth models, A1. Characterization, A3. Molecular beam epitaxy, B1. Nitrides, B2. Semiconducting III-V materials

1. Introduction

AlGa_{1-x}N_x is an attractive material for ultraviolet (UV) optoelectronic devices because of its wide bandgap tunability (3.4 eV to 6.2 eV) by controlling the composition [1]. However, high Al-content AlGa_{1-x}N_x devices have low efficiency due to increases in dopant activation energy and dislocation density [2–6]. These issues make it difficult to use high Al-content AlGa_{1-x}N_x for device applications. One way to overcome these problems is to grow AlGa_{1-x}N_x into a nanowire structure rather than a thin film structure. Many studies have reported the features and benefits of nanowire structures [7–11].

Plasma-assisted molecular beam epitaxy (PA-MBE) is a widely used method for growing axial AlGa_{1-x}N_x nanowires. PA-MBE enables the growth of high-density self-organized nanowires without the use of pre-patterned masks or additional catalysts [12–14]. For this growth of nanowires, the nitrogen flux must be higher than the total group-III metal flux to satisfy the nitrogen-rich conditions [15–17]. Under these conditions, the composition of AlGa_{1-x}N_x nanowires can be easily controlled by changing the flux ratio of Al and Ga. In contrast, the nitrogen flux, composed of a single element, N, has less effect on the composition as compared

with the metal fluxes. Hence, the nitrogen flux tends to be overlooked in AlGa_N nanowire growth, and metal fluxes have been commonly used to control the characteristics of AlGa_N nanowires [18,19].

For Ga_N nanowires, many studies have reported on the effects of various growth parameters, such as Ga flux, growth temperature, or nitrogen species, etc. [20–24]. Based on the studies of Ga_N nanowires, many growth parameters have been investigated to optimize the growth conditions for AlGa_N nanowires. Among those, it has been reported that reducing nitrogen flow rate in the growth of AlGa_N nanowires can improve compositional uniformity and suppress the formation of defects [25–27]. This suggests that the nitrogen flow rate can affect some characteristics of AlGa_N nanowires. However, no detailed studies have been reported on that.

In this study, we investigate the effects of the nitrogen flow rate on the morphology and composition of AlGa_N nanowires grown by PA-MBE. It has been found that using a low nitrogen flow rate when growing AlGa_N nanowires improves the structural uniformity and increases the Al composition. We discuss the cause of the composition change by suggesting a composition change model and show that the composition is affected by the nitrogen flow rate, depending on the growth temperature.

2. Experimental details

AlGa_N nanowires were grown by PA-MBE (VG-V80). A radio frequency (RF) plasma source (Arios Inc., IRFS-504) was used for the nitrogen activation. All samples were grown on Si(111) substrates. The growth temperature was measured with an IR pyrometer calibrated by the Si(111)-7×7 to 1×1 transition occurred at 860°C using reflection high energy electron diffraction

(RHEED) [28].

The native oxide on the Si surface was removed using buffered oxide etchant. The substrate was mounted on an indium-free molybdenum holder and loaded into the MBE load-lock chamber. Prior to growth, the substrate was pre-outgassed at 300°C for 1 h in a buffer chamber to remove water vapor and then transferred to the growth chamber. After that, the sample was annealed at 783°C to deoxidize the Si surface until there was a clear appearance of the Si(111)-7×7 RHEED pattern. At the first stage of growth, a thin AlN buffer layer was grown to improve the verticality and the nucleation of the nanowires [13,16,21]. GaN nanowires, about 30 nm in length, were grown on an AlN buffer layer at 746°C to make a GaN nanowire template. This not only allowed the maintaining of the nanowire structure during the growth of AlGaIn segments but also made it possible to compare the structural changes due to the nitrogen flow rate. After that, AlGaIn segments were axially grown on the GaN nanowire template. In this study, two sets of AlGaIn nanowire samples were used. All AlGaIn segments were grown for 2 h, and the beam equivalent pressures (BEPs) of Ga and Al were fixed at 6.0×10^{-8} mbar (0.0323 ML/s) and 3.0×10^{-8} mbar (0.0240 ML/s), respectively. The first set of samples were grown under nitrogen flow rates in the range of 0.3 to 2.0 standard cubic centimeters per minute (sccm) with fixed metal fluxes at 783°C to confirm the influence of nitrogen flow rate on the morphology and composition of the AlGaIn nanowires (Figures 2–5). The second set of samples at flow rates of 0.7 sccm and 2.0 sccm were grown at temperatures of 746, 765, 783, 802, and 821°C with fixed metal fluxes to confirm the relationship between growth temperature and nitrogen flow rate on the composition of the AlGaIn nanowires (Figure 6).

The light intensity of the plasma, which is proportional to the nitrogen flux, was measured by an optical emission detector (OED) to confirm the change in the nitrogen flux with the nitrogen flow rate. Scanning electron microscopy (SEM) was used to observe the morphology of the

AlGa_N nanowires. Statistical analysis of the SEM images was conducted using the open-source software ImageJ. Photoluminescence (PL) measurements were carried out at room temperature using a 266 nm diode-pumped solid-state laser at 5 mW. X-ray diffraction (XRD) 2 θ - ω scans were performed to confirm the change in the composition of AlGa_N nanowires. All measurements were made for the ensembles of nanowires. The formation of an Al-rich shell, which can affect the structure and composition of the AlGa_N nanowires, was not considered because this topic is too broad and complex to be dealt with at the same time [29].

3. Results and discussion

Fig. 1 shows the optical signal measured from the light intensity of the nitrogen plasma using the OED. The optical signal became stronger with an increase in the nitrogen flow rate. Generally, the amount of active nitrogen species, which are directly associated with the nitrogen flux, is proportional to the light intensity of the nitrogen plasma [30–34]. Therefore, the optical signal indicates that the nitrogen flux increased logarithmically with a nitrogen flow rate from 0.3 to 2.0 sccm. We used the results of previous experiments on AlN thin film growth to confirm whether the AlGa_N nanowires were grown under nitrogen-rich conditions. Under the same growth condition as those used for growing the AlGa_N nanowires in Figs. 2–5, an AlN thin film was grown by adjusting only the Al BEP at 0.3 sccm, and the thickness of the AlN film had changed little when the Al BEP exceeded 4×10^{-7} mbar (not shown). This means that the Al BEP, which satisfied the slight Al-rich or intermediate conditions, was around 4×10^{-7} mbar at 0.3 sccm. The sum of the Al and Ga BEPs used in the growth of AlGa_N nanowires was 9×10^{-8} mbar. Because the difference between these two BEPs is very large, the growth atmosphere at 0.3 sccm used for the AlGa_N nanowire growth can be regarded as nitrogen-rich. Together with Fig. 1, this implies that all of the AlGa_N nanowires using a

nitrogen flow rate in the range of 0.3 to 2.0 sccm were grown under nitrogen-rich conditions.

Fig. 2 shows SEM images of AlGa_N nanowires grown at various nitrogen flow rates. There were observable differences in the structures between the samples grown at 0.3–1.0 sccm and the samples at 1.3–2.0 sccm. In the top view images, it can be seen that the samples grown at 0.3–1.0 sccm had less coalescence than those samples grown at 1.3–2.0 sccm. Furthermore, the nanowalls marked with red arrows in the SEM images were prominently formed at 1.3–2.0 sccm due to the increased coalescence [34,35]. In cross-sectional view images, the contour of the top of the AlGa_N nanowires grown at 0.3–1.0 sccm was flatter and the length variation was smaller than at 1.3–2.0 sccm. This shows that the lengths of AlGa_N nanowires grown at 0.3–1.0 sccm were more uniform than those grown at 1.3–2.0 sccm. The observed trend in morphology is similar to that reported for Ga_N nanowires according to the V/III flux ratio using Ga flux [22].

The length, diameter, and density of the AlGa_N nanowires were measured from the SEM images, and their average values are expressed in Fig. 3. In the process of measuring their length, very short nanowires of around 100 nm or less located at the cut surface were considered to have been damaged during the sample cutting, and thus were not included. To measure the diameter and density, the coalesced structures were separated using a watershed algorithm, and nanowires that were too short or too small to be seen in the SEM images were excluded. The length of nanowires gradually increased with the nitrogen flow rate from 0.3 to 1.0 sccm but decreased after 1.3 sccm (Fig. 3(a)). Meanwhile, an increase in diameter and a subsequent decrease in density were observed in the range of 0.3 to 1.0 sccm, but the changes were small after 1.3 sccm (Fig. 3(b), (c)). Because of the range of the error bars, it is difficult to clearly recognize the trend in the average diameter in the Fig. 3(b), but the average diameters increased by around 9.7% from 54.4 to 59.7 nm with increasing nitrogen flow rate. Although the AlGa_N

nanowires were grown on the GaN nanowire templates which have the same structural conditions, the large change in average diameter means that the nitrogen flow rate had a significant effect on this characteristic. From the error bars of the length in Fig. 3(a), the length uniformity can be confirmed. The increase in the length of the error bars indicates that length uniformity was degraded with an increase in the nitrogen flow rate. The error bars of the diameters in Fig. 3(b) increased gradually, but the change was not noticeable. As already shown in Fig. 2, nanowalls prominently formed after 1.3 sccm of nitrogen due to much coalescence occurring between the nanowires. This shows that more coalescence occurred as the nitrogen flow rate increased. Since the value of the diameter was measured by dividing the coalesced nanowire top-surface by the watershed algorithm, the uniformity of the actual diameter can be considered to have been degraded with increasing nitrogen flow rate. Therefore, we can conclude that the morphology of AlGaIn nanowires was made more uniform by reducing the nitrogen flow rate. Because the nitrogen flow rate affects the diffusion length, these morphological changes in the AlGaIn nanowires are assumed to have originated from the change in the diffusion lengths of the Ga and Al atoms [37]. This assumption is consistent with the context for the cause of the morphological change in the GaN nanowires by the V/III flux ratio [22].

Fig. 4(a) shows normalized PL spectra of the AlGaIn nanowires. Even though there was no change in the metal fluxes, the PL spectra gradually shifted toward lower energy with an increase in the nitrogen flow rate. Fig. 4(b) presents the PL peak energy and full width at half maximum (FWHM) of the AlGaIn nanowires as a function of the nitrogen flow rate. The PL peak energy shifted from 4.30 to 4.00 eV with a nitrogen flow rate from 0.3 to 2.0 sccm. The shift in PL peak energy suggests that the nitrogen flow rate affected the Al-content of AlGaIn nanowires. A notable point of interest is the relationship between the FWHM and the nitrogen flow rate. In general, alloy fluctuation is proportional to the Al composition of AlGaIn up to

about 70–80%, which causes a broadening of the FWHM [38,39]. However, the FWHM values of the grown AlGaN nanowires gradually decreased despite the increase in the PL peak energy. It has been reported that the compositional modulation is reduced when the nitrogen flow rate is low [25]. In addition, alloy fluctuation is known to affect the FWHM of AlGaN [40]. According to the literatures, the decrease in FWHM can be attributed to the improved compositional uniformity of each AlGaN nanowire resulting from the enhanced diffusion of the Al and Ga adatoms by lowering the nitrogen flow rate.

XRD measurements were conducted to determine whether the shift in PL peak energy was resulted from the change in the composition of the AlGaN nanowires. Fig. 5(a) shows XRD 2θ - ω scans for the (002) reflection of the AlGaN nanowires. As the nitrogen flow rate increased, the AlGaN peaks gradually shifted to lower angles. However, the GaN peaks were almost fixed at 34.85° . The shift in the AlGaN peaks clearly shows that the composition was changed by the nitrogen flow rate. From the XRD reflection, the Al composition was calculated by the equation $c_0(x) = c_0^{GaN}(1 - x) + c_0^{AlN}x$, where $c_0(x)$ is the c-plane lattice distance obtained from Bragg's equation, and c_0^{GaN} and c_0^{AlN} are the theoretical lattice parameters of GaN and AlN, respectively. In this calculation, c_0^{GaN} was 5.186 and c_0^{AlN} was 4.981 [41]. For a comparison with the Al composition calculated from the XRD, the Al composition corresponding to the PL peak energy was determined by $E_g^{Al_xGa_{1-x}N} = E_g^{GaN}(1 - x) + E_g^{AlN}x - bx(1 - x)$, where $E_g^{Al_xGa_{1-x}N}$ is the PL peak energy of AlGaN nanowires, E_g^{GaN} and E_g^{AlN} are the band gap energy of GaN and AlN, and b is the direct gap bowing parameter; E_g^{GaN} and E_g^{AlN} were set to 3.4 eV and 6.2 eV, and b was 1.3 eV [41]. Fig. 5(b) presents the Al composition calculated from the XRD reflection and PL peak energy as a function of the nitrogen flow rate. The Al composition from XRD decreased from 45.7% to 34.4% with as the nitrogen flow rate increased from 0.3 to 2.0 sccm. Similarly, the Al composition from PL decreased from 43.6%

to 31.6% with the same flow-rate range. There are several reasons for the difference in Al composition: the effect of strain, the change in PL peak energy according to laser power, and the parameters used in calculations. Although there were slight differences in the calculated Al compositions, both results show that the Al composition of AlGa_N nanowires can be changed by the nitrogen flow rate.

To explain the cause of the change in Al composition, we describe the relationship between the nitrogen flow rate and the incorporation of Al and Ga atoms. For Al incorporation, the Al incorporation probability at temperatures close to the growth temperatures used for the AlGa_N nanowire growth has been reported to be almost a constant 1 in both nitrogen-rich and metal-rich conditions [42,43]. This means that the nitrogen flow rate has little effect on the Al incorporation. Furthermore, Al atoms can be preferentially incorporated over Ga atoms because an Al–N bond is stronger than a Ga–N bond [42,44]. Therefore, Al incorporation is less sensitive to variation in the nitrogen flow rate than Ga incorporation. However, Ga incorporation depends on the growth atmosphere as well as the nitrogen flow rate. In metal-rich conditions, the Ga incorporation rate is determined only by the difference between the nitrogen flux and the Al flux. In nitrogen-rich conditions, the Ga incorporation can be affected by excess nitrogen remaining after reacting with the group-III metal fluxes. The excess nitrogen decreased the Ga desorption by increasing the Ga capture probability [45]. Similarly, the activation energy of GaN decomposition has been reported to increase with an increase in V/III flux ratio [46].

By extending our results with those previously reported, we propose a composition change model considering the nitrogen flow rate for AlGa_N. Under metal-rich conditions, there is no additional increase in Ga incorporation to more than the amount of nitrogen flux minus Al flux because there is no excess nitrogen. Therefore, the nitrogen flow rate cannot have a significant

effect on the composition of AlGa_N. On the other hand, excess nitrogen can exist under nitrogen-rich conditions, and the amount of excess nitrogen can be varied in proportion to the nitrogen flow rate. Under this condition, the Al incorporation is almost constant regardless of the change in nitrogen flow rate, but the Ga incorporation can be increased by excess nitrogen, which reduces the Ga desorption [44–46]. As a result, the Al composition can be changed by the nitrogen flow rate under nitrogen-rich conditions.

We have shown that the change in the Al composition is due to the excess nitrogen affecting the Ga desorption. Since the Ga desorption depends on the temperature, the effects of the nitrogen flow rate on the composition could be affected by the growth temperature. Fig. 6 shows the PL peak energy of the AlGa_N nanowires as a function of growth temperature at 0.7 and 2.0 sccm. Under both nitrogen flow rates, the PL peak energy increased exponentially with growth temperature. Because Ga desorption is promoted by an increase in growth temperature, the shift in the PL peak energy can be attributed to the change in Ga desorption [45,47,48]. The change in the PL peak energy was 4.03–4.39 eV at 0.7 sccm (corresponding to an Al composition of 32.9%–47.0%), and 3.97–4.15 eV at 2.0 sccm (corresponding to an Al composition of 30.2%–37.7%). The difference in PL peak energy caused by the nitrogen flow rate depends on the growth temperature. The difference in the PL peak energy at 0.7 and 2.0 sccm is 0.06 eV at 746°C (2.7 percentage points for Al composition) but increases to 0.24 eV at 821°C (9.3 percentage points for Al composition). This can be described based on the composition change model. At low temperatures, the number of Ga atoms that can be affected by excess nitrogen is small because of the low Ga desorption rate. This means that the Ga incorporation is less affected by the nitrogen flow rate. However, at high temperatures, the number of Ga atoms that can be affected by excess nitrogen is increased due to an increase in Ga desorption, which makes a large difference in Ga incorporation as the nitrogen flow rate

changes. Therefore, the difference in PL peak energy between the 0.7 and 2.0 sccm samples at 821°C was greater than the difference at 746°C. Since the change in PL peak energy can be considered as a change in Al composition, it can be concluded that the composition of AlGaIn nanowires is affected by the nitrogen flow rate, depending on the growth temperature.

4. Conclusion

The effects of the nitrogen flow rate on AlGaIn nanowires grown by PA-MBE were investigated. It was confirmed that the nitrogen flow rate had a significant effect on the morphology and composition of the AlGaIn nanowires. The structural uniformity of the AlGaIn nanowires was improved by lowering the nitrogen flow rate. This was assumed to originate from the change in the diffusion lengths of the Ga and Al atoms. The PL peak energy was inversely proportional to the nitrogen flow rate. The change in PL peak energy was caused by a change in the composition of the AlGaIn nanowires. We presented a compositional change model to explain the cause of the change in composition. The amount of Ga atoms generated or supplied by GaN decomposition or Ga effusion cell is changed by the Ga desorption, depending on the growth temperature. At that time, the excess N suppresses the Ga desorption by recombining the Ga atoms and causes a change in the Al composition of AlGaIn. It was also confirmed that the influence of the nitrogen flow rate on the Al composition varied with the growth temperature. These results provide insight into the role of the nitrogen flow rate in the growth of AlGaIn nanowires and suggest that more sophisticated growth control is possible by considering the nitrogen flow rate.

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Fig. 1. Nitrogen flow rate dependence of the optical intensity emitted from nitrogen plasma, as measured by an optical emission detector.

Fig. 2. SEM images of AlGaIn nanowires grown at various nitrogen flow rates: (a) 0.3 sccm, (b) 0.7 sccm, (c) 1.0 sccm, (d) 1.3 sccm, (e) 1.6 sccm, and (f) 2.0 sccm. In the two images for each nitrogen flow rate, the left is a top view and the right is a cross-sectional view. The red arrows indicate nanowalls. All of the AlGaIn nanowires shown in this figure were grown at 783°C with fixed metal fluxes.

Fig. 3. Structural changes in the AlGaIn nanowires as a function of nitrogen flow rate: (a) average length, (b) average diameter, and (c) density. Each error bar represents two standard deviations, and the dotted lines are fitted polynomial curves.

Fig. 4. Photoluminescence (PL) characterization of the AlGaIn nanowires: (a) normalized PL spectra of samples grown at various nitrogen flow rates (the arrow indicates the direction of increasing nitrogen flow rate) and (b) PL peak energy and FWHM as a function of the nitrogen flow rate. The dashed lines are fitted polynomial curves.

Fig. 5. (a) X-ray diffraction (XRD) 2θ - ω scans for the (002) reflection of the AlGaIn nanowires grown at various nitrogen flow rates. The XRD patterns were aligned on the basis of the Si (111) substrate peak at 28.45° . (b) Calculated Al compositions of the AlGaIn nanowires from the XRD reflections and the PL spectra.

Fig. 6. PL peak energy of the AlGaIn nanowires as a function of growth temperature (746–821°C) at nitrogen flow rates of 0.7 sccm (blue circles) and 2.0 sccm (red triangles).

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Highlights

- The structural uniformity can be improved by lowering the nitrogen flow rate.
- The composition is affected by nitrogen flow rate under nitrogen-rich conditions.
- Excess nitrogen causes a change in composition by suppressing Ga desorption.