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High growth rate metal organic vapor phase epitaxy GaN

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ABSTRACT

High growth rate GaN of 28 μm/h was demonstrated by using an atmospheric pressure multi-wafer metal organic vapor phase epitaxy reactor. FWHM of X-ray diffraction of (0 0 2) and (1 0 2) reflection was about 250 and 400 arcsec for the layer grown with a growth rate less than 12 μm/h. FWHM for the sample with the highest growth rate of 28 μm/h was 300 and 560 arcsec, respectively. Carbon contamination was increased up to 6×10^{17} cm^{-3} for 28 μm/h sample as input V/III ratio was decreased in accordance to the increased growth rate. Limiting factors to the growth rate were discussed in comparison to hydride vapor phase epitaxy.

1. Introduction

High growth rate technology of GaN by metal organic vapor phase epitaxy (MOVPE) is a promising technology for a thick low dislocation density template as an alternative to a native bulk GaN substrate since the device structure can be grown successively in a same reactor. GaN with dislocation density of low 10^8 cm^{-3} can be grown on sapphire substrate by atmospheric pressure MOVPE by using conventional two-step growth technique [1]. However, the growth rate of MOVPE GaN is limited to a few micrometers per hour in large-scale production equipment at atmospheric pressure. In the attempt of growing high-quality nitride semiconductors including AlGaN, we have been developing high flow speed three-flow-gas-injection atmospheric pressure MOVPE reactor since the mid-90s [2]. The details of the three-flow-gas-injection and their results are described in previous papers [2–4].

A recent understanding of obstacles for obtaining high growth rate of GaN by MOVPE would be summarized as following. To put it simply, high growth rate of GaN is hindered by particulate generation in vapor phase. Creighton et al. [5] observed nanometer-sized particles in an inverted stagnation point flow reactor by employing a high flow rate condition of organo-metals. Nanometer-sized particulates were observed on top of a thermal boundary layer by in-situ laser scattering. Dauelsberg et al. [6] reported an experimental and simulation study of GaN MOVPE as a function of thermal gradient in vapor phase and flow speed. They concluded that a large temperature gradient in the vapor phase in a shower head reactor can result in a condensation of nanometer-sized particles and their migration into a relatively cool part of the reactor, followed by removal of precursors from the growing region. They have suggested a high flow speed is critical to eliminate particulate generation in a horizontal reactor. Hirako and Ohkawa [7] also reported $[GaN]_4$ molecules condense at an entrance region of a horizontal reactor, where there is a large temperature gradient in the vapor phase.

In this paper, we will describe that high flow speed reactor, which can grow AlGaN at atmospheric pressure, is useful for high growth rate GaN. By using a high flow speed reactor, the growth rate can be extended near the criteria of HVPE.

2. Experiment

The GaN layers were grown by using a commercial production scale multi-wafer reactor (Taiyo Nippon Sanso corp., SR23K). The reactor is capable of growing 10 × 2 in or 8 × 3 in at a time. We have employed the three-flow-gas-injection with flow speed of more than 1 m/s at a wafer center. The gas injector is located at the center of a rotational circular plate, in which each wafer is located so as to surround the central gas injector and rotated mechanically on its axis. GaN layers were grown at atmospheric pressure entirely over this study. Ammonia (NH_3) and trimethylgallium (TMG) were used as precursors. Hydrogen and nitrogen were used as carrier gases. To enhance the structural quality of the GaN buffer, we used *c*-plane sapphire with an off-orientation of 0.15° towards the *m*-plane. The grown samples were characterized by standard four-crystal X-ray diffraction and Lehighton sheet resistance meter. Residual carbon concentration was measured by secondary ion mass spectrometer (SIMS).

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3. Results and discussion

The utility of the SR23K reactor for reducing parasitic reactions has been previously demonstrated with AlGaN growth. By using this reactor, AlGaN with Al composition of 5% and 9% can be grown at more than 2.5 and 1 μm/h at atmospheric pressure, respectively. This suggests that a parasitic reaction is effectively suppressed in this reactor. The details of the growth of AlGaN will be reported elsewhere. By using SR23K, GaN was grown at a growth rate up to 28 μm/h. In Fig. 1, the growth rate of GaN is shown as a function of normalized TMG supply rate. The maximum growth rate was limited only by a limitation of TMG supply. The surface morphology of all the samples was smooth regardless of growth rate. Fig. 2 shows the ω-scan XRD FWHM of the GaN (0 0 2) and (1 0 2) reflections as a function of growth rate. In this experiment, NH_3 flow rate was fixed at 100 SLM, and the TMG supply rate was changed. V/III ratio was 300–3000 according to the growth rate. Each high-temperature grown GaN layer was directly deposited on a low-temperature buffer layer. The total thickness of the samples was fixed at about 4 μm. The FWHM of the symmetric (0 0 2) reflection was less than 300 arcsec, while the FWHM of the asymmetric (1 0 2) reflection was 350, 390 and 560 arcsec for the growth rate of 2.4, 12 and 28 μm/h, respectively. It is notable that the XRD FWHM of these reflections are not very much affected up to the growth rate of 12 μm/h, even though the high-temperature GaN layer is directly grown on a low-temperature buffer layer. It is well established that an optimal nucleation density and succeeding lateral growth is important to reduce dislocation density [8]. Trapezoidal facet formation is enhanced during initial growth stage by relatively low V/III ratio [9]. Density of high-temperature grown nuclei tends to decrease by low V/III ratio, followed by lateral growth and bending of dislocations [10]. The lateral to vertical growth rate ratio seems smaller in case of the highest growth rate of 28 μm/h, which resulted in broader line width of (1 0 2) reflection.

Since the V/III ratio affects the electrical properties of GaN, the carbon concentration and sheet resistance were measured for these samples. Table 1 summarizes carbon concentration and sheet resistance measurements of GaN layers as a function of V/III ratio and the growth rate. At the V/III ratio of 600 (growth rate of 12 μm/h), carbon concentration was $1.5 \times 10^{17}\,cm^{-3}$. At the V/III ratio of 300 (growth rate of 28 μm/h), carbon concentration was $6 \times 10^{17}\,cm^{-3}$. Probably due to the carbon contamination, the sheet resistance of GaN was 16,000 Ω/sq (nominal sheet resistance by Lehighton) for the highest growth rate sample with V/III ratio of 300; however, it should be noted that the sheet resistance is also affected by the growth process of initial coalescence without regard to the residual carbon concentration. When the growth condition of early coalescence is adopted, sheet resistance tends to be high. When the retarded coalescence condition is adopted, current leakage channels are often formed near the interface of the epitaxial layer and the sapphire substrate. From these results, the usable growth rate range, which allows us to conductively dope the film, would be lower than 10 μm/h.

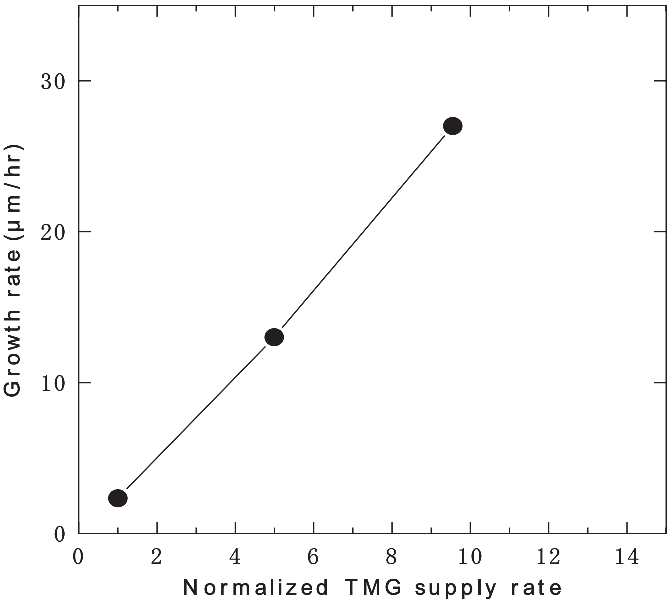

Fig. 1. GaN growth rate is shown as a function of normalized TMG supply rate.

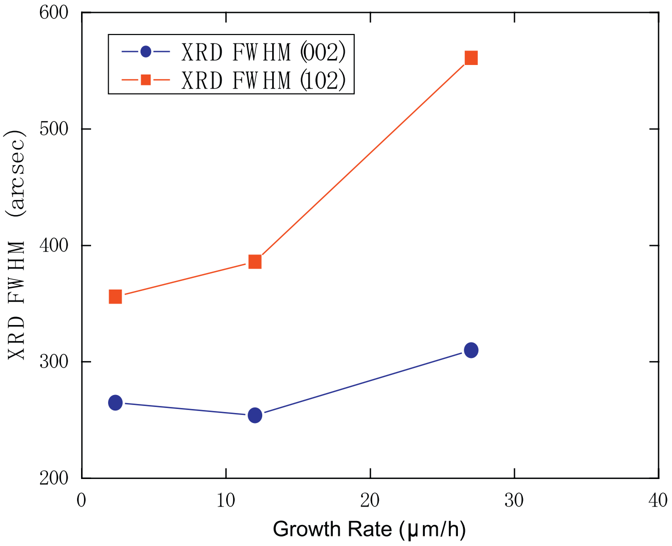

Fig. 2. FWHM of ω-scan XRD of (0 0 2) and (1 0 2) reflection are shown as a function of growth rate of GaN.

Table 1
Carbon concentration and sheet resistance of GaN is shown as a function of growth rate NH_3 flow rate was kept constant at 100 SLM. Sheet resistance was measured by Lehighton

Growth rate (μm/h)	2.4	12	28
V/III ratio	3000	600	300
Carbon concentration (cm^{-3})	2.5×10^{16}	1.5×10^{17}	6.0×10^{17}
Sheet resistance (Ω/sq)	1200	4500	16000

In comparison with hydride vapor phase epitaxy (HVPE), the reported growth rate of GaN as a function of V/III ratio is plotted in Fig. 3. It is noteworthy that a recently reported GaN growth rate by HVPE [11] is on the same line as the present work for MOVPE, while the old data for HVPE in Refs. [12–15] are below the line. Growth rate data of HVPE of Ref. [11] and the present MOVPE data are on a common straight line. The growth rate difference of HVPE [11] and the present MOVPE study can be explained mostly by Ga source supply rate, by assuming that the rate limiting process is diffusion controlled and the order of NH_3 flow rate is comparable. Because the growth rate of a surface reaction limited case is always lower than that of a diffusion-limited growth condition, different growth conditions in Refs. [12–15] may partly explain the scattered HVPE growth rate data in Fig. 3; however, because the growth temperatures of these references are very similar (in the range from 1000 to 1050 °C), a growth equipment related reason would be more probable. Incomplete reaction of HCl and metal Ga could also be considered. The limitation of the

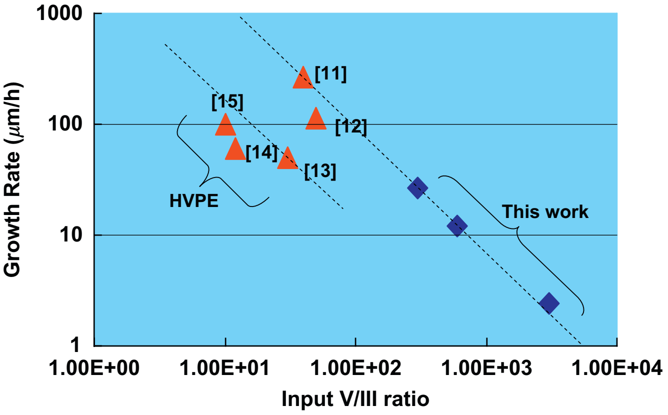

Fig. 3. Growth rate of GaN by HVPE in literatures and those of the present work by MOVPE is shown as a function of V/III ratio [11–15].

maximum growth rate of GaN by MOVPE partly comes from the reaction between GaN molecules formed in vapor phase and the stability of these resultant particles, since the GaN molecule is supposed to be a major by-product in vapor phase for atmospheric pressure MOVPE. The TMG-NH_3 adduct reaction can also be responsible for the particulate generation. The adduct process would be important at an upstream region where the decomposition process does not proceed very much in the vapor phase [16]. When there was flow turbulence at upstream region, we have observed growth rate saturation [3,17]. Growth rate saturation is also reported in a case with a long residence time in a reaction zone [18]. This implies there could be some critical residence time for growth rate saturation. In case of a long residence time, small GaN clusters, which were formed by any of a number of causes, can result in particulate growth under supersaturation of precursors. Since the maximum growth rate in the present report is not the true limit, we can expect a higher growth rate for GaN by increasing the TMG supply.

It is useful to consider whether growth rate of GaN by high flow speed MOVPE can reach the criteria of HVPE. Provided that the particulate generation by adduct process expected at upstream region is well suppressed by proper flow design and gas phase temperature distribution, we may focus on the stability of GaN clusters in growing region.

It is also interesting to consider the role of HCl in vapor phase reaction in HVPE. HCl is a reactant to produce GaCl in source region in HVPE. This HCl is usually almost perfectly consumed in the source region, but HCl is produced again through the reaction between GaCl and NH_3 in growth region. When GaN clusters are formed in the HVPE vapor phase, the concentration of GaN monomolecules around the cluster would be decreased by consumption through deposition on the cluster surface, which would increase the local HCl concentration. This higher concentration of HCl would enhance the reverse reaction by HCl to decompose GaN cluster into GaCl and NH_3, which may effectively eliminate GaN cluster formation and growth. It is also notable that a high concentration of NH_3 can act to stabilize GaN clusters by suppressing GaN decomposition. Without an efficient etching reaction in vapor phase and because of a typically high V/III ratio, the maximum obtainable growth rate of MOVPE GaN could be smaller than that of HVPE. From the above considerations, cluster formation in vapor phase should be strictly controlled in case of MOVPE. In order to eliminate the possibility of the adduct reaction path, low V/III ratio would be recommended, because adduct decomposition is enhanced by excessive NH_3 [3]. Actual limitation of growth rate of MOVPE GaN is open to continued discussion at present.

4. Summary

By using high flow speed production scale MOVPE reactor, GaN growth rate of 28 μm/h was obtained. It was shown that for conductive doping capabilities, the usable growth rate in terms of electrical and structural property was less than 10 μm/h.

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