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Study of carbon concentration in GaN grown by metalorganic chemical vapor deposition

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ABSTRACT

We investigated the C concentration in GaN as a function of the V/III ratio and growth rate for a p–n junction diode structure on a bulk GaN substrate by metalorganic chemical vapor deposition (MOCVD). The C concentration was independent of the growth rate for growth at atmospheric pressure. Moreover, the C concentration in GaN was 3.3×10^{15} cm^{-3} at a V/III ratio of 5000 with a growth rate of 2.3 μm/h and 4×1015 cm^{-3} at a V/III ratio of 3700 with a growth rate of 4.7 μm/h. Both of the major and minor carrier concentrations in the drift layers of a p–n junction structure were optimized at the reasonable growth rate in terms of the short growth time. The C impurity concentration was well controlled at a concentration on the order of 10^{15} cm^{-3}.

1. Introduction

A low power consumption for a power supply system is important for conserving energy to achieve a reduction in CO_2 emissions. GaN electron devices are very attractive owing to the physical properties of GaN, notably its large electron saturation velocity and high breakdown voltage. To date, horizontal AlGaN/GaN electron device architectures on Si substrates have been extensively studied owing to the low cost of large-diameter Si substrates. However, the study of vertical GaN power devices has recently attracted attention for high-power devices because the price of GaN substrates is decreasing [1–3]. For this application, a slightly Si-doped GaN layer that is tens of micrometers thick is required to achieve a high breakdown voltage; furthermore, the carrier concentration must be suppressed to 10^{16} cm^{-3} in order to provide a breakdown voltage of several kilovolts. Also, the residual impurity concentration influences increase of on-resistance in high breakdown voltage devices. It was reported that a part of C atoms incorporated in GaN can create energy bands between the deep level and the shallow acceptor level and compensate donors [4,5]. Because metalorganic chemical vapor deposition (MOCVD) is generally used for GaN production, C is incorporated into the films from the methyl ligand of the trimethylgallium (TMG) used as a gallium source [6]. High growth pressures, a high temperature, and high V/III ratios are effective in producing GaN films with a low C concentration with MOCVD [7]. However, a high V/III ratio implies a high NH_3 flow rate, and the TMG input must also decrease to obtain a high V/III ratio; therefore, the resulting growth rate will not be high. A low growth rate is not practical for the production of vertical devices. In this report, the growth conditions for obtaining a reasonable growth rate of 2.3–4.7 μm/h and the C concentration in GaN were investigated.

2. Experimental

In this study, GaN samples were grown using a laminar-flow-type MOCVD reactor system (Taiyo Nippon Sanso Co., SR4000). Both reactors have a trilayered gas-injection nozzle and are designed to enable AP growth at high-flow conditions [8–11]. TMG and NH_3 were used as the source gases for Ga and N, respectively. Silane (SiH_4) was used as an n-type dopant. Bulk GaN substrates (Mitsubishi Chemical Co.) were used for GaN growth. The FWHMs of the X-ray rocking curve (XRC) for the (002) and (102) planes of the 3-μm-thick GaN template on sapphire as a reference were 220″ and 290″, respectively.

Unintentionally doped (ud)-GaN or n-GaN with a thickness of 2.5–3.0 μm has been directly grown on GaN substrates and GaN templates. The growth conditions in this experiment are listed in Table 1. To investigate the effect of C incorporation, the NH_3 flow rate was varied while the TMG flow rate was constant (Series A),

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Table 1
Growth conditions for ud-GaN and Si-doped GaN.

Series	Layer	Pressure (atm)	Tg (°C)	TMG molar fraction	V/III ratio	SiH_4/TMG (%)
A	ud-GaN	1	1125	6.72×10^{-5}	1800	–
A B				6.72×10^{-5}	3700	–
A				6.72×10^{-5}	5000	–
B				1.15×10^{-4}	3700	–
B				3.36×10^{-5}	3700	–
C	n-GaN			6.72×10^{-5}	5000	4.18×10^{-6}
C				6.72×10^{-5}	5000	5.21×10^{-6}
C				6.72×10^{-5}	5000	8.33×10^{-6}

A: varying NH_3 flow and a constant TMG flow rate.
B: varying TMG flow rate for a constant V/III ratio.
C: varying SiH_4 flow rate with a constant TMG flow rate and V/III ratio.

and the TMG and NH_3 flow rates were simultaneously varied to maintain a constant V/III ratio (Series B). In addition, slightly Si-doped GaN was grown on a bulk GaN substrate (Series C) to confirm the effect of carrier compensation at a low C concentration.

X-ray diffraction (XRD) measurements were conducted to measure the XRCs. Moreover, secondary ion mass spectrometry (SIMS) and capacitance-voltage (CV) measurements were performed to characterize the impurity concentrations. The detection limits for C and Si were $1\text{–}2\times10^{15}$ cm^{-3} and 5×10^{14} cm^{-3}, respectively.

3. Results and discussion

3.1. Residual C concentration in ud-GaN

Fig. 1 shows the dependence of the C concentration on the V/III ratio (Series A). The data for the C concentrations in the GaN layers grown on 4-in. and 6-in. sapphire substrates with different reactor sizes were fitted with a single line. The C concentration is inversely proportional to the V/III ratio to concentrations on the order of 10^{15} cm^{-3} without regard to the reactor size when the growth pressure and temperature were the same. The growth rate of series A samples were about 2.3 μm/h.

The C concentration in the GaN layer on the GaN substrate exhibited approximately 30% smaller values than those on sapphire, and the C concentration reached 3.3×10^{15} cm^{-3} at a V/III ratio of 5000. The reason for the difference in C concentrations for GaN growth on different substrate materials is not yet known exactly.

Fig. 2 shows the C concentration when the TMG molar fraction increases to 1.15×10^{-4} with a constant V/III ratio of 3700 (Series B). A C concentration of 4×10^{15} cm^{-3} at a growth rate of 4.7 μm/h was obtained. The linear increase in the growth rate with the increase in the TMG molar fraction indicates that the gas-phase reaction is well-controlled. Also, the C concentrations were not changed by changing the growth rate. From these results, it was realized that the C concentration in the GaN layer is independent of the growth rate for a constant V/III ratio. The major reaction pathway for GaN growth is the elimination of the methyl group in the TMG:NH_3 adduct molecules when there is a sufficient supply of NH_3, which is predicted by quantum chemical calculations [12,13]. The above results illustrating the effect of the V/III ratio on the C concentration can be understood knowing that CH_4 is a very stable molecule and rarely contributes to C incorporation.

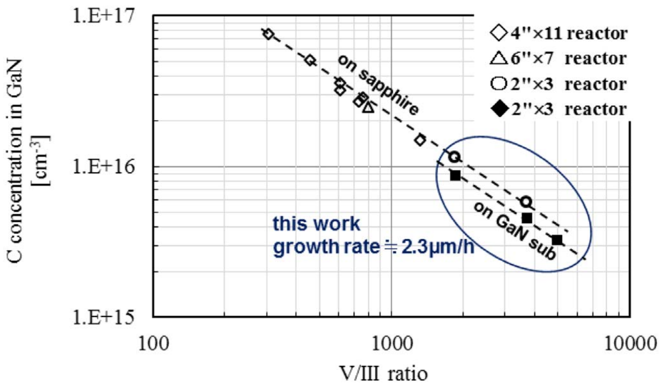

Fig. 1. C concentration in GaN layer as a function of the V/III ratio for the samples in Series A. The plot includes data for GaN layers grown with different size reactors which have same concept (high-flow-rate reactor).

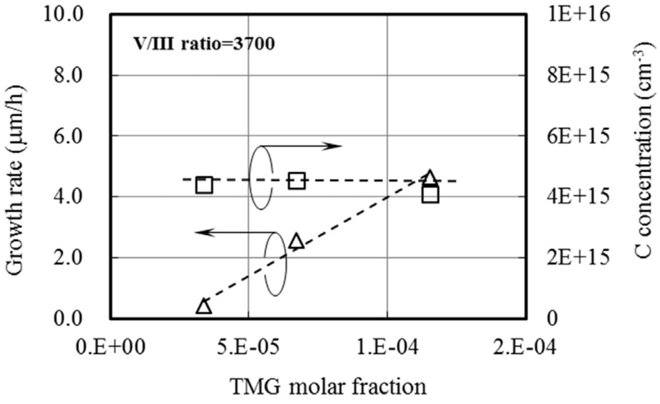

Fig. 2. Growth rate of GaN and the C concentration in the GaN layer as a function of the TMG molar fraction (Series B). The V/III ratio was kept constant to increase the TMG and NH_3 inputs simultaneously.

It is important to consider the growth rate and C concentration for growing a thick and low carrier concentration n-type GaN. From the results of Fig. 1, C concentration is inversely proportional to the V/III ratio:

$$n_C \propto \left(\frac{F_N}{F_G}\right)^{-1} \tag{1}$$

where n_C is C concentration, F_N is NH_3 molar fraction, and F_G is TMG molar fraction. Also, the result in Fig. 2 shows that the growth rate is linearly proportional to TMG molar fraction:

$$G_r \propto F_G \tag{2}$$

where G_r is the growth rate. If the gas-phase pre-reaction between NH_3 and TMG is well-controlled, those experimental results give an equation for growth rate as follows:

$$G_r = aF_N \bullet n_C + b \tag{3}$$

where a and b are constant. The relationship of growth rate and C concentration acquired from previous experiments as shown in Figs. 1 and 2 are plotted in Fig. 3. Further, the dotted lines are expected growth rates as a function of C concentration based on Eq. (3). The growth rate is proportional to C concentration, the increase of the C concentration is due to the decrease of the V/III ratio because the TMG flow rate increased for growth rate up at the constant of the NH_3 flow rate. This figure supports optimization of practical process conditions for high breakdown voltage devices.

3.2. C compensation effect in n-GaN

High-purity GaN (C concentration of 3.3×10^{15} cm^{-3} at a growth rate of 2.3 μm/h) was slightly doped with Si to confirm the carrier compensation ratio. Fig. 4 shows the relationship between

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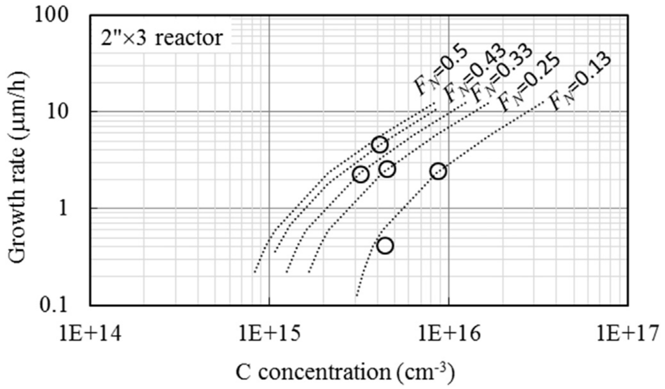

Fig. 3. The relationship between the growth rate and the C concentration as a function of NH_3 molar fraction. The dotted lines are the expected growth rates derived from Eq. (3).

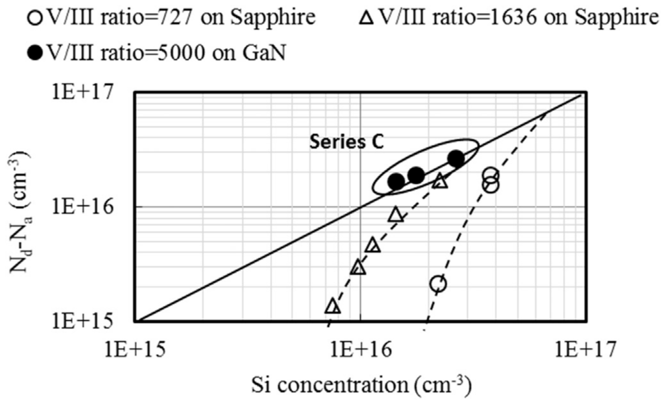

Fig. 4. Free carrier concentration (Nd–Na) in slightly Si-doped GaN on bulk GaN as a function of the solid Si concentration in GaN (Series C by SR4000). The results are shown in comparison with those for Si-doped GaN on sapphire, which was prepared with lower V/III ratios (727 and 1636) and a different reactor size (UR25k).

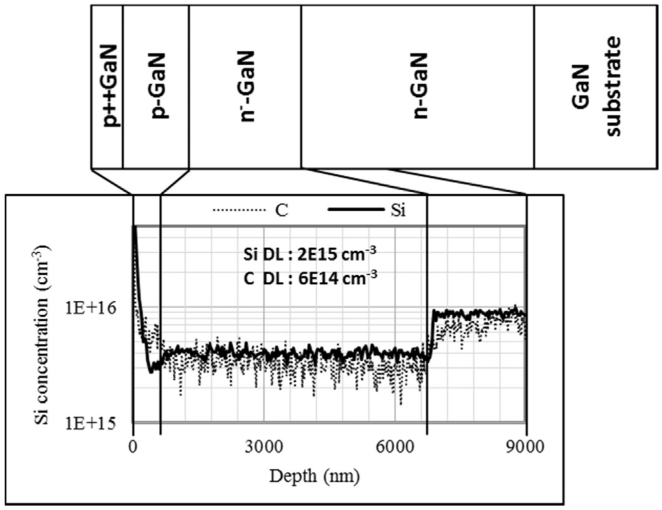

Fig. 5. Example of an in-depth profiles of the C and Si concentrations measured by SIMS in ud-GaN and slightly Si-doped GaN. The growth rates of ud-GaN and Si-doped GaN are 2.3 and 5.4 μm/h, respectively. The oxygen concentration is below the detection limit of SIMS (DL: 2.0×10^{15} cm^{-3}).

the Si dopant concentration and the net donor concentration (N_d–N_a). In our previous experiment (the open circles and triangles), some of the donors were compensated since the V/III ratios were low. In addition, we found that a lower V/III ratio caused an increase in the compensation ratio, which suggests that an increase in the C concentration results in an increase in the compensation ratio. The straight line in Fig. 4 indicates the ideal relationship between the Si dopant concentration and the activated donor concentration. The data in this experiment (Series C) fit this ideal straight line, indicating that the incorporated Si is fully activated. The Si concentration was in the range of approximately 1–3 × 10^{16} cm^{-3}. From these results, the compensation effect for growth on a GaN substrate almost disappeared when the C concentration was sufficiently low, and the donor concentration can be controlled by only the Si concentration.

Based on design method in Fig. 3, a p–n junction diode structure was also demonstrated. The optimized growth rate in terms of the C concentration for each layer was considered. A 30-μm-thick n-GaN layer was grown at 5.4 μm/h, and a 6 μm-thick n⁻-GaN was subsequently grown at 2.3 μm/h. A p-type GaN layer was then grown. Mg was used as a p-type dopant, and the Mg concentration of p-GaN was 1 × 10^{18} cm^{-3}. A simplified schematic of the p–n junction structure and its SIMS depth profiles are shown in Fig. 5. The C concentrations in n⁻-GaN and n-GaN layers were 3.3 × 10^{15} cm^{-3} and 7.3 × 10^{15} cm^{-3}, respectively. We confirmed that the both of C and Si incorporation in n⁻-GaN and n-GaN layers was well-controlled, as designed.

4. Conclusions

The C incorporation in GaN was investigated as a function of the V/III ratio and growth rate at atmospheric pressure by high-flow-speed MOCVD. The C concentration is inversely proportional to the V/III ratio to a concentration on the order of 10^{15} cm^{-3}. The growth rate was 2.3 μm/h at a C concentration of 3.3 × 10^{15} cm^{-3}. We also realized a growth rate of 4.7 μm/h at a C concentration of approximately 4 × 10^{15} cm^{-3}. These are very promising results for the growth of vertical electron devices on bulk GaN substrates. Both of the major and minor carrier concentrations in the drift layers were optimized at the reasonable growth rate in terms of the short growth time. The C impurity concentration was well controlled at a concentration on the order of 10^{15} cm^{-3}.

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