Origin of acceptor diffusion into silicon substrate during GaN growth by metal organic chemical vapor deposition

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This study investigated the change in carrier concentration near the surface of a silicon substrate during gallium nitride (GaN) growth with an aluminum nitride (AlN) buffer layer. It was observed that aluminum, gallium, and carbon diffused into the silicon substrate during the growth process and that the carrier concentration increased with increasing concentration of aluminum and gallium impurities. The gallium that diffused into the silicon substrate was identified as having originated from the gallium that decomposed on the reactor wall during the growth process and the gallium introduced onto the silicon substrate during GaN growth. In contrast, the amount of aluminum that diffused into the substrate was influenced by the duration of the trimethylaluminium (TMAI) flow: a long duration of the TMAI flow step before AlN growth led to a high aluminum concentration near the substrate surface. © 2019 The Japan Society of Applied Physics

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1. Introduction

Gallium nitride (GaN) has attractive properties for use in high-power and high-frequency devices, such as a wide bandgap, high breakdown electric field, high electron mobility, high saturated electron velocity, and high thermal conductivity.1–3 In particular, GaN power transistors fabricated on silicon substrates are superior in terms of cost, and many works have therefore studied GaN power devices on silicon substrates.4–7 The high electron mobility transistor (HEMT), which is a horizontal device, is one of the preferred applications of the GaN-on-silicon technology.5–10 A GaN HEMT can be operated at high-power and high frequency through utilization of a two-dimensional electron gas generated at the AlGaN/GaN interface by the spontaneous and piezoelectric polarization of the interface.11–13 It has been reported that removal of the silicon substrate increases the blocking voltage of a GaN-on-silicon HEMT.14–16 These works suggest that in addition to the lower breakdown field strength of silicon than of GaN, a leakage current path present along the silicon substrate surface also contributes to a low blocking voltage. However, removal of the substrate makes the device fabrication process complicated. Since leakage current is an important parameter influencing the performance of HEMT devices, the source of this current should be eliminated. A high-resistivity substrate is desirable for high-frequency devices because it reduces the parasitic capacitance between the device and the substrate.11,17,18 However, gallium and aluminum can diffuse into the silicon substrate during GaN growth, which would lead to a decrease in the substrate resistivity and degradation of the device performance.19

As described above, the behavior of carriers near the interface of a silicon substrate affects the device performance, and control of the resistivity of the substrate surface is likely to be a crucial task for enhancing the performance of GaN devices. Therefore, in this study, we identified the routes of aluminum and gallium diffusion into the interfacial region of a silicon substrate during the metal organic chemical vapor deposition (MOCVD) growth process.

2. Experimental methods

Samples were grown in a low-pressure MOCVD system including a horizontal reactor (Nihon EMC GRC-210). The flow channel was made of quartz and carbon. Trimethylaluminium (TMAl) and trimethylgallium (TMGa) were used as group-III precursors for growth of the AlN layer and GaN layer, respectively. Ammonia (NH3) was used as a group-V precursor, and hydrogen (H2) was used as the carrier gas. P-type two inch silicon(111) wafers grown by the float-zone technique were used as substrates.20 The resistivity of the substrates was higher than 1000 Ω cm. The substrates were cleaned with hydrofluoric acid to remove native silicon oxide prior to epitaxial growth. In the MOCVD reactor, the silicon substrates were heated to the growth temperature in H2 ambient. An AlN layer was used as the buffer layer for the GaN growth.21 The AlN layer was grown at two different temperatures to obtain high crystal quality. During growth of the AlN layer, TMAI was first introduced into the reactor for several seconds at 980 °C before the introduction of NH3. Then, NH3 was introduced into the reactor for 1 min along with the TMAI flow. Subsequently, the temperature was increased to 1140 °C while maintaining the flow of the precursors for 2 min, and the AlN layer grew continuously at 1140 °C for 7 min. The total thickness of the AlN layer was 0.1 μm. The TMAI and NH3 flow rates during AlN growth were 17 μmol min–1 and 0.25 SLM, respectively. After AlN growth, a 1 μm GaN layer was grown at 1050 °C for 30 min. The TMGa and NH3 flow rates during GaN growth were 100 μmol min–1 and 5 SLM, respectively. The reactor pressures during the AlN growth and GaN growth were 133 and 400 hPa, respectively. The reactor was cleaned in H2.
and NH₃ ambient before the next growth cycle: H₂ was first introduced at the maximum temperature of 1200 °C for 18 min, and NH₃ was then introduced at 1040 °C for 10 min.

In this study, seven samples were prepared to investigate which processes affect the aluminum and gallium concentrations near the substrate surface. The preparation conditions of samples and the process flow for each sample are summarized in Table I and depicted in Fig. 1, respectively. The samples were divided into four groups. Sample A consisted of only the AlN layer on the silicon substrate, where the AlN layer was grown under TMAl preflow step for 12 s by the above-described two-step growth process. For samples in group B, the durations of the TMAl flow step before AlN growth were 6 s, 12 s, 18 s, and 24 s (these samples are hereafter denoted as B6, B12, B18, and B24, respectively); then, the AlN buffer and GaN layer were grown under the same conditions as those described above. Sample C was a silicon substrate that was heated in the same temperature sequence as that adopted in the AlN growth, i.e., 980 °C and 1140 °C, in NH₃ ambient and H₂ ambient without TMAl supply; that is, no AlN and GaN films were grown. Sample D was prepared as follows: after preparation of sample A, i.e., AlN growth on the silicon substrate under the above-described conditions, the sample was removed from the MOCVD reactor and subjected to additional heat treatment at 1050 °C for 30 min in N₂ ambient in another lateral furnace that was free of gallium contamination. That is, in the preparation of both samples A and D, the duration of the TMAl flow step before AlN growth was fixed at 12 s.

The concentrations of impurities in the silicon substrates and AlN layers were evaluated by secondary ion mass spectrometry (SIMS). Before SIMS analysis of samples A, B, and D, they were thinned to several micrometers via polishing of the bottom surface, and the measurement was begun from the bottom surface of the substrates to prevent detection of aluminum and gallium in the AlN and GaN layers, respectively. Carrier concentrations were measured by spreading resistance analysis. The samples were beveled at an angle of 0.01° via polishing. Then, the profiles of the carrier concentrations were obtained through measurements at different positions along the beveled surface and thus at different depths below the substrate interface.

3. Results and discussion

The profiles of impurities and carrier concentrations below the surface of the silicon substrate in sample B12 are shown in Fig. 2. Specifically, Fig. 2(a) shows the distributions of aluminum, gallium, and carbon concentrations in B12, and Fig. 2(b) shows the difference between the distribution of the carrier concentration in this sample and the distribution of the sum of aluminum and gallium concentrations extracted from Fig. 2(a). In both plots, the origin on the horizontal axis represents the interface between the AlN buffer layer and the silicon substrate. It can be seen that aluminum, gallium, and carbon diffused into the silicon substrate during the growth of the GaN and AlN layers. The nitrogen and hydrogen concentrations were below the detection limit: 5 × 10¹⁴ cm⁻³ and 1 × 10¹⁶ cm⁻³, respectively. The detected carbon seems to have originated from the group-III precursors or components of the MOCVD reactor. The distribution of the sum of the aluminum and gallium concentrations in Fig. 2(b) agrees with that of the carrier concentration at a depth of 0–1 μm. Additionally, the carbon present in silicon does not affect the carrier concentration. Therefore, it was considered that the carrier concentration in Fig. 2(b) did not include the influence of carbon. Consequently, it was inferred that aluminum and gallium were activated as acceptors in the silicon substrate. However, at depths greater than 1 μm, the carrier concentration was lower than the sum of the aluminum and gallium concentrations. Other impurities were thought to have compensated for the carrier, and the concentration of the impurities was estimated to be about 1 × 10¹⁵ cm⁻³. Pankove et al. reported that atomic hydrogen neutralizes shallow acceptors in silicon. In our study, the hydrogen concentration was lower than 1 × 10¹⁶ cm⁻³. It was possible that the hydrogen used in the growth process diffused into silicon and passivated the aluminum and gallium acceptors.

To investigate the sources of the aluminum and gallium that diffused into the silicon substrate, the growth processes were isolated. Figure 3(a) shows the difference in the distributions of the aluminum and gallium concentrations near the silicon substrate surface between samples A and C. The temperature profiles in the preparation processes of both these samples were identical. In the case of sample A, H₂, TMAl, and NH₃ were introduced into the reactor and the AlN layer was grown. In contrast, in the case of sample C, H₂ and 

![Fig. 1. Process flow and structures of samples.](image-url)
NH₃ were introduced into the reactor and no film was grown on the sample. A comparison of samples A and C elucidates the influence of the TMAl supply on aluminum diffusion into the silicon substrate. In Fig. 3(a), the solid and dashed lines indicate the profiles of the elements in samples A and C, respectively. Figure 3(b) shows the distribution of the gallium concentration in the AlN buffer layer in sample A, and Fig. 3(c) shows a schematic drawing of the structure of sample A. The interface between the AlN layer and the silicon substrate was defined as zero depth, and positions within the silicon substrate and the AlN layer were considered to be at positive and negative depths, respectively. The increase in the gallium concentration near the zero depth as observed in Fig. 3(b) was identified by the SIMS analysis as being a result of the matrix effect caused by the roughness of the bottom of the crater.

As shown in Fig. 3(a), gallium diffused into the silicon substrate in both samples A and C. The TMGa precursor was not introduced into the reactor during the preparation process of either of these samples. Therefore, the source of the gallium detected in the silicon substrate had to be the gallium contamination that originated from GaN-based deposits in the reactor. As can be seen in Fig. 3(a), the gallium concentration near the silicon substrate surface in sample A was higher than that in sample C. From Fig. 3(b), the average concentration of gallium in the AlN buffer layer in sample A was determined to be $5.2 \times 10^{18}$ cm$^{-3}$. This high gallium concentration in the AlN buffer layer is assumed to have led to the high concentration of aluminum near the silicon substrate surface. When the AlN layer was grown, a high concentration of gallium was present in the layer during its growth. When the AlN layer was not grown, the gallium absorbed onto the silicon substrate surface was desorbed in the H₂ atmosphere. For this reason, the gallium concentration in the silicon substrate without the AlN layer was considered to be lower than that in the silicon substrate with the AlN layer. Aluminum diffused into the silicon substrate in sample A but was not observed in sample C. This result implies that aluminum contamination did not originate from the reactor wall; rather, aluminum diffused into the silicon substrate only during the AlN growth.

To examine the diffusion of aluminum from the AlN layer into the silicon substrate, the profiles of aluminum in samples A and D were compared. Sample A was composed of the AlN layer grown on the silicon substrate. Sample D was prepared by subjecting sample A to additional heat treatment at 1050 °C, which was the growth temperature of GaN. Figure 4 shows the profiles of aluminum in the silicon...
substrates in samples A (solid lines) and D (dashed lines). The aluminum concentrations near the surface after heat treatment were lower than those before heat treatment. The total aluminum concentrations in the silicon substrates at depths of 0–3 μm in samples A and D were $5.7 \times 10^{12}$ cm$^{-2}$ and $2.4 \times 10^{12}$ cm$^{-2}$, respectively. The aluminum concentration in the silicon substrate did not increase after the additional heat treatment. This result reveals that aluminum did not diffuse from the AlN layer into the silicon substrate during heat treatment. Kumagai et al. reported that the decomposition rate of AlN was very low at temperatures below 1300 °C. Therefore, in our study, it was deduced that the TMAl flow step before AlN growth, and not the thermal decomposition of the AlN layer, was the source of the aluminum in the silicon substrate.

Figure 5(a) shows the difference in the distributions of aluminum and gallium concentrations between samples A and B12, where the latter is simply sample A with a GaN layer on top. The solid and dashed lines indicate the profiles of the aluminum and gallium elements in samples A and B12, respectively. Samples A and B12 had the AlN/silicon substrate and GaN/AlN/silicon substrate structures, respectively. The comparison in Fig. 5(a) reveals the effect of the GaN growth process on the diffusion of impurities into the silicon substrate. The diffusion depths of both aluminum and gallium in sample B12 were greater than those in sample A. These results suggest that the TMGa precursor supplied during the GaN growth diffused into the silicon substrate through the AlN layer. In the AlN and GaN layers in these samples, no pits or meltback etching was observed. Hiramatsu et al. and Lu et al. reported that an AlN layer grows with a columnar structure, and Lahrèche et al. reported that numerous grain boundaries are present in the AlN layer. Because diffusion easily occurs through grain boundaries, it was considered here that gallium diffused into the AlN layer through the grain boundaries.

The duration of the TMAl flow step before AlN growth was varied to investigate the influence of this step on the diffusion of impurities into the silicon substrate. Figure 6(a) shows the difference in the depth profiles of aluminum and gallium in the silicon substrates in samples B12 and B24, i.e., when the durations of the TMAl preflow step were 12 s and 24 s, respectively. The amount of aluminum that diffused into the silicon substrate increased with increasing duration. The total gallium concentrations in the silicon substrates at depths of 0–2 μm in samples B12 and B24 were $8.8 \times 10^{11}$ cm$^{-2}$ and $5.9 \times 10^{11}$ cm$^{-2}$, respectively. The amount of diffused gallium remained almost unchanged irrespective of the duration of the TMAl preflow step. Figure 6(b) shows the total amount of aluminum that diffused into the silicon substrate at depths of 0–4 μm as a function of the duration of the TMAl preflow step. The total amount of diffused aluminum was found to increase with increasing duration. This result reveals that the duration of the TMAl preflow step affects the aluminum concentration in the silicon substrate. It is believed that when the duration is longer, aluminum does not react with nitrogen on the silicon substrate and the
aluminum concentration in the substrate consequently increases. A longer duration also provides aluminum with a greater opportunity to react with silicon.

4. Conclusions

Changes in the carrier concentration near the surface of a silicon substrate after GaN and AlN growth were investigated. Aluminum, gallium, and carbon diffused into the substrate during the growth process, and the carrier concentration increased with increasing concentration of impurities. Gallium that decomposed on the reactor wall and the gallium supplied during GaN growth were the sources of the gallium that diffused into the silicon substrate. The amount of aluminum that diffused into the silicon substrate was significantly influenced by the duration of the TMAI flow step before AlN growth.

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**Fig. 6.** (Color online) Difference in distributions of aluminum and gallium concentrations in silicon substrate between samples B12 and B24, i.e., when durations of TMAI flow step before AlN growth were 12 s and 24 s, respectively. (b) Dependence of total amount of aluminum diffused into silicon substrate on duration of TMAI preflow step.