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Ex situ dry cleaning of reactor component of nitride metal organic chemical vapor deposition using chlorinated gases

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Abstract

We have demonstrated an ex situ method of cleaning reactor parts of metal organic chemical vapor deposition (MOCVD) equipment for nitride semiconductors. The etching rate of GaN by Cl_2 gas was sufficiently high compared with that of BCl_3 gas and HCl gas. The etching rates of GaN and $Al_{0.1}Ga_{0.9}N$ with 5% Cl_2 at 750 °C were higher than 30 and 2 μm/h, respectively. We confirmed that there was no contamination of Fe, Ni, Cr and Cl in the GaN film by Cl_2 gas dry cleaning.

Keywords: A1. Dry cleaning; A3. Metalorganic chemical vapor deposition; B1. Chlorine; B1. Nitrides

1. Introduction

A high throughput of the nitride semiconductor growth process is crucial for minimizing the production cost. GaN, AlGaN and InGaN films are deposited on reactor parts, such as the tray, susceptor and flow channel, in the metalorganic chemical vapor deposition (MOCVD) chamber during the epitaxial growth process. The deposits on the wafer susceptor and reactor wall can cause a particulate generation and also brings about the gradual change of the thermal condition of the growth ambient, which results in a shift of the growth temperature. Therefore, these parts must be frequently cleaned to improve the yields of the epi-process by removing the deposits. Reactor parts with deposits are routinely cleaned in every growth run by introducing H_2 gas into the reactor at a susceptor temperature above 1000 °C. However, it is very difficult to remove the deposit of Al containing nitride alloys only by thermal cleaning. Moreover, these parts are sometimes deformed during cleaning at a high temperature. As a result, ex situ wet cleaning in hot phosphoric acid is conducted once in every few growth runs. However, hot phosphoric acid is very dangerous. Therefore, there has been a strong demand for the dry gas cleaning method of removing Al containing nitride alloys from the reactor components of GaN MOCVD equipment. To this end, we have developed an ex situ dry cleaning method to remove the deposits on reactor components as well as ensuring safety during cleaning.

We have tested HCl gas, BCl_3 gas and Cl_2 gas diluted by N_2 gas as candidates for cleaning gas. Since Cl_2 and H_2 react explosively, we cannot use H_2 as a carrier gas. The expected reaction by-products are $GaCl_3$, $AlCl_3$ and $InCl_3$. They have a high enough vapor pressure at a temperature higher than 500 °C.

We measured secondary ionization mass spectrometry (SIMS) of GaN, which was grown by using reactor components just after cleaning to examine the potential contamination from gas cleaning by measuring the heavy metals and chlorine.

2. Experimental procedure

In this experiment, two types of quartz glass tube reactors were used. First, a small reactor (inner diameter of 48 mm, indicated as "reactor A") was used to study the chemistry of this cleaning method. Cl_2, HCl and BCl_3 gases were compared in terms of the etch rates of GaN and $Al_{0.1}Ga_{0.9}N$. After the temperature of the reactor was

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stabilized at the set point, the cleaning gas was supplied into reactor A at the flow rates ranging from 0.109 to 1.09 slm. GaN and $Al_{0.1}Ga_{0.9}N$/GaN films grown on sapphire substrates by MOCVD were used as samples. The efficiency of the dry cleaning was investigated by measuring the weight loss of samples. The sample thickness was also measured by scanning electron microscopy (SEM). The amount of residual Ga on the specimen surface was measured by X-ray fluorescence spectrometer (XRF). Next, a large dry cleaning reactor, with an inner diameter of 360 mm (indicated as "reactor B"), was used for cleaning the components of the existing multi-wafer MOCVD. For reactor B, only Cl_2 gas was used. The flow rates of N_2 and Cl_2 gases for reactor B were 4.56 and 0.24 slm, respectively, so that the Cl_2 gas concentration was 5%. SIMS measurement of GaN was conducted for the layer grown using the reactor components cleaned with Cl_2 gas.

3. Results and discussion

First, the effect of gas concentration on etching rate was investigated using reactor A. The gas flow velocity, reaction pressure, reaction temperature, and reaction time were 1 cm/s, 101 kPa, 750 °C, and 1 h, respectively. Fig. 1 shows the cleaning efficiency as a function of gas concentration for Cl_2 , HCl, and BCl_3 gases. The cleaning efficiency is defined as the percentage of the removed amount to the deposits. Etching gas, 5% Cl_2, completely etched the 2.7-μm-thick GaN film for 1 h, while the cleaning efficiency for 30% HCl gas was less than 90% and that for 5% BCl_3 gas was about 50%. The etching rate of GaN using 5% Cl_2 gas was estimated to be more than 27 μm/h because 2.7-μm-thick GaN was completely etched within 0.1 h. In a similar manner, AlGaN/GaN(0.2 μm/3.0 μm) was completely etched within 0.1 h. From this result, we can know that the etching rate of GaN is even higher than 30 μm/h. Even if we assume the etching rate of GaN is 30 μm/h, the etching rate for $Al_{0.1}Ga_{0.9}N$ is much higher than 2 μm/h. The etching rates of 2 μm/h for AlGaN and 30 μm/h for GaN are high enough for cleaning wall deposit with regard to conventional visible LED production, because AlGaN thickness is several tens nm and GaN thickness is several microns [1,2].

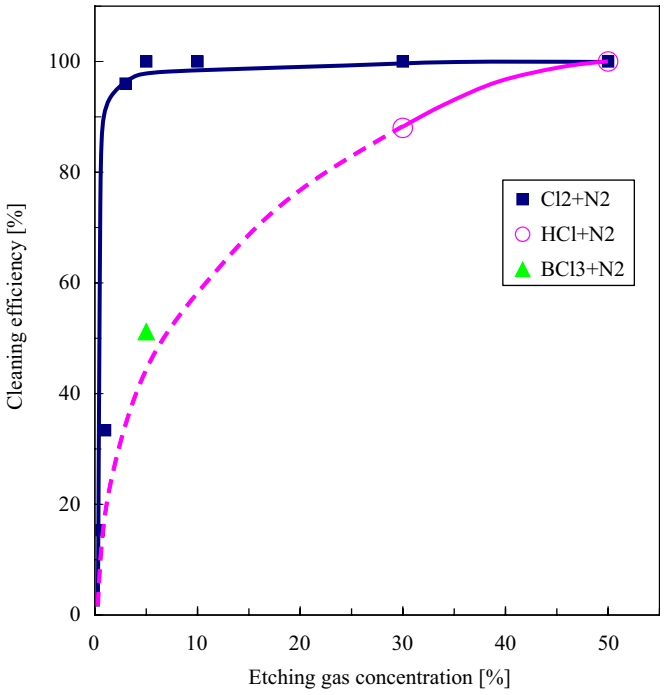

Fig. 1. The effect of gas concentration on cleaning efficiency. Sample: 2.7-μm-thick GaN film on sapphire substrate, reaction time: 1 h, reaction pressure:101 kPa, reaction temperature: 750 °C, dilution gas: N_2, total gas flow: 1.09 slm.

In the case of HCl gas, a white material was deposited on the inner surface of the quartz glass tube downstream of the reactor. Such a white deposit was not observed when Cl_2 gas was used. A solution of the white deposit in water was analyzed using ion chromatography and inductively coupled plasma mass spectrometer (ICP-MS). Some ions, such as Cl^-, NH_4^+ and Ga^{3+}, were detected in the solution; thus, it was supposed that the main components of the white deposit were NH_4Cl and $GaCl_3$, which were derived from the following reactions:

$$3HCL + GaN \rightarrow GaCl_3 + NH_3, \quad (1)$$

$$NH_3 + HCL \rightarrow NH_4Cl. \quad (2)$$

It is notable that monochloride material like GaCl, which has a key role in hydride vapor phase epitaxy, is less important under hydrogen free condition. GaCl involves a reaction as follows:

$$GaN + HCl + H_2 \rightarrow GaCl + NH_3, \quad (3)$$

which is less probable without hydrogen. In addition, GaCl is consumed through the reaction:

$$GaCl + 2HCl \rightarrow GaCl_3 + H_2. \quad (4)$$

Koukitu reported that GaN growth rate is very much enhanced under hydrogen free condition by thermodynamic analysis. In other word, the etching reaction by HCl is suppressed with inert carrier gas [3].

From the above results, we found that Cl_2 gas was the most suitable cleaning gas among the candidates. Therefore, we used only Cl_2 gas for the succeeding experiments.

A 4.8-μm-thick GaN film was processed using reactor A. Cl_2 gas diluted to 5% in N_2 carrier gas was supplied at process temperatures from 650 to 750 °C. Fig. 2 shows the cleaning efficiency as a function of reaction time. The cleaning efficiency is almost proportional to the reaction time. The etching rate of the GaN film increased with the process temperature, the etching rate increased by a factor of 6 as the process temperature increased by 50 °C. The inset in Fig. 2 shows an Arrhenius plot of the reaction coefficient k calculated from the slope in Fig. 2. The

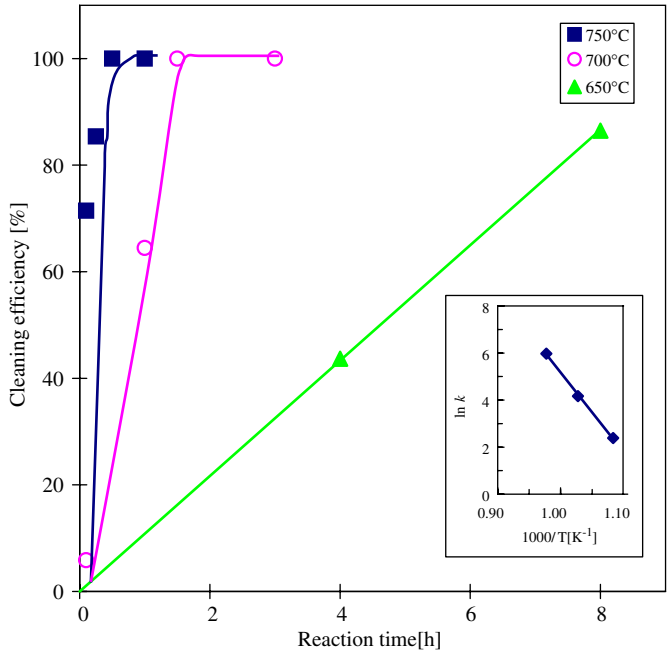

Fig. 2. Cleaning efficiency as a function of reaction time. The inset shows in Arrhenius plot of the reaction coefficient k calculated from the slope in Fig. 2. Cleaning gas: Cl_2, dilution gas: N_2, gas concentration:5%, total gas flow: 1.09 slm, reaction pressure: 101 kPa.

Arrhenius equations shown below:

$$k = A \exp(-E_a/k_B T), \quad (5)$$

where A, E_a, k_B, and T represent frequency factor, activation energy, Boltzmann factor, and temperature, respectively. The frequency factor A and activation energy E_a were estimated to be 9.76×10^{16} and 2.92 eV/K, respectively.

We also developed a large cleaning reactor (reactor B) for a mass-production multi-wafer MOCVD system. The temperature distribution in the working region in the reactor B was controlled to within 10 °C. A quartz glass platelet, which was placed in the MOCVD reactor, was tested. The process pressure, process temperature, and time were 101 kPa, 750 °C, and 30 min, respectively. We supplied 5% of Cl_2 gas into the reactor. Fig. 3 shows the quartz glass platelet before and after the cleaning process, respectively. The deposit on the platelet contained GaN, InGaN, AlGaN and AlN after many growth runs of LED structures. The quartz glass platelet was transparent after the cleaning process. After the cleaning process, we detected 0.12 mass% Ga residues on the specimen surface by XRF measurement. The effect of the cleaning process on GaN film was also investigated in terms of residual heavy metal contamination and chlorine. Fig. 4 shows the SIMS depth profile of GaN film grown using components just after cleaning by Cl_2 gas. Concentration of Cl, Ni, Fe and Cr were all less than detection limit. It is expected that the ex situ cleaning process will improve the epi-process throughput by a factor of 1.5 using two sets of MOCVD reactor components alternately for mass production.

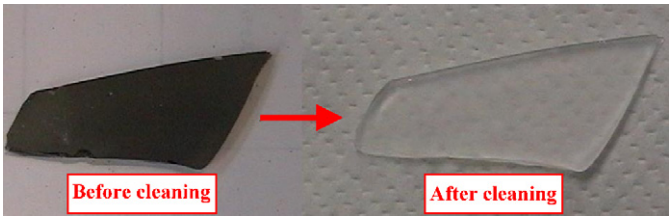

Fig. 3. Photos of a quartz glass platelet of flow channel. Left side: before cleaning, right side: after cleaning. The sample was cleaned in the reactor B. Cleaning gas: Cl_2, dilution gas: N_2, gas concentration: 5%, total gas flow: 1.09 slm, reaction time: 30 min, reaction pressure: 101 kPa, reaction temperature: 750 °C.

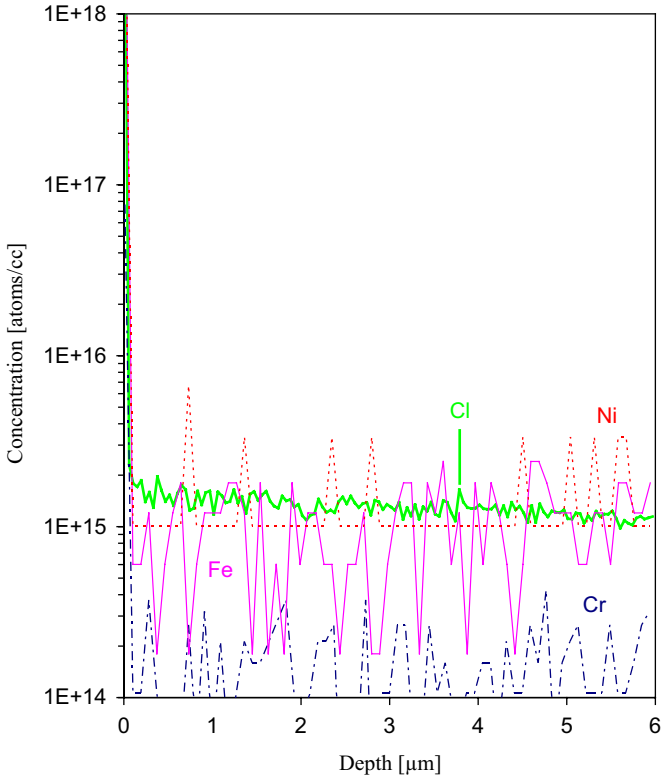

Fig. 4. SIMS depth profile of GaN film grown using components just after cleaning by Cl_2 gas. Cl, Ni, Fe and Cr were at quantities less than the detection limit.

4. Summary

We have examined the possibility of the thermal etching of GaN and $Al_{0.1}Ga_{0.9}N$ using Cl_2, HCl and BCl_3 gases. Among them, Cl_2 gas was the most efficient for ex situ cleaning of the reactor components of nitride semiconductor MOCVD equipment. The etching rates were higher

than 30 μm/h for GaN and much higher than 2 μm/h for $Al_{0.1}Ga_{0.9}N$ at 750 °C.

After the cleaning process, we detected 0.12 mass% Ga residues on the specimen surface by XRF measurement. We confirmed that there was no contamination of Fe, Ni, Cr and Cl in the GaN film by Cl_2 gas dry cleaning. The ex situ cleaning process would be useful for a mass-production nitride MOCVD.

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