Observation and Suppression of Growth Pits Formed on 4H-SiC Epitaxial Films Grown Using Halide Chemical Vapor Deposition Process

Yoshiaki Daigo, Keisuke Kurashima, Shigeaki Ishii, and Ichiro Mizushima

***Abstract*—In this study, the origin of growth pits on the surface of 4H-silicon carbide epitaxial films grown using a chemical vapor deposition reactor was clarified by evaluating the surface morphology of substrates immediately before the epitaxial growth and of epitaxial films. When the film was grown under non-optimized conditions, we found that numerous Si particles were formed on the surface of the substrate before the epitaxial growth and that the numerous growth pits on the subsequently grown epitaxial film were originated from Si particles. We observed that, by increasing the HCl flow rate through the outer nozzles in the gas inlet, which has a double-pipe structure consisting of inner and outer nozzles, the growth pit density was successfully decreased.**

***Index Terms*—4H-SiC, epitaxial growth, growth pits, Si particles.**

I. INTRODUCTION

4H- SILICON carbide (4H-SiC) semiconductors have been used for fabricating high-efficiency power devices owing to their excellent physical properties such as wide bandgap, high breakdown electric field strength, and high thermal conductivity. In order to widely utilize 4H-SiC power devices, the development of epitaxial growth techniques based on the chemical vapor deposition (CVD) method, which is essential for forming an active layer on the power device, is progressing. In the past, several experimental efforts, such as increasing the growth rate [1], [2] and reducing the defect density [3], [4] of 4H-SiC epitaxial films, have been made to improve productivity and yield.

When the 4H-SiC epitaxial films are grown using a conventional CVD process based on the SiH_4-C_3H_8-H_2 reaction gas system, in which SiH_4, C_3H_8, and H_2 gases are used as the Si, C, and carrier gases, respectively, Si clusters are likely to be generated through homogeneous nucleation in the gas phase or on the growing surface at high SiH_4 concentrations [5]. Because the Si clusters generated through homogeneous nucleation have harmful effects on epitaxial growth, such as decreasing the growth rate [6] and forming defects [7], the available growth conditions for the mass production of 4H-SiC epitaxial films are restricted to a narrow range in which no homogeneous nucleation occurs. By contrast, a halide CVD process based on the SiH_4-C_3H_8-H_2-HCl reaction gas system is unlikely to generate Si clusters [1], [2], [4], [6] and is expected to realize a high growth rate and low defect density in 4H-SiC epitaxial films.

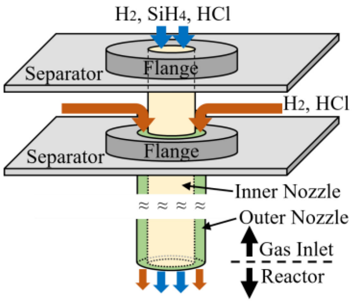

Fig. 1. Schematic of a gas nozzle having a double-pipe structure.

In the halide CVD process, the reaction between SiH_4 and HCl gases is believed to form stable $SiCl_2$ species, which prevent homogeneous nucleation [1]. This leads to a considerable increase in the growth rate and suppression of Si cluster formation under high SiH_4 concentrations. However, even when halide CVD is used for the epitaxial growth of 4H-SiC films, numerous growth pits are formed on the epitaxial film surface [4]. In the present study, one of the origin of numerous growth pits on 4H-SiC films grown using the halide CVD process was clarified, and a technique to suppress the formation of numerous growth pits was presented.

II. EXPERIMENTAL METHODS

The samples were prepared using a vertical CVD system (EPIREVO^{TM} S8, NuFlare Technology, Inc.). A gas inlet was placed on the top of the CVD reactor, and process gases were introduced into the reaction space through several gas nozzles in the gas inlet. For the epitaxial growth, SiH_4, C_3H_8, HCl, and H_2 gases were used as process gases, whereas SiH_4 and C_3H_8 gases were introduced separately into the reactor. The gas nozzles consisted of a double-pipe structure, as shown in Fig. 1. SiH_4 gas, which was mixed with HCl gas and

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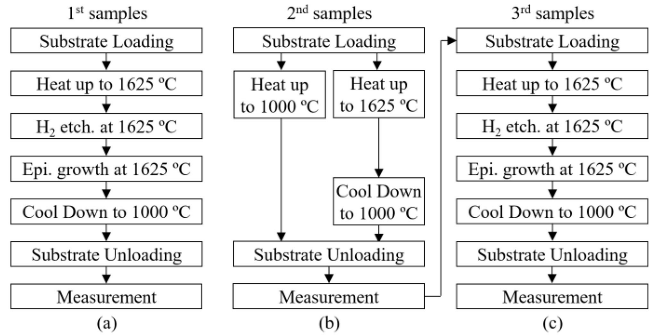


Fig. 2. Process flows during sample fabrications.

diluted with H_2 gas, was introduced into the reactor through the inner nozzles. Furthermore, HCl gas diluted with H_2 gas was introduced into the reactor through the outer nozzles that surrounded the inner nozzles. Using this configuration, the formation of Si byproducts on the tips of nozzles was suppressed and the repeatability of the thickness and doping concentration of 4H-SiC films was improved [9].

In this study, three types of samples were prepared using the process flows shown in Fig. 2. Two epitaxial films were grown as 1st samples following the process flow shown in Fig. 2(a). These films were grown on 4H-SiC bare substrates under non-optimized and optimized conditions. In the process flow shown in Fig. 2(a), the substrate temperature was increased up to 1625 °C under the H_2 ambient condition, and approximately 10-μm thick epitaxial films were grown after H_2 etching toward the substrate surface. Two substrates, for which the heating process was performed as shown in Fig. 2(b), were prepared as 2nd samples after epitaxial growth using non-optimized condition. In the process flow shown in Fig. 2(b), the substrate temperature was increased to the target temperature under the H_2 ambient condition and was then lowered to the transfer temperature without epitaxial growth. The target temperatures for the two 2nd samples were 1000 and 1625 °C, respectively. The 3rd sample was an epitaxial film grown on the substrate for which the heating process was performed; the process flow was same as those shown in Fig. 2(a) and film was grown under optimized condition.

The samples prepared in this study were measured by optical microscope with bright-field and dark-field images and Raman spectroscopy.

III. RESULTS AND DISCUSSION

1st samples were grown on a bare substrate following the process flow shown in Fig. 2(a). Fig. 3 shows the bright-field images of two 1st samples grown under non-optimized and optimized conditions. For film growth under non-optimized conditions, the Cl/Si ratio, which was calculated using the total flow rate of HCl gas and the total flow rate of SiH_4 gas, was set to 11.5, and the flow rate ratio of HCl gas passing through the outer gas nozzles was 4.3% of the total HCl gas flow rate. Numerous growth pits were observed on the surfaces of films grown under non-optimized conditions. These growth pits were always observed under non-optimized conditions, even when the substrate was replaced with several other substrates. For film growth under optimized conditions, the Cl/Si ratio was maintained at 11.5, and the flow rate ratio of HCl gas passing through the outer gas nozzles was changed to 10.9%. Compared with the epitaxial film grown under the non-optimized condition, numerous growth pits were not observed on the film grown under the optimized condition, and this result was repeatedly observed even when the substrate was replaced with other substrates.

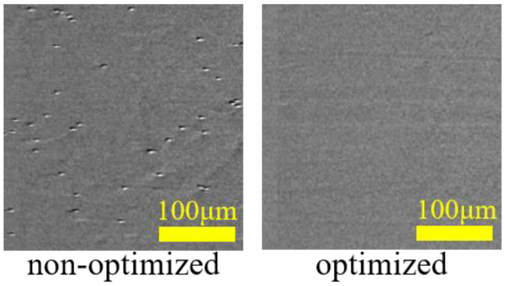


Fig. 3. Bright-field images of the surfaces of 4H-SiC epitaxial films (1st samples) prepared following the process flow shown in Fig. 2(a).

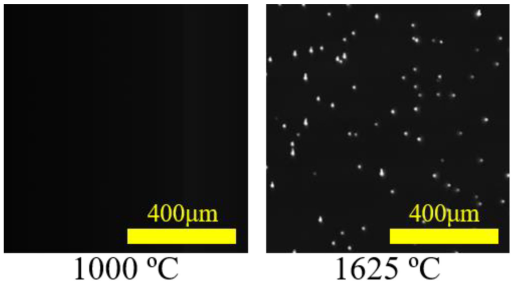


Fig. 4. Dark-field images of the surfaces of 4H-SiC substrates (2nd samples) prepared following the process flow shown in Fig. 2(b).

To analyze the substrate surface immediately before epitaxial growth using non-optimized condition, a heating process without epitaxial growth was performed for the two substrates, as shown in Fig. 2(b). Fig. 4 shows the bright-field and dark-field images of the surface of 2nd samples, which were heated to target temperatures of 1000 and 1625 °C, respectively. For the substrate heat-treated at 1000 °C, a pitch-black background in the dark-field image was observed, and no clear foreign materials appeared to adhere to the surface of the substrate. Needless to say, no clear foreign materials were found, even for the substrates that were transferred into the CVD system without introducing them into the CVD reactor. For the substrate heat-treated at 1625 °C, on the other hand, numerous foreign materials were clearly observed as numerous bright spots in dark-field images.

To clarify the structural properties of foreign materials on the substrate, Raman measurements were performed at positions where foreign materials were observed and were not observed. Fig. 5 shows the Raman spectra of the substrate heat-treated at 1625 °C. At the position where foreign materials were not observed, three intense peaks at approximately 200, 790, and 1000 cm^{-1}, and a weak peak at approximately 600 cm^{-1} were observed. At the position where foreign

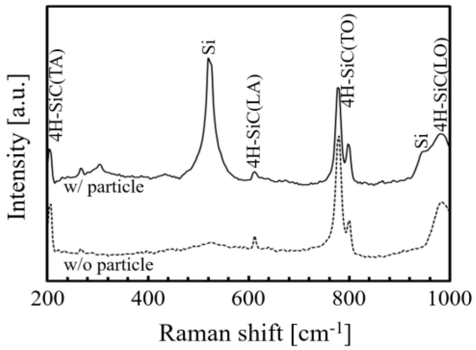
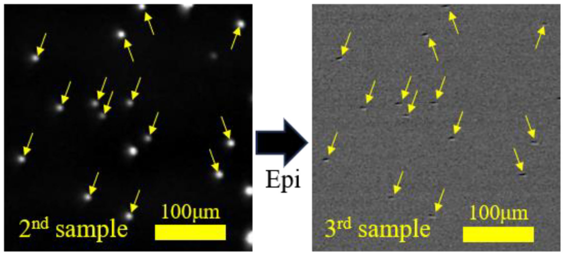


Fig. 5. Raman spectra of the 4H-SiC substrate heat-treated at 1625 °C shown in Fig. 4.



(a) (b)

Fig. 6. Correlation between dark-field image for the substrate (2^{nd} sample) that was heat-treated at 1625 °C shown in Fig. 4 and bright-field image for the epitaxial film (3^{rd} sample) grown on the same 2^{nd} sample.

materials were observed, two intense peaks at approximately 520 and 900 cm^{-1} were observed. The intense peaks at approximately 200, 790, and 1000 cm^{-1} as well as a weak peak at approximately 600 cm^{-1} were associated with the 4H-SiC crystal, although the two intense peaks at approximately 520 and 900 cm^{-1} were associated with the Si crystal. Therefore, the foreign materials observed on the heat-treated substrates were Si particles.

Fig. 6 shows the correlation between the Si particles and the growth pits on the epitaxial film. The epitaxial film as 3^{rd} sample was grown on one of the 2^{nd} samples which was heat-treated at 1625 °C, and was measured by bright field image. Fig. 6 shows the typical position of the same coordinate between the substrate heat-treated at 1625 °C and the epitaxial film on the same substrate. Numerous growth pits were observed on the epitaxial film at positions where numerous Si particles were formed.

In our previous paper [9], we found that Si byproducts are formed on the tips of gas nozzles when the HCl gas as an outer gas does not pass through the outer gas nozzles. This is because the films were grown on the gas nozzles with a double-pipe structure, and SiH_4 gas mixed with HCl gas and C_3H_8 was separately introduced into the reactor. Owing to this configuration, byproducts on the gas nozzles are likely to be formed as the Si phase rather than the 3C-SiC phase. Furthermore, we found that the formation of Si byproducts on the tip of gas nozzles can be easily suppressed by adding HCl gas to the outer gases passing through the outer gas nozzles. Under non-optimized conditions, we considered that the suppression of Si byproduct formation was insufficient owing to the addition of a small amount of HCl gas. Furthermore, Si byproducts appeared to be thermally decomposed during the heating process as well as appear to act as the origin of Si particle formation. Under optimized conditions, because the HCl gas concentration passing through the outer nozzles was increased, Si byproducts could be sufficiently removed. Thus, numerous growth pits were not observed owing to the suppression of Si byproducts formed on the gas nozzles.

IV. CONCLUSION

In this study, the origin of numerous growth pits on the surface of 4H-SiC epitaxial films grown using a CVD reactor was clarified by evaluating the surface morphology of the substrates immediately before the growth of epitaxial. When the film was grown under non-optimized conditions, we found that numerous Si particles were formed on the substrate surface before epitaxial growth and that the numerous growth pits on the subsequently grown epitaxial film originated from the Si particles. The formation of Si byproducts was suppressed by increasing the HCl flow rate through the outer nozzles in the gas inlet, which had a double-pipe structure consisting of inner and outer nozzles; thus, the density of the growth pit was successfully decreased.

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