Silicon carbide (SiC) has been considered as a promising wide bandgap material for high power, high frequency, and high temperature devices owing to its high breakdown field (~3 × 10^6 V/cm), high thermal conductivity, high saturated electron drift velocity (~2 × 10^7 cm/s), and chemical stability. Due to the commercialization of its large single-crystal wafer up to size of 6 inch and excellent electrical and thermal properties, SiC has become a better candidate for high-power and high-frequency devices compared to the Si-face. Therefore, it is essential to determine the dependence of the quality of epitaxial layers on substrate polarity. Although many SiC polytypes, most of the recent work has focused to on-axis substrate has attracted much attention, because of two main advantages. First, it can reduce basal plane dislocations (BPDs), which are known as killer defects for power device applications. Second, it can diminish crystal waste in slicing ingots for producing wafers. However, the epitaxial growth on low off-angle 4H-SiC substrates exhibits a difficulty in controlling the morphology of epitaxial film, especially macro step-bunching. The step-bunching behavior of 4H-SiC is one of the major problems that should be eliminated, and there has been a lot of research in this area. Recently, the off-angle reduction from 8° to on-axis substrates has been considered as a promising wide bandgap material for high power, high frequency, and high temperature devices owing to its high breakdown field (~3 × 10^6 V/cm), high thermal conductivity, high saturated electron drift velocity (~2 × 10^7 cm/s), and chemical stability. Due to the commercialization of its large single-crystal wafer up to size of 6 inch and excellent epitaxial growth technique, SiC becomes a better candidate for application in high-power and high-frequency electronic devices compared to the other wide-bandgap materials such as GaN, ZnO, and diamond. Among the many SiC polytypes, most of the recent work has focused on 4H-SiC owing to its high saturated electron drift velocity and commercial availability.

Recently, the off-angle reduction from 8° to on-axis substrate has attracted much attention, because of two main advantages. First, it can reduce basal plane dislocations (BPDs), which are known as killer defects for power device applications. Second, it can diminish crystal waste in slicing ingots for producing wafers. However, the epitaxial growth on low off-angle 4H-SiC substrates exhibits a difficulty in controlling the morphology of epitaxial film, especially macro step-bunching. The step-bunching behavior of 4H-SiC is one of the major problems that should be eliminated, and there has been a lot of research in this area.

The 4H-SiC epitaxial films were deposited on the n-type 4° off-axis 4H-SiC Si-face and C-face substrates by in situ H2 pre-etching and homoepitaxial growth of 4H-SiC have been carried out on 4° off-axis Si-face and C-face substrates by low-pressure chemical vapor deposition. We systematically analyzed H2 etching characteristics and epitaxial growth of 4H-SiC substrates on two different polarities using an organosilicon source material, bistrimethylsilylmethane (C7H20Si2). The effects of the growth conditions, such as growth temperature and source flow rate on the surface morphology, crystallinity, polytype conversion, defect generation, and structural imperfection of the epilayers on different polar surfaces, were investigated. High-quality epitaxial layers were successfully grown at low temperature range of 1320-1440 °C on the Si-face and 1500 °C on the C-face. A low source flow rate of 5–10 sccm was also preferred to grow defect-free epilayers.© 2015 The Electrochemical Society. [DOI: 10.1149/2.011508jss] All rights reserved.

Experimental

The 4H-SiC epitaxial films were deposited on the n-type 4° off-axis 4H-SiC Si-face and C-face substrates using an organosilicon source material, bistrimethylsilylmethane (BTMSM; C7H20Si2). BTMSM, containing both C and Si components, is nontoxic and nonflammable. It also makes lower temperature growth possible compared to a silane (SiH4) source. Our research group previously performed SiC epitaxial growth using BTMSM as a precursor, but most efforts have been focused on Si-face substrates. The effects of the growth conditions, such as growth temperature and source flow rate on the surface morphology, crystallinity, polytype conversion, defect generation, and structural imperfection of the epilayers on different polar surfaces, were investigated. This study has successfully identified the optimized experimental conditions for in situ surface preparation and epitaxial growth on C-face as well as Si-face substrates using the BTMSM.

Comparative Study of 4H-SiC Epitaxial Layers Grown on 4° Off-Axis Si- and C-Face Substrates Using Bistrimethylsilylmethane Precursor

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In situ H2 etching and homoepitaxial growth of 4H-SiC have been carried out on 4° off-axis Si-face and C-face substrates by low-pressure chemical vapor deposition. We systematically analyzed H2 etching characteristics and epitaxial growth of 4H-SiC substrates on two different polarities using an organosilicon source material, bistrimethylsilylmethane (C7H20Si2). The effects of the growth conditions, such as growth temperature and source flow rate on the surface morphology, crystallinity, polytype conversion, defect generation, and structural imperfection of the epilayers on different polar surfaces, were investigated. High-quality epitaxial layers were successfully grown at low temperature range of 1320–1440 °C on the Si-face and 1500 °C on the C-face. A low source flow rate of 5–10 sccm was also preferred to grow defect-free epilayers. 

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the growth chamber was fixed at 180 Torr. The epitaxial growth was performed for 2 hr. The surface morphology of in situ H₂-etched substrates and epitaxial films was observed using a Nomarski microscope (NMS, Nicon, Eclipse LV100D) and atomic force microscopy (AFM, JEOL, JSPM-5200). X-ray diffraction (XRD) analysis was conducted by a PANalytical high resolution X-ray diffractometer with a 2 kW Cu radiation source. Double-axis crystal XRD was used to evaluate the crystallinity. Micro-Raman spectroscopy was performed to determine the existence of polytype conversion using a Horiba Jobin-Yvon LabRam HR spectrometer and detected with a liquid-nitrogen-cooled CCD detector. The 514.5 nm line of an Ar-ion laser was used as an excitation source, and the laser power on the sample was maintained at around 100 μW to avoid heating of the sample by the measuring laser beam. The laser spot diameter was about 1 μm. The Raman signal was collected in a backscattering geometry using a ×100 microscope objective lens. Cross-sectional observation for epilayers by scanning electron microscopy (SEM) was performed to determine the thickness of epilayers. The background doping concentration of epilayers was determined from capacitance–voltage (C–V) measurements of Ni/SiC Schottky diodes (contact diameter: 300 μm).

**Results and Discussion**

*In situ surface preparation of 4° off-axis Si-face and C-face SiC substrates using hydrogen.* — H₂ etching of substrates, prior to the epitaxial growth, is a prerequisite process to gain the optimal surface; the process removes the damaged layer, surface native scratches, and incomplete nucleation generation sites. The experiment was conducted for 10 min, while the etching temperatures were 1450 C and 1500 C to reveal the different characteristics between each face of the substrates. Figure 1 presents AFM images of 4° off-axis Si-face and C-face 4H-SiC wafers and hydrogen etched wafers obtained at 1450 C and 1500 C. Figures 1a and 1b present the bare substrates of the Si-face and C-face, showing native scratches. Root-mean-square (RMS) roughnesses of the substrates were 0.94 nm and 0.67 nm, respectively. Figure 1c shows irregular macro step-bunching morphology and an RMS roughness of 5.32 nm when the surface of the Si-face was etched at 1500 C, whereas a smooth surface without scratch or step-bunching and having an RMS roughness of 0.4 nm could be obtained at 1450 C (Fig. 1e). There was no step-bunching on C-face SiC at 1500 C (Fig. 1d) with an RMS roughness of 1.84 nm, but some clusters, which cause several defects in epitaxial growth, were found. Nevertheless, with a hydrogen etching temperature of 1450 C, no step-bunching nor clusters were observed with an RMS roughness of 0.45 nm (Fig. 1f).

As shown in the Figure 1, macro step-bunching only occurred on the Si-face SiC when the etching temperature was 1500 C. It is believed that step bunching occurs as a result of enhanced surface etching under high temperatures in a hydrogen atmosphere. Since the Si-face possesses high surface-free energy, surface expends in order to reduce the energy during the etching process, resulting in the formation of step-bunching. Because the C-face is more chemically active than the Si-face, the high temperature of 1500 C in the hydrogen etching process may generate more clusters on C-face than on the Si-face. Such clusters should be removed, since such clusters are the origin of crystallographic defects during epitaxial growth. Therefore, in order to acquire smooth layers on the two different faces, we conducted the surface preparation at a temperature of 1450 C in a hydrogen environment for 10 min prior to the epitaxial growth.

**4H-SiC epitaxial layers grown on 4° off-axis Si-face substrates using BTMSM.** — Figure 2 shows the Nomarski micrograph and AFM image of the 4H-SiC epitaxial layer grown on a Si-face substrate at 1400 C. The BTMSM carrier gas flow rate was 10 sccm. By using BTMSM source, which operates at a temperature 200–300 C lower than the usual SiC epitaxial growth temperature of 1600 C using a gas source including SiH₄ and C₃H₈, a good surface morphology without defects or step-bunching and having a low RMS roughness of 0.2–0.8 nm could be obtained over a broad temperature range of 1320 to 1440 C. Unlike the report on the increasing density of defects with a lower growth temperature, the epitaxial layer grown in this experiment showed no defects on the surface. It is believed that the smooth surface is obtained owing to the bonding characteristics of the BTMSM source, which has an alternate and tetrahedral Si–C bonding structure like the crystal phase of SiC.

Figure 3 presents the AFM step profiling of SiC epilayers grown at 1280, 1360, and 1440 C. The step morphology at the growth temperatures of 1280 C illustrates high RMS roughness of 20–30 nm owing to 3D nucleation and growth. Layer-by-layer growth or step-flow growth occurred with the growth temperature of 1360 C, resulting an RMS roughness of 0.7–0.8 nm; and growth temperature of 1440 C, resulting an RMS roughness of 0.2–0.3 nm, respectively.

Figure 4 shows the RMS roughness determined from the AFM image of the 4H-SiC epitaxial layer, which was grown at various growth temperatures and flow rate of BTMSM carrier gas. We evaluated the RMS roughnesses five times for each sample in order to ensure reliability. As the growth temperature decreases or the flow

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*Figure 1. AFM images of (a) Si-face (b) C-face bare substrate, (c) Si-face (d) C-face substrate after H₂ etching at 1500°C, and (e) Si-face (f) C-face substrate after H₂ etching at 1450°C.*
Figure 2. (a) AFM image and (b) Nomarski micrograph of 4H-SiC epitaxial layer grown at 1400 °C on 4° off-axis Si-face substrates. (BTMSM Source flow rate: 10 sccm).

Figure 3. Peak to valley of height profile data of AFM images of 4H-SiC epilayers grown on 4° off-axis Si-face substrates at various conditions.

The rate of BTMSM carrier gas increases above 15 sccm, the RMS roughness of the epitaxial layers increases by 10–100 times, rendering a non-specular and rough surface. It is assumed that there was insufficient step flow growth, and some parts of the terrace were affected by 3D nucleation and growth. Micro-Raman spectroscopy was conducted to verify the formation of the single polytype. As a result, we could observe that the 4H-SiC polytype was fairly well grown at a growth temperature of 1320–1440 °C, as seen in Figure 5. However, macro step-bunching, which have a step height of 5–7 nm, occurred with a growth temperature of 1500 °C, as shown in Fig. 6. The main reasons for the step-bunching are minimization of the surface energy, impurity effect, and step kinetics. It is therefore assumed that the higher surface free energy of the Si-face generated step-bunching. In addition, step-kinetics explain the phenomenon in terms of our epitaxial growth, that is, the Schwoebel effect. The atoms during the growth and etching processes are usually influenced by the Ehrlich-Schwoebel (ES) barriers of materials. Since SiC is a material with a normal ES barrier, adatoms naturally move into the internal site of the step, which is called a kink site. Therefore, more atoms would flow into the larger terraces during the growth process to reduce the step-bunching, while increasing etching atoms during the etching process would induce step-bunching. In summary, materials with the normal ES barrier generate more step-bunching during etching, rather than the growth process. In our experiment, epitaxial growth was carried out under 1500 °C as sources were sufficiently supplied, but hydrogen etching was excessively performed to generate step-bunching. Additionally, macro step-bunching on the Si-face, during the hydrogen etching process at 1500 °C, is observed before epitaxial growth. Thus, if the growth process is conducted under 1500 °C, there would be no step-bunching generated by excessive hydrogen etching.

Figure 4. RMS roughness of AFM image in 4H-SiC epitaxial layer, which was grown at various growth temperatures and flow rates of BTMSM carrier gas.
4H-SiC epitaxial layers grown on 4° off-axis C-face substrates using BTMSM.— Figure 7a shows Nomarski micrographs of 4H-SiC epitaxial layers grown at various growth conditions on 4° off-axis C-face substrates. The epilayers show a non-specular surface until the growth temperature increases to 1450°C, indicating epitaxial growth did not occur. Eventually, the grown layer on the C-face generates epitaxial growth at 1500°C, which is 100°C higher than that on the Si-face SiC substrates. Epitaxial growth is influenced by critical supersaturation ratio and surface diffusion length of the adatom on the surface. Critical supersaturation ratio of the C-face SiC shows a markedly lower value than that of the Si-face, irrespective of temperature. This indicates that adatoms generate nucleation easier and more frequently on the C-face substrates. Therefore, it requires atoms to diffuse into the kink site more rapidly to gain step flow growth before 3D growth occurs. Therefore, a higher growth temperature would be necessary to acquire more energy. It is known that the longer length of surface diffusion on the C-face substrate suppresses rapid nucleation and 3D growth. However, considering a higher value of the C/Si ratio decreases the surface diffusion length, and the value of the BTMSM source used in this study has a fairly high value of 3.5, the value of the critical supersaturation ratio rather than the surface diffusion length would play the dominant factor. Thus, the C-face will require a higher growth temperature of 1500°C compared to the Si-face of 1400°C.

As shown in Fig. 7a, two types of defects, complex triangular (TD) defects and inverted pyramid (IP) defects, were observed; TD are planar defects, and IP defects are concave contour-shaped defects with 0.15 μm depth, as shown in the AFM image provided in Fig. 7b. Previous studies reported that C atoms generate more C-C bonding under a C-rich growth environment, resulting in defects. This corresponds with the results of our experiments where BTMSM is a C-rich
source with a C/Si value of 3.5. As discussed earlier, clusters were increasingly formed at 1500°C during the hydrogen etching process. Although the temperature of the hydrogen etching process was conducted at 1450°C, defects were observed when the growth temperature was 1500°C. When the growth temperature was further increased to 1550°C, the density of defects decreased while the sizes became larger. The observed triangular-shaped defects are generally formed owing to interrupted step-flow growth, thus it is assumed that the mobility of the adatoms on the surface increased with higher growth temperature, to make adatoms resistant to interrupted step flow growth. In addition, the reason for bigger defects is that clusters became more influenced during the hydrogen etching process as the growth temperature was 1550°C. It was possible to decrease the number of these defects by reducing the flow rate of BTMSM carrier gas from 10 sccm to 5 sccm, which resulted in a decrease of C-C bonding. This occurs because the amount of source from the CVD process has decreased while the C/Si ratio remains the same, and the amount of source was low enough to reduce the growth rate and enable stable growth.

Figure 8 shows the AFM image and the peak to valley of the height profile of the AFM image of 4H-SiC epitaxial layer grown at 1500°C on 4° off-axis C-face substrates. The peak to valley of the height profile data of the AFM image in Fig. 8b shows that the grown epitaxial layers have an RMS roughness of 0.501 nm.

Figure 9 shows the FWHM difference of 4H-SiC (0004) rocking curves before and after the epitaxial grown on the C-face substrates as a function of (a) growth temperature and (b) BTMSM source flow rate. For comparison, the rocking curves were taken before and after the epitaxial growth. FWHM of all the substrates lay in the range of 16 to 25 arcsec. The substrates having the strong mosaicity or FWHM more than 25 arcsec were not used for the growth. The FWHM of the rocking curve for the epilayers monotonously decreases with increasing growth temperature from 1350°C to 1550°C, indicating better crystallinity at higher temperature (Fig. 9a). Here, the BTMSM flow rate was fixed at 10 sccm. Moreover, the FWHM of the epilayers grown above 1450°C are lower than those of the substrates. At 1500°C, the FWHM of 16.56 arcsec was much lower than that of the substrate, 20.88 arcsec. However, the FWHM of the epilayers grown at a BTMSM flow rate of 15 sccm is slightly higher (22.68 arcsec) than that of the substrates (18 arcsec) (Fig. 9b). The step-flow growth mode is enhanced with high temperature and low supersaturation, so crystallinity degradation can be prevented by high growth temperature and low supersaturation.

Figure 10 shows the Raman spectra of the epilayers grown on C-face substrates at various growth temperatures (BTMSM flow rate of 10 sccm). At a growth temperature of 1300°C, peaks at 796 cm⁻¹ and 971 cm⁻¹ were observed, indicating the formation of 3C-SiC structures. A single polytype with a non-specular surface was observed at 1400°C, and sharper FLO peaks, indicating better crystallinity of the grown layers, were observed at 1500°C.

Figure 11 shows that a complex triangular defect was observed at a BTMSM flow rate of 15 sccm on the C-face grown at 1500°C. As the source flow rate increased to 15 sccm, a good quality surface was not achieved, as the appearance of black spots generated defects of complex shape. The surface became rougher and the number of defects increased. This is observed as the number of adatoms in terraces reaches a certain level that disturbs the step flow growth. This defect has an overall triangular shape, but left and right-side wings
were composed of inverted pyramid defects. In Fig. 11a, the starting point of the complex triangular defects, that is the black spots, reveals peaks related to the 3C-SiC structure. Investigating the FTO peak, the ratio of two peaks was different from that of a surface without defects, indicating the amount of 3C inclusion is much higher (Fig. 11b). Figure 11c shows the Raman intensity ratio map of the peak at 796 cm$^{-1}$ (3C-TO phonon mode) to the peak at 776 cm$^{-1}$ (4H-TO phonon mode) for the defect. Most of the 3C-SiC structure is possessed in black spots and the central part of the triangular defect exhibits less inclusion but still shows a 3C-SiC structure. The IP defects on both sides of the wings show 4H structures, but a 3C structure could be observed at their edge. In the initial growth process, the step flow growth occurs with an abundant amount of source flow to start nucleation and growth in the middle of the terrace and incur defective regions.

The size of the defective region was about 32 μm, as shown in Fig. 12a. Since this study employed 4° off-angle substrates, the thickness of such a defective region can be calculated to be ∼2.2 μm. The actual thickness of the epilayer itself was 2.1 μm when observed by SEM. Therefore, it is inferred that such a defect was initiated from the interface between the substrate and epilayer.

The inverted pyramid defect in Fig. 13 is called an isolated inverted pyramid, since it was independently generated compared to the complex shaped defects illustrated in Fig. 11, when the flow rate of BTMSM carrier gas was 10 sccm. The ratio of the FTO peak was analyzed through micro-Raman spectroscopy to compare defect-free and defective regions. The results revealed the defective region possesses more 3C-SiC structures than the defect-free region, which is contrary to previous reports. Some research groups insisted that defects are composed of 4H, while other research groups insisted that it is composed of 3C.13,31 This study revealed that the dents in the central area of IP defects, shown in Fig. 11c, were composed of 4H-SiC structures, whereas the edge parts were composed of 3C-SiC structures.

**Background doping concentration and the growth rate of two polar face substrates.**—The background doping concentration of epitayers was determined from capacitance-voltage (C-V) measurements of Ni/SiC Schottky diodes (contact diameter: 300 μm). Under the optimal condition for Si-face substrates (growth temperature: 1400 °C, flow rate: 10 sccm), background doping concentration of grown epitayer was $1.67 \times 10^{16}$ cm$^{-3}$, whereas the optimal condition for C-face, whose temperature is 1500 °C and the flow rate is 5 sccm, was $2.04 \times 10^{16}$ cm$^{-3}$. The result shows higher value of background...
doping concentration on C-face than Si-face, because the difference between face polarities leads to the easier incorporation of N-impurity.\textsuperscript{13} The absolute background doping level is relatively higher than $\sim 10^{14}$ cm$^{-3}$ of the SiC epilayers grown by using SiH$_4$ and C$_3$H$_8$.\textsuperscript{32}

To observe the thickness of epitaxial layers, SEM was utilized to reveal a little increase on growth rate with higher temperature and flow rate of BTMSM carrier gas for both C and Si-faces, although overall level of growth rate was low in this study. In this study, we used BTMSM source under cold-wall reactor, therefore resulted low growth rate about 1.0 $\mu$m/hr. However, in the follow-up research, we observed that the growth rate of SiC epilayer on Si-face substrate increased up to $\sim 5.0$ $\mu$m/hr when using a hot-wall reactor; growth temperature was 1425°C and the flow rate was 10 sccm. Therefore, it is assumed that the type of reactor also affects the growth rate of SiC epilayer. Detailed analysis on the properties of SiC epilayers grown on such conditions is under progress.

**Conclusions**

In situ H$_2$ etching and homoepitaxial growth of 4H-SiC have been carried out on 4$^\circ$ off-axis Si-face and C-face 4H-SiC substrates by low-pressure CVD. H$_2$ etching characteristics and epitaxial growth behavior on two different polarities using an organosilicon source of BTMSM (C$_9$H$_{17}$Si$_2$) were systematically analyzed and discussed. When the temperature of in situ H$_2$ etching was 1500°C, the Si-face and C-face showed macro step-bunching and some clusters, respectively, whereas both faces showed fairly good quality when treated at 1450°C for 10 min. High-quality 4H-SiC epitaxial layers with free of crystallographic defects and step-bunching were demonstrated on both Si-face and C-face substrates. The optimal growth temperature on the Si-face substrate was 1320–1440°C with a BTMSM source flow rate of 5–10 sccm, while the growth temperature should be increased to 1500°C on the C-face substrate with a lower source flow rate of 5 sccm. A mechanism for the observed generation of step-bunching and surface morphological defect on both substrates depending on the growth temperature and source flow rate was also proposed.

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