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Low Temperature Heteroepitaxial Growth of 3C-SiC on Silicon Substrates by Triode Plasma Chemical Vapor Deposition using Dimethylsilane

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Abstract: The investigation of the dependence of the cubic silicon carbide (3C-SiC) film characteristics on the reaction pressures, growth temperatures and hydrogen dilution rates was carried out by rapid thermal triode plasma CVD using dimethylsilane as a source gas. The stoichiometric 3C-SiC films with good crystallinity and crystal orientation were successfully grown at 1100-1200°C. The crystallinity and the crystal orientation of SiC films grown at large dilution rate of above 200 and growth pressure of 0.3-0.7 Torr were better than those grown at small dilution rate and high growth pressure. Under large dilution rate, large amount of hydrogen radicals can be generated. It is speculated that excessive carbon atoms or weak bonds formed in SiC films were effectively extracted by the large amount of hydrogen radicals.

Key words: Silicon carbide, triode plasma CVD, dimethylsilane, heteroepitaxial growth, stacking faults

INTRODUCTION

Silicon carbide (SiC) is a wide band-gap semiconductor with large saturated electron drift velocity, large breakdown electric field and large thermal conductivity. Therefore, this material is of great interest for high temperature and high-power applications (Müller *et al*., 2006; Okumura, 2006; Yasui *et al*., 2008). Among many polytypes, cubic silicon carbide (3C-SiC) with zincblende crystal structure can also be grown on Si substrates (Matsunami *et al*., 2004). Unlike the other polytypes (4H-or 6H-SiC), 3C-SiC can be grown at lower temperature (below 1300°C) and be epitaxially grown on Si substrates. Usually, SiC films are grown on Si substrate by Chemical Vapor Deposition (CVD) using silane (SiH_4) and hydrocarbon gases such as propane (C_3H_8) (Ishida *et al*., 1997; Matsunami, 2004). However, this method requires high growth temperature (~1300°C), which may induce high tensile stress because of the difference in thermal expansion coefficient between Si and SiC and the formation of the voids in Si substrates.

In order to overcome these problems, the use of single precursor gases such methylsilanes instead of SiH_4 and C_3H_8 are useful, because they contain Si-C bonds in their molecules and are decomposable at low temperature. In addition, simplified Chemical Vapor Deposition (CVD) apparatus can be utilized because they are non-pyrophoric gases. Application of reactive plasma is a useful method to accelerate chemical reactions at low temperatures. In order to apply the reactive plasma to the epitaxial growth of SiC, however, the incidence of energetic charged particles on the surface of the growing films must be reduced.

In the previous study, we presented the triode plasma Chemical Vapor Deposition (CVD) method and the introduction of negative DC biases on the grid electrode, low electron temperature and low space potential below the grid were obtained (Yasui *et al*., 1999, 2005). The preliminary results on the growth of crystal SiC film using dimethylsilane (DMS) diluted with hydrogen were presented (Yasui *et al*., 1998, 1999). In those previous studies, hydrogen dilution rate and growth pressure were not changed widely.

In this study, we present the experimental results of low-temperature epitaxial growth of 3C-SiC on Si (100) and (111) substrates by rapid thermal triode plasma CVD (RTP-CVD) using dimethylsilane (DMS) and hydrogen radicals without carbonization process. Namely, the effects of hydrogen dilution rate, reaction pressure and temperature on the quality of SiC films will be reported. The crystallinity of SiC films were characterized using X-ray diffraction spectroscopy.

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MATERIALS AND METHODS

Heteroepitaxial growth of 3C-SiC on Si Substrates was performed in an Triode Plasma CVD apparatus (Fig. 1) using H_2 and DMS. The grid electrode (135 mm in diameter, wire diameter = 0.3 mm, wire spacing = 1.25 mm) inserted between the cathode and anode electrodes was connected to a dc electric source. By supplying negative dc bias on the grid (Vg), rf discharge was confined between the grid and the cathode. Anode was insulated from the grounded chamber. In this experiment, the substrate holder was made electrically floated. As a source gas, DMS, kept at 0°C in a stainless steel cylinder, was admitted into the afterglow region below the grid. Hydrogen gas was admitted into the discharge region above the grid passing through a hydrogen gas purifier. Experimental conditions are as follows: H_2 flow rate 112 sccm, gas feed ratio (H_2/DMS) 40-1500, total gas pressure during growth 0.1-1.4 Torr, substrate temperature 1000-1200°C, rf power 100W, grid bias Vg = -100V.

After degreasing, dipping in buffered HF and rinsing in dionized water, Si (100) and (111) substrates were immersed in boiling ultra-pure water. After evacuating the growth chamber to 10^{-7} Torr, the substrate temperature was raised to 350°C. Substrates were heated on a carbon heater and substrate temperature was measured using an

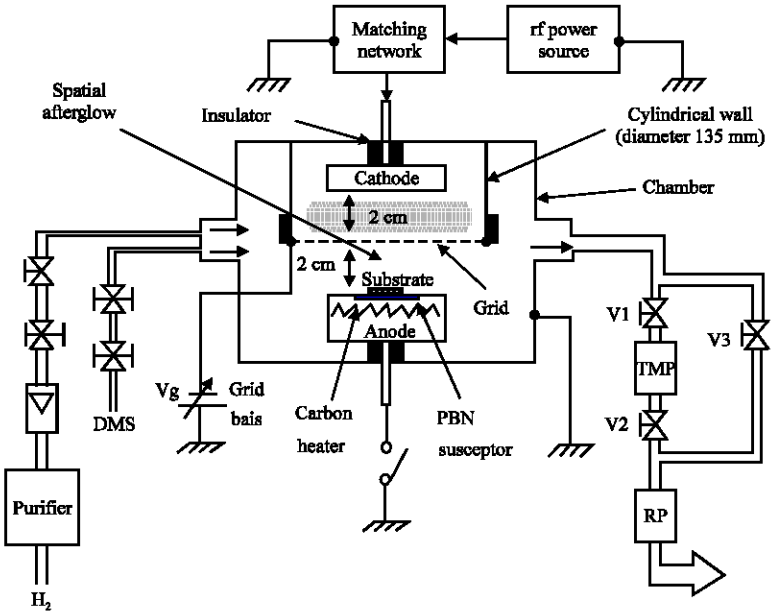

Fig. 1: Schematic diagram of rapid thermal triode plasma CVD apparatus

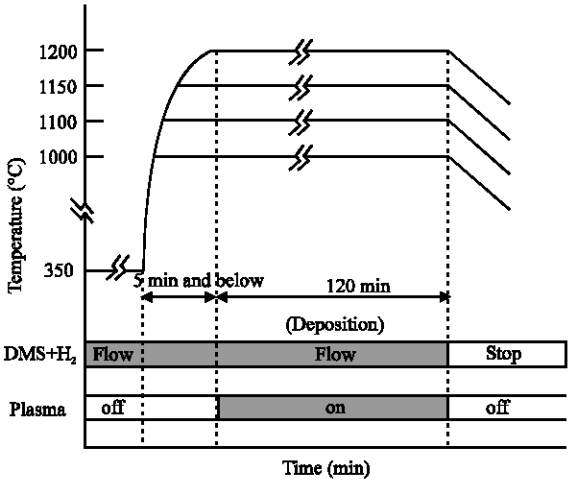

Fig. 2: The time chart for SiC epitaxial growth by rapid thermal triode plasma CVD

optical pyrometer. With the supply of source gas, substrate temperature was rapidly raised from 350°C to growth temperature in hydrogen and DMS flows, followed by the epitaxial growth, as shown in Fig. 2.

Crystallinity of SiC films was evaluated using an X-ray diffractometer (RIGAKU, RAD-IIIA) equipped with a graphite monochromator.

RESULTS AND DISCUSSION

Figure 3a and b shows the growth rate of SiC film grown on Si (100) substrate by rapid thermal triode plasma CVD as a function of growth pressure and dilution rate (H_2/DMS), respectively. The values of Fig. 3a shows the hydrogen dilution rate. The dilution rates at 0.3 and 1.4 Torr were very close. Considering these two dilution rates, it is clear that the growth rate increase with the growth pressure. It was considered that large plasma etching effect has become more dominant at the low growth pressure condition compared to high growth pressure. This assumption is supported by the experimental data shown in Fig. 3b where the growth rate decreases with the hydrogen dilution rate. The films grown at small dilution rate were thicker than those grown at large dilution rate. The same characteristics were also seen for Si (111) substrate. From these results, plasma etching effect becomes more dominant at high density hydrogen plasma condition.

Figure 4a shows the variation in the full width at half maximum (FWHM) of X-ray diffraction peak of SiC (200) grown by rapid thermal triode plasma CVD as a function of the hydrogen dilution rate (H_2/DMS). The film thickness was 0.3-0.8 μm. As shown in Fig. 3b, the films grown at small dilution rate were thicker than those grown at large dilution rate. At the same growth condition, the crystallinity of SiC epitaxial films was improved with the

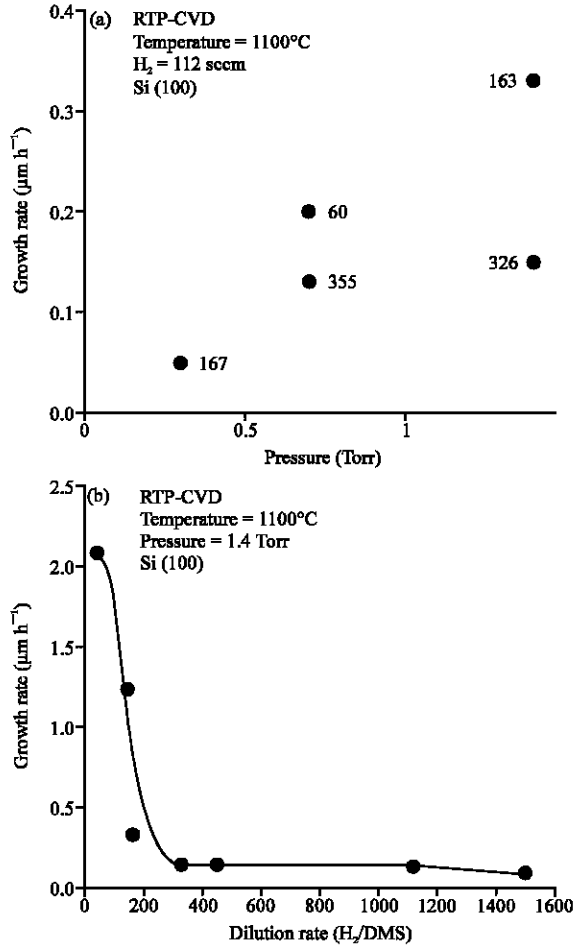

Fig. 3: The growth rate of SiC films grown on Si(100) substrate by rapid thermal triode plasma CVD as a function of (a) growth pressure and (b) the dilution rate (H_2/DMS)

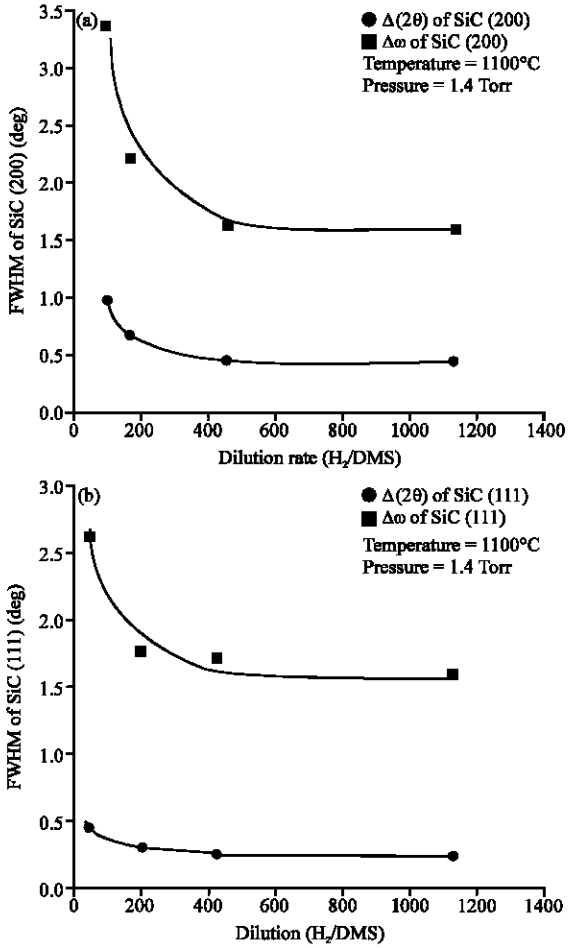

Fig. 4: The variation in the FWHM values of X-ray diffraction peak of SiC (200) and (111) grown by rapid thermal triode plasma CVD as a function of the dilution rate (H_2/DMS)

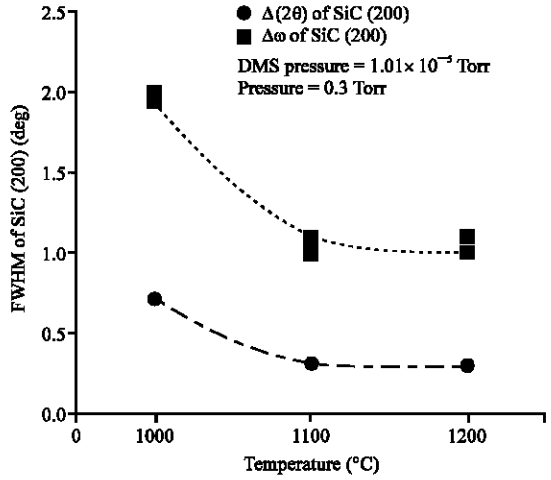

Fig. 5: The variation in the FWHM values of X-ray diffraction peak of SiC (200) and (111) grown by rapid thermal triode plasma CVD as a function of the substrate temperature

film thickness. The FWHM values of X-ray diffraction peaks decreased with the hydrogen dilution rate, as shown in Fig. 4a. From the result, it is clear that the crystallinity and the crystal orientation of SiC films grown at large dilution rate were better than those grown at small dilution rate. FWHM values of X-ray diffraction peak of SiC (111) also decreased with the hydrogen dilution rate, as shown in Fig. 4b. Under large dilution rate, large amount of hydrogen radicals can be generated. It is speculated that excessive carbon atoms or weak bonds formed in SiC films were effectively extracted by the large amount of hydrogen radicals.

Figure 5 shows the variations in the FWHM values of X-ray diffraction (θ-2θ) and ω-rocking curve of SiC (200) grown by rapid thermal triode plasma CVD as a function of the substrate temperature. Hydrogen dilution rate during SiC growth was 300. It is shown in this Fig. 5 that SiC epitaxial films with good crystallinity and crystal orientation have not been obtained at temperature of 1000°C. To date, those grown at 1100°C showed fairly good crystallinity and crystal orientation. Figure 6a and b shows the variation in the volume ratio of the domains epitaxially grown to those containing stacking faults. Data of SiC films grown on Si (100) crystals were used. The volume of the domains epitaxially grown was evaluated from the area of SiC (200) peak obtained from X-ray rocking curves and that of domains containing stacking faults was evaluated from the area of SiC (111) peak appeared ±15.8° deviated from the substrate surface ((100) plane).

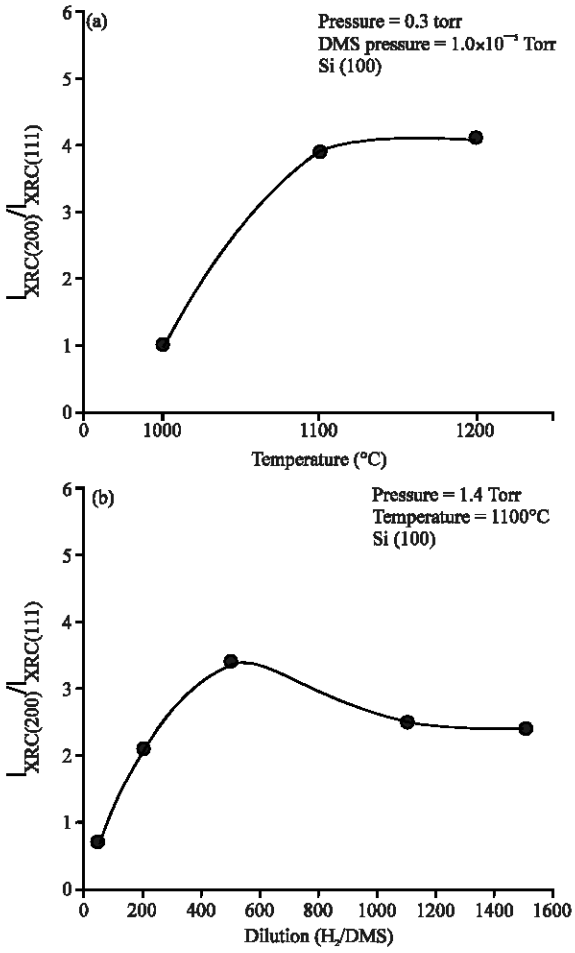

Fig. 6: Variation in the volume ratio between the domains epitaxially grown and those containing stacking faults as a function of the growth temperature and dilution rate

As shown in Fig. 6a, the integrated intensity ratio of the rocking curves between the domains epitaxially grown and those containing the stacking faults was smallest at low temperature (1000°C). At high temperatures (>1100°C), on the other hand, the integrated intensity ratio increased 3 times. At low temperatures, the extraction of excessive methyl groups from the growing film surface is not adequate by thermal energy. The generation of the stacking faults is also considered to be induced by the existence of the excessive carbon and hydrogen atoms.

Figure 6b shows the dependence of volume ratio between the domains epitaxially grown and those containing stacking faults on the dilution rate of DMS. The ratio shows high values at large dilution rate (>200). Again, it shows that the hydrogen radicals generated in H_2 plasma have enhanced the extraction of the excessive

carbon atoms and break the weak bonds and have reduced the volume of the domains containing the stacking faults.

CONCLUSION

The investigation of the dependence of the SiC film characteristics on the growth pressure, growth temperature and hydrogen dilution rate was carried out by rapid thermal triode plasma CVD method using DMS as a source gas. The hydrogen dilution rate of above 200 and total growth pressure of 0.3-0.7 Torr are considered as the best growth conditions. From X-ray rocking curve measurements, the domain which includes stacking faults in films grown at these conditions was drastically reduced. The growth rate increase with the growth pressure due to the decrease in plasma etching effect. Under large dilution rate, large amount of hydrogen radicals can be generated. It is speculated that excessive carbon atoms or weak bonds formed in SiC films were effectively extracted by the large amount of hydrogen radicals.

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