High-purity and high-quality 4H–SiC grown at high speed by chimney-type vertical hot-wall chemical vapor deposition

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4H–SiC layers have been homoepitaxially grown at a high growth rate of 25 μm/h by chimney-type vertical hot-wall chemical vapor deposition at 1700 °C. Through photoluminescence measurement, the intrinsic defect, so-called L_1 peak, was found to be reduced under a C-rich condition. In the deep level transient spectroscopy measurement, the Z_1 center was also found to be suppressed under a C-rich condition. For a 75-μm-thick epilayer, the net donor concentration was reduced to as low as 5×10^{12} cm^{-3}. In low-temperature photoluminescence, free exciton peaks are dominant, indicating high purity of the epilayer. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1456968]

Silicon carbide (SiC) is a strong candidate for low-loss high-power devices, high-temperature and high-frequency devices, owing to its superior characteristics such as high breakdown field strength, high thermal conductivity, and high saturation drift velocity.[1] While SiC growth technology has made tremendous progress and SiC devices showing better performance than conventional Si or GaAs counterparts have been reported, there exist various problems in the growth technology to realize SiC devices utilizing its outstanding properties completely.

In general, homoepitaxial growth is carried out by chemical vapor deposition (CVD) at around 1500–1600 °C utilizing step-controlled epitaxy.[2] Although the SiC growth technology has made significant progress, the quality of SiC epilayer is required to be improved for real devices.[3,4] Moreover, a higher growth rate is desirable for high-power devices, considering that the typical growth rate at around 1500–1600 °C is 2–6 μm/h.[2,5]

In the last several years, a few attempts of high-temperature growth have been reported, which offers a great potential for the growth of high-purity thick epitaxial layers with a high growth rate. For example, high growth rates from 10 to 25 μm/h have been achieved using vertical hot-wall CVD configurations.[6,7] One challenge in fast epitaxial growth so far is to reduce a relatively high concentration of deep levels, called the D_I center,[8] found as the L_1 peak in photoluminescence measurements.

In this letter, the authors describe the epitaxial growth of 4H–SiC at 1700 °C in an originally designed vertical hot-wall chimney-type CVD reactor and the characterization of these epilayers. The authors found that the formation of the D_I and the Z_1 centers[9] could be suppressed in growth under a C-rich condition, and realized successful fast epitaxial growth of high-purity and high-quality 4H–SiC without the L_1 peak.

The epitaxial growth was performed on *n*-type 8° off-axis 4H–SiC(0001) by vertical hot-wall chimney-type CVD in a SiH_4–C_3H_8–H_2 system at 1700 °C.[10] The substrates were placed in a SiC-coated graphite susceptor, heated by radio-frequency induction. The C/Si ratios were varied in the range from 0.6 to 0.8 with a fixed SiH_4 flow rate of 16.3 sccm at a reactor pressure of 100 Torr. A typical flow rate of H_2 was 3–5 slm. No intentional *in situ* etching by H_2 or HCl prior to CVD was employed.

Epilayers were characterized by a Nomarski microscope, atomic force microscopy, x-ray diffraction, photoluminescence (PL), and deep level transient spectroscopy (DLTS). The thickness of the epitaxial layers was measured on as-cleaved cross sections using a scanning electron microscope (SEM), and thereby the growth rate was obtained. The net donor concentration was determined by capacitance–voltage (C–V) measurements on a Ni/4H–SiC Schottky structure with a frequency of 1 kHz–1 MHz. DLTS spectra were acquired on Ni/4H–SiC Schottky diodes with 1.5–4.0 mm diameter. The reverse bias and pulse voltage applied during the DLTS measurements were −5 and 5 V with a frequency of 1 MHz, respectively. The 325 nm radiation from a He–Cd laser was used as an excitation source in the PL measurements.

Table I summarizes the major properties of three epilayers grown for 1 h with respective C/Si ratios of 0.6, 0.7, and 0.8. The H_2 flow rate was fixed at 3 slm. High growth rates from 22 to 25 μm/h were obtained. A mirror-like surface morphology without wavy pits and triangular defects was observed by Nomarski microscopy, and atomic force microscopy showed a relatively smooth surface with a small roughness (rms) of around 0.2 nm in the area of 2×2 μm^2. Even in the area of 10×10 μm^2, the roughness was small, 0.5–0.6 nm. The reason for a relatively large roughness of 0.947 nm for the epilayer grown with a C/Si ratio of 0.8 may come from an accidental failure in setting the substrate on the susceptor. The full width at half maximum (FWHM) obtained

TABLE I. Major properties of epilayers grown with C/Si ratios of 0.6, 0.7, and 0.8.

C/Si (SiH_4=16.3 sccm)	0.6	0.7	0.8
Growth rate (μm/h)	22	25	25
rms (nm) (2×2 μm^2)	0.249	0.200	0.947
N_d-N_a (cm^{-3})	4×10^{14}	2×10^{14}	1×10^{14}
Z_1 center (cm^{-3})	5×10^{13}	1×10^{13}	6×10^{12}

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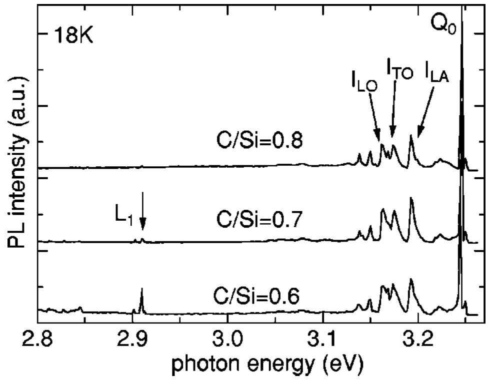

FIG. 1. PL spectra at 18 K of 4H–SiC epilayers grown for 1 h.

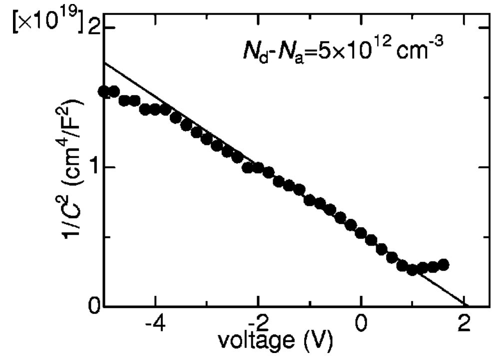

FIG. 2. $C-V$ characteristic of 4H–SiC epilayer grown with a C/Si ratio of 0.7 for 3 h.

by x-ray rocking curves sensitive to a lattice tilt and crystal bending was as narrow as 9.7–14 arcsec. Considering that the resolution for the FWHM of SiC(0001) perfect crystal is 6–8 arcsec in the present x-ray rocking curve measurement, the result indicates a high quality for the epilayer.

The net donor concentration was estimated to be 4, 2, and 1×10^{14} cm^{-3} for C/Si ratios of 0.6, 0.7, and 0.8, respectively. The incorporation of N was reduced under a C-rich condition, in agreement with the "site-competition epitaxy"[11] principle. In the DLTS measurement, the deep Z_1 center trap at $E_c-0.66$ eV was detected. The Z_1 center concentration was reduced from 5×10^{13} cm^{-3} to as low as 6×10^{12} cm^{-3} by increasing the C/Si ratio from 0.6 to 0.8. The ratio of Z_1 center concentration to net donor concentration is not constant for different C/Si ratios, suggesting no relation between the Z_1 center and N concentrations. In the DLTS measurements for an epilayer with a donor concentration of 1×10^{16} cm^{-3}, the Z_1 center concentration was similar (low 10^{13} cm^{-3}) to the epilayer shown in Table I. The epilayer was grown under the same condition as the sample grown with a C/Si ratio of 0.7 in Table I, but the high donor concentration was accidentally obtained due to a system problem. This result implies that the Z_1 center is not related to impurities such as N but to C/Si ratios in the CVD growth. The previous report[12] also describes that there was no correlation between the Z_1 center and doping concentrations, and the Z_1 center is believed to be an intrinsic defect complex including a Si antisite or C vacancy, not containing specific impurities.

Figure 1 represents the PL spectra at 18 K for the epilayers grown with C/Si ratios of 0.6, 0.7, and 0.8 for 1 h. Because an epilayer of about 20 μm is too thin to investigate the PL from only the epilayer, the Q_0 peak (recombination of excitons bound at N donors), coming from the substrate, is strong. While the relatively strong L_1 peak (thought to be recombination through intrinsic defects) can be observed for the epilayer grown with a C/Si ratio of 0.6, the L_1 peak becomes weaker with C/Si=0.7, and it can be hardly seen with C/Si=0.8. The result suggests that the origin of the L_1 peak decreases under a C-rich condition. Although the correlation between the Z_1 center and the L_1 peak is not well understood,[9] the formation of both defects is suppressed under a C-rich condition.

Epitaxial growth was carried out for 3 h with a C/Si ratio of 0.7 with a H_2 flow rate of 5 slm. The thickness was determined to be 75 μm by SEM, indicating a growth rate of 25 μm/h. Although several pits exist, a relatively good morphology was obtained. The net donor concentration was extremely low, estimated to be 5×10^{12} cm^{-3} (Fig. 2). One of the reasons for this low doping level is considered to be a baking effect. Residual nitrogen in the reactor is removed during a CVD run, and therefore, the incorporation of N gradually decreases with increasing growth time. For this epilayer, the DLTS measurement was made on a Schottky structure with 4.0 mm diameter. Although the very high resistivity due to the low doping concentration leads to the lack of reliability in the result, a Z_1 center concentration of 1×10^{12} cm^{-3} was detected. No clear reason for the lower trap concentration of this thick epilayer compared to the thin epilayer in Table I has been identified yet. The stress between the substrate and the epilayer may cause the higher trap concentration, and the creation of trap may be suppressed with increasing the thickness of epilayer. More detailed investigation is required, but the decrease of trap concentration with increasing the thickness of the epilayer is advantageous for power devices.

The PL spectrum at 18 K from this sample is represented in Fig. 3. The epilayer thickness of 75 μm is enough for the laser light not to penetrate into the substrate, and so the emission is only from the epilayer. The strong free exciton peaks (I_{LA},I_{TA},I_{LO},I_{TO}) and weak Q_0 peak are observed. The free exciton peaks are much stronger than the Q_0 peak, indicating the high purity and high quality of the epilayer. No other peaks such as B-, Al-, and Ti-related peaks can be seen, suggesting very little contamination of impurities. The L_1 peak, which is often observed in epilayers grown at a high

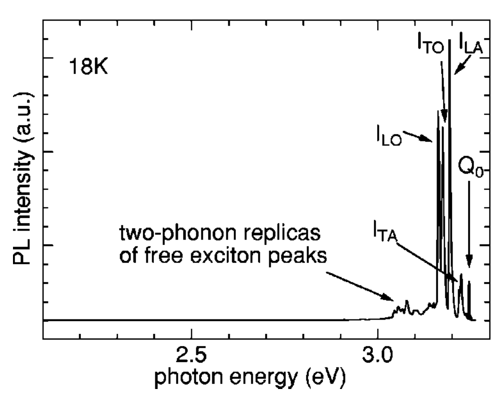

FIG. 3. PL spectrum at 18 K of 4H–SiC epilayer grown with a C/Si ratio of 0.7 for 3 h.

growth rate,[6,7] cannot be seen in this epilayer grown at 25 μm/h. It implies that the origin of L_1 peak, attributed to intrinsic defects, is not always created by high-speed growth.

Fast homoepitaxial growth of 4H–SiC by vertical hot-wall chimney-type CVD at 1700 °C was investigated. A good surface morphology was attained at a high growth rate of 25 μm/h. The net donor concentration was reduced to 5×10^{12} cm^{-3} by increasing growth time. The formation of the D_I and the Z_1 centers was found to be suppressed by increasing the C/Si ratio and increasing the thickness. The formation of the L_1 peak is not necessarily associated with a very high growth rate but to a C/Si ratio in the growth condition. In the PL measurement at 18 K, no L_1 peak was observed in a thick epilayer grown at 25 μm/h with a C/Si ratio of 0.7.

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