Fast Epitaxial Growth of High-Purity 4H-SiC(000$\bar{1}$) in a Vertical Hot-Wall Chemical Vapor Deposition

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4H-SiC(000$\bar{1}$) epitaxial layers with a 14–28-μm thickness have been grown at high growth rates of 14–19 μm/h by chimney-type, vertical hot-wall, chemical vapor deposition (CVD) at 1,750°C. The 3C hillocks are formed on the epilayers grown under relatively low C/Si ratios. When grown at a relatively higher C/Si ratio of 0.6, the hillock density has been decreased to 1 cm^{-2}. Under the C-rich condition, the concentrations of residual impurity (nitrogen) and intrinsic defects ($Z_{1/2}$ and $EH_{6/7}$) have been reduced. When growth has been performed at low C/Si ratios of 0.4 and 0.5, all the micropipes in the substrates (more than 100 micropipes for each condition) have been closed during CVD growth.

Key words: SiC, C face, epitaxial growth, high purity, deep-level transient spectroscopy (DLTS)

INTRODUCTION

Silicon carbide (SiC) has several attractive properties, such as high breakdown field and high thermal conductivity. The SiC devices are accordingly promising for high-power and high-temperature applications, and high-voltage (300–600 V) Schottky barrier diodes are now on the market. In recent years, development of SiC metal-oxide-semiconductor field-effect transistors (MOSFETs) has been extensively investigated as an ideal unipolar switching device. However, the slow oxidation rate and large channel resistance in MOS devices on the 4H-SiC (0001)Si face have hindered the realization of high-performance MOSFETs. The 4H-SiC(000$\bar{1}$)C face has superior properties, such as a fast oxidation rate[1] and the high quality of the MOS interface, compared to the (0001)Si face.[2] In bulk growth of 4H-SiC, the 4H-SiC(000$\bar{1}$)C face has been usually employed because of polytype stability on the face.[3] In epitaxial growth on the C face, macrostep bunching can be prevented, and a rather smooth surface is obtained.[4] However, investigations on chemical vapor deposition (CVD) of 4H-SiC(000$\bar{1}$) have been very limited because the background doping level is high, and the growth "window", in which the specular surface can be obtained, is narrow.[4] Fast epitaxial growth on the C face has been especially difficult because fast growth (higher than 5 μm/h) usually leads to poor morphology because of the high nucleation rate on this face. Recently, CVD growth on the 4H-SiC has been attracting renewed attention.[5]

In this study, the authors succeeded in the fast growth of high-purity 4H-SiC(000$\bar{1}$) epilayers with a specular surface by CVD at high growth temperature. Electrical and structural properties of 4H-SiC (000$\bar{1}$) epilayers are investigated.

EXPERIMENTAL

Homoepitaxial growth was performed on 8° off-axis 4H-SiC(000$\bar{1}$) and (0001) substrates (size: 6 mm × 20 mm) by chimney-type, vertical hot-wall CVD in a SiH_4-C_3H_8-H_2 system at 1,750°C.[6] On these substrates, uniformity of morphology, thickness, and doping concentration were very good, although growth on a 2-in. wafer has not been tried. The C/Si ratio was changed from 0.4 to 0.7 with a fixed SiH_4 flow rate of 24.3 sccm. The typical reactor pressure and the H_2 flow rate were 100 torr and 5 slm, respectively. No intentional doping was employed, regarding the results presented in this paper. Thickness and growth rate were estimated by

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using cross-sectional scanning electron microscopy (SEM).

Epilayers were characterized by a Nomarski optical microscope (both reflection and transmission modes), atomic force microscopy (AFM), SEM, and micro-Raman scattering spectroscopy using an Ar laser (λ = 488 nm) in the back-reflection geometry at room temperature. Electrical properties were assessed by capacitance-voltage and deep-level transient spectroscopy (DLTS) on a Ni/4H-SiC Schottky structure with a probe frequency of 1 MHz.

RESULTS AND DISCUSSION

In most CVD runs, a mirror-like surface was attained at high growth rates of 14–19 μm/h, which are 3–6 times higher than values reported for CVD growth on 4H-SiC(000$\bar{1}$).[4,5] The high growth temperature may contribute to suppress two-dimensional nucleation and, thereby, to smooth morphology even at high growth rate. The growth rate showed little dependence on the C/Si ratio within the range investigated in this study, indicating the growth rate is mainly determined by the supply of Si species. The growth rate on the (000$\bar{1}$) face was comparable to that on the (0001) face.

On the surface of commercial (000$\bar{1}$) wafers, surface damages are introduced by an unoptimized polishing process. In fact, when epitaxial growth was performed on as-received (000$\bar{1}$) wafers, randomly oriented shallow grooves, originating from surface scratch, appeared on the epilayer surface. Because the (000$\bar{1}$) face has the fastest oxidation rate in SiC, this damage could be removed by performing sacrificial oxidation on as-received substrates prior to epitaxial growth. In this work, the defective morphology was successfully removed by sacrificial oxidation at 1,150°C for 4 h.

Figure 1 shows the Nomarski micrographs and AFM images of 4H-SiC(000$\bar{1}$) epilayers grown with various C/Si ratios from 0.4 to 0.7. "Hillocks" elongated along the off-direction are observed on the epilayers grown with low C/Si ratios of 0.4 and 0.5. The hillock density was decreased from 15 cm^{-2} to 1 cm^{-2} by increasing the C/Si ratio from 0.4 to 0.6. A small root mean square roughness of 0.15 nm for a 2 μm × 2 μm area, together with the low hillock density, was obtained when growth was performed with a C/Si ratio of 0.6 (Fig. 1). The further increase in C/Si ratio to 0.7 resulted in a rough surface with significant macrostep formation.

The shape and structure of hillocks were characterized by SEM and micro-Raman scattering. A typical SEM image of a hillock is shown in Fig. 2a. The SEM image was taken at a 45° inclination from the sample surface. The peak height of this hillock is estimated to be 15 μm for 28-μm-thick epilayers. Micro-Raman scattering spectra were acquired from the hillock (point A in Fig. 2a) and the flat region (point B) and shown in Fig. 2b. At the region without a hillock (point B), three peaks are detected at 776.9 cm^{-1}, 796.5 cm^{-1}, and 964.1 cm^{-1}. The intensive peak at 776.9 cm^{-1} and a weaker one of 796.5 cm^{-1} are assigned to be the folded modes of transverse optic (FTO) branches of 4H-SiC, and they have the reduced wave vectors of 2/4 and 0.[7] The peak detected at 964.1 cm^{-1} can be assigned to be the folded longitudinal optic (FLO) mode of 4H-SiC, corresponding to the Γ point. This result indicates that no inclusion of foreign polytypes is detected for the flat region. In the Raman spectrum from the hillock region (point A), three peaks at 776.9 cm^{-1}, 796.5 cm^{-1}, and 970.9 cm^{-1} (the strongest: 796.5 cm^{-1}) are detected. Because 3C-SiC exhibits characteristic peaks at 796.5 cm^{-1} for FTO and 970.9 cm^{-1} for FLO modes, the present Raman spectrum indicates that the hillock is of 3C-SiC polytype. The peak at 776.9 cm^{-1} may originate from the 4H-SiC region underneath the hillock because the penetration depth of excitation light is greater than 100 μm.

The hillocks tend to generate in epilayers grown at low C/Si ratios (Si-rich condition) in this study. Though hillocks were also observed in Refs. 4 and 5, the growth condition in which hillocks are easily generated is different from the present case; hillocks generated under a C-rich condition in previous works while under a Si-rich condition in the present study. More recently, Tsuchida et al. reported that the hillock density could be reduced under both low- and high-C/Si ratio conditions.[8] Further investigation is required to clarify the mechanism of hillock formation.

On epilayers grown with C/Si ratios of 0.4 and 0.45, shallow grooves along the off-direction were observed, as shown in Fig. 3a. Careful observation using a transmission optical microscope revealed that micropipes in substrates were closed during epitaxial growth. Figure 3b shows an AFM image near a closed micropipe. In this figure, two kinds of pits, a large pit and small pits, are observed. Both pits are highly elongated along the [1$\bar{1}$00] direction (perpendicular to the off-direction). The large pit has a width of about 1 μm and depth of 25 nm, and small ones have about half width (0.5 μm) but similar depth (20 nm). Although the formation mechanism of these pits is not clear at present, the pits may be formed by "step retardation" at closed-core screw dislocations, which are created by micropipe dissociation. In the case of micropipe closing during CVD on SiC(0001), Kamata et al. reported that several pits are formed near a closed micropipe.[9]

For epilayers grown with C/Si ratios of 0.4 and 0.45, all the micropipes (more than 100 micropipes for each sample) were closed. For epilayers grown with relatively higher C/Si ratios, however, some or all of the micropipes penetrated into epilayers from substrates. Figure 4 shows the relation between the micropipe closing ratio and C/Si ratio for (0001) and (000$\bar{1}$) epilayers. As is the case for growth on the (0001) face,[10] micropipes were easily closed at low C/Si ratios for the (000$\bar{1}$) face as well. From Fig. 4, the C/Si ratio window, where micropipes are closed during epitaxial growth, seems to shift to the C-rich

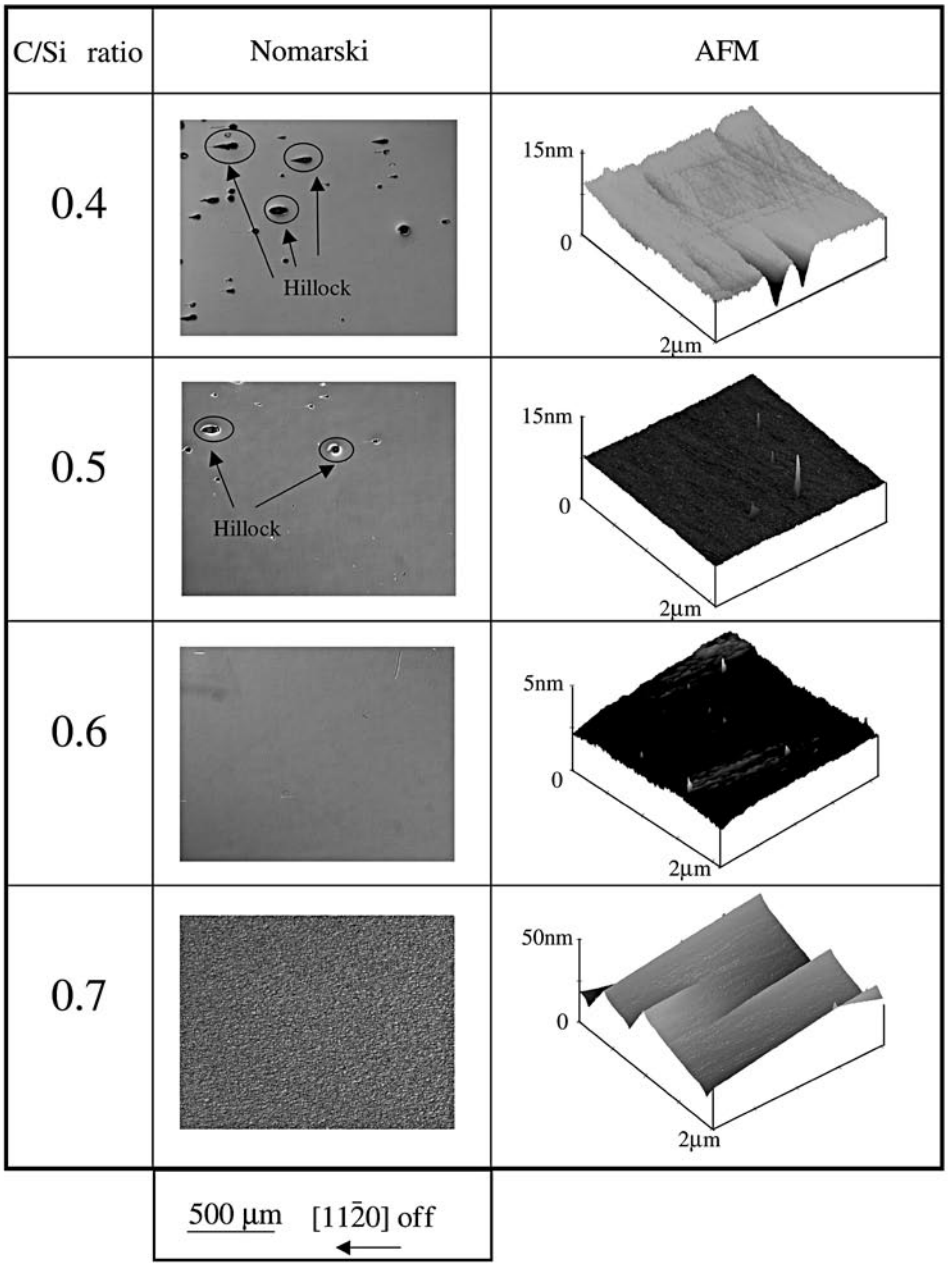
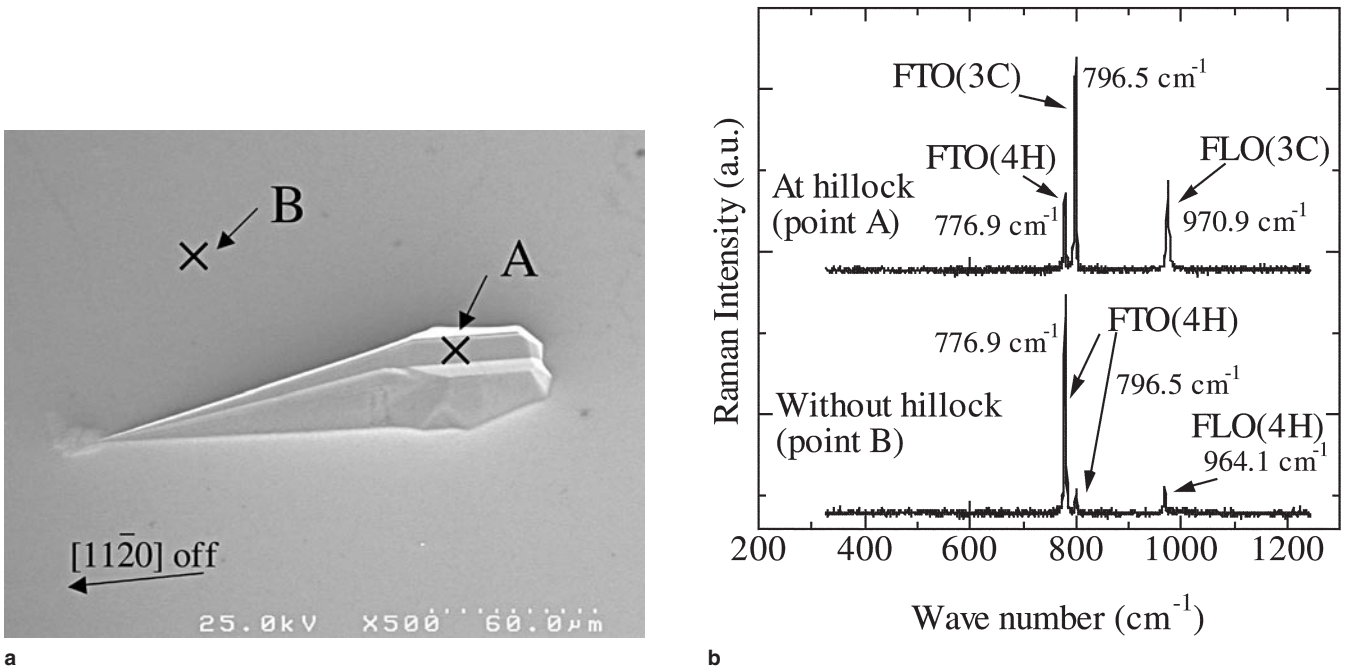


Fig. 1. Nomarski and AFM images of 4H-SiC(000$\bar{1}$) epilayers grown under various C/Si ratios from 0.4 to 0.7.

condition in (000$\bar{1}$) growth. The wider C/Si ratio range for micropipe closing on 4H-SiC(000$\bar{1}$) has also been reported recently.[8] It has been suggested that micropipes may be closed when micropipes and surface steps interact effectively.[10] One possible reason is that the speed of spiral growth at the micropipe core might be slower on (000$\bar{1}$), which results in more interaction between surface steps and micropipe core.

Figure 5 shows the relation between the net donor concentration of (0001) and (000$\bar{1}$) epilayers and the C/Si ratio measured on a Ni/4H-SiC Schottky structure. The net donor concentration of (000$\bar{1}$) epilayers is about one order of magnitude higher than that of (0001) epilayers grown under the same condition, in agreement with previous reports.[4,5,11] However, the net donor concentration decreased to 4.9×10^{14} cm^{-3} by increasing the C/Si ratio to 0.6. High temperature (1,750°C), low pressure (100 torr), and optimum C/Si ratio (C/Si = 0.6) during growth contribute to the high purity of the epilayer. High-temperature and low-pressure growth enhances desorption of nitrogen atoms from the growing surface,[11–13] and a relatively high C/Si ratio brings about a "site competition" effect.[14]

Although the net donor concentration of SiC (000$\bar{1}$) epilayers is almost constant irrespective of C/Si ratio in atmospheric-pressure CVD,[4,11] the net donor concentration was reduced by increasing the C/Si ratio in this study, where the epitaxial growth was performed at a low pressure of 100 torr. Kojima et al. also reported the reduction of donor concentration by



a b

Fig. 2. (a) SEM image of a hillock and (b) Raman spectra acquired from a hillock and a flat region without a hillock.

increasing C/Si ratio in low-pressure, hot-wall CVD at 1,600°C.[5] The reason why the site competition effect on (000$\bar{1}$) is pronounced at low pressure is unknown. The surface Si coverage may be easily reduced because Si evaporation (desorption) is enhanced at low pressure.

The DLTS measurements were made on a Schottky structure with a 800-μm diameter in the wide temperature range from 90 K to 800 K, typical results of which are shown in Fig. 6a. As observed for 4H-SiC(0001) epilayers, two peaks at 310 K and 620 K are dominant for 4H-SiC(000$\bar{1}$) epilayers.

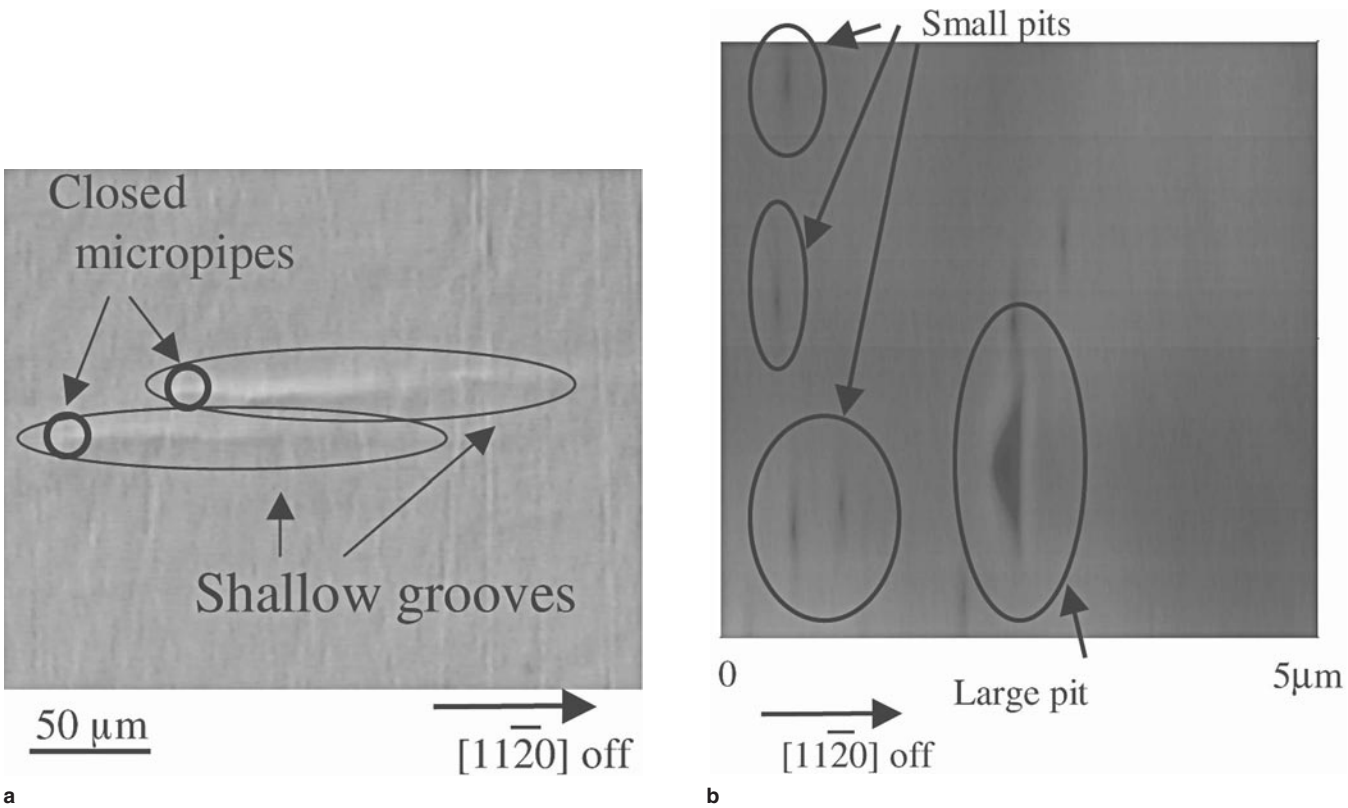


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Fig. 3. (a) Surface morphology near a closed micropipe and (b) AFM image around a closed micropipe.

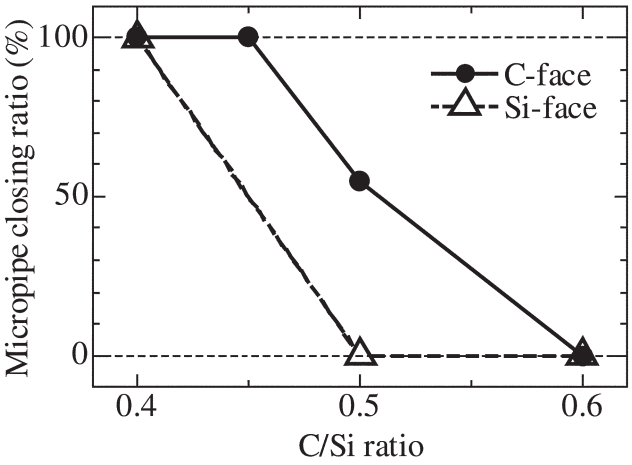


Fig. 4. Relation between micropipe closing ratio and C/Si ratio in CVD growth on 4H-SiC(0001) and (000$\bar{1}$).

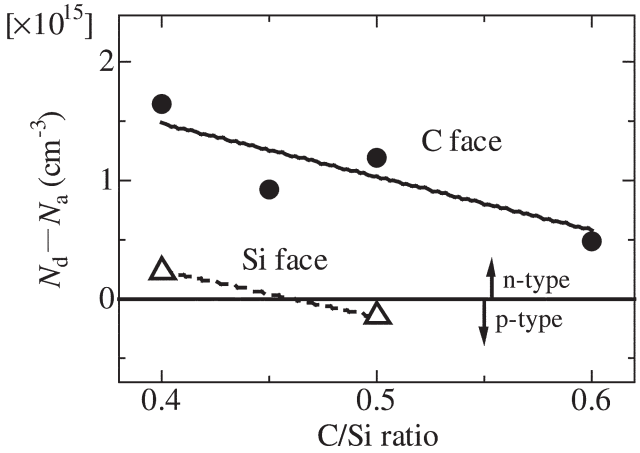
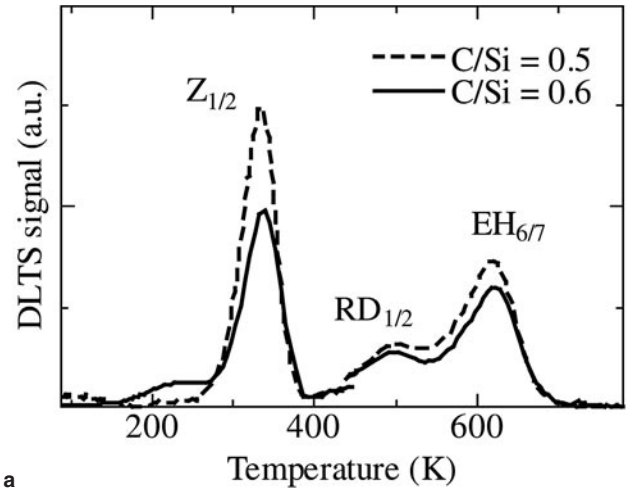


Fig. 5. C/Si ratio dependence of net donor concentration for 4H-SiC(0001) and (000$\bar{1}$) epilayers.



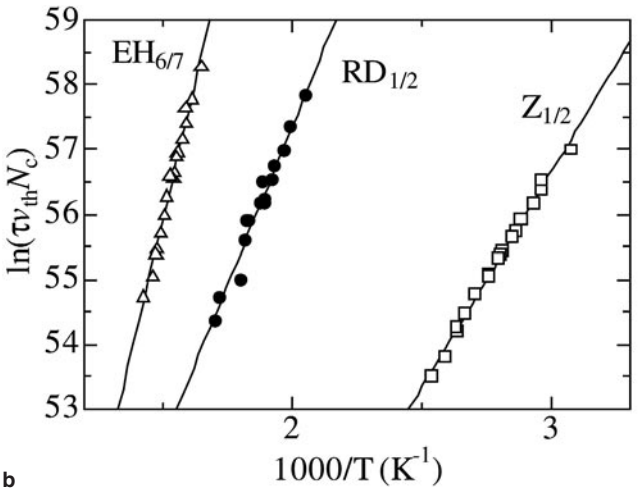


Fig. 6. (a) DLTS spectra of 4H-SiC(000$\bar{1}$) epilayers grown with C/Si ratios of 0.5 and 0.6 and (b) Arrhenius plots of emission-time constant assuming a temperature-independent capture cross section.

From the Arrhenius plots of emission-time constant assuming a temperature-independent capture cross section (Fig. 6b), these peaks could be assigned as the $Z_{1/2}$ center located at $E_c - 0.64$ eV[15] and $EH_{6/7}$ center at $E_c - 1.5$ eV[16] (E_c: the conduction band edge). The $Z_{1/2}$ center concentration of the epilayers grown under C/Si ratios of 0.5 and 0.6 was 1.5×10^{13} cm^{-3} and 1.0×10^{13} cm^{-3}, respectively. The $EH_{6/7}$ center concentration was also decreased from 7.0×10^{12} cm^{-3} to 6.0×10^{12} cm^{-3} by increasing the C/Si ratio from 0.5 to 0.6. Both the $Z_{1/2}$ and $EH_{6/7}$ concentrations of (000$\bar{1}$) epilayers were comparable to those of (0001) epilayers.[6] Another peak was detected at 500 K. This DLTS peak can be attributed to the $RD_{1/2}$ center (trap concentration: 2.7–3.0 $\times 10^{12}$ cm^{-3}, $E_c - 0.9$ eV),[15] which can be also seen in (0001) epilayers.

CONCLUSIONS

By CVD at a high temperature of 1,750°C in a chimney-type, hot-wall reactor, the authors succeeded in the growth of high-purity 4H-SiC(000$\bar{1}$) epilayers with high growth rates of 14–19 μm/h. A relatively high C/Si ratio (C/Si = 0.6) led to specular surface and low donor (4.9×10^{14} cm^{-3}) and trap ($Z_{1/2}$: 1.0×10^{13} cm^{-3}, $EH_{6/7}$: 6.0×10^{12} cm^{-3}) concentrations. As observed for the (0001) epilayers, micropipes were closed at low C/Si ratios during CVD on 4H-SiC(000$\bar{1}$).

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