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Reduction of doping and trap concentrations in 4H–SiC epitaxial layers grown by chemical vapor deposition

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High-purity and thick 4H–SiC(0001) epilayers have been grown by a horizontal hot-wall chemical vapor deposition (CVD) system, which was designed and built at the authors' group. The background donor concentration has decreased by reducing pressure during CVD, and a low donor concentration of $1-3\times10^{13}\,\mathrm{cm}^{-3}$ was achieved by CVD growth at 80 Torr. The free exciton peaks dominated in low- and room-temperature photoluminescence spectra without titanium or point-defect related peaks. The electron mobility reaches 981 $\mathrm{cm}^2/\mathrm{V\,s}$ at room temperature and 46 200 $\mathrm{cm}^2/\mathrm{V\,s}$ at 42 K. The total trap concentration could be reduced to $4.7\times10^{11}\,\mathrm{cm}^{-3}$ by increasing the input C/Si ratio. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1413724]

Through recent progress in silicon carbide (SiC) growth and device processing technologies, high-voltage (300 and 600 V) 4H–SiC Schottky diodes have been realized as commercial products.[1] The major advantages of SiC Schottky diodes, a unipolar device, include fast switching speed and negligibly small switching loss, owing to the absence of injected minority carriers. Although the theoretical specific on-resistance of SiC unipolar devices is more than two orders of magnitude lower than that of Si devices,[2,3] the on-resistance becomes unacceptably high for several kilovolts (>3–5 kV) SiC unipolar devices. For such high-voltage applications, SiC bipolar devices have promise, owing to the effect of conductivity modulation. In order to fabricate 5 kV SiC bipolar devices, for example, lightly doped ($<2\times10^{15}\,\mathrm{cm}^{-3}$) and thick (>40 μm) SiC epilayers with a sufficiently long minority carrier lifetime (>1 μs) are required. On the other hand, thick SiC crystals with ultrahigh purity and low trap concentration are of scientific importance for characterization of intrinsic or defect-related properties.

Chemical vapor deposition (CVD) has been a standard technique to produce device-quality SiC epilayers.[4] The background doping concentration of SiC epilayers has been reduced to $0.7-2\times10^{14}\,\mathrm{cm}^{-3}$ either by utilizing the site-competition concept[5] or by employing hot-wall type reactors.[6–8] Although an exceptionally low doping concentration of $2\times10^{13}\,\mathrm{cm}^{-3}$ has been recently reported for 4H–SiC epilayers grown at high growth rates by a vertical radiant-heating reactor,[9] the deep level concentration is in the same order as the doping concentration. In this letter, the authors describe the homoepitaxial growth of 4H–SiC(0001) by a home-made hot-wall CVD system. The lowest doping and deep level concentrations are simultaneously achieved.

A hot-wall CVD technique has been demonstrated to grow high-quality and thick SiC epilayers,[6,7] and its prototype CVD system is commercially available. The authors of this letter, however, designed and built a horizontal hot-wall CVD reactor, with which these experimental works have been done. Although the susceptor configuration used in this study is similar to that previously reported,[6] special care was paid to the purity of SiC-coated susceptor and thermal insulator as well as to the susceptor design. The susceptor is 100 mm long and has a gas flow channel with a height of approximately 10 mm. A single 2 in. wafer can be loaded in this system, but in the present work, small pieces (5–10 mm □) cut from 8° off-axis 4H–SiC(0001) wafers were used. Source gases were $\mathrm{SiH_4}$ and $\mathrm{C_3H_8}$ with a $\mathrm{H_2}$ carrier gas purified by a Ag–Pd cell. After loading substrates and pumping down to 10^{-6} Torr, the CVD process, consisting of *in situ* $\mathrm{C_3H_8+H_2}$ etching[10] and epitaxial growth, has started. The susceptor temperature was kept at 1500 °C during the *in situ* etching and epitaxial growth. The typical flow rates of $\mathrm{SiH_4}$, $\mathrm{C_3H_8}$, and $\mathrm{H_2}$ were 1.5 sccm, 0.75 sccm, and 5.0 slm, respectively, if not specified. Most CVD growth runs were carried out at reduced pressure in the range from 60 to 240 Torr, at which a growth rate of 5 μm/h was obtained under the typical condition. Typical growth time was 5–10 h, by which 25–50 μm thick epilayers were produced. The details of growth kinetics such as growth rate and surface morphological defects will be published elsewhere,[11] and this letter shall focus on the characterization of epilayers.

Figure 1 shows the donor concentration of unintentionally doped epilayers versus the reactor pressure during CVD. The net donor concentration was determined by

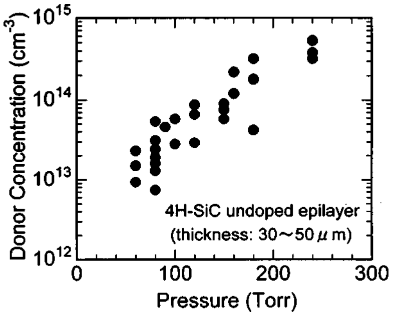

FIG. 1. Pressure dependence of donor concentration for unintentionally doped epilayers. The donor concentration was determined by $C-V$ characteristics of 1.5 mmϕ Ni/4H–SiC Schottky structure processed on 30–50 μm thick epilayers grown on highly doped *n*-type substrates.

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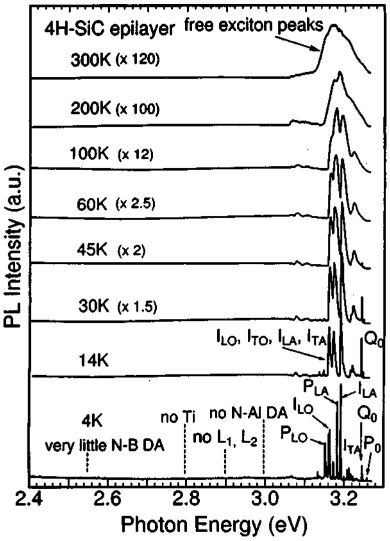

FIG. 2. PL spectra at several temperatures from 4 to 300 K obtained from a 50 μm thick undoped 4H–SiC epilayer grown at 80 Torr.

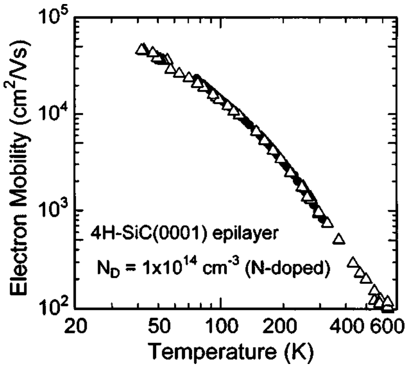

FIG. 3. Temperature dependence of electron mobility for a 20 μm thick 4H–SiC epilayer doped to $1.5\times10^{14}\,\mathrm{cm}^{-3}$. Solid circles and open triangles denote the data measured at the authors' group and University of Erlangen, respectively.

capacitance–voltage ($C-V$) measurements on 1.5 mmϕ Ni/4H–SiC Schottky structure with 30–50 μm thick undoped epilayers grown on highly doped *n*-type substrates. The donor concentration showed a significant decrease by reducing the pressure. Preliminary experiments on intentional nitrogen doping have also indicated that the doping efficiency of nitrogen is suppressed at low pressure, in agreement with previous reports.[12,13] A probable reason for this effect might be the enhanced desorption of nitrogen from the growing surface at reduced pressure. In the present growth system, the reproducible donor concentration is $1-3\times10^{13}\,\mathrm{cm}^{-3}$ by CVD growth at 80 Torr, and the lowest value obtained so far is $7\times10^{12}\,\mathrm{cm}^{-3}$, which are about one-order-of-magnitude lower than typical values reported from several groups.[4–8] In addition to the growth at low pressure, the use of pure susceptor and graphite thermal insulator may contribute to the reduction of unwanted impurities. The authors of this letter suggest that the doping concentration was not very sensitive to the C/Si ratio or to the gas flow rates, though the mechanism is not clear at present.

The 4H–SiC epilayers showed smooth surfaces, and the surface defect density was in the range of 100–300 cm^{-2}. In atomic force microscopy analyses, no macrostep formation was observed for 30–50 μm thick epilayers, leading to a small surface roughness of 0.2 nm. High-resolution x-ray diffraction measurements revealed that the full width at half maximum of the 4H–SiC(0004) peak ($2\theta=35.6°$) in a rocking curve (ω scan) was as small as 9.0 arcs.

Figure 2 represents the photoluminescence (PL) spectra at several temperatures from 4 to 300 K obtained from a 50 μm thick 4H–SiC epilayer grown with a C/Si ratio of 1.5 and at a pressure of 80 Torr. A He–Cd laser ($\lambda=325\,\mathrm{nm}$) was used as an excitation source. The net donor concentration of this epilayer determined from $C-V$ measurements was $2\times10^{13}\,\mathrm{cm}^{-3}$. At 4 K, the PL spectrum is dominated by free exciton peaks denoted by the I series and peaks of excitons bound to neutral-nitrogen donors labeled by the P (nitrogen at the hexagonal site) or Q (nitrogen at the cubic site) series. Phonons involved in the recombination are represented as the subscripts of labels. Impurity- or defect-related PL peaks such as aluminum-bound exciton ($4Al_0$ at 3.249 eV),[14] Ti (C_0 at 2.790 eV),[15] and D_1 center (L_1 at 2.902 eV)[16] were not observed. After thermal quenching of the P series at 20 K and the Q series at 50 K (not shown), free exciton peaks govern the PL spectra. The free exciton peaks exhibited longer tails towards the high-energy side with increasing temperature, due to the increase of kinetic energy of free excitons.

Hall effect measurements were performed on a 20 μm thick 4H–SiC epilayer grown on a semi-insulating substrate. The epilayer was intentionally doped with nitrogen to $1.5\times10^{14}\,\mathrm{cm}^{-3}$ in order to ensure the formation of Ni ohmic contacts. The sample was $5\times5\,\mathrm{mm}^2$ in size and was processed into a clover-leaf structure by reactive ion etching with CF_4+O_2 gases. The free electron concentration was $1.1\times10^{14}\,\mathrm{cm}^{-3}$ at room temperature. Figure 3 shows the temperature dependence of electron mobility for this lightly doped 4H–SiC epilayer. In the mobility calculation, a Hall scattering factor of unity was assumed. In Fig. 3, solid circles and open triangles denote the data measured at the authors' group and University of Erlangen, respectively. The agreement is very good between the two measurement systems. A high mobility of 981 $\mathrm{cm}^2/\mathrm{V\,s}$ was obtained at room temperature, and it reaches 46 200 $\mathrm{cm}^2/\mathrm{V\,s}$ at 42 K, indicating very small impurity scattering. This value is a very high mobility measured in SiC polytypes determined by the Hall effect.

Figure 4 represents the deep level transient spectroscopy (DLTS) spectra for 30 μm thick 4H–SiC epilayers grown

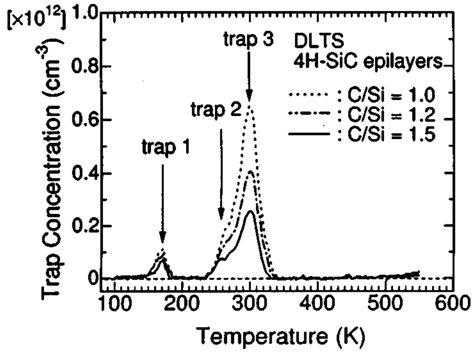

FIG. 4. DLTS spectra for 30 μm thick 4H–SiC epilayers grown with C/Si ratios of 1.0, 1.2, and 1.5, respectively. The epilayers have donor concentrations of $5-6\times10^{13}\,\mathrm{cm}^{-3}$. The reverse bias and pulse voltages applied during the measurement were -5 V and 5 V, respectively.

TABLE I. Trap parameters of defect centers observed in 4H–SiC epilayers grown by hot-wall CVD.

Trap	Activation energy (eV)	Capture cross section (cm^2)	Possible origin[a]
1	0.35 ± 0.02	$(2-5)\times10^{-15}$	ID_4
2	0.52 ± 0.05	$(7-10)\times10^{-16}$	ID_9
3	0.65 ± 0.02	$(4-9)\times10^{-15}$	Z_1

[a] See Ref. 17.

with C/Si ratios of 1.0, 1.2, and 1.5, respectively. All the epilayers were grown at 80 Torr with a growth rate of 5 μm/h, and have a donor concentration of $5-6\times10^{13}\,\mathrm{cm}^{-3}$. The DLTS signals were taken from 1.5 mmϕ Ni/4H–SiC structure. The reverse bias and pulse voltages applied during DLTS measurements were -5 V and 5 V, respectively. Under this measurement condition, a 10–12 μm deep region from the surface was monitored. The DLTS spectra exhibited two clear peaks at 170 K (trap 1) and 300 K (trap 3). At the lower-temperature flank of the peak for trap 3, a small shoulder is observed. This shoulder (trap 2) was analyzed after subtracting the component of trap 3. Table I summarizes the trap parameters estimated from the Arrhenius plots of emission time constants for the traps 1, 2, and 3, assuming temperature-independent capture cross sections. The activation energies for three traps were determined to be 0.35, 0.52, and 0.65 eV. From the activation energies and capture cross sections, the observed deep levels can be assigned to the ID_4, ID_9, and Z_1 centers,[17] as shown in Table I.

By increasing the C/Si ratio from 1.0 to 1.5, the total deep level concentration could be reduced from 9.5×10^{11} to $4.7\times10^{11}\,\mathrm{cm}^{-3}$, which is one order of magnitude lower than typical concentrations reported $(4-20\times10^{12}\,\mathrm{cm}^{-3})$.[4,8,9,18,19] In particular, the generation of the Z_1 center, the major trap, could be suppressed by increasing the C/Si ratio. Although the authors of this letter prepared nitrogen-doped epilayers with donor concentrations up to $5\times10^{14}\,\mathrm{cm}^{-3}$, as well as epilayers grown at various growth rates from 1.5 to 6.2 μm/h, DLTS measurements on these samples revealed no clear correlation between the trap concentrations and doping concentration or growth rate. As shown in Fig. 4, the growth under C-rich conditions is a key factor to obtain the lower Z_1-center concentration. All the defect centers observed in this study are believed to be intrinsic defect complexes, which do not contain specific impurities,[17] but the exact defect structures have not been identified yet. The present study implies that a Si antisite (Si_C) or C vacancy (V_C), which may be easily created under Si-rich conditions, might be included in the Z_1 center. DLTS measurements were also made at 300–550 K in the long transient-time range from 20 ms to 2 s, but no new deep level signals were detected. Thus, the authors of this letter conclude that the concentration of deep levels located in the range from $E_C-0.7$ to $E_C-1.3$ eV (E_C: the conduction band edge) may be lower than $5\times10^{10}\,\mathrm{cm}^{-3}$, assuming a capture cross section of $1\times10^{-15}\,\mathrm{cm}^2$.

In summary, high-purity and thick 4H–SiC(0001) epilayers were grown by horizontal hot-wall CVD. A typical growth rate was 5 μm/h at 1500 °C under a pressure of 80 Torr. The background donor concentration exhibited a significant decrease by reducing the reactor pressure, and a low donor concentration of $1-3\times10^{13}\,\mathrm{cm}^{-3}$ was achieved at 80 Torr. The free exciton peaks dominated in low- and room-temperature PL spectra without Ti or point-defect related peaks. High electron mobilities of 981 $\mathrm{cm}^2/\mathrm{V\,s}$ at room temperature and 46 200 $\mathrm{cm}^2/\mathrm{V\,s}$ at 42 K were obtained by Hall effect measurements. DLTS analyses revealed three types of deep levels, the Z_1 center being dominant. The total deep level concentration could be reduced to $4.7\times10^{11}\,\mathrm{cm}^{-3}$ by increasing the C/Si ratio to 1.5.

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