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

Author(s)
Kimoto, Tsunenobu; Nakazawa, Satoshi; Hashimoto, Koichi; Matsunami, Hiroyuki

Citation

Issue Date
2001-10-22

URL
http://hdl.handle.net/2433/24206

Copyright 2001 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.

Type
Journal Article

Textversion
publisher

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

Tsunenobu Kimoto, Satoshi Nakazawa, Koichi Hashimoto, and Hiroyuki Matsunami

*Department of Electronic Science and Engineering, Kyoto University, Yoshidahonnouchi, Sakyo, Kyoto 606-8501, Japan*

(Received 2 May 2001; accepted for publication 17 August 2001)

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 $1 \times 10^{13}$ 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 cm$^2$/V s at room temperature and 46,200 cm$^2$/V s at 42 K. The total trap concentration could be reduced to $4.7 \times 10^{11}$ 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. 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, the on-resistance becomes unacceptably high for several kilovolts (~600 V) SiC unipolar devices. For several 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 ($<2 \times 10^{15}$ cm$^{-3}$) and thick ($>40 \mu m$) SiC epilayers with a sufficiently long minority carrier lifetime ($>1 \mu s$) 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. The background doping concentration of SiC epilayers has been reduced to $0.7 \times 2 \times 10^{14}$ cm$^{-3}$ either by utilizing the site-competition concept or by employing hot-wall type reactors. Although an exceptionally low doping concentration of $2 \times 10^{13}$ cm$^{-3}$ has been recently reported for 4H–SiC epilayers grown at high growth rates by a vertical radiant-heating reactor, 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, 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, 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$^2$) cut from 8° off-axis 4H–SiC(0001) wafers were used. Source gases were SiH$_4$ and C$_3$H$_8$ with a 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* C$_3$H$_8$+H$_2$ etching 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 SiH$_4$, C$_3$H$_8$, and 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, 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

---

*Electronic mail: kimoto@kuee.kyoto-u.ac.jp*
surface defect density was in the range of 100–300 cm
2. The mechanism is not clear at present.

to the C/Si ratio or to the gas flow rates, though the mecha-
suggest that the doping concentration was not very sensitive
reduction of unwanted impurities. The authors of this letter
ceptor and graphite thermal insulator may contribute to the
addition to the growth at low pressure, the use of pure sus-

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 (0001) peak (2θ = 35.6°) in a rock-
ing 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 undoped 4H–SiC epilayer grown at 80 Torr.

capacitance–voltage (C–V) measurements on 1.5 mm φ 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 ni-ogen is suppressed at low pressure, in agreement with pre-
vious reports. A probable reason for this effect might be
the enhanced desorption of nitrogen from the growing sur-
facet at reduced pressure. In the present growth system, the
reproducible donor concentration is 1–3 x 10
13 cm
–3 by
CVD growth at 80 Torr, and the lowest value obtained so far
is 7 x 10
12 cm
–3, which are about one-order-of-magnitude
lower than typical values reported from several groups.4–5 In
addition to the growth at low pressure, the use of pure sus-
ceptor 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 mech-
nism is not clear at present.

The 4H–SiC epilayers showed smooth surfaces, and the

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 exhib-
it 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
x 10
14 cm
–3 in order to ensure the formation of Ni ohmic
contacts. The sample was 5 x 5 mm
2 in size and was pro-
cessed into a clover-leaf structure by reactive ion etching
with CF
4 +O
2 gases. The free electron concentration was
1.1 x 10
14 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 agree-
ment is very good between the two measurement systems. A
high mobility of 981 cm
2/V s was obtained at room tempera-
ture, and it reaches 462 000 cm
2/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. 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 x 10
14 cm
–3. Solid circles and open triangles
denote the data measured at the authors’ group and University of Erlangen,
respectively.

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 concen-
trations of 5–6 x 10
13 cm
–3. The reverse bias and pulse voltages applied
during the measurement were –5 V and 5 V, respectively.

Downloaded 24 Dec 2006 to 130.54.130.229. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp
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 $5 \times 6 \times 10^{13}$ cm$^{-3}$. The DLTS signals were taken from 1.5 mm thick 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, 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 $9.5 \times 10^{11}$ to $4.7 \times 10^{11}$ cm$^{-3}$, which is one order of magnitude lower than typical concentrations reported ($4 \times 20 \times 10^{12}$ 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 $5 \times 10^{14}$ 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, but the exact defect structures have not been identified yet. The present study implies that a Si antisite (Si$_{\text{C}}$) or C vacancy (V$_{\text{C}}$), 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 $5 \times 10^{10}$ cm$^{-3}$, assuming a capture cross section of $1 \times 10^{-15}$ cm$^2$.

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

<table>
<thead>
<tr>
<th>Trap</th>
<th>Activation energy (eV)</th>
<th>Capture cross section (cm$^2$)</th>
<th>Possible origin$^{a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.35±0.02</td>
<td>$(2-5) \times 10^{-15}$</td>
<td>ID$_4$</td>
</tr>
<tr>
<td>2</td>
<td>0.52±0.05</td>
<td>$(7-10) \times 10^{-16}$</td>
<td>ID$_9$</td>
</tr>
<tr>
<td>3</td>
<td>0.65±0.02</td>
<td>$(4-9) \times 10^{-15}$</td>
<td>Z$_1$</td>
</tr>
</tbody>
</table>

$^{a}$See Ref. 17.

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 $1 \times 3 \times 10^{13}$ 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 $981 \text{cm}^2/\text{V} \cdot \text{s}$ at room temperature and $46 \text{200 cm}^2/\text{V} \cdot \text{s}$ 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 $4.7 \times 10^{11}$ cm$^{-3}$ by increasing the C/Si ratio to 1.5.

The authors express deep gratitude to Dr. G. Pensl and M. Laube at the University of Erlangen–Nürnberg for their Hall effect measurements. This work was supported by a Grant-in-Aid for Specially Promoted Research (No. 09102009) from the Ministry of Education, Science, Sports, and Culture of Japan, and also by NEDO. Kyoto University Venture Business Laboratory is also acknowledged for the use of characterization systems.