Impacts of growth parameters on deep levels in *n*-type 4H-SiC

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Deep levels in *n*-type 4H-SiC epilayers have been investigated by deep level transient spectroscopy. The $Z_{1/2}$ and $EH_{6/7}$ centers are dominant in epilayers grown with low C/Si ratios during chemical vapor deposition. By increasing the C/Si ratio, the $Z_{1/2}$ and $EH_{6/7}$ concentrations are decreased, while an unknown trap (the UT_1 center, $E_c-1.45$ eV) is introduced. The $Z_{1/2}$ and $EH_{6/7}$ concentrations are not changed by increasing the growth rate from 14 to 23 μm/h at a fixed C/Si ratio. By increasing growth temperature from 1550 to 1750 °C, however, the $Z_{1/2}$ and $EH_{6/7}$ concentrations are significantly increased. From these results, the formation of $Z_{1/2}$ and $EH_{6/7}$ centers are mainly affected by the C/Si ratio and growth temperature rather than the growth rate. These phenomena can be explained with a model that both $Z_{1/2}$ and $EH_{6/7}$ centers are related to a carbon vacancy, which has been recently proposed by the authors. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2437666]

I. INTRODUCTION

Silicon carbide (SiC) is an attractive material for realizing high-power, high-temperature, and high-frequency devices, owing to its superior properties such as wide band gap, high breakdown field, high thermal conductivity, and high saturation electron drift velocity.[1] 4H-SiC has been regarded as the most promising polytype for fabricating vertical-type high-voltage devices, due to higher bulk mobility and smaller anisotropy. To realize SiC power devices with high blocking voltage of more than several kilovolts, bipolar devices such as pin diodes, thyristors, and insulated gate bipolar transistors possess great promise in terms of lower on-resistance owing to the effect of conductivity modulation.[2,3] Long minority carrier lifetime is required for effective conductivity modulation. Although the lifetime of SiC epilayers has been investigated by several groups,[4–7] it does not exceed 1–2 μs, which is a-few-orders-of-magnitude smaller than that of high-purity silicon. Since deep levels may play an important role in limiting the carrier lifetime, the concentration should be decreased.

In as-grown *n*-type 4H-SiC epilayers, the $Z_{1/2}(E_c-0.65$ eV) (Ref. 8) and $EH_{6/7}(E_c-1.55$ eV) (Ref. 9) centers are two major deep levels, detected by deep level transient spectroscopy (DLTS).[10] Their concentrations are decreased by increasing the C/Si ratio[11,12] during chemical vapor deposition (CVD). However, many features remain unknown about formation of the deep levels during CVD growth of SiC.

In this work, the authors have tried to clarify the growth parameters (C/Si ratio, growth rate, growth temperature, etc.), which affect formation of the deep levels in *n*-type 4H-SiC. The key issue to reduce trap concentration in conjunction with possible origins is discussed.

II. EXPERIMENT

Epitaxial growth was performed on 8° off-axis 4H-SiC(0001) n^+ substrates by horizontal hot-wall CVD in a SiH_4-C_3H_8-H_2 system.[13] Epitaxial growth was performed at 1550–1750 °C with a typical reactor pressure of 80 Torr. The growth rate was varied in the range from 9.3 to 54 μm/h by changing the SiH_4 flow rate from 4 to 20 sccm. The C/Si ratio was varied from 0.8 to 2.0 by changing the C_3H_8 flow rate at a fixed SiH_4 flow rate. The flow rate of H_2 carrier gas was 10 slm. Most epilayers were intentionally doped with nitrogen.

The net donor concentration of epilayers, determined by capacitance-voltage measurement, was in the range from 2.2×10^{14} cm^{-3} to 1.8×10^{16} cm^{-3}. Nickel was thermally evaporated onto the sample surface as Schottky contacts with a thickness of approximately 70 nm. Ohmic contacts were formed with silver paste on the backside of highly doped *n*-type substrates. Typical diameter of the Schottky contacts was 1500 μm.

Deep levels were investigated by DLTS in the temperature range from 100 to 700 K. If not specified, the reverse bias was kept at −5 V, and the pulse voltage applied during the DLTS measurements was 0 V (pulse height: 5 V). The period width of 0.2 s was employed for all the DLTS mea-

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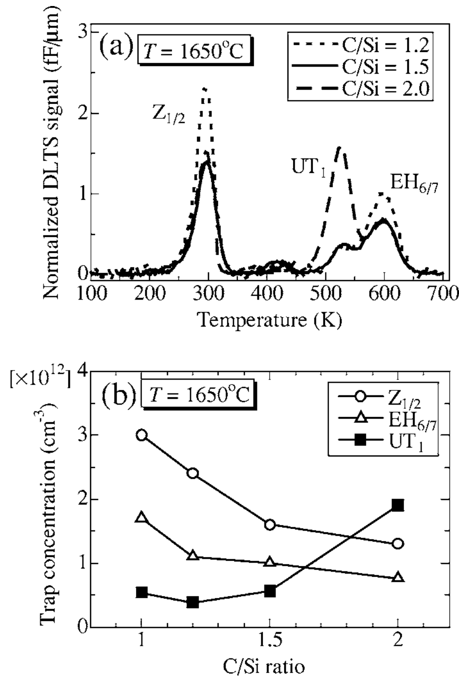

FIG. 1. (a) Normalized DLTS spectra of as-grown n-type 4H-SiC epilayers grown at 1650 °C with various C/Si ratios of 1.2, 1.5, and 2.0. The DLTS signals are normalized by depletion layer width. (b) C/Si ratio dependence of the $Z_{1/2}$, $EH_{6/7}$, and UT_1 concentrations.

surements performed in this study. A Fourier transform analysis[14] of the measured transients was employed. A temperature-independent capture cross section was assumed when analyzing the DLTS data. In this article, the trap concentrations are corrected by considering the lambda effect.[15]

III. RESULTS

Figure 1(a) shows the DLTS spectra normalized by depletion layer width of the n-type 4H-SiC epilayers grown with C/Si ratios of 1.2, 1.5, and 2.0. The epilayers were grown with the SiH_4 flow rate of 8.0 sccm at 1650 °C. The growth rate and thickness of the samples were almost constant at 24 μm/h and 24 μm, regardless of the C/Si ratio in this range. As shown in Fig. 1(a), two peaks at 295 and 600 K were dominant in the samples grown with the C/Si ratios of 1.2 and 1.5. According to the Arrhenius plot of emission time constant, the capture cross section and activation energy were 2×10^{-14} cm^2 and 0.61 eV for the trap at 295 K, and 1×10^{-13} cm^2 and 1.54 eV for the trap at 600 K. From the results, these peaks can be assigned to the $Z_{1/2}$ center[8] and the $EH_{6/7}$ center.[9] In Fig. 1(b), the dependence of the trap concentrations on the C/Si ratio is shown. The trap concentrations were decreased by increasing the C/Si ratio and reduced to 1.3×10^{12} cm^{-3} ($Z_{1/2}$) and 7.6×10^{11} cm^{-3} ($EH_{6/7}$) at the C/Si ratio of 2.0. Therefore, formation of the $Z_{1/2}$ and $EH_{6/7}$ centers is pronounced under Si-rich conditions.

In the DLTS spectrum of the epilayer grown with a C/Si ratio of 2.0, a sharp peak at 500 K (labeled UT_1) was observed. According to the Arrhenius plot, the UT_1 center is energetically located at $E_c-1.45$ eV. The UT_1 concentration was lower than mid 10^{11} cm^{-3} in epilayers grown with C/Si ratios of 1.0 and 1.2 and became the most dominant (1.9 $\times10^{12}$ cm^{-3}) with a C/Si ratio of 2.0. As shown in Fig. 1(b), the UT_1 concentration tends to increase by increasing the C/Si ratio. The center might be related to carbon interstitials, carbon antisites, or silicon vacancies, since they are easily introduced under the C-rich condition.[16] However, this center could not be observed in the electron-irradiated samples,[8,9,17,18] in which the defects mentioned earlier will exist in high concentration. Therefore, the UT_1 center may relate to a more complicated defect like a defect cluster or a complex, including a defect which is easily introduced under C-rich condition.

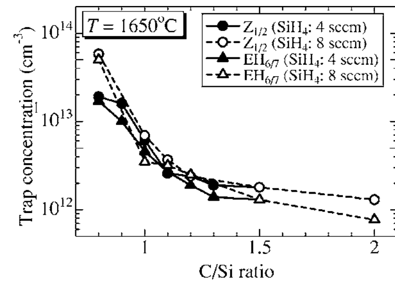

FIG. 2. C/Si ratio dependence of $Z_{1/2}$ and $EH_{6/7}$ concentrations in 4H-SiC epilayers grown with a SiH_4 flow rate of 4 sccm (growth rate ~14 μm/h) and 8 sccm (growth rate ~23 μm/h) at 1650 °C.

Figure 2 shows the C/Si ratio dependence of the $Z_{1/2}$ and $EH_{6/7}$ concentrations in epilayers grown at the SiH_4 flow rate of 4 and 8 sccm at a fixed growth temperature of 1650 °C. The growth rate was 14 μm/h for a SiH_4 flow rate of 4 sccm and 23 μm/h for 8 sccm when the epilayers were grown with a C/Si ratio of 1.5. As shown in Fig. 2, the $Z_{1/2}$ and $EH_{6/7}$ concentrations decreased by more than one order of magnitude when the C/Si ratio was changed from 0.8 to 2.0. Interestingly, the $Z_{1/2}$ concentration does not depend on the growth rate (14 and 23 μm/h) as far as the growth was carried out with a given C/Si ratio from 1.0 to 1.5 (and at a given temperature of 1650 °C). The same tendency is observed for the $EH_{6/7}$ center. In the sample grown with higher growth rate of 54 μm/h (SiH_4 flow rate =20 sccm, C/Si ratio =1.0 or 1.2, not shown), the trap concentrations (both $Z_{1/2}$ and $EH_{6/7}$) were also similar to those in Fig. 2. Therefore, the growth rate does not directly influence the formation of the $Z_{1/2}$ and $EH_{6/7}$ centers and the C/Si ratio gives a much larger impact on the defect formation than the growth rate.

Figure 3 shows the DLTS spectra of epilayers grown with a fixed C/Si ratio of 1.5 at various temperatures from 1550 to 1750 °C. The growth rate of the samples used for

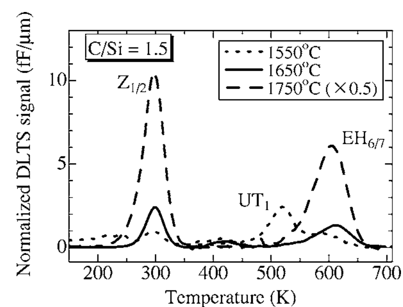

FIG. 3. DLTS spectra of as-grown n-type 4H-SiC epilayers grown with a fixed C/Si ratio of 1.5 at various temperatures of 1550, 1650, and 1750 °C.

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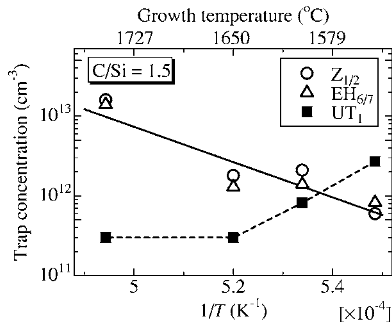

FIG. 4. Arrhenius plot of the $Z_{1/2}$, $EH_{6/7}$, and UT_1 concentrations in the epilayers grown with a fixed C/Si ratio of 1.5. The solid line denotes the least square fit.

this experiment was very close to each other (approximately 14–17 μm/h). As seen in Fig. 3, the introduction of the UT_1 center seems to be enhanced in growth at relatively low temperature. On the other hand, the DLTS signals for the $Z_{1/2}$ and $EH_{6/7}$ centers were significantly increased by increasing growth temperature, in good agreement with a previous result obtained in chimney-type CVD at 1740–1840 °C.[19] Figure 4 shows the Arrhenius plot of the $Z_{1/2}$, $EH_{6/7}$, and UT_1 concentrations. By increasing growth temperature from 1550 to 1750 °C, the UT_1 concentration was decreased from 2.7×10^{12} cm^{-3} to below the detection limit (about 1–3 $\times10^{11}$ cm^{-3}). For the $Z_{1/2}$ and $EH_{6/7}$ centers, on the other hand, the trap concentrations were increased from 6.0 $\times10^{11}$ cm^{-3} to 1.6×10^{13} cm^{-3} for the $Z_{1/2}$ center and from 8.3×10^{11} cm^{-3} to 1.4×10^{13} cm^{-3} for the $EH_{6/7}$ center. Therefore, it is effective for reducing the $Z_{1/2}$ and $EH_{6/7}$ concentrations to decrease growth temperature and to increase the C/Si ratio.

IV. DISCUSSION

Storasta *et al.* reported that the $Z_{1/2}$ and $EH_{6/7}$ centers may be related to carbon displacement [generation of carbon vacancies (V_C) and carbon interstitials (C_i)] according to their DLTS results on 4H-SiC epilayers irradiated with low-energy (80–300 keV) electrons.[17] C_i may be thermally much more unstable than V_C due to its high mobility.[20,21] Considering thermal stability of the centers up to 1500–1600 °C,[18,22–24] the $Z_{1/2}$ and $EH_{6/7}$ centers may not be C_i-related but V_C-related defects, which is in agreement with a report by Litton *et al.*[25] The authors also made extensive study on the $Z_{1/2}$ and $EH_{6/7}$ centers in 4H-SiC epilayers irradiated with low-energy electrons and speculated that both centers may originate from a same defect, probably containing V_C.[18] The formation of V_C is suppressed under C-rich condition and enhanced under Si-rich condition. This may be the reason why the $Z_{1/2}$ and $EH_{6/7}$ concentrations were decreased under C-rich condition.

According to a simple model on the formation of vacancies in solids,[26] the concentration of neutral carbon vacancies (N_{V_C}) in thermal equilibrium is given by

$$N_{V_C} = N_0 \exp\left(\frac{\Delta S}{k}\right)\exp\left(-\frac{\Delta H}{kT}\right) = A \exp\left(-\frac{\Delta H}{kT}\right), \qquad (1)$$

where N_0 is the concentration of C lattice sites, ΔS the effective entropy of formation of neutral carbon vacancy, k the Boltzmann constant, ΔH the effective enthalpy of formation (formation energy) of neutral carbon vacancy, T the absolute temperature, and A the constant. From the slope of the Arrhenius plot shown in Fig. 4, the activation energies for formation of the $Z_{1/2}$ and $EH_{6/7}$ centers were estimated to be 4.6 ± 0.3 eV, which shows agreement with the formation energy calculated for V_C in 4H-SiC [for example, 4.41–4.49 eV (Ref. 16) and 5.48 eV (Ref. 27)]. The obtained activation energy is also close to those obtained for *n*-type epilayers grown by chimney-type hot-wall CVD at 1740–1840 °C (4.3 eV for the $Z_{1/2}$ center and 4 eV for the $EH_{6/7}$ center).[19] Thus, the increase in the $Z_{1/2}$ and $EH_{6/7}$ concentrations with increasing growth temperature follows the same tendency as the equilibrium V_C concentration in SiC. If the $Z_{1/2}$ and $EH_{6/7}$ centers are attributed to or contain V_C,[17,18] the high trap concentration in epilayers grown at high temperature may be reasonably understood. On the other hand, the UT_1 center does not follow this trend, probably because the UT_1 center may originate from a completely different defect complex.

V. SUMMARY

In summary, the authors investigated impacts of CVD parameters on deep levels in as-grown *n*-type 4H-SiC. The formation of $Z_{1/2}$ and $EH_{6/7}$ centers were governed mainly by the C/Si ratio and growth temperature rather than the growth rate. The C-rich condition is favorable to suppress the formation of the $Z_{1/2}$ and $EH_{6/7}$ centers. This is probably because both the centers are V_C-related defects. The $Z_{1/2}$ and $EH_{6/7}$ concentrations were increased by increasing growth temperature in a similar manner to the temperature dependence of concentration of neutral V_C in thermal equilibrium. Therefore, it is important to choose the proper C/Si ratio and growth temperature (relatively high C/Si ratio from a stoichiometric point and not too high growth temperature) in order to grow high-quality epilayers at high growth rate. The UT_1 center could be detected in the epilayers grown with a high C/Si ratio and/or a low growth temperature.

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