Characteristics of the intrinsic defects in unintentionally doped 4H–SiC after thermal annealing

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Abstract

Thermal annealing effects on the characteristics of intrinsic defects in unintentionally doped 4H–SiC were investigated. The 4H–SiC samples were prepared by Low-Pressure Chemical Vapor Deposition (LPCVD) technique. Results show that there is only one Electron Spin Resonance (ESR) peak and a broad, from green to yellow, photoluminescence (PL) band were detected. These results are attributed to the native defects of carbon vacancy ($V_{C}$) and complex carbon compound vacancy. The concentration of the intrinsic defects increases and reaches its maximum annealing at 1573 K, then decreases with the anneal temperature. Both ESR and PL have significant changes when the samples were annealed for 60 min. The concentration variation in unintentionally doped 4H–SiC is process dependent and is related to the interaction among the various intrinsic defects during the annealing. The silicon capping layer may also play an important role for these defect interactions particularly when the annealing was lasted for 60 min.

1. Introduction

The electrical characteristics of a 4H–SiC film strongly depend on defect centers. It was shown that most of the intrinsic defects inside the band gap produced during the crystal growth can be activated electrically. These defects even affect the doping efficiency [1]. The deep level defects affect conductivity and carrier lifetime of semiconductors [2–4]. It is interesting to study the dependence of these defects on the process temperature as it is crucial to achieve the required electrical properties. A large number of theoretical [5,6] and experimental [7–9] studies on the thermal stability of intrinsic defects in various SiC have been reported in literature.

Electron paramagnetic resonance (EPR) spectroscopy reveals the existence of at least three different paramagnetic intrinsic defects in high-quality SiC [10,11], which are vacancy, divacancy and anti-site vacancy pairs. Some studies [12,13] further suggested these defects may also in complex forms depending on cluster sizes. The carbon vacancy ($V_{C}$) and cluster-related $V_{C}$ are the well-known intrinsic defects in high-purity SiC and can be characterized directly by Electron Spin Resonance (ESR). Low-Pressure Chemical Vapor Deposition (LPCVD) is one of the effective methods to prepare high-quality 4H–SiC films. However, the characteristics of native defects in unintentionally doped 4H–SiC prepared by LPCVD are still an unresolved issue. In this study isochronous annealing on the deposited samples were carried out in different temperature in the range of 1273–1873 K. ESR and PL measurements were performed on each of the annealing samples. We demonstrate the annealing effects on the intrinsic defects and some mechanisms are proposed to explain the ESR and PL results.

2. Experiments

The samples used in this investigation were unintentionally doped epitaxial 4H–SiC grown on the SiCrystal substrates by using LPCVD technique. The substrates were n-type with doping concentration of about $5 \times 10^{18}$ cm$^{-3}$. The donor concentration of the unintentionally doped epitaxial layer was about $1.1 \times 10^{15}$ cm$^{-3}$ due to the residual N$_2$ in the system. The isochronous annealing from 10 min to 60 min were performed in Ar ambient in the CVD reactor at temperature in the range of 1273–1873 K. Photoluminescence (PL) measurements were performed at 10 K, by using 325 nm wavelength He–Cd laser as the excitation light source. The ESR measurements were obtained by using a JES-FA200 spectrometer operated at about 9.0 GHz. The ESR data were taken with an external magnetic field with direction along the epitaxial direction and at a temperature of 110 K.

3. Results and analysis

Fig. 1 shows the ESR spectra of as-grown sample, in which C and P represent the direction of the magnetic field that are perpendicular and parallel to the epitaxial direction, respectively. It is obvious that the ESR spectrum is in aelotropism, and the C intensity is larger than that of P [14]. In order to analyze legibly, the magnetic field perpendicular to the epitaxial direction was chosen for...
the following ESR spectra. In ESR spectra is a reflection of the resonance between the microwave power and magnetic intensity caused by the SiC intrinsic defects and can be described by:

$$h\nu = g\beta H$$  \hspace{0.5cm} (1)

In Eq. (1), $h$ is the Planck constant, $\nu$ the microwave frequency, $\beta$ the Bohr magnetic, and $H$ the center magnetic field of ESR signal. From this equation, $g$ vector can be evaluated by:

$$g = \frac{h\nu}{\beta H} = 0.714484 \frac{\nu/\text{MHz}}{H/\text{G}}$$  \hspace{0.5cm} (2)

From Eq. (2), the $g$ vectors of ESR spectra in Fig. 1 can be determined and they are $g_C = 1.97522$ and $g_P = 1.97323$, respectively. These values are essentially the same as those for carbon vacancy and its complex compounds. On the other hand, the line width is another important parameter which is the magnetic distance between the apex and vale. The line width in Fig. 1 is more than 6 mT which is much larger than that of an ideal carbon vacancy (0.03 mT) [14] at 77 K. The higher measurement temperature may be major cause for the wider line width [15].

Fig. 2 shows the ESR spectra of 4H–SiC epilayers annealed for 10, 30 and 60 min. It can be seen that the major ESR features of the annealed samples are same as that of as-grown ones, which suggests that the native defects should also be composed by the carbon vacancy and its complex compounds. In Figs. 1 and 2, the total concentration of intrinsic defects can be characterized by ESR intensity $\phi$ which can be expressed as:

$$\phi \propto Y \times (\Delta H_{pp})^2$$  \hspace{0.5cm} (3)

where $Y$ represents the summation of apex values and vale values, and $\Delta H_{pp}$ is the line width. Detailed information of intrinsic defects with different annealing conditions is shown in Table 1. The total concentration of the intrinsic defects, as a function of annealing conditions, is also plotted in Fig. 3.

From Table 1 and Fig. 3, it is noted that the total concentration of intrinsic defects first increases and then decreases with the
annealing temperature. It reaches its maximum at 1573 K for annealing duration of 10 min and 30 min. However, samples annealed for 60 min has different temperature dependence for the defect concentration. In addition, the line widths of the annealed samples also agree with that of the as-grown sample although the annealed samples have lower defect density.

Photoluminescence measurements were conducted at 10 K. Fig. 4 shows the PL spectrum of the as-grown sample. A broad yellow and green luminescence band peaks at 526 nm is observed. Fig. 5 shows the PL results samples with 30 min and 60 min annealing. Sample with 30 min annealing has a dominant luminescence in green band. Samples with 60 min annealing has a total different behavior. The PL intensities besides the peak increase and luminescence peak is broadened as the annealing temperature increases. In addition, the total concentration of intrinsic defects decrease after the thermal annealing and which is consistent with the ESR results.

The luminescence caused by the recombination of donor and acceptor can be modeled by:

\[
\hbar \nu = E_g - (E_A + E_D) + e^2/\varepsilon r
\]

Here \(E_g\) represents the band gap energy, \(E_A\) and \(E_D\) are the energy levels of acceptor and donor, respectively, and \(\varepsilon r\) is the dielectric constant. The wavelength of luminescence calculated from (4) is less than 526 nm. There is an obvious difference between the calculated and experimental data. We suggest that an energy level, \(E_x\) may exist in the band gap of SiC, and the yellow and green luminescence are caused by the recombination of shallow donor and deep acceptor with \(E_x\). There are different characteristics of green luminescence [5,8,7]. The PL spectrum at 10 K is asymmetrical because of the asymmetrical distribution of the carbon vacancies and its re-

| Table 1 | ESR parameters of annealed unintentionally doped 4H–SiC. |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | As-grown | 10 min | 30 min | 60 min | 10 min | 30 min | 60 min | 10 min | 30 min | 60 min |
| | 1273 K | 1573 K | 1873 K | 1273 K | 1573 K | 1873 K | 1273 K | 1573 K | 1873 K | 1273 K | 1573 K | 1873 K |
| Y (a.u.) | 1309.25 | 489.12 | 431.62 | 469.25 | 396.50 | 638.62 | 442.37 | 554.00 | 386.75 | 477.13 |
| g vector | 1.9752 | 1.9738 | 1.9665 | 1.9712 | 1.9704 | 1.9724 | 1.9736 | 1.9727 | 1.9702 | 1.9725 |
| \(\phi\) (a.u.) | 57,533 | 21,494 | 25,778 | 22,250 | 20,016 | 32,238 | 16,950 | 27,668 | 19,195 | 24,837 |

Fig. 3. The dependence of total concentration of intrinsic defects on different anneal treatment parameters.

Fig. 4. PL spectrum of as-grown sample.

Fig. 5. PL results in annealed sample. (a) Anneal time 30 min (b) anneal time 60 min.
lated defects [9]. It indicates that the broad green luminescence originates from several independent radiative transitions.

For 10 min and 30 min annealing, the ESR and PL spectra suggest that the total concentration of intrinsic defects first increase and then decrease as the annealing temperature rising from 1273 K to 1873 K. This result should be due to the interaction among the intrinsic defects during the annealing process. The increase of total defect concentration may be resulted from the splitting of some clusters into small size defects [12]. Whereas the decrease of the total defect concentration may be induced by the following defect transformation [12,16–19]:

\[
\begin{align*}
V_{3\text{SiC}} & \rightarrow V_{\text{C}} & (5) \\
V_{\text{Si}} & \rightarrow V_{\text{C}}C_{\text{Si}} & (6) \\
V_{\text{C}}V_{\text{Si}} & \rightarrow V_{\text{C}}C_{\text{Si}}V_{\text{C}} & (7) \\
V_{\text{C}} + V_{\text{Si}} & \rightarrow V_{\text{C}}V_{\text{Si}} & (8) \\
V_{\text{C}}V_{\text{Si}} + nV_{\text{C}} & \rightarrow -(V_{\text{C}})_nV_{\text{Si}} & n = 1, 2, 3, 4 & (9) \\
V_{\text{C}}V_{\text{Si}} + V_{\text{Si}} & \rightarrow V_{\text{C}}V_{\text{Si}}CV_{\text{Si}} \rightarrow V_{\text{C}}V_{\text{Si}}V_{\text{C}}C_{\text{Si}} & (10)
\end{align*}
\]

In Refs. [16–18], the intrinsic defects \(V_{3\text{SiC}}, V_{\text{Si}}\) and \(V_{\text{C}}V_{\text{Si}}\) are metastable and the interactions given in (5)–(7) may occur easily if sufficient energy is provided. Meanwhile, reactions (8)–(10) may occur with additional external energy [12,17,19]. The interactions from (5)–(10) ultimately lead to the change of the total concentration of intrinsic defects during the isochronous annealing.

Both ESR and PL results demonstrate that the annealing effect on total defects concentration is different for 10 min and 30 min annealing and for 60 min annealing. The 60 min annealing may cause some silicon atom to escape and leading to more silicon vacancies. This result is similar to the observation reported earlier [20].

4. Conclusion

In this work, we study the annealing effect on defect levels of the 4H–SiC film. The annealing was conducted at various temperatures in the range of 1273–1873 K for 10–60 min. The defect properties were studied by using ESR and PL. From the ESR and PL measurement, we found that the intrinsic defects in unintentionally doped 4H–SiC include carbon vacancy (\(V_{\text{C}}\)) and complex compounds related carbon vacancy. We further found that the total concentration of intrinsic defects increases with the increases of annealing temperature. The defect density reaches its maximum at 1573 K and then decreases with the increasing annealing temperature. For longer annealing duration of 60 min, the silicon atoms released from the SiC film result in the defect generation.

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