Relationship of annealing time and intrinsic defects of unintentionally doped 4H-SiC*

Cheng Ping(程 萍)†, Zhang Yu-Ming(张玉明),
Zhang Yi-Men(张义门), and Guo Hui(郭 辉)

Key Laboratory of Wide Band-Gap Semiconductor Materials and Devices, School of Microelectronics, Xidian University, Xi'an 710071, *China*

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With annealing temperature kept at 1573 K, the effects of annealing time on stability of the intrinsic defects in epitaxial unintentionally doped 4H-SiC prepared by low pressure chemical vapour deposition have been studied by electron spin resonance (ESR) and low temperature photoluminescence. This paper reports the results shown that annealing time has an important effect on the intrinsic defects in unintentionally doped 4H-SiC when annealing temperature kept at 1573 K. When the annealing time is less than 30 min, the intensity of ESR and photoluminescence is increasing with annealing time prolonged, and reaches the maximum when annealing time is 30 min. Then the intensity of ESR and photoluminescence is rapidly decreased with the longer annealing time, and much less than that of as-grown 4H-SiC when annealing time is 60 min, which should be related with the interaction among the intrinsic defects during the annealing process.

Keywords: intrinsic defects, annealing time, low temperature photoluminescence, electron spin resonance
PACC: 7850, 6116N, 7855

1. Introduction

Silicon carbide (SiC) is an attractive wide band-gap semiconductor material for developing high-temperature, high-frequency and high-power electron devices. One of the key issues in the SiC technology is to develop high-purity semi-insulating (HPSI) substrates for high-frequency high-power devices. Undoped HPSI SiC substrates have been developed in recent years by physical vapour transport (PVT)[1,2] and by high-temperature chemical vapour deposition (HTCVD).[3,4] In HPSI SiC materials, the silicon vacancy ($V_{\rm Si}$),[5,6] the carbon vacancy ($V_{\rm C}$),[7−9] and many other defects were observed.[10] These defects may behave as recombination centres or can act as traps for electrons or holes, limiting the lifetime of carrier, affecting the drift mobility, breakdown voltage and so on. It is therefore important to study this technologically relevant and critical issue for designing and processing electronic devices. Both theoretical[11] and experimental[12−14] studies on the thermal stability and nature of intrinsic defects of SiC can be found in the literatures.

It is proved that some defects, such as micropipe, can be effectively prevented in epitaxial growth of semi-insulating SiC by low pressure (LP) chemical vapour deposition (LPCVD). While few literatures reported characters and thermal stability of the intrinsic defects in epitaxial unintentionally doped (UD) SiC prepared by LPCVD, in which the impurity concentration is less than that prepared by PVT and HTCVD, the effect of annealing time on the intrinsic defects has not been reported. We have recently explored the stability of intrinsic defects in UD 4H-SiC prepared by LPCVD with anneal treatment between 1273 K and 1873 K, which shows that 1573 K is a key annealing temperature on the change of concentration of native defects. In present paper, the different annealing time at 1573 K is carried out. The concentration of the samples after each annealing step is detected by electron spin resonance (ESR) and photoluminescence (PL).

2. Experimental details

The samples used in this experiment are epitaxial UD 4H-SiC grown by LPCVD technique. The 4H-SiC crystal substrates were purchased from SiCrystal AG

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†Corresponding author. E-mail: chpzmm@yahoo.com.cn
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company, which are in 50.8 cm size. The isothermal annealing series, in the annealing time range 10 min to 60 min and with a constant annealing temperature of 1573 K, was carried out in a CVD reactor with Ar ambience. After the heat treatment, scanning electron microscope (SEM) measurements were done by JSM-6360. The measurements were performed at 10 K, and a 325 nm wavelength He–Cd laser was used as the excitation light source in the low temperature PL measurements. The ESR measurements were implemented using a JES-FA200 spectrometer operating near 9.0 GHz equipped by a nitrogen gas flow system with temperature control. All the presented ESR data are taken with the external magnetic field B oriented along the crystal c-axis. Optimum data is obtained at 110 K. To analyse the spectra characters, the line width is computed by magnetic distance between apex and vale in ESR spectra, and relative intensity of the intrinsic defects is obtained by formula $\vartheta \propto Y \times (\Delta H_{\rm pp})^2$, where Y is summation of apex value and vale value, and $\Delta H_{\rm pp}$ represents the line width. JSM-6360 equipment was used to obtain figure of the sample's faces.

3. Results and discussion

The SEM is used to investigate the surface morphology of sample. Figure 1 shows the images of the surface morphology after different annealing time treatments, which are obvious that the annealing time has effect on the faces. There are some shorter furrows when annealing time is 30 min. The more annealing time the more furrows and the furrows are parallel each other and larger in size, as shown with arrows in Figs. 1(c) and 1(d).

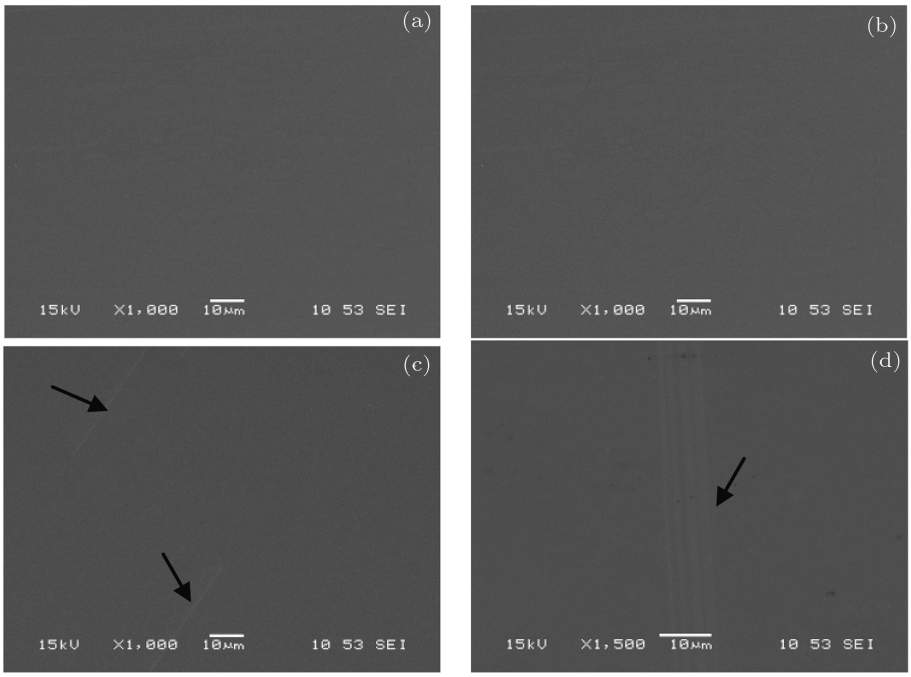


Fig. 1. Surface morphology in different annealing time at 1573 K (a) as-grown, (b) 10 min, (c) 30 min, (d) 60 min.

Meanwhile Table 1 lists the atom percentage of C and Si in SiC for different samples. It can be seen that the ratio of C atom to Si atom in different samples is quite similar with as-grown UD 4H-SiC from x-ray energy spectrum analysis from this table. It can be seen the effect of annealing time on concentration of intrinsic defects in UD 4H-SiC is faint so that the effect caused by surface on the intrinsic defects can be neglected.

Table 1. The ratio of C atom to Si atom in different samples.

	as-grown	1573 K, 5 min	1573 K, 10 min	1573 K, 30 min	1573 K, 60 min
C atom/%	50.97	51.01	52.26	53.44	53.50
Si atom/%	49.03	48.99	47.74	46.56	46.50

One of the ESR results which are annealed at 1573 K is shown in Fig. 2, and all of the rest ESR results are the same as those in Fig. 2. The ESR peak in annealed samples is the same as that of as-grown,[15] which demonstrates that the kinds of native defects are carbon vacancy and its complex compounds too. Figure 3 presents the relationship between the concentration and the annealing time with annealing temperature kept at 1573 K.

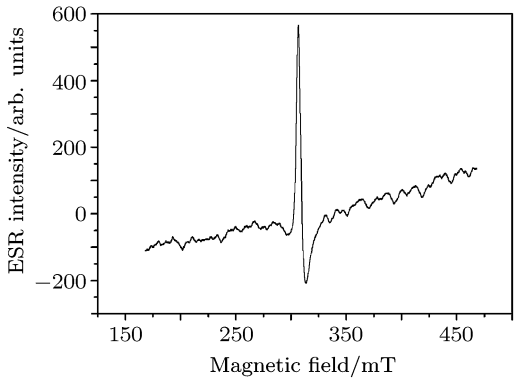


Fig. 2. ESR result of annealed sample at 1573 K under 110 K.

Figure 3 shows that the intrinsic defects obviously vary with annealing time. Firstly the ESR intensity of intrinsic defects is increasing with the annealing time prolonged from 10 min to 30 min, and then rapidly decreasing when the annealing time is increased from 30 min to 60 min. The results are concordant with low temperature PL.

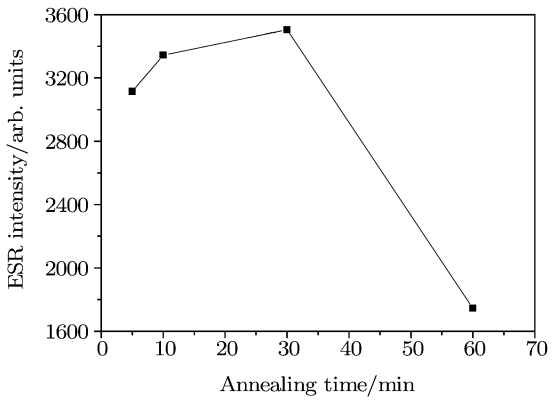


Fig. 3. Dependence of concentration of intrinsic defects and annealing time at 1573 K.

Figure 4 shows the low temperature PL measurement results of samples annealed under different time at 1573 K, and a broadband yellow and green luminescence with PL peak about 526 nm and 580 nm is observed. The intensity of luminescence becomes strong and the luminescence band becomes broad with annealing time increased from 5 min to 30 min, and then the intensity of luminescence is weak when annealing time increased to 60 min, which is attributed to the lattice vibration and lattice scattering. Due to the luminescence caused by the recombination of donor and acceptor, the following equation can be obtained:

$$h\upsilon = E_{\mathrm{g}} - (E_{\mathrm{A}} + E_{\mathrm{D}}) + e^2/\varepsilon_{\mathrm{r}}. \quad (1)$$

Here the wave of luminescence calculated according to Eq. (1) is less than 526 nm obtained from Fig. 4. There are an obvious difference between the calculation and experiments. So an energy level E_x may be located in the bandgap of SiC, and the yellow and green luminescence is caused by the recombination of shallow donor and deep acceptor level E_x. There were different attitudes on the green luminescence, and several explanations were given.[16−18] The PL spectrum at 10 K is asymmetrical because of the asymmetrical distribution of the vacancies of carbon and its extended defects.[19] It indicates that the broadband green luminescence originates from the combination of several independent radiative transitions.

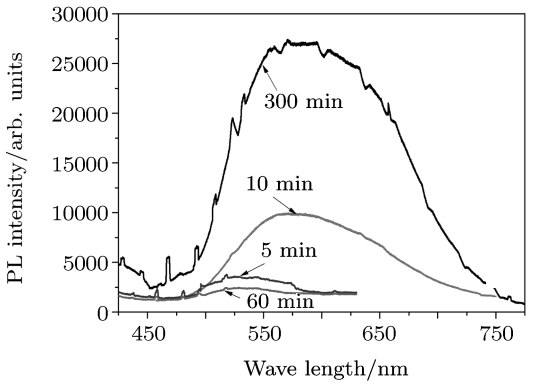


Fig. 4. The PL results of UD 4H-SiC after annealing at 1573 K.

From Fig. 4 we can conclude that the PL intensity of UD 4H-SiC is increased with annealing time prolonged from 5 min to 30 min, and rapidly decreased when annealing time increased from 30 min to 60 min. The PL results are identical to the results of Fig. 3, so we believe that both annealing time and temperatures have an obvious effect on intrinsic defects of UD 4H-SiC. The characters of ESR and PL may be related with the interactions among the intrinsic defects during the annealing process. In the anterior line, the ESR and PL intensity of the intrinsic defects increases with prolonging annealing time, which may be resulted from some of the clustering splitting to small defects.[20] The part of latter may be induced

by the transform and evolvement among intrinsic defects, which can be described as follows:

$$V_{\rm C}V_{\rm Si} \rightarrow V_{\rm C}C_{\rm Si}V_{\rm C}^{[21]}, \quad (2)$$

$$V_{\rm C} + V_{\rm Si} \rightarrow V_{\rm C}V_{\rm Si}^{[22]}, \quad (3)$$

$$V_{\rm C}V_{\rm Si} + nV_{\rm C} \rightarrow (V_{\rm C})_n V_{\rm Si}^{[23]}, \quad n = 1, 2, 3, 4, \quad (4)$$

$$V_{\rm C}V_{\rm Si} + V_{\rm Si} \rightarrow V_{\rm C}V_{\rm Si}CV_{\rm Si} \rightarrow V_{\rm C}V_{\rm Si}V_{\rm C}C_{\rm Si}^{[20]}. \quad (5)$$

As formulas (4) and (5) presented, there are one or more defects combining just one kind of defects, which make the quantity of intrinsic defects rapidly decreasing. This may result in the concentration of intrinsic defects in UD 4H-SiC rapidly decreasing when the annealing time is increased from 30 min to 60 min. Meanwhile by using formulas (2) to (5), the variation of intrinsic defect during annealing treatment induces the PL peak changed from 526 nm to 580 nm.

4. Summary

The dependence of concentration of intrinsic defects in UD 4H-SiC prepared by LPCVD on annealing time are studied by ESR. With annealing temperature kept at 1573 K, the effect of annealing time on concentration of the intrinsic defects in epitaxial UD 4H-SiC can be expressed as follows: when annealing time is less than 30 min, the concentration of the intrinsic defects is increased with the increase of annealing time, and reached its maximum when annealing time is 30 min. However the ESR and PL intensity of the intrinsic defects is rapidly decreased with the increase of annealing time. When annealing time is 60 min, the ESR and PL intensity of intrinsic defects is much less than that of as-grown 4H-SiC.

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