Properties of carbon-doped GaN using isobutane as a dopant

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Abstract. Carbon doping is an effective method to obtain semi-insulating GaN buffer, which is a necessity to prevent current leakage, in the high-electron-mobility-transistor device structure. The properties of intentionally carbon-doped GaN using isobutane gas as a dopant has been studied in detail. The carbon incorporation efficiency has been measured by secondary ion mass spectrometry. It is found that the carbon concentration could be directly controlled by the flow rate of isobutane precursor. The surface morphology of carbon-doped gallium nitride epitaxial layers has been investigated by optical microscopy and atomic force microscopy. The growth mode of GaN layers changes from step-flow to island growth, when the incorporated carbon concentration is higher than $1\times10^{19}\text{ cm}^{-3}$. In order to evaluate the structural quality of intentionally carbon-doped GaN, the full-width-at-half-maximum values are extracted from the rocking curves in six different reflections measured by high resolution X-ray diffraction. Raman spectroscopy is utilized to evaluate the physical properties of the carbon-doped GaN epitaxial layer.

1. Introduction

Wide band gap semiconductor gallium nitride (GaN) is considered to be a very promising material in the applications of optoelectronics [1] and high-frequency and high-power devices [2] due to its remarkable properties.

In the GaN-based high-electron-mobility-transistors (HEMT) structure, a semi-insulating buffer is necessary in order to decrease leakage current [3]. Nowadays, there are two common ways to obtain the semi-insulating GaN buffer layers, i.e., iron doping and carbon doping [4-7]. The drawback of iron doping is the memory effect during the growth. Iron will exist on the surface of GaN epitaxial layer for a while, even if the iron precursor is shut down [8]. In this point of view, the growth of semi-insulating GaN by carbon doping is preferred.

For the chemical vapour deposition (CVD) technique, the conventional way of incorporating carbon into GaN film is using the carbon atoms from the gallium precursor [9]. By varying the growth condition, the carbon doping rate could be controlled. However, this kind of method has difficulties in maintaining growth uniformity and reproducibility when process temperature and pressure are changed. Therefore, a new way of carbon doping is emerged and studied. In this new method, an optimal unintentionally doped GaN growth condition is selected first. At this condition, the concentration of carbon source from the gallium precursor is suppressed under the detection limit of SIMS. Then a carbon gas precursor is put into the reactor to dope GaN. The carbon incorporation efficiency could be easily managed by tuning the flow of the carbon precursor. Few studies have been made in this field. Sweden researchers have
discussed the device performance of a HEMT structure, which buffer layer was doped by the propane gas [10].

In this paper, a detailed study of intentionally carbon-doped GaN by isobutane (i-C4H10) precursor is reported. Morphological, structural and physical properties of the carbon-doped GaN epitaxial layers are investigated.

2. Experimental details
In this section, detailed information of sample preparation and characterization techniques is described.

2.1. Sample preparation
All the experiments were carried out in a metal-organic CVD (MOCVD) reactor with substrate rotation. The GaN epitaxial layer was grown on the 4H-SiC on-axis substrates with a 100 nm thick aluminum nitride (AlN) interlayer. The process pressure used in the present study was kept at 5000 Pa. Trimethylgallium (TMGa), trimethylaluminum (TMAI), and ammonia (NH3) were used as precursors for Ga, Al, and N, respectively. A mixture of hydrogen (H2) and nitrogen (N2) was used as carrier gas. The growth temperature of GaN layers was fixed at 1060 °C. The growth rate of all the GaN samples is around 0.8 m/h at this temperature. Isobutane gas is a gaseous precursor, which was chosen as a carbon dopant during the growth of GaN layers. The V/III ratio used in this study was kept at 1200.

2.2. Characterization technique
Secondary ion mass spectrometry (SIMS) measurement was performed in order to detect the impurity concentrations. The detect limit for carbon (C) impurity is around $1 \times 10^{16}$ cm$^{-3}$. Optical microscopy and atomic force microscopy (AFM) were utilized to examine the morphology and surface roughness of the grown epitaxial layers. Root-mean-square (RMS) value is used in this study to quantify the surface roughness in AFM measurements. High resolution X-ray diffraction (HRXRD) equipped with a triple-axis configuration was used to measure the rocking curves. Raman spectroscopy was done at room temperature with excitation laser wavelength of 532 nm.

3. Results and discussion
In this section, the experimental results and discussion regarding carbon incorporation efficiency, surface morphology, crystalline quality as well as Raman spectroscopy are presented.

3.1. Carbon incorporation efficiency

![Figure 1](image.png)

Figure 1 Carbon concentration versus depth of an isobutane-doped GaN sample measured by SIMS.

The optimal growth condition to obtain a high quality unintentionally doped GaN epitaxial layer in our reactor is at a temperature of 1060 °C with a reduced pressure of 5000 Pa. Carbon concentration of undoped GaN layers is under the SIMS detection limit at this temperature. Therefore, i-C4H10 gas
precursor is added at the abovementioned process condition when growing carbon-doped GaN layers. In order to study the relation between carbon incorporation efficiency and flow rate, a sample with several GaN layers were grown. Firstly, a 0.6 µm undoped GaN epitaxial layer was grown, followed by six carbon-doped layers with different flow rates of i-C₄H₁₀ precursor. Finally, the carbon gas precursor was shut down and a thin undoped GaN was grown. Figure 1 shows the SIMS measurement done in the center of this sample. There’s a variation at the depth of 0.6 µm in the figure due to the carbon precursor was added into the reactor at this point. The used flow rate of i-C₄H₁₀ gas is given in the figure. When the flow rate of i-C₄H₁₀ precursor is higher than 5 ml/min, the carbon concentration profile is very stable.

3.2. Surface morphology
In order to study the surface morphology, a few 1 µm thick GaN samples intentionally doped by i-C₄H₁₀ precursor with only one concentration were deposited at 1060 °C. Figure 2 is the AFM images performed on the surface of these samples. An unintentionally doped GaN sample is shown in figure 2(a) for comparison. Its surface roughness is 0.178 nm over a 3×3 µm² area. The surface roughness of GaN layer increases to 0.212 nm, when increasing the flow rate of i-C₄H₁₀ precursor to 10 ml/min, shown in figure 2(b). Figure 2(c) is the AFM image of GaN epitaxial layer doped by 25 ml/min i-C₄H₁₀ gas. Its surface becomes rougher but still remains to step-flow growth mode. Its surface roughness is 0.272 nm over a 3×3 µm² area and 0.765 nm over a 10×10 µm². However, when further increase the flow rate of carbon precursor to 50 ml/min, the GaN epitaxial layer change to island growth, as shown in figure 2(d).

Figure 2  AFM images of carbon-doped GaN epitaxial layers with i-C₄H₁₀ precursor flow rate of (a) 0 ml/min, (b) 10 ml/min, (c) 25 ml/min, and (d) 50 ml/min, respectively.
Figure 3 Optical microscope images of (a) an unintentionally doped GaN epitaxial layer, and (b) a carbon-doped GaN layer using 50 ml/min i-C₄H₁₀ gas.

Figure 3(a) is the typical optical microscope image for unintentionally doped samples. Its surface is very smooth, which could hardly see any feature. Figure 3(b) is the optical image of the same sample presented in figure 2(d). The surface of this sample becomes rougher and has decorative pattern. The information of i-C₄H₁₀ flow rate, C concentration and related surface roughness measured in the area of 3×3 μm² are summarized in table 1. When the carbon precursor are 5 ml/min, 10 ml/min, 25 ml/min and 50 ml/min, the incorporated carbon concentration could reach to the lever of 3.5×10¹⁷ cm⁻³, 1×10¹⁸ cm⁻³, 4.5×10¹⁸ cm⁻³ and 1.3×10¹⁹ cm⁻³, respectively. Meanwhile, the surface of the GaN epitaxial layers doped by i-C₄H₁₀ gas becomes rougher as the incorporated carbon concentration increases.

Table 1 Carbon precursor flow rate, carbon concentration and corresponding surface roughness in an area of 3×3 μm².

| i-C₄H₁₀ flow rate (ml/min) | 0    | 5    | 10   | 25   | 50   |
|---------------------------|------|------|------|------|------|
| C concentration (cm⁻³)    | undoped | 3.5E17 | 1E18 | 4.5E18 | 1.3E19 |
| RMS (nm)                  | 0.178 | 0.2  | 0.212 | 0.272 | 0.388 |

3.3. Structural quality

HRXRD was measured on the centre part of the intentionally carbon-doped GaN samples with different i-C₄H₁₀ gas flow. In order to evaluate the structural quality, the full-width-at-half-maximum (FWHM) values were extracted from the rocking curves and listed in table 2. The (002), (004) and (006) reflections could reveal the screw type of threading dislocations, while the (101), (102), (103), (104) and (302) reflections are related to the edge type of threading dislocations. Generally, the carbon doping will deteriorate the structural quality of GaN epitaxial layers. The FWHM values increase as the flow rate of i-C₄H₁₀ gas goes up from 0 ml/min to 25 ml/min. However, when further increase the carbon precursor flow rate, the FWHM values decrease for all the reflections. This may because the growth mode has been changed from step-flow growth to island growth as observed in the AFM pictures.

Table 2 FWHM values extracted from XRD rocking curves with different reflections for i-C₄H₁₀ doped GaN.

| reflection | (002) | (004) | (006) | (101) | (102) | (103) | (104) | (302) |
|------------|-------|-------|-------|-------|-------|-------|-------|-------|
| undoped    | 223   | 211   | 210   | 297   | 69    | 237   | 222   | 298   |
| 5 ml/min   | 259   | 235   | 234   | 362   | 313   | 288   | 273   | 362   |
| 25 ml/min  | 300   | 277   | 270   | 393   | 349   | 325   | 302   | 385   |
| 50 ml/min  | 171   | 161   | 155   | 380   | 313   | 270   | 237   | 373   |

3.4. Raman spectroscopy

Raman measurement has been carried out at room temperature at the centre part of an i-C₄H₁₀ doped GaN sample with a carbon concentration of 1×10¹⁸ cm⁻³, shown in the figure 4. The GaN E₂ (high) peak positioned at 567.5 cm⁻¹ is quite strong. The relatively weak GaN E₂ (low) and A₁ (LO) phonon modes
are at 143.5 cm$^{-1}$ and 733.6 cm$^{-1}$, respectively. The weak peaks at 266 cm$^{-1}$, 610 cm$^{-1}$, 799 cm$^{-1}$ and strong peaks at 776 cm$^{-1}$ are all related to the SiC substrate. There is also a very weak E2 (high) peak located at 657 cm$^{-1}$, which is contributed from the 100 nm thick AlN interlayer.

Figure 4 Raman spectrum of the i-C$_4$H$_{10}$ doped GaN sample with a C concentration of $1\times10^{18}$ cm$^{-3}$.

4. Conclusions
In this paper, the morphological, structural and physical properties of intentionally carbon-doped GaN epitaxial layers by i-C$_4$H$_{10}$ precursor were studied. The carbon precursor was added into the reactor at the optimized growth condition for undoped GaN. The incorporated carbon concentration could be directly controlled by the flow rate of i-C$_4$H$_{10}$ gas. The carbon incorporation efficiency was studied by SIMS measurements. The growth mode of i-C$_4$H$_{10}$ doped GaN layers, observed from AFM images, changed from step-flow growth to island growth when the doped carbon concentration was higher than $1\times10^{19}$ cm$^{-3}$. The structure quality of GaN layers with different carbon doping levels was studied by HRXRD. In general, the structure quality of the intentionally carbon-doped GaN film would decline with the increased flow rate of i-C$_4$H$_{10}$ precursor. Nevertheless, the crystal quality got better at the carbon concentration of $1\times10^{19}$ cm$^{-3}$, which could be explained by the alternation of growth mode. Raman measurement was performed on a GaN sample with a carbon concentration of $1\times10^{18}$ cm$^{-3}$ in order to study its physical property.

Acknowledgments
This work was financially supported by National Natural Science Foundation of China (Grant No. 61804044) and Natural Science Foundation of Hebei Province (Grant No. F2018202234).

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