Preparation of 50mm 3C-SiC/Si(111) as Substrates Suited for IV-Nitrides

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Abstract: 50mm SiC films with high electrical uniformity are grown on Si(111) by a newly developed vertical low-pressure chemical vapor deposition (LPCVD) reactor. Both in-situ n- and p-type doping of 3C-SiC are achieved by intentional introduction of ammonia and boron into the precursor gases. The dependence of growth rate and surface morphology on the C/Si ratio and optimized growth conditions is obtained. The best electrical uniformity of 50mm 3C-SiC films obtained by non-contact sheet resistance measurement is ±2.58%. GaN films are grown atop the as-grown 3C-SiC/Si(111) layers using molecular beam epitaxy (MBE). The data of both X-ray diffraction and low temperature photoluminescence of GaN/3C-SiC/Si(111) show that 3C-SiC is an appropriate substrate or buffer layer for the growth of III-nitrides on Si substrates with no cracks.

Key words: 3C-SiC/Si (111); LPCVD; GaN
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1 Introduction

It has been shown that III-nitrides are important materials for optoelectronic devices, such as blue and ultraviolet (UV) light emitting diodes (LEDs), laser diodes (LDs), and high temperature/high frequency transistors [1, 2]. Much effort has been made to the growth of III-nitrides on sapphire substrates because of their commercial availability and excellent surface preparation [3]. However, the large lattice mismatch and the difference in thermal expansion coefficients of GaN and sapphire cause large stress in GaN films during growth and a threading dislocation (TD) density as high as $10^{10}$ cm$^{-2}$ [4]. On the other hand, difficulties arise in cleavage and formation of back contacts in this material system. Silicon carbide (SiC) is one of the most suitable materials for the substrate of III-nitride semiconductors, since lattice mismatch between SiC and III-nitrides in perpendicular direction to [0001] is much smaller (3%) than that between sapphire and III-nitrides [5]. Further, SiC has a higher thermal conductivity (4.9 W/cm · K) suited for efficient heat radiation. Among over 250 different SiC polytypes, only 3C-SiC with cubic crystal structure can be grown on conducting Si substrates [6, 7], which has the potential to solve the difficulties mentioned above. In this paper, SiC films have been grown on Si(111) for its applications to

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the substrates of III-nitride semiconductors by a newly developed vertical LPCVD. The growth rate, surface morphology, interface property between SiC and Si(111), both in-situ n- and p-type doping as well as the electrical uniformity have been investigated systematically. The growth of GaN films on as-grown 3C-SiC/Si(111) has been performed using MBE method. The data of both X-ray diffraction and low temperature photoluminescence show that 3C-SiC is an appropriate substrate or buffer layer for the growth of III-nitrides on Si substrates.

2 Experiment

A vertical LPCVD quartz reaction chamber heated inductively has been developed and employed to get 50nm 3C-SiC/Si with high electrical and thickness uniformity. As shown in Fig. 1, it has two water-cooled stainless steel flanges at the ends of quartz tube. A high-purity SiC-coated graphite susceptor with a solenoid coil RF heating provides a temperature up to 1400°C. The temperature measured by a pyrometer through the quartz side is the record of the susceptor temperature. The precursor gases can be introduced through a flat plate with a number of small holes.

![Fig. 1 Schematic diagram of the vertical LPCVD reaction chamber](image)

The heteroepitaxial growth of 3C-SiC on 50nm Si (111) substrates with resistivity of 10-12 Ω·cm has been performed by LPCVD at a pressure of around 1.3 × 10⁻³Pa. Prior to the growth, the Si substrates are subjected to a pre-growth etching in hydrogen with a flow rate of 3000sccm at about 1100°C for 10min. The diagram of growth process is shown in Fig. 2. SiH₄, C₂H₆, and Pd-cell purified H₂ are used as precursor gases. The typical flow rates of SiH₄, C₂H₆, and H₂ are 0.5-5sccm, 0.25-1sccm, and 3000sccm, respectively. For intentional doping of 3C-SiC, NH₃ (0-0.16sccm), and B₂H₆ (0-3.5sccm) are used as the n- and p-type dopants, respectively.

![Fig. 2 Growth process diagram of 3C-SiC grown on Si(111) substrates](image)

The GaN samples are grown on as-grown 3C-SiC/Si(111) using a homemade MBE system. Prior to initiation of GaN growth, an AlN buffer layer (about 100nm thick) is grown at 500-600°C. This is followed by the growth of GaN epilayers. The thickness of the unintentionally doped GaN epilayers is about 700nm.

The surface morphology of both 3C-SiC and GaN films are investigated using Nomarski optical microscope. The electrical properties are characterized using Hall effect measurement and Napson NC-40 non-contact sheet resistance measurement. The growth rate of 3C-SiC films are determined by observing the cross sectional interface through Nomarski optical microscope. The N doping is characterized using secondary ion mass spectroscopy (SIMS). Optical properties of GaN samples are investigated by low temperature (ranging from 10 to 270K) photoluminescence (PL) technique.
3 Results and discussion

A critical requirement of epitaxy is to produce specular layers. It is shown that the C/Si ratio (atomic ratio of C and Si in supplied source gases) in SiC growth is an important factor to get a mirror-like surface, especially, for the growth of III-V nitrides on as-grown 3C-SiC surface. The surface morphology of 3C-SiC has been investigated with respect to the C/Si ratio by keeping the SiH₄ gas flow rate a constant, and to the SiH₄ gas flow rate maintaining the C/Si ratio a constant at 6. The mirror-like surfaces without any features are obtained for C/Si ratio in the range from 3 to 20. However, rough surfaces with high-density growth pits are observed for C/Si ratio of less than 3. The moderate value of C/Si ratio to get a mirror-like surface is around 6, which is greater than that reported in Ref. [1]. The reason is mainly that the C₂H₆ has a lower cracking temperature, while C₂H₂ used in Ref. [1] has a higher one. At the optimized growth temperature of 3C-SiC, higher C₂H₂ gas flow rate is needed to stoichiometric 3C-SiC film.

Figures 3(a) and (b) show the dependence of growth rate on C/Si ratio and SiH₄ gas flow rate, respectively. Figure 3(a) shows that the growth rate maintained approximately constant with increasing the C/Si ratio from 2 to 20 while keeping SiH₄ flow rate constant as 0.5 sccm. Under the optimized condition, the growth rate of 3C-SiC is nearly proportional to the SiH₄ flow rate with a constant C/Si ratio of 6. This result indicates that the growth rate is limited by SiH₄ flow rate. The optimized growth rate ranges from 0.8 to 3μm/h.

Fig. 3 Growth rate of 3C-SiC on Si as a function of (a) C/Si ratio with a constant SiH₄ flow rate of 0.5 sccm and (b) SiH₄ flow rate under a constant C/Si ratio of 6

Table 1 shows the sheet resistance distribution of four doped and undoped 3C-SiC/Si samples. As shown in the right of Table 1, number 1, 2, 3, 4, and 5 represent the different position on the 50mm 3C-SiC/Si wafer. No. 1 is the center. Other four numbers represent four different positions with each 15mm away from the center. The 1.0μm thick undoped, N and B doped 3C-SiC layers have a sheet resistance variation of less than ±5%. The best uniformity achieved is about ±2.48%. But the major challenge is to grow 3C-SiC with good uniformity in both thickness and doping. Because the developed LPCVD system is single wafer reactor, the run-to-run reproducibility is still to be investigated.

Table 1 Sheet resistance distribution of four 3C-SiC/Si samples obtained using Napon NC-40 non-contact sheet resistance measurement system (unit: Ω/sq)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Average</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. N-doped</td>
<td>212.9</td>
<td>218</td>
<td>216.6</td>
<td>224.1</td>
<td>218.5</td>
<td>218.0</td>
<td>±2.48</td>
</tr>
<tr>
<td>2. B-doped</td>
<td>118</td>
<td>117.5</td>
<td>109.6</td>
<td>105.8</td>
<td>110.9</td>
<td>112.4</td>
<td>±5.4</td>
</tr>
<tr>
<td>3. Undoped</td>
<td>151.4</td>
<td>154.6</td>
<td>154.8</td>
<td>159.3</td>
<td>166.6</td>
<td>157.3</td>
<td>±4.83</td>
</tr>
<tr>
<td>4. Undoped</td>
<td>177.5</td>
<td>168.5</td>
<td>178.7</td>
<td>182.3</td>
<td>182.0</td>
<td>177.8</td>
<td>±3.88</td>
</tr>
</tbody>
</table>
Figure 4 shows (a) the nitrogen concentration depth profile and (b) the schematic diagram of NH₃ flow rate with the growth time. The inset shows the atomic concentration depth profile of Si, C, and N. During the growth, the NH₃ flow rate was increased from 0.01 sccm to the maximum value of 0.16 sccm and then decreased to 0.01 sccm with each step grown for 5 min except 10 min for the highest NH₃ flow rate of 0.16 sccm, while the SiH₄ and CH₄ flow rates were maintained at 0.5 sccm and 3.5 sccm, respectively. In the first and the last 5 min, no NH₃ gas is added to the precursor gases. The depth profile of the incorporated nitrogen concentration is asymmetric and not forming a staircase as the designed NH₃ flow rate sequence as shown in Fig. 4(b). The nitrogen concentration in the left side is higher than that in the right side. This can be explained by a memory effect or re-evaporation of N from the heated susceptor and the remaining NH₃ in the precursor gases. For the first and the last two undoped layers, the difference of nitrogen concentration is also remarkable.

![Fig. 4](image)

**Fig. 4** SIMS depth profile of a nitrogen doped 3C-SiC epilayer grown on Si(111) with different NH₃ flow rate. The C/Si ratio and the SiH₄ flow rate were maintained at 7 and 1 sccm during the growth. (b) Schematic diagram of flow rate of NH₃ with the growing time. The inset shows the atomic concentration depth profile of Si, C, and N.

In situ B-doping is also performed using B:H₆ as the p-type dopant. Hall effect measurement is employed to characterize the electrical properties. 50 nm n-type Si wafers with a resistivity of 10–12Ω·cm are used as substrates. It is shown that with decreasing B:H₆ flow rate, hole mobility increases from around 58 cm²/V·s to 180 cm²/V·s, while the hole concentration decreases from 10¹⁹ cm⁻³ to 8–9 × 10¹⁸ cm⁻³. The highest hole concentration is about 10¹⁹ cm⁻³. For the undoped p-type 3C-SiC, the highest hole mobility is close to 200 cm²/V·s at room temperature with a hole concentration of approximately 9.2 × 10¹⁸ cm⁻³.

The GaN films have been grown on as-grown 3C-SiC/Si(111). The cracks are often observed on GaN grown on bare Si substrates. However, no cracks were observed on 3C-SiC because of lattice constant of GaN being closed to that of 3C-SiC. Figure 5 shows a typical X-ray diffraction pattern of GaN/3C-SiC/Si(111). Only GaN(0002) peak at 34.6° (FWHM = 0.18°) and its secondary diffraction (0004) peak at 73.1° are observed. No peaks corresponding to other planes of GaN are seen. This result indicates that the GaN films grown on 3C-SiC(111) substrates are epitaxial and crystalline. The rocking curve widths of GaN samples on three different 3C-SiC/Si substrates with 3C-SiC thickness of 200, 500, and 1000 nm are 0.57°, 1.37°, and 1.6°, respectively. These data are close to those reported in Ref. [11].

![Fig. 5](image)

**Fig. 5** X-ray diffraction of a GaN film grown on as-grown 3C-SiC/Si(111) substrate by MBE. The film thickness is about 750 nm (GaN(0002) FWHM = 0.18°). The inset shows the rocking curve (FWHM = 0.57°).
Figure 6 shows the low temperature (10K) PL spectra of GaN epilayers grown on (a) 3C-SiC/Si(111) and (b) Si(111) for comparison. The spectra for all GaN epilayers on both substrates exhibit near band-edge luminescence and yellow band luminescence that is commonly observed in GaN photoluminescence spectra\textsuperscript{[12]}. For the near-band-edge emission, the 3.49 eV peak can be attributed to the donor bound exciton emission\textsuperscript{[13]}. There are also DAP (donor-acceptor pair) at 3.29 eV, LO\textsubscript{1} (phonon replica related peak) at 3.23 eV and LO\textsubscript{2} peaks at 3.12 eV with higher intensity than the donor bound exciton emission. For the yellow band emission, the peak energy on 3C-SiC (centered at 2.25 eV) is smaller than that on Si (centered at 2.4 eV), while the relative intensity on 3C-SiC is higher than that on Si. This can be explained by the contribution of 3C-SiC photoluminescence at 2.29 eV at low temperature.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6.png}
\caption{Low temperature (10K) PL spectra of GaN epilayers grown on 3C-SiC/Si(111) (a) and Si(111) (b).}
\end{figure}

4 Conclusion

50mm SiC films with high electrical uniformity can be grown reproducibly on Si(111) for their applications to the substrates of III–V nitride semiconductors by a newly developed vertical low-pressure chemical vapor deposition (LPCVD) reactor. Both in situ n- and p-type doping of 3C-SiC are achieved by intentional introduction of ammonia and boron into the precursor gases. The dependence of growth rate and surface morphology on the C/Si ratio and optimized growth conditions are obtained. The best electrical uniformity of 50mm 3C-SiC films obtained by non-contact sheet resistance measurement is ± 2.48%. GaN films have been grown atop the as-grown 3C-SiC/Si(111) layers using molecular beam epitaxy. The data of both X-ray diffraction and low temperature photoluminescence of GaN/3C-SiC/Si(111) show that 3C-SiC is an appropriate substrate or a buffer layer for the growth of III-nitrides on Si substrates with no cracks.

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可用于IV族氮化物生长的50mm 3C-SiC/Si(111)衬底的制备

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摘要：利用新研制出的垂直式低压CVD（LPCVD）SiC生长系统，获得了高质量的50mm 3C-SiC/Si（111）衬底材料。系统研究了3C-SiC的n型和p型掺杂技术，获得了生长速率和表面形貌对反应气体中SiH4流量和C/Si原子比率的依赖关系。利用Hall测试技术、非接触式方块电阻测试方法和SIMS，分别研究了3C-SiC的电学特性和均匀性和故意控制掺杂的N浓度横向分布。利用MBE方法，在50mm 3C-SiC/Si（111）衬底上进行了GaN的外延生长，并研究了GaN材料的表面、结构和光学特性。结果表明3C-SiC是一种适合于高质量无裂纹GaN外延生长的衬底或缓冲材料。

关键词：3C-SiC/Si(111)衬底；LPCVD；GaN

PACC: 6170T；7360P；7855

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