Homoepitaxial Growth and Characterization of 4H-SiC Epilayers by Low-Pressure Hot-Wall Chemical Vapor Deposition

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Abstract: Horizontal air-cooled low-pressure hot-wall CVD (LP-HW CVD) system is developed to get highly qualitative 4H-SiC epilayers. Homoepitaxial growth of 4H-SiC on off-oriented Si-face (0001) 4H-SiC substrates is performed at 1500°C with a pressure of 1.3×10³ Pa by using the step-controlled epitaxy. The growth rate is controlled to be about 1.0 μm/h. The surface morphologies and structural and optical properties of 4H-SiC epilayers are characterized with Nomarski optical microscopy, atomic force microscopy (AFM), X-ray diffraction, Raman scattering, and low temperature photoluminescence (LTPL). N-type 4H-SiC epilayers are obtained by in-situ doping of NH₃ with the flow rate ranging from 0.1 to 3 sccm. SiC p-n junctions are obtained on these epilayers and their electrical and optical characteristics are presented. The obtained p-n junction diodes can be operated at the temperature up to 400°C, which provides a potential for high-temperature applications.

Key words: 4H-SiC; HW CVD; homoepitaxial growth; off-oriented substrates

1 Introduction

Silicon carbide (SiC) takes the form of many polytypes, which are classified by the stacking sequence and cycle along the c-axis direction. 4H-, 6H-, and 3C-SiC are three interesting polytypes. In particular, most attentions are paid on 4H-SiC polytype. The unique thermal and electronic properties of SiC make it an attractive semiconductor for electronic devices designed to operate in extreme conditions, such as high voltage, high temperature, high frequency, and high radiation. It is shown that homoepitaxial growth has been key technology to fabricate SiC devices. The growth on off-oriented α-SiC (0001) substrates by chemical vapor deposition (CVD) with step-controlled epitaxy utilized at around 1500°C is standard technique to produce device-quality epilayers. For power devices with high breakdown voltage, high quality and thick epitaxial layers are needed. To fulfill these requirements, hot-wall CVD systems, both horizontal and vertical, have been proposed and developed and SiH₄ + C₃H₈+ H₂ gas system has been used mainly. It is desired to grow epitaxial layer with other carbon material easily dissociated at higher temperature. Heteroepitaxial growth of SiC on Si using C₃H₈ as carbon source material has been already reported in previous works.

In this paper, we report on the developed horizontal hot-wall CVD reactor and homoepitaxial growth of 4H-SiC on off-oriented 4H-SiC(0001) Si planes using SiH₄ + C₃H₈ + H₂ system. The surface morphologies, structural, and optical properties of...
4H-SiC epilayers are characterized with Nomarski optical microscope, SEM, AFM, X-ray diffraction, Raman scattering, and low temperature PL measurements. Preliminary results of the 4H-SiC p-n junction diodes are also presented.

2 Experiment

An air-cooled horizontal quartz reactor heated inductively was designed and built in the authors' group and was employed for the homoepitaxial growth of 4H-SiC. The schematic drawing of the chamber is shown in Fig. 1(a). A high-purity SiC-coated graphite susceptor with a solenoid coil RF heating provides a temperature up to 1600°C. The susceptor is a round high-purity graphite bar with a rectangular-shaped hole in the center. The 4H-SiC substrates were placed on the inside bottom surface of the hole as shown in Fig. 1(a). The graphite foam wrapped around the susceptor was used as the thermal insulation and to reduce the thermal losses. The susceptor temperature is measured by a pyrometer through the glass window in the center of the downstream flange.

The precursor gases of SiH4 and C2H2 and carrier gas of H2 are introduced through a flat, water-cooled stainless steel flange via a number of small holes. A palladium cell is used to supply high-purity hydrogen to the growth process. The substrates used in this study were commercially available n- and p-type 4H-SiC with Si-terminated (0001) faces 8° off-axis toward 41-20 direction. The typical flow rates of SiH4 and H2 were 0.5 and 3000sccm. The C/Si ratio in the gas phase ranged from 1 to 6. The growth temperature and pressure were typically 1500°C and 1.3×105Pa, respectively. Ammonia (NH3) was employed for intentional n-type doping. Prior to deposition, the substrates were etched at 1500°C for 30 min in H2. Figure 1(b) shows the growth process.

The surface morphology was characterized by Nomarski differential interference microscopy and AFM, X-ray diffraction, Raman, and low temperature PL were performed to determine the structural and optical properties. Electroluminescence measurements were carried out with Ti/Au ohmic contacts to determine characteristics of the 4H-SiC p-n junction diodes.

3 Results and discussion

The as-received polished wafers are specular but exhibited high-density random scratches as shown in Fig. 2(a). A flat 4H-SiC substrate surface is needed for the subsequent epitaxial growth. The surface morphology of 4H-SiC substrates is studied in three different ways: high temperature annealing in H2, oxidation and subsequent HF etching, and high temperature annealing in H2 and C2H2. Figure 2(b) shows the AFM image of the 4H-SiC substrate surface exposed to H2 at 1350°C for 3h in a 3000sccm H2 environment. The RMS with the image size of 2μm × 2μm is 0.220nm, while that by oxidation/etching and annealing in H2 and C2H2 are 0.784 and 1.592nm, respectively. It is well known that the height of a single double-layer of Si and C atoms is 0.25nm that is stacked in the c-direction to form the various SiC polytypes. This result
would lead us concluding that an atomically flat and damage free SiC surface, ideal for epitaxial growth, can be obtained by H₂ annealing at 1350°C.

Most time has been spent on optimizing the morphology of 4H-SiC epitaxial layers, which is critical for the device fabrication. It has been shown that as the growth temperature decreases, the range of growth condition to obtain a smooth surface becomes narrower. To obtain optimized growth condition, the dependence of the surface morphology of 4H-SiC epilayers on the C/Si ratio was investigated systematically. Figure 3 shows Nomarski micrographs of 4H-SiC epilayers grown at 1500°C with C/Si ratio of (a) 6.0, (b) 3.0, (c) 2.0, and (d) 1.0. The SiH₄ flow rate is 0.5sccm and kept at constant in the whole growth process and four different runs. The best RMS obtained by AFM is 0.592nm. It can be seen from Fig. 4 that the epilayer surface becomes smooth as the C/Si ratio decreases from 6.0 to 1.0. The surface becomes specular when the C/Si is around 1-2.

Typical surface defects, namely, round pits, wavy steps, grooves, and triangular defects, are observed on 4H-SiC epilayers grown at C/Si ratio of 2.0 and 1.0 as shown in Fig. 4. It is shown that these surface defects are induced by the structural defects penetrating from the substrates. But the surface defect density, especially the round pits, for our samples grown under optimized conditions is much less than that in Ref. [10]. To eliminate this type of defects, the growth conditions (C/Si ratio and SiH₄ flow rate) and pregrowth substrate surface modifications have to be optimized further.
With decreasing C/Si ratio further (less than 1) or increasing the SiH₄ flow rate, Si-droplets or those originated from Si-droplets (not shown here) have been observed. A too high SiH₄ concentration in the gas phase can lead to the condensation of Si-droplets on the wafer, which then evaporate leaving traces on the epilayers. We have observed that at moderate C/Si ratio of around 2.0 and SiH₄ flow rate of 0.5 sccm, the Si-droplets can be eliminated completely. Chemical analysis of molten KOH at 500°C is used for etching studies. The hexagonal, shell-like, rounded etch pits as well as etch pits lines are found to be randomly distributed over the surface. It is shown that the epilayer inherits both the structure and the defects density of the substrate in the growth of SiC on off substrates.

The crystallinity of the as-grown 4H-SiC epilayer is evaluated using Rigaku D/max-2400 X-ray diffractometer. Figure 5 shows a typical XRD wide scan between 20°–90° for an epilayer. A strong peak at 35.45°, with a full width at half maximum of 0.14°, is due to diffraction from the (0004) planes of 4H-SiC. No other feature is evident besides the (0004) patterns, thus indicating good 4H-SiC crystalline structure. High-resolution X-ray diffraction measurements showed that the full width at half maximum (FWHM) of the 4H-SiC (0004) peak is approximately 10arcsec, which is comparable to that in Ref. [12].

Raman scattering spectroscopy is a powerful tool to characterize SiC non-destructively. Figure 6 shows the Raman spectrum for a typical 10μm-thick 4H-SiC epilayer obtained at room temperature in the back-scattering configuration. Typical Raman peaks of 4H-SiC polytype at 206.5 (TA, E₂g), 777.8 (TO, E₂g), 797.8 (TO, E₁), and 966.3 (LO, A₁) cm⁻¹ corresponding to the reasonably well-ordered 4H-SiC (within 0.5 cm⁻¹) are observed as described in Ref. [13]. This result confirms that the 4H-SiC epilayers can be grown homoepitaxially on the off-orientation 4H-type substrates with high crystal quality.

![Fig. 6 Typical Raman spectrum of the 4H-SiC epilayer](image)

Low temperature PL is also employed to characterize the epitaxial layers. Figure 7 shows the photoluminescence spectrum at 15K and the dependence of PL spectral change on temperature ranging from 15 to 100K. As shown in Fig. 7(a), the spectrum is composed of zero-phonon lines of A₀, Bₐ, and C₀ and their phonon replicas in energy region of 2.8–3.2 eV. Including all other polytypes, the energies of four phonons in SiC are $E_{TA} \approx 28$, $E_{LA} \approx 68$, $E_{TO} \approx 95$, $E_{LO} \approx 107$ and 118 meV, respectively. Zero-phonon line of A₀ attributes to the recombination of a free electron with a hole trapped at Al acceptor in this case. 4H-SiC has one cubic and one hexagonal site in its crystal structure. The energy levels of N donors on these two sites have a significant difference, which brings about two series of luminescence in donor-acceptor recombinat-

![Fig. 5 Typical X-ray diffraction pattern for a 10μm thick 4H-SiC epilayer with FWHM of 0.14°](image)
tion, i.e., B and C series. It is obtained that the energy difference between B₀ and C₀ peaks in Fig. 7 is 60 meV, which is close to the difference in ionization energies (58 meV) of N donors at cubic sites (124 meV) and hexagonal sites (66 meV). The A, B, and C series peaks kept unchanged, while the intensity decreases with increasing temperature from 15 to 60 K. However, when temperature is larger than 80 K, the A, B, and C series peaks disappeared and a new broad PL peak centered at around 2.460 eV is present. The exact explanation of this new broad PL peak is probably related to deep boron centers. These results further show that 4H-SiC can be homoepitaxially grown by step-controlled epitaxy on off-oriented substrates.

![Image](image_url)

**Fig. 7** (a) Photoluminescence spectrum at 15 K, and (b) the PL spectral change with temperature in the range from 15 to 100 K for a 10-μm-thick 4H-SiC epilayer.

4H-SiC p-n junction diodes are fabricated by growing N-doped or undoped (n-type) epilayers on Al-doped 4H-SiC substrates. The electrical properties of 4H-SiC epilayers and p-n junction diodes have been reported in Ref. [15] with the electroluminescence. For example, Figure 8 shows the typical blue-violet electroluminescence (EL) spectrum (452.0 nm: 2.747 eV) of a 4H-SiC p-n junction diode biased at a forward voltage of 27 V. The inset shows the photograph of EL with the forward I-V curve at (a) room temperature and (b) 400°C, respectively. It can be seen from Fig. 7 and Fig. 8 that the main EL peak position is completely different from that in PL, indicating different EL and PL mechanisms. It has been proposed that the D–A pair recombination is a dominant light-emission mechanism in EL. The light generation mechanism for 4H-SiC LEDs is phonon-assisted donor-acceptor (D–A) pair recombination between nitrogen donors and aluminum acceptors. The 4H-SiC p-n junction can operate at temperature up to 400°C as shown in the inset. This indicates the advantage of 4H-SiC devices operating at high temperature.

![Image](image_url)

**Fig. 8** Blue-violet EL spectrum (452.0 nm: 2.74 eV) of a 4H-SiC p-n junction diode. The inset is the photograph of EL with the forward I-V curve at room temperature (a) and 400°C (b), respectively.

### 4 Conclusion

Horizontal LP-HWCVD system is developed. Homoepitaxial growth of 4H-SiC on off-oriented Si-face (0001) 4H-SiC substrates has been performed with the step-controlled epitaxy used. An atomically flat SiC substrate surface with RMS of 0.220 nm and 4H-SiC epilayer surface with RMS of...
0.59nm are obtained by H2 annealing at 1350°C and optimized growth condition, respectively. Results of X-ray diffraction, Raman scattering, and low temperature PL indicate that 4H-SiC can be homoepitaxially grown by step-controlled epitaxy on off-oriented substrates. Both the electrical and optical characteristics show that the obtained 4H-SiC p-n junction diodes can be operated at high temperature up to 400°C, which indicates a potential for high-temperature applications.

References

4H-SiC 低压热壁 CVD 同质外延生长及特性

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摘要: 为了获得高质量 4H-SiC 外延材料, 研制出一套水平式低压热壁 CVD(DI-LP-HWCVD) 生长系统, 在单晶衬底上, 利用“台阶控制生长”技术进行了 4H-SiC 的同质外延生长, 增加生长温度和压力分别为 1500℃和 1.3×10^5 Pa, 生长速率控制在 1.0μm/h 左右。采用 Nomarski 光学显微镜、扫描电镜(SEM)、原子力显微镜(AFM)、X 射线衍射、Raman 散射以及低温透射光光谱等技术, 研究了 4H-SiC 的表面形貌、结构和光学特性,以及用 HRXRD 作为 n 型掺杂剂的 4H-SiC 原位掺杂技术, 并在此基础上获得了 4H-SiC p-n 结二级管以及它们在室温及 400℃下的电致发光特性, 实验结果表明 4H-SiC 在 Si 不能工作的高温环境下具有极大的应用潜力。

关键词: 4H-SiC; 低压热壁 CVD; 同质外延生长; 原位生长
PACC: 8115H: 6105: 7855


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