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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 $10^{10}\mathrm{cm}^{-2}$[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 (4.9W/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 50mm 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℃. 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.

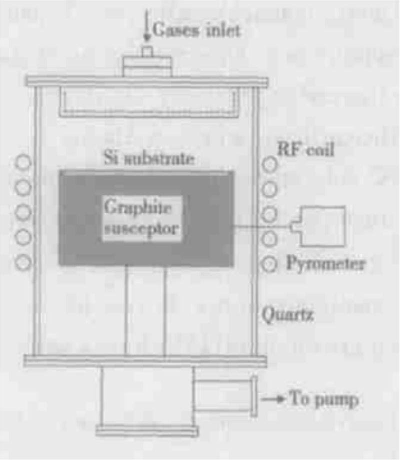

Fig. 1 Schematic diagram of the vertical LPCVD reaction chamber

The heteroepitaxial growth of 3C-SiC on 50mm Si(111) substrates with resistivity of 10~12Ω·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℃ for 10min. The diagram of growth process is shown in Fig. 2. SiH_4, C_2H_4, and Pd-cell purified H_2 are used as precursor gases. The typical flow rates of SiH_4, C_2H_4, and H_2 are 0.5~5sccm, 0.25~1sccm, and 3000sccm, respectively. For intentional doping of 3C-SiC, NH_3 (0~0.16sccm), and B_2H_6 (0~3.5sccm) are used as the n- and p-type dopants, respectively.

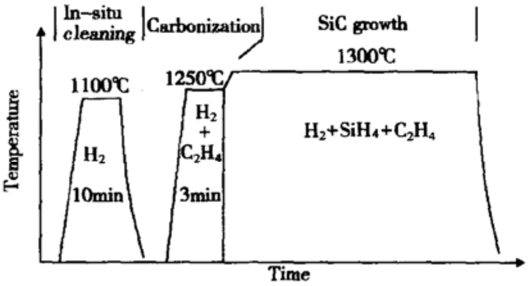

Fig. 2 Growth process diagram of 3C-SiC grown on Si(111) substrates

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℃. 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[8], 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 SiH$_4$ gas flow rate a constant, and to the SiH$_4$ 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 C$_2$H$_4$ has a lower cracking temperature, while C$_3$H$_8$ used in Ref. [1] has a higher one. At the optimized growth temperature of 3C-SiC, higher C$_2$H$_4$ 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 SiH$_4$ 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 SiH$_4$ flow rate constant as 0.5sccm. Under the optimized condition, the growth rate of 3C-SiC is nearly proportional to the SiH$_4$ flow rate with a constant C/Si ratio of 6. This result indicates that the growth rate is limited by SiH$_4$ flow rate. The optimized growth rate ranges from 0.8 to 3μm/h.

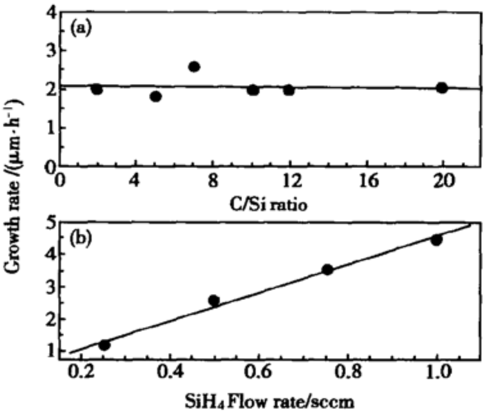

Fig. 3 Growth rate of 3C-SiC on Si as a function of (a) C/Si ratio with a constant SiH$_4$ flow rate of 0.5sccm and (b) SiH$_4$ flow rate under a constant C/Si ratio of 6

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 Napson NC-40 non-contact sheet resistance measurement system (unit: Ω/sq)

Sample No.	1	2	3	4	5	Average	%
1. N-doped	212.9	218	216.6	224.1	218.5	218.0	±2.48
2. B-doped	118	117.5	109.6	105.8	110.9	112.4	±5.4
3. Undoped	151.4	154.6	154.8	159.3	166.6	157.3	±4.83
4. Undoped	177.5	168.5	178.7	182.3	182.0	177.8	±3.88

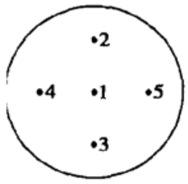

Figure 4 shows (a) the nitrogen concentration depth profile and (b) the schematic diagram of NH_3 flow rate with the growth time. The inset shows the atomic concentration depth profile of Si, C, and N. During the growth, the NH_3 flow rate was increased from 0.01sccm to the maximum value of 0.16sccm and then decreased to 0.01sccm with each step grown for 5min except 10min for the highest NH_3 flow rate of 0.16sccm, while the SiH_4 and C_2H_4 flow rates were maintained at 0.5sccm and 3.5sccm, respectively. In the first and the last 5min, no NH_3 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 NH_3 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 NH_3 in the precursor gases. For the first and the last two undoped layers, the difference of nitrogen concentration is also remarkable.

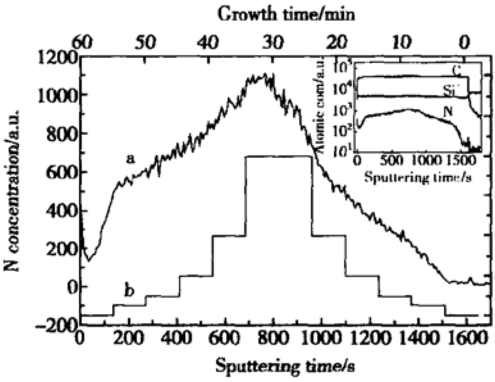

Fig. 4 SIMS depth profile of a nitrogen doped 3C-SiC epilayer grown on Si(111) with different NH_3 flow rate The C/Si ratio and the SiH_4 flow rate were maintained at 7 and 1sccm during the growth. (b) Schematic diagram of flow rate of NH_3 with the growing time The inset shows the atomic concentration depth profile of Si, C, and N.

In situ B-doping is also performed using B_2H_6 as the p-type dopant. Hall effect measurement is employed to characterize the electrical properties. 50mm n-type Si wafers with a resistivity of 10~12Ω·cm^2 are used as substrates. It is shown that with decreasing B_2H_6 flow rate, hole mobility increases from around $58cm^2/V\cdot s$ to $180cm^2/V\cdot s$, while the hole concentration decreases from $10^{19}cm^{-3}$ to 8~$9\times10^{16}cm^{-3}$. The highest hole concentration is about $10^{19}cm^{-3}$. For the undoped p-type 3C-SiC, the highest hole mobility is close to $200cm^2/V\cdot s$ at room temperature with a hole concentration of approximately $9.2\times10^{16}cm^{-3}$.

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[9,10]. 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 1000nm are 0.57°, 1.37°, and 1.6°, respectively. These data are close to those reported in Ref. [11].

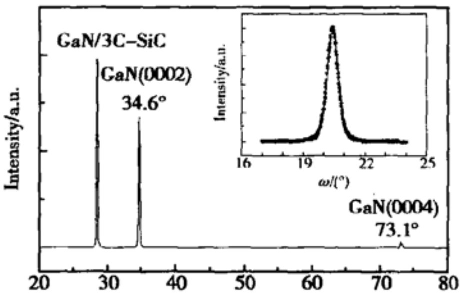

Fig. 5 X-ray diffraction of a GaN film grown on as-grown 3C-SiC/Si(111) substrate by MBE The film thickness is about 750nm (GaN (0002) FWHM = 0.18°). The inset shows the rocking curve (FWHM = 0.57°).

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[12]. For the near-band-edge emission, the 3.49eV peak can be attributed to the donor bound exciton emission[13]. There are also DAP (donor-acceptor pair) at 3.29eV, LO_1 (phonon replica related peak) at 3.23eV and LO_2 peaks at 3.12eV with higher intensity than the donor bound exciton emission. For the yellow band emission, the peak energy on 3C-SiC (centered at 2.25eV) is smaller than that on Si (centered at 2.4eV), 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 2.29eV at low temperature.

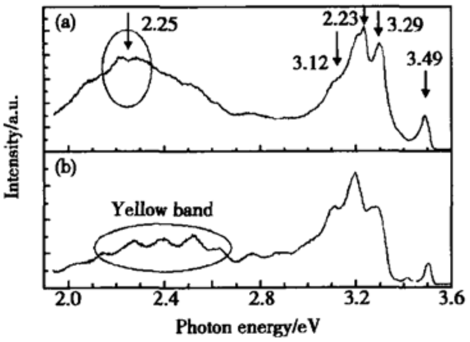

Fig. 6 Low temperature (10K) PL spectra of GaN epilayers grown on 3C-SiC/Si(111) (a) and Si(111) (b)

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型原位掺杂技术,获得了生长速率和表面形貌对反应气体中SiH_4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、均匀性和故意调制掺杂的N浓度纵向分布.利用MBE方法,在原生长的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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