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Structural and Optical Performance of GaN Thick Film Grown by HVPE*

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Abstract: Thick GaN films were grown on GaN/sapphire template in a vertical HVPE reactor. Various material characterization techniques, including AFM, SEM, XRD, RBS/Channeling, CL, PL, and XPS, were used to characterize these GaN epitaxial films. It was found that stepped/terraced structures appeared on the film surface, which were indicative of a nearly step-flow mode of growth for the HVPE GaN despite the high growth rate. A few hexagonal pits appeared on the surface, which have strong light emission. After being etched in molten KOH, the wavy steps disappeared and hexagonal pits with $\{10\bar{1}0\}$ facets appeared on the surface. An EPD of only $8\times10^6\mathrm{cm}^{-2}$ shows that the GaN film has few dislocations. Both XRD and RBS channeling indicate the high quality of the GaN thick films. Sharp band-edge emission with a full width at half maximum (FWHM) of 67meV was observed, while the yellow and infrared emissions were also found. These emissions are likely caused by native defects and C and O impurities.

Key words: GaN; HVPE; CL; RBS/channeling; yellow emission; infrared emission
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1 Introduction

GaN is a promising material for optoelectronic device applications, such as laser diodes and light-emitting diodes in the visible and ultraviolet spectrum, as well as for electronic devices, due to its wide band gap and good thermal stability. Because of a lack of native substrates, these semiconductor devices have been grown on many alternative substrates, such as sapphire and SiC. However, there is a large lattice mismatch between the GaN epitaxial layer and the foreign substrate, resulting in a large number of dislocations. Bulk GaN samples have been grown with several different techniques, including the high-temperature, high-pressure, near-equilibrium growth method[1], the sodium flux method[2], the ammonothermal method[3], and hydride vapor phase epitaxy (HVPE)[4~7]. HVPE is so far the best among these methods for growing large diameter, thick GaN films because of its high growth rate. These thick layers, once removed from the foreign substrate, have the potential to provide lattice-matched and thermally-matched homo-substrates for further epitaxial growth of high quality GaN with a low dislocation density for different heterostructure devices.

In this paper, the homo-epitaxial thick GaN film was grown on a thin GaN template grown by metal-organic chemical vapor deposition (MOCVD) in a vertical HVPE system. The surface morphology of the GaN film was investigated to understand the growth mechanism on the composite substrate. We also analyzed the optical properties of thick GaN film and discussed the origin of the yellow luminescence.

2 Experiment

First, 2μm GaN templated GaN films (on sapphire) grown by MOCVD were prepared. Next, the thick GaN film was grown by HVPE on the GaN template in the vertical quartz reactor with rotating graphite susceptor at atmospheric pressure, as shown in Fig. 1. The substrate was

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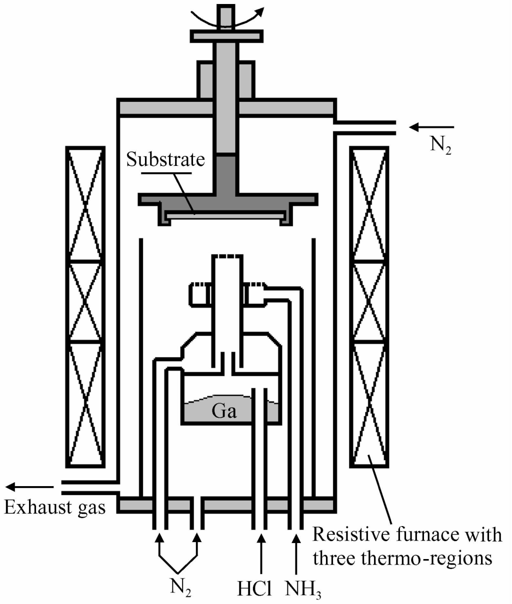

Fig. 1　Schematic diagram of reactor in HVPE system

top-mounted to remove contamination, and the heating was applied in three separate sections, with a conventional resistive surface. HCl diluted by N_2 was reacted with liquid Ga at 850℃ to form GaCl gas and was then transported into the growth zone where it directly reacted with NH_3 at 1050℃. The NH_3 flow rate was held at 1000mL/min, while the HCl flow rate was typically 10～20 mL/min. The total flow rate of the NH_3/N_2 mixture passing the NH_3 inlet was fixed at 1. 3L/min. The total flow rates of $GaCl/N_2$ via the showerheads were 710～720mL/min. In addition, a 3L/min main N_2 flow to drive reactants and purge the complete reactor was used from the reactor bottom. The film thickness measurements were made using cross-sectional SEM. A thick GaN film of over 80μm was obtained after one hour of growth on the thin GaN layer by MOCVD, so the growth rate exceeded 80μm/h.

The morphology on the surface of the GaN film was analyzed by a JSM-5600LV scanning electronic microscope (SEM) and a Nanoscope Ⅲ atomic force microscope (AFM) before and after being etched in molten KOH for 5min. The crystal quality of the epitaxial film was characterized by X-ray diffraction (XRD) and RBS/Channeling analysis. The X-ray diffraction was measured with a Philips X'Pert Pro MRD system. The Rutherford back scattering (RBS) measurements used 4. 0 MeV He^+ ions, with an incident angle of 7° and a scattering angle of 165°, and a fixed surface barrier detector. Photoluminescence spectra (PL) were excited with the 325nm line from a He-Cd laser, with an excitation density of about $10W/cm^2$. Cathodoluminescence (CL) was measured in an Oxford instruments MonoCL2 system on a JEOL field-emission scanning electron microscope with an e-beam accelerating voltage of 15kV. The chemical composition was investigated with a PHI-5702 multi-functional X-ray photoelectron spectroscope (XPS) operating with AlKα radiation as the excitation source and the binding energy of contaminated carbon (C1s at 284. 8eV) as the reference.

3　Results

The examined thick GaN film typically shows a relatively smooth surface morphology, as shown in Fig. 2(a). Well-defined stepped/terraced structures can be seen on the film surface. The terrace widths are several microns separated by 6～10nm high steps as measured by AFM. This is indicative of a nearly step-flow mode of growth for HVPE GaN even though the growth rate of GaN reached 80μm/h. In addition, a small number of hexagonal pits can be seen on the surface in Fig. 2(c), which originate at the large scale columnar assemblies of structural defects close to the thick film-template interface[8]. The dimensions of the hexagonal pits exceed 35μm due to the high growth rate of the GaN film. These pits affect the optical properties of GaN. Their panchromatic CL map is shown in Fig. 2(d). The intensity of CL is spatially inhomogeneous, and stronger luminescence is observed inside the hexagonal pits. We attribute the strong luminescence localized at the hexagonal zone to structural defects, i. e., high electron concentration in the hexagonal pits.

A surface morphology image of GaN film etched in molten KOH (360℃) for 5min is shown in Fig. 3. After etching, wavy steps disappear and hexagonal pits with $\{10\bar{1}0\}$ facets appear on the GaN surface. There are two kinds of pits, i. e., large pits with a diameter of about 10μm and depth of about 1400nm, and small pits with a diameter less than 4μm and depth less than 400nm. The diameter of the large pits is almost the same, while that of small pits is different and discrete. According to TEM results[9], the etch pits

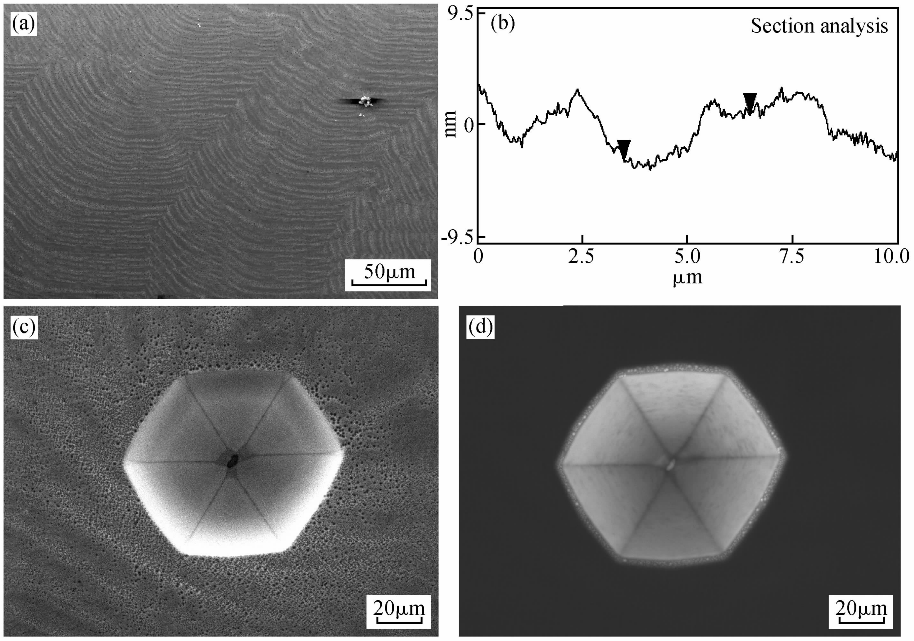

Fig. 2　(a) Surface morphology of thick GaN film;(b) AFM analysis;(c),(d) SEM and panchromatic CL images of a hexagonal pit on the film surface,respectively

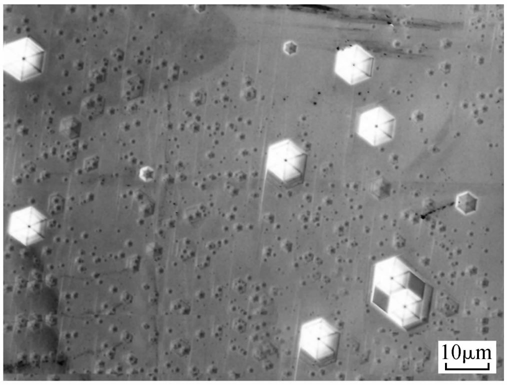

Fig. 3　Surface morphology after etching for 5min in molten KOH

originated from the mixed dislocations in the GaN film,so EPD may act as the evaluation approach for dislocation density. That the total etch-pit density is $8\times10^{6}\mathrm{cm}^{-2}$ illustrates the high quality of the GaN film. However,the large etch pit density is only $1\times10^{5}\mathrm{cm}^{-2}$,and its appearance may be caused by dislocation bunching or nanopipes in the GaN film. A careful investigation of the initial growth stage needs to be carried out to clarify the reason.

Figure 4(a) shows the FWHM of the ω-mode scan for the (0002) plane of the thick film grown by HVPE. The narrowest linewidth of 590″ is found for GaN film. This shows that the thick

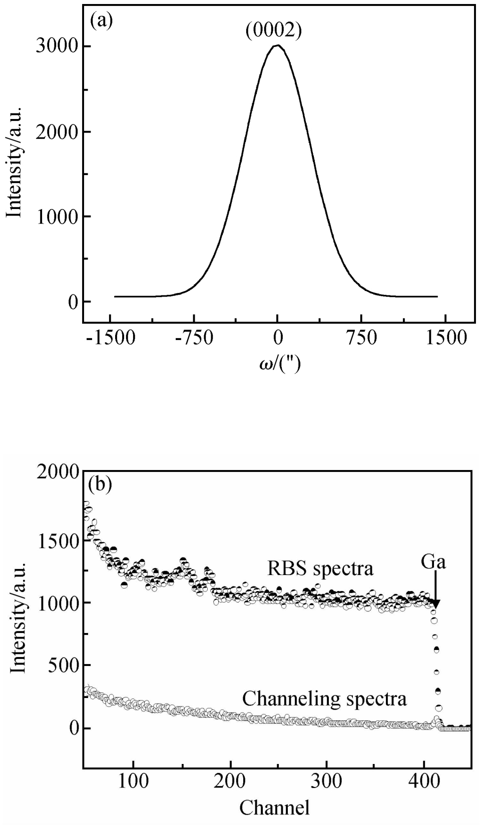

Fig. 4　X-ray rocking curve (a) and RBS/⟨0001⟩ aligned channeling spectra (b) of thick GaN films grown by HVPE

film has high crystal quality in spite of the high growth rate. At the same time, Rutherford backscattering spectroscopy and channeling experiments are also applied to verify the crystalline perfection, as illustrated in Fig. 4(b). Because the film thickness is much thicker than the penetration depth of α particles with the energy of 4.5MeV (about 5μm), all signals are obtained from the upper surface region of the film. The 〈0001〉 aligned channeling spectrum shows that the minimum RBS channeling yield is as low as 1.8%, which again proves that the GaN films grown by HVPE are of high crystalline quality and highly 〈0001〉 orientation.

A typical room-temperature PL spectrum of the GaN film is shown in Fig. 5(a). Sharp band-edge emission with a full width at half maximum (FWHM) of 67meV is observed, which is indicative of high quality material. However, a broad yellow band and an infrared band also appear near 575nm (2.15eV) and 975nm (1.27eV), respectively. The origin of yellow band has not been well established and is a subject of debate. It may be due to a shallow donor-deep acceptor transition[10,11], a deep donor-shallow acceptor transition[12], or a level-to-level transition broadened by large non-uniform strain in the vicinity of dislocations[13]. In our undoped GaN film, there are C and O impurities according to the XPS spectra in Fig. 5(b). These impurities may be related to the strong yellow emission. In addition, infrared emission (975nm) is found for the first time in undoped GaN film. We speculate that native defects such as vacancies or native interstitial atoms, likely recombined with C and O impurities leads to the yellow and infrared emission. Careful investigation will be carried out to clarify the infrared emission.

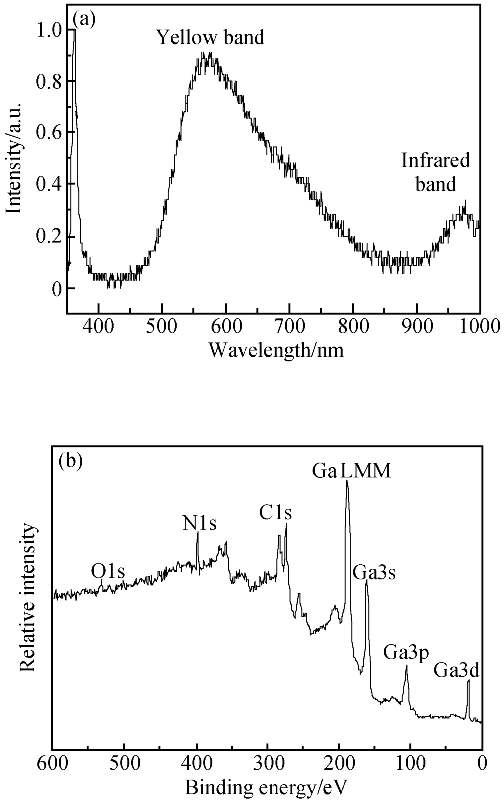

Fig. 5 Room-temperature photoluminescence spectrum (a) and XPS spectrum (b) of thick GaN film

4 Conclusion

In this paper, high quality HVPE-grown thick GaN film was studied by various techniques. Stepped/terraced structures appeared on the film surface, indicating a step-slow mode of growth for HVPE GaN in spite of the growth rate. A small number of hexagonal pits with the dimensions of 35μm were found on the surface, which have strong light emission. An EPD of only $8\times10^6 cm^{-2}$ indicates that the GaN film had few dislocations. That minimum RBS channeling yield was as low as 1.8% verified the high quality of the film. A sharp band-edge emission with a full width at half maximum of 67meV was observed. However, yellow and infrared emission also appeared. These emissions were likely related to the C and O impurities.

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HVPE 生长 GaN 厚膜的结构和光学性能*

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摘要： 采用自制的立式 HVPE 设备，在 GaN/蓝宝石复合衬底上生长了 GaN 厚外延膜，利用 AFM，SEM，XRD，RBS/Channeling，CL，PL 以及 XPS 等技术分析了厚膜的结构和光学性能. 结果表明，外延层表面具有台阶结构，接近以层流生长方式二维生长，一些六角形的坑出现在膜表面，坑区具有很强的发光. 腐蚀试验显示 EPD 仅 8×10^6 cm^{-2}；XRD 和 RBS/channeling 表明 GaN 膜具有较好的晶体质量；PL 结果也证明外延层具有高的质量，出现了尖锐的带边峰，半高宽仅 67meV，同时出现了黄带和红外带，这些带的出现可能是由本征缺陷和 C，O 等杂质引起的.

关键词： 氮化镓；氢化物气相外延；阴极荧光谱；卢瑟福背散射/沟道；黄发射；红外发射

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