

文章类型:

DOI: 10.15541/jim20250481

Research on Growth of GaN Single Crystals on Sapphire Patterned-porous Thin Film Composite Substrate

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Abstract: Due to the large lattice mismatch and thermal mismatch between gallium nitride (GaN) and hetero-substrates, high-density mismatch dislocations are introduced in the GaN epitaxial layer, thereby reducing the performance and lifetime of the devices. The most fundamental solution to this problem is to grow GaN on GaN homo-substrate. In this paper, GaN films were first grown on a patterned sapphire substrate using metal-organic chemical vapor deposition method. Then, the GaN films were wet-etched to fabricate a sapphire patterned-porous film composite substrate. Subsequently, GaN single crystals were grown on this substrate, and GaN bulk single crystals were obtained by self-peeling. The feasibility of this process was experimentally verified. The test results of X-ray diffraction (XRD), Raman spectroscopy, photoluminescence spectroscopy (PL), and cathodoluminescence spectroscopy (CL) confirm that the crystalline and quality of grown GaN single crystals were improved. At the same time, the growth mechanism of GaN single crystals on the sapphire patterned-porous thin film composite substrate is expounded, providing a new idea for improving the quality of self-stripping GaN single crystals.

Key words: pattern; porous; composite; GaN

The third-generation semiconductors refer to the wide bandgap semiconductor materials such as gallium nitride (GaN), silicon carbide (SiC), diamond, and zinc oxide (ZnO). Compared with the traditional first-generation and second-generation semiconductor materials like silicon (Si), the third-generation semiconductor GaN has unique properties such as large bandgap width, high breakdown electric field, high thermal conductivity, high electron saturation drift velocity, and small dielectric constant, which make it show great potential in optoelectronic devices, power electronics, radio frequency microwave devices, lasers, and detectors. Therefore, it has become a hot topic in the semiconductor research fields of various countries^[1-3].

GaN crystals have a high melting point (above 2200 °C), but their decomposition point is around 900 °C, *i.e.*, at the

melting point, the existence of GaN requires an extremely high equilibrium nitrogen pressure (above 6 GPa). Thus there is a lack of natural GaN bulk single crystal materials in nature^[4]. Common GaN crystal growth methods include high-pressure nitrogen solution growth method^[5], ammonia thermal method^[6], fluxing agent method^[7], hydride vapor phase epitaxy (HVPE), *etc.* Due to the lattice mismatch and thermal expansion coefficient mismatch in heterogeneous epitaxy, the epitaxial layer usually generates a high density of dislocations and cracks, which significantly reduces the quality of GaN crystals and consequently severely degrades the performance and lifespan of the devices^[8]. To reduce the defect density and obtain high-quality GaN crystals, two-step growth technology, buffer layer technology, substrate surface treatment, flexible substrate technology, lateral epitaxial

收稿日期: 2025-12-04; 收到修改稿日期: 2026-01-22; 网上出版日期: XXXX-XX-XX

基金项目: 国家自然科学基金(52202265, 52302004, 52502007, 62434010); 山东省泰山学者计划(tsqn202306330); 山东省自然科学基金(ZR2021MB034, ZR2022QF044, ZR2022MF229); 山东大学晶体材料全国重点实验室(KF2104)

National Natural Science Foundation of China (52202265, 52302004, 52502007, 62434010); Taishan Scholars Program of Shandong Province (tsqn202306330); Natural Science Foundation of Shandong Province (ZR2021MB034, ZR2022QF044, ZR2022MF229); State Key Laboratory of Crystal Materials, Shandong University (KF2104)

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growth, *etc.* have gradually been developed^[9-12]. The development of GaN crystal growth is led by companies such as Mitsubishi, Sumitomo, and SCIOCS in Japan, and Kyma in the United States. Although China started relatively late in the field of GaN semiconductor materials, it has accumulated a considerable amount of basic research and technical reserves. Among them, Suzhou Navier and Zhongjia have achieved mass production of 2-inch GaN crystals, and institutions such as Shandong University and the 46th Research Institute of China Electronics Technology Group Corporation have also made significant progress^[13]. In 2020, Mitsubishi Corporation in Japan^[14] successfully fabricated GaN single crystal substrates with a low dislocation density of $1.4 \times 10^3 \text{ cm}^{-2}$ on ammonia-thermal GaN seeds by the HVPE method. Zhongjia Semiconductor has developed 2-inch GaN self-supporting substrates with dislocation densities ranging from 4×10^5 to $7 \times 10^5 \text{ cm}^{-2}$ and has begun mass production and sales. The State Key Laboratory of Crystal Materials at Shandong University has also conducted research on the growth and processing of GaN single crystals^[15-18]. They have mastered the key technology for 2-inch single crystal homoepitaxial growth, reducing the GaN dislocation density to $5 \times 10^6 \text{ cm}^{-2}$.

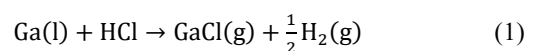
The main problem in GaN crystal growth is the lack of suitable seed crystals. Currently, most commercial GaN-based devices use sapphire, GaAs, and Si as seed crystals for heteroepitaxial growth. However, these seed crystals have larger lattice mismatch and thermal mismatch compared to GaN, resulting in significant stress and high dislocation density in the grown GaN single crystals, which seriously impairs the performance of GaN-based devices. Therefore, choosing a seed crystal that can effectively reduce the stress and dislocation density of epitaxial GaN crystals is the key to growing high-quality GaN crystals. After GaN is grown on a patterned sapphire substrate (PSS), a porous structure is prepared, which can effectively block dislocation propagation and improve the quality of GaN crystals. Therefore, actively conducting research on growing GaN crystals on sapphire patterned-porous thin film composite substrates is of great significance for obtaining GaN crystals with low dislocation density and stress-free self-deposition. Thus, after growing GaN films on PSS in this paper, a porous structure was prepared by chemical etching methods, and GaN single crystal growth was carried out and its performance was studied, laying a foundation for the subsequent growth of high-quality GaN single crystals.

1 Experimental

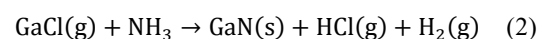
1.1 Experimental method

For the experiment, a piece of 4 inch patterned sapphire substrate (PSS) was used (Pattern diameter of $3 \mu\text{m}$ and a period of $6 \mu\text{m}$). Then, a layer of GaN film was grown using the MOCVD method. The film thickness is 3.5 nm . Subsequently, the GaN film on the PSS was etched using a H_3PO_4 solution at a temperature range of 230°C to 260°C for 5 min to form a porous structure as shown in Fig. 1. Unlike the porous structure in Ref. [18], which has deep pores and a long corrosion time, resulting in large pores and deep structures with long dimensions, in this paper, the porous structure has a shorter corrosion time. The gallium nitride film on the sapphire is roughened, and subsequent growth is then carried out. As hot H_3PO_4 solution can etch the poorer quality parts of GaN^[19-20], Chen, *et al.* found many hexagonal holes when etching GaN grown by Metal Organic Chemical Vapor Deposition (MOCVD) with H_3PO_4 solution. Based on the burgers vector of the threading dislocation and the distribution of dislocations on the surface, they believed that the etched holes were threading dislocations in GaN single crystal^[21]. The experiment compared the use of sapphire substrate and sapphire patterned substrate. The samples used in the experiment were all cleaned before the GaN single crystal was grown. In the experiment, *a*, *b*, and *c* represent the sapphire substrate, sapphire patterned substrate, and sapphire patterned-porous thin film composite substrate, respectively.

The growth of GaN single crystal in this experiment was carried out using a self-developed HVPE single crystal growth furnace. The Ga source used for growing GaN crystals was 99.99999% high-purity metallic Ga, and 99.99999% high-purity NH_3 was used as the N source, while 99.999% purity N_2 was employed as the carrier gas. The basic principle of HVPE method for growing GaN is that in the low-temperature zone (850°C), metallic Ga reacts with HCl to generate GaCl:



Subsequently, GaCl was transported to the high-temperature zone (1050°C) using high-purity N_2 and then reacted with NH_3 :



GaN is formed through deposition. In this experiment, a nucleation layer was first formed during growth, and then

gradually merged and grew into a GaN single crystal. After 12 h of growth, a 1 mm GaN crystal was grown. During the cooling process at the end of growth, the thermal stress between the sapphire substrate and the GaN crystal directly acted on the interface. The bond between the interface and the substrate was very weak, enabling the self-peeling of the sapphire substrate from the GaN crystal, and thus obtaining a bulk GaN single crystal.

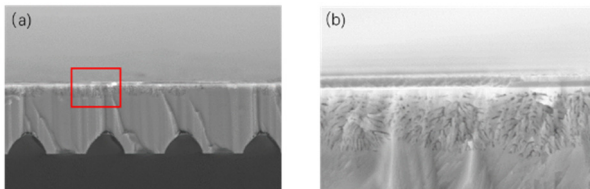


Fig. 1 The wet etching porous structure

(a) Sapphire pattern-porous thin film composite substrate; (b) Zoomed-in view of the square box

1.2 Characterization

Scanning electron microscopy (SEM Gemini560) is utilized to observe the surface morphology of the GaN crystal. Raman spectroscopy (excitation wavelength 532 nm) is employed to characterize the stress in GaN crystal. X-ray diffraction (XRD) using symmetric (002) and asymmetric (102) reflections of GaN is used to characterize the crystalline quality of HVPE-grown GaN. The photoluminescence spectrum (PL excitation wavelength 320 nm) is used to measure the luminous intensity of GaN crystals. Cathodoluminescence (CL) spectroscopy at room temperature is used for imaging the surface of HVPE-grown GaN to observe the dislocation situation.

2 Results and analysis

2.1 Surface morphology of sapphire patterned-porous thin film composite substrate growth layer

Fig. 2 shows the surface images of the GaN single crystals grown on different substrates (a), (b), and (c) after processing. The wafer diameter is 2 inches and the thickness is 400 μm . As can be seen from the figure, the number of pits on the surface varies: (a) about 20 pits, (b) about 10 pits, and (c) less than 5 pits. The pits are formed during the growth process. This may be due to the formation of islands during the GaN nucleation process. There is no connection between islands during further growth, and ultimately they closely come together to form a smooth surface. This may be related to the different substrates. These stress differences arise from the reduction of the interaction between the surface patterned

structure and the porous structure of sapphire. The porous structure enables a partial release of stress during the growth process. This leads to the relief of stress differences among different substrates.

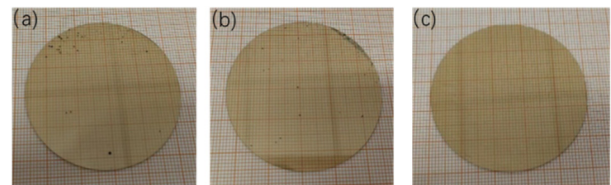


Fig. 2 GaN crystals grown on different substrates

(a) Sapphire substrate; (b) PSS; (c) Sapphire patterned-porous thin film composite substrate

2.2 Interface of GaN single crystal growth on sapphire patterned-porous thin film composite substrate

Fig. 3 shows the SEM image of GaN single crystal grown on a sapphire patterned-porous thin film composite substrate using the HVPE method. It can be seen that after the GaN single crystal was grown on the patterned sapphire substrate using the HVPE method, the porous structure on the patterned sapphire substrate was filled as shown in Fig. 3(a). Additionally, there are still gaps when observed at a magnified scale, as shown in Fig. 3(b). This indicates that during the growth of GaN on the sapphire patterned composite substrate, the porous structure recombined with the Ga atoms and N atoms during the growth process, and the original defects were destroyed, which may prevent the original defects from further extension, thereby improving the crystal quality of GaN. If the quality of the crystals continues to improve, the gaps may decrease or even disappear, as shown in Fig. 3(b).

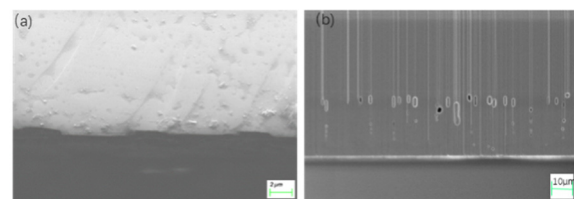


Fig. 3 SEM cross-sectional view of GaN crystal grown on sapphire patterned-porous thin film composite substrate

(a) Interface of sapphire and GaN growth; (b) Zoomed-in view of the interface

2.3 X-ray rocking curve of GaN single crystal on sapphire patterned-porous thin film composite substrate

Fig. 4 shows the X-ray rocking curves of GaN single crystals grown on sapphire substrate, PSS, and sapphire patterned-porous thin film composite substrate. As can be seen in Fig. 4, compared with the samples grown on the substrate,

the full width at half maximum of the (002) plane of the GaN single crystal grown on the sapphire patterned-porous film composite substrate has decreased from 153 arcsec to 95 arcsec, and the full width at half maximum of the (102) plane has decreased from 292 arcsec to 135 arcsec. The crystal quality has been significantly improved. The GaN single crystal grown on the PSS has a full width at half maximum of the (002) plane reduced to 117 arcsec and that of the (102) plane reduced to 168 arcsec, and the crystal quality has also improved. In the X-ray rocking curve test, the diffraction signal of the (002) plane can more directly reflect the epitaxial quality in the c-axis direction and the lattice integrity of the crystal. Meanwhile, the diffraction signal of the (102) plane is more sensitive to edge dislocations, in-plane stress, and

grain orientation differences. Such defects are more difficult to completely eliminate during crystal growth, which results in the half-width of the (102) plane diffraction peak usually being larger. The quality of the GaN crystals grown in this work is slightly different from that of the GaN single crystals with homogeneous epitaxial growth in Ref. [15-18] (the half-width of the (002) plane is 48 arcsec and the half-width of the (102) plane is 67 arcsec). The process in this paper can be further optimized on the porous structure, and it is expected to continue to improve the crystal quality. The GaN grown on the porous composite substrate has relatively better quality. This may be because the micropattern and porous structure have a better stress release effect during the GaN growth process.

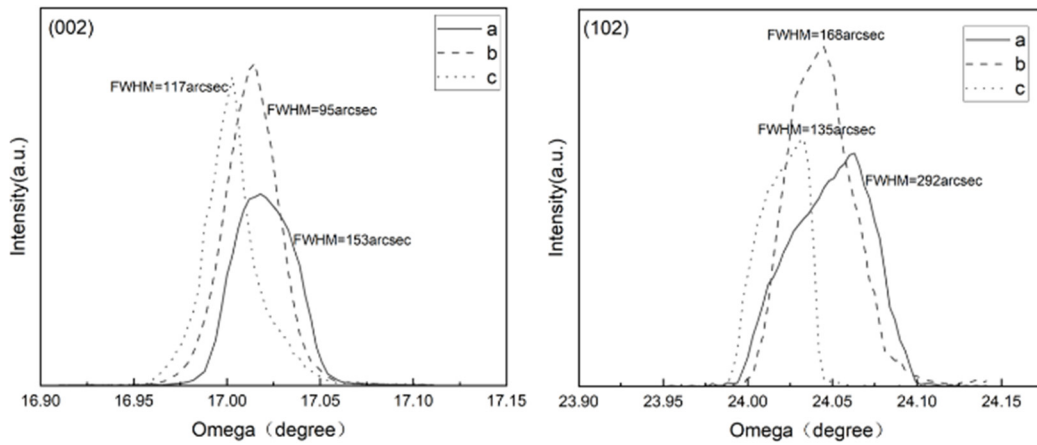


Fig. 4 X-ray rocking curves of the (002) and (102) planes of GaN single crystals grown on different substrates
(a) Sapphire substrate; (b) PSS; (c) Sapphire patterned-porous thin film composite substrate

2.4 Raman spectra of GaN single crystal on sapphire patterned-porous thin film composite substrate

Fig. 5 shows the Raman spectra of GaN single crystals grown on sapphire substrate, PSS, and sapphire patterned-porous thin film composite substrate. In Fig. 5, it can be seen that the E2 mode peak position of GaN grown on the flat substrate is 567.697 cm^{-1} , that on PSS is 567.713 cm^{-1} , and that on the sapphire patterned-porous thin film composite substrate is 567.662 cm^{-1} . The peak positions of the E2 mode of GaN grown on the three different substrates have all shifted towards longer wavelengths. The phonon vibration frequency is related to the stress in the material. When the stress changes, the frequency position of the phonon Raman peak will shift. Generally, the E2 phonon mode in the Raman spectrum is used to characterize the stress of GaN crystals^[22]. The stress can be calculated by the following formula^[23]:

$$\sigma = \frac{\Delta\omega}{4.3} \text{ (cm}^{-1} \cdot \text{GPa}^{-1}) \quad (3)$$

In the formula, σ represents stress, $\Delta\omega$ is the frequency shift of the E2 phonon mode, and the position of the E2 phonon mode of unstrained GaN single crystal is $(567.1 \pm 0.1) \text{ cm}^{-1}$ ^[24]. Through the formula, we calculated that the GaN single crystals grown on sapphire substrates, PSS, and sapphire pattern-porous thin film composite substrates are all under a compressive stress state, with stress values of 0.143, 0.139, and 0.131 GPa, respectively. The results obtained from the calculation indicate that the GaN single crystals grown on the sapphire pattern-porous thin film composite substrate have effectively released the stress, which is conducive to the growth of high-quality GaN crystals as the growth substrate. The smaller residual stress improves the mechanical strength of the substrate^[25], effectively reducing the cracking of the crystals. If the size and period of the pattern on the sapphire substrate are changed, for example, when adopting a nano-pattern structure, or if the size and depth of

the porous structure are altered, such as by extending the etching time or increasing the etching temperature, the stress of the GaN film may be altered. Continued growth of the GaN single crystal may result in a reduction of the stress.

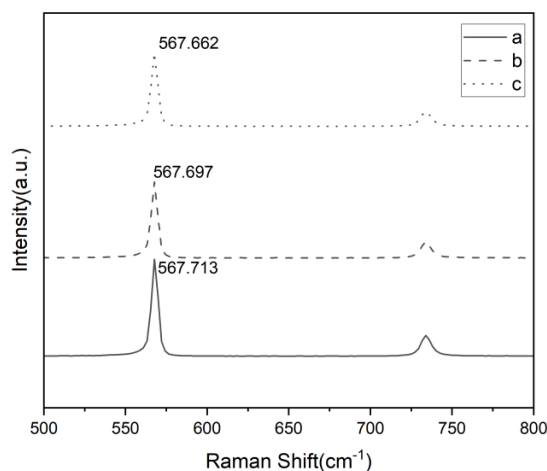


Fig. 5 Raman spectra of GaN single crystals grown on different substrates

(a) Sapphire substrate; (b) PSS; (c) Sapphire patterned-porous thin film composite substrate

2.5 Photoluminescence spectra (PL) of GaN single crystals on sapphire patterned-porous thin film composite substrate

Fig. 6 shows the photoluminescence spectra of GaN single crystals grown on the sapphire substrate, PSS and sapphire patterned-porous thin film composite substrate. The PL represents a curve showing the distribution of light emission intensity as a function of photon energy. By analyzing the photoluminescence spectra, we can obtain information about the material structure and physical properties, and the spectra also reflect the competition between radiative recombination and non-radiative recombination. The photoluminescence spectrum depends on the radiative recombination process of non-equilibrium carriers in the experimental sample and is related to factors such as the band structure of the material, defect conditions, and doping level. It indirectly indicates the optical quality of the crystal. As shown in Fig. 6, the GaN crystals grown on all three substrates exhibit strong edge emission peaks around 363 nm. Since the dislocations in GaN crystals act as non-radiative recombination centers, they reduce the luminescence efficiency of GaN crystals^[26-27]. Compared with GaN crystals grown on planar substrates, the intensity of the edge emission peaks of GaN crystals grown on sapphire patterned substrates has increased. Moreover, the intensity of the edge emission peaks of GaN crystals grown

on the sapphire patterned-porous film composite has continued to increase, which is 19.4% higher than that of crystals grown on sapphire substrates. This indicates that the dislocation density of GaN crystals grown on the sapphire patterned-porous film composite substrate has significantly decreased. Consequently, the crystal quality has been improved, and the optical quality has also been significantly enhanced.

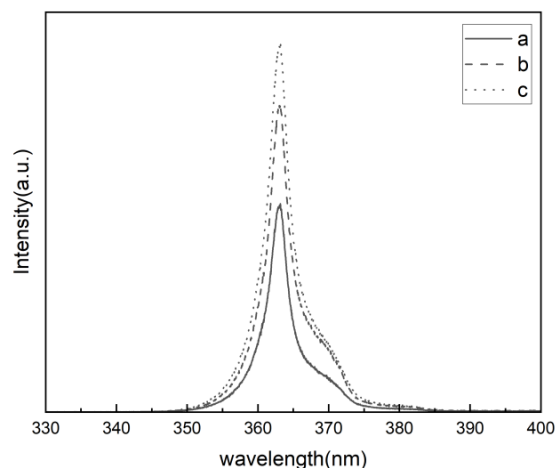


Fig. 6 PL spectra of GaN single crystals grown on different substrates

(a) Sapphire substrate; (b) PSS; (c) Sapphire patterned-porous thin film composite substrate

2.6 Cathodoluminescence Spectra (CL) of GaN Single Crystals on sapphire patterned-porous thin film composite substrate

Fig. 7 shows the cathodoluminescence test image of a GaN single crystal. The densities of black dots in Fig. 7 are approximately 8.0×10^6 , 4.0×10^6 , and $2.3 \times 10^6 \text{ cm}^{-2}$ respectively. The density of black dots is related to the non-radiative carrier recombination at dislocations^[28]. Therefore, the density of black dots is close to the dislocation density in the GaN single crystal. This proves that the crystal quality of the GaN single crystal grown on the sapphire patterned-porous thin film composite substrate has been improved, which effectively reduces defects.

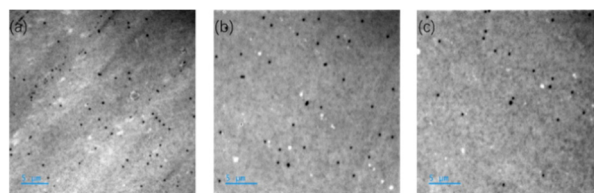


Fig. 7 CL spectra of GaN single crystals grown on different substrates (a) Sapphire substrate; (b) PSS; (c) Sapphire patterned-porous thin film composite substrate

3 Mechanism of reducing dislocations by growing GaN on

sapphire patterned-porous thin film composite substrate

During the growth process, NH_3 fills the entire growth area, and the N source is in excess. The diffusion of the Ga source determines the growth process. Compared with N atoms, the density of Ga atoms is higher, and they can easily diffuse onto the substrate under the action of gravity and be adsorbed by the bottom atoms and surface atoms to form GaN. Therefore, GaN nucleation islands appear at the bottom of the substrate holes and on the surface that has not formed holes. With the increase of nucleation time, the nucleation islands at the bottom of the holes in the porous substrate gradually grow and fill the film pores, and then gradually grow and merge. As GaN gradually covers the entire surface of the porous substrate, the nucleation islands at the hole positions stop growing, and the GaN nucleation islands grown at the hole positions cannot completely fill the pores. Therefore, a pore layer appears at the growth interface, effectively inhibiting the upward extension of dislocations in GaN, thereby improving the quality of GaN single crystal. Shao, *et al.*^[29] pointed out that there are three different types of dislocations in GaN crystals, namely a-type dislocation, c-type dislocation, and mixed a+c-type dislocation, and the three types of dislocations correspond to different Burgers vectors:

$$\vec{b}_a = \frac{1}{3} \langle 11\bar{2}0 \rangle, \vec{b}_c = \langle 0001 \rangle, \vec{b}_{a+c} = \frac{1}{3} \langle 11\bar{2}3 \rangle$$

It should be pointed out that in this paper, three-coordinate, four-coordinate, and three-coordinate structures have equivalent relationships, and (hkl) is equivalent to (hki) , where $i = -h-k$. The GaN prepared in this paper is a (001) face crystal, and along the [001] direction, there exist edge threading dislocations and screw threading dislocations in GaN. Due to different dislocations corresponding to different Burgers vectors, different dislocations can only appear in certain specific directions. The half-width of the rocking curve in the symmetric direction (001) corresponds to the density of edge threading dislocations, while the density of mixed dislocations is related to the half-width of the asymmetric direction rocking curve (FWHM)^[30-32]. This is also the basic principle of using XRD rocking curves to characterize the internal dislocation density of the crystal. As shown in Fig. 4, the rocking curves in the (002) and (102) directions are used to reflect the internal dislocation situation of the crystal: the smaller the half-width of the rocking curve, the lower the dislocation density and the higher the crystal quality.

4 Conclusions

In conclusion, we have demonstrated the feasibility of growing GaN single crystals on sapphire patterned-porous thin film composite substrates, and the quality of GaN crystals exponentially grown^[33] on the prepared sapphire patterned-porous thin film composite substrates has significantly improved. The preparation process of the sapphire patterned-porous thin film composite substrate has easily controllable conditions, making it a simple and efficient method. We have studied the growth mechanism of GaN crystals on sapphire patterned-porous thin film composite substrates. The sapphire patterned-porous film composite substrate further reduces the dislocation density^[34] and stress in GaN growth, and plays an important role in improving the quality of GaN crystals. The work has significant reference value for the growth of high-quality GaN crystals.

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蓝宝石图形-多孔薄膜复合衬底生长 GaN 单晶研究

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摘要: 氮化镓(GaN)及其合金材料因具有宽禁带、高载流子迁移率、高击穿电压、化学性质稳定等优点, 在半导体发光二极管、激光二极管、光电探测器、高频高功率微波器件等领域具有广阔的应用前景。由于GaN与异质衬底之间存在较大的晶格失配和热失配, 导致在GaN外延层中引入高密度的失配位错而降低器件的性能与寿命。解决这个问题最根本的方法就是在GaN同质衬底上进行外延生长。本研究采用金属有机化学气相沉积法首先在蓝宝石图案化衬底上生长氮化镓薄膜, 然后湿法腐蚀氮化镓薄膜, 制备出蓝宝石图形-多孔薄膜复合衬底, 再在其上生长氮化镓单晶, 自剥离得到氮化镓体块单晶, 实验证明了此工艺的可行性。通过X射线衍射(XRD)、拉曼光谱、光致发光光谱(PL)、阴极荧光光谱(CL)测试结果证实, 在蓝宝石图形-多孔薄膜复合衬底上生长GaN单晶的质量和光学质量都有所提高。同时阐述了蓝宝石图形-多孔薄膜复合衬底上生长GaN单晶的生长机制, 为生长提高自剥离GaN单晶质量提供了新的思路。

关 键 词: 图形; 多孔; 复合; GaN

中图分类号: TQ174

文献标志码: A

文章编号: