Investigation of GaN Growth Directly on Si (001) by ECR Plasma Enhanced MOCVD*

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Abstract: Direct growth of GaN films on Si(001) substrate at low temperatures (620~ 720℃) by electron cyclotron resonance (ECR) microwave plasma enhanced metalorganic chemical vapor deposition (PEMOCVD). The crystalline phase structures of the films are investigated. The results of high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) indicate that high *c*-axis oriented crystalline wurtzite GaN is grown on Si(001) but there is an amorphous layer formed naturally at GaN/Si interface. Both faces of the amorphous layer are flat and sharp, and the thickness of the layer is 2nm approximately cross the interface. The analysis supports that β-GaN phase is not formed owing to the N_xSi_y amorphous layer induced by the reaction between N and Si during the initial nucleation stage. The results of XRD and atomic force microscopy (AFM) indicate that the conditions of substrate surface cleaned in situ by hydrogen plasma, GaN initial nucleation and subsequent growth are very important for the crystalline quality of GaN films.

Key words: PEMOCVD; GaN/Si(001) interface; crystalline phase structure

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1 Introduction

The application of GaN material system for the blue-ultraviolet light-emitting device and high-temperature electronics has attracted much attention. Growth of good-quality GaN film has been investigated with different growth techniques[1~5], including MOCVD, molecular beam epitaxy (MBE) and its plasma-assisted type technique, and various substrate, such as sapphire[1,2], GaAs[3,4], SiC[5] and Si[5~8]. Si substrate for GaN growth presents several obvious advantages, for example, low cost, good electrical condition, especially well-established silicon device technique for future GaN devices onto silicon-based large scale integrated circuit . Despite of its importance, it is difficult to grow good-quality GaN on Si directly for such a large mismatched system. Commonly, GaN films are grown on Si with intermediate layer, such as SiC[5], AlN[7,8], GaAs[3,4], or others. There are a few studies of the direct growth of GaN on Si(001)[6] and Si(111)[7] substrates. And the reactions between GaN and Si are responsible for the degradation of the GaN/Si interface[6,9]. Some works try to prevent these reactions by low growth temperature[6,8]. Low processing temperature is indispensable for device application of materials to avoid some problems. such as thermal stress, dopant redistribution, and out-doping.

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In this paper the direct growth of GaN on Si (001) at low temperature by ECR PEMOCVD in a homemade ECR semiconductor processing device (ESPD)[4,10] is investigated, and the crystalline phase structure of GaN film grown and β-GaN phase formation are investigated as well. There are two reasons to select Si(001) substrate for the purpose of investigation. First, the character of atom staking sequence along 〈111〉 direction for zinc-blend structure is different from the one for wurtzitic structure[4]. Si(111) surface is favorable for h-GaN (0001) growth[7,8]. Second, the occurrence of an epitaxial "cube-on-cube" orientation due to the coincidence lattice between β-GaN and Si (001) is possible[6]. The *c*-GaN epitaxial films have been grown on GaAs(001) substrate successfully by a similar technique in ESPD[8,10]. The main objective of this work is to investigate the effect of pre-processing of Si substrate by H-plasma, the initial growth technique under the plasma environment, Ⅲ-Ⅴ ratio and substrate temperature on crystalline quality and crystalline phase structure of GaN film grown directly on Si (001) without any intentional inter-mediate layer, and especially occurrence condition of β-phase by a lot of experiments.

2 Experiment

The samples were grown in ESPD with a base pressure of 1.33×10^{-4}Pa. The main difference of ESPD from normal MOCVD equipment is the multi-cusp cavity-coupling ECR plasma source (MEP)[11] to provide active species of nitrogen and hydrogen for the first time. A significant character of MEP is almost free of static magnetic field in the reactor of ESPD. MEP can provide a uniform unmagnetized plasma with highly activate function (high energy electrons) and low ion damage (low energy ions and low space potential) for plasma processing of semiconductor[9,10]. The Langmuir probe and ion energy analyzer on the reactor were used to measure plasma parameters. A batch of quartz optical fiber inserted into the reactor was connected to a monochrometor with high-resolution to monitor relative concentration of active species in plasma, such as, hydrogen, and nitrogen radical. A more detail description of ESPD may be found elsewhere[10,11].

The epitaxy procedure of GaN films on Si (100) was shown in Fig. 1. Prior to growing GaN films, the Si substrates were cleaned and pre-processed in situ by hydrogen plasma at $T_H\approx450\sim550$℃ with a microwave power $P_w\approx550\sim600$W for $t_H\approx25\sim35$min, so that the native oxide layer was removed, and a fresh flat surface can be obtained for the growth of GaN film. Then, when TMGa was introduced into the reactor with H_2 carrier by a gas-puffed circle distant 5cm from the substrate, the GaN growth was started directly on Si(001) substrate by a two-step process including a buffer layer growth at low temperature $T_B\approx400\sim600$℃ for $t_B\approx20$nm thick and growth of GaN at high temperature $T_G\approx620\sim720$℃. The H-plasma was replaced by N-plasma to provide nitrogen radicals with a microwave power of 350~450W.

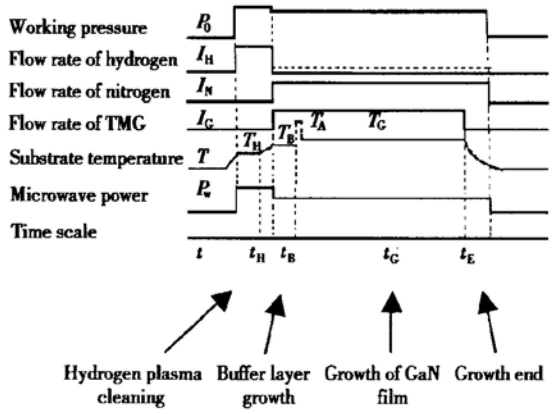

Fig. 1 Epitaxy procedure of GaN film grown directly on (001)Si by ECR-PEMOCVD

The GaN films were characterized by XRD in this work. The surface morphology of the buffer layers and GaN films were observed by AFM. The HRTEM observations of the GaN films were carried out by the high-resolution transmission electron microscope—JEOL-2010 (energy of electron beam = 200keV, resolution = 0.19nm) to investigate the microstructure of GaN films. The cross-section TEM dark-field image of the sample was obtained by using Phylips CM-12 (electron beam energy E_e = 100eV and magnification = 143k)

3 Results and discussion

3.1 H-plasma cleaning of Si(001) substrates in situ

To remove the native oxide layer on the surface of Si(001) substrates and to build a fresh substrate surfaces with atomic level flatness for GaN film growth with a good quality, H-plasma cleaning of the surface of substrates[19,20] in situ at 400~550℃ with P_w ≈ 500~600W for 15~35min was investigated. The experimental results show that H-plasma cleaning temperature T_H, time t_H and microwave power P_w have important effects on the crystalline quality and structure of GaN films. The FWHM and relative intensity of the (0002) XRD peak of GaN epilayers grown under different T_H for the same other conditions are shown in Fig. 2. The results show that when t_H < 20min and T_H < 500℃

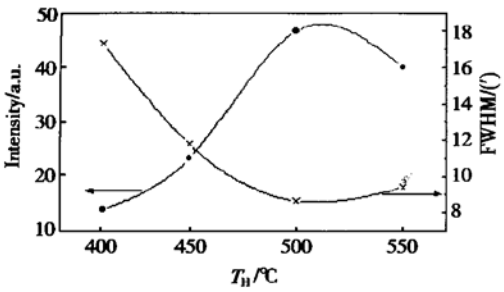

Fig. 2 Dependence of FWHM and intensity of XRD (0002) diffraction of GaN film on H-plasma cleaning temperature T_H under the same condition t_H ≈ 30min, P_w = 600W, V/III = 300, T_B = 500℃(20min) T_G = 620℃(5h)

or t_H > 35min and 550℃ > T_H, the crystalline quality is poor because there are few effects on substrates in former and the substrates surface is damaged in latter. The optimum conditions of H-plasma cleaning are T_H ≈ 550~500℃ and t_H ≈ 26~30min for P_w ≈ 600W.

3.2 Growth of buffer layer

The results of experiments show that a buffer layer with a smooth surface and good crystal quality is necessary for a GaN epilayer with good quality. The AFM images (2000nm × 2000nm) of GaN buffer layers grown at different temperature T_B are shown in Fig. 3. The surface of the buffer layer grown at 450℃ looks flat with small crystalline

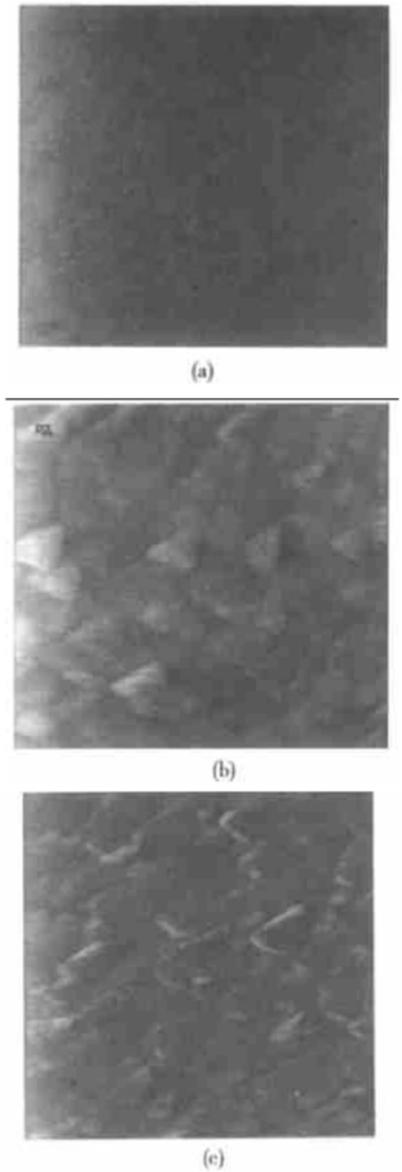

Fig. 3 Plan-view AFM images(2000nm × 2000nm) of buffer layers grown on Si(001) substrates at different growth temperatures (a) T_B = 450℃; (b) T_B = 500℃, (c) T_B = 550℃

grains as shown in Fig. 3 (a). This indicates a polycrystalline structure. We know from Fig. 3 (a), (b) and (c) that the higher T_B, the larger crystalline grain and the better crystalline grain orientation in the condition. The buffer layers with good quality are obtained under the growth condition of $T_B \approx$ 550℃, $t_B \approx$ 20min (the thikness≈250mn) and $P_w \approx$ 400W, as shown in Fig. 3 (c). The effects of crystal quality of the buffer layer on GaN epilayer quality are concerned in the following.

3.3 Growth of GaN films

The different growth conditions are further investigated. Figure 4 and Fig. 5 show AFM images and XRD diffraction patterns of GaN film of the samples A, B, and C grown under the conditions shown in Table 1. The I_N and I_{Ga} are flow rate of N_2 and TMG, respectively. It can be seen from the Fig. 4 (a) that the shape and orientation of the crystal grains of sample A are very poor and the surface is very rough. Correspondingly, the XRD diffraction pattern indicates two small peaks, the (0002) diffraction peak and ($10\bar{1}0$) diffraction peak of GaN as shown in Fig. 5 (a). This is due to poor quality of substrate surfaces obtained at a low cleaning temperature (450℃) and poor nucleation uniformity of GaN buffer layer induced by low mobility of Ga particles on the surface grown with big I_{Ga} at low growing temperature (620℃). Shape and orientation of crystal grains of sample B are better than that of sample A as shown in Fig. 4(b). Correspondingly, only strong (0002) diffraction peak of GaN film with FWHM ≈ 12′ can be seen from Fig. 5 (b). But we can also see from Fig. 4 (b) that the film surface is not smooth. This is due to fast growing of buffer layer at high temperature (600℃). It can be seen from the Fig. 4 (c) that the film surface of the sample C is smooth. The orientation of the crystal grains of sample C is better and crystal grains are bigger than that of samples A and B. Correspondingly, a strong (0002) diffraction peak of GaN with FWHM ≈ 9min (the film thickness≈0.5μm) is shown in Fig. 5 (c). Both of Fig. 5 (b) and (c) show high *c*-axis orientation of GaN growth.

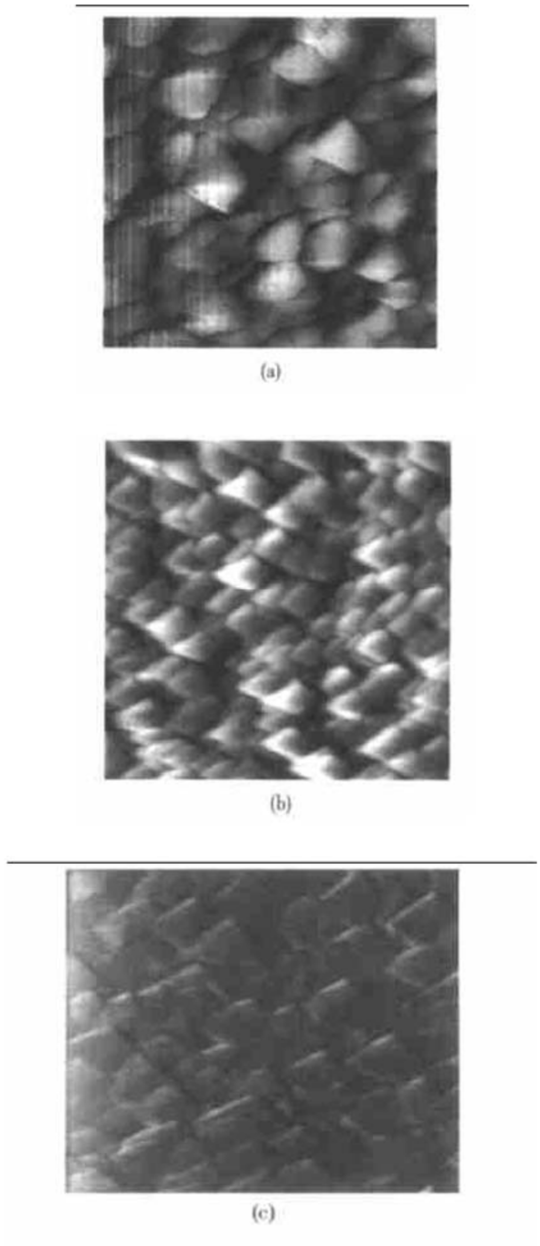

Fig. 4 Plan-view of AFM images (2000nm × 2000nm) (a) Sample A; (b) Sample B; (c) Sample C

Table 1 Growth conditions of samples A, B, and C

Sample	A	B	C
V/III	200	267	267
I_N(sccm)/I_{Ga}(sccm)	20/2.0	20/1.5	20/1.5
T_H(℃)/t_H(min)	450/30	500/30	500/30
T_B(℃)/t_B(min)	500/20	600/20	500/20
T_G(℃)/t_G(h)	620/5	720/5	700/5

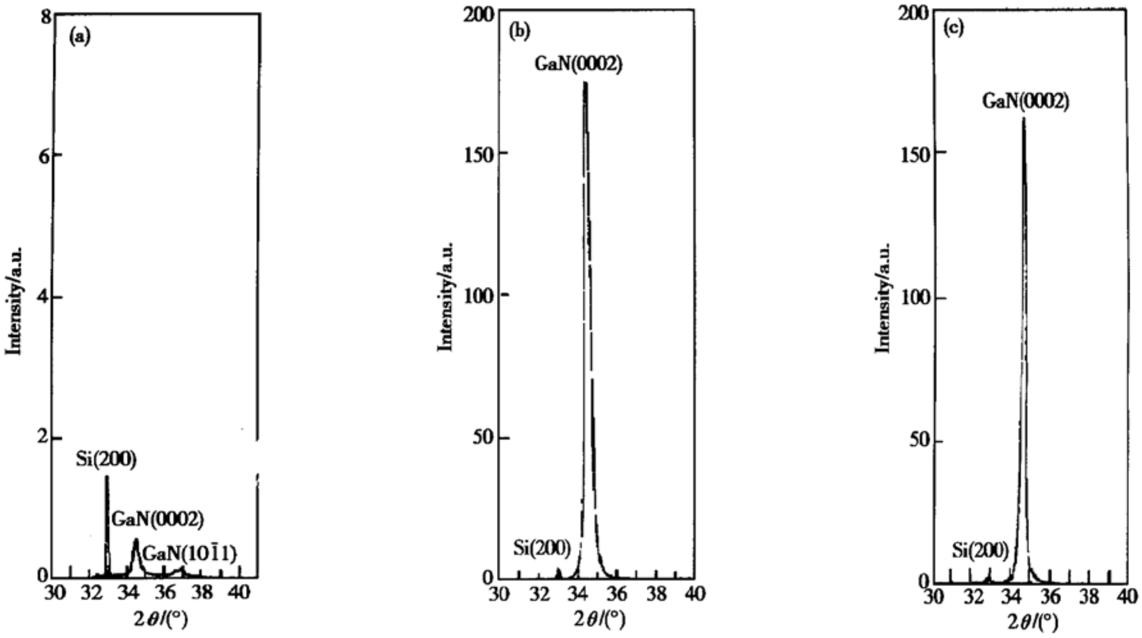

Fig. 5 XRD spectra of GaN films of samples A, B, and C

Figure 6 shows FWHMs and intensities of (0002) XRD peaks of GaN films grown on Si (001) under different Ⅴ/Ⅲ ratio for the same T_H

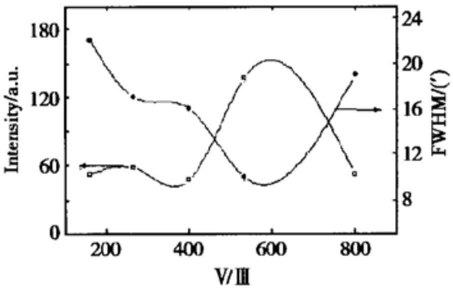

Fig. 6 Dependence of FWHM and intensity of XRD (0002) diffraction peaks of GaN epilayers on Ⅴ/Ⅲ rate

= 500℃, t_H = 30min, T_B = 550℃, t_B = 20min, T_G = 620℃, and P_w = 600W for H-plasma cleaning and P_s = 400W for two steps growth of GaN films. It is found that for a certain microwave power and growth temperature: (1) there is an optimum range of I_N and Ⅴ/Ⅲ ratio for growing GaN with high c-axis orientation as shown in Fig. 6; (2) when $I_N <$ 20sccm, crystalline quality of GaN epilayers becomes poor. This is caused by density decrease of N active particles of N-plasma with I_N decrease and N active particles density are too low to grow; (3) when N active particles increase with I_N increase to 60sccm, GaN (10$\bar{1}$1) diffraction peak at $2\theta \approx 36.9°$ appears. This can be explained as follows: more nitrogen particles is not favorable for mobilization of Ga particles on the growth surface. It is found that when Ⅴ/Ⅲ ratio is decreased from 500 to 200 or I_{Ga} is increased, the increase of growth temperature is favorable for improvement of crystalline quality of GaN epilayer as compared with Fig. 5(c).

The microstructure of the GaN films grown directly on Si(001) with a homoepitaxy layer on it is investigated by TEM, as shown in Fig. 7. The growth condition is the some to that of Fig. 6 except that Ⅴ/Ⅲ ratio is 540. Figure 7 (a) and (b) display two typical parts of the [110] HRTEM micrograph of the GaN films. It can be seen from Fig. 7(a) and (b) that no epitaxial growth of β phase occurred on Si (001) and a hexagonal GaN film is grown on an amorphous-like layer formed at GaN/Si interface. Both interface of the amorphous layer are atomical flat and the thickness of layer is fairly uniform for about 2nm. The layer is believed to be Si_xN_y formed in the initial nucleation stage of GaN growth owing to the interaction of the active N with the Si (001) surface[7] having no evident degradation observed. However, the crystallographic orientation shown in Fig. 7(a) demonstrates the heteroepitaxial relationship between the GaN epilyer and Si(001) substrate preserved as GaN (0001)/Si (001). Figure 7 (b) shows that there are domains of {0$\bar{1}$11} crystallographic orientation in the GaN film. This crystalline structure is characterized by XRD pattern with a strong (0002) diffraction peak and a small (10$\bar{1}$1) diffraction peak as shown in Fig. 8. The cross-section TEM dark-field image of the sample displays the characteristic columnar structure of α-GaN with a transition zone of homoepitaxy, a flat GaN/Si interface and a uniform thickness for about 500nm as shown in Fig. 7(c).

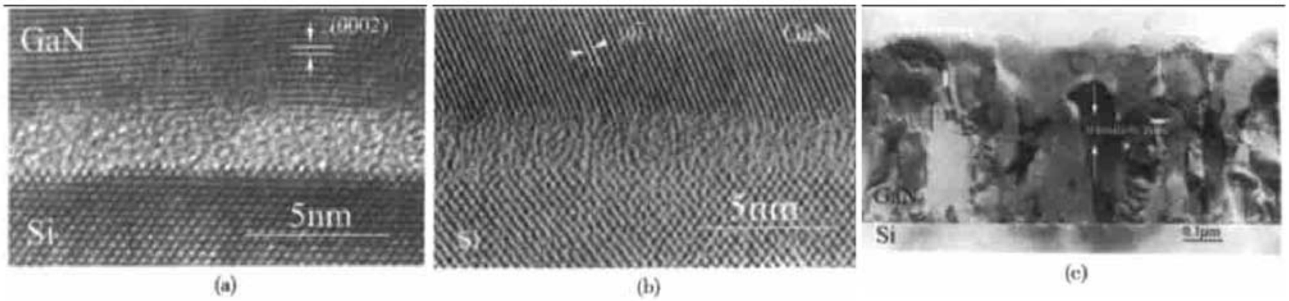

Fig. 7 HRTEM micrographs showing (a) epitaxial relationship of GaN (0001)/Si (001), (b) {0$\bar{1}$11} crystallographic orientation area, and both (a) and (b) showing the presence of amorphous layer at the interface; TEM dark-field image (c) showing characteristic columnar structure of α-GaN with a transition zone of homoapitaxy in the GaN film

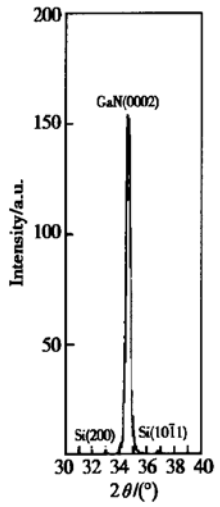

Fig. 8 XRD spectrum of GaN with homoepitaxy layer grown on Si(001) by ECR PE-MOCVD on ES-PD under the growth condition of Fig. 7(a)

A lot of experiment results show that β-GaN phase is not achieved and *c*-axis oriented crystalline α-GaN films are obtained even at low growth temperature of buffer layer. The studies demonstrate that the amorphous SiN layer formation is owing to the interaction between the active N and the Si (001) surface, and the amorphous layer acts as initial nucleation layer for the formation of h-GaN phase[6]. While epitaxial "cube-on-cube" orientation has occurred for growth of β-GaN on GaAs (001)[3,4] due to the coincidence lattice, the same effect is hampered for GaN-on-Si(001) due to the formation of the amorphous SiN layer at GaN/Si (001) interface[6].

4 Summary

The *c*-axis oriented crystalline h-GaN films are grown directly on Si (001) by ECR PE-MOCVD at low temperature using activated nitrogen species provided by cavity-coupling type ECR plasma source MEP for the first time. The FWHM of GaN (0002) diffraction peak from 0.5μm thick GaN film is 9′. HRTEM micrograph demonstrates that no β phase epitaxial growth occurred and α-GaN film is grown on an amorphous layer with a sharp interface and a uniform thickness for about 2nm at GaN/Si interface. The cleaning of Si (001) substrates surface in situ by H-plasma at low temperature is essential for growing GaN films. The buffer layer with flat surface and good crystal quality is necessary for epitaxial growth of GaN film with good quality. β-GaN phase is not achieved at low temperature, even at 400℃ for a buffer layer growth.

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GaN 在 Si(001) 上的 ECR 等离子体增强 MOCVD 直接生长研究*

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摘要: 研究了用电子回旋共振(ECR)等离子体增强金属有机物化学气相沉积(PEMOCVD)技术在 Si(001) 衬底上, 低温(620~ 720℃)下 GaN 薄膜的直接外延生长及晶相结构. 高分辨透射电镜(HRTEM)和 X 射线衍射(XRD)结果表明: 在 Si(001) 衬底上外延出了高度 c 轴取向纤锌矿结构的 GaN 膜, 但在 GaN/Si(001) 界面处自然形成了一层非晶层, 其两个表面平坦而陡峭, 厚度均匀(≈2nm). 分析认为, 在初始成核阶段 N 与 Si 之间反应所产生的这层 Si_xN_y 非晶层使 GaN 的 β 相没有形成. XRD 和原子力显微镜(AFM)结果表明, 衬底表面的原位氢等离子体清洗, GaN 初始成核及后续生长条件对 GaN 膜的晶体质量非常重要.

关键词: PEMOCVD; GaN/Si (001) 界面; 晶相结构

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