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Effects of *in situ* Annealing on Optical and Structural Properties of GaN Epilayers Grown by HVPE

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Abstract: Effects of *in-situ* annealing on the structural and optical properties of Gallium nitride (GaN) layers grown on (0001) sapphire by hydride vapor phase epitaxy (HVPE) are studied. The properties of GaN epilayers are improved by *in-situ* annealing at growth temperature under ammonia (NH_3) atmosphere. X-ray diffraction (XRD) analysis shows that the full width at half maximum (FWHM) of the rocking curves narrows as the annealing time increases. Raman scattering spectroscopy shows that E_2(high) peak positions shift to the low frequency region. Compared to without annealing and epilayers annealed with bulk GaN, the E_2(high) peak position of epilayers becomes closer to that of bulk GaN as the *in situ* annealing time increases. The biaxial compressive stress decreases after *in-situ* annealing. Photoluminescence (PL) examination agrees well with XRD and Raman scattering analyses. These results suggest that the optical and structural properties of GaN epilayers can be improved by *in situ* annealing.

Key words: GaN; *in situ* annealing; HVPE
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1 Introduction

In recent years, GaN has attracted attention because of its potential applications in optoelectronic and microelectronic devices such as blue lighting-emitting diodes[1], blue laser diodes[2], and high-power electronic devices[3] and because of its wide band gap, high breakdown field, and high saturation drift velocity[4]. However, the growth of high performance GaN devices is obscured due to the absence of thermal constant and lattice matched substrates. Thus, hydride vapor phase epitaxy (HVPE) is a promising technique for the growth of quasi-homogenous substrates, because of its high growth rate and relatively high quality in comparison with other bulk growth techniques. In order to obtain high-quality GaN epitaxial films, it is important to optimize the growth process, including growth temperature, and control the gases ratio and annealing after growth. A number of investigations on the thermal annealing process for GaN epilayers have been reported[5~7], but there are few reports on *in situ* annealing after HVPE-GaN growth[8]. To further improve the qualities of GaN epilayers, we have investigated the effects of the *in situ* annealing process on the crystalline qualities.

In this letter, we focus on the influence of *in situ* annealing on HVPE-GaN epilayers. We present the results of optical and structural studies of GaN epilayers grown by HVPE on sapphire substrates with different annealing times at the same temperature. The crystalline optical and structural performances of GaN layer are characterized by X-ray diffraction (XRD), Raman scattering, and photoluminescence (PL) measurements.

2 Experiment

The templates used for HVPE-GaN growth were grown by molecular beam epitaxy (MBE) on *c*-plane sapphire. In order to make a fair comparison, the templates were grown under the same conditions. The growth was carried out at atmospheric pressure in a home-built vertical HVPE system. First, HCl gas passed through a Ga boat and reacted with melt Ga to form GaCl in the source zone. Then, GaCl was transported to the growth zone and reacted with NH_3 to form GaN. During the growth process, the flow rates of HCl remained at 15sccm. The source zone temperature was held at 850℃ and the growth zone temperature was 1050℃. Details of reactor and growth conditions are reported in Ref. [9]. When the growth of GaN films are completed, the samples remained in the system at growth temperature for annealing under NH_3 ambience. The annealing time of growth-GaN varied from 0 to 1, 2, and 3h for samples A, B, C, and D, respectively.

XRD was carried out with a Philips X'pert dif-

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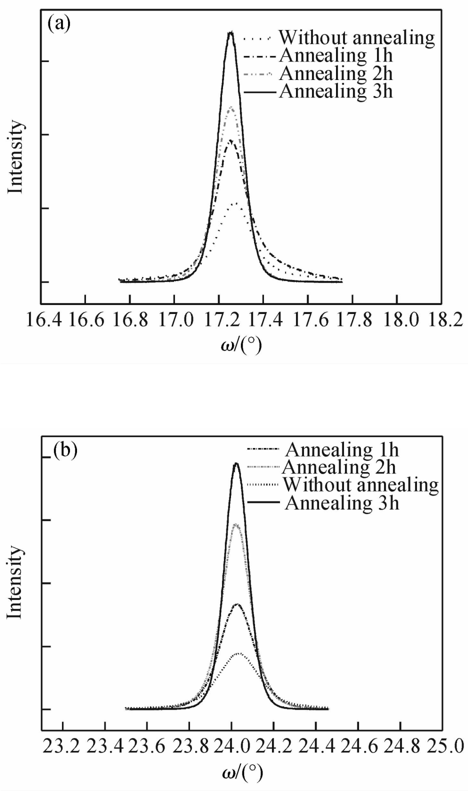

Fig. 1 (a) Rocking curves for the symmetric (0002) reflections of GaN epilayers for different annealing times; (b) Rocking curves for the asymmetric ($10\bar{1}2$) reflections of GaN layers for different annealing times

fractometer (X'pertpro MPD) with CuKα1 radiation. The samples were characterized by spatially resolved micro-Raman scattering in the back scattering geometry at room temperature. The laser was an argon ion laser operating at 514.5nm (2.41eV). The spectral resolution was 0.2cm^{-1} and the lateral resolution during Raman mapping was less than 1.0μm. Photoluminescence measurement was performed at room temperature with modulated laser optical excitation from a Verdi-V6/Mira900/THG-266 laser system at 4mW. The signal was dispersed by a monochromator with 1800lines/mm grating and detected by a photo counting detector.

3 Results and discussion

These samples differed in the annealing time after growth. Their thicknesses were about 20μm after 20min of growth. To investigate the crystalline quality, we measured the X-ray rocking curves of the GaN. Figure 1 (a) shows the rocking curves for the symmetric (0002) reflections of GaN layers for different annealing times. The full width at half maximum (FWHM) of the rocking curves reflects the material's crystalline quality. In Fig. 1 (a), the FWHM of HVPE-GaN after annealing for 0, 1, 2, and

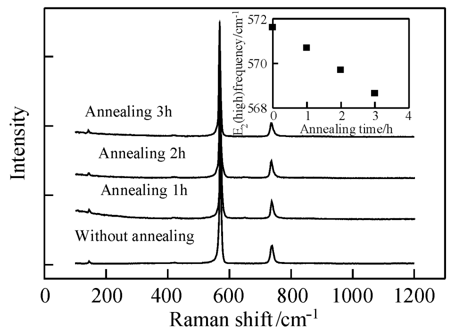

Fig. 2 Raman spectra of without annealed and annealed GaN
The inset shows the E_2 (high) frequency of GaN epilayers decreased as the annealing time increased.

3h are 0.185°, 0.171°, 0.152°, 0.129°, respectively. The rocking curves of symmetric planes are normally responsive to mosaic dislocations but insensitive to the pure edge threading dislocations because these planes are undistorted by pure threading dislocations (TDs) and the (0002) plane rocking curves can be broadened by screw and mixed TDs[10]. The narrow peak of (0002) diffraction suggests that some screws and mixed TDs are reduced. The FWHM values presented in the rocking curves from the samples become narrower as the annealing time of GaN increases. These results suggest that the crystalline quality became better as the annealing time increased.

Additionally, asymmetric reflections compared with the symmetric reflections is indicative of a defect structure with a large pure edge TDs content since the (0002) peak is only broadened by screw and mixed TDs while the ($10\bar{1}2$) peak is broadened by all TDs[11]. For the rounded analysis of defects of GaN epilayers, the rocking curves for asymmetric ($10\bar{1}2$) is shown in Fig. 1 (b). The narrow peak of ($10\bar{1}2$) indicates induced defects. The FWHM values of the ($10\bar{1}2$) reflection decrease from 0.228° to 0.131° as the annealing time increases from 0 to 3h. Thus, the crystalline quality is improved when the annealing time increases.

The layer is highly strained at the initial growth stage due to the quick coalescence and the lattice mismatch between the epitaxial films and the substrates, and structural defects probably occur. In the case of the growth process annealing, there is time for the strain to relax and grains can coalesce and grow in size. In order to elucidate the relationship between strain relaxation and *in situ* annealing, Raman scattering analyses of GaN were performed. The shift of the E_2 (high) mode is related to the biaxial stress in the GaN epilayers. The shift of the E_2 (high) mode towards higher frequency corresponds to the state of compressive stress in the samples studied. As shown in Fig. 2, the peaks of the E_2 mode from samples A, B,

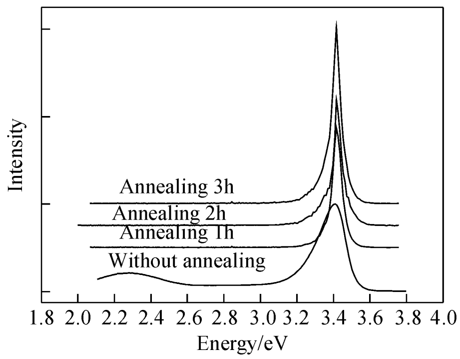

Fig. 3 Comparison between PL spectra recorded on the as-grown and the annealed samples in NH_3 The inset shows the FWHM of PL narrowed as annealing time increased.

C, and D were detected at 571.6, 570.7, 569.7, and 568.6cm^{-1}, respectively. The shift of the E_2 line for the annealed samples is less than that for sample A without annealing.

Based on these values, we calculated the biaxial compressive stress using the well-known formula as follows: $\Delta\omega_\gamma = \kappa_\gamma \sigma_{\chi\chi}$[12,13], where $\Delta\omega_\gamma$ is the Raman shift, $\sigma_{\chi\chi}$ is the biaxial stress, and κ_γ is the stress coefficient. κ_γ of GaN was taken to be 2.56cm^{-1}/GPa from the literature and $\Delta\omega_\gamma$ is the shift of E_2(high) mode from the peak position of a bulk GaN (567.8cm^{-1})[14]. The average residual stress in the sample D is about 0.3GPa, while in the sample A without annealing it is about 1.48GPa. Therefore, the biaxial compressive strain was relaxed after *in situ* annealing. Thus, the *in situ* annealing process improved the crystalline qualities at the surface of the GaN strained layer resulting from the relaxation of the residual compressive strains caused from disordered lattice distribution.

In order to investigate the effect of *in situ* annealing on optical properties, a PL measurement of GaN samples annealed for different time in NH_3 atmosphere was performed. The variation of PL spectra and intensity for the GaN samples are shown in Fig. 3. The broad band between 2.0 and 2.4eV in the PL spectra is known as yellow luminescence (YL). In general, it is believed that this YL not only involves electronic states associated with native defects such as vacancies, antisites, and interstitials in material[15], but is also strongly related to the density of screw-type and edge-type dislocations[16,17]. In Fig. 3, YL is observed in sample A but not observed in samples B, C, and D, indicating that the *in situ* annealing can decrease the defects in GaN epilayers. Room-temperature PL spectra of GaN crystal are dominated by the band-edge transition at 3.39eV. From the relative intensity of the band-edge PL peaks, the sample D shows the maximum enhancement of the PL intensity and the smallest FWHM value. These results imply that the *in situ* annealing improves the crystalline quality of HVPE-GaN epilayers.

4 Conclusion

In summary, the effects of *in situ* annealing on the optical and structural characteristics of GaN layers grown by HVPE on (0001) sapphire were investigated. XRD, Raman scattering, and PL were used to characterize the samples. The improved results are considered to be due to the decrease of defects and the relaxation of biaxial compressive strain in HVPE-GaN epilayers by *in situ* annealing. The results suggest that *in situ* annealing is an effective method to improve the optical and structural properties of GaN epilayers.

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原位退火对 HVPE 生长的 GaN 外延层光学性质和结构的影响

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摘要：研究了原位退火对用氢化物外延方法在(0001)面蓝宝石衬底上生长的氮化镓(GaN)外延薄膜的结构和光学性能的影响.测试表明,氨气气氛下在生长温度进行的原位退火,明显提高了 GaN 外延膜的质量.X 射线衍射(XRD)分析表明,随着原位退火时间的增加,(0002)面和($10\bar{1}2$)面摇摆曲线的半峰宽逐渐变窄.喇曼散射谱显示样品退火后 E_2(high)峰位向低频区移动;随着退火时间的延长,趋向于块状 GaN 的峰位.可见,原位退火使 GaN 外延膜中的双轴应力明显减少.光致发光的测试结果与 XRD 和喇曼散射谱的结论一致.表明原位退火能有效提高 GaN 外延膜的结构和光学性能.

关键词：GaN；原位退火；氢化物气相外延
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