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Micro-Raman Spectroscopy Characterization of GaN Grown on Maskless Periodically Grooved Sapphire Fabricated by Wet Chemical Etching

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Abstract: Micro-Raman spectroscopy is performed to characterize GaN films grown on the patterned sapphire (0001) fabricated by wet chemical etching. The stress distributions are characterized by the frequency shift in the micro-Raman spectroscopy measurements. Residual stress state and carrier concentration in the mesa and wing region are assessed. The wing region shows lower compressive stress and less carrier concentration in comparison with mesa region. That is due to the interactions between sapphires and GaN as the result of differences in the coefficients of thermal expansion are excluded in the wing region by adopting maskless periodically grooved sapphire, thus less compressive stress and lower background carrier concentration can be achieved by this method.

Key words: GaN; MOCVD; Micro-Raman spectroscopy

蓝宝石图形衬底上生长 GaN 的微区拉曼光谱研究

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摘 要: 采用微区拉曼光谱对生长在湿法腐蚀获得的无掩膜周期性图形蓝宝石衬底上 GaN 材料做了研究, 结果显示, 侧向外生长区域具有较低的压应力。采用湿法腐蚀结合原子力显微镜对材料的位错进行了表征, 侧向外延区域显示了低的位错密度, 具有较高的晶体质量。另外通过对不同生长区域的拉曼纵光学声子与等离子体激元形成的耦合模高频支进行拟合, 结果显示侧向外延区域具有较低的背底载流子浓度。研究认为, 由于采用图形衬底, 侧向外延区域悬空生长降低了位错密度, 同时侧向外延区域不与蓝宝石接触, 因此采用该方法生长的 GaN 材料具有较低的压应力和较低的背底载流子浓度。

关 键 词: 氮化镓; 金属有机化学气相沉积; 微区拉曼光谱

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1 Introduction

GaN-based bandgap semiconductors have drawn a lot of attractions due to their current and potentials toward optoelectronic devices^[1-3]. However, large lattice mismatches between GaN and the substrate often lead to high defect densities. Recent evidences have shown that the dislocations act as nonradiative centers, which influence performance and cause degradation of GaN-based devices^[4]. Many effective methods have been developed to minimize dislocation densities. Epitaxial-lateral-overgrowth (ELO) is one of the most important techniques to reduce dislocation densities^[5]. Recently, high quality GaN film grown on maskless periodically grooved sapphire by wet chemical etching has been reported^[6]. Compared with the usually used patterned substrate made by dry etching, wet etching can avoid the mechanical damages on the grooved surface, which is promising way to get higher quality GaN-based materials films.

In this paper, micro-Raman scattering spectra were carried out to characterize GaN grown on (0001) maskless periodically sapphire substrates by metal organic chemical vapor deposition (MOCVD). Residual stress state and carrier concentration in the mesa and wing region is assessed. The wing region show lower compressive stress and less carrier concentration in comparison with mesa region. That is due to the interactions between sapphire and GaN as the result of differences in the coefficients of thermal expansion are excluded in the wing region by adopting maskless periodically grooved sapphire, thus less compressive stress and lower background carrier concentration can be achieved by this method.

2 Experiments

Unintentional doped 1.5 μm thick GaN films were grown on maskless patterned sapphire by MOCVD. Fig. 1 shows the schematic of

fabrication procedure for patterned sapphire. The sapphire substrates were patterned along with 3 μm wide mesa and 3.5 μm wide wing with standard photolithographic procedures, which was obtained by wet chemical etching in the solution of $V(\text{H}_2\text{SO}_4) : V(\text{H}_3\text{PO}_4) = 3 : 1$, followed by dipping in the solution of $V(\text{HF}) : V(\text{H}_2\text{O}) = 1 : 10$ for removal of SiO_2 . Thermal annealing process was carried out at around 1070 $^\circ\text{C}$, followed by the growth of thick GaN nucleation layer on the sapphire wafer at temperature of 520 $^\circ\text{C}$. Typical GaN growth temperature is 1100 $^\circ\text{C}$. Trimethylgallium (TMGa) and ammonia (NH_3) were used as precursors for Ga and N, respectively, and H_2 as carrier gas. Micro-Raman scattering experiments were carried out in backscattering geometry at room temperature, which were performed with multichannel modular triple Raman systems (JY-T6400), a 100X microscope objective lens was used for focusing the laser beam and collection of the scatter light. Under such conditions, the spatial resolution of instrument is about 1 μm , the solid-state diode laser(532 nm) was used as an excited source. Hot wet chemical etching was performed in a mixture of $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4$ with a volume ratio of 3:1 at 280 $^\circ\text{C}$ for 15 min to reveal the density of threading dislocations. The morphology and distribution of etch pits is measured by atomic force microscopy (NanoScope III a-D3000 AFM).

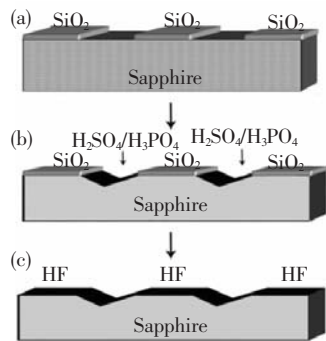


Fig. 1 Schematic of the procedure for GaN grown on maskless periodically grooved sapphire by wet chemical etching

3 Results and Discussion

Typical Raman spectra for the sample is shown in Fig. 2. Two dominant peaks in both regions corresponded to E_2 (high) and A_1 (LO) photon mode, which is in agreement with selection rules^[7]. E_2 (high) photon mode is known to be affected by stress, the E_2 (high) of mesa and wing region is 570.4 cm^{-1} and 569.7 cm^{-1} , both regions are larger than strain free crystal sample whose E_2 mode is located at 567.2 cm^{-1} ^[8], so both regions are under compressive stress. For GaN, the E_2 (high) mode shifts linearly with stress with $2.9 \text{ cm}^{-1}/\text{GPa}$ for biaxial stress^[8]. The compressive stresses calculated in the mesa and wing region are 1.1 GPa and 0.86 GPa , respectively. The mesa is under large compressive stress than the wing region, so more relieved stress was achieved in wing region by this method. General crystalline quality can be accessed by the width of the E_2 (high) line^[9]. The line width of E_2 (high) for the mesa and wing region is 2.83 cm^{-1} and 2.57 cm^{-1} respectively, a minimum in linewidth was detected in the wing region.

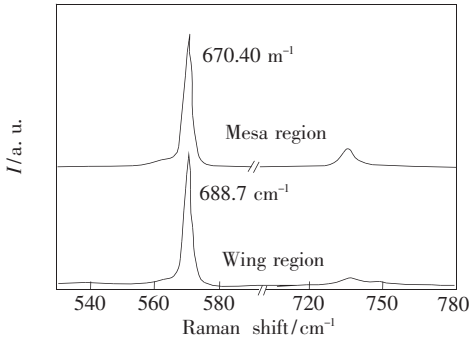


Fig. 2 Micro-Raman spectroscopy of mesa and wing region for GaN grown on grooved sapphire

Hot wet etching with mixed $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4$ solutions are performed to reveal the dislocation distribution. It has been reported that hot wet etching combining with AFM can effectively characterize dislocations^[10]. Typical AFM images of the etched surface morphology of two samples are showed in Fig. 3 with a measuring scale of $20 \mu\text{m} \times 20 \mu\text{m}$.

The diameter of the pits is almost uniform,

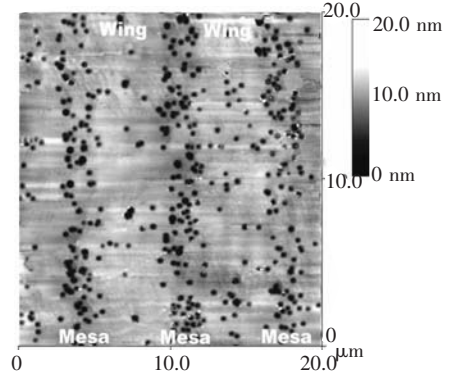


Fig. 3 Etched surface morphology of GaN sample on maskless periodically grooved sapphire

which have been attributed to the surface termination of threading dislocations. The pits are regularly spaced and arranged, the pits concentrated in the mesa region, in contrast, the wing region contains fewer etch pits. It displayed the crystalline quality in the wing region is better than that in the mesa region, which further confirmed the micro-Raman E_2 (high) linewidth observation.

In general, the carrier concentrations for doped GaN can be obtained from Hall measurements, but it was difficult to measure undoped GaN because of high resistivity. It has been proved carrier concentrations obtained from Raman scattering methods and Hall measurements agree well^[11]. From the energy position of the LPP^+ mode we were able to estimate the free-carrier concentration. The dotted line in the Fig. 4 shows the experimental micro-Raman spectra in the range from 720 cm^{-1} to 770 cm^{-1} . The solid, dashed, and dotted lines are $A(\text{LO}) + \text{LPP}^+$, $A_1(\text{LO})$, and LPP^+ , respectively. Since the shape of the $A_1(\text{LO})$ line is assumed to be Lorentzian, experimental data was fitted by Lorentzian fitting, a fairly good fit has been obtained. The position of LPP^+ in the mesa and wing region is 750.88 cm^{-1} and 742.65 cm^{-1} respectively. A convenient empirical formula has been proposed for deducing carrier density from the observed frequency shift $\Delta\omega (\text{cm}^{-1})$ of the LPP^+ mode frequency^[12].

$$n = 1.1 \times 10^{17} \text{ cm}^{-3} \Delta\omega^{0.764}$$

The free carrier concentration in the mesa

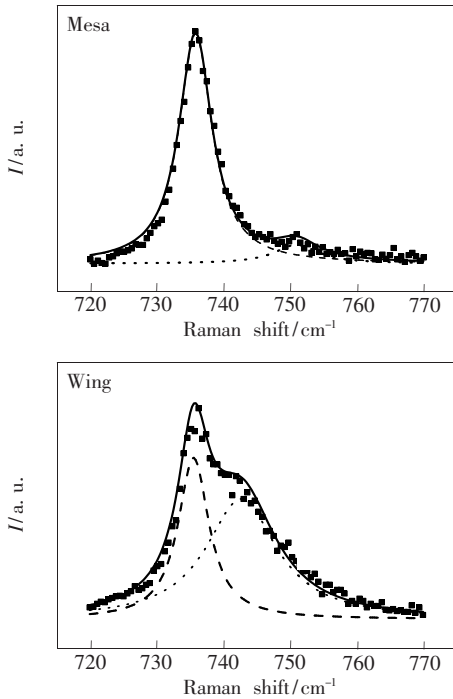


Fig. 4 Solid squares are the experimental micro-Raman data from the mesa and wing region of GaN sample grown on patterned sapphire. The solid, dashed, and dotted lines are $A(LO) + LPP^+$, $A_1(LO)$, and LPP^+ , respectively, obtained by fitting.

and wing region determined from the formula is $8.65 \times 10^{17} \text{ cm}^{-3}$ and $4.68 \times 10^{17} \text{ cm}^{-3}$ respectively. A minimum carrier concentration is shown in the wing region.

4 Conclusion

Using micro-Raman spectra, the stress and free carrier concentration in the wing and mesa regions of $1.5 \mu\text{m}$ thick GaN films grown on pattern sapphire substrates was studied. The results show that wing regions display a minimum in compressive stress and a reduced carrier concentration compared to that of the mesa regions. That is due to the interactions between sapphire and GaN as the result of differences in the coefficients of thermal expansion are excluded in the wing region by adopting maskless periodically grooved sapphire, thus less compressive stress and lower background carrier concentration can be achieved by this method. In addition, narrower linewidth of E_2 photon mode reveals higher quality GaN in the wing region.

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