Evaluations of GaN film grown on patterned Si (111) templates substrates

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Low stress, low defect density GaN was successful grown on circle array patterned Si (111) substrate using AlN as the nucleation buffer followed by two steps growth of the GaN film. Raman measurement shows a reduction of in plane biaxial stress for the GaN film grown on patterned substrate. The slight blue-shift of the band edge PL peaks further provides the evidence that the tensile stress in the GaN film was relaxed in the patterned Si substrate. It's believed that the grain boundaries of the polycrystalline AlN buffer layer and the dislocations in the GaN film grown helped to relieve the stress induced by the lattice and the thermal coefficient mismatches during growth.

1. Introduction

The GaN material is receiving much attention due to the current and potential applications in high power high frequency electronic devices, light emitting diodes (LEDs), laser diodes (LDs), and photo detectors (PDs).1) Using Si substrates for the growth of GaN has been a subject of great interest owing to its low cost, large size, and good thermal and electrical conductivities. However, large mismatches in lattice parameter and thermal expansion coefficient between GaN and the Si substrate lead to the formation of cracks and high dislocation density. Therefore, thick GaN epilayer on Si substrate for device fabrication is hard to achieve without cracks. Furthermore, the melt etching of Si during the grown of GaN layer results in the formation of polycrystalline GaN on Si substrate. Many techniques have been employed to improve the crystalline quality of GaN epilayers grown on Si substrates.2-6) Selective area growth and lateral epitaxial overgrowth were found effective in alleviating the defect issue.7) In this work, we utilize the periodic circle array patterned Si (111) substrate as the template for the growth of GaN by metal-organic chemical vapor deposition (MOCVD). The structural and optical properties of GaN films grown are then measured and analyzed.

2. Experimental

The GaN epilayers in this study were grown on Si (111) substrate using EMCORE D-180 MOCVD reactor and the growth details are similar to that described in the previous report.8) Prior to the growth, periodic circle pattern with depth of 500 nm was fabricated on the Si substrate by standard photolithography and followed by Inductively Coupled-Plasma (ICP) etching with the mixture of BCl_3,Cl_2, and Ar gases.

Subsequently, the patterned Si template was chemically cleaned with $H_2SO_4 : H_2O_2 : H_2O$ (3:1:1) solution for 5 min followed by DI water rinse and blown dry with nitrogen gas before it was loaded in the reactor for MOCVD growth. Scanning electron microscopy (SEM) was used to observe the surface morphologies of the GaN films grown. The crystal quality of the sample grown was investigated using transmission electron microscopy (TEM) (JEOL 2010) with field emission gun microscopy operating at 200KV. Besides, photoluminescence (PL) emissions of the samples were investigated using He–Cd laser (325 nm) at room temperature. The Raman spectra of the sample were obtained at room temperature using Ar^+ laser with 488 nm incident wavelength.

3. Results and Discussion

SEM micrograph of the patterned Si prepared by ICP dry-etching method is inserted at the top left corner of Fig. 1 (a). The diameter and depth of the circular pattern are 4.5 μm and 500 nm, respectivily. As can be seen from this figure, the patterns are uniformly arranged and having homogeneous size distribution. Several growth runs were carried out to investigate the nature of GaN grown at different growth durations. Fig. 1 (a) to (f) are the SEM micrographs of the GaN films grown at different durations of (a) 20 min, (b) 30 min, (c) 40 min (d) 50 min (e) 60 min and (f) 70 min. At short growth time, GaN grew as isolated islands with valley and ridge regions as shown in Fig.1 (a). It can be observed that the GaN material grown on patterned Si substrate has a hexagonal shape during the initial stage of growth. The insert SEM micrograph at the lower right corner of Fig. 1 (a) shows that the small GaN islands at the intersections of the large hexagonal GaN islands grown from the patterned areas also have hexagonal pyramid shapes. The islands started to coalesce to form larger mesas as the growth time increased as shown in Fig.1 (b). At growth time of 40 min, partial coalescence took place at the valley regions and the cavities on the GaN film shrunk to smaller size as shown in Fig. 1(c). In the initial stage, the GaN grown on patterned Si has hexagonal pyramid shape with (0001) top facet and six side facets. The top facet and side facets form ~61° angle with respect to each other. Therefore the inclined facets are atomically flat {-1101} planes. With further growth, the GaN layer on the valley and ridge regions coalesced and formed a continuous film, as shown in Fig. 1 (d) to (e). Based on the growth parameters, the growth of GaN with smooth surface was achieved with two steps. The first step is the “coalescence stage” which was accomplished at 1000℃, in this step, the growth parameters was tuned so that the film grew faster in the vertical direction, Fig. 1 (a) to (e) show the film grown at the first step. The smoothing of the surface was achieved by adjusting the growth parameters with a different Ⅲ/Ⅴ ratio and at a higher temperature so that the laterally growth will dominate, this is considered as the second step. The film after the second step growth is shown in Fig.1 (f).

In order to better understand the growth mechanism and the dislocation distribution, GaN grown on the patterned Si was investigated by TEM. The cross-sectional TEM images of GaN on periodic patterned Si are shown in Fig. 2 and Fig. 3. Island nucleation is a typical growth mechanism for the AlN buffer layer, the layer exhibits the well-known columnar structure with tilts and twists between the subgrains. As can be seen in Fig. 2 (a), there are numerous subgrains in the AlN buffer layer, these subgrains are misoriented with respect to each other. These subgrains retained their particular orientations upon coalescence during the epilayer growth, resulting in many dislocations at the coalescence boundaries. High resolution image of the AlN/Si interface is shown in Fig. 2 (b), evidencing that the AlN film is polycrystalline with small subgrains. This is different from AlN grown on plane Si substrate without patterns which is usually crystalline. The reason for the difference is that for the patterned substrate, the AlN film may grow from the sidewall as well from the bottom of the pattern. Fig 3 (a) shows a large density of threading dislocations at the GaN/AlN interface at the bottom of the patterned valley region, but dislocation annihilation occurred as the GaN layer grew thicker, resulting in a significant reduction of the threading dislocation density at the top of the GaN film. Defects at the coalescence boundaries are marked by the arrowheads in Fig. 3 (b), most of these coalescence dislocations terminated at the boundary of the second step growth layer. Such phenomena are quite similar to the report by Hersee *et.*9) During the second step lateral growth stage, the threading dislocations terminated at the boundary of the lateral growth layer, and the dislocation density was greatly reduced. Therefore, a reduction of dislocations density was achieved, and the second step lateral growth film had much lower dislocation density. The result is quite similar to that reported by Feltin *et.*10) Either in the AlN buffer and or in the GaN film, the dislocations at the AlN grain boundaries and the coalescence dislocations of GaN film could help to relieve the strains induced by the lattice and thermal expansion coefficient mismatches.

To determine the in-plane residual stress in the GaN films, the samples were subjected to room temperature Raman measurements. The room temperature Raman spectra of the E_2-high for the samples are presented in Fig. 4. The spectra show strong E_2 (TO)-high under z(x_)-z scattering geometry. The E_2 (high) phonon scattering was utilized to characterize the tensile stress distribution. The E_2 (high) phonon peak is known to shift by in-plane stress only. For GaN grown on patterned Si and on non-patterned Si samples (with the same growth condition), the Raman spectra of E_2 (TO) phonon peaks were 564.10 cm^{-1} and 563.56 cm^{-1}, respectively. The residual stresses in the samples were calculated from the measured wave number shifts of the

E_2-high mode in the Raman spectra.11) The values of tensile stresses in GaN films (GaN on patterned Si = 0.79 GPa, GaN on non-patterned Si = 0.916 GPa) were calculated using the E_2 phonon peak observed at 567.5 cm^{-1} for a 400 μm thick free standing, strain free GaN and the relation $\Delta\omega = K\sigma_{xx}$ cm^{-1} GPa^{-1} . Here $\Delta\omega$ is phonon peak shift, σ is biaxial stress and K= 4.3 is the pressure coefficient.12) For GaN grown on patterned Si, the in-plane stress was 15.9% lower than that of GaN grown on the non-patterned Si. Compared with the reported results, the residual stress in the GaN films here is slightly lower than that reported by Hersee *et al.*9) (0.84~0.88 GPa) and Wang *et al.*13) (0.81 GPa) which grew GaN on nano-patterned substrates prepared by interferometric lithography, while higher than that reported by Liang *et al.*11) (0.68 GPa) and Zang *et al.*14) (0.57) GPa which used nanopore array Si as the template for GaN growth.

Fig. 5 shows the room temperature PL spectra of GaN grown on patterned and non-patterned substrates. A strong band edge emission of GaN on patterned Si is seen at the energy of 3.408 eV, which indicates that the GaN film is of hexagonal phase rather than cubic GaN (excitonic emission around 3.2 eV). The increase in the peak intensity also indicates that the crystalline quality was improved for GaN grown on patterned substrates. An enhancement in PL intensity for GaN grown on patterned substrates may also be due to the internal reflection on the patterned sidewall of the subs0trate. This periodic pattern improves the light-efficiency due to the stronger back scattering effect relative to other methods such as stripe pattern and nanoporous substrates.[15)] The slightly blueshift of the band edge PL peaks further supports the evidence of relaxation of tensile stress in GaN films through periodic pattern on Si substrate.

4. Conclusions

In summary, smooth GaN surface with low defect density was successfully grown on the patterned substrate using AlN as the nucleation layer followed by two steps growth of the GaN layer. TEM micrograph shows that the buffer AlN film grown is polycrystalline and the coalescence dislocations in the GaN film during first step growth were terminated at the boundary of the GaN film grown at second step. Thus, the GaN film grown by two steps growth demonstrated low defect density even though the GaN film grown at the first step had high dislocation density. The dislocations at the AlN polycrystalline boundaries and the coalescence dislocations at the GaN film helped to accommodate the stresses induced by the lattice and thermal expansion mismatches during growth. The room temperature Raman measurement shows a reduction of in plane biaxial stress in the GaN grown on patterned substrate compared to the GaN film grown on blank Si substrate. The slightly blueshift of the band edge PL peaks further provides the evidence that the tensile stress in the GaN film was relaxed in the periodic patterned Si substrate. These results demonstrate the potential of using the circle array patterned substrate for low stress high quality GaN growth on Si substrate.

Acknowledgement

This work was supported by the Ministry of Economic Affairs and the National Science Council of Taiwan under the contracts: NSC97-2221-E-009-156-MY2 and NSC98-2923-E-009-002-MY3

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Figure Captions

Fig. 1. SEM images of GaN grown on patterned Si substrate for the growth time of (a) 20 min (b) 30 min (c) 40 min (d) 50 min (e) 60 min (f) 70 min; Photo inserted at the top left corner of Fig. (a) shows the circular pattern with depth and diameter of 500 nm and 4.5 μm respectively; Inserted at the lower right corner of Fig. (a) shows the small GaN islands at intersections also have hexagonal pyramid shapes.

Fig. 2. High resolution TEM image showing the AlN buffer layer with subgrains of different orientations.

Fig. 3.The cross-section TEM images of GaN film grown by two step growth on circle array periodic patterned Si (111) substrate, (a) Image from the bottom of the valley region (b) Image from the ridge region.

Fig. 4. Raman spectra of GaN films grown on patterned and non-patterned substrates.

Fig. 5. Room temperature PL spectra of GaN epilayers grown on patterned and non-patterned Si substrates.

Fig. 1.

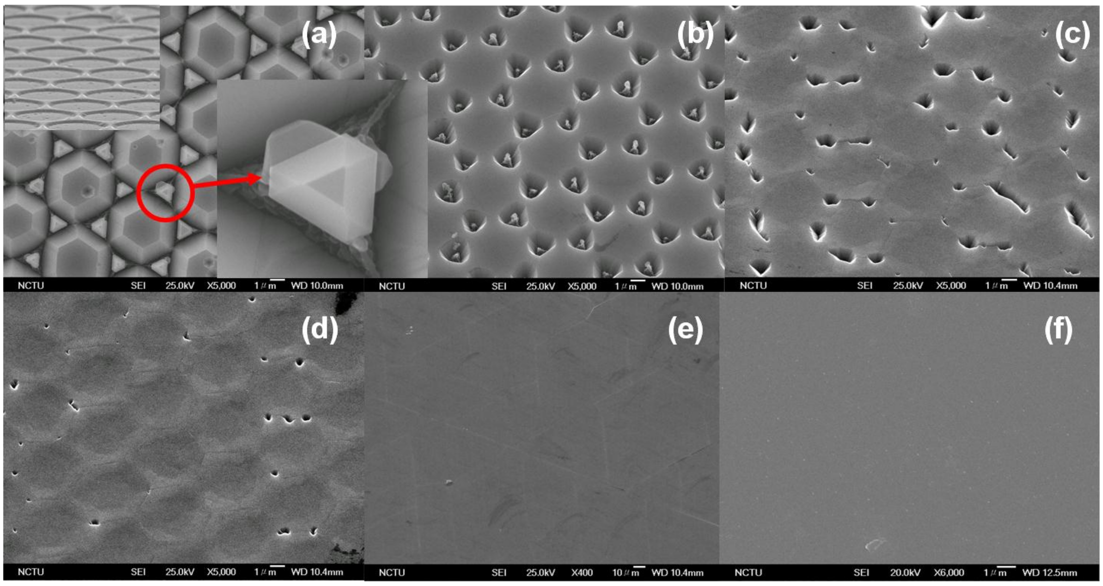

(a)
(b)
(c)
NCTU SEI 25.0kV X5,000 1 μm WD 10.0mm
NCTU SEI 25.0kV X5,000 1 μm WD 10.0mm
NCTU SEI 25.0kV X5,000 1 μm WD 10.4mm
(d)
(e)
(f)
NCTU SEI 25.0kV X5,000 1 μm WD 10.4mm
NCTU SEI 25.0kV X400 10 μm WD 10.4mm
NCTU SEI 20.0kV X6,000 1 μm WD 12.5mm

Fig. 2.

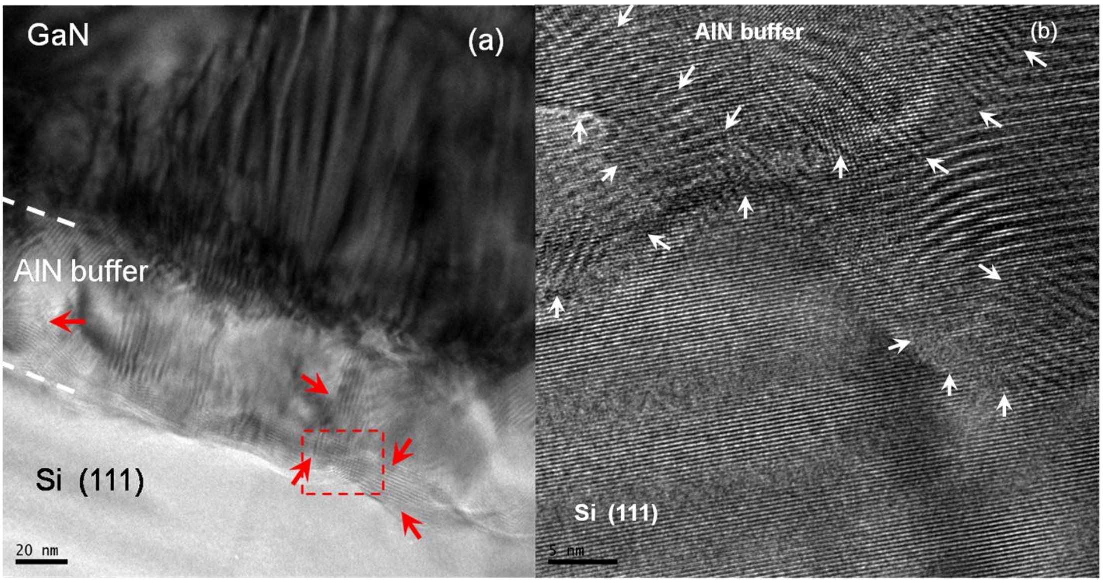


Fig. 3.

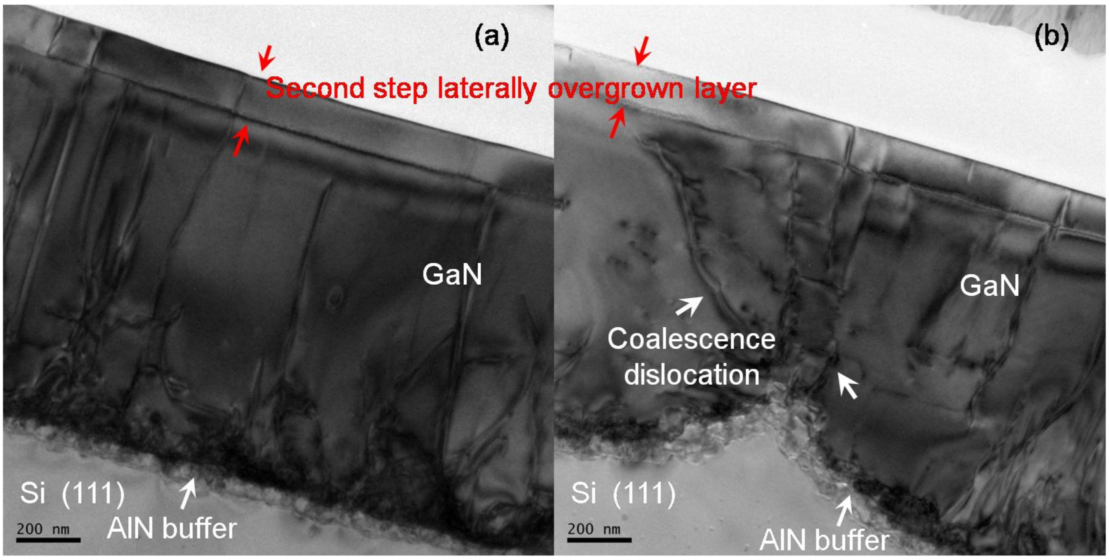

(a)
Second step laterally overgrown layer
GaN
Si (111)
200 nm
AlN buffer
(b)
GaN
Coalescence dislocation
Si (111)
200 nm
AlN buffer

Fig. 4.

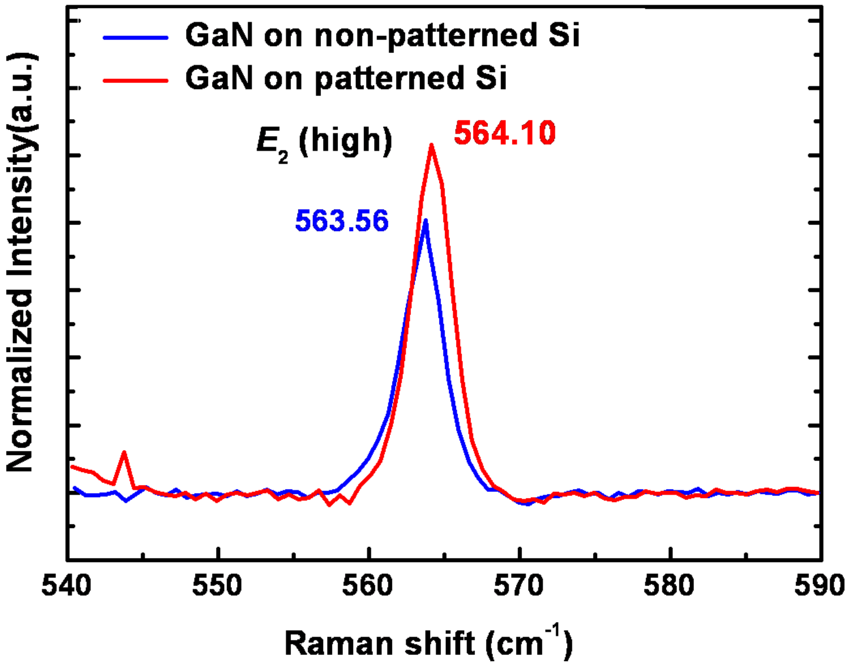
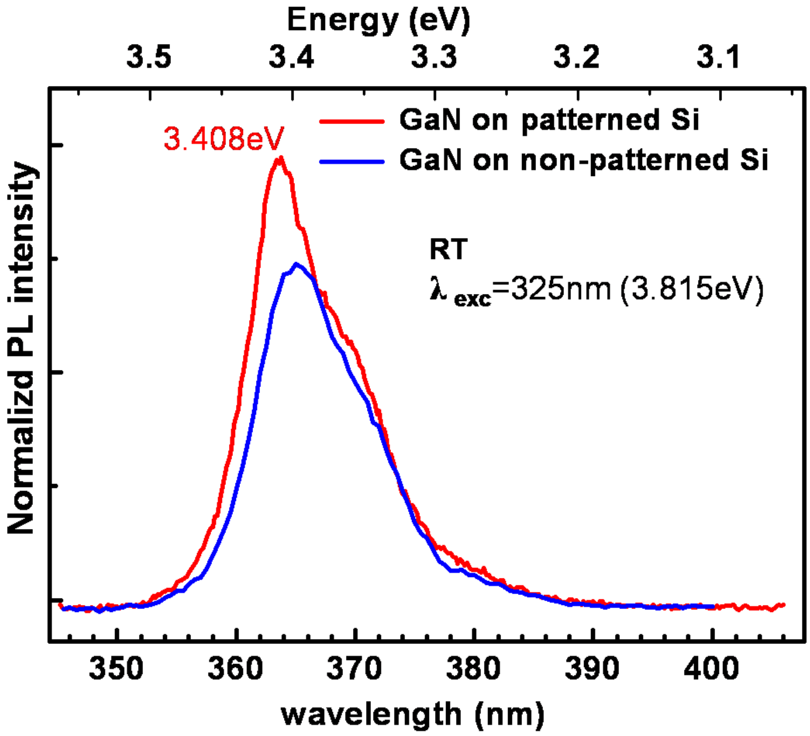

GaN on non-patterned Si
GaN on patterned Si
E_2 (high)
564.10
563.56
Normalized Intensity(a.u.)
540
550
560
570
580
590
Raman shift (cm^{-1})

Fig.5.


Energy (eV)
3.5
3.4
3.3
3.2
3.1
3.408eV
GaN on patterned Si
GaN on non-patterned Si
RT
λ exc=325nm (3.815eV)
Normalizd PL intensity
350
360
370
380
390
400
wavelength (nm)