

Growth and Characterization of crack-free GaN films grown on cracked Si-doped GaN templates

E. K. Sia, M. S. Hao and S. J. Chua

Institute of Materials Research & Engineering, 3 Research Link, Singapore 117602

I. M. Tiginyanu

Institute of Applied Physics, Technical University of Moldova, MD-2004 Chisinau, Moldova

V. Ichizli, K. Mutamba and H. L. Hartnagel

Institut für Hochfrequenztechnik, Technische Universität Darmstadt, D-64283 Darmstadt, Germany

J. Zhang and S. Tripathy

Centre for Optoelectronics, Electrical and Computer Engineering, National University of Singapore, Engineering Drive 3, Singapore 119260

Abstract

Continuous GaN films were grown on the top of cracked Si-doped n^+ -GaN epilayers by MOCVD techniques. Raman-scattering studies of the samples indicated strain-free top GaN film. The biaxial compressive stress estimated by using X-ray diffraction analysis was as low as 0.036 GPa for sample grown under optimized conditions. The results obtained show that the use of an intermediate relaxed n^+ -GaN:Si layer is perspective for growing high quality GaN films.

I. INTRODUCTION

Gallium nitride based materials are characterized by large direct band gaps, which make them suitable for optoelectronic applications in both visible and ultraviolet regions of the electromagnetic spectrum.¹ Due to the infancy of good quality GaN substrates, GaN epilayers are usually grown on foreign substrates such as sapphire (Al_2O_3) and silicon carbide (SiC). However, GaN layers grown on these substrates experience large lattice mismatches and differences in thermal expansion coefficients resulting in built-in biaxial stresses up to 1 GPa.^{2,3} Thus considerable research efforts were focused at developing technologies that can enable to reduce the residual strain in GaN epitaxial layers grown on foreign substrates. These include the two-step method where a low-temperature thin AlN ⁴ or GaN ⁵ buffer layer is incorporated; epitaxial lateral overgrowth (ELO) techniques;⁶⁻¹⁰ and recently porous GaN method.¹¹⁻¹⁴ It has been shown that a significant reduction in the defect densities in GaN epilayers can be obtained using ELO on a patterned $\text{GaN}/\text{Al}_2\text{O}_3$ substrate.¹⁵⁻¹⁸ This approach permitted the fabrication of laser diodes having long continuous wave (cw) lifetimes of about 10,000 hours.¹⁹

We have found that a high quality continuous GaN films can be grown on cracked Si-doped GaN by carefully selecting the growth parameters.²⁰ In this work, a systematic characterization of the GaN film properties was carried out using SEM, in-situ optical reflectance, Raman scattering (RS) and X-ray diffraction (XRD) analyses. The obtained data demonstrate the perspectives of the proposed approach for growing high quality GaN films.

II. EXPERIMENT

Samples A and B were grown in a low-pressure metalorganic chemical vapor deposition (MOCVD) reactor equipped with an *in situ* reflectivity measurement system. Ammonia (NH_3) was used as nitrogen (N) source and trimethylgallium (TMGa) as gallium (Ga) source with hydrogen (H_2) as the carrier gas. Silicon doping was achieved by introducing H_2 diluted silane (50 ppm) into the gas stream. The deposition procedure for the two samples was a sequential growth of: (1) a GaN buffer layer with a thickness of 25 nm on (0001) *c*-plane sapphire (Al_2O_3) substrate at the growth temperature of 500°C; (2) an undoped layer (u-GaN) followed by a Si-doped layer (n^+ -GaN) each with a thickness of 1 μm at the growth temperature of 1000°C; and finally, (3) an undoped layer (u-GaN) with a thickness of 1 μm at the growth temperature of 1000°C. The silane flow in step (2) was 40 and 30 sccm for samples A and B, respectively.

RS characterization was carried out at room temperature using a JY-T64000 set-up. An Ar^+ laser ($\lambda = 514.5 \text{ nm}$) was used as an excitation source. The scattered radiation was analyzed in a backscattering geometry by a triple grating monochromator connected to a computer-controlled system for scanning and data acquisition. The accuracy of the Raman measurements is 0.2 cm^{-1} with a lateral spectral resolution of 1.5 μm . In our scattering geometry, the [0001] and $[\bar{1}1\bar{2}0]$ directions of the film were the *z*-axis and *x*-axis, respectively, and the $z(yy)\bar{z}$ (parallel) configuration was used to detect the E_2 (TO) (High) phonon mode. X-ray measurements were performed using a high-resolution x-ray diffractometer Philips X'Pert MRD equipped with a Cu sealed anode and a four-crystal monochromator in Ge (220) configuration.

III. RESULTS AND DISCUSSION

A. SEM and Reflectivity

Fig. 1 shows the plan-view SEM and optical micrographs of the GaN epilayers grown on cracked Si-doped GaN templates. For sample A, crack lines are apparent from the SEM picture as shown in Fig. 1a. For sample B, the growth conditions were optimized to reduce the density of cracks as seen in Fig. 1b.

Additional analysis carried out using an optical microscope evidenced two different kinds of line, namely thick and fine lines as illustrated in Fig. 1c and Fig. 1d for samples A and B, respectively. The thick lines are cracks on the top GaN surface of sample A, while the thin lines are cracks from the intermediate Si-doped n^+ -GaN layers of both samples A and B. However, the cracks from the intermediate Si-doped n^+ -GaN layer were covered by the top u-GaN layer. By adjusting the optical microscope, the underneath cracks could be brought into and out of focus indicating that the cracks were indeed buried and confined within the intermediate Si-doped n^+ -GaN epilayer. In addition, etching by inductively coupled plasma (ICP) into the intermediate Si-doped n^+ -GaN layer brought unambiguously these crack lines to light.

Optical reflectivity was used to monitor the development of epitaxial growth surface and growth rate for GaN growth in our MOCVD system. Fig. 2 shows a plot of the *in-situ* reflectivity intensity vs growth time for typical growth process of high quality GaN layers on cracked Si-doped GaN templates recorded by using a light source with a wavelength of 650 nm. The intensity of reflectivity started to oscillate when the first u-GaN epilayer began to develop at high

growth temperature. Shortly after Silane was introduced for the growth of Si-doped n^+ -GaN epilayer, the intensity of reflectivity decreased gradually with growth time until it reached its minimum. This gradual decrease of reflectivity intensity revealed that the surface of the Si-doped n^+ -GaN epilayer was no longer mirror-like due to the formation of microcracks. On the other hand, during the growth of the second u-GaN layer, the oscillations of reflectivity intensity recovered. The oscillation recovery of the reflectivity intensity revealed that the u-GaN layer grown on top of the cracked Si-doped n^+ -GaN layer has high crystal quality and good surface morphology.

According to Refs. 21 and 22, cracks in high Si-doped n^+ -GaN epilayers are due to biaxial tensile stress. The observation of cracks during growth means that biaxial tensile strains occurred in the high Si-doped n^+ -GaN epilayer at the growth temperature, which is consistent with the results reported by Hearne *et al.*²³ Since the incorporation of Si in the GaN lattice has a negligible effect on the lattice constant of GaN,²⁴ the biaxial tensile stress experienced by the high Si-doped n^+ -GaN epilayer may be attributed to the lattice and thermal coefficient mismatches against Al_2O_3 substrate.

The literature data show that the tensile stress in GaN films increases with Si doping, resulting in a reduction of the critical thickness from about 5 μm for undoped GaN to about 2 μm for a Si-doped GaN with a Si concentration of $2 \times 10^{19} \text{ cm}^{-3}$.^{22, 24, 25} Once the critical thickness of the Si-doped n^+ -GaN epilayer is exceeded, cracks will develop. Due to the formation of cracks, the Si-doped n^+ -GaN epilayer becomes relaxed. In our opinion, it is the lattice relaxation in the Si-doped n^+ -GaN that inhibits further propagation of cracks into the top u-GaN film. The growth of a continuous high quality u-GaN layer on cracked Si-doped n^+ -GaN may be explained by bridging effect. i.e., during the vertical growth of the top u-GaN layer, a diffusion-induced lateral extension may occur resulting in covering cracked regions of the high Si-doped n^+ -GaN epilayer.

Upon cooling down, a biaxial compressive stress as high as 1 GPa would be expected to develop in an epilayer grown stress-free at the growth temperature.²⁶ Therefore, cracks do not occur during the cooling process. According to the epitaxial relation adopted for GaN on Al_2O_3 and the lattice constants, a GaN layer will be under compression at the growth temperature if it is coherently grown on Al_2O_3 substrate. Above a critical thickness, this biaxial compression can, to a lesser or a greater extent, be relaxed by a network of misfit dislocations at the GaN/ Al_2O_3 interface. However, there is no dislocation mechanism that would switch the sign of the crystallographic mismatch from compressive to tensile.²² Although the occurrence of tensile stress in Si-doped n-GaN epilayer during growth is still not clear, it is considered to be associated with coalescence of islands.^{22,24}

B. Raman scattering

According to the factor group analysis, at the Γ point, optical phonons belong to the irreducible representations $A_1(Z)$, $2B$, $E_1(X,Y)$ and $2E_2$, where X, Y and Z in parentheses represent the polarization directions and denote [100], [010] and [001] crystallographic directions of the Al_2O_3 substrate. Raman-active phonons belong to $A_1(Z)$ (polar), $E_1(X,Y)$ (polar) and $2E_2$ (non-polar) modes and IR-active ones to $A_1(Z)$ and $E_1(X,Y)$ modes. $2B$ modes are silent. Since the $A_1(Z)$ and $E_1(X,Y)$ symmetries are also infrared active, the polar optical modes split into longitudinal (LO) and transverse (TO) components by the long-range electric field. Raman selection rules indicate

that the $A_1(\text{LO})$ and the E_2 modes are expected in the $z(yy)\bar{z}$ (parallel) configuration while the $z(xy)\bar{z}$ configuration allows only E_2 modes.²⁵ The E_1 mode is forbidden in the back scattering from (0001) surfaces. In our scattering geometry, the $[0001]$ and $[11\bar{2}0]$ directions of the film correspond to the z -axis and x -axis, respectively.

Fig. 3 shows the room temperature Raman spectrum of sample B taken in the $z(yy)\bar{z}$ configuration. $E_2(\text{TO})$ (high) and $A_1(\text{LO})$ phonons were observed at 567.5 and 733.2 cm^{-1} , respectively. Apart from that, an LO-phonon-plasmon (LOPC) coupled mode was evidenced at 950 cm^{-1} . This LOPC feature reflects the contribution of the n^+ -GaN:Si layer to the RS signal. The estimated²⁶ free-carrier concentration in the buried n^+ -GaN:Si film equals $3.2 \times 10^{19} \text{ cm}^{-3}$.

The $E_2(\text{TO})$ phonon consideration was used for the purpose of evaluating biaxial stress. Raman spectra were taken from different areas of the GaN epilayers grown on cracked Si-doped GaN templates. Fig. 4 shows the E_2 (TO) (High) phonon RS bands taken for sample A with the Ar^+ laser beam focused into the crack of the top-layer (thick line) as well as away from the crack [indicated as (I) and (II), respectively, in Fig. 1a]. Since the Ar^+ laser beam was directed into the crack, the Raman signal came mainly from the high Si-doped n^+ -GaN layer.

The Si-doped n^+ -GaN layer of sample A exhibits a Raman shift of 569.8 cm^{-1} . The E_2 (TO) (High) phonon frequency for a 400 μm thick hydride vapor phase epitaxy (HVPE) GaN layer was observed at 567.5 cm^{-1} and assumed to correspond to stress-free material.²⁷ So, the Si-doped n^+ -GaN epilayer exhibits a hardening effect, i.e., an upward frequency shift of $\Delta\omega_{E_2} = 2.3 \text{ cm}^{-1}$. As a result, the stress tensor component σ_{zz} , which was estimated by using the model of a biaxially strained layer,²⁸ was approximately 0.3 GPa for Si-doped n^+ -GaN epilayer of sample A. The same value is expected for Si-doped n^+ -GaN epilayer of sample B.

Fig. 5 shows the E_2 (TO) (High) phonon frequencies measured for sample A and B with the Ar^+ laser beam focused away from the crack [indicated as (II) in Fig. 1a]. In this case, the Raman signals came mainly from the top continuous u-GaN layers. The measured Raman frequencies proved to be the same, i.e. 567.5 cm^{-1} , for samples A and B. This coincides with the RS data for the stress-free top u-GaN layers, which indicates that the top u-GaN layers grown using this approach described in this contribution were stress free.

C. X-Ray diffraction

From x-ray diffraction measurements, the biaxial compressive stress ε_{zz} normal to the substrate can be estimated from the double-axis rocking curves for (hkl) reflection in symmetric diffraction geometry. The relationship between strain ε_{zz} and interatomic spacing d for a partially relaxed thin layer is given in Ref. 29. According to this approach, the interatomic spacings above and below the interface in a partially relaxed GaN layer are not equivalent and hence have to be determined independently. In this case, the angular positions of two reflections for the GaN layer and similarly for the under-layer have to be measured. Then the difference in the interplanar spacing parallel and perpendicular to the interface can be determined. The interplanar spacing normal to the interface is given as²⁹

$$\{d_z\}_{\text{Relax}} = K_z \frac{1-\nu}{1+\nu} \left\{ \frac{d_z}{K_z} + \frac{\nu}{1-\nu} \left(\frac{d_x}{K_x} + \frac{d_y}{K_y} \right) \right\} \quad (1)$$

Here, ν is the Poisson ratio for the phase along the direction normal to the surface. The parameters K are related to the choice of reflection in the measurement. Since the [0001] direction of the hexagonal GaN epilayer is normal to surface plane, suitable reflection planes for calculation of K_x , K_y and K_z are $(10\bar{1}5)$, $(\bar{2}114)$ and (0002), respectively. In addition, as the $(10\bar{1}5)$ reflection has a K_x value equivalent to the d_x separation in the plane, i.e., equivalent to the separation of $(10\bar{1}0)$ in the plane, and the $(\bar{2}114)$ reflection has a K_y value equivalent to $(\bar{2}110)$, then equation (1) can be simplified as

$$\{d_z\}_{\text{Relax}} = \frac{1-\nu}{1+\nu} \left\{ d_z + \frac{\nu}{1-\nu} (2K_z) \right\} \quad (2)$$

From the above expression, only K_z value needs to be determined. For the (0002) plane, $K_z = 2.591 \text{ \AA}$.

For our partially relaxed GaN epilayer, the interatomic spacings normal to the surface plane d_z were evaluated using the values of the incident and scattering angles, i.e., ω and $2\omega'$ for the (0002) and (0004) planes. The measured d_z and calculated $\{d_z\}_{\text{Relax}}$, ϵ_{zz} and σ_{zz} values for GaN epilayers grown on cracked Si-doped GaN templates are summarized in Table 1.

Note that there is a good correlation between stress values estimated from XRD ($\sigma_{zz} = 0.036 \text{ GPa}$) and Raman scattering analyses (stress-free) of sample B.

IV. CONCLUSION

The strain relaxation for u-GaN films grown on Si-doped n^+ -GaN epilayers was evaluated. The heterogeneous strain, estimated from the E_2 phonon frequency shifts, was found to be negligible for the top u-GaN films. In addition, the biaxial compressive stresses estimated from x-ray diffraction were 0.141 and 0.036 GPa for sample A and B respectively. The value of stress obtained for sample B correlates well with that derived from the XRD analysis. Thus, the use of an intermediate n^+ -GaN:Si epilayer is a promising approach for growing stress-free u-GaN films by MOCVD techniques.

ACKNOWLEDGEMENTS

This work was financially supported by Singapore National Science and Technology Board (NSTB) and Fujitsu Quantum Devices Singapore (FQDS). One of the authors (E. K. S.) would like to thank Prof. P. Fewster for useful discussion on XRD data.

REFERENCES

1. M. Hao, S. J. Chua, X. H. Zhang, W. Wang, E. K. Sia, L. S. Wang, A. Ramam, P. Li, and W. Liu, *Phys. Rev. B.*, **63**, 121308-1 (2001).
2. K. Hiramatsu, T. Detchprohm, and I. Akasaki, *Jpn. J. Appl. Phys.*, Part 1 **32**, 1528 (1993).
3. M. Mynbaeva, A. Titkov, A. Kryzhanovski, I. Kotousova, A. S. Zubrilov, V. V. Ratnikov, V. Yu. Davydov, N. I. Kuznetsov, K. Mynbaev, D. V. Tsvetkov, S. Stepanov, A. Cherenkov, and V. A. Dmitriev, *MRS Internet J. Nitride Semicond. Res.* **4**, 14 (1999).
4. H. Amano, N. Sawaki, I. Akasaki, and Y. Toyada, *Appl. Phys. Lett.*, **48**, 353 (1986).
5. S. Nakamura, *Jpn. J. Appl. Phys.*, Part 2, **30**, L1750 (1991).
6. S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, Y. Sugimoto, T. Kozaki, H. Umemoto, M. Sano, and K. Chocho, *Appl. Phys. Lett.*, **72**, 211 (1998).
7. D. Kapolnek, S. Keller, R. Ventury, R. Underwood, P. Kozodoy, S. DenBaars, and U. Misra, *Appl. Phys. Lett.*, **71**, 1204 (1997).
8. T. Zheleva, O. H. Nam, M. Bremser, and R. Davis, *Appl. Phys. Lett.*, **71**, 2472 (1997).
9. C. Sasaoka, H. Sunakawa, A. Kimura, M. Nido, A. Usui, and A. Sakai, *J. Cryst. Growth*, **189/190**, 61 (1998).
10. P. Kozodoy, J. Ibbetson, H. Marchand, S. Fini, S. Keller, J. Speck, S. DenBaars, and U. Mishra, *Appl. Phys. Lett.*, **73**, 975 (1998).
11. M. Mynbaeva, A. Titkov, Kryzhanovskii, V. Ratnikov, K. Mynbaev, H. Huhtinen, R. Laiho, and V. Dmitriev, *Appl. Phys. Lett.*, **76**, 1113 (2000) and the references therein.
12. M. Mynbaeva, and D. Tsvetkov, *Inst. Phys. Conf. Ser.* **155**, 365 (1997).
13. S. O. Kucheyev, J. S. Williams, C. Jagadish, J. Zou, V. S. J. Craig, and G. Li, *Appl. Phys. Lett.* **77**, 1455 (2000).
14. S. O. Kucheyev, J. S. Williams, J. Zou, C. Jagadish, and G. Li, *Appl. Phys. Lett.* **77**, 3577 (2000).
15. Z. Yu, M. A. L. Johnson, T. Menulty, J. D. Brown, J. W. Cook, and J. F. Schetzina, *MRS Internet J. Nitride Semicond. Res.* **3**, 6 (1998).
16. S. Haffouz, B. Beaumont, and P. Gilbert, *MRS Internet J. Nitride Semicond. Res.* **3**, 8 (1998).
17. B. Beaumont, V. Bousquet, P. Vennéguès, M. Vaille, A. Bouillé, P. Gilbert, S. Dassoneville, A. Amokran, and B. Sieber, *Phys. Status Solidi A* **176**, 567 (1999).
18. V. Bousquet, P. Vennéguès, B. Beaumont, M. Vaille, and P. Gibart, *Phys. Status Solidi B* **216**, 691 (1999).
19. S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Matsushita, and T. Mukai, *MRS Internet J. Nitride Semicond. Res.* **4S1**, G1.1 (1999).
20. S. J. Chua, M. Hao, J. Zhang, and E. K. Sia, *Physica Status Solidi*, **228** (2001) (in press).
21. N. Itoh, J. C. Rhee, T. Kawabata, and S. Koike, *J. Appl. Phys.* **58**, 1828 (1985).
22. E. V. Etzkorn, and D. R. Clarke, *J. Appl. Phys.* **89**, 1025 (2001).
23. S. Hearne, E. Chason, J. Han, J. A. Floro, J. Figiel, J. Hunter, H. Amano, and I. S. T. Tsong, *Appl. Phys. Lett.*, **73**, 356 (1999).
24. L. T. Romano, C. G. van de Walle, J. W. Ager III, W. Götz, and R. S. Kern, *J. Appl. Phys.*, **87**, 7745 (2000).
25. C. A. Arguello, D. L. Rousseau, and S. P. S. Porto, *Phys. Rev.*, **181**, 1351 (1969).

26. P. Perlin, J. Camassel, W. Knap, T. Taliercio, J. C. Chervin, T. Suski, I. Grzegory, and S. Porowski, Appl. Phys. Lett., **67**, 2524 (1995).
27. S. Tripathy, R. K. Soni, H. Asahi, K. Iwata, R. Kuroiwa, K. Asami and S. Gonda, J. Appl. Phys., **85**, 8386 (1999).
28. V. Y. Davydov, N. S. Averkiev, I. N. Goncharuk, D. K. Nelson, I. P. Nikitna, A. S. Polkovnikov, A. N. Smirnov, M. A. Jacobson and Q. W. Semchinova, J. Appl. Phys. **82**, 5097 (1997).
29. P. F. Fewster, X-ray Scattering from Semiconductors, Imperial College Press (2000).

Table Captions

Table 1: Stress values of GaN epilayers grown on cracked Si-doped GaN templates derived from XRD analysis.

	d_z (Å)	$\{d_z\}_{\text{Relax}}$ (Å)	ϵ_{zz} ($\times 10^{-4}$)	σ_{zz} (GPa)
A	2.587	2.589	4.837	0.141
B	2.589	2.590	1.544	0.036

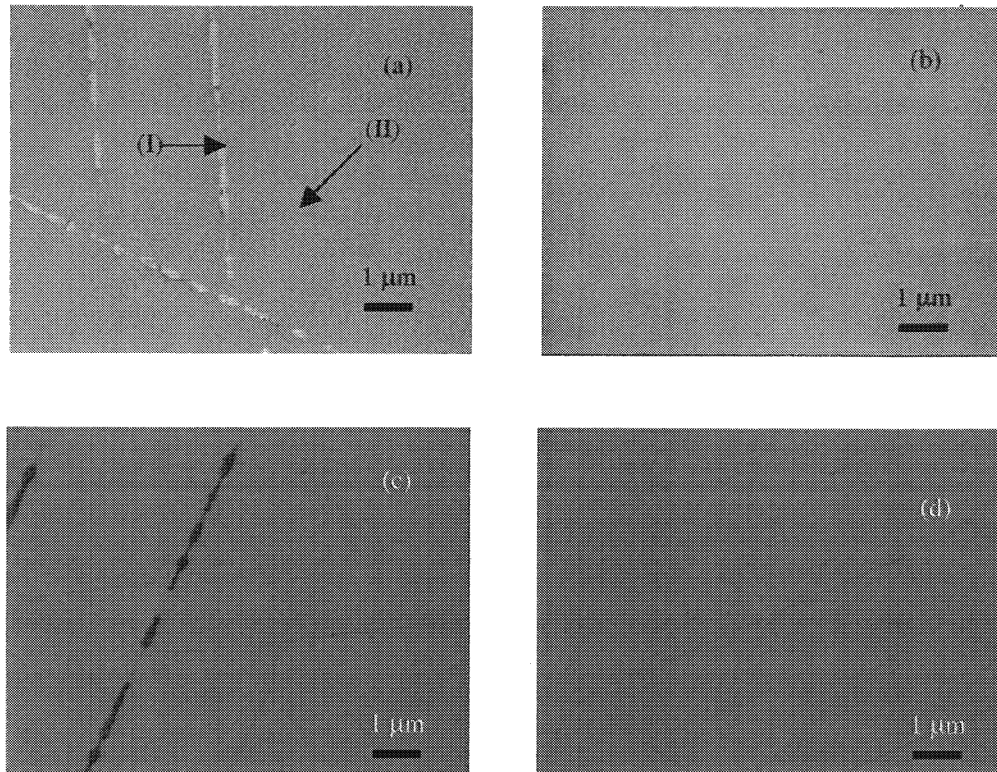


Fig. 1: SEM and optical micrographs of GaN epilayers grown on high Si-doped cracked n^+ -GaN epilayer.

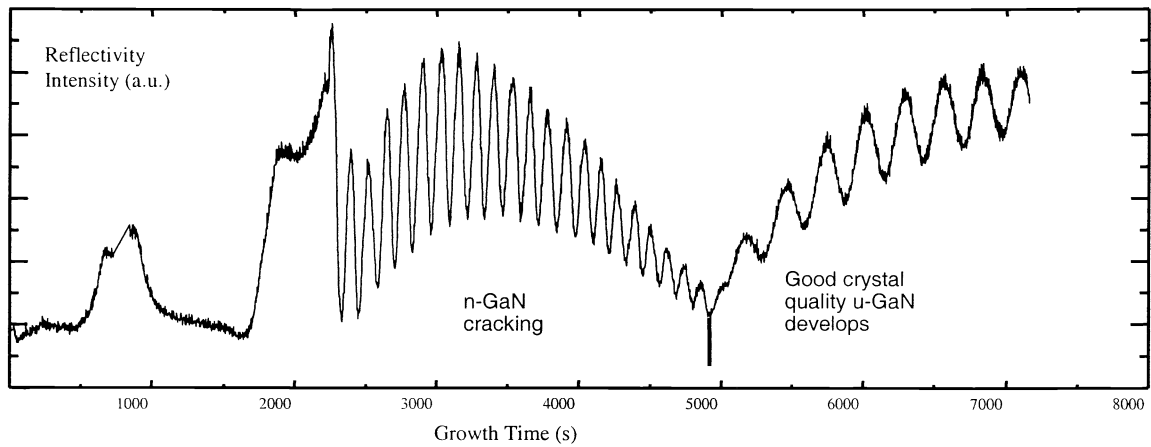


Fig. 2: Typical reflectivity intensity versus growth time. The reflectivity oscillation decreases to a minimum indicating the formation of cracks in the high Si-doped n^+ -GaN epilayer and increases again with the growth of the second u-GaN layer claiming its high crystal and morphological quality.

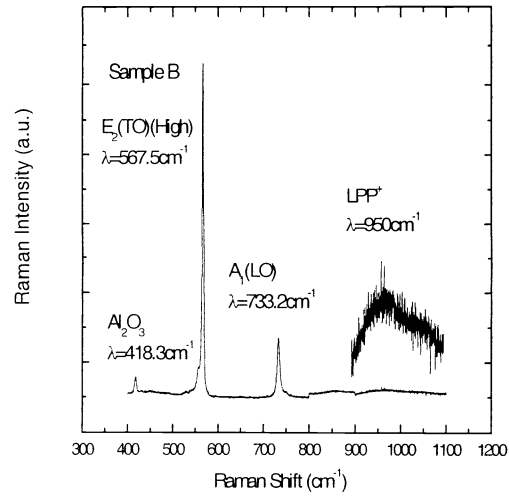


Fig. 3: Room temperature Raman spectrum of sample B.

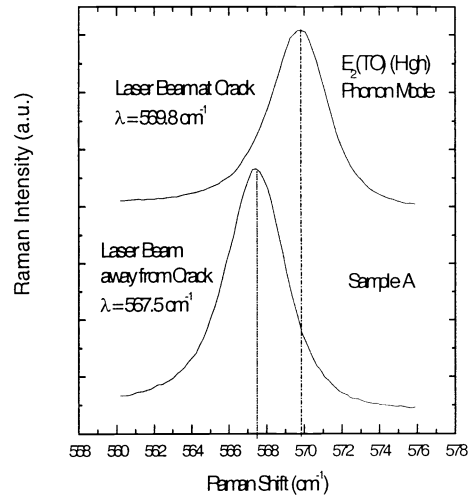


Fig. 4: Raman shift of the E_2 (TO)(High) optical phonon for sample A with Ar⁺ laser beam focused into the crack and away from it.

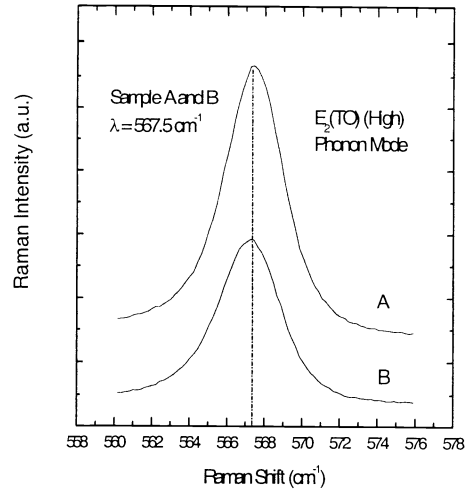


Fig. 5: Raman shift of the E_2 (TO)(High) optical phonon for GaN epilayers grown on cracked Si-doped GaN templates with laser beam focused away from cracks.