X-ray and Raman analyses of GaN produced by ultrahigh-rate magnetron sputter epitaxy

Cite as: Appl. Phys. Lett. **81**, 1797 (2002); https://doi.org/10.1063/1.1506781
Submitted: 15 May 2002 • Accepted: 22 July 2002 • Published Online: 26 August 2002

Minseo Park, J.-P. Maria, J. J. Cuomo, et al.

X-ray and Raman analyses of GaN produced by ultrahigh-rate magnetron sputter epitaxy

Minseo Park,[a] J.-P. Maria, and J. J. Cuomo
Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695

Y. C. Chang, J. F. Muth, and R. M. Kolbas
Department of Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina 27695

R. J. Nemanich
Department of Physics, North Carolina State University, Raleigh, North Carolina 27695

E. Carlson and J. Bumgarner
Kyma Technologies, Incorporated, 8829 Midway West Road, Raleigh, North Carolina 27617

(Received 15 May 2002; accepted for publication 22 July 2002)

Thick films of GaN were studied by x-ray diffraction and Raman spectroscopy. The GaN thick films were deposited on (0001) sapphire using ultrahigh-rate magnetron sputter epitaxy with typical growth rates as high as 10–60 μm/min. The width of the x-ray rocking curve from the (0002) reflection for the sample produced by this technique is ~300 arcsec, which is unprecedented for GaN produced by a sputtering-type process. Our recent sample shows an x-ray rocking curve width of 240 arcsec. Only allowed modes were observed in the polarized Raman spectra. The background free carrier concentration is lower than 3×10^{16} cm^{-3}. The phonon lifetime of the Raman $E_2^{(2)}$ mode of the sputtered GaN was comparable to that of bulk single crystal GaN grown by sublimation. The quality of the film was uniform across the wafer. The film was thermally stable upon annealing in N_2 ambient. The x-ray and Raman analyses revealed that the sputtered GaN films are of high crystalline quality. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1506781]

Recently, wide band gap III–V nitrides semiconductors such as gallium nitride (GaN) have attracted significant attention for potential optoelectronic application in the blue to ultraviolet spectral region. The quality of GaN epitaxial layers grown by both molecular beam epitaxy (MBE) and organometallic vapor phase epitaxy (OMVPE) has been significantly improved in recent years. However, relatively little attention has been paid to the sputtering process as a viable technique by which to produce high quality epitaxial films of GaN. After pioneering work by Hovel and Cuomo,[1] only a handful of research projects has been carried out on sputter growth of GaN.[2–8] Conventionally, the sputter process has not been portrayed as a viable method suitable for single crystal growth of GaN. However, we have demonstrated that high quality GaN films can be grown using sputtering. The x-ray rocking-curve width for our sample is ~300 arcsec, which is unconventional for the GaN films deposited by sputtering. Our recent sample shows an x-ray rocking curve width of 240 arcsec. The smallest value reported up to now was 620 arcsec, which was produced by Webb *et al.* using magnetron sputter epitaxy.[9] Note that the rocking curve width for an OMVPE sample can be as low as 30 arcsec.[10] In the present investigation, x-ray and Raman analyses were used to assess the optical and structural properties of GaN thick films produced by magnetron sputter epitaxy.

The GaN layers were deposited using ultrahigh-rate dc reactive magnetron sputter epitaxy with a target of 99.9999% pure gallium contained in a stainless steel cup. This growth technique is capable of growing high quality GaN layers on large area substrates (up to 4 in.) through the use of a large area Ga target (6 in.) at growth rates as high as 10–60 μm/min. The deposition chamber was pumped to a pressure of 1×10^{-6} Torr and backfilled with a gas mixture of argon and nitrogen. The gas ratios and flows were controlled by mass flow controllers with combined flow rate of around 75 sccm. The GaN layers were deposited on single crystal (0001) sapphire substrates (2 in.) that were heated using a graphite filament up to 1200 °C. The layers were grown under various conditions of sputtering atmosphere and substrate temperature. X-ray rocking curve measurement was performed using the Bede 200 double crystal x-ray diffractometer. The x-ray pole figure and x-ray ϕ scan were obtained using a Bruker x-ray diffractometer. Raman spectroscopy was performed at room temperature using backscattering geometry with the 514.5 nm (2.41 eV) line of an Ar ion laser and an ISA U-1000 scanning double monochromator to disperse the Stokes Raman scattering spectra.

Figure 1(a) shows an x-ray (0002) rocking curve for GaN films on (0001) sapphire deposited by ultrahigh-rate magnetron sputter epitaxy. The full width at half maximum (FWHM) of the (0002) rocking curve for the sample which was used for this study is ~300 arcsec. Pole figure analysis [inset in Fig. 1(a)] and x-ray ϕ scan [Fig. 1(b)] unambiguously reveal the sixfold symmetry of the hexagonal crystal. Table I summarizes the physical properties of the GaN thick films produced by sputtering.

[a]Author to whom correspondence should be addressed; electronic mail: m_park@ncsu.edu

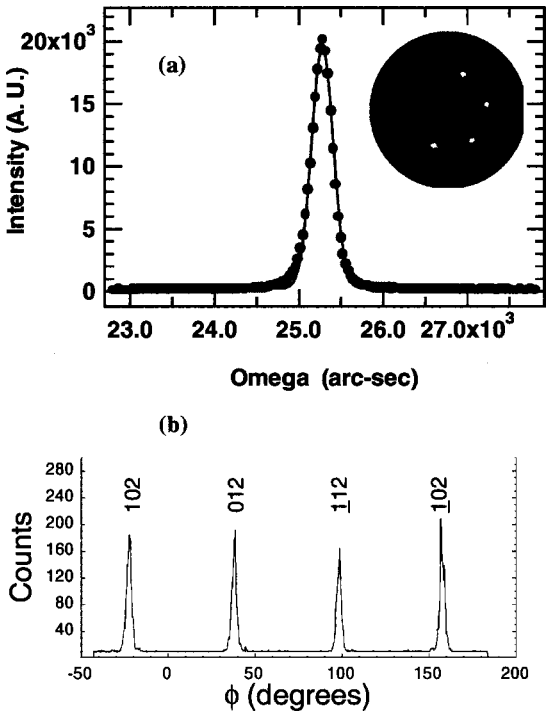

FIG. 1. (a) X-ray rocking curve from (0002) reflection. The inset shows the x-ray pole figure. (b) X-ray ϕ scan of the sputtered GaN.

Hexagonal GaN has a wurtzite structure with C_{6v}^4 space group. Group theory predicts $A_1(z)+2B_1+E_1(x,y)+2E_2$ optical modes at the Γ point of the Brillouin zone of GaN,[11] where the two E_2 modes are Raman active, the A_1 and E_1 modes are both Raman and IR active, and the two B_1 modes are silent. Since the A_1 and E_1 modes are polar, they split into longitudinal optical (LO) and transverse optical (TO) components. According to the Raman selection rule, only the $E_2^{(1)}$, $E_2^{(2)}$, and A_1(LO) modes should be observed in the $z(x,-)\underline{z}$ scattering geometry of our experiment. Figure 2 shows a Raman spectrum of GaN deposited on sapphire, where only the allowed Raman modes were observed. Since the GaN is transparent to 514.5 nm, the E_g mode of sapphire was also observed at 750 cm^{-1}.

TABLE I. Summary of the physical properties of GaN produced by magnetron sputter epitaxy.

	This work	Other work[a]
FWHM of the rocking curve	300 arcsec[b]	3600 arcsec[c] 2196 arcsec[d] 620 arcsec[e]
FWHM of the Raman $E_2^{(2)}$ peak	4.8 cm^{-1}	9 cm^{-1} [f]
FWHM of the Raman A_1 (LO) peak	8.8 cm^{-1}	12 cm^{-1} [g]
Phonon lifetime ($E_2^{(2)}$)	1.6 ps	1.4 ps[h] (sublimation)
Phonon lifetime [A_1 (LO)]	0.7 ps	
Free carrier concentration	$<3\times10^{16}$ cm^{-3}	
Biaxial residual stress	~0.26 GPa	

[a]The values are for the sputtered samples unless specified.
[b]Reference 19.
[c]Reference 5.
[d]Reference 3.
[e]Reference 9
[f]Reference 3.
[g]Reference 3.
[h]Reference 15.

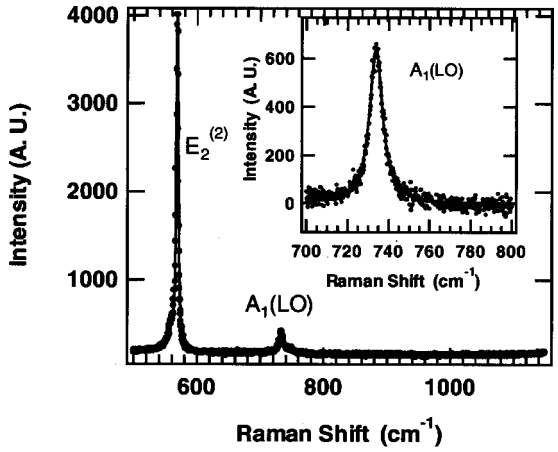

FIG. 2. Raman spectrum of sputtered GaN. The inset shows the high resolution Raman spectrum of A_1 (LO) mode.

In polar semiconductors, a LO phonon couples strongly to a plasmon through the macroscopic electric field.[12] The coupling between plasma and the LO phonon produces two coupled LO phonon-plasmon (LPP) modes, ω_+ (LPP^+) and ω_-(LPP^-).[13] In GaN, where plasmon damping is significant, the coupling will be displayed as a shift of LO phonon mode. The plasma frequency can be deduced by fitting the coupled A_1 (LO) phonon-plasmon peak to the following expression,[14]

$$I_A = \text{const}\cdot A(\omega)\cdot \text{Im}\{-\varepsilon(\omega)^{-1}\}, \tag{1}$$

where ω is the Raman shift, $\varepsilon(\omega)$ is the dielectric function, and $A(\omega)$ is related to deformation potential and the electro-optic mechanism. The plasma frequency (ω_p) can be obtained by line shape analysis of the coupled mode. Finally, the free carrier concentration (n) can be calculated using

$$\omega_p = \left(\frac{4\pi n e^2}{\varepsilon_\infty m^*}\right)^{1/2}, \tag{2}$$

where n is the free carrier concentration and m^* is the effective mass of the free carrier. The inset in Fig. 2 shows the high resolution Raman spectrum of the coupled A_1 (LO)-plasmon mode. The spectrum of sapphire was removed by collecting a Raman spectrum from the backside of the sample, followed by spectral subtraction. Plasma frequency of $\omega_p = 50.6$ cm^{-1} was obtained by fitting the spectrum with Eq. (1). Using Eq. (2), the calculated free carrier concentration (n) of the GaN is $<3\times10^{16}$ cm^{-3}. This value is considered maximum since this method will produce the same value of free carrier concentration even though the free carrier concentration is lower than this.

Figure 3 shows Raman spectra of E_2 mode as a function of the spectrometer slit width. The plot of FWHM versus the spectrometer slit width is shown in the inset in Fig. 3. The so-called zero-slit width of 3.4 cm^{-1} was determined using the method used by Bergman *et al.*[15] By using the uncertainty relation,

$$\Delta E\cdot\tau\sim\hbar, \tag{3}$$

the phonon lifetime of the sputtered GaN can be calculated.[16] The phonon lifetime of the sputtered GaN (1.6 ps) is comparable to that of single crystal GaN grown by sublimation (1.4 ps).[15] It should be noted that the x-ray rocking curve

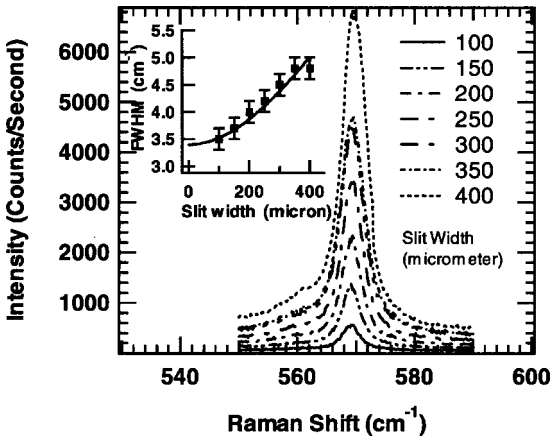

FIG. 3. Raman spectrum of $E_2^{(2)}$ mode as a function of the monochromator slit size. The inset shows a plot of the FWHM of $E_2^{(2)}$ mode vs the slit size.

width and Raman peak width (phonon lifetime) are not necessarily determined by the same defect structure.

Kisielowski *et al.* found that biaxial stress of 1 GPa shifts the $E_2^{(2)}$ Raman peak of GaN 4.2 ± 0.3 cm^{-1}.[17] Based on this formula and on the Raman peak position, it was determined that our thick films are under compressive residual stress of ~0.26 GPa. (The peak position of $E_2^{(2)}$ mode for stress-free bulk GaN used for this calculation is 567.9 cm^{-1} at room temperature.[18])

Figure 4(a) shows the x-ray rocking curve width and FWHM of the Raman $E_2^{(2)}$ peak for different regions of GaN

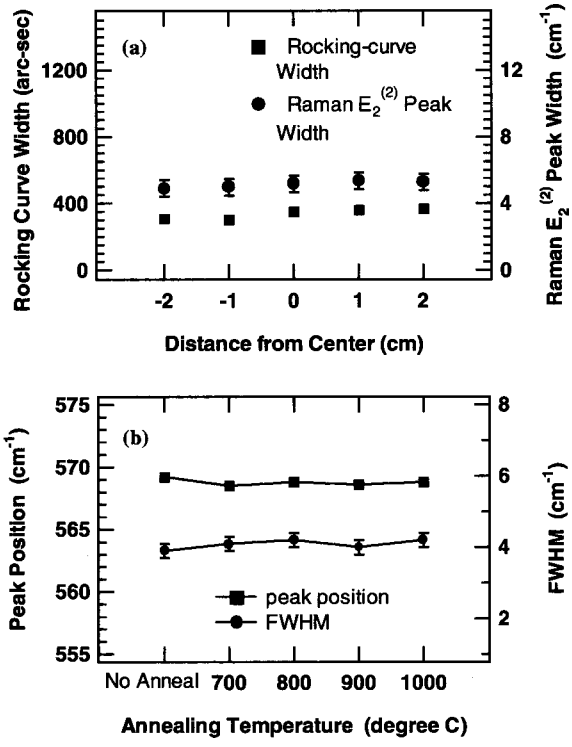

FIG. 4. (a) X-ray rocking curve width and FWHM of $E_2^{(2)}$ mode collected from different regions of the GaN film. (b) Peak position and FWHM of $E_2^{(2)}$ mode as a function of the N_2 annealing temperature.

thick films deposited on a 2 in. sapphire wafer. No significant change in x-ray rocking curve width or FWHM of the Raman peak was observed. Therefore, it can be concluded that the quality of the film was uniform across the wafer.

The sample was annealed under N_2 atmosphere sequentially from 700 to 1000 °C for 30 min each, and its effect on structural properties was investigated by Raman spectroscopy. The forbidden mode was not observed in the Raman spectrum for the annealed sample. No substantial change in peak position and FWHM of Raman $E_2^{(2)}$ mode was observed [Fig. 4(b)], which indicates that the films are thermally stable under N_2 at that temperature range.

In summary, thick films of sputtered GaN were studied by x-ray diffraction and Raman spectroscopy. The FWHM of the x-ray rocking curve for our sample is ~300 arcsec, which is the smallest value of GaN produced by a sputtering type process. Only the allowed modes were observed in the polarized Raman spectra. The background free carrier concentration was lower than 3×10^{16} cm^{-3}. The phonon lifetime of the Raman $E_2^{(2)}$ mode of the sputtered GaN was comparable to that of the bulk single crystal GaN grown by sublimation. The quality of the film was uniform across the wafer. The film was thermally stable upon annealing in N_2 ambient. The x-ray and Raman analyses revealed that the sputtered GaN films are of high crystalline quality.

One of the authors (M.P.) would like to thank E. Pupa, CEO of Kyma Technologies, Inc., for financial support of this work. The authors also thank Dr. A. I. Kingon for allowing them access to his x-ray diffractometer. Rocking curve measurement by M. Reed and Dr. N. El-Masry is greatly appreciated.

[1] H. J. Hovel and J. J. Cuomo, Appl. Phys. Lett. **20**, 71 (1972).
[2] S. Zembutsu and M. Kobayashi, Thin Solid Films **129**, 289 (1985).
[3] W. J. Meng and T. A. Perry, J. Appl. Phys. **76**, 7824 (1994).
[4] H. Tang, J. Webb, J. Bardwell, B. Leathem, S. Charbonneau, and S. Raymond, J. Electron. Mater. **29**, 268 (2000).
[5] K. Kubota, Y. Kobayashi, and K. Fujimoto, J. Appl. Phys. **66**, 2984 (1989).
[6] P. Singh, J. M. Corbett, J. B. Webb, S. Charbonneau, F. Yang, and M. D. Robertson, J. Vac. Sci. Technol. A **16**, 786 (1998).
[7] J. Ross and M. Rubin, J. Mater. Res. **8**, 2613 (1993).
[8] T. L. Tansley and R. J. Egan, Thin Solid Films **164**, 441 (1988).
[9] J. B. Webb, D. Northcott, S. Charbonneau, F. Yang, D. J. Lockwood, O. Malvezin, P. Singh, and J. Corbett, Mater. Sci. Forum **264**, 1229 (1998).
[10] M. A. di Forte-Poisson, F. Huet, A. Romann, M. Tordjman, D. Lancefield, E. Pereira, J. Di Persio, and B. Pecz, J. Cryst. Growth **195**, 314 (1998).
[11] W. Hayes and R. Laudon, *Scattering of Light by Crystals* (Wiley, New York, 1978).
[12] M. V. Klein, in *Light Scattering in Solids*, edited by M. Cardona (Springer, Berlin, 1975), p. 147.
[13] A. Mooradian and G. B. Wright, Phys. Rev. Lett. **16**, 999 (1966).
[14] H. Yugami, S. Nakashima, and A. Mitsuishi, J. Appl. Phys. **61**, 354 (1987).
[15] L. Bergman, D. Alexon, P. L. Murphy, R. J. Nemanich, M. Dutta, M. A. Stroscio, C. Balkas, H. Shin, and R. F. Davis, Phys. Rev. B **59**, 12977 (1999).
[16] M. Kuball, J. M. Hayes, Y. Shi, and J. H. Edgar, Appl. Phys. Lett. **77**, 1958 (2000).
[17] C. Kisielowski, J. Krüger, S. Ruvimov, T. Suski, J. W. Ager III, E. Jones, Z. Liliental-Weber, M. Rubin, E. R. Weber, M. D. Bremster, and R. F. Davis, Phys. Rev. B **54**, 17745 (1996).
[18] M. Giehler, M. Ramsteiner, P. Waltereit, O. Brandt, K. H. Ploog, and H. Obloh, J. Appl. Phys. **89**, 3634 (2001).
[19] E. Carlson, Kyma Technologies, Inc. (private communication).