Optical Characterization of High Quality GaN Produced by High Rate Magnetron Sputter Epitaxy

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ABSTRACT

The thick films of GaN were investigated using X-ray diffraction, micro-Raman spectroscopy and photoluminescence spectroscopy. The thick films of GaN were prepared on (0001) sapphire using high rate magnetron sputter epitaxy with growth rates as high as 10-60 μm/min. The width of the X-ray rocking curve ((0002) reflection) for the sample produced by this method is ~300 arc-sec. Only the allowed modes were observed in the polarized Raman spectra. The background electron concentration is lower than 3×10^{16} cm^{-3}, which was determined from the Raman spectra. The phonon lifetime determined from Raman $E_2^{(2)}$ mode was 1.6 ps, which is comparable to that of bulk single crystal GaN grown by sublimation (1.4 ps). The full-width-at-half-maximum of the near band-edge photoluminescence peak obtained at 77K is ~100 meV.

INTRODUCTION

Wide band gap III-V nitrides semiconductors such as gallium nitride (GaN) are important materials for optoelectronic applications in the short-wavelength spectral region. GaN can be prepared using a variety of techniques such as organometallic vapor phase epitaxy (OMVPE) and molecular beam epitaxy (MBE). It can also be produced using sputtering, but the sputtering process has not been considered as a method to produce high quality epitaxial films of GaN. After the sputtered GaN was synthesized by Hovel and Cuomo [1], only a few worker have reported on sputter epitaxy of GaN [2-7].

Recently, we have demonstrated that high quality GaN films can be grown using sputtering, and the full-width-at-half-maximum of X-ray rocking-curve for this sample is ~300 arc-sec. The smallest value reported until now was 620 arc-sec, which was produced by Webb *et al.* using magnetron sputter epitaxy [7]. Values for the FWHM of (0002) rocking curves for thin GaN films grown *via* HVPE directly on sapphire have been previously reported in the range of 200 to 600 arc-sec [8, 9, 10]. Note that FWHM for GaN grown by OMVPE can be as low as ~30 arc-sec [11].

In the present investigation, we have used X-ray diffraction, micro-Raman scattering, and photoluminescence spectroscopy to assess the crystal quality of the sputtered GaN.

EXPERIMENTAL

Thick films of GaN were prepared on sapphire substrates using high-rate DC reactive magnetron sputter epitaxy. As a target, pure gallium (99.9999%) was contained in a large area stainless steel cup (6 in.). This sputtering technique allows the growth of high quality GaN layers on large area substrates (up to 4 in.) with growth rates as high as 10-60 μm/min. The deposition chamber was pumped to a pressure of $1x10^{-6}$ Torr and backfilled with a gas mixture of argon and nitrogen. The GaN layers were deposited on single crystal (0001) sapphire substrates (2 in.) that were heated up to 1200 ºC using a graphite filament. The layers were grown under a variety of conditions of sputtering atmosphere and substrate temperature. The thickness of the film is 20 μm.

X-ray rocking curve measurements were carried out using the Bede 200 double crystal X-ray diffractometer. Micro-Raman spectroscopy was performed at room temperature using backscattering geometry with the 514.5 nm line of an Ar^+ laser and an ISA U-1000 scanning double monochromator to disperse the Stokes Raman scattering spectra. The excitation laser beam was focused to a small spot (2 μm in diameter) with a microscope objective, and the power of the laser was fixed to 140 mW. The frequency-tripled output of a pulsed Ti: Sapphire laser (280 nm and 250 fs at 76 MHz) was used as the UV excitation source for photoluminescence spectroscopy. The sample was mounted on an oxygen-free highly conductive copper plug and placed on the cold finger of a liquid nitrogen dewar. The photoluminescence (PL) signal was collected, collimated and focused on to the entrance slits of a 0.32 m spectrometer, and the emission was detected using a cooled GaAs photomultiplier dc coupled to an electrometer.

RESULTS AND DISCUSSION

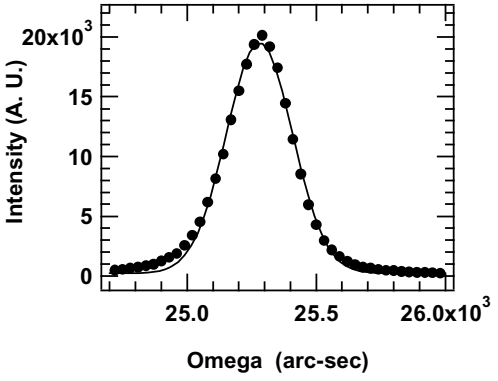

FIGURE 1. X-ray rocking curve from (0002) reflection

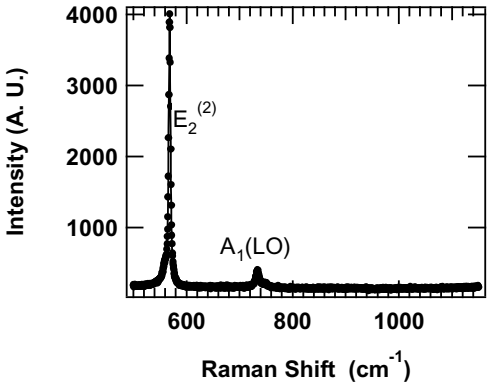

FIGURE 2. Raman spectrum of sputtered GaN

Figure 1 presents an X-ray rocking-curve for GaN film deposited on (0001) sapphire. The FWHM of the (0002) rocking curve for the sample which was used for this investigation is ~300 arc-sec. Hexagonal GaN has a wurtzite structure which belongs to the C_{6v}^4 space group. According to group theory, $A_1(z) + 2B_1 + E_1(x,y) + 2E_2$ optical modes occur at the Γ point of the Brillouin zone of GaN [17]. Among these optical modes, the two E_2 modes are Raman active, the A_1 and E_1 modes are both Raman and

infrared active, and the two B_1 modes are neither Raman nor infrared active. The A_1 and E_1 modes split into longitudinal optical (LO) and transverse optical (TO) components due to their polar nature. Only the $E_2^{(1)}$, $E_2^{(2)}$, and A_1(LO) modes are allowed with the z(x,-)$\underline{z}$ scattering geometry of our experiment. Figure 2 shows polarized Raman spectra of the GaN grown on sapphire. As can be seen from the figure, only the allowed phonon modes were observed. A high-resolution spectrum of the $E_2^{(2)}$ mode is shown in Figure 3(a).

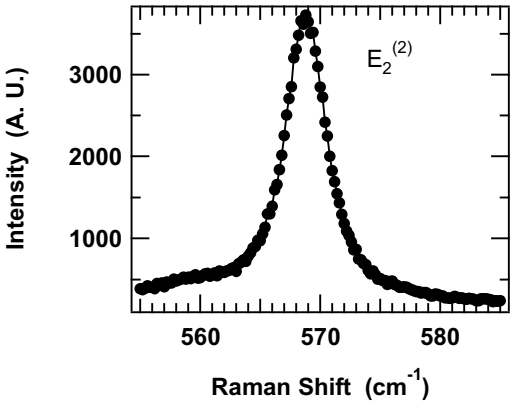

FIGURE 3(a). High resolution Raman spectrum of $E_2^{(2)}$ mode.

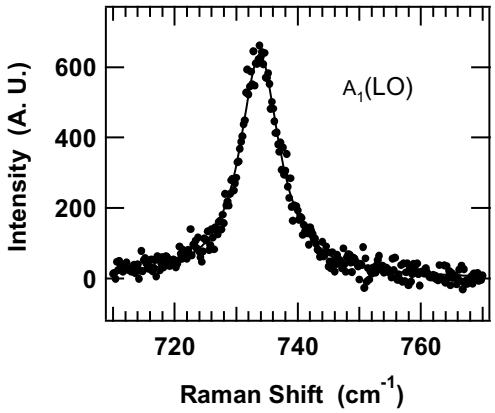

FIGURE 3(b). High resolution Raman spectrum of A_1(LO) mode.

A longitudinal optical (LO) phonon couples with a plasmon through the macroscopic electric field in the case of polar semiconductors such as GaAs and GaN [12]. The coupling is *via* the macroscopic electric fields of the phonons and plamons. The coupling between the plasmons and the LO phonon generates two coupled LO phonon-plasmon (LPP) modes, which are referred to as ω_+ (LPP^+) and ω_- (LPP^-) [13]. The frequency of these coupled modes varies as a function of the free carrier concentration. This effect was suggested by Varga [14], and first experimentally observed in GaAs by Mooradian and Wright [13]. In the case of GaN where plasmon damping is substantial, the coupling will be manifested as a shift of the LO phonon mode. The plasma frequency can be obtained by fitting the coupled mode to the following formula [15];

$$I_A = \text{Constant} \bullet A(\omega) \bullet \text{Im}\{-1/\varepsilon(\omega)\} \quad , \tag{2}$$

where ω is the Raman shift, $\varepsilon(\omega)$ is the dielectric function which has a phonon and a plasmon contribution, and $A(\omega)$ is the interference term which contains Faust-Henry coefficient. The $A(\omega)$ is expressed as

$$\begin{aligned} A(\omega) = 1 + 2C\frac{\omega_{TO}^2}{\Delta}\left[\omega_P^2\gamma(\omega_{TO}^2 - \omega^2) - \omega^2\Gamma(\omega^2 + \gamma^2 - \omega_P^2)\right] \\ + C^2\left\{\omega_P^2\left[\gamma(\omega_{LO}^2 - \omega_{TO}^2) + \Gamma(\omega_P^2 - 2\omega^2)\right] + \omega^2\Gamma(\omega^2 + \gamma^2)\right\}\left(\frac{\omega_{TO}^4}{\Delta(\omega_{LO}^2 - \omega_{TO}^2)}\right) \end{aligned} \quad , \tag{3}$$

where

$$\Delta = \omega_p^2\gamma\left\{(\omega\Gamma)^2 + (\omega_{TO}^2 - \omega^2)^2\right\} + \omega^2\Gamma(\omega^2 + \gamma^2)(\omega_{LO}^2 - \omega_{TO}^2), \tag{4}$$

and C is the Faust-Henry coefficient [16], ω_p is the plasma frequency, ω_{TO} and ω_{LO} are the TO and LO phonon frequencies, respectively, and Γ and γ are the phonon and plasmon damping constants, respectively. The parameter ω_P, Γ, γ, and C can be obtained

from least-square fitting. Finally, the free carrier concentration is calculated from the plasma frequency by using

$$\omega_P = \left(\frac{4\pi n e^2}{\varepsilon_\infty m^*} \right)^{\frac{1}{2}} , \qquad (5)$$

where n is the free carrier concentration and m* is the effective mass of the free carriers.

Figure 3(b) shows the high resolution Raman spectrum of the coupled A_1(LO)-plasmon mode. Note that the spectrum from sapphire was removed by collecting Raman spectrum from the backside of the sample, followed by spectral subtraction. By fitting the spectrum with eq. (2), a plasma frequency of ω_p=50.6 cm^{-1} was obtained. By using eq. (5), the calculated free carrier concentration of the sputtered GaN is $<3\times10^{16}$ cm^{-3}. This value is considered as maximum since this is the detection limit for this method.

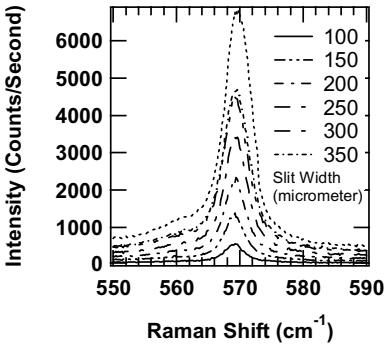

FIGURE 4. Raman spectrum of $E_2^{(2)}$ mode as a function of the monochromator slit width.

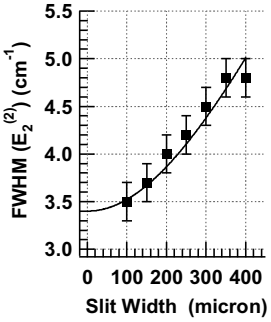

FIGURE 5. The plot of FWHM of the $E_2^{(2)}$ mode *vs*. slit width.

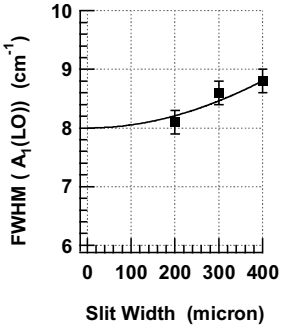

FIGURE 6. The plot of FWHM of the A_1(LO) mode *vs*. slit width.

Figure 4 shows the Raman spectra of the E_2 mode as a function of the spectrometer slit width. The plot of FWHM *vs*. spectrometer slit width is shown in Figure 5. The "zero-slit width" of 3.4 cm^{-1} was determined using the method used by Bergman *et al*., and the detailed procedure can be found elsewhere [17]. According to the uncertainty relation,

$$\Delta E \bullet \tau \sim \hbar \qquad (6)$$

where τ is the phonon lifetime, and ΔE is the Raman line width. The phonon lifetime of the sputtered GaN can be calculated using eq. (6) [18]. 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 is well recognized that incorporation of impurities and point defects substantially reduces phonon lifetimes, broadening the Raman peak. Note that the Raman E_2 mode in GaN is not affected by variation in the free carrier concentration. Similarly, phonon lifetime of A_1(LO) mode was determined to be 0.7 ps (Figure 6).

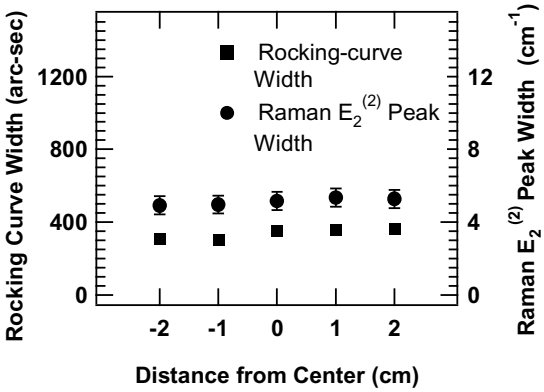

FIGURE 7. X-ray rocking curve width and FWHM of $E_2^{(2)}$ mode collected from different region of the GaN film.

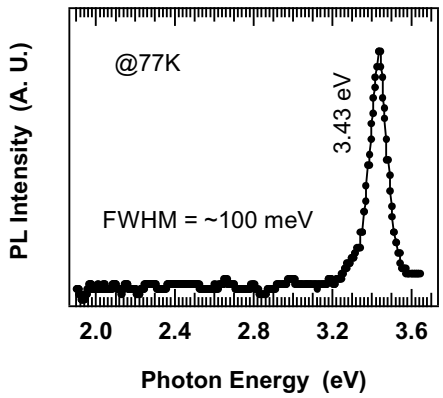

FIGURE 8. Photoluminescence spectrum of the sputtered GaN.

Figure 7 shows the X-ray rocking curve width and FWHM of the Raman $E_2^{(2)}$ peak for different regions on the sputtered GaN films. No substantial variation in X-ray rocking curve width or FWHM of the Raman peak was found, which implies that the quality of the film was uniform across the wafer. Figure 8 shows the photoluminescence spectrum of the same film. The "yellow luminescence" peak was not detected from the spectrum. The FWHM of the near band-edge photoluminescence peak obtained at 77K is ~100 meV. For comparison, the FWHM of the PL peak for samples grown by OMVPE is ~40 meV.

CONCULSIONS

The thick films of GaN were investigated using X-ray diffraction, micro-Raman spectroscopy and photoluminescence spectroscopy. The thick films of GaN were prepared on (0001) sapphire using high rate magnetron sputter epitaxy with growth rates as high as 10-60 μm/min. The width of the X-ray rocking curve ((0002) reflection) for the sample produced by this method is ~300 arc-sec. Only the allowed modes were observed in the polarized Raman spectra. The background electron concentration is lower than 3×10^{16} cm^{-3}, which was determined from the Raman spectra. The phonon lifetime determined from Raman $E_2^{(2)}$ mode was 1.6 ps, which is comparable to that of bulk single crystal GaN grown by sublimation (1.4 ps). The full-width-at-half-maximum of the near band-edge photoluminescence peak obtained at 77K is ~100 meV.

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