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Permalink
https://escholarship.org/uc/item/2km9p440

Journal
Applied Physics Letters, 80(8)

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Publication Date
2002-07-31
Correlations between spatially resolved Raman shifts and dislocation density in GaN films

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Spatially resolved Raman spectra were measured on thick GaN samples with known dislocation density grown by hydride vapor phase epitaxy. The frequencies of the E\textsubscript{2} (high) and E\textsubscript{1} (transverse optical) phonons shift to lower wave number over a distance of 30 µm from the sapphire substrate/GaN interface. The shifts are linearly correlated with the dislocation density suggesting that the strain due to the lattice mismatch at the interface determines both quantities.
One of the key issues for the performance of GaN based device structures is the control of growth-induced defects and their impact on optoelectronic and transport properties. Despite the impressive progress in device applications a deeper understanding of defect and impurity issues is necessary for continued rapid development in the areas of light emitting and laser diodes, ultraviolet detectors, and high voltage unipolar and bipolar devices.\(^1\) Raman spectroscopy has proven to be an informative and nondestructive technique in III–V material characterization including local structure determination and stress analysis.\(^2\) In low temperature, spatially resolved measurements shifts in the luminescence band and the \(E_2\) Raman mode have been observed with decreasing distance to the substrate interface.\(^3\) These were attributed to vertical strain and doping gradients. In a highly Si doped GaN material the quenching of the \(A_1\) Raman line by donor impurities has been used to image spatially varying carrier concentrations in faceted GaN crystallites.\(^4\) In quasibulk n-type GaN electron beam and optical depth profiling has recently been employed to measure the minority hole diffusion length as a function of distance from the GaN/sapphire substrate interface.\(^5\) The observed decrease in photoluminescence intensity and minority carrier diffusion length with decreasing distance from the interface was attributed to reduced carrier mobility and lifetime at the interface, due to scattering at threading dislocations. To relate strains present in the material due to a GaN/sapphire lattice mismatch we have performed spatially resolved Raman measurements and correlated them with dislocation density. The \(E_2\) (high) and \(E_1\) transverse optical (TO) phonons show shifts toward higher frequencies at the GaN/sapphire interface, which are linearly related with a spatial variation in dislocation density.

The samples under investigations were grown at the MIT Lincoln Laboratory by hydride vapor phase epitaxy.\(^6\) Several different films with thickness from 36 to 64 µm were used in our experiments. Room-temperature Hall measurements showed n-type electrical conductivity for these samples, with electron concentrations (at the surface) ranging from \(8\times10^{16}\) to \(1.2\times10^{17}\) cm\(^{-3}\), and mobilities of 580–750 cm\(^2\)/V s, respectively. The samples were then cleaved, to obtain a surface perpendicular to the growing direction on which the investigation could be made.
Raman spectra were measured with a single-grating spectrometer (HR 640, Instruments SA) equipped with a thinned back-illuminated charge-coupled device (CCD) detector (TKB 1024, Princeton Instruments) and a homebuilt microattachment. A holographic notch filter rejected the Rayleigh line. Raman scattering was excited with the 514.53 nm line of an Ar\(^+\) ion laser at a power of 10 mW. An infinity corrected microscope objective focused the laser beam to a spot size of about 1 µm in diameter. Due to the high sensitivity of the Raman system a very narrow entrance slit of the spectrometer (5 µm) was employed, and the spectra were measured in the second order of the diffracted light. The acquisition time of individual spectra was less than 30 s at a spectral resolution of 1 cm\(^{-1}\). During the entire experiment the drive of the spectrometer was not moved to avoid drifts of the wavelength position. The narrow slit and binning the CCD chip in the vertical direction effectively provided a confocal aperture and 1–2 µm depth resolution. The excitation beam was parallel to the surface of the interface and therefore perpendicular to the growth direction of the GaN layers. Sample positioning was performed with a translation stage allowing submicron increments.

Figure 1 presents the Raman spectra at various distances from the GaN/sapphire interface over a range of 64 µm. The data were collected with a backscattering geometry. The propagation direction of the laser beam was perpendicular to the c axis, but not along one of the principle axes so the \(A_1\) (TO), \(E_1\) (TO), \(E_1\) (LO), and \(E_2\) (high) modes are observed at 532, 558, 744, and 567 cm\(^{-1}\), respectively. These frequencies are measured 60 µm away from the interface and are in good agreement with literature data.\(^2\) Due to limitations of the Rayleigh filter the \(E_2\) (low) mode (144 cm\(^{-1}\)) was not investigated. The raw data presented in Fig. 1 show a shift of the \(E_1\) (TO) and \(E_2\) (high) modes to higher frequency with decreasing distance from the sapphire substrate. We did not observe any significant changes in full width at half maximum of the spectral bands. The precision in the determination of the frequency shifts could be further increased by fitting Lorenzian lines to the Raman peaks. Since the line shape remains constant we estimate that spectral shifts of 0.1 cm\(^{-1}\) can be reliably detected.\(^7\)

The peak frequencies of the Raman modes are shown as a function of the distance from the GaN/sapphire interface in Fig. 2. The shift of the \(E_2\) (high) and \(E_1\) (TO) phonons to higher energy when approaching the GaN/sapphire interface is clearly visible for
measurements in both directions, i.e., from the interface to the surface and backward. In addition, an independent experiment was conducted with another sample from the same batch. The shifts of the frequencies with distance are very reproducible; a small difference (0.2 cm\(^{-1}\)) in the absolute wave number is within the error of the calibration. The E\(_2\) Raman mode is known to be affected by stress\(^8,9,10,11\). In GaN films large compressive stresses causing frequency shifts of +4.5 cm\(^{-1}\) compared to single crystals have been observed\(^9\). The small changes in the E\(_2\) (high) and E\(_1\)(TO) modes, presented here, indicate the good quality of our films. Approximating the zero-stress E\(_2\) phonon frequency by the value measured far from the interface (567.2 cm\(^{-1}\)) we find a strain induced shift of +1 cm\(^{-1}\). This corresponds to a compressive strain of 0.42 GPa within 5 µm of the GaN/sapphire interface based on the stress determination in Ref. 9. The absence of a significant shift in the A\(_1\) phonon may be related to the direction of the optical phonon eigenvectors with respect to the c axis. Among the Raman active modes A\(_1\) is the only one with displacements along the c axis\(^12,2\) as opposed to the E\(_2\)(high) and E\(_1\) (TO) vibrations.

Figure 3 presents the correlation between the peak frequencies of the E\(_2\) and E\(_1\) Raman modes and the dislocation density. Data for the dislocation density as a function of distance from the sapphire/GaN interface were obtained from transmission electron microscope (TEM) measurements\(^5\). The two phonon frequencies depend linearly on the dislocation density over an order of magnitude range. The average dislocation distance calculated from the density varies from 0.35 to 0.69 µm at a distance of 8–32 µm from the interface, respectively. A similar shift in the E\(_2\) Raman mode has been reported in Ref. 3 and been attributed to vertical strain. In the films discussed here, shifts are not only observed for the E\(_2\) (high) but also for the E\(_1\) (TO) mode. These as well as the linear correlation with dislocation density may be attributed to the biaxial strain due to lattice mismatch of the sapphire substrate. The same biaxial strain is responsible for the formation and multiplication of dislocations near the interface during film growth. The local strain associated with dislocations (and thus a direct relationship) is more complex, because it depends on the particular arrangement of dislocations and involves both tensile compressure and shear components. The strain is extremely high near the core of the dislocation but decreases with the square of the distance away from the core.
We note that the shifts, observed in Fig. 2 for the \( E_2 \) (high) and \( E_1 \) (TO) modes may be related to the directions of the vibrational displacements of the Ga and N atoms relative to the threading dislocations. Both displacements are perpendicular to the \( c \) axis of the wurtzite GaN lattice and also to the direction of threading dislocations propagation. Wu et al.\(^\text{13} \) have shown that above \( \sim0.5 \) \( \mu m \) to the film free surface the threading dislocations are straight and show little interaction with most of the threading segments being perpendicular to the surface. Larger Raman shifts are indeed observed in regions at higher dislocation density and for the \( E_2 \) (high) and \( E_1 \) (TO) modes. A less pronounced shift for the \( A_1 \) (TO) mode with eigenvectors parallel to the \( c \) axis is also consistent. On the other hand, we did not find significant shifts of the \( E_1 \) (LO) mode although the displacement vectors are perpendicular to the \( c \) axis. The reason is not clear at the present time and may lie in the more complex local strains.

In summary, micro-Raman spectroscopy shows a high frequency shift for the \( E_2^\text{high} \) (high) and \( E_1 \) optical phonons at the GaN/sapphire interface. We were able to correlate independently obtained data on dislocation density and vibrational modes which are connected to the strain due to lattice mismatch at the interface.

The authors would like acknowledge financial support from the University of Central Florida through the Presidential equipment initiative program. R. J. Molnar (Lincoln Lab) and D. C. Look (AFRL) are acknowledged for providing bulk GaN samples. The TEM group (J.J., M.B., and Z.L.-W.) acknowledges financial support from the Air Force Office of Scientific Research, through the U.S. Department of Energy under Order No. AFOSR-ISSA-00-0011, and thanks W. Swider for her excellent TEM sample preparation and NCEM in Berkeley for the use of TEM facility.

References

Figure Captions

Fig. 1. Raman spectra of a 64 µm thick GaN film measured with 514.5 nm excitation. Inset shows \( E_1 \) (TO) and \( E_2 \) (high) modes for various distances from the GaN interface.

Fig. 2. Peak frequencies of the Raman \( E_2 \) (high) and \( E_1 \) (TO) modes as a function of distance to the substrate interface. The solid lines represent exponential fits to the data points with asymptotic values of 567.2 and 558.3 cm\(^{-1}\), respectively. The open symbols show results from a second experiment on a sample grown under the same conditions.

Fig. 3. Correlation between peak position of the \( E_1 \) (TO) and \( E_2 \) (high) Raman modes and dislocation density. Data from two different samples (64 and 36 µm thick) are shown.