Second order Raman spectroscopy of the wurtzite form of GaN

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We report on Raman scattering by phonon pairs in GaN films grown on sapphire substrates by plasma-enhanced molecular beam epitaxy. The first order data are consistent with results obtained from GaN bulk crystals of the wurtzite structure. The A_1 and the much weaker E_2 symmetry components of the second order scattering have been identified. Two-phonon spectra are dominated by contributions due to longitudinal optical phonons. © *1995 American Institute of Physics.*

Gallium nitride (GaN) has attracted considerable attention recently.[1] Its wide, direct band gap of 3.4 eV, makes it a promising candidate for semiconductor device applications in the blue and ultraviolet regions. There have been a few works describing Raman scattering studies of GaN in its wurtzite form.[2–6] However, there have been no reports of *second order* spectra to the best of our knowledge. In this paper, we present such results in thin films of GaN. Our first order measurements confirm the single crystalline nature of the samples. The dominant contribution to the second order Raman scattering was found to be from the fully symmetric A_1 component.

Nominally undoped GaN films were grown on c-plane (0001) sapphire substrates using plasma-enhanced molecular beam epitaxy.[7] Four samples of varying thickness (2.7 to 3.2 μm) and electron concentration ranging from 1×10^{17} to 1×10^{19} cm^{-3} were studied. X-ray data reveal that the films crystallize in the wurtzite structure with the (0001) axis parallel to the direction of growth. The Raman scattering measurements were performed at room temperature using a Dilor XY multichannel spectrometer and the 4880 Å line of an argon ion laser. Consistent results were obtained in all four samples. Spectra were recorded in the $z(y,y)\bar{z}$ and $z(y,x)\bar{z}$ backscattering geometries. Here, z (and $\bar{z}$) are parallel to the hexagonal axis and x, y are mutually orthogonal, arbitrary directions in the plane of the films. The notation $a(b,c)d$ is such that a,d denote the directions and b,c represent the polarizations of the incident and scattered light, respectively.[8]

The point group of wurtzite is C_{6v} leading to $A_1+E_1+2E_2$ Raman active modes.[5] Since the A_1 and E_1 symmetries are also infrared active, they split into longitudinal (LO) and transverse (TO) components. The Raman selection rules dictate that the A_1(LO) and the E_2 modes are expected in the $z(y,y)\bar{z}$ configuration and that the $z(y,x)\bar{z}$ configuration allows only E_2 modes. The E_1 mode is forbidden for backscattering off (0001) faces. Figure 1 shows the Raman spectrum of one of our films in the $z(y,y)\bar{z}$ configuration. Since both GaN and sapphire are transparent to the blue light of the incident laser, the spectra consists of a superposition of scattering from the GaN film and sapphire. The first order GaN phonons are indicated by arrows. Consistent with earlier reports[5] and Raman selection rules, the peak at ~570 cm^{-1} is due to the high frequency E_2 mode (the low frequency E_2 phonon is at ~144 cm^{-1}).[3] The A_1(LO) phonon at ~738 cm^{-1} can be barely resolved from the tail of the E_g mode of sapphire at 751 cm^{-1}. Its energy is consistent with the value reported in Ref. 2, but is blue shifted by ~30 cm^{-1} from that in Ref. 3; this is tentatively ascribed to effects due to stress. The positions of the other discrete, first order Raman peaks in Fig. 1 agree well with the values reported earlier for sapphire.[9] Other than the narrow first order lines, the spectrum shows a continuum, at about twice the energy of the A_1(LO) phonon, which is nearly thirty times weaker than the first order scattering. This feature, on top of a relatively strong luminescence background whose origin is still unclear, is ascribed to second order Raman scattering from GaN and sapphire. In order to discern the contribution due to GaN, Raman measurements were performed under identical scattering conditions on a sapphire sample.[10] After normalization of the second order data from both samples with respect to the first order sapphire peak at 418 cm^{-1}, the sapphire contribution was subtracted to obtain the resultant contribution due to GaN alone. This procedure was used for both the $z(y,y)\bar{z}$ (A_1+E_2) and the much weaker $z(y,x)\bar{z}$ (E_2) configuration. After comparing the results in both geometries and taking leakages into account, the individual contributions of A_1 and E_2 symmetries were obtained. This is shown in Fig. 2. Second order Raman spectra probe the continuum of phonon pairs with wave vectors of equal magnitude but opposite directions.[8] This is clearly evident in the measured spectra, in contrast to the discreteness of the first order Raman scattering due to zone-center phonons. Since modes with wave vectors throughout the Brillouin zone are involved, the second order intensity reflects the phonon density of states, which in turn is related to the phonon dispersion. From Fig. 2, it can be seen that the fully symmetric A_1 contribution is much stronger than that of E_2 symmetry with a cutoff at ~1490 cm^{-1} in both spectra. The band at ~1467 cm^{-1} in Fig. 2(a) is slightly lower than twice the energy of the first order, zone-center, A_1(LO) phonon. This is attributed to overtone scattering due to two phonons of the corresponding branch near the edge of the Brillouin zone, where the phonon den-

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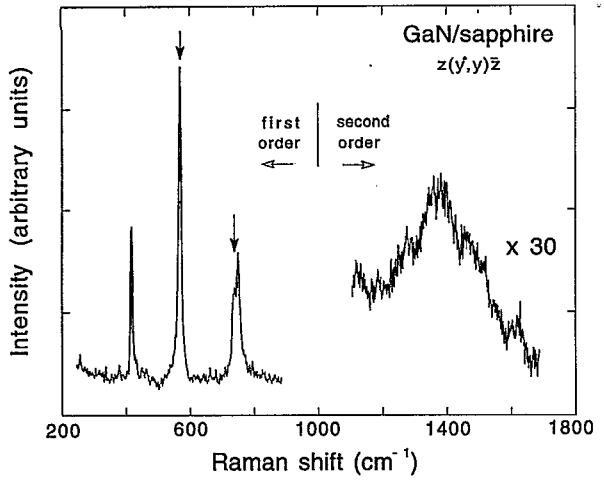

FIG. 1. First and second order Raman scattering from GaN and sapphire. The positions of the zone-center optical phonons in GaN are marked by arrows; the other peaks are due to sapphire. The continuous structure above ~1000 cm^{-1} is due to second order scattering from GaN and sapphire.

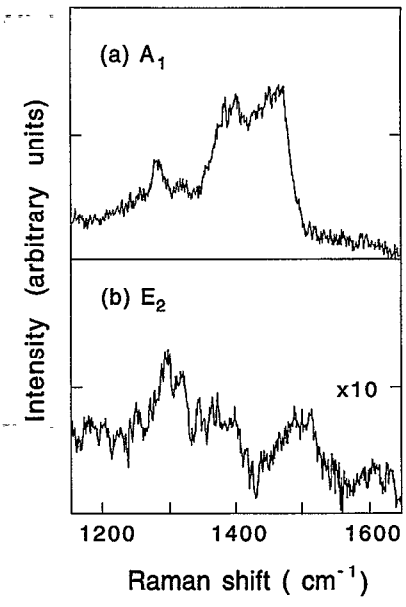

FIG. 2. Second order Raman scattering contribution of (a) A_1 and (b) E_2 symmetry in GaN. The intensity of the A_1 component is nearly ten times stronger than that of the E_2 component.

sity of states is largest. The other prominent features in the A_1 spectrum in Fig. 2(a) are at 1282 and 1387 cm^{-1}. Taking into account the raw data and the low signal-to-noise ratio of the E_2 spectrum, only the features at 1297 and 1318 cm^{-1} can be unequivocally assigned to E_2 scattering from GaN. The structures at higher shifts are most likely due to the substrate and A_1 leaks. The bands in Fig. 2(a) and 2(b) as listed above, are assigned to additional maxima in the density of states, associated with other critical points. Their origin is not known due to the lack of theoretical calculations or measurements of dispersion curves for phonons in GaN. Because of the strong first order Raman peaks from GaN and sapphire, we could not measure second order scattering at lower energies. Furthermore, it was not experimentally possible to determine second order scattering of E_1 symmetry. We would like to note here that due to the lack of availability of good quality samples of GaN grown on other substrates, additional data confirming the nature of the second order scattering in the wurtzite form of GaN could not be obtained.

In summary, we have reported first and second order Raman scattering from thin films of wurtzite GaN grown on sapphire. The zone-center, A_1(LO) and E_2 phonons, were seen in first order scattering with line shapes and selection rules which are consistent with the single crystalline nature of the samples. The A_1 and E_2 symmetry contributions to the second order Raman scattering were obtained. The A_1 symmetry component was found to be dominant.

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