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Ultraviolet Raman study of $A_1(LO)$ and E_2 phonons in $\ln_x Ga_{1-x}N$ alloys

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We report on ultraviolet Raman spectroscopy of $In_xGa_{1-x}N$ thin films grown on sapphire by metal-organic chemical vapor deposition. The $A_1(LO)$ and E_2 phonon mode behavior was investigated over a large compositional range (0 < x < 0.50). Compelling evidence is presented for one-mode behavior for the $A_1(LO)$ phonon, and data suggestive of two-mode behavior are presented for the E_2 phonon. © 2001 American Institute of Physics. [DOI: 10.1063/1.1330760]

In recent years interest has increased in the group III nitrides as hopeful candidates for the fabrication of lightemitting diodes and laser diodes operating throughout the visible region and into the UV range. AlN, GaN, and InN are an important set of semiconductors because their direct band gaps span the range 1.9 to 6.2 eV.¹ In principle, this complete set of ternary allows for any band gap within this range. This tunability of the energy band gap, combined with the fact that they generate efficient luminescence, has motivated the study and fabrication of high-performance optical devices based on the group III nitrides. Potential applications range from high-density optical storage devices to projection and other bright displays. Presently much work and progress has been done in AlN, GaN, and their alloys. The growth of InGaN alloys, with a band gap energy range of 1.9 to 3.4 eV, however, has proven to be very difficult. One of the main difficulties with InGaN growth is the large difference in interatomic spacing between GaN and InN of roughly 11%. This large difference can give rise to a solid miscibility gap and highly strained InGaN alloys.² As a result, phase separation in the alloy becomes a major concern. Until recently, there has been little attention given to the phonon mode behavior over a wide compositional range in the hexagonal wurtzite $In_xGa_{1-x}N$ system.

Mid- and deep-UV Raman spectroscopy have been used here as an effective tool for studying the issue of compositional inhomogeneities and spinodal decomposition in InGaN thin films. In addition, mode behavior over a large compositional range was investigated, and we have found compelling evidence for one-mode behavior for the $A_1(LO)$ phonon mode, while our data is suggestive of two-mode behavior for the E_2 mode consistent with the previously found behavior in AlGaN.^{3,4}

In this work, we study the Raman scattering spectra of $In_xGa_{1-x}N$ alloys, grown on (0001) sapphire substrates us-

ing a specially designed metal-organic chemical vapor deposition (MOCVD) reactor and growth conditions that have been described elsewhere.⁵ A buffer layer of GaN was grown on each substrate prior to the growth of the InGaN films. The growth temperature of the $In_xGa_{1-x}N$ layer was between 690 °C and 780 °C. Variation of the growth temperature and the hydrogen gas flow rate determined the percent concentration of InN. Eight films were examined in the compositional range 0 < x < 0.50. The composition *x* was determined by calculating the shift of the 0002 XRD InGaN peak relative to the 0002 peak position of GaN, and applying Vegard's law.

Raman scattering experiments of thin $In_xGa_{1-x}N$ films, using visible laser frequencies, typically provide additional Raman peaks from buffer layers and substrates. In addition, InGaN films with low InN compositional content emit strong interfering broadband luminescence in visible regions. The excitation of Raman scattering in the UV avoids both of these problems. The Raman spectral region of interest is well above any emitted photoluminescence, and there is strong absorption of the UV laser light in the film, resulting in a larger Raman signal and an absence of Raman peaks from layers below the film. The deep-UV Raman spectra were excited with the 244 nm line of a frequency-doubled Coherent Inc. Innova 300 FreD Argon Ion laser. The incident beam was focused onto the sample to a spot size of approximately 2 mm in height and 50 μ m in width. The intensity of the light on the surface of the sample, in this configuration, was on the order of 65 W/cm². The scattered light was collected in a backscattering geometry and imaged onto the entrance slit of a SPEX 1877 TripleMate spectrometer, equipped with a UV-enhanced liquid-nitrogen-cooled charge coupled device (CCD). Specialized high-reflectance dielectric mirrors were used for steering the laser beam, and a single plano convex lens, of UV grade fused silica, was used to focus the

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FIG. 1. Raman spectra of InGaN films. The dotted lines represent the positions of the E_2 mode for InN and GaN at 488 and 738 cm⁻¹. (a) Spectra excited with the 244 nm line of the frequency doubled Ar ion laser. (b) Spectra excited with the 325.2 nm line of a HeCe laser. The positions of the A_1 (LO) frequencies are marked.

scattered light. The Raman spectra were obtained with a 3600 gr/mm grating, providing 0.8 cm⁻¹ resolution. The mid-UV Raman spectra were excited with the 325 nm line of a HeCd laser. The laser light was focused on the sample through a specialized $100 \times$ UV microscope objective down to a spot size of approximately 0.3 μ m with a power density around 16.7×10^5 W/cm². The scattered light was analyzed with a UV JY LabRam Infinity equipped with a UV-enhanced liquid-nitrogen-cooled CCD. The Raman spectra were obtained with a 2400 gr/mm grating providing 3 cm⁻¹ resolution. For both of these situations Raman scattering by the A_1 (LO) and E_2 phonons are symmetry allowed from the (0001) surfaces of the hexagonal wurzite structures.

Figure 1(a) shows Raman spectra excited with the 244 nm (5.1 eV) line of the frequency-doubled Ar ion laser. The dashed lines indicate the Raman frequencies of the E_2 mode for InN and GaN. The value for the E_2 mode in InN was taken from other references.^{3–6} Several Raman peaks due to

scattering from air overlap the region of the $A_1(LO)$ peak. Analysis of the $A_1(LO)$ peak positions, for the data taken with the 244 nm line, was not included for this reason. However, qualitative observations regarding the ratio of $A_1(LO)$ to E_2 peak intensities are made. For the GaN and the films with low InN concentration, the intensity of the $A_1(LO)$ mode, with respect to the E_2 mode, is small. The absence of the $A_1(LO)$ mode has been previously observed in GaN and has been attributed to a high free carrier concentration in the film; the free carriers form plasmon waves that interact and, in turn, damp the LO phonons.^{7,8} The free carrier concentration of the GaN film used for Fig. 1(a) was found to be 8.4 $\times 10^{16}$ cm⁻³ by Hall measurements. The free carrier concentrations in the InGaN films are of the order of 10^{18} cm⁻³, and the concentration increases with higher In concentrations. Despite this, the films with higher InN concentration show an increase in the $A_1(LO)$ intensity with respect to the E_2 mode. Inushima *et al.* reported Raman spectra of InN films in which the $A_1(LO)$ mode intensity was also greater than the E_2 mode intensity.⁹ Their films were grown on (0001) sapphire substrates with a carrier density of 3 $\times 10^{20}$ cm⁻³ by Hall measurements. They ascribed this effect to the presence of a deep depletion layer on the air exposed surface of InN.

Figure 1(b) shows Raman spectra excited with the 325.2 nm (3.81 eV) line of the HeCd laser. The dashed lines again show the position of the E_2 mode for InN and GaN. Raman spectra for GaN could not be obtained due to the strong photoluminescence resulting from excitation just above the band gap of the material. In these spectra the case is the opposite of that observed in Fig. 1(a). The E_2 mode intensity is weak with respect to the $A_1(LO)$ mode for low concentrations of InN in the film. The $A_1(LO)$ mode is easily detected, and though not shown here, even second- and third-order A_1 (LO) phonons could be observed. This is presumably due to a resonant Raman effect at this laser energy. Also worth noting, the $A_1(LO)$ mode develops an additional low-energy feature for In concentrations higher than 15%. The shoulder and the large full width at half maximum (FWHM) of the $A_1(LO)$ peaks in Fig. 1(b) have tentatively been assigned to compositional inhomogeneities and spinodal decomposition effects present in InGaN films that have been previously discussed.^{2,10,11} This issue will be addressed more completely in a future publication.

Figure 2 shows the frequencies of the $A_1(LO)$ and E_2 modes as a function of alloy composition. The filled circles represent the peak positions of the $A_1(LO)$ mode in Fig. 1(b). The peak positions of the $A_1(LO)$ mode, in Fig. 1(a), are not shown due to the presence of interfering air peaks, which made assignment of peak positions difficult. The crosses and unfilled circles in Fig. 2 represent the E_2 mode frequencies from Figs. 1(a) and 1(b), respectively. The peak positions were determined by fitting the spectra in Figs. 1(a) and 1(b). Each spectral feature was fitted to a function that was a cross product of Lorentzian and Gaussian peak functions. The $A_1(LO)$ peaks in Fig. 1(b), which exhibited a low-energy shoulder, were fit with two peak functions. The sample with 35.6% In concentration was fit with an additional high-energy shoulder. The $A_1(LO)$ peak positions



FIG. 2. Percent InN concentration versus frequency for the $A_1(LO)$ and E_2 modes. $A_1(LO)$ mode for 325.2 nm data. E_2 mode for both 244 and 325.2 nm. The bars at x=1 represent data points for InN taken from the following Refs. In descending order, Refs. 6, 13, 12, 9, and 14 for the $A_1(LO)$ mode, and Refs. 6, 13, 12, and 9 for the E_2 mode.

used in Fig. 2 are marked in Fig. 1(b). These positions are assumed to be due to the majority phase of the alloy in the films, and the low-energy shoulder is tentatively assigned to the phase-segregated regions of higher In concentration. Similar InGaN films were analyzed by $\theta - 2\theta$ x-ray diffraction. The x-ray data for films with concentrations above 40% In concentration showed a diffraction peak for the majority phase along with a shoulder that was fitted with several Gaussian distribution functions.¹¹ The authors ascribed this feature to phase separation occurring in the films. The value for the $A_1(LO)$ mode in InN was taken from other references. $^{6,9,12-14}$ The A_1 (LO) frequencies shift linearly as a function of percent InN composition. The experimental values presented here fit well with a linear extrapolation to the InN endpoint. This is indicative of one-mode behavior for the $A_1(LO)$ mode. The one-mode behavior of the $A_1(LO)$ phonon is in good agreement with theoretical calculations based on a modified random element isodisplacement model (MREI) for the ternary family of semiconductors $AB_{1-x}C_x$.¹⁵ It has also been shown experimentally that the $A_1(LO)$ phonon in $Al_xGa_{1-x}N$ wurzite structures obeys a one-mode behavior.^{3,4}

The E_2 phonon frequencies shown in Fig. 2, for the 244 and 325.2 nm laser lines, show a good consistent linear fit for the InN compositional range of 0 < x < 0.50. However, the extrapolated line for the E_2 data intersects between 30 and 40 cm⁻¹ lower at x=1 than the previously reported E_2 mode frequencies for InN. It has been shown experimentally that the E_2 phonon mode in the Al_xGa_{1-x}N wurzite structure displays a two-mode-type behavior.^{3,4} The phonon behavior in a mixed crystal of an $AB_{1-x}C_x$ ternary system falls into two main classes, referred to as one- and two-mode behavior. Phonons exhibiting one-mode behavior have only one set of frequencies that show nearly linear dependency with the composition x, from the AB component to the AC component. The $A_1(LO)$ mode in $In_rGa_{1-r}N$ exhibits this behavior. On the other hand, the frequencies of phonons in the two-mode class of materials exhibit a nonlinear dependence with composition x. Also, for an intermediate composition x in the two-mode class of materials, two sets of frequencies are usually observed in the spectra. One set of frequencies is due to the modes of the lighter AB component and one set for the heavier AC component. These components in the In_xGa_{1-x}N crystal are GaN and InN. The absence of the InN set of frequencies in the spectra may be due to the large FWHM for peaks close to 50% In concentration, making it difficult to detect weak peaks in that spectral region.

In summary, we present the results of a Raman scattering study for a series of $In_xGa_{1-x}N$ films from x=0 to 0.50, where the Raman scattering was excited with two different UV frequencies. Our results show the behavior of the $A_1(LO)$ and E_2 modes as a function of composition. The $A_1(LO)$ mode follows a one-mode behavior while the E_2 mode appears to follow two-mode behavior consistent with AlGaN studies.

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