phys. stat. sol. (a) **179**, R4 (2000)
Subject classification: 68.55.Nq; 78.30.Fs; 78.55.Cr; S7.14

Evidence for Phase Separation in InGaN by Resonant Raman Scattering

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(Submitted March 21, 2000; accepted April 6, 2000)

Introduction The InGaN material system has attracted much attention since the possibility arises to produce light emitting diodes and laser diodes covering the spectral range of the UV and the whole visible [1]. Much effort has been placed into shifting the emission to longer wavelengths by introducing higher amounts of indium into the alloy, which was found to decrease the crystal quality. Recently, the production of a laser diode with 200 h lifetime emitting at 450 nm was reported [2]. The difficulty of growing high quality InGaN crystals is usually explained by the theoretically predicted limited solubility of indium in GaN leading to a miscibility gap [3,4]. It was pointed out that this accounts for the bulk solubility, but the surface solubility being more relevant for vapour phase growth is more extensive [5].

Resonant Raman scattering was used to investigate compositional fluctuations in thin InGaN films [6] and InGaN/GaN heterostructures [7]. In both Refs. [6] and [7] temperature was used to tune the effective band gap. By doing so the resonance condition was fulfilled for regions with different indium molar fraction. A change of the A_1(LO) mode frequency was observed depending on the indium concentration of the probed sample volume. In this paper we want to show that resonant Raman scattering can also probe regions with a very small indium concentration, i.e. there is evidence of phase separation, even if no GaN-like features are observed under non-resonant excitation conditions.

Experimental Details The 1 μm thick InGaN samples were grown by molecular beam epitaxy on *c*-plane sapphire followed by a 30 nm GaN buffer layer [8]. Here, we report on three samples having an average indium concentration of 5%, 10% and 20%. Raman measurements were carried out in backscattering geometry $z(..)\underline{z}$ using a cooled charge-coupled device detector. Non-resonant Raman-scattering experiments were performed at room temperature using the 568.3 nm line of an Ar^+/Kr^+ mixed-gas laser for excitation to avoid the strong luminescence background. The accuracy is 0.5 cm^{-1}. For resonant excitation at room temperature the 363.8 nm Ar^+ line was chosen. Signal detection and analyses were carried out with a Dilor UV spectrometer having a resolution of 3 cm^{-1}. For standard photoluminescence (PL) at 4.2 K the samples were excited at 325 nm.

Results and Discussion Figure 1 shows the normalized PL spectra of the three samples at 4.2 K. With increasing indium concentration the main emission peak from the InGaN shifts to lower energies. The maximum intensity is found at 2.80, 2.67 and 2.61 eV, respectively. For all three samples we find an emission line at 3.36 eV which is two orders of magnitude weaker than the main emission. This luminescence was previously reported for zincblende and wurtzite GaN and assigned to excitons localised at extended defects [9], but its origin is still under discussion. However, we do not observe the typical free or donor-bound exciton luminescence of GaN.

In Fig. 2 non-resonant Raman spectra are depicted. We observe the E_2 phonon mode which shifts to lower frequency with increasing indium concentration. The E_2 frequency vs. molar indium fraction is shown in the inset of Fig. 2, where the data points for pure GaN and InN are also indicated. We achieve a similar relation like Harima et al. [10] did for a smaller composition range.

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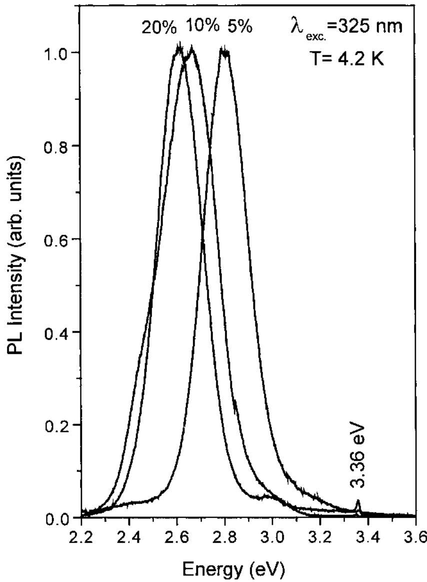

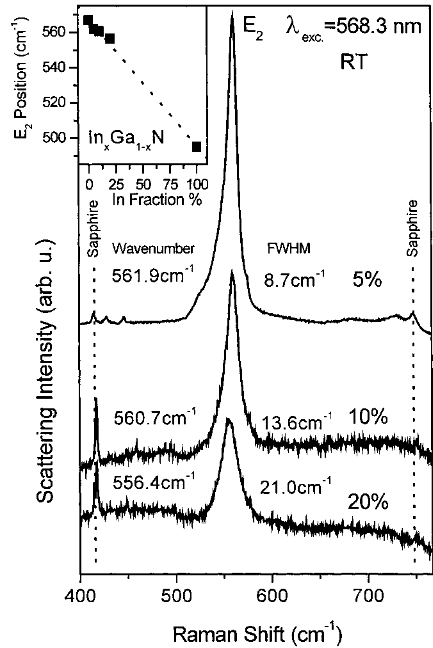

Fig. 1. Normalized PL spectra of three InGaN samples with different indium concentrations recorded at 4.2 K

Fig. 2. RT Raman spectra at non-resonant excitation. The inset shows the E_2 frequency vs. indium concentration. The dotted line represents a linear approximation

Furthermore the linewidth of the E_2 mode increases with the indium concentration, which results from compositional fluctuations. This also may account for the fact that we do not observe the A_1(LO) mode, which is allowed by selection rules in the $z(..)\underline{z}$ scattering geometry. Only for the 5% sample a weak broad band around 730 cm^{-1} is discernible. We suggest that in the samples with 10% and 20% indium the A_1(LO) mode disappears in the background due to strong line broadening.

Excitation at 363.8 nm, i.e. close to the band gap of GaN at room temperature, drastically changes the Raman spectra (see Fig. 3). We find three phonon modes at 734 cm^{-1}, 1462 cm^{-1} and 2186 cm^{-1} on a luminescence background, which are the 1LO, 2LO and 3LO lines of pure GaN [11]. The frequency of the multiple LO bands is slightly lower than the A_1(LO) frequency multiplied by 2 or 3 since for the multiphonon processes the phonons are no longer restricted to the centre of the Brillouin zone. For excitation close to the fundamental band gap scattering by LO phonons via the Fröhlich interaction occurs and

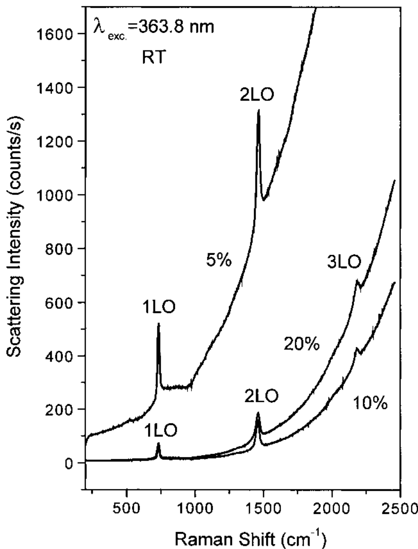

Fig. 3. RT Raman spectra of the three InGaN samples under excitation close to the GaN band gap

gives rise to strongly enhanced multiple LO phonon emission. In our spectra we do not observe the E_2 phonons which interact only via the deformation-potential mechanism even if allowed by selection rules.

The penetration depth of the exciting laser light is 79 nm (5%), 46 nm (10%) and 42 nm (20%), respectively, as derived from ellipsometric data. Therefore we can exclude that the GaN signal stems from Raman scattering within the buffer layer. We rather think that our results evidence a phase separation in the InGaN material system. Using EDX such phase separation has been observed in InGaN layers [12].

In summary, we have shown that resonant Raman scattering is an effective non-destructive tool to probe phase separation in InGaN samples. Even small quantities of the GaN phase can be detected, which are not seen in PL or non-resonant Raman spectra.

Acknowledgements The authors would like to thank Dilor Company for supplying their UV spectrometer and C. Cobet (TU Berlin) for carrying out the ellipsometric measurements. A. Kaschner is grateful for an Ernst-von-Siemens scholarship. Part of this work was supported by Deutsche Forschungsgemeinschaft and Volkswagen-Stiftung.

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