

Evidence for Phase-Separated Quantum Dots in Cubic InGaN Layers from Resonant Raman Scattering

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The emission of light in the blue-green region from cubic $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys grown by molecular beam epitaxy is observed at room temperature and 30 K. By using selective resonant Raman spectroscopy (RRS) we demonstrate that the emission is due to quantum confinement effects taking place in phase-separated In-rich quantum dots formed in the layers. RRS data show that the In content of the dots fluctuates across the volume of the layers. We find that dot size and alloy fluctuation determine the emission wavelengths.

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Group-III nitride semiconductors have led to high efficient quantum well (QW) structure light emitting diodes (LEDs) operating in the blue-green region of the spectrum and laser diodes (LDs) emitting violet light [1]. The $\text{In}_x\text{Ga}_{1-x}\text{N}$ layers are the active media in these devices. This has motivated several investigations of the structural and optical properties of the InGaN alloys in both hexagonal (*h*) [2–6] and cubic (*c*) [7–9] structures. Despite all this effort, the optical emission mechanism in the available LEDs and LDs remains a controversial issue and is a subject of ongoing discussion in the literature. The fact that emission is observed with energy below the alloy band gap and that the high efficiency carrier recombination is insensitive to defects led to the conclusion that carrier localization effects are taking place in the emission process. Different mechanisms have been proposed for the origin of the carrier localized states in the device QW structures. For *h*-based QWs, the piezoelectric (PZ) field across the well would localize the carriers in the lowest potential at the interfaces, lowering the recombination energy [5]. From theory it has been shown that exciton localization effects would arise from the localization of the hole wave function related to the In atoms [10]. In the so-called localized exciton model, In composition fluctuation in the InGaN well would produce potential minima active for carriers localization [2]. Another model is the recombination of carriers localized within quantum dots (QDs) [2,3]. Alloy fluctuations and the QDs formation would originate from thermodynamic equilibrium phase separation taking place at the InGaN growth temperature [11]. Recently, it has been proposed that the excitons are confined within QDs with almost InN composition but with radii increasing with the In content in the alloy [6]. According to this model the emission wavelength would depend on the dots size rather than on the alloy

fluctuation. The presence of In-rich phases or inclusions in InGaN epitaxial layers arising from phase separation effects is well established [9,12]. It is quite consistent then to associate such phases with a recombination channel in the emission process. However, *there is no direct proof* so far that the observed below-band-gap emission originates from such phases. Moreover, *there is also no demonstration* that they are QDs. In the present investigation we demonstrate that the blue-green below-band-gap photoluminescence (PL) from the *c*-InGaN is directly linked to In-rich separated phases in the alloy. Polarized resonant Raman scattering (RRS) measurements show that the emission originates from self-formed phase-separated nanometer scale QDs. Since spontaneous polarizations do not exist in cubic structures and coherent growth of InGaN layers on GaN(001) cubic buffer does not give rise to PZ fields [13], the investigations performed here are essential to clearly establish the role of In-rich separated phases (QDs) in the luminescence emission mechanism.

The $\text{In}_x\text{Ga}_{1-x}\text{N}$ ($0.07 \leq x \leq 0.33$) samples analyzed here are grown on GaAs (001) substrates by plasma assisted molecular beam epitaxy (MBE) using a GaN layer as a buffer. Details about the growth and structural analysis of the films are given in Ref. [9]. The PL measurements were carried out at room temperature (RT) and $T = 30$ K, with standard photomultiplier detection, and using the 2.81 eV line of a HeCd laser for excitation. The excitation energy was below the GaN band gap in order to avoid luminescence from the GaN buffer. The Raman scattering measurements were performed at RT with the Jobin-Yvon T64000 micro-Raman system. The focus was a spot of about $2 \mu\text{m}$ diameter. Several different lines of an Ar^+ and a Kr^+ ion laser were used in order to achieve resonance.

The PL spectra obtained from the $c\text{-In}_x\text{Ga}_{1-x}\text{N}$ layers with $x = 0.07, 0.19,$ and 0.33 are shown in Fig. 1. The emission lines were fitted to Gaussian line shapes leading to the energies of the PL peaks (E) and the linewidths (full width at half maximum) Γ . The results are shown in Table I. For the layer with $x = 0.07$ we notice in the spectra the presence of a second small peak at higher energies. Two Gaussian functions were used to fit the spectrum at RT. Only the results for the main peak are shown in Table I. At RT (30 K) a redshift of 127 meV (197 meV) was observed for the PL peak as the In content was increased from 0.07 to 0.33. In a first step to identify the origin of the observed luminescence we show that the PL emission energies fall far below the gap energies of the respective InGaN layers. In Fig. 2 a comparison is made between the emission energies (E) obtained by us (full circles) with the measured energies of the fundamental absorption edges of the $c\text{-InGaN}$ layers. The open circles are recent data from spectroscopic ellipsometry studies [14] carried out on samples grown in our group and the triangles are results of absorption measurements [7,8] obtained also on MBE-grown epitaxial layers. The solid curve in Fig. 2 is a parabolic fit of the data by assuming the value 1.9 eV for the $c\text{-InN}$ gap energy. It is clear from Fig. 2 that the PL emission observed by us cannot be related to the alloy gap energy. In $c\text{-GaN}$ a defect-

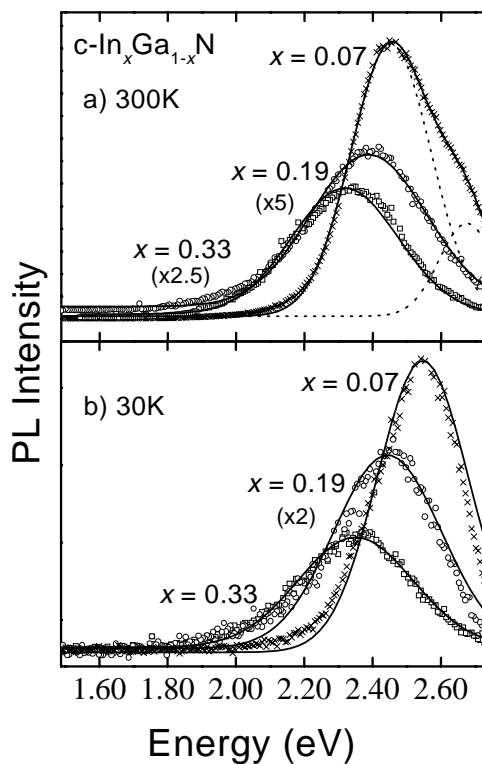


FIG. 1. PL spectra of $c\text{-In}_x\text{Ga}_{1-x}\text{N}$ layers. (a) At RT; (b) at $T = 30$ K. The solid lines are fittings to Gaussian line shapes. The dashed lines are the Gaussian functions used to fit the spectrum for the sample with $x = 0.07$.

related process has been observed at 2.4 eV by cathodoluminescence at low excitation densities [15]. However, luminescence of this transition is totally suppressed at low temperatures which is not observed in our PL experiments. Therefore, we can rule out defect-related processes and analyze the emission observed by us in terms of quantum confinement effects. Recent x-ray diffraction (XRD) analysis of our samples [9,12] showed that our $\text{In}_x\text{Ga}_{1-x}\text{N}$ layers are fully relaxed and contained strained crystalline cubic In-rich separated phases with nearly the same composition ($x \approx 0.8$) in all analyzed samples. For the $x = 0.33$ layer an In-poor phase with $x = 0.20$ was also detected, leading to the conclusion that spinodal decomposition effects may take place in our samples [11]. In the following we show that the emission observed by us originates from an In-rich phase present in the layers. Recently, we found in our samples that both the TO and LO phonons exhibit a one-mode type behavior, and the frequencies lie on straight lines connecting the corresponding values obtained for $c\text{-GaN}$ and $c\text{-InN}$ epitaxial layers [9]. Theoretical calculations confirmed these results [16]. Those findings lead to a straightforward way to determine the alloy composition in $c\text{-InGaN}$ layers by using the Raman technique. By measuring the frequency of the LO phonon we can access the value of x . The same process can be used to determine the composition of the In-rich phases in the layers provided that excitation energies which tune electronic transitions associated with them are used. This procedure allows one to observe a selective resonance of an extra phonon when the photon energy of the outgoing beam approaches the emission energy. Since the phonon frequency is very sensitive to the alloy composition, the alloy fluctuation in the layer and in the In-rich separated phase has also been obtained from Raman scattering experiments on different spots of the sample. Figure 3 shows the Raman spectra for the $c\text{-In}_x\text{Ga}_{1-x}\text{N}$ layers with $x = 0.19$ and 0.33 , recorded in backscattering geometry using excitation energies of 2.40 and 2.60 eV, respectively. Each spectrum after background subtraction consists of three peaks. To obtain the frequency position, the linewidth, and the integrated intensity of the peaks each spectrum was fitted using three Lorentzian line shapes. The highest (lowest) frequency peak in each spectrum corresponds to the LO (TO) phonon mode of the layer [9]. The intensity of the intermediate peak (S) when measured as a function of the incident beam energy displays a clear resonance character. It is selectively enhanced in the blue-green range of our measurements and disappears in the red or violet regions. From the ratio between the integrated intensities of the S and LO peaks we obtained the profiles which yield clear resonances with a maximum at about 2.4 eV for the $x = 0.33$ sample. Thus, the spectra in Fig. 3 were recorded under resonant conditions. For the $x = 0.33$ layer the measured energy of the S phonon is 78 meV. This leads to the value 2.32 eV for the resonant electronic transition, in perfect agreement with the PL emission

TABLE I. The In mole fraction x in $c\text{-In}_x\text{Ga}_{1-x}\text{N}$ layers as measured by XRD, the PL emission energy E , linewidth Γ , the average In mole fraction \bar{x} in the In-rich phase, and the confinement energy ΔE .

x	E (eV)	E (eV)	Γ (meV)	Γ (meV)	\bar{x}	ΔE (eV)
	300 K	30 K	300 K	30 K		
0.33	2.318	2.350	313	337	0.76 ± 0.06	0.326
0.19	2.388	2.444	339	314	0.72 ± 0.09	0.396
0.07	2.445	2.547	240	264		0.453

energy observed by us in this sample at RT, 2.318 eV. The RRS experiments are probing directly the vibrational properties of regions of our sample which act as the source for the below gap emission. Their fingerprint is the S phonon which we identify as a LO phonon propagating in these regions [12]. By measuring the LO frequencies at different spots on the sample we achieve the average values of the In content in the layer and in the In-rich separated phase. For the $x = 0.33$ sample we found the value $\bar{x} = 0.34 \pm 0.01$ for the layer averaged In composition. The values of \bar{x} found for the In-rich phases in the $x = 0.19$ and $x = 0.33$ samples are shown in Table I. The S intensity in the $x = 0.07$ layer is close to the detection limit of the Raman method, probably due to the small scattering volume in this sample. Figure 3 shows the remarkable fact that the position of the S maximum for the $x = 0.19$ and 0.33 samples is almost identical, indicating that this Raman line is due to In-rich regions with nearly the same In composition, as observed from XRD experiments. The RRS data we just described link the emission observed in the $c\text{-In}_x\text{Ga}_{1-x}\text{N}$ layers to the In-rich phases present in the samples. From the XRD and RRS data we

conclude that In-rich phases with $x \approx 0.8$ are the source of the observed emission in our samples. According to Fig. 2, the emission energies are found to fall above the gap energy of the alloy with $x = 0.8$; therefore they cannot be ascribed to band-to-band transitions. Carrier confinement effects are taking place with related confinement energies, ΔE , indicated in the figure. The values of ΔE are listed in Table I for our samples. We believe that the luminescence is due to radiative recombination of electron-hole pairs which are created (a) in the InGaN layer and are captured in the In-rich regions and (b) due to excitation of these regions itself. The existence of the latter process, which was also observed in semiconductor nanocrystals embedded in vitreous media is corroborated by the observation of luminescence from the $x = 0.07$ sample, where the layer gap energy exceeds the excitation energy [17]. Polarized RRS experiments provide a suitable tool to identify the In-rich separated phases as QDs [18]. In Fig. 4 the RRS spectra of the $c\text{-In}_{0.33}\text{Ga}_{0.67}\text{N}$ sample taken in the $z(xx)\bar{z}$ and $z(yx)\bar{z}$ geometries are shown. If we take into consideration the fact that QD radial modes are allowed (forbidden) in the parallel (crossed) polarization, we conclude that the outstanding signal marked by an arrow

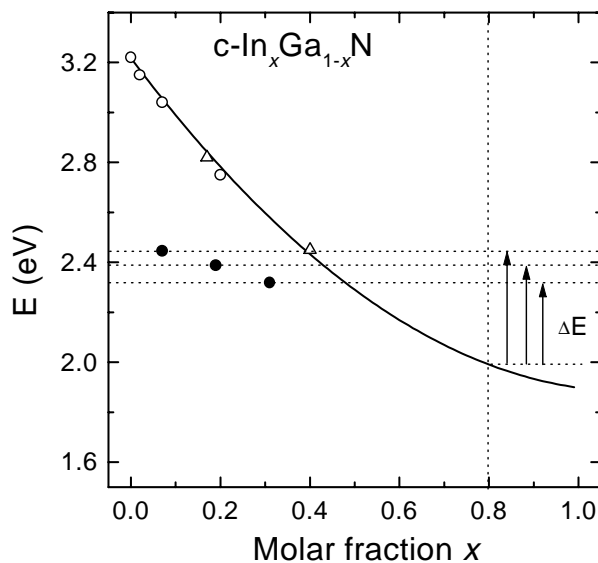


FIG. 2. Dependence of emission energies (full circles) on the In concentration for the $c\text{-InGa}_{1-x}\text{N}$. Open circles (Ref. [14]) and triangles (Refs. [8,9]) are experimental results for the gap energies. The solid line is a parabolic fit to the experimental data. The dashed lines indicate the QD confinement energies, ΔE .

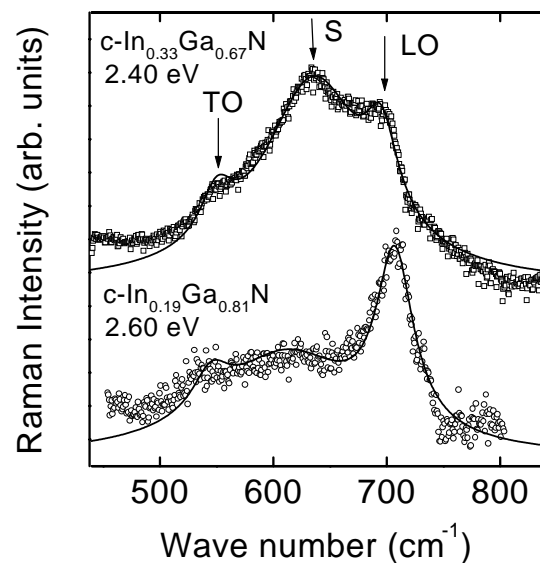


FIG. 3. Resonant Raman spectra for $c\text{-In}_x\text{Ga}_{1-x}\text{N}$ layers. The spectra were recorded for the indicated excitation energies. TO and LO are the layer phonon modes and S the LO phonon of the In-rich phase.

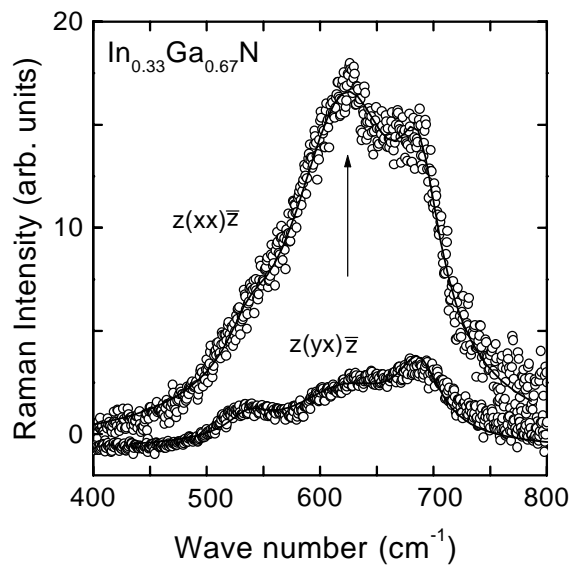


FIG. 4. Polarized resonant Raman spectra for the c - $\text{In}_{0.33}\text{Ga}_{0.67}\text{N}$ layer, excited with 2.40 eV. The solid lines are fittings to Lorentzian line shapes. The arrow points to the quantum dot related signal.

in the figure is due to QD vibrations. In the $z(yx)\bar{z}$ geometry the corresponding peak almost disappears, as should occur according to symmetry restrictions. It is interesting to note (Ref. [18]) that for not too small dots the observed frequency occurs basically at the LO frequency of the dot material, say, the alloy with $x \approx 0.8$. For a perfect c - $\text{In}_{0.33}\text{Ga}_{0.67}\text{N}$ layer the LO mode should not appear in the $z(xx)\bar{z}$ spectrum being forbidden by selection rules. However, it is seen with considerable intensity compared to the QD scattering. The structural analysis of our layers reveals that they consist of small crystals which are not perfectly aligned along the growth axis. Those crystals could well contribute to the observed LO scattering in the $z(xx)\bar{z}$ configuration. From ΔE listed in Table I we estimate the size of the dots as about 3 nm by taking the values $m_e^* = 0.10$ and $m_h^* = 0.84$ for the c - InN effective masses [19]. Since the confinement energy decreases as the size of the dot increases we reinforce the idea that the dot size plays a role on the origin of the redshift observed in the PL spectra [6]. However, the entries in Table I show that the In-content fluctuation in the dots is about 10% of their average composition \bar{x} . Therefore, the alloy fluctuations may also contribute to the redshift and the linewidths of the observed luminescence. Probably the small peak observed in the PL spectra from the $x = 0.07$ layer is due to the presence of two different kinds of dots.

In summary, we have shown that light emission from c - InGaN epitaxial layers is directly linked to In-rich phase-

separated quantum dots spontaneously formed by spinodal decomposition taking place in the layers. We conclude that both dot size and In-content fluctuations in the dots play an important role on the emission characteristics. These findings are an important contribution to the solution of the controversial issue related to the origin of light emission in nitride-based LEDs and LDs.

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