Phase separation suppression in InGaN epitaxial layers due to biaxial strain

A. Tabata, L. K. Teles, L. M. R. Scolfaro, J. R. Leite, A. Kharchenko, T. Frey, D. J. As, D. Schikora, K. Lischka, J. Furthmüller, and F. Bechstedt

Citation: Applied Physics Letters **80**, 769 (2002); doi: 10.1063/1.1436270
View online: http://dx.doi.org/10.1063/1.1436270
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/80/5?ver=pdfcov
Published by the AIP Publishing

Phase separation suppression in InGaN epitaxial layers due to biaxial strain

A. Tabata,[a] L. K. Teles, L. M. R. Scolfaro, and J. R. Leite[b]
Universidade de São Paulo, Instituto de Física, Caixa Postal 66318, 05315-970 São Paulo, SP, Brazil

A. Kharchenko, T. Frey, D. J. As, D. Schikora, and K. Lischka
Universität Paderborn, FB-6 Physik, D-33095 Paderborn, Germany

J. Furthmüller and F. Bechstedt
Institut für Festkörpertheorie und Theoretische Optik, Friedrich-Schiller-Universität, D-07743, Jena, Germany

(Received 16 July 2001; accepted for publication 28 November 2001)

Phase separation suppression due to external biaxial strain is observed in $In_xGa_{1-x}N$ alloy layers by Raman scattering spectroscopy. The effect is taking place in thin epitaxial layers pseudomorphically grown by molecular-beam epitaxy on unstrained GaN(001) buffers. *Ab initio* calculations carried out for the alloy free energy predict and Raman measurements confirm that biaxial strain suppress the formation of phase-separated In-rich quantum dots in the $In_xGa_{1-x}N$ layers. Since quantum dots are effective radiative recombination centers in InGaN, we conclude that strain quenches an important channel of light emission in optoelectronic devices based on pseudobinary group-III nitride semiconductors. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1436270]

The light emission process in optoelectronic devices based on group-III nitride semiconductors is still a matter of controversy in the literature.[1] However, there is strong evidence that an important emission mechanism originates from phase-separated quantum dots (QDs) formed by spinodal decomposition taking place in the InGaN alloys, the active media in these devices.[2–4] Spinodal decomposition occurs below a critical temperature and for a range of the alloy composition which defines a miscibility gap at a given temperature. It has been recognized from theory for a long time that the critical temperature lowers significantly due to biaxial strain in coherently grown semiconductor epitaxial layers and the miscibility gap may even be suppressed.[5,6] Evidence that strain associated with thin InGaN layers in InGaN/GaN double heterostructures could suppress phase separation has been recently reported.[7] A deep understanding of the role played by strain on phase separation in InGaN layers is highly desirable. The control of strain parameters is important to monitor the QDs formation in the active region of the devices.

In this letter, we show that external biaxial strain suppress spinodal phase separation in thin InGaN epitaxial layers pseudomorphically grown on thick unstrained cubic (*c*) GaN(001) buffer layers. The InGaN films are terminated by a top GaN layer forming GaN/InGaN/GaN double heterostructures. By monitoring the alloy composition and thickness for a fixed growth temperature, we control the presence of biaxial strain induced by the rigid GaN buffer in the InGaN layers. We start by first showing from *ab initio* calculations of the alloy free energy *taking strain into account* that the biaxial strain is expected to induce a suppression of the miscibility gap leading to a single homogeneous phase for the InGaN alloys. We use high resolution x-ray diffraction (HRXRD) reciprocal space maps to select the strained layers. We have shown recently that micro-Raman is an accurate tool to observe separate phases in InGaN epitaxial layers.[4,8] Micro-Raman spectroscopy measurements are also used in this work to demonstrate conclusively the suppression of the spinodal phase separation process in strained quantum wells.

The *c*-GaN/$In_xGa_{1-x}N$/GaN double heterostructures were grown on GaAs(001) substrates by molecular-beam epitaxy using a rf plasma nitrogen source. The GaN buffer layers were grown at $T=720\,^{\circ}C$ with thicknesses of about 400 nm. The *c*-InGaN films were deposited at lower growth temperatures of 600 °C. The films were deposited at growth rates of 40 nm/h. The GaN cap layers, of about 30 nm thick, were grown at low temperatures of about 600 °C in order to reduce In desorption and interdiffusion. The growth front was continuously monitored by reflection high-energy electron diffraction and the diffraction patterns exhibited a cubic symmetry along all major azimuths.

We selected two sets of samples (436, 437 and 438, 439) where the InGaN layers were grown under identical conditions but two different thicknesses, one above and the other below the critical one. The characteristics of these layers are shown in Table I. Two double heterostructures were planned to contain relaxed thicker alloy layers (samples 436 and 438). The other two were tailored to comprise pseudomorphic strained thinner InGaN layers (samples 437 and 439). According to our theoretical predictions, the relaxed InGaN layers in samples 436 and 438 undergo phase separation while in samples 437 and 439 the biaxial strain stabilizes a single homogeneous phase against spinodal decomposition.

In order to investigate the effects of a biaxial strain on the miscibility of the $In_xGa_{1-x}N$ alloy in a microscopic scale

[a]Permanent address: Universidade Estadual Paulista, Caixa Postal 473, 17033-360 Bauva, S.P., Brazil.
[b]Author to whom correspondence should be addressed; electronic mail: jrleite@macbeth.if.usp.br

TABLE I. $In_xGa_{1-x}N$ alloy composition x as obtained from micro-Raman and XRD measurements. L_W is the layer thickness, LO and S are the longitudinal optical phonon mode frequencies of the layers, and of the In-rich separated phases, respectively.

Sample No.	L_W (nm)	LO (cm^{-1})	x (Raman)	x (XRD)	S (cm^{-1})	x (Raman)	x (XRD)
436	30	685	0.36	0.33	630	0.61	0.54
438	30	701	0.26	0.27	621	0.65	0.55
437	3	672	0.45	0.45	⋯	⋯	⋯
439	3	689	0.35	0.37	⋯	⋯	⋯

we calculated the Helmholtz free energy $F(x,T)$ which allowed us to access the $T-x$ phase diagram and obtain the critical temperature for miscibility. We express the thermodynamic potential F of the alloy as $F(x,T)=F_0(x,T)+\Delta F(x,T)$, where $F_0(x,T)=(1-x)F_{GaN}(T)+xF_{InN}(T)$, and $\Delta F(x,T)=\Delta U(x,T)-T\Delta S(x,T)$. F_0 describes the free energy of a macroscopic mixture of the GaN and InN components whose free energies are F_{GaN} and F_{InN}, respectively. ΔF gives the mixing free energy as a sum of the mixing enthalpy of the alloy (ΔU) and the mixing free entropy (ΔS). The calculation of the mixing free energy was carried out by combining the cluster expansion method within the framework of the generalized quasichemical approximation and *ab initio* density functional theory-local density approximation. Details of the calculations are given in Ref. 9.

Figure 1 shows the mixing free energy $\Delta F(x,T)$ for the $In_xGa_{1-x}N$ alloy as a function of composition calculated for the temperature range of interest. Results are shown for the alloys in two extreme strain conditions: [Fig. 1(a)] fully relaxed (unstrained) and [Fig. 1(b)] pseudomorphically grown on a rigid GaN(001) buffer layer. Figure 1(a) shows that for the alloy growth temperature, ≈870 K, the composition of our relaxed layers $x\approx 0.4$ lies inside a wide miscibility gap region. The critical temperature extracted from our calculated $T-x$ phase diagram is about 1295 K, thus above the alloy growth temperature. On the other hand, when the biaxial strain effects are introduced, ΔF in Fig. 1(b) exhibits a pronounced single minimum in the entire range of the alloy composition. The $T-x$ phase diagram undergoes a dramatic change. Spinodal decomposition taking place in our unstrained samples is predicted to be fully suppressed in the samples under biaxial strain.

HRXRD measurements with a Philips High Resolution Diffractometer are used to investigate the strain conditions in our samples. Figure 2 depicts the distribution of the scattered x-ray intensity in reciprocal space [reciprocal space map (RSM)] of the asymmetric $(\bar{1}13)$ Bragg reflexes of samples 436 and 437 (RSM's of 438 and 439 are similar). Also included are the positions of the Bragg reflexes of GaN and of fully strained (pseudomorphic) and fully relaxed InN as well as the relaxation lines (dashed), which indicate the position of Bragg reflexes of partially relaxed InGaN with a given

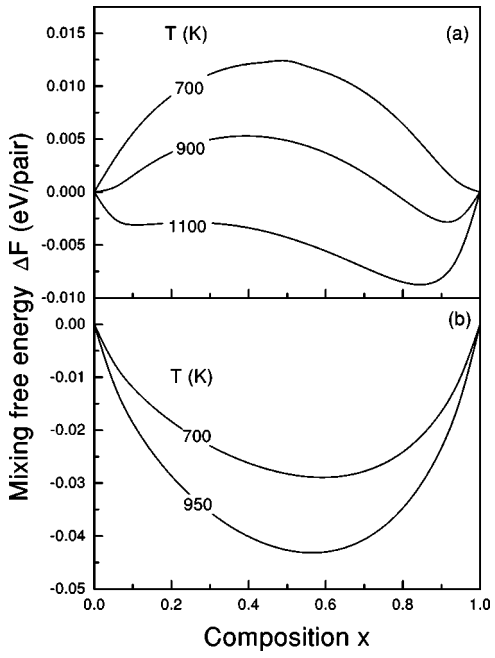

FIG. 1. Mixing free energy (ΔF) of inhomogeneously strained c-$In_xGa_{1-x}N$ alloys as a function of composition x for different temperatures. (a) unstrained and (b) pseudomorphically grown on a rigid GaN(001) buffer.

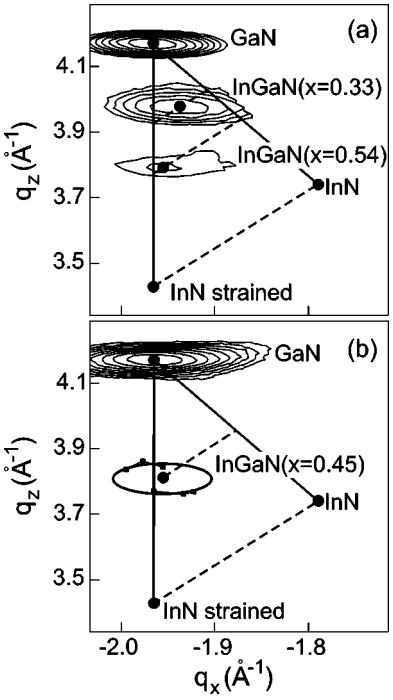

FIG. 2. Distribution of the scattered x-ray intensity in reciprocal space (reciprocal space maps) of the asymmetric $(\bar{1}13)$ Bragg reflexes of c-GaN/$In_xGa_{1-x}N$/GaN double heterostructures (a) sample 436 and (b) sample 437. The width of the alloy layers in these heterostructures is given in Table I. The position of the maximum intensity of the GaN and InGaN Bragg reflexes are indicated by dots. The full lines show the calculated positions of the Bragg reflexes of strained $In_xGa_{1-x}N$ and relaxed $In_xGa_{1-x}N$ layers of varying In content. The dashed lines show the position of the Bragg reflex of a partially relaxed InGaN layer of a given composition.

composition. The RSM of sample 436 shows Bragg reflexes of InGaN with two different compositions ($x=0.33$ and 0.54). The position of the $x=0.33$ reflex reveals that the degree of relaxation in this layer is about 50% while the in-plane lattice parameter of the strained In-rich phase is almost equal to that of GaN. Since the InGaN layer of sample 437 is only 3 nm thick the intensity of the corresponding Bragg reflex is low. However, a careful analysis of a number of line scans reveals only one intensity maximum which is indicated in Fig. 2(b). From its position, the In content of the layer is found to be $x=0.45\pm0.03$. The in-plane lattice parameter is equal to the GaN lattice spacing indicating that the InGaN layer of this heterostructure is fully strained. The alloy composition in our samples as obtained from x-ray diffraction (XRD) measurements is shown in Table I.

In order to clearly demonstrate that biaxial strain suppress spinodal decomposition in our samples, we use the micro-Raman spectroscopy technique recently adopted by us to investigate the structural and optical properties of c-$In_xGa_{1-x}N$ epitaxial layers.[4,8] We showed that the alloy composition x in the layer and in the In-rich separated phase can be obtained by measuring the frequencies of the longitudinal optical (LO) phonon propagating in these regions of the sample. Particularly, the LO phonon propagating in the In-rich separated phase (QDs), labeled by us as S phonon, allows the identification of this phase and an approximate determination of its composition x.

Our Raman scattering measurements were performed at room temperature with the Jobin–Yvon T64000 micro-Raman system. Figure 3 shows the Raman spectra for the c-GaN/InGaN/GaN samples, recorded in backscattering geometry. Assuming Lorentzian line shapes, the observed peaks in each spectrum were fitted after background subtraction and their frequencies were determined and are indicated by arrows in Fig. 3. The c-GaN phonon frequencies, 555 cm^{-1} transverse optical (TO) and 741 cm^{-1} (LO) are clearly identified in the spectrum of each sample.[10] The other peaks are originated from the c-$In_xGa_{1-x}N$ alloy and correspond to the TO and LO phonon modes of the layer and to the LO phonon propagating in the In-rich separated phases (S). The fact that the LO phonon frequency of c-$In_xGa_{1-x}N$ varies linearly with x allows us to determine the alloy composition in our layers and in the In-rich phases.[8] The results are shown in Table I. They are in good agreement with the XRD data.

The remarkable difference between the spectra of samples 438, 436, and 437, 439 in Fig. 3 is the absence of the S peak for the latter. For the 438, 436 samples, the fingerprint (S) of the phase-separated In-rich QDs is clearly observed as pronounced peaks between the TO and LO peaks of the InGaN layers. On the other hand, the S peak disappears from the spectra of the samples 437 and 439. It could be argued that phase separation is correlated to the length of time required to grow the InGaN films. Since the time to grow the thicker layers is about ten times (50 min) than that to grow the thinner ones (5 min), this would explain the absence of separated phases in samples 437 and 439. To check this point, we performed a set of annealing experiments on samples 437 and 439, in steps of 1 h up to 10 h at 600 °C, each step followed by Raman experiments. Within the detection limit of our equipment, there was no evidence for the presence of the S peak in the spectra of those samples.

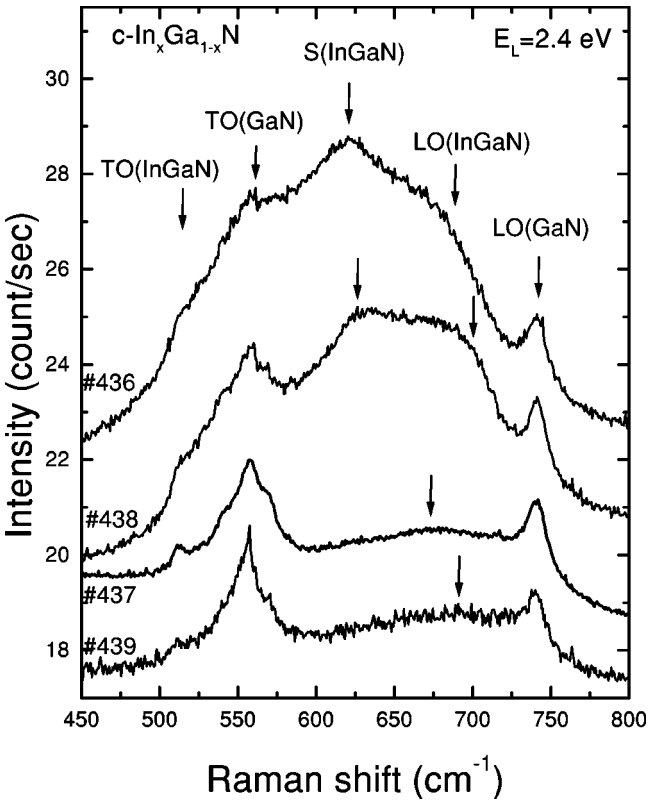

FIG. 3. Raman spectra for c-GaN/$In_xGa_{1-x}N$/GaN double heterostructures recorded for the excitation energy $E_L=2.4$ eV. The arrows indicate the phonon frequencies of the TO and LO modes of c-GaN and c-InGaN layers and of the LO mode ascribed to the In-rich separated phase (S).

In conclusion, we show that in the two samples where the InGaN layers are strained, the phase separation did not take place. We consider this fact, the undoubted demonstration that phase separation induced by spinodal decomposition in InGaN layers can be suppressed by biaxial strain, as expected from theory.

The authors acknowledge Dr. E. Silveira for the annealing experiments and Dr. A. Zunger for stimulating discussions. This work was supported by FAPESP, CNPq, and DFG.

[1] T. Wang, J. Bai, S. Sakai, and J. K. Ho, Appl. Phys. Lett. **78**, 2617 (2001).
[2] S. Chichibu, T. Azuhata, T. Sota, and S. Nakamura, Appl. Phys. Lett. **69**, 4188 (1996); *ibid.* **70**, 2822 (1997).
[3] K. P. O'Donnell, R. W. Martin, and P. G. Middleton, Phys. Rev. Lett. **82**, 237 (1999).
[4] V. Lemos, E. Silveira, J. R. Leite, A. Tabata, R. Trentin, L. M. R. Scolfaro, T. Frey, D. J. As, D. Schikora, and K. Lischka, Phys. Rev. Lett. **84**, 3666 (2000).
[5] A. Zunger, in *Handbook of Crystal Growth*, edited by D. T. J. Hurle (Elsevier, New York, 1994), Vol. 3, p. 998.
[6] S. Y. Karpov, MRS Internet J. Nitride Semicond. Res. **3**, 16 (1998).
[7] R. Singh, D. Doppalapudi, T. D. Moustakas, and L. T. Romano, Appl. Phys. Lett. **70**, 1089 (1997).
[8] E. Silveira, A. Tabata, J. R. Leite, R. Trentin, V. Lemos, T. Frey, D. J. As, D. Schikora, and K. Lischka, Appl. Phys. Lett. **75**, 3602 (1999).
[9] L. K. Teles, J. Furthmüller, L. M. R. Scolfaro, J. R. Leite, and F. Bechstedt, Phys. Rev. B **62**, 2475 (2000).
[10] A. Tabata, R. Enderlein, J. R. Leite, S. W. da Silva, J. C. Galzerani, D. Schikora, M. Kloidt, and K. Lischka, J. Appl. Phys. **79**, 4137 (1996).