Compositional dependence of the strain-free optical band gap in $In_xGa_{1-x}N$ layers

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(Received 18 September 2000; accepted for publication 29 January 2001)

The effect of strain on the compositional and optical properties of a set of epitaxial single layers of $In_xGa_{1-x}N$ was studied. Indium content was measured free from the effects of strain by Rutherford backscattering spectrometry. Accurate knowledge of the In mole fraction, combined with x-ray diffraction measurements, allows perpendicular strain (ϵ_{zz}) to be evaluated. Optical band gaps were determined by absorption spectroscopy and corrected for strain. Following this approach, the strain free dependence of the optical band gap in $In_xGa_{1-x}N$ alloys was determined for $x \leqslant 0.25$. Our results indicate an ''anomalous,'' linear, dependence of the energy gap on the In content, at room temperature: $E_g(x) = 3.39 - 3.57x$ eV. Extension of this behavior to higher concentrations is discussed on the basis of reported results. © *2001 American Institute of Physics.*
[DOI: 10.1063/1.1358368]

Light emitting devices based on the ternary alloy $In_xGa_{1-x}N$ have been developing at an impressively fast rate over the last decade.[1] The emission wavelength in these devices is tuned by adjusting the indium content in the active layer. Despite such technological developments, the semiconductor alloy at the core of these light emitters is, from a fundamental point of view, a poorly understood material. Most of their properties are simply estimated from the two binary compounds, GaN and InN, in particular the band gap energy is expected to vary between 3.42 and 1.89 eV at room temperature (RT). However, the tendency for phase segregation and ordering[2] can greatly influence an alloy's optical properties. Actually some authors[3,4] argue that phase segregation, on a nanometer scale,[5] can account for the extraordinary light emission properties in $In_xGa_{1-x}N$, despite the huge dislocation density in the devices' active regions.

The bandgap variation for $In_xGa_{1-x}N$ has not yet been established, independently of state of strain. A deviation from a linear dependence of the fundamental gap has been postulated, with a wide range of bowing parameters, in the literature.[6–14] Several sources of error hamper the establishment of a consensual relation. In some studies the measured quantity is the luminescence peak energy, with ignores the Stokes' shifted[15,16] of emission with respect to the band edge. When the gap is derived from optical absorption or photoluminescence excitation experiments, a difficulty arises from the spectral broadening, which hinders a clear identification of the band edge energy. On the other hand, accurate determination of In content is difficult in $In_xGa_{1-x}N$ layers. Frequently, this quantity is derived from x-ray diffraction (XRD) using Vegard's law[17] directly, without properly considering the state of strain in the samples.

In this letter, Rutherford backscattering (RBS) is used to accurately determine the alloy composition independent of the effects of strain. Subsequent XRD measurements permit the evaluation of strain in all samples and also the magnitude of the band gap correction due to strain.

The samples studied are nominally undoped wurtzite $In_xGa_{1-x}N$ layers, grown by metalorganic chemical vapor deposition on GaN/Al_2O_3 substrates. Thin (<75 nm), fairly thick (~200 nm), and thick (>500 nm) samples with a reasonable range of compositions ($x \leqslant 0.25$) were considered. RBS measurements were performed on a standard geometry with a 1 mm collimated beam of 2 MeV He^+ ions. XRD was done in a high-resolution double-crystal diffractometer, using the Cu $K\alpha_1$ line.

Random and aligned RBS spectra from an $In_xGa_{1-x}N/GaN/Al_2O_3$ heterostructure are shown in Fig. 1. The full curve is a computer simulation of the random spectra using RUMP.[18] High statistics and a good simulation provide an accurate value for the In mole fraction (x). For this sample (B), $x = 0.099 \pm 0.005$, a thickness of 50 ± 5 nm and a $\chi_{\min}$ of 2.4% along ⟨0001⟩ were also determined. Measured values of $\chi_{\min}$, a crystal quality factor, are good compared to other reported values for samples with similar In content.[19]

Composition values determined by RBS are not sensitive to the state of strain in the sample.[20] However, XRD measures an averaged value for the lattice constants of layers, which may or may not be strained. Figure 2 shows a ω–2θ map of the GaN and $In_xGa_{1-x}N(00.2)$ diffraction peaks. The lattice constants c_{GaN} and c_{InGaN} are directly given by $c = l^* \lambda_{\mathrm{Cu}\,K\alpha_1}/(2\sin\theta_B)$, for any allowed $(00.l)$ reflection. For sample B, $c_{\mathrm{GaN}} = 0.5187$ nm and $c_{\mathrm{InGaN}} = 0.5252$ nm.

In order to calculate the In content from XRD results, using *only* the lattice constant c_{InGaN} two extreme assumptions are usually considered for the state of strain.

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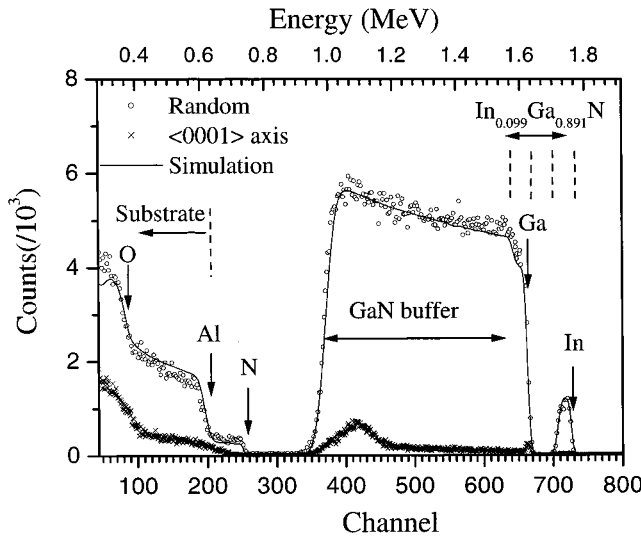

FIG. 1. Random, aligned, and simulated RBS spectra from an $In_{0.099}Ga_{0.89}N/GaN/Al_2O_3(0001)$ sample. Vertical arrows indicate the scattering energies of the different chemical elements. Horizontal arrows indicate the depth location in the sample.

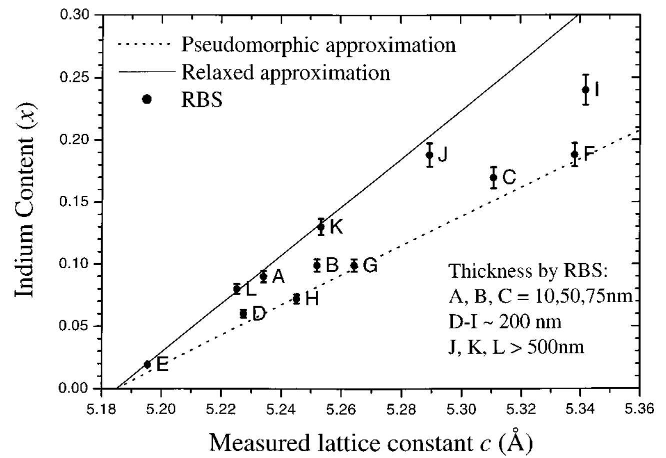

FIG. 3. Indium content determined by RBS correlated with the values of lattice constant c measured by XRD. The composition determined by RBS is compared with the values that would be obtained under the two assumptions discussed in the text. The parameters used were $c_{GaN}=0.51850$, $a_{GaN}=0.31892$ nm (Ref. 24) and $c_{InN}=0.57033$, $a_{InN}=0.35378$ nm (Ref. 25), c_{13} and c_{53} of 103, 405, and 92, 224 GPa (Ref. 26) for GaN and InN respectively.

(i) The layer is fully relaxed. Vegard's law assumes that the lattice constants of a *relaxed* ternary compound $A_xB_{1-x}N$ will scale linearly with x between AN and BN lattice parameters.

(ii) Pseudomorphic growth. In the case of biaxially strained hexagonal wurtzite structures, such as $In_xGa_{1-x}N/GaN$, distortion of the unit cell must be considered. In order to separate the influence of strain and composition effects on c_{InGaN}, both lattice parameters a_{InGaN} and c_{InGaN}, have to be measured.[21] Therefore applying Hooke's law, x can be determined solving:

$$[c_{InGaN}-c_0(x)]+2\frac{C_{13}(x)c_0(x)}{C_{33}(x)a_0(x)}[a_{InGaN}-a_0(x)]=0, \qquad (1)$$

where c_0 and a_0 are the relaxed parameters given by Vegard's law and $C_{i,j}(x)$ are the linearly interpolated elastic constants from the binary semiconductors. Nevertheless, it is often assumed that for thin layers, say below 100 nm, $In_xGa_{1-x}N$ grows pseudomorphically ($c_{InGaN}=c_{GaN}$) to the GaN buffer.[7,13,22] In this case measuring only c_{InGaN} and solving Eq. (1), x can be calculated.[23]

Both situations, (i) and (ii), are represented in Fig. 3 together with the value of x determined by RBS. One can see that for thick samples direct application of Vegard's law using c_{InGaN} provides a good agreement with RBS data, indicating that these layers are almost fully relaxed. For $In_xGa_{1-x}N$ layers with thickness below, say 300 nm, the state of strain is not easy to predict on thickness considerations alone. For example, sample B is partially relaxed while a thinner one (A) is almost fully relaxed, and a thicker one (G) is pseudomorphic. Critical thicknesses can, for some samples, be well above the values calculated using the relaxation models,[27,28] as pointed out in Ref. 22. The partial relaxation observed in thin samples is an important point, since if the pseudomorphic assumption were generally made for these layers, x values would be underestimated,[6] and inconsistent over-corrections in the band gap value due to strain would be performed. From this discussion, it is evident that strain should be evaluated for each sample.

Once the strain-free composition of the $In_xGa_{1-x}N$ layers is known by RBS, perpendicular strain, $\epsilon_{zz}=(c_{InGaN}-c_0)/c_0$, can be determined. In the absence of better knowledge regarding deformation potentials for $In_xGa_{1-x}N$, $dE_g/d\epsilon_{zz}=15.4$ eV, obtained experimentally from the dependence of GaN band gap on the strain,[29] was used to correct the band gaps. Therefore, the alloy's relaxed energy gap is given as

$$E_g^{rel}(\mathrm{InGaN})\cong E_g^{abs}-\epsilon_{zz}^{InGaN}\times\frac{dE_g^{GaN}}{d\epsilon_{zz}}. \qquad (2)$$

The absorption curves for several concentrations were fitted to a sigmoidal expression, $\alpha(E)=\alpha_0/\{1+\exp[(E_g^{abs}-E)/\Delta E]\}$, providing a reproducible criterion to determine the band gap in $In_xGa_{1-x}N$ layers. This procedure, rather than using an unclear threshold, was used to determine E_g^{abs}, the "effective band gap," and the broadening parameter (ΔE), equivalent to an Urbach tail.[30]

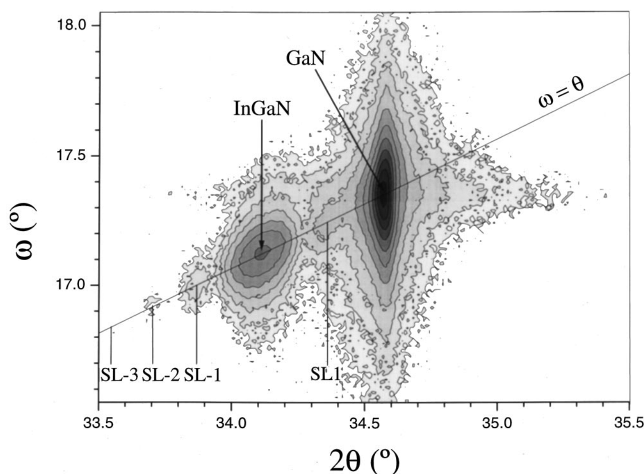

FIG. 2. ω–2θ map of the $In_xGa_{1-x}N$ and GaN (00.2) reflections. Satellite peak (SL_i) separation yields an $In_xGa_{1-x}N$ layer thickness of about 55 nm, in agreement with the RBS determined value.

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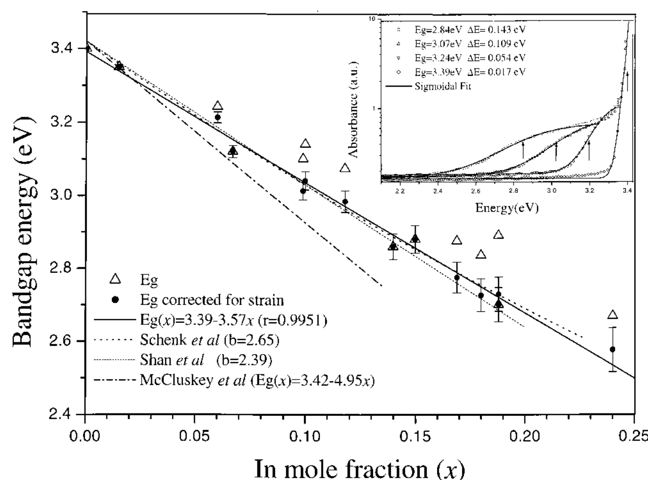

FIG. 4. Strain-free optical band gap as a function of In content obtained from RBS. The inset shows experimental absorption curves and the sigmoidal fit of $In_xGa_{1-x}N$ layers with different In mole fractions at RT.

In Fig. 4, the strain-free optical bandap is plotted as a function of x. The inset presents some absorption curves and the corresponding sigmoidal fits. The dependence of $E_g(x)$ is shown to be linear with x. A least-squares fit to the data yields to $E_g(x)=3.39-3.57x$ ($r=0.9951$). Together with our measurements a set of experimental results from other works are represented. Our data are in agreement with the works by Shan *et al.*[12] and Schenk *et al.*[6] where In content was measured by RBS and XRD (considering strain relaxation) and band gap determined at RT by photoreflectance and photothermal deflection spectroscopy, respectively. However, our results differ from those obtained by McCluskey *et al.*[9] This can be explained by the different criteria used to define the band gap. In Ref. 9 the threshold for the start of the $In_xGa_{1-x}N$ absorption was used. Another factor, is the possibility of an over correction for strain in the band gap, for layers assumed pseudomorphic, when a partial relaxation may have occurred.

The linear behavior of $E_g(x)$ observed in Fig. 4 is distinct from a simple interpolation between the gap energies of the binary compounds. It is clear that the decrease of the band gap occurs faster than it would be expected in that case. This work only considers $x \leqslant 0.25$, however if this linear trend was maintained a value of 1.89 eV, the band gap of pure InN, would be reached at $x=0.42$. The interest of this extrapolation arises from the fact that an absorption edge below 1.89 eV was measured for thick $In_xGa_{1-x}N$ layers with $x \geqslant 0.4$.[31] Moreover, intrinsic infrared emission from $In_xGa_{1-x}N$ epilayers has also been reported.[16]

The quadratic correction to Vegard's law may also suit our data in a short range of compositions. However this approach does not seem satisfactory to describe the behavior of $In_xGa_{1-x}N$ alloys, since the bowing parameter, b, has to change in order to fit data for a wider range of x. This clear deviation from the ''normal'' (small b and constant with x) quadratic term has been discussed in terms of a strong compositional dependence of the bowing parameter.[13] As it is shown in this work, different approaches used to estimate In mole fraction, combined with different criteria to define the band gap in $In_xGa_{1-x}N$ and uncertain assumptions about strain, may also lead to a variety of $E_g(x)$ curves.

In order to open the way to an understanding of the physical reason behind this unusual behavior of the band gap with composition, ''electronic,''[32] chemical clustering or any other, the alloy's properties should preferentially be referred to a comparable situation of relaxed material.

S.P. acknowledge financial support from FCT (Portugal), and discussions with Professor K. P. O'Donnell.

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