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Publication V

O. Reentilä, M. Mattila, M. Sopanen, and H. Lipsanen, *Simultaneous determination of indium and nitrogen contents of InGaAsN quantum wells by optical in-situ monitoring*, Applied Physics Letters **89** 231919 (2006)

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Simultaneous determination of indium and nitrogen contents of InGaAsN quantum wells by optical *in situ* monitoring

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(Received 13 September 2006; accepted 24 October 2006; published online 6 December 2006)

In situ monitoring of metal-organic vapor phase epitaxial growth of InGaAsN/GaAs multiquantum wells is studied. The complex refractive index of InGaAsN is determined for several indium and nitrogen contents based on the fits to the reflectance curve. Taking advantage of the different effects caused by the incorporation of indium and nitrogen on the complex refractive index of InGaAsN, the InGaAsN quantum well nitrogen and indium contents are simultaneously determined *in situ*.
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In recent years, the need to monitor material growth has increased, for example, due to the complicated growth procedures of gallium-nitride-related materials.[1] In addition to the well-established field of application of *in situ* monitoring, the monitoring of thick layer growth, it has been also reported that growth of thin layers can be observed and analyzed.[2–5]

It is commonly known that there are difficulties in determining the indium and nitrogen contents of InGaAsN quantum wells exclusively from x-ray diffraction (XRD) curves because only the lattice constant of the quarternary alloy material can be obtained by XRD. Thus, either the indium or the nitrogen content needs to be fixed in order to determine the other one. Therefore, it is necessary to determine the composition of the quarternary alloy using several measurement techniques and simulations, e.g., photoluminescence (PL) measurements and the band anticrossing (BAC) model[6] combined with XRD results.

Here we show that the InGaAsN composition can be determined directly from the reflectance data measured during multiquantum-well (MQW) structure growth. When the growth rate of each layer is known, the indium and the nitrogen content can be determined simultaneously from the real and imaginary parts of the complex refractive index of InGaAsN ($n_{\mathrm{complex,InGaAsN}}=n_{\mathrm{InGaAsN}}+i\kappa_{\mathrm{InGaAsN}}$).

Samples were fabricated by a vertical low-pressure metal-organic vapor phase epitaxy (MOVPE) system using trimethylindium (TMIn), trimethylgallium (TMGa), tertiarybutylarsine (TBAs), and dimethylhydrazine (DMHz) as precursors for indium, gallium, arsenic, and nitrogen, respectively. All the layer structures were grown on semi-insulating, 350-μm-thick GaAs substrates using hydrogen as the carrier gas. Two GaAs buffer layers were grown below the actual (In)GaAs(N)/GaAs MQW structure. The growth temperatures for the buffers and the MQW structure were 650, 575, and 575 °C (thermocouple readings), respectively.

After growth, the samples were characterized by high-resolution x-ray diffraction (HR-XRD) measurements (in ω-2θ configuration) as well as by PL measurements. The GaAsN samples were annealed *ex situ* at 700 °C to increase the photoluminescence intensity. The BAC model was utilized together with the XRD and PL results to solve the compositions of the quarternary alloy samples. GaAsN nitrogen contents and InGaAs indium contents as well as all the layer thicknesses were determined from the XRD curves directly. In addition, atomic force microscopy (AFM) was utilized to study the surface morphology of several samples. All HR-XRD and AFM measurements were performed for the as-grown samples.

The *in situ* monitoring system was a normal incidence reflectance setup with a halogen lamp as the light source. The reflectance signal was detected at 635 nm, which is partially absorbed into all the layers grown for this study. The *in situ* data were compared with theoretical reflectance curves calculated using a well-known matrix method. In the fitting procedure the complex refractive index of the GaAs barrier layers was fixed to $n_{\mathrm{complex,GaAs}}=4.0-0.3i$.[5] The growth rate of each layer (QW or barrier) was also fixed in the fitting procedure, to minimize the number of free parameters. Growth rates were obtained from the HR-XRD measurements. A more detailed description of the fitting method can be found in Ref. 5.

Figure 1 shows a typical reflectance curve measured during MOVPE growth of an InGaAsN/GaAs MQW structure. The growth regions of the QWs (increasing reflectance) and the barriers (decreasing reflectance) are denoted and the the-

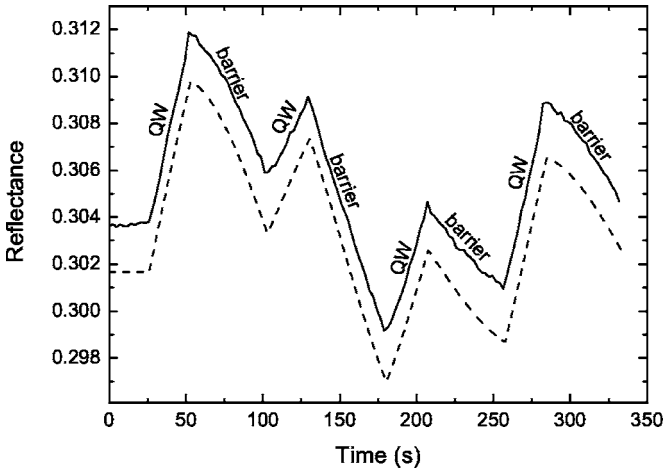

FIG. 1. Typical reflectance curve measured during the growth of an InGaAsN/GaAs MQW structure consisting of four QWs and four barriers (solid line) and a theoretical reflectance curve of the same structure (dashed line). The vertical offset between the curves is added for clarity.

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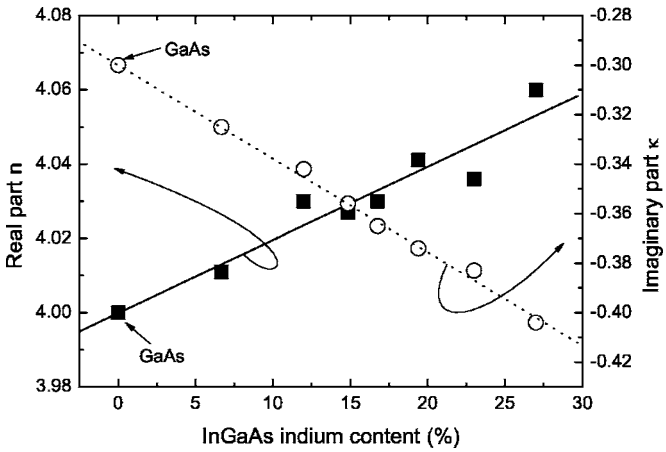

FIG. 2. Measured n_{InGaAs} (squares) and κ_{InGaAs} (open circles) for different indium contents. Linear dependencies were observed for both parts.

oretical reflectance curve is also shown in Fig. 1. The vertical offset is added for clarity. A very good agreement between the measured and calculated curves was obtained. The values $n_{InGaAsN}=4.022$ and $\kappa_{InGaAsN}=-0.479$ were obtained by the fitting procedure.

A similar fitting procedure to the one shown in Fig. 1 was performed on the reflectance data measured during the growth of all the (In)GaAs(N)/GaAs MQW structures. To demonstrate the change of the reflectance with varying only the indium content in the QWs, Fig. 2 shows the real and imaginary parts of $n_{complex,InGaAs}$ as a function of the InGaAs QW indium content in the range of 0%–27%. Both κ_{InGaAs} and n_{InGaAs} depend linearly on the indium content and the linear fits forced via the GaAs data points are also shown in the figure. Because of the linear dependencies, the InGaAs indium content can be determined using either one of them.

Introducing nitrogen into (In)GaAs leads to significant changes in the material characteristics already at small concentrations, see, for example, Refs. 3, 4, and 7. The effects can be seen also in the complex refractive index. The imaginary and real parts of the dilute nitride refractive indices with different indium and nitrogen contents are shown in Figs. 3 and 4.

Figure 3 shows the values of $\kappa_{InGaAsN}$ as a function of

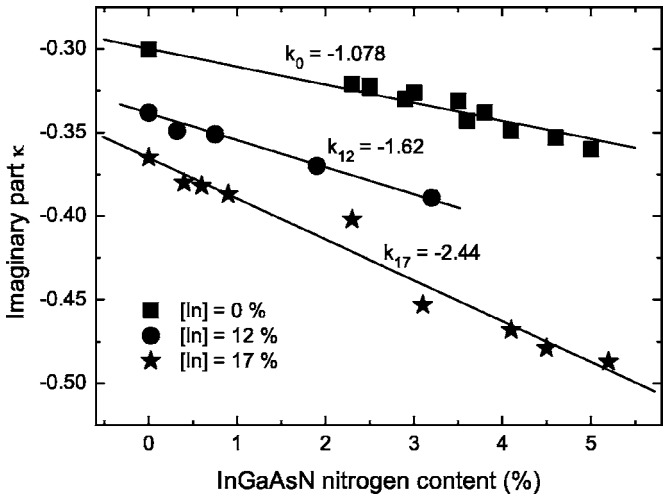

FIG. 3. Measured values of κ as a function of the QW nitrogen content. Samples with different indium contents are denoted with different symbols. Linear fit to each data set is also shown.

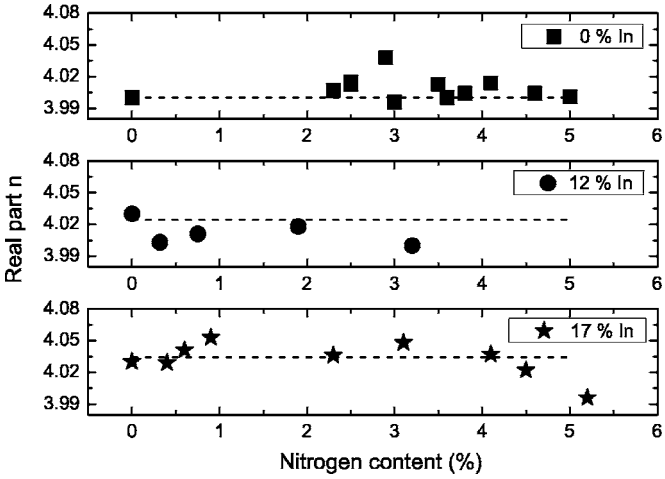

FIG. 4. Values of n as a function of the QW nitrogen content with different InGaAsN indium contents. The dashed lines in each figure are the calculated values for the InGaAs reference samples based on the linear fit in Fig. 2.

the QW nitrogen content for samples containing different amounts of indium. $\kappa_{InGaAsN}$ differs significantly from κ of the reference InGaAs sample and $\kappa_{InGaAsN}$ decreases as the nitrogen content increases. A linear fit forced via the InGaAs reference point of each indium series is shown in the figure. Slopes −1.078, −1.463, and −2.44 were obtained for the indium contents of 0%, 12%, and 17%, respectively. The absolute value of the slopes increases as the indium content of the samples increases, i.e., the effect of the nitrogen incorporation on $\kappa_{InGaAsN}$ increases with increasing indium content.

Figure 4 shows the real part of the InGaAsN refractive index as a function of the QW nitrogen content. It is observed that the obtained data points for $n_{InGaAsN}$ are somewhat scattered around the InGaAs values derived from the linear fit in Fig. 2, regardless of the nitrogen content.

The real part of the complex refractive index, $n_{InGaAsN}$, is sensitive to possible surface roughness appearing during growth. Therefore, to exclude the possibility of the effects of the growth time surface roughening on $n_{InGaAsN}$, an AFM study of several GaAsN MQW samples was performed. No indication of surface roughening could be found on the surface of the topmost GaAs capping layer (thickness of the layer was 15–22 nm depending on the sample), not even on the sample with the largest nitrogen content (5%). This was expected because in Ref. 5 it was already demonstrated that variance in the values of n tend to be larger than the variance in κ. Nevertheless, the data shown here indicate that regardless of the indium content of the sample, the dependence of $n_{InGaAsN}$ on nitrogen content is practically negligible. This straightforwardly leads to a conclusion that the indium content of not only InGaAs QWs but also InGaAsN QWs can be determined unambiguously from $n_{InGaAsN}$.

If the indium content of the quarternary alloy InGaAsN is determined from $n_{InGaAsN}$, $\kappa_{InGaAsN}$ remains to be used in determining of the nitrogen content of InGaAsN. This means that when the growth rate of each layer is known, the overall composition of InGaAsN quantum wells, i.e., the indium and nitrogen contents separately, can be determined simply by measuring the complex refractive index of the QW material during growth. However, it is quite clear from Figs. 2 and 4 that more work is needed to make the measurement of n more accurate. We have shown earlier that the determination of n is sensitive to many unidealities.[5] For example, lamp

intensity fluctuation during reflectance measurement directly causes an error to the value of n. Moreover, n is determined in the fitting process by the overall level and shape of the whole reflectance curve whereas κ correlates straightforwardly with the slope $\Delta R/\Delta t$ measured during growth of the first QW. The largest errors in indium content of n_{InGaAs} are 5% units, and in the case of the quarternary material the errors for some data points are even larger. However, typical errors are much smaller.

In this letter we have shown that when the growth rates of InGaAsN QWs and GaAs barriers are known, an *in situ* determination of the InGaAsN complex refractive index is possible. Furthermore, the QW indium and nitrogen contents can be determined simultaneously using the complex refractive index. Because of the very weak nitrogen content dependence and linear indium content dependence of n_{InGaAsN}, the indium content can be determined from n_{InGaAsN} independently of the amount of nitrogen. Then, the linear nitrogen content dependence of $\kappa_{\mathrm{InGaAsN}}$ can be used to determine the nitrogen content. Thus, the reflectance measured during the growth of the structure provides an *in situ* tool to determine the full composition of the quarternary alloy system.

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