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Nitrogen content of GaAsN quantum wells by in situ monitoring during MOVPE growth

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Abstract

Metal–organic vapor phase epitaxial growth of GaAsN quantum wells is monitored by in situ reflectance measurements. Correlation between the change in the reflectance intensity and nitrogen content of the quantum well is established. The reflectance as a function of time also reveals if there is deterioration of the crystalline quality during growth. This method together with X-ray diffraction and photoluminescence characterization is applied to analyze GaAsN growth using various reactor pressures and TBAs/III molar flow ratios.
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1. Introduction

Nowadays it is a well-known fact that introducing a small percentage of nitrogen into (In)GaAs leads to strong bowing of the band gap energy making the material a potential candidate for long-wavelength applications. However, the research of the dilute nitride compounds GaAsN and especially InGaAsN has come to the result that introducing nitrogen to (In)GaAs degrades the material quality in a severe way making it not the optimal active medium for long-wavelength active devices. It has been observed, though, that dilute nitride material has shorter carrier recombination time than its nitrogenless counterpart, which means that nitrogen makes the material faster [1]. A semiconductor saturable absorber mirror (SESAM) is a passive component consisting of a Bragg mirror and an absorber region, which is favorable to have a very short recovery time. Therefore, SESAM structures including InGaAsN quantum wells (QW) as the absorber material are suitable for fast mode locking of lasers operating at 1.3 and 1.55 μm [1–3].

The in situ monitoring methods for both metal–organic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE) provide a large amount of information not only about the material growth but also about the material itself. Growth rate, layer composition and temperature of the substrate may also be determined depending on the in situ method in use. In MOVPE systems, usually the growth of relatively thick layers, such as AlAs/GaAs Bragg mirror stacks or typical GaN growths, is monitored optically, see for example, Refs. [4,5]. Here, we demonstrate that thin layers, such as QWs, cannot only be monitored [6] but also partially analyzed during MOVPE growth.

In addition, despite the rather good knowledge of the growth parameters for the dilute nitride growth by MOVPE and MBE, the effect of the growth pressure in MOVPE systems has not been thoroughly examined. Typically, the MOVPE reactor pressure during growth is either atmospheric or around 100 Torr. Here, the MOVPE growth pressure dependence of GaAsN material parameters is discussed.

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2. Experimental procedure

Several GaAsN samples were fabricated in order to examine the growth of GaAsN and the influence of the growth pressure on dilute nitride growth. GaAsN was chosen instead of the quarternary alloy InGaAsN to decrease the number of material parameters affecting the growth: the TMIn flow to the reactor used to grow InGaAsN is known to influence the nitrogen incorporation into the sample [7].

A close-coupled showerhead MOVPE system was used to grow the samples. The growth temperature was 575 °C (a thermocouple reading). Trimethylgallium (TMGa), tertiarybutylarsine (TBAs) and dimethylhydrazine (DMHy) were used as precursors for gallium, arsenic and nitrogen, respectively. Carrier gas was hydrogen (H_2). The reactor pressure during the growth was either 100, 300 or 700 Torr.

All samples were grown on semi-insulating 350 μm thick (1 0 0) GaAs substrates and consisted of four GaAsN QWs and GaAs barriers. No extra capping was added on top of the uppermost barrier. Based on the relation between the growth rate and group III flow in MOVPE growth, the real growth rate indicates that about 65% of TMGa was decomposed in the reactor at the used temperature. The molar flows to the reactor were the same in all the examined pressures as were the molar flow ratios. The DMHy/III molar flow ratio was kept constant at 81 for all the samples.

During the growth an in situ reflectance measurement was performed at 635 nm using a filtered halogen lamp as a light source. Light at 635 nm is absorbed into both GaAs and GaAsN QWs, but reflectance signal is still adequate to provide a possibility to monitor the growth procedure. Similar systems are widely used in growth of GaN and related III-N materials.

High-resolution X-ray diffraction (XRD) and photoluminescence (PL) measurements were performed to the samples after growth. A high-resolution X-ray diffractometer was used to determine the compositions and layer thicknesses of all the samples. Simulation results were fitted to all XRD data. PL measurements were performed for annealed samples at 10 K. Pump beam power was 6 mW. Small pieces of all the samples were annealed for 10 min at 700 °C in a TBAs flow at atmospheric pressure to improve the optical quality of the material and to enable the PL measurements.

3. Results and discussion

Fig. 1 shows the QW nitrogen content based on XRD measurements as a function of TBAs/III molar flow ratio used during the QW growth. The nitrogen content increases superlinearly with increasing TBAs/III molar flow ratio and, as a consequence, with decreasing DMHy/V molar flow ratio. Similar behavior is detected at all pressures. The DMHy/V molar flow ratio decreases from 0.94 to 0.85 with increasing TBAs/III molar flow ratio (from 5 to 14). The optimal TBAs/III molar flow ratio at all growth pressures seems to be even larger than the values examined here. Regardless of the TBAs/III molar flow ratio, the largest nitrogen contents are obtained at 100 Torr and the largest nitrogen content is achieved using a TBAs/III molar flow ratio of 12.5. Using a larger TBAs/III molar flow ratio at 100 Torr led to deterioration of the material quality. However, TBAs/III molar flow ratio of 14 was successfully used at 300 Torr. The QW nitrogen contents varied from 2% to around 5% as the growth pressure and TBAs/III molar flow ratio were varied.

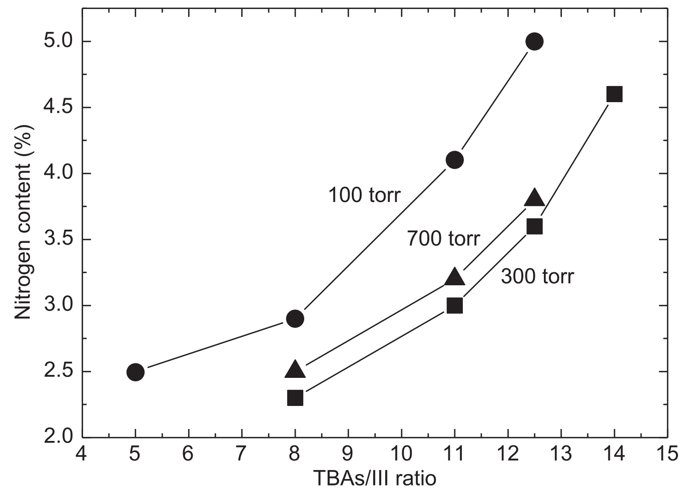

Fig. 1. Nitrogen content as a function of TBAs/III molar flow ratio at various pressures. The superlinear dependence can be observed regardless of the growth pressure.

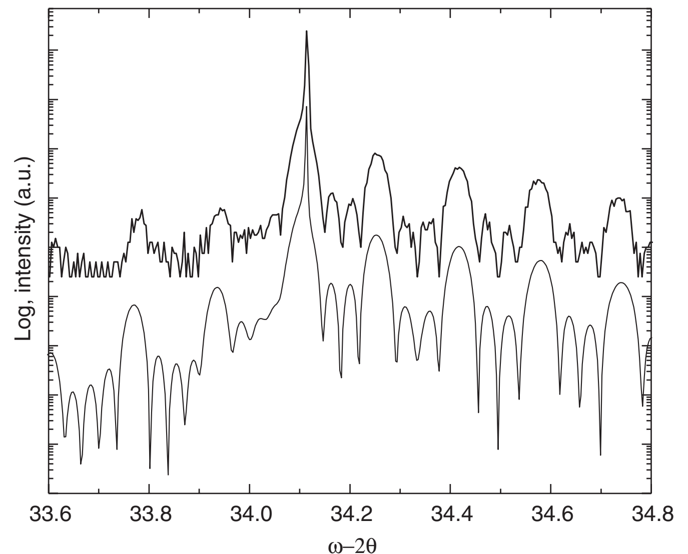

Fig. 2. XRD measurement (upper curve) and a simulation result (lower curve) fitted to the measurement from a GaAsN/GaAs MQW sample containing 3.1% nitrogen. The vertical offset between the measured and simulated curves is added for clarity.

Fig. 2 shows a measured XRD curve from a GaAsN MQW sample with 3.1% nitrogen grown at 700 Torr. XRD

measurements were performed for un-annealed samples. The simulation result fitted to the measurement is shown in the figure right below the measured curve. The measurement and the simulation are in good agreement for all the samples. By XRD characterization, for the 100 Torr grown samples the GaAsN QW and GaAs barrier thicknesses were about 7 and 16 nm, respectively. The growth rate was 0.26 nm/s for the QWs and 0.32 nm/s for the barriers. The samples grown at 300 and 700 Torr were found to have thicker QW (10 nm) and barrier (19–22.5 nm) layers than the samples grown at 100 Torr. The growth rates for 300 and 700 Torr samples were 0.36 nm/s for the QWs and 0.39–0.45 nm/s for the barriers. The different increase in the growth rate for QWs and barriers with increasing growth pressure may be caused by the rather large DMHy flow affecting the growth rate of GaAsN layers more significantly at higher pressures. This, however, was not studied in detail in this paper.

It is quite clearly seen from Fig. 1, that the nitrogen content of the samples grown at 300 and 700 Torr is smaller than that of the samples grown at 100 Torr. It is possible that the overall growth conditions which are optimized at low pressure are not as optimal at higher pressures. For example, the increasing growth rate might diminish the nitrogen incorporation into the sample. However, we suggest that the optimal TBAs/III molar flow ratio is a function of growth pressure and, in addition, it decreases as the growth pressure increases. Here, we need to consider the growth rate as a key parameter: the growth rate increases with increasing growth pressure. It is possible to calculate the effective TMGa molar flow to the reactor from the growth rate. Naturally, this effective TMGa molar flow is larger at 300 and 700 Torr than the TMGa molar flow at 100 Torr which makes the effective TBAs/III molar flow ratio smaller. An examination that is based on the effective TBAs/III molar flow ratio introduced above, results in an optimal TBAs/III molar flow ratio which is pressure dependent. The pressure dependence of the optimal TBAs/III molar flow ratio would explain the nitrogen content differences in our samples grown with the same nominal TBAs/III molar flow ratio but at different pressures. Furthermore, the explanation of the somewhat contradictory optimal TBAs/III molar flow ratio results obtained by others [8,9] might lie in this effective TBAs/III molar flow ratio.

Fig. 3 shows low-temperature photoluminescence (LTPL) spectra measured from the annealed samples grown at 300 Torr. LTPL peaks are at 1051, 1125, 1180 and 1321 nm with nitrogen contents of 2.3%, 3.0%, 3.6% and 4.6%, respectively. The intensity of the peaks decreases and the full-width half-maximum (FWHM) increases as the nitrogen content is increased. The PL peak at 1051 nm is over 30 times more intense than the peak at 1321 nm. The samples grown at 300 Torr appeared to be of the best optical quality. In addition, the samples grown at 100 Torr, which is a typical growth pressure in low-pressure MOVPE systems, showed significantly lower LTPL intensity with similar nitrogen contents than the samples grown at higher pressures.

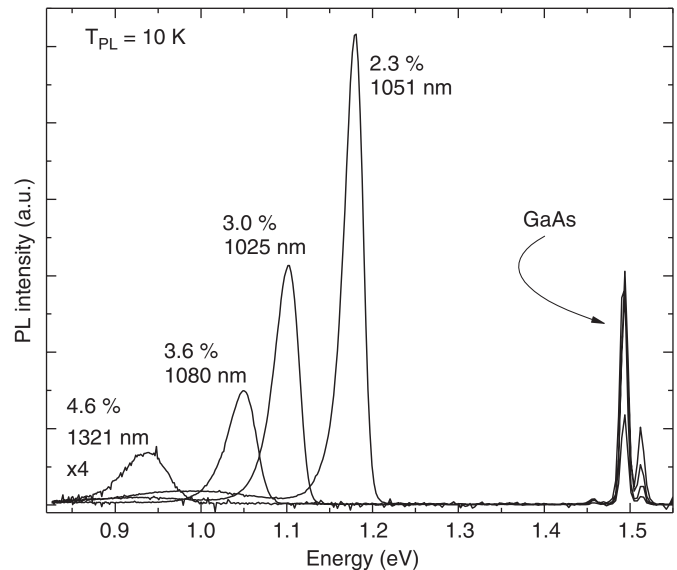

Fig. 3. Photoluminescence spectra of the samples grown at 300 Torr. Nitrogen contents are shown in the figure together with the peak luminescence wavelength. The peaks around 1.5 eV originate from GaAs.

The LTPL measurements of the samples indicate a bowing parameter of −14 eV for GaAsN. The value for the bowing parameter is a rather rough estimate because quantization effects have been neglected and the LTPL measurements were performed for annealed samples. Also, the samples examined here contained a relatively large amount of nitrogen (from 2% to 5%) and the bowing parameter could be different for smaller nitrogen contents [10]. However, the result is in good agreement with previous reports [8,11,12].

Fig. 4 shows a typical reflectance signal measured during a whole MQW growth run. The sample was grown at 300 Torr and contains 4.6% nitrogen. Reflectance varies as a function of temperature and as the surface of the sample changes. Different origins of the change in the reflectance are denoted in the figure. The penetration depth of 635 nm to GaAs is about 250 nm at 650 °C [4]. The layers examined here, i.e., the QW and barrier layers, are so thin, that the interference fringes typical for thick layers are not seen. Thick layers, however, might be useful to examine the refractive index of GaAsN. For example, in situ monitoring of thick GaAs and AlAs layers has been used to study the refractive indices of GaAs and AlAs [4].

Fig. 5 shows an enlargement from Fig. 4 leaving only the reflectance data of the MQW growth region into consideration. The difference between the refractive indices of GaAs and GaAsN causes the change in the reflectance and therefore the reflectance changes originating from the QWs and barriers are clearly seen. The lines in the figure are linear fits to the reflectance data during QW and barrier layer growth. The first QW was selected for closer inspection because of the simplicity of the reflection at a

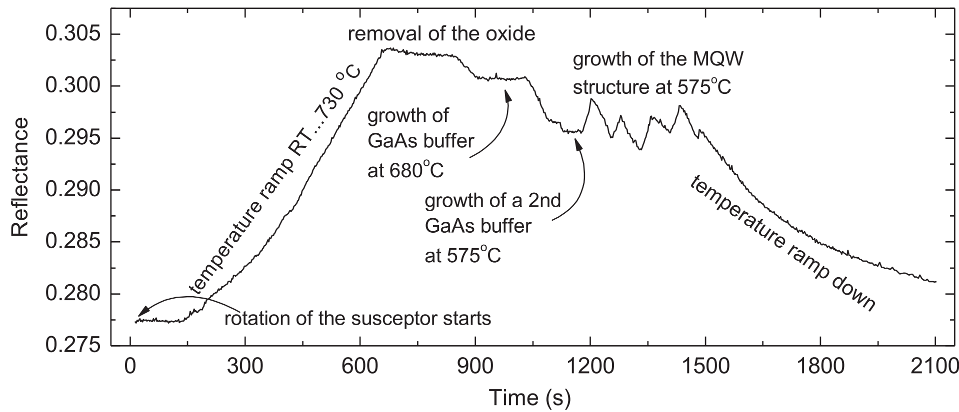

Fig. 4. In situ reflectance measured during a MOVPE run. Different phases of growth are denoted in the figure.

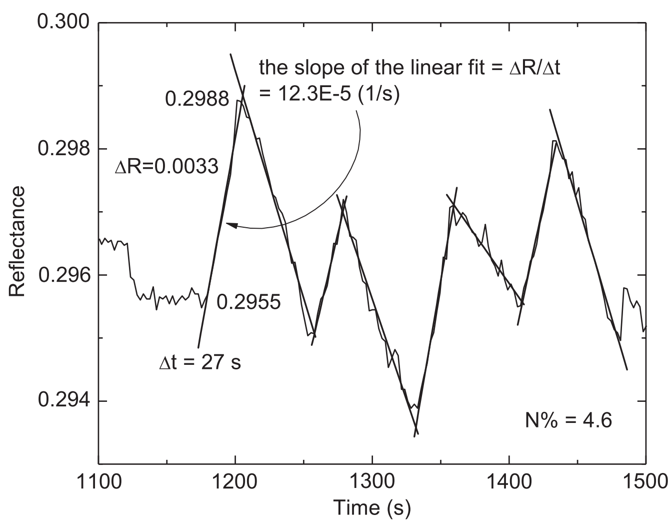

Fig. 5. Reflectance measured during the MQW growth. Reflectance increases during QW growth and decreases during barrier growth. Linear fits to the data are shown as solid lines.

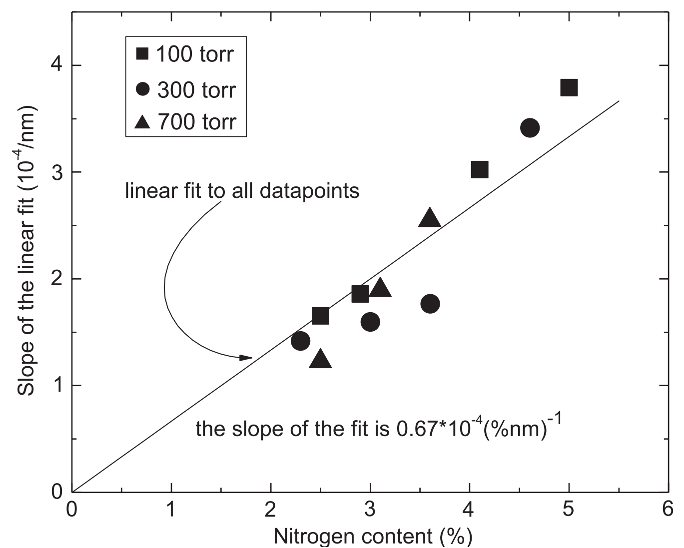

Fig. 6. Slopes of the linear fits to the reflectance data measured during the first QW growth as a function of the nitrogen content in the QW. Samples grown at different pressures are denoted with different symbols. The solid line is a linear fit to all the data points. The fit is fixed at origin.

single GaAsN/GaAs interface instead of the whole stack of QWs below, e.g., the uppermost QW. The particular parameters ΔR and Δt denoted in Fig. 5 are used to determine the slopes $\Delta R/\Delta t$ of the linear fits.

The difference in the refractive indices between GaAs and GaAsN increases when the nitrogen content of the GaAsN layer increases. This causes the slope of the QW growth reflectance data being proportional to the QW nitrogen content. The slopes obtained from the linear fits to the reflectances of the first QW data are shown in Fig. 6. Data points measured from samples grown under different reactor pressures are denoted with different symbols. To eliminate the growth rate dependence of the slope $\Delta R/\Delta t$ a mathematical correction was used to translate it to $\Delta R/\Delta d$, where d is the thickness of the layer. Because ΔR is assumed to be linearly proportional to d, the original data were divided by growth rate. The slope of the QW growth is found to be linearly dependent on the nitrogen content of the sample. The line fitted to all the data points is shown in the figure as a solid line and has a slope of 0.67×10^{-4} $(\%\,\mathrm{nm})^{-1}$. The linear fit is fixed to zero at origin (GaAs on GaAs). Because the slope $\Delta R/\Delta d$ depends on the QW nitrogen content, the nitrogen content can be roughly estimated already when the QW structure is grown.

Fig. 7 shows examples of the reflectance data measured during the growth of two samples. QW and barrier growth regions are denoted in the figure. Atomic force microscopy (AFM) and XRD results (not shown here) support the conclusion that the crystalline quality of the sample shown in Fig. 7b is poor. This can be also seen from the measured reflectance data. In the case of the high-quality sample (Fig. 7a) the reflectance from GaAs is about 0.296 before and after the growth of the MQW structure. When the reflectance data of the curve b is studied, it becomes clear that the reflectance from the topmost GaAs barrier is significantly lower than in the beginning of the growth of the MQW structure. The decrease of the reflectance of the

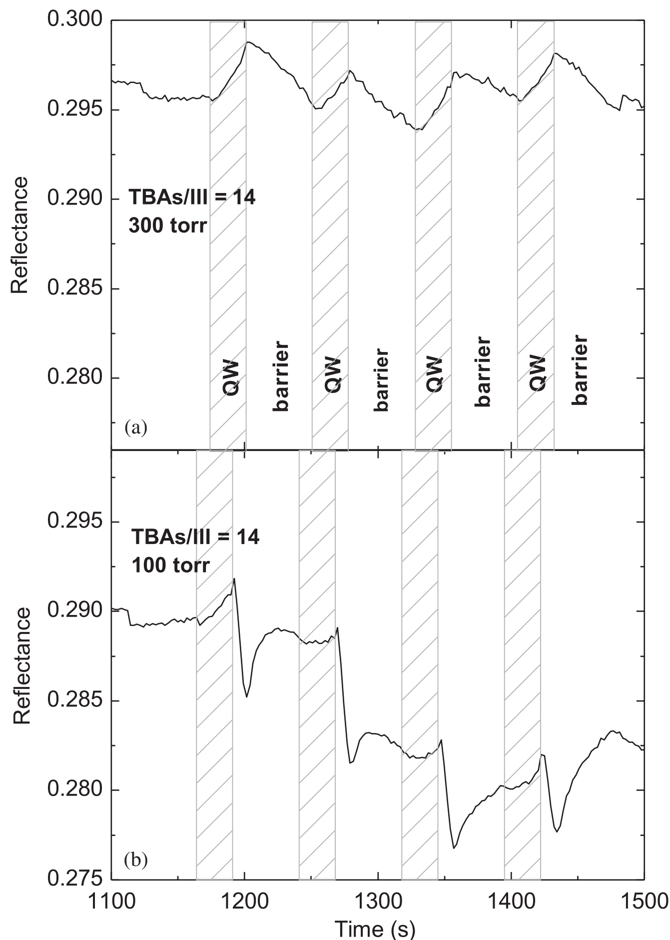

Fig. 7. In situ reflectance data measured during the growth of a (a) high-quality and (b) poor-quality MQW sample. QW and barrier growth regions are denoted.

sample of poor crystalline quality seems to occur just after the growth region of the QW layers: the reflectance increases slightly during the QW growth and at the beginning of the barrier growth a drastic decrease of the reflectance can be observed. This indicates a significant roughening of the sample surface as the growth of the QW ends and the DMHy is switched off from the reactor. Based on these results, we report that the crystalline quality of the sample can be roughly determined already during the MOVPE growth of the structure.

The deterioration of the sample grown at 100 Torr with TBAs/III = 14 may be caused by the relaxation of the structure due to exceeding the critical thickness of GaAsN on GaAs. If extrapolated, the 100 Torr curve in Fig. 1 indicates a nitrogen content of 6% with TBAs/III molar flow of 14. The critical thickness decreases strongly as the nitrogen content increases: a simple approximation gives about 23 nm for the critical thickness of $GaAs_{0.94}N_{0.06}$ on GaAs.

4. Conclusions

Several GaAsN MQW samples have been fabricated by MOVPE using different reactor pressures. The nitrogen content of the samples varied from 2% to 5%. XRD and LTPL measurements were carried out to determine the nitrogen content and layer thicknesses of the samples. After annealing, the samples grown at 300 Torr were of the best optical quality.

In situ monitoring of GaAsN MQW structure was examined and the change in the reflectance was found to be proportional to the nitrogen content of the QWs. In addition, the crystalline quality of the sample could be roughly estimated already during the growth.

The effect of the reactor pressure during growth of the samples was also investigated. The growth rate increases with increasing reactor pressure and the nitrogen content was found to be strongly dependent on the TBAs/III molar flow ratio in all the samples.

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