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Comparison of H_2 and N_2 as carrier gas in MOVPE growth of InGaAsN quantum wells

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Abstract

Differences in sample quality and nitrogen incorporation in InGaAsN quantum well samples grown by metal-organic vapor phase epitaxy using either H_2 or N_2 as the carrier gas are studied by several ex situ methods. The nitrogen incorporation increases while the indium content and the growth rate of the quantum wells decrease when using N_2 as the carrier gas instead of H_2. Also, the hydrogen incorporation into the quantum well is reduced by one order of magnitude. In addition, the in situ reflectance monitoring technique is used to monitor the material quality of the sample and the slope of the reflectance change is shown to be linearly dependent on the quantum well nitrogen content.

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1. Introduction

Ever since the promising results of Kondow et al. [1] about strong nitrogen-introduced band gap bowing of InGaAsN, the nitrogen incorporation has been one of the main problems in the material fabrication. Another problem to be solved is the material quality, which decreases strongly with increasing nitrogen content.

To overcome the obstacles in the nitrogen incorporation process, growth parameters have been carefully optimized for both molecular beam epitaxial (MBE) and metal-organic vapor phase epitaxial (MOVPE) systems. A respectable amount of articles has been published over growth topics of dilute nitrides. Although the use of N_2 carrier gas has been observed to increase the nitrogen incorporation [2,3], the possibilities of N_2 carrier gas have not been examined extensively.

Here we compare nominally similar multiple-quantum well (MQW) structures grown with both N_2 and H_2 as the carrier gas. We also use an in situ reflectance technique for monitoring the growth of the quantum wells. The technique has been previously utilized to determine the quality and composition of (In)GaAsN samples [4,5] and is used here to compare the growth of the samples with the two different carrier gases.

2. Experimental procedure

The samples were grown by a low-pressure MOVPE system on 350 μm thick semi-insulating (1 0 0) oriented GaAs substrates. The rotation speed of the susceptor was 100 rpm. Either nitrogen (N_2) or hydrogen (H_2) was used as the carrier gas. The growth temperature during the growth of all the quantum well structures was 575 °C (a thermo-couple reading). Trimethylindium (TMIn), trimethylgallium (TMGa), tertiarybutylarsine (TBAs) and dimethylhydrazine (DMHy) were used as precursors for indium, gallium, arsenic and nitrogen, respectively. Regardless of the carrier gas chosen, the manifold gas for the precursors was always hydrogen.

The samples consisted of four InGaAsN/GaAs QWs fabricated on two GaAs buffers grown at 650 and 575 °C. No extra capping was added on the topmost GaAs barrier. The TBAs/III molar flow ratio for all the QWs was 2.23

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and DMHy/III and DMHy/V molar flow ratios were 0–24 and 0–0.91, respectively. TMIn, TMGa and TBAs molar flows were kept constant during the growth of all QWs as the DMHy flow was varied to introduce different amounts of nitrogen into the QWs.

The in situ monitoring of the samples was realized with a normal-incidence reflectance setup with a halogen lamp as a light source and data collected at 635 nm. The sampling speed of 1.7 Hz was a consequence of the susceptor rotation speed (100 rpm).

To characterize the samples, photoluminescence (PL) and high resolution X-ray diffraction (HR-XRD) measurements were performed. Together with the results obtained from the PL and XRD measurements, band anti-crossing model (BAC) [6] was utilized to determine the nitrogen and indium contents of the samples. In addition, the hydrogen depth profile of a couple of samples was measured by secondary ion mass spectroscopy (SIMS).

3. Results and discussion

Fig. 1 shows the QW nitrogen content as a function of the DMHy molar flow for samples grown with N_2 (circles) and H_2 (squares) as the carrier gas. The inset of Fig. 1 shows the difference in nitrogen content as a function of the DMHy molar flow. The nitrogen incorporation is clearly enhanced when N_2 is used as the carrier gas. Both curves in Fig. 1 have a similar shape: the nitrogen incorporation is not a linear function of the DMHy molar flow irrespective of the carrier gas. We have earlier reported this sort of behaviour for samples grown in H_2 [5] with a threshold value of 850 μmol/ min for the nitrogen incorporation. When N_2 is used as the carrier, the threshold value is much smaller, approximately 500 μmol/ min. The superlinear dependence of the QW nitrogen content as a function of the nitrogen precursor flow was earlier found by Miyamoto et al. [7] for both GaAsN and InGaAsN using DMHy as the nitrogen precursor.

By combining XRD and PL measurement results and BAC modelling, the indium contents of the QWs were determined to be 18% and 14% for samples grown in H_2 and N_2, respectively, indicating a lower indium content when grown with N_2. The reason for this might be the growth temperature. We suspect that because of the lower thermal conductivity of nitrogen gas, the substrate surface is slightly warmer when N_2 is used as the carrier gas. At the used growth temperature the TMGa precursor is only partly decomposed and the fraction of the decomposed molecules is strongly dependent on the temperature. Because of this, very small changes in the susceptor surface temperature can lead to different concentrations of decomposed TMGa and thus different indium contents. This decreased indium content may have a positive effect on the nitrogen incorporation as it is reported that large indium contents prevent efficient nitrogen incorporation (see for example, Refs. [7,8]). However, we do not believe that the increase in the nitrogen content in the N_2 grown samples is entirely explained by the different indium contents of the samples.

By XRD measurements and simulations, the growth rate of the samples grown using N_2 as the carrier was found to be 37% smaller when compared to samples grown with H_2. We consider the decrease in the growth rate to be caused by the smaller diffusion coefficient of metal-organics in nitrogen than in hydrogen, as was also proposed in Ref. [3].

Fig. 2 shows the depth profile of the hydrogen concentration in a sample grown with H_2 as the carrier gas and with 3.1% of nitrogen in the QWs. The sample was grown with a DMHy molar flow of 1200 μmol/ min. The

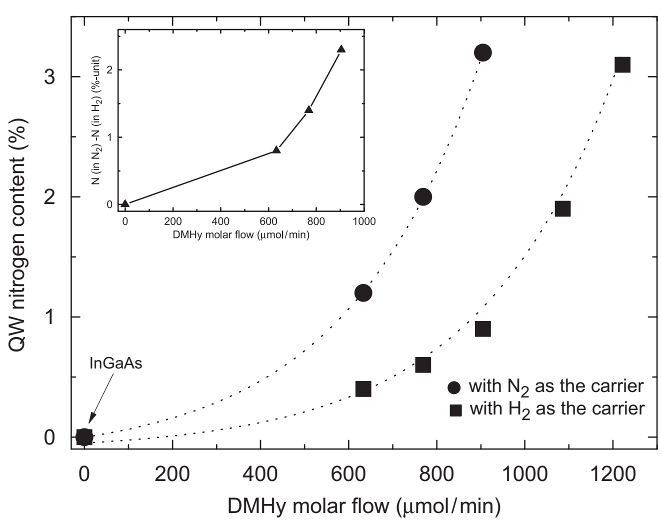

Fig. 1. The QW nitrogen content as a function of the DMHy molar flow in samples grown with H_2 (squares) and N_2 (circles) as the carrier gas. The dotted lines are guides to the eye. The inset shows the QW nitrogen content difference between samples grown in N_2 and in H_2 as a function of the nitrogen precursor molar flow.

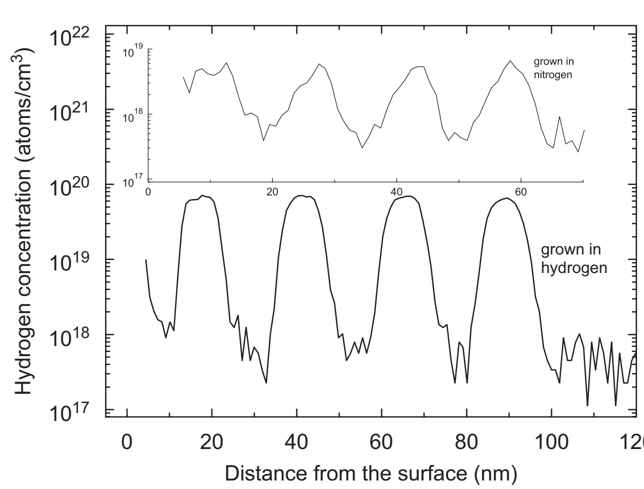

Fig. 2. Hydrogen depth profile measured by SIMS. The sample was grown under H_2 and with DMHy molar flow of 1200 μmol/ min and nitrogen content of 3.1%. The inset shows the depth profile of the hydrogen content in the sample grown with N_2 as a carrier and with DMHy molar flow of 800 μmol/ min and nitrogen content of 2.1%. Note the different scales in the figure and the inset.

hydrogen concentration is over two orders of magnitude larger in the QWs than in the barriers. This is supposed to be caused by the easily forming and strong hydrogen–nitrogen bond. The hydrogen is suspected to originate from the hydrogen in the precursors, because molecular hydrogen is not incorporated into the structure as easily as atomic hydrogen. Also, the hydrogen incorporation into the structure seems to be a MOVPE-related problem, as reported by Ptak et al. [9].

However, the hydrogen incorporation into the QWs is decreased to less than 1×10^{19} atoms/cm^3 when N_2 is used as the carrier gas (inset of Fig. 2). The sample was grown with DMHy molar flow of about 800 μmol/ min. This indicates that even if the molecular hydrogen does not infiltrate into the QWs, it may assist some reactions which support the formation of the hydrogen–nitrogen bonds and therefore increase the hydrogen incorporation.

Fig. 3 shows a typical in situ reflectance curve measured during the MQW structure growth when H_2 is used as the carrier gas. The nitrogen content of the QWs is about 1%. The reflectance signal increases as the QWs are grown and decreases during the growth of the barriers. All samples grown with H_2 as the carrier gas showed similar shape of reflectance curves. The changes in the reflectance signal originate from the different refractive indices of the QW and barrier materials, i.e., InGaAsN and GaAs. The total change in reflectance during the QW growth, ΔR, increases as either the indium or the nitrogen content of the samples increases. The method has been explained in more detail in our previous publications [4,5]. In addition, with this method we have already managed to determine the relation between the QW nitrogen content and the ΔR when the QW indium content is fixed [5].

The in situ reflectance data can also be used to roughly estimate the quality of the samples. The inset of Fig. 3 shows two examples of in situ reflectance curves measured during two growth runs where N_2 was used as the carrier gas. The noisier appearance of these curves compared to the one measured during H_2 growth is a consequence of the smaller growth rate in N_2 grown samples. The sample from which the upper curve has been measured has a QW nitrogen content of 3.2%, whereas the nitrogen content of the sample connected to the lower curve could not be determined.

The lower curve lacks the typical shape of in situ reflectance curve, which clearly indicates that the quality of the sample is poor. Indeed, poor crystal quality was detected when XRD measurements were performed and no PL was observed even after annealing the sample. Because a DMHy molar flow of 1100 μmol/ min was used to grow the sample, we come to a conclusion that the nitrogen content of the QW increased high enough to cause the deterioration of the material or to prevent the growth of the high quality QWs. This kind of threshold concentration for high-quality growth has also been observed elsewhere [10,11]. If the curve from Fig. 1 is extrapolated, the growth with DMHy molar flow of 1100 μmol/ min would lead to a nitrogen content of 5.9% when N_2 is used as the carrier gas, which indicates that a limit of good quality dilute nitride material is approached.

Fig. 4 shows the growth rate corrected slopes $\Delta R/\Delta d$ of the first QWs of the samples grown with H_2 (squares) and N_2 (open circles) as the carrier gas. The growth rate correction is done by dividing the slopes $\Delta R/\Delta t$ by the growth rate $\Delta d/\Delta t$ of each QW. Only the first QWs are discussed for the sake of simplicity. The $In_{0.18}Ga_{0.82}As$ (with no nitrogen) on GaAs data point is marked in the figure. Naturally, the GaAs on GaAs data point would lie in the origin, because of no refractive index difference between the layer and the substrate.

The $\Delta R/\Delta d$ depends linearly on the QW nitrogen content. Because of the smaller indium content of the

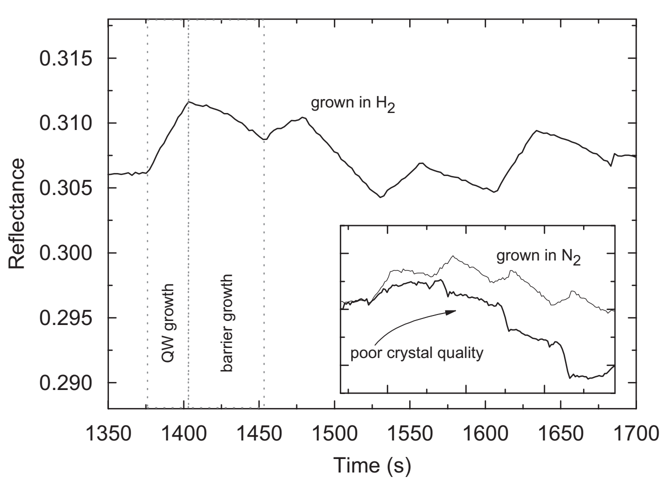

Fig. 3. Typical in situ reflectance curve measured during a MQW growth. The carrier gas was H_2. In the inset, the reflectance curves of a good quality (upper curve) and a poor quality (lower curve) MQW growth using N_2 as the carrier gas are shown.

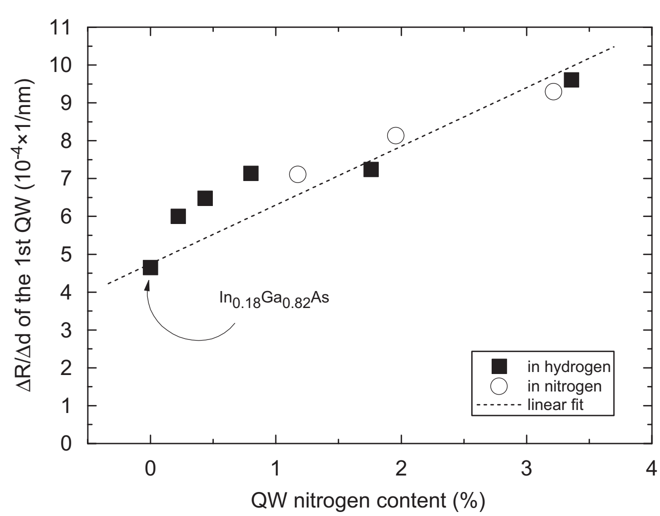

Fig. 4. Growth rate corrected slopes of the reflectance change of the 1st QWs ($\Delta R/\Delta d$) as a function of QW nitrogen content. Data points from samples grown with H_2 and the N_2 as the carrier gas are marked with squares and open circles, respectively. Also the data point of InGaAs on GaAs is denoted.

samples grown with N_2 as the carrier gas, we would have expected the data points of those samples to be slightly lower than the points of the H_2 grown samples. This slight discrepancy might be caused by the smaller reflectance changes ΔR of the N_2 grown samples, which is caused by the smaller growth rate. Smaller ΔR makes it more difficult to examine the data with a high reliability. However, irrespective of the carrier gas, a linear dependence was observed. To thoroughly study the $\Delta R/\Delta d$ vs. nitrogen content of the samples grown with N_2 as the carrier gas, a larger growth rate and thicker QWs are required.

4. Conclusions

We have studied MOVPE grown InGaAsN/GaAs MQW samples using both H_2 and N_2 as the carrier gas. The nitrogen incorporation was found to increase when N_2 was used as the carrier. However, the indium content of the samples grown with N_2 was lower and the growth rate was found to decrease by about 37% compared to samples grown with H_2 as the carrier gas. Also, the hydrogen concentration in the quantum wells was found to be one order of magnitude smaller when the sample was grown in N_2.

In addition, we have utilized the in situ reflectance monitoring technique to obtain information about the growth. It is clearly seen from the reflectance data that an attempt to introduce a too large nitrogen content into the QWs leads to deterioration of the material quality already during the growth. Also, the growth rate corrected slope of the reflectance change is found to be a linear function of the QW nitrogen content for both carrier gases.

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