

Dimethylhydrazine: a potential competitor for ammonia for the growth of GaInN structures?

V. Pérez-Solórzano¹⁾, B. Santic²⁾, A. Gröning¹⁾, M. Jetter¹⁾, M. Seip³⁾, H. Schweizer¹⁾, **F. Scholz¹⁾**

1) 4.Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany, 2) R. Boskovic Institute, Bijenicka 54, HR-10002 Zagreb, Croatia, 3) Akzo Nobel Chemicals HPMO, Hannah-Arendt-Str. 3–7, 35037 Marburg, Germany

1. Introduction

In the last years, important progress in the fabrication and process techniques for semiconductor materials has been done, resulting in the commercialization of blue laser diodes based on GaInN/GaN structures[1]. The growth of GaInN quantum wells (QWs) with high In-content is still a difficult issue due mainly to the very different physical properties of GaN and InN. At the typical GaN growth temperatures, no InN incorporation can be expected due to the high volatility of the In atoms. On the other hand, the cracking of the commonly used group V precursor, ammonia, is not efficient enough at lower temperatures, requiring V/III-ratios greater than 10.000 to ensure a good optical quality and increasing drastically the amount of waste material producing during the growth.

Finding a new nitrogen precursor, which decomposes easily at lower temperatures, may simplify the growth of InN-containing structures. Such a precursor could be Dimethylhydrazine (DMHy), a liquid source releasing atomic nitrogen at temperatures between 320 and 800°C, as shown in the investigations from Bourret et al. [2]. This group succeeded in growing stoichiometric GaN at 630°C with a very low DMHy/TEGa-ratio of 14. Sato et al. [3] obtained excellent GaN crystalline quality with a full width at half maximum (FWHM) of the x-ray rocking curve of about 81 arcsec. At normal growth conditions for GaN, DMHy also acts as fairly efficient source for carbon, degrading the optical properties of the samples. This can only partly be overcome by the growth at higher pressures and lower temperatures [4]. Therefore, DMHy is less suitable for GaN or AlGaIn growth under normal growth conditions ($T_G > 1000^\circ\text{C}$), whereas no investigations are yet known about the growth of GaInN with DMHy at lower temperatures around 700–800°C. DMHy has already been systematically used as nitrogen source for the growth of GaInAsN with growth temperatures below 600°C [5].

In this paper, we present some results from our recent investigations about the use of DMHy for the growth of GaInN/GaN-structures at temperatures between 760–800°C.

2. Experimental

Our samples were grown in an horizontal MOVPE reactor with rectangular cross-section (Aixtron AIX 200 RF) at a reactor pressure of 100 mbar. First, a buffer structure consisting of 800 nm $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$ followed by a 1 μm GaN layer were grown on (0001)-oriented 6H-SiC at 1120°C using NH_3 as nitrogen precursor and H_2 as carrier gas and main dilution. Then the growth temperature was reduced to grow a GaInN-QW with a nominal thickness of 3 nm, supplying 7 $\mu\text{mol}/\text{min}$ TEGa and 42 $\mu\text{mol}/\text{min}$ TMIn. Only for the growth of this GaInN-QW, the DMHy was fed into the reactor as nitrogen precursor. Different DMHy carrier gases (H_2 and N_2) and mixtures of the two nitrogen precursors (NH_3 or DMHy) were used as described in more detail below. Besides the DMHy carrier gas in some experiments, nitrogen was used for all other carrier and dilution gases during the GaInN-QW growth. For optical characterization, the samples were capped with 30 nm GaN. In order to avoid the In-desorption, we grew the first few nms of the capping layer at the same temperature as GaInN has been grown, and then the temperature was increased to 1120°C, to ensure a good surface morphology of the whole structure.

The samples were characterized by photoluminescence (PL) using the 325 nm line of a He-Cd laser and by cathodoluminescence (CL). In-content and growth rate were determined by the analysis of symmetrical (002) and asymmetrical (105) reflections using high resolution x-ray diffraction (HRXRD) on these layers as well as on

GaInN–GaN superlattice structures grown under the same conditions. From these structures, we could not observe a change of the growth rate when applying DMHy as additional nitrogen source.

3. Results

First, we have grown some reference layers using 9 l/min NH₃ and no DMHy, where the GaInN quantum well was grown at different temperatures. As expected from our early results [6], the PL–energy position changed according to an increased In incorporation. The sample grown at 760°C showed a PL–energy of 2,86 eV, which was confirmed by x–ray diffraction reciprocal space mapping, obtaining an In–content of about 26%.

Since GaInN–QWs grown only with DMHy as nitrogen source presented poor structural quality and no luminescence, we have grown our samples reducing the NH₃ flow from 9 l/min to 6,7 l/min and then gradually introducing DMHy. A strong blue shift of the CL–peak position from 2,86 eV to 3,28 eV is produced for GaInN–QWs grown at 800°C when the DMHy–flow was increased until 3 mmol/min and carried with H₂. (fig. 1, squares)

Investigations fo Piner *et al.* [7] have shown a rapid decrease of the In–content of GaInN–QWs at 750°C, even when small amounts of H₂ were introduced into the reactor. In order to clarify the origin of the blue shift, we have grown the same structures with the same H₂ flow, but keeping the DMHy–bubbler closed.

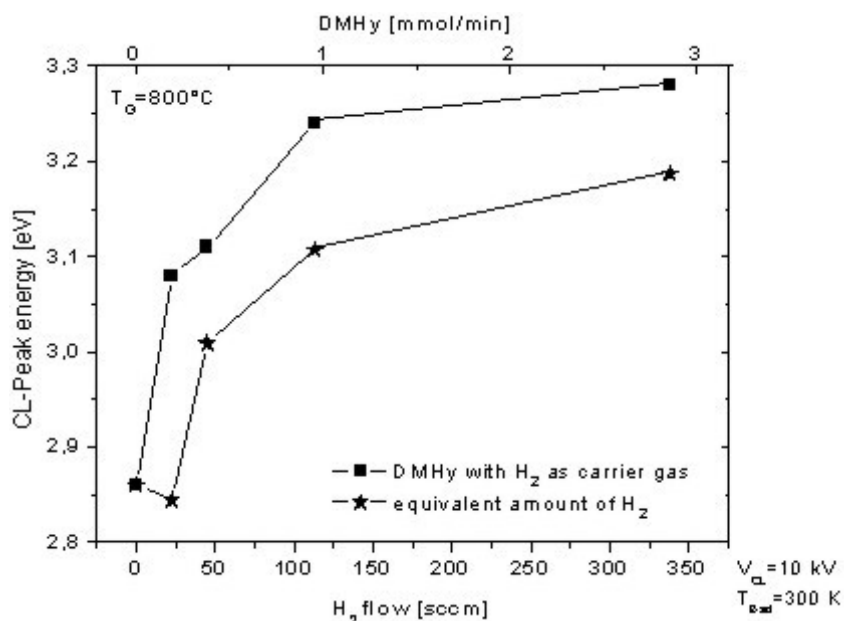


Fig. 1: Influence of the amount of H₂ present in the reactor on the CL–energy position of the nom. 3 nm GaInN–QW (growth temperature set to 800°C)

As expected, also these layers show a blue shift on the CL–energy (fig. 1, stars). However, they still contain significantly more In than the corresponding layers grown with DMHy.

Making use of the possibilities of our MOVPE–machine, and keeping in mind the fact described above, we decided to grow our samples while minimizing the quantity of H₂ present in the reactor. Therefore, N₂ was used as carrier gas for DMHy.

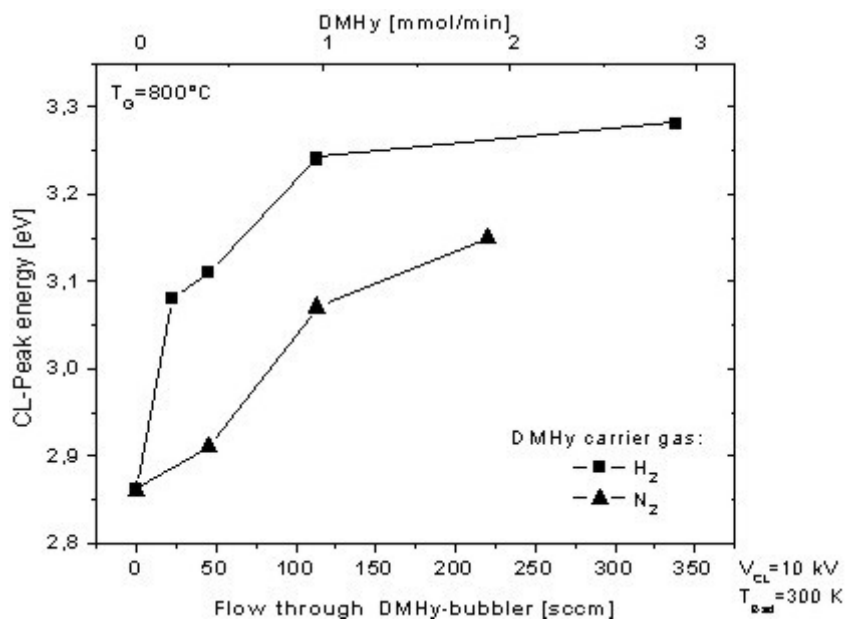


Fig. 2: Comparison of the CL–peak position of our samples grown with H₂ and N₂ as carrier gas at a growth temperature of 800°C.

A much lower but still significant shift of 270 meV was observed when carrying the DMHy with N₂ confirming the negative effect of DMHy on the In–incorporation efficiency.

If we are interested in GaInN–layers with high InN–content, the growth temperature should be further reduced to avoid the desorption of In atoms from the surface. Then, any potential advantages of DMHy are expected to increase.

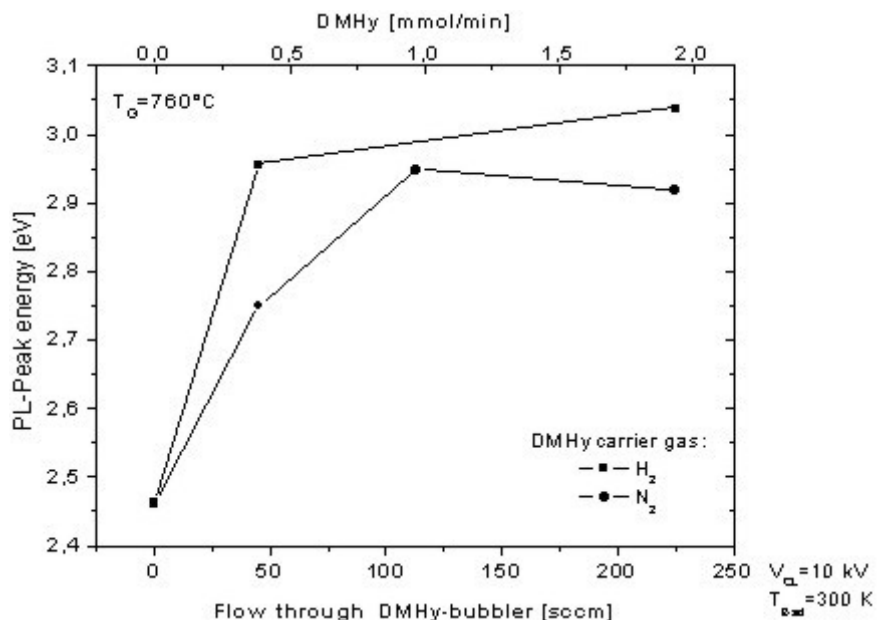


Fig. 3: Dependence of the PL–Peak energy with the carrier gas and amount of DMHy for a growth temperature of 760°C.

However, we obtained quite similar results at a growth temperature of 760°C. Now, even a small amount of DMHy (45sccm=0,4 mmol/min) provokes an increase of the PL–energy of about 500 meV for H₂ used as carrier gas. This corresponds to a reduction of the In–content of the layer from 26% to 10%.

4. Conclusions

From our results, we can conclude that the incorporation of InN into GaInN is reduced when DMHy is used as nitrogen precursor, whereas no influence on the growth rate was observed. This may be explained by the additional amount of hydrogen which is released from the methyl–group of the DMHy molecule itself. Unfortunately, this effect is quite strong even for low growth temperatures. Thus, DMHy seems to be less suitable for the growth of GaInN, although it is a good nitrogen precursor for lower growth temperatures in other material systems. These results confirm those findings of Piner et al. [7] that the hydrogen, which may be released from NH₃ does not significantly influence the In–incorporation and thus its concentration is very low under typical GaInN growth conditions.

Further investigations are necessary to clarify the influence of carbon and other residual materials coming from the decomposition of the DMHy–molecule on the optical and structural properties of GaInN grown at low temperatures.

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6. References

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