

Growth of galliumnitride on sapphire and silicon using propylamine as nitrogen precursor

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Abstract. In the present work, gallium nitride was grown by MOCVD from trimethylgallium and ammonia with and without the addition of propylamine. The usage of propylamine showed considerable advances, concerning the morphology, compared to the standard mixture. The elemental composition as well as the Raman spectra were measured and show that GaN films with only small amounts of impurities were deposited. GaN growth was found on sapphire and silicon substrates. In gas phase studies of TMG/propylamine mixtures at different temperatures, two Lewis acid-base-complexes were detected, which dissociate at higher temperatures.

1 INTRODUCTION

Gallium nitride has received considerable attention due to its wide band gap. The excellent properties of GaN-based materials have resulted in promising applications including light-emitting and laser diodes, ultraviolet detectors, microwave devices and high-temperature electronics [1-3]. This has motivated investigation of the crystal growth and the mechanism of GaN deposition.

Several materials technologies, including liquid-phase epitaxy (LPE), molecular-beam epitaxy (MBE) and metalorganic chemical vapour deposition (MOCVD) have been developed for the growth of the thin film epitaxial structures that are required for the realisation of GaN materials. Although these techniques still suffer from some disadvantages, such as high deposition temperature, low growth efficiency and high defect density, MOCVD is often the preferred method for GaN deposition.

Typically, trimethylgallium (TMG) is used as the gallium source, and ammonia as nitrogen precursor [3]. However, GaN films deposited using this mixture often exhibit a more or less pronounced yellow colour, an indication of impurities. Hydrazoic acid (HN_3) [4,5] as well as hydrazine (H_2NNH_2) [6] and its derivatives [7,8] were used for the growth of GaN, in spite of the high toxicity or explosiveness of these compounds. While novel single-source precursors are being designed to improve the deposition process [9], alkyl amines have not received much attention as a potential substitute for ammonia. Recently, Beaumont et al [10] have used triethylamine and t-butylamine, but they conclude that these precursors are not suitable for GaN deposition, and ammonia remains the most widely and effectively employed nitrogen precursor in the CVD of GaN films. In a study of Rushworth et al. who used tert-butylamine and TMG as precursors, gallium droplets were deposited [11]. In our study, three closely related precursor systems were studied: the deposition of GaN from TMG with ammonia, with n-propylamine alone and with a mixture of propylamine and ammonia.

2 EXPERIMENT

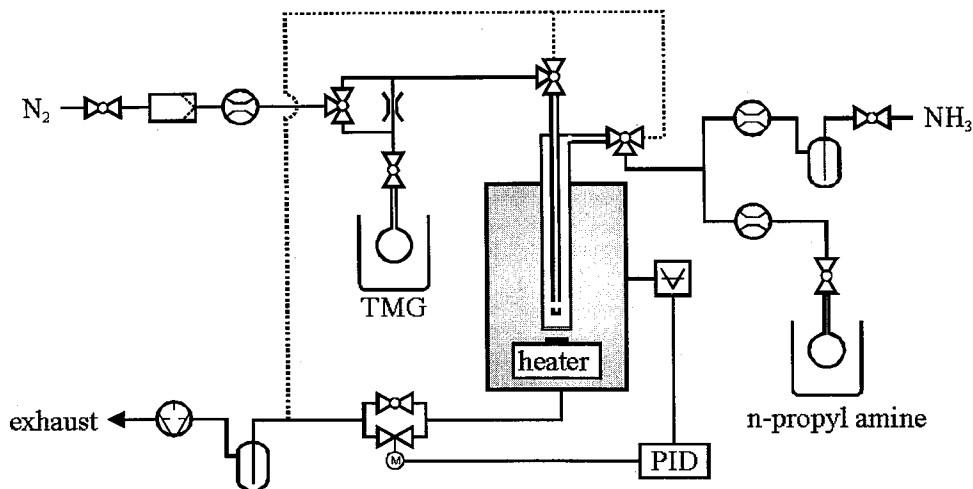


Figure 1. Experimental set up of the cold-wall CVD reactor with stagnation-point geometry.

The experimental set up of the MOCVD system, as depicted in Fig. 1, will be described briefly. Propylamine was purified by distillation, collecting the fraction between 48 and 49 °C. An aluminium reactor was used at a total pressure of 45 mbar and with a distance between the gas entrance and the substrate of 10 mm. The substrate materials were sapphire (orientation [0001]) and silicon [100]. The substrate was cleaned in an ammonia atmosphere at 1000 °C for 5 min, the ammonia flow was 0.8 slm. While maintaining the substrate temperature at 1000 °C, TMG and propylamine were introduced separately into the reactor. Nitrogen was used as a carrier gas for TMG at a partial pressure of 1.96 mbar (total flow of TMG + N_2 : 0.04 slm), and the fraction of TMG in this flow was estimated with the TMG vapour pressure to be about 20% (0.008 slm). Propylamine was added at a flow of 0.08 slm corresponding to a partial pressure of 3.91 mbar. The mixing of the TMG-containing gas flow and the nitrogen precursor-containing gas flow occurs inside the tube at 16 mm distance from the substrate. The total linear flow velocity is calculated to be 147 cm/s. The deposition time was 45 min. For a comparison, some of the experiments were repeated without propylamine addition under otherwise identical conditions; the ratio of nitrogen precursor to gallium precursor was only slightly affected by this procedure. The resulting films were inspected with scanning electron microscopy (SEM) and Raman spectroscopy. The composition of four samples was measured by Bergmaier and Dollinger applying elastic recoil detection (ERD), further information on this method can be found in Ref. [12].

The gas phase composition of the TMG/n-propylamine mixture was determined between 20 and 630 °C using the molecular-beam sampling mass-spectrometry method. The experimental set up was given elsewhere [13], where the experimental procedure was also discussed, so only these new results will be summarised here. The ionization energy was fixed to 20 eV, as a compromise between signal intensities and the amount of fragmentation. In the interpretation of the mass spectrometric results, a loss of one methyl group has to be taken into account, as was discussed in our previous work [13].

3 RESULTS AND DISCUSSION

3.1 Deposition experiments

3.1.1 TMG and propylamine

Several attempts (more than 25) to deposit gallium nitride of reasonable quality out of a TMG/n-propylamine mixture on sapphire as well as on silicon failed. The deposition experiments were performed between 400 and 1000 °C. At the lowest temperature, no deposition was observed, at higher temperatures the deposits were gray or black, and therefore obviously not GaN. However, in the SEM some amorphous, or at least unresolvable structures were observed, instead of the expected gallium droplets. From these experiments it was concluded that either the amount of nitrogen-containing radicals was too small, which is unlikely, because the pyrolysis of propylamine takes place at lower temperatures than the pyrolysis of ammonia, or some reducing agent was necessary to react with the produced hydrocarbons from the pyrolysis of n-propylamine. These considerations led to the following experiments.

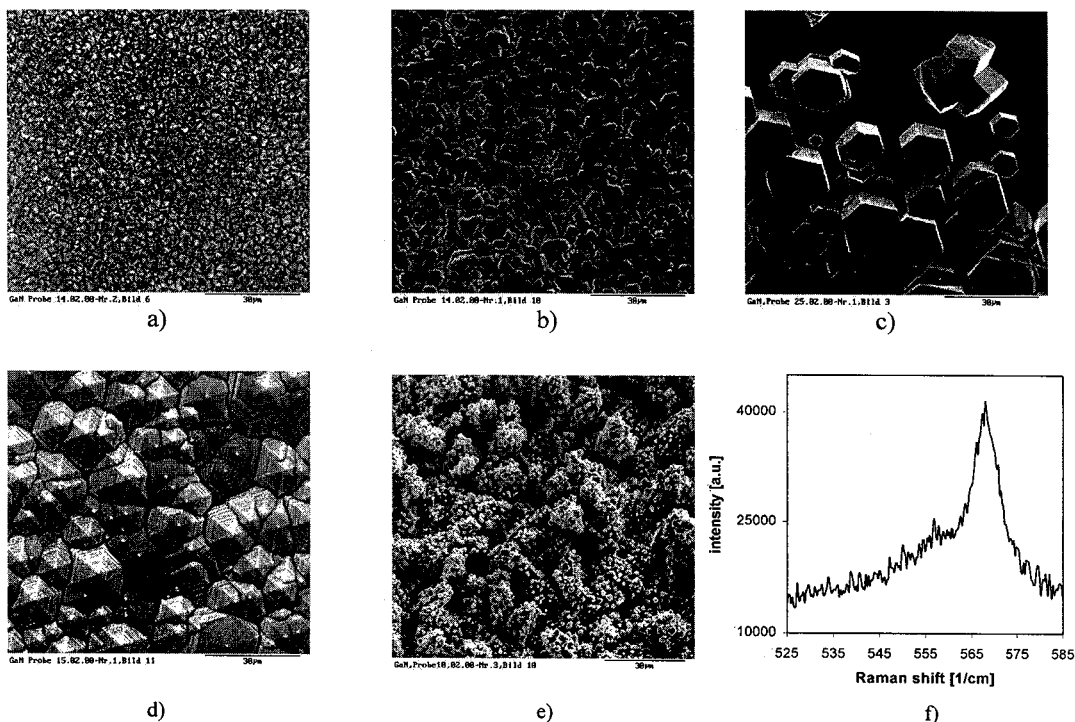


Figure 2. SEM pictures of 5 samples deposited on sapphire and a corresponding Raman spectrum. a), b), c) d) show deposits with propylamine addition at 800, 900, 950 and 1000 °C respectively. e) GaN deposited at 1000 °C without propylamine addition. f) The Raman spectrum of sample c).

3.1.2 TMG and Ammonia, the effect of propylamine addition

Ammonia was chosen as co-reactant, because it is a reducing agent and it will increase the concentration of NH_2 radicals after reaction with alkyl radicals. At 700 °C, no deposition was found, but at temperatures between 800 and 1000 °C, GaN films were deposited on sapphire using the TMG/ ammonia mixture with propylamine. While the sample at 800 °C is dark, the films which were deposited at higher temperatures

are transparent, as would be expected for GaN. Four SEM pictures of deposits at 800, 900, 950 and 1000 °C are shown in Figure 2 a-d. These images show that the samples at 950 °C and 1000 °C are highly oriented; it should be mentioned in addition that the SEM picture at 950 °C is from a peripheral region, therefore part of the film is not closed. From the crystal height in this region, a growth rate of 7-10 $\mu\text{m/h}$ is estimated. Well-defined hexagonal prisms can be recognised in this region. The film is closed at 1000 °C, and sizes of individual crystals are about 7-15 μm . Most crystals exhibit terraces and show a needle-like structure in the centre, which might be due to the growth of a hexagonal pyramid, with some secondary nucleation at the tip. Raman spectra taken at 488 nm using an argon ion laser verify that GaN was deposited at 950 and 1000 °C. At lower temperatures, the Raman peak was not detectable. This might in part be a problem of lower film thicknesses; Fig. 2 f shows the E_2 peak of GaN at 568 cm^{-1} [14,15] for the sample deposited at 950 °C with propylamine added. Two of the samples were analysed by ERD [16], the films deposited at 800 °C and at 900 °C. At the lower temperature, the ratio of Ga:N is 1.6, with a high level of impurities of oxygen and carbon ($x_{\text{O}}=0.06$ and $x_{\text{C}}=0.04$). At 900 °C the ratio of Ga:N is $1(\pm 0.05)$, with the main impurity being carbon with $x_{\text{C}}=0.02$, the oxygen impurity levels being below 1%.

Figure 2e shows a sample deposited on sapphire at 1000 °C using a TMG/ammonia mixture without propylamine addition. This sample exhibits a light yellow colour typically associated with impurities. The morphology indicates poor crystal definition in a coherent polycrystalline film. The addition of propylamine thus leads to some considerable improvement of the grown films with respect to orientation. In a further series, GaN was deposited on silicon, using both gas mixtures. Two typical SEM pictures are shown in Figure 3. Both samples were deposited at 1000 °C. Again it was found that propylamine addition led to an improved film quality, with mainly hexagonal surfaces present, while trigonal surfaces were prevailing without propylamine addition. The composition and impurities of a sample deposited at 900 °C was analysed by ERD; the result is very similar to the one on sapphire.



Figure 3. SEM pictures of two GaN samples, both deposited at 1000 °C on silicon. a) with propylamine addition, b) without propylamine addition.

3.1.3 Gas phase studies

In addition to our previous work on the temperature-dependent gas phase composition of TMG ammonia mixtures [13], we have studied the propylamine/TMG system in the temperature range between 300 and 900 K. A typical mass spectrum is shown in Fig. 4. It should be mentioned that gallium consists of two isotopes, Ga^{69} and Ga^{71} with a ratio of 60/40. From the presence of such double peaks, the gallium-

containing species can easily be resolved. In addition to the TMG fragmentation peaks (Ga, MMG ($=\text{GaCH}_3^+$) and DMG ($=\text{Ga}(\text{CH}_3)_2^+$)), two additional peak groups were resolved: one group at 158/160 u and a second at 217/219 u. From our previous experience with EI mass spectra of organo-gallium compound it is clear that these peaks are due to two Lewis acid-base complexes after losing one methyl group (Me), because of fragmentation. The lower mass group should be due to $(\text{CH}_3)_3\text{Ga}:[\text{NH}_2(\text{C}_3\text{H}_7)]$ (-Me) the higher mass group is the complex of TMG with two propylamine molecules: $(\text{CH}_3)_3\text{Ga}:[\text{NH}_2(\text{C}_3\text{H}_7)]_2$ (-Me).

The intensity for the second group decreases already at 100 °C below the detection limit, while $(\text{CH}_3)_3\text{Ga}:[\text{NH}_2(\text{C}_3\text{H}_7)]$ (-Me) can be detected up to 300 °C. However, the presence of these complexes at 1000 °C, although the reaction times are strongly reduced, seems unlikely.

It seems more probable that the pyrolysis of propylamine would produce additional N-containing radicals, like NH_2 . Therefore some attempts were made to resolve such species. At higher temperatures ($T > 400$ °C), strong peaks at 15 and 16 u were detected, but these peaks were mainly originating from CH_3 and CH_4 and not from NH_2 and NH . So this mechanistic hypothesis cannot be confirmed with these experiments.

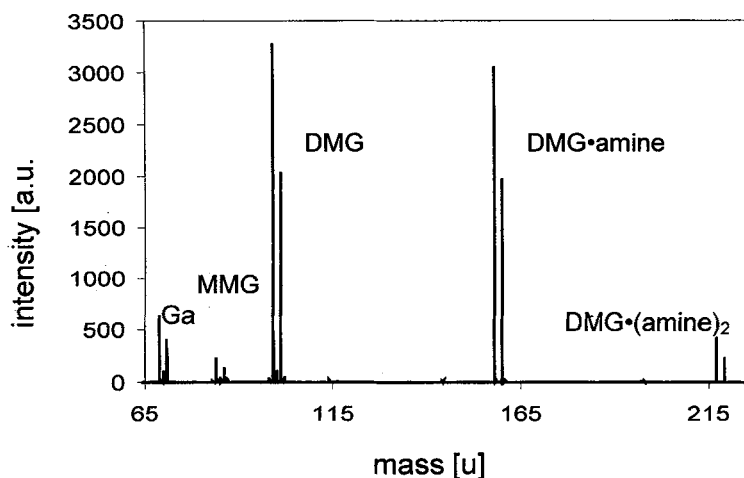
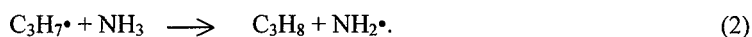
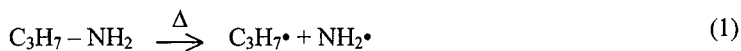


Figure 4. A typical mass spectrum measured in a TMG/propylamine mixture, measured at room temperature.

4 CONCLUSIONS

Although the chemical mechanism is presently unclear, it is evident that comparatively small amounts of propylamine have a significant effect on the GaN crystal growth and film morphology, while GaN deposition substituting NH_3 completely by alkyl amines was not successful (see also Ref. [10]). Propylamine should be a more effective source of NH_2 due to the lower C-N bonding enthalpy in comparison to that of the H-N bond. Although NH_2 was not directly detected, due to strong signals of CH_4 , this mechanism seems to be the most likely process. The main role of ammonia could be to act as a reaction partner for hydrocarbon intermediates (e.g. propyl) and so to generate further NH_2 radicals



Propylamine as a nitrogen precursor also offers the interesting possibility of reducing the deposition temperature due to its lower thermodynamic stability, but so far relatively strong deviations of stoichiometry and high levels of contamination were found at 800 °C.

In summary, transparent, pure, polycrystalline GaN films with a significantly improved crystal morphology were obtained in this work using a new gas phase mixture. Two Lewis acid-base complexes were detected in the gas phase, which dissociate at too low temperatures to be involved in the deposition mechanism. While the chemical mechanism causing this effect awaits further investigation, the addition of propylamine to the "standard" TMG/ammonia reaction system provides a new approach for the deposition of high-quality gallium nitride films.

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