Synthesis and Characterization of Bis(tris(dimethylamido)-gallium as a Precursor for MOCVD of GaN Thin Films

Kai junge Puring, Stefan Cwik, In-depth-Practical, Chair of Inorganic Chemistry II, Ruhr-University Bochum (RUB)

Gallium nitride is a material which has become famous for its use in blue light emitting devices. In this work the alternative precursor bis(tris(dimethylamide)gallium) $[Ga(NMe_2)_3]_2$ to common ones such as trimethylgallium (TMG) has been synthesized and was used for the MOCVD of GaN. The precursor was synthesized in high purity and exhibits promising thermal properties for its use in MOCVD. The GaN thin films, produced in this work exhibit mostly an amorphous structure and promising gallium to nitrogen ratios. However, huge sulfur contaminations are abundant in these thin films due to sulfur condensation in the reactor lines from prior usage of the reactor for thermal annealing of sulfide samples.

A film is called a thin film, if its thickness is in the range from a few atomic layers to a few micrometers. The application of thin films covers a wide range from optoelectronics and microelectronics[1] to decorative and protective coatings[2]. A prominent example, which shows applicability in optoelectronics is GaN. This material has a direct band gap of 3.4 eV and hence shows applicability in blue and violet light emitting devices.[1a] Nevertheless, it has been a huge task to obtain high quality GaN thin films by several deposition methods. While hydride vapor phase epitaxy (HVPE) and molecular beam epitaxy (MBE) exhibited low growth rates and hence are not suitable for industrial fabrication. Metal-organic chemical vapor deposition (MOCVD) was found to be the method of choice for the growth of GaN thin films. Chemical vapor deposition (CVD) is a deposition method, which is based on the reactive formation of thin films by a reaction of gaseous precursors on a heated substrate. In case of MOCVD, metal-organic precursors are used. A huge advantage of CVD methods over other deposition methods (e.g. PVD) is that these are not line-of-sight methods and hence can be used to deposit thin films on complicated structures. While MOCVD with trimethylgallium (TMG) and ammonia (NH_3) as a precursor offered high growth rates and a large scale-up possibility, a large lattice mismatch between GaN and common substrates such as sapphire(1000) caused problems with the crystalline uniformity of these thin films. Therefore an AlN buffer layer was implemented to obtain high quality thin films of GaN.[3] Another issue with GaN thin films was the n-type behavior of these films due to nitrogen deficiency. However, in order to obtain functional light emitting devices a p-type GaN is mandatory to create a p-n-junction. These p-type GaN layers were received by Mg doping and subsequent low energy electron beam irradiation (LEEBI) or thermal annealing treatments.[4] Due to GaN having a band gap of 3.4 eV and hence emitting light at approximately 380 nm a doping with indium was necessary to obtain blue light emitting devices.[5] With these improvements the high power light emitting diodes have been obtained.

In this work an alternative precursor for MOCVD, namely bis(tris(dimethylamide)gallium) $[Ga(NMe_2)_3]_2$, will be synthesized and characterized in respect to its purity and thermal properties. Additionally this precursor will be used to deposit high quality GaN thin films in a home-built horizontal MOCVD reactor. Herein the growth behavior of GaN thin films, using this precursor are investigated.

The precursor syntheses were performed under an inert argon atmosphere using common Schlenk techniques. Air and moisture sensitive chemicals were stored under inert argon atmosphere in a glove box. All used solvents were dried and purified using an MBraun SPS-Solvent Purification System. Glassware, used for synthesis, was silylated with 1,1,1,3,3,3-hexamtheyldisilazan before usage. The synthesis of bis(tris(dimethylamide)gallium) $[Ga(NMe_2)_3]_2$ was done by the salt metathesis reaction of gallium(III)chloride and lithium dimethylamide (Figure 1), as described in the literature.[6] The precursor was finally obtained as colorless crystals by crystallization from hexane. For MOCVD of GaN on Si(100) substrates with the previously mentioned compound as precursor, a home built cold-wall reactor, equipped with resistive heating was used. For the depositions the reactor pressure was set to 0.1 mbar, while the carrier (N_2) and reactive gas (NH_3) flows were 25 sscm and 50 sscm, respectively. Deposition temperatures in the range from 200 °C to 600 °C were chosen, while the bubbler temperature was set to 60 °C.

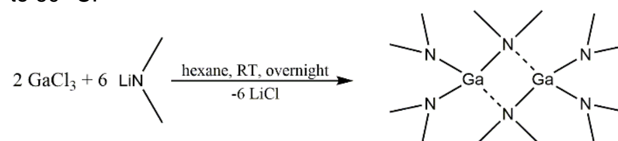

Figure 1. Synthesis of bis(tris(dimethylamide)gallium) $[Ga(NMe_2)_3]_2$.

The bis(tris(dimethylamide)gallium) precursor was obtained in 33 % yield in high purity according to ^{1}H and ^{13}C NMR spectroscopy. The thermal properties of the precursor were investigated with thermogravimetry (TG) / differential thermal analysis (DTA). The respective spectra are depicted in Figure 2. The onset of evaporation is observed at 104 °C. From there, the precursor evaporates in one single step until a temperature of 211 °C is reached. At this point the mass loss ceases and a constant rest mass of 14.3 wt% remains. When comparing this rest mass value with calculated rest mass values of GaN (20.7 wt%), Ga_2O_3 (46.4 wt%) and elemental Ga (17.3 wt%). Hence, a clean decomposition of the precursor can be presumed. Due to the sufficient thermal properties and high purity the precursor is suitable for MOCVD applications.

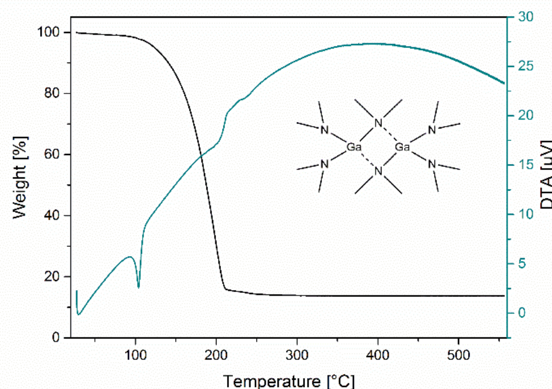

Figure 2: TG / DTA of bis(tris(dimethylamide)gallium) measured with a heating rate of 5 °C / min and an N2 flow rate of 300 ml / min

The GaN thin films grown on Si(100) substrates at a pressure of 0.1 mbar, flow rates of 25 sscm (N_2) /50 sscm (NH_3) in a temperature range from 200 °C to 600 °C were characterized in repect of composition by nuclear reaction analysis (NRA) / Rutherford backscattering (RBS) and structure and morphology by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Table 1: Composition of GaN films, obtained by NRA/RBS analyses.

Deposition Temperature	Composition [atm.%] Ga	N	S	C	O
200 °C	32.97	49.67	8.90	5.16	3.30
300 °C	37.97	49.69	9.21	1.46	1.67
400 °C	41.74	49.93	7.02	0.68	0.63
500 °C	46.58	34.01	18.76	0.22	0.44
600 °C	47.90	27.78	19.46	2.78	2.07

The composition of GaN thin films, obtained by NRA/RBS analyses is shown in Table 1. The expected ratio of gallium and nitrogen atom in the GaN thin films is 1. The observed nitrogen values range from 0.6 deficient to 1.5 excess nitrogen levels in comparison to gallium. Hence the implementation of nitrogen into the thin films is highly dependent of the deposition temperature. While at lower temperatures (200 °C to 400 °C) a nitrogen excess in the range from 1.2 to 1.5 is observed, at higher temperatures (500 °C to 600 °C) a nitrogen deficiency in the range from 0.6 to 0.9 is observed. In general relatively high contamination values of sulfur are observed these range from 7.02 atm.% to 19.46 atm.%, whereas films, deposited at lower temperatures (up to 400 °C) show lower sulfur contaminations. The sulfur contamination is caused by thermal annealing processes of sulfide thin films in the same reactor, which were done prior these depositions, and hence condensation of sulfur in the reactor lines. Contamination levels of carbon (caused by incorporation of ligand fragments of the precursor) and oxygen are in the range from 0.22 atm.% to 5.16 atm.% and from 0.44 atm.% to 4.17 atm.%, respectively. These contamination levels are higher at very low and very high temperatures and get minimal at a deposition temperature of 500 °C. In summary, the film, deposited at 400 °C exhibits the best Ga : N ratio of 1.2, while having by far the least sulfur (7.02 atm.%) and the second least carbon (0.68 atm.%) and oxygen (0.63 atm.%) contamination levels.

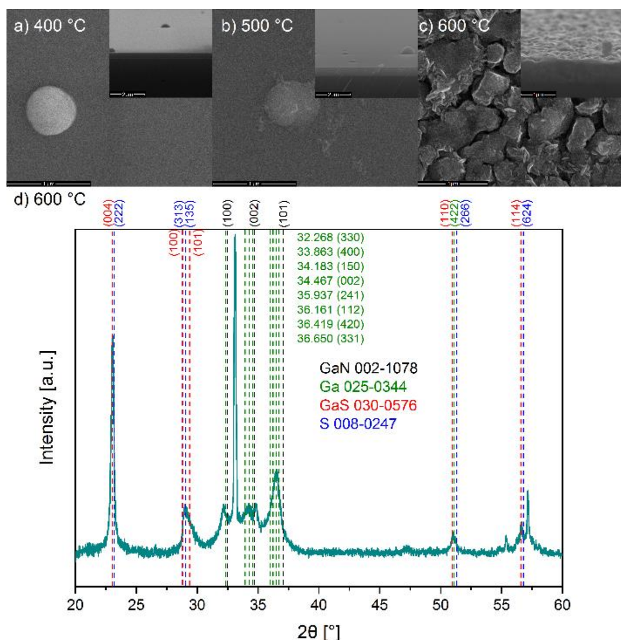

Figure 3: SEM images of GaN thin films deposited on Si(100) at a pressure of 0.1 mbar, flow rates of 25 sscm (N2) / 50 sscm (NH3) at temperatures of a) 400 °C, b) 500 °C and c) 600 °C and the XRD pattern of the GaN thin film, deposited at 600 °C (d).

The structure and morphology of the GaN thin films were investigated by SEM (Figure 3a – c) and XRD (Figure 3d). The thin films, deposited at 400 °C and 500 °C are amorphous, smooth and dense, as the SEM images show. The amorphous nature is verified by XRD pattern of the respective thin films. On these smooth thin films, small drops of presumably elemental Gallium are present. The formation of Gallium drops during CVD processes was already observed by Koleske *et al.*[7] The only crystalline GaN thin film was deposited at 600 °C as it is obviously seen on the SEM images (Figure 3c) and in the XRD. This thin film features relatively large crystallites and is less dense and smooth in comparison to the amorphous samples. In the XRD pattern, four different phases can be detected: A wurtzite GaN (JCPDS: 002-1078), a Ga (JCPDS: 025-0344), a GaS (JCPDS: 030-0576) and an α-sulfur (JCPDS: 008-0247) phase.

The precursor bis(tris(dimethylamide)gallium $[Ga(NMe_2)_3]_2$ has been synthesized in high purity and characterized in respect to its structure and thermal properties. GaN thin films were obtained using this precursor and characterized in respect to their structure, morphology and composition. GaN thin films were obtained at temperatures, as low as 200 °C, whereas a crystalline thin film only could be obtained at 600 °C. While all thin films were contaminated by relatively large amounts of sulfur, the 400 °C sample shows the most promising composition. The crystallinity of the amorphous films can be presumably enhanced by thermal annealing and has to be proved by further studies. Additionally the depositions have to be repeatedly excecuted in a clean reactor in order to reduce the grade of sulfur contamination.

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