

Growth of GaN Layer from the Single-Source Precursor (Et₂GaNH₂)₃

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In recent years, there has been a great interest in new routes for depositing GaN films in the application of III–V semiconductors. We report herein on the deposition of highly crystalline GaN films by low-pressure MOCVD (in the low-temperature range of 500–700 °C and the pressure range of 77–177 mbar) using the single-source precursor (Et₂GaNH₂)₃. This process was investigated for a variety of substrates (Si(100) and polycrystalline Al₂O₃) using a cold wall chemical vapor deposition reactor. The thickness of films grown under these conditions ranged from 6 to 8 μm, and the growth rates varied from 7 to 8 μm/h. Films deposited at lower temperatures (500–550 °C) had a pale yellowish color and were amorphous. At 600 °C slightly gray colored films were obtained, while above 650 °C high-quality crystalline films were formed, which show diffraction patterns characteristic of the hexagonal wurtzite structure. The films are consistent with the 1:1 stoichiometry of GaN and have carbon and oxygen as impurities; however, cracks were not evident on the surface by SEM examination up to a magnification of 30 000. In contrast, samples of GaN deposited under high-vacuum conditions (up to 10⁻² mbar) have neither a 1:1 stoichiometry nor a smooth surface morphology. Atomic force microscopy, scanning electron microscopy, Auger electron microscopy, and energy-dispersive X-ray analyses were used for the study of the structure, composition, and morphology of the films.

Introduction

The Group 13 nitrides of AlN, GaN, and InN and their alloys have high industrial and scientific interest due to their applications in short-wavelength light-emitting diodes (LEDs), laser diodes (LDs), high-temperature electronics, and ultrahigh-density optical storage systems, respectively.^{1–9} These materials have excellent physical properties such as wide direct energy band gap, strong atomic bonding, and formation of a continuous

range of solid solutions and superlattices.^{10–13} Gallium nitride and related compounds (e.g., AlGaInN and GaInN) are promising materials for the development of optoelectronic devices in the region of blue to ultraviolet light emission, due to a direct energy band gap of 3.45 eV for GaN at room temperature.^{14–16}

Several techniques, such as halide-based vapor phase epitaxy (HVPE),^{17–19} molecular beam epitaxy (MBE),^{20,21} and metalorganic chemical vapor deposition (MOCVD)^{22–27} have been used to grow epitaxial GaN

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films. The deposition of GaN by MOCVD has traditionally been carried out using mixtures of trimethylgallium or triethylgallium and ammonia at very high substrate temperatures (over 1000 °C). These conditions are necessary due to the high thermal stability of ammonia (15% pyrolyzed at 950 °C; <5% pyrolyzed at 700 °C)¹⁸ but leads to the problem of nitrogen effusion from the film, even though the ratio of the ammonia flow rate to the flow rate of the Group 13 source is as high as 2000.^{18,28} Therefore the films typically have a high-background n-type carrier concentration, resulting in uncontrollable p-type doping.²⁹ Furthermore, the choice of substrate material is limited by high substrate temperatures and results in residual strains in the layer.

With the use of a "single-source" precursor having a preformed Ga–N bond, an alternative route to GaN is possible. The main advantages of this new method are significantly lower growth temperatures, the absence of large quantities of toxic ammonia gas, and easy process control.^{30–36}

Herein, we report on GaN film growth using diethylgallium amide as a single-source precursor. In a recent report,^{25,37} the process using the compound (Et₂GaNH₂)₃ needs additional ammonia to decrease the carbon content and to increase the quality of GaN film. The good results from the similar system of (Me₂AlNH₂)₃ reported by Interrante et al.³⁸ are a good evidence of the above argument. With this in mind we have developed a system for GaN deposition that does not need additional ammonia during the pyrolytic decomposition of the precursor. The precursor having an ethyl ligand was selected due to the facile removal of ethylene from the growth zone by β-hydride elimination.

Experimental Section

Synthesis of (Et₂GaNH₂)₃. Ammonia (about 20 mL), which had been previously dried over sodium metal, was condensed on to a solution of 3.12 g (20 mmol) of Et₃Ga in toluene (20 mL) at –78 °C. After the reaction mixture was stirred for 1 h at this temperature, the solution was allowed to warm slowly to room temperature and subsequently it was stirred for another 2 h. The excess ammonia was allowed to evaporate through a valve during this period. The reaction mixture was then refluxed for 1 h, and the solvent was removed under reduced pressure. The product, a colorless

liquid, was distilled in vacuo from the resulting residue. Yield: 2.28 g (15.9 mmol), 80%. Anal. calcd for (Et₂GaNH₂)₃: C, 32.1; H, 8.1; N, 9.4. Found: C, 33.5; H, 8.3; N, 9.7. ¹H NMR (250 MHz, C₆D₆): δ 0.1–0.2 (br NH₂), 0.24 (q, *J* = 8.1 Hz, –CH₂–), 0.32 (q, *J* = 8.1 Hz, –CH₂–), 1.16 (t, *J* = 8.1 Hz, CH₃), 1.25 (t, *J* = 8.1 Hz, CH₃). MS (EI): *m/z* 402 ([M₃ – Et]⁺, 19) (M = Et₂GaNH₂), 259 ([M₂ – Et]⁺, 18), 129 ([Et₂Ga]⁺, 100%). Boiling point: ca. 55 °C at 0.05 mbar.

MOCVD Experiments. For film growth, GaN was deposited on Si(100) and polycrystalline Al₂O₃ (rubalith 710 from Hoechst Ceramtec) substrates, respectively, under two regimes of pressures (up to 10^{–2} mbar and the range of 77–177 mbar) with N₂ as a carrier gas. The Si substrates (dimension 10 × 10 mm²) were degreased with 2-propanol, rinsed with distilled water, and treated with hydrofluoric acid for 1 min. The substrate was rinsed again with distilled water and then treated with dry nitrogen prior to film deposition. The Al₂O₃ substrates were degreased in organic solvents (acetone, 2-propanol) and etched in a solution of H₂SO₄:H₃PO₄ (3:1) using common procedures.

The MOCVD growth experiments were carried out in two types of CVD apparatus as described below.

High-Vacuum CVD (HVCVD) Apparatus. The high-vacuum experiments (up to 10^{–2} mbar) were performed using a cold wall stainless steel globular reactor which is described in detail elsewhere.³⁹ The precursor was loaded into a fritted glass bubbler in a drybox. To increase the saturation of the carrier gas with the precursor, two bubblers were switched in line. Moreover, two glass vessels were connected at both sides of the bubbler, to equalize pressure between the bubblers. After the substrate was loaded in the reactor, the system was evacuated to a pressure of 10^{–7} mbar for 1 h. The system was filled with purified nitrogen gas and was evacuated (to 10^{–7} mbar) for 1 h again. A distance of 20 mm was maintained between the substrate and the precursor dosing line during all the experiments. The substrate was heated by means of a resistively heated furnace, and the temperature was measured by a thermocouple, which was placed directly under the substrate. While the apparatus was evacuated, the substrate was heated to 750 °C for 20 min. The temperature of the substrate and the pressure in the reactor were adjusted before film growth. The bubbler was maintained at room temperature, and the dosing line (from the bubbler into the reactor) was heated to 70 °C to prevent condensation of the precursor. Film growth was conducted using a carrier gas flow rate of 5–10 mL/min at a pressure of 1 × 10^{–2} mbar and a substrate temperature of 500–700 °C for 1 h.

Low-Pressure CVD (LPCVD) Apparatus. Low-pressure CVD experiments in the pressure range of 77–177 mbar were performed using a vertical cold wall reactor of inverted geometry, which prevented the temporal fluctuations of material transport even at a low flow rate using a high source vapor pressure (Figure 1). The system was equipped with a rotary oil pump (capable of a pressure of 1 × 10^{–4} mbar) and a deoxygenation material containing reactive chromium oxide (Oxisorb-w from Messer Griesheim) and a vacuum controller with a magnetic valve (Divatron DT 1 from Leybold), with which the pressure in the reactor can be manipulated in a range of 1–2000 mbar. To prevent diffusion of water molecules from the rotary oil pump toward the CVD apparatus, two traps cooled with liquid nitrogen were placed between the reactor and the pump. The substrate was mounted on the stainless steel substrate-holder with an incline of 45 degrees to the reactor wall and heated resistively. The holder was then placed in the middle of the vertical quartz reaction tube.

Generally, all the "single-source" precursors (nearly all III–V compounds) have very low vapor pressures (≪1 mbar at room temperature), and therefore the III–V films are usually grown under mass transport limited conditions. To ensure sufficient delivery of the precursor to the substrate for a convenient growth rate, the organometallic precursor was

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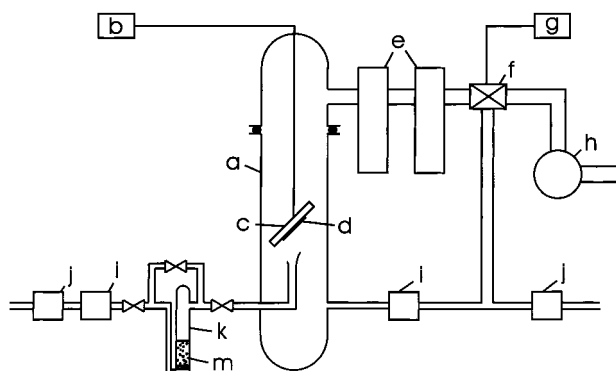


Figure 1. Scheme of the low-pressure vertical cold wall CVD reactor: (a) quartz reactor tube, (b) heating substrate devices, (c) substrate carrier and heating furnace, (d) substrate, (e) cold trap, (f) magnetic valve, (g) pressure measurement and control device, (h) pump system, (i) mass flow controller, (j) gas purifying system, (k) bubbler, (m) precursor.

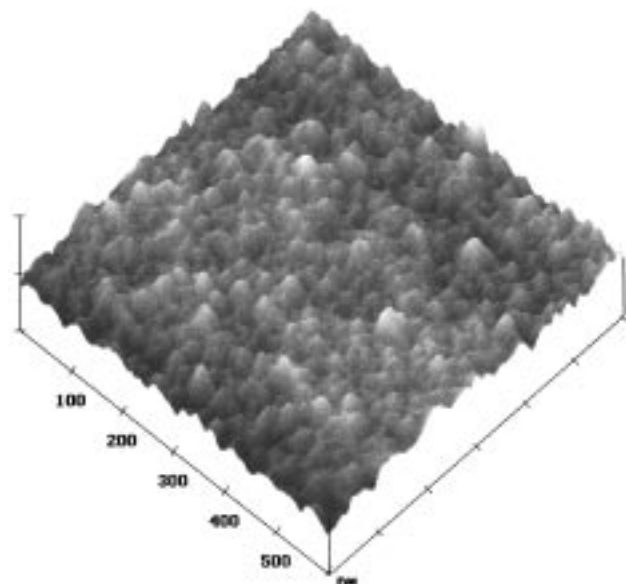


Figure 2. AFM image of the surface of GaN film (from reactor 1) deposited on Si(100) substrate at 500 °C using a pressure of 1×10^{-2} mbar in contact modes X (100 nm/div) and Z (100 nm/div).

introduced through a quartz dosing line (5.0 mm i.d.) with a trumpet-shaped outlet, to focus directly on the substrate. A distance of 10 mm was maintained between the substrate and the precursor dosing line during all the experiments. By connecting the fritted glass bubbler to the bottom of the quartz tube, it was not necessary to heat the dosing line. In the case of low-pressure CVD experiments, depositions were carried out in the reactor at pressures of 77–177 mbar using N_2 as carrier gas at typical flow rates of 70–100 mL/min. The temperature of substrate was kept in the range of 500–700 °C.

Characterization. The structure, composition, and morphology of the films were characterized by several techniques including X-ray power diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), Auger electron microscopy (AES), and energy-dispersive X-ray (EDX) analyses, respectively. **AES Measurements.** Auger electron spectroscopy data were obtained using a Physical Electronics PHI 595 scanning Auger spectrometer at a base pressure of 10^{-9} mbar. The spectrometer was equipped with a cylindrical mirror electron energy analyzer (CMA) having an integral, coaxially mounted electron gun. Auger electron spectra were recorded with an energy resolution of 0.5%. Surface compositions of the deposited GaN films were analyzed using AES.

An AES depth profile was obtained using a 3 keV Ar^+ ion beam (current density $1 \mu A$) over an area of $0.3 \times 0.3 \text{ mm}^2$. The sputtering rate for the GaN films was estimated to be 3 nm min^{-1} . **AFM Analyses.** Atomic force microscopy was performed using a Nanoscope III (Digital Instrument, Santa Barbara, CA). Head types E and J: E, $X 28.1 \text{ nm V}^{-1}$, $Y 31.0 \text{ nm V}^{-1}$, $Z 5.60 \text{ nm V}^{-1}$; J, $X 328 \text{ nm V}^{-1}$, $Y 377 \text{ nm V}^{-1}$, $Z 11.6 \text{ nm V}^{-1}$; 256×256 points; E_{max} , X , 12 364 nm, Y , 13 640 nm, Z , 2462 nm; J_{max} , X , 144 320 nm, Y , 165 880, Z , 5104 nm; asymmetric Si tips with 17° and 25° vertex angles; cantilever with spring constant 23–92 $N \text{ m}^{-1}$; images were taken in constant height mode, plane-fit and low-pass filter. Measurements made on several films were reproducible. Cross-sections were obtained for each sample in the depth-profile analysis. Measurements were made from the base of each peak to its maximum height. **XRD Analyses.** X-ray power diffraction studies were performed using a D 500 diffractometer from Siemens equipped with the thin film package and a graphite monochromator. Monochromated Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) was used. The instrumental resolution in the θ - 2θ mode is approximately 0.02° in 2θ , and the samples were analyzed by a conventional θ - 2θ scan (JCPDS-ICDD Card No. 2-1078 and 5-0601).

Results and Discussion

Two different CVD reactors were used in the present study: (1) a reactor, in which the gas-phase precursor was deposited on the substrate at very low pressure (up to 10^{-2} mbar) to increase the diffusion at the surface of the substrate, (2) a cold wall quartz glass tube reactor which allowed convenient control of pressure in the range of 1–2000 mbar. Due to the presence of native oxide on Si(100) and the use of polycrystalline Al_2O_3 substrates, an epitaxial film growth was not expected. After the experiment, the materials were analyzed by a variety of techniques, including XRD, AFM, SEM, EDX, and AES.

The deposited GaN film from the $(Et_2GaNH_2)_3$ precursor in the temperature range of 500–700 °C using reactor 1 showed a variation in morphology depending on the substrate temperatures. At temperatures less than 550 °C the films were amorphous, yellowish-colored, and stoichiometric in composition in agreement with previously reported results.^{32,40–41} The composition of the film deposited at 500 °C and 1×10^{-2} mbar was established by energy-dispersive X-ray analyses. The bulk composition of the film was 47% Ga, 45% N, and 8% contamination (including 5.6% O, 1.43% C, and other impurities). However, it was not possible to analyze the composition by Auger electron spectroscopy due to preferential sputtering of nitrogen.³⁰ Figure 2 shows an AFM image of GaN film deposited on Si(100) under the same conditions and taken in contact mode (a surface of $0.6 \times 0.6 \mu\text{m}^2$ was scanned). The image reveals very small pyramidal type features, terminated with peaks. The pyramids shown in Figure 2 have bases with diagonals ranging from 10 to 30 nm and elevations ranging from 10 to more than 50 nm. Increasing the deposition temperature from 600 to 700 °C caused the layer to develop a darker appearance, and small glitter droplets were scattered in all directions on the resulting film. The diameter of these droplets was up to 50 μm as shown in Figure 6a. It can be seen from

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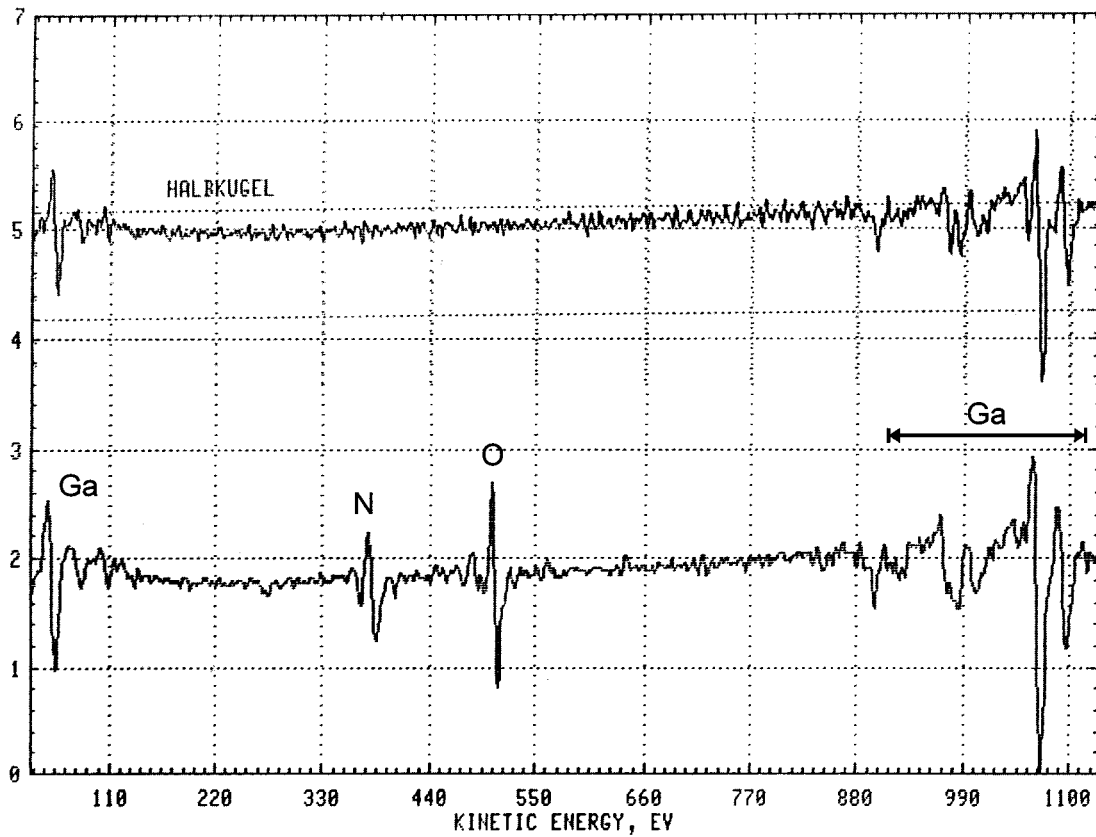


Figure 3. (a, top) Auger electron spectra of Ga droplet on GaN film (from reactor 1) deposited on Si(100) substrate at 700 °C using a pressure of 1×10^{-2} mbar. (b, bottom) First derivative Auger electron survey spectra showing the principal Auger transition peaks of the GaN film (from reactor 2) deposited on polycrystalline Al_2O_3 at 650 °C using a pressure of 177 mbar.

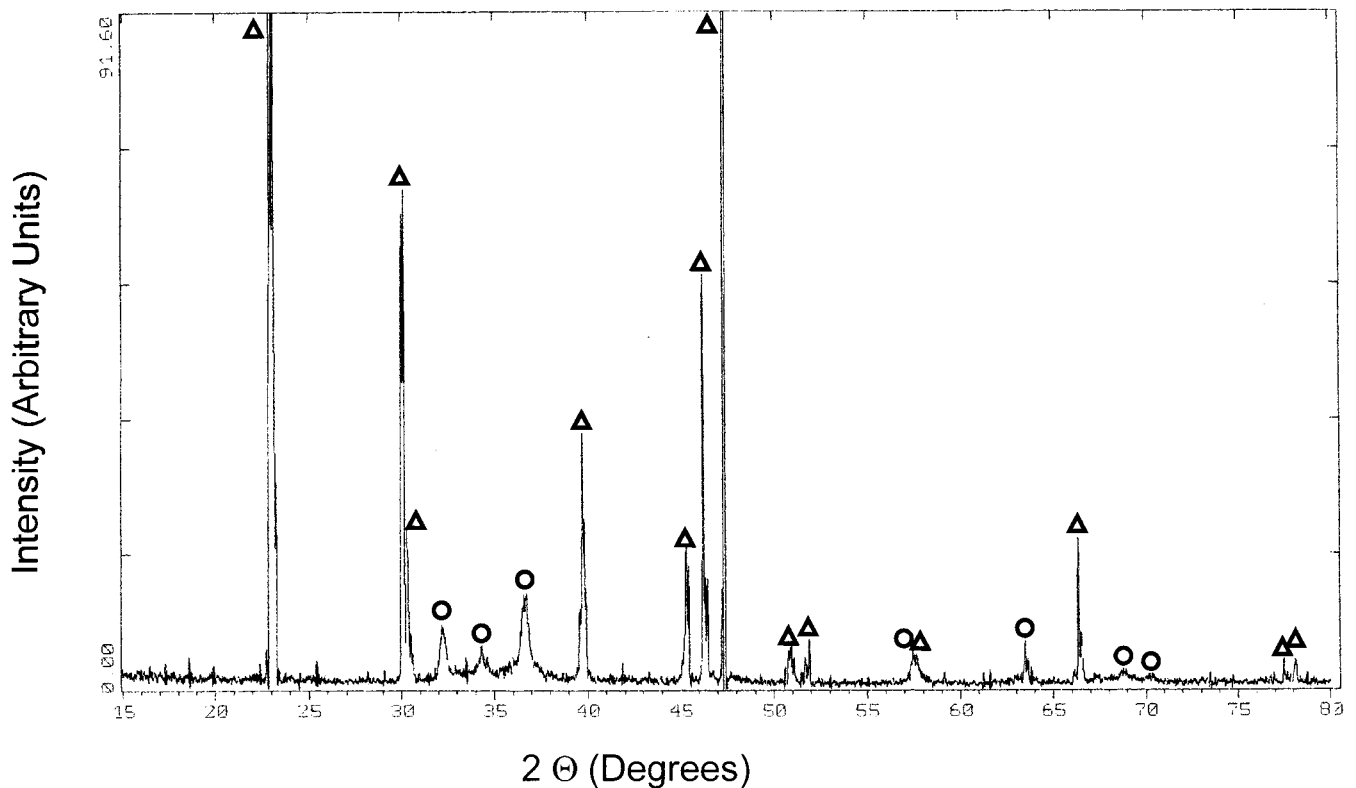


Figure 4. X-ray diffraction pattern of GaN film grown on a Si(100) substrate at 650 °C using a pressure of 10^{-2} mbar. The peaks from the wurtzitic polycrystalline GaN film are indicated with ○ and the peaks from the metallic Ga are indicated with Δ.

the Auger electron spectroscopy analyses (Figure 3) that the small glitter droplets consist of metallic gallium. The

XRD analyses performed on the GaN film grown on Si(100) at 650 °C and at a pressure of 1×10^{-2} mbar

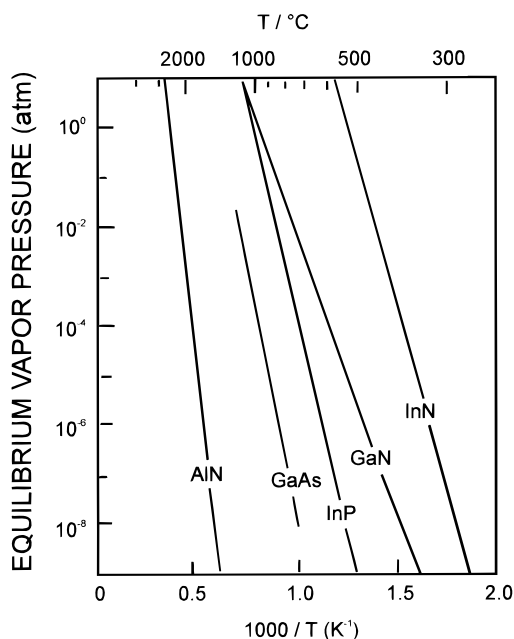


Figure 5. Equilibrium vapor pressure of Group 13 nitrides.⁴⁴

confirmed the presence of metallic gallium, as well as revealing the presence of very small peaks of wurtzitic polycrystalline GaN (Figure 4).^{42,43} One of the reasons for the growth of Ga droplets and nonstoichiometric nitride might be the loss of NH_3 at these growth conditions. Gladfelter et al.⁴⁴ reported the syntheses of N-deficient nitride material caused by the loss of NH_3 using $(\text{H}_2\text{GaNH}_2)_3$. The study of the decomposition of $(\text{Et}_2\text{GaNH}_2)_3$ in the range of 60–600 °C by EI-MS confirmed the absence of NH_3 . Another reason for the growth of Ga droplets might be the lower Gibbs free energy of the constituents compared to the free energy for GaN at the growing temperature which favors the decomposition into gallium and nitrogen.⁴⁵ The N_2 equilibrium pressure above GaN is shown in Figure 5.⁴⁶ To confirm the above-mentioned observations, several experiments were carried out in conditions likely to yield the Ga droplets according to the diagram in Figure 5. The films were deposited on Si(100) at a temperature of 700 °C and at the pressure 1×10^{-2} mbar. The morphologies of the resulting films were examined using a SEM. Figure 6a shows a film with very well developed Ga droplets with diameters up to 50 μm . When the Ga droplet has reached a certain size the adhesion between the drop and the substrate and between the drop and the GaN film respectively is not sufficient to prevent it from leaving the film. Because of the inverted reactor geometry, the drop follows the law of gravity and falls off the film (Figure 6b). In Figure 6c the craters can be seen in the very flat and smooth Si substrate. The EDX analyses show that the bulk composition of the film deposited at 650 °C has a composition of 52% Ga, 41% N, and 7% contamination (including oxygen and carbon).

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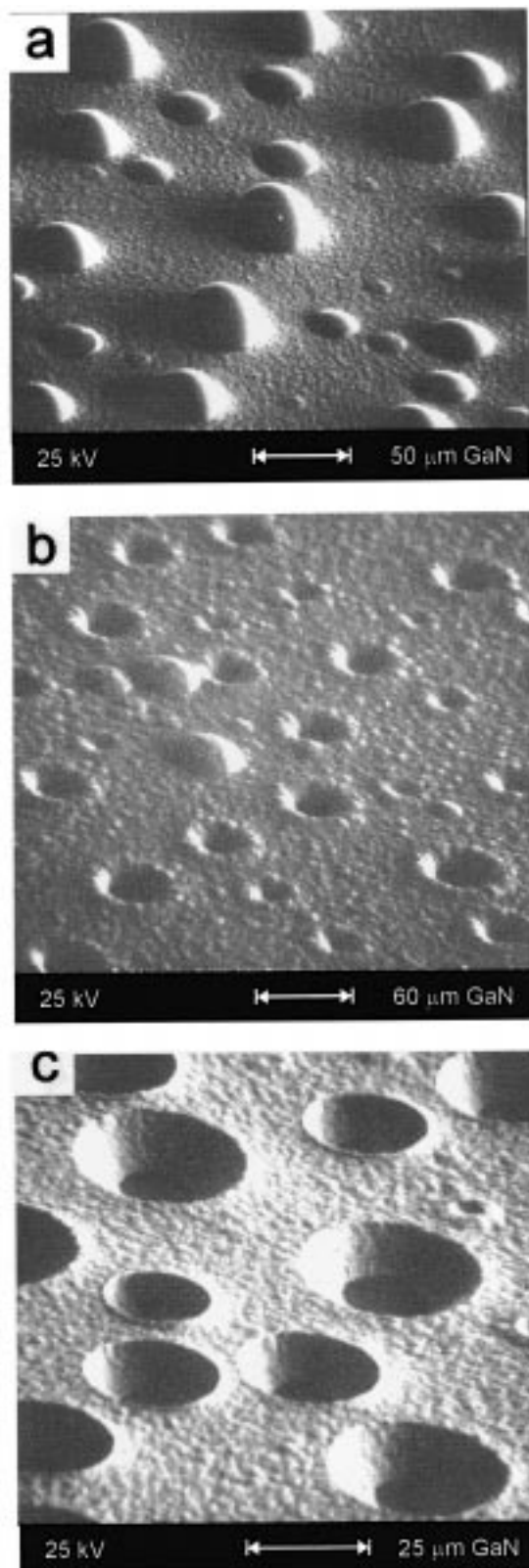


Figure 6. (a, top) SEM photograph of Ga droplets on GaN film (from reactor 1) deposited on Si(100) substrate at 700 °C using a pressure of 1×10^{-2} mbar. (b, middle) SEM photograph of Ga droplet and the crater in the film deposited on Si(100) substrate at the same parameter like a. (c, bottom) SEM photograph of crater: the trace of the Ga droplet on the film deposited on Si(100) substrate at the same parameter like a.

The $[\text{Ga}]/[\text{N}]$ atom ratio increases slightly to 1.3 when the deposition temperature is increased to 700 °C. Due to the poor morphology and the incorrect composition

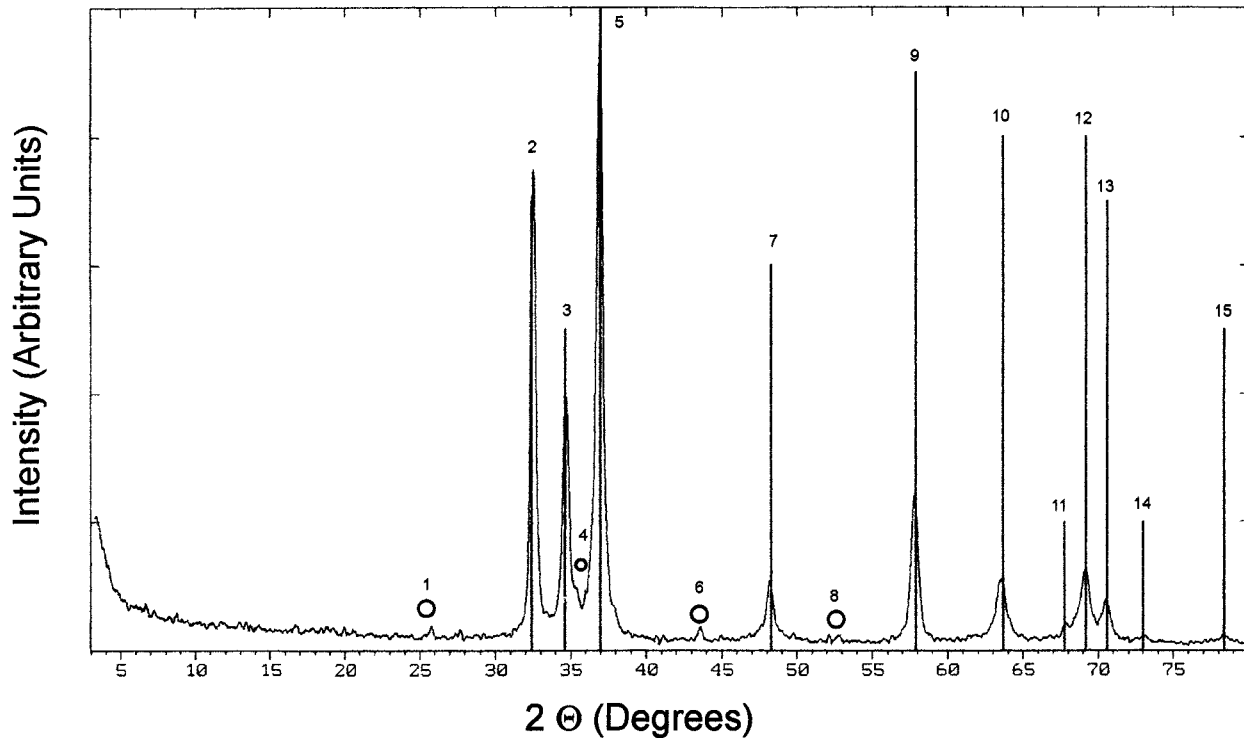


Figure 7. X-ray diffraction pattern of GaN film (from reactor 2) grown on a polycrystalline Al_2O_3 substrate at 650°C using a pressure of 177 mbar. The peaks from the substrate are indicated with \circ . The diffraction peaks seen are (1) 25.6° , (0112) Al_2O_3 ; (2) 32.4° , (1010) GaN; (3) 34.6° , (0002) GaN; (4) 35.1° , (1014) Al_2O_3 ; (5) 36.9° , (1011) GaN; (6) 43.4° , (1123) Al_2O_3 ; (7) 48.3° , (1012) GaN; (8) 52.6° , (0224) Al_2O_3 ; (9) 57.9° , (1120) GaN; (10) 63.6° , (1013) GaN; (11) 67.8° , (2020) GaN; (12) 69.1° , (1122) GaN; (13) 70.6° , (2021) GaN; (14) 73.0° , (0004) GaN; (15) 78.3° , (2022) GaN.

of the film grown at a very low pressure, no further experiments were conducted.

The study of GaN film growth from $(\text{Et}_2\text{GaNH}_2)_3$ precursor in a temperature range from 500 to 700°C using reactor 2 at higher pressures than in reactor 1 shows the potential of this precursor to yield high-quality GaN. The variety of colored films formed at different temperatures is comparable to the results found with reactor 1. Interestingly the film deposited at 700°C was even darker compared to the film from reactor 1 at the same temperature. Generally, the films were uniform, but slightly rougher than those films grown in reactor 1. As expected, the films deposited at 550°C were poorly crystalline. Films deposited above 600°C consist of crystalline hexagonal GaN. Figure 7 shows the X-ray spectrum of a $4.25\ \mu\text{m}$ thick GaN film deposited on polycrystalline Al_2O_3 at 650°C and 177 ± 3 mbar; sharp peaks for wurtzitic polycrystalline GaN are apparent.⁴² The lattice constant of $5.188 \pm 0.003\ \text{\AA}$ obtained for this sample is in good agreement with previously reported data.^{47–49} Figure 3b shows the principal Auger transition peaks for the same GaN film before the sputtering, which was characterized using XRD. Gallium, nitrogen, and oxygen were observed.

Table 1 summarizes the EDX analyses of the GaN films deposited in the temperature range of 500 – 700°C . The $[\text{Ga}]/[\text{N}]$ atom ratio increased slightly (1.01 to

Table 1. Energy Dispersive X-ray Analyses of GaN Films Deposited from $(\text{Et}_2\text{GaNH}_2)_3$ (low-pressure reactor 2)

growth pressure (mbar)	growth temp ($^\circ\text{C}$)	film composition (atom %)			
		Ga	N	C	O
77	500	46.2	45.7	1.6	6.5
77	550	46.1	45.9	1.9	6.2
77	600	47.0	44.9	1.7	6.3
177	650	46.8	45.0	1.9	6.1
177	700	46.3	45.8	2.0	5.9

1.04) as the temperature increased. Interestingly, the carbon content did not increase with growth temperature and the relatively low carbon content of 2% might be related to facile evolution of ethylene via β -hydride elimination. Generally, a large amount of oxygen in the film was detected in the EDX analyses. Auger electron spectroscopy was used in an effort to discover the source of oxygen in the film. The oxygen content at the surface was as much as 17%, but after sputtering more than $200\ \text{\AA}$, this figure decreased to a constant level of 3%. This indicated that the oxygen content is caused by exposure to air during the transport to the AES instrument. However, to account for the residual 3%, it was clear that there had to be another oxygen source during the process of film deposition. Two possible sources of oxygen are (i) imperfect reactor conditions (leaking) and (ii) the precursor was not ultrapurified. A deposition with very low growth rate ($20\ \text{\AA}/\text{min}$) was carried out at 650°C and 177 mbar using reactor 2 without a trap between the reactor and the rotary oil pump. The oxygen level in the $10.7\ \mu\text{m}$ thick film reached the value of 28 atomic percent. In light of a previous report,³⁰ the high residual water partial pressure in the apparatus ($\sim 10^{-8}$ Torr) could have led to the high oxygen content.

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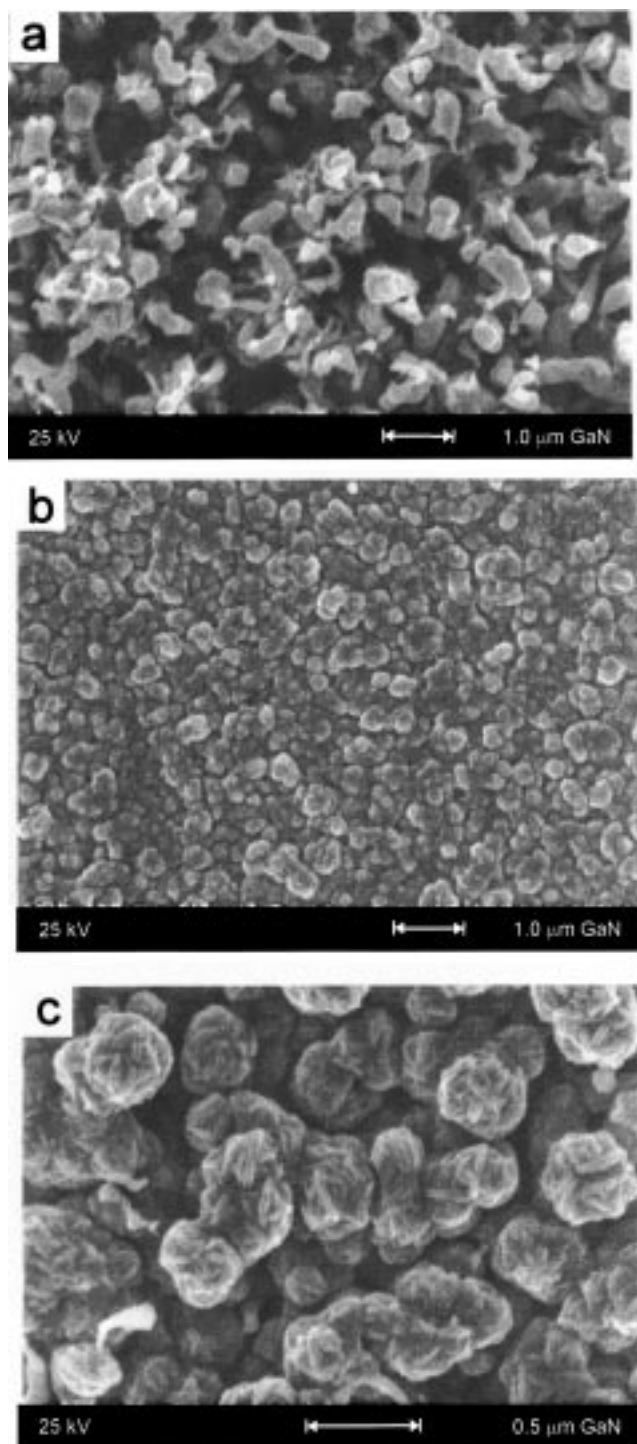


Figure 8. (a, top) SEM photograph of GaN film (from reactor 2) grown on a polycrystalline Al_2O_3 substrate at 550 °C and 77 mbar. (b, middle) SEM photograph of GaN grown on a polycrystalline Al_2O_3 substrate at 650 °C and 177 mbar. (c, bottom) SEM photograph of GaN film grown on a polycrystalline Al_2O_3 substrate at 700 °C and 177 mbar.

The morphologies of the films were examined with SEM. Figure 8a shows a film deposited on polycrystalline Al_2O_3 at 550 °C and 77 mbar. The film has a

very poor morphology and a very small degree of crystallinity, an observation which was confirmed by XRD. In contrast, the film grown at 650 °C and 177 mbar exhibited improved morphology accompanied by nanoparticle formation in the size range 50–150 nm (Figure 8b). Figure 8c shows the SEM of the same film with magnifications up to 30 000. The image of the film deposited at 700 °C and 177 mbar revealed the presence of agglomerated particles in the layer; the particles ranged in size up to several hundred nanometers. The good quality of crystallinity was confirmed by the XRD studies.

In contrast to the previous report³² that the film growth rate using $(\text{Me}_2\text{GaN}_3)_n$ (vapor pressure of 0.05 Torr at 55 °C) increased 5-fold when the temperature was raised from 450 to 600 °C, the GaN growth rate using $(\text{Et}_2\text{GaNH}_2)_3$ is relatively temperature insensitive. In our studies, even at relatively low temperature (500 °C) the film growth rate is very high (6.7 $\mu\text{m}/\text{h}$) and this rate increased only slightly as the temperature was raised to 650 °C (7.2 $\mu\text{m}/\text{h}$). The deposition rate remained constant in the temperature range 650 to 700 °C. These observations can be explained on the basis of the mass-transport system which ensures the delivery of sufficient precursor to the substrate (see Experimental Section) and by facile β -hydride elimination of ethylene which takes place even at low temperatures. This suggests that during the deposition of GaN films from $(\text{Et}_2\text{GaNH}_2)_3$ no dominant mechanisms play an obvious role in determining the deposition rate. Obviously this system is not affected by the diffusion of precursor species through the boundary layer above the substrate throughout the temperature range studied. However, the rate of deposition is controlled by the decomposition kinetics of the precursor.

Conclusion

GaN films were grown from $(\text{Et}_2\text{GaNH}_2)_3$ using a cold wall MOCVD apparatus in the absence of ammonia at low temperatures and reduced pressure. The films deposited above 600 °C have a good quality of crystallinity without cracks but not a very smooth surface morphology. Presently we are improving and extending our methodology of the CVD process to the epitaxial growth of GaN film on single crystalline Al_2O_3 and other group 13 nitrides (e.g., AlN and InN).

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