Journal of Electronic Materials, Vol. 14, No. 5, 1985

MOCVD EPITAXIAL GROWTH OF SINGLE CRYSTAL GaN, AlN AND $Al_xGa_{1-x}N$

M. Matloubian* and M. Gershenzon

Departments of Electrical Engineering and Materials Science
University of Southern California
Los Angeles, CA 90089

(Received January 16, 1985: revised June 10, 1985)

Ga begins to deposit from a stream of trimethylgallium (TMG) in H_2 at a minimum temperature of 475°C. Addition of sufficient amounts of NH_3 results in the growth of textured polycrystalline GaN on basal plane sapphire substrates above 500°C. A minimum temperature of 800°C is required for the epitaxial growth of GaN on the substrate. Under similar conditions, but with the TMG replaced with trimethylaluminum (TMA), polycrystalline AlN begins forming at 400°C (in the absence of NH_3, the TMA starts pyrolyzing at 300°C), but single crystal growth of AlN requires a temperature of at least 1200°C. Epitaxial single crystal layers of $Al_xGa_{1-x}N$ can be grown in the temperature range 800-1200°C, the minimum temperature being approximately proportional to x, but preferential deposition of AlN on the hot walls of the reactor (>400°C) precludes precise control of the alloy composition. This predeposition of AlN can be retarded by keeping the walls below 400°C by using a water-cooled jacket, by rapid flow-rates, or by injecting the TMA through a nozzle close to the surface of the substrate.

Key Words: Metalorganic chemical vapor deposition, epitataxy, AlGaN.

*Present address: Texas Instruments,Inc., Dallas, Texas

0361-5235/85/1401-0633 $3.00 © 1985 AIME

MOCVD of AlGaN

Introduction

GaN and AlN are direct gap semiconductors with room temperature bandgaps of 3.45 and 6.2 eV, respectively, and there is no miscibility gap in the solid solution system $Al_xGa_{1-x}N$ [1]. Thus the $Al_xGa_{1-x}N$ system may be well suited as the materials basis for an electrooptic device technology spanning the complete ultraviolet range.

The congruent melting temperatures and the corresponding equilibrium N_2 pressures are extremely high for both GaN (T>2300°C, P>40,000 atm [2]) and AlN (T>3100°C, P>100 atm [3]). In the Ga-N system, a N_2 solubility of 2% in Ga requires a temperature of 1500°C at a N_2 pressure of 16,000 atm for 3-phase equilibrium [2]. Hence, melt growth as well as normal liquid phase epitaxy can be ruled out. At the highest temperatures at which NH_3, a more reactive source of N, is kinetically stable with respect to decomposition into N_2 and H_2, 1150°C, the solubility of GaN in Ga is only 0.003% [4], again too small for conventional liquid phase epitaxy. Thus, the $Al_xGa_{1-x}N$ alloys are most easily prepared from the vapor phase.

Baranov et al. [5] used halide transport vapor phase epitaxy (VPE) to grow $Al_xGa_{1-x}N$, for $0<x<0.45$, and Hagen et al. [1] used a variation of the same technique to demonstrate the existance of an alloy system for all values of x. Yoshida et al. [6] synthesized $Al_xGa_{1-x}N$ by reactive molecular beam epitaxy (RMBE), and Khan et al. [7] used low pressure metalorganic chemical vapor deposition (LP MOCVD) to grow this material.

In this report, we describe the conditions necessary to grow single crystal layers of $Al_xGa_{1-x}N$ epitaxially on basal plane sapphire substrates by atmospheric pressure MOCVD over the entire range of x, starting with trimethylgallium (TMG), trimethylaluminum (TMA), NH_3 and H_2.

Experimental

Basal plane sapphire substrates were degreased by standard organic cleaners and etched in hot $H_3PO_4:H_2SO_4$, 1:1 solution, for 15 minutes. The substrate was then loaded on a silicon carbide coated graphite susceptor, centered in a vertical quartz reactor with a 4.5 cm inside diameter

(Fig. 1). RF induction was used to heat the susceptor and the temperature was monitored by a Pt/Pt-10% Rh thermocouple and correlated with the readings from an optical pyrometer. Prior to film growth, the substrate was heated in hydrogen to 1200°C for 15 min to remove any trace of contaminants and produce a surface suitable for epitaxy. The substrate was then cooled to the growth temperature, and a 2 slm flow of ammonia was started and maintained until the end of the growth. TMG and TMA were carried to the reactor by bubbling 0-10 sccm of hydrogen through TMG held at 0°C, and 0-100 sccm of hydrogen through TMA held at 20°C respectively. The metalorganic flow was further diluted by the addition of 1 slm hydrogen before entering the reactor. Additional hydrogen was added to the ammonia line, when necessary, to increase the total flow rate.

The crystallinity of the grown layers was determined by x-ray Bragg diffraction using CuK_α radiation, and reflection electron diffraction (RED) with a 150 keV accelerating voltage. The Al and Ga fractions in the $Al_xGa_{1-x}N$ films

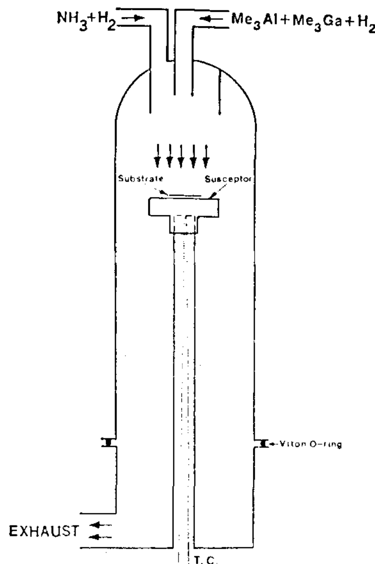


Fig. 1. Schematic diagram of the MOCVD vertical quartz reactor.

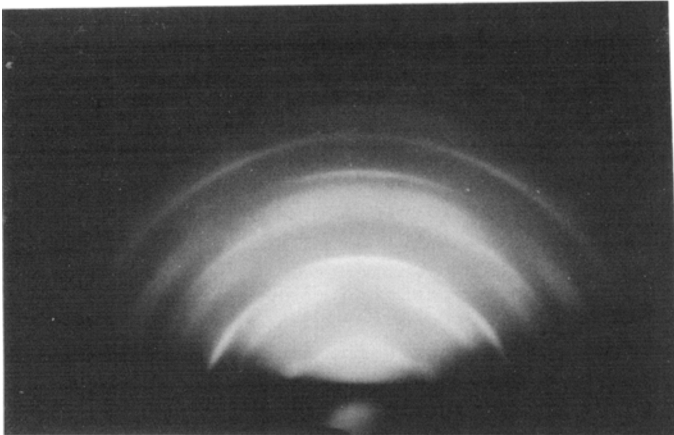
were obtained by x-ray energy dispersive spectroscopy (EDS). Electron probe microanalyzer (EPMA), with a detectivity of 0.01 at.%, was used to detect the impurities in the films. The thickness of the layers was determined by masking part of the substrate with a small piece of sapphire during deposition, and measuring the growth step using a surface profilometer. Some electrical properties of the films were measured by the Van der Pauw Hall effect technique.

Results

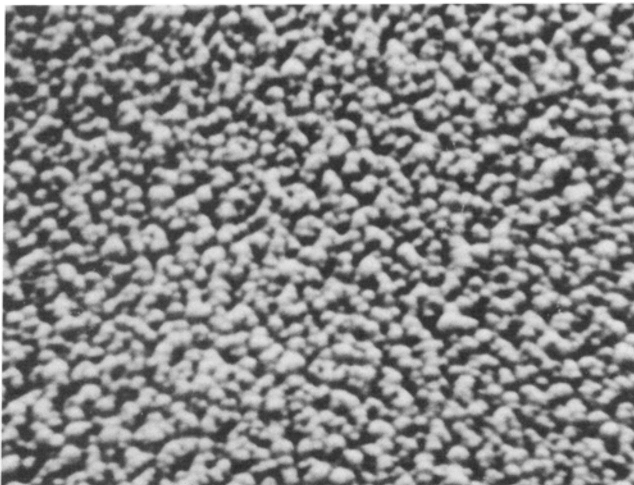
In the absence of ammonia, but with additional H_2 replacing the normal NH_3 flow, metallic Ga is deposited from a stream of TMG in hydrogen at a minimum temperature of 475°C. By addition of sufficient ammonia (see above), polycrystalline, but textured, GaN begins depositing at a minimum temperature of 500°C on basal plane sapphire with the c-axis of the GaN film normal to the substrate surface. (Only Bragg reflections due to (0001) planes of GaN separated by a distance of 5.189 Å were observed.) Reflection electron diffraction (RED) spectra of these films show discontinuous arcs which are indicative of a textured structure (Fig. 2a). The GaN films grown at 500°C are very planar (Fig. 2b). Single crystal GaN films were obtained at substrate temperatures between 800 and 1000°C. At 1100°C the high decomposition and reevaporation rate of GaN resulted in voids in the grown layer. The films grown at 500°C appear yellow in transmitted white light because of a large impurity concentration of oxygen. The oxygen concentration in the GaN films was found to vary from about 10 at.% at 500°C to 0.05 at.% at 800°C, to below EPMA detectivity (<0.01 at.%) at 900°C.

From a similar set of experiments, TMA in hydrogen was found to begin pyrolyzing at 300°C, consistent with a previously reported value [8]. The addition of ammonia retards the TMA decomposition, and textured polycrystalline AlN starts to deposit at 400°C. However, a minimum substrate temperature of 1200°C is necessary to obtain single crystal AlN on sapphire [9,10].

Single crystal $Al_xGa_{1-x}N$ layers can be grown on sapphire between 800-1200°C with the minimum temperature for epitaxy approximately proportional to x. However, at such high temperatures, the reactor walls become heated to



(a)



(b)

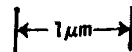


Fig. 2. (a) Reflection electron diffraction from a GaN film grown at 500°C, (b) secondary electron micrograph of a GaN film grown at 500°C.

temperatures above 400°C and AlN preferentially deposits on the walls. (No gas phase decomposition is observed.) This depletes the gas stream of TMA, and precludes control of the alloy composition. This can be seen in Fig. 3, where the Al fraction in the grown film is shown to decrease as the substrate temperature is increased. With equal molar flow rates of TMG and TMA entering the reactor, at 400°C, only polycrystalline AlN deposits; from 500-800°C polycrystalline $Al_xGa_{1-x}N$ with varying compositions are grown, and at 900°C, where single crystal layers are obtained, almost no Al is incorporated into the lattice.

The AlN predeposition can be avoided either by preventing the TMA from striking the hot walls, or by cooling the reactor walls below 400°C. The first method can be achieved by ejecting the metalorganics through a nozzle, very close to the substrate, or by using higher flow rates. (Operating at reduced pressures [7] should have a similar effect.)

Various amounts of hydrogen were added to the gas stream to increase the total flow rate in our reactor from 3 slm to 7.5 slm, resulting in an increase in the average gas

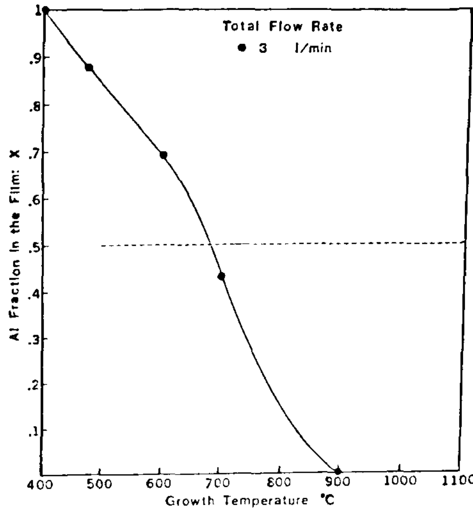


Fig. 3. AlN mole fraction in the $Al_xGa_{1-x}N$ films grown at different temperatures with equal molar fluxes of TMA and TMG entering the reactor.

velocity from 6 cm/sec to 15 cm/sec. The effect of the increased flow rates on the alloy composition is shown in Fig. 4. At each temperature, increasing the total flow rate resulted in an increase of the Al concentration in the film. For equal fluxes of TMA and TMG entering the reactor, with a total flow rate of 7.5 slm, single crystal $Al_xGa_{1-x}N$ layers were grown at 1100°C with x=0.1. By increasing the TMA to TMG flux ratio, $Al_xGa_{1-x}N$ films with larger x values were grown.

Addition of a nozzle (1 cm^2 in diameter) to introduce the TMA and TMG about 2 cm from the substrate (Fig. 5), with a total flow rate of 5 slm, resulted in single crystal $Al_xGa_{1-x}N$ films with x=0.15 at 1000°C. Use of a narrow nozzle, or one closer to the substrate, results in higher x values in the film, but this leads to excessive nonuniformity of the grown layers. (Substrate rotation was not used here.) Metalorganic nozzles have been used before in the MOCVD growth of pure AlN [9,10].

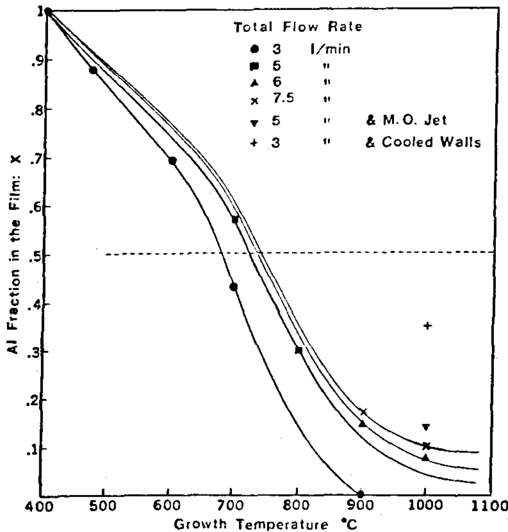


Fig. 4. AlN mole fraction in the $Al_xGa_{1-x}N$ films grown at different temperatures and total flow rates but with equal molar fluxes of TMA and TMG entering the reactor.

MOCVD of AlGaN

Another modification that was made to prevent AlN predeposition was to install a water-jacket surrounding the reactor so that the TMA entering the reactor would not contact any surface above 400°C before reaching the substrate (Fig. 5). Using the water-jacket, and with equal fluxes of TMA and TMG entering the reactor at the relatively low total flow rate of 3 slm, $Al_xGa_{1-x}N$ films with x=0.35 were obtained at 1000°C. By varying the ratio of the TMA and TMG fluxes, and adjusting the substrate temperature accordingly, single crystal $Al_xGa_{1-x}N$ films were grown on sapphire over the entire range of x (Fig. 6). Typical growth rates were 1-2 um/hr.

The $Al_xGa_{1-x}N$ layers were smooth and transparent. The films were examined by optical and electron microscopes. Only growth steps could be seen on the good layers (Fig. 7a), but near the edges of the substrate, and on films deposited at higher growth rates, hexagonal pyramids, bounded by $(10\bar{1}2)$ planes were observed (Fig. 7b).

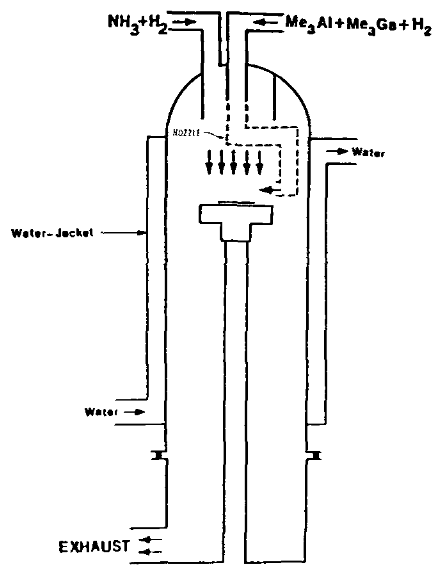


Fig. 5. Schematic diagram of the MOCVD reactor with the installed water jacket.

MOCVD of AlGaN

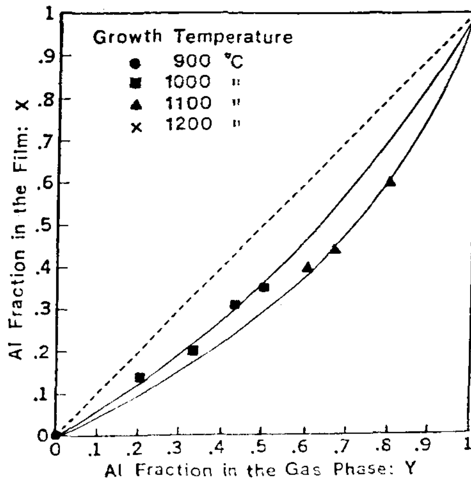


Fig. 6. AlN mole fraction in the $Al_xGa_{1-x}N$ films, grown in the water-cooled reactor, as a function of TMA mole fraction in the gas phase.

Sharp diffraction spots along with diffuse Kikuchi lines, indicative of high crystalline quality, were observed in the RED spectra of the films (Fig. 8). X-ray Bragg diffraction was used to find the lattice constant of the $Al_xGa_{1-x}N$ films. Resolution of the CuK_α doublet was noted in the x-ray Bragg diffraction of most layers (Fig. 9). This translates into less than 0.1% nonuniformity in the lattice constant of the film.

All the $Al_xGa_{1-x}N$ films were n-type. The carrier concentrations in the GaN films were in the mid-10^{19} cm^{-3} range with a mobility of 75 cm^2/V-sec. The resistivity of the $Al_xGa_{1-x}N$ films increased with x, becoming semi-insulating for x>0.4.

Conclusions

The preferential predeposition of AlN on the hot walls (>400°C) of the conventional MOCVD reactor could be reduced by using rapid flow rates, or more effectively, by water-cooling the reactor walls. Single crystal layers of

MOCVD of AlGaN

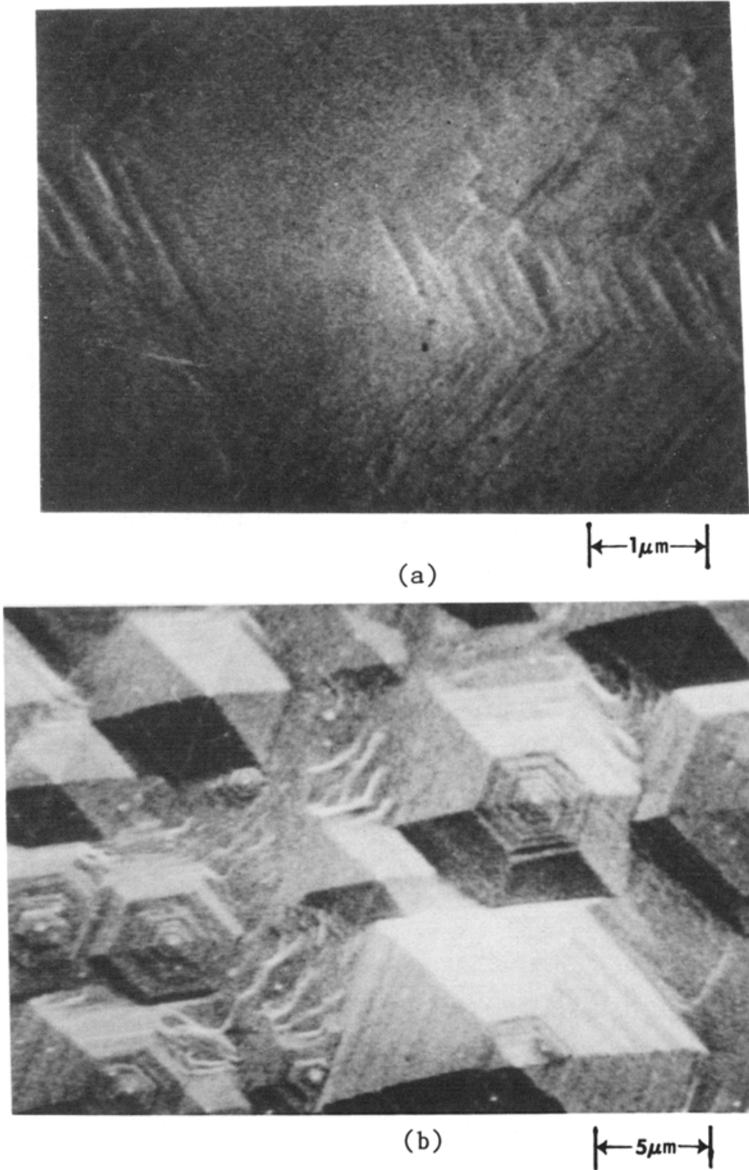


Fig. 7. Secondary electron micrograph of $Al_xGa_{1-x}N$ film showing (a) smooth surface structure, (b) hexagonal pyramid structure.

MOCVD of AlGaN

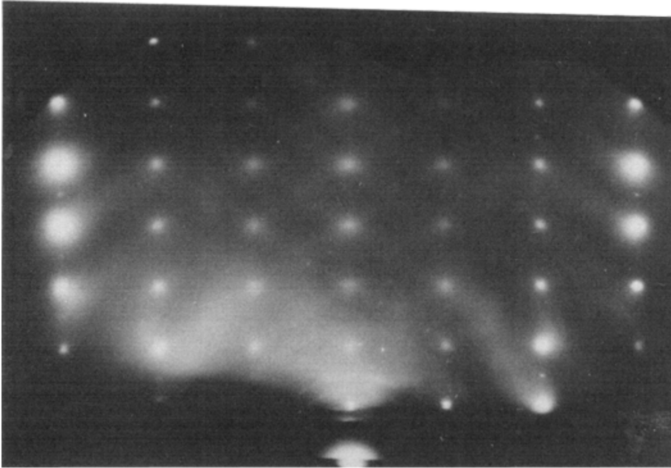


Fig. 8. Reflection electron diffraction spectra from a single crystal film.

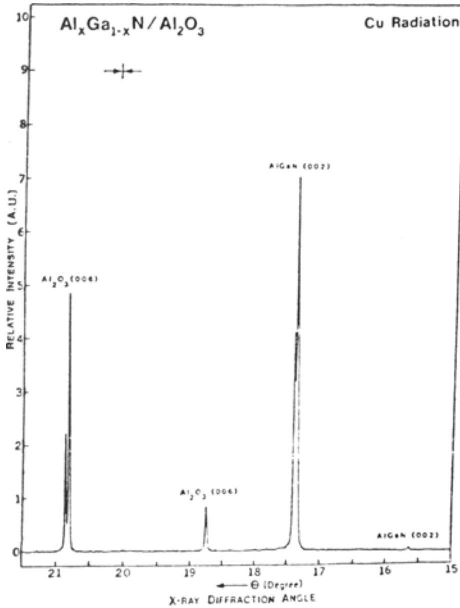


Fig. 9. X-ray diffraction spectra from a single crystal $Al_xGa_{1-x}N$ film with x=0.1 from EDS measurment.

$Al_xGa_{1-x}N$ could then be grown on basal plane sapphire, with controlled values of x from 0 to 1, in the temperature range of 800-1200°C, with the minimum temperature being approximately proportional to x.

Acknowledgements

We are grateful to Honeywell, Inc., for supporting this work, to Dr. Moshe Shiloh of the Sorey Nuclear Laboratory, Israel, whose original experiments here indicated the importance of determining the minimum deposition temperatures, and to Bu-Chin Chung and Kevin Sayyah for many helpful discussions.

References

1. J. Hagen, R. D. Metcalfe, D. Wickenden and W. Clark, J. Phys. C 11, L143 (1978).

2. J. Karpinski, J. Jun and S. Porowski, J. Cryst. Growth 66, 1 (1984).

3. G. A. Slack and T. F. McNelly, J. Cryst. Growth 36, 263 (1976).

4. R. A. Logan and C. D. Thurmond, J. Electrochem. Soc. 119, 1727 (1972).

5. B. Baranov, L. Daweritz, V. B. Gutan, G. Jungk, H. Neumann and H. Raidt, Phys. Stat. Sol. (a) 49, 629 (1978).

6. S. Yoshida, S. Misawa and S. Gonda, J. Appl. Phys. 53, 6844 (1982).

7. M. A. Khan, R. A. Skogman, R. G. Shulze and M. Gershenzon, Appl. Phys. Lett. 43, 492 (1983).

8. L. M. Yeddanapalli and C. C. Shubert, J. Chem. Phys. 14, 1 (1946).

9. J. K. Liu, K. M. Lakin and K. L. Wang, J. Appl. Phys. 46, 3703 (1975).

10. M. Morita, N. Uesugi, S. Isogai, K. Tsubouchi and N. Mikoshiba, Japan. J. Appl. Phys. 20, 17 (1981).