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Chemical Vapor Deposition of Gallium Nitride from Diethylgallium Azide

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Pyrolysis of diethylgallium azide in a conventional hot-wall chemical vapor deposition reactor at 350 °C followed by in situ annealing at 600 °C results in gallium nitride films. Film purity has been determined by electron microprobe, Auger electron spectroscopy, and Rutherford backscattering spectroscopy. The films are stoichiometric GaN, with carbon and oxygen content below 2%. Film structure has been examined by X-ray diffraction and by scanning and transmission electron microscopy. The films are polycrystalline and show diffraction patterns characteristic of the expected hexagonal wurtzite structure. Mass spectroscopic analysis of the product gases suggests the films are formed by successive β-hydride eliminations of ethylene from the ethyl groups and loss of nitrogen from the azide. The effect of annealing, as studied by infrared spectroscopy, is the loss of hydrogen from the film with a concomitant increase in gallium–nitrogen bonding.

Introduction

Gallium nitride is a wide-gap semiconductor ($E_g = 3.39$ eV) with several potential uses in optoelectronics.[1] Unfortunately, practical methods for the chemical vapor deposition (CVD) of this material are not available. Gallium nitride has previously been deposited by the reaction of gallium metal, hydrogen chloride, and ammonia,[2] the reaction of gallium tribromide or trichloride with ammonia,[3,4] the reaction of triethylgallium chloride and ammonia,[5,6] and the pyrolysis of the ammonia or trimethylamine adducts of trimethylgallium.[7] All of these previously reported syntheses suffer from major drawbacks, including corrosive hydrogen halide byproducts, relatively high (>600 °C) temperatures, and/or poor film purity.

Evans, Gladfelter, and co-workers[8,9] have recently reported the low-pressure CVD of aluminum nitride using diethylaluminum azide at temperatures between 450 and 500 °C. The molecule decomposes to give AlN, nitrogen, hydrogen, ethylene, and ethane as the products. Although the films contain some carbon and oxygen, the low deposition temperature, the preformed III–V bond in the precursor, the absence of a strong N–H bond, and the possibility of removing carbon via β-hydride elimination make this route to group III nitrides very attractive. Therefore, we wish to report the deposition of gallium nitride of excellent purity from diethylgallium azide using a low-temperature (350 °C) deposition step, following by a higher temperature (600 °C) annealing step.

Experimental Section

Diethylgallium azide has previously been prepared by the reaction of triethylgallium and chloroazide.[10] It may be more conveniently prepared by a procedure similar to the one used by Prince and Weiss[11] to synthesize diethylaluminum azide. Finely ground sodium azide was dried at 115 °C for 3 days in a vacuum drying pistol. Diethylgallium chloride was added to a slurry of rigoursly dried benzene containing a slight excess of sodium azide. After stirring 48 h, the solution was filtered, and the benzene was removed by vacuum distillation to give a nearly quantitative yield of diethylgallium azide as a colorless liquid that distills without decomposition (bp 130 °C, 3 Torr). The compound was characterized by infrared spectroscopy.[10]

Single-crystal silicon wedges used for transmission infrared spectroscopy, scanning electron microscopy (SEM), and Auger spectroscopy were degreased in organic solvents and dipped in 10% HF until the surface was hydrophobic. Flat pieces of highly oriented pyrolitic graphite for Rutherford backscattering spectroscopy (RBS) were cleaved to remove the outer contaminated layers.

Deposition of GaN was carried out in the horizontal hot-wall low-pressure CVD reactor shown in Figure 1. The three-zone furnace was adjusted to give a constant temperature center zone of approximately 15 cm in length. The precursor was loaded into a fritted glass bubbler in a drybox. During deposition, the bubbler and the lines into the reactor were maintained at 80 °C. In a typical experiment, the substrates were loaded on a quartz boat, the load lock was evacuated, and the boat was passed into the reactor by using a magnetically coupled manipulator. Graphite substrates were heated under high vacuum at 800 °C for 2 h to remove water. The base pressure of the deposition system prior to the start of deposition was typically 10^{-9} Torr at 350 °C. Purified helium at a flow rate of 30 cm^3/min was allowed to flow into the reactor through an inlet separate from the precursor bubbler. The pumping was then switched from the turbomolecular pump to a mechanical pump (protected by a burnoff furnace at 900 °C), and the pressure was adjusted to 2 Torr by using an automatic throttle control valve. At this point, purified He was passed through the bubbler at 2–5 cm^3/min, resulting in a growth rate at substrate temperatures between 350 and 450 °C of 15–50 Å/min. (In this temperature range, the growth rate was dependent only on the flow of gas through the bubbler, implying that we were depositing films under mass transport limited conditions rather than surface kinetic controlled conditions.) Following deposition, some of the samples were subjected to in situ postdeposition annealing at 600 °C in a helium ambient for several hours.

Results and Discussion

Diethylgallium azide begins to decompose to give films at temperatures as low as 275 °C by using the apparatus described above; however, most depositions were done at substrate temperatures of 350–450 °C due to low growth rates below 350 °C. Typical run times were 1–4 h resulting in films 0.2–1.0 μm thick. All films adhered well to Si and C substrates and were smooth and continuous when ex-

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(1) Shintani, A.; Minagawa, S. *J. Electrochem. Soc.* **1976**, *123*, 1725.
(2) Maruska, H. P.; Tiefjen, J. J. *Appl. Phys. Lett.* **1969**, *15*, 327.
(3) Chu, T. L. *J. Electrochem. Soc.* **1971**, *118*, 1200.
(4) Born, P. J.; Robertson, D. S. *J. Mater. Sci.* **1980**, *15*, 303.
(5) Nicki, J. J.; Just, W.; Bertingers, R. *Mater. Res. Bull.* **1974**, *9*, 1413.
(6) Nicki, J. J.; Just, W.; Bertingers, R. *Mater. Res. Bull.* **1975**, *10*, 1097.
(7) Seifert, W.; Franzheld, R.; Bonich, F.; Buttler, E. *Cryst. Res. Technol.* **1986**, *21*(1), 9.
(8) Schulze, R. K.; Mantell, D. R.; Gladfelter, W. L.; Evans, J. F. *J. Vac. Sci. Technol. (A)* **1988**, *A6*, 2162.
(9) Boyd, D. C.; Haasch, R. T.; Mantell, D. R.; Schulze, R. K.; Evans, J. F.; Gladfelter, W. L. *Chem. Mater.* **1989**, *1*, 119.
(10) Muller, J.; Dehnicke, K. *J. Organomet. Chem.* **1968**, *12*, 37.
(11) Prince, M. I.; Weiss, K. *J. Organomet. Chem.* **1966**, *5*, 584.

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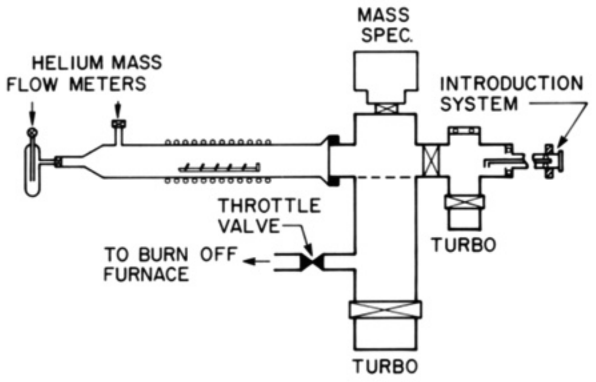

Figure 1. Horizontal hot-wall low-pressure CVD reactor.

amined with an optical microscope.

Film Composition. The ratio of gallium to nitrogen in these films could not be established with any certainty by Auger spectroscopy because of preferential sputtering of nitrogen. Electron microprobe analysis showed that the bulk composition of the films was 51% Ga and 48% N with an estimated uncertainty of 2%. Rutherford backscattering analysis indicated that the films were 49% Ga and 51% N, again with an uncertainty estimated to be 2%. We conclude from these results that the films are stoichiometric GaN.

Although Auger spectroscopy was not useful for bulk analysis, it was useful for estimating carbon and oxygen impurity levels. For films deposited at or below 350 °C, carbon levels were near or below the limit of detection (<2%) but rose to more than 10% in films deposited at 450 °C. The low growth rates (less than 15 Å/min) of films grown below 350 °C resulted in high (more than 5%) oxygen content, presumably because the rate of oxidation of the growth surface due to residual water and oxygen was comparable to film growth rate. (Mass spectroscopic analysis of the reactor ambient indicated the residual water partial pressure to be $\sim 10^{-8}$ Torr when using the mechanical pump. This partial pressure would correspond to an oxidation rate of up to 1 monolayer/min and is consistent with the observed oxygen content of the film.) Oxygen levels in films deposited at 350 °C and exposed to air were extremely high (>20%) but were not uniform through the film. After several hundred angstroms were sputtered into the the bulk, the measured oxygen level abruptly fell to less than 2 at. %. We believe this indicated that oxidation following exposure to air was responsible for the high oxygen content. By in situ annealing of the films at 600 °C for several hours in helium, the films were no longer sensitive to air exposure and had oxygen contents of less than 2%.

The air sensitivity of the as-deposited films could be explained by high hydrogen content in these films. To study relative hydrogen content and examine the effects of annealing, films were deposited on silicon wedges (polished slightly off-axis to suppress interference effects), and transmission infrared spectra were recorded. Figure 2 shows the spectra of films deposited at 350 °C (and quickly placed in the FTIR spectrometer) and deposited at 350 °C and annealed at 600 °C for 6 h. The two overlapping bands in the as-deposited films are due to Ga–H (2070 cm^{-1}) and Ga–H$_2$ (1930 cm^{-1}) stretches. (The assignment of these bands is based on the observation that the 1930-cm^{-1} band was not observed in samples deposited at 450 °C.) No absorptions in the 3200–3500-cm^{-1} region were discernible, indicating little or no N–H bond formation. The as-deposited film also shows a broad band at 550 cm^{-1}, which becomes considerably sharper after annealing. This band is due to the Ga–N stretching modes. These infrared spectra are consistent with the deposition of a highly hydrogenated gallium nitride, which undergoes loss of hydrogen with an increase in gallium–nitrogen bond formation on annealing.

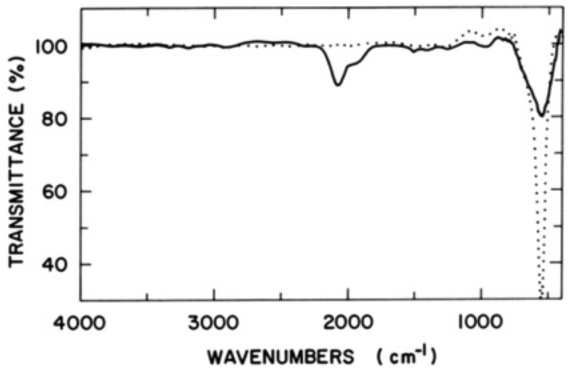

Figure 2. Infrared spectra of GaN films deposited at 350 °C (solid line) and deposited at 350 °C and annealed at 600 °C for 6 h (dotted line).

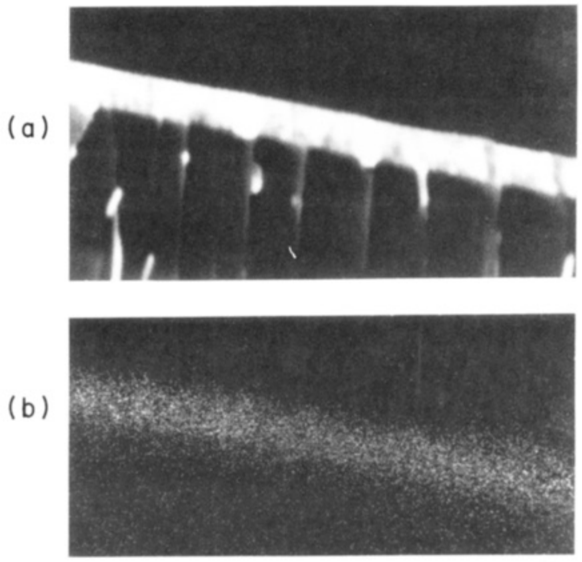

Figure 3. (a) Scanning electron micrograph of a 3300-Å GaN film on a cleaved Si substrate. (b) X-ray dot map of the same film showing uniform distribution of Ga.

Film Structure. The structure and morphology of the annealed films were studied by several techniques. Scanning electron microscopy (obtained on a ISI-DS130S microscope operated at an accelerator voltage of 7 kV to reduce charging) showed that GaN films deposited by this technique are smooth and featureless. Figure 3a shows a cross-sectional view of a 3300-Å GaN film deposited on a cleaved silicon substrate. Figure 3b is a gallium X-ray dot map (obtained by using a PGT TS20 EDAX accessory) of the same view showing uniform distribution of gallium throughout the film. X-ray diffraction patterns were obtained with a Guinier camera using Cu Kα_1 radiation and showed the expected hexagonal wurtzite structure with measured lattice constants of $a = 3.185 \pm 0.005$ Å, $b = 5.185 \pm 0.005$ Å.[12] Electron diffraction data of several thin films supported on a carbon coated copper grid were obtained by using a Phillips 301 (100-keV accelerating voltage) transmission electron microscope. An electron diffraction pattern of a typical film is shown in Figure 4.

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[12] Literature values: $a = 3.182$, $c = 5.173$ Å, from: Shunk, F. A. *Constitution of Binary Alloys, Second Supplement*; McGraw-Hill: New York, 1969; p 359.

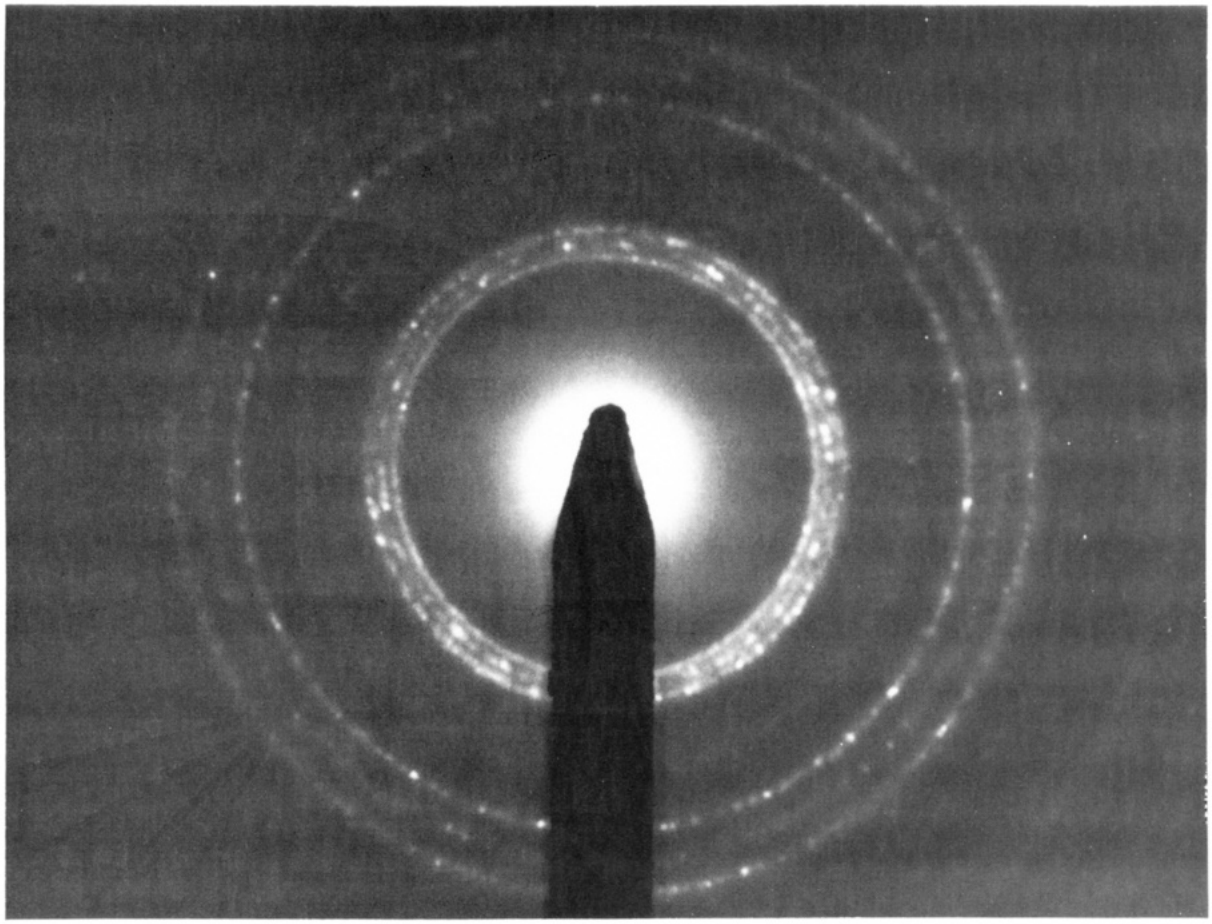

Figure 4. Electron diffraction pattern of CVD GaN film.

The rings correspond to reflections of the expected hexagonal wurtzite structure, and the measured interplanar spacings and *hkl* assignments agree with those in the literature for GaN.[13]

Film Growth Mechanism. Mass spectroscopic analysis of the volatile byproducts showed only hydrogen, nitrogen, and ethylene formed in depositions below 350 °C. With increasing temperature, significant amounts of ethane were produced. Using published sensitivity factors and cracking patterns,[14] the ratio of $m/e = 30$ to $m/e = 28$ could be used to estimate relative amounts of ethane and ethylene, respectively. At a deposition temperature of 450 °C, the hydrocarbon products were composed of roughly 70% ethylene, 30% ethane, and traces of methane. (A similar distribution of hydrocarbon products has been observed in the deposition of AlN from diethylaluminum azide at 500 °C.[9]) Our results suggest that the formation of ethane rather than ethylene as the C_2 product correlates with carbon incorporation in the film, although the mechanism of carbon incorporation may not be related to the mechanism of C_2 loss from the growing film. (Other factors such as higher growth rates at higher temperatures trapping the hydrocarbon fragment or relative rates of carbide versus nitride growth may be responsible.) Still, the importance of low-temperature deposition to reduce carbon levels is clearly indicated, and we believe that a likely explanation for our results is that at low temperatures (below 350 °C), only successive β-hydride elimination occurs. As the deposition temperature increases, the loss of ethane via reductive elimination following the initial loss of ethylene[9] becomes energetically possible, as does some as-yet-unknown process of carbon incorporation. Our observation of $Ga-H_2$ species in the films deposited at 350 °C is also consistent with successive β-hydride elimination.

Conclusion

Gallium nitride has been deposited by the thermal decomposition of diethylgallium azide at 350 °C, followed by annealing at 600 °C. The films are polycrystalline, stoichiometric GaN with carbon and oxygen levels below 2%.

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[13] Juza, R.; Hahn, H. *Z. Anorg. Chem.* **1938**, *239*, 285.

[14] O'Hanlon, J. F. *A User's Guide to Vacuum Technology*; Wiley: New York, 1980, and references therein.