

Growth of AlN by metalorganic molecular beam epitaxy

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Thin film AlN has been grown on Al₂O₃ and GaAs substrates by metalorganic molecular beam epitaxy using amine bonded alane precursors and either tertiarybutylamine or nitrogen from a compact electron cyclotron resonance (ECR) plasma source operating at 2.45 GHz. Typical growth pressures were in the 0.5–1×10⁻⁴ Torr range. The growth rates, impurity backgrounds, and surface morphologies were examined for both nitrogen sources and both the solid and liquid alanes. In general, growth efficiencies were good for both alane precursors, allowing for deposition of the low temperature, ~400 °C, AlN buffers needed for subsequent growth of GaN and InGaAlN alloys. Low growth temperatures could not be obtained using tertiarybutylamine, presumably due to poor decomposition efficiency of the source at low temperatures. The structural quality of material grown at high temperatures from the ECR plasma was measured by atomic force microscopy, high resolution x-ray diffraction, and transmission electron microscopy, indicating single crystal material with a surface roughness of ~8 Å and an x-ray full width half-maximum of 430 arcsec. This ECR plasma-derived material was of sufficient quality to allow for the growth of multiple quantum well InGaAlN structures. © 1995 American Institute of Physics.

Due to its high thermal conductivity and stability, chemical inertness, and ability to passivate III–V surfaces, there has been considerable interest in the growth of AlN films for microelectronics packaging, passivation, and dielectric applications.¹ Recently, the development of blue-emitting optical devices² based on group III–N materials as well as the potential for nitride-based high temperature electronic device applications have stimulated development of epitaxial growth techniques for AlN and Al-containing group III-nitride ternaries of high electrical and optical quality. Several techniques have been investigated including metalorganic chemical vapor deposition (MOCVD),³ plasma-assisted molecular beam epitaxy (MBE),⁴ and metalorganic molecular beam epitaxy (MOMBE).^{5,6} Problems inherent in methods based on metalorganic precursors include the incorporation of unwanted impurities including oxygen, hydrogen, and carbon. For the N source, an atomic beam of elemental N generated from a clean source such as N₂ would be expected to provide the cleanest material. However, the use of plasma sources in UHV growth systems is a potential barrier to process scale-up and does not allow for selective growth based on catalytic group V precursor decomposition. Therefore, chemical rather than plasma-based *n* sources are desired. In this letter, the properties of films grown by MOMBE using different amine-bonded alane sources are compared. As well, the first attempt at UHV nitride growth with an amine precursor is reported.

AlN samples were grown on 2 in. diameter semi-insulating (100) GaAs substrates or (0001) sapphire substrates at 700–725 °C in an Intevac Gas Source Gen II. Films grown with the electron cyclotron resonance (ECR) nitrogen

plasma were preceded by a low temperature AlN buffer grown with a substrate temperature of 425 °C. The aluminum sources, trimethylamine alane (TMAA) and dimethylethylamine alane (DMEAA), were transported using a He carrier gas in order to avoid possible hydrogen passivation effects, a common problem in MOCVD grown GaN films.^{7–9} For layers grown with the plasma, an ECR plasma source (Wavemat MPDR 610) operating at 2.45 GHz and 200 W forward power was used to provide the nitrogen flux. Growth rates for samples utilizing the plasma source ranged from ~50 to 60 Å/min. The tertiarybutylamine (*t-butyl*/NH₂) was maintained at ~17 °C and was introduced using vapor source control. The growth rate obtained using *t-butyl*/NH₂ was ~67 Å/min. Further details of the growth system have been given previously.¹⁰

Structural quality was examined by atomic force microscopy (AFM) using a DI-Nanoscope III in tapping mode, high resolution x-ray diffraction (HRXRD) utilizing a Philips 5-crystal system, and transmission electron microscopy (TEM) using a JEOL 200CX. Secondary ion mass spectrometry (SIMS) analysis was performed using either a PHI 6300 or a Cameca IMS 4f system.

SIMS analysis of AlN grown with TMAA shows extremely high concentrations of both carbon and oxygen, on the order of several atomic percent; see Fig. 1. These very high concentrations have been verified by Auger electron spectroscopy as well. Similar oxygen levels have also been observed in AlAs grown with TMAA,¹⁰ and are believed to arise from residual ether left over from the synthesis of the precursor. DMEAA, by contrast, is not synthesized with oxygen containing solvents, and consequently produces much lower oxygen backgrounds in AlAs. Thus it is not surprising to find that the oxygen levels observed in AlN grown from this source are lower by several orders of magnitude. Inter-

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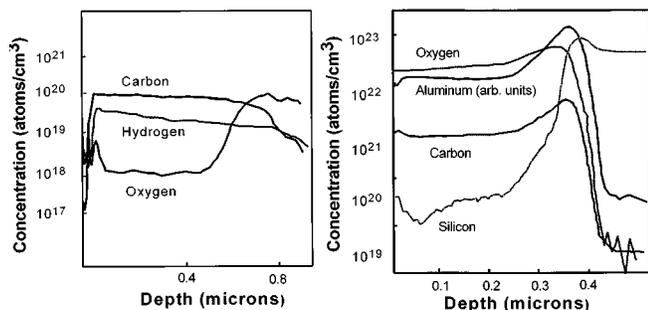


FIG. 1. SIMS profiles of AlN layers grown at 700 °C using a N₂ plasma and DMEAA (left) and TMAA (right).

estingly, both sources produce high carbon backgrounds. For the material from TMAA, it is likely that some of this carbon is due to the decomposition of the ether at the growth surface. For the DMEAA, however, the only plausible sources of carbon are the ligands attached to the amine. Carbon incorporation is not observed in AIAs grown from this source, suggesting that the lower temperatures used for deposition of the AIAs, ~500–550 °C, are more suitable for use with this precursor. Experiments to confirm this are in progress. Finally it should be noted that the hydrogen background is quite high as well. Again the only plausible source is the alane precursor. While the background will most likely decrease as the carbon level is reduced, the potential for dopant passivation exists, and must be addressed, either by enhancing the removal of hydrogen from the growth surface or by removing it from the lattice through postgrowth annealing.

Optical emission spectroscopy of the output of the ECR source indicates that a significant atomic nitrogen fraction is produced under the conditions used for deposition of the AlN, though the presence of peaks at 335, 326, 390, and 391 nm shows there to be some N₂ and N₂⁺, respectively, in the beam. By contrast, the use of amine precursors is expected to produce only atomic species at the surface. Tertiary-butylamine has been used for deposition of AlN in MOCVD,¹² but has not yet been explored for use in UHV, where surface catalysis is generally required for decomposition at the growth front. Examination of the decomposition



FIG. 2. Selected area diffraction pattern of AlN grown from ECR N₂ and DMEAA showing an (0001)_{AlN}|| (0001)_{Sub}; [1010]_{AlN}|| [1120]_{Sub} orientation relationship. The brighter epitaxial film spot pattern shows minimal streaking, indicating single crystal material.

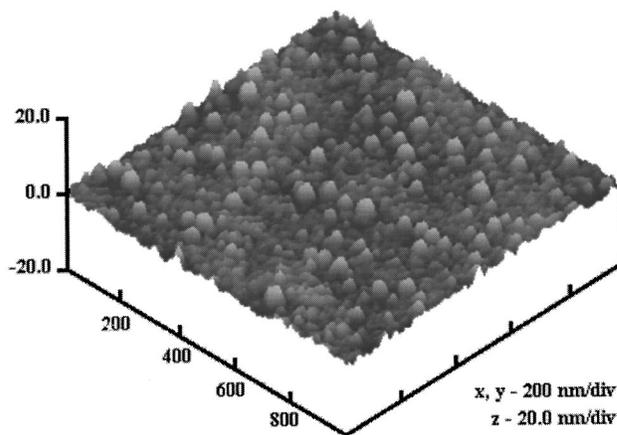


FIG. 3. AFM surface scan of AlN grown from ECR N₂ plasma and DMEAA on (0001) sapphire.

by-products over a range of growth temperatures shows that the pyrolysis of the butyl group from the amine increases gradually with temperature over the range 100–800 °C. However, it was not until 800 °C that a significant increase in hydrogen evolution was observed, suggesting that the remaining NH₂ fragment does not decompose until relatively high substrate temperatures. This observation would thus explain the fact that we were unable to obtain growth of AlN at low temperatures using *t-butyl*/NH₂. At 700 °C, growth does occur; however, the films are amber in color, as opposed to the colorless, transparent appearance of those layers grown with the plasma. Also, the films grown by *t-butyl*/NH₂ wet-etched substantially faster than the ECR plasma-derived AlN, indicating lower quality material.

When examined with SIMS, the layers grown with the chemical nitrogen source show an order of magnitude higher concentration of oxygen as well, probably due to residual oxygenated solvents left from synthesis. The carbon and hydrogen levels are approximately the same in both layers, again suggesting that the alane precursor is the major source of these contaminants. Consequently, though higher growth temperatures would probably improve the decomposition efficiency of the *t-butyl*/NH₂, such temperatures would also increase the decomposition of the dimethylethylamide ligand

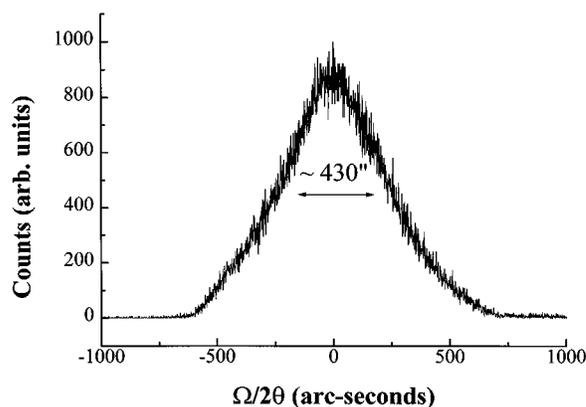


FIG. 4. High resolution x-ray diffraction rocking curve from AlN grown from ECR N₂ plasma and DMEAA. FWHM for this sample was 430 arcsec.

on the DMEAA, resulting in even further carbon contamination. In light of these results, it is unlikely that monosubstituted ammonias like *t-butyl*/NH₂ will be suitable for deposition of the nitrides. It is more likely that nonhydrogen bonded amines will prove to be more useful, though this has not yet been demonstrated.

The AlN grown with DMEAA and ECR N₂ plasma proved to be of sufficient epitaxial quality and surface smoothness to act as a base layer in an InGaN multiple quantum well microdisk laser structure. Cross-section TEM indicated that this AlN was defective single crystal, as exhibited in the selected area diffraction pattern taken from the laser structure base layer shown in Fig. 2. Further details of the processing and characterization of the microdisk laser structure will be presented elsewhere. XRD analysis of the plasma-grown AlN showed a FWHM of 430 arcsec, comparable to typical values reported in the literature for material grown by MOCVD (Fig. 3). By contrast, no peak was detected for the material grown using *t-butyl*/NH₂. The poor crystallinity of the *t-butyl*/NH₂-grown layer may be a reflection of poor stoichiometry due to insufficient nitrogen at the growth surface. Surface analysis of the ECR plasma-grown layer with AFM showed the layer to be quite smooth with an average surface roughness of ~8 Å, as shown in Fig. 4. Surface roughness of the substrate prior to growth was found to be 14 Å, indicating that planarization has occurred during growth.

DMEAA and a N₂ plasma were found to produce the highest quality material in terms of oxygen impurity background and crystallinity. The surface roughness, 8 Å, and

FWHM, 430 arcsec, are the best yet reported for epitaxial AlN grown from molecular beams. Growth from a chemical precursor, *t-butyl*/NH₂, was demonstrated, although the crystal quality was not good. The hydrogen background was found to be independent of the group V precursor, suggesting that the alane is the primary source. Similarly, the carbon background was the same in the samples grown under the different sources, suggesting that the amines generated upon the decomposition of the alane are themselves decomposing. It is believed that lower growth temperatures may help to alleviate this effect.

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