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Aluminum nitride substrate growth by halide vapor transport epitaxy

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Abstract

High-quality AlN layers with thickness up to 50 μm have been grown by HVTE at growth rates up to 60 $\mu\text{m}/\text{h}$ at deposition temperatures of 1000–1100°C in the pressure range of 50–760 Torr. The HVT process uses an aluminum chloride amine adduct as the aluminum source and ammonia for the nitrogen. This new technique eliminates the main difficulties of the conventional HVPE growth, where aluminum oxidation and the strong reactivity of aluminum chloride with quartz create the potential for oxygen contamination. The crystalline layer quality as determined by X-ray rocking curve measurement shows FWHM of 300–900 and 500–1300 arcsec for (002) and (102) planes, respectively. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Aluminum nitride has potential as a substrate material for a wide range of optical and electronic applications from UV sensors to high power RF devices. The properties that make it attractive are its high thermal and low (insulating) electrical conductivity [1], high UV transparency [2], high acoustic wave velocity [3], and its excellent lattice and thermal expansion match with GaN [4].

Although 15 mm diameter boules of AlN have been demonstrated [5], the manufacturing process involves sublimation at very high temperatures and is similar to the most common SiC manufac-

turing process. It has taken many years for the SiC foundries to ramp up to 50 and 75 mm diameter boules and it is likely that AlN production will take a similar number of years. A hybrid approach involving the deposition of a thick AlN layer on large diameter sapphire substrates offers a near term, low cost solution.

Several techniques for growth of aluminum nitride layers on a variety of substrates have been exploited, including reactive sputtering [6], MBE [7], MOCVD [8] and VPE [9]. However, only VPE has a high growth rate for well-oriented AlN film growth. This paper covers the recent successful growth of AlN films by a modified VPE process.

The choice of VPE source materials and precursors is critical to the AlN crystal quality. The simplest hydride VPE approach to growth of aluminum nitride employs the reaction between

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aluminum chloride (formed by the reaction of molten aluminum and HCl gas) and ammonia. However, the molten aluminum and the aluminum chloride gas are very reactive and easily reduce the silica hardware. To eliminate the molten aluminum problem, some researchers prefer the direct reaction of solid AlCl_3 and NH_3 [10]. In this case also there is potential oxygen contamination because of the strong reactivity between AlCl_3 and fused silica.

An alternate approach is to pre-synthesize the adduct and heat the entire reactor inlet to avoid adduct condensation on the cold spots. A few authors have discussed adduct preparation [11,12] and some have discussed very briefly the adduct properties [13–15]. The use of the aluminum chloride amine adduct circumvents the high affinity of pure aluminum for oxygen and the strong reactivity of aluminum chloride to the quartz reactor walls. At the same time, the adduct contains within itself both sources—of aluminum and nitrogen. Thus, the deposition can be easily controlled by the temperature and gas flow rate. In what follows, we present our recent successful growth of AlN films by the HVTE process using the preformed adduct.

2. Experimental procedure

The halide vapor transport epitaxy (HVTE) system for III-nitride layer growth is designed

(Fig. 1) to include: (1) three-zone furnace with computer controlled independent power supplies for each zone; (2) quartz tube reactor 1200 mm long and 50 mm in diameter and (3) mass flow controllers working in the range 1–850 sccm for each source of gas—ammonia, nitrogen and hydrogen, with the possibility for precise gas mixing either outside or inside the reactor. At the outlet: (4) an automatic control butterfly valve MKS type 153; (5) a programmable MKS pressure reader for an accuracy of 1 Torr in the pressure range 1–1000 Torr; (6) a mechanical pump; and (7) oil and water air locks.

Before each run the quartz tube of the reactor was evacuated and heated for 12 h at 500°C. After that the substrate (sapphire template with 1 μm thick MOCVD AlN or GaN layer) and the adduct boat were placed in proper positions and the system was maintained for another 12 h at 100°C in vacuum. An RGA chemical test for water vapor, oxygen, nitrogen and ammonia contamination followed. When the RGA chemical analysis indicated less than 10^{-5} Torr the epitaxial growth process was initiated in the pressure range 50–760 Torr, deposition temperature 1000–1100°C, adduct temperature 250–360°C, and gas flow rates 170–400 sccm for N_2 and H_2 and 5–100 sccm for NH_3 .

For the HVTE process, adducts of the type $\text{AlCl}_3-x\cdot\text{NH}_3$ ($x=1-6$) are produced. The adduct was prepared at low temperature, taking precautions against any possible oxygen contamination. The weights of the initial chemical components

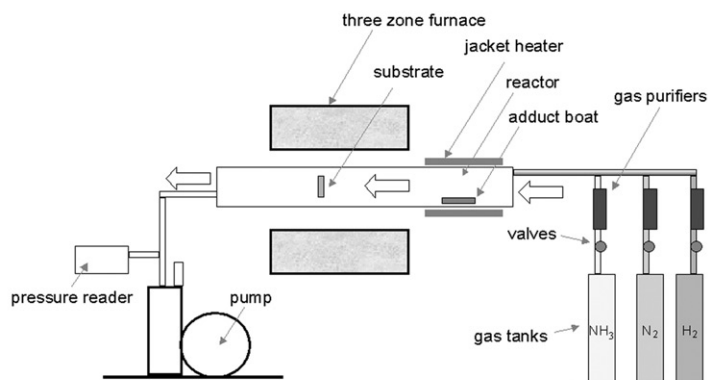


Fig. 1. HVTE system designed and used for the aluminum nitride layer growth.

were recorded, and after each synthesis run the complex was analyzed by X-ray diffractometer *Philips APD 3720*. The equilibrium vapor pressure over this adduct at different temperatures was investigated and compared to the literature (see Fig. 2). The data shows a good agreement with the other authors—it is between the data obtained for mono- and tri-amine type of adducts. By comparison, the adduct partial pressure is considerably lower than the vapor pressure of either AlCl_3 or ammonium chloride NH_4Cl .

3. Results

3.1. Growth rate and layer thickness

More than 50 experiments were conducted under various growth conditions using GaN and AlN 1 μm thick MOCVD templates on (0001) sapphire substrate. AlN layers were grown to thicknesses up to 50 μm with good crystal quality at a growth rate from 5 to 60 $\mu\text{m}/\text{h}$. The results illustrate the following points:

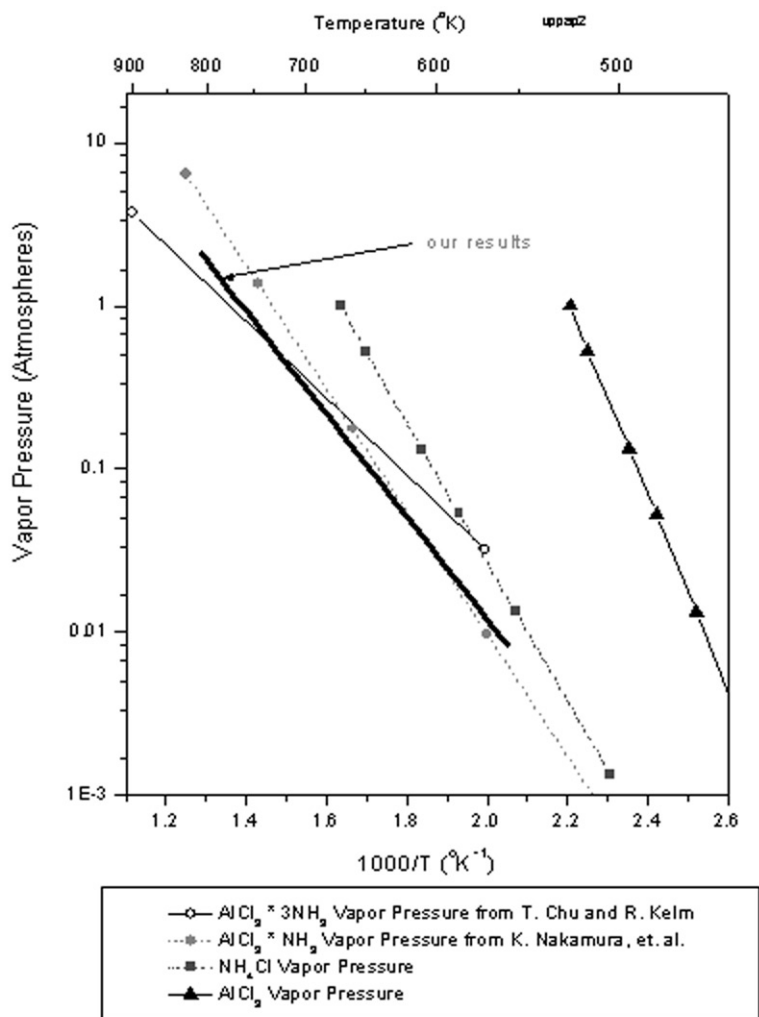
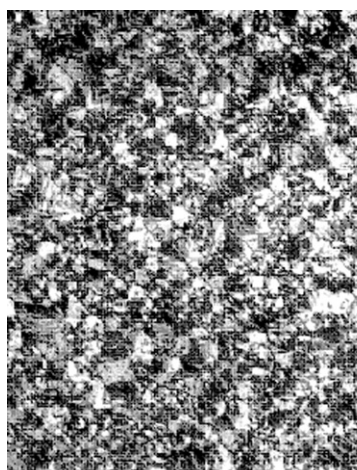


Fig. 2. Adduct partial pressure versus the adduct temperature—a comparison of recent results with some previously published data.

- (1) AlN layers grown on AlN-MOCVD templates have much higher crystal quality than those grown on GaN templates.
- (2) A higher deposition temperature than is used for GaN growth is favored for layer quality. Higher substrate temperature is not a problem when AlN instead of GaN templates are used.
- (3) The growth rate depends not only on the type of adduct and temperature, but also on the ammonia overpressure. Factors increasing the growth rate are: the N_2/NH_3 ratio, the aluminum content and temperature of the adduct.
- (4) The growth rate increases with lower ambient pressure (higher gas flow velocity), which also allows more flexibility in substrate wafer positioning.

3.2. Surface morphology

Surface morphology was studied using a *NO-MARSKI* optical microscope under a magnification of $20\text{--}100\times$. The structure is dominated by oriented hexagonal platelets as shown in Fig. 3. The growth conditions affect the surface morphology of the layers, where an increase of 10°C in the deposition temperature results in a 30X increase of the size of hexagons.



3.3. Transmission electron microscopy

TEM images of the layer structure in cross-section show a clear distinction between the layers (Fig. 4) and a reduced density of threading dislocations compared to the template layer.

3.4. X-ray diffraction rocking curves and $\Omega/2\theta$ scan

AlN crystal structure was investigated with a high resolution, triple-axis X-ray diffractometer with a four-crystal monochromator using $\text{Cu K}\alpha$ radiation. A high resolution X-ray rocking curve technique is employed to analyze the crystalline quality of epitaxial AlN. Instead of scanning the $\Omega/2\theta$ using a narrow receiving slit, we used an Ω -scan with a large beam diameter to examine the in-plane alignment. In this measurement the incident angle θ and the reflection angle are fixed and symmetrical for each Bragg angle. Typically, the full-width at half-maximum (FWHM) of this measurement is much larger than the $\Omega/2\theta$ scan commonly used as an indicator of lattice strain.

The best samples are exhibited by X-ray rocking curve FWHM in the range of $300\text{--}500$ arcsec for reflection (002) and (102), respectively. A significant improvement of the crystal quality in comparison with the MOCVD templates was also observed (see Table 1).



Fig. 3. Ten degrees increase of the deposition temperature from 1050°C (left figure) to 1060°C (right figure) resulted in about 30 times increase of the size of the surface hexagons.

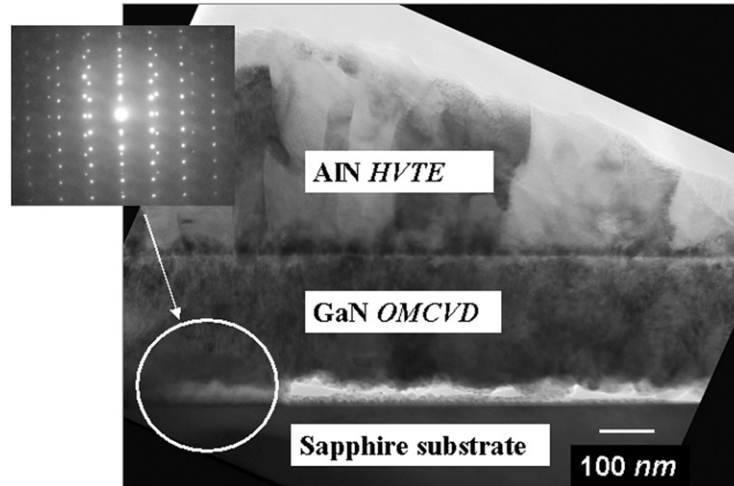


Fig. 4. A cross sectional TEM micro-image showing the AlN columnar layer structure with reduced dislocation density. TEM by Wendy Sarney, ARL.

Table 1

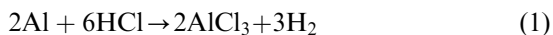
A series of runs comparing the rocking curves for MOCVD templates with HVPE layers grown upon them

Run #	Reactor pressure (Torr)	Flow rates (sccm)		Growth rate ($\mu\text{m/h}$)	MOCVD template RC (arcsec)		HVTE layer RC (arcsec)	
		N ₂	NH ₃		002	102	002	102
115	50	255	75	3	1073	1855	961	1350
114	781	255	75	5	1073	1855	702	1001
112	765	170	100	12	1073	1855	681	958
126	782	340	25	49	549	1215	757	1196
124	777	300	50	5	549	1215	467	795
125	781	300	50	5	549	1215	366	512

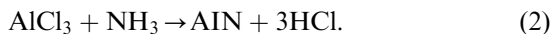
4. Discussion

In general, a VPE process for aluminum nitride growth can be carried out using one of the three schemes:

1. Direct reaction between molten Al and HCl to form AlCl₃,



which definitely brings a significant risk for oxidation of the molten aluminum, and a further reaction between AlCl₃ and NH₃ in an ammonia stream:



It should be noted that the above reaction (2) requires a temperature greater than 600°C. Aluminum nitride could be produced at much lower temperature (about 350°C) by the reaction: $\text{AlCl}_3 + 4\text{NH}_3 \rightarrow \text{AlN} + 3\text{NH}_4\text{Cl}$. (3)

However, this reaction produces undesirable ammonium chloride NH₄Cl as a byproduct. In addition, the gases NH₃ and HCl may easily combine to form NH₄Cl even at 250°C in a competing reaction:



2. Using anhydrous aluminum trichloride AlCl₃ in a reaction (see reaction (2)) with ammonia NH₃.

In this case it should be noted that the reaction (2) is exothermic and—more important—the $\text{AlCl}_3/\text{NH}_3$ mixture has high reactivity with silica. Oxygen contamination from the quartz tube then becomes transported to the growing film, curtailing or altering the physical properties of the AlN material.

3. A third approach is to use an adduct made in advance, whose heavy molecule contains the two reactants— AlCl_3 and NH_3 —and to heat the compound to its decomposition temperature at or near the substrate surface, in order to ensure a reaction of the type (2). The advantage of such a process is that, using a narrow heater with a sharp temperature profile, one can adjust the deposition conditions near the substrate. The rest of the reactor tube can be held at a relatively low temperature, sufficient only to prevent adduct vapor condensation during the gas transport.

Comparing our data with a survey of previous results it appears that there has been a progression from amorphous coatings to high-quality crystalline layers. While growth of thick, amorphous AlN is possible on different, even metallic, surfaces, the growth of well-oriented crystalline AlN epi-layers is not fully developed yet. The technique employed here produces uniform layers with thickness up to 50–60 μm at growth rates of about 60 $\mu\text{m}/\text{h}$ and economic gas regimes, which makes it a highly efficient process. The best results for the peak width of the 002 and 102 rocking curve reflections are in the range of 300–500 arcsec, respectively. Crystal quality of the HVTE layers was generally improved over the AlN MOCVD templates.

5. Summary

High-quality AlN layers with thickness up to 50 μm have been grown by HVTE. The deposition temperature and the total reactor pressure were in the range of 1000–1100°C and 50–760 Torr, respectively. This new technique eliminates the main difficulties of conventional HVPE growth, where aluminum oxidation and the strong reactiv-

ity of aluminum chloride with quartz create the potential for oxygen contamination.

The layer quality, as determined by X-ray rocking curve measurements (with a high resolution Philips instrument using omega scan), shows a FWHM of about 300 and 500 arcsec for (0 0 2) and (1 0 2) planes, respectively. Trace element impurity measurements by GDMS depth profile analysis indicate $7.5 \times 10^{19}/\text{cm}^3$ oxygen. Tests are under way to evaluate this material as a substrate for GaN-based devices.

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