Investigations into the Growth of AlN by MOCVD using Tri-*tert*-butylaluminium as an Alternative Aluminium Source

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Thin films of AlN have been deposited at 500 and 600 °C by atmospheric-pressure MOCVD using the precursors tri-*tert*-butylaluminium (Bu^t_3Al) and *tert*-butylamine (Bu^tNH_2). Growth rates of 0.5 μm h^{-1} were obtained at 500 °C. Post-growth oxidation of the AlN films was prevented by the deposition of a protective Al overlayer using Bu^t_3Al.

Aluminium nitride (AlN) is an important material with a variety of applications such as passive barrier layers and substrates in silicon integrated circuits, high-frequency acoustic wave devices, high-temperature windows and dielectric optical enhancement layers in magneto-optic multilayer structures.[1] In addition, the ternary alloy $Al_xGa_{1-x}N$ has a large potential application in optoelectronic devices operating in the UV–blue spectral region.[2] The development of these various applications is critically dependent on the capability to deposit thin films of AlN at low to moderate substrate temperatures.

Conventional ceramic processes, such as the direct nitriding of Al powder at high temperature (>1440 °C) are unsuitable for the controlled deposition of thin AlN layers.[3] Therefore, the physical vapour deposition technique of vacuum sputtering is generally employed. However, this suffers from the disadvantages of limited scale and poor conformal step coverage. There has thus been a concerted effort[4] to develop metal–organic chemical vapour deposition (MOCVD) techniques which have the advantages of large-area growth capability, excellent conformal step coverage and precise control of layer thickness.

The deposition of AlN by MOCVD has traditionally been carried out using mixtures of trimethylaluminium (Me_3Al) and ammonia (NH_3).[5,6] However, the high thermal stability of NH_3 necessitates the use of high substrate temperatures (typically >900 °C). This leads to the problem of nitrogen loss from the AlN film which is only partially alleviated by the use of high V:III ratios (*e.g.* >2000:1).

AlN growth has been achieved at lower substrate temperatures (400–800 °C) using a variety of 'single-source' precursors, which already contain an intramolecular (Al—N) bond. These include $[Al(NR_2)_3]_2$, $[HAl(NR_2)_2]_2$ (R = Me, Et),[7] $[Me_2AlNH_2]_3$,[8] $[Et_2AlN_3]_3$[9] and $[Me_2AlNR_2]_2$ ($R = Pr^i$).[10] However, these precursors have only very low vapour pressures (<1 Torr at room temperature) which necessitates the heating of source and reactor inlet lines and the use of high-vacuum MOCVD reactors.

It is therefore desirable to develop alternative precursors which may be more conveniently utilized in MOCVD, and the volatile nitrogen source hydrazine (N_2H_4) has been used in combination with Me_3Al to grow AlN at temperatures as low as 220 °C.[11] However, N_2H_4 is an extremely toxic ($TLV_{(skin)}$ 0.01 ppm) and unstable compound which has been reported to decompose on contact with stainless steel. These factors are likely to seriously restrict its large-scale application in MOCVD.

The successful deposition of AlN from the single-source precursors $[Me_2AlNR_2]_2$[10] and $[Et_2AlN_3]_3$[9] has encouraged us to investigate methods of forming similar species *in situ* in the vapour phase prior to layer growth. This approach aims to combine the advantages of convenient source temperatures and high growth rates associated with the use of high vapour pressure reagents, with the low growth temperatures associated with single-source precursor molecules. Thus, we have recently demonstrated[12] the successful deposition of AlN in the temperature range 400–600 °C by atmospheric pressure MOCVD using the volatile primary alkylamines, *tert*-butylamine (Bu^tNH_2) and isopropylamine (Pr^iNH_2) in combination with Me_3Al. It was proposed[12] that the directly bonded species $[Me_2AlNHR]_2$ was formed in the gas phase prior to AlN deposition, and the recent report[13] of AlN growth by high-vacuum CVD using $[Me_2AlNHR]_2$ ($R = Bu^t$, Pr^i) strongly supports this proposal. Similarly, the combination of Me_3Al and trimethylsilylazide (Me_3SiN_3) proved suitable for the deposition of AlN at 300–450 °C.[14] Significantly, Auger electron spectroscopy (AES) failed to detect silicon in the films, and this was attributed[14] to the formation of dimethylaluminium azide (Me_2AlN_3) in the gas phase, together with tetramethylsilane (Me_4Si) which allows the efficient transport of Si species away from the growth zone.

However, the AlN films deposited from mixtures of Me_3Al–RNH_2 or Me_3Al–Me_3SiN_3 were found to contain oxygen (2.0–8.0 atom%), due possibly to post-growth oxidation, together with variable levels of residual carbon (2.7–17.0 atom%). The carbon contamination was attributed[12,14] to the use of the methyl-based Al precursor Me_3Al, which has been shown to lead to significant levels of carbon contamination in Al films[15] and AlGaAs epitaxial layers[16] grown by MOCVD.

Recently, some of the present authors have shown that the new Al precursor tri-*tert*-butylaluminium (Bu^t_3Al) can be used to deposit high-purity Al in the temperature range 300–450 °C by low-pressure CVD.[17] This has encouraged us to investigate Bu^t_3Al as an alternative precursor to Me_3Al for the deposition of AlN by MOCVD, and these results are presented herein.

In an effort to prevent post-growth oxidation of the AlN films, Bu^t_3Al was also used to deposit a protective Al overlayer, which provides evidence of its usefulness and versatility as a new Al source for MOCVD.

Experimental

General Techniques

AES was carried out on a Varian scanning Auger spectrometer. The atomic compositions quoted are from the bulk of the film (depth from surface >2000 Å) and were obtained by combining AES with sequential ion bombardment until comparable compositions were obtained for consecutive data

points. Film thicknesses were estimated by the time taken to sputter through the layer using Ar^+-ion bombardment.

Proton nuclear magnetic resonance (^1H NMR) data were obtained on a Bruker WM 250 spectrometer operating at 250 MHz and microanalytical data (C, H, N analysis) were provided by the Microanalytical Services Department of the University of Liverpool.

Scanning electron microscopy (SEM) was performed on a Cambridge Stereoscan 360 microscope.

Aluminium Nitride Film Growth

The reagents used were Bu^t_3Al, synthesized as described previously[17] and Bu^tNH_2. The Bu^tNH_2 was dried and deoxygenated prior to use by distillation over sodium under a nitrogen purge.

The AlN films were deposited at atmospheric pressure in a simple cold-wall horizontal quartz reactor (Electro Gas Systems Ltd) using radiant substrate heating. The substrates used were Si(111) single-crystal wafers and these were cleaned (20% nitric acid–deionized water), degreased with acetone and dried before use.

Trace oxygen and moisture were removed from the hydrogen carrier gas by passing it through a Nanochem resin purification unit. The Bu^tNH_2 was further purified during use by passage through a Nanochem purifier.

The Bu^t_3Al and Bu^tNH_2 sources were operated at room temperature (22 °C) and were mixed in a 'T-piece' at the reactor inlet. This was heated to 60 °C to prevent condensation of any adducts formed in the gas phase.

In order to prevent post-growth oxidation of the deposited AlN films, a protective Al overlayer was subsequently deposited at low pressure (15 Torr) using the Bu^t_3Al precursor alone. A full summary of growth conditions is given in Table 1.

Results and Discussion

AlN films were successfully deposited using Bu^t_3Al and Bu^tNH_2 at substrate temperatures between 500 and 600 °C. Below 500 °C, the AlN growth rate was found to be prohibitively low, whilst at temperatures >600 °C film growth was limited by severe reagent depletion. The atomic composition of the films was determined by AES and these data are summarized in Table 2. These data show that all the films have an Al:N ratio close to unity, although in film 3 nitrogen is present in slight excess.

The most obvious feature of the AES data is the significant reduction of oxygen contamination resulting from the growth of the protective Al overlayer in films 2 and 3. This strongly suggests that post-growth oxidation has occurred in the uncapped AlN film (1), and further suggests that post-growth oxidation was largely responsible for the relatively high levels of oxygen contamination (2.0–8.0 atom%) observed previously[12,14] in AlN films grown using mixtures of $Me_3Al–RNH_2$ and $Me_3Al–Me_3SiN_3$. The residual oxygen (between 0.4 and 1.3 atom%) remaining in the capped AlN films and in the Al overlayer can be attributed to trace oxygen in the relatively unsophisticated MOCVD reactor used in this study.

The uncapped AlN films were extremely hard and scratch-resistant and demonstrated specular surface morphology. Scanning electron microscopy (SEM) data for a typical uncapped AlN film grown at 500 °C on Si(111) (Fig. 1)

Table 2 Auger electron spectral analysis of AlN films grown on Si(111) using mixtures of Bu^t_3Al and Bu^tNH_2

	atomic composition (%)				
film no.	Al	N	C	O	Al:N
1 (uncapped)	41.4	39.3	6.9	10.4	1.05
2 (Al capping layer)	98.2	—	0.5	1.2	—
(AlN layer)	49.7	44.3	4.7	1.3	1.21
3 (AlN layer)	45.7	46.6	7.2	0.4	0.98

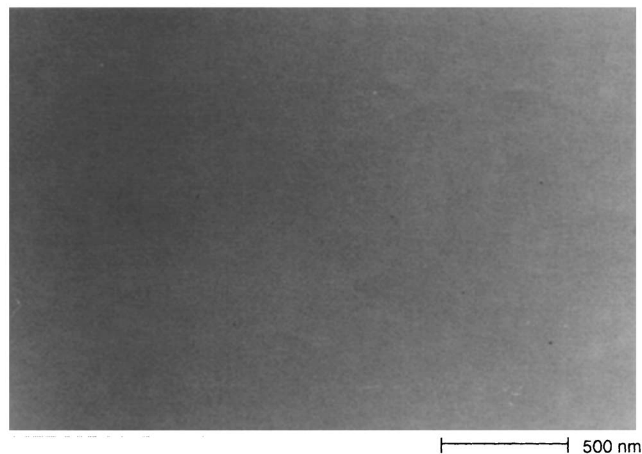

Fig. 1 Scanning electron micrograph of an AlN film grown at 500 °C on Si(111) from a $Bu^t_3Al–Bu^tNH_2$ mixture

Table 1 Growth conditions used to deposit AlN films from mixtures of Bu^t_3Al and Bu^tNH_2[a]

	run no.		
	1 (uncapped)	2 (Al capped)	3 (Al capped)
(*a*) AlN Growth (cell pressure 760 Torr)			
H_2 carrier gas flow through Bu^t_3Al (sccm)[b]	200	200	200
H_2 carrier gas flow through Bu^tNH_2 (sccm)	50	50	50
substrate temperature/°C	500	500	600
growth rate/μm h^{-1} [c]	0.5	—	—
approximate V:III ratio[d]	36	36	36
(*b*) Al capping layer (cell pressure 15 Torr)			
H_2 carrier gas flow through Bu^t_3Al (sccm)	—	50	50
substrate temperature/°C	—	400	400
duration of growth/min	—	3	1

[a] Bu^t_3Al and Bu^tNH_2 sources at 22 °C; substrates Si(111) single-crystal wafers. [b] Standard cm^3 min^{-1}. [c] Estimated from AES sputter time. [d] Based on an estimated Bu^t_3Al vapour pressure of *ca.* 2 Torr at 22 °C (vapour pressure Bu^tNH_2 = 340 Torr at 25 °C).

indicate that the film is amorphous and structureless, with no grains evident on a 500 nm scale.

A further significant feature to emerge from the AES data (Table 2) is that, despite the use of Bu^t_3Al as an alternative to Me_3Al, the AlN films still contain residual carbon at a level of between 5 and 7 atom%. These carbon levels are similar to those observed in AlN films grown using Me_3Al–Bu^tNH_2 mixtures ($C \approx 3$–9 atom%),[12] which indicates that Bu^t_3Al offers no significant advantage over Me_3Al for AlN growth from R_3Al–RNH_2 mixtures. This is a surprising result in view of the marked contrast in the purity of Al films deposited at 450 °C from Bu^t_3Al ($C \approx 0.2$–0.5 atom%)[17] compared with Al films deposited at similar substrate temperatures from the methyl-based precursors Me_3Al[15] or $Me_2AlH(NMe_3)$[18] in which carbon levels of up to 39 atom% have been observed. This suggests that the decomposition of the [Al–R] group may not be the only factor controlling carbon incorporation in AlN films grown from R_3Al–RNH_2 mixtures. The decomposition of the organic radical of the primary alkylamine (RNH_2) may also play a role which suggests that carbon incorporation may vary according to the nature and pyrolysis characteristics of the RNH_2 precursor. This proposal is supported by the greatly increased carbon levels (14–17 atom%) observed in AlN films grown using Me_3Al–Pr^iNH_2 compared with films grown from Me_3Al–Bu^tNH_2 mixtures.[12] In addition, the carbon contamination was shown to increase with increasing V : III ratios, in marked contrast to the trend generally observed in the growth of GaAs and AlGaAs by MOVPE;[16] this provides further evidence that the RNH_2 precursor may play a critical role in carbon contamination.

Information concerning the possible growth mechanism has been obtained by the *ex-situ* addition of Bu^tNH_2 (12.9 g, 0.17 mol) to $Bu_3{}^tAl$ (16.0 g, 0.08 mol) in dry pentane solution (25 cm^3). Removal of volatiles *in vacuo* left a colourless crystalline product which was highly soluble in benzene. This was shown to be the 1:1 adduct, $[Bu^t_3Al(NH_2Bu^t)]$ by ^1H NMR data and elemental microanalysis (Table 3).

The $[Bu^t_3Al(NH_2Bu^t)]$ adduct was observed to melt at 70–80 °C, and at 115 °C a gas was evolved. Further heating of the compound at 115–120 °C for 30 min led to a white powder which was only sparingly soluble in benzene. This precluded meaningful ^1H NMR data and elemental microanalysis (Table 3) was also inclusive, although these data suggest that the decomposition product may have the molecular formula $[Bu^t_2Al(NHBu^t)]_n$ ($n = 2$, 3). The low solubility of this compound in benzene is consistent with the proposed oligomeric structure.

Table 3 Analytical data for 1:1 adduct formed from the reaction between Bu^t_3Al and Bu^tNH_2

^1H NMR data ([$^2H_6$]benzene)	δ		
	0.85 (s, 9 H, N-Bu^t) 1.25 (s, 27 H, Bu^t-Al) 2.5 (s, 2 H, N-H)		
elemental microanalysis	C (%)	H (%)	N (%)
found	70.74	14.49	4.83
calcd. for $[Bu^t_3Al(NH_2Bu^t)]$	70.77	14.14	5.16
elemental microanalysis of decomposition product^a	C (%)	H (%)	N (%)
found	66.67	13.65	5.74
calcd. for $[Bu^t_2Al(NHBu^t)]_n$	67.54	13.25	6.56

^{a}Formed by heating the 1:1 adduct at 115–120 °C for 30 min. Decomposition product essentially insoluble in [$^2H_6$]benzene.

During the growth of AlN from Bu^t_3Al–Bu^tNH_2 mixtures, a crystalline deposit was observed to form at the reactor inlet if this was left unheated, and it is likely that this is the $[Bu^t_3Al(NH_2Bu^t)]$ adduct. Previous studies,[19,20] which are supported by the present work, have shown that such adducts readily form elimination products of the type $[R_2AlNHR']_n$ on heating, and therefore such species may be expected to form in the hot boundary layer adjacent to the substrate. Subsequent pyrolysis of the directly bonded species $[Bu^t_2AlNHBu^t]_n$ on or near the substrate surface leads to the deposition of AlN. This proposal is strongly supported by the recently reported growth of AlN by vacuum CVD using $[Me_2AlNHR]_2$ ($R = Pr^i$, Bu^t).[13]

The level of carbon contamination in AlN films deposited from $[R_2AlNHR]_2$ precursors, which have been either presynthesized or formed *in situ* in the gas phase, will depend strongly on the mechanism by which the alkyl radicals bound to Al or N are desorbed from the growth surface. For Pr^i and Bu^t radicals there is a ready desorption route *via* the β-hydride elimination of alkene;[21] however, the continued presence of carbon in AlN grown from Bu^t_3Al–Bu^tNH_2 mixtures indicates that some surface decomposition of the Bu^t radical has occurred. The decomposition of the Bu^t radical is likely to be promoted by the presence of Al on or near the growth surface.[21] This may lead to methyl abstraction from the Bu^t radical, leading to surface-adsorbed methyl radicals which subsequently decompose to deposit carbon.

The mechanism of AlN deposition from $[R_2AlNHR']_n$ species may be similar to that occurring in the growth of GaAs from the single-source molecule $[Me_2GaAsBu^t_2]_2$.[22] In these studies it was proposed that the facile β-hydride elimination of alkene from the bulky and sterically hindered *tert*-butyl group leads to the formation of a strong intramolecular III–V bond during pyrolysis which facilitates the growth of stoichiometric GaAs.

The precise mechanism of AlN deposition from R_3Al–RNH_2 mixtures has not been established. However, the low growth temperatures (400–600 °C) and low V : III ratios used in this, and previous[12] studies, compared with those used for Me_3Al–NH_3 combinations, suggests that 'directly bonded' species of the type $[R_2AlNHR]_2$ are the active precursors to AlN deposition.

Conclusions

AlN films have been deposited by atmospheric-pressure MOCVD using Bu^t_3Al in combination with Bu^tNH_2. Growth rates of 0.5 μm h^{-1} were obtained at substrate temperatures of 500 °C. The use of a protective Al overlayer, deposited from Bu^t_3Al, was shown to lead to a significant reduction in oxygen contamination of the AlN films. However, residual carbon was present at levels of between 5 and 7 atom%, and it is suggested that the decomposition of the organic radical in Bu^tNH_2 may play a role in carbon incorporation.

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