

# Spectroscopic Study of AlN Film Formation by the Sequential Reaction of Ammonia and Trimethylaluminum on Alumina

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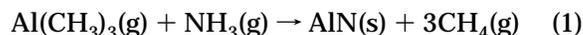
Aluminum nitride is grown on an alumina substrate by several sequential exposures to trimethyl aluminum and ammonia. Broad similarities are evident between the chemistry in this case and that found for the reaction between trimethylaluminum and water except that temperatures in excess of 500 K are required to form AlN layers whereas alumina is formed at room temperature. It is found, using infrared spectroscopy to examine the surface species formed during repeated sequential adsorption of trimethylaluminum and ammonia, that trimethylaluminum initially reacts to form an adsorbed dimethylaluminum species. This reacts with ammonia to initially form a Lewis acid–base adduct which subsequently reacts to form bridging and terminal NH<sub>2</sub> species. The first methyl group in the adsorbed species is found to be more reactive than the second, an effect that was also noted for reactions with water. The ultimate formation of AlN films by several sequential exposures to trimethylaluminum and ammonia is confirmed using X-ray photoelectron spectroscopy and gravimetrically by weighing the samples after several trimethylaluminum and ammonia exposure cycles.

## Introduction

Organometallic chemical vapor deposition (OMCVD) provides a useful strategy for growing thin, inorganic films, particularly of III–V compounds, by the reaction of volatile precursors (in this case a metal alkyl and a nonmetal hydride) to deposit the film and evolve methane.

It has been demonstrated in previous work<sup>1</sup> that it is possible to grow alumina films on an alumina substrate by several sequential applications of trimethylaluminum (TMA) and water at room temperature; a film of ~1 Å thickness on average being deposited in each TMA + water cycle. The reaction was shown to be initiated by the formation of a dimethylaluminum (Al(CH<sub>3</sub>)<sub>2</sub>(ads)) surface species at 300 K by reaction of trimethylaluminum with hydroxyl groups on the alumina surface. Alumina formation proceeds by a sequential reaction of the remaining methyl groups with water, the first methyl group being significantly more labile than the second. Note that this growth strategy is similar to that known as atomic layer epitaxy (ALE) where thin films are grown by repeated exposure of a heated substrate to the reactants.<sup>2–7</sup>

Here a similar reaction between trimethylaluminum and ammonia has been used to grow aluminum nitride films:



In this case, an AlN film several layers thick is grown by sequentially adsorbing trimethyl aluminum and ammonia. The reactivity of TMA-derived surface species with ammonia is significantly lower than for the corresponding alumina formation reaction at room temperature and proceeds at a significant rate only at >500 K (see below). This observation is in accord with recent XPS data which showed the formation of an aluminum nitride monolayer by reaction of a TMA-derived overlayer on alumina only after heating to ~600 K.<sup>8,10</sup>

Results in the following for reaction between ammonia and a dimethyl aluminum monolayer in this paper are in good agreement with those for similar experiments by other groups<sup>8,9</sup> and also for a co-adsorbed TMA + NH<sub>3</sub> layer.<sup>10</sup> These experiments are extended to examining the growth chemistry of thin films several layers in thickness by repeated sequential exposure of the surface to up to four deposition cycles of TMA and ammonia.

## Experimental Methods

The apparatus used for these experiments has been described in detail in a previous publication.<sup>1</sup> Briefly, however, aluminum oxide was made in ultrahigh vacuum (UHV) by oxidation of a clean aluminum foil (773 K, 3 × 10<sup>-6</sup> Torr of oxygen for 180 s) and hydroxylation of the surface has been

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described previously.<sup>1</sup> The sample was mounted to a carousel geometry manipulator and cleaned using a protocol described by Paul and Hoffman.<sup>11</sup> Auger spectra were collected using a retarding-field analyzer (RFA) using a 2 kV electron beam.

Transmission infrared spectra were obtained using an evacuable cell described elsewhere<sup>1</sup> and were collected using a MIDAC FTIR spectrometer with a globar source and a DTGS detector operating at 4 cm<sup>-1</sup> resolution for 400 scans. Self-supported, pressed  $\gamma$ -alumina pellets (Aksochimie, BET surface area = 187 m<sup>2</sup>/g) ~0.1 mm-thick were prepared to be used as substrates.<sup>1</sup> Gasses were introduced into the UHV chamber by means of a variable leak valve and into the infrared cell via a glass stopcock.

The TMA (Aldrich Chemicals, 97%) was transferred to a glass vial and out-gassed using repeated freeze-pump-thaw cycles. The ammonia (Matheson, 99.9%) was transferred from the cylinder to a glass bulb and purified by means of several bulb-to-bulb distillations between a dry ice/acetone mixture and liquid nitrogen. D<sub>2</sub>O was placed into a glass vial via a septum by means of a syringe and also purified by repeated freeze-pump-thaw cycles. Ammonia, water, and trimethylaluminum were introduced into the infrared cell directly from the bulbs, and the ammonia was cooled to 195 K by immersing it in a mixture of dry ice + acetone. The ammonia vapor pressure under these conditions is 43.5 Torr.

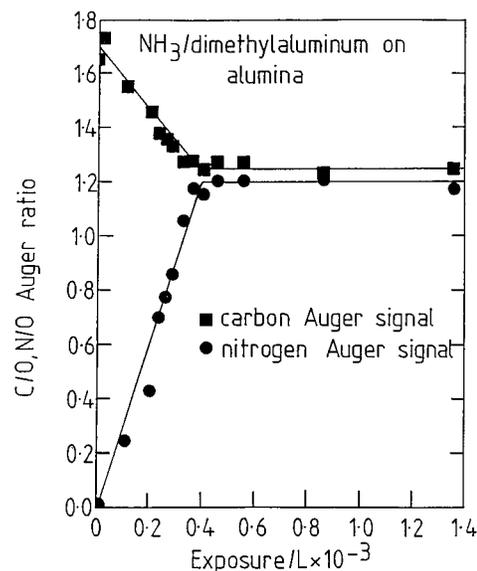
XPS data were collected using a VG-ESCALAB photoelectron spectrometer using nonmonochromated Mg K $\alpha$  radiation and a 100 mm-radius hemispherical electron analyzer and photoelectrons were detected using a channeltron. Spectra were collected using an analyzer pass energy of 10 eV and a step size of 0.1 eV. Peak positions were calibrated using the aluminum peak of aluminum oxide referenced at 74 eV binding energy<sup>12</sup> which yielded a C 1s binding energy due to background carbon at the generally accepted value of 286.4 eV.<sup>13</sup>

The self-supported alumina pellets were removed from the IR cell in a glovebag under a nitrogen atmosphere for XPS analysis and pulverized with a mortar and pestle. Still under nitrogen, the powder sample was pressed onto an indium foil which in turn was affixed to the spectrometer's sample chuck. The chuck was then transferred to the analysis chamber, again using the glovebag, so that intervening exposure to air was kept to a minimum.

Gravimetric analysis of the samples was carried out by placing alumina powder in a glass tube. Glass wool was placed into the neck of the tube to avoid any loss of alumina powder during evacuation of the cell. The alumina was outgassed in vacuo at 400 K and initially exposed to TMA at room temperature. To ensure that the sample was saturated with TMA, the cell was then evacuated and reexposed to fresh TMA twice more. This procedure resulted in no further detectable change in mass. The sample was then exposed to water at 300 K to form alumina and again, to ensure complete reaction, the cell was evacuated and reexposed to fresh water vapor twice more. This procedure was repeated a total of four times and the net mass change of the sample measured. Similar gravimetric experiments were performed for AlN layers using an identical protocol, but in this case the sample was reacted sequentially with TMA and ammonia at 573 K.

## Results

It has been shown<sup>1</sup> that TMA adsorbs onto a hydroxylated alumina surface in ultrahigh vacuum to form dimethylaluminum species ((CH<sub>3</sub>)<sub>2</sub>Al(ads)). This is completely removed by water at room temperature in two distinct rates; the first methyl group in the adsorbed dimethyl species reacting more rapidly (by a factor of 30) than the second.<sup>1</sup> Figure 1 shows results of a similar experiment for reaction of ammonia with TMA-derived



**Figure 1.** Plots of the carbon and nitrogen Auger intensities as a function of ammonia exposure in ultrahigh vacuum to an hydroxylated alumina surface that had been exposed to TMA at room temperature.

surface species on planar alumina carried out at room temperature where surface carbon and nitrogen concentrations are monitored using Auger spectroscopy following exposure to ammonia. The carbon Auger signal intensity (KLL transition at 273 eV kinetic energy) decreases as a function of ammonia exposure while the nitrogen Auger signal (KLL Auger transition; 381 eV kinetic energy) increases concomitantly. However, in contrast to the behavior with water, the surface carbon is not completely removed by reaction with ammonia at 300 K, implying a lower reactivity of adsorbed TMA with ammonia than with water. The carbon Auger signal decreases by  $25 \pm 3\%$ ; only a quarter of the surface methyl groups are removed. A corresponding increase in the nitrogen signal is also noted which is  $2.6 \pm 0.1$  times larger than the decrease in carbon Auger signal. Using standard Auger sensitivities,<sup>14</sup> this yields an N:C stoichiometric ratio for the increase in amount of nitrogen to the decrease in the amount of carbon of ~1.6 after exposure of the TMA-covered surface to ammonia in ultrahigh vacuum. That is, about 1.6 nitrogens are added for each carbon removed.

Figure 2 shows the results of a similar room-temperature ammonia exposure experiment, in this case, carried out using high-surface-area  $\gamma$ -alumina which had been partially dehydroxylated by heating under vacuum at 400 K for 2 h leading to a surface hydroxyl coverage of  $\sim 11 \times 10^{14}$  OH/cm<sup>2</sup>.<sup>15</sup> This figure displays the methyl bending mode at  $\sim 1217$  cm<sup>-1</sup> following initial exposure to TMA and illustrates the changes caused by exposure to ammonia at 300 and 423 K. The behavior of the remainder of the spectrum is in good agreement with that found by other workers.<sup>1,8-10</sup> This peak is not only reduced in intensity but also narrows and is shifted to a frequency of 1212 cm<sup>-1</sup> as ammonia

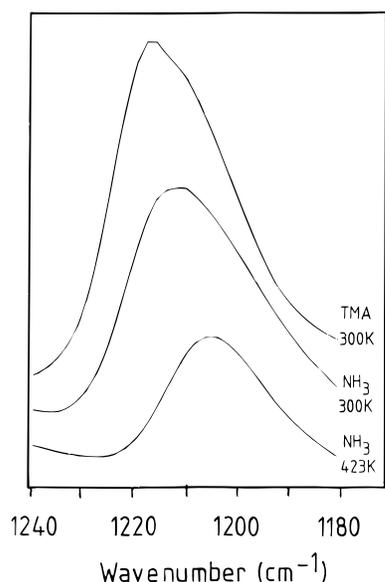
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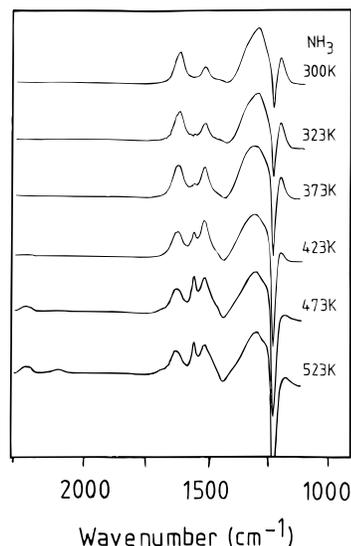


**Figure 2.** Methyl bending spectral region of TMA adsorbed at 300 K on high-surface-area alumina pretreated at 400 K and following exposure to ammonia at 300 and 423 K, respectively.

is added. This narrowing and shift in peak position has been shown to be due to the conversion of dimethylaluminum at the surface into a monomethylaluminum species,<sup>16</sup> indicating the partial removal of the first methyl groups by reaction between ammonia and the surface at 300 K and the formation of monomethylaluminum at higher temperatures (423 K). In addition, exposure of the TMA-treated alumina surface to ammonia at 300 K results in the formation of methane as identified by IR. However this production of methane is small compared to that of the corresponding reaction with water.

Figure 3 displays infrared difference spectra of TMA-saturated  $\gamma$ -alumina that has been reacted with ammonia (43.5 Torr) for 10 min at various temperatures. The reaction temperature is indicated adjacent to each spectrum, which were obtained by subtracting the spectrum for TMA-covered, hydroxylated alumina from each of them, and is in excellent agreement with those found by others.<sup>8-10</sup> The N-H stretching region (from 3100 to 3500  $\text{cm}^{-1}$ ), although normally valuable in determining molecular structures,<sup>17-19</sup> is not of much use in this investigation because it is obscured by the hydroxyl stretching feature, which makes it difficult to reliably identify peaks or obtain detailed information regarding the nature of the adsorbed species. The peak assignments in the spectra are displayed in Table 1 and are discussed further below.

Initial exposure of the TMA-covered surface to ammonia at 300 K (Figure 3) results in the appearance of peaks at 1614 and 1286  $\text{cm}^{-1}$ , associated with the adduct, the formation of some bridging amino species indicated by a peak at 1512  $\text{cm}^{-1}$ , and a decrease in intensity of the methyl bending modes as shown in Figure 2. Further heating to  $\sim 373$  K shows that the



**Figure 3.** Series of difference infrared spectra of  $\gamma$ -alumina pretreated at 400 K and saturated with TMA and then exposed to ammonia (43.5 Torr) for 10 min and annealed in the presence of ammonia at various temperatures. The annealing temperatures are displayed adjacent to the corresponding spectrum. All spectra were collected after 10 min evacuation following exposure to ammonia.

amount of adduct remains unchanged while the bridging amino group peaks grow by  $\sim 20\%$ . As the sample is heated further to a temperature of 423 K, a new peak begins to emerge at 1552  $\text{cm}^{-1}$ . This peak continues to grow further at higher reaction temperatures until all of the intensity due to methyl bending modes is consumed so that annealing under ammonia at 523 K results in *complete* removal of the surface methyl groups with methane being detected in the gas phase. The negative excursion at 1217  $\text{cm}^{-1}$  corresponds to complete absence of methyl bending modes in the original infrared spectrum.

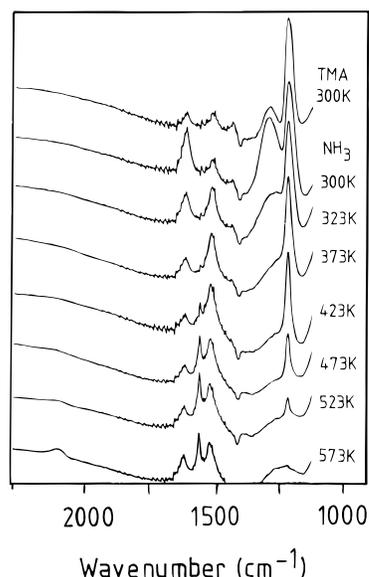
It is known<sup>16</sup> that heating  $\gamma$ -alumina that has been partially dehydroxylated and saturated with TMA results in the same overall effect on the methyl bending modes, i.e., reduction in the intensity and change in peak shape, due to reaction with surface hydroxyl species, as observed when heating under ammonia.<sup>16</sup> To investigate the effect of the level of hydroxylation on the reaction with alumina, a new pellet was prepared and annealed at 873 K for 12 h under vacuum, resulting in a much diminished surface hydroxyl concentration of  $\sim 3 \times 10^{14}$  OH/ $\text{cm}^2$ .<sup>15</sup> This sample was treated with TMA and then ammonia in the same manner as the pellet that was dehydroxylated at 400 K, and the resulting spectra are shown in Figure 4 and displayed as a function of reaction temperature. The overall spectral changes are identical to those observed for the 400 K dehydroxylated pellet with the exception of a marked decrease in intensity of the 1614 and 1286  $\text{cm}^{-1}$  peaks (associated with the adduct) as the annealing temperature increases. When comparing the thermal stability of the dimethylaluminum species in the presence of ammonia on dehydroxylated alumina (Figure 3) and in the absence of ammonia gas on hydroxylated alumina,<sup>16</sup> it is observed that the temperature range over which the methyl bending modes are removed is similar in both cases. This indicates that, when the  $\gamma$ -alumina pellet is fully dehydroxylated, there is competition between hydroxyls groups on the surface and

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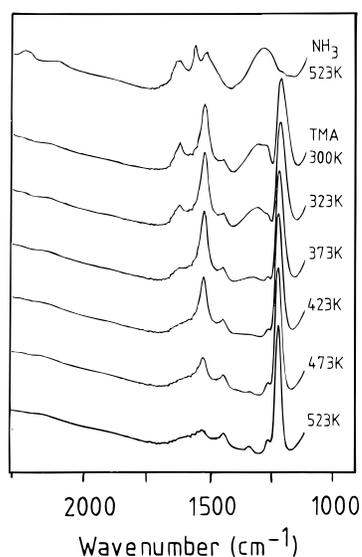
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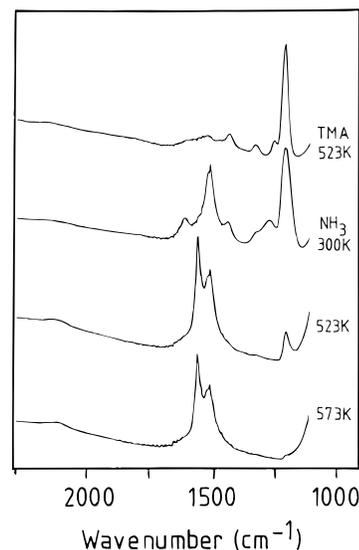
**Figure 4.** Series of infrared spectra of  $\gamma$ -alumina pretreated at 873 K saturated with TMA, then exposed to ammonia (43.5 Torr) for 10 min, and annealed in the presence of ammonia at various temperatures. The annealing temperatures are displayed adjacent to the corresponding spectrum. All spectra were collected after 10 min evacuation following exposure to ammonia.



**Figure 5.** Infrared spectra following a second exposure to TMA. The top spectrum is that of the sample taken, after heating at 523 K in ammonia, from Figure 3. This surface was exposed to TMA at various temperatures which are displayed adjacent to the corresponding spectrum.

the complexed ammonia for reaction with methyl groups of the surface dimethyl aluminum.

The partially dehydroxylated (400 K) pellet was subject to a *second* cycle of TMA(g)/NH<sub>3</sub>(g) treatment. Thus, further reactions are carried out now not on an alumina substrate but on a previously deposited (AlN) film. The infrared spectra following this second cycle are presented in Figures 5 and 6. After completion of the C-H removal by heating the sample under ammonia at 525 K (see top spectrum of Figure 5), the surface is reexposed to TMA at 300 K (Figure 5). Subsequent TMA exposures were carried out at increasing temperatures, and Figure 5 displays the resulting spectra where the reaction temperatures are marked



**Figure 6.** Infrared spectra following a second exposure to NH<sub>3</sub>(g). The top spectrum is that obtained after heating at 523 K in TMA, taken from figure 5. This surface was exposed to NH<sub>3</sub>(g) at various temperatures which are displayed adjacent to the corresponding spectrum.

adjacent to the corresponding spectrum. Figure 6 displays the last spectrum of Figure 5 (following TMA treatment at 523 K) for reference and documents subsequent changes in that spectrum as the sample is reexposed to ammonia at 300, 523, and 573 K. Two more TMA/NH<sub>3</sub> cycles were carried out (resulting in a total of four NH<sub>3</sub>/TMA cycles) by sequentially exposing TMA and ammonia at 573 K. The chemistry of these cycles were identical to that of the second cycle (depicted in Figures 5 and 6) as observed by FTIR so that the chemistry on the initially formed AlN layer is identical with that on subsequent layers.

Finally, it is noted that, at a temperature of 523 K, a small peak begins to develop at 2148 cm<sup>-1</sup> (which is initially detectable at a reaction temperature of 473 K) and grows as the temperature increases. At 523 K, another peak begins to grow at 2108 cm<sup>-1</sup>. The latter peak, upon annealing rapidly to 973 K, becomes the dominant feature of the spectrum. After this process, there is no evidence of either the 1512 or of the 1552 cm<sup>-1</sup> peaks. The peak at 2108 cm<sup>-1</sup> is tentatively assigned to an Al-N=N group,<sup>20,21</sup> although it can also possibly be attributed to C≡N vibrations.<sup>20</sup>

The alumina dehydroxylated at 873 K was subject to the same procedure and the chemistry after the second cycle of TMA and ammonia is no different from that of the sample dehydroxylated at 400 K.

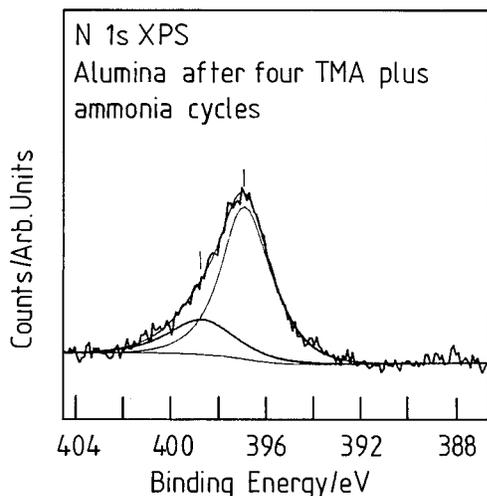
The formation of AlN is usually indicated in the IR spectrum by the presence of peaks at ~650 or at ~690 cm<sup>-1</sup> due to amorphous and ordered AlN respectively.<sup>22,23</sup> The corresponding one-phonon peak appears at ~340 cm<sup>-1</sup>,<sup>22,23</sup> out of the range of the infrared spectrometer. However, no AlN peaks are detected even after four cycles of TMA/ammonia in the range 630–700 cm<sup>-1</sup>. The inability to detect AlN peaks with the

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**Figure 7.** X-ray photoelectron spectrum (XPS) displayed between 386 and 404 eV corresponding to the 1s orbital of nitrogen. The sample was obtained from the powder of the pellet pretreated at 400 K used in the FTIR studies following four cycles of TMA/NH<sub>3</sub> at 523 K. Curve fitting reveals two peaks with binding energies of 396.8 and 398.7 eV.

IR spectrometer may possibly be explained by noting that  $\gamma$ -alumina shows strong IR adsorption due to its lattice modes in the region 400–1000 cm<sup>-1</sup>. The formation of AlN is however confirmed using XPS. The pressed pellets used for FTIR studies and which had been subject to four sequential TMA and ammonia cycles at 573 K are first pulverized and then transferred to the XPS analysis chamber. Shown in Figure 7 is the N(1s) region of the spectrum. The binding energies are calibrated by internally referencing to the Al(2p) peak at 74 eV,<sup>12</sup> yielding peaks at 396.8 ± 0.2 and 398.7 ± 0.2 eV binding energy (BE). The components of the spectra were fit using a standard least-squares package. The peak at 398.7 ± 0.2 eV BE is assigned to an Al–N=N species based on the XPS of organic polymers.<sup>24</sup> Note that the presence of Al–N=N is in agreement with the FTIR observation of a peak at ~2100 cm<sup>-1</sup> referred to above. The binding energy of the larger peak centered at 396.8 ± 0.2 eV is in good agreement with values in the literature for AlN (ref 25 gives 396.8 eV; ref 26 gives 396.7 eV). The formation of AlN is also confirmed in the infrared experiments by exposing a surface that has been subject to several TMA and ammonia cycles to water (in this case D<sub>2</sub>O). Aluminum nitride can react slowly with water<sup>27</sup> and forms alumina and ammonia. When this sample is exposed to D<sub>2</sub>O, copious amounts of ND<sub>3</sub> are formed. The amount of ammonia evolved for reaction of an alumina powder sample coated with AlN was measured. In this case, 40.8 mg of alumina powder was placed in a glass tube (total volume 0.203 L), evacuated to ~1 × 10<sup>-7</sup> Torr, and partially dehydroxylated at 400 K. The sample was then reacted sequentially in ammonia and trimethyl-aluminum four times as described above to form aluminum nitride. The coated alumina sample was then

exposed to water which infrared spectroscopy shows evolved substantial amounts of ammonia (see above). The excess water was removed by placing a coldfinger attached to the tube in an ice/salt cold bath (at a temperature of 255 K) and the residual pressure measured by means of a capacitance manometer attached to the tube. The final pressure reading (9.9 ± 0.5 Torr) allows the amount of AlN that reacts with water to be calculated and yields and estimated layer thickness of 2.0 ± 0.1 Å. This leads to an average increase in film thickness per cycle of ~0.5 Å. Note, however, that a portion of the ammonia is likely to dissolve in the water leading to an underestimate of the film thickness.

The gravimetric experiments outlined above were also carried out to determine whether a film of AlN had indeed been formed by sequential TMA + NH<sub>3</sub> cycles. The procedure was initially tested for alumina films grown from TMA and water where it has been shown that a film of ~1 Å average thickness is deposited in each cycle.<sup>1</sup> The average film thickness  $t$  is calculated from

$$t = \frac{1}{\rho(\text{Al}_2\text{O}_3)A} \frac{\Delta m}{m_0}$$

where  $\rho(\text{Al}_2\text{O}_3)$  is the alumina density (3.97 g/cm<sup>3</sup> (ref 27)) and  $A$  the specific alumina surface area (187 m<sup>2</sup>/g).  $m_0$  is the initial mass of the pellet and  $\Delta m$  the mass change per TMA + H<sub>2</sub>O deposition cycle. For  $m_0 = 43$  mg,  $\Delta m = 2.5 \pm 0.2$  mg/cycle and substitution into the above equation yields  $t = 0.75 \pm 0.06$  Å/cycle, a value in reasonable agreement with previous measurements.<sup>1</sup> This value is similar to that found for ALE growth of alumina on planar substrates where a film of ~550 Å grows after 500 deposition cycles.<sup>28</sup>

Similar experiments were carried out for the growth of AlN films from TMA and ammonia yielding  $t = 0.73 \pm 0.03$  Å/cycle. It was also confirmed, by weighing the sample after each exposure cycle, that the mass increased by this amount after *each* cycle.

## Discussion

**Assignments of the IR Bands.** Previous work has shown that ammonia reacts with adsorbed dimethyl-aluminum to form an acid–base adduct (H<sub>3</sub>N→Al)<sup>29</sup> and a bridging NH<sub>2</sub> (Al–NH<sub>2</sub>→Al) species.<sup>30,31</sup> Figure 3 shows the effect of heating a TMA-covered alumina surface, which has been partially dehydroxylated at 400 K, in ammonia. At an annealing temperature of 423 K, this shows the saturation of the 1512 cm<sup>-1</sup> peak and the clear appearance of a peak at 1552 cm<sup>-1</sup>. The latter continues to grow until all the methyl groups are removed. The 1552 cm<sup>-1</sup> peak has been ascribed by some workers<sup>32</sup> to a three-coordinated nitrogen of a terminal NH<sub>2</sub>. The assignment, however, is based on the work done in ref 33 which identifies it as a Si–NH<sub>2</sub>

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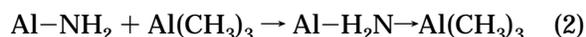
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**Table 1. Peak Assignments for Surface Species Formed by Reaction of Trimethylaluminum and Ammonia on Alumina**

frequencies/cm <sup>-1</sup>	species
1614, 1286	adduct: H <sub>3</sub> N→Al
1512	bridging amino
1552	terminal amino

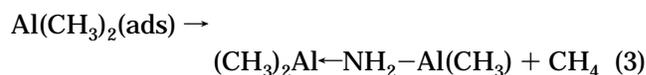
and not as Al–NH<sub>2</sub>. Insights into the origin of the 1512 and 1552 cm<sup>-1</sup> features can be obtained from the data of Figure 5 which show that TMA reacts at 300 K very quickly with the species responsible for the peak at 1552 cm<sup>-1</sup>, reducing its intensity to zero. At the same time, the intensity of the peak at 1512 cm<sup>-1</sup> more than doubles. These simultaneous changes suggest that the first species is easily converted to the latter upon TMA exposure at 300 K. Worthy of note is the lack of reactivity toward TMA of the species responsible for the band at 1512 cm<sup>-1</sup>; it requires heating under TMA to 523 K before it is fully consumed. These simultaneous changes have been assigned to the reactive conversion of a terminal amino group to a bridging amino<sup>30</sup> which, being saturated, shows little reactivity to TMA. The difficulty with such an assignment comes from stoichiometry, which requires a methyl group to be eliminated by reaction with hydrogen yielding, not a bridging NH<sub>2</sub>, but a bridging NH. The formation of a bridging secondary amine Al–NH–Al (imine) by reaction of a NH<sub>2</sub> with a neighboring methyl group to liberate methane would seem to account for a first step in the growth of an AlN film. Unfortunately, it is impossible in our system to determine from FTIR alone the presence of a secondary amine since this species exhibits a very weak bending mode<sup>34</sup> and, although secondary amines display a strong single peak in the 3400–3100 cm<sup>-1</sup> range,<sup>20</sup> they are obscured by the simultaneous presence of NH<sub>2</sub> species and hydrogen-bonded hydroxyls. An alternative explanation for the conversion of a terminal NH<sub>2</sub> to a bridging species on TMA exposure (Figure 5) is that TMA adsorption forms an acid–base adduct with terminal NH<sub>2</sub> species:



This postulate effectively rationalizes the spectroscopic changes exhibited by dosing an ammonia-covered surface with TMA so that the following peak assignments are therefore made on this basis: the 1614 and 1286 cm<sup>-1</sup> features are assigned to an adduct (H<sub>3</sub>N→Al); the 1512 cm<sup>-1</sup> feature to a bridging NH<sub>2</sub> and the 1552 cm<sup>-1</sup> peak to a terminal species and are summarized in Table 1. The relative weakness of the imine mode probably renders this undetectable in infrared.

**Chemistry of Trimethylaluminum and Ammonia on Alumina.** It is evident from the XPS data (Figure 7), from reactions with D<sub>2</sub>O, and from gravimetric analyses that aluminum nitride films several layers in thickness can be grown on  $\gamma$ -alumina by the repeated sequential addition of TMA and ammonia. Growth takes place in a similar fashion to that observed for aluminum oxide formed by the reaction of TMA and water described elsewhere<sup>1</sup> but where alumina is formed by reaction at room temperature while aluminum nitride grows by reaction with ammonia at 573 K.

Figure 3 displays the infrared spectra collected following exposure of ammonia to an alumina surface covered with dimethylaluminum. It shows the changes in intensities of the peaks at 1614 and 1286 cm<sup>-1</sup> (due to the adduct), at 1512 (due to bridging NH<sub>2</sub>), and 1552 cm<sup>-1</sup> (due to terminal NH<sub>2</sub> groups) and at 1212 cm<sup>-1</sup> (due to methyl wagging modes) at temperatures up to 373 K. These results indicate an initial formation of an acid–base adduct between surface dimethylaluminum and ammonia and the initial appearance of peaks due to bridging NH<sub>2</sub> species. This information, in conjunction with the observed 25% decrease in the C KLL Auger intensity, and the relatively small amount of methane that is formed compared to reaction with water suggests that the initial reaction on the surface proceeds as:



The nitrogen-increase to carbon-decrease Auger intensity ratio is  $2.6 \pm 0.1$  and, using standard Auger sensitivities,<sup>14</sup> yields an N:C stoichiometric ratio of  $\sim 1.6$ . However, the reaction depicted in eq 3 suggests that nitrogen-increase to carbon-decrease stoichiometry should yield a 1:1 ratio as oppose to the experimentally measured value of  $\sim 1.6$ . This implies that, in addition to the formation of bridging amines, some ammonia can coordinate to aluminum forming an acid–base adduct. These species give rise to the observed 1512 cm<sup>-1</sup> peak for the bridging amine and 1614 and 1286 cm<sup>-1</sup> features for the adduct.

Further heating of dimethylaluminum species on alumina (Figure 3) or on a previously deposited film (Figure 6) to 373 K in the presence of ammonia results in additional growth and ultimate saturation of the 1512 cm<sup>-1</sup> peak (bridging NH<sub>2</sub>) and a slight further diminution of the intensity of the methyl bending modes (1217 cm<sup>-1</sup>) connoting completion of the chemistry indicated by eq 3 on the high-surface-area sample corresponding to the Auger data obtained in ultrahigh vacuum (Figure 1).

A further rapid diminution in intensity of the 1217 cm<sup>-1</sup> methyl stretching peak is noted on warming to above 423 K, and the adduct concentration decreases and Al–NH<sub>2</sub> species start to appear (1552 cm<sup>-1</sup> peak). A detailed examination of the methyl stretching region (Figure 2) indicates that monomethylaluminum species predominate on this surface under these conditions.<sup>4</sup> This suggests that the dimethylaluminum moiety shown in eq 3 may further react with ammonia as

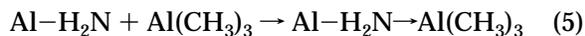


In addition, since AlN is finally produced (Figure 7), bridging NH<sub>2</sub> species may also react with methyl groups to form NH species. Curiously, however, there is only a slight decrease in intensity of the peak associated with this species (at 1512 cm<sup>-1</sup>). This may mean that, as existing bridging amino groups are consumed, others are formed.<sup>8–10</sup>

Film growth can be extended by the addition of further TMA to a sample that has been heated to 573 K in ammonia. TMA adsorption at 300 K results in terminal groups converting to bridging species (Figure 5). This effect has been ascribed above to a direct

(34) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Wiley: London, 1960; p 248.

coordination of TMA to a terminal  $\text{NH}_2$ :



which suggests that the initial reaction of TMA with terminal  $\text{NH}_2$  species at the surface is analogous to that found for the reaction with ammonia and adsorbed TMA-derived species both of which react via acid-base adduct formation. Slight heating to  $\sim 373$  K shows a preferential reaction of methyl groups with remaining  $\text{Al-NH}_3$  adduct since peaks at 1614 and 1286  $\text{cm}^{-1}$  decrease in intensity while the 1512  $\text{cm}^{-1}$  peak remains approximately constant in intensity. In addition, the methyl bending mode narrows and shifts slightly indicating reaction with methyl species in TMA.<sup>16</sup> Concomitant formation of methane detected by infrared corroborates this view. Further heating of the sample in an ambient pressure of TMA to above  $\sim 400$  K results in a decrease in intensity of the 1552  $\text{cm}^{-1}$  mode indicating TMA reaction with terminal  $\text{NH}_2$  species. This must result in the formation of  $\text{NH}$  species which are essentially undetectable in infrared due to their small cross section. Heating to  $> 500$  K results in a surface that consists primarily of surface methyl groups and the almost complete removal of any nitrogen-containing surface species.

The behavior found here is in good agreement with that of triorganoaluminum compounds when they react with ammonia and proton-bearing amines.<sup>35</sup> The first alkane molecule is readily lost, commonly at or slightly above ambient temperature, and the second alkane molecule is eliminated at higher temperatures. The formation of a more highly associated imide is most often not complete until the temperature reaches 473 K.

Addition of ammonia to this AlN surface (Figure 6) results in essentially identical chemistry as described above, leading to the complete removal of surface methyl groups by heating to  $\sim 600$  K in ammonia and the presence of bridging and terminal  $\text{NH}_2$  groups. This sample can be exposed to TMA which results in essentially identical spectral changes as shown in Figure 5. The surface can therefore be repeatedly sequentially heated in ammonia and trimethylaluminum to deposit a film of aluminum nitride several layers in thickness. The formation of an AlN film is clearly demonstrated by the XPS from the data shown in Figure 7 which is in good agreement with the spectrum of a monolayer of AlN formed by reaction of ammonia with TMA-derived surface species.<sup>8-10</sup> Additional evidence is provided by reaction of this layer with  $\text{D}_2\text{O}$  which yields exclusively gas-phase  $\text{ND}_3$  with no partially deuterated ammonia showing the complete reactive dehydrogenation of the ammonia ( $\text{NH}_3$ ) used to form the film.

### Conclusions

It is possible to grow aluminum nitride films by the sequential reaction of trimethylaluminum and ammonia in a manner analogous to the growth of alumina by sequential reaction between TMA and water. TMA initially reacts forming an adsorbed dimethyl species which, upon exposure to ammonia, forms an acid-base adduct. The adduct in turn reacts with the methyl groups producing methane and  $\text{NH}_2$  bonded to aluminum center(s). Aluminum nitride formation is found to be less facile than the formation of aluminum oxide.

The first methyl group in the adsorbed dimethyl species is found to be much more reactive than the second, a tendency found for the reaction with both ammonia and water. This effect may be the result of direct chemical modification of the final methyl groups by the more electronegative oxygen or nitrogen.

(35) Wiberg, E. *FIAT Rev. Ger. Sci. Inorg. Chem.* **1948**, 2,155.