

# Nucleation and Growth of AlN: Self-Limiting Reactions and the Regeneration of Active Sites Using Sequential Exposures of Trimethylaluminum and Ammonia on Silica at 600 K

M. E. Bartram,\* T. A. Michalske, and J. W. Rogers, Jr.†

Sandia National Laboratory, Albuquerque, New Mexico 87185-5800

R. T. Paine

Chemistry Department, University of New Mexico, Albuquerque, New Mexico 87131

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The sequential reactions of trimethylaluminum (TMA) and ammonia have been studied in the 1-Torr pressure regime at 600 K with FTIR (Fourier transform infrared spectroscopy) and XPS (X-ray photoelectron spectroscopy). Transmission FTIR spectra acquired through a silica substrate reveal that extended ammonia exposure can overcome the desorption of ammonia from the methylaluminum:ammonia surface adduct identified previously. This increases the number of reactions between methyl groups and ammonia on adjacent adducts and thereby maximizes the population of bridging amino groups on the surface (Al-NH<sub>2</sub>-Al). The resulting NH<sub>2</sub> species can then react with TMA from an additional exposure to produce a new layer of methylaluminum species. Repetitions of these sequential reactions demonstrate that the respective TMA and ammonia reactions are self-limiting, regenerating active sites suitable for promoting chemisorption of the next precursor for the layer-by-layer growth of aluminum nitride. These studies suggest that in addition to providing transport for the source elements, functional groups that remain chemisorbed on the surface may also be used to enhance the uptake of the next precursor and influence bond directionality during film growth at low temperatures. Although the crystallinity of the aluminum nitride film is expected to be limited by the amorphous nature of the silica substrate, the results from a simple conformational analysis suggest a general rule that can be applied to any substrate; if a concerted reaction between dissimilar functional groups is the only mechanism available for growth, then this mechanism will ultimately limit long-range order in the resulting film.

## Introduction

Demanding applications in the field of microelectronics and the challenges associated with the fabrication of integrated circuitry require effective methods for growing chemically resilient materials that possess desirable combinations of physical properties. As pointed out in a recent comprehensive review,<sup>1</sup> aluminum nitride is a refractory material, with a wide bandgap, a high thermal conductivity, and a thermal expansion coefficient similar to silicon. In addition, it is piezoelectric with a high acoustic wave velocity and is transparent in the visible and near-infrared regions. Because of these properties, aluminum nitride should have wide application in microelectronic and optoelectronic devices as methods are improved that allow it to be grown on surfaces in a crystalline form, at low temperatures, and with high purity.

Significant progress in the development of methods for the growth of aluminum nitride has been achieved recently. Dc magnetron reactive sputtering,<sup>2</sup> reactive molecular beam deposition,<sup>3</sup> laser-induced deposition,<sup>4</sup> and hot

filament catalysis techniques<sup>5</sup> are important examples that use novel enhancements to influence aluminum nitride deposition. Single-source precursors designed to deposit equal quantities of aluminum and nitrogen have been the subjects of comprehensive studies.<sup>6-11</sup> The use of separate sources for aluminum and nitrogen has also been investigated. These include AlCl<sub>3</sub> and ammonia reacting above 800 K,<sup>12</sup> and Al<sub>2</sub>[N(CH<sub>3</sub>)<sub>2</sub>]<sub>6</sub> and ammonia reacting near 500 K to achieve 1000 Å/min depositions<sup>13</sup> and at higher temperatures to achieve 1500 Å/min depositions.<sup>14</sup> The

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\* Present address: Department of Chemical Engineering, University of Washington, Seattle, WA 98195.

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simplest sources used have been trimethylaluminum (TMA) and ammonia,<sup>15-17</sup> with 600 K as the lowest deposition temperature.<sup>18</sup>

There are several fundamental issues that are relevant to each of these methods for aluminum nitride growth. Perhaps most central are the mechanisms for Al-N bond formation and the conditions that lead to Al-N bond retention as well as dissociation. The functional groups contained in precursors are normally thought of only in terms of transporting the element of interest to the substrate. However, at low temperatures these groups must also be considered as potential adsorbates since they may have significant lifetimes on the surface. The effect of these adsorbates must be understood since they have the potential to enhance or inhibit reactions, undergo side reactions that lead to the incorporation of impurities, and affect the morphology of the aluminum nitride film. To address these subjects, we have conducted studies of the reactions between the simplest forms of the aluminum and nitrogen precursors: TMA and ammonia. Silica was selected as the substrate for these reactions because of its transparency to infrared wavelengths and the ease of derivatizing this surface with aluminum alkyls. While the first study focused primarily on the nucleation of an aluminum nitride precursor at 300 K (a methylaluminum: ammonia surface adduct<sup>19</sup>) and its subsequent decomposition, the present study focuses on the growth of aluminum nitride at 600 K and the factors that influence the propagation of Al-N bonding at low temperatures. The chemistry established in the first paper that is essential to this paper is summarized at the beginning of the Results section.

In this work, a methylaluminum-derivatized silica substrate<sup>20</sup> is given high ammonia exposures at 600 K to form bridging amino groups (Al-NH<sub>2</sub>-Al) on the surface. The amino groups on this new surface are then reacted with TMA at 600 K to produce a new layer of aluminum alkyl functional groups. Sequential exposures of NH<sub>3</sub> and TMA are cycled repeatedly in this fashion to demonstrate that the reactions are self-limiting with active sites being regenerated for the reactions that follow on each new surface. The direct correlation between the consumption of reactive sites on one layer and the formation of complementary reactive sites on the next layer suggests that the respective functional groups may be used for more than transporting the element of interest to the surface and may play a significant role in directing the growth of aluminum nitride. This effect is expected to influence the morphology of the resulting thin film. As an example, a simple conformational analysis is presented to suggest that mechanisms involving concerted reactions between dissimilar functional groups on the surface have the potential to *limit* long-range order in the thin film.

## Experimental Section

The FTIR (Fourier transform infrared spectroscopy) experiments were carried out in a stainless steel vacuum system having a base pressure of  $2 \times 10^{-8}$  Torr. The apparatus was equipped with two 80 L/s turbomolecular pumps, an ion gauge, a capacitance manometer, a quadrupole mass spectrometer, a high-pressure chamber, and an IR cell with CsI windows. The apparatus was suspended in the standard sample compartment of a Nicolet model 740 FTIR with a Plexiglass cover sealed around the IR cell to maintain the purity of the nitrogen purge. The vibrational spectra were recorded from 400 to 4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> using an MCT-B detector. A new background spectrum was acquired before each transmission spectrum by moving the bellows mounted sample out of the IR beam. These spectra were then ratioed to obtain the absorbance spectrum. This also removed the effects of adsorbates on the CsI windows and impurities in the nitrogen purge. The spectra were obtained in vacuum after the TMA and the ammonia exposures. For the experiments that used FTIR to follow the extent of the reactions as a function of time, such as those corresponding to Figures 4 and 5, the reactant was evacuated from the IR cell, the spectrum was recorded, and then the exposure was continued. All of the vibrational spectra were taken with the surface at room temperature. In a few cases, spectra were also recorded at the reaction temperature to show that the room-temperature spectra were an accurate representation of irreversible changes that had taken place. Each of the spectra presented in this paper (with the exception of those in Figure 3) are the result of subtracting the spectrum of the clean surface from the spectrum of the adsorbate covered surface after normalization to the intensities of the peak at 1860 cm<sup>-1</sup>. This substrate vibrational band has been assumed to have an absorption cross section that is insensitive to the degree of dehydroxylation of the surface.<sup>21</sup>

Cab-O-Sil M5 silica was the substrate used in all of the experiments. This was supported on a tungsten electroformed screen that was used for resistive heating. A new sample was prepared for each set of experiments by pressing the silica into the screen. Cleaning was accomplished by heating at 900 K for 5 min in 50 mTorr of O<sub>2</sub>. This was followed by annealing at 1200 K for 30 min. Cleaning and annealing effectively removed all of the hydrocarbon impurities on all of the surfaces as judged by FTIR. X-ray photoelectron spectroscopy (XPS) analysis of a silica surface prepared in this manner showed it to be free of impurities.

TMA obtained from Alfa Products was purified by freezing the bottle in liquid nitrogen and then pumping away the volatile impurities.<sup>22</sup> With the exception of some methane produced by decomposition of TMA on the walls and the filaments of the chamber, impurities in the TMA could not be detected in the gas phase with FTIR or mass spectroscopy. The spectra obtained were in agreement with published vibrational spectra<sup>23,24</sup> and mass spectra<sup>25</sup> of gas-phase TMA. NH<sub>3</sub>, obtained from Alphagaz, was used without further purification. Impurities in the ammonia could not be detected with FTIR or with mass spectroscopy. All of the TMA and NH<sub>3</sub> exposures were given sequentially, maintaining a continuous flow at a constant pressure.

XPS analysis of the surface exposed to TMA and NH<sub>3</sub> was performed in a Vacuum Generators ESCALAB 5 Surface Spectrometer with a base pressure of  $5 \times 10^{-10}$  Torr. The Mg K $\alpha$  nonmonochromatic X-ray source was operated at 220 W (11 kV and 20 mA), and the hemispherical electron energy analyzer was operated in a constant analyzer energy mode. This gave a working resolution of 0.92 eV including X-ray broadening. Binding energies were referenced to Si<sub>2p</sub> established at 103.4 eV in SiO<sub>2</sub><sup>26</sup> and were reproducible to  $\pm 0.1$  eV.

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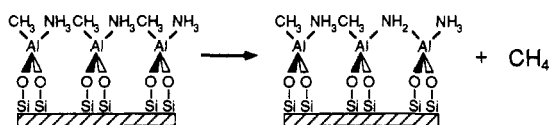
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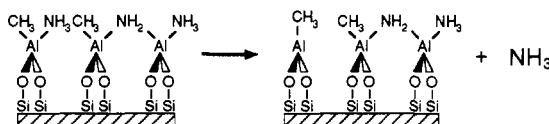
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## Reaction 1



## Reaction 2

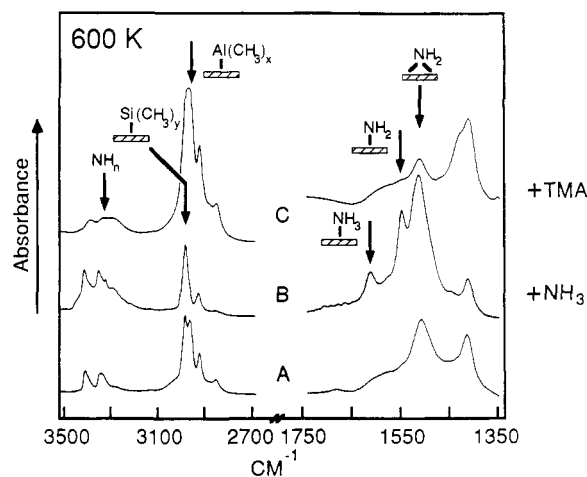


**Figure 1.** Chemistry of the methylaluminum:ammonia surface adduct on silica.<sup>19</sup> Reaction 1 shows schematically how decomposition occurs to yield bridging amino groups and methane. Desorption of ammonia competes with this by reaction 2. Methyl groups bonded to silicon, formed on the surface during the initial reaction between TMA and silica, are not shown.

## Results

The choice of experimental conditions was based on information obtained from established work in which FTIR was used to determine that a methylaluminum:ammonia surface adduct is formed by exposing a methylaluminum derivatized silica surface to  $\text{NH}_3$  at 300 K.<sup>19</sup> In addition to FTIR, isotopic labeling studies using deuterated ammonia and thermal desorption mass spectroscopy revealed that the thermal decomposition of the surface adduct between 300 and 600 K likely proceeds by two reaction pathways (Figure 1).<sup>19</sup> In a concerted event, the methyl group of one adduct reacts with the  $\text{NH}_3$  of an adjacent adduct via interadsorbate hydrogen transfer with loss of methane and formation of bridging amino groups, increasing the number of Al-N bonds (reaction 1). Although either of the remaining functional groups can react with other adjacent adducts to continue this reaction, the desorption of ammonia can also take place, disrupting the propagation of contiguous Al-N bonding on the surface (reaction 2).<sup>19</sup> On a saturated surface, both reactions 1 and 2 reach their endpoints by 600 K. Above 600 K, decomposition of the bridging amino groups begins to take place.<sup>19</sup> Thus, a reaction window centered at 600 K exists between the decomposition reactions of the surface adduct and the subsequent decomposition of the resulting amino groups. With respect to the reaction of TMA with  $\text{NH}_n$  surface species, it has been suggested that carbide formation resulting from TMA side reactions is minimized at this same temperature.<sup>18</sup>

**Regeneration of Active Sites and the Formation of Aluminum Nitride.** The FTIR spectra in Figure 2 show how exposing the decomposed surface adduct to ammonia at 600 K exploits the reaction window to maximize the populations of bridging amino groups (Al-NH<sub>2</sub>-Al) and Al-N bonds on the surface. Features of the clean silica substrate have been removed by digital subtraction. Proposed surface species and their bond orders with respect to the surface (denoted by hatched rectangles) are represented schematically in the figure. FTIR spectrum A in Figure 2 is representative of a saturation coverage of the methylaluminum:ammonia surface adduct formed at 300 K that is then heated at 600 K.<sup>19</sup> This spectrum displays the vibrational features of three species on the surface that have been discussed previously:<sup>19</sup>  $\text{NH}_2$  groups bridging between aluminum centers ( $\delta_{\text{NH}_2}$  at 1510  $\text{cm}^{-1}$ ,



**Figure 2.** FTIR spectra in which features of the clean silica substrate preannealed at 1200 K have been removed by digital subtraction. The surface adduct formed initially at 300 K was heated at 600 K (A), then given a saturation ammonia exposure of 1 Torr for 40 min at 600 K (B), and then given a saturation TMA exposure of 2 Torr for 40 min at 600 K (C). Bond orders are suggested by the lines drawn between each species and the surface represented by the hatched rectangles.

$\nu_{\text{symNH}_2}$  at 3327  $\text{cm}^{-1}$ , and  $\nu_{\text{asymNH}_2}$  at 3399  $\text{cm}^{-1}$ ), methyl groups bonded to aluminum ( $\delta_{\text{CH}_3}$  unresolved at  $\approx 1438$   $\text{cm}^{-1}$ ,  $\nu_{\text{symCH}_3}$  unresolved at  $\approx 2894$   $\text{cm}^{-1}$ ,<sup>20</sup> and  $\nu_{\text{asymCH}_3}$  at 2942  $\text{cm}^{-1}$ ), and methyl groups bonded to silicon ( $\delta_{\text{CH}_3}$  at 1413  $\text{cm}^{-1}$ ,  $\nu_{\text{symCH}_3}$  at 2901  $\text{cm}^{-1}$ , and  $\nu_{\text{asymCH}_3}$  at 2963  $\text{cm}^{-1}$ ). The methyl groups bonded to aluminum and to silicon arise from the dissociative chemisorption of TMA during the initial aluminum alkyl derivatization step.<sup>20</sup> The hydroxyl groups<sup>27</sup> and the strained siloxane bridges including both two-membered Si-O rings<sup>28,29</sup> and three-membered Si-O rings<sup>30</sup> normally associated with the surface of silica, are consumed completely during the chemisorption of TMA.<sup>20</sup>

Spectrum B in Figure 2 shows the effects of exposing the surface characterized by spectrum A to 1 Torr of ammonia at 600 K for 40 min. This represents a saturation coverage since further exposure produces no changes in the vibrational spectrum. Clearly, the increased intensities of the features in the N-H stretching region (3200 to 3450  $\text{cm}^{-1}$ )<sup>31-33</sup> show that the populations of N-H species are increased by this reaction. The N-H bending region has vibrational bands sufficiently resolved to propose specifically that bridging  $\text{NH}_2$  groups (1510  $\text{cm}^{-1}$ )<sup>19</sup> have increased by a factor greater than 2. Further,  $\text{NH}_2$  groups with three-coordinate nitrogen bonded to aluminum (nonbridging amino groups at 1550  $\text{cm}^{-1}$ )<sup>31</sup> and  $\text{NH}_3$  bonded to aluminum (1617  $\text{cm}^{-1}$ )<sup>19</sup> are now present on the surface. Note that the vibrational peaks representative of the methyl groups bonded to aluminum are consumed during the uptake of the N-H species on the surface. The changes are most evident at 2942  $\text{cm}^{-1}$  but can also be seen

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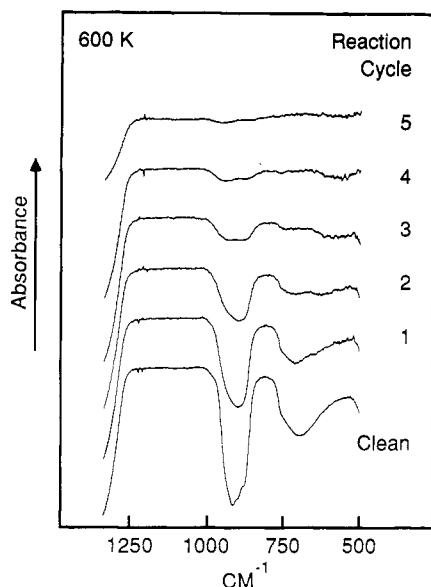
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**Figure 3.** FTIR spectra beginning with silica annealed at 1200 K. Each reaction cycle corresponds to a saturation TMA exposure followed by a saturation ammonia exposure at 600 K. Note that the "clean" spectrum shows that silica is not transparent to IR below 1300  $\text{cm}^{-1}$  with the exception of the regions from 850 to 950  $\text{cm}^{-1}$  and from 600 to 750  $\text{cm}^{-1}$ . Features attributable to aluminum nitride become more intense with each reaction cycle, "filling in" these two transparent regions.

at 1438  $\text{cm}^{-1}$  and  $\approx 2894 \text{ cm}^{-1}$  using a more sensitive scale. The frequencies and the intensities of the silicon methyl peaks (1413, 2901, and 2963  $\text{cm}^{-1}$ ) remain essentially unchanged by the ammonia exposures suggesting that these groups do not take part in the reaction. Nevertheless, it is reasonable to expect that steric inhibition from these spectator groups as well as the amorphous substrate will limit the efficiency of Al-NH<sub>2</sub>-Al formation on this test surface. This limited efficiency may explain why the NH<sub>2</sub> groups with three-coordinate nitrogen and the NH<sub>3</sub> shown in spectrum B are not converted to bridging NH<sub>2</sub> groups on the surface.

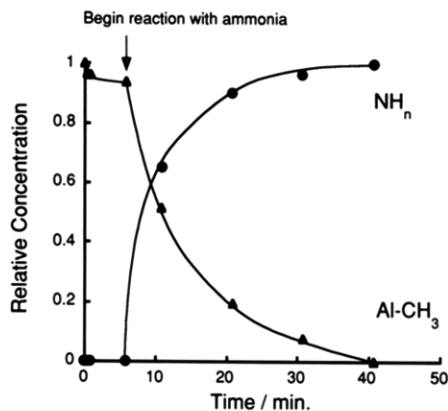
The new surface with NH<sub>n</sub> species characterized by spectrum B in Figure 2 furnishes new reactive sites for the subsequent reaction with TMA at 600 K (2 Torr of TMA for 40 min). Evidence for this can be seen in spectrum C, where the peaks associated with aluminum methyl groups are now observable (1438, 2894, and 2942  $\text{cm}^{-1}$ )<sup>19</sup> and the N-H stretching and bending modes are reduced in intensity (regions near 3400 and 1550  $\text{cm}^{-1}$ ). This represents a saturation coverage since changes in the vibrational spectrum are not observed upon further exposure. The new surface can be treated repeatedly with these sequential ammonia-TMA reaction cycles at 600 K to yield vibrational spectra that are virtually identical to B and C in Figure 2.

Displacement reactions could be consistent with these observations. However, the appearance of new vibrational features at lower frequencies that become more intense with each reaction cycle suggests instead that a new species is formed continuously as a result of the sequential exposures. This is shown in Figure 3. The spectrum labeled "clean" at the bottom of the figure is that of the silica substrate before reaction with TMA or NH<sub>3</sub>. It is important to emphasize that the spectral features are (1) due only to the absorbance of silica<sup>19</sup> and are (2) *not* subtracted from the other spectra in the figure. Therefore, the clean spectrum shows that silica is *not* transparent to IR below 1300  $\text{cm}^{-1}$  with the exception of the regions from

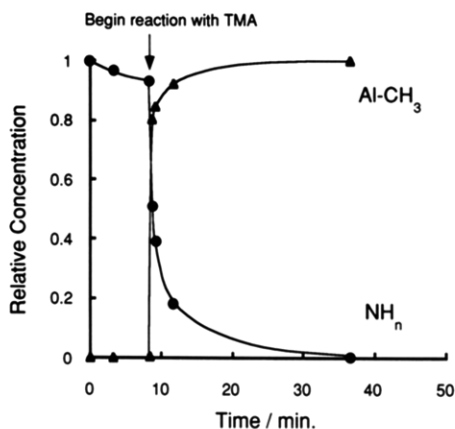
850 to 950  $\text{cm}^{-1}$  and from 600 to 750  $\text{cm}^{-1}$ .<sup>19</sup> The remaining spectra in the figure show the changes in the substrate that occur with each sequential TMA and NH<sub>3</sub> exposure at 600 K; poorly resolved but intense signals grow in with each reaction cycle that "fill up" the two transparent regions. Considering that the vibrational mode for polycrystalline aluminum nitride of a single-crystalline type has a frequency of  $\approx 680 \text{ cm}^{-1}$  and a full-width-at-half-maximum of  $\approx 300 \text{ cm}^{-1}$ ,<sup>10</sup> it is reasonable to expect that the increasing absorbance in the two initially transparent regions is due to the growth of aluminum nitride on the amorphous surface. The spectrum at the top of Figure 3 shows that after five reaction cycles the combined aluminum nitride and silica absorbances leave the substrate opaque to infrared in the frequency range of the figure.

Collectively, the information presented in Figures 2 and 3 suggests that layer-by-layer growth takes place as a result of repetitive treatments with NH<sub>3</sub> and TMA at 600 K. XPS analysis of the surface after numerous reaction cycles indicates that nitrogen is present in the form of both a nitride (397.5 eV) and NH<sub>n</sub> species (399.9 eV) on the surface. This is in good agreement with previous work in which TMA reacted with ammonia to produce a nitride and NH<sub>n</sub> species on Si(100) with binding energies of 397.3 and 399.8 eV.<sup>18</sup> XPS also shows that the nitride layer is sufficiently thick to render silicon undetectable and has a level of carbon approximately 10% of that measured for carbon in the initial substrate treated with TMA. An oxide is also present; however, this can be attributed to the oxygen-nitrogen exchange expected for an aluminum nitride film exposed to air during the transfer of the substrate from the IR chamber to the XPS chamber. This complication makes it difficult to estimate the aluminum to nitrogen stoichiometry of the film deposited by sequential exposures. However, Al/N  $\approx 1$  has been observed with XPS when Si(100) was given sequential exposures of ammonia and TMA at 600 K.<sup>18</sup>

**Self-Limiting Reactions Using Sequential Exposures of TMA and NH<sub>3</sub>.** Vibrational spectra B and C in Figure 2 represent the endpoints of the NH<sub>3</sub> and TMA reactions at 600 K. These spectra alone provide evidence that the growth of one functional group takes place at the expense of the other. However, the integrated peaks of the N-H and the C-H stretching modes obtained from numerous vibrational spectra recorded during the course of NH<sub>3</sub> and TMA reactions at 600 K, serve to emphasize that there is a direct correlation between the consumption of the reactive sites on one layer and the generation of the complementary reactive sites on the next. This is shown in Figure 4 for the reaction with NH<sub>3</sub> at 600 K. The integrated values of the N-H and C-H peaks, taken as direct measures of the NH<sub>n</sub> and the aluminum alkyl concentrations on the surface, are normalized to unity and plotted as a function of time. The initial substrate is silica derivatized with a saturation coverage of methyl aluminum species.<sup>20</sup> The plot shows that before the surface is exposed to ammonia, the population of these species is diminished by a purely thermal process at 600 K but then reaches a constant value after about 5 min. When 1 Torr of NH<sub>3</sub> is admitted to the chamber, the rate of methyl group elimination is substantially enhanced (compared to the thermal process in the absence of ammonia) with all aluminum alkyls being removed at approximately 40 min. Note that the increase in the NH<sub>n</sub> concentration is directly correlated with the depletion of aluminum alkyls and that it also reaches a constant value when all methyl



**Figure 4.** Populations of  $\text{NH}_n$  and methyl groups bonded to aluminum as a function of time during the reaction of ammonia (1 Torr) with methylaluminum derivatized silica at 600 K.

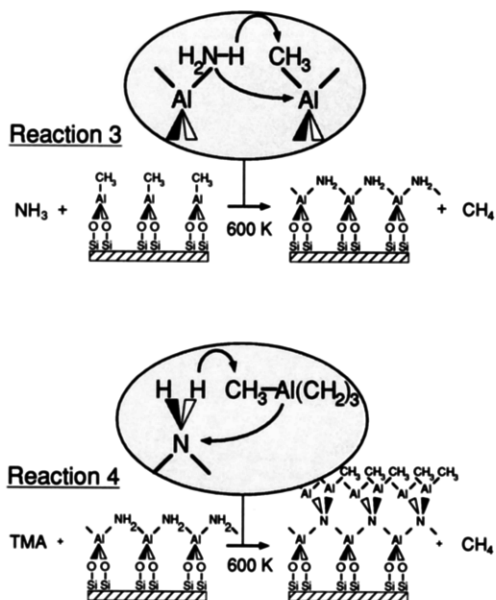


**Figure 5.** Populations of  $\text{NH}_n$  and methyl groups bonded to aluminum as a function of time during the reaction of TMA (2 Torr) with  $\text{NH}_n$  species bonded to aluminum on the surface at 600 K.

groups bonded to Al are removed. Therefore, the reaction of ammonia with the aluminum alkyl derivatized surface is self-limiting under these conditions. The vibrational spectrum of the endpoint of this reaction is equivalent to that shown in Figure 2 as spectrum B.

The data in Figure 4 imply that nearly 10% of the methyl groups bonded to aluminum decompose or desorb in some form<sup>20</sup> at 600 K before exposing the surface to 1 Torr of ammonia. Side reactions associated with the removal of these groups have been discussed previously<sup>20</sup> and may be responsible for the carbon contamination detected with XPS. Assuming a first-order dependence on the ammonia pressure for these reactions, a 100-Torr ammonia exposure may be expected to remove the methyl groups before the thermally induced side reactions can lead to significant carbon incorporation.

Data from the experiment that complements the preceding one are shown in Figure 5. The surface that results from the preceding experiment (a  $\text{NH}_n$ -terminated surface) is first heated to 600 K in vacuum. The plot shows that the concentration of  $\text{NH}_n$  species decreases by a thermal process but approaches a constant value at 8 min. When the surface is exposed to 2 Torr of TMA, the concentration of  $\text{NH}_n$  species is diminished by 50% in less than 2 min. The reaction does not reach completion until nearly 25 min later at which time the aluminum alkyls deposited on the surface as well as the few  $\text{NH}_n$  species that do remain on the surface undergo no further changes. Thus, the reaction of TMA with the surface of  $\text{NH}_n$  species that includes bridging amino groups ( $\text{Al-NH}_2\text{-Al}$ ) is also self-



**Figure 6.** At 600 K, reaction of ammonia with methyl aluminum derivatized silica is self-limiting and maximizes the population of bridging amino groups (reaction 3). These serve as active sites for subsequent reaction with TMA (reaction 4). This reaction is also self-limiting and regenerates active sites that can be used again for reactions with ammonia as in reaction 3. Possible transition states are shown above the reactions. The schematic representations of the reactions are idealized to highlight the chemistry that leads to aluminum nitride growth. Other surface species are also formed during the reactions as described in the text. For clarity in reaction 4, some of the  $-\text{CH}_3$  groups are not shown on the new layer of methylaluminum species.

limiting at 600 K. The vibrational spectrum of the endpoint of this reaction is equivalent to that shown in Figure 2 as spectrum C.

## Discussion

The experiments presented in the Results provide strong evidence that layer-by-layer growth of aluminum nitride on silica can be achieved with sequential exposures of TMA and  $\text{NH}_3$  at 600 K. The increase in the population of bridging amino groups at 600 K demonstrates that ammonia exposures can overcome the desorption of ammonia to maximize contiguous Al-N bonding on the methylaluminum-derivatized surface. Each of the respective TMA and ammonia reactions are self-limiting and produce reactive sites suitable for promoting chemisorption of the next precursor.

In the remainder of this section, mechanisms responsible for this chemistry are proposed. In addition, specific rules are presented that may be applied generally to the growth of films at low temperatures.

**Mechanisms for the Formation of Al-N Bonds at 600 K.** Reaction 3 of Figure 6 shows schematically how Al-N bond formation may occur during ammonia exposure at 600 K. Considering that adjacent adducts formed at 300 K react to produce methane and bridging amino groups<sup>19</sup> and that the depletion of methyl groups bonded to aluminum is directly correlated with the formation of bridging amino groups at 600 K, we propose specifically that the first step in the reaction at 600 K is the formation of an intermediate equivalent to the surface adduct identified previously at 300 K.<sup>19</sup> As shown in reaction 3, the next steps which constitute an interadsorbate reaction

mechanism are (1) the reaction between a hydrogen from ammonia and a methyl group bonded to aluminum to form methane and (2) the formation of a new bond between nitrogen and an adjacent aluminum. The degree to which these two steps are concerted depends on when the bond is broken between the methyl group and the aluminum. If ammonia from an adduct hydrogenates the methyl group via a four-centered transition state, bond breaking and bond making will be simultaneous and the reactions will be concurrent (direct hydrogenation). Conversely, ammonia bonded to aluminum could lower the barrier to the liberation of methyl radicals observed previously in the absence of ammonia above 600 K.<sup>35</sup> At one extreme, given a high capture probability between the free radical liberated from one adduct and the hydrogen abstracted from the adjacent adduct (stimulated free-radical hydrogen abstraction), Al-N bond formation will follow with the overall reaction sequence occurring in a concerted fashion. At the other extreme, however, if the capture probability between adjacent adducts is low, the free radical will be available to abstract hydrogen from ammonia or methyl groups bonded to other adducts. Such noninteradsorbate reaction pathways would not be expected to lead to further Al-N bond formation.

The previous discussion suggests that both the direct hydrogenation and the high capture probability hydrogen abstraction mechanisms may involve concerted reactions between the functional groups on the surface with the transition states being highly organized as shown in reaction 3. This would place stringent requirements on the proximity and orientations of neighboring adsorbates.<sup>19</sup> If such a transition state does occur, it follows that the placement of the resulting bridging amino group will be related directly to the directionality of the functional groups undergoing reaction. Considering this supposition and the experimental results, we suggest that in addition to providing transport for the source elements, *functional groups may also determine bond directionality during growth as well as enhance the uptake of the next precursor on the surface at low temperatures.*

The direct hydrogenation mechanism as well as the two extremes of the hydrogen abstraction mechanisms are consistent with our data. With respect to the removal of methyl groups (Figure 4), the enhanced rate could reflect the power of ammonia bonded to a methyl aluminum surface species to either hydrogenate methyl groups or liberate methyl radicals at 600 K. With respect to the NH<sub>n</sub> species present on the surface after the ammonia reaction at 600 K (Figure 2), the presence of nonbridging amino groups may indicate that the amorphous substrate does not provide the spacing between adducts necessary for hydrogenation of a methyl group to be matched quantitatively by amino bridge formation. Alternatively, the presence of nonbridging amino groups could be the result of free radicals abstracting hydrogen from adducts on one of the other layers in the Cab-O-Sil M-5 silica substrate instead of reacting with adducts immediately adjacent.

In consideration of TMA reacting with the surface containing NH<sub>n</sub> species, the correlation between the removal of NH<sub>n</sub> vibrational features and the accumulation of Al-methyl species suggest that TMA may react with the hydrogens bonded to nitrogen at 600 K. This could occur by a methyl group from TMA removing a hydrogen

from the NH<sub>n</sub> group to form methane and an aluminum alkyl amide species. One possible interpretation of this is shown schematically by reaction 4 in Figure 6. Although the figure shows that two methyl groups bonded to each aluminum may result from this, it is also possible that this species could react with an additional NH<sub>n</sub> species to produce methane and a bridging monomethyl aluminum (N-AlCH<sub>3</sub>-N). In either case, the aluminum center would be three-coordinate and could undergo adduct formation with ammonia during the next reaction sequence as readily as the initial methyl aluminum derivatized surface.

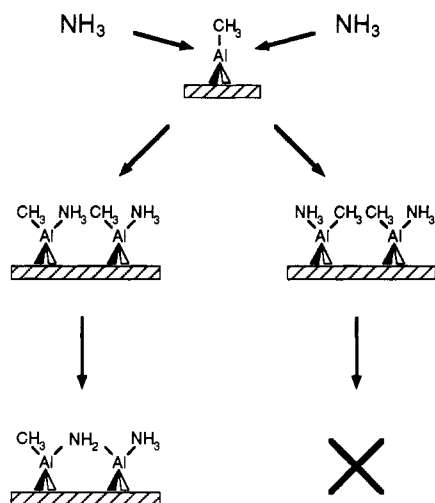
The result of the sequential reactions of TMA and ammonia are presented in Figure 6 in sufficient detail to show how the reactions could continue indefinitely, with each element in the film being tetrahedrally coordinated. Although Figure 6 is idealized it does illustrate that if no other factors were considered, sequential reactions of TMA and ammonia could have the potential to lead to the extended six-membered Al-N rings expected for hexagonal aluminum nitride.<sup>9,34</sup> Our FTIR and XPS results imply this type of growth may have been achieved to some degree on the silica test-surface.

**Limits on Long-Range Order Imposed by Concerted Reactions between Dissimilar Functional Groups during Growth.** The presence of unreacted ammonia and amino groups with three-coordinate nitrogen makes it quite clear that quantitative conversion of chemisorbed ammonia to bridging amino groups was not achieved on the test surface. Although the amorphous character of the substrate and the Si-CH<sub>3</sub> spectator groups produced during the initial reaction of TMA with silica are expected to limit the propagation of contiguous Al-N bonding as well as diminish the purity of an aluminum nitride film, the following discussion points out that these influences alone may not be the cause of incomplete conversion of methyl aluminum species and ammonia to aluminum nitride on the surface.

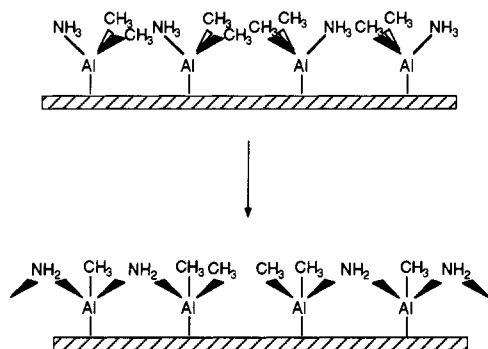
Since adjacent adducts must have orientations that place the methyl and ammonia groups in close proximity for the formation of a Al-NH<sub>2</sub>-Al bridge to occur via an interadsorbate reaction, a large number of surface adducts must at some point achieve specific orientations with respect to one another to accomplish the series of cross-linking events required for the propagation of contiguous Al-NH<sub>2</sub>-Al bridging. That is, *the achievement of periodic bonding must begin with specific periodic orientations of surface species.* This requirement should be less stringent for growth requiring reactions between adsorbates having the same functional groups on the surface. Conversely, this requirement should be rigorous for concerted reactions between dissimilar functional groups as in the case of sequential reactions of TMA and ammonia at 600 K.

A simple conformational analysis demonstrates that the achievement of periodic orientations on a large scale will be difficult whether the adsorbates are rotationally inhibited or rotationally free. The analysis is strictly qualitative, using schematic representations of adsorbates to consider the degree to which reactive combinations of dissimilar groups can be achieved on a surface. For simplicity, only cross sections of the surfaces are shown in the figures that follow. However, the same conclusions can be reached considering the entire surfaces. Although the reactions we have proposed for the sequential TMA-ammonia system are used for illustration, the analysis applies to any chemical system in which (1) there is no diffusion of adsorbates and (2) the propagation of bonding

(35) Squires, D. W.; Dulcey, C. S.; Lin, M. C. *J. Vac. Sci. Technol. B* 1985, 3, 1513.



**Figure 7.** Possible reaction limitations for rotationally inhibited surface species using the products of the TMA and ammonia reactions as examples. Reaction with ammonia can occur on either side of the aluminum alkyl leading to both reactive and unreactive combinations of adjacent adducts.



**Figure 8.** Possible reaction limitations for rotationally free surface species using the products of the TMA and ammonia reactions as examples. Reaction of one pair of adducts may influence the alignment of the next. However, initiation of reactions at different points on the surface will lead to an unreactive pair of functional groups.

on the surface occurs via a concerted reaction between dissimilar functional groups.

An example of rotationally inhibited adsorbates is shown in Figure 7. In this case, a monomethyl aluminum species has two bonds to the surface, fixing its conformation. Reaction with ammonia can take place at either side to yield equivalent adducts. However, this will result in two different combinations of adjacent adducts. One combination will have the ammonia and methyl group next to each other and react as in the left side of Figure 7. The other possibility will have the same functional groups next to each other as in the right side of Figure 7 and does not result in the formation of bridging amino groups. This same argument applies to adducts with single bonds to the surface that may have rotation restricted by crowding from other adsorbates.

The inherent limitation of achieving periodic orientations with rotationally free adsorbates is shown in Figure 8. With only a single bond to the surface the alignment that brings the ammonia next to the methyl group is allowed regardless of the side with which ammonia reacts initially. The reaction at one adduct should influence the alignment of the next. This should hold true whether the adducts are present at the same time or formed sequentially and react one at a time. However, the initiation of reactions at numerous locations on the surface will ultimately result

in the same functional groups being next to each other. As a result, the propagation of Al-N bonding will come to an end as shown in Figure 8. Interestingly, if one of the adjacent methyl groups could be liberated as a free radical, a new site for ammonia bonding to aluminum would become available. Reaction between the ammonia and the remaining methyl group would then complete the Al-NH<sub>2</sub>-Al bonding.

On the basis of these arguments, we postulate a general rule: *if a concerted reaction between dissimilar functional groups is the only mechanism available for growth, then this mechanism will ultimately limit long-range order in the resulting film.* It follows that this will also significantly influence the morphology. Similar limitations on the final coalescence of larger aluminum nitride precursors such as [(CH<sub>3</sub>)<sub>2</sub>AlNH<sub>2</sub>]<sub>3</sub> have also been suggested<sup>8</sup> and as shown in the preceding paragraph, must be overcome by the involvement of more than one reaction mechanism to achieve long-range order. Certainly, if crystalline aluminum nitride can be produced from sequential reactions of TMA and ammonia at 600 K on a surface more ideal than our silica test surface, a mechanism in addition to an interadsorbate reaction must also contribute to growth. These conclusions also imply that depositions of crystalline aluminum nitride at low temperatures,<sup>2,4,14-16</sup> regardless of the precursors involved, do not depend only on concerted reactions between dissimilar functional groups.

## Summary

Studies of low-temperature reactions between TMA and ammonia have revealed that functional groups remaining on the surface during deposition can influence the growth chemistry. Self-limiting reactions are observed for both of the reactants and yield new reactive sites that can be used to continue the growth of aluminum nitride at 600 K. In addition to enhancing the uptake of the next precursor on the surface, chemisorbed functional groups may determine the placement of bonds formed during the decomposition reaction. It is proposed that the first step in the reaction of ammonia with the methylaluminum-derivatized surface is the formation of an adduct on the surface at 600 K. Subsequent reaction produces methane and an amino bridge via a direct hydrogenation mechanism and/or a stimulated free-radical hydrogen abstraction mechanism. Since the functional groups involved in the reaction are dissimilar and must be in close proximity to each other for interadsorbate reactions, the orientations of the surface adducts may be the limiting factor in achieving contiguous Al-N bonding. This conclusion is extended to propose the general rule that growths controlled by only concerted reactions between dissimilar functional groups will have limited long-range order.

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