Mechanistics of Early Stage Growth of AlN on Alumina: TMAl and NH_3

D. C. Bertolet and J. W. Rogers, Jr.*

Department of Chemical Engineering, BF-10, University of Washington,
Seattle, Washington 98195

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The reactions of trimethylaluminum and ammonia on γ-alumina were studied by Fourier transform infrared spectroscopy to explore their feasibility as precursors for the low-temperature growth of AlN thin films. Trimethylaluminum reacts with hydroxyl groups on the alumina surface to form primarily a dimethylaluminum species singly bound to oxygen. When this species is subsequently exposed to ammonia at room temperature, a weakly bound ammonia: aluminum alkyl adduct is formed, along with amide ($-NH_2-$) covalently bonded to aluminum, formed by the hydrogenation of one of the methyl groups. Upon heating to 820 K, the $-NH_2-$ remains on the surface, while the ammonia and the majority of the methyl groups are desorbed. These data indicate that a stable Al–N complex can be created on alumina at room temperature; however, the reaction probability is quite low.

Introduction

A number of current and emerging technologies require the low-temperature deposition of thin films of wide-bandgap materials on technologically important substrates. The interest in these films is driven by their unique combination of electrical, thermal, mechanical, and dimensional properties. For instance, AlN, the material of interest here, has a bandgap of 6.2 eV, high thermal conductivity (230 W/mK), a thermal expansion coefficient (33×10^{-7} K^{-1}) closely matched to that of silicon, a dielectric constant of 8.8, it is chemically inert,[1] it is refractory with a melting point of 2750 K, and it is piezoelectric with a high surface acoustic wave velocity. Thus, it finds applications as passivation and dielectric layers for high temperature semiconductors (e.g., SiC and diamond), microelectronics packaging material, and films for surface acoustic wave (SAW) devices for chemical sensors. If suitable doping procedures can be developed, AlN may itself develop into a useful, wide-bandgap semiconductor, particularly for extending optical devices into the UV range.

One method of preparing wide-bandgap thin films is by metal–organic chemical vapor deposition (MOCVD). The MOCVD technique has many attractive features, including high deposition rates, the potential for depositing a wide variety of materials (metals, insulators, and semiconductors), purity of films, operation at high pressures (UHV is not required), and the ability to form abrupt interfaces and deposit conformal coatings.[2] MOCVD of AlN thin films was first proposed by Manasevit[3] using trimethylaluminum (TMAl) and ammonia (NH_3), and several groups followed suit.[4-9] Epitaxial AlN films have been grown successfully on Si(001),[8,9], Si(111),[5,8,9] and Al_2O_3-(0001)[4,5,7] substrates by MOCVD, but epitaxial deposition has never been observed at substrate temperatures below 1423 K; typically higher temperatures are required. Deposition of thin films of these materials at high temperature creates a major impediment to their use because many applications require substrates which cannot tolerate a high-temperature processing step.

The MOCVD process is quite complex involving both homogeneous and heterogeneous reactions, and fundamental investigations of the inherent surface reaction mechanisms have been limited.[10,11] Fewer still have studied the chemistry involved in AlN thin-film processing. However, because of the interest in depositing aluminum metal and AlGaAs for microelectronic applications, reactions involving TMAl as an aluminum source have received considerable attention. Mechanistic studies of the decomposition of TMAl on Cu, Al, quartz, and GaAs substrates were reported by Squire et al.,[12,13] on Si(100) by Gow et al.,[14-16] and on Si(111) by Ishida et al.[17]

Chemisorption of TMAl on silica has been reported by several groups.[18-26] In general TMAl was found to react with surface siloxane and silanol groups, but the rate at

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which this happens is a matter of some controversy. Bridged surface species were formed by reaction between the TMAl and more than one reactive surface site. The coadsorption of TMAl and NH_3 on silica[27] and Si(100)[28] has also recently been reported, and a comparison of this work with the present results on alumina will be given when relevant.

The overall goal of this investigation is to study the fundamental chemistry and physics associated with the initial stages of growth of AlN thin films from aluminum- and nitrogen-containing source gases (TMAl and NH_3) on alumina and to explore the potential for reduced processing temperatures.

Experiment

Deposition and infrared (IR) spectroscopy were performed in a stainless steel vacuum chamber with a base pressure of 1×10^{-8} Torr. The system was equipped with two turbomolecular pumps, an ion gauge, a capacitance manometer, a quadrupole mass spectrometer, and a gas-handling manifold incorporating a leak valve and ballast. The chamber was mounted partially within, and externally O-ring sealed to, the sample compartment of a Bruker IR98 FTIR system, such that the entire IR beam path could be evacuated. Dual O-ring-sealed, differentially pumped KBr windows were employed to pass the IR beam through the high-vacuum chamber, and the sample was moved in and out of the IR beam path with a bellows assembly.

The IR data was recorded from 4000 to 1000 cm^{-1} at a resolution of 4 cm^{-1}, using a KBr beam splitter and a DTGS detector. For each spectrum, a new reference scan, with the sample out of the beam path, was taken to calculate absorbance and eliminate the effects of background changes (if any), such as deposition on the KBr windows. Unsubtracted absorbance spectra presented below were baseline linearized, because IR light scattering by the alumina powder increases at larger wavenumbers producing a sloping baseline in the raw absorbance plots. Subtracted spectra were not normalized before subtraction.

The γ-alumina substrate for all experiments was aluminum oxide C (Degussa AG, Frankfurt, FRG) with an as-received surface area of 100 m^2/g and an average particle diameter of 20 nm. A new sample was prepared for each set of experiments by hand pressing the alumina powder into a tungsten electroformed mesh; the alumina was mounted as-received. The mesh was spot-welded between two tantalum wires connected to power feedthroughs, such that the mesh served as a resistive heating element. A chromel–alumel thermocouple was spot welded to the top center portion of the mesh to monitor temperature. At higher temperatures, a temperature gradient across the sample area could be observed visually, with the thermocouple at the hot spot. Consequently, the temperature was rescaled to agree with known chemical reactions on alumina surfaces; specifically the behavior of hydroxyl groups[29] and ammonia.[30] The uncertainty in the upper range of the temperatures used in this study was not critical to our interpretation of the data.

Semiconductor-grade trimethylaluminum (TMAl, Akzo Chemicals, Inc., Deer Park, TX) was purified before each set of experiments by freezing the bottle in liquid nitrogen and pumping away the volatile impurities. Both FTIR and mass spectra of gas-phase TMAl agreed well with published data.[31] No impurities were evident, with the exception of methane produced from reactions of TMAl with the chamber walls and filaments. Anhydrous ammonia (Matheson Gas Products, Secaucus, NJ) was used without further purification. IR[32] and mass spectra of NH_3 were in agreement with well-known standards, and no impurities were detected. Both the TMAl and NH_3 exposures were achieved either by continuous flow at constant pressure or in a static mode for pressures greater than 1 Torr, with all exposures reported in langmuirs (1 langmuir = 10^{-6} Torr s). TMAl dosing was performed with the substrate at 470 K, while for NH_3 dosing, the substrate was at room temperature.

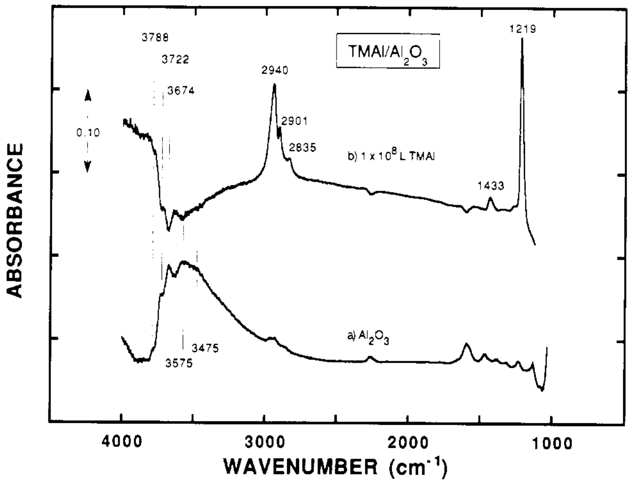

Figure 1. FTIR spectra of alumina powder substrate before (a) and after (b) a TMAl dose of 1×10^8 langmuirs. Spectrum b is a difference spectrum plotted after subtraction of the features due to clean alumina (curve a) to illustrate adsorbate-derived features.

Results and Discussion

TMAl on Alumina. Shown in Figure 1a, is an absorbance spectrum for "clean" alumina annealed for 12 h at 390 K in vacuum. The peaks at 3674, 3722, and 3788 cm^{-1} are assigned to isolated surface hydroxyl stretching vibrations,[30] and the broad bands at about 3575 and 3475 cm^{-1} are hydrogen-bonded surface hydroxyl stretches.[29] Weak bands near 2800 cm^{-1} indicate the presence of a trace amount of hydrocarbon impurity. Also shown in Figure 1 (curve b) is an absorbance spectrum after a saturation TMAl exposure of 1×10^8 langmuirs. The absorbance spectrum of the clean alumina (curve a) has been subtracted from the raw data to show only the changes brought on by the adsorbates. The $-CH_3$ stretching region consists of three resolved peaks centered at ~ 2900 cm^{-1}. The positions and relative intensities of the three peaks agree extremely well with those of TMAl vapor (dimer) measured in our laboratory, and others.[31] We therefore assign the peaks at 2940, 2901, and 2835 cm^{-1} to $-CH_3$ antisymmetric stretching modes, $-CH_3$ symmetric stretching modes, and the first overtone of the antisymmetric $-CH_3$ bend, respectively. The bands at 1219 and 1433 cm^{-1} also closely match gas-phase data, and are assigned to symmetric and antisymmetric $-CH_3$ bending modes, respectively. The relatively weak band at about 1263 cm^{-1} is assigned to the symmetric bend of bridged $-CH_3$ in the TMAl dimer, indicating a small amount of dimeric TMAl is present. The negative peaks in the –OH stretching

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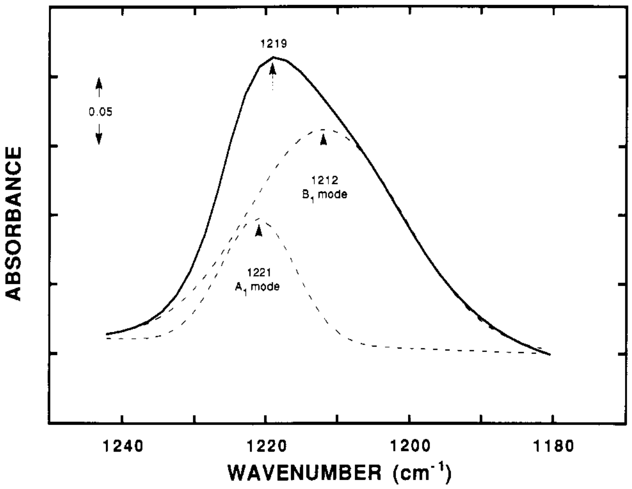

Figure 2. Curve fit of two Gaussians to the $-CH_3$ symmetric bending modes (A_1 and B_1) obtained after a 1 × 10^8-langmuir dose of TMAl to an alumina substrate.

region indicate that the TMAl has reacted with the surface hydroxyl groups. Roughly one-fourth of the original −OH band integrated intensity remains after TMAl saturation, likely because a portion of the −OH groups are inaccessible from the surface.

When TMAl is exposed to the alumina surface, presumably one of the $-CH_3$ groups reacts with a hydroxyl to liberate methane, leaving a dimethylaluminum (Me_2Al) species singly bound to oxygen. For TMAl on silica surfaces,[26] it has been proposed that the Me_2Al proceeds to react with another adjacent hydroxyl or oxygen, such that bridged-bonded monomethylaluminum (MeAl) is the dominant species on the surface at room temperature. In the case of alumina however, our data suggest that the majority species is a single-bound Me_2Al species, for reasons as follow. Closer examination of the lineshape of the $-CH_3$ symmetric bend peak at 1219 cm^{-1} reveals the presence of two modes, as illustrated in Figure 2, in which two Gaussian peaks have been fitted to the data. We curve-fitted Gaussians as opposed to Lorentzians because the observed peak linewidths are too large to be attributed to intrinsic broadening. Instead we believe the dominant broadening mechanism is due to the heterogeneous nature of the surface surrounding individual surface species, giving rise to a Gaussian line shape. The symmetric $-CH_3$ bending modes were curved-fitted for TMAl exposures between 1 × 10^7 and 6 × 10^9 langmuirs, corresponding to a change in total integrated peak area of a factor of 32. Over this range, the positions of the two curve-fitted peaks were consistent within 1 cm^{-1}, while the peak separation was 8.4 ± 1.1 cm^{-1}. The ratio of the integrated intensities of these peaks was 3.8 ± 0.72. We interpret each of these minor variations in line shape to be independent of coverage within experimental error.

If a C_{2v} symmetry is assumed for a surface Me_2Al (with freely rotating methyl groups), then two symmetric $-CH_3$ bending modes corresponding to the A_1 (both methyl bends in-phase) and B_1 (out-of-phase) representations are expected.[33] A similar $-CH_3$ symmetric bend doublet has been observed for solid dimethylsilane.[34] In addition, we have performed ab inito calculations on dimethylaluminum chloride with C_{2v} symmetry, which yielded two symmetric $-CH_3$ bending modes separated by 3–5 cm^{-1}. For a carbon–carbon bond angle of 120°, simple vectoral addition of the dipole changes in each methyl group would predict a 3:1 ratio for the intensities of the two modes, in fair agreement with the observed values of 3.8 (±0.7):1. The full width at half-maximum of the A_1 peak (higher cm^{-1}) was consistently about 2 times smaller than that of the B_1 peak. Because the A_1 mode dipole moment is perpendicular to the surface, while the B_1 moment is parallel, random surface irregularities should have a greater influence on the energy of the B_1 mode, resulting in a wider peak.

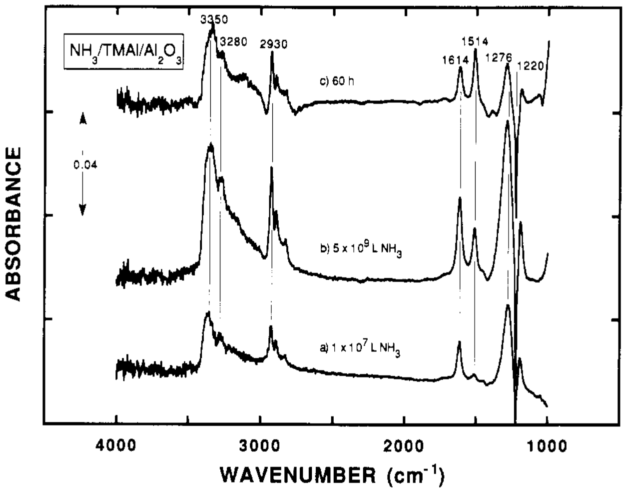

Figure 3. FTIR difference spectra for NH_3 exposures of (a) 1 × 10^7, (b) 5 × 10^9, and (c) 5 × 10^9 langmuirs followed by 60 h at room temperature. The spectrum of the TMAl derivatized surface, taken immediately prior to NH_3 exposure, was subtracted from each spectrum to highlight the features due to NH_3 interactions.

If instead, a homogeneous MeAl species is considered as a possible surface species, then only one symmetric $-CH_3$ bending mode is expected, clearly not what we observe. Perhaps one could speculate that either a mixture of Me_2Al and MeAl, or two forms of surface MeAl are present, each with a distinct symmetric $-CH_3$ bending mode. In this case it is unlikely that the relative coverages of each species would remain constant over the wide range of TMAl exposures studied here.

The CH_3 stretching region is more difficult to analyze, because for C_{2v} symmetry, four antisymmetric (three of which are IR active) and two symmetric modes would be predicted. Curve-fitting analysis of our data suggests the presence of six peaks (one of which is the antisymmetric bend overtone), but the high degree of peak overlap precludes reliable peak identification. However, as in the case for the symmetric bending modes, the overall line shape of this group of peaks did not change significantly with increasing TMAl exposure, supporting the argument for a single dominant surface species (Me_2Al).

NH_3/TMAl on Alumina. Figure 3 shows spectra for a series of increasing doses (1 × 10^7 and 5 × 10^9 langmuirs) of NH_3 to the TMAl derivatized alumina surface discussed above. Here, the spectrum of the TMAl-derivatized surface taken immediately before NH_3 exposure has been subtracted, such that only features associated with the addition of NH_3 appear. In the plot for a 1 × 10^7 langmuir dose (curve a), the peaks located at 1276 and 1614 cm^{-1}

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are assigned, based on IR data for the TMAl–NH_3 adduct,[35] to symmetric and antisymmetric –NH_3 bending vibrations, respectively. In the N–H stretching region at least three bands are present, roughly located at 3350, 3280, and 3200 cm^{-1}, but are relatively noisy due to weaker source intensity and increased light scattering by the alumina particles at these higher wavenumbers. Peri[36] observed –NH_3 stretching vibrations at 3400 and 3355 cm^{-1} for ammonia adsorption on alumina at room temperature, and –NH_2– stretches at 3386 and 3355 cm^{-1} at higher temperatures. For our data, the signal-to-noise levels preclude precise peak assignments for –NH_3 and –NH_2– when both species are present on the surface at the same time.

The three peaks in the –CH_3 stretching region ($\sim$2900 cm^{-1}) and the positive and negative peaks at 1194 and 1220 cm^{-1} represent shifts to lower energy of the –CH_3 stretches and bends, respectively, and the magnitude of these shifts increased with higher NH_3 doses. The peak positions of the –CH_3 stretching features shifted down by 2–8 cm^{-1}, and the total integrated area of the –CH_3 stretching region increased by about 10%. A similar shift in the peak locations of the –CH_3 stretch was observed for TMAl and NH_3 on silica[27] and was attributed to the formation of an aluminum alkyl:ammonia surface adduct. An increase in the –CH_3 stretch intensity was also present but was not discussed.[37] It is reasonable to assume that the mechanism causing the shift in energy could also result in an increase in the oscillator strength. With the respect to the two –CH_3 symmetric bending modes, both peaks shifted down in energy a total of 2–4 cm^{-1}, and while the total integrated area for both peaks did not change significantly, their area ratio *dropped monotonically* from 3.7 to 2.8.

The band at 1514 cm^{-1} closely matches those observed at 1510 cm^{-1} for NH_2 on alumina[36] and at 1514 cm^{-1} for the Me_2Al–amide trimer $[(CH_3)_2AlNH_2]_3$,[38–40] which were attributed to the bending mode of NH_2 with *four-coordinate* nitrogen. The Me_2Al–amide trimer can be synthesized by the pyrolysis of the $Me_3Al{:}NH_3$ adduct at temperatures as low as 350 K.[41] It has been proposed that a similar structure, in which –NH_2– is bridge-bonded between adjacent aluminum centers, is formed on the surface of silica upon exposure of TMAl and NH_3 and subsequent heating to 600 K.[27] Our data indicate a similar –NH_2–bridge-bonded reaction also occurs on alumina. Note that the frequency of the four-coordinate –NH_2– bending mode differs significantly from that of three-coordinate –NH_2, which has been observed at 1550 cm^{-1}.[42]

After the final NH_3 dose of 5×10^9 langmuirs, the sample was left for 60 h under vacuum at room temperature, and the resulting spectrum is shown as curve c of Figure 3. The intensities of all of the –NH_2-related vibrations have decreased, and on the basis of the area of the –NH_3 bend peaks, roughly 50% of the –NH_3 originally bound to the surface has desorbed or reacted to form –NH_2–. The area of the –NH_2– bend (1514 cm^{-1}) increased by about 30%. Meanwhile, the peak positions of the –CH_3 bending modes shifted back up in energy 1–2 cm^{-1}, while their areas, both total and relative, did not change significantly. Both the peak positions and areas of the –CH_3 stretching modes also shifted back, but not completely, toward their pre-ammonia exposure values.

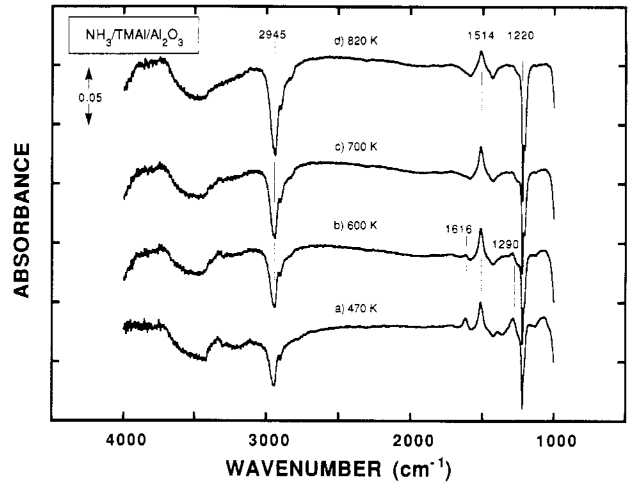

Figure 4. FTIR difference spectra of the TMAl/NH_3 derivatized surface sequentially annealed for 3 min at (a) 470, (b) 600, (c) 700, and (d) 820 K. The spectrum of the TMAl derivatized surface, taken immediately prior to NH_3 exposure, has been subtracted from each spectrum to highlight the features due to NH_3 interactions.

Thus, the peak shifts as well the change in total –CH_3 stretch intensity appear to be correlated to the concentration of adsorbed NH_3. However, the change in relative areas of the two –CH_3 symmetric bending modes, observed after exposure of the TMAl-derivatized surface to ammonia, is apparently the result of a more permanent reaction, since the area ratio was not affected by the loss of ammonia during the 60-h wait at room temperature. Recalling that the –NH_2– symmetric bending mode intensity did not decrease but instead increased slightly during the 60-h wait, it becomes reasonable to associate this change in –CH_3 bending modes to the reaction which forms –NH_2–, in which the ammonia hydrogenates one of the methyl groups which then leaves the surface as methane. The MeAl surface species would have a single –CH_3 symmetric bending mode, and with the resultant mixture of MeAl and Me_2Al on the surface, a change in the lineshape of the –CH_3 symmetric bend peaks would be expected. The probability of this –NH_2– forming reaction is apparently quite low, however, as the total number of –CH_3 present has not decreased enough for the change in relative intensity of the C–H stretching or bending modes to be measurable. It is likely that the proximity and orientation of adjacent Al–NH_3 and Me_2Al species is limiting the extent of reaction. It is also possible that the loss of –CH_3 is being obscured by the increase in oscillator strength which occurs with the formation of the NH_3 adduct.

Presented in Figure 4 are spectra for the TMAl/NH_3-saturated surface described above after a series of 3-min anneals at increasingly higher temperature up to a maximum of 820 K. As the temperature increases, the –NH_3 related peaks all lose intensity and disappear by 820 K, while the –NH_2– asymmetric bend peak retains about 50% of its integrated intensity. Meanwhile the –CH_3 stretch and bend peaks become increasingly negative, up

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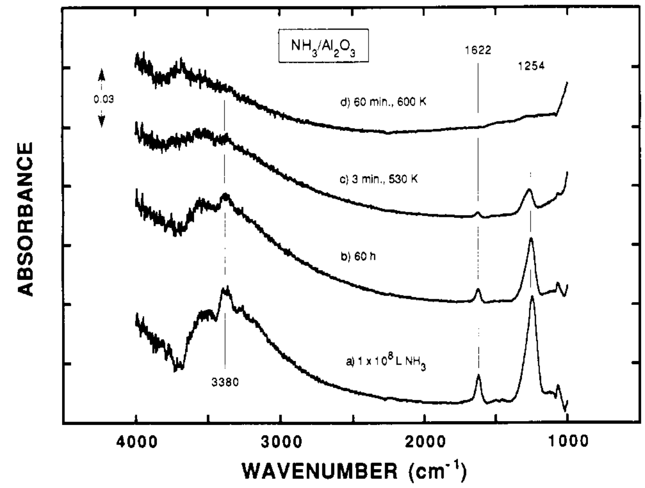

Figure 5. FTIR difference spectra of alumina after (a) an exposure of 1 × 10^8 langmuirs of NH_3, (b) 60 hours at room temperature, (c) 3 min at 530 K, and (d) 60 min at 600 K. The spectrum of clean alumina, taken immediately prior to NH_3 exposure, has been subtracted from each spectrum to highlight the features due to NH_3 interactions.

to 820 K at which point the $-CH_3$ peaks retain about 20–40% percent of their original integrated area. For the case of silica, Bartram et al.[27] reported a 2-fold increase in $-NH_2-$ population upon heating to 600 K. For alumina, however, only about a 20% increase in $-NH_2-$ population occurs, because the reaction apparently occurs to near completion at room temperature. Most importantly, the formation of the bridge-bonded $-NH_2-$ species implies a stable, covalent bond between the nitrogen and aluminum, the first step in forming an extended network of covalently bonded N and Al, i.e., AlN. The $-NH_2-$ bending mode intensity does eventually decrease at elevated temperature, which could be a result of dehydrogenation of the $-NH_2-$ complex to form Al–N–Al bonds. Unfortunately, we must rely on the NH_x modes to identify aluminum and nitrogen interactions because the IR modes of the Al–N bond occur in a region in which the alumina substrate is opaque.

To ensure that the formation of the $-NH_2-$ species was soley a result of the interaction of ammonia with aluminum-methyl complexes, NH_3 was exposed to clean alumina which had been annealed in vacuum overnight at 390 K. Shown in Figure 5 are absorbance spectra for an NH_3 dose of 1 × 10^8 langmuirs on clean alumina, which was subsequently sequentially annealed for 3 min at several temperatures between 390 to 600 K. In the bottom plot, taken immediately after the dose, the symmetric and antisymmetric NH_3 bending, and the NH_3 stretching modes are exhibited at 1254, 1622, and ~3380 cm^{-1}, respectively. Note that the symmetric NH_3 bend is at a significantly lower wavenumber than the case for the TMAl-derivatized surface, supporting the contention of a NH_3:Me_2Al adduct. Conspicuously lacking in the spectrum however, is the antisymmetric $-NH_2-$ bend. After the sample was left for ~60 h, the intensities of the NH_3 peaks decreased by about a factor of 2 (see Figure 5), similar to the case for NH_3 on the TMAl-derivatized surface. As the sample was sequentially annealed up to 600 K, the NH_3 continued to desorb, and after 60 min at 600 K, no $-NH_3$ features could be resolved. Most importantly, no $-NH_2-$ peaks appeared. These results are consistent with the work of Peri[36] for NH_3 on alumina predried at 673 K, in which no $-NH_2-$ was formed and no $-NH_3$ peaks were observed after heating to 673 K.

Conclusions:

The surface chemistry of TMAl and NH_3 on γ-alumina was studied by Fourier transform infrared spectroscopy. When TMAl is exposed to a hydroxylated alumina surface, the dominant surface species formed is Me_2Al singly bound to oxygen. This conclusion is primarily based on the consistent observation of a pair of symmetric $-CH_3$ bending modes corresponding to the A_1 and B_1 representations of C_{2v} symmetry, for TMAl coverages varying by a factor of 32. Upon subsequent exposure of NH_3 to a TMAl-derivatized alumina surface, a portion of the NH_3 reacts with the surface Me_2Al liberating methane, and leaving $-NH_2-$ covalently bonded to MeAl on the surface, as evidenced by the appearance of the $-NH_2-$ bending mode, as well as a change in the relative intensities of the symmetric $-CH_3$ bending modes. In addition, some of the NH_3 forms a weakly-bound adduct with the Me_2Al, manifested in the $-CH_3$ stretching and bending peak position shifts which were proportional to the NH_3 coverage. In contrast, for a similarly prepared clean alumina surface, NH_3 is weakly adsorbed, but no $-NH_2-$ modes are detected, even after heating to 600 K which desorbs the NH_3. Thus, it is specifically the interaction of NH_3 and Me_2Al which leads to the formation of the $-NH_2-$ species. Similar behavior has been observed from the reaction of TMAl and NH_3 on silica surfaces.[27] After heating to 820 K, all the NH_3 and about 70% of the $-CH_3$ groups are removed, while about 50% of the $-NH_2-$ population is retained. The important overall result is that stable Al–N bond networks have been formed at temperatures as low as 300 K. However, this reaction probability is quite low as the appearance of $-NH_2-$ did not correspond to a measurable decrease in $-CH_3$ population. The reaction to form $-NH_2-$ was most likely limited by the proximity and orientation of the Me_2Al species on the surface, as well as the thermal desorption of weakly bound NH_3. Work involving the exposure of NH_3 at elevated temperatures, as well as repeated cyclic exposures of TMAl and NH_3 is currently underway in our laboratory.

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