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If, as our results suggest, kogation and etching are properties of functional groups, polyfunctional molecules may do both, and the resultant effect could be very subtly balanced.

Given the composition of kogation as some sort of reduced form of carbon, possibly polymeric, the kogation processes might take any one of the forms described as follows, and all may operate independently: (1) Kogation is produced by a radical polymerization process at high temperatures. (2) Kogation is produced by a base-catalyzed polymerization at high temperatures. (3) Kogation is produced by decomposition at elevated temperatures that is predominantly anaerobic.

Conclusions

Kogation and etching in thermal ink jet devices are derived from the thermal activation of ink ingredients. Etching can arise from high pH, radicals, or both. Kogation can arise from chemicals with a preponderance of carbon. Relatively low amount (ca. 0.1%) of an offensive component can produce poor performance. The fraction of the offensive chemical that decomposes to either etch or kogate is probably small, on the order of 0.01%. The interaction of etching and kogation is complicated and can give rise to all possible combinations: net etching, net kogation, or no adverse behavior.

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Mechanism of Nucleation and Atomic Layer Growth of AlN on Si

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We have studied by X-ray photoelectron spectroscopy the adsorption and decomposition of trimethylaluminum (TMA) on Si(100), the low-temperature formation of AlN from pyrolysis of TMA and NH_3, and have demonstrated a mechanism for atomic layer growth of AlN at 600 K. TMA adsorbs dissociatively to Si at temperatures above 300 K. At <650 K adsorption is self-limiting at <1 monolayer, with most carbon remaining in the form of CH_3. At higher temperatures, decomposition of the TMA is rapid, and continuous deposition is observed with production of carbides as the primary product. Coadsorption of TMA and NH_3 at room temperature leads to formation of Al–N covalent bonding as well as a surface adduct species, Al:N, which is converted quantitatively to Al–N at higher temperature. At substrate temperatures <550 K, coadsorption of TMA and NH_3 is self-limiting at less than a monolayer, while above this temperature reaction to form AlN is rapid and continuous deposition is observed. Self-limiting adsorption of TMA at <650 K and rapid, site-selective reaction with NH_3 to form AlN at >550 K satisfy the conditions for atomic layer growth of AlN at 600 K using sequential exposures of TMA and NH_3. The chemical nature of the interfacial and growth surface are discussed.

Introduction

We have undertaken extensive studies of the low-temperature chemical vapor deposition (CVD) of AlN[1,2] because of the many potential applications of this material in microelectronic and sensor technologies and as a model system for the study of low-temperature preparation of ceramic thin films in general. CVD offers many advantages in terms of process flexibility and control of material properties but demands a great deal of understanding of the mechanisms and kinetics of film growth to realize these advantages.

To this end, we previously investigated the adsorption and decomposition of trimethylaluminum (TMA) on SiO_2[1] and the initial stages of AlN formation from TMA and NH_3 on SiO_2.[2] In these studies we demonstrated the dissociative chemisorption of TMA on this substrate and the transformations of the organic ligands over the temperature range of interest to CVD processes. We inferred from infrared spectroscopic evidence that adsorbed alkylaluminum species form a Lewis acid–base adduct with NH_3 which may serve as a precursor to formation of an Al–N covalently bonded network at temperatures <600 K. We have also proposed that elimination of methane from the surface can occur via inter- and intraadsorbate reactions between methyl groups from the alkylaluminum species and H from the NH_3. Recently Yu et al.[3] demonstrated preparation of high-quality AlN at low temperature by surface reaction of TMA and NH_3 on Si and Al_2O_3 substrates.

Here we conduct similar studies of initial stages of AlN growth from TMA and NH_3 on Si, in part to complement the infrared studies, as well as to demonstrate the control of film growth that can be achieved by controlling the surface chemistry. In this case we have demonstrated a mechanism for atomic layer growth of AlN.

Atomic layer growth of III–V semiconductor materials by chemical vapor deposition techniques has been demonstrated by a number of laboratories.[4–9] This process

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offers the possibility of exquisite control of layer thickness and interface abruptness in heterostructure devices, "δ doping" of crystals for unique device applications, conformal coatings on high aspect ratio three-dimensional structures, low-temperature deposition conditions to minimize interface diffusion and material degradations, and others.[9]

Atomic layer growth has been achieved in a number of process variations, but all involve a two-step process in which alternating monolayers of material are adsorbed to the surface in sequential exposure steps, with transformation to the desired film taking place during the exposures or with additional energy input during one step, such as by laser irradiation.[8]

Two important aspects of the atomic layer growth process that appear to be essential are a self-limiting adsorption of one or both of the precursor gases[6,10] and site-selective incorporation of components into the proper surface configuration.[11,12] The first requirement leads to the control of growth to the atomic scale and is accomplished by control of the adsorption or decomposition kinetics of the precursor gases on the surface. Limited decomposition results in dissociative adsorption but leaves a surface passive, preventing further adsorption of that precursor. The second requirement leads to control of the stoichiometry and structure of the film. Selective adsorption of a component into preferred surface sites fixes the composition and structure of the growing film.

III–V compounds are ideal candidates for atomic layer growth because the decomposition of the group III alkyl precursors can be controlled at low temperatures to give self-limiting adsorption, and the complementary acid–base characteristics of the electron deficient group III (Lewis acid) and electron-rich group V (Lewis base) components lead naturally to site-selective incorporation.

In this paper we investigate the adsorption and decomposition of TMA and the formation of AlN from low-temperature pyrolysis of TMA and NH_3 on Si surfaces using X-ray photoelectron spectroscopy. The objectives of this study are to understand in more detail the mechanisms of TMA decomposition and the fate of the organic ligands in TMA pyrolysis and to confirm the mechanisms of Al–N bond formation from coadsorption of TMA and NH_3. We demonstrate that the necessary conditions for atomic layer growth are satisfied in this system and that atomic layer growth of AlN can be accomplished at about 600 K.

Experimental Section

The experiments were carried out in a VG ESCALAB 5 X-ray photoelectron spectrometer, with sample dosing directly in the analysis chamber. Background pressure in the instrument was typically 1×10^{-10} Torr. Residual gas analysis with a quadrupole mass spectrometer and surface structural analysis with LEED were also available.

Samples were 1 cm^2 Si(100) single-crystal wafers, heated resistively by passing current through a 0.5-μm Ta film deposited on the back of the Si wafer. The temperature was measured with a W-5% Re/W-25% Re thermocouple inserted into a well drilled in the side of the Si sample. Samples were cleaned by sputtering with 3-keV Ar^+, followed by annealing to >1300 K until no residual C or O was observed by XPS and a sharp LEED pattern of the 2 × 1 reconstructed Si(100) surface was obtained.

Trimethylaluminum was obtained from Alfa Products. A small quantity was vacuum distilled into a stainless steel sample vial and purified before each use by several freeze–pump–thaw cycles to remove accumulated methane from the sample. The alkylaluminum compound was admitted to the sample chamber through a gas doser containing a small orifice (2–25 μm diameter, depending on the dosing pressure desired) and a glass microchannel capillary array. The sample was positioned approximately 1 cm from the capillary array to ensure uniform flux of gas to the surface. Doses were estimated on the basis of the calculated conductance of the orifice and the sample reservoir pressure but must be considered quite uncertain due to the slow decomposition of the gas in the doser manifold and adsorption and slow desorption of TMA from the walls of the vacuum chamber. Significant quantities of methane were observed in the analysis chamber both during and after dosing, indicative of adsorption and decomposition of the precursor in the instrument. Because of the rapid hydrolysis of TMA the experiments were extremely sensitive to the presence of residual water vapor in the vacuum chamber. However any water remaining after baking the system was effectively gettered by the first exposure of the chamber to the alkylaluminum compound, and no further problem was encountered. Ammonia was admitted to the chamber through a leak valve, and doses were estimated on the basis of the pressure reading in the main chamber and exposure time.

Sample dosing was followed immediately by XPS analysis. All measurements were performed using a Mg Kα X-ray source operated at 15 kV and 300 W. The hemispheric energy analyzer was used in constant analyzer energy mode with a pass energy of 20 eV, giving an instrumental line width, including broadening due to the X-ray source linewidth, of approximately 1.0 eV. All binding energies are referenced to the Fermi energy of gold ($Au(4f_{7/2}$ = 84.0 eV). Integrated peak intensities were quantified by using standard elemental sensitivity factors[13] corrected for transmission characteristics of the analyzer, which were found to be in excellent agreement with measured standards.

For adsorbed organometallic films, however, consistently higher levels of C were measured than are contained in the molecules. In the case of TMA, room-temperature molecular adsorption indicated a C/Al ratio of approximately 4, using the standard sensitivity factors. Since the major carbon-containing impurity in the vacuum chamber is CH_4, which has negligeable sticking probability, we conclude that this calculated ratio is in error. This error could be due to attenuation of the Al(2p) photoelectrons by the pendant CH_3 groups on the surface. In any case we have used molecularly adsorbed TMA at room temperature with a C/Al ratio of 3 as an internal standard for the C(1s) sensitivity factor.

Results and Discussion

TMA Adsorption and Decomposition. TMA adsorption and decomposition on Si has been studied by a number of authors.[14-16] At room temperature and below, TMA adsorbs readily, forming multilayers below 200 K and a stable monolayer composed of TMA dimers up to approximately 300 K and monomers up to approximately 400 K.[14,15] In the present experiments saturation of the surface is observed at temperatures up to 600 K for doses greater than about 100 langmuirs. Quantitative estimates[17]

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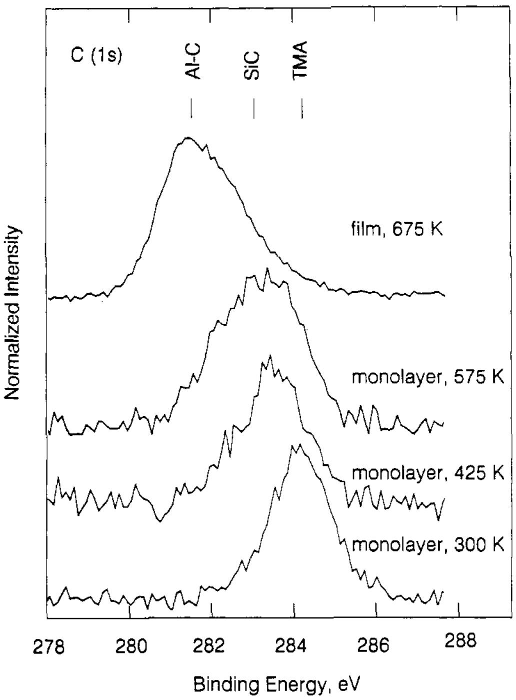

Figure 1. C(1s) X-ray photoelectron spectra of Si samples dosed with TMA at 300–675 K. Intensities are normalized to equal peak heights. Exposures at 300–575 K result in self-limiting submonolayer coverage with some evidence of dissociation to carbidic species at higher temperatures. Continuous deposition at 675 K results in a thick film of aluminum carbide.

of the saturation coverage made from the integrated peak intensities, elemental sensitivity factors, and the inelastic mean free paths[18] for photoelectrons from the Si substrate and the Al-containing film give a maximum of 1.5×10^{14} cm^{-2} for TMA. The XPS spectrum of the adsorbed TMA layer obtained here agrees well with previous reports.[14,15]

At room temperature saturation occurs for Al coverage of approximately one-eighth to one-quarter of a monolayer (compared to the surface density of Si(100)). Further adsorption is prevented by site blocking by dissociated organic fragments and steric effects of remaining pendant organic ligands on the Al atom. Dissociation and desorption of the organic ligands are often rate controlling in CVD processes and represent a major source of C contamination of the resulting film. We have followed the evolution of the organic ligands in the decomposition of TMA by observing changes in quantity and bonding environment of the C in the XPS measurements, shown in Figure 1. At room temperature, the C(1s) binding energy of 284.3 eV is identical with that of multilayer TMA films,[14] and the width (approximately 1.75 eV) and symmetry of the peak indicate primarily a single bonding type. Methyl groups attached to either Al or Si sites populate the surface. Self-limiting adsorption is also observed on surfaces heated to 425 and 575 K; however, the C(1s) peak broadens substantially and shifts to lower binding energy, indicative of formation of carbidic species. C(1s) binding energies for Si–C and Al–C occur at approximately 283.1[19,20] and 281.5 eV,[21] respectively, and could account for the C(1s) binding energy shifts observed here. The C(1s) line for a thick film of aluminum/aluminum carbide formed by pyrolysis of TMA at 675 K is also shown in Figure 1. These changes in the C(1s) spectrum for adsorption at different temperatures are very similar to those observed by Gow et al.[15] upon annealing a molecular layer of TMA to high temperatures.

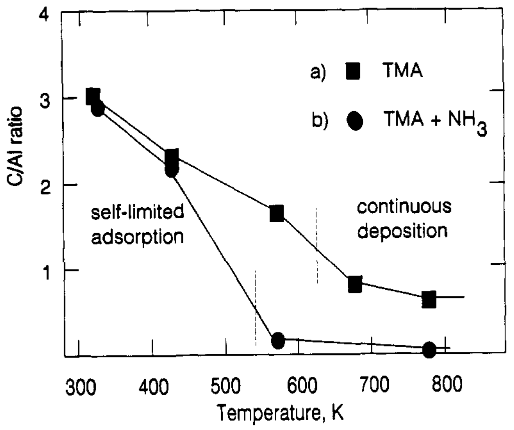

Figure 2. C/Al ratio in (a) adsorbed TMA and (b) coadsorbed TMA + NH_3 as a function of temperature. Points to the left of the dotted lines represent submonolayer films formed by self-limiting adsorption. Points to the right of the dotted lines represent thicker films formed by continuous deposition.

The formation of SiC at the interface upon adsorption of TMA to Si is potentially deleterious to the interface properties of Al or AlN films with Si. No obvious contribution to the Si(2p) line from Si–C bonding was observed, but the large escape depth of the Si(2p) photoelectron from the bulk (25 Å)[18] and photoelectron detection normal to the surface makes surface features of the bulk element difficult to detect. Ishida et al.[22] reported formation of SiC from TMA adsorption on clean Si and annealing at 600–875 K, and Gow et al.[15] reported EELS features consistent with formation of Si–C bonds. Bartram et al.[1] observed a similar phenomenon on SiO_2, with Si–CH_3 bonds formed by dissociation of TMA.

The amount of carbon retained in the film and the extent of dissociation of the alkylaluminum precursor is shown in Figure 2a. The C/Al ratio for TMA adsorption at room temperature to 575 K indicates a large fraction of the C is retained by the film in the self-limited adsorption regime (up to approximately 650 K). Passivation of the surface by undissociated organic ligands prevents further adsorption and formation of a thick film. Above about 650 K continuous deposition is observed and the C/Al ratio becomes constant at about 0.6. This is consistent with formation of an aluminum carbide phase along with metallic Al upon pyrolysis of TMA. The dehydrogenation of the surface observed in Figure 1 is seen here to be accompanied by a decrease in the total residual carbon. The most obvious explanation, proposed by Gow et al.[15] is H abstraction by CH_3 leading to desorption of CH_4 and a hydrogen-deficient, carbidic surface.

It is clear that reactions and desorption of the C-containing ligands in alkylaluminum pyrolysis are key to the residual contamination of the films. Dissociation of the parent molecule at the interface may also lead to CH_x adsorption to the substrate and possible SiC formation at higher temperature. We concur with Gow et al.[15] that this transfer of CH_x from the TMA to the Si substrate is a serious drawback to the use of TMA in film growth on Si. Triethylaluminum (TEA) and other larger alkylaluminum compounds capable of undergoing β-hydride elimination

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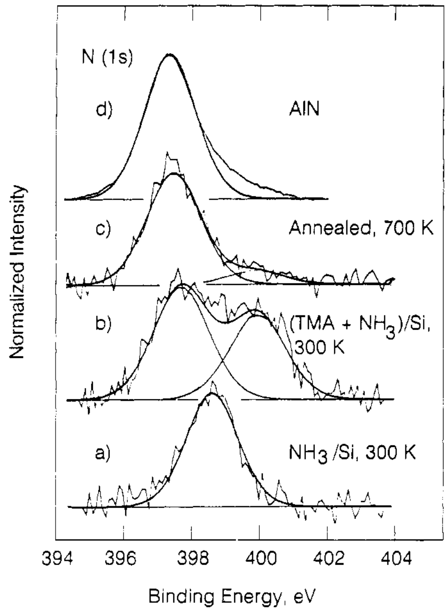

Figure 3. N(1s) X-ray photoelectron spectra for (a) adsorbed NH_3, (b) coadsorbed TMA + NH_3 at 300 K, (c) the coadsorbed film annealed at 700 K, and (d) an AlN film grown at 900 K. Peak intensities are normalized.

reactions have been observed to result in less C contamination than TMA.[23-25]

TMA and NH_3 Adsorption and AlN Formation. The adsorption of TMA and NH_3 and their conversion to AlN is conveniently studied by observation of the N(1s) line in XPS. NH_3 is known to adsorb to Si(100) at near room temperature to form a quarter monolayer of NH_2.[26] Heating of this layer to >700 K leads to hydrogen desorption and formation of Si_3N_4.[27] In Figure 3 we show the evolution of the N(1s) feature upon (a) adsorption of NH_3 at room temperature, (b) simultaneous exposure to TMA and NH_3 at room temperature, and (c) annealing the coadsorbed film to 700 K. The adsorbed NH_2 feature observed at 398.4-eV binding energy in (a) is replaced by two distinct features upon coadsorption with TMA. The lower binding energy feature at 397.3 eV is characteristic of a nitride and agrees well with XPS measurements of AlN formed by reactive evaporation[28] and by ion implantation.[29] Annealing of this film to 700 K results in the quantitative conversion of all the N(1s) intensity to this low binding energy feature, seen in (c). This feature is identical with that observed for an AlN film formed at 800 K by continuous pyrolysis of TMA and NH_3, shown in (d).

The higher binding energy feature at 399.8 eV is consistent with donation of the N lone-pair electrons (Lewis base) to form a bond with the empty nonbonding orbital of the alkylaluminum (Lewis acid). A chemical shift to higher binding energy indicates less efficient screening of the core level due to withdrawal of valence electron density on the atom being observed. This type of bonding would represent an analogue to the well-known gas-phase adduct formed between TMA and NH_3,[30] consisting of NH_3 bound to an adsorbed alkylaluminum species via the adduct bond. A similar shift to higher binding energy in the N(1s) line is observed for the gas-phase adduct $BH_3{:}N(CH_3)_3$.[31]

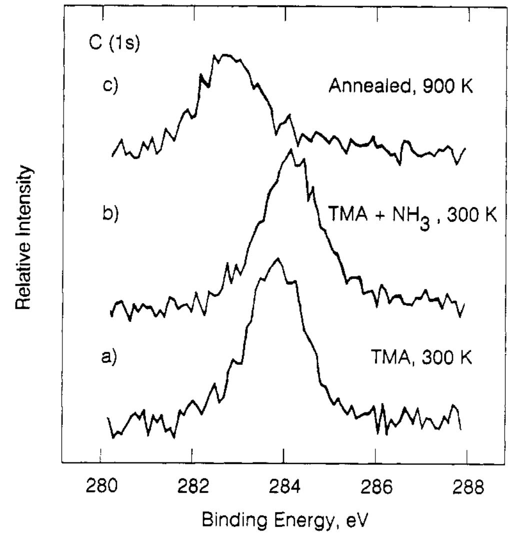

Figure 4. C(1s) spectra for (a) adsorbed TMA, (b) coadsorbed TMA + NH_3 at room temperature, and (c) the coadsorbed film annealed to 900 K. Peak intensities are relative.

Two important aspects of Figure 3 should be noted. First, the covalent Al–N bond formation that eventually leads to AlN is readily formed at room temperature. Second, the formation of surface adduct species (Al:N) leads directly to Al–N covalent bond formation upon annealing to higher temperature. The integrated intensity of the entire N(1s) region remains constant during the annealing procedure, with all of the Al:N intensity converted to Al–N.

Recently, Bartram, et al.[2] have presented infrared spectroscopic evidence for the existence of a surface adduct of TMA and NH_3 on SiO_2. The infrared measurements clearly show the existence of NH_3 adsorbed to an alkylaluminum surface species, which is converted to NH_2 upon heating. Bartram has suggested that this is evidence for such a surface adduct as a direct precursor to the formation of covalent Al–N–Al species in a tetrahedrally bonded AlN network, lending support to the conclusions of XPS measurements presented here.

Decomposition of the surface adduct by annealing to form Al–N covalent bonds is accompanied by loss of carbon from the surface and dehydrogenation of the residual carbon. Figure 4 shows C(1s) spectra for TMA adsorbed at room temperature (a), TMA and NH_3 coadsorbed at room temperature (b), and the coadsorbed film after annealing at 900 K. The binding energy and intensity of the C(1s) feature is nearly identical for the two room-temperature adsorbed films, indicating little change in the C environment, as expected for formation of the surface adduct. Upon annealing, the C(1s) intensity decreased by approximately 50%, and the binding energy shifted to lower values, characteristic of carbide formation.

The presence of NH_3 facilitates the removal of C from the surface as is evident by comparisons of the residual C fraction in the AlN and AlC films. C/Al ratios for samples dosed simultaneously with TMA and NH_3 as a

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function of temperature are shown in Figure 2b. Adsorption saturates at a fraction of a monolayer for temperatures <500 K. Carbon retention is high in these films as well, as shown in Figure 2b. As the temperature is raised above 550 K, however, residual C is reduced to much lower values than that observed for the TMA pyrolysis alone (Figure 2a). Continuous deposition (as judged by attenuation of the substrate Si(2p) photoelectron intensity) is also apparent at lower temperatures than for the TMA alone. Decomposition of the adsorbed NH_x to form a nitride with loss of H also occurs here at significantly lower temperature than is observed for H_2 desorption from adsorbed NH_2 on Si.[26]

It is possible that desorption of CH_4 due to hydrogenation of CH_3 by H from the NH_3 is responsible for the loss of C from the film. We have no direct evidence from these experiments that this is the case, however. This mechanism for CH_4 formation has been proposed earlier for TMA and trimethylgallium (TMG) decomposition on Si,[15] and recent thermal desorption experiments using TMA and ND_3 adsorbed on SiO_2 have revealed CH_3D evolved at >600 K.[2]

In contrast to the methane desorption mechanism discussed above is the case of GaAs growth from TMG and arsine, where CH_3 radical desorption from the surface is observed as the predominant product.[32-34] In this case the presence of arsine is also observed to increase the rate of Ga–CH_3 dissociation, but hydrogenation of the CH_3 is not observed. We cannot entirely rule out this mechanism in the TMA dissociation.

The Al/N ratio in the monolayer and multilayer films grown by both sequential and simultaneous dosing of the substrate was determined from the XPS data. NH_3 doses were always in excess of the TMA dose by a factor of 2–10. In all cases, the ratio of Al/N incorporated into the film was >1 at $T < 550$ K where adsorption is self-limiting and approximately 1 at higher temperatures where multilayer film formation occurs. This is an important consideration in control of the resulting film composition. Availability of Al sites for N incorporation is limited by dissociation of the Al–CH_3 bond. However, given sufficient lability of the Al–C bonds, reaction of the NH_3 is selective at the Al site, and the stoichiometry is fixed. Likewise, it appears that TMA preferentially incorporates at N sites on the surface, although it will react at Al sites at >650 K. This site selectivity leads to automatic stoichiometry control similar to that observed in growth of GaAs. All that is required is a sufficient excess of group V source to maintain a high concentration of preferential surface sites for group III incorporation.

Atomic Layer Growth of AlN. The observations of self-limiting adsorption of TMA at $T < 650$ K and site-selective reaction of NH_3 at Al surface sites at $T > 550$ K suggest that an atomic layer growth process for AlN is possible at 550–650 K. Sequential exposures of the sample to TMA and NH_3 should lead to incorporation of Al during the TMA cycle until the adsorption saturates and incorporation of N during the NH_3 cycle until Al sites are depleted, with elimination of CH_3 from the surface during the NH_3 exposure.

This process should be successful only in this narrow temperature range. At temperature higher than about 650 K, adsorption of TMA is no longer self-limiting. Decomposition of the CH_3 ligands lead to further adsorption of TMA and formation of carbidic species. At temperatures lower than about 550 K, the elimination of CH_3 and reaction with HN_3 are slow, resulting in no adsorption past the first monolayer, as indicated in Figure 2b. Only at approximately 550–650 K is both TMA adsorption self-limiting and reaction with NH_3 facile.

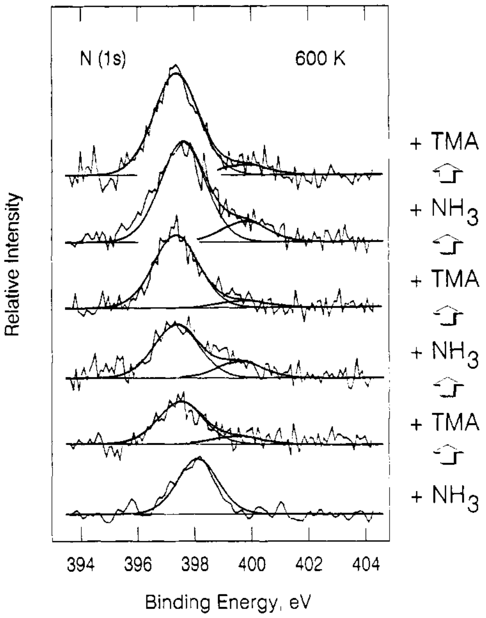

Figure 5. N(1s) spectra for sequential doses of NH_3 and TMA at 600 K. Peak intensities are relative.

Sequential doses of NH_3 and TMA of approximately 1000 langmuirs at 10^{-6} Torr and 600 K were given to a Si(100) sample with XPS spectra obtained after each half cycle. The N(1s) feature serves as a useful diagnostic for the growth of the AlN film and the chemical state of the growth surface. N(1s) spectra are shown in Figure 5 for three full cycles of NH_3 and TMA exposure. The initial NH_2 feature observed on the Si surface is converted primarily to Al–N upon adsorption of the first TMA dose. A small quantity of the high binding energy surface adduct feature (Al:N) is also observed. The C(1s) signal (discussed below) increased dramatically at this point, exhibiting a binding energy consistent with surface CH_3 termination. The next dose of NH_3 produces nearly equal increases in both the Al–N and Al:N intensities. The Al:N feature disappears almost entirely with subsequent TMA exposure. This sequence is repeated for each successive cycle of NH_3 and TMA exposure. LEED observations after three cycles showed only faint 1 × 1 substrate spots, with a high background, indicating little or no ordering of the deposited film.

The quantity of Al, N, and C on the surface during each point in this dosing sequence is shown in Figure 6. The attenuation of the Si substrate signal indicates that the amount of AlN deposited per full cycle is actually only about one-eighth to one-quarter of a molecular layer for an AlN crystalline film. This is consistent with the above observation of self-limited adsorption of TMA at about one-eighth monolayer. As earlier, we suppose this is due to site blocking by the pendant and dissociated methyl groups on the TMA.

The site-selective nature of the growth process is evident from the fixed 1/1 stoichiometry of the AlN film after the second and third full cycles. (It was not feasible to extend these experiments past three cycles because of the difficulty of maintaining an oxygen-free surface during the long exposure and analysis times required for these ultrahigh-vacuum experiments.)

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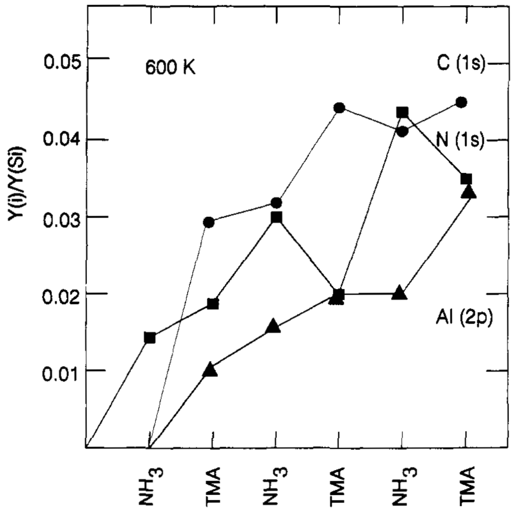

Figure 6. Quantitative yields of Al(2p), N(1s), and C(1s) relative to the Si(2p) bulk photoelectron yield for the sequential dosing experiment of Figure 5.

There remains a large amount of residual carbon in the film, apparently in the form of undissociated CH_3 as well as carbidic species, as judged from the C(1s) binding energy. At these conditions of temperature and pressure, the elimination of CH_3 is apparently not rapid enough to liberate all of the carbon. The major contribution to the C(1s) signal occurs during the first TMA exposure, while succeeding doses add decreasing amounts of residual carbon. CH_3 dissociation and transfer to Si substrate sites, as observed by Gow,[15] is consistent with this observation and suggests that much of the residual carbon may be contained in the interfacial layer, which would eventually be converted to SiC.

The observation of the Al:N adduct species on the surface after the NH_3 dose also indicates that the temperature (or time) of the exposure is not sufficient to convert all of the adduct to Al–N, resulting in retention of CH_3. After the NH_3 dose both Al–N and Al:N peak intensities increase (see Figure 5), whereas after the TMA dose, the Al–N remains constant while Al:N decreases, resulting in a decrease in the total N signal (see Figure 6). Some NH_3 is apparently desorbed from the surface before or during the TMA dose, originating exclusively from the Al:N surface species. This suggests that the surface adduct species is not a reactive site for adsorption of TMA and can actually result in loss of nitrogen from the surface by decomposition of the relatively weak Al:N bond.

We have not attempted to optimize the growth of AlN, nor have we progressed in the atomic layer growth sequence past the interfacial layer (for the reason cited above). However these experiments demonstrate that atomic layer growth of AlN is possible, and we have outlined the restrictive conditions under which successful atomic layer growth can occur in this system. The temperature must be kept low enough to prevent rapid decomposition of the TMA and formation of carbidic species but high enough to promote complete conversion of the Al:N surface adduct species to Al–N with elimination of CH_3. The mechanism of dissociation and desorption of carbon-containing products in this system is still unclear and requires further work to clarify the nature of the atomic layer growth process.

Summary

We have studied the adsorption and decomposition of trimethylaluminum on Si(100) and the low-temperature formation of AlN from pyrolysis of TMA and NH_3 and demonstrated a mechanism for atomic layer growth of AlN by self-limiting adsorption of TMA and site-selective reaction of NH_3 and TMA at 600 K.

TMA adsorbs dissociatively with a high sticking probability to Si at temperatures above 300 K. At temperatures below 650 K adsorption is self-limiting at <1 monolayer, with most carbon remaining in the form of CH_3. At higher temperatures, decomposition of the TMA is rapid, leading to thick film formation, loss of about 80% of the carbon, and production of carbides (AlC and perhaps SiC). Transfer of CH_3 from TMA to the Si substrate and eventual formation of SiC may be an important drawback to the use of TMA in film growth processes on Si.

Coadsorption of TMA and NH_3 at room temperature leads to formation of Al–N covalent bonding as well as a surface adduct species, Al:N. Upon annealing to >500 K, this adduct is converted quantitatively to Al–N, accompanied by elimination of carbon from the surface. This observation confirms both the existence of a Lewis acid–base adduct between adsorbed alkyl aluminum species and ammonia and that this adduct is a direct precursor to the formation of covalent Al–N bonding. At substrate temperature <550 K, coadsorption of TMA and NH_3 is self-limiting at less than a monolayer, while above this temperature reaction is rapid to form a thick film of AlN.

Self-limiting adsorption of TMA at <650 K and rapid, site-selective reaction with NH_3 to form AlN at >550 K suggest that an atomic layer growth process for AlN is possible at about 600 K by using sequential exposures of TMA and NH_3. This proposal is confirmed. Sequential dosing at 10^{-6} Torr and 600 K leads to self-limiting adsorption of TMA and conversion to stoichiometric AlN, with approximately one-eighth of a monolayer of AlN deposited per dosing cycle. Significant C retention in the film and incomplete conversion of the Al:N surface adduct to Al–N suggest a narrow range of conditions in which this process is effective. No indication of crystalline film formation at these temperatures was observed, likely due to the large degree of residual C contamination at the AlN/Si interface.

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