Low-Pressure Deposition of TiN Thin Films from a Tetrakis(dimethylamido)titanium Precursor

C. M. Truong, P. J. Chen, J. S. Corneille, W. S. Oh, and D. W. Goodman*
Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255
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We demonstrate that, at low reagent pressures (<10^{-4} Torr), the prevalent TiN film deposition mechanism operates exclusively on the reactions between tetrakis(dimethylamido)titanium (TDMAT) and NH3 at the growth surface. Our surface spectroscopic analyses indicate that film deposition in the low-pressure regime is also capable of delivering TiN with very low residual carbon levels. Spectroscopic evidence supporting this surface-reaction pathway to TiN films is presented in this report. The kinetics of the reactions between TDMAT and NH3 on TiN surfaces are also explored. In addition, we also discuss a proposed mechanistic framework for this low-pressure deposition process.

I. Introduction

Research in recent years has shown the potential and viability of metal oxide chemical vapor deposition (MOCVD) processes which utilize tetrakis(dimethylamido)titanium (TDMAT) and NH3 for the commercial production of TiN films.1-5 It is commonly accepted that the reactions of TDMAT and NH3 at low temperatures can deliver TiN films which are suitable for applications in VLSI device technology.6,7 Current TDMAT/NH3 MOCVD deposition systems are operated at moderate to high atmospheric pressures where the process is driven by rapid reactions in the gas phase. However, these high-pressure processes must be judiciously regulated in order to obtain film products of desirable properties.8 Carbon residue is the primary impurity in these CVD TiN films. In general, the complete removal of the carbon-containing functional groups from the products requires sufficient reaction time between TDMAT and NH3. On the other hand, too extensive reactions usually lead to nonconformal TiN films. Despite a great deal of effort, no satisfactory description of this complex chemistry has been offered, and it remains a challenge to control the deposition operations in order to simultaneously achieve good step coverage and film purity from the gas-phase reactions.

In this investigation, we demonstrate that, at pressures below 10^{-4} Torr, the deposition of TiN is solely sustained by the reactions of the precursors at the growth surface. In the absence of gas-phase reactions at reduced pressures, the surface reaction pathways can also produce TiN films possessing low carbon content. We have, therefore, elected to pursue the surface chemistry of the TDMAT precursors, with the goal of developing an understanding of this largely overlooked mechanism for TiN film deposition.

II. Experimental Section

The ultrahigh vacuum (UHV) systems utilized in this study are equipped with a number of surface characterization techniques including X-ray photoelectron and Auger electron spectroscopy (XPS and AES), FT-IRAS and thermal desorption mass spectroscopy (TD-MS). All X-ray photoelectron spectra were acquired at normal incidence, using a Perkin-Elmer double-pass cylindrical mirror analyzer, Model 15-255G, and with an unmonochromatized Al Kα X-ray radiation source. The thermal desorption mass spectra were recorded from a UTI 100C quadrupole mass spectrometer (housed in a differentially-pumped shroud) and with a linear heating rate of 5 K/s.

The reflection infrared measurements (FT-IRAS) were conducted in a similar UHV system which is also equipped for TD-MS and Auger analysis. The Fourier-transform spectrometer is a Mattson Cygnus 100, equipped with a narrow band MCT detector. The infrared spectra were collected at 4 cm^{-1} resolution and averaged from 128 scans. The reflection geometry of the vacuum infrared cell allows the beam to impinge on the sample at near grazing incidence (~85°). The infrared cell is fitted with KBr windows and interfaced to the ultrahigh vacuum region via a differentially-pumped sliding seal. In this vacuum chamber, the sample can be directly transferred into the cell where infrared measurements can be obtained over a wide pressure range (10^{-9} Torr to atmospheric pressures). Gaseous reagents can be readily admitted into the cell through an effusive doser which is mounted about 1 cm from the sample surface. The infrared cell can also be quickly evacuated using a turbomolecular pump.

The TDMAT precursor was used as obtained from Schuch-P Chemicals, without further purification. However, the more volatile contaminants in the TDMAT container were evacuated by prolonged freeze-pump-thaw cycles. Semiconductor grade (99.999%) ammonia was obtained from Matheson Gas Products. In all experiments, the TDMAT vapor was generated by warming the liquid to 40-50 °C, and admitted to the vacuum chamber without diluents, via nozzle dosers and controlled by variable leak valves. Anhydrous hydrazine, obtained from Aldrich Chemicals, was subjected to repeated freeze-pump-thaw purification cycles before admission into the vacuum systems. In addition, the purities of the reagent fluxes (TDMAT, NH3, and N2H2) are also monitored using the residual gas analyzer (RGA).

Clean W(110) and Ta(110) metal substrates were prepared by repeatedly oxidizing the crystals in O2, followed by flashing to 2200 K, until the Auger or XPS signals of C and O contaminants were below the instrumental detection limit. However, in the studies of Ti surfaces, fresh titanium metal was evaporated in situ onto the W substrate at UHV, before each experiment.

III. Results

A. Adsorption and Reaction of TDMAT on W, Ta, and Ti Surfaces. To develop an understanding of the mechanistic
details of a surface process, characterization of the adsorption and reaction of the precursor molecules on the substrate is essential. Although not directly pertinent to the film growth processes which occur at many atomic layers beyond the substrate surface, these studies address the issues related to the initial film growth (e.g., film composition and morphology, etc.) at the film–substrate interface. These investigations of TDMAT precursor chemistry on metal surfaces should contribute to a better understanding of the implications of substrate reactivity on the film interface. Furthermore, the interactions of the precursor molecules with Ti surfaces are particularly important due to the common utilization of titanium in device metallization processes and to its very strong reactivity.

1. TDMAT Adsorption and Decomposition on W(110) and Ta(110). The thermal desorption spectra of TDMAT on W(110) are shown in Figure 1, for increasing exposures. Molecular desorption of TDMAT from the W(110) surface is only observed for exposures above 6 langmuirs. The feature at ~220 K is attributed to the condensed TDMAT multilayer. The desorption states between 230 and 280 K saturate near 12 langmuirs and are assigned to the unreacted fraction of chemisorbed TDMAT. Subsequent XPS intensity analyses indicate that this fraction amounts to 15–20% of the total chemisorbed TDMAT layer on W(110).

The corresponding thermal desorption spectra of the 45-amu, 16-amu, and 2-amu fragments are shown in Figure 2. The 45-amu channel monitors the evolution of dimethylamine during the dissociation of the adsorbed TDMAT molecule. Between 200 K and 280 K, the signal is cluttered by the cracking fragments of the parent TDMAT molecule. However, a dimethylamine desorption feature can be clearly discerned at ~310 K.

The decomposition of adsorbed TDMAT becomes more extensive above 350 K, where the evolution of methane (16-amu channel) clearly indicates the dissociation of the remaining dimethylamido ligands. The temperature range for hydrogen desorption is similar to that reported for recombinative desorption of hydrogen from clean W(110). However, above 450 K the H2 TD-MS spectrum is further complicated by the convolution with hydrogen evolution from the further decomposition of the dimethylamido ligands.

The reflection infrared spectra of Figure 3 provide further details on the decomposition of TDMAT on solid surfaces. This figure only shows results obtained for TDMAT adsorbed on the W(110) surface; however, analogous spectral features are also recorded for TDMAT on the Ta(110) and polycrystalline Re surfaces. After annealing to 250 K, the condensed TDMAT is removed and the decomposition of the chemisorbed TDMAT is made apparent by the emergence of an absorption band at 1590 cm⁻¹. A similar absorption band has been reported for the dissociation of TDMAT in the gas phase by Dubois et al., but at a higher temperature (above 580 K). The authors attributed this band to a species containing a C=N bond but did not elaborate on the assignment. The C=N stretching frequency of organic imine compounds are commonly observed in the range 1690–1640 cm⁻¹. For an imine ligand which is bonded to a metal center via the nitrogen end (i.e., the Ti–N=C configuration), it is conceivable that the C=N stretch frequency is similarly shifted to a lower frequency. This bonding configuration has led to frequency red shifts of a similar magnitude in metal–ketones and metal–aldehyde complexes. In these complexes, the ketone or aldehyde ligands are bonded to the metal center through the oxygen atom (known as the n(1)(O) configuration). The perturbation of the C=O bond by the metal center reduces the frequency of the ν(C=O) mode by 90–100 cm⁻¹. A similar effect can reasonably be expected for organometallic complexes with N-bonded imine ligands.
Many organometallic imine complexes which contain a similar metal–N bonding configuration have been reported in the literature. For temperatures below ~350 K, the intensity of the 1590 cm\(^{-1}\) peak increases with annealing temperature, whereas the intensity of the \(\nu(NC_2)\) deformation mode steadily decreases. The structure shown in Figure 4A is proposed for this decomposition product of adsorbed TDMAT. A plausible mechanism for the formation of such a species is depicted in Figure 4A. A similar scheme also is proposed by Fix, Gordon, and Hoffman. The decomposition mechanism begins with a \(\beta\)-hydrogen abstraction step and follows by the elimination of a dimethylamido group (as dimethylamine). In the Fix–Gordon–Hoffman mechanism, shown in Figure 4B, the decomposition product would then be a Ti–N–C metalacycle instead of a N-bonded Ti-imine complex. A notable difference between the IR spectra of adsorbed TDMAT (this study) and the ones reported for gaseous TDMAT (Dubois, Zegarsky, and Girolami) is the absence of the absorption band at 1273 cm\(^{-1}\) in the former. The proposed Fix–Gordon–Hoffman mechanism satisfactorily explains the IR absorption band at 1273 cm\(^{-1}\) but leaves the strong band at 1590 cm\(^{-1}\) unaccounted for.

The presence of this N-bonded Ti-imine structure can also explain the restructurering of the \(\nu(CH)\) absorption bands at temperatures above 250 K. Similar changes in the \(\nu(CH)\) absorption bands are also found in the IR spectrum of the gas-phase decomposition product of TDMAT. For TDMAT adsorbed on W(110) and Ta(110) (not shown), the characteristic absorption bands of N-bonded aliphatic CH\(_2\) groups (at 2760 cm\(^{-1}\)) are attenuated steadily with increasing annealing temperatures. Concurrently, two strong peaks at 2940 cm\(^{-1}\) and 2865 cm\(^{-1}\) in the \(\nu(CH)\) region steadily gain intensity (see Figure 5). These bands can be satisfactorily attributed to \(\nu(CH)\) stretching modes of the Ti–N=CH\(_2\) group.

The \(\nu(CH)\) stretching modes of vinyllic compounds (i.e., the \(==CH_2\) modes) commonly occur at higher frequencies than their aliphatic counterparts. For a vinyl \(==C-H\) group, the \(\nu(CH)\) mode is typically in the \(~3020–3100\) cm\(^{-1}\) range. However, in aldehyde compounds, the characteristic \(\nu(CH)\) stretching modes of the \(==C-H\) group are shifted to \(~2850\) and \(~2750\) by the charge-withdrawing oxygen atom. The nitrogen atoms in imine compounds are not as strongly electronegative, and hence do not affect the \(\nu(CH)\) stretch frequency of the \(sp^2\) hybridized CH group as greatly as the oxygen atoms in aldehyde compounds.

In this present work, similar infrared absorption bands are observed for Ta(110) and also for Re(poly crystalline) surfaces, when the adsorbed TDMAT is annealed to temperatures above 250 K. Subsequent to the TDMAT exposures at 100 K and annealing the sample to 1000 K, Auger analyses show significant amounts of carbon and nitrogen residues (more discussion in later sections). In contrast, these infrared absorption features are completely absent in similar measurements of TDMAT adsorption on polycrystalline Cu and Al surfaces. In agreement with earlier reports in the literature, our Auger analyses indicate that the compound adsorbs molecularly and reversibly on these latter surfaces. Considering the contrasting infrared and thermal desorption measurements recorded from W, Re, and Ta surfaces versus those obtained from Cu and Al surfaces, one is tempted to speculate that the "deep" decomposition channel of TDMAT on solid surfaces (in which the amido ligands are dissociated) proceeds via the formation of Ti-coordinated imine complexes. It is also worth noting that on all of the metal substrates where the 1590 cm\(^{-1}\) peak is observed (W, Ta, and Re), there is no mass spectroscopic indication of the evolution of N-methylimine (parent fragment, \(m/e = 43\)) from the surface upon high-temperature annealing.

Figure 6 shows C(1s) and N(1s) XPS spectra of a 10-langmuir exposure of TDMAT on W(110), recorded after annealing to the indicated temperature.
undergo further dissociation which leads to the carbon residues binding energies. The emergence of these spectral features begins to emerge. Compared to the measurements made on be easily resolved. Subsequent to annealing the W( 110) of TDMAT with Ta( 110) and Re surfaces.

that, on the average, two of the original four dimethylamido ligands in a chemisorbed TDMAT molecule are eliminated. From similar thermal desorption and XPS data of Figure 2.

The final Ti:N:C stoichiometry subsequent to annealing the surface to 700 K, obtained from the analyses of XPS intensities, is consistently on the order of 1:1.5:3. These results suggest that, on the average, two of the original four dimethylamido ligands in a chemisorbed TDMAT molecule are eliminated “cleanly” as dimethylamine. The remaining two ligands undergo further dissociation which leads to the carbon residues in the TiN deposits. From similar thermal desorption and XPS measurements, analogous conclusions can also be applied to the interaction of TDMAT with Ta(110) and Re surfaces.

2. TDMAT Adsorption and Decomposition on Ti. Thermal desorption spectra of TDMAT adsorbed on a Ti surface are shown in Figure 7 as a function of TDMAT exposure. For exposures above 8 langmuirs, molecular desorption of TDMAT begins to emerge. Compared to the measurements made on W(110) and Ta(110) surfaces, the chemisorbed TDMAT evolves from the Ti surface at a slightly lower temperature (~235–240 K). The desorption peak is also significantly narrower.

Figure 7. Thermal desorption spectra (m/e = 224) of increasing exposures of TDMAT on a Ti surface at 90 K.

gives rise to the small shoulder at high binding energy in the N(1s) spectrum at 90 K, which disappears upon annealing to above 200 K. In all the experiments of this study, dimethylamine adsorbs on W and Ta as “a spectator” and desorbs molecularly below 230 K. This molecular desorption of dimethylamine can also be seen in the 45-amu TDMS spectrum of Figure 2.

At annealing temperatures below 400 K, both the C(1s) and the N(1s) exhibit a slight reduction in intensity, due to desorption of some of the dimethylamido ligands. However, no significant change in the N(1s) binding energy or peak shape is apparent in any of the spectra recorded below 400 K. This is disappointing but not surprising since amine, imine, and even cyanide compounds have very similar N(1s) binding energy, and cannot be easily resolved. Subsequent to annealing the W(110) surface to 500 K, both the C(1s) and the N(1s) signal intensities are further attenuated and also display new features at low binding energies. The emergence of these spectral features indicates that some of the C–N bonds have been cleaved. The XPS spectra are, in fact, consistent with the thermal desorption data of Figure 2 which show the evolution of methane from 350 K to 600 K. Further heating to temperatures above 650 K eliminates all remaining hydrogen-containing species from the W(110) surface. The corresponding C(1s) and N(1s) XPS spectra show peaks at binding energies which are characteristic of metal carbides and nitrides.

The strong reactivity of Ti toward adsorbed TDMAT can also be seen in the XPS spectra of Figure 9. Subsequent to annealing the surface to 300 K, much of the N(1s) XPS intensity is located below 398 eV, indicating that most of the C–N bonds are already cleaved. The C(1s) spectrum at 300 K shows that about half of the methyl groups are decomposed to carbide deposits (below 281 eV). When the surface is heated from 300 K to 650 K, the C(1s) XPS intensity of the hydrocarbonaceous carbon (above 283 eV) is transferred wholly into that of carbide carbon. This conservation of the C(1s) and N(1s) intensities is consistent with the absence of methane desorption, dimethylamine desorption, and desorption of other carbon-containing or nitrogen-containing volatile by-products from the Ti surface in the TDMS measurements. Therefore, we are convinced that much of the C remained entrapped on the Ti surface upon dissociation of the chemisorbed TDMAT layer.

being essentially complete below 275 K. Subsequent XPS intensity analysis shows that this unreacted fraction of the TDMAT amounts to less than 7% of the total chemisorbed TDMAT. In sharp contrast to the results observed for the W(110) and Ta(110) surfaces, the 12-amu, 14-amu, 16-amu, and 45-amu TD-MS spectra display no desorption features above that of the condensed layer. The 2-amu desorption spectrum also shows that the hydrogen evolution from a TDMAT-covered Ti surface is complete below 600 K.

The corresponding IR spectra of 20 langmuirs of TDMAT adsorbed on the Ti surface are shown in Figure 8, as a function of annealing temperature. After annealing the Ti surface to 250 K, the complete decomposition of TDMAT is evidenced by the disappearance of the characteristic v(NC2) vibrational mode (~980 cm⁻¹). The spectral transformation in the ν(CH) region of the spectra of Figure 8 differs completely from that of the spectra of TDMAT on W(110) or TDMAT on Ta(110). The distinct restructuring of the CH stretching modes which is observed for TDMAT adsorbed on W(110) and Ta(110) is absent in the spectra of Figure 8. In addition, no absorption band in the 1600 cm⁻¹ region is detected. These results indicate that the adsorbed TDMAT is extensively dissociated by the Ti surface at temperatures below 250 K. In fact, most of the dimethylamido ligands themselves are also readily decomposed at this temperature.

Figure 8. Reflectance infrared spectra of multilayers of TDMAT condensed on a Ti surface at 100 K, acquired after annealing to the indicated temperature.
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Figure 9. C(1s) and N(1s) XPS spectra of 20 langmuirs of TDMAT adsorbed on a Ti surface, recorded after annealing to the indicated temperature.

Figure 10. C(1s) XPS spectra of TiN, films grown from TDMAT pyrolysis on (a) Ta surface and (b) on Ti surface at 600 K.

3. TiC\textsubscript{N} Film Growth from TDMAT. The implication of the substrate reactivity on the deposition of TiN films is best illustrated by the film profiles of Figure 10. In Figure 10, C(1s) XPS spectra of TiC\textsubscript{N} films are shown as a function of film thickness. The TiC\textsubscript{N} films are deposited by exposing the Ta (Figure 10a) or Ti surface (Figure 10b) to a continuous flux of TDMAT (~1 x 10\textsuperscript{-7} Torr) at 600 K. On the Ti surface, the initial deposit contains almost exclusively Ti-bound carbon. The reactivity of the titanium metal is once again manifested by the enrichment of carbidic carbon at the film–Ti interface. For multilayer film growth, this Ti-C interface is gradually buried by the growing TiC\textsubscript{N} film. Beyond the first 10 or so atomic layers, the TiC\textsubscript{N} film assumes the composition commonly observed for films which are grown from the pyrolysis of TDMAT. The chemical nature of the carbon incorporated in the film undergoes transition from a carbide-like carbon at the film–Ti interface to an organic carbon in the bulk film, as is clearly shown by the C(1s) binding energy shift as a function of film thickness. Analyses of the XPS C(1s) peak intensity of the film show that, upon heating the deposited TiC\textsubscript{N} film to temperatures above 750 K, a small fraction (~20%) of the hydrocarbonaceous carbon desorbs as methane. The Auger and XPS analysis also indicate that further heating of the TiC\textsubscript{N} films to temperatures above 1000 K leads to the evolution of hydrogen and the consequential transformation of the remaining residues to carbidic carbon.

B. Surface Reaction-Controlled TiN Film Deposition Mechanism. 1. Evidence of a Surface Mechanism for TiN Deposition. The deposition of TiN films is generally believed to be chiefly governed by the direct reaction between TDMAT and NH\textsubscript{3} in the gas phase. The mechanism has been shown to commence with the transammination of the TDMAT precursor by NH\textsubscript{3}.\textsuperscript{7,18} The subsequent surface decomposition of the products of this initial step would ultimately deposit TiN on the substrate. However, the rate constant for the gas-phase transammination reaction at 24 °C is reported to be ~1 x 10\textsuperscript{-16} cm\textsuperscript{3}/(molecules).\textsuperscript{19} This rate corresponds to roughly one reaction event in 1 million molecular collisions. It follows that under the low reagent pressure conditions (less than 10\textsuperscript{-4} Torr) of this study, direct reactions between gaseous TDMAT and NH\textsubscript{3} must be negligible and certainly cannot be credited for the observed TiN film formation. Nevertheless, gas-phase reactions are not simply dismissed from this work without the support of convincing spectroscopic evidence.
pressure was approximately

Upon removal of the NH3 pressures. Simultaneous fluxes of TDMAT and NH3 were upon the addition of NH3. In the absence of gas-phase reaction, this can only occur through surface processes involving adsorbed films deposited from the simple pyrolysis of TDMAT are primary indicator for the existence of such a surface reaction (or reactions), to rationalize the observed growth of TiN films. The XPS analyses of these films are shown in Figure 14. These XPS spectra clearly show that elevating the growth temperature adversely affects the carbon content in the product film. A reasonable rationalization is that at high substrate temperatures the competing TDMAT pyrolysis channel is favored over the one involving an adsorbed NH3 species. In agreement with reports in the literature, we have shown in the previous section that film products of TDMAT pyrolysis are heavily contaminated with carbon residues. In fact, at 700 K the C/N atomic ratio reaches the same magnitude of that observed for TiC2N films deposited via pyrolysis of TDMAT. Furthermore, an ammonia pressure of 2 \times 10^{-6} Torr is not sufficient to maintain an adequate surface concentration of the appropriate NH3 species to compete with the pyrolysis channel. However, the high C/N ratios of TiN films grown at 700 K can be reversed by further elevating the NH3 pressure to a background pressure of 5 \times 10^{-7} Torr, the estimated TDMAT flux is ~0.2 monolayer/s. The film deposition was allowed to proceed for 2 h before the controlling leak valves were shut off and all the gaseous reagents or products were evacuated. The XPS spectra were then recorded with the sample held at 600 K, in order to avoid the re-adsorption of residual TDMAT in the background.

The impact of NH3 on the carbon content of the deposited TiN films is quite apparent in Figure 13. The C/N atomic ratio was significantly reduced, from 1.5 for the TiN film grown without NH3 to 0.25, upon the addition of 5 \times 10^{-6} Torr of NH3 during the film deposition (see spectrum d). As mentioned above, at these pressures the formation of the TiN films observed in these experiments can only be attributed to surface-mediated reactions.

Having demonstrated the dominant role of surface processes at low reagent pressures, we proceed to examine the effects of the growth conditions on the composition of the TiN film. In a series of deposition experiments, TiN films were deposited at a constant TDMAT pressure (~3 \times 10^{-7} Torr) and NH3 pressure (~2 \times 10^{-6} Torr). The XPS analyses of these films are shown in Figure 14. These XPS spectra clearly show that elevating the growth temperature adversely affects the carbon content in the product film. A reasonable rationalization is that at high substrate temperatures the competing TDMAT pyrolysis channel is favored over the one involving an adsorbed NH3 species. In agreement with reports in the literature, we have shown in the previous section that film products of TDMAT pyrolysis are heavily contaminated with carbon residues. In fact, at 700 K the C/N atomic ratio reaches the same magnitude of that observed for TiC2N films deposited via pyrolysis of TDMAT. Furthermore, an ammonia pressure of 2 \times 10^{-6} Torr is not sufficient to maintain an adequate surface concentration of the appropriate NH3 species to compete with the pyrolysis channel. However, the high C/N ratios of TiN films grown at 700 K can be reversed by further elevating the NH3 pressure to compensate for the higher surface temperature. An encouraging observation from these measurements is that the direct reaction channel which produces clean TiN films can be sustained when
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Figure 14. XPS spectra of TiN films, deposited from $5 \times 10^{-7}$ Torr of TDMAT and $2 \times 10^{-6}$ Torr of NH$_3$: (a) at 500 K, (b) at 600 K, and (c) at 700 K.

Figure 15. Auger spectra of TiN films deposited at 500 K and at indicated TDMAT/NH$_3$ pressure ratio.

a sufficient coverage of the necessary NH$_3$ species is maintained at the growth front.

In agreement with the XPS measurements at very low reagent pressures ($<10^{-3}$ Torr), AES measurements (shown in Figure 15) of TiC$_x$N$_y$ films grown in the $10^{-5}-10^{-2}$ Torr pressure range also provide similar evidence of surface-reaction-controlled TiN film growth. In the temperature range 550–650 K, steady reductions in the carbon content are achieved by increasing the NH$_3$ partial pressure, from the steady-state film growths under combined flux of TDMAT and NH$_3$. These same effects were observed for deposition attempts on a number of substrate materials including Ti, SiO$_2$, and W (data not shown), suggesting the nonselective nature of the nucleation/film growth process under the conditions examined.

The basic chemistry of adsorbed TDMAT and NH$_3$ on TiN surfaces has not received much attention and remained poorly understood. In an early publication, Dubois and co-workers reported no reactivity between adsorbed TDMAT and NH$_3$ on solid surfaces under UHV conditions. Our present TDMAT/NH$_3$ co-adsorption studies at UHV (not shown) indeed corroborate the observations of these authors. However, the results of previous sections have shown that the absence of surface reactions at UHV conditions does not a priori rule out a growth mechanism which operates on the substrate surface at more elevated precursor pressures. Under steady-state film growth conditions, the reactive adsorption of TDMAT and NH$_3$ can lead to the formation of intermediate surface species. The presence of these reactive intermediates at sufficient concentrations can open up reaction channels which, under the nonequilibrium conditions of the thermal desorption experiments, are rendered inaccessible by the competing desorption channels of the reactants.

Since our interest now lies in the chemistry occurring at the growth front, all the measurements reported in the following sections are performed on TiN-covered surfaces. In all cases, before each adsorption measurement, clean TiN overlayers were prepared on the W(110) sample by reacting TDMAT with NH$_3$ in the $1 \times 10^{-5}$ Torr pressure range, at a substrate temperature of 550 K. Our efforts are mainly focused on gathering spectroscopic information necessary for characterizing the key elementary steps involved in the TiN film growth from TDMAT and NH$_3$. The objective of these experiments is to develop a realistic mechanistic framework which encompasses the more important surface reactions. For the purpose of formulating an investigating strategy, the deposition of TiN in the absence of gas-phase reactions is simply conceptualized as consisting of the following classes of surface processes: (I) the adsorption and desorption of the reagents TDMAT and NH$_3$; (II) the decomposition of TDMAT on the TiN surface, a nominally unimolecular process which is responsible for carbon-rich TiC$_x$N$_y$ films; and (III) the surface reaction(s) between adsorbed TDMAT and NH$_3$ (or their dissociation fragments), a nominally bimolecular process which accounts for the deposition of clean TiN products.

The limitations of experiments within the ultrahigh vacuum regime only allow direct determinations of kinetic information of some of these surface processes. Thermal desorption mass spectroscopy acquires kinetic data in the low-temperature, low-pressure limits for the adsorption and desorption of the reagents; however, extrapolations of these data into the elevated temperature and pressure regimes of CVD reactor operations are generally reliable. Similarly, the decomposition pathways of TDMAT on TiN film surfaces can be studied using surface spectroscopic techniques, and the associated kinetic parameters can also be estimated from measurements at ultrahigh vacuum.

Given the limited amount of kinetic data available from these studies, the more complex surface (bimolecular) reactions between TDMAT and NH$_3$ cannot be characterized in as much detail as the above surface processes. However, the overall investigation should provide a basis for the development of TDMAT/NH$_3$ CVD processes which operate via surface reaction mechanisms. Optimal operating windows for such processes should be realized with the precursor steady-state coverages and the deposition temperatures such that the TDMAT/NH$_3$ reactions are kinetically favored and the competing decomposition reaction impeded. To achieve this end, a knowledge of the precursor adsorption/desorption kinetics is essential. In addition,
the results from the numerous deposition experiments in this section should also provide many useful insights into such optimization efforts.

2. \( \text{NH}_3 \) Adsorption on TiN Surfaces. In consideration of the results of section B.1, a new bimolecular reaction pathway is anticipated with the addition of \( \text{NH}_3 \), since TiN products containing reduced carbon contamination levels are readily obtained. However, the thermal desorption spectra of adsorbed \( \text{NH}_3 \) (not shown) on a TiN surface which is precovered with a chemisorbed layer of TDMAT is analogous to those recorded for a TDMAT layer on a clean TiN surface. None of the monitored mass channels exhibits new or distinct desorption features which can be taken as indication of a surface reaction between TDMAT and \( \text{NH}_3 \). Likewise, our results (not shown) also indicate that under UHV conditions, \( \text{NH}_3 \) exhibits no observable reactivity toward the dissociation products of adsorbed TDMAT, which are prepared by repeatedly exposing the TiN surface to the TDMAT flux and annealing to 500 K. (In essence, this was an attempt to react \( \text{NH}_3 \) with a surface which is saturated with partially decomposed TDMAT molecules.)

Under ultrahigh vacuum conditions, \( \text{NH}_3 \) adsorbs molecularly and reversibly on TiN surfaces. However, a small \( \text{H}_2 \)-desorption state can be discerned at 700 K, indicating that a small fraction of the adsorbed \( \text{NH}_3 \) is dissociated by the TiN surface. Unfortunately, we could not quantify this amount of dissociated \( \text{NH}_3 \) using electron spectrosopic techniques, due to the lack of sufficient \( \text{N}(1s) \) signal and to the interference of the TiN substrate. On the other hand, the amorphous quality of the TiN substrate would render any comparison of \( 2\text{-amu} \) integrated thermal desorption peak areas (relative to the \( \text{H}_2 \) evolution from the reference W(100) surface) unreliable.

The 17-amu thermal desorption spectra, shown in Figure 16, of \( \text{NH}_3 \) chemisorbed on a TiN film surface show that the major evolution state of chemisorbed \( \text{NH}_3 \) occurs near 430 K. The desorption temperature is well below the film growth temperature and the onset temperature for the first Ti-ligand bond scission (see Figure 17b and next section, B.3). These \( \text{NH}_3 \) TD-MS spectra and the TD-MS spectra of TDMAT on TiN surface (discussed in the following section) can reasonably explain the reported failure of adsorbed TDMAT and \( \text{NH}_3 \) to react on the substrate surface at UHV conditions. It is clear that the desorption channels of TDMAT and \( \text{NH}_3 \) are kinetically more favored in this case.

Information of the \( \text{NH}_3 \) binding energy on a TiN film surface, in principle, can be obtained from analysis of the corresponding desorption spectra. However, the amorphous nature of the TiN substrate presents poorly defined, inhomogeneous binding sites and is believed to be responsible for the broadening of the desorption peaks. This distortion of the TD-MS spectra prevents any meaningful coverage-dependent leading edge analysis to be reliably applied to the desorption spectra. Nevertheless, a reliable estimate of the binding energy can be made using the Redhead formula and the measured desorption peak temperature. Such an analysis gives a \( \text{NH}_3 \) binding energy value of approximately 24 kcal/mol on TiN, for the \( \text{NH}_3 \) chemisorption state near 400 K.

3. TDMAT Adsorption on TiN Surfaces. Shown in Figure 17a are TD-MS spectra of TDMAT (\( m/e = 224 \)) adsorbed on a TiN surface. The condensed TDMAT layers desorb at a near constant peak temperature of 210 ± 10 K. The molecular TDMAT desorption from the chemisorbed submonolayer can be observed in the temperature range 220–350 K. This
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The thermal desorption spectra of Figure 17b show the mass fragments which evolve from the decomposing fraction of the chemisorbed TDMAT. The first major decomposition product is dimethylamine, desorbing at ~510 K. This temperature is comparable to the gas-phase pyrolysis step observed by Dubois et al. Following this initial elimination of a (CH₃)₂ ligand, further elimination of ligand groups from the precursor-derived surface intermediate becomes more difficult and hence occurs at higher temperatures. This, in turn, results in more extensive dissociation. The second major product desorbs at ~630 K as indicated by the evolutions in the 42-amu and 41-amu channels. Tracking this product is the desorption band of C₅H₆. At this high temperature, the desorption of methane is clearly reaction-limited. It is clear that the dissociation above 600 K goes beyond scission of the Ti–NR₂ bonds. It is more likely that the carbon incorporation into the film is the result of this “deep” dissociation step and subsequent steps in which the N(CH₃)₂ ligands are broken. Conceivably, the reduction of the titanium center from TiV to TiIII could also occur concurrently at this stage. On TiN surfaces, the Ti(2p) XPS spectra of TDMAT cannot be analyzed due to the emission from the substrate Ti atoms. However, for the measurements recorded on W(110) and Ta(110) surfaces, a comparable “extent” of TDMAT dissociation is consistently accompanied by a ~2 eV shift of the Ti(2p) peak to lower binding energy. To complement these thermal desorption measurements, mass spectrometric studies of the interaction of TDMAT with the TiN surfaces were also performed at steady-state conditions, with continuous impinging fluxes of TDMAT. The results of these steady-state studies are detailed in the Discussion.

4. Surface Reaction of TDMAT with NH₃. Representative kinetic measurements for the TDMAT/NH₃ surface reaction are shown in Figure 18. In these measurements, the attenuation of the XPS W(4f) emission of the W(110) substrate with increasing deposition time is interpreted as a measure of the thickness of the TiN film which, in turn, serves as an indicator of the reaction. All of the depositions shown in the figure are carried out at comparable background TDMS pressures of ~1 × 10⁻⁶ Torr (corresponding to ~1 ML/min) and an excess ammonia pressure of ~1 × 10⁻⁶ Torr. The initial growth rate (at less than 5 min) appears to be independent of the surface temperature. This seemingly anomalous growth characteristic may simply be due to the stronger reactivity of the W substrate which catalyzes the decomposition of TDMAT, equalizing the growth rates for all of the attempted deposition temperatures. The TiN growth rate at 400 K is very slow and, interestingly, raising the TDMAT pressures to ~3 × 10⁻⁷ Torr results in no noticeable increase in the growth rate (within the experimental uncertainties). However, when a constant TDMAT pressure of ~1 × 10⁻⁶ Torr (and NH₃ pressure at ~1 × 10⁻⁶ Torr) is maintained, raising the substrate temperature to 500 K more than doubles the deposition rate. On the other hand, the growth rate at 600 K exhibits only a modest increase relative to the deposition run at 500 K. For comparable TDMAT pressures, conducting the deposition experiment at 700 K (data not shown) brings no further enhancement in the TiN growth rate. We suspect that, at surface temperatures above 500 K, the deposition experiments using this low TDMAT pressure are already becoming TDMAT flux-limited and, therefore, their intrinsic reaction rates cannot be realized.

The TiN films which are realized at 600 K and below in these low-pressure experiments consistently exhibit low residual carbon levels (the achieved C/N ratios are on the order of 0.25 to 0.35). After the growth process, a fraction of the carbon residues are actually hydrocarbons and can be removed (as desorbing methane) by annealing the deposited films to temperatures above 700 K. In fact, the ultimate C/N ratios on the order of 0.2 are achieved by the postdeposition anneals. During the high-temperature annealing, significant amounts of residual hydrogen are also observed evolving from the films in the temperature range of 750–950 K. This temperature range actually differs from the temperature range which is recorded for TiC,Nₓ films which are deposited from the surface pyrolysis of TDMAT (i.e., in the absence of NH₃). When annealed to 900 K, the latter TiCₐNₓ films produce mostly methane. Hydrogen evolution from the TiCₐNₓ films is not observed until the sample is heated to above 1000 K. The integrated TDMS peak area also reveals that, for a comparable film thickness, there is less methane evolved from the TiN films during the anneal. Conversely, the TiN films which are deposited by reacting TDMAT with NH₃ liberate more hydrogen upon annealing to 1000 K. Furthermore, for the thin (<100 Å) TiN films which are deposited in our experiments, the amount of desorbing hydrogen increases with increasing film thickness. Unfortunately, in this investigation we were not able to quantitatively determine the residual hydrogen and residual CHₓ contents for either the TiN films or the TiCₓNₓ films.

IV. Discussion

A. Surface Reaction Kinetics. The complex growth behavior, particularly at low temperatures, indicates that the deposition rate is affected by the TDMAT + NH₃ reaction rate and the surface coverages of the reagents. The variation of the reactive sticking coefficient of the TDMAT precursor as a function of surface temperature also appears to be a primary factor. In a series of steady-state TDMAT adsorption experiments, the mass spectrometer signals of TDMAT fluxes,
molecularly scattered from a TiN-covered W(110) surface, were measured as a function of surface temperature (monitoring \( m/e = 224 \)), and for increasing incident fluxes (the background pressure rise was between \( 10^{-7} \) Torr and \( 10^{-6} \) Torr). The scattering profiles of these experiments are shown in Figure 19. The mass spectrometric scattering intensity provides a measure of the reactive sticking coefficient of TDMAT on the TiN surface under steady-state conditions.

In Figure 19, significant losses of mass spectrometric signal begin near 400 K, indicating the onset of TDMAT decomposition at the TiN surface. These profiles show that the reactive sticking probability of TDMAT on TiN is low at 400 K but rises very quickly with increasing surface temperature. This trend of reactivity is in very good agreement with the observed growth kinetics. At temperatures above 600 K, the complete disappearance of scattering signal, on the other hand, indicates rapid rates of surface pyrolysis. In fact, the results of deposition experiments (by reacting TDMAT with \( 1 \times 10^{-6} \) Torr of NH\(_3\)), which were conducted at temperatures above 600 K, must be discarded from our kinetic data set, due to the high carbon contamination levels (an indication that the film growth has considerable contribution from the competing pyrolysis reaction).

**B. Surface Reaction of TDMAT with Adsorbed NH\(_3\).** In light of the presence of H\(_2\) evolution, following the adsorption of NH\(_3\) on the TiN surface (the reader is referred to the results in section B.2), larger concentrations of surface amines (−NH\(_2\)) and imines (−NH) can conceivably be produced under realistic CVD conditions from the dissociation of NH\(_3\) on heated TiN surfaces. Generally, these species are more strongly adsorbed on solid surfaces\(^{22-25}\) and can have reactivities toward TDMAT which are significantly different from that of adsorbed NH\(_3\). These TiN deposition experiments on the W(110) surface, using TDMAT and hydrazine (N\(_2\)H\(_4\)), are only intended to help shed further insights into the mechanism of the surface reactions between TDMAT and surface NH\(_3\) groups. In order to enhance the coverages of these ammination agents (−NH or −NH\(_2\) groups) for the purpose of mechanistic studies at ultrahigh vacuum conditions, hydrazine (N\(_2\)H\(_4\)) was substituted for ammonia in the experiments of this section.

In general, at temperatures below 300 K, hydrazine decomposes very rapidly on solid surfaces producing adsorbed H, NH\(_3\), amine (−NH\(_2\)), and imine (−NH) groups, and, at temperatures above 500 K, atomic nitrogen.\(^{20-23}\) For the same reason stated above, when adsorbed on TiN surfaces, photoelectron spectroscopic characterizations of hydrazine and its decomposition products are seriously hindered by the interference of the underlying TiN films. However, the N(1s) XPS spectra which are recorded following hydrazine exposures to TiN surfaces do exhibit observable emission bands (appearing as shoulders of the nitride N(1s) peak) at binding energies above 399 eV in the temperature range 280–520 K. These features can only be interpreted as fingerprints of adsorbed −NH\(_2\) or −NH groups, since at these temperatures NH\(_3\) desorbs completely from the TiN surface. Our gas-phase infrared measurements also indicate that, at pressures above \( 10^{-3} \) Torr, reacting mixtures of hydrazine and TDMAT produce gaseous dimethylamine and TiN solid condensates (at the nozzle inlets). The formation of dimethylamine suggests that the gas-phase chemistry of the N\(_2\)H\(_4\)/TDMAT system is quite analogous to that of the NH\(_3\)/TDMAT system (i.e., involving a transammination reaction).

The use of hydrazine is purposed to alleviate the need to excessively raise the NH\(_3\) pressure (in UHV experiments) in order to obtain saturation concentrations of adsorbed −NH\(_2\) species at the TiN growth front. Our principal interest is to assess the reactivity of molecularly chemisorbed TDMAT molecules and also the reactivities of the dissociated TDMAT derivatives, in an environment that is enriched or even saturated with reactive ammination agents.

In Figure 20, the attenuation of the W(4f) XPS signal from the substrate is again used as a measure of TiN growth rate for a series of deposition experiments at different TDMAT fluxes (\( 1 \times 10^{-7} \) and \( 5 \times 10^{-7} \) Torr) and an excess but constant hydrazine pressure (\( \sim 5 \times 10^{-7} \) Torr). Despite the abundance and the stronger reactivities of the −NH and −NH\(_2\) groups which are produced on the TiN surface by the dissociation of hydrazine, sustained TiN film growths cannot be achieved in our experiments at surface temperatures below 350 K. In congruence with the results obtained in deposition experiments using NH\(_3\) (see Results, section B.4), the TiN deposition rate in these hydrazine experiments is similarly slow at 390 K and also exhibits little dependence on the TDMAT fluxes. In a trend analogous to the experiments using NH\(_3\), dramatic increases in the TiN growth rate are observed for the depositions at surface temperatures higher than 400 K.

In consideration of this reactivity information and the adsorptive behavior of TDMAT on TiN surfaces, as illustrated by the scattering data, we speculate that molecularly chemisorbed TDMAT is not the primary participant in the surface reaction which finally delivers the TiN product. Thermal desorption measurements indicate that molecular TDMAT is
weakly adsorbed on TiN surface. However, the derivative Ti species, produced by a "clean" removal of one of more amido ligands, are more strongly bound to TiN. Under the nonequilibrium conditions of thermal desorption measurements, only a small fraction of the chemisorbed TDMAT produces these partially dissociated Ti-D(NMe2), species during the temperature ramping. At temperatures where the "clean" amido-ligand removal step commences, the surface concentration of TDMAT would have been heavily depleted.

On the other hand, the scattered data suggest that a buildup of the more strongly bound species on the TiN, growth front can be achieved from steady fluxes of TDMAT and slightly higher surface temperature (>400 K). We speculate that these TDMAT-derived species, being more strongly bound than molecular TDMAT (and possibly more reactive), are becoming dominant on the TiN growth front at high surface temperatures (450 K < T < 600 K), and are actually responsible for the observed increase in the growth rate. Generally, in organometallic complexes the Ti center has a tendency to expand its coordination number. A chemisorbed TDMAT derivative which is stripped of one or more of its amido ligands (hence becoming less coordinatively-saturated), can become more susceptible to nucleophilic attacks by NH3 (or other NH2 groups) than a molecularly chemisorbed TDMAT molecule. It is conceivable that TiN deposition is actually carried by the transamination of these partially dissociated TDMAT molecules with adsorbed NH3 (or NH2) on the surface.

In Figure 21, a representative XPS characterization of a TiN film deposited from TDMAT and hydrazine at 500 K is shown. For hydrazine/TDMAT molecular ratios larger than 0.2, the produced films have very low carbon doping levels and also tend to be nitrogen-rich. The achieved C/Ti atomic ratios are on the order of 0.15 to 0.2. These low C/Ti ratios are remarkable in that they can be achieved in experiments which are clearly deficient in the amine-containing agents. (Preceding these deposition experiments, i.e., prior to covering the W(110) crystal with a TiN overlayer, the N2H4 molecular flux impinging on the W(110) surface is first estimated using the N(1s) XPS peak intensity of chemisorbed hydrazine, against the same of a saturation coverage of N adatoms on the W(110) sample). These results suggest that, besides the transamination step, there must exist additional avenues for the removal of the carbon-containing ligands from the Ti-containing reaction intermediates.

The lack of adequate infrared absorbance signal levels foiled all of our further attempts to monitor the steady-state reactions of TDMAT and NH3/N2H4 at elevated temperatures and pressures (above 500 K and 10^-6 Torr) and to detect reactive species which may be present under film growth conditions. Furthermore, emissions from the Ti and N atoms of the TiN underlying layer effectively impede the use of electron spectroscopy for the detection and identification of the reaction intermediates on TiN surfaces. These experimental obstacles leave us with no other available spectroscopic methods to directly study the reactions on the TiN surfaces. Without direct spectroscopic evidence we can only speculate on the surface reactions leading to the formation of TiN, relying only on the deposition kinetic information. The cartoons in Figure 22 illustrate our rationalization, proposed in analogy to the corresponding gas-phase and solution-phase mechanisms. By virtue of the abundance of adsorbed NH3 (x = 1, 2, 3) species under deposition conditions, a plausible surface reaction mechanism most likely involves a surface-mediated transamination reaction between adsorbed NH3 and Ti-(NMe2)x groups as the initial step. Following this step, the NH3 ligand in the adsorbed Ti precursor could subsequently open up additional intramolecular pathways to further eliminate the carbon-containing N-(CH3)2 ligands. Conceivably, a second N-(CH3)2 could be liberated as dimethylamine via an α-hydrogen transfer from the substitute NH3- to one of the remaining N-(CH3)2 groups. The successive α-hydrogen transfer within the intermediate molecule could also benefit from the decrease in the N-H bonding energy, from 110 kcal/mol for H-NH2 to 95 and 80 kcal/mol for H-NH and H-N, respectively. We should also point out that this scheme does not necessarily exclude subsequent direct transamination between a Ti(NR2)xNH- intermediate (hereafter referred to as amino-alkylamino-titanium) and another NH2 group.

Finally, the oligomerization of the adsorbed amino-alkylamino-titanium intermediates at the growth surface is also a plausible reaction step in the surface mechanism. A reaction scheme involving this step can be drawn in analogy to the conventional mechanism which is commonly proposed for the solution-phase chemistry of alkylamino-titanium compounds (see Figure 22B). Subsequent to the initial transamination steps, some of the remaining dimethylamino ligands can also be eliminated from the adsorbed amino-alkylamino-titanium intermediate as a result of a coordination–polymerization reaction with a neighboring amino-alkylamino-titanium group. The α-hydrogen-containing amino ligands are potentially bifunctional. At sufficient high surface densities, the intermolecular α-hydrogen abstraction may occur concurrently with the
intramolecular α-hydrogen transfer. We speculate that the evolution of hydrogen in the temperature range of 750 to 950 K, during the post-deposition annealing of the TiN films (see Results, section B.4), originates from these surface Ti-N oligomers. Its occurrence at this very particular temperature range can be reasonably accounted for by the scission of the μ-nitrogen–hydrogen chemical bonds (i.e., the hydrogens on the N-bridges). The thermal desorption measurements (see Results, section B.2) show that the hydrogen which is produced by the surface-dissociated NH₃ desorbs from the TiN surface at 700 K. Therefore, residual adsorbed hydrogen (following the deposition process) cannot account for this high-temperature hydrogen evolution from the TiN films.

As indicated in the Results, section A.3, the evolution of hydrogen which originates from the scission of the stronger C–H bonds in the residual methyl groups does not occur below 1000 K (for the N-bonded methyl groups; the bond strength is on the order of 95 kcal/mol). On the other hand, the desorption of hydrogen from the dissociation of adsorbed amino groups generally completes well below 700 K (i.e., the overall process of (1) the surface decomposition M–NH₂ → H(a) + N(a) step (2) the subsequent recombinative desorption 2H(a) → H(g) step) (also see Results, section A.2).

V. Conclusions

From the perspective of film conformality, a strong driving force for pursuing the development of MOCVD processes for TiN films is that a growth mechanism which involves surface reactions often yields uniform step coverages. An important prerequisite for the success of this deposition pathway is the low reactive sticking coefficient of the precursor molecule. The nonreactive scattering of the precursor molecule by the surface (and also the surface mobility of the precursor) ensures efficient reagent transport to device structures which have high aspect ratios.

Preliminary data on atmospheric-pressure CVD systems using TDMAT/NH₃ indicate very poor step coverage of the resulting TiN films. This has been tentatively attributed to a high reactive sticking coefficient of the gas-phase intermediates, which is accepted as an intrinsic property of the TDMAT/NH₃ reaction system. Since the growth mechanism which relies on the gas-phase reaction fails to provide acceptable film conformality, the next logical step is to turn to a surface-reaction driven mechanism, which is singularly controlled by surface reactions, will necessarily deliver better film conformality. Clearly, only direct characterizations of TiN films grown on test structures (vias or trenches) under well-controlled surface reaction conditions can provide a definite answer to this question.

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References and Notes

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