

MODEL STUDIES OF LOW TEMPERATURE TITANIUM NITRIDE THIN FILM GROWTH

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Abstract—The reaction of tetrakis(dimethylamido)titanium [Ti(NMe₂)₄, tdmat] and ammonia to yield titanium nitride (TiN) thin films and gas phase dimethylamine (HNMe₂) is discussed. Film growth is dominated by gas phase reactions which lead to the formation of large, oligomeric clusters of the form :



These decompose on the surface of the growing film at temperatures ≥ 450 K. By isotopically labelling the ammonia with ¹⁵N or deuterium, we conclude that both the nitrogen in a *clean* TiN film and the nitrogen bound hydrogen (deuterium) in the gaseous dimethylamine product are derived *exclusively* from ammonia. Evidence for carbon contamination through the intermediacy of a Ti—N—C metallocycle is provided. Our observations are compared with the known thermal chemistry of titanium dialkylamides in solution.

INTRODUCTION

Titanium nitride (TiN) thin films are used as coatings in a variety of important technologies due to their hardness (greater than that of sapphire). corrosion resistance, high melting point (\sim 3200 K), gold colour, and good electrical and thermal conductivity (better than that of pure titanium). Because of these unique properties and its excellent adherence to most metals, semiconductors and insulators, TiN also shows promise as a barrier layer in ultra-large scale integrated circuits.¹⁻³ The deposition of pure, conformal titanium nitride thin films on a wide variety of substrates continues to be a challenge, however. While reactive sputter deposition of pure titanium in a nitrogen-argon atmosphere can be used to coat flat metallic substrates,¹⁻³ conformal coverage of complex shapes and the coating of soft or damage-sensitive materials is still difficult.

Chemical vapour deposition (CVD) techniques hold the promise of solving some of these problems.

For example, the reaction of titanium tetrachloride (TiCl₄) with nitrogen and hydrogen⁴ or with ammonia⁵⁻⁹ leads to the formation of high-purity titanium nitride thin films. Although both the step coverage and the sheet resistivity are excellent, reactions must be carried out at substrate temperatures above 850 K. This temperature can be reduced somewhat by employing tert-butylamine as both the reductant and the nitrogen source.^{10,11} Attempts at lowering the deposition temperature further have involved either plasma assisted processes^{12,13} or the use of volatile titanium subchlorides¹⁴ or alkylamides as the titanium source.¹⁵⁻¹⁹ For example, a low temperature (450-700 K) process has been by demonstrated recently mixing tetrakis (dimethylamido)titanium (Ti(NMe₂)₄, tdmat), a volatile yellow liquid,¹⁵⁻¹⁸ and ammonia in the gas phase. Similar reactivity is seen with other titanium alkylamides including Ti(NEt₂)₄ and Ti(NMe₂)₃-('Bu).¹⁵⁻¹⁹ The deposition chemistry is complex, however, and is dominated by the formation of reactive gas phase intermediates and/or clusters.²⁰ Despite these difficulties, high quality titanium nitride can be grown from tdmat and ammonia in a low temperature process. The resulting films cannot contain

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chlorine (which might cause corrosion problems) and therefore have excellent long-term reliability.

A stoichiometric reaction between tdmat and NH_3 can be written by analogy with the known reaction of TiCl₄ with ammonia⁵:

$$6 \operatorname{Ti}(\mathrm{NMe}_2)_4 + 8 \operatorname{NH}_3 \rightarrow 6 \operatorname{TiN} + 24 \operatorname{NHMe}_2 + \mathrm{N}_2.$$
(1)

Although nitrogen is bonded directly to titanium in the metallorganic precursor, the presence of ammonia is crucial to the growth of pure TiN: films grown in the absence of ammonia contain significant amounts of carbon, even when the deposition is conducted in excess hydrogen.^{21,22} Alternatively, the reaction can be written as:

$$2 \operatorname{Ti}(NMe_2)_4 + 4 \operatorname{NH}_3 \rightarrow$$

$$2 \operatorname{Ti}N + 4 \operatorname{NHMe}_2 + N_2 + 2 \operatorname{H}_2. \quad (2)$$

The formation of molecular nitrogen in eqs (1) and (2) (which can account for the reduction in the formal oxidation state of the titanium centre from +4 in the precursor to +3 in the product film) has never been established. Similarly, the presence of molecular hydrogen in eq. (2) has never been confirmed as a reaction product. Alternatively, homolytic Ti—N bond cleavage to form alkylamido radicals (i.e. $\cdot NMe_2$ or $\cdot NH_2$) has been proposed to account for the decrease in Ti oxidation state.^{23,24}

We have attempted to unravel the chemistry of TiN thin film growth at low temperatures by exploring the surface and gas phase reactions of tetrakis(dimethylamido)titanium with ammonia using Fourier transform infrared spectroscopy and molecular beam/mass spectrometry.^{20,25} Our mechanistic and isotopic labelling studies allow us to predict the source of nitrogen in the growing film as well as the mechanism of carbon contamination. In addition, we have determined the source of the nitrogen bound hydrogen in the dimethylamine product.^{20,25} In order to extrapolate these results to more "realistic" growth conditions, we constructed a novel gas source which allowed us to mix the reactants at high pressure, but carry-out film growth in high vacuum.²⁰ Some of our findings are summarized here and these observations are compared to the known thermal chemistry of titanium alkylamides in solution.

PYROLYSIS OF PURE TDMAT AND CARBON INCORPORATION

Since titanium and nitrogen are bonded directly in tdmat, one might expect the pyrolysis of this material to lead to the formation of TiN thin films.

Previous studies have shown that this is indeed the case, however, as noted above, the films are contaminated with carbon²¹⁻²³ and are sub-stoichiometric in nitrogen.²³ Carbon occurs in two forms: bonded directly to titanium and bonded to nitrogen or to other carbon atoms.^{22,23} In early experiments, Sugiyama et al. suggested that titanium alkylamides (Ti $(NR_2)_4$, R = Me, Et, n-Pr, and n-Bu) decompose through the successive elimination of amide fragments to give a low valent metal amide, followed by elimination of alkyl groups to yield the metal nitride.²¹ While homolytic Ti-N and Ti-C bond cleavage may occur for more sterically crowded ligands (e.g. cyclic NC₄H₈ and 'Bu),^{23,26} it is unlikely that this will occur in tdmat. Further, mass spectral analysis of the exhaust gases runs counter to the argument of direct bond cleavage since the major volatile products of tdmat pyrolysis are dimethylamine and ammonia.²¹ Thus, intramolecular hydrogen atom transfer must be occurring^{27,28} leaving behind elemental carbon. Other processes to remove carbon such as β -hydride elimination from Ti(NEt₂)₄ or Ti(NMe₂)₃('Bu) are probably occurring to a limited extent.23

We have probed the source of carbon in the growth of titanium nitride thin films by following the pyrolysis of tdmat in the gas phase using transmission infrared spectroscopy (see Fig. 1)²⁵ and mass spectrometry.²⁰ At temperatures below ~450 K the infrared spectrum is characteristic of the intact precursor [Fig. 1(a); mode assignments are discussed in refs. 25, 29, and 30]. Above ~500 K, however, intense new bands at 1590, 1505, 1276, 900, and ~750 cm⁻¹ become visible [Fig. 1(b)].²⁵



Fig. 1. Gas phase infrared spectra of 0.07 Torr of tetrakis-(dimethylamido)titanium at the indicated nozzle temperatures. No significant decomposition is observed until \sim 450K. Tentative mode assignments are discussed in ref. 25.

While a detailed analysis of the spectrum is difficult, several of the new bands deserve comment. Most importantly, the strong band at 1276 cm⁻¹ is clear evidence for the formation of species that contain Ti-N-C three-membered rings.^{25,31} This ring stretching frequency is *ca* 200 cm⁻¹ higher than those of normal N-C single bonds due to the presence of some partial double bond character and, possibly some mixing in of other modes.³¹



Such species could form via loss of dimethylamine (characterized by N—H bending modes at ~1500 and ~750 cm⁻¹) from Ti(NMe₂)₄,³² leaving behind a product that contains a Ti(NMeCH₂) metal-locycle (see below).

Although three-membered Ti—N—C rings have not been detected directly in the thermolysis of titanium dialkylamides in solution, they have been observed in the chemistry of other transition metals such as niobium, tantalum, and tungsten.^{29,33} If we assume that similar reactions can occur with tetrakis (dimethylamido)titanium, then we may write the initial step in the thermolysis pathway as follows:

$$Ti(NMe_2)_4 \rightarrow Ti(NMeCH_2)(NMe_2)_2 + HNMe_2.$$
(3)

Such a structure is consistent with the IR spectrum in Fig. 1(b). Both Fix *et al.*²³ and Girolami and coworkers³⁴ proposed that the decomposition of this intermediate can lead to the formation of strong Ti—C bonds and therefore to carbon incorporation into the growing TiN thin film.

Attempts to detect these same species on surfaces under ultra-high vacuum conditions proved unsuccessful. While tdmat has a near unit sticking probability on aluminum, copper, and titanium disilicide substrates at 300 K,^{25,35} infrared studies indicate that the dimethylamido groups remain intact. New C-H and C-N stretching vibrations are observed on TiSi₂ substrates at temperatures between 400 and 600 K, although there is not enough evidence to assign these bands to a metallocyclic intermediate.²⁵ Complete dissociation of the ligand is found above \sim 650 K leaving the surface covered with titanium. nitrogen, and significant amounts of carbon.²⁵ Xray photoelectron spectroscopic analysis of TiN thin films grown from pure tdmat provides evidence for both titanium and nitrogen bound carbon.²¹⁻²³ In addition, significant amounts of carbon and oxygen are observed at grain boundaries.^{20,22,23}

SOURCE OF NITROGEN IN TIN

There are two possible sources of nitrogen in titanium nitride thin films grown from a mixture of tdmat and ammonia : $Ti(NMe_2)_4$ and NH_3 . Isotopic labelling studies involving the reaction of ¹⁵NH₃ and ¹⁴N-tdmat and *ex situ* Rutherford back-scattering (RBS) analysis can be used to differentiate between these two possibilities.²⁰ An incident alpha particle energy of 3.5 MeV is chosen to provide a clean separation of ¹⁵NH₃ : ¹⁴N-tdmat yield different levels of carbon incorporation²⁰ and confirm the existence of at least two reaction pathways.

When high levels of carbon contamination $(\sim 20\%)$ are found in a film, almost no ¹⁵N is observed indicating that an intramolecular process [i.e. eq. (3)] is dominating the chemistry.²⁰ As the ¹⁵NH₃: ¹⁴N-tdmat ratio is raised, the level of carbon contamination decreases until for a film containing 12 atomic per cent of carbon, 80% of the nitrogen is ¹⁵N. Raising the ammonia to tdmat ratio further yields material with a $\sim 5\%$ level of carbon with virtually all of the nitrogen present in the film as ¹⁵N. A representative RBS spectrum of this latter material is shown in Fig. 2.³⁶ The results of these studies lead us to conclude that all of the nitrogen in a clean TiN thin film is derived from the ammonia via an intermolecular process. Residual nitrogen from the titanium precursor can lead to carbon impurities.

The reaction of $Ti(NMe_2)_4$ with ammonia falls into the general class of processes known as transamination reactions. Early transition metal dial-



Fig. 2. RBS spectrum of a film grown from tdmat and $^{15}NH_3$. A flow rate ratio of $^{15}NH_3$: ^{14}N -tdmat in helium was 3:1 with a source pressure of ~55 Torr. Growth occurred on a Si(100) wafer held at 570 K. The incident alpha particle energy was 3.5 MeV to resolve ^{14}N and ^{15}N . Analysis of this spectrum yields 49% Ti, 38% ^{15}N , 2.5% ^{14}N , 5% O, and 5.5% C. The intensity of the carbon peak is enhanced dramatically due to a resonance at this energy (see ref. 20).

kylamido complexes are known to undergo these reactions with both primary and secondary amines.³⁷⁻³⁹ For secondary amines, transamination reactions often result in partial ligand exchange and in the isolation of mixed amido complexes via a four-centre transition state:

$$Ti(NMe_{2})_{4} + n HNR_{2} \rightarrow \begin{bmatrix} R_{2}N - H \\ Ti - NMe_{2} \end{bmatrix} \rightarrow$$
$$Ti(NMe_{2})_{4-n}(NR_{2})_{n} + n HNMe_{2}, \quad (4)$$

where n varies from 1 to 3. A comparable reaction can be written for ammonia :

$$Ti(NMe_2)_4 + n NH_3 \rightarrow$$

$$Ti(NMe_2)_{4-n}(NH_2)_n + n HNMe_2, \quad (5)$$

although under most reaction conditions oligomeric products are expected (see ref. 38 and below). If all of the dimethylamido ligands in eq. (5) are replaced by amido groups, then further pyrolysis of this species should lead to the formation of clean titanium nitride films.

SOURCE OF HYDROGEN IN HNMe₂

As postulated in eq. (5) and demonstrated previously,^{20,21,25} the major gas phase product of the reaction of tdmat and ammonia is dimethylamine. For example, the infrared data in Fig. 3 show that as the titanium precursor is consumed [loss of intensity at 949 cm⁻¹ (\bigcirc) characteristic of the NC₂ symmetric stretch],^{25,29,30} dimethylamine is formed



Fig. 3. The intensity of the NC₂ symmetric stretch (●, 949 cm⁻¹) of the tetrakis(dimethylamido)titanium precursor is plotted as a function of time after reaction with ammonia at 320 K. As the concentration of Ti(NMe₂)₄ decreases, the amount of product dimethylamine (characterized by the intensity of the NH bending vibration at 735 cm⁻¹, ▲) grows. The shapes of the curves are a function of the mixing rate and are not characteristic of the reaction rate (see ref. 25).

[increase in intensity of the NH bend at 735 cm^{-1} (\blacktriangle)].⁴⁰ There are two potential sources of the hydrogen bound nitrogen in this product. Hydrogen atom transfer from an adjacent methyl group can occur via an intramolecular process [i.e. by eq. (3)]. This reaction has been observed in the pyrolysis of tdmat in the absence of ammonia.^{21,25} Alternatively, the ammonia molecule can serve as the source of hydrogen by forming an amido group via a transamination reaction [i.e. by eq. (5)]. Again these two possibilities can be sorted out using isotopic labelling experiments. The infrared spectra in Fig. 4 show that while the reaction of tdmat and NH₃ leads to the formation of gas phase HNMe₂ [Fig. 4(a)], the reaction of tdmat with ND₃ yields DNMe₂ [Fig. 4(b)].⁴¹ The modes which are most characteristic of these species are the N-H (D) bends at 1485 (1245) and 735 (590) cm^{-1} . Complete mode assignments are discussed in ref. 40. Complementary mass spectrometry studies yield identical results.20

The reaction between tdmat and ammonia is extremely rapid in the gas phase, even at 300 K (see refs. 25, 42, 43, and Fig. 3). Recent estimates using a flow-tube reactor coupled to a Fourier transform infrared spectrometer yield a bimolecular rate constant of $(1.1 \pm 0.1) \times 10^{-16}$ cm³ mol⁻¹ s⁻¹ at 298 K.⁴² Furthermore, despite the larger steric bulk, facile gas phase reactions are also observed in mixtures of tetrakis(diethylamido)titanium and ammonia (to yield diethylamine, see, for example, Fig. 5) and tetrakis(dimethylamido)titanium and methyl amine (to yield primarily dimethylamine).²⁵ As expected,



Fig. 4. Infrared spectra of the gas phase products of tetrakis(dimethylamido)titanium and (a) NH_3 and (b) ND_3 . Analysis of these spectra yield $HNMe_2$ and $DNMe_2$ as the two reaction products, respectively. Mode assignments are discussed in the text as well as in ref. 41.



Fig. 5. Gas phase infrared spectra showing that the reaction of tetrakis(diethylamido)titanium (Ti(NEt₂)₄, (a) with ammonia (b) yields diethylamine. The vibrational spectrum of pure HNEt₂ is shown in (c) for comparison. All spectra were recorded at ~ 300 K.

these latter reactions are slower than the reaction of Ti(NMe₂)₄ with NH₃ (refs 15, 25 and 37). Although the N—H bond strength decreases from 110 kcal/mol⁻¹ in ammonia to 95 kcal/mol⁻¹ in dimethylamine,⁴⁴ there is no reaction with dimethylamine as the reductant.^{25,45} This observation is consistent with the known solution chemistry of Ti(NMe₂)₄ toward secondary amines.^{21,45} These observations are also consistent with the proposed transamination reactions discussed in eqs (4) and (5) above.⁴⁶

SEARCH FOR REACTION INTERMEDIATES

The ability to deposit titanium nitride thin films on a wide variety of substrates (including glass and plastic)¹⁵ at temperatures below 470 K implies that some form of gas phase activation must be occurring. Furthermore, optimum growth occurs when the reactants are mixed at near atmospheric pressure¹⁵ and no growth is observed when a hot surface is exposed to low fluxes of tdmat and NH₃.^{25,43} Based on the chemistry discussed above, the most likely first step in the mixing process is a gas phase transamination reaction [see eq. (5)]. Monomeric intermediates may not be required for the growth of TiN thin films, however, since recent studies of the deposition of aluminum nitride have demonstrated that the active growth species is a gas phase cluster of ~ 1 nm in size.⁴⁷ Furthermore, TiN thin films deposited on substrates held at 470 K are microcrystalline with grain sizes between 2 and 5 nm.¹⁵ Minimal annealing should be taking place at this temperature.

Solution phase transamination of titanium alkylamides with primary amines generally yield oligomeric products. Only one example of a partial transamination reaction with a primary amine is known, and that product is dimeric containing two bridging N'Bu groups:^{38,48}

$$2 \operatorname{Ti}(\mathbf{NMe}_2)_4 + 2 \operatorname{H}_2 \mathbf{N}' \mathbf{Bu} \rightarrow$$
$$\operatorname{Ti}_2(\mu - \mathbf{N}' \mathbf{Bu})_2(\mathbf{NMe}_2)_4 + 4 \operatorname{HNMe}_2. \quad (6)$$

Organotitanium cluster compounds containing bridging dimethylamido and imido groups have also been synthesized recently by this method.⁴⁹ Further, imido groups have been implicated as intermediates in the growth of TiN from mixtures of TiCl₄ and 'Bu.¹⁰ More often, however, transamination with primary amines proceeds to completion to give high molecular weight (>1100 amu), 3-dimensional polymeric products that have not been structurally characterized :^{38,50}

$$Ti(NMe_2)_4 + 2H_2NR \rightarrow$$

$$1/x [Ti(NR)_2]_x + 4 HNMe_2$$
, (7)

 $\mathbf{R} = \mathbf{Pr}$ or Bu. The repeat unit is thought to be of the form³⁸:



These materials can be converted to almost pure titanium nitride by heating to ~ 1250 K in a stream of dry ammonia.⁵⁰

The decomposition of tdmat in liquid ammonia occurs essentially instantaneously at room temperature to yield a brick-red precipitate characterized as a mixed amido (NH_2) /bridging imido (NH) complex.⁵¹ The idealized stoichiometry is $Ti_3(NMe_2)(NH_2)_2(N)_3$. Vacuum pyrolysis of this material at 410 to 430 K yields gas phase ammonia and dimethylamine and presumably a polymeric titanium(IV) nitrido complex with the approximate composition $Ti_3 N_4$.

$$Ti_3(NMe_2)(NH_2)_2(N)_3 \rightarrow Ti_3N_4 + HNMe_2 + NH_3.$$
(8)

HARVARD Ex. 2106, p.5

Reduction to Ti(HI) occurs by loss of N_2 at ≤ 950 K

$$Ti_3N_4 \to 3 TiN + 1/2 N_2$$
, (9)

or by reaction with hydrogen⁵¹

$$Ti_3N_4 + 3/2H_2 \rightarrow 3TiN + NH_3.$$
 (10)

The reduction of the initial polymer to titanium nitride is quantitative, although trace carbon contamination may be caused by the decomposition of any residual dimethylamido groups.⁵¹ This latter conclusion is consistent with the results of the ¹⁵N labelling studies discussed above.

Attempts to identify reactive intermediates in the gas phase have proved unsuccessful to date. The results of our molecular beam/mass spectrometry and growth studies are consistent with the formation of large, oligomeric clusters as precursors to film growth, however.²⁰ For example, the mass spectra in Fig. 6 (recorded under growth conditions) show that when ammonia [trace (b)] is added to pure tdmat [trace (a)], all of the peaks between ~ 90 and 240 amu decrease in intensity. Since a film is deposited and gas phase dimethylamine is formed (peaks characteristic of dimethylamine between 10 and 50 amu increase in intensity), gas phase reactions must be taking place. The products of this reaction are greater than 240 amu, however. Based on precedents established in the solution chemistry discussed above, we postulate an intermediate of the form



where n varies with the number of gas phase collisions in the mixing region and each oligomer is terminated by dimethylamido groups. If the NH₃: tdmat ratio is small, then n is small and the film will be contaminated with carbon.³² Conversely, if the NH₃: tdmat ratio is large, n is large and the film stoichiometry should be essentially independent of the exact gas mixture. Finally, if the cluster size becomes too large, then powdery, highly porous films should result. All of these predictions are born out by experiment.²⁰ Film colour, resistivity, and microstructure are also sensitive functions of the NH₃: tdmat ratio.¹⁵⁻¹⁸

The relatively poor step coverage measured in

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Fig. 6. (a) Mass spectrum of pure $Ti(NMe_2)_4$ at room temperature. The carrier gas flow rate was 0.2 sccm. In (b), 3 sccm of NH₃ was added to the source. The loss of peak intensity in (b) is not because of scattering inside the mass spectrometer ionizer or to wall reactions, but is due the formation of large oligomeric clusters (see ref. 20). The source pressure was held constant at 13 Torr in both experiments.

a number of experiments indicates that whatever species is formed in the gas phase, it must have a high sticking coefficient and low surface mobility at the growth temperature.^{20–24} Indeed, the sticking coefficient must be much greater than that of either ammonia or dimethylamine since these latter species are not trapped in the growing film. Finally, since film growth slows at low substrate temperatures, the decomposition of this intermediate must be thermally activated on the surface. In addition, film properties are a sensitive function of the substrate temperature. For example, film purity, colour, resistivity, and crystallinity all improve with increasing substrate temperature.^{16–19}

The growth of TiN films from TiCl₄ and ammonia is also dominated by gas phase chemistry.^{5,6,9,53} In contrast to the reactions observed for titanium alkylamides, however, mixing TiCl₄ and ammonia at low temperatures leads to the formation of stable, isolatable adducts such as TiCl₄ • nNH₃, n = 2–8 and salts (NH₄Cl).^{5,6,9,53} These adducts decompose in a step-wise fashion in the presence of excess ammonia forming TiClN first and finally TiN and HCl. This latter process only occurs at elevated temperatures (>700 K) with an activation energy of ~15 kcal mol^{-1,9} Chlorine incorporation into the growing film and salt particle formation are drawbacks of this chemistry, however.

Evidence for species intermediate between tdmat and TiN is provided by infrared spectroscopy.^{25,51} Mixing these reactants at room temperature leads to the formation of a non-volatile yellow powder containing titanium, dimethylamido groups, and amido or imido ligands with a complex stoichiometry [see Fig. 7(a)].²⁵ Modes characteristic of both NH_n (n = 1 or 2, N—H stretch at 3100–3400 cm^{-1} and N—H bend at 1594 cm^{-1}) and NMe_n $(n = 1 \text{ or } 2, CH_3 \text{ stretch at } 2800-3000 \text{ cm}^{-1}, CH_3)$ deformation at 1450 cm⁻¹, and CH₃ rock at 1120 cm^{-1}) species are found. The spectrum is similar to that observed from the reaction of tdmat and liquid ammonia.51 The observed vibrations must be characteristic of a reaction product (as opposed to a decomposition or thermolysis product) since there is a significant shift in the NH stretching bands upon deuteration of the ammonia [Fig. 7(b) $v_{ND} = 2300-$ 2500 cm⁻¹, $\delta_{\rm ND} \simeq 910$ cm⁻¹). This product cannot be dimethylamine since this species will not stick to the surface at 300 K.

Residual hydrogen present in the titanium amido and imido intermediates discussed above must either desorb as molecular hydrogen [see, for example, eq. (2)] or be incorporated into the growing film. Recent hydrogen forward recoil scattering measurements on TiN thin films grown from tdmat and ammonia show that the amount of residual hydrogen in the films can be quite large.¹⁵ For example, films deposited at 420 K contain approximately 33 atom per cent hydrogen! This value decreases to about 10 atom per cent as the substrate temperature is increased to 670 K.¹⁵ Hydrogen is most likely bonded at grain boundaries since the X-ray powder pattern of these films is consistent with that of pure TiN [15]. Hydrogen is also present in films grown from TiCl₄ and ammonia.⁷



Fig. 7. Transmission infrared spectra of the residual yellow powder deposited on the windows of the gas cell after the reaction of tetrakis(dimethylamido) titanium with (a) NH₃ and (b) ND₃ at 325K. The isotope shift of the NH (ND) stretching $(3250 \rightarrow \sim 2400 \text{ cm}^{-1})$ and bending $(1200 \rightarrow 900 \text{ cm}^{-1})$ vibrations is a clear indication that hydrogen (deuterium) is incorporated into the product (see ref. 20).

CONCLUSIONS

Although the mechanism of titanium nitride thin film growth from the reaction of tetrakis (dimethylamido)titanium and ammonia is now well established, several questions still remain. First, when the titanium atoms in tdmat are reduced from Ti^{IV} to Ti^{III}, what are the oxidized product(s): N_2 ? H_2 ? both? or some yet to be identified species? Second, given our detailed knowledge of the rapid transamination reaction between tdmat and ammonia, how can this chemistry be controlled to yield higher quality (i.e. purer, denser, lower resistivity) materials? While one could argue that this is a process engineering problem and that the solution requires the optimization of flow rates, mixing patterns, and the like, it is possible that more straightforward solutions may be found by chemically modifying the reactants. Such studies are currently underway in many laboratories.

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- 35. TiSi₂ was chosen as a substrate due to its importance in making low resistance contacts to TiN. Both aluminum and copper are likely materials to be deposited on top of TiN barrier layers in integrated circuit fabrication.
- 36. Small amounts of oxygen incorporation in our films

always occurs upon exposure to air during the transfer from the growth to the analysis chambers. See ref. 20.

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