

Infrared Studies of the Surface and Gas Phase Reactions Leading to the Growth of Titanium Nitride Thin Films from Tetrakis(dimethylamido)titanium and Ammonia

Lawrence H. Dubois and Bernard R. Zegarski

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Gregory S. Girolami

School of Chemical Sciences and Materials Research Laboratory,
University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

ABSTRACT

The reaction of tetrakis(dimethylamido)titanium ($\text{Ti}(\text{NMe}_2)_4$) with ammonia has been studied in the gas phase and on titanium disilicide, aluminum, and copper surfaces using infrared spectroscopy. In the gas phase the main product of this reaction, dimethylamine, forms rapidly even at 300 K, and a fine yellow powder is deposited on the windows of the IR cell. Under ultrahigh vacuum conditions there is no reaction between $\text{Ti}(\text{NMe}_2)_4$ and NH_3 on any of the three surfaces studied at temperatures between 300 and 650 K. Heating pure $\text{Ti}(\text{NMe}_2)_4$ to temperatures >550 K in the gas phase, leads to species that contain Ti-N-C metallacycles and N=C double bonds. The thermal decomposition of $\text{Ti}(\text{NMe}_2)_4$ on both TiSi_2 and Al surfaces at temperatures up to 650 K yields films that contain titanium, nitrogen, and a significant amount of carbon. No decomposition is observed on copper; instead, molecular desorption occurs below 400 K. Our observations are compared with the known thermal chemistry of titanium dialkylamides in solution.

As the density of transistors in integrated circuits grows in each succeeding generation, the reliability of each individual device becomes increasingly important. Of equal importance is the reliability of the many meters of "wire" connecting these devices. At present, electrical contact to these devices is made through a barrier layer consisting of sputter-deposited titanium and titanium-tungsten alloys. The purpose of this layer is to limit interdiffusion between the metal (typically aluminum/copper/silicon alloys) and the silicon device while still allowing for good electrical (ohmic) contact. Titanium nitride (TiN) is a promising new material for this purpose due to its low resistivity ($\sim 22 \mu\Omega\text{-cm}$) and excellent barrier properties.¹⁻³ TiN has the additional advantage of adhering well to aluminum, silicon, and SiO_2 .

The growth of high quality titanium nitride thin films has been accomplished by a variety of techniques. The two most useful are reactive sputter deposition¹⁻³ and chemical vapor deposition.⁴⁻⁹ The problem with many of these techniques is that to form a layer with good barrier properties, the substrate must be quite hot during the deposition process or the layer must be postannealed at an elevated temperature. In addition, step coverage problems continue to plague physical deposition techniques. Recently the growth of high quality [<1 atomic percent (a/o) carbon and oxygen] TiN thin films at low temperatures from the reaction of tetrakis(dimethylamido)titanium ($\text{Ti}(\text{NMe}_2)_4$) and ammonia has been demonstrated.⁸⁻¹¹ Reaction temperatures were varied from 470 to 850 K at pressures between 0.3 and 760 Torr.⁸⁻¹¹ The highest purity films were deposited at atmospheric pressure with substrates held near 470 K.⁸ [Most of the gas phase species consist of an inert buffer gas such as helium since the vapor pressure of $\text{Ti}(\text{NMe}_2)_4$ at 300 K is ~ 0.15 Torr.]¹²

By analogy with the reaction of titanium tetrachloride (TiCl_4) and ammonia,⁵ a stoichiometric reaction can be written



Although both Ti and N appear in the metallorganic precursor, the presence of ammonia is crucial: films grown from pure $\text{Ti}(\text{NMe}_2)_4$ contain significant amounts of carbon, even when the deposition is conducted in the presence of excess hydrogen.^{13,14} Moreover, the observation of molecular nitrogen (which can account for the reduction in the

formal oxidation state of the titanium center from +4 in the precursor to +3 in the product film) has never been established. To gain a better understanding of the mechanisms responsible for the growth of TiN thin films at low temperatures, we have begun to explore both the surface and gas phase reactions of tetrakis(dimethylamido)titanium with ammonia using Fourier transform infrared spectroscopy. We compare our observations to the known thermal chemistry of titanium alkylamides in solution.

Experimental

Surface experiments were carried out in a turbomolecular and titanium sublimation pumped ultrahigh vacuum system (base pressure $\sim 1 \times 10^{-10}$ Torr) described elsewhere.¹⁵ The chamber was equipped with a single-pass cylindrical mirror analyzer for Auger electron spectroscopy (AES), 4-grid low-energy electron diffraction optics, a mass spectrometer, an ion sputtering gun, and two differentially pumped KBr windows for the infrared experiments. IR radiation from a conventional, nitrogen-purged Fourier transform infrared spectrometer (Mattson Instruments) was incident on all solid samples at $\sim 85^\circ$ and the scattered, p-polarized light collected by a liquid-nitrogen-cooled narrow band MCT detector. Typically 2048 scans from 900 to 4000 cm^{-1} were recorded at 4 cm^{-1} resolution (total acquisition time ~ 8 min).

Polycrystalline titanium disilicide (TiSi_2) surfaces were chosen as the primary substrates for study due to their importance in making low resistance contacts to TiN. These substrates were prepared in a separate chamber by E-beam evaporation of $\sim 2200 \text{ \AA}$ of titanium (Metron, 99.97%) onto a clean Si(100) wafer held at 300 K. The wafer was cleaved into 1.2×1.2 cm samples which, in turn, were mounted on a rotatable molybdenum heater stage in the UHV-IR system. TiSi_2 was formed by first annealing the sample at 670 K for 1 h to form TiSi followed by heating to 900–920 K for several hours to grow the disilicide.¹⁶ Temperatures were measured using a Chromel-Alumel thermocouple pressed against the surface by a titanium-covered tantalum tab. Samples were cleaned by repeated cycles of neon ion bombardment (1 keV, 5 $\mu\text{A}/\text{cm}^2$) at both 300 and 900 K followed by annealing at the latter temperature for several minutes. Sample cleanliness was checked by AES. A limited number of adsorption studies were performed on aluminum and copper substrates since these metals are likely materials to be deposited on top of TiN barrier layers

Table I. Vibrational mode assignments for tetrakis(dimethylamido)titanium and dimethylamine.^a

Assignment ^b	8 L/TiSi ₂ ^c	Ti(NMe ₂) ₄			NHMe ₂ gas phase ^d
		8 L/Al(100) ^c	Gas phase ^c	Neat liquid ^b	
		2968, sh ^e	2964	2959	2982
		2931	2943	2934	2955, 2962
CH ₃ stretch	2920, sh	2920	2918	2907	
	2880	2871	2865	2855	
			2852	2838	
			2827	2814	
CH ₃ sym stretch	2833	2823	2779	2768	2791
NH bend	2785	2771			1485
CH ₃ deform	1478	1474	1458	1440, 1450	1463
	1464	1436	1424	1413	1441
	1279	1268	1254	1249	1240
CH ₃ rock	1177	1163	1156	1152	1158
	1146, sh	1126	1121	1145	
NC ₂ asym stretch	1065	1069	1059	1057	1022
NC ₂ sym stretch	989	976, 947	949	945	925, 930
NH bend	—	—	—	—	735
TiN ₄ asym stretch	—	—	594	590	—

^a All frequencies in cm⁻¹.^b From Ref. 18. The observed frequencies are not shifted significantly in a cyclohexane solvent.¹⁹^c From Fig. 1a and b.^d From Ref. 20.^e sh = shoulder.

in integrated circuit fabrication. Al(100) and Cu(100) single crystal samples were oriented, cut, polished, and cleaned using standard techniques.

Gas phase experiments were carried out in a stainless steel cell constructed from a 2-3/4 in. metal-seal 6-way cross. The cell was equipped with KBr windows, a 40 liter/s turbomolecular pump, and a capacitance manometer for pressure measurement. The precursor was introduced into the IR cell through a ~6-mm long, 3-mm diameter stainless steel tube wrapped with insulated constantan wire for heating. Temperatures were measured with a Chromel-Alumel thermocouple spot welded to the end of the tube. The opening of the tube was positioned ~4 mm from the focus of the infrared spectrometer. The transmitted light was detected using a liquid nitrogen cooled, wide band MCT detector. Typically 1024 scans from 500 to 4000 cm⁻¹ were collected at 4 cm⁻¹ resolution (total acquisition time ~4 min). For kinetic runs, 128 scans were collected at 16 cm⁻¹ resolution (< 30 s acquisition time).

Volatile impurities (principally the *n*-hexane solvent used in the synthesis of the precursor) were removed from the tetrakis(dimethylamido)titanium (purchased from Strem) by pumping on the sample at room temperature. Tetrakis(diethylamido)titanium was synthesized according to the procedure of Bradley and Thomas¹⁷ and again purified by pumping. Ammonia (anhydrous, 99.99+%), methyl- (98+%), dimethyl- (99+%), and trimethyl- (99%) amines were obtained from Aldrich and used as received. Gas dosing in the ultrahigh vacuum (UHV) system was performed by backfilling the chamber. Doses were uncorrected for the varying sensitivity of the ion gauge to the different gases.

Results

Before describing the reactions of tetrakis(dimethylamido)titanium with ammonia, we present a summary of the chemistry of pure Ti(NMe₂)₄ both on surfaces and in the gas phase.

Thermal decomposition of Ti(NMe₂)₄.—Surface studies.—Figure 1a shows single reflection infrared spectra recorded after exposure of TiSi₂, Al(100), and Cu(100) surfaces to saturation doses of tetrakis(dimethylamido)titanium at 300 K. The IR spectrum of gas phase Ti(NMe₂)₄ is shown at the bottom of Fig. 1a for comparison. The low-frequency portion of the spectra are displayed in Fig. 1b. Mode assignments are summarized in Table I. AES indicates that, upon adsorption, there are significant amounts of carbon containing species present on the surface (note that this molecule is extremely electron-beam sensitive).

Thus, the poor signal-to-noise ratios in Fig. 1 are due to the low oscillator strength of the precursor and not to low surface coverages. The initial sticking coefficient of the precursor at 300 K must be near unity on all three surfaces since saturation occurs at 8 L on TiSi₂, 4 L on Al(100), and

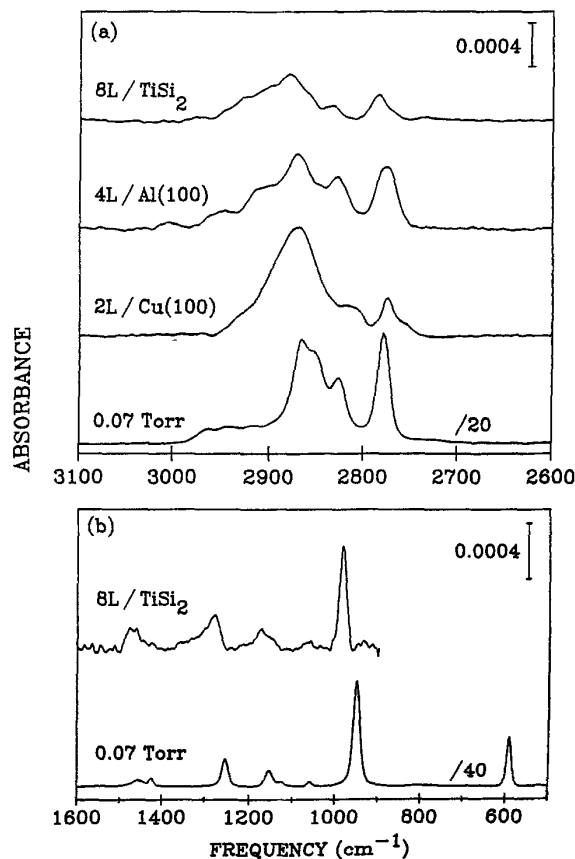


Fig. 1. (a) Reflection-absorption infrared spectra in the CH stretching region of saturation doses of tetrakis(dimethylamido)titanium adsorbed on TiSi₂ (top), Al(100), and Cu(100). The vibrational spectrum of 0.07 Torr of Ti(NMe₂)₄ (bottom) is shown for comparison. All spectra were recorded at 300 K at 4 cm⁻¹ resolution; (b) low-frequency modes. Mode assignments are discussed in Table I.

2 L on Cu(100). The vibrational spectra (both the relative peak intensities and the peak frequencies) are independent of gas dose (and hence independent of surface coverage). The presence of both CH and CN modes in all of the vibrational spectra and the similarity of these spectra to that of pure $\text{Ti}(\text{NMe}_2)_4$ ^{18,19} show that the dimethylamido groups remain essentially intact when the precursor is adsorbed on these surfaces at room temperature.

To probe the reactivity of $\text{Ti}(\text{NMe}_2)_4$, clean TiSi_2 surfaces were exposed to 8 L (saturation dose) of $\text{Ti}(\text{NMe}_2)_4$ at 300 K and the vibrational spectra recorded as the surface temperature was raised (Fig. 2). Significant changes in the spectra are seen at ~400 K: the intensity of the CH_3 symmetric stretch at 2785 cm^{-1} decreases and a new peak at *ca.* 2850 cm^{-1} grows in. Above 400 K, the intensities of all the remaining peaks decrease slowly. We have shown in a separate experiment that dimethylamine, the expected product of this decomposition reaction, does not stick to a clean TiSi_2 surface at 300 K. No peaks characteristic of this species were observed (Table I). Although a detailed assignment of the peaks in Fig. 2 is not possible at present, based on our AES studies, the molecule is decomposing on the surface.

In Fig. 3 we show Auger spectra of (a) the nominally clean TiSi_2 surface (the presence of trace carbon and oxygen impurities is seen at 272 and 510 eV, respectively), and (b) the same surface after exposure to 8 L of $\text{Ti}(\text{NMe}_2)_4$ at 300 K followed by ramping the surface temperature to 500 K. After dosing, the relative intensities of both the carbon (272 eV) and the nitrogen peaks (~380 eV) increase while that of the Si peak (92 eV) decreases. [The absolute ratio of Ti to N (or C) is difficult to determine due to overlap of the titanium (387 eV) and nitrogen (~380 eV) peaks. The ratio of the peaks at 387 eV (Ti + N) to 418 eV (Ti) in an authentic sample of TiN recorded under the same conditions is 2.76. This ratio is significantly greater than the ratio of ~1.2 measured here for films prepared on TiSi_2 substrates.]²¹ The surface is being covered with a layer containing titanium, nitrogen, and carbon. Similar behavior is observed when comparable experiments are performed on Al(100). The growth of thick carbon-contaminated titanium nitride films also has been seen from the decomposition of $\text{Ti}(\text{NMe}_2)_4$ on a variety of surfaces at temperatures between 570 and 850 K.^{13,14,22}

In contrast, when a Cu(100) surface is exposed to $\text{Ti}(\text{NMe}_2)_4$ at 300 K and subsequently flashed to 400 K, AES

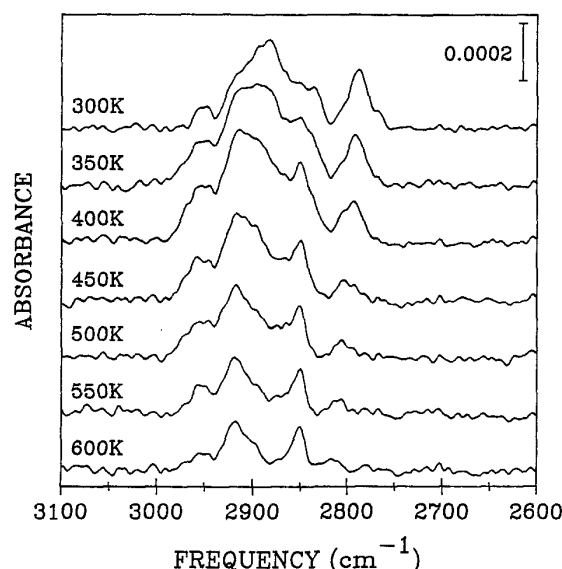


Fig. 2. The top trace shows the infrared spectra of an 8 L (saturation dose) of tetrakis(dimethylamido)titanium adsorbed on a TiSi_2 substrate at 300 K. The temperature was raised in 50 K steps and the succeeding spectra were recorded. Significant decomposition is observed at temperatures above 400 K (see text).

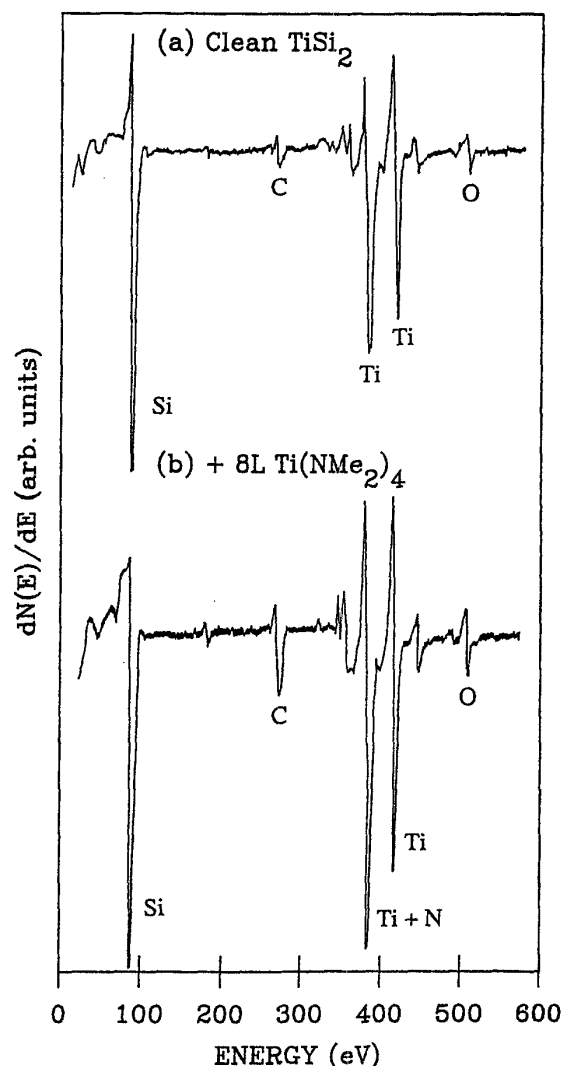


Fig. 3. Auger electron spectra of a nominally clean TiSi_2 substrate (upper trace) and after exposure to 8 L of $\text{Ti}(\text{NMe}_2)_4$ at 300 K and subsequent flashing to 500 K. The decomposition of the precursor is not clean and significant amounts of carbon are left on the surface. Identical Auger spectra are recorded even if the adsorbate is exposed to several hundred Langmuirs of NH_3 at temperatures between 300 and 500 K.

indicates that a clean copper substrate is regenerated. Since an analysis of the IR data (Fig. 1, Table I) shows that no decomposition is taking place, we conclude that desorption from Cu(100) surfaces is molecular.

Gas phase studies.—When 0.07 Torr of pure tetrakis(dimethylamido)titanium is heated in the gas phase, a new species forms as shown by the series of infrared spectra in Fig. 4. Little change in the transmission infrared spectrum is seen until the nozzle is heated above ~450 K: at this temperature, intense new bands at 1590, 1505, 1276, and ~900 cm^{-1} become visible. Due to the complexity of these spectra a detailed mode analysis is difficult, although tentative assignments are summarized in Table II. Several of the new IR bands are worthy of 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. Such species could form via loss of dimethylamine from $\text{Ti}(\text{NMe}_2)_4$, leaving behind a product that contains a $\text{Ti}(\text{NMeCH}_2)$ metallacycle.

The thermolysis of the related tantalum complex $\text{Ta}(\text{NMe}_2)_5$ reportedly gives such a metallacycle (see below);

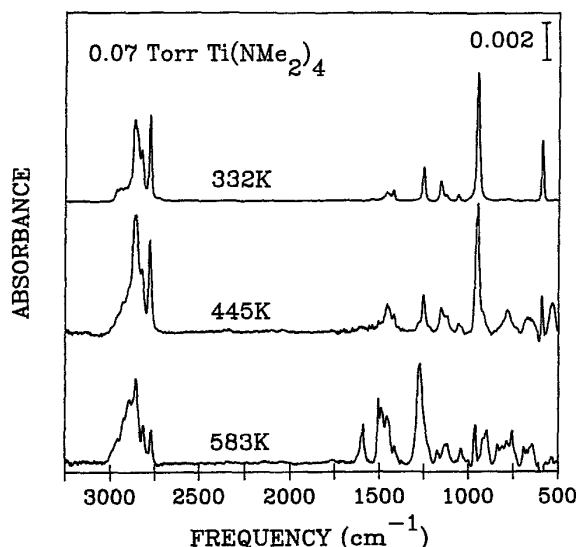
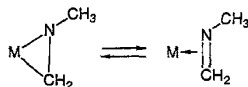


Fig. 4. Gas phase infrared spectra of 0.07 Torr of tetrakis(dimethyl-amido)titanium at the indicated nozzle temperatures. No significant decomposition is observed until ~ 450 K. Tentative mode assignments for the lower trace are summarized in Table II.

the infrared spectrum of this thermolysis product contained an intense absorption at 1235 cm^{-1} which was assigned to the stretching vibration of the ring N—C bond.²³ 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.



If these effects are more pronounced for metallacycles of titanium *vs.* tantalum, then the different frequencies of the N—C stretching mode in the two thermolysis products can be explained. An alternative assignment for the strong 1276 cm^{-1} band to a CH_3 rocking mode seems less likely because such modes typically occur near 1150 cm^{-1} with only weaker bands appearing at higher frequencies.

Also noteworthy in the spectra of Fig. 4 is the absorption at 1590 cm^{-1} observed when $\text{Ti}(\text{NMe}_2)_4$ is heated to 583 K. This band may be assigned to species that contain N=C

Table II. Tentative mode assignments for $\text{Ti}(\text{NMe}_2)_4$ heated to 583 K in the gas phase.^a

Assignment	Observed frequencies ^b
	2957
	2926
CH stretch	2893
	2858
	2816
	2771
N=C stretch	1590
NH bend	1505, 1490
CH ₃ deformation	1457, 1416
Ti-N-C stretch	1276
CH ₃ rock	1173
	1130, 1117
NC ₂ asym stretch	1040
	961
NC ₂ sym stretch	917, 899
	836, 809
NH bend	785, 756

^a All frequencies in cm^{-1} .

^b Data from Fig. 4, bottom trace.

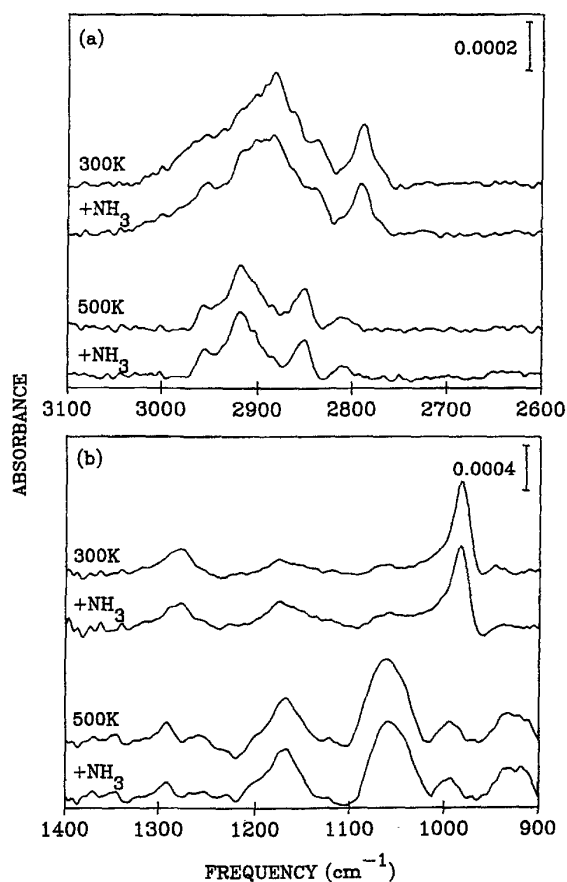


Fig. 5. Reflection-absorption infrared spectra of an 8 L (saturation dose) of tetrakis(dimethylamido)titanium adsorbed on a TiSi_2 substrate at 300 K both before and after reaction with 20 L of ammonia. Similar sets of spectra were recorded after raising the substrate temperature to 500 K and again exposing the precursor to 20 L of NH_3 ; (a) the CH stretching vibrations, (b) the low-frequency vibrational modes.

double bonds. Interestingly, the formation of N=C double bonds by the thermolysis of transition metal dialkylamides is not observed generally, although such species would be similar to the metallacycles that are known to form. Finally, weak N—H bending modes at *ca.* 1500 cm^{-1} may be evidence for the formation of small amounts of dimethyl amine.

Reactions of $\text{Ti}(\text{NMe}_2)_4$ with ammonia.—Surfaces studies.—When a clean polycrystalline titanium disilicide surface is exposed to ammonia at temperatures between 300 and 500 K, no reaction is observed under our experimental conditions. Similarly, if the same surface is saturated with a layer of $\text{Ti}(\text{NMe}_2)_4$ and then exposed to NH_3 at temperatures between 300 and 600 K, no reaction is seen (see Fig. 5 for representative infrared spectra recorded at 300 and 500 K). This lack of reactivity between $\text{Ti}(\text{NMe}_2)_4$ and NH_3 on surfaces is in sharp contrast to what is observed in the gas phase.

Gas phase studies.—Tetrakis(dimethylamido)titanium and ammonia react rapidly in the gas phase as shown by the series of infrared spectra in Fig. 6. In this experiment, the gas cell was first charged with 0.095 Torr of $\text{Ti}(\text{NMe}_2)_4$ at 300 K, then 730 Torr of a 0.2% mixture of ammonia in nitrogen was added ($\text{NH}_3:\text{Ti}(\text{NMe}_2)_4$ ratio of $\sim 1.5:1$). As the reaction proceeds over the course of several minutes, the only product observed is dimethylamine (for reference, the infrared spectrum of pure dimethylamine is shown at the bottom). No partial decomposition species or adducts containing both titanium and ammonia were detected. Similar

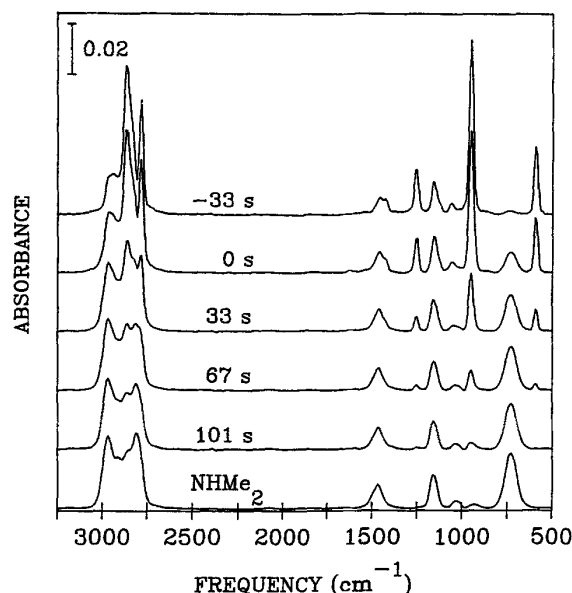


Fig. 6. Gas phase infrared spectra recorded both before and after reacting 0.095 Torr of $\text{Ti}(\text{NMe}_2)_4$ with 730 Torr of a 0.2% mixture of NH_3 in N_2 . The reaction took place at 320 K and the only product detected was dimethylamine (spectrum shown at bottom). The rate of the reaction was controlled by the rate of mixing. The spectral resolution was 16 cm^{-1} .

results are obtained if pure ammonia is used, or if the titanium precursor is first diluted in nitrogen. [Similar results were obtained also from the reaction of tetrakis(diethylamido)titanium with ammonia. In this case the only gas phase product found by IR was diethylamine.] The reaction between tetrakis(dimethylamido)titanium and deuterated ammonia yields predominantly monodeuterated dimethylamine (NDMe_2). Some protonated amine is formed, we believe, due to wall reactions (see below).

A more detailed view of the kinetics of the reaction of $\text{Ti}(\text{NMe}_2)_4$ and NH_3 is shown by the data in Fig. 7a. Here the intensity of the NC_2 symmetric stretch (949 cm^{-1}), a mode characteristic of the precursor, is plotted as a function of time both before and after admitting NH_3 to the system. Before the addition of ammonia ($t < 0$), the amount of tetrakis(dimethylamido)titanium decreases slowly due to wall reactions. Consistent with this, we observe a slow increase in the system total pressure (Fig. 7b) and the growth of a weak band at 735 cm^{-1} (NH bend, open squares) characteristic of dimethylamine (Table I). The increase in the system pressure indicates that several product NHMe_2 molecules are produced for each titanium precursor consumed.

After the ammonia is added to the system ($t = 0$), the intensity of the NC_2 stretch of the precursor decreases rapidly while the intensity of the NH bend of the dimethylamine product grows. By varying the flow of the two reactants into the IR cell, we conclude that the rate of this reaction is controlled by the speed at which the two reactants mix. Thus the intensity decay curve in Fig. 7a is not characteristic of the kinetics of this reaction. The reaction can be slowed down substantially, however, by reacting the tetrakis(dimethylamido)titanium with methylamine (Δ). In this case, the gas phase product also is predominantly dimethylamine. Under our experimental conditions, there is no reaction between the precursor and dimethylamine (\bullet), trimethylamine, or hydrogen (not shown). [In solution (where the reagent flux is extremely high) the reaction of $\text{Ti}(\text{N}(\text{CD}_3)_2)_4$ with HNMe_2 occurs in approximately 2 h at 298 K .^{24,25}

If the reaction of $\text{Ti}(\text{NMe}_2)_4$ and NH_3 is allowed to proceed in a flow mode for ca. 20 min, then a fine yellow powder is deposited on the KBr windows of the IR cell. The

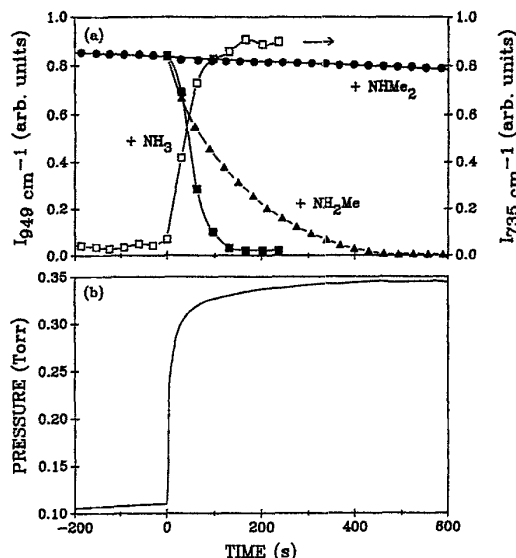


Fig. 7. (a) The intensity of the NC_2 symmetric stretch (949 cm^{-1}) of the tetrakis(dimethylamido)titanium precursor is plotted as a function of time both before and after reaction with ammonia (\blacksquare), methylamine (Δ), and dimethylamine (\bullet) in the gas cell. As the concentration of $\text{Ti}(\text{NMe}_2)_4$ decreases in the reaction with NH_3 , the amount of product dimethylamine (characterized by the intensity of the NH bending vibration at 735 cm^{-1} , \square) grows; (b) the total pressure in the cell as a function of time. All reactions were carried out at 320 K.

infrared spectrum of this species is shown in the upper trace of Fig. 8. We believe this yellow powder is a non-volatile oligomer that contains titanium, dimethylamido groups, and amido (NH_2) or imido (NH) ligands. Modes characteristic of both NH_n ($n = 1$, or 2, NH stretch at $3100\text{--}3400\text{ cm}^{-1}$ and NH bend at 1594 cm^{-1}) and NMe_n ($n = 1$ or 2, CH_3 stretch at $2800\text{--}3000\text{ cm}^{-1}$, CH_3 deformation at 1450 cm^{-1} , and CH_3 rock at 1120 cm^{-1}) groups are found. 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. 8, lower trace $\nu_{\text{ND}} = 2300\text{--}2500\text{ cm}^{-1}$, $\delta_{\text{ND}} = 910\text{ cm}^{-1}$).

Discussion

Surface reactions.—At 300 K the dimethylamido groups from adsorbed $\text{Ti}(\text{NMe}_2)_4$ remain intact on all three substrates (TiSi_2 , Al, Cu) as shown by the similarity of the

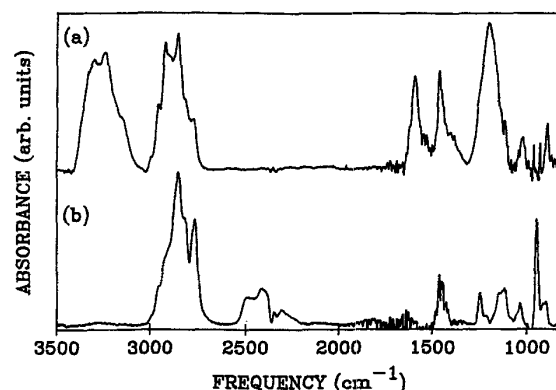


Fig. 8. Transmission infrared spectra of the residual yellow powder deposited on the windows of the gas cell after the reaction of tetrakis(dimethylamido)titanium with (a) NH_3 , and (b) ND_3 , at 325 K. The isotope shift of the NH (ND) stretching ($3250 \rightarrow \sim 2400\text{ cm}^{-1}$) and bending ($1200 \rightarrow 900\text{ cm}^{-1}$) vibrations is a clear indication that hydrogen (deuterium) is incorporated into the product.

vibrational spectra with that of the parent compound (Fig. 1, Table I). There appears to be no dependence of the vibrational spectra on coverage, which indicates that adsorbate-adsorbate interactions are weak on all three substrates. Moreover, migration of the ligands away from the central titanium atom is unlikely on copper since a clean Cu(100) surface is regenerated when the crystal is flashed to 400 K.

In contrast, thermal decomposition of $\text{Ti}(\text{NMe}_2)_4$ does occur on both TiSi_2 and aluminum surfaces. At temperatures between 300 and 600 K indicating that the adsorbate does not dissociate completely to carbon, nitrogen, and hydrogen adatoms since CH and CN stretching vibrations are still approved. Above 650 K, however, these vibrations disappear and thermal decomposition of adsorbed tetrakis(dimethylamido)titanium must be complete. As expected, decomposition does not yield clean titanium nitride: carbon contamination is seen by AES on both TiSi_2 and aluminum substrates. This observation is consistent with the results of several previous studies which showed that clean TiN thin films could be grown only from $\text{Ti}(\text{NMe}_2)_4$ in the presence of excess ammonia.^{8-11,13,14,22} An understanding of the solution chemistry of titanium dialkylamides provides a clear explanation for this behavior (see below).

Under UHV conditions there is no surface reaction between adsorbed tetrakis(dimethylamido)titanium and ammonia, irrespective of which molecule is adsorbed first. In contrast, in the gas phase the dimethylamido groups of the tetrahedrally coordinated precursor are sufficient to protect the central titanium atom from reaction with ammonia. Evidently, the structure of the molecule is distorted or the thermal motion of the ligands is suppressed by the presence of the surface such that attack by ammonia is no longer a facile process.

One might expect that at elevated surface temperatures, where the titanium precursor is partly decomposed (Fig. 2), exposure to ammonia would lead to at least some reaction (Fig. 5). Evidently at 300 K, such a reaction is prevented by the inability of ammonia to dissociate on either titanium disilicide or aluminum. At elevated temperatures the dissociation of ammonia may be prevented by the surface carbon that is generated during decomposition of the $\text{Ti}(\text{NMe}_2)_4$ precursor. The flux of both ammonia and $\text{Ti}(\text{NMe}_2)_4$ to the surface under our reaction conditions is exceedingly low and this may account, in part, for the low reactivity observed in UHV. This low reactivity is in sharp contrast to what is observed at elevated pressures in the gas phase.

Gas phase reactions.—As noted above, the growth of clean titanium nitride thin films from the reaction of $\text{Ti}(\text{NMe}_2)_4$ and NH_3 has been observed only at elevated pressures.¹² This implies that gas phase reactions may be as important as they are in the reaction of TiCl_4 and ammonia.^{5,26} Our infrared studies show that the reaction of tetrakis(dimethylamido)titanium and ammonia proceeds rapidly in the gas phase, even at 300 K. Dimethylamine is the only infrared active product observed in the gas phase, and a fine yellow powder is deposited on the windows of the IR cell.

Despite the larger steric bulk, facile gas phase reactions are observed in mixtures of tetrakis(diethylamido)titanium and ammonia (to yield diethylamine) and tetrakis(dimethylamido)titanium and methyl amine (to yield primarily dimethylamine). As expected, these latter reactions are slower than the reaction of $\text{Ti}(\text{NMe}_2)_4$ with NH_3 (Fig. 7a, Ref. 8, 17). Although the N—H bond strength decreases from 110 kcal/mol in ammonia to 95 kcal/mol in dimethylamine,²⁷ the reaction effectively shuts down, an observation consistent with the known solution chemistry of $\text{Ti}(\text{NMe}_2)_4$ toward secondary amines.^{14,24,25} [In solution (where the reagent flux is extremely high), the reaction of $\text{Ti}(\text{N}(\text{CD}_3)_2)_4$ with HNMe_2 occurs is approximately 2 h at 298 K.]

In no case was there any spectroscopic evidence for the formation of adducts between $\text{Ti}(\text{NMe}_2)_4$ and either NH_3 or H_2NMe . Analysis of the yellow powder deposited on the cell

walls may provide some insight into the mechanism of the reaction of $\text{Ti}(\text{NMe}_2)_4$ with NH_3 . Although this species is a nonvolatile oligomer, it does contain the type of functional groups expected to play a key role in the decomposition chemistry of titanium dialkylamides (see below).

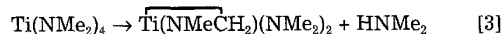
In the absence of ammonia, metallacyclic intermediates can be formed by heating pure tetrakis(dimethylamido)titanium in the gas phase (Fig. 4), but this species does not lead to the formation of clean TiN films. Based on the presence of a characteristic N—C stretching mode at 1276 cm^{-1} , we believe that this metallacycle contains a $\text{Ti}(\text{NMeCH}_2)$ three-membered ring. Further information about potential reaction intermediates can be gained through an understanding of the chemistry of titanium alkylamides in solution.

Chemistry of dialkylamido complexes.—*Thermochemistry.*—The thermolysis of tetrakis(dimethylamido)titanium has not been investigated previously. A variety of related complexes of stoichiometry $\text{Ti}(\text{NEt}_2)_3\text{R}$, where R is an alkyl group such as methyl, ethyl, etc., have been studied, however.²⁸ Heating bulk samples of these compounds to ca. 420 K results in the liberation of one equivalent of the alkane (RH). The hydrogen atom source was shown to be the diethylamido groups on the basis of a deuterium labeling study. Although the titanium-containing product of this reaction was not characterized, the results suggest that a 3-membered metallacycle should be formed



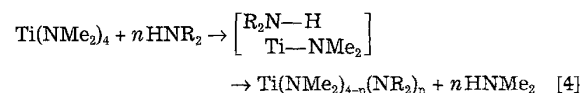
Although these three-membered Ti—N—C rings have not been detected directly in the thermolysis of titanium dialkylamides, they have been observed in the chemistry of other transition metals such as niobium, tantalum, and tungsten.^{23,29}

If we assume that these reactivity patterns are also characteristic of tetrakis(dimethylamido)titanium, then we may write the initial step in the thermolysis pathway as follows

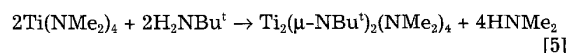


Such a structure is consistent with the IR spectrum obtained upon thermolysis of $\text{Ti}(\text{NMe}_2)_4$ in the gas phase (Fig. 2). It has been proposed previously³⁰ that the formation of titanium-carbon bonds via Eq. 3 can explain how carbon contaminants become incorporated into "TiN" films grown from $\text{Ti}(\text{NMe}_2)_4$ in the absence of ammonia. In the present context, this reaction accounts for the presence of carbon left on both the TiSi_2 and aluminum substrates after the heating experiments.

Transamination reactions.—The reaction of $\text{Ti}(\text{NMe}_2)_4$ with ammonia falls into the general class of processes known as transamination reactions. Early transition metal dialkylamido complexes are well known to undergo these reactions with both secondary (HNR_2) and primary (H_2NR) amines.^{17,31,32} For secondary amines, transamination reactions often result in partial ligand exchange and in the isolation of mixed amido complexes

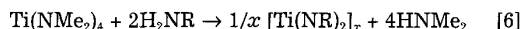


where n varies from 1 to 3. One example of a partial transamination reaction with a primary amine is known, and that product is dimeric containing two bridging NBu^t groups³¹



Organotitanium cluster compounds containing bridging dimethylamido and imido groups also have been synthesized recently by this method.³³ Further, imido groups have been implicated as intermediates in the growth of TiN from

mixtures of TiCl_4 and *tert*-butylamine.³⁴ More often, however, transamination with primary amines proceeds to completion to give polymeric products that have not been structurally characterized³¹



Similar reactions involving zirconium analogues have resulted in products formulated as $[\text{Zr}(\text{NHR})_4]_x$ and $[\text{Zr}(\text{NR})(\text{NHR})_2]_x$, but again these species have not been structurally characterized.³² Monomeric intermediates may not be required for the growth of TiN thin films 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.³⁵

Little information is available about the chemical pathway by which early transition metal dialkylamide complexes react with ammonia. One study claims that the zirconium complex $\text{Zr}(\text{NEt}_2)_4$ reacts with ammonia to give $[\text{Zr}(\text{NH}_2)_4]_x$, which quickly condenses to $[\text{Zr}(\text{NH})(\text{NH}_2)_2]_x$ and finally to $[\text{Zr}(\text{NH})_2]_x$ after 24 h at 330 K.³² Although little evidence is offered in support of these formulations, such a sequence is reasonable and is consistent with the better established reactivity patterns shown by transition metal dialkylamides toward both primary and secondary amines.

The fine yellow powder formed from the reaction of $\text{Ti}(\text{NMe}_2)_4$ with ammonia in our gas cell must be related chemically to some of the transamination products discussed above. Specifically, a polymeric, mixed amido complex of stoichiometry $\text{Ti}(\text{NMe}_2)_{4-x}(\text{NH}_2)_x$ may best describe the chemical composition of this material. Alternatively, the powder may contain imido groups. Both possibilities are consistent with the IR spectra shown in Fig. 8. Further characterization studies of this material, which is the first isolated chemical intermediate in the growth of TiN from ammonia and a titanium dialkylamide complex, are presented elsewhere.

Conclusions

The growth of titanium nitride thin films from a mixture of $\text{Ti}(\text{NMe}_2)_4$ and NH_3 is unusual in that gas phase reactions may be as important as the surface chemistry. Specifically, the surface reactions responsible for the growth of TiN films involve intermediates that are formed by the gas phase reactions of $\text{Ti}(\text{NMe}_2)_4$ with ammonia. The presence of these reactive intermediates may obviate the surface nucleation problem and allow TiN films to be deposited on a wide variety of substrates. In addition, the removal of carbon containing fragments in the gas phase may inhibit metallacycle formation and lead to cleaner film growth. More attention must be paid to the process parameters (*i.e.*, flow rate, mixing ratio, temperature, etc.) to obtain optimum film properties, however. Thus, the details of how the reactants are mixed in the gas phase is critical to the growth of high quality films. The use of an inert buffer gas (typically helium) may play a crucial role in promoting the formation of gas phase intermediates.

Our study has advanced understanding the reaction mechanism by showing that the gas phase thermolysis of $\text{Ti}(\text{NMe}_2)_4$ in the absence of ammonia leads to the formation of species containing $\text{Ti}-\text{N}-\text{C}$ three-membered rings and $\text{N}=\text{C}$ double bonds. The presence of ammonia completely changes the chemistry taking place and leads instead to a rapid transamination reaction. The products are dimethylamine and a titanium compound containing NH or NH_2 groups (or both). More work is needed to further characterize this gas phase intermediate.

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REFERENCES

1. M.-A. Nicolet, *Thin Solid Films*, **52**, 415 (1978).
2. M. Wittmer, B. Studer, and H. Melchior, *J. Appl. Phys.*, **52**, 5722 (1981).
3. S. Kanamori, *Thin Solid Films*, **136**, 195 (1986).
4. S. Kurtz and R. G. Gordon, *ibid.*, **140**, 277 (1986).
5. N. Yokoyama, K. Hinode, and Y. Homma, *This Journal*, **138**, 190 (1991).
6. M. J. Buiting, A. F. Otterloo, and A. H. Montree, *ibid.*, **138**, 500 (1991).
7. T. Akahori and A. Tanihara, 1991 Int. Conf. Solid State Dev. and Mat., Yokohama, 180 (1991).
8. R. M. Fix, R. G. Gordon, and D. M. Hoffman, *Mater. Res. Soc. Symp. Proc.*, **168**, 357 (1990).
9. K. Ishihara, K. Yamazaki, H. Hamada, K. Kamisako, and Y. Tarui, *Jpn. J. Appl. Phys.*, **29**, 2103 (1990).
10. A. Katz, A. Feingold, S. Nakahara, S. J. Pearton, E. Lane, M. Geva, F. A. Stevie, and K. Jones, *J. Appl. Phys.*, **71**, 993 (1992).
11. J. A. Prybyla and L. H. Dubois, Submitted to *This Journal*.
12. Cyanamid, Technical Data Sheet.
13. K. Sugiyama, S. Pac, Y. Takahashi, and S. Motojima, *This Journal*, **122**, 1545 (1975).
14. A. Katz, A. Feingold, S. J. Pearton, S. Nakahara, M. Ellington, U. K. Chakrabati, M. Geva, and E. Lane, *J. Appl. Phys.*, **70**, 3666 (1991).
15. B. R. Zegarski and L. H. Dubois, *Surf. Sci.*, **262**, L129 (1992).
16. See, for example, G. Ottaviani, *J. Vac. Sci. Technol.*, **16**, 1112 (1979).
17. D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, 3857 (1960).
18. H. Bürger, H. Stammreich, and Th. T. Sans, *Monatsh. Chem.*, **97**, 1276 (1966).
19. D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. (A)*, 980 (1969).
20. G. Gamer and H. Wolff, *Spectrochim. Acta*, **29A**, 129 (1973).
21. B. R. Zegarski and L. H. Dubois, Unpublished observations.
22. R. M. Fix, R. G. Gordon, and D. M. Hoffman, *Chem. Mater.*, **2**, 235 (1990).
23. Y. Takahashi, N. Onoyama, Y. Ishikawa, S. Motojima, and K. Sugiyama, *Chem. Lett.*, 525 (1978).
24. W. A. Nugent, D. W. Ovenall, and S. J. Holmes, *Organometallics*, **2**, 161 (1983).
25. M. H. Chisholm and M. W. Exline, *J. Am. Chem. Soc.*, **99**, 792 (1977).
26. Y. Saeki, R. Matsuzaki, A. Yajima, and M. Akiyama, *Bull. Chem. Soc. Jpn.*, **55**, 3193 (1982).
27. *Handbook of Chemistry and Physics*, 67th ed., CRC Press, Boca Raton, FL (1986).
28. H. Bürger and H.-J. Neese, *J. Organomet. Chem.*, **21**, 381 (1970).
29. C. Airolidi, D. C. Bradley, and G. Vuru, *Trans. Met. Chem.*, **4**, 64 (1979).
30. G. S. Girolami, J. A. Jensen, J. E. Gozum, and D. M. Pollina, *Mater. Res. Soc. Symp. Proc.*, **121**, 429 (1988).
31. D. C. Bradley and E. G. Torrible, *Can. J. Chem.*, **41**, 134 (1963).
32. R. K. Bartlett, *J. Inorg. Nucl. Chem.*, **28**, 2448 (1966).
33. M. E. Gross and T. Siegrist, Submitted to *Inorg. Chem.*
34. C. H. Winter, P. H. Sheridan, T. S. Lewkebandara, M. J. Heeg, and J. W. Proscia, *J. Am. Chem. Soc.*, **114**, 1095 (1992).
35. H. J. Kim, Y. Egashira, and H. Komiyama, *Appl. Phys. Lett.*, **59**, 2591 (1991).