

Spontaneous Evolution of Silica-Supported Ti Amide Fragments to Imine and Imido Complexes

Marcel Beaudoin and Susannah L. Scott*

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

Received October 26, 2000

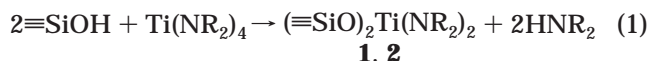
Summary: Upon prolonged exposure to vacuum, $(\equiv\text{SiO})_2\text{-Ti}(\text{N}(\text{CH}_2\text{R})_2)$ ($\text{R} = \text{H}$, **1**), Me (**2**)) evolves to an *N*-methyl-methylenimine complex (**3**; $\text{R} = \text{H}$) or an ethylimido complex (**5**; $\text{R} = \text{Me}$). The change in the reaction mechanism depending on the nature of the molecular precursor accounts for the lower level of carbon contamination in TiN films formed from the complex with the higher initial carbon content.

Volatile homoleptic tetrakis(dialkylamido)titanium complexes have been investigated as halogen-free single-source precursors for the low-temperature chemical vapor deposition of very thin films of cubic titanium nitride, TiN,^{1,2} which is the material of choice for diffusion barriers, adhesion layers, and low-resistance contacts in microelectronic devices.³ Vapor deposition of a volatile titanium complex gives films with better step coverage than does sputtering of the metal, but $\text{Ti}(\text{NR}_2)_4$ -derived films tend to be highly contaminated by carbon.² Co-deposition with ammonia has been used successfully³ to reduce the amount of C in the films, presumably via transamination reactions.⁴ However, even in the presence of NH_3 , the nature of the extruded ligands is known to influence the ultimate composition of the film.⁵ Curiously, the use of $\text{Ti}(\text{NMe}_2)_4$ gives lower quality films with higher carbon content and higher resistivity than $\text{Ti}(\text{NEt}_2)_4$,^{3,6} despite the higher carbon content, lower volatility, and greater steric resistance to transamination by NH_3 of the latter molecular precursor.

Although mechanisms for the deposition reactions and subsequent transformations of metal amido complexes have been proposed by analogy to solution chemistry,⁴ calculations,⁷ analysis of gas-phase spectra in CVD reactors,^{8,9} mass spectral fragmentation patterns of the molecular precursors,¹⁰ and kinetic simulations,⁶ intermediates on the surface have not been isolated and mechanisms for the surface reactions remain specula-

tive. Nevertheless, the nature of the thermal reactions of the amido complexes upon interaction with the oxidized (i.e., silica) surface of silicon wafers are of great relevance, since film quality appears to be highest under low-pressure deposition conditions, where surface reactions predominate.^{3,11,12} In our investigation of the reactions of $\text{Ti}(\text{NR}_2)_4$ with silica surfaces, we discovered quantitative thermal transformations which lead to isolable intermediates. A dramatic difference in behavior between dimethyl- and diethylamido derivatives accounts for their different propensities to form clean TiN films.

The initial product of the gas–solid reaction of $\text{Ti}(\text{NEt}_2)_4$ with a silica surface¹³ partially dehydroxylated at 200 °C¹⁴ has already been reported.¹⁵ A yellow grafted bis(amido)titanium(IV) fragment is obtained by reaction with adjacent surface hydroxyls (eq 1). An analogous



1, 2
R = Me (**1**), Et (**2**)

reaction stoichiometry has now been confirmed for $\text{Ti}(\text{NMe}_2)_4$.¹⁶ The sole volatile product of eq 1 is the amine, HNET_2 or HNMe_2 , of which 2 equiv was recovered. Combustion analysis of each supported complex in 300 Torr of O_2 at 750 °C led to the evolution of 4.1 and 7.9 equiv of CO_2 per Ti from **1** and **2**, respectively.

Although both **1** and **2** are indefinitely stable under static vacuum (ca. 10^{-4} Torr) at room temperature, both are thermally unstable to prolonged evacuation. The thermolytic reactions were followed by in situ IR spectroscopy. During 10 h of evacuation at room temperature, the IR spectrum of **1** shows a reproducible and linear (i.e., zero order) decrease in $\nu(\text{C-H})$ absorbance

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(13) The silica used in all experiments is Aerosil, a pyrogenic, nonporous silica from Degussa Corp. Its surface area, 200 m^2/g , is unchanged by thermal treatment at the temperatures used in this study.

(14) Silica which has been partially dehydroxylated by treatment under dynamic vacuum ($<10^{-4}$ Torr) at 200 °C for a minimum of 4 h has a reproducible hydroxyl content of 0.86 mmol/g (Rice, G. L.; Scott, S. L. *Langmuir* **1997**, *13*, 1545–1551). The silica was always cooled to room temperature before its surface was modified with the molecular Ti complexes.

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(16) Upon complete reaction of the surface hydroxyls with $\text{Ti}(\text{NMe}_2)_4$, the solid contains 1.93 ± 0.04 wt % Ti, corresponding to 0.49 Ti per hydroxyl (average of 12 experiments). The amount of HNMe_2 liberated during grafting corresponds to 1.99 ± 0.04 per Ti. Our methods for the quantification of grafting reactions have been described previously.¹⁵

* To whom correspondence should be addressed.

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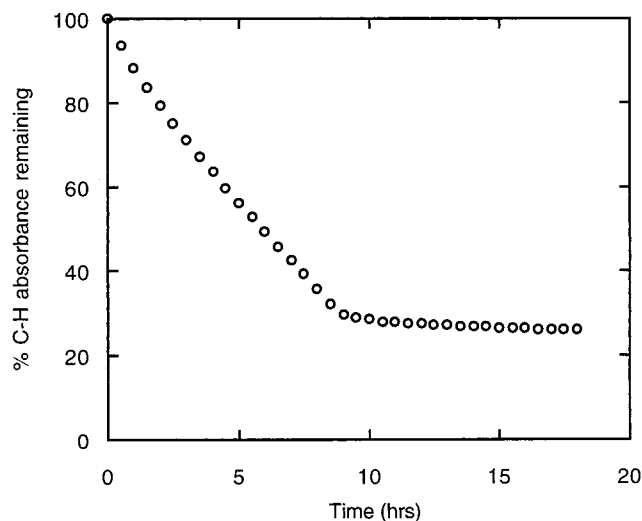


Figure 1. Integrated absorbance in the region 3100–2650 cm^{-1} as a function of the time of evacuation of $(\equiv\text{SiO})_2\text{Ti}(\text{NMe}_2)_2$.

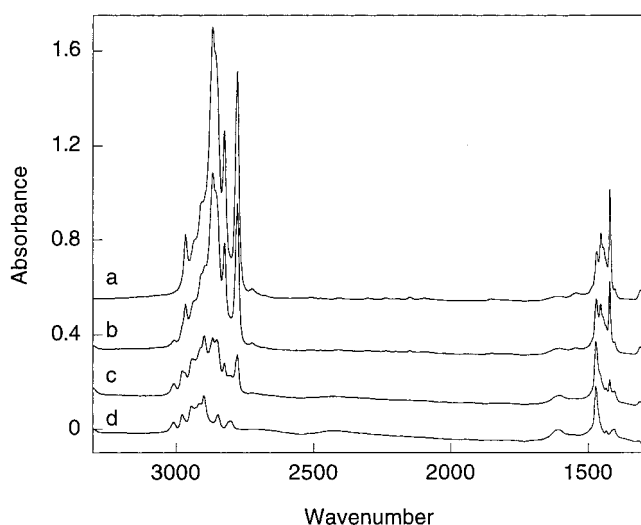
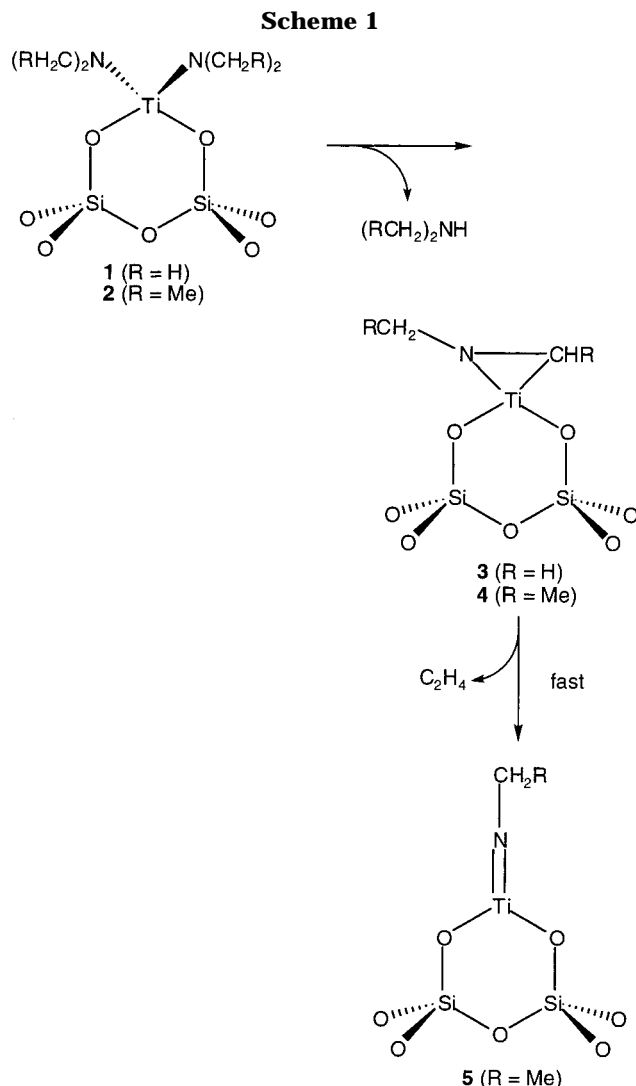


Figure 2. In situ IR spectra (vertically offset) recorded during the room-temperature evacuation of $(\equiv\text{SiO})_2\text{Ti}(\text{NMe}_2)_2$ (**1**) at the following times: (a) 0 h; (b) 3 h; (c) 8 h; (d) 11.5 h. The silica background spectrum has been subtracted.

of $76 \pm 1\%$ (average of seven experiments; Figure 1) as well as a dramatic change in appearance (Figure 2). The color of the modified silica pellet changes from bright yellow to very pale yellow. Further evacuation gave no changes in the IR spectrum, although evacuation at a higher temperature (60°C) resulted in a more rapid loss of hydrocarbon intensity from the surface. The trapped volatiles consist exclusively of HNMe_2 . Combustion of the product **3** at 750°C in 300 Torr of O_2 completely removed the remaining hydrocarbon intensity. Since 2.1 CO_2/Ti was recovered, we conclude that **3** contains two of the four original carbon atoms of **1**.

A similar loss of hydrocarbon intensity from the in situ IR spectrum occurs upon exposure of **2** to prolonged dynamic vacuum, although the reaction is much slower than that of **1** at room temperature.¹⁷ After 16 h of

(17) The rates of these ligand extrusion reactions are strongly pressure-dependent; we note that the quality of TiN films formed by the CVD route is also pressure-dependent.^{3,11}



evacuation at 60°C , the IR spectrum shows a $72 \pm 2\%$ decrease in $\nu(\text{C-H})$ absorbance (average of seven experiments). The trapped volatiles are a mixture of HNMe_2 and C_2H_4 . Combustion of the resulting material, **5**, in O_2 resulted in the formation of 1.8 CO_2/Ti . We conclude that **5** contains two of the eight original carbon atoms of **2**.

The products of both thermal reactions are consistent with initial intramolecular β -H abstraction by a coordinated amido ligand and subsequent liberation of amine (Scheme 1). In the case of **1**, this reaction yields an *N*-methylmethylenimine complex, **3**.¹⁸ The intense $\nu_s(\text{NC}_2)$ vibrations^{8,19,20} of **1** at 956 and 946 cm^{-1} disappear as the thermolysis reaction proceeds, and a weak new band at 1608 cm^{-1} was observed. The ^{13}C CP/MAS spectrum of **3** does not show any new resonance²¹

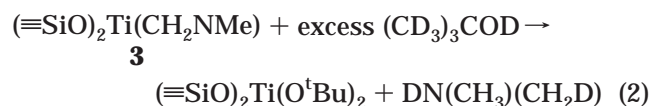
(18) The appearance of new bands at 1590 and 1276 cm^{-1} has been reported as evidence for the presence of N-bonded η^1 -imine¹² and N,C-bonded η^2 -imine⁸ complexes, respectively, during the thermolysis of $\text{Ti}(\text{NMe}_2)_4$. We do not observe a new vibration between 1200 and 1300 cm^{-1} , but this region is difficult to access because of the intense absorption of the silica. We note also that low-frequency vibrational assignments are particularly problematic for metal amido, imine, and imido complexes in which metal-N modes are strongly coupled to other vibrational modes associated with the alkyl groups.^{28,30}

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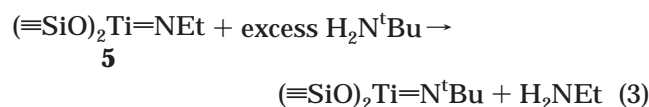
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attributable to the methylene carbon.²² However, reaction of **3** with *tert*-butyl alcohol-*d*₁₀ yielded dimethylamine deuterated at carbon (eq 2).²³



The formation of η^2 -imine metal complexes has ample precedent in the molecular chemistry of the metal amides.^{23,24} For example, Cp*Ta(NMe₂)Me₃ undergoes intramolecular β -H migration to give methane and Cp*Ta(η^2 -CH₂NMe)Me₂.²¹ Intramolecular β -H transfer reactions have also been suggested, although imine complexes were not directly observed, in CVD processes involving metal amides.^{4,25} Elimination of HNET₂ was the major product in the thermolysis of V(NEt₂)₄ at 373 K,⁹ while an equimolar amount of EtN=CHMe was evolved at 473 K. The weak band at 1608 cm⁻¹ in the spectrum of **3** is assigned to $\nu(\text{C}=\text{N})$, implying that some of the imine ligands may be η^1 -N-bonded in the presence of residual HNMe₂ on the surface.

The imine is not liberated from the supported complex **3** at low temperatures (<100 °C). However, the presumed imine intermediate **4** releases C₂H₄ to give the ethylimido complex **5**. The spontaneous formation of imido ligands during the synthesis of molecular dialkyl-amido metal complexes is well-established.²⁶ Alkenes as well as dialkylamines have been detected upon thermal transformation of isolable dialkylamido²⁸ and imine²³ complexes of the early transition metals to imido derivatives. Imido intermediates have also been postulated in the CVD mechanism for titanium nitride.²⁷ We assume that **5** is mononuclear, since supported metal complexes **1** and **2** are not mobile under anhydrous conditions (and especially in the absence of residual surface hydroxyl groups). Terminal imido complexes of Ti are rare²⁹ but have been demonstrated to undergo imido group exchange.³⁰ Upon treatment of **5** with excess *tert*-butylamine, ethylamine was liberated (eq 3).

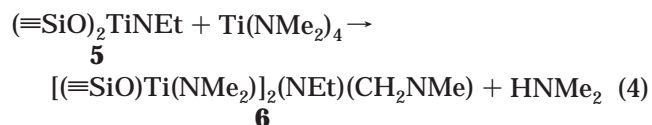


Calculations suggest that terminal imido complexes should retain coordinated amine;⁷ therefore, our observation that the diethylamine is removed by evacuation during the generation of **5** suggests that another ligand

is available to replace it. Complex **5** may be stabilized by additional interactions with oxygen atoms of the silica surface, as in [(≡SiO)₂Ti(NEt)(≡SiOSi≡)_{*n*}]. Since such siloxane “ligands” are themselves readily displaced, complexes such as **5** are expected to be more susceptible to transamination by NH₃ than either of their immediate precursors **1** and **2** or molecularly adsorbed Ti(NR₂)₄, which for steric reasons are reluctant to undergo nucleophilic substitution.²⁶

Our finding that Ti(NEt₂)₄, although less volatile, undergoes greater loss of carbon than Ti(NMe₂)₄ is consistent with the observation that TiN films based on Ti(NEt₂)₄ contain fewer carbon impurities than those made with Ti(NMe₂)₄ (both in the presence of ammonia).³ Indeed, 75% of the carbon is readily lost from **2**, whereas only 50% of the carbon is lost from **1**. Imido ligands have been suggested as the major source of N in metal nitride films, while the Ti–C bonds in imine complexes such as **3** and **4** have been proposed to lead to C incorporation.^{9,10,27,31,32}

The formation of imidotitanium complexes was expected to facilitate the adsorption of the second layer of Ti(NR₂)₄ on the surface.⁶ Our silica surface, after complete reaction with Ti(NR₂)₄, contains 1.9 wt % Ti and no residual hydroxyl groups and does not react further with Ti(NR₂)₄. However, after transformation of **2** to **5**, followed by subsequent exposure to Ti(NMe₂)₄ vapor, a stoichiometric reaction occurs in which the chemisorbed Ti content of the material doubles, to 3.9 wt %. At the same time, 1.0 equiv of HNMe₂ is liberated. These results suggest the occurrence of reaction 4. This



grafting *in the absence of hydroxyl groups* resembles the spontaneous reaction of (≡SiO)₂Ti(O^{*i*}Pr)₂ with Ti(O^{*i*}Pr)₄ to yield dinuclear (≡SiO)₂Ti₂(μ-O)(O^{*i*}Pr)₄.¹⁵ We suggest that **6** is also dinuclear and that likely bridging ligands are ethylimido and *N*-methylmethylenimine. The formation of μ, η^2 -CH₂NMe ligands by H atom transfer from dimethylamido ligands coordinated to polynuclear tungsten²⁸ and titanium³³ frameworks has been reported. Transamination reactions of Ti(NR₂)₄ with monoalkylamines commonly lead to polynuclear products containing bridging imido ligands.^{10,34} The structure of **6** as well as the transamination reactions of **1** and **2** with monoalkylamines and NH₃ are presently under investigation.³⁵

Acknowledgment. This work was supported by an NSERC Strategic Grant.

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