$HNMe_2$ Inhibits the Reaction of $Ti(NMe_2)_4$ with NH_3: Implications for the Chemical Vapor Deposition of TiN and Related Nitrides

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The chemical vapor deposition (CVD) of TiN diffusion barriers for metalization is critical to future generations of integrated circuits.[1] As the feature size of integrated circuits becomes smaller than 0.5 μm, one of the only techniques that gives good step coverage on these high aspect ratio features is CVD. Currently there are two viable CVD processes for TiN: $TiCl_4 + NH_3$[2] and $Ti(NR_2)_4$ (R = Me, Et) + NH_3.[3] The $TiCl_4$ process gives TiN with excellent step coverage, but the temperature is too high for integrated circuits and Cl contamination is a problem. $Ti(NR_2)_4 + NH_3$ gives good step coverage at low temperature with no Cl contamination. As a result, there has been intense recent interest in this CVD system.[3−7]

Gas phase chemical reactions play an important role in TiN CVD from $Ti(NR_2)_4$ and NH_3. NH_3 is required to produce low-carbon, low-resistivity films. Gas-phase transamination to produce HNR_2 was demonstrated and apparently serves to remove carbon from the precursor in situ.[7] Although the higher vapor pressure of $Ti(NMe_2)_4$ makes it more desirable as a starting material, the resulting step coverage is insufficient for integrated circuit applications. $Ti(NEt_2)_4$ gives much better step coverage, but its low vapor pressure is problematic.[5] Using a flow tube reactor, we have measured the gas-phase kinetics of $Ti(NMe_2)_4 + NH_3$ and found the rate constant at 24 °C to be large for these stable molecules, $k = (1.2 \pm 0.2) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (3.8 ± 0.6 Torr^{-1} s^{-1}).[8] The rate constant for $Ti(NEt_2)_4$ is much smaller[9] and this apparently leads to better step coverage. The gas-phase reaction of $Ti(NMe_2)_4$ is fast and probably results in the formation of intermediates with high sticking coefficients or low surface mobility.[10] This work shows that the gas-phase reaction of $Ti(NMe_2)_4$ with NH_3 is strongly inhibited by $HNMe_2$. This result has important implications for the mechanism of the reaction. Furthermore, it points to the use of amines to control the reaction of amido compounds with NH_3 to improve the properties of TiN and other nitride materials.

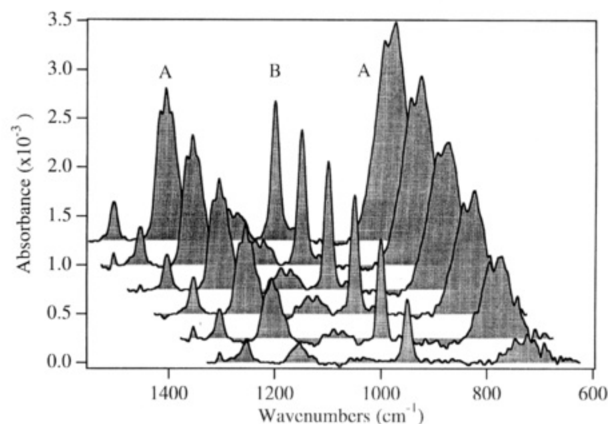

Figure 1. IR spectra of the reaction of $Ti(NMe_2)_4$ with NH_3 as a function of added $HNMe_2$. The peak labeled B is for $Ti(NMe_2)_4$, and the peaks labeled A are for $HNMe_2$. The $HNMe_2$ pressure increases from front to rear (0, 0.051, 0.098, 0.148, 0.198, 0.248, 0.297 Torr) the NH_3 pressure is constant at 0.46 Torr, and the reaction time is 0.60 s. Each spectrum is offset by 2.5×10^{-4} absorbance units and 25 cm^{-1}.

The technique used for these measurements is a flow tube reactor interfaced to an FTIR spectrometer described previously.[8,11] Separate flows of $Ti(NMe_2)_4$ and NH_3 were mixed in a 1-m-long, Teflon-coated, stainless steel tube via a sliding injector. Reactants and products were monitored downstream, and the reaction time is controlled by the variable distance between the injector and the focused IR beam at a constant flow velocity. Mass flow meters measured the separate gas flows of buffer (He), bubbler (He), window purge (Ar), NH_3 (9.77% in He), and $HNMe_2$ (16.8% in He). The total pressure was 10.0 Torr, and the temperature was 24 ± 1 °C. The gas flow was held constant by compensating changes in NH_3 or $HNMe_2$ flow with buffer gas. The spectrometer was operated at 8 cm^{-1} resolution, and 256 scans were averaged. Reference spectra of NH_3 were subtracted from the data to remove overlapping bands.

Figure 1 shows the IR spectra when $Ti(NMe_2)_4$ is reacted with NH_3 in the presence of $HNMe_2$. The injector position was held at 30 cm and the flow velocity was 49.7 cms^{-1} for a reaction time of 0.60 s. Holding the total gas flow and the NH_3 pressure constant (0.46 Torr), the partial pressure of $HNMe_2$ was varied (0, 0.051, 0.098, 0.148, 0.198, 0.248, 0.297 Torr). The band labeled B at 950 cm^{-1} is the NC_2 stretch for $Ti(NMe_2)_4$,[12]

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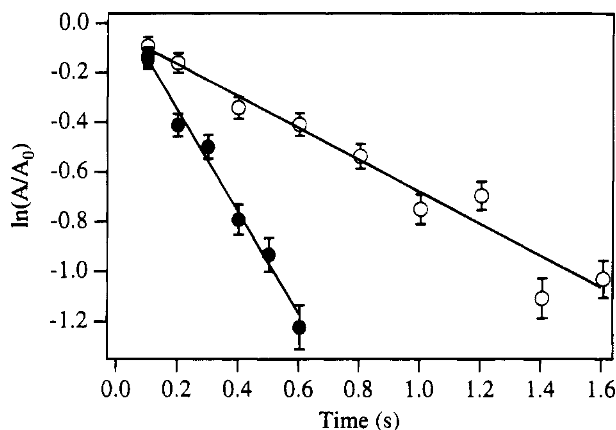

Figure 2. Effect of $HNMe_2$ on the reaction rate of $Ti(NMe_2)_4$ with NH_3. The NH_3 pressure is 0.46 Torr. The slope is k_{obs}, and the open points are with added $HNMe_2$ (0.198 Torr), and the solid points are without $HNMe_2$.

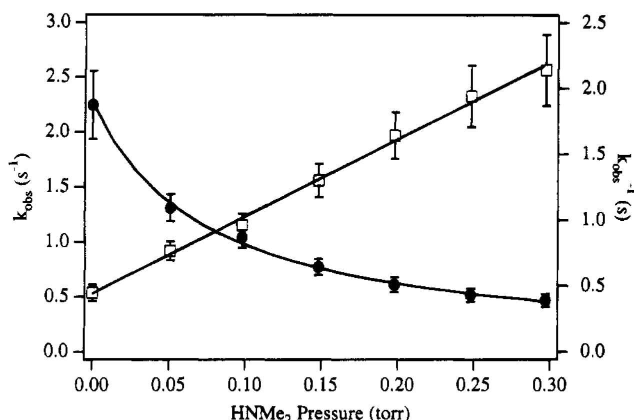

Figure 3. Dependence of k_{obs} on $HNMe_2$ pressure. Both k_{obs} (●) and $(k_{obs})^{-1}$ (□) are shown. The NH_3 pressure is held constant at 0.46 Torr.

and the bands labeled A at 1156 and 730 cm^{-1} are both for $HNMe_2$ (CH_3 rock and NH bend, respectively).[13] As the partial pressure of $HNMe_2$ is increased at constant NH_3 pressure, the amount of $Ti(NMe_2)_4$ clearly *increases*. Addition of sufficient $HNMe_2$ to the gas stream almost completely inhibits the reaction of $Ti(NMe_2)_4$ with NH_3 over this time scale.

Figure 2 shows the decay rates of $Ti(NMe_2)_4$ under conditions of 0.46 Torr of NH_3 with and without added $HNMe_2$. The data are plotted as $\ln(A/A_0)$ vs t where A is the absorbance of $Ti(NMe_2)_4$ at time t, A_0 is the absorbance of $Ti(NMe_2)_4$ in the absence of NH_3, and $\ln(A/A_0) = -k_{obs}t$. Both semilog plots are linear, indicating a simple first order decay for both conditions. The rate constant (k_1) is calculated from the slope (k_{obs}) and the NH_3 pressure where $k_{obs} = k_1(NH_3)$. In the absence of $HNMe_2$, the rate constant is the same as that observed earlier, $k_1 = (1.4 \pm 0.2) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}. In the presence of 0.198 Torr of $HNMe_2$, the rate constant is reduced significantly to $k_1 = (0.43 \pm 0.03) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}. Figure 3 shows that k_{obs} is inversely dependent on $HNMe_2$ concentration. Using data as in Figure 1, k_{obs} was calculated from $\ln(A/A_0)$ and the reaction time. Also shown is a linear dependence of $(k_{obs})^{-1}$ on $HNMe_2$. $HNMe_2$ clearly inhibits the reaction of $Ti(NMe_2)_4$ with NH_3.

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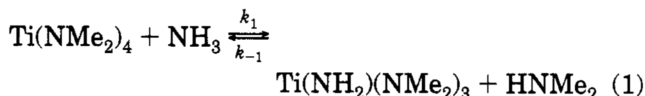
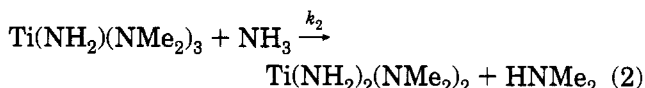
The mechanistic implication of Figures 1–3 is clear: the reaction between $Ti(NMe_2)_4$ and NH_3 must be reversible. Bradley et al. showed that the transamination reactions between numerous amido compounds and amines are at equilibrium in solution.[14] Therefore it is reasonable to propose the first step in the mechanism as reversible transamination to form the transient intermediate $Ti(NR_2)_3(NH_2)$ as shown in (1). The subsequent reactions are of particular interest since they control which species reach the surface. Two reasonable possibilities are reaction with NH_3 in a second transamination step to form $Ti(NH_2)_2(NMe_2)_2$ (2) or elimination of $HNMe_2$ to form an imido complex (3):



$$Ti(NMe_2)_4 + NH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ti(NH_2)(NMe_2)_3 + HNMe_2 \quad (1)$$



$$Ti(NH_2)(NMe_2)_3 + NH_3 \xrightarrow{k_2} Ti(NH_2)_2(NMe_2)_2 + HNMe_2 \quad (2)$$

$$Ti(NH_2)(NMe_2)_3 \xrightarrow{k_3} Ti({=}NH)(NMe_2)_2 + HNMe_2 \quad (3)$$

Using the steady-state approximation on $Ti(NR_2)_3(NH_2)$ for the two mechanisms (1)–(2) and (1)–(3), the respective expressions for k_{obs} are[15]

$$k_{obs} = \frac{k_1 k_2 (NH_3)^2}{k_{-1}(HNMe_2) + k_2(NH_3)} \quad (4)$$

$$k_{obs} = \frac{k_1 k_3 (NH_3)}{k_{-1}(HNMe_2) + k_3} \quad (5)$$

With no added $HNMe_2$, both expressions give the observed linear dependence of k_{obs} on NH_3, $k_{obs} = k_1(NH_3)$, and the derived bimolecular rate constant represents the forward transamination reaction (k_1). Both expressions also predict the observed linear dependence of $(k_{obs})^{-1}$ on $HNMe_2$. The key difference is the order with respect to NH_3 in the presence of excess $HNMe_2$; (5) is first order, while (4) is second order. At the highest $HNMe_2$ pressure used (0.297 Torr), the dependence of k_{obs} on NH_3 from 0 to 0.5 Torr was linear with a zero intercept. While this is not conclusive, we favor the mechanism (1)–(3) for several additional reasons. $Ti({=}NH)(NMe_2)_2$ could easily give bridging imido complexes such as those previously postulated as intermediates in this system.[5] A similar imido complex has been isolated as an intermediate in TiN CVD from $TiCl_4$ and NH_3[16] and there are several other related examples as well.[17] Experiments are in progress to further elucidate the mechanism.

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These results are apparently the first to show that a transamination reaction between a metal amido compound and NH_3 is reversible. This has important implications for the CVD of TiN from $Ti(NR_2)_4$ precursors since the addition of amines to the gas flow may provide a simple method for controlling the extent of gas-phase reaction and therefore the properties of TiN. Furthermore, metal amido precursors are useful CVD precursors for numerous nitride materials,[18] and this result will provide others an important consideration in understanding and controlling the chemistry of these CVD systems as well. We are currently exploring the effect added amine has on the properties of TiN deposited as well as the generality of this effect for the gas-phase reactions of other metal amido compounds with NH_3.

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