*Chem. Mater.* **1994**, *6*, 260–261

# Flow-Tube Kinetics of Gas-Phase Chemical Vapor Deposition Reactions: TiN from $Ti(NMe_2)_4$ and $NH_3$

Bruce H. Weiller* and Brenda V. Partido

*Mechanics and Materials Technology Center*
*The Aerospace Corporation*
*PO Box 92957/M5-753*
*Los Angeles, California 90009-2957*

*Received October 14, 1993*
*Revised Manuscript Received December 20, 1993*

TiN is a material with a unique combination of properties including high hardness, good electrical conductivity, a high melting point, and chemical inertness.[1] This makes it useful for a range of applications that include wear-resistant coatings for machine tools and bearings and thermal control coatings for windows.[2] However, one of the most significant applications of TiN is as a diffusion barrier for metallization layers in integrated circuits.[3] Here good conformal coatings of TiN on high-aspect-ratio features may hold the key to the next generation of integrated circuits.

The CVD reaction of $Ti(NR_2)_4$ (R = Me, Et) with $NH_3$ is a promising new method to deposit TiN since it gives films at low temperature with good purity[4] and good step coverage.[5] An important feature of this system is that a gas-phase reaction between $Ti(NMe_2)_4$ and $NH_3$ is apparently required in order to deposit low-carbon films of TiN.[6] Significantly, no surface reaction between coadsorbed $Ti(NMe_2)_4$ and $NH_3$ could be observed under UHV conditions.[7] Therefore, to optimize this process and design improved CVD reactors, it is important to examine the relevant gas-phase reactions and their relationship to the properties of the material produced. This includes the spectroscopic identification of the reactive intermediates and quantitative measurements of the rates of relevant reactions for input into kinetic models of the deposition process.

We have developed a technique that is ideal for this purpose—a flow-tube reactor coupled to an FTIR spectrometer. In the flow-tube experiment,[8] two reactive flows are mixed in a long tube via a movable injector, and reactants and products are monitored downstream, in this case by FTIR spectroscopy. The reaction time is controlled by the variable distance between the injector and the focused IR beam at a constant flow velocity. Here we demonstrate the use of the flow tube reactor for studies of CVD kinetics by measuring the gas-phase rate constant for the reaction between $Ti(NMe_2)_4$ and $NH_3$ for the first time.

The flow-tube reactor[9] is a 1-m-long, 1.37-in.-i.d., Teflon-coated, stainless steel tube equipped with a sliding injector port. To ensure good mixing, $Ti(NMe_2)_4$ is injected counter-current to the main flow using a Pyrex loop with many equally spaced holes. The observation region is a cross equipped with purged windows, capacitance manometers, and a throttle-valve controller to maintain constant pressure. Mass flow meters measure the separate flows of buffer gas, bubbler, and purge flows, and the flow of a dilute mixture of $NH_3$ in buffer gas (6–7%). The He and Ar buffer gases used were ultrahigh-purity grade, and the $NH_3$ was electronic grade. The total pressure and gas flow into the reactor was held constant by compensating changes in the $NH_3$ 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.

To confirm that the apparatus produces reliable kinetics data, we have measured the rate constant for the reaction of $O_3$ with isobutene. For this experiment, a mixture of He and $O_2$ flowed into an ozone generator and then into the sliding injector. We measured the decay of $O_3$ as a function of reaction time (distance) and isobutene partial pressure and determined the rate constant to be $(13.8 \pm 0.1) \times 10^{-18}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (10 Torr, 25 °C).[10] This is in excellent agreement with the best literature value, $(13.6 \pm 0.2) \times 10^{-18}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (760 Torr, 25 °C), obtained using a very different technique.[11]

When $Ti(NMe_2)_4$ is reacted with $NH_3$ in the flow-tube reactor, the IR spectra show the removal of $Ti(NMe_2)_4$ and formation of $HNMe_2$. The relatively intense $NC_2$ symmetric stretch at 949 $cm^{-1}$ is a good signature for $Ti(NMe_2)_4$,[7] and we use it to monitor the number density of $Ti(NMe_2)_4$. With 0.245 Torr of $NH_3$ in the reactor, we observe the decay of $Ti(NMe_2)_4$ on the time scale of <2 s and the concomitant formation of $HNMe_2$ as identified by its peaks at 1485, 1158, and 735 $cm^{-1}$.[12] This is consistent with the results of Dubois et al.[7] and is expected for a transamination reaction.[13] However, in this work, the kinetics are not determined by reagent mixing times (see below), and we confirm that $HNMe_2$ is a direct product from the reaction of $NH_3$ with $Ti(NMe_2)_4$.

Figure 1 shows the disappearance of $Ti(NMe_2)_4$ as a function of time and $NH_3$ pressure. Plots of $\ln(A/A_0)$ versus time are shown for three $NH_3$ pressures, where $A$ is the integrated absorbance of the $NC_2$ stretch, and $A_0$ is the average absorbance in the absence of $NH_3$.[14] Using available vapor pressure data[15] and assuming that the

---

* To whom correspondence should be addressed.

(1) Schwarzkopf, P.; Kieffer, R. *Refractory Hard Metals*; Macmillan: New York, 1953.

(2) Kurtz, S. R.; Gordon, R. G. *Thin Solid Films* **1986**, *140*, 277–290.

(3) Musher, J. N.; Gordon, R. G. *J. Electron. Mater.* **1991**, *20*, 1105.

(4) (a) Fix, R. M.; Gordon, R. G.; Hoffman, D. M. *Mater. Res. Soc. Symp. Proc.* **1990**, *168*, 357–362. (b) Fix, R. M.; Gordon, R. G.; Hoffman, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 7833–7835. (c) Ishihara, K.; Yamazaki, K.; Hamada, H.; Kamisako, K.; Tarui, Y. *Jpn. J. Appl. Phys.* **1990**, *29*, 2103–2105. (d) Fix, R. M.; Gordon, R. G.; Hoffman, D. M. *Chem. Mater.* **1991**, *3*, 1138–1148.

(5) Raaijmakers, I. J.; Vrtis, R. N.; Yang, J.; Ramaswami, S.; Lagendijk, A.; Roberts, D. A.; Broadbent, E. K. *Mater. Res. Soc. Symp. Proc.* **1992**, *260*, 99–105.

(6) Prybyla, J. A.; Chiang, C.-M.; Dubois, L. H. *J. Electrochem. Soc.* **1993**, *140*, 2695–2702.

(7) Dubois, L. H.; Zegarski, B. R.; Girolami, G. S. *J. Electrochem. Soc.* **1992**, *139*, 3603–3609.

(8) Keyser, L. F. *J. Phys. Chem.* **1984**, *88*, 4750–4758 and references therein.

(9) Weiller, B. H. *Mater. Res. Soc. Symp. Proc.* **1993**, *282*, 605.

(10) We have also measured the rate constant at 5 Torr and find no significant difference.

(11) Japar, S. M.; Wu, C. H.; Niki, H. *J. Phys. Chem.* **1974**, *78*, 2318.

(12) Gamer, G.; Wolff, H. *Spectrochim. Acta.* **1973**, *29A*, 129.

(13) (a) Bradley, D. C.; Gitlitz, M. H. *J. Chem. Soc. A* **1969**, 980–984. (b) Bradley, D. C.; Torrible, E. G. *Can. J. Chem.* **1963**, *41*, 134–138. (c) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857–3861.

(14) In a time-dependent experiment, $A_0$ would be the absorbance at zero time. We cannot obtain $A_0$ this way since at zero time (distance), the injector would block the IR beam. Instead we substitute the $NH_3$ flow with buffer gas and measure the $Ti(NMe_2)_4$ absorbance. This is equivalent since we have shown that in the absence of $NH_3$, there is no dependence of the $Ti(NMe_2)_4$ absorbance on the position of the injector over the length of the flow tube. We record $A_0$ before and after each kinetic run to confirm that there has been no change in the $Ti(NMe_2)_4$ concentration due to bubbler fluctuations.

0897-4756/94/2806-0260$04.50/0

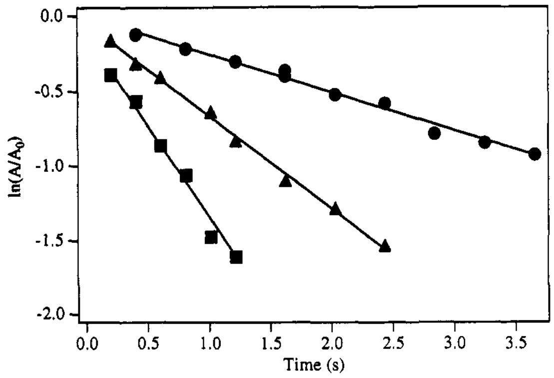

**Figure 1.** Plot of $\ln(A/A_0)$ versus time for the reaction of Ti$(NMe_2)_4$ with $NH_3$ where $A$ is the absorbance of $Ti(NMe_2)_4$ and $A_0$ is the absorbance in the absence of $NH_3$. Data for three different $NH_3$ pressures are shown: 0.090 (●), 0.179 (▲), and 0.357 (■) Torr. The buffer gas is helium and the total pressure is 10.0 Torr.

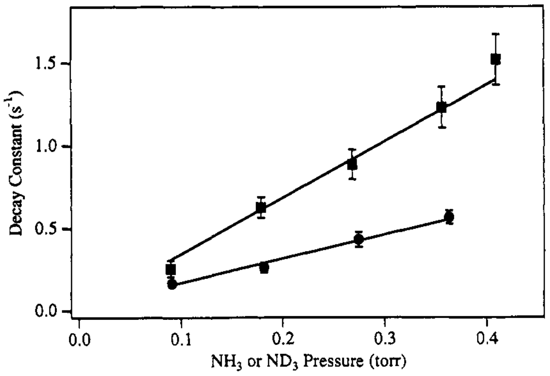

**Figure 2.** Plot of the decay constants of $Ti(NMe_2)_4$ versus $NH_3$ (■) or $ND_3$ (●) pressure. The slopes give the bimolecular rate constants, $k_h = (1.1 \pm 0.1) \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k_d = (4.5 \pm 0.5) \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, or $k_h/k_d = 2.4 \pm 0.4$.

bubbler flow is saturated, the upper bound on the partial pressure of $Ti(NMe_2)_4$ is 0.006 Torr. Therefore, the $NH_3$ density (>0.1 Torr) is in excess, pseudo-first-order conditions apply, and we expect a linear plot of $\ln(A/A_0)$ versus time. As Figure 1 shows, the data are in good agreement with this expectation and were fit to a line using weighted least-squares. The slopes of these lines give the observed decay constant at each $NH_3$ pressure.

Figure 2 shows that the observed decay constants are linearly dependent on $NH_3$ pressure, as expected for pseudo-first-order conditions. The slope of Figure 2 is the bimolecular rate constant: $k = (1.1 \pm 0.1) \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.[16] To our knowledge, this is the first measurement of the rate constant for a transamination reaction. The rate constant is surprisingly large considering that both $Ti(NMe_2)_4$ and $NH_3$ are stable closed-shell molecules and that the temperature is only 24 °C. It should be noted that the use of argon or helium buffer gas has no effect on the measured rate constant, and, therefore, the mixing time is insignificant compared to the measurement time. This is supported by calculations of the diffusional mixing time using estimates of the diffusion constant for $Ti(NMe_2)_4$.[17]

We have also determined the rate constant using $ND_3$ and find a significant isotope effect. Under conditions identical to those used with $NH_3$, we find good kinetics data for the removal of $Ti(NMe_2)_4$, except now the rate constant is significantly smaller. Figure 2 shows the decay constants obtained as a function of $ND_3$ pressure. The resulting rate constant is $k_d = (4.5 \pm 0.5) \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, or $k_h/k_d = 2.4 \pm 0.4$. This result is significant because it is a clear indication that H-atom transfer is involved in the rate-limiting step of the reaction. This is consistent with earlier studies that showed the reaction of $ND_3$ with $Ti(NMe_2)_4$ gives $DN(CH_3)_2$, presumably from cleavage of a N–D bond in $ND_3$.[6,7]

These results are consistent with transamination reactions that remove the $NMe_2$ ligands in $Ti(NMe_2)_4$. One possible mechanism for this is a concerted bimolecular reaction proceeding through a four-center transition state as discussed previously.[18] Another possibility is the formation of a weak adduct between $NH_3$ and $Ti(NMe_2)_4$, followed by H-atom transfer and elimination of $HNMe_2$. Similar adducts have been observed from the reaction of $TiCl_4$ with $NH_3$,[19] but none are known for $Ti(NR_2)_4$. The difference between these two possibilities centers on the relative stability of the postulated adduct which should depend on identity of R. Clearly steric interactions are an issue,[13c] and for R larger than Me the formation of an adduct is more questionable. However, in both mechanisms close approach of $NH_3$ to the Ti center is required, and if this is rate limiting, a significant isotope effect would not be expected.

Our results provide the first quantitative data on this key gas-phase reaction in the initial stages of the CVD of TiN. The extent of gas-phase reaction appears to have a profound impact on the quality of the TiN produced by this process, with too much reaction giving lower-quality films.[5,6] The species responsible for film growth may be determined by the rate of the transamination reaction measured here. To design an optimized CVD reactor for this process, there is great interest in developing a quantitative model that includes reaction kinetics and our data should be valuable in this effort. Work in progress is aimed at identifying the mechanism for this reaction and the intermediate(s) responsible for film growth. Temperature-dependent kinetics measurements are planned as well as experiments with other related precursors. Finally we note that many other main-group and transition-metal nitride materials can be formed from analogous chemistry;[4b,d,20] similar mechanisms have been proposed, and this technique should prove useful in understanding and modeling those systems as well.

**Acknowledgment.** This work was supported by The Aerospace-Sponsored Research Program. We thank Professor R. G. Gordon and Dr. L. H. Dubois for helpful discussions and for communication of results prior to publication, Dr. N. Cohen for useful consultations regarding kinetics issues, and Dr. L. R. Martin for the loan of the ozone generator. We also thank the reviewers for their thoughtful comments.

---

(15) The vapor pressure at 25 °C is 0.11 Torr: Roberts, D., The Schumacher Corporation, personal communication.

(16) In these units, the gas kinetic (collision) rate constant for this reaction is ~5 × $10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

(17) For this calculation we used an estimate of the collision radius for $Ti(NMe_2)_4$ of 4.5 Å. The resulting diffusion constant in helium is ~3.5 times larger than in argon at room temperature.

(18) Chisholm, M. H.; Rothwell, I. P. Amido and Imido Metal Complexes. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987.

(19) Saeki, Y.; Matsuzaki, R.; Yajima, A.; Akiyama, M. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3193–3196.

(20) (a) Gordon, R. B.; Hoffman, D. M.; Riaz, U. *Mater. Res. Soc. Symp. Proc.* **1992**, *242*, 445–450. (b) Gordon, R. G.; Hoffman, D. M.; Riaz, U. *Chem. Mater.* **1992**, *4*, 68–71. (c) Gordon, R. G.; Riaz, U.; Hoffman, D. M. *J. Mater. Res.* **1992**, *7*, 1679–684.