Gas Phase Photoproduction of Diatomic Metal Nitrides During Metal Nitride Laser Chemical Vapor Deposition

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Recent spectroscopic studies of luminescent fragments produced during gas-phase photolysis of metal-containing precursors for laser-assisted chemical vapor deposition (LCVD)[1] have shown that atoms or small molecules having the elemental compositions of the final deposits are produced in the gas phase.[2−10] For example, luminescence from both atoms and diatomics of metals are observed during the deposition of gold,[2] and both metal and chalcogen are observed during the deposition of II/VI semiconductors.[3,4] It has also been found that diatomic molecules are formed containing the desired metal combined with an undesired heteroatomic impurity that contaminates the final film. For example, when metal hexafluoroacetylacetonates are used as the precursor molecules, diatomic metal fluorides are observed during LCVD of Cr, Ni, and Cu,[9,10] and diatomic metal carbide is observed during the LCVD of Pt.[10] These studies demonstrate that both desired and undesired species are produced in the purely gas-phase component of the CVD process. To date there have been no demonstrations of gas-phase formation of diatomic molecules having the same stoichiometry as that of the desired solid-phase deposit.

As a test case, we chose to examine metal nitride deposition (metal = titanium, zirconium, hafnium) from the corresponding metal amide $M(NEt_2)_4$ precursor and search for diatomic metal nitride formation in the gas phase. The metal nitrides are of current interest for microelectronics; TiN in particular is used as a diffusion barrier material in the metalization structures of microelectronic devices.[11] An additional motivation for studying single source precursors for metal nitride formation is the absence of simple sources of nitride ion. Unlike metal sulfides and selenides, for example, where the desired metal cation can react with the chalconide anion, metal nitride preparations must employ different strategies such as the one utilized in this work. Both pyrolysis and photolysis of gaseous $Ti(NEt_2)_4$ in the presence of ammonia has been shown to deposit clean TiN.[12−20] The transamination reactions that occur during the thermal CVD involving ammonia have been well studied and are necessary to produce stoichiometric TiN; pyrolysis of the metal amide in the absence of ammonia results in films where the carbon content is usually greater than that of nitrogen. Laser-assisted CVD of $Ti(NEt_2)_4$ in the presence of ammonia also produced stoichiometric TiN; under irradiation the electrical resistivity of the films was reported to be lowered.[19,20]

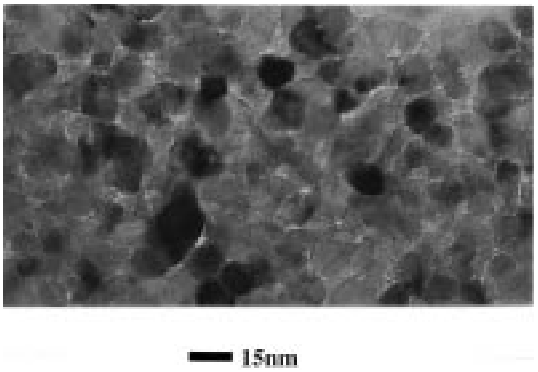

Figure 1. Transmission electron microscopy image of the film photodeposited on quartz. The particle size is 11 ± 3 Å.

In this note, we show that photolysis of $M(NEt_2)_4$ (M = Ti, Zr, Hf) produces MN molecules in the gas phase. MN production occurs in the absence of ammonia gas but is enhanced in the presence of ammonia. We also verify that laser assisted CVD occurs at 355 and 308 nm under the fluence conditions used in the spectroscopic study. Surprisingly, transmission electron microscopy reveals that the deposit consists of nanostructured grains.

Solid thin films of TiN were formed by irradiating $Ti(NEt_2)_4$ gas at 355 nm. The CVD precursor (∼0.1 g) was heated to its boiling temperature (∼110−130 °C) in a reservoir cell under vacuum (10^{-2} Torr) and introduced into a CVD cell with quartz windows by using He as the carrier gas. Other gases (e.g. NH_3) could be introduced if desired via a different dosing line. The photodepositions were carried out by irradiating a 0.5 cm diameter circle on substrates with ∼50 mJ/pulse at 20 Hz. Deposits were formed on both quartz and Si (100). The TiN thin films are rough on the surface and consist of granules as shown by transmission electron microscopic analysis (Figure 1). The TEM image shows 11 ± 3 nm diameter granules of TiN on the quartz substrate. Auger electron spectroscopy and EDS comparison with a TiN standard indicate that the films are stoichiometric TiN within the experimental uncertainty; a small amount of oxygen contamination is detected, while almost

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(1) For reviews, see: (a) Eden, J. G. *Photochemical Vapor Deposition*; Wiley: New York, 1992. (b) Hitchman, M. L.; Jensen, K. F. *Chemical Vapor Deposition: Principles and Applications*; Academic Press: San Diego, 1993. (c) Kodas, T. T.; Hampden-Smith, M. J. *The Chemistry of Metal CVD*; Weinheim: New York, 1994. (d) Chaiken, J., Ed. Laser Chemistry of Organometallics. *ACS Symp. Ser.* **1993**, 530.
(2) Wexler, D.; Zink, J. I.; Tutt, L. W.; Lunt, S. R. *J. Phys. Chem.* **1993**, *97*, 13563.
(3) Cheon, J.; Talaga, D. S.; Zink, J. I. *J. Am. Chem. Soc.* **1997**, *119*, 163.
(4) Cheon, J.; Zink, J. I. *J. Am. Chem. Soc.* **1997**, *119*, 3838.
(5) Cheon, J.; Talaga, D. S.; Zink, J. I. *Chem. Mater.* **1997**, *9*, 1208.
(6) Schendel, J.; Wehry, E. L. *Anal. Chem.* **1988**, *60*, 1759.
(7) Willwohl, H.; Wolfrum, J. *Appl. Surf. Sci.* **1992**, *54*, 89.
(8) Baraichotte, D.; Garrido, C.; van den Bergh, H. J. *Appl. Surf. Sci.* **1990**, *46*, 9.
(9) Talaga, D. S.; Zink, J. I. *Inorg. Chem.* **1996**, *35*, 5050.
(10) Talaga, D. S.; Hanna, S. D.; Zink, J. I. *Inorg. Chem.* **1998**, *37*, 2880.
(11) Littau, K.; Dixit, G.; Havemann, R. H. *Semiconductor Int.* **1994**, *July*, 183.
(12) Fix, R. M.; Gordon, R. G.; Hoffman, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 7833.
(13) Fix, R.; Gordon, R. G.; Hoffman, D. M. *Chem. Mater.* **1991**, *3*, 1138.
(14) Hoffman, D. M. *Polyhedron* **1994**, *13*, 1169.
(15) Cundari, T. R.; Morse, J. M. *Chem. Mater.* **1996**, *8*, 189.
(16) Weiller, B. H. *J. Am. Chem. Soc.* **1996**, *118*, 4975.
(17) Prybyla, J. A.; Chiang, C.-M.; Dubois, L. H. *J. Electrochem. Soc.* **1993**, *140*, 2695.
(18) DuBois, L. H. *Polyhedron* **1994**, *13*, 1329.
(19) Illmann, U.; Ebert, R.; Reisse, G.; Freller, H.; Lorenz, P. *Thin Solid Films* **1994**, *241*, 71.
(20) Ishihara, S.; Hanabusa, M. *J. Appl. Phys.* **1998**, *84*, 596.

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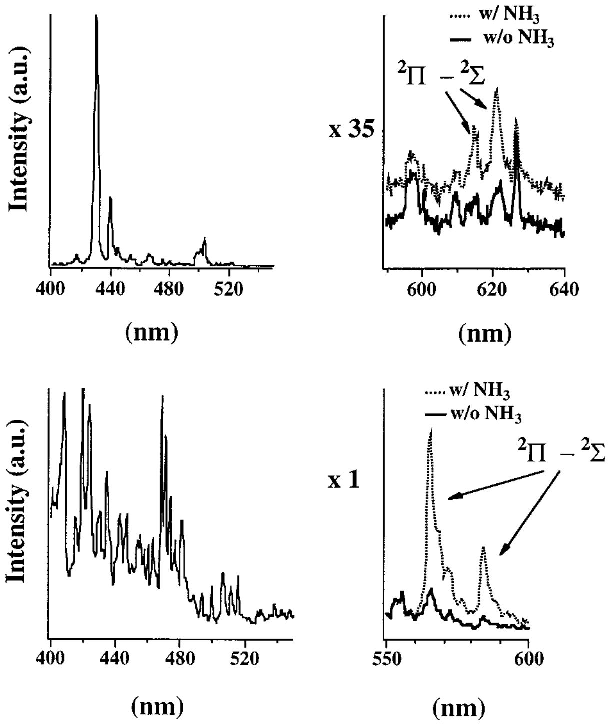

Figure 2. Emission spectra during photolysis of $Ti(NEt_2)_4$ (top) and $Zr(NEt_2)_4$ (bottom) in the gas phase. Two spectral regions are shown. The 400−550 nm region is dominated by the emission of the metal atom. The bands at 613.9 and 619.9 nm in the spectrum from $Ti(NEt_2)_4$ and the bands at 564.2 and 587.9 nm in the spectrum from $Zr(NEt_2)_4$ are the $^2\Pi \rightarrow {}^2\Sigma$ emissions from diatomic TiN and ZrN, respectively. The intensities of these bands increase in the presence of ammonia gas (dotted lines).

no carbon is present, similar to the results reported for 193 nm irradiation.[19,20]

We spectroscopically examine the photofragmentation reactions that lead to the deposition under two gas-phase conditions: a gas cell at about 10^{-1} Torr and the collision-free conditions of a supersonic expansion molecular beam (10^{-6} Torr). The former reproduces the conditions used for the deposition of films and includes molecular collisions (but not collisions with surfaces), while the latter restricts the photochemistry to intramolecular reactions.

Luminescence was observed when each of the metal amide complexes was irradiated at 308 nm in a 6-way cross gas cell under conditions similar to those used for the deposition studies. The luminescence spectra from the fragmentation of $Ti(NEt_2)_4$ and $Zr(NEt_2)_4$ are shown in Figure 2. The region between 400 and 500 nm in each spectrum is dominated by the emission of the metal atoms. These atomic lines are well-known and the assignment is unambiguous.[21,22] In addition to the atomic lines, well-known emission bands from CH (431.4, 432.4 nm) and C_2 (468.4, 469.8, 471.5, 473.7 nm) are observed.[23] Similar assignments are made for the emission spectrum obtained when the Hf complex is photolyzed. The identification of bare Ti, Zr, or Hf atoms and diatomic ligand fragments shows that extensive fragmentation takes place.

The most important luminescence for the purposes of this note are the bands at 613.9 and 619.9 nm in the spectrum of $Ti(NEt_2)_4$ and the bands at 564.2 and 587.9 nm in the spectrum from $Zr(NEt_2)_4$ (Figure 2). In both cases, the emission bands have been assigned to the $A^2\Pi_{3/2} \rightarrow X^2\Sigma^+$ and $A^2\Pi_{1/2} \rightarrow X^2\Sigma^+$ transitions, respectively, in diatomic MN.[24−26] (Because emission from HfN has not been reported in the literature, it is not known if any of the unassigned bands in the spectrum involving $Hf(NEt_2)_4$ arise from HfN.) The spectra in Figure 2 unambiguously show that TiN and ZrN are produced in the purely gas phase component of the deposition process. Furthermore, these diatomics are not the result of reactions with a source of nitrogen other than the amide ligand; only the precursor molecules and He buffer gas are present in the cell.

To test for the effects of other nitrogen sources on MN emission, ammonia gas was added to the cell. The addition of ammonia gas resulted in a dramatic increase in the intensity of the TiN and ZrN emission (Figure 1, inset). Ammonia increased both the rate of film deposition and the purity of the film. Similar trends during pyrolytic CVD were attributed to ammonia coordination followed by enhanced elimination of NR_2H.[16−18] Our luminescence studies show that ammonia is not necessary for gas-phase MN formation but rather that it enhances MN formation.

To test whether the MN formation was intramolecular or whether it required intermolecular reactions, the photofragmentation was studied in the collision free environment of a molecular beam. To identify MN as well as of other photofragments, time-of-flight mass spectroscopy was used. Mass spectroscopy confirmed the formation of the bare metal and the ligand fragments observed in the emission spectra. Large peaks from the amide ligand and partially dissociated metal complexes (the heaviest being $Hf(NEt_2)_3$) were also observed. Most importantly, mass selection provided unambiguous identification of the HfN diatomic.

The results reported in this note prove that diatomic metal nitrides are produced in the gas phase under laser-assisted CVD conditions. The amide ligand can act as the source of the nitride, and the photoreaction produces the metal nitride via an intramolecular process in the absence of collisions. When collisions are frequent, MN is also produced when the only reactants are the precursor molecules, but the production of MN is enhanced in the presence of ammonia gas. Characterization of the TiN photodeposit shows that 11 ± 3 nm crystalline nanoparticles of TiN are formed. These results suggest that interesting nucleation pathways are followed that may enable nanocrystals to be collected and that photolysis is a convenient method of making solid metal nitrides.

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(21) Wiese, W. L.; Martin, G. A. *Wavelength and Transition Probabilities for Atoms and Atomic Ions*; U.S. Gov. Printing Office: Washington, DC, 1980.

(22) Striganov, A. R.; Sventitskii, N. S. *Tables of Spectral Lines of Neutral and Ionized Atoms*; IFI/Plenum: New York, 1968.

(23) Pearse, R. W. B.; Gaydon, A. G. *The Identification of Molecular Spectra*, 3rd ed.; Chapman and Hall: London, 1976.

(24) Dunn, T. M.; Hanson, L. K.; Rubinson, K. A. *Can. J. Phys.* **1970**, *48*, 1657.

(25) Bates, J. K.; Dunn, T. M. *Can. J. Phys.* **1976**, *54*, 1216.

(26) Chan, C. M−T; Li, H.; Sze, S.-K.; Cheung, A. S−C. *J. Mol. Spectros.* **1996**, *180*, 145.