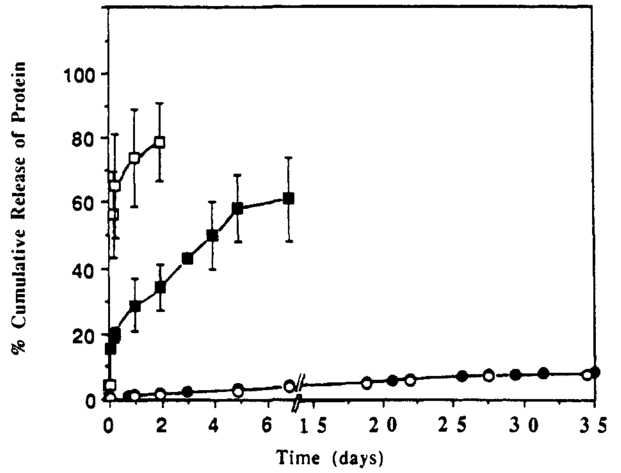

Figure 2. Release rates of FITC-BSA (□) and β-gal (■) from PCPP spheres coated with 21.5-kDa PLL.[4,5] FITC-BSA release rates from liposomes (○) and MELs (●), composed of egg hydrogenated phosphatidylcholine (PPC) and cholesterol (CH), 1:1 molar ratio.[7]

Ca-PCPP matrices efficiently entrapped fluorescein isothiocyanate labeled bovine serum albumin (FITC-BSA) and β-galactosidase (β-gal), with MWs of 68 and 540 kDa (kilodaltons), respectively; 60% and 80% of FITC-BSA and β-gal, respectively, were recovered in Ca-PCPP spheres. The process enabled high retention of β-gal activity, comparable to its aqueous activity.[5,6]

Ca-PCPP spheres aggregate and adhere to glass, suggesting surface-charge effects. To neutralize charge (i.e., carboxylic groups), microspheres were reacted with the positively charged polyelectrolyte poly(L-lysine) (PLL).[4a] This not only diminished aggregation but sustained release rates of FITC-BSA (by 20%) and β-gal (by 80%) (Figure 2).[4b] Presumably, the complex PCPP-PLL creates a permselective membrane on the microsphere surface, similar to alginate-PLL membranes.[2b]

FITC-BSA release was further sustained by encapsulating it first in liposomes that were then entrapped in PCPP-PLL, providing microencapsulated liposomes (MELs) with an additional controllable barrier, i.e., lipid bilayer.[7] Liposome entrapment did not interfere with ionic cross-linking and, when coated with 21.5 kDa PLL, Ca-PCPP retained the liposomes for over 50 days. FITC-BSA release was significantly reduced and was similar to that of unencapsulated liposomes with the same lipid composition (Figure 2). The lipid bilayer is presumably rate-limiting for MELs.

PCPP degradation was studied in phosphate-buffered saline (PBS), at 37 °C for 90 days. The medium was collected periodically and assayed for backbone degradation products, i.e., ammonia, using ion activity measurements and inorganic phosphate.[8] No degradation products were detected, implying that PCPP does not degrade.

To examine cellular toxicity, liver cells[9a,b] were seeded on Ca-PCPP films coated with PLL.[5] One hour after seeding, cells had attached to the films; washing with media did not remove the cells. Microscopic inspection and viability assays[9c,d] revealed live cells. Five days later, live cells were still observed on the films. Preliminary studies also indicated that hybridoma cells survive microencapsulation.[4a,5]

Acknowledgment. H.R.A. and K.B.V acknowledge the NIH (Grant No. HL11418), M.C.B. acknowledges a Fulbright grant, and S.C, M.C., and R.L. acknowledge the NIH (Grant No. A124764).

Supplementary Material Available: Details of the encapsulation process and the preparation of Ca-PCPP films, a graph showing the β-gal activity in PBS and Ca-PCPP matrices, and a figure showing hybridoma cells in PCPP spheres via phase contrast microscopy (3 pages). Ordering information is given on any current masthead page.

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[5] Supplementary material available: detailed encapsulation process (1 paragraph); preparation of Ca-PCPP films (1 paragraph); β-gal activity in PBS and Ca-PCPP matrices (1 figure); hybridoma cells in PCPP spheres via phase contrast microscopy (1 figure).

[6] β-Gal activity assay using o-nitrophenyl β-galactopyranoside as a substrate.

[7] (a) Liposomes of PPC (Avanti Polar Lipids) and CH (Sigma), 1:1 molar ratio, were prepared by reverse-phase evaporation.[7b] To prepare MELs, 1 mL of (FITC-BSA)-laden liposomes (66-88 μmol of lipid) was mixed with 1 mL of 5% (w/v) PCPP and the mixture was sprayed as microdroplets into the $CaCl_2$ solution.[4,5] (b) Szoka, F.; Papahadjopoulos, D. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 4194.

[8] Phosphate was quantified colorimetry by reducing a molybdenum phosphate heteropolyacid with ascrobic acid (Sigma, kit No. 670).

[9] (a) Liver cells were isolated from male fisher rats.[9b] (b) Selgen, P. O. In *Methods in Cell Biology*; Prescott, E., Ed.; Academic Press: New York, 1976; p 13. (c) Cell viability was followed by tetrazolium salt assay.[9c] (d) Mosmann, T. J. *Immunol. Methods* **1983**, *65*, 55.

Solution-Phase Reactivity as a Guide to the Low-Temperature Chemical Vapor Deposition of Early-Transition-Metal Nitride Thin Films

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Recently there has been an interest in using inorganic and organometallic compounds as precursors for the synthesis of inorganic thin films by chemical vapor deposition (CVD).[1] In the CVD process, reactions are thought to occur both in the gas phase and at the gas phase-substrate surface interface.[2] It remains to be demonstrated that well-developed solution reaction chemistry is relevant to such complicated systems,[3-6] and concurrently, whether or not solution reactivity can be used as a guide in the selection of precursors for the designed synthesis of target materials.

In the early 1960s, Bradley and co-workers reported that dialkylamido complexes undergo facile transamination reactions in solution (eq 1).[7] With primary amines, reaction 1 leads to imido-bridged oligomers if the alkyl substituent is small (eq 2)[8,9] and to dimer formation in the case of t-$BuNH_2$ (eq 3).[8,10] The formation of formal M-N multiple bonds by successive amine elimination reactions in eqs 2 and 3 suggests that a combination of transamination and amine elimination reactions involving volatile metal amido complexes could be the basis for the CVD synthesis of stoichiometric metal nitride thin films if ammonia were the co-reactant.[11,12]

$$MNR_2 + HNR'_2 \rightarrow MNR'_2 + HNR_2 \qquad (1)$$

$$M(NMe_2)_4 + RNH_2 \rightarrow [M({=}NR)_2]_x + HNMe_2 \qquad (M = Ti, Zr) \quad (2)$$

$$2M(NMe_2)_4 + 2t\text{-}BuNH_2 \rightarrow [M_2(NMe_2)_2(\mu\text{-}NR)]_2 + 4HNMe_2 \quad (3)$$

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Table I. Compositions and Growth Rates for Films Deposited at 200 °C on Silicon[a]

precursors	growth rates, Å/min	N/M ratios[b]	stoichiometries
$Zr(NEt_2)_4 + NH_3$	200–500	1.35	Zr_3N_4
$Nb(NEt_2)_4 + NH_3$	200	1.35	Nb_3N_4
$V(NMe_2)_4 + NH_3$	120–200	1.10	VN
$Mo(NMe_2)_4 + NH_3$	100–150	1.45	$\approx Mo_2N_3$

[a] Film compositions and thicknesses obtained by RBS. [b] The error in these numbers is estimated to be ±0.05.

Herein we show that the solution-phase chemistry illustrated by eqs 1–3 is applicable to a CVD system by synthesizing thin films of M_3N_4 (M = Zr, Nb) from $M(NR_2)_4$ and ammonia precursors at low temperatures. We also describe the synthesis of films with stoichiometries Mo_2N_3 and VN from $M(NMe_2)_4$ and ammonia. Periodic trends explain the contrasting result obtained for vanadium.

The CVD apparatus consisted of an atmospheric-pressure laminar-flow rectangular glass reactor described previously.[11,13] Purified helium was used as carrier gas for the inorganic complexes as well as a diluent for ammonia.

Thin coatings (500–5000 Å) were successfully deposited when $Zr(NEt_2)_4$,[7] $Nb(NEt_2)_4$,[14] $V(NMe_2)_4$,[15] or $Mo(NMe_2)_4$[16] and ammonia precursors were used at temperatures from 200 to 400 °C. When the ammonia reactant was omitted in the process, no deposition was observed below 350 °C.[3,17] In general, the films are smooth and pinhole-free and show good adhesion (Scotch tape test) to a variety of substrates including glass, silicon, and vitreous carbon. Film thicknesses and compositions were obtained by Rutherford backscattering spectrometry (RBS);[18] stoichiometries and growth rates are listed in Table I. In all cases, oxygen and carbon contaminants in the films are below the detection limits of RBS, indicating that these elements are present at less than 2–3 atom % (see Figure 1).[19] In general, growth rates could be increased by increasing the vapor pressure of the $M(NR_2)_4$ precursors, which was accomplished by heating the bubbler assembly containing the compounds.

According to the RBS analysis, the reactions between $Zr(NEt_2)_4$ or $Nb(NEt_2)_4$ and ammonia gave zirconium and niobium nitrides with stoichiometries Zr_3N_4 and Nb_3N_4 (Figure 1a,b). To our knowledge, this is the first CVD route to Zr_3N_4 coatings, although Zr_3N_4 films have been prepared previously via physical deposition processes[20,21] and the compound in powder form has been synthesized from ZrI_4 and ammonia at 750 °C.[22,23] There are only a few reports of a Nb_3N_4 phase in the literature, and Nb_3N_4 films have never been prepared.[24,25] Zr_3N_4 is a dielectric, metastable phase, with a structure corresponding to a rhombohedral distortion of the cubic ZrN lattice.[20] We have found that Nb_3N_4 is a conductor (≈3000 μΩ cm).

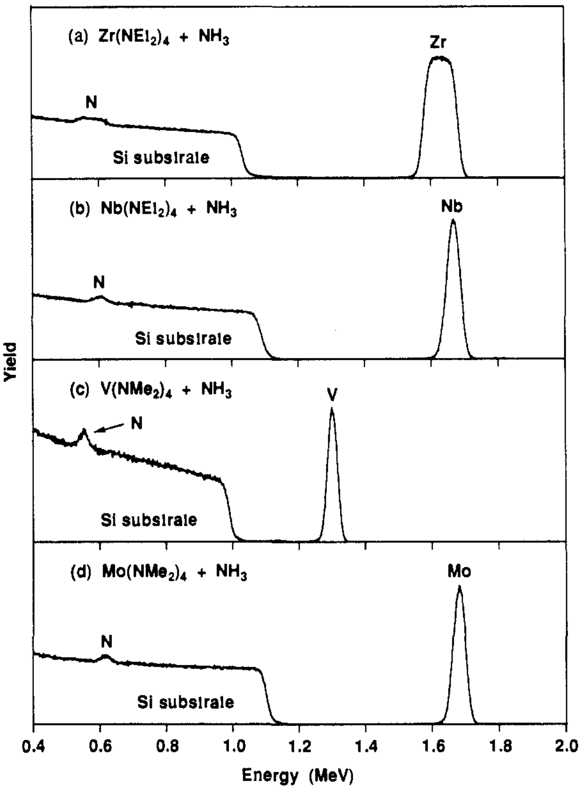

Figure 1. RBS spectra for films deposited on silicon at 200 °C. A He^+ beam was used with an energy of 2.0 MeV, except for part c, obtained at 1.8 MeV.

Transmission electron micrographs for Zr_3N_4 and Nb_3N_4 films deposited at 200 °C indicate that they are composed of small microcrystallites (≈2 nm). The electron diffraction rings for the Zr_3N_4 were sharp, and the pattern was consistent with one reported for a dual ion beam deposited material.[20] The diffraction rings for Nb_3N_4 were broad, indicating that the crystallites are smaller than those of Zr_3N_4.

In contrast to the reactions involving zirconium and niobium, the reaction of $V(NMe_2)_4$ and ammonia at 200 °C led to a gold-colored vanadium nitride that, according to an RBS analysis (Figure 1c), has only a slight excess of nitrogen (V:N, 1:1.1).[26] Thus, vanadium behaves similarly to titanium, for which a TiN stoichiometry was observed for films deposited from $Ti(NMe_2)_4$ and NH_3.[11] The mechanisms of the reductions in the $V^{IV}(NMe_2)_4$ and $Ti^{IV}(NMe_2)_4$ reactions with NH_3 are not known, but the contrasting chemistry we observe between the first- and second-row transition elements can be rationalized on the basis of periodic

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trends; that is, the heavier transition-metal $M(NR_2)_4$ compounds are more difficult to reduce, leading to unusually nitrogen rich stoichiometries.

Interestingly, preliminary studies indicate that the reaction of $Mo(NMe_2)_4$ and ammonia is more complicated and leads to a nitrogen-rich film with a N to Mo ratio of ≈1.45, suggesting a stoichiometry close to Mo_2N_3 (Figure 1d). The films are gold-colored and conductive.

In conclusion, we have prepared very pure, high-quality early-transition-metal nitride thin films by low-temperature CVD from $M(NR_2)_4$ and ammonia precursors. This system provides access to metal nitride coatings with stoichiometries not available by other chemical routes. In general, periodic trends explain the stoichiometrics. Finally, by successfully employing the $M(NR_2)_4/NH_3$ system, we have shown that solution chemistry can be used as a guide for the design of low-temperature CVD reactions.

Acknowledgment. We are grateful to the National Science Foundation (DMR-88-02306) for support of this work. We thank Yuan Z. Lu for his help in obtaining the TEM data. The RBS spectra were acquired by using the Cambridge Accelerator for Materials Sciences housed in the Harvard Materials Research Laboratory, an NSF-funded facility (DMR-86-14003).

Supplementary Material Available: Transmission electron micrographs and electron diffraction patterns for Zr_3N_4 and Nb_3N_4 thin films and a listing of X-ray photoelectron binding energies (5 pages). Ordering information is given on any current masthead page.

Additions and Corrections

Intermediates and Transition States in Chloride Ion/Acyl Chloride Displacement Reactions [*J. Am. Chem. Soc.* **1987**, *109*, 589–590]. CHAU-CHUNG HAN and JOHN I. BRAUMAN*

I (J.I.B.) have become aware that the data in Figure 1e of this paper were changed so as to enhance some of the peaks and diminish others, in order to reflect the observations in a spectrum that was acquired but not saved. Extensive subsequent studies,[1] however, have failed to reproduce the result reported. Consequently, I believe that the conclusion reported in this paper does not follow from these experiments, although it is consistent with other experiments[2] and with quantum calculations.[3,4]

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Photochemical Dehydrogenation of Alkanes Catalyzed by *trans*-Carbonylchlorobis(trimethylphosphine)rhodium: Aspects of Selectivity and Mechanism [*J. Am. Chem. Soc.* **1989**, *111*, 7088–7093]. JOHN A. MAGUIRE, WILLIAM T. BOESE, and ALAN S. GOLDMAN*

Page 7093: In the second paragraph before the Conclusion, the first sentence should read "... k_3 and k_4 are of course expected to be strongly dependent on the alkane substrate." In the same paragraph, the quantum yield for cyclohexane and cyclooctane dehydrogenation in the absence of added CO is misstated as $\Phi_{obs} = 0.97$. The correct value is 0.097, as indicated in Figure 4 and ref 29.

Reaction-Surface Topography for Hydride Transfer: Ab Initio MO Studies of Isoelectronic Systems CH_3O^- + CH_2O and CH_3NH_2 + $CH_2NH_2^+$ [*J. Am. Chem. Soc.* **1990**, *112*, 530–537]. IAN H. WILLIAMS,* ANDREA B. MILLER, and GERALD M. MAGGIORA*

Page 531: Figure 3, showing the important molecular orbitals discussed in the text, is incorrectly labeled. The HOMOs should be orbitals $7a_1$ and $7a_g$ (*not* $6b_1$ and $6b_u$), and the LUMOs should be $7b_1$ and $7b_u$ (*not* $7a_1$ and $7a_g$). The sentence in the last two lines of the left-hand column of page 531 should read as follows: Cartesian force constants computed analytically within CADPAC were employed in normal-mode analyses, using the CAMVIB program,[14] to characterize each critical point.

Uroporphyrinogen III Methylase Catalyzes the Enzymatic Synthesis of Sirohydrochlorins II and IV by a Clockwise Mechanism [*J. Am. Chem. Soc.* **1990**, *112*, 5343–5345]. MARTIN J. WARREN, MARIO D. GONZALEZ, HOWARD J. WILLIAMS, NEAL J. STOLOWICH, and A. IAN SCOTT*

Page 5344: In Scheme II structures **8** and **11** are incorrect and should contain only one methyl group as shown in the revised version given below, which also shows the conversion of **8** and **11** to **9** and **12** by further C-methylation. This graphical error in no way alters the conclusions of the work as discussed in the text.