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Chemical Vapor Deposition of Vanadium, Niobium, and Tantalum Nitride Thin Films

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Vanadium, niobium, and tantalum nitride thin films were synthesized from homoleptic dialkylamido metal complexes and ammonia by atmospheric pressure chemical vapor deposition with high growth rates at low substrate temperatures (200–400 °C). Depositions were successfully carried out on silicon, glass, vitreous carbon, and boron substrates. The films showed good adhesion to the substrates and were chemically resistant. The films were characterized by Rutherford backscattering spectrometry, X-ray photoelectron spectroscopy, ellipsometry, and transmission electron microscopy. Reflectance and transmission spectra for the tantalum nitride films were also recorded. Hydrogen in the films was determined by hydrogen forward recoil scattering spectrometry. The vanadium nitride coatings were slightly nitrogen-rich VN (N/M ratio 1.05–1.15). They were polycrystalline as deposited and displayed metallic properties. The niobium nitride films had N/M ratios of 1.35 ± 0.05 and were golden colored by reflection and conducting. In contrast, the tantalum nitride films had N/M ratios of 1.7 ± 0.1 and were transparent, pale yellow colored in transmission and insulating. The stoichiometry and physical properties suggest that the films consist of Ta_3N_5. The hydrogen content of the films diminished as the deposition temperature increased, but all had significant amounts of hydrogen present.

Preparations of vanadium, niobium, and tantalum nitride thin films by chemical vapor deposition (CVD) generally involve reaction of the volatile metal chlorides with a nitrogen/hydrogen mixture at high temperatures.[2,3] Although the common products of the reactions are the MN phases (eq 1), stoichiometries such as M_2N and Nb_4N_3 have also been obtained depending on the deposition conditions employed:

$$MCl_x + {}^1/_2N_2 + (x/2)H_2 \xrightarrow{>900\ ^\circ C} MN + xHCl \qquad (1)$$
$$M = V, x = 4; \quad M = Nb \text{ or } Ta, x = 5$$

Superconducting fcc NbN thin films have also been prepared by reacting niobium pentachloride, ammonia, and hydrogen at temperatures greater than 900 °C (eq 2),[4]

$$NbCl_5 + NH_3 + H_2 \xrightarrow{>900\ ^\circ C} NbN + 5HCl \qquad (2)$$

$$3TaCl_5 + 5NH_3 \xrightarrow{600\text{–}1000\ ^\circ C} Ta_3N_5 + 15HCl \qquad (3)$$

but a similar reaction between $TaCl_5$ and ammonia (eq 3) produces the tetragonal phase Ta_3N_5.[2] More recently, cubic TaN films have reportedly been synthesized from a $Ta(NEt)(NEt_2)_3/Ta(\eta^2\text{-}EtN{=}CMeH)(NEt_2)_3/H_2$ mixture at 500–650 °C.[5]

We have attempted to find low temperature CVD routes to nitride thin films so that delicate substrates can be coated. Recently, we reported that polycrystalline TiN, Zr_3N_4, and Hf_3N_4 films can be deposited at temperatures as low as 200 °C from the corresponding homoleptic metal dialkylamido complexes ($M(NR_2)_n$) and ammonia.[6] Transammination reactions are undoubtedly key to the formation of nitrides from these precursors. Because transammination is a general reaction of early transition metal dialkylamido complexes, a similar approach employing homoleptic group 5 metal amide complexes and ammonia is also expected to give nitride films at low temperatures. Herein we show that this is in fact the case by reporting the low-temperature preparation of group 5 nitride thin films employing the $M(NR_2)_n/NH_3$ precursor system.[7]

Experimental Section

The compounds $V(NMe_2)_4$, $Nb(NEt_2)_4$, $Nb(NMe_2)_5$, and $Ta(NMe_2)_5$ were synthesized from the metal chlorides and lithium dialkylamides as described by Bradley and co-workers.[8–10] $V(NMe_2)_4$, $Nb(NMe_2)_5$, and $Ta(NMe_2)_5$ are sublimable solids whereas $Nb(NEt_2)_4$ is a viscous liquid. The synthesis of $Nb(NEt_2)_4$ from $LiNEt_2$ and $NbCl_5$ deserves special note. In our hands, the preparation led to a viscous liquid with properties similar to those described for $Nb(NEt_2)_4$. Proton NMR studies of the distilled liquid indicated, however, that although the material did consist mostly of a paramagnetic compound, presumably $Nb(NEt_2)_4$, there were also at least two additional

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diagmagnetic compounds always present as minor components. Because the major component apparently is $Nb(NEt_2)_4$ we will hereafter in this paper refer to the mixture simply as $Nb(NEt_2)_4$. Prior to use, the solid compounds were purified by sublimation.

Depositions were carried out in an atmospheric-pressure laminar-flow rectangular glass reactor heated from below as described in a previous paper.[6] Ultrahigh-purity helium, which had passed through a gettering furnace and a Nanochem gas purifier (Model L-50 t), was used as carrier gas for the metal-containing precursor and as diluent for the ammonia. Electronic grade ammonia, obtained from Matheson, was purified by using a Nanochem resin. The CVD system, loaded with the substrates, was purged for at least 2 h before each deposition. Under these conditions, analysis of the helium outflow showed that it contained less than 0.1 ppm of O_2 and H_2O. During depositions, helium was passed through a stainless steel bubbler containing the metal precursor, and this mixture then flowed through a 2-mm i.d. delivery line to the reaction chamber. Approximately 2 cm before this delivery line entered the reaction chamber, the metal compound/He mixture was combined with ammonia gas diluted in helium ($\approx$10% NH_3). The combined mixtures then flowed over the hot substrate. Outflow from the reaction chamber exited to an oil bubbler. After each deposition the films were allowed to cool slowly in the reactor under a flow of helium.

Silicon and glass substrates were cleaned by immersion in H_2O_2:H_2SO_4 (1:4) for 10 min and then rinsed with deionized water. The vitreous carbon and boron substrates, which were obtained from Atomergic Chemetals Corp., were degreased with $C_2F_3Cl_3$. The glass substrates were either Corning 7059 low-sodium glass or normal soda lime glass. The silicon substrates were ⟨100⟩ test-grade p- or n-doped wafers.

Rutherford backscattering (RBS) analyses (General Ionics Model 4117) were performed by using a 2.0-MeV He^+ beam for films deposited on silicon and vitreous carbon and a 1.8-MeV beam for films deposited on boron. (It should be noted that boron gives a nuclear reaction with He^+ at a nuclear resonance of 2.06 MeV).[11] A beam of 2-MeV He^+ was used for hydrogen forward recoil spectrometry (FRS). For FRS the sample was tilted so that the incident beam arrived at a 15° angle with respect to the sample. In this configuration the detector and incident beam were at an angle of 150°.

X-ray photoelectron spectroscopy (XPS) was carried out by using a Surface Science Lab SSX-100 system equipped with a 3-keV Ar^+ sputter gun. The electron-energy analyzer was calibrated to the Au $4f_{7/2}$ line at 84 eV. XP spectra depth profiles were collected in the unscanned mode by using the monochromatized Al/Kα excitation with a spot size of 600 μm and the electron-energy analyzer set for a pass energy of 150 eV. The experimental detector width was 18.6 eV in this configuration. The base pressure was 10^{-7} Torr with the Ar^+ gun on. Higher resolution XP spectra of the metal and nitrogen signals were collected in the scanned mode (20-eV window) with a spot size of 300 μm and a pass energy of 50 eV after removing the surface oxide layer by sputtering. In this configuration the Ar^+ gun was off during the data acquisition and the base pressure was less than 10^{-8} Torr. The binding energies of insulating samples were referenced to the adventitious surface carbon 1 s line set at 284.6 eV.

Transmission electron micrographs and electron diffraction patterns were obtained on a Philips EM420T scanning transmission electron microscope at 120 kV. Film refractive indexes were measured by using a fixed-wavelength (6228 Å) ellipsometer (model Rudolf Auto-El II).

Results

Film Preparation. The homoleptic metal amido compounds $M(NMe_2)_5$ (M = Nb and Ta) or $M(NR_2)_4$ (M = V, R = Me; M = Nb, R = Et)[8-10] and ammonia (10% diluted in He) were used as precursors for the chemical vapor deposition of thin films at substrate temperatures ranging from 200 to 400 °C. Depositions were successfully carried out on silicon, glass, boron, and vitreous carbon. In the absence of ammonia, no depositions occured below 300 °C and coatings obtained at 350 °C were easily wiped away from the substrates.[12]

Table I. Typical Conditions during Depositions of Group 5 Nitride Films

precursors	bubbler temp, °C	total He flow, L/min	deposition temp, °C	growth rate,[a] Å/min
$V(NMe_2)_4/NH_3$	50	0.8	200	200
$Nb(NEt_2)_4/NH_3$	130	2.1	200	750
$Nb(NMe_2)_5/NH_3$	100	2.1	200	2000
$Ta(NMe_2)_5/NH_3$	105	1.6	200	2000

[a] Film thicknesses determined by RBS.

All of the coatings were smooth (featureless by SEM), nonporous, and pinhole-free and showed good adhesion to the substrates when pulled at with adhesive tape. Films 1000–3000 Å thick deposited on silicon were not damaged (as judged by visual inspection) when placed in concentrated HCl or aqua regia for approximately 10 min. In concentrated HF the films appeared to lift off of the substrates.

The films obtained from $V(NMe_2)_4$ or $Nb(NEt_2)_4$ and ammonia were mirror-like with a reflected gold color. Thick coatings (ca. 2000 Å) obtained from $Nb(NEt_2)_4$ and ammonia were entirely aborbing with a silvery shine. $Nb(NMe_2)_5$ and ammonia produced metallic-like films similar to those obtained when $Nb(NEt_2)_4/NH_3$ was used. $Ta(NMe_2)_5$ and ammonia gave yellowish transparent films which showed the brightly colored interference bands on silicon wafers typical of insulating layers with high refractive indexes.

Typical deposition conditions are presented in Table I. Film growth rates were dependent on the vapor pressure of the metal-containing precursor and could be increased by heating the precursor feed lines and precursor bubbler with heating tape. The temperature of the substrate did not influence the growth rates, but higher substrate temperatures did make the area covered by the deposit smaller. Higher carrier gas flows could be used to counteract the temperature effect. Qualitatively, ammonia reacted faster with the niobium and tantalum complexes than with the vanadium precursor, a periodic trend that was also observed for analogous group 4 precursors.[6]

Composition. Film stoichiometries were determined by using Rutherford backscattering spectrometry (RBS). X-ray photoelectron spectroscopy (XPS) depth profiles were carried out in order to obtain chemical bonding information and composition data complementary to the RBS results. XPS was also useful for the detection of low levels of carbon and oxygen contamination in the coatings because XPS is more sensitive than RBS for light element detection.[13]

According to the RBS data, films made from $V(NMe_2)_4$ and ammonia contained nitrogen and vanadium with N/V ratios of 1.05–1.15 (see Figure 1a) which can be interpreted as slightly nitrogen-rich VN. This suggests that vanadium was reduced from V(IV) to V(III) during the deposition, a result similar to that observed for titanium.[6] The carbon

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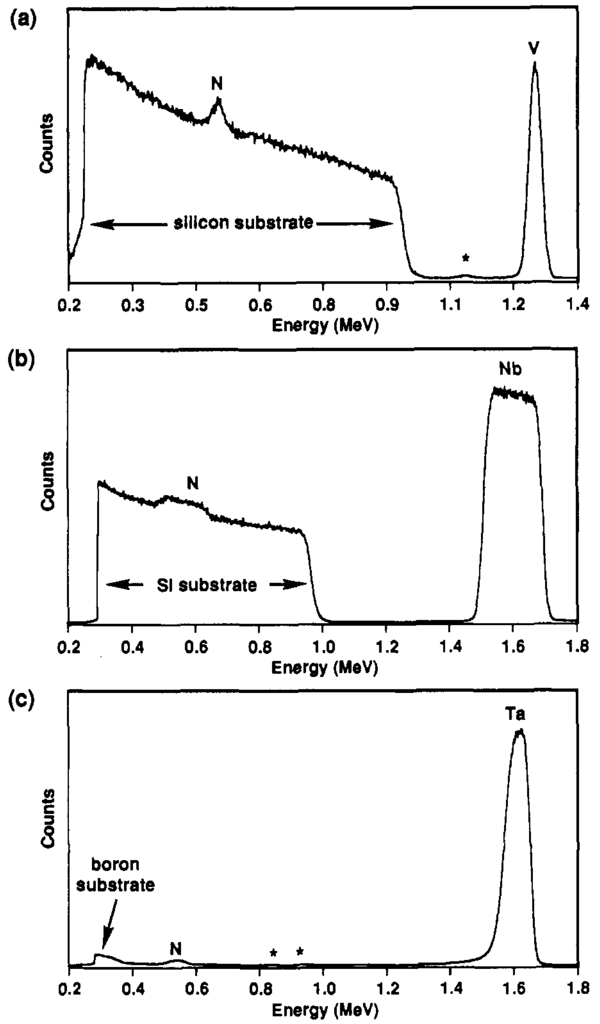

Figure 1. Rutherford backscattering spectra for films deposited at 200 °C from $V(NMe_2)_4$ and ammonia on a silicon substrate (a), from $Nb(NMe_2)_5$ and ammonia on a silicon substrate (b), and from $Ta(NMe_2)_5$ and ammonia on a boron substrate (c). The starred peak in (a) is an unidentified impurity. The starred peaks in (c) were present in spectra obtained for the uncoated boron substrate.

and oxygen levels were below the detection limits of RBS, indicating that the films contained less than 3–4 atom % of these elements. Consistent with the RBS results, XPS depth profiles showed that the bulk of the films contained less than 1 atom % of oxygen and carbon. The amount of carbon in the films did not vary as the deposition temperature was changed. A carbon and oxygen contaminated surface layer approximately 50 Å thick was present on all of the films due to their exposure to air before analysis.

Films obtained from $Nb(NEt_2)_4$ and ammonia had N/NB ratios of 1.35±0.05 as determined by RBS, suggesting a Nb_3N_4 stoichiometry. $Nb(NMe_2)_5$ and ammonia produced coatings with the same stoichiometry (Figure 1b), implying a reduction of Nb(V) to Nb(IV) during the deposition. Films obtained from $Ta(NMe_2)_5$ and ammonia had nitrogen-to-metal ratios of 1.7 ± 0.1, which is consistent with the Ta_3N_5 phase (Figure 1c).

X-ray photoelectron analysis of the niobium and tantalum nitride films indicated that they contained less than 1 atom % of carbon contamination. The amount of carbon contamination did not vary with deposition temperature. The oxygen content in the films was 2–4 atom % for Nb_3N_4 and less than 1–2 atom % for Ta_3N_5.

Table II. Hydrogen-to-Metal Ratios as a Function of Deposition Temperature for Films Deposited on Silicon[a,b]

	deposition temp, °C		
precursors	200 H/M	300 H/M	400 H/M
$V(NMe_2)_4/NH_3$	0.50	0.45	0.20
$Nb(NEt_2)_4/NH_3$	1.15	0.65	
$Nb(NMe_2)_5/NH_3$	1.15	0.70	0.20
$Ta(NMe_2)_5/NH_3$	0.90	0.80 (at 250 °C)	0.35

[a] Determined by FRS. [b] The error in the ratios is estimated to be ±0.05.

The vanadium, niobium, and tantalum to nitrogen ratios in the films did not vary significantly as the temperature of deposition was changed.

Hydrogen forward recoil spectrometry (FRS) was used to measure the hydrogen content in the films. A titanium nitride film for which the hydrogen content had already been determined (33 atom %) by using FRS (gypsum standard) was used as a calibration standard. The hydrogen-to-metal ratios are presented in Table II. The ratios were determined by assuming an identical hydrogen scattering cross section for all samples.

The data indicate that the films had a large hydrogen content and that the hydrogen content decreased as the deposition temperature was increased. Both niobium precursors produced films with hydrogen contents that were identical within experimental error. The niobium and tantalum nitride films were significantly more hydrogen-rich than the vanadium nitride films. A similar trend was observed in a study involving the preparation of group 4 nitrides from metal amido and ammonia precursors in that M_3N_4 (M = Zr, Hf) films were more hydrogenated than TiN.[6]

Morphology and Crystal Structure. All of the films examined were featureless by scanning electron microscopy. Transmission electron microscopy (TEM) revealed that the films had a fine granular structure with poorly defined grains.

Selected area electron diffraction produced sharp ring patterns for the vanadium nitride films (Figure 2) indicating that the films were at least partially polycrystalline as deposited. The diffraction pattern is consistent with that reported in the powder diffraction file for cubic *Fm*3*m* (225) VN.[14] There is no indication of a preferred orientation. The calculated lattice parameter is 4.14(1) Å, which is identical to the value for bulk VN (4.139 16(4) Å).[14] The grain size was about 2 nm. Films deposited at 400 °C had the same microstructure and grain size, but the microcrystallites were better-defined and produced a sharper diffraction pattern.

Ammonia and $Nb(NEt_2)_4$ or $Nb(NMe_2)_5$ yielded films with similar, nearly featureless microstructures. The diffraction patterns for the films showed broad rings, suggesting an amorphous material or a polycrystalline material with very small crystallites. Unlike the VN films, higher deposition temperatures (400 °C) did not produce films that gave sharper diffraction rings. Tantalum nitride films deposited at 200 and 400 °C had nearly featureless microstructures and also produced broad electron diffraction rings. A lattice parameter could not be obtained.

XPS Analysis. Binding energies are referenced to the Au $4f_{7/2}$ transition at 84.0 eV for all samples except

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(14) VN: Index Card Nos. 35-768. *Powder Diffraction File*; McClune, W. F., Ed.; JCPDS International Centre for Diffraction Data: Swarthmore, PA.

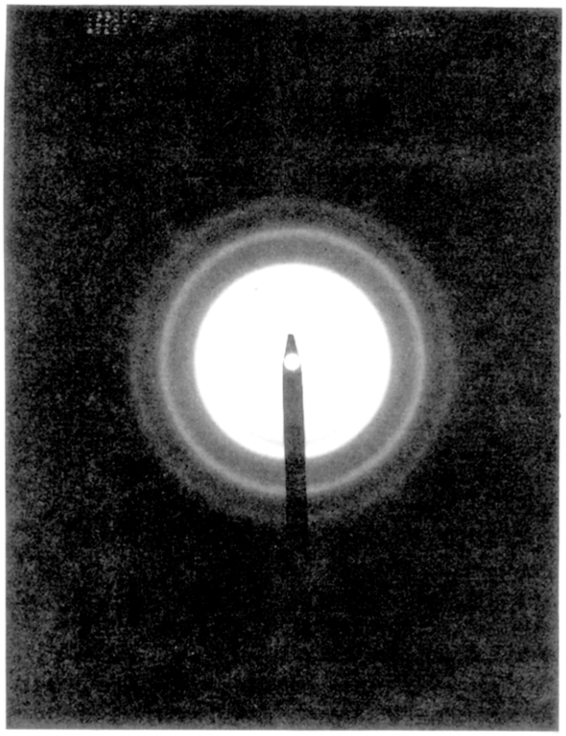

Figure 2. Electron diffraction pattern for a vanadium nitride film deposited at 200 °C on mica.

Table III. X-ray Photoelectron Binding Energies (eV) for Films Deposited at 200 °C on Silicon Substrates[a]

precursors	N 1s binding energy	metal line	binding energy
$V(NMe_2)_4/NH_3$	397.0	V $2p_{3/2}$	513.1
$Nb(NEt_2)_4/NH_3$	397.4	Nb $3d_{5/2}$	204.1
$Nb(NMe_2)_5/NH_3$	397.2	Nb $3d_{5/2}$	203.9
$Ta(NMe_2)_5/NH_3$	396.9	Ta $4f_{7/2}$	24.0

[a] All data was referenced to the Au $4f_{7/2}$ line at 84.0 eV, except for Ta_3N_5, which was referenced to C 1s at 284.6 eV. The error in these values is estimated to be ±0.2 eV.

tantalum nitride which showed charging during collection. For the latter the binding energies are referenced to the adventitious surface carbon 1s line set at 284.6 eV. The nitrogen 1s and metal binding energies for the various films are reported in Table III. The binding energies reported in the table were recorded after sputtering the sample with a 3-keV Ar^+ gun for 2–5 min in order to remove a superficial oxide layer. Binding energies were reproducible to ±0.3 eV. Depth profiling showed that the binding energies were constant throughout the interior of the films. The binding energies did not vary as a function of the temperature of deposition.

For vanadium nitride, the binding energies of the V $2p_{3/2}$ and N 1s electrons were 513.1 and 397.0 eV, respectively (Figure 3). V $2p_{3/2}$ binding energies for VN_x of 514.5 ($x = 0.94$; powders) and 513.8 eV ($x = 1.5$; sputtered amorphous films) have been reported.[15,16] For the same materials, the N 1s binding energies were reported to be 397.6 and ≈397 eV, respectively.

$Nb(NEt_2)_4$ or $Nb(NMe_2)_5$ and ammonia yielded films with nearly identical binding energies for the Nb $3d_{5/2}$ and N 1s electrons (204 and 397.3 eV, respectively). These values are consistent with those reported for amorphous $NbN_{0.9}$ films deposited by sputtering,[16] but the Nb $3d_{5/2}$ binding energy is significantly lower than the value reported for NbN powders (207 eV).[17] The binding energy of the Ta $4f_{7/2}$ electron in Ta_3N_5 was intermediate between tantalum metal and tantalum oxide as is typical for early transition metal nitrides.[18]

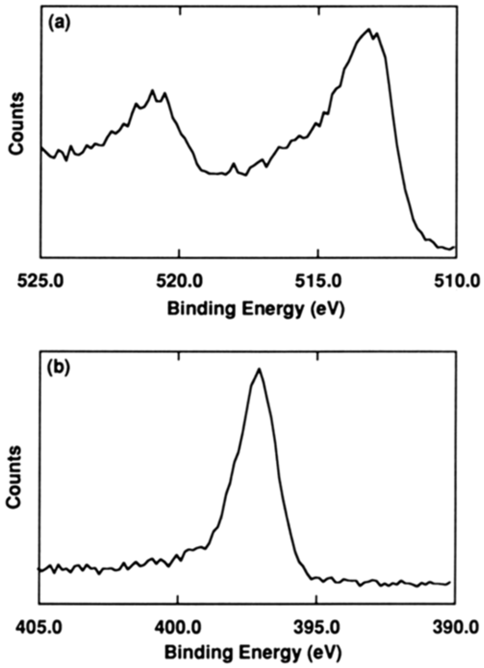

Figure 3. X-ray photoelectron spectra for a VN film deposited at 200 °C on silicon in the V 2p (a) and N 1s (b) regions.

Table IV. Selected Physical Properties for Films Deposited at 200 °C[a]

coating	resistivity,[a] μΩ cm	optical band gap,[a] eV	refractive index[c]
VN	ca. 10^3		1.5–1.7
Nb_3N_4	10^3–10^4		2.5–2.9
Ta_3N_5	$>10^6$	2.7[b]	3.0–3.1

[a] Films deposited on 7059 glass. [b] Error estimated to be ±0.2 eV. [c] Films deposited on silicon.

Electrical and Optical Properties. Sheet resistances were measured for coatings deposited on 7059 glass by using the four-point probe method. Film resistivity was calculated by multiplying the sheet resistance by the film thickness (obtained by RBS). Film refractive indexes were measured by using a fixed-wavelength (6228 Å) ellipsometer.

The vanadium and niobium nitride films were conductors (Table IV). The resistivity of the VN films was approximately 10^3 μΩ cm. This value is higher than the resistivities reported for bulk VN (85 μΩ cm)[19] and $VN_{1.5}$ thin films prepared by sputtering (10^2–10^4 μΩ cm).[16] A similar discrepancy was noted for TiN in our previous work.[6] The higher resistivities we observe may be a consequence of differences in nitrogen and/or hydrogen content or the small grain size of our material. The

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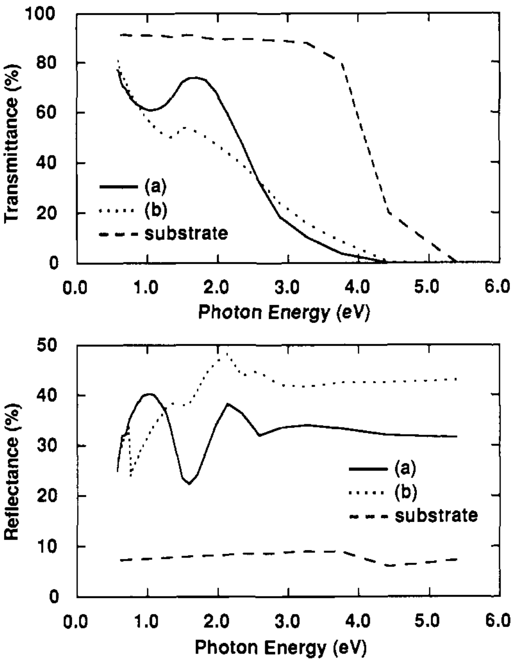

Figure 4. Top: transmission spectra for Ta_3N_5 films (ca. 3000 Å thick) deposited at 200 °C (a) and 400 °C (b) on 7059 glass. Bottom: reflectance spectra for Ta_3N_5 films (ca. 3000 Å thick) deposited at 200 °C (a) and 400 °C (b) on 7059 glass.

niobium nitride films had resistivities of 10^3–10^4 $\mu\Omega$ cm. The resistivities were not dependent on the temperature of deposition. The tantalum nitride films were insulating (i.e., they had sheet resistances higher than 100 kΩ/square), consistent with previous reports.[2,20]

Refractive indexes are tabulated in Table IV. Within experimental error, the indexes were not dependent on film deposition temperatures.

Transmission and reflectance spectra for Ta_3N_5 films deposited at 200 and 400 °C are presented in Figure 4. An optical band gap of 2.7 eV for Ta_3N_5 was obtained from the optical transmission measurements by plotting $(\alpha h\nu)^{1/2}$ vs $h\nu$, where α is the absorption coefficient ($\alpha = -\log T/T_0$; T = sample optical transmission; T_0 = substrate optical transmission) and $h\nu$ is the photon energy, and then taking as the bandgap the intercept of the abscissa from an extrapolation of the linear portion of the curve to $\alpha = 0$.[21] The plot (Figure 5) shows a linear dependence of $(\alpha h\nu)^{1/2}$ on $h\nu$ for $h\nu$ greater than the bandgap. This type of behavior is observed for materials with an indirect band gap and with bands that are free-electron like.[21] The bandgap value reported here should be interpreted with caution because α was not corrected for interference effects due to reflection.

Discussion

The composition and physical data for our vanadium nitride films are consistent with a slightly nitrogen-rich VN phase in which there is little or no carbon or oxygen contamination. Although the material apparently has an excess of nitrogen, electron diffraction does not indicate a lattice expansion. This suggests there are metal site vacancies in the lattice. Another possibility is that the excess nitrogen is present in the form of NH, NH_2, and/or N–N groups, which result from the incomplete decomposition of putative intermediates. This latter possibility would also account for the hydrogen in the films and suggests that the material is composed of VN crystallites imbedded in a amorphous material in which V–NH, V–NH_2, and similar groups are incorporated.

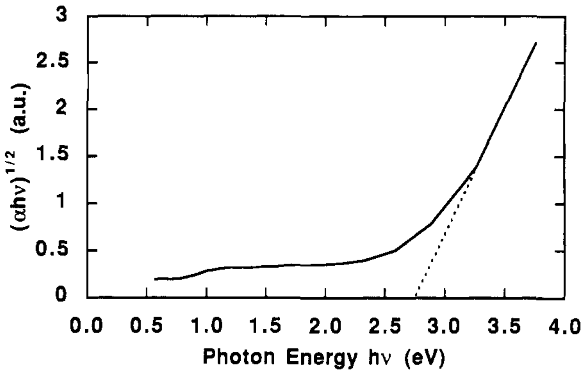

Figure 5. $(\alpha h\nu)^{1/2}$ vs $h\nu$ (solid line) plot for a tantalum nitride film deposited on 7059 glass at 200 °C. The dotted line represents the best fit for the linear portion of the curve.

$Ta(NMe_2)_5$ and ammonia deposit amorphous tantalum nitride films with a N/Ta ratio of ca. 1.7. The films are transparent (yellow colored by transmitted light) and insulating with a bandgap of around 2.7 eV. The stoichiometry and physical properties are consistent with the known Ta_3N_5 tetragonal phase which is reported to be a high resistivity material that forms yellow-colored transparent films.[2,20]

Films obtained from ammonia and $Nb(NEt_2)_4$ or $Nb(NMe_2)_5$ display nearly identical properties and stoichiometries; for example, they both have a metallic appearance, are electrical conductors and have nitrogen-to-metal ratios of around 1.35. The latter suggests an unusual Nb_3N_4 stoichiometry. Although there has been extensive work on niobium nitrides because of interest in the low temperature superconducting δ-NbN phase,[3,22] a Nb_3N_4 stoichiometry has been mentioned only sporadically.[23] A theoretical discussion of Nb_3N_4 has also appeared.[24]

Because our niobium nitride films are amorphous it is difficult to assess whether they are composed of an actual Nb_3N_4 phase or are perhaps a mixture of the several known niobium nitride phases.[3,22] An additional complication is the hydrogen in the films, which, like the vanadium and tantalum nitride films, could be present in the form of NH, NH_2, and/or N–N groups.

Solution Chemistry Analogies. The contrasting behavior of Nb(V) $Nb(NMe_2)_5$ and Ta(V) $Ta(NMe_2)_5$ in these CVD reactions, on the one hand apparently to produce Nb(IV) Nb_3N_4 and on the other to yield Ta(V) Ta_3N_5, parallels the solution chemistry of the amido compounds in that Ta(V) is a stable oxidation state (more stable than Ta(IV)) whereas Nb(V) tends to be reduced under mild conditions.[9,10] This is well-illustrated by Bradley's studies on the thermal decomposition (in vacuo) of $M(NR_2)_5$ complexes (M = Nb, Ta). For example, the niobium complex Nb(NMe-*n*-Bu)$_5$ decomposes to give almost exclusively Nb(IV) Nb(NMe-*n*-Bu)$_4$ and a small

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amount of Nb(V) [Nb(N-*n*-Bu)(NMe-*n*-Bu)$_3$] (eq 5), whereas in the case of tantalum, the trend is reversed and [Ta(N-*n*-Bu)(NMe-*n*-Bu)$_3$] is the major decomposition product from the thermal decomposition of Ta(NMe-*n*-Bu)$_5$ (eq 6). Bradley proposed that dialkylamido radicals are involved in these reactions.

$$\mathrm{Nb(NMe\text{-}}n\mathrm{\text{-}Bu)_5} \xrightarrow{150\ ^\circ\mathrm{C}} \underset{\text{major}}{\mathrm{Nb(NMe\text{-}}n\mathrm{\text{-}Bu)_4}} + \underset{\text{minor}}{[\mathrm{Nb(N\text{-}}n\mathrm{\text{-}Bu)(NMe\text{-}}n\mathrm{\text{-}Bu)_3}]} \quad (5)$$

$$\mathrm{Ta(NMe\text{-}}n\mathrm{\text{-}Bu)_5} \xrightarrow{160\text{–}180\ ^\circ\mathrm{C}} \underset{\text{major}}{[\mathrm{Ta(N\text{-}}n\mathrm{\text{-}Bu)(NMe\text{-}}n\mathrm{\text{-}Bu)_3}]} + \underset{\text{minor}}{\mathrm{Ta(NMe\text{-}}n\mathrm{\text{-}Bu)_4}} \quad (6)$$

By analogy to the solution studies, the reductions that occur in the synthesis of our films may also be a consequence of M–NR$_2$ homolytic bond cleavage, which would produce an amido radical NR$_2$ (R = H or Me) and the required V(III) or Nb(IV) center.[9]

Comparison to Analogous Group 4 Nitride Preparations. There are three results from our study of the group 5 metal nitrides that parallel those found in our study of the group 4 nitrides:[6]

(1) The film thickness profiles depend on gas flow rates. This suggests that the deposition process is controlled by gas-phase reactions. The absence of substrate selectivity and the formation of powder by homogeneous nucleation in the gas phase during the depositions also suggest that gas-phase reactions dominate the process.

(2) The niobium and tantalum amido precursors react qualitatively faster with ammonia than the vanadium complex as judged by where the film deposited along the flow direction. A similar partitioning of reactivity between first row and the heavier congeners was also observed for the group 4 elements.

(3) In general the films are free of carbon contamination. This suggests that all the dialkylamido ligands are eliminated by gas-phase reactions prior to hitting the substrate surface.

These observations and the fact that early transition metal dialkylamido complexes display a common solution chemistry suggest that the depositions of the group 4 and 5 metal nitrides proceed via the same mechanism. On the basis of known solution reactivity, we have proposed the mechanism involves ammonia transammination reactions, which generate M–NH$_2$ intermediates in situ, and α-hydrogen activation reactions.[6] A recent gas-phase study of the mechanism of TiN deposition from Ti(NMe$_2$)$_4$/NH$_3$ support these notions.[25]

Conclusion

Homoleptic dialkylamido complexes and ammonia precursors produce group 5 metal nitride thin films with low carbon contamination at temperatures as low as 200 °C. V(NMe$_2$)$_4$ and ammonia give polycrystalline VN films containing less than 1 atom % of C and O contamination. Similarly, hydrogenated films with a Nb$_3$N$_4$ stoichiometry are produced from ammonia and Nb(NMe$_2$)$_5$ or Nb(NEt$_2$)$_4$, and hydrogenated Ta$_3$N$_5$ films result from ammonia and Ta(NMe$_2$)$_5$. Our results suggest that in the CVD processes the redox behavior and reactivity with ammonia of the metal precursors parallel solution chemistry trends.

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