

ties are electronic in nature as evidenced by charge polarization experiments. Interestingly, elevated conductivities were found at quite low nickel compositions with PVA/Ni(113)TTO, PVA/Ni(57)TTO, PVA/Ni(28)TTO, PVA/Ni(11)TTO, and PVA/Ni(6)TTO all exhibiting electrical conductivities of 10^{-3} – 10^{-4} Ω^{-1} cm $^{-1}$. This might be attributable to the fact that this diffusion-controlled reaction necessarily begins at the film surface. Migration of Ni $^{2+}$ from the film bulk toward the surface in the swollen membrane may lead to a higher concentration of poly(nickel tetrathiooxalate) forming at the film surface. In fact, scanning electron microscopy shows the surface morphology of the conducting PVA/NiTTO composites to be significantly rougher than films prior to reaction with TEATTO. XPS studies show the initially octahedrally coordinated nickel ions in the surface of the PVA/Ni $^{2+}$ to change to square-planar coordination upon formation of PVA/NiTTO.¹⁵ These results are backed up by FT-IR and elemental analysis. The C–O stretch and O–H bend/CH $_2$ wag absorbances in PVA/Ni(6)TTO do not shift relative to PVA/Ni(6). Elemental analyses show extremely high Ni/S ratios of 2.4/4 for PVA/Ni(57)TTO and 6/4 for PVA/Ni(11)TTO where the expected ratio for complete reaction is expected² to be $\leq 1/4$. Thus, though a significant amount of reaction occurs in the outer layer of the membrane leading to large changes in electrical and optical properties, the TTO ligand has not penetrated into the major portion of the film interior. It should be noted that this process does not lead to a film of poly(nickel tetrathiooxalate) on top of PVA as these films can be polished with no loss of conductivity.

All of the films prepared were mechanically durable, flexible, and quite strong. No evident loss of mechanical integrity was observed when compared to PVA films prepared using the same techniques. There is little change in thermal stability as measured by thermogravimetric analysis in N $_2$. PVA begins thermally degrading at ca. 250 °C, PVA/Ni(6) at 260 °C, PVA/Ni(11)TTO at 260 °C, and PVA/Ni(6)TTO at 225 °C.

Finally, these films can be significantly stretch oriented. For example, PVA/Ni(6)TTO, having the highest NiTTO content, could be stretched at 50 °C to 700% of its original length. Orientation of the film led to a significant decrease in conductivity from 10^{-3} to $\leq 10^{-9}$ Ω^{-1} cm $^{-1}$, both parallel and perpendicular to the stretch direction. In that the poly(nickel tetrathiooxalates) are known to be oligomeric,^{1–3} separation of these stacked oligomers during orientation most likely leads to the observed decrease in conductivity. An interesting phenomenon is observed in these stretch-oriented materials in that they behave as optical polarizers. A homogeneous and transparent sample of PVA/Ni(113)TTO [σ (unoriented) = 10^{-3} Ω^{-1} cm $^{-1}$] was stretched to ca. twice its original length. When held parallel with a polarizing film the film remained transparent, but when crossed with the polarizing film the film became opaque. It is expected that, upon stretching, the rodlike molecules of poly(nickel tetrathiooxalate) are oriented by the poly(vinyl alcohol) chains leading to this optical anisotropy.

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Silicon Dimethylamido Complexes and Ammonia as Precursors for the Atmospheric Pressure Chemical Vapor Deposition of Silicon Nitride Thin Films

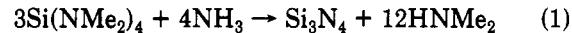
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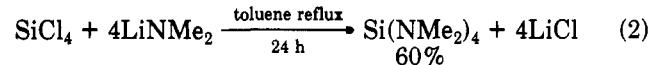
Silicon nitride thin films are widely used in the microelectronics industry as diffusion barriers, passivation layers, and the active charge storage elements in metal-nitride–oxide semiconductor nonvolatile memory products.¹ Silicon nitride films are normally prepared either by atmospheric pressure chemical vapor deposition (APCVD) using silane and ammonia² as precursors or by low-pressure chemical vapor deposition (LPCVD) using dichlorosilane and ammonia.³ The temperature range for both processes is 700–900 °C. Growth rates at temperatures below 800 °C range from 50 (LPCVD)³ to 150 Å/min (APCVD)² but are up to 1000 Å/min for the APCVD process at 900 °C.

We recently reported the APCVD synthesis of high-quality TiN thin films using the dual-precursor system tetrakis(dimethylamido)titanium, Ti(NMe₂)₄, and ammonia.⁴ Because in many aspects the solution chemistries of Ti(NMe₂)₄ and Si(NMe₂)₄ are similar,⁵ we reasoned that an analogous precursor mixture composed of Si(NMe₂)₄ or a more volatile hydride-containing derivative and ammonia would provide a clean route to silicon nitride films (e.g., eq 1). Herein, we report the successful APCVD



preparation of high-quality silicon nitride coatings using silicon dimethylamido complexes, Si(NMe₂)_nH_{4-n} ($n = 2$ –4), and ammonia as precursors. The films have been deposited at 600–750 °C with growth rates from 50 to 550 Å/min.

The precursor tetrakis(dimethylamido)silane, Si(NMe₂)₄, was synthesized by the reaction of SiCl₄ with an excess of LiNMe₂ in refluxing toluene (eq 2).^{6,7} The use of toluene



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Table I. Growth Rates, Film Compositions, and Refractive Indexes for Films Deposited at 750 °C on Silicon^a

precursor(s)	growth rates, Å/min	at. % Si	at. % N	Si/N	at. % C	at. % O	n_f^b
Si(NMe ₂) ₄ + NH ₃	430	45	55	0.81	c	c	1.86
Si(NMe ₂) ₃ H + NH ₃	460	43	57	0.76	c	c	1.86
Si(NMe ₂) ₂ H ₂ + NH ₃	550	42	58	0.74	c	c	1.84
Si(NMe ₂) ₄	200	31	24	1.3	30	15	1.82
Si(NMe ₂) ₃ H	200	33	28	1.2	22	17	1.78
Si(NMe ₂) ₂ H ₂	250	28	24	1.2	31	17	1.79

^aAll at. % compositions were determined by RBS. ^bRefractive index. ^c<2-3%, below detection limit of RBS.

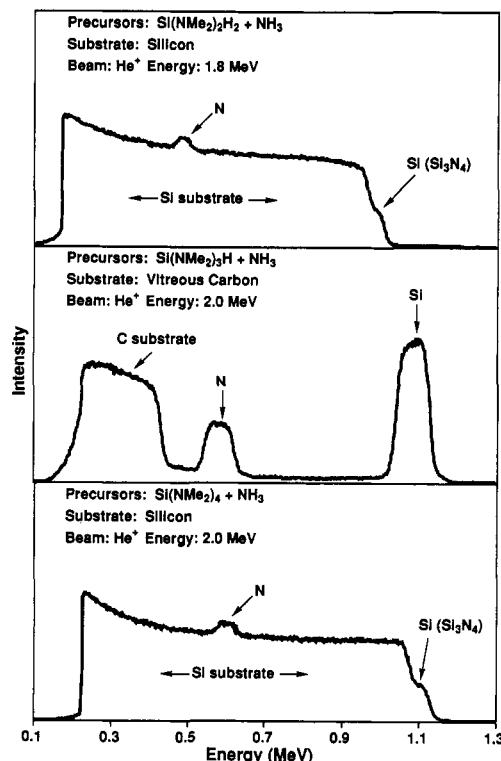


Figure 1. RBS spectra for films deposited at 750 °C using Si(NMe₂)₂H₂ and NH₃ (top), Si(NMe₂)₃H and NH₃ (middle), and Si(NMe₂)₄ and NH₃ (bottom) as precursors.

in eq 2 is important; lower boiling solvents, such as benzene or tetrahydrofuran, produced mixtures of Si(NMe₂)₃Cl and Si(NMe₂)₄, which were difficult to separate by distillation. Tris(dimethylamido)silane, Si(NMe₂)₃H, was obtained commercially (Petrarch Systems) and used without further purification, and bis(dimethylamido)silane, Si(NMe₂)₂H₂, was synthesized by the literature method.⁸

Depositions were carried out in an atmospheric-pressure laminar-flow rectangular quartz reactor.^{4,9} Purified helium was used as a carrier gas for the silicon-containing precursors as well as a diluent for ammonia. The precursors Si(NMe₂)₄ (bp 196 °C) and Si(NMe₂)₃H (bp 142 °C) were maintained at room temperature in the bubbler assembly, whereas the more volatile Si(NMe₂)₂H₂ (bp 93 °C) was cooled to 0 °C (high concentrations of Si(NMe₂)₂H₂ in the carrier gas led to undesirable powder formation).

(6) To a slurry of LiNMe₂ (2.5 g, 49.0 mmol) in toluene (25 mL) at 0 °C was added dropwise SiCl₄ (1.25 g, 7.4 mmol) in toluene (10 mL). After warming to room temperature, the mixture was refluxed for 24 h and then filtered (Celite). The flask was washed with pentane (2 × 10 mL), and the washings were filtered. The filtrates were combined, and the solvent was then removed in vacuo, leaving a yellow liquid. This liquid was vacuum distilled to give colorless Si(NMe₂)₄ (0.9 g, 4.4 mmol, 60%); ¹H NMR (C₆D₆) δ 2.50 (s). For an alternative method, see ref 7.

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Depositions were successfully carried out on silicon, vitreous carbon, boron, and quartz substrates at temperatures from 600 to 750 °C. The films were characterized by ellipsometry (Rudolph Research Auto EL II), FT-IR (Bio-Rad Model FTS-40), X-ray photoelectron spectroscopy (XPS; Surface Science Lab SSX-100) and Rutherford backscattering spectrometry (RBS; General Ionics Model 4117). The films were featureless by scanning electron microscopy and were amorphous by X-ray diffraction.

Film thicknesses, which were determined by ellipsometry and RBS, were up to 3000 Å, and growth rates ranged from 50 to 550 Å/min (Table I). The highest growth rates were obtained with Si(NMe₂)₂H₂ and ammonia at 750 °C. The Si(NMe₂)₂H₂/NH₃ system also produced films at 600 °C. All of the films showed good adhesion (Scotch tape test). They did not dissolve in concentrated HCl, H₃PO₄, or aqua regia but readily dissolved in 48% hydrofluoric acid.

Transmittance FT-IR spectra for the films obtained at 750 °C showed a strong band at 850 cm⁻¹, characteristic of the Si-N vibration in Si₃N₄.¹⁰ Weak bands at 2205 and 3340 cm⁻¹ were also observed, which are characteristic of Si-H and N-H stretches, respectively. On the basis of the intensities of the N-H and Si-H bands, which are comparable to the intensities of the same stretches in other Si₃N₄ films obtained by CVD, we estimate that the amount of hydrogen in the films is 8–10 at. %.¹¹

Rutherford backscattering spectra for films obtained by using the Si(NMe₂)_nH_{4-n} compounds and ammonia are shown in Figure 1, and film compositions based on the spectra are presented in Table I. All of the films have Si/N ratios of 0.72–0.81, close to the value of 0.75 expected for stoichiometric Si₃N₄. Oxygen and carbon peaks were not observed in the spectra, indicating that the oxygen and carbon contents are less than 2–3%, the detection limit of RBS. Although the compositions in Table I do not take into account hydrogen, which cannot be detected by RBS, these results show that the film compositions are close to stoichiometric Si₃N₄.

An XPS depth profile showed that the films were of uniform composition, consistent with the RBS analysis.¹² We could not reliably establish the Si/N ratio by XPS for comparison with the RBS results because of preferential sputtering of nitrogen.¹³ We did employ XPS to estimate

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(12) X-ray photoelectron spectra (Surface Science Lab SSX-100) were collected in the unscanned mode by using the monochromatized Al K α excitation line with a spot size of 600 μ m and the electron energy analyzer set for a pass energy of 150 eV. The spectrometer was equipped with a 3-keV Ar⁺ sputter gun and an electron flood gun, set at 2 eV during data collection. The base pressure was 10⁻⁷ torr with the Ar⁺ gun on.

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the carbon and oxygen content of the films, however, and on this basis, the carbon content is estimated to be less than 0.5 at.-% and the oxygen 1.5-3 at.-%. The source of the oxygen contamination is probably oxygen diffusion from the quartz reactor, whereas the carbon must come from the amide ligands in the silicon-containing precursors. The binding energies of the Si 2p and N 1s peaks were 101.8 and 397.5 eV, respectively, which are in accord with literature values for stoichiometric Si_3N_4 .¹⁴ The absolute binding energies were referenced to the C 1s peak at 284.6 eV.

The refractive indexes (n_f) of the films were also determined (Table I). They varied from 1.84 to 1.89. Refractive indexes for silicon nitride films are normally 1.8-2.0, with values below 1.9 indicating the presence of small amounts of oxygen contamination.^{14,15}

In control experiments, film depositions using the $\text{Si}(\text{NMe}_2)_n\text{H}_{4-n}$ compounds without ammonia were carried out at 750 °C.¹⁶ For all three precursors, films were obtained but at slower growth rates and with large amounts of carbon (22-30%) and oxygen (15-17%) contamination (Table I). The high oxygen content in these films is probably due to the extended time the precursors and films were exposed to oxygen-containing impurities in the carrier gas at 750 °C, which is a reflection of the slow growth rates.

In conclusion, we have shown $\text{Si}(\text{NMe}_2)_n\text{H}_{4-n}$ ($n = 2-4$) compounds and ammonia are promising precursors to silicon nitride coatings at 750 °C. Our preparation provides higher growth rates than the existing APCVD and LPCVD routes at comparable temperatures. Also, the $\text{Si}(\text{NMe}_2)_n\text{H}_{4-n}$ precursors appear to be safer to handle than SiH_4 and SiH_2Cl_2 , which is another advantage over existing systems.¹⁷

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Synthesis of the New Highest T_c Ambient-Pressure Organic Superconductor, κ -(BEDT-TTF)₂Cu[N(CN)₂]Br, by Five Different Routes

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The synthesis of new superconducting compounds is a topic of intense interest today. Very recently the superconducting transition temperature (T_c) of a new BEDT-TTF-based superconductor [BEDT-TTF or "ET" is bis-

(ethylenedithio)tetrathiafulvalene, $\text{C}_{10}\text{H}_8\text{S}_8$], κ -(ET)₂Cu[N(CN)₂]Br, was raised to a new high for these systems (resistive onset $T_c = 12.5$ K, midpoint 11.2 K).^{1,2} The previous highest T_c was observed in κ -(ET)₂Cu(NCS)₂ (resistive midpoint 10.4 K).³ Since the introduction of polymeric anions into the synthesis of ET-based materials^{4,5} and the development of useful structure-property correlations for β -phase ET superconductors,⁶ numerous new superconducting materials have been prepared, including recently, e.g., α -(ET)₂(NH₄)Hg(SCN)₄ ($T_c = 1.15$ K)⁷ and β_m -(BEDT-TTF)₃Cu₂(NCS)₃ ($T_c = 1.06$ K),⁸ but κ -(ET)₂Cu(NCS)₂ and κ -(ET)₂Cu[N(CN)₂]Br represent the only organic superconductors to break the 10 K barrier. In contrast to the synthesis of κ -(ET)₂Cu(NCS)₂, which is usually carried out by use of electrocrystallization of ET in the presence of CuSCN and SCN⁻ anion, the synthesis of κ -(ET)₂Cu[N(CN)₂]Br can be achieved by use of different starting materials, and thus provides an opportunity to probe the complex solution chemistry involved during electrocrystallization. In this communication we report five synthetic routes, and the related solution chemistry, for the electrocrystallization of κ -(ET)₂Cu[N(CN)₂]Br. One of these syntheses, which is the easiest to use (entry 3, Table I), utilizes all commercially available materials.

The new organic superconductor κ -(ET)₂Cu[N(CN)₂]Br belongs to the orthorhombic space group $Pnma$, $Z = 4$, $a = 12.942$ (3) Å, $b = 30.016$ (4) Å, $c = 8.539$ (3) Å, $V = 3317$ (1) Å³ (298 K).¹ The donor molecular packing motif is typical of κ -phase salts. The polymeric anion Cu(N(CN)₂)Br⁻, consists of tricoordinated Cu(I) with two bridging (NC)₂N(CN)⁻ ligands forming a zigzag chain and a terminal bromide to complete the coordination around the Cu atom.¹ On the basis of the anion stoichiometry, the polymeric chain can be synthesized, in principle, from CuBr with N(CN)₂⁻ or from CuN(CN)₂ with Br⁻. We have explored these possibilities, and the results are summarized in Scheme I.

The CuBr/N(CN)₂⁻ system leads to at least three different anionic species depending on the reaction conditions. We have found that the reaction of CuBr with 2 equiv of dicyanamide anions (as the PPh₄⁺ salt)⁹ in re-

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