

# Low-Temperature Atmospheric Pressure Chemical Vapor Deposition of Polycrystalline Tin Nitride Thin Films

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The atmospheric pressure chemical vapor deposition of tin nitride thin films from tetrakis(dimethylamido)tin(IV) and ammonia precursors is reported. The films were characterized by transmission electron microscopy, X-ray photoelectron spectroscopy, Rutherford backscattering spectrometry, and forward recoil spectrometry. The films were deposited on soda lime, borosilicate, and quartz glass and silicon substrates at substrate temperatures of 200–400 °C with growth rates up to 1000 Å/min. The films were smooth, adherent, and chemically inert. Rutherford backscattering analysis showed that the N/Sn ratio was 1.45–1.50. The ratio was independent of deposition temperature. The hydrogen concentration, measured by forward recoil spectrometry, ranged from 18 atom % at 200 °C to 15 atom % at 400 °C. Transmission electron microscopy revealed that the films deposited at 200 °C were amorphous whereas films deposited at 300 and 400 °C were polycrystalline. The films were conductive with resistivities in the range of  $(2-9) \times 10^{-3} \Omega \text{ cm}$ . A bandgap of 1.94–2.25 eV was estimated from transmission spectra.

## Introduction

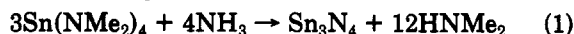
Thin films of the group 14 nitrides are useful in a variety of technological applications because of their physical and chemical properties. For example, silicon nitride is a chemically inert insulator that is used in microelectronic devices as a diffusion barrier, dielectric layer, and passivation layer.<sup>1</sup> Germanium nitride has properties similar to silicon nitride and has been tested as a dielectric layer and a diffusion mask in germanium-based devices.<sup>2</sup>

Interestingly, tin nitride has not been as extensively studied as its lighter congeners. For example, there appear to be only two early reports in the literature concerning the synthesis of bulk tin nitride (from  $\text{SnCl}_4$  and ammonia by dc discharge),<sup>3,4</sup> and it was not until 1975 that Remy and Hantzpergue first reported the preparation of tin nitride thin films.<sup>5,6</sup> The films, which were prepared by reactive cathodic sputtering, were amorphous, and the composition was determined by chemical analysis to be  $\text{Sn}_3\text{N}_4$  with an excess of nitrogen. In contrast to insulating silicon and germanium nitride, the tin nitride films were conductive. The dependence of the electrical conductivity on temperature suggested semiconductor behavior, and a bandgap of 3.55 eV was estimated from transmission spectra. The conductivity was attributed to free tin present in the material. Since the reports by Remy and Hantzpergue, the synthesis of conductive tin nitride films from  $\text{SnCl}_4$  and ammonia has been published in a patent.<sup>7</sup> They are apparently no reports in the literature concerning the preparation of crystalline tin nitride in bulk or thin film form.

We recently reported that homoleptic main-group dialkylamido complexes and ammonia were excellent precursors for the atmospheric pressure chemical vapor deposition (APCVD) of nitride thin films; for example, films of  $\text{AlN}^8$  and  $\text{GaN}^9$  were obtained from the  $\text{Al}_2(\text{NMe}_2)_6/\text{NH}_3$  and  $\text{Ga}_2(\text{NMe}_2)_6/\text{NH}_3$  precursor mixtures, respectively, at substrate temperatures as low as 200 °C and with growth rates of up to 1000 Å/min. Similarly, films of amorphous  $\text{Si}_3\text{N}_4$  were obtained at 600–750 °C from ammonia and  $\text{Si}(\text{NMe}_2)_{4-x}\text{H}_x$  ( $x = 0-2$ ) precursors.<sup>10</sup> The growth rates for  $\text{Si}_3\text{N}_4$  were as high as 500 Å/min, which were significantly higher than the more common APCVD

routes at comparable temperatures. The  $\text{M}(\text{NR}_2)_n/\text{NH}_3$  system was also used for the low-temperature (200 °C) synthesis of early-transition-metal nitride thin films such as  $\text{TiN}$  and  $\text{Zr}_3\text{N}_4$ .<sup>11-13</sup>

The successful applications of the  $\text{M}(\text{NR}_2)_n/\text{NH}_3$  precursor system prompted us to extend the approach to the synthesis of tin nitride thin films (eq 1). Herein we describe the synthesis of conductive polycrystalline tin nitride thin films from tetrakis(dimethylamido)tin(IV),  $\text{Sn}(\text{NMe}_2)_4$ , and  $\text{NH}_3$  precursors.



Prior to this study, tetrakis(dimethylamido)tin was examined by Sugiyama and co-workers as a possible single-source precursor for the chemical vapor deposition of tin nitride thin films.<sup>14</sup> At temperatures above 300 °C,  $\text{Sn}(\text{NMe}_2)_4$  deposited only grayish coatings which were identified as tin metal by X-ray diffraction.<sup>14</sup>

## Experimental Section

The compound  $\text{Sn}(\text{NMe}_2)_4$  was prepared by reaction of  $\text{SnCl}_4$  with  $\text{LiNMe}_2$ .<sup>15</sup> It is a pale yellow, air- and moisture-sensitive liquid with a reported boiling point of 51 °C at 0.15 mmHg.<sup>15</sup>

(1) See: *Proceedings of the Symposium on Silicon Nitride Thin Insulating Films*; Kapoor, V. J., Stein, H. J., Eds.; Electrochemical Society Proceedings, 1983; Vol. 83-8, and references therein.

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(15) Jones, K.; Lappert, M. F. *J. Chem. Soc.* 1965, 1944.

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Depositions were carried out in an atmospheric pressure laminar flow rectangular quartz reactor heated from below, which was described previously.<sup>13,16</sup> Ultrahigh-purity helium, passed through a gettering furnace followed by a Nanochem gas purifier, was used as a carrier gas for the organometallic precursor and as a diluent for the ammonia. With no precursors in the helium stream, analyses of the helium outflow showed an oxygen concentration of less than 0.5 ppm. Higher oxygen concentrations led to oxygen incorporation in the films. Electronic grade ammonia was passed through a Nanochem gas purifier and diluted with helium before it was mixed with the precursor. During depositions, helium was passed through a stainless steel bubbler assembly containing the tin precursor and this mixture then flowed through a 2-mm-i.d. delivery line to the reaction chamber. The helium/Sn(NMe<sub>2</sub>)<sub>4</sub> mixture was mixed with the diluted ammonia approximately 1 cm before the entrance to the reactor.

Silicon and quartz substrates were cleaned by immersion in a 1:4 hydrogen peroxide/sulfuric acid mixture for 10 min and then rinsed with deionized water. The glass substrates (borosilicate or soda lime) were etched for 1 min in HF/HNO<sub>3</sub> (1:10) and then rinsed with deionized water.

Rutherford backscattering spectrometry (RBS) and forward recoil spectrometry (FRS) were performed on a General Ionics Model 4117 spectrometer. A He<sup>+</sup> beam of energy 2 MeV was used for most of the analyses. RBS data analyses were performed by using the program SPECTRUM ANALYSIS, written by Patrick Smith, Division of Applied Sciences, Harvard University. It is a Fortran program based on algorithms from a book by Chu et al.<sup>17</sup> FRS was used to determine hydrogen concentrations in the films. For the FRS experiments, the angle of the incident beam relative to the sample surface was adjusted to 15°. In this configuration, the detector and incident beam were at an angle of 150°. A gold-coated piece of mica with composition K<sub>2</sub>Al<sub>3</sub>SiO<sub>12</sub>H<sub>2</sub> was used as the calibration standard. FRS analyses were carried out using the simulation subroutines in the program RUMP, which is RBS modeling software based on a paper by Doolittle.<sup>18</sup>

X-ray photoelectron spectroscopy (XPS) was carried out by using a Surface Science Lab SSX-100 system equipped with a 3-keV Ar<sup>+</sup> sputter gun. XPS depth profiles were collected in the unscanned mode by using the monochromatized Al K $\alpha$  excitation line with a spot size of 600  $\mu$ m, and the electron energy analyzer set for a pass energy of 150 eV. Higher resolution spectra were collected in the scanned mode with a spot size of 300  $\mu$ m and a pass energy of 50 eV. The base pressure was 10<sup>-7</sup> Torr with the Ar<sup>+</sup> gun on and 10<sup>-10</sup> Torr with the gun off.

Samples for TEM were prepared by depositing films on carbon coated mica. The transmission electron micrographs and electron diffraction patterns were obtained on a Philips EM240T scanning transmission electron microscope at 120 kV. Absorption and transmission spectra were obtained on a Varian 2390 spectrophotometer. Film resistivities were measured by the four point probe method on a Veeco Model FPP-100 instrument.

## Results

**Deposition and General Characteristics.** Films of tin nitride were successfully deposited from Sn(NMe<sub>2</sub>)<sub>4</sub> and NH<sub>3</sub> precursors on silicon and soda lime, borosilicate, and quartz glass substrates. Substrate temperatures were varied in the range 200–400 °C. In a control experiment, no film deposition was observed on silicon at 200 °C in the absence of ammonia.

In a typical experiment, the temperature of the precursor bubbler assembly was maintained at 90 °C while the delivery lines to the reactor were held at 125 °C. Under these conditions, films up to 3000 Å thick were obtained at growth rates of 1000 Å/min for substrate temperatures between 200 and 400 °C. Growth rates were increased by increasing the temperature of the bubbler assembly, but too much heating led to the formation of rough films,

Table I. Composition of Tin Nitride Films

deposition temp, °C	N/Sn ratio <sup>a</sup>	H concn, <sup>b</sup> atom %
200	1.50	18.0
300	1.45	17.5
400	1.45	15.0

<sup>a</sup>The error in these values is estimated to be  $\pm 0.05$ . <sup>b</sup>The error in these values is estimated to be  $\pm 1$  atom %.

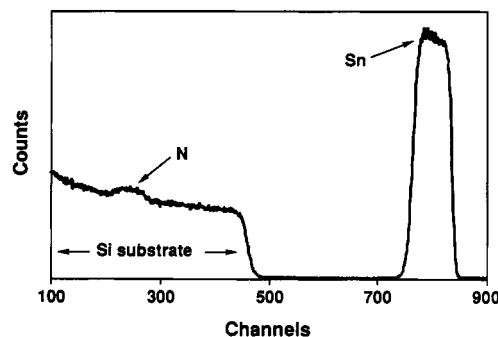


Figure 1. RBS spectrum for a tin nitride film deposited on silicon at 200 °C (2.0-MeV He<sup>+</sup> beam).

presumably because the concentration of Sn(NMe<sub>2</sub>)<sub>4</sub> in the gas stream was too high. The highest growth rates were obtained on substrates placed near the inlet of the reactor.

The films showed interference patterns on all substrates, and they adhered well by the Scotch tape test criterion. Except as noted above, the films were smooth. They were chemically inert to organic solvents and did not readily dissolve in concentrated mineral acids (tested 2–3 min in hydrochloric, nitric, sulfuric, and 48% hydrofluoric acids). The films were etched rapidly when they were sprinkled with powdered zinc followed by droplets of dilute hydrochloric acid.

**Characterization.** Film compositions were determined by RBS (Table I). Figure 1 shows a representative RBS spectrum for a tin nitride film deposited at 200 °C. No oxygen or carbon signals were detected, indicating that these elements were present in low concentrations (<2–3 atom %). Films grown at higher temperatures also showed no oxygen or carbon contamination. The N/Sn ratio did not vary appreciably with temperature; for example, it was 1.50 for films deposited at 200 °C and 1.45 at 400 °C.

Hydrogen concentrations in the films were determined by forward recoil spectrometry (Table I). The films obtained at all three temperatures were hydrogenated, with the hydrogen concentration varying from 18 atom % at 200 °C to 15 atom % at 400 °C.

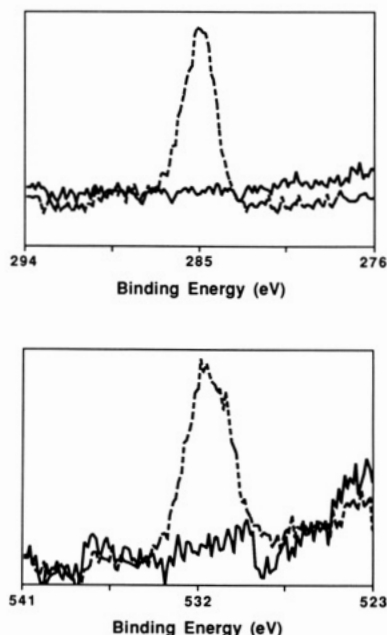
XPS analyses were carried out in an attempt to estimate the amount of carbon and oxygen in the films. After sputtering to a constant composition, however, no carbon or oxygen signals were observed (e.g., Figure 2). This is consistent with the RBS results, which showed that oxygen and carbon contamination was low or not present at all.

An interesting feature of the XPS spectra was the binding energies of the tin peaks (Figure 3). Before sputtering, the binding energies of the Sn 4d<sub>3/2</sub> and Sn 4d<sub>5/2</sub> were 494.69 and 486.25 eV, respectively, which corresponded to the binding energies of tin in SnO<sub>2</sub>. After sputtering into the bulk of the sample, the binding energies of the Sn 4d<sub>3/2</sub> and Sn 4d<sub>5/2</sub> peaks were 493.13 and 484.69 eV, respectively, which corresponded to the binding energies of tin metal. The composition data and observed electrical and optical properties (see below) of the films, however, were consistent with the formation of a tin nitride film, not tin metal. This discrepancy suggested that the tin at the clean tin nitride sample surface was reduced by the 3-keV Ar<sup>+</sup> sputter beam. Such a reduction has pre-

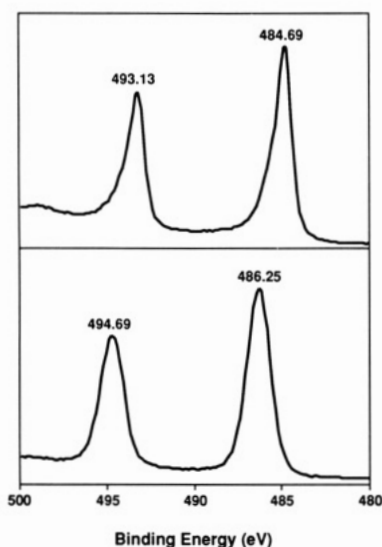
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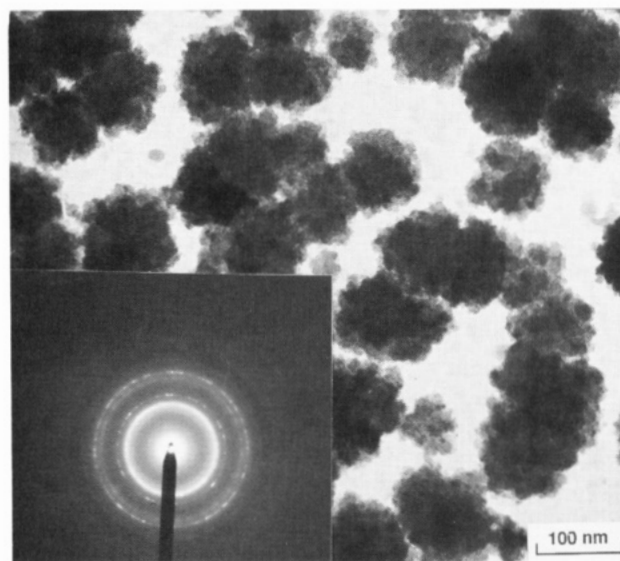
**Figure 2.** XPS spectra in the C(1s) (top) and O(1s) (bottom) regions for a tin nitride film deposited at 200 °C on silicon. The dashed curves were obtained before sputtering and the solid curves after sputtering for 2 min with Ar<sup>+</sup>.



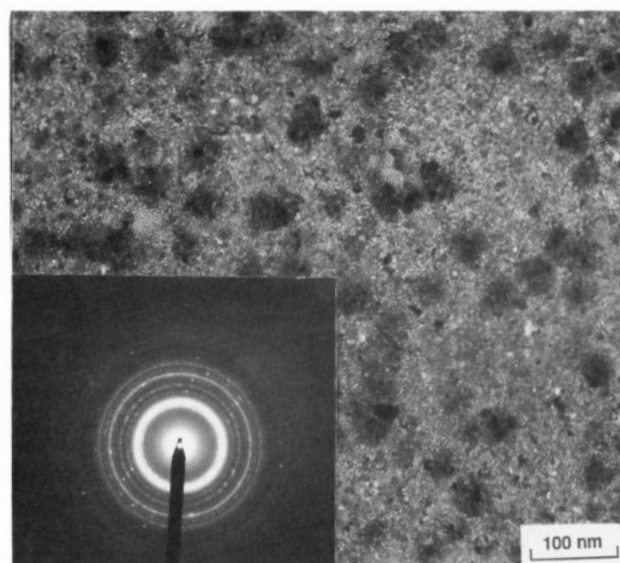
**Figure 3.** Sn(3d) region of the XPS spectrum for a tin nitride film deposited at 200 °C on silicon. The bottom spectrum was obtained before sputtering and top spectrum after sputtering for 2 minutes.

viously been observed for the metal atom in oxides of some transition metals (e.g., tantalum in Ta<sub>2</sub>O<sub>5</sub>).<sup>19</sup> Consistent with this interpretation, a lower energy Ar<sup>+</sup> sputter ion (1 keV) produced shoulders on the Sn 4d<sub>3/2</sub> and 4d<sub>5/2</sub> peaks at 494.18 and 485.82 eV, respectively, which can perhaps be assigned as the binding energies for tin in tin nitride.

**Microstructure.** TEM micrographs and diffraction patterns were obtained for tin nitride films deposited at 200, 300, and 400 °C. The films deposited at 200 °C showed diffuse diffraction rings characteristic of an amorphous material or a crystalline material with extremely small crystallites. Sharper diffraction rings were observed for the films deposited at 300 (Figure 4) and 400 °C (Figure 5), which suggested they were composed of



**Figure 4.** TEM micrograph and electron diffraction pattern (inset) for a tin nitride film deposited at 300 °C.



**Figure 5.** TEM micrograph and electron diffraction pattern (inset) for a tin nitride film deposited at 400 °C.

**Table II. Observed Spacings (Å) between Lattice Planes for Tin Nitride Films**

5.20, 3.11, 2.92, 2.82, 2.63, 2.38, 2.02, 1.84, 1.66, 1.59, 1.49, 1.38, 1.20
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polycrystalline materials. The observed spacings between lattice planes are presented in Table II. The spacings do not correspond to the reported powder diffraction pattern for tin metal<sup>20</sup> and, to our knowledge, a pattern for tin nitride has not been reported. The sharper diffraction rings and the difference in relative intensities of the rings for the films deposited at 400 °C versus those deposited 300 °C probably arose because the sample prepared at 400 °C was thicker than the sample prepared at 300 °C (600–800 vs 300 Å).

Depositions carried out at 200 °C produced smooth, featureless films. Films deposited at 300 °C, on the other hand, appeared to be composed of islands of crystallites where the crystallites were approximately 10 nm in diam-

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(20) Sn: Index No. 5-0390 and 4-0673. Powder diffraction File; McClune, W. F., editor in chief; JCPDS International Center for Diffraction Data, Swarthmore, PA, 1990.

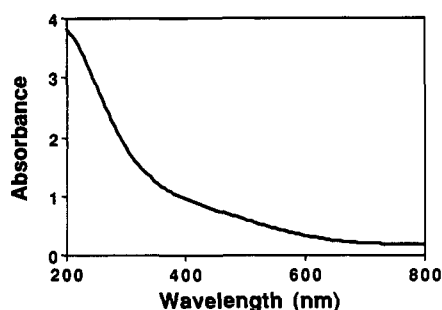


Figure 6. Absorption spectrum for a tin nitride film deposited on quartz at 200 °C.

eter (Figure 4). The micrograph shown in Figure 5 was taken of a thick film (600–800 Å) deposited at 400 °C. This film had a granular structure with crystallites approximately 10 nm in diameter.

**Electrical and Optical Properties.** Films approximately 1500–2000 Å thick deposited on quartz were used to study electrical and optical properties. The resistivity was  $(8-9) \times 10^{-3} \Omega \text{ cm}$  for films deposited at 200 and 400 °C and  $(2-3) \times 10^{-3} \Omega \text{ cm}$  for films deposited at 300 °C. These numbers should be considered estimates because the film thicknesses varied along the substrate due to the design of our reactor. The variation made an accurate determination of resistivity impossible.

The absorption spectrum for a film 2000 Å thick deposited at 200 °C is shown in Figure 6. The films weakly absorbed at low energies ( $\leq 400 \text{ nm}$ ). The transmitted color was yellow.

Optical bandgaps for the films were estimated from transmission spectra by plotting  $(\alpha h\nu)^{1/2}$  vs  $h\nu$ , where  $\alpha$  is the absorption coefficient and  $h\nu$  the photon energy. These measurements revealed that the bandgap decreased with the temperature of deposition. For films deposited at 200, 300, and 400 °C, the band gaps were calculated to be  $2.25 \pm 0.05$ ,  $2.05 \pm 0.05$ , and  $1.94 \pm 0.05 \text{ eV}$ , respectively. Reflectance spectra showed that the films had a low reflectance in the visible and near-infrared regions. For the films deposited at 200 and 400 °C, no increase in relative reflectivity was observed in infrared reflectance spectra, indicating that these films had low electron concentrations. The films deposited at 300 °C showed a 60% reflectivity in the infrared and the electron concentration in these films was estimated from the plasma wavelength<sup>21</sup> to be around  $10^{20} \text{ cm}^{-3}$ .

Refractive indexes were measured by ellipsometry at 632 nm. There was no discernible change in the indexes with deposition temperature, and the indexes varied widely (2.8–3.3) for each individual sample tested. The variation in refractive index may reflect a variation in physical properties in the films along the gas flow in the reactor.

### Discussion

Films of tin nitride were deposited from  $\text{Sn}(\text{NMe}_2)_4$  and  $\text{NH}_3$  precursors on silicon and glass substrates at temperatures as low as 200 °C with growth rates of up to 1000 Å/min. The N/Sn ratio was 1.5, and the hydrogen concentration was in the range 15–18 atom %. On the basis of these data, a  $\text{Sn}_3\text{N}_{4.5}\text{H}_{1.5}$  stoichiometry is calculated.

The hydrogen and excess nitrogen in the films are probably incorporated in amorphous material surrounding  $\text{Sn}_3\text{N}_4$  crystallites.<sup>13</sup> This would explain the TEM micrographs and electron diffraction data, which suggest that the films are composed of some crystalline material (presumably  $\text{Sn}_3\text{N}_4$ ). In the amorphous material the excess nitrogen and hydrogen may be present in the form of N–H and N–N groups.<sup>13</sup>

The physical properties of our films were different from those reported by Remy and Hantzpergue for reactively sputtered amorphous tin nitride films.<sup>5,6</sup> For example, the optical bandgaps of our films were in the range 1.9–2.25 eV, whereas the value reported by Remy and Hantzpergue was  $3.55 \pm 0.05 \text{ eV}$ . Also, the resistivity of our films  $(2-9) \times 10^{-3} \Omega \text{ cm}$  was considerably lower than the resistivity of the sputtered films (1.43–66.7  $\Omega \text{ cm}$ ).

The films prepared by Remy and Hantzpergue were more nitrogen rich (N/Sn  $\approx 2$ ) than ours and contained no hydrogen. It is possible that these differences in stoichiometry may account for the disparity in physical properties between their films and ours. Also, Remy and Hantzpergue postulated that free tin in the sputtered tin nitride led to the conductivity they observed.<sup>5,6</sup> We cannot exclude the possibility of small amounts of free tin in our samples, but on the basis of the RBS data, there would not be sufficient free tin mixed with a semiconducting or insulating  $\text{Sn}_3\text{N}_4$  phase to account for the low resistivity. It is possible that traces of oxygen or lattice vacancies in a semiconducting  $\text{Sn}_3\text{N}_4$  phase give rise to the conductivity we observe (i.e., a doped semiconducting description is appropriate). We are presently attempting to prepare pure, bulk crystalline tin nitride in order to study its properties for comparison with the films.

The deposition of tin nitride films from  $\text{Sn}(\text{NMe}_2)_4$  and ammonia is another illustration of the applicability of the  $\text{M}(\text{NR}_2)_n/\text{NH}_3$  precursor system for the chemical vapor deposition of metal nitride thin films. The mechanism of formation for tin nitride is probably similar to the mechanism we have proposed for analogous systems;<sup>9,11-12</sup> that is, rapid substitution of one or more  $\text{NMe}_2$  groups by  $\text{NH}_2$  groups (transamination) followed by  $\alpha$ -hydrogen activation and intramolecular elimination of  $\text{HNMe}_2$ . The absence of carbon in the films suggests that the  $\alpha$ -hydrogen activation occurs cleanly.

### Conclusion

Films of tin nitride were successfully deposited at low temperatures from tetrakis(dimethylamido)tin(IV) and ammonia. The films were adherent, chemically inert, and conductive. Films deposited at 300 °C and above were polycrystalline with a crystallite size of approximately 10 nm. To our knowledge, this is the first report of the preparation of polycrystalline tin nitride.

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**Registry No.**  $\text{Sn}_3\text{N}_4$ , 12142-83-5;  $\text{Sn}(\text{NMe}_2)_4$ , 1066-77-9;  $\text{NH}_3$ , 7664-41-7; Si, 7440-21-3;  $\text{H}_2$ , 1333-74-0.

(21) Jin, Z. C.; Hamberg, I.; Granquist, C. G. *Appl. Phys. Lett.* 1987, 51, 149.