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Chemical Vapor Deposition of Metal Nitrides, Phosphides and Arsenides

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Report by
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We recently demonstrated that dialkylamido complexes, such as $\text{Si}(\text{NMe}_2)_4$, are promising precursors to nitride thin films. On this basis we reasoned that transition metal and main group disilazide complexes in which the silicon has dialkylamido substituents (e.g., $[\text{N}(\text{Si}(\text{NMe}_2)_3)_2]^-$) are potential precursors to ternary silicon nitride films. Bulky disilazide ligands are known to stabilize main group and transition metal complexes with low coordination numbers, an important consideration in making volatile compounds for deposition studies. Reaction of dimethylamine with $\text{Cl}_3\text{SiN}(\text{H})\text{SiMe}_3$ in hexane solution at 25 °C gave the bulky disilazane $[(\text{Me}_2\text{N})_3\text{Si}]\text{N}(\text{H})\text{SiMe}_3$ in 73% yield. Reaction of $[(\text{Me}_2\text{N})_3\text{Si}]\text{N}(\text{H})\text{SiMe}_3$ with *n*-butyl lithium in benzene at 0 °C produced the lithium complex $[(\text{Me}_2\text{N})_3\text{Si}]\text{N}(\text{Li})\text{SiMe}_3$ in 82% yield. $\text{LiN}[\text{Si}(\text{NMe}_2)_3]_2$ was prepared in 92% yield from the reaction of $\text{HN}(\text{SiCl}_3)_2$ and seven equivalents of LiNMe_2 in hexane. $\text{LiN}[\text{Si}(\text{NMe}_2)_3]_2$ is converted to the amine (83% yield) by reaction with $[\text{H}_2\text{NMe}_2]\text{Cl}$ in THF. The new compounds were characterized spectroscopically, and the X-ray crystal structures of $[(\text{Me}_2\text{N})_3\text{Si}]\text{N}(\text{Li})\text{SiMe}_3$ and $\text{LiN}[\text{Si}(\text{NMe}_2)_3]_2$ were determined. $[(\text{Me}_2\text{N})_3\text{Si}]\text{N}(\text{Li})\text{SiMe}_3$ and $\text{LiN}[\text{Si}(\text{NMe}_2)_3]_2$ are dimeric in the solid state, forming four-membered Li_2N_2 rings. In both cases dimethylamido groups bridge between silicon and lithium, giving three-coordinate lithium in $\{[(\text{Me}_2\text{N})_3\text{Si}]\text{N}(\text{Li})\text{SiMe}_3\}_2$ and four-coordinate lithium in $\{\text{LiN}[\text{Si}(\text{NMe}_2)_3]_2\}_2$. Use of the lithium salts to introduce the novel disilazides as ligands in transition metal and main group compounds may prove difficult because of the encapsulation of the Li-N bonds by the dimethylamido groups.

Because amido precursors are volatile, easily synthesized, and relatively safe to handle, we decided to examine their use as precursors to main group oxide thin films. $\text{Sn}(\text{NMe}_2)_4$ and $\text{Si}(\text{NMe}_2)_4$ react with oxygen in an atmospheric pressure chemical vapor deposition reactor to give SnO_2 and SiO_2 films, respectively. The films were deposited on quartz, silicon, and glass substrates at substrate temperatures of 250–400 °C. Rutherford backscattering spectroscopy, elastic recoil spectroscopy, scanning electron microscopy, X-ray diffraction, Auger electron spectroscopy, X-ray photoelectron spectroscopy, four-point probe measurements, ellipsometry, and FTIR spectroscopy were used to characterize the films. The films are stoichiometric tin oxide (avg. $\text{O}/\text{Sn} = 2.00 \pm 0.10$) and slightly oxygen rich silicon oxide (avg. $\text{O}/\text{Si} = 2.20 \pm 0.10$). The tin oxide films contain less than 1 atom % C and 0.3 atom % N and the silicon oxide less than 0.2 atom % C and 0.3 atom % N. The silicon oxide deposited at 350 °C has a hydrogen content of 9 ± 5 atom %, but no detectable hydrogen is observed in any of the tin oxide films. The growth rates for tin oxide range from 650 to 10,000 Å/min and for silicon oxide from 380 to 900 Å/min. The silicon oxide films are insulators, whereas the tin oxide films are conductors with resistivities in the range 10^{-1} – 10^{-3} Ω cm. The silicon oxide deposited at 350 °C is amorphous by X-ray diffraction, but tin oxide deposited at 350 °C is crystalline cassiterite with some (101) orientation. The refractive indexes for the silicon dioxide films are 1.458 ± 0.003 and do not vary significantly with deposition temperature. The refractive indexes for the tin oxide films vary from 2.064–2.867.

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