
Silicon Nitride from Organosilazane Cyclic and Linear Prepolymers

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Silicon nitride coatings are generally produced by CVD techniques which involve mixtures of gases, typically SiH_4/NH_3 or $\text{SiCl}_4/\text{NH}_3$ in carriers. The fabrication of passivation layers and dielectric coatings demand consistent electrical, mechanical and etch (chemical) properties. Operationally, this is difficult to accomplish since silicon nitrides of variable stoichiometry are deposited from gas mixtures depending on compositional, thermal, and surface variation in the deposition environment. Proposals for alternate silicon nitride sources that should lead to more uniform stoichiometry include single monomer approaches. Reinberg¹ has reported trisilylamine $[(\text{H}_3\text{Si})_3\text{N}]$ as a silicon nitride source, but the material is difficult to prepare and is pyrophoric. Other approaches to silicon nitride sources are found in the ceramic field. These include polysilazane, polyorganosilazanes and a variety of non-volatile resinous materials such as sesquisilazanes which are not suitable for the production of thin films of silicon nitride. Moreover, polysilazanes in which there is no carbon substitution have poor storage stability,² while previously reported organosilazanes yield high levels of silicon carbide on pyrolysis.^{3,4,5}

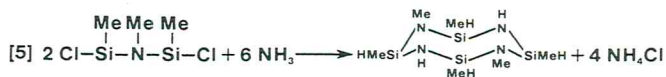
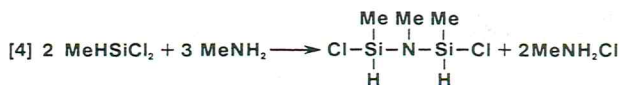
In this report the formation of silicon nitride from cyclic and linear organosilazane prepolymers is reported. The materials having the following structure were prepared in cyclic and linear forms. Poly(1,1-dimethylsilazane) is included for comparison with earlier work.

Table I.

Structure & Physical Properties of Organosilazanes

	Cyclic		Polymer	
	n	bp	sp. gr.	visc.
[1] $\left[\begin{array}{c} \text{Me} \quad \text{H} \\ \quad \\ \text{Si} \quad \text{N} \\ \quad \\ \text{Me} \end{array} \right]_n$	3	186-8°		>1000 ctsk.
[2] $\left[\begin{array}{c} \text{Me} \quad \text{Me} \\ \quad \\ \text{Si} \quad \text{N} \\ \quad \\ \text{H} \end{array} \right]_n$	3	56°/5mm	.99	600-700 ctsk.
[3] $\left[\begin{array}{c} \text{Me} \quad \text{Me} \\ \quad \\ \text{Si} \quad \text{N} \\ \quad \\ \text{H} \end{array} \right]_{n/2} \left[\begin{array}{c} \text{Me} \quad \text{H} \\ \quad \\ \text{Si} \quad \text{N} \\ \quad \\ \text{H} \end{array} \right]_{n/2}$	4	202-206°	1.04	150-250 ctsk.

The cyclic silazanes are readily prepared by one or two stage aminolysis reactions, e.g.



The linear polymers are prepared by catalytic reequilibration of the cyclic materials at 225-300°C. They are soluble in hydrocarbons.

Essentially identical compositions result from the pyrolysis of cyclic or linear organosilazanes at pyrolysis temperatures of 350°C or greater. Complete conversion to ceramic occurs at temperatures exceeding 700°C. Slight changes in morphology without changes in elemental composition appear to occur at higher temperatures.

Table II.

Polymer	Thermal Characteristics		
	Principal Endotherm*	Silicon Nitride** Content%	Yield%
1.	440-450°	30-40	5-10
2.	375-385°	50-60	15-20
3.	286-287°	80-85	50-55

1,1-dimethylsilazanes and 1,2-dimethylsilazanes have the same ratio of silicon, nitrogen, and hydrogen. The 1,2-dimethylsilazanes undergo conversion at lower temperatures to higher levels of silicon nitride at higher yields. This may be accounted for by the lower bond dissociation of N-CH₃ compared to Si-CH₃.⁶ The dramatic yield enhancement in the 1,2-dimethylsilazane-1-methylsilazane copolymer may be accounted for by several factors: The carbon content is lower, the bond dissociation energies of N-CH₃ vs. Si-CH₃, and the ability of the relatively basic nitrogen to react with silicon hydride generating hydrogen byproduct. It should be noted that although the base interaction with silicon hydride is the likely cause of poor stability in inorganic polysilazanes, the methyl substituted silicon hydrides appear to have acceptable stability.

REFERENCES

1. A. R. Reinberg, Single Component Monomer for Silicon Nitride Deposition, U.S. Patent 4,200,666 (1980).
2. D. Seyferth, G. H. Wiseman, C. Prud'homme, J. Amer. Ceram. Soc. **66**, C13 (1983).
3. B. A. Mazaev, B. N. Talanov, M. M. Eleen, Inorganic Materials, **19**, 2044 (1983).
4. C. L. Beatty, "Ultrastructure Processing of Advanced Structural and Electronic Materials," ed. L. Hench, Noyes Data (1984).
5. D. Ya Zhinkin, E. A. Semenova, M. V. Sobolevskii, K. A. Andranov, Plastics, Massy, **12**, 16 (1963).
6. R. Walsh, Acc. Chem. Res. **14**, 246 (1981).

* Determined by DSC 10°/min under N₂.

** Calculation from stoichiometries, balance SiC.

Figure 1.

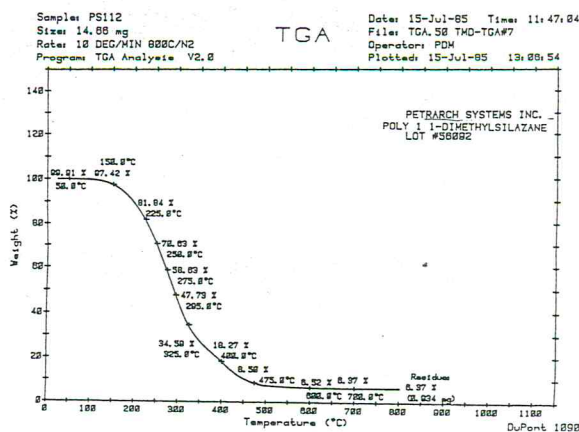


Figure 2.

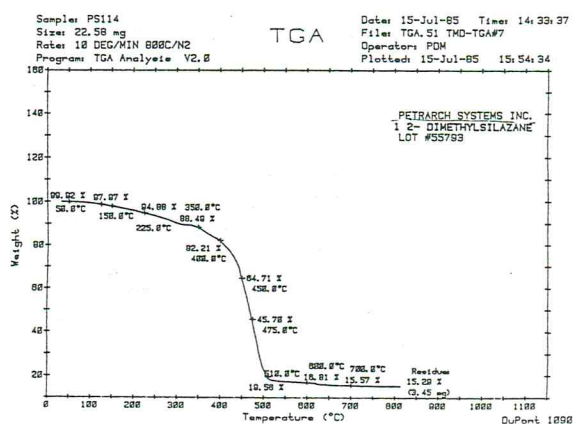
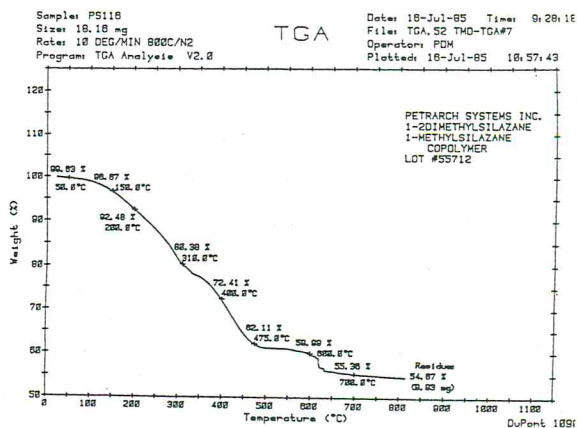


Figure 3.



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