JOURNAL OF MATERIALS SCIENCE 29 (1994) 4883–4888

# Conversion mechanism of perhydropolysilazane into silicon nitride-based ceramics

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The pyrolysis of perhydropolysilazane in anhydrous ammonia has been studied up to 1000 °C through the analysis of the gas phase and the characterization of the solid residue by thermogravimetric analysis, Fourier transform–infrared analysis, X-ray photoelectron spectroscopy, X-ray diffraction and $^{29}$Si cross-polarization magic angle spinning–nuclear magnetic resonance. The pyrolysis mechanism involves three main steps: (1) below 400 °C, evaporation of residual solvent; (2) from 400–600 °C, reaction with ammonia leading to an increase of nitrogen content and formation of preceramic polymer–ceramics intermediate solid with a three-dimensional network; (3) from 600–1000 °C, completion of the formation of an amorphous hydrogenated solid with composition close to silicon nitride.

## 1. Introduction

There has been much interest in the use of organometallic polymers as precursors to high-performance ceramics such as silicon nitride [1–5] and silicon carbide [6–10]. Some of the potential advantages in the preparation of ceramic materials from these precursors include: (1) compositional homogeneity in the final products, (2) high-purity ceramic products with uniform microstructure, amorphous to microcrystalline, (3) the preparation of refractory ceramics at relatively low temperatures, and (4) the ability to form fibres, coatings and near net-shaped structures [11].

Polycarbosilane has been developed for producing SiC-based ceramics [6, 7]. The pyrolysis mechanism of the polycarbosilane has been studied [12–15]. Bouillon *et al.* suggested [16] that the pyrolysis mechanism involves three main steps: (1) from 550–800 °C, an organometallic mineral transition leading to an amorphous hydrogenated solid built on tetrahedral SiC, $SiO_2$ and silicon oxycarbide entities, (2) from 1000–1200 °C, a nucleation of SiC resulting in SiC nuclei surrounded with aromatic carbon layers, and (3) above 1400 °C, a SiC grain-size coarsening consuming the residual amorphous phases and giving rise simultaneously to a probable evolution of SiO and CO.

We have reported the production of high ceramic yield perhydropolysilazane synthesized by thermal polymerization of the oligomer–$(SiH_2NH)_x$–in the presence of ammonia in pyridine. This polymer is an excellent precursor for high-purity silicon nitride fibres [1, 17–19]. Yokoyama *et al.* [20] suggested that this amorphous silicon nitride fibre has either α- or β-$Si_3N_4$-like structures or a mixture of them. The conversion mechanism of perhydropolysilazane into ceramics should be understood in order to have better control of composition and microstructure in the final ceramics. Nitridation of perhydropolysilazane in ammonia and its rate-determining steps have been studied [21]. However, the structural change during the pyrolysis is not completely known. This paper describes the conversion mechanism of perhydropolysilazane into ceramics in anhydrous ammonia.

## 2. Experimental procedure

### 2.1. Preceramic polymer synthesis

Initially 15 kg dry pyridine was charged into a 40 l jacketed reactor. While the pyridine was stirred at 0 °C, 1.5 kg dichlorosilane was added at a rate of 0.75 kg $h^{-1}$ to form dichlorosilane–pyridine adduct suspended in the pyridine. After the adduct formation, gaseous $NH_3$ at a flow rate of 100 nl $h^{-1}$ at 6 kg $cm^{-3}$ was bubbled into the adduct suspension. Reaction between the dichlorosilane–pyridine adduct ammonia gave soluble perhydrosilazane oligomer and $NH_4Cl$ precipitate. The oligomer in pyridine was separated from the $NH_4Cl$ precipitate by filtration.

A solution containing 5 wt % oligomeric perhydrosilazane in pyridine and anhydrous ammonia were charged in a 40 l jacketed reactor. The solution was held at constant pressure at 120 °C for 4 h. After cooling to room temperature, the solvent and $NH_3$ were removed by distillation at 50–70 °C under 5–7 mm Hg to give a white powder (perhydropolysilazane, $M_n \approx 2400$ Da).

### 2.2. Pyrolysis

Prior to pyrolysis, the polymer was ground to a powder with a mean particle size of 4–8 μm. Polymer samples were pyrolysed in an infrared image furnace (ULVAC E 45). Initially, the furnace tube was flushed with anhydrous ammonia at room temperature.

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The polymer was pyrolysed by heating from room temperature to given temperatures (ranging from 400–1000 °C) at heating rate of 10 °C min$^{-1}$, holding at given temperatures for an additional 5 min and finally cooling to room temperature at 200 °C min$^{-1}$. All heating was completed under flowing anhydrous ammonia (1 nl min$^{-1}$).

### 2.3. Characterization

The analysis of the gaseous species resulting from the pyrolysis was performed under helium by flash pyrolysis using a Curie point pyrolyser (at 300, 423, 670 and 1040 °C, Japan Analytical Industry JHP-3). The gaseous species formed during the pyrolysis were transported with a helium flow to a chromatograph (Hewlett Packard 5890A) and the identification of the gaseous species was performed with a mass-spectrometer (Jeol JMS-DS303).

Thermogravimetric analysis (TGA) was performed on the polymer up to 1000 °C at heating rate of 10 °C min$^{-1}$ under flowing anhydrous ammonia (Rigaku TG8110D). X-ray diffraction (XRD) measurements were performed on untreated and pyrolysed perhydropolysilazane with Cu$K_\alpha$ radiation using an automated powder diffractometer equipped with a monochrometer (Rigaku RINT 1400).

Nuclear magnetic resonance with cross-polarization magic angle spinning (CPMAS–NMR) spectra were recorded on MSL-300 Bruker spectrometer. A $^{1}$H 90° pulse of 4.5 μs, contact time of 3 ms, and a delay between pulses of 10 s were used for $^{29}$Si NMR spectra.

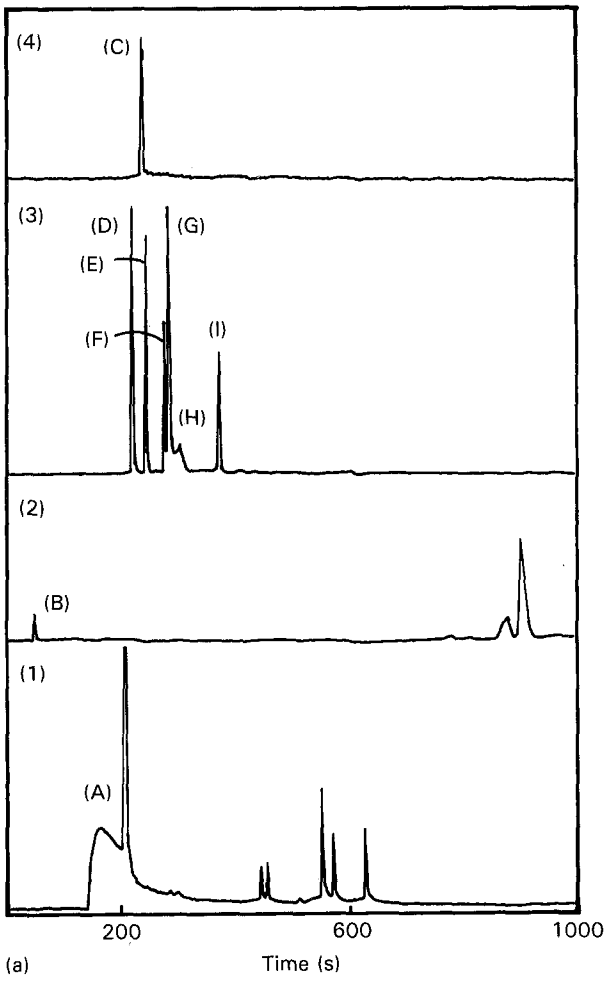
X-ray photoelectron spectroscopy (XPS) spectra were recorded with Mg$K_\alpha$ (1253.6 eV) as the excitation source (Kratos XSAM-800). The analyses were performed under a residual pressure of less than $6.65 \times 10^{-7}$ Pa on the pyrolysed samples. The sample was cleaned by Ar$^{+}$ ion bombardment (20 mA intensity, 3.5 kV energy) prior to XPS analysis. The XPS data recorded on pyrolysed samples were calibrated utilizing the C 1s binding energy in carbon (284.6 eV as a standard).

Infrared (IR) spectra were recorded on KBr pellets containing powder samples (Jeol JIR-5500). Elemental analyses for silicon, nitrogen, carbon, oxygen and hydrogen were obtained for the polymer and the pyrolysed samples.

## 3. Results and discussion

### 3.1. Analysis of the gaseous species

The chromatograms and mass spectra recorded during the flash pyrolysis of perhydropolysilazane at



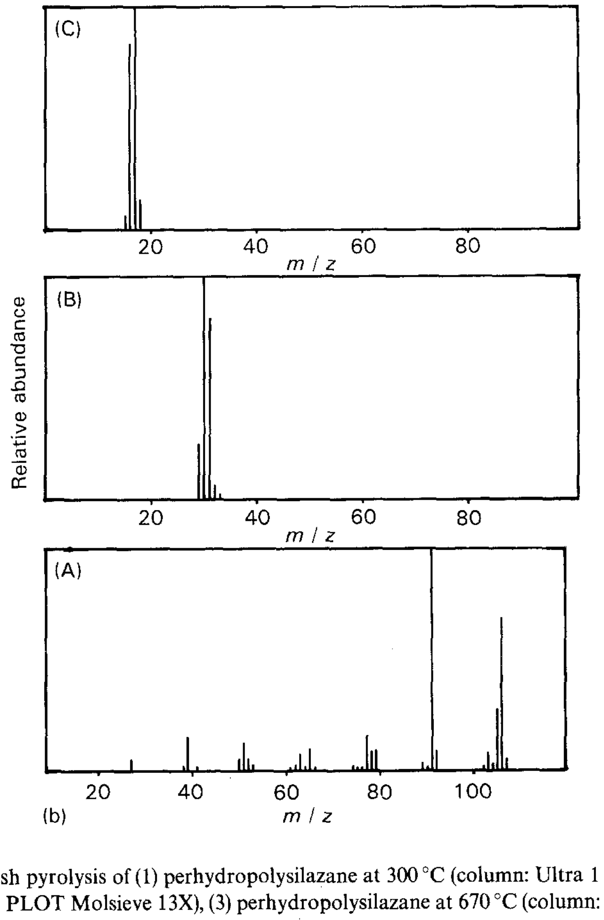


*Figure 1* (a) Chromatograms of the gaseous species resulting from the flash pyrolysis of (1) perhydropolysilazane at 300 °C (column: Ultra 1 cross-linked methyl silicone), (2) perhydropolysilazane at 420 °C (column: PLOT Molsieve 13X), (3) perhydropolysilazane at 670 °C (column: PONA cross-linked methyl silicone), and (4) 600 °C pyrolysed perhydropolysilazane at 1040 °C (column: PONA). Mass spectra of (a) xylene, (b) silane, and (c) ammonia ($m$ = ion mass, $z$ = ion charge). (c) Mass spectra of low molecular weight silazane compounds and their proposed structures, resulting from the flash pyrolysis of perhydropolysilazane at 670 °C. (d) Mass spectra of low molecular weight silazane compounds and their proposed structures, resulting from the flash pyrolysis of perhydropolysilazane at 670 °C.

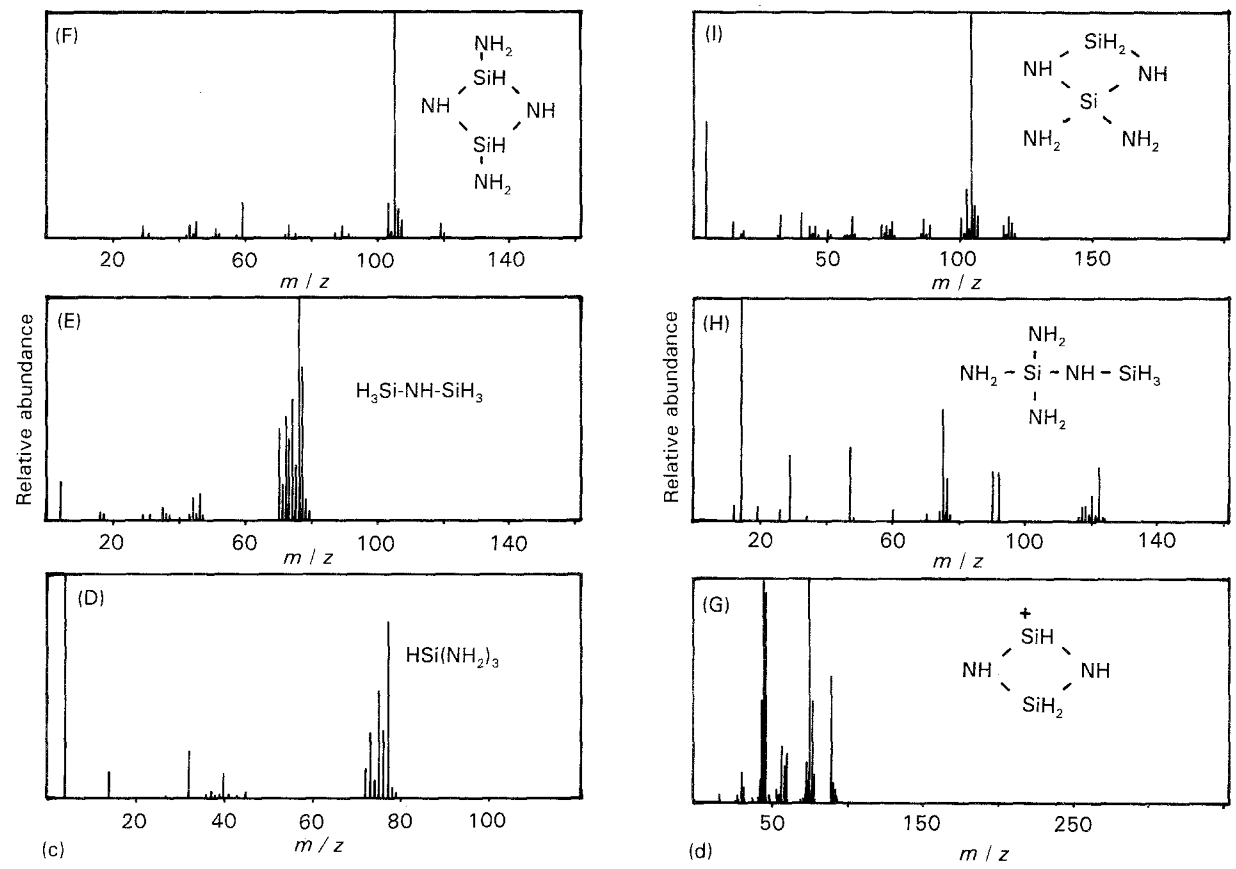


*Figure 1* Continued

TABLE I Elemental analysis of polymer and polymer-derived ceramics

| | Composition (wt %) | | | | |
|---|---|---|---|---|---|
| Sample | Si | N | O | C | H |
| Perhydropolysilazane | 60.40 | 29.80 | 0.80 | 5.00 | 4.00 |
| 400 °C pyrolysed perhydropolysilazane | 62.80 | 31.00 | 1.10 | 1.30 | 3.60 |
| 500 °C pyrolysed perhydropolysilazane | 59.70 | 35.10 | 1.20 | 0.50 | 3.20 |
| 600 °C pyrolysed perhydropolysilazane | 57.40 | 38.80 | 0.90 | 0.20 | 2.70 |
| 1000 °C pyrolysed perhydropolysilazane | 57.90 | 38.60 | 0.80 | 0.20 | 2.40 |

increasing temperatures are given in Fig. 1. The main species which have been identified are hydrocarbons, hydrogen, ammonia and low molecular weight silazane compounds for high temperature. Hydrogen and ammonia are detected from all pyrolysis conditions. Below 400 °C, hydrocarbons contribute significantly to the gas evolution; these are mainly residual solvent and its derivatives and impurities (Fig. 1b). Up to 400 °C, evolution of a small amount of $SiH_4$ is observed (Fig. 1b). Above 400 °C, low molecular weight silazane compounds contribute mainly to the gas evolution (Fig. 1c and d).

## 3.2. Preceramic polymer–ceramics transition

The results of the elemental analyses performed on untreated and pyrolysed samples are given in Table I. The empirical ratios of untreated and pyrolysed samples are found to be $SiN_{0.97}O_{0.02}C_{0.19}H_{1.85}$, $SiN_{0.99}O_{0.03}C_{0.05}H_{1.61}$ (400 °C), $SiN_{1.18}O_{0.04}C_{0.02}H_{1.50}$ (500 °C), $SiN_{1.35}O_{0.03}C_{0.01}H_{1.32}$ (600 °C) and $SiN_{1.33}O_{0.02}C_{0.01}H_{1.16}$ (1000 °C), respectively. As can be seen from these results, the Si/N atomic ratio is almost the same in the polymer as it is in its 400 °C pyrolysed sample. From 400–600 °C, the nitrogen content increases. The values of Si/N in the 600 and 1000 °C pyrolysed samples were found to be close to the value of silicon nitride. The oxygen may accidentally accumulate during the polymer synthesis, sample grinding, loading and transfer steps.

The TGA curve of perhydropolysilazane in an $NH_3$ atmosphere is shown in Fig. 2. Three regions are apparent in the TGA curve. The first region, below 400 °C, shows a weight loss of nearly 4%. Analysis of gaseous species and results of elemental analyses suggest that the weight loss in the first region results mainly from the loss of residual solvent. The second region, from 400–600 °C, shows a weight gain of 8% and is due to the nitridation [21]. Ammonia is thought to react with low molecular weight silazane

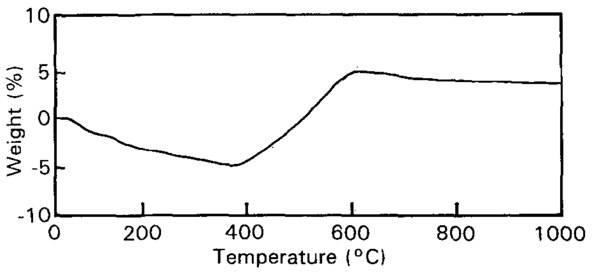


*Figure 2* TGA of perhydropolysilazane (ammonia flow 100 cm$^3$ min$^{-1}$; heating rate 10 °C min$^{-1}$).

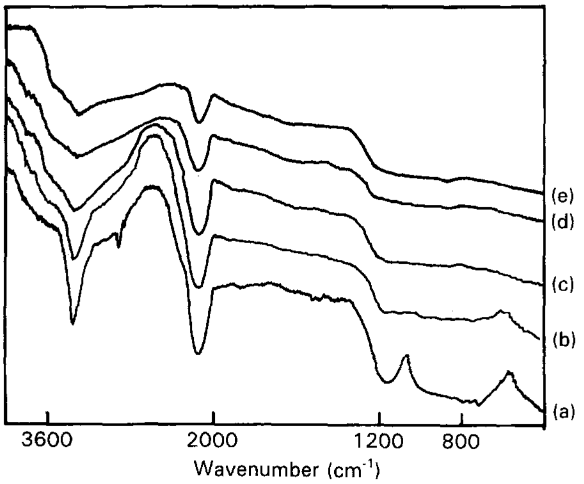


*Figure 3* FT–IR spectra of (a) untreated, (b) 400 °C pyrolysed, (c) 500 °C pyrolysed, (d) 600 °C pyrolysed, and (e) 1000 °C pyrolysed perhydropolysilazane.

compounds which will volatilize in the helium atmosphere and suppresses those volatiles. The third region, from 600–1000 °C, shows a slight weight loss of 2%. Analysis of the gaseous species of the 600 °C pyrolysed sample at about 1000 °C (Fig. 1a) shows evolution of $NH_3$ but low molecular weight silazane compounds cannot be detected. Nitridation is completed in the second region.

IR spectra for untreated and pyrolysed samples are shown in Fig. 3. Absorptions of the untreated sample at 3400 and 1200 cm$^{-1}$ indicate the presence of N–H groups, that at 2100 cm$^{-1}$ indicates the presence of Si–H groups, whereas the strong broad band at 800–1000 cm$^{-1}$ indicates Si–N–Si moieties [5]. Upon pyrolysis, the peak intensity at 2100 cm$^{-1}$ decreases slowly up to 1000 °C. The spectrum of the 1000 °C pyrolysed sample still exhibits the presence of N–H, Si–H and Si–N bonds. The absence of resolved features in the 800–1000 cm$^{-1}$ band has been attributed to the amorphous nature of silicon nitride [22, 23]. This spectrum indicates that the 1000 °C pyrolysed sample is an amorphous hydrogenated solid.

$^{29}$Si CPMAS-NMR spectra of untreated and pyrolysed samples are shown in Fig. 4. A comparison between untreated and 400 °C pyrolysed samples shows a slight decrease of the intensity of the peak at − 51 p.p.m. assigned to $SiH_3N$ units while the peak due to $SiHN_3/SiH_2N_2$ at − 37 p.p.m. shows the same chemical shift. Above 500 °C, the peak at − 51 p.p.m.

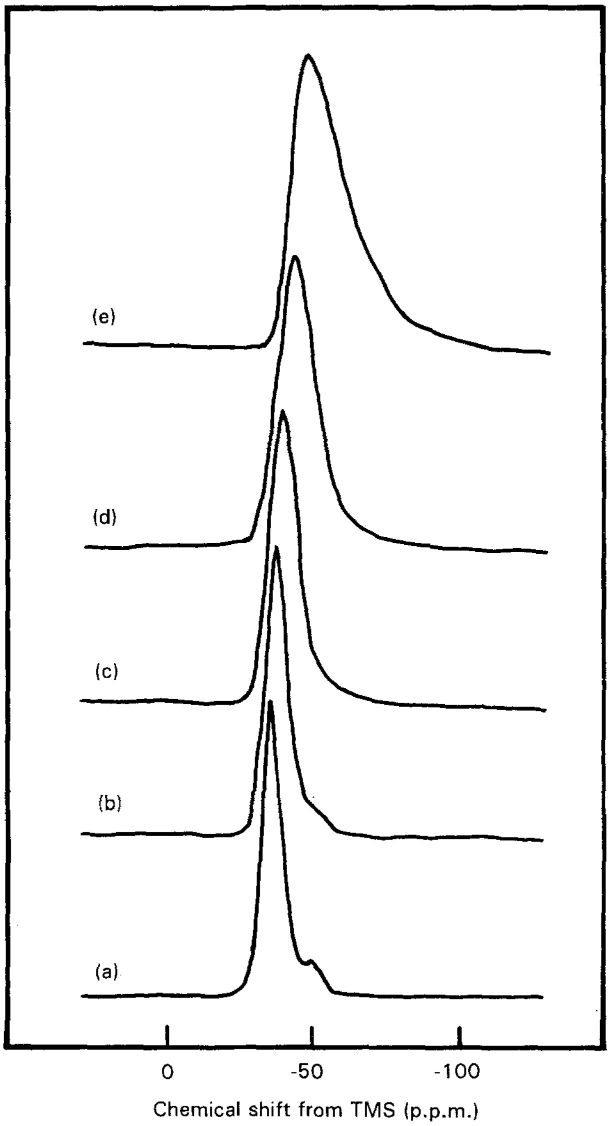


*Figure 4* $^{29}$Si CPMAS–NMR spectra of (a) untreated, (b) 400 °C Pyrolysed, (c) 500 °C pyrolysed, (d) 600 °C pyrolysed, and (e) 1000 °C pyrolysed perhydropolysilazane.

disappears. These results agree with decrease of the intensity of Si–H absorption in the IR spectra. From 500–1000 °C, the pyrolysed samples present one peak whose chemical shift decreases from − 37 p.p.m. to − 46 p.p.m. The chemical shift with the pyrolysis temperature is represented in Fig. 5. Below 400 °C, the chemical shift of the peak due to $SiHN_3/SiH_2N_2$ units does not vary. From 400–1000 °C, the position of the peak shifts towards a value corresponding to the amorphous $Si_3N_4$ phase [24]. In the same temperature range, the linewidth of the peak increases. These phenomena and TGA results indicate that from 400–600 °C, the reaction between $NH_3$ and Si–H bonds in the polymer leads to the building of an Si–N three-dimensional network. However, the solid obtained in this temperature range is thought to be a preceramic polymer–ceramics intermediate. From 600–1000 °C, the formation of an amorphous hydrogenated solid which has an $\alpha$- or $\beta$-$Si_3N_4$-like structure is completed.

Fig. 6 shows X-ray diffraction patterns of the polymer and the pyrolysed samples. In the 600 and 1000 °C pyrolysed samples, a very broad peak at about $2\theta = 20°–40°$ is observed. This broad peak is attributed

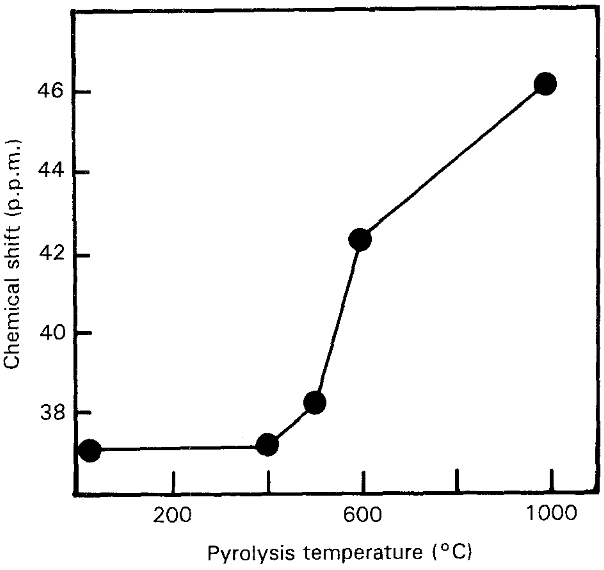


*Figure 5* Chemical shift ($^{29}$Si CPMAS-NMR spectra) of the pyrolysed perhydropolysilazane as a function of pyrolysis temperature.

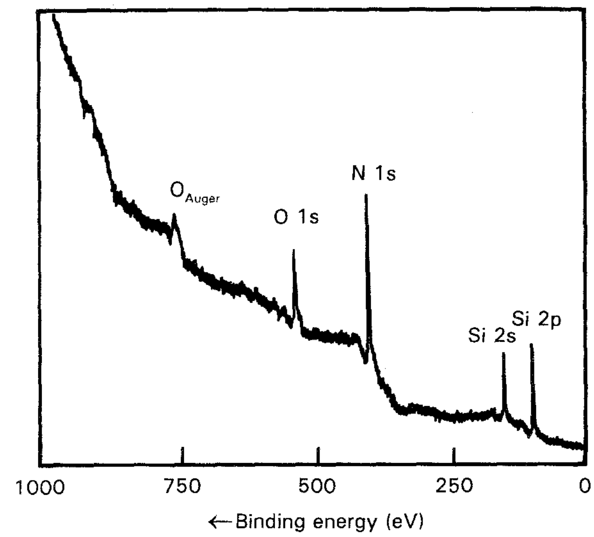


*Figure 7* XPS spectrum of 1000 °C pyrolysed perhydropolysilazane.

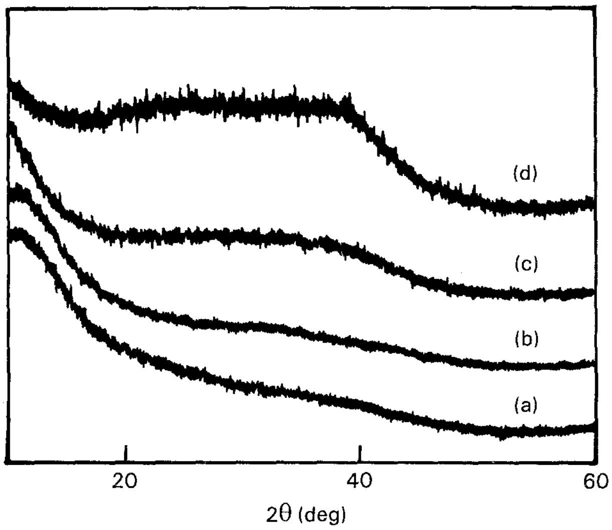


*Figure 6* X-ray powder diffraction patterns of (a) untreated, (b) 400 °C pyrolysed, (c) 600 °C pyrolysed, and (d) 1000 °C pyrolysed perhydropolysilazane.

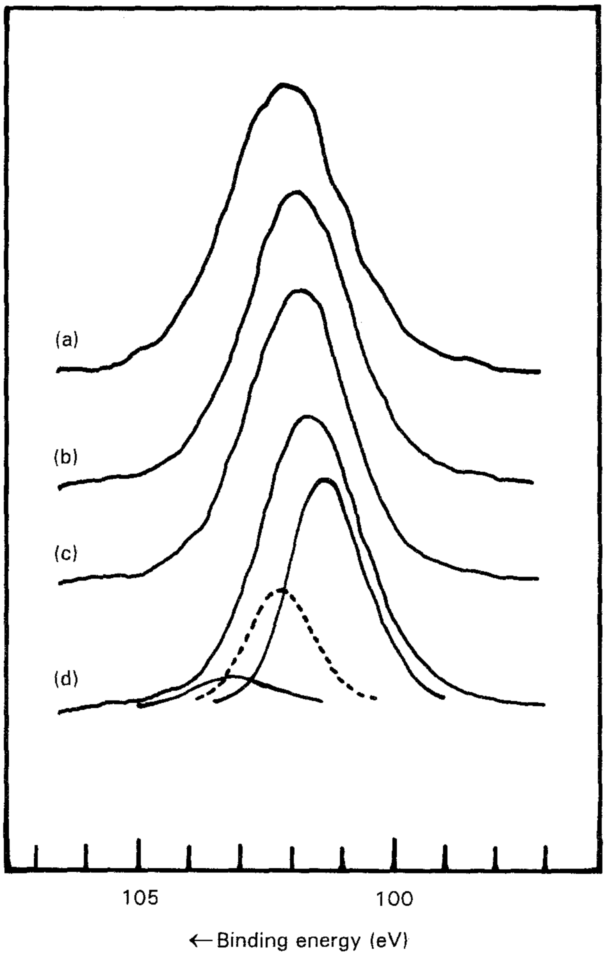


*Figure 8* XPS spectra (Si 2p) of (a) 400 °C pyrolysed, (b) 500 °C pyrolysed, (c) 600 °C pyrolysed, and (d) 1000 °C pyrolysed perhydropolysilazane.

to the amorphous nature of silicon nitride, which is not apparent in the polymer and the 400 °C pyrolysed sample. This result suggests that Si–N structure is built from 400–600 °C and the formation is completed between 600 and 1000 °C. The product obtained by pyrolysis of perhydropolysilazane at 1000 °C in ammonia is considered to be amorphous, consisting of silicon, nitrogen, oxygen and hydrogen.

The pyrolysed samples were also characterized by XPS (Fig. 7). The pyrolysed sample is mainly made of silicon, nitrogen and oxygen. A semiquantitative analysis of the chemical bonds is possible by using the deconvolution of the Si 2p peak of the high-resolution spectra (Fig. 8). The Si 2p peak can be analysed on the basis of three components: the first at 101.4 eV is assigned to Si–N bonds [25], the second at 103.5 eV is assigned to Si–O bonds [26], and the third at an intermediate energy of 102.1 eV could be assigned to silicon atoms bound to both nitrogen and oxygen. From 400–600 °C, the peak shifts from 102.0 eV to 101.7 eV, whereas from 600–1000 °C, the peak does not shift. In the temperature range from 400–600 °C, the increase of the Si–N component is due to the formation of an Si–N three-dimensional network. From 600–1000 °C, the formation of an amorphous solid is completed. These results are in good agreement with the results of elemental analyses, TGA, XRD, IR and $^{29}$Si CPMAS–NMR measurements.

Taki *et al.* have proposed [27] that nitridation of polycarbosilane begins from 500 °C and is completed at 700 °C from $^{29}$Si and $^{13}$C NMR spectra. Burns and Chandra [28] have reported that the most effective temperature for nitridation and carbon removal for polycarbosilane, hydridopolysilazane, methylchloropolysilane and silsesquiazanes is in the range 673–873 K which has been derived from the elemental composition. This temperature range is consistent with our result for perhydropolysilazane. The difference between the results of Taki *et al.* [27] and of Burns and Chandra [28] and ours might be due to the pyrolysis conditions and the particle size of the polymer powder. Because carbon removal is rendered unnecessary for perhydropolysilazane, nitridation of perhydropolysilazane seems to be more controllable than that of carbon-containing preceramic polymers.

## 4. Conclusion

The pyrolysis of perhydropolysilazane has been studied up to 1000 °C in anhydrous ammonia. The pyrolysis mechanism involves three main steps. (1) Below 400 °C, an evaporation of residual solvent is the main reason for the weight loss. The structure of the polymer does not change markedly. (2) From 400–600 °C, ammonia reacts with Si–H bonds in the polymer to build an Si–N three-dimensional network. The solid with polymer-like structure converts into a solid with $Si_3N_4$-like structure. (3) From 600–1000 °C, the formation of hydrogenated solid is completed. The structure of the solid does not change markedly. The composition of this solid is revealed to be close to $Si_3N_4$. It is important to control the nitridation step, from 400–600 °C, to achieve better control of the composition, microstructure and properties of the final ceramics.

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*Received 7 January 1993*
*and accepted 21 March 1994*