JOURNAL OF MATERIALS SCIENCE **34** (1999) 2199 – 2206

Gas-phase synthesis of amorphous silicon nitride — reaction paths and powder characteristics

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The gas phase reaction between $SiCl_4$ and NH_3 is investigated in the temperature range between 525 and 800 °C at atmospheric pressure and at conditions typical for powder synthesis. By means of mass spectrometric in-situ measurements it was possible to detect the gaseous compounds H_2NSiCl_3, $H_2NSiCl_2NH_2$, $Cl_3SiNHSiCl_3$, $NH_2Cl_2SiNHSiCl_3$, $(SiCl_2NH)_3$ and $Si_3(NH)_3Cl_5NH_2$. The reactions taken place in the gas phase are very fast and result in the formation of a fine, chlorine containing product. Powders sampled at a reaction temperature of 800 °C have an average molar ratio Si : N : Cl of 1 : 1, 33 : 0.28. Based on the proved gaseous intermediates and the composition of the powders reaction paths resulting in the formation of powders are derived. α-Si_3N_4 powders with a high sintering activity are obtained after thermal dechlorination of the synthesis products in ammonia atmosphere followed by a crystallization process between 1200 and 1500 °C. © *1999 Kluwer Academic Publishers*

1. Introduction

Silicon nitride ceramics are promising materials for high temperature applications. The achievement of ceramics combining high hardness, wear resistance, low density, chemical stability and high mechanical resistance requires powders with high purity, uniform crystal size, low agglomeration and a high α-Si_3N_4 content [1, 3]. Using silicon nitride powders of improved purity result in better high temperature properties [2]. In this way, silicon nitride powder production by gas phase reaction of $SiCl_4$ with NH_3 has been seen for many years as an alternative to conventional carbothermal or direct nitridation processes. Depending on temperature, molar ratio $SiCl_4/NH_3$ and retention time, the reaction leads to amorphous products of various composition. Mainly chlorine containing powders are formed. Only a high temperature gas-solid separation offers the possibility to prevent the formation of NH_4Cl as a byproduct. Thus, additional processing steps are necessary to separate NH_4Cl and to produce chlorine free, amorphous silicon nitride or silicon imide nitride. Crystalline α-Si_3N_4 is obtained by thermal treatment of these compounds at temperatures above 1200 °C [3–5]. For the development of favourable synthesis conditions it is important to characterize the reactions taking place in the gas phase. However, only investigations at conditions typical for CVD processes are known so far. Mass spectrometric measurements of the $SiCl_4$-NH_3-reaction at temperatures and pressures in the range of 800–1200 °C and up to 106 mbar indicated the occurrence of silicon containing species in the gas phase [6]. A reaction mechanism which is in agreement with that of the reaction of $SiCl_4$ with NH_3 at temperatures below 0 °C was proposed. But these investigations [7] were carried out with an excess of ammonia and thus it is impossible to conclude reaction paths favourable for powder production.

This paper describes mass spectrometric investigations to detect gaseous intermediates formed by the reaction between $SiCl_4$ and NH_3 at elevated temperatures and atmospheric pressure and possible reaction paths leading to powder formation. The characteristics of powders precipitated at reaction temperature are described. Further processing steps leading to α-Si_3N_4 are summarized.

2. Experimental

The main part of the developed experimental setup is a vertically positioned hot wall quartz reactor with a special gas input system and a connection to a quadrupol mass spectrometer (Fig. 1). The reactor has a length of 300 mm and an inner diameter of 20 mm at the top and 35 mm diameter and 450 mm length at the bottom. It was heated by an electrical resistance heating wire. Temperature controller and thermocouple were used for temperature control and measurement. The reactants were led into the tube by a special gas input system. The inner quartz tube was used simultaneously for $SiCl_4$ (99.999%) and N_2 (99.999%) gas input whereas

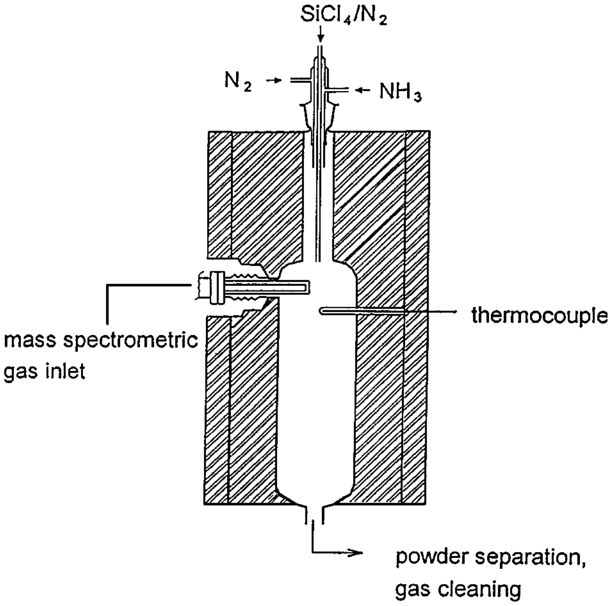

Figure 1 Experimental setup.

the outer tube was used only for N_2. The middle tube served for NH_3 (99.96%; additional dried by KOH) input. Ammonia and N_2 were premixed and warmed up until they reached the end of the inner $SiCl_4$ tube.

The distance between the $SiCl_4$ input tube and the QMS gas inlet was 15 mm. It followed from the short distance that retention time all over the studied temperature range was lower than 0.1 s at a total flow of 3.5 mol/h. The used QMS (type QMG 421 made by BALZERS AG) enabled measurements in the mass range up to 512 m/e. The apparatus consists mainly of

- a two-stage gas inlet (nozzles of boron nitride with orifices of 0.1 mm in each case),
- a (200 × 8) mm molybdenum quadrupole mass filter,
- a cross-beam ion source,
- a detector (optionally 90°-off axis multiplier (SEM) or Faraday cup and
- a pumping unit (two turbo molecular pumps with two backing diaphragma vacuum pumps).

For identification of intermediates SEM was always used. The energy for ionization was kept constant at 70 eV.

All gas flows were controlled by means of mass flow controllers (MKS instruments). The total flow rate varied in the range of 150–300 cm^3/min for NH_3 and was 1000 cm^3/min for N_2. $SiCl_4$ was dosed by a peristaltic pump in such a way that the liquid was pumped continuously into a heated boiler and after that was transported to the reactor in a heated pipe with nitrogen as carrier gas. The amount of $SiCl_4$ was controlled both by the pump parameters and a burette which was discontinuously filled with liquid $SiCl_4$. A variation of the $SiCl_4/NH_3$ ratio could be reached by increasing the $SiCl_4$ volume flow while the other flows are kept constant.

To identify the formed intermediates, the measured intensity distribution was compared with the intensity distribution which can be expected theoretically. For a compound of the formal composition $Si_wCl_xN_yH_z$ the theoretical intensity distribution was calculated on the basis of the natural frequency of isotopes resulting from solution of the term $({}^{28}Si + {}^{29}Si + {}^{30}Si)^w \cdot ({}^{35}Cl + {}^{37}Cl)^x \cdot ({}^{14}N + {}^{15}N)^y \cdot {}^1H^z$. The peak of the lightest isotopic combination in an isotopic pattern is named basic peak.

3. Results and discussion

The reaction between $SiCl_4$ and NH_3 is very fast, and gaseous intermediates can be detected only by direct measurement on the boundary between the $SiCl_4/N_2$ and the NH_3 gas flow. This technique has the disadvantage, that the real mixing ratio between $SiCl_4$ and NH_3 is unknown at the place of measurement. However, only this method allows a detection of the formed gaseous intermediates. Because the intensities of all silicon containing species decrease with rising temperature, the identification of intermediates is described on the basis of the experiments at 525 °C. The formation of the following silazanes was proved [8].

3.1. Aminotrichlorosilane (ATCS)—Cl_3SiNH_2

Aminotrichlorosilane is the first compound formed by the reaction of $SiCl_4$ with NH_3 (Equation 1).

$$SiCl_4 + NH_3 \rightarrow Cl_3SiNH_2 + HCl \qquad (1)$$

The basis peak of the molecule ion lies at 149 amu and characterises the molecule ion $Cl_3SiNH_2^+$ (Fig. 2). It is no problem to assign mass numbers at 149–155 amu to ATCS, because the existence of other fragment species in this mass range can be excluded. The isotopic distribution of the $ATCS^+$ molecule ion is summarized in Table I.

3.2. Diaminodichlorosilane (DADCS)—$Cl_2Si(NH_2)_2$

The occurrence of the mass peak 130 amu in a characteristic isotopic pattern (before the typical $SiCl_3^+$-pattern) proved the formation of diaminodichlorosilane, because a fragmentation path of other species cannot lead to this mass number (Fig. 2). Further fragment ions cannot be used for identification due to the possibility of their formation as a result of fragmentation of other compounds.

TABLE I Comparison of calculated and measured data for $ATCS^+$ molecule ion

Mass (amu)	Intensity (calc.)	Intensity (exp. data)
149	99.4	99
150	5.4	6
151	100	100
152	5.3	5
153	34.6	35
154	1.7	1
155	4.4	6

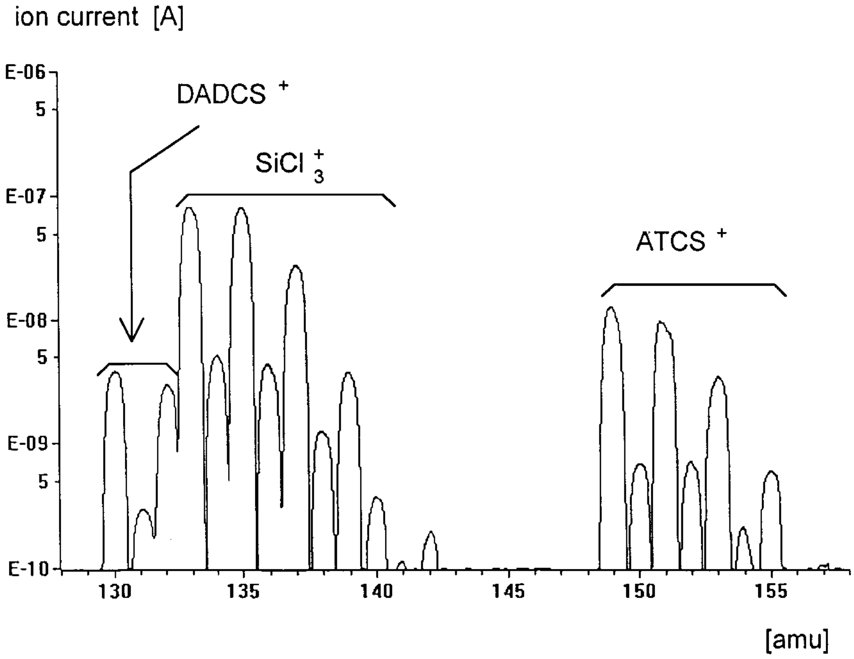

Figure 2 Mass spectrum of the $SiCl_4$ ammonolysis at 525 °C.

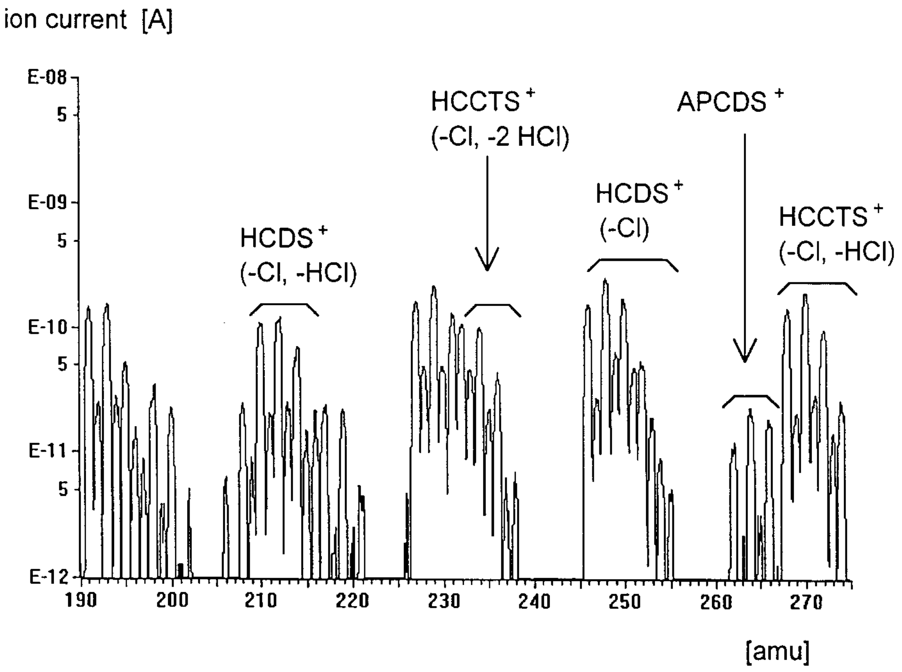

Figure 3 Mass spectrum of the $SiCl_4$ ammonolysis at 525 °C.

3.3. Hexachlorodisilazane (HCDS)—Cl_3Si-NH-$SiCl_3$

Hexachlorodisilazane is the first representative of chain-like silazanes. The basis peak of the HCDS molecule ion appears at 281 amu followed by a 283 amu mass peak, both with low intensities (Fig. 4). Further peaks of the isotopic pattern are overlapped by the APCCTS(-Cl)$^+$-fragment ion (especially at 285 amu). In accordance with literature data for pure HCDS [9], the formation of the fragment ions HCDS(-Cl)$^+$ and HCDS(-Cl, -HCl)$^+$ was proved at 246 and 210 amu (Fig. 3). The intensities are in good accordance with theoretical isotopic distribution (Table II). The

TABLE II Comparison of calculated and measured data for HCDS(-Cl)$^+$ fragment ion

Mass (amu)	Intensity (calc.)	Intensity (exp. data)
246	59.2	59
247	6.2	8
248	100	100
249	10.3	15
250	68.9	66
251	6.9	10
252	24.6	21
253	2.4	4
254	4.7	3

formation of the fragment ion $\mathrm{Cl_3SiNHSiCl_2^+}$ can be explained by a reaction according to Equation 2.

$$\mathrm{Cl_3SiNHSiCl_3^+} \rightarrow \mathrm{Cl_3SiNHSiCl_2^+} + \mathrm{Cl} \tag{2}$$

The peak intensities at mass number 249, 251 and 253 amu are slightly higher than the theoretical values. It is assumed, that the reason is a small overlapping effect of the APCCTS(-Cl,-HCl)$^+$ fragment ion.

3.4. Aminopentachlorodisilazane (APCDS)—$\mathrm{Cl_3Si\text{-}NH\text{-}SiCl_2NH_2}$

The mass number at 262 amu is assigned to the basic peak of the APCDS$^+$ molecule ion (Fig. 3). An isotopic pattern characteristic for the $\mathrm{Si_2Cl_5}$-system is obtained. Overlapping with signals resulting from a fragmentation based on hexachlorocyclotrisilazane was visible beginning at 268 amu. Thus, only the signals at 262, 264 and 266 amu can be used for aminopentachlorodisilazane identification. Two intensive fragment ions, formed according to Equations 3 and 4, are assigned to APCDS, too.

$$\underset{262\,\text{amu}}{[\mathrm{Cl_3SiNHSiCl_2NH_2}]^{+\bullet}} \rightarrow \underset{227\,\text{amu}}{[\mathrm{Cl_2SiNHSiCl_2NH_2}]^{+}} + \mathrm{Cl}^{\bullet} \tag{3}$$

$$\underset{227\,\text{amu}}{[\mathrm{Cl_2SiNHSiCl_2NH_2}]^{+}} \rightarrow \underset{191\,\text{amu}}{[\mathrm{ClSiNSiCl_2NH_2}]^{+}} + \mathrm{HCl} \tag{4}$$

3.5. Hexachlorocyclotrisilazane (HCCTS)—$\mathrm{(SiCl_2NH)_3}$

Mass peaks at 339–347 amu—the last mass signals in the detectable range up to 512 amu—were assigned to the molecule peak of HCCTS (Fig. 4). Total isotopic pattern at 339–347 amu conforms to the theoretical expected values of an $\mathrm{Si_3Cl_6N_3H_3}$-system (Table III). Due to the absence of overlapping effects, there is good agreement between the theoretical and the measured intensity distribution.

TABLE III Comparison of calculated with measured data for HCCTS$^+$ molecule ion

Mass (amu)	Intensity (calc.)	Intensity (exp. data)
339	48.7	46
340	8.0	7
341	100	100
342	16.1	14
343	87.2	84
344	13.7	10
345	41.9	37
346	6.4	4
347	12.0	7

In addition to the HCCTS$^+$ molecule peak, fragment ion peaks at 304, 268 and 232 amu were assumed to belong to HCCTS. The formation takes place according to Equations 5–7.

$$\underset{339\,\text{amu}}{[\mathrm{Si_3Cl_6(NH)_3}]^{+\bullet}} \rightarrow \underset{304\,\text{amu}}{[\mathrm{Si_3Cl_5(NH)_3}]^{+}} + \mathrm{Cl}^{\bullet} \tag{5}$$

$$\underset{304\,\text{amu}}{[\mathrm{Si_3Cl_5(NH)_3}]^{+}} \rightarrow \underset{268\,\text{amu}}{[\mathrm{Si_3Cl_4N(NH)_2}]^{+}} + \mathrm{HCl} \tag{6}$$

$$\underset{268\,\text{amu}}{[\mathrm{Si_3Cl_4N(NH)_2}]^{+}} \rightarrow \underset{232\,\text{amu}}{[\mathrm{Si_3Cl_3N_2(NH)}]^{+}} + \mathrm{HCl} \tag{7}$$

The HCCTS(-Cl)$^+$ ion species with a basic peak at 304 amu exist predominantly. This confirms results obtained in mass spectrometric investigations of pure HCCTS [10].

3.6. Aminopentachlorocyclotrisilazane (APCCTS)—$\mathrm{Si_3Cl_5(NH)_3NH_2}$

Before the HCCTS molecule peak in the mass spectra, a signal group appears at 320–327 amu whose intensity

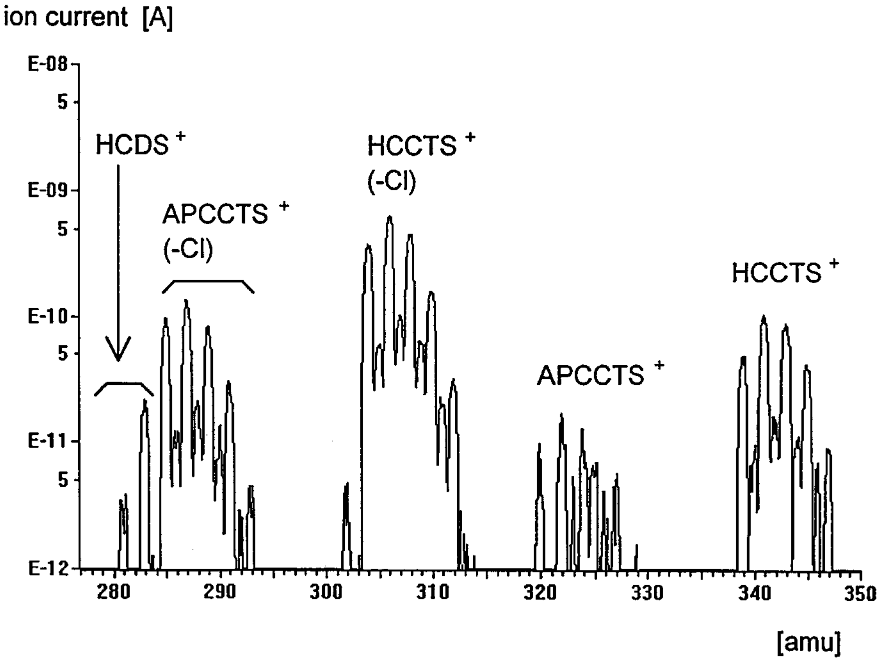

Figure 4 Mass spectrum of the $\mathrm{SiCl_4}$ ammonolysis at 525 °C.

is one order of magnitude lower (Fig. 4). The difference between the two basic peaks is 19 amu. It is impossible to explain this mass difference by fragmentation of HCCTS. Therefore, it can be assumed that these peaks are due to another molecule ion, namely that of APCCTS. The isotopic distribution conforms with a Si_3Cl_5-system at mass numbers 320, 322 and 324 amu, but not so well at 325 and 327 amu. Fragmentation of APCCTS according to Equations 8 and 9 results in peak groups beginning at 285 amu and at 249 amu.

$$\underset{320\,\text{amu}}{[Si_3Cl_5(NH)_3NH_2]^{+\bullet}} \rightarrow \underset{285\,\text{amu}}{[Si_3Cl_4(NH)_3NH_2]^{+}} + Cl^{\bullet} \tag{8}$$

$$\underset{285\,\text{amu}}{[Si_3Cl_4(NH)_3NH_2]^{+}} \rightarrow \underset{249\,\text{amu}}{[Si_3Cl_4N(NH)_2NH_2]^{+}} + HCl \tag{9}$$

Fig. 5 represents the curve of the relative intensities of signals typical for the different compounds as a function of temperature. Here, the relative intensity characterises the intensity of the signal with respect to that of the ^{14}N signal. The rising HCl content reflects the increase of the degree of conversion of $SiCl_4$ with increasing temperature. This is confirmed by the decrease of the ammonia signal at 17 amu. Aminotrichlorosilazane and Diaminodichlorosilazane are the predominate intermediates. All other compounds have intensities which are 1 to 3 orders of magnitudes lower. The decreasing contents of all silazanes show the acceleration of the reaction with increasing temperature. Only small amounts of HCDS and APCDS are present in the gas phase. The cyclic compounds HCCTS has higher concentrations, indicating a higher stability in the investigated temperature range. It is important to note that the gas phase contains, even at high ammonia contents and great retention times, unreacted $SiCl_4$ while no or only extremely small amounts of gaseous silazanes can be detected. Ammonia reacts with the formed gaseous intermediates or with the solids rather then with $SiCl_4$. The same was found for reactions of $SiCl_4$ with ammonia at low temperatures [7].

Based on the results of the mass spectrometric investigations the following reaction path is probable for $SiCl_4$ ammonolysis in the temperature range between 525 and 800 °C (Fig. 6):

$SiCl_4$ reacts with NH_3 producing Cl_3SiNH_2. There are two paths for a further reaction. The reaction with $SiCl_4$ leading to the formation of $SiCl_3NHSiCl_3$ or the reaction with ammonia producing $SiCl_2(NH_2)_2$. No formation of $SiCl(NH_2)_3$ or $Si(NH_2)_4$ was detected.

It is known, that hexachlorodisilazane decomposes at temperatures above 300 °C to solids [7, 11]. This means, it is a metastable compound in the investigated temperature range. Only high $SiCl_4$ contents or low reaction temperatures should lead to the preferred presence of hexachlorodisilazane in the gas phase. It can be expected that a fast further reaction with ammonia resulting in the formation of aminopentachlorodisilazane takes place. However, aminopentachlorodisilazane can be formed also by reactions both of $SiCl_2(NH_2)_2$ and $SiCl_3NH_2$. The low concentrations of APCD indicate a fast further reaction.

The reaction of known dihalosilanes (R_2SiCl_2) with ammonia results in the formation of silylamines, cyclosilazanes or polysilazanes depending on the used reactants and the reaction conditions [12, 13]. The formation of ring systems with 3 or 4 Si atoms is preferred. The proved presence of hexachlorocyclotrisilazane in the gas phase indicates, that $SiCl_2(NH_2)_2$ shows a reaction behaviour equivalent to that of known dihalosilanes. However, links for a formation of gaseous 4-ring systems were not found. Amiopentachlorodisilazane acts as an intermediate in the process of hexachlorocyclotrisilazane formation according to Fig. 6. Aminopentachlorocyclotrisilazane can be formed by reactions both of hexachlorocyclotrisilazane with ammonia and aminopentachlorodisilazane with diaminodichlorosilane. As mentioned above, the reaction in the gas phase is very fast and results in the formation of amorphous, chlorine containing powders with an uniform spherical shape and a particle size $<1\ \mu m$.

Table IV contains the results of the chemical analysis of powders sampled in the reaction zone. These powders were precipitated at 800 °C and separated from

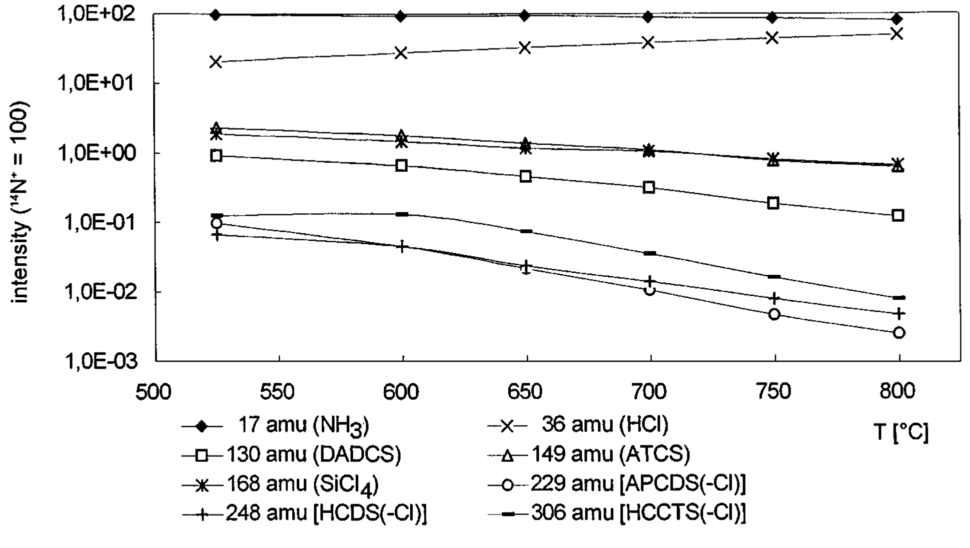

Figure 5 Temperature dependence of signal intensities of the formed gaseous silazanes.

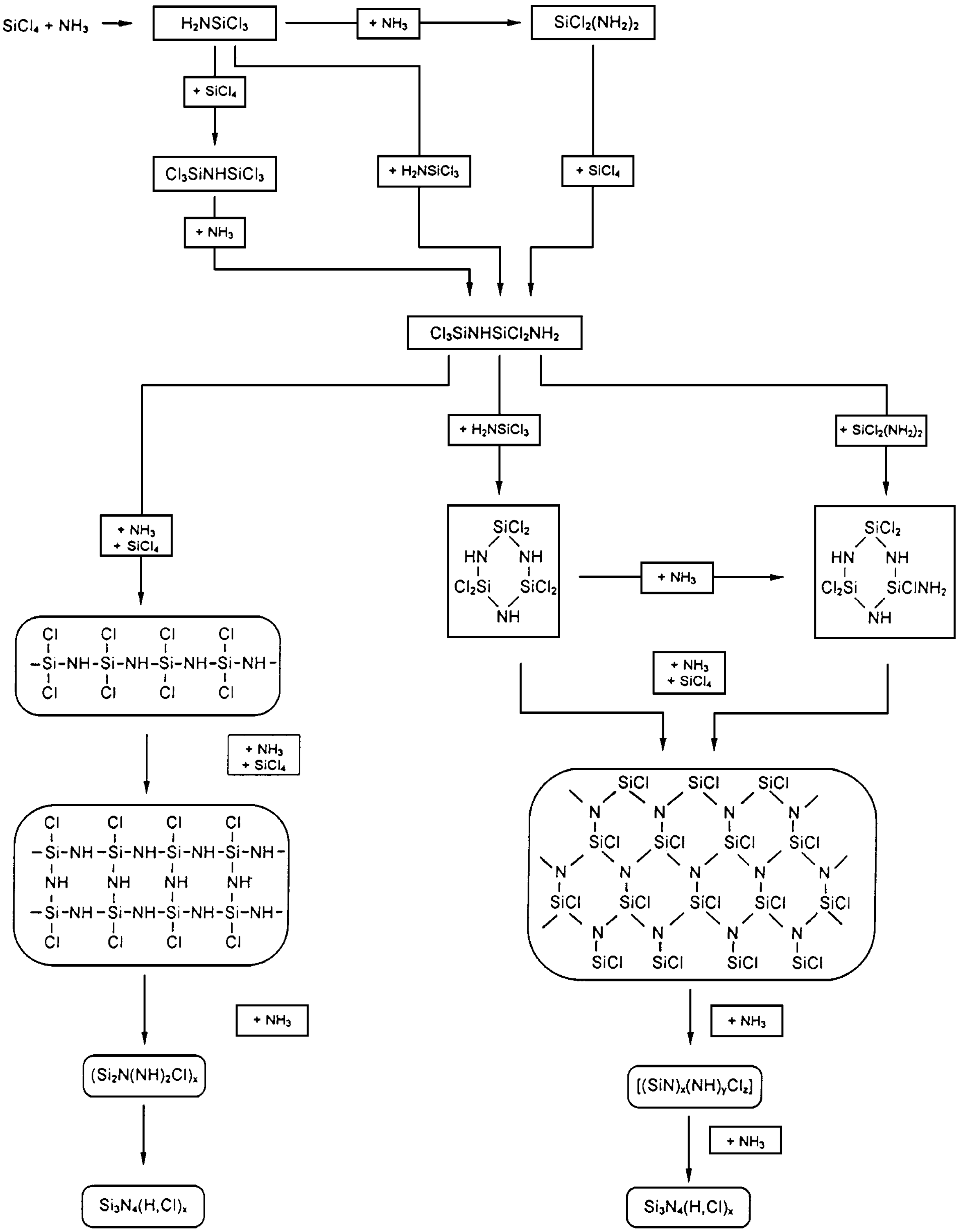

Figure 6 Reaction paths resulting in the formation of amorphous silicon nitrides.

the reaction system after cooling to room temperature. There are no differences in the powder composition as a function of the $SiCl_4/NH_3$ input ratio. The average composition is 47.24 wt% Si, 31.2 wt% N, 16.67 wt% Cl [14]. This is equivalent to a molar ratio Si : N : Cl of 1 : 1.33 : 0.28. The IR-spectra of all powders are identical. Fig. 7 represents a typical spectrum. Signals indicating Si-Cl groups are not visible. However, the Si-Cl vibrations lie in an area which is also characterised by the occurrence of the signals of Si-N groups. Overlapping can be possible and thus, detection of the Si-Cl-signal becomes impossible. The signal at 1400 cm^{-1} indicates traces of NH_4Cl. This was probably formed during the cooling process of the reaction system from HCl and NH_3 traces present.

Thermal treatment of the powders in ammonia atmosphere leads to amorphous, chlorine free products. The formation of powders containing a high α-Si_3N_4

TABLE IV Composition of powders sampled at 800 °C

Molar input ratio $SiCl_4/NH_3$	wt % Si	wt % N	wt % Cl	mol Si	mol N	mol Cl
3/5.5	46.21	32.71	15.33	1	1.42	0.26
3/5.9	46.62	30.12	18.3	1	1.30	0.31
3/6.0	46.53	30.47	17.11	1	1.31	0.29
3/6.1	46.62	30.12	18.3	1	1.30	0.31
3/6.15	46.53	30.47	17.11	1	1.31	0.29
3/6.26	47.59	31.66	17.15	1	1.33	0.29
3/6.3	46.37	29.25	19.61	1	1.27	0.34
3/6.71	46.83	31.96	15.69	1	1.37	0.27
3/7.1	46.1	29.16	19.61	1	1.27	0.34
3/7.8	48.85	31.31	14.21	1	1.29	0.23
3/8.2	49.25	32.56	14.04	1	1.33	0.23
3/8.6	49.38	34.62	13.55	1	1.41	0.22

content is achieved by an additional crystallization process at temperatures between 1200 and 1500 °C. The obtained materials have a high sintering activity resulting in Si_3N_4 ceramics parts with a room temperature strength of about 1000 MPa [15].

4. Conclusions

Based on the proved gaseous intermediates and the composition of the powders sampled in the reaction zone the following two reaction paths resulting in the formation of powders are possible (Fig. 6):

- Further reactions of aminopentachlorodisilazane resulting in the formation of solid polysilazanes such as $(Cl_2SiNH)_x$ and $(Si_2(NH)_3Cl_2)_x$ and their thermal decomposition to $Si_3N_4(H, Cl)_x$.
- Formation of cyclic compounds such as $(ClSiN)_x$ and subsequent Cl substitution caused by reactions with gaseous ammonia.

The first reaction path is in accordance with the ammonolysis of $SiCl_4$ at low temperature. However, the formed solid polysilazanes undergo even in the reaction zone thermal decomposition processes and further reactions with ammonia. These reactions are similar to that, described for the thermal decomposition of $(Si(NH)_2)_n/NH_4Cl$ mixtures [11].

Due to the increased formation of cyclic gaseous compounds with increasing temperature it is probable that high temperatures favour the second reaction path. After the formation of the cyclic compound $(ClSiN)_x$, which was firstly described in [16], gradual further reaction with unreacted ammonia results in the formation of compounds with the formal composition $Si_3N_4(H, Cl)_x$.

Both reaction paths are characterized by overlapping of reactions taken place in the gas phase and further reactions of the formed solids. Unreacted ammonia is precipitated as NH_4Cl after cooling of the gases to room temperature. In conclusion, it is expected that the preferred reaction path strongly depends on the concrete reaction conditions such as temperature, retention time and total amounts of $SiCl_4$ and NH_3 in the gas phase.

Gas phase ammonolysis of $SiCl_4$ at elevated temperatures provides an excellent opportunity to produce

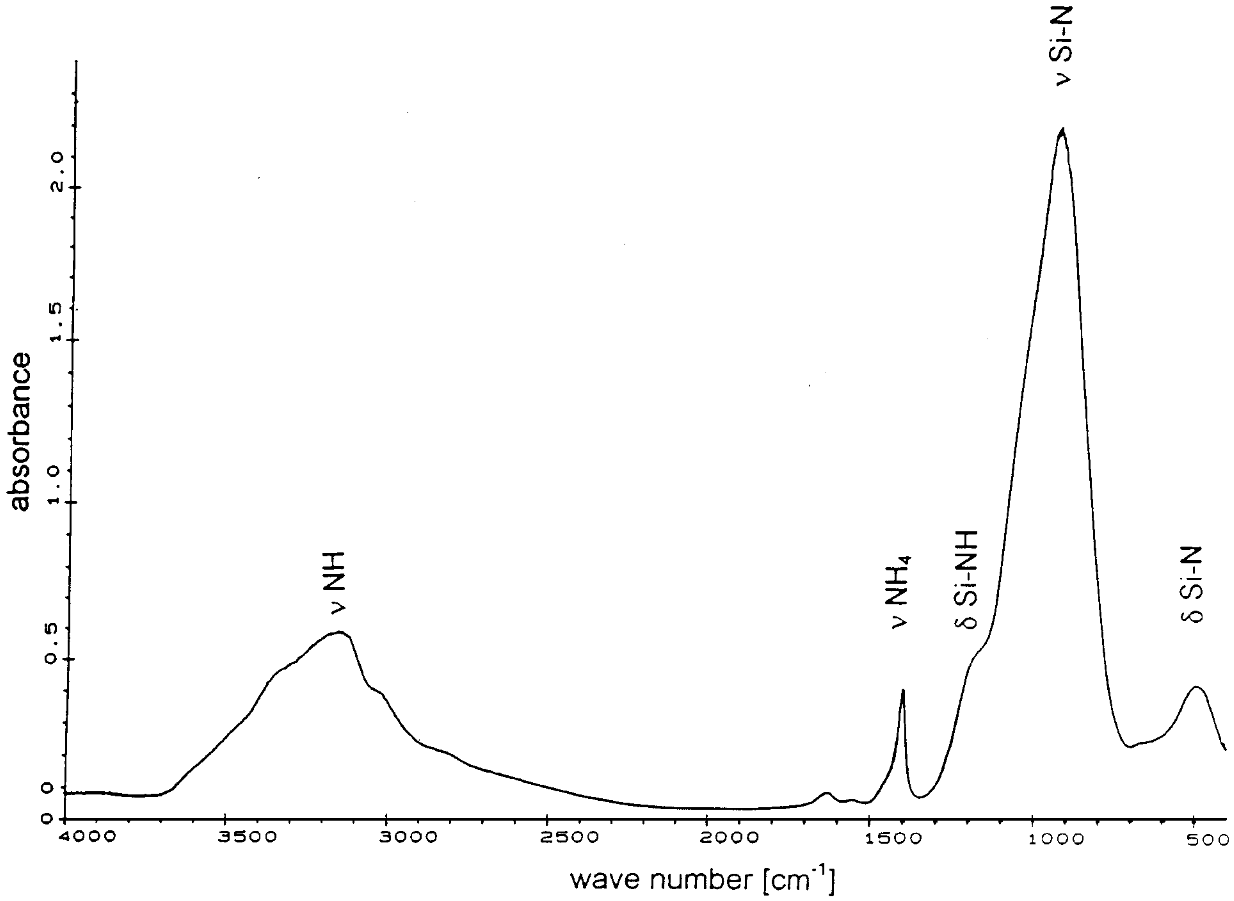

Figure 7 IR-spectra of a powder sampled at 800 °C.

high quality α-Si_3N_4 powders. That requires thermal treatment of the chlorine containing synthesis product in ammonia atmosphere and a crystallization process in the temperature range between 1200 and 1500 °C.

Acknowledgement

This work was supported by the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie.

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Received 15 September 1997
and accepted 12 November 1998