Journal of the European Ceramic Society 21 (2001) 947–958

www.elsevier.com/locate/jeurceramsoc

Synthesis of α-silicon nitride powder by gas-phase ammonolysis of CH_3SiCl_3

Gerald Ziegenbalg [a,*], Ulrich Breuel [a], Eila Ebrecht [b], Horst Holldorf [a], Reinhold Brink [c]

[a] *Freiberg University of Mining and Technology, Institute of Technical Chemistry, D-09596 Freiberg, Germany*
[b] *Freiberg University of Mining and Technology, Institute of Analytical Chemistry, D-09596 Freiberg, Germany*
[c] *Bayer AG, Werk Uerdingen, Geschäftsbereich Chemikalien, Geschäftsfeld Bayer Solar, Rheinuferstraße 7-9, D-47829 Krefeld-Uerdingen, Germany*

Received 15 June 2000; received in revised form 6 September 2000; accepted 21 September 2000

Abstract

An alternative to silicon tetrachloride mostly used for silicon nitride production by gas phase ammonolysis is CH_3SiCl_3. While powders resulting from ammonolysis of CH_3SiCl_3 at room temperature have a constant composition, high temperature reactions result in materials showing a strong dependence on the reaction conditions. Increasing reaction temperature leads to powders with increasing silicon content, while the chlorine content decreases. Mixtures of non stoichiometric, chlorine and carbon containing silicon nitride intermediates and ammoniumchloride are obtained. Gaseous reaction products are HCl, $SiCl_4$, CH_4 and H_2. Quantitative mass spectrometric analysis of the exhaust gases allowed to balance the reactions. ^{29}Si and ^{13}C CP-MAS-NMR powder characterisation was used to deduce the reactions taking place in the gas phase. An overlapping of radical forming and substitution reactions is probable. Dechlorination of the powders in ammonia at 900°C followed by a crystallization step at 1500°C results in crystalline α-Si_3N_4 which is equivalent to powders obtained by ammonolysis of $SiCl_4$.

Keywords: CH_3SiCl_3; Powders-gas phase reaction; Si_3N_4

1. Introduction

Silicon nitride is one of the most interesting materials for the production of advanced ceramics. Mainly processes based on gas phase ammonolysis of reactive silicon compounds have a great potential to produce powders with high chemical purity, low oxygen content and excellent sinterability.[1–3] For large scale powder production, only the use of $SiCl_4$ has been discussed up to now. Other chlorosilanes are used to produce Si–N layers by means of cvd processes. Due to its low costs in respect to other chlorosilanes, CH_3SiCl_3 can be seen as an alternative raw material for silicon nitride powder production. However, only little is known about the reaction behaviour of methyltrichlorosilane with ammonia at elevated temperatures and atmospheric pressure as well as the composition and properties of the resulting products. Especially the question whether carbon free products can be obtained is of great importance.

Methyltrichlorosilane is a preferred starting material for the deposition of SiC layers in chemical vapour deposition processes. Many experimental investigations and thermodynamic calculations concern the mechanism of SiC layer formation.[4–13] The following model is probable:

- cleavage of the Si–CH_3 bond resulting in the formation of methyl radicals and their decomposition into carbon and hydrogen,
- reaction of hydrogen with $SiCl_3$ radicals leading to the formation of elementary silicon and HCl,
- deposition both of carbon and silicon on the surface that has to be treated,
- formation of SiC by a solid–solid-reaction.

The uniformity of the deposited SiC layer as well as its composition is determined by the temperature, the

* Corresponding author. Tel.: +49-3731-39-4374; fax: +49-3731-39-2324.
E-mail address: ziegenb@server.compch.tu-freiberg.de

0955-2219/01/$ - see front matter
PII: S0955-2219(00)00275-2

CH_3SiCl_3 input concentration, the absolute pressure and the presence of additional species such as hydrogen.

In the present study CH_3SiCl_3 ammonolysis is investigated both at room temperature in an unheated tube reactor and at temperatures between 680 and 900°C. The obtained powders are characterised by chemical analysis as well as physico-chemical methods. In connection with a quantitative exhaust gas analysis, it becomes possible to derive reaction paths resulting in powder formation.

2. Experimental

Powder synthesis was carried out in a hot wall reactor (Fig. 1) consisting of an indirectly heated SiSiC tube, a gas-solid cooling unit and a powder collection system.[3,14] The SiSiC tube had a length of 700 mm and an inner diameter of 52 mm. Before starting the synthesis, the temperature profile of the reactor was measured and correlated to the temperature measured at the outer side of the reactor by a Pt-PtRh thermocouple. In the following, all given reaction temperatures characterise the temperature measured inside the reactor, 5 cm below the mixing unit. The reactants are brought into the reaction zone separately. Mixing is achieved by a mixing unit of special design. The average retention time of the gases in the reaction zone after mixing lies between 1 and 2 s.

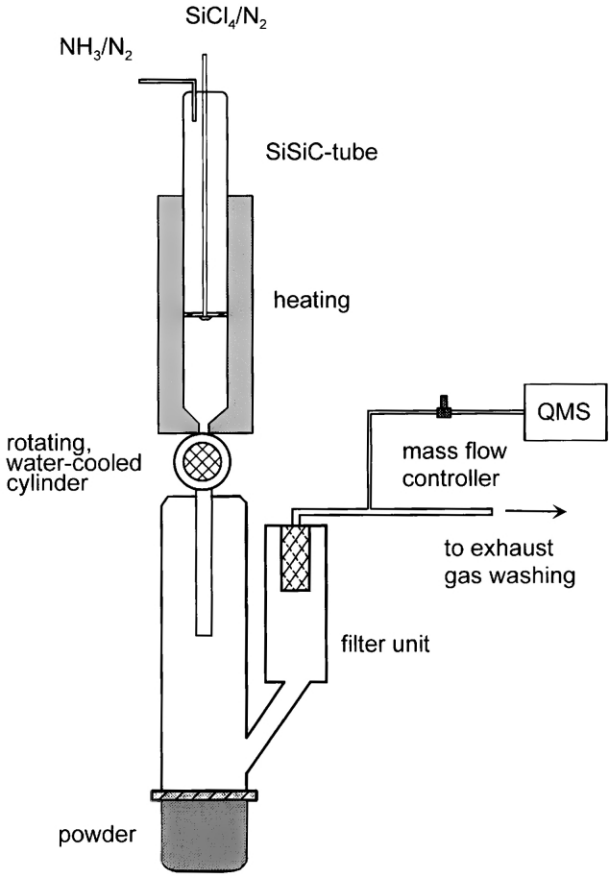

Fig. 1. Experimental setup.

The gas–solid cooling unit is a rotating, water cooled cylinder. The gas–solid mixture leaving the reactor hits on the surface of the cylinder and is cooled rapidly. Both ammoniumchloride and the silicon nitride intermediate are deposited. Powder separation from the cylinder is achieved by a scraper. The main advantage of the cooling unit is that a fast decrease of the gas temperature is achieved preventing the formation of layers of unprecipitated NH_4Cl in the adjacent parts of the apparatus. Powder collection is achieved by sedimentation caused by a reduction in gas velocity and a filter unit. To prevent pollution by oxygen the powders are collected in plastic bags, which are closed after the end of the synthesis and transported in a glove box. Further handling is carried out only under nitrogen atmosphere. A bypass installed in the exhaust gas pipe allows continuous gas sampling for mass spectrometric analysis. The used QMS (type QMG 421 made by BALZERS AG) enables quantitative gas analysis. The system was calibrated with gas mixtures of known composition before starting the measurements.

All gas flows were controlled by means of mass flow controllers (MKS instruments). The total flow rate varied in the range between 0.3 and 2 l/min for NH_3 and between 2 and 6 l/min for N_2. A peristaltic pump served for CH_3SiCl_3 dosage. The amount of CH_3SiCl_3 was controlled both by the pump parameters and by weighting the CH_3SiCl_3 container before and after dosing. Changing the NH_3 gas flow while the other flows were kept constant allowed a variation of the CH_3SiCl_3/NH_3 input ratio.

Powder composition was determined by chemical analysis. Silicon was gravimetrically determined as SiO_2 after fusing a powder sample in a Na_2CO_3/K_2CO_3 mixture. Nitrogen analysis was based on the determination of NH_3 generated during a treatment of the sample with a hot NaOH solution. The Cl-analysis was carried out as potentiometric titration with 0.1 N $AgNO_3$ solution after fusing of the sample in KOH. The analyser Foss–Heraeus CHN–O-Rapid served for carbon analysis.

3. Results

The reaction between gaseous CH_3SiCl_3 and NH_3 in an unheated tube results in the formation of powders with an average composition of 12±1 wt% Si, 25±2 wt.% N, 49±1 wt.% Cl, 5±1 wt.% C, which is equivalent to a molar Si:N:Cl:C ratio of 1:4.2:3.2:1. It is a strong exothermal reaction leading to a drastic temperature increase in the zone in which the reactants come in contact. All ammonia brought into the reaction zone is converted in solid products. XRD investigations

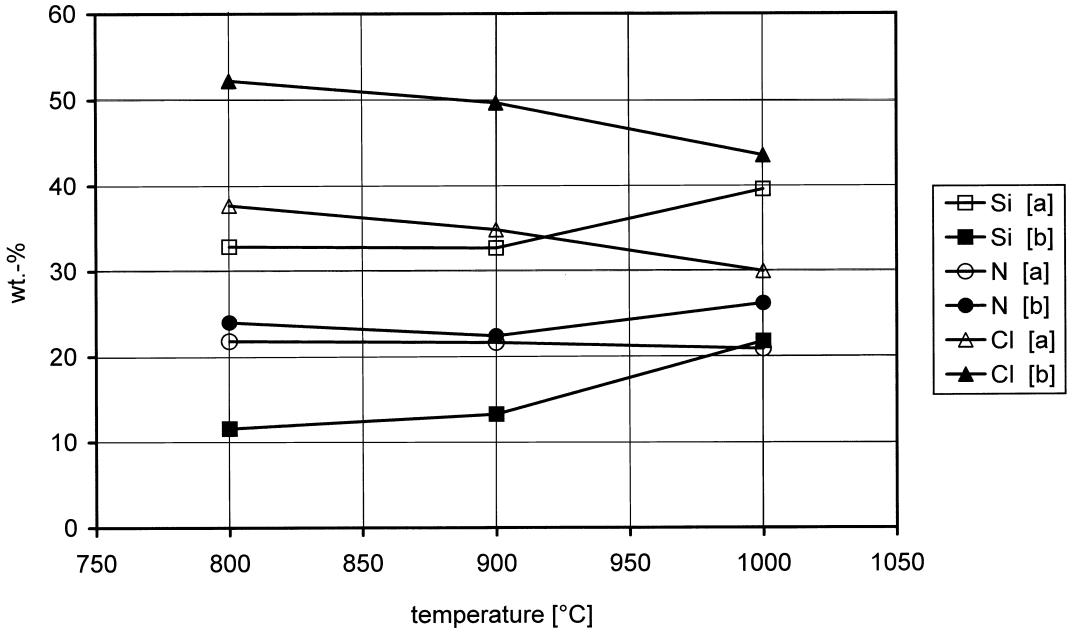

Fig. 2. Composition of powders synthesised between 800 and 1000°C depending on the molar input ratio CH_3SiCl_3/NH_3 (a) 3.49/3; (b) 1.5/3.

Table 1
Composition of synthesis products formed at a reaction temperature of 800°C

Input ratio mol NH_3/3 mol CH_3SiCl_3	Powder composition (wt.%)			
	Si	N	Cl	C
1.75	35.30	17.58	37.22	4.3
2.53	32.88	21.82	37.69	3.6
3.76	25.86	23.44	41.42	2.5
5.04	21.21	24.31	43.92	1.8
6.69	13.95	26.09	52.27	1.0

showed the presence of the low temperature modification of ammoniumchloride (α-NH_4Cl, cubic, CsCl type). Crystalline silicon containing compounds were not formed. The exhaust gases contain the carrier gas nitrogen and unreacted CH_3SiCl_3. HCl is present only in traces. Gaseous carbon containing compounds were not detected. By changes in the input ratio, it is impossible to vary the powder composition. Complete conversion of CH_3SiCl_3 requires an excess of ammonia, e.g. a molar input ratio greater than 1:3.

Thermal treatment of the powder leads to ammonium chloride decomposition in the temperature range between 180 and 350°C. The occurring weight loss of 75% is in accordance with the value calculated on the basis of the chlorine content. Further thermal treatment results at temperatures of 1500°C in the formation of α-Si_3N_4.

The course of CH_3SiCl_3 ammonolysis at high temperatures differs from that in an unheated tube reactor. Typical powder compositions obtained at 800°C are summarized in Table 1. Fig. 2 shows the course of

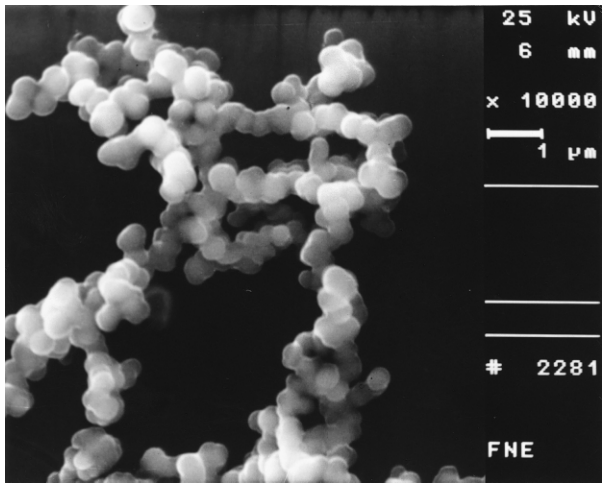

Fig. 3. SEM of a synthesis product produced at 800°C.

powder composition depending on the reaction temperature at two different CH_3SiCl_3/NH_3 input ratios. With increasing amounts of ammonia, powders are formed having lower Si but higher Cl contents. The carbon contents decrease with increasing ammonia. At constant CH_3SiCl_3/NH_3 input ratios, rising reaction temperature results in powders with increasing Si and decreasing Cl contents. The synthesis products are uniform having a spherical shape and an average particle diameter less than 1 μm (Fig. 3). Due to gas–solid separation at room temperature the powders contain α-NH_4Cl as a byproduct. Other crystalline phases cannot be detected by XRD measurements. Thermoanalytical investigations indicate that the NH_4Cl content cannot be calculated on the basis of the chlorine content of the

synthesis products. The mass loss occurring in the first decomposition step between 180 and 350°C is lower than the chlorine content suggests (Table 2). Non stoichiometric chlorine containing intermediates are formed which are similar to powders obtained by ammonolysis of $SiCl_4$ [3,14]. Also, high ammonia input concentrations do not result in the formation of chlorine-free Si–N–C products. After NH_4Cl decomposition, further thermal treatment leads to continuous weight loss. DTA signals showing phase transformations or defined decomposition steps cannot be detected in the temperature range between 350 and 900°C (Fig. 4).

Quantitative analysis of the exhaust gases allowed to balance the reactions leading to powder formation. Apart from unreacted CH_3SiCl_3, HCl, CH_4, $SiCl_4$ and H_2 are present in the gases. Additional test series with mixtures of ammonia and nitrogen showed no significant ammonia decomposition. The hydrogen present in the exhaust gases is a result of thermal decomposition of CH_3SiCl_3. The typical course of exhaust gas composition is shown in Fig. 5. The diagram contains the measured concentrations in vol.%. While — as was expected — the CH_3SiCl_3 and $SiCl_4$ concentrations decrease with rising ammonia contents, the CH_4 concentrations increase. The HCl concentration goes through a maximum. To calculate the degree of conversion of CH_3SiCl_3 or the yields of the gaseous reaction products, it is necessary to include into the calculations the volume change occurring during the reaction. The composition of the exhaust gases can be used to calculate the degree of conversion of CH_3SiCl_3 or the yields of the gaseous reaction products. However, it is necessary to include into these calculations the volume change of the gas phase occurring during the reaction. Two gaseous reactants produce a solid (containing NH_4Cl and the amorphous silicon nitride intermediate) and four gaseous compounds. The volume change depends on the absolute concentrations of the reactants, their molar input ratio and the degree of conversion.

Because nitrogen is an inert compound in the investigated temperature range, input and exhaust amounts must be equal. This means that a factor defined by Eq. (1) can be used for the correction of the measured concentrations [Eq. (2)]. The degree of conversion and the yields defined by Eqs. (3)–(7) (The equations are given in the Appendix) allow a quantitative description of the reactions taken place. Due to the formation of $SiCl_4$ as byproduct the total conversion of CH_3SiCl_3 is not equivalent to the CH_3SiCl_3 conversion into powder and must be regarded separately. The HCl yield characterises the ammoniumchloride and chlorine content of the powder indirectly. An HCl yield of one would indicate the formation of a chlorine-free powder. In the

Table 2
Comparison of calculated and thermogravimetrically determined NH_4Cl contents

Input ratio n $NH_3/3$ CH_3SiCl_3	Cl content of the synthesis product (wt.%)	Thermogravimetric mass loss up to 400°C	Calculated NH_4Cl content on the basis of the Cl-content
1.75	37.22	12.48	56.16
2.53	37.69	20.76	56.87
3.76	41.42	43.43	62.49
5.04	43.92	56.32	66.27
6.69	52.27	67.22	78.86

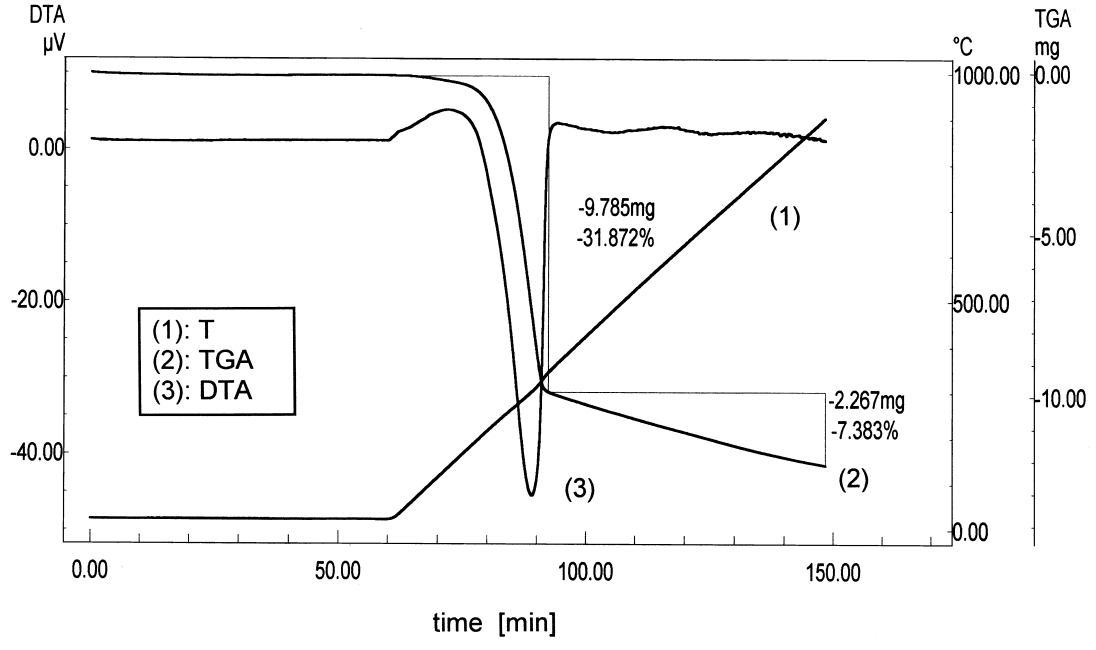

Fig. 4. Characteristic course of the thermal decomposition of synthesis products.

same manner, a CH_4 yield equal to one would show the formation of a product without carbon.

The degree of CH_3SiCl_3 conversion increases with rising reaction temperature (Fig. 6). Above 850°C complete CH_3SiCl_3 conversion occurs. A comparison of Figs. 6 and 7 indicates that the differences between total CH_3SiCl_3 conversion and CH_3SiCl_3 conversion into powder are low at 624 and 650°C. A significant formation of $SiCl_4$ occurs only at temperatures above 800°C. Thus, increasing differences are visible between total CH_3SiCl_3 conversion and conversion into powder. The $SiCl_4$ yield decreases with increasing ammonia content. High ammonia contents are necessary to achieve complete conversion (Fig. 8). To find favourable synthesis conditions it is important to discuss the curve of the HCl yield. With increasing ammonia content the HCl yield

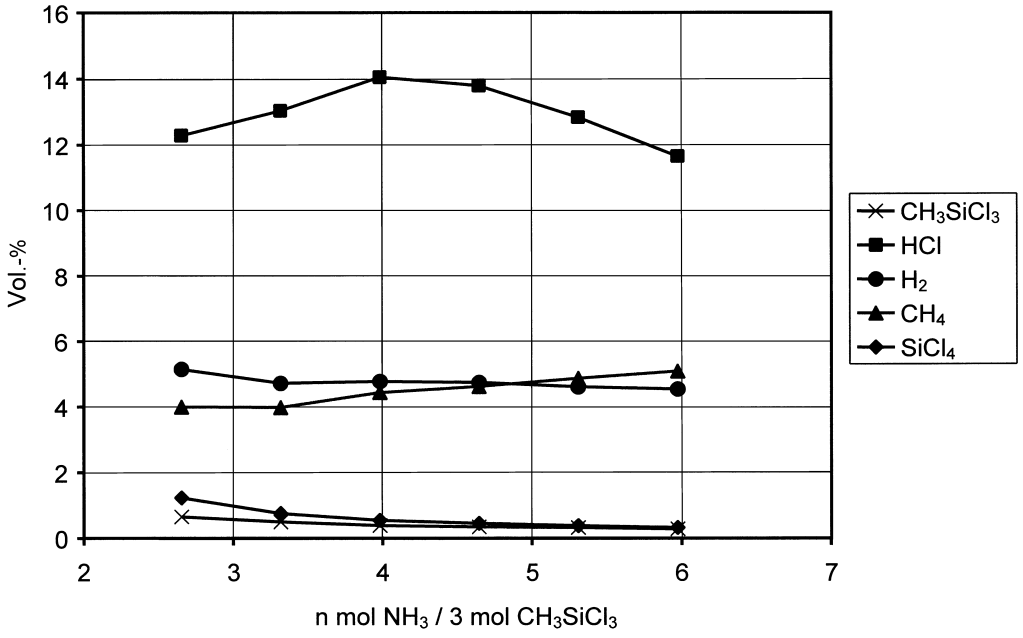

Fig. 5. Course of exhaust gas composition.

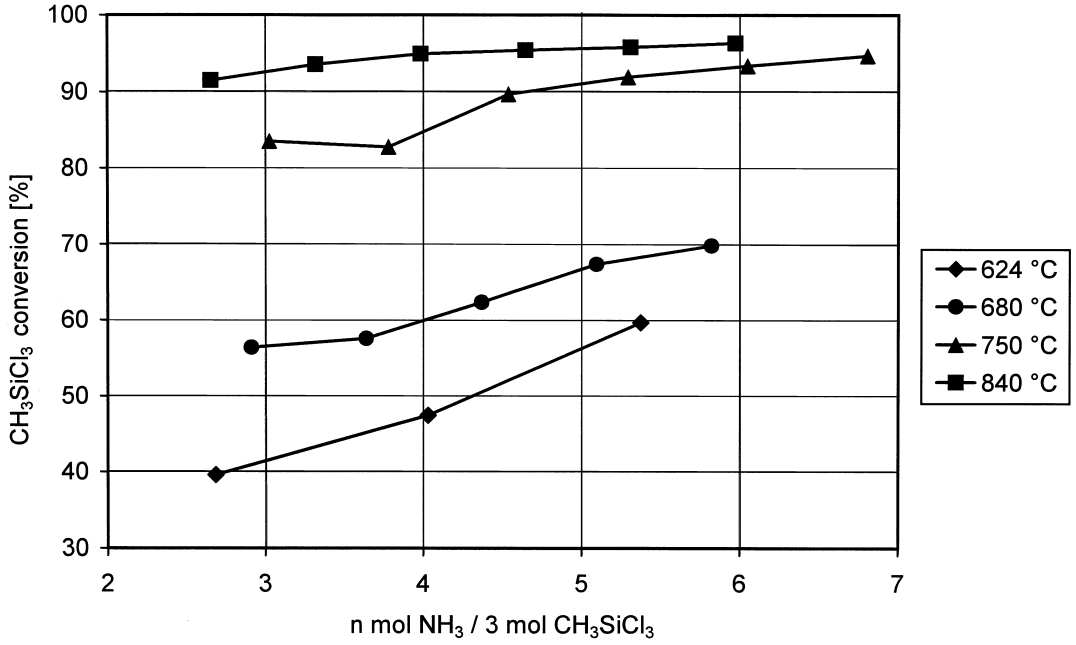

Fig. 6. Degree of CH_3SiCl_3 conversion depending on the reaction temperature and the molar input ratio NH_3/CH_3SiCl_3.

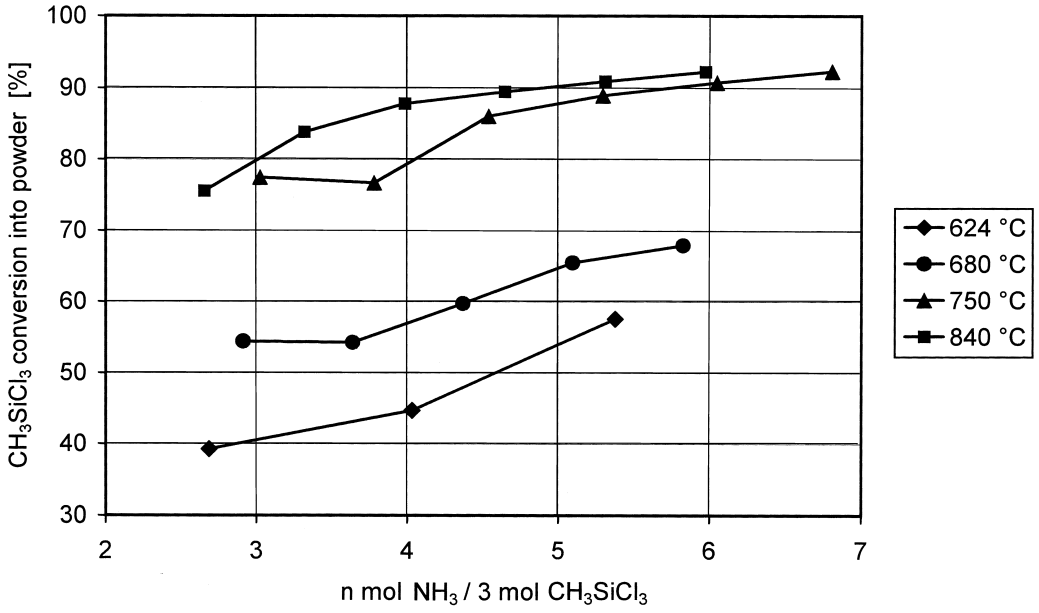

Fig. 7. Degree of CH_3SiCl_3 conversion into powder depending on the reaction temperature and the molar input ratio NH_3/CH_3SiCl_3.

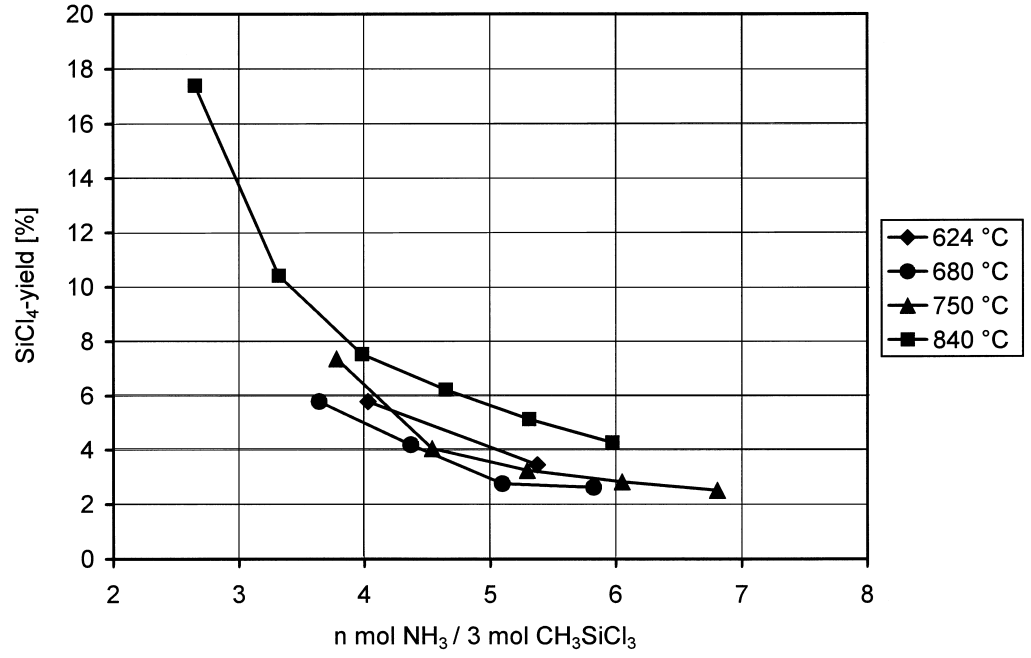

Fig. 8. $SiCl_4$ yield depending on the reaction temperature and the molar input ratio NH_3/CH_3SiCl_3.

increases and reaches a maximum at a $NH_3/3CH_3SiCl_3$ ratio between 3.5 and 4 (Fig. 9). Further increase of the ammonia input content does not result in an equivalent increase of the CH_3SiCl_3 conversion and thus, after cooling, increasing ammoniumchloride precipitation occurs. Powders with a minimum content of ammoniumchloride are obtained for the $NH_3/3CH_3SiCl_3$ input ratio that leads to a maximal HCl yield. The CH_4 yield increases both with rising reaction temperature and increasing ammonia input content (Fig. 10). This is in good agreement with the composition of the produced powders.

Increasing reaction temperature does not only result in a higher CH_3SiCl_3 conversion but leads also to powders characterised by different structural units. ^{29}Si CP-MAS-NMR investigations showed that powders obtained in an unheated reaction tube are characterised by $CH_3Si(NH_x)_3$ units. With increasing reaction

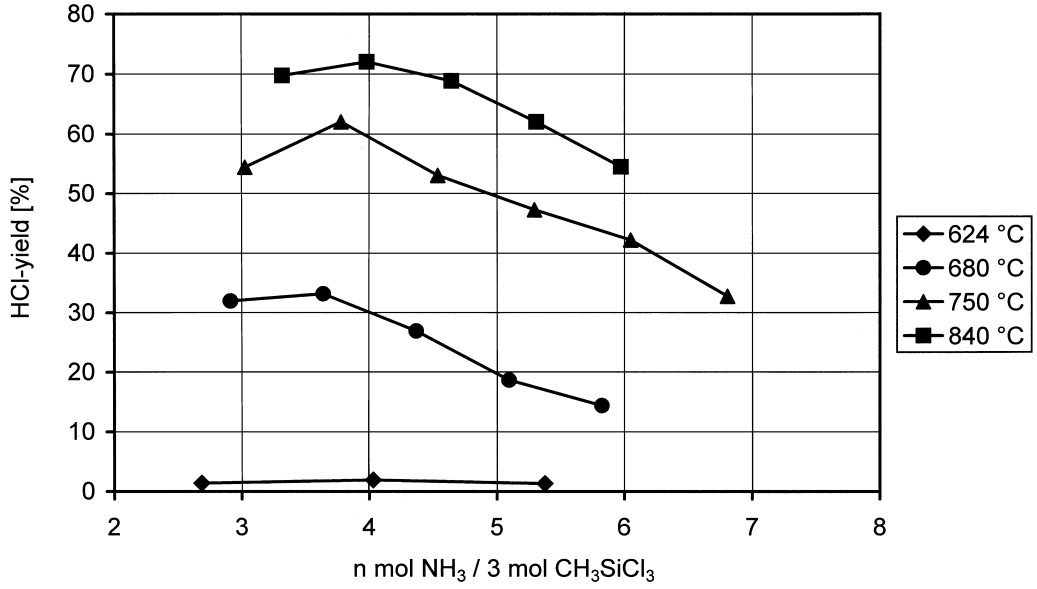

Fig. 9. HCl yield depending on the reaction temperature and the molar input ratio NH_3/CH_3SiCl_3.

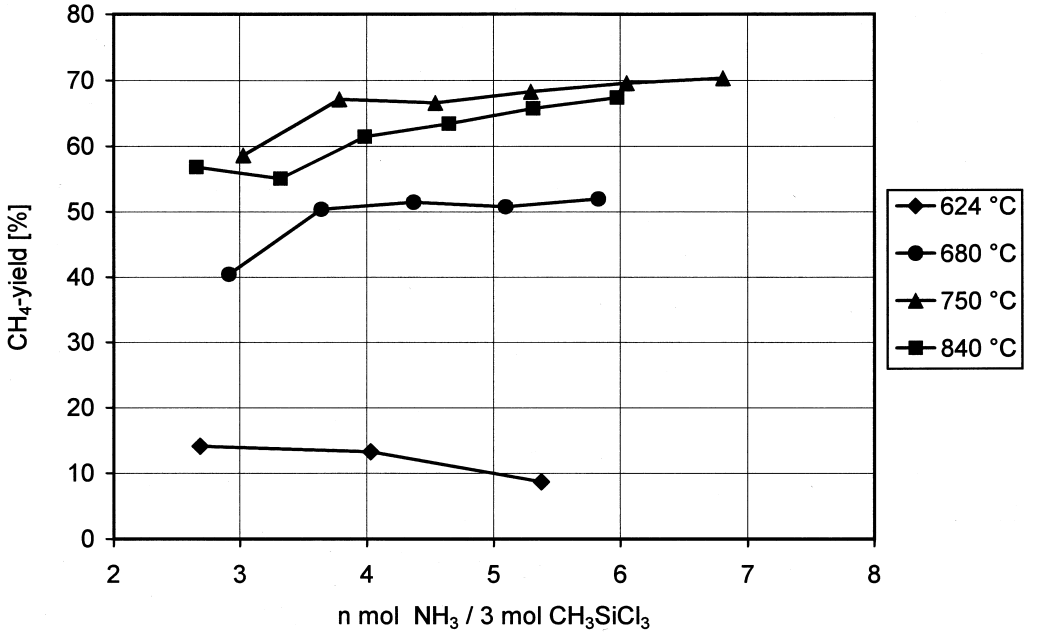

Fig. 10. CH_4 yield depending on the reaction temperature and the molar input ratio NH_3/CH_3SiCl_3.

temperature their intensity decreases and the $Si(NH_x)_4$ unit becomes dominant. In the temperature range between 700 and 800°C both units are present, while at higher temperatures only signals related to $Si(NH_x)_4$ units are found (Fig. 11). The signals used for identification are summarised in Tables 3 and 4.[15–24] Although the chemical analysis indicated that the formed powders have to be characterised as Si–N–Cl intermediates, signals related to Si–Cl bonds are only visible in the ^{29}Si CP-MAS-NMR spectra of powders synthesised at low temperatures. It is assumed that in powders synthesised at temperatures above 800°C chlorine is present in the form of strongly chemisorbed HCl.

The structural differences between the powders are visible in the ^{13}C CP-MAS-NMR spectra as well (Fig. 12). The low temperature synthesis product is characterised by the $CH_3Si(NH_x)_3$ unit. With increasing reaction temperature, the intensity of the signals resulting from that unit decreases. But it is important to note that even at a reaction temperature of 980°C, CH_3 groups are still present in the powder. Rising reaction temperature results in powders characterised by

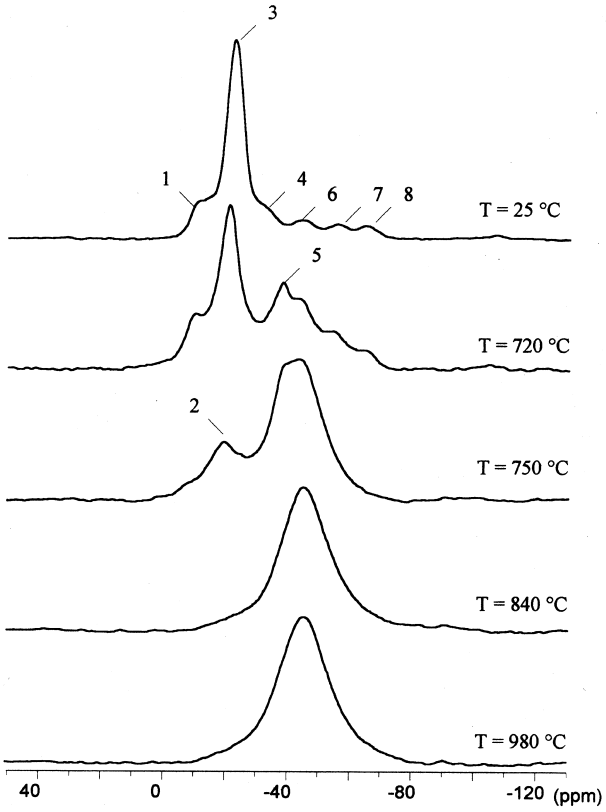

Fig. 11. ^{29}Si CP-MAS NMR-spectra of synthesis products depending on the reaction temperature (the numbers on the graphs are equivalent with Table 3).

Table 3
Identification of ^{29}Si CP-MAS NMR-signals

No.	Range	Structural unit
1	−2 ppm to −15 ppm	$CH_3ClSi(NH_x)_2$-units[a]
2	−19 ppm to −25 ppm	$CH_3Si(NH_x)_3$-units[a]
3	−25 ppm to −30 ppm	$CH_3Si(NH_x)_3$-units with $Si(NH_x)_4$-units in the near vicinity[a]
4	−32 ppm to −37 ppm	$Si(NH_x)_4$-units with $CH_3Si(NH_x)_3$-units in the near vicinity[a]
5	−41 ppm to 42 ppm	$Si(NH_x)_4$-units with $CH_3Si(NH_x)_3$-units and $Si(NH_x)_4$-units in the near vicinity[a], NH is dominant
6	−44 ppm to −48 ppm	$Si(NH_x)_4$-units[a], (amorphous Si_3N_4)
7	−54 ppm to −66 ppm	Si-oxynitides
8	−70 ppm to −72 ppm	[SiO_3]-units, [SiO_3N]-units
9	−81 ppm to 108 ppm	[SiO_4]-units (Q-groups)

[a] Lower values indicate fewer H on N.

Si–CH_2–Si and Si–C=C bonds. Aromatics can be proved, too. The curves of the intensity of selected signals are summarised in Figs. 13 and 14.

Powders obtained by ammonolysis of CH_3SiCl_3 can be converted into pure α-Si_3N_4. This requires, in a first step, the separation of ammoniumchloride and secondly a dechlorination. Ammoniumchloride separation is

Table 4
Identification of ^{29}C CP-MAS NMR-signals

No.	Range	Structural unit
1	−0.5 ppm–5 ppm	$CH_3Si(NH_x)_3$-units $CH_3Si(NH_x)O$-units
2	12 ppm–17 ppm	[Si–CH_2–Si]
3	22.2 ppm–27 ppm	[Si–CH_2–Si], SiC
4	122 ppm–138 ppm	[C=C], aromatics
5	155 ppm	[Si–C=C]

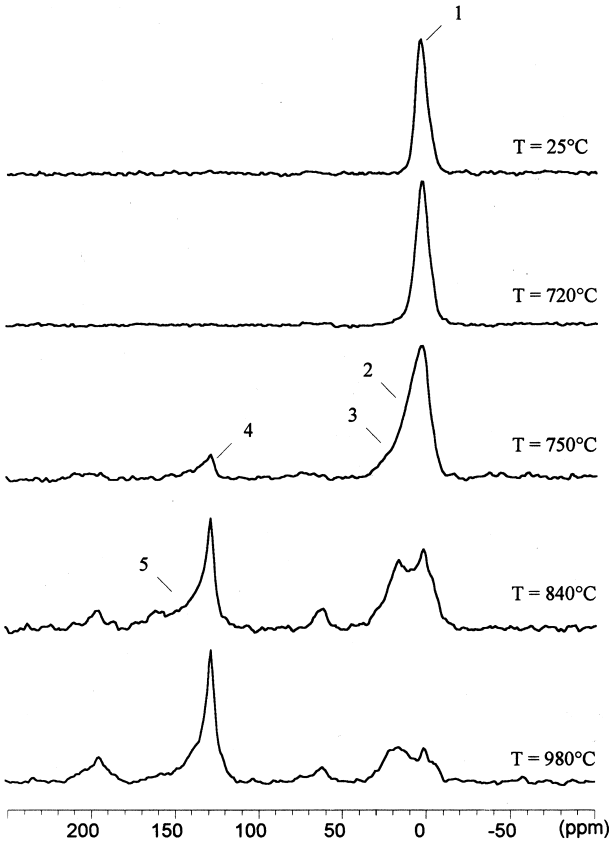

Fig. 12. ^{13}C CP-MAS NMR-spectra of synthesis products depending on the reaction temperature (the numbers on the graphs are equivalent with Table 4).

achieved by thermal treatment in nitrogen atmosphere at temperatures above 300°C. The resulting powders contain up to 12 wt.% chlorine. Fast and quantitative dechlorination takes place in an ammonia atmosphere at 900°C. A reduction of the carbon content of the powders is connected with the dechlorination. A crystallisation process at 1500°C produces α-Si_3N_4 with a high purity. Carbon contents lower than 0.1 wt.% indicate complete destruction of Si–C bonds during the thermal treatment. The powders are equivalent to powders produced by $SiCl_4$ ammonolysis (Table 5) [25].

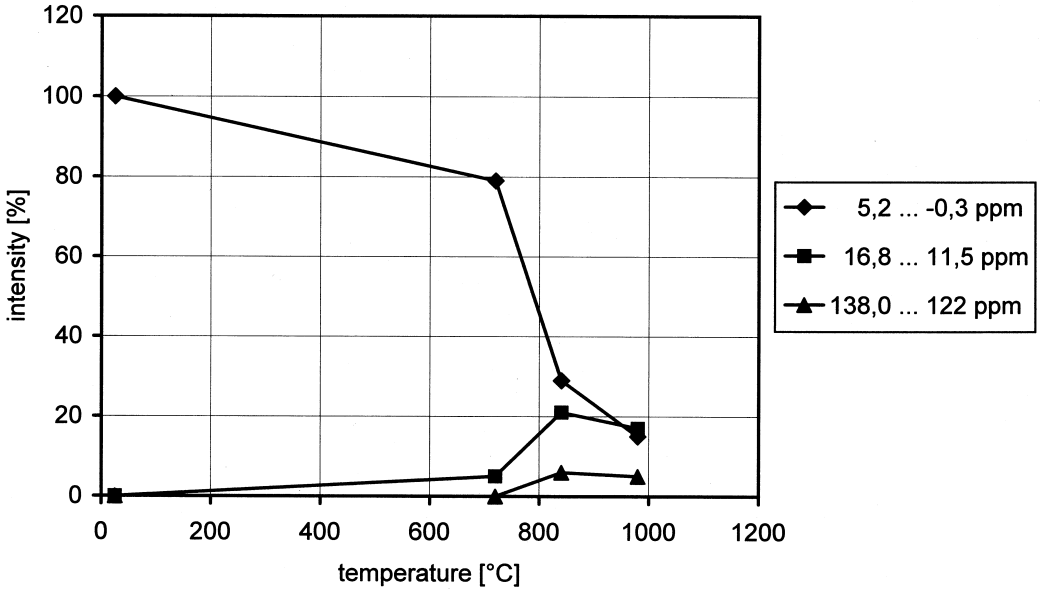

Fig. 13. Course of ^{13}C signals depending on the synthesis temperature.

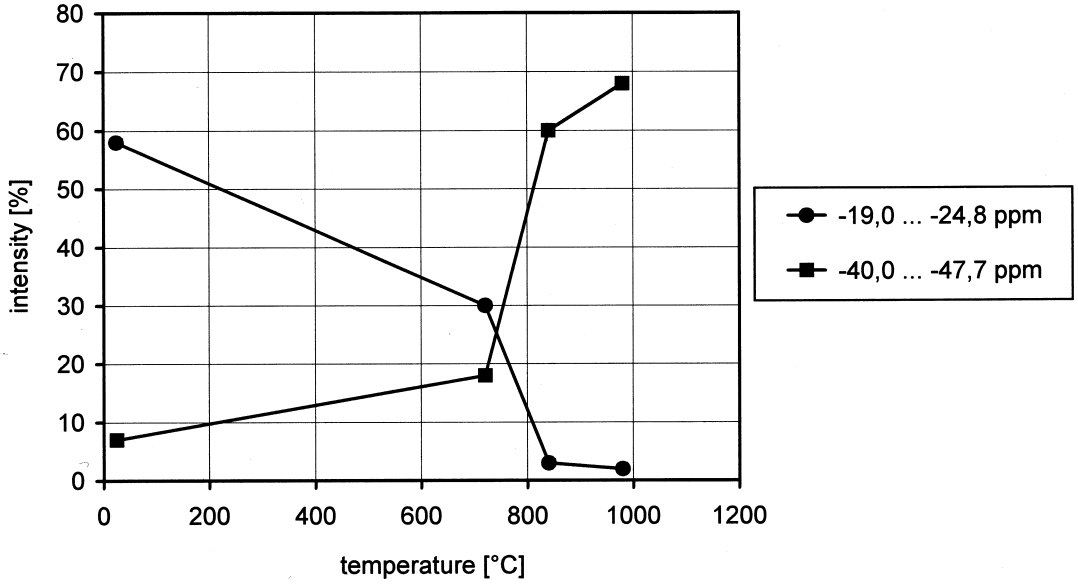

Fig. 14. Course of ^{29}Si signals depending on the synthesis temperature.

Table 5
Composition of crystallised α-Si_3N_4

	Powder composition			
	Synthesis product of CH_3SiCl_3-ammonolysis	Thermal treatment of the synthesis product in ammonia (950°C, 8 h)	α-Si_3N_4 produced by CH_3SiCl_3-ammonolysis (4 h at 1500°C)	α-Si_3N_4 produced by $SiCl_4$-ammonolysis [25]
Cl	31.34 wt.%	540 ppm	780 ppm	<0.15 wt.%
O	0.7 wt.%	1.3 wt.%	0.85 wt.%	1.2 wt.%
C	n.d.	0.45 wt.%	0.17 wt.%	<0.05 wt.%
Fe	n.d.	n.d.	51 ppm	<0.01 wt.%
BET	n.d.	n.d.	8.0 m^2/g	10–13 m^2/g

4. Discussion

The ammonolysis of CH_3SiCl_3 at low temperatures is a substitution reaction. Reaction paths are likely similar to $SiCl_4$ ammonolysis at low temperatures (Fig. 15). The Si–C bond is not broken and the powders contain $CH_3Si(NH_x)_3$ units. Produced HCl will be precipitated immediately by present NH_3.

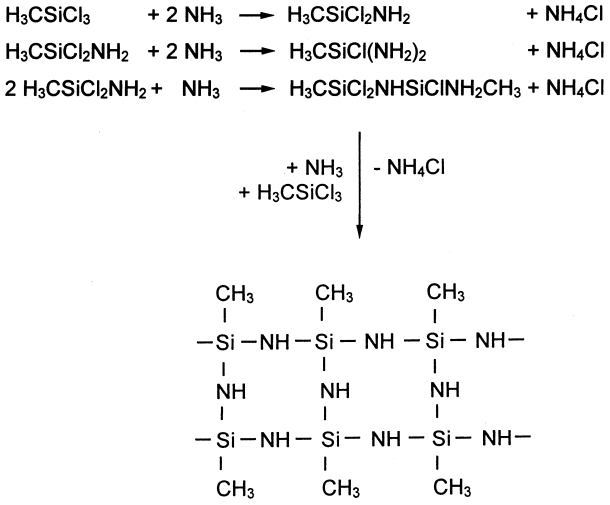

Fig. 15. Reaction paths leading to powder formation at low temperatures.

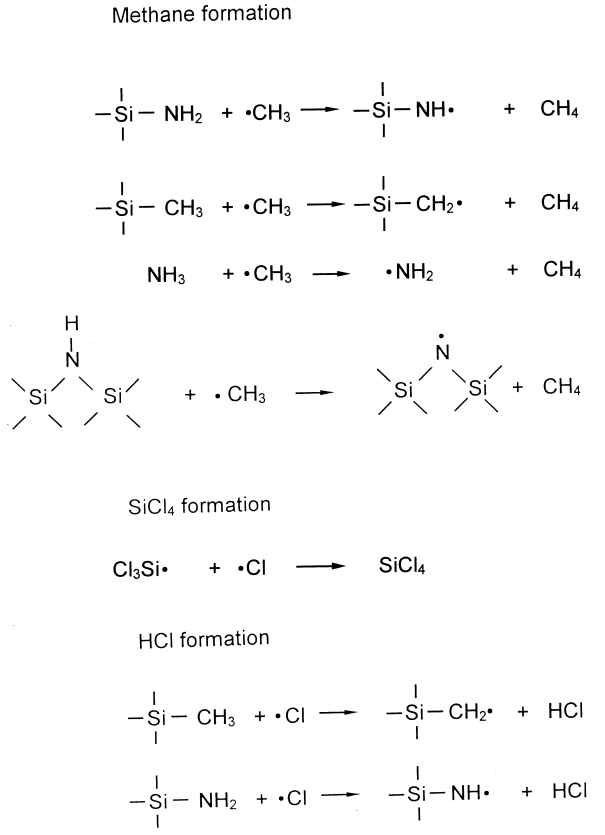

Fig. 16. CH_4, $SiCl_4$ and HCl producing radical reactions.

With increasing reaction temperature a superposition with radical reactions occurs. These are based on the thermal decomposition of Si–CH_3 or Si–Cl bonds. Radical producing reactions are favoured at high temperatures and produce Si–CH_2–Si units or aromatic systems. The cleavage of Si–Cl bonds results in the formation of •Cl radicals which form $SiCl_4$. NH_3 supports the radical formation, reflected by the increase of the CH_4 yield with rising NH_3 input concentrations. Possible radical reactions leading to the formation of HCl, $SiCl_4$ and CH_4 are summarized in Fig. 16. Fig. 17 shows reaction paths resulting in the formation of Si–CH_2–Si, Si–CH_2–CH_2–Si and Si_3N-groups. In contrast to cvd processes leading to the formation of SiC layers, gas phase ammonolysis of CH_3SiCl_3 is characterised by nucleophilic substitution reactions as well as radical forming processes. Powder formation requires a homogeneous nucleation in the gas phase and thus synthesis conditions charcterised by high CH_3SiCl_3 and NH_3 input concentrations are favourable. It is probable, that an overlapping of gas–gas and gas–solid reactions takes place. This means that synthesis products formed in first steps will undergo further reactions while passing the reaction zone.

To derive favourable synthesis conditions, two aspects have to be regarded:

- High degree of CH_3SiCl_3 conversion into powder.
- Formation of a minimal amount of NH_4Cl as a byproduct.

At constant CH_3SiCl_3/NH_3 input ratios high temperatures favour the conversion of CH_3SiCl_3 as well as a high HCl yield. On the other hand, with increasing reaction temperature an increasing formation of Si–C and C=C bonds takes place. These have a high stability. The reduction of the carbon content during thermal treatment of the synthesis products in ammonia atmosphere is lower than for powders produced at lower temperatures.

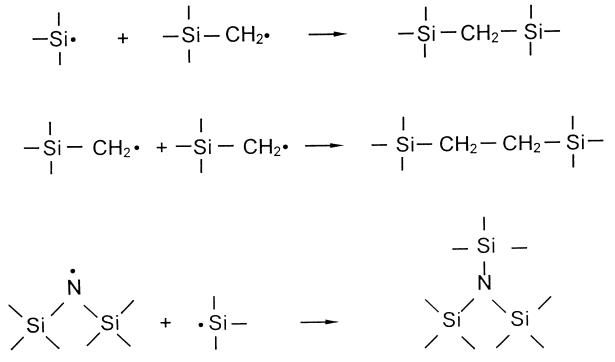

Fig. 17. Radical reactions leading to Si–CH_2–Si, Si–CH_2–CH_2–Si and Si_3N-groups.

Synthesis conditions resulting in powders with a minimum of NH_4Cl as a byproduct can be selected on the basis of the HCl content of the exhaust gas. The maximum HCl yield characterises the conditions leading to a powder with a minimum NH_4Cl content. Further increase in the ammonia content will result in increasing CH_3SiCl_3 and $SiCl_4$ conversion into silicon–nitrogen intermediates, but this is connected with the strongly rising NH_4Cl contents. In conclusion, CH_3SiCl_3 is a promising compound for synthesising α-Si_3N_4 with a high quality. Favourable synthesis conditions can be selected both on the basis of mass spectrometric analysis of the exhaust gases and chemical composition of the formed powders. It is necessary to include into these considerations also the aftertreatment processes. The selection of favourable synthesis conditions is an optimisation task concerning all process steps.

Acknowledgements

The present work was supported by the Bundesministerium für Bildung und Forschung and Bayer AG.

Appendix

Corrector factor

$$f = \frac{\text{vol\%.N}_{2(\text{output})}}{\text{vol.\%.N}_{2(\text{input})}} \quad (1)$$

$$n\text{CH}_3\text{SiCl}_{3(\text{output})} = \frac{n\text{CH}_3\text{SiCl}_{3\text{output,measured}}}{f} \quad (2)$$

Degree of CH_3SiCl_3 conversion

$$X_{\text{CH}_3\text{SiCl}_3} = \frac{n_{\text{CH}_3\text{SiCl}_{3(\text{input})}} - n_{\text{CH}_3\text{SiCl}_{3(\text{output})}}}{n_{\text{CH}_3\text{SiCl}_{3(\text{input})}}} \quad (3)$$

CH_3SiCl_3 conversion into powder

$$X_{\text{CH}_3\text{SiCl}_{3,\text{powder}}} = \frac{n_{\text{CH}_3\text{SiCl}_{3(\text{input})}} - n_{\text{CH}_3\text{SiCl}_{3(\text{output})}} - n_{\text{SiCl}_{4(\text{output})}}}{n_{\text{CH}_3\text{SiCl}_{3(\text{input})}}} \quad (4)$$

$SiCl_4$ yield

$$Y_{\text{SiCl}_4} = \frac{n_{\text{SiCl}_{4(\text{output})}}}{n_{\text{CH}_3\text{SiCl}_{3(\text{input})}} - n_{\text{CH}_3\text{SiCl}_{3(\text{output})}}} \quad (5)$$

HCl yield

$$Y_{\text{HCl}} = \frac{n_{\text{HCl}_{(\text{output})}}}{3^*(n_{\text{CH}_3\text{SiCl}_{3(\text{input})}} - n_{\text{CH}_3\text{SiCl}_{3(\text{output})}})} \quad (6)$$

CH_4 yield

$$Y_{\text{CH}_4} = \frac{n_{\text{CH}_{4(\text{output})}}}{n_{\text{CH}_3\text{SiCl}_{3(\text{input})}} - n_{\text{CH}_3\text{SiCl}_{3(\text{output})}}} \quad (7)$$

References

1. Ziegler, G., Heinrich, G. and Wötting, G., Review — relationships between processing, microstructure and properties of dense and reaction-bonded silicon nitride. *J. Mater. Sci.*, 1987, **22**, 3041.
2. Lange, H., Wötting, G. and Winter, G., Siliciumnitrid — vom Pulver zum keramischen Werkstoff. *Angew Chem.*, 1991, **103**, 1606.
3. Ziegenbalg, G., *Reaktionen, Zwischenprodukte und Verfahren zur Herstellung von amorphen Si_3N_4-Pulvern durch Umsetzung von $SiCl_4$ mit NH_3 in der Gasphase*. Freiberger Forschungshefte, Reihe Angewandte Naturwissenschaften, Heft C 477, 208p. TU Bergakademie Freiberg, 1999.
4. Bonnke, M. and Fitzer, E., Pyrolytisches Siliziumkarbid. *Ber. Dtsch. Keram. Ges.*, 1966, **43**(2), 180.
5. Von Muench, W. and Pettenpaul, E., Preparation of pure and doped silicon carbide by pyrolysis of silane compounds. *J. Electrochem. Soc., (Solid State Science and Technology)*, 1978, **125**(2), 294.
6. Hopfe, V., Wagner, O., Klobes, B. and Marx, G., In situ FTIR emission spectroscopy on chemical vapour deposition processes. *Journal of Molecular Structure*, 1990, **217**, 115.
7. Chin, J., Gantzel, P. K. and Hudson, R., The structure of chemical vapor deposited silicon carbide. *Thin Solid Films*, 1997, **40**, 57.
8. Minato, K. and Fukuda, K., Chemical vapour deposition of silicon carbide for coated fuel particles. *J. Nucl. Mater.*, 1987, **149**, 233.
9. Allendorf, M., Melius, C. F. and Osterheld, T. H., Thermodynamics and kinetics of methyltrichlorosilane decomposition. In: *Proceedings of the Electrochemical Society* (1993) 93-2 (*Proc. 12th Int. Symp. Chem. Vap. Deposition*), 1993, pp. 20.
10. Rai-Choudhury, P. and Formigoni, N. P., β-Silicon carbide films. *J. Electrochem. Soc.*, 1969, **116**, 144.
11. Yeheskel, J., Agam, S. and Dariel, M.S., Mass-spectrometric study of silicon-carbide CVD from MTS (methyltrichlorosilane) and hydrogen. In: *Proceedings of the Electrochemical Society* (1990) 90-12 (*Proc. Int. Conf. Chem. Vap. Deposition* 11th, 1990, p. 696.
12. Schintlmeister, W., Wallgram, W. and Gigl, K., Herstellung von CVD-SiC Schichten bei mittleren Beschichtungstemperaturen. *High Temp.- High Pressure*, 1986, **18**(2), 211.
13. Chappel, M. J. and Millman, R. S., The fabrication of ceramic coated carbon fibre duplex elements. *J. Mater. Sci.*, 1974, **9**, 1933.
14. Ziegenbalg, G., Pätzold, C., Šingliar, U. and Brink, R., Gasphasensynthesen — ein attraktiver Weg zur Herstellung von nitridischen Pulvern. *Chemische Technik*, 2000, **52**(2), 95.
15. Lipowitz, J., Rabe, J. A. and Carr, T. M., Characterization of the reaction products of symmetrical dimethyltetrachlorodisilane with hexamethyldisilazane by ^{29}Si NMR spectroscopy. *Spectr. Lett.*, 1987, **20**, 53.
16. Lewis, R. H. and Maciel, G. E., Magnetic resonance characterization of solid-state intermediates in the generation of ceramics by pyrolysis of hydridopolysilazane. *J. Mater. Sci.*, 1995, **30**, 5020.
17. Jiliang, H., Scarlete, M. and Harrod, J. F., Silicon nitride and silicon carbonitride by the pyrolysis of poly(methylsiladiazane). *J. Am. Ceram. Soc.*, 1995, **78**, 3009.

18. Ando, I. and Webb, G. A. (ed.), *Annual Reports on NMR Spectroscopy,* Vol. 25, Academic Press, London, 1993.
19. Lewis, R. H., Wind, R. A. and Maciel, G. E., Investigations of cured hydridopolysilazane-derived ceramic fibres via dynamic nuclear polarization. *J. Mater. Res*., 1993, **8**, 649.
20. The Aldrich Library of ^{13}C and ^{1}H-FT-NMR spectra, Edition 1, Aldrich Chemical Company Inc., 1993.
21. Brodie, N., Majoral, J. P. and Disson, J. P., An NMR study of the step by pyrolysis of a polysilazane precursor of silicon nitride. *Inorg. Chem*., 1993, **32**, 4646.
22. Fiebolin, H., *Ein und zweidimensionale NMR-Spectroskopie*. VCH, Weinheim, 1992.
23. Hayashi, S., In *Annual Reports on NMR Spectroscopy,* Vol. 28, ed. I. Ando and G. A. Webb, Academic Press, London, 1996.
24. Williams, E. A., In *The Chemistry of Organosilicon Compounds*, Part 1, ed. S. Patai and Z. Rappaport, John Wiley and Sons, Chichester, 1989.
25. Brink, R. and Woditzsch, P., Synthesis of Si_3N_4 powder by gas phase reaction of chlorosilanes with ammonia. *Cfi/Ber. DKG*., 1998, **75**(7), 22.