Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of the European Ceramic Society 32 (2012) 1873–1881

www.elsevier.com/locate/jeurceramsoc

Phase separation of a hafnium alkoxide-modified polysilazane upon polymer-to-ceramic transformation—A case study

Emanuel Ionescu[a,*], Benjamin Papendorf[a], Hans-Joachim Kleebe[b], Hergen Breitzke[c], Katharina Nonnenmacher[b], Gerd Buntkowsky[c], Ralf Riedel[a]

[a] *Technische Universität Darmstadt, Institut für Materialwissenschaft, Petersenstrasse 23, D-64287 Darmstadt, Germany*

[b] *Technische Universität Darmstadt, Institut für Angewandte Geowissenschaften, Schnittspahnstrasse 9, D-74287 Darmstadt, Germany*

[c] *Technische Universität Darmstadt, Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Petersenstrasse 20, D-64287 Darmstadt, Germany*

Abstract

The polymer-to-ceramic transformation of a hafnium alkoxide-modified polysilazane was investigated via thermogravimetric analysis coupled with *in situ* mass spectrometry (TG/MS), nuclear magnetic resonance (MAS NMR) and transmission electron microscopy (TEM). The results indicate that the structural evolution of the polysilazane upon ceramization is strongly affected by the modification with hafnium alkoxide. Thus, the content of carbon in the ceramic backbone was relatively low, whereas a large amount of SiN_4 sites and a segregated carbon phase was present in the sample. Furthermore, this study revealed the formation of a SiHfCNO amorphous single phase ceramic via pyrolysis of the polymer at 700 °C, whereas at higher pyrolysis temperatures precipitation of hafnia was observed, leading to an amorphous hafnia/silicon carbonitride ceramic nanocomposite. The precipitation of hafnia was shown to not rely on decomposition processes, but to be a result of rearrangement reactions occurring within the ceramic material.

Keywords: Precursors; Polymer-derived ceramics (PDCs); Nanocomposites; Transition metal oxides

1. Introduction

During the last decades, a continuously growing research interest has been given to amorphous ceramics[1] which are prepared via solid state thermolysis from preceramic polymers.[2] Their polymer-to-ceramic conversion[3] leads to polymer-derived ceramics (PDCs) which have been shown to possess a unique combination of properties. Especially materials of the ternary system Si–C–N[4] as well as quaternary ceramics Si–M–C–N(O) (M = B[5], Al[6,7], Zr[8]) exhibit excellent stability against decomposition and crystallization as well oxidation resistance up to high temperatures (as for amorphous SiCN and SiBCN ceramics), good mechanical and interesting electrical properties.[1]

One of the most intriguing features of the PDCs is their amorphous nature, which is a result of a non-equilibrium state thereof and cannot be realized by using other preparative techniques. As a consequence of their covalent bonding, they have been found to possess near-zero steady state creep[9,10] and high resistance against crystallization processes at temperatures far beyond 1000 °C.[1]

Numerous studies on the amorphous microstructure and its high-temperature evolution of SiCN ceramics have been reported in the last 15 years. Thus, a wide variety of experimental techniques, such as X-ray and neutron diffraction (XRD and ND),[11–14] transmission electron microscopy (TEM)[15,16] and nuclear magnetic resonance (NMR),[17] as well as modeling approaches (e.g. molecular dynamics: MD,[18,19] reverse Monte Carlo method: RMC,[20] and density-functional-theory-based molecular dynamics),[21] have been used in order to understand the nano/microstructure and the high-temperature stability.

Furthermore, polysilazane-based precursors have been used in order to fabricate silicon carbonitride nanocomposite ceramics such as SiBCN,[5] SiAlCN(O)[6,22] or SiZrCN(O).[8] Whereas SiBCN has been intensively studied with respect to its synthesis, processing and properties, the polymer-to-ceramic transformation processes and the nano/microstructure evolution of other SiMCN(O) materials is not well known as yet. These materials are mainly prepared by chemical modification of suitable polysilazanes with metal alkoxides and subsequent ceramization and lead to silicon carbonitride ceramic nanocomposites containing

---

[*] Corresponding author. Tel.: +49 06151 166344; fax: +49 06151 166346.
E-mail address: ionescu@materials.tu-darmstadt.de (E. Ionescu).

0955-2219/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2011.09.003

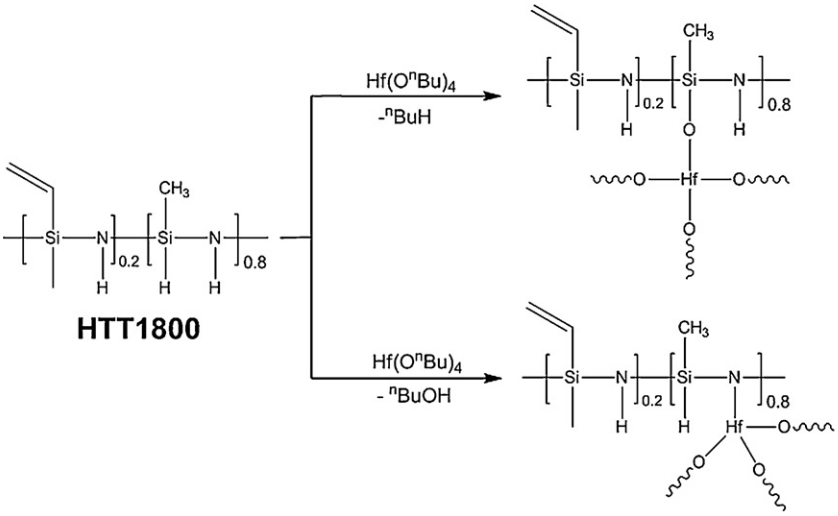

Fig. 1. Chemical modification pathways of polysilazane HTT1800 with hafnium alkoxide.[22]

a finely dispersed metal oxide phase (e.g. ZrO_2, Al_2O_3). However, no reliable information is available so far on the phase separation process of the metal oxide phase upon pyrolysis of the polysilazane precursors, which leads to the formation of the metal oxide precipitates.

The present paper describes a case study on the precipitation of hafnia upon pyrolysis of a hafnium alkoxide-modified polysilazane by means of TGA/MS, ^{29}Si MAS NMR and TEM techniques. To the best of our knowledge, this is the first systematic case study on the segregation of amorphous metal oxide in alkoxide-modified polysilazanes upon ceramization.

2. Experimental procedure

Polysilazane HTT1800 (Clariant, Sulzbach am Taunus, Germany) was used as polymer precursor and was chemically modified in inert atmosphere (Schlenk technique) by using a hafnium alkoxide. Thus, 10.5 ml of HTT1800 were mixed with 4.5 ml hafnium(IV) *n*-butoxide (Sigma–Aldrich) and stirred for 30 min at room temperature. The mixture was cross-linked at 250 °C (heating rate 50 °C/h) for 180 min and subsequently pyrolyzed in argon atmosphere for 2 h at 400, 700, 900 and 1100 °C.

The polymer-to-ceramic transformation of the hafnium *n*-butoxide modified polysilazane was studied by means of TGA/MS on a simultaneous thermal analysis device (STA 449C Jupiter, Netzsch, Germany) coupled with a quadrupole mass spectrometer (QMS 403C Aëolos, Netzsch, Germany). The measurements were done under flowing argon, with a heating rate of 5 °C/min up to 1450 °C.

Elemental analyses for nitrogen and oxygen were performed by means of hot gas extraction techniques using a LECO C-200 and a LECO TC-436 analyzer.

All NMR experiments were carried out on a Bruker AVANCE II$^+$ spectrometer at 400 MHz proton resonance frequency, employing a Bruker 4 mm double resonance MAS probe at spinning rates of 10 kHz at room temperature. Single pulse (SP) ^{29}Si NMR spectra were recorded using a 90° pulse of 9 μs and recycle delays of 120 s. Conversely, in case of SP ^{13}C NMR spectra, a 90° pulse of 4 μs and recycle delays of 20 s were adopted. ^{29}Si and ^{13}C chemical shifts were referenced with respect to TMS by utilizing the external standards Kaolin and Adamantane, respectively.

Transmission electron microscopy (TEM) was performed using a CM20STEM (FEI, Eindhoven, The Netherlands) operating at 200 kV on TEM-foils obtained from the pyrolyzed bulk samples. Sample preparation followed standard ceramographic techniques involving cutting, ultrasonic drilling, dimpling and Ar-ion thinning to perforation followed by light carbon coating to minimize charging under the incident electron beam.

3. Results and discussion

The chemical modification of the polysilazane HTT1800 with hafnium *n*-butoxide was reported recently.[23] It was shown that hafnium *n*-butoxide undergoes reactions with both Si–H and N–H reactive groups present in HTT1800, as shown in Fig. 1. Thus, the reaction of hafnium *n*-butoxide with the Si–H bonds of HTT1800 occurs upon release of butane and formation of ≡Si–O–Hf≡ units, whereas the reaction with the N–H bonds leads to =N–Hf≡ units and the evolution of butanol.

The polymer-to-ceramic transformation of the polysilazane HTT1800 modified with hafnium *n*-butoxide was investigated by means of TGA coupled with *in situ* mass spectrometry (MS) from ambient temperature up to 1400 °C. The TGA study reveals that the transformation of the precursor into ceramic material occurs in several steps and exhibits a ceramic yield of ca. 53% (Fig. 2a). In the temperature range from ambient temperature to ca. 350–400 °C cross-linking of the precursor takes place. This relies mainly on hydrosilylation and vinyl polymerization processes[3,4] (see Fig. 3a and b), which however occur without mass loss. Thus, the detected mass loss during the cross-linking of the precursor (ca. 25 wt%) was assigned to the evolution of oligomers with low molecular weight. At temperatures from 400 to ca. 700 °C additional mass loss was detected (ca. 20 wt%), which was attributed to the ceramization

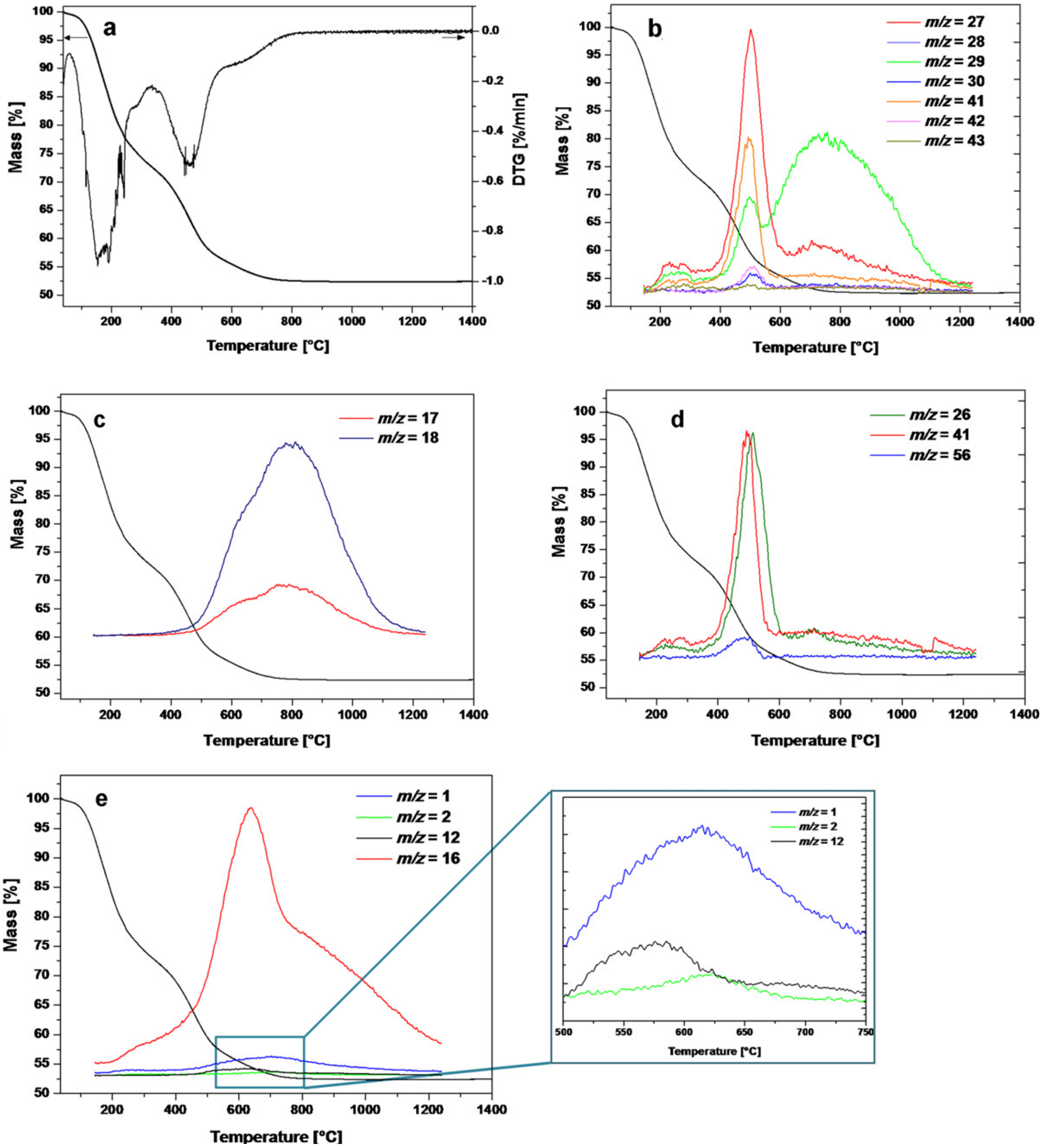

Fig. 2. (a) TG and DTG (first derivative of the TG) curves showing the polymer-to-ceramic transformation of the hafnium alkoxide modified precursor; (b–e) TG and QMID ion current curves (QMID – quasi multiple ion detection) describing the evolution of volatile species during polymer-to-ceramic transformation of the sample (b: fragments of amines; c: ammonia ($m/z = 17$) and water ($m/z = 18$); d: fragments of butene; e: hydrogen ($m/z = 1$ and 2) and methane ($m/z = 16$)).

process of the modified polysilazane to yield SiHfCNO ceramic. The ceramization process was found to be completed at temperatures around 750 °C, since no mass change was recorded at higher temperatures. Within the ceramization step different rearrangement and decomposition processes were attributed to volatiles which were detected by means of *in situ* MS. In the temperature range from 400 to 550 °C strong evolution of amines was detected via MS (Fig. 2b), thus indicating that transamination processes occur; this was further supported by *ex situ* MAS NMR investigation on samples pyrolyzed at 400 and 700 °C (see discussion below). Furthermore, the generation of amines can also be assigned to reactions of ≡Si–N= bonds with alkoxy end groups present within the cross-linked polymer (Fig. 3d).

At temperatures from 500 to ca. 750 °C hydrogen evolution takes place (Fig. 2e) as a result of dehydrocoupling reactions (of e.g. =N–H or still non-reacted ≡Si–H groups) or decomposition processes of hydrocarbon substituents. Also within the same temperature range a strong evolution of ammonia (Fig. 2c) and methane (Fig. 2e) was detected, thus confirming the ceramization process leading to a homogeneous SiHfCNO ceramic.

Furthermore, at temperatures of 450–750 °C butene and water evolution was detected by means of MS and was assigned to the decomposition of butoxy end groups at hafnium centers.[24]

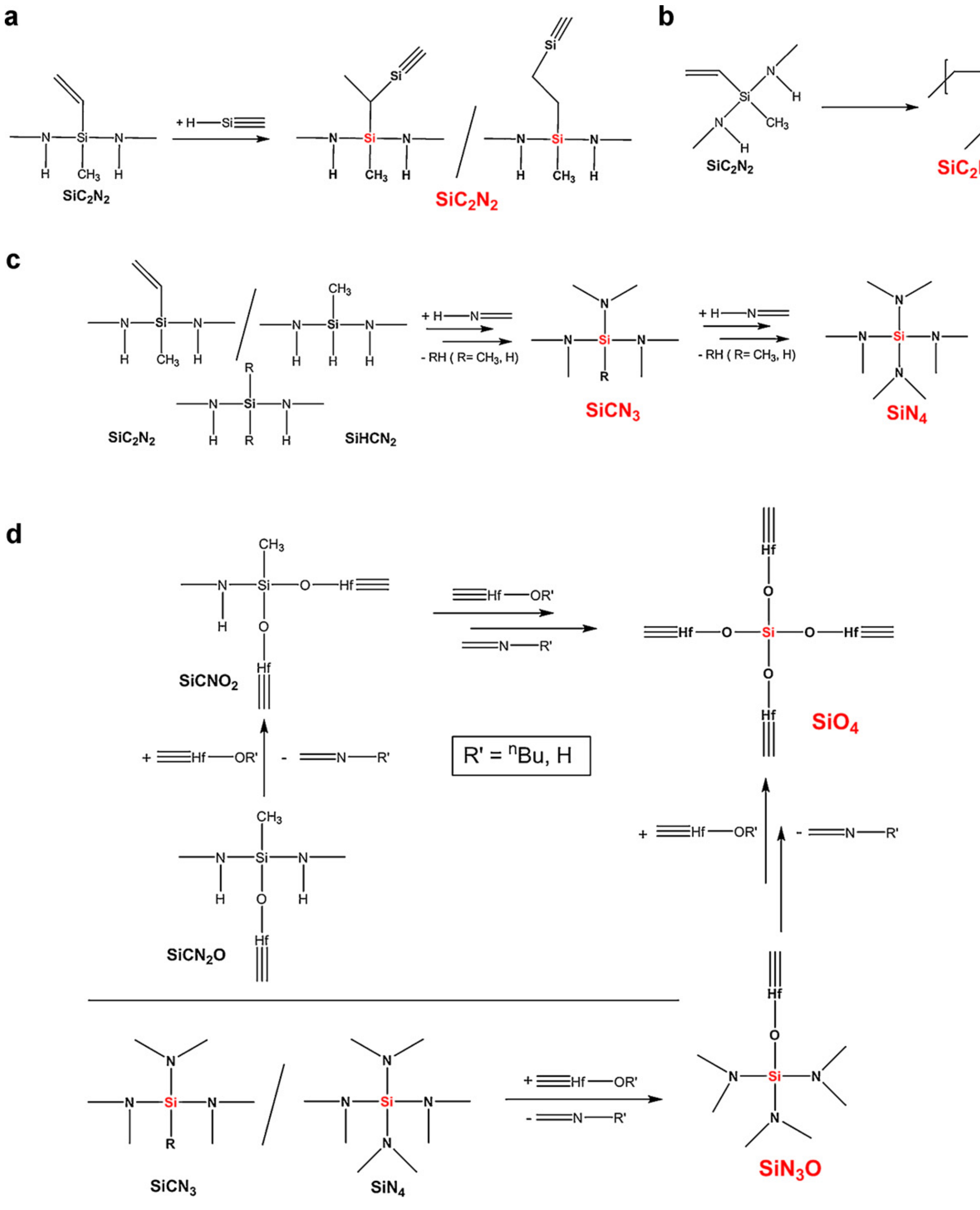

Fig. 3. Possible rearrangement reactions hafnium alkoxide modified polysilazane upon polymer-to-ceramic transformation: (a) hydrosilylation reaction; (b) vinyl polymerization; (c) transamination; (d) reactions of amino groups (at Si centers) with alkoxy end substituents (at hafnium). Whereas reactions (a) and (b) occur without mass loss, hydrocarbons and amines are released during reactions (c) and (d).

The polymer-to-ceramic transformation of the hafnium alkoxide modified polysilazane HTT1800 was also investigated by means of ^{29}Si MAS NMR. The sample pyrolyzed at 400 °C shows the presence of Si sites with mixed bonds (SiC_xN_{4-x}), thus a signal at ca. −4 ppm was assigned to SiC_2N_2 sites (with sp^3 hybridized C), whereas the signals at −25.6 ppm (highest intensity) and −45.7 ppm were attributed to $SiCN_3$ and SiN_4 centers (Fig. 4).[25,26] Additionally, the presence of a peak at −65.5 ppm was observed, which was assigned to SiN_3O centers.

The SiC_2N_2 sites develop upon cross-linking due to hydrosilylation reactions between $H_2C{=}CH–Si≡$ (vinyl) and ≡Si–H groups as well as vinyl polymerization processes (Fig. 3a and b). Both processes lead to the transformation of sp^2 hybridized vinyl carbon atoms into sp^3 hybridized carbon, as revealed by the chemical shift of the SiC_2N_2.[17] Interestingly, the intensity of the SiC_2N_2 signal was relatively low, indicating that at this temperature SiC_2N_2 centers are not stable and undergo further rearrangement processes. This is a rather unusual behavior for

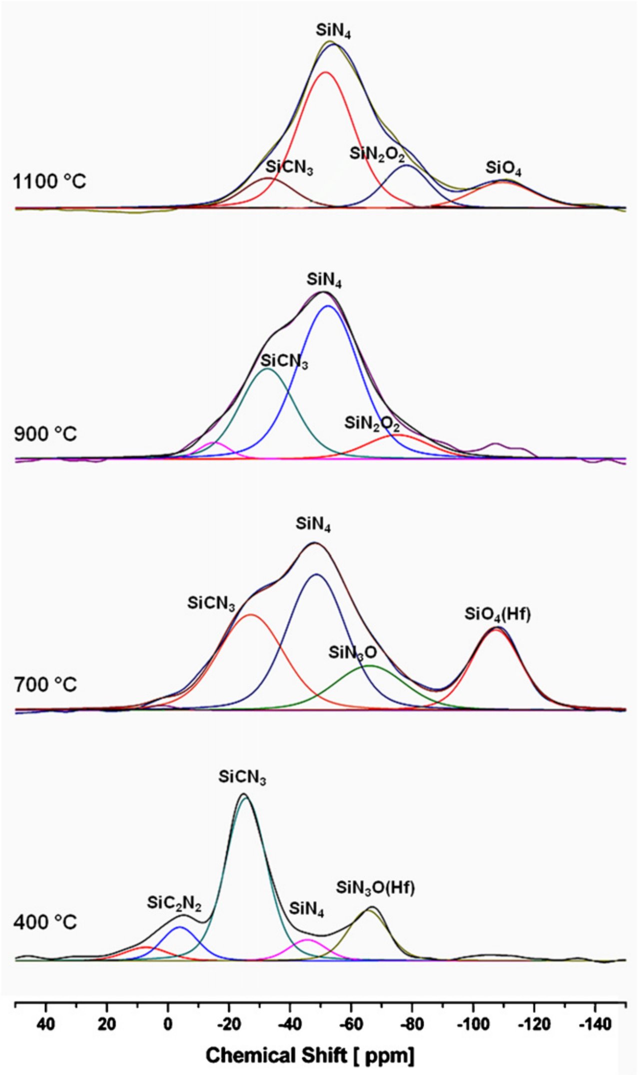

Fig. 4. ^{29}Si MAS NMR spectra of hafnium alkoxide modified polysilazane pyrolyzed at different temperatures.

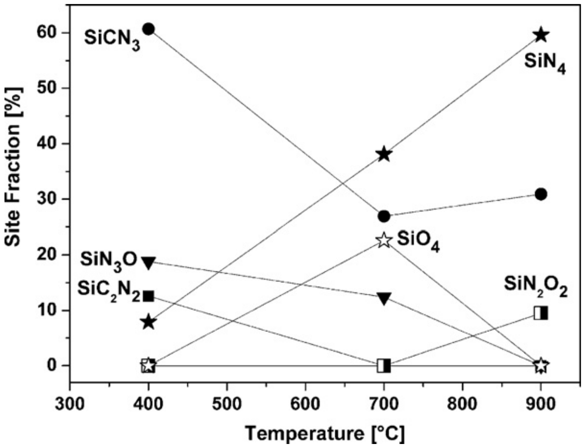

Fig. 5. SiC_xN_{4-x} and SiN_xO_{4-x} site fractions of the alkoxide modified polysilazane samples as function of the temperature.

polysilazanes, consisting of SiC_2N_2 sites which are stable up to high temperatures (e.g. 1100 °C).[17] The reason for the different reaction behavior of our sample is seen in its modification with hafnium alkoxide; however, this has not been clarified so far.

The most probable rearrangement process occurring at SiC_2N_2 sites (which leads to the formation of $SiCN_3$) involves transamination reactions upon release of gaseous hydrocarbons, as supported by *in situ* mass spectrometry (Fig. 3c). Also the formation of SiN_4 sites can be explained as resulting from transamination reactions of SiC_2N_2 and $SiCN_3$.

Besides the mixed bond sites SiC_xN_{4-x}, the sample pyrolyzed at 400 °C shows an additional signal in the ^{29}Si NMR spectrum, which was assigned to SiN_3O centers. Their formation relies on the presence of hafnium alkoxy end groups within the polymeric precursor and their reaction with ≡Si–N= units to form ≡Si–O–Hf≡ groups and volatile amines (see Figs. 2b and 3d). The presence of the SiN_3O signal in the MAS NMR spectrum of the sample pyrolyzed at 400 °C supports our previous observation that hafnium alkoxide modification occurs upon reaction not only with N–H bonds but also with Si–H functions in HTT1800 (see Fig. 1) as well as the fact that hafnium is molecularly distributed throughout the material.

The MAS NMR spectrum of the sample pyrolyzed at 700 °C reveals the presence of $SiCN_3$ and SiN_4 (main signal) sites. The amount of $SiCN_3$ was found to decrease with respect to the sample pyrolyzed at 400 °C, whereas the amount of SiN_4 sites has increased (Table 1 and Fig. 5). Furthermore, no SiC_2N_2 sites were detected, indicating that they have fully rearranged to $SiCN_3$ and SiN_4 via transamination processes. In addition to the SiN_3O sites, SiO_4 centers are formed at 700 °C, thus revealing further rearrangement processes of SiN_3O via reactions of ≡Si–N= sites with butoxy groups (see Fig. 3d). The SiO_4 signal (−107 ppm) was found to be shifted towards low field as compared to pure silica (−112 ppm),[27,28] indicating that hafnium is attached to oxygen. This effect was also observed in hafnia and zirconia modified silicon oxycarbide ceramic nanocomposites.[29,30]

The SiN_4 signal exhibits the highest intensity in the sample pyrolyzed at 900 °C, revealing a further increase of the SiN_4 sites (ca. 60%) with respect to the sample pyrolyzed at 700 °C (Table 1). Whereas no SiC_2N_2 sites were detected and the amount of $SiCN_3$ (ca. 30%) has slightly increased (Table 1 and Fig. 5). Thus, the sample pyrolyzed at 900 °C shows a different distribution of the Si sites as compared to other polysilazane derived materials: a relatively similar polysilazane (i.e. VS/MS, $\{[(H_2C{=}CH)SiH\text{–}NH]_{0.5}\text{–}[(H_3C)SiH\text{–}NH)_{0.5}\}$) was reported to consist upon pyrolysis at 850 °C of ca. 32% SiC_2N_2, 35% $SiCN_3$ and 33% SiN_4,[25] hence emphasizing the presence of an uniform distribution of mixed bonds within amorphous SiCN materials. In our case, the pyrolyzed sample at 900 °C revealed the presence of a large amount of SiN_4 and the disappearance of the SiC_2N_2 sites, indicating that the nanostructure of the alkoxide-modified materials is different from that of polysilazane-derived SiCN. Interestingly, no SiN_3O or SiO_4 signals were detected, whereas only a small amount of SiN_2O_2 sites was present in the sample. The strong decrease of the oxygen containing sites is a consequence of the phase separation of hafnia upon pyrolysis at 900 °C, which has been further supported by TEM investigation

Table 1
^{29}Si MAS NMR chemical shifts and the fractions corresponding to SiC_xN_{4-x} as well as SiN_xO_{4-x} sites ($x = 0$, 1 and 2) for the alkoxide modified polysilazane samples pyrolyzed at 400, 700, 900 and 1100 °C.

Temperature [°C]	SiC_2N_2		$SiCN_3$		SiN_4		SiN_3O		SiN_2O_2		SiO_4	
	[ppm]	[%]	[ppm]	[%]	[ppm]	[%]	[ppm]	[%]	[ppm]	[%]	[ppm]	[%]
400	−3.9	12.6	−25.6	60.7	−45.7	7.9	−65.5	18.8	–	0	–	0
700	–	0	−27.0	26.9	−48.7	38.1	−66.1	12.4	–	0	−107	22.6
900	–	0	−32.6	30.9	−52.5	59.6	–	0	−75.2	9.5	–	0
1100	–	0	−32.9	12.0	−51.6	60.1	–	0	−78.1	15.2	−110	12.7

(see below). It can thus be concluded that the pyrolysis of the hafnium alkoxide-modified polysilazane at 900 °C leads to a ceramic nanocomposite material comprising of amorphous hafnia finely dispersed within an amorphous SiCN(O) matrix. Additional elemental analysis of the samples pyrolyzed at 700 and 900 °C revealed that the hafnia precipitation relies only on rearrangement reactions within the material and is not a result of decomposition processes, since the oxygen content was found to be the same in all ceramic samples (Table 2). This is further supported by the results of the TG analysis which has shown no mass loss at temperatures beyond 750 °C (Fig. 2a).

The sample pyrolyzed at 1100 °C exhibits in the ^{29}Si NMR spectrum the presence of SiC_xN_{4-x} mixed bonds sites, i.e. $SiCN_3$ and SiN_4 (predominant), as well as of oxygen containing sites SiN_2O_2 and SiO_4. The elemental analysis of this sample indicates following chemical composition: $SiC_{0.55}N_{1.09}O_{0.47}Hf_{0.07}$. Under the assumption that the oxygen is bonded to hafnium and silicon, nitrogen is bonded only to silicon and carbon can be carbidic or "free"; a formal phase composition can be calculated, as is shown in Table 3.

The chemical composition of the SiHfCNO ceramic material pyrolyzed at 1100 °C confirms the observation made by means of MAS NMR concerning its nanostructure. Thus, an increased fraction of silicon nitride was calculated (54.31 wt%), which is in very good agreement with the MAS NMR data (60.1% SiN_4 sites within the material). Furthermore, a low amount of carbon incorporated within the ceramic network (carbidic $Si\underline{C}_xN_{4-x}$ carbon) has been calculated on the basis of the chemical composition (i.e. ca. 0.6 wt% SiC, Table 3), which is rather unusual for polysilazane-derived SiCN(O) ceramics, consisting of a single amorphous SiC_xN_{4-x} phase (mixed bonds).[31] This fact furthermore reveals that carbon is mainly present as a segregated phase ("free" carbon) within the ceramic, as also shown by MAS NMR (Fig. 6). Thus, the sample prepared via pyrolysis at 1100 °C consists of hafnia nanoparticles dispersed within a SiCN(O) matrix showing mainly separated bonds, i.e. SiN_4 and free C, and only a small amount of $SiCN_3$ sites.

Table 2
Nitrogen and oxygen content of the samples pyrolyzed at 700, 900 and 1100 °C. The oxygen content remains practically constant upon pyrolysis of the sample in this temperature range, i.e. no decomposition occurs.

Temperature [°C]	N [wt%]	O [wt%]
700	23.12	10.28
900	23.63	10.26
1100	21.85	10.76

The evolution of the carbon within the samples at different temperatures is shown in Fig. 6. The ^{13}C MAS NMR spectrum of the sample pyrolyzed at 400 °C exhibit a signal at ca. 2 ppm, which was assigned to methyl groups bonded at silicon centers. Further signals at 13.2 ppm ($OCH_2CH_2CH_2\underline{C}H_3$), 19.0 ppm ($OCH_2CH_2\underline{C}H_2CH_3$), 35.2 ppm ($OCH_2\underline{C}H_2CH_2CH_3$) and 63.1 ppm ($O\underline{C}H_2CH_2CH_2CH_3$) correspond to end butoxy groups bonded to hafnium centers. Furthermore, at this temperature the segregation of carbon ("free" carbon) can be detected, as revealed by the broad signal at 136 ppm.[32–35] Upon pyrolysis at 700 °C the Si–CH_3 signal decreases strongly and by

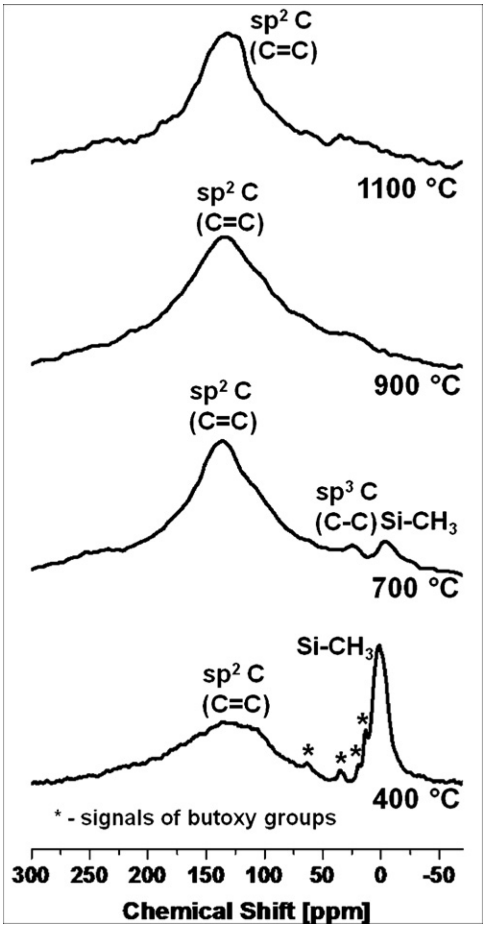

Fig. 6. ^{13}C MAS NMR spectra of the samples pyrolyzed at 400, 700, 900 and 1100 °C.

Table 3
Calculated mol and weight fractions of HfO_2, SiO_2, Si_3N_4, SiC and "free" carbon for the alkoxide-modified sample pyrolyzed at 1100 °C using its chemical composition.

	$Si_xC_yN_zO_wHf_v$		$SiC_{0.55}N_{1.09}O_{0.47}Hf_{0.07}$		
	Amount [mol]	Fraction [mol%]	Amount [mol]	Fraction [mol%]	Fraction [wt%]
HfO_2	v	$[4v/(4y+2w+z)] \times 100$	0.07	6.60	21.15
SiO_2	$(w-2v)/2$	$[2(w-2v)/(4y+2w+z)] \times 100$	0.17	16.04	14.65
Si_3N_4	$z/4$	$[z/(4y+2w+z)] \times 100$	0.27	25.47	54.31
SiC	$x-\{[(w-2v)/2]+(3z/4)\}$	$\{4\{x-\{[(w-2v)/2]+(3z/4)\}\}/(4y+2w+z)\} \times 100$	0.01	0.95	0.58
"Free" C	$y-\{x-\{[(w-2v)/2]+(3z/4)\}\}$	$\{4[y-\{x-\{[(w-2v)/2]+(3z/4)\}\}]/(4y+2w+z)\} \times 100$	0.54	50.94	9.31
Sum	$(4y+2w+z)/4$	100	1.06	100	100

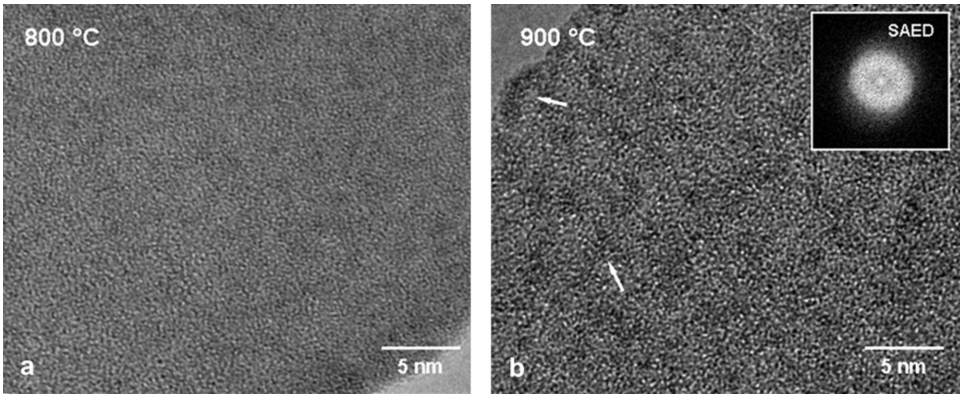

Fig. 7. (a) High-resolution TEM image of the sample pyrolyzed at 800 °C. Similar to the sample heat treated at 900 °C, this sample also was fully amorphous and revealed no clear evidence for HfO_2 nanocrystallites and (b) high-resolution TEM micrograph of the sample annealed at 900 °C. A slightly stronger contrast variation, as indicated by arrows, was observed. This percolation network is assumed to be the initial state of the HfO_2 formation.

further increasing the pyrolysis temperature to 900 or 1100 °C, no additional signals beside that of "free" carbon are observed in the spectra. Thus, it can be concluded that the main fraction of carbon within the ceramized hafnium alkoxide modified polysilazane is present within the material as segregated "free" carbon phase. This was further supported by Raman spectroscopy.

Transmission electron microscopy was utilized to study the microstructural evolution of the Hf-modified samples annealed at 700 and 900 °C. Unfortunately, the material pyrolyzed at 700 °C could not be studied, since it viciously reacted with water and/or ethanol during TEM-foil preparation, which was noticeable by a pronounced color change. Therefore, an additional sample was prepared pyrolyzed at 800 °C. This sample and the material annealed at 900 °C showed no chemical reactivity and hence both materials were prepared for TEM analysis.

The micro/nanostructure of the sample annealed at 800 °C is shown in Fig. 7a. No crystalline phases or local phase separation was observed. Electron diffraction only showed a diffuse halo, indicative for an amorphous material. No clear evidence for local precipitation of hafnia was found. It is therefore concluded that the phase separation into SiCN and nanosized HfO_2 has not yet occurred. It should be noted that indications for local SiO_2 enrichments, as indicated by NMR data, was also not observed. It is assumed that the domain size of those amorphous silica-rich regions is on the order of 1–2 nm, embedded in the also amorphous SiCN matrix, which cannot be imaged via high-resolution TEM. As the resulting TEM image is a projection of all nanodomains within the observed sample volume onto the imaging screen, SiO_2-rich regions cannot be individually distinguished, when the TEM-foil thickness is approximately 20–30 nm.

The sample annealed at 900 °C, however, only showed a slightly stronger variation in contrast, as compared to the material pyrolyzed at 800 °C. Here, small contrast variations (indicated by arrows in Fig. 7b) were observed which are attributed to the segregation of an amorphous Hf-containing phase. It should be noted that those variation in local contrast within the amorphous matrix, under the assumption of a constant sample thickness, can only be due to local changes in chemistry; i.e., local variation in atomic number. It is therefore concluded that this percolation network of the darker regions represents the formation of an amorphous Hf-containing phase, which at higher temperatures will lead to the formation of nanosized hafnia precipitates. Hence the TEM observations support the NMR data, since the percolation network of the Hf-bearing phase corresponds to the reduction of Si–O–Hf units detected by NMR upon pyrolysis at 900 °C.

4. Conclusions

This paper describes a systematic study on the polymer-to-ceramic transformation and phase separation of a hafnium alkoxide-modified polysilazane upon pyrolysis. Correlated

TGA/MS, MAS NMR and TEM investigations revealed that the hafnium-containing polysilazane transforms at 700 °C into an amorphous single phase ceramic, i.e. SiHfCNO. Upon pyrolysis at higher temperatures (ca. 900 °C), amorphous hafnia nanoparticles begin to precipitate throughout the SiCN(O) matrix, as revealed by NMR and TEM.

The presented hafnium alkoxide-modified samples differ strongly from polysilazane-derived SiCN ceramics concerning their structural composition. Thus, our ceramics show mainly separated bonds (e.g. SiN_4 sites and segregated "free" carbon phase), whereas SiCN ceramics derived from polysilazanes consists of mixed bonds (i.e. SiC_xN_{4-x}). The different structural composition of the SiHfCNO ceramic with respect to other polysilazane-derived silicon carbonitride ceramics is a consequence of the molecular structure of the preceramic polymer, which contains hafnium alkoxide units, drastically affecting its rearrangement processes upon polymer-to-ceramic transformation. Furthermore, NMR and TEM studies have elucidated the hafnia precipitation process, which is a result of rearrangement processes occurring in two steps: in the first step nitrogen containing Si sites react with alkoxide groups at moderate temperatures (400–700 °C) and lead to the formation of SiO_4 sites bearing Hf; in a second step the precipitation of hafnia phase throughout the SiCN(O) matrix occurs at $T > 800$ °C, leading to an amorphous hafnia/silicon carbonitride ceramic nanocomposite.

Acknowledgements

This work was financially supported by the German Research Fundation (DFG) within the Priority Programme SPP1181 NANOMAT (IO64/1–2). Funding from Ministry of Higher Education, Research and the Arts in Hesse, Germany (AdRIA: Adaptronik – Research, Innovation, Application) is also gratefully acknowledged. The authors thank Ms. C. Fasel for performing the TGA/MS measurements and Mr. S. Schmid for the deconvolution of the MAS NMR spectra. RR also thanks the Fonds der Chemischen Industrie for continuous financial support.

References

1. Colombo P, Mera G, Riedel R, Sorarù GD. Polymer-derived ceramics: 40 years of research and innovation in advanced ceramics. *J Am Ceram Soc* 2010;**93**:1805–37.
2. Riedel R, Ionescu E, editors. Special triple issue "Preceramic polymers". *Soft Mater* 2006;**4**(1–3):105–299.
3. Ionescu E, Gervais C, Babonneau F. Polymer-to-ceramic transformation. In: Colombo P, Riedel R, Soraru GD, Kleebe HJ, editors. *Polymer derived ceramics: from nano-structure to applications.*. Pennsylvania: Destech Publications; 2010. p. 108–26.
4. Kroke E, Li Y, Konetschny C, Lecomte E, Fasel C, Riedel R. Silazane derived ceramics and related materials. *Mater Sci Eng R* 2000;**26**:97–199.
5. Riedel R, Kienzle A, Dressler W, Ruwisch L, Bill J, Aldinger F. A silicoboron carbonitride ceramic stable to 2000 °C. *Nature* 1996;**382**:796–8.
6. An L, Wang Y, Bharadwaj L, Zhang L, Fan Y, Jiang D, Sohn Y-H, Desai VH, Kapat J, Chow LC. Silicoaluminum carbonitride with anomalously high resistance to oxidation and hot corrosion. *Adv Eng Mater* 2004;**6**:337–40.
7. Wang Y, Fei W, An L. Oxidation/corrosion of polymer-derived SiAlCN ceramics in water vapor. *J Am Ceram Soc* 2006;**89**:1079–82.
8. Saha A, Shah SR, Raj R. Oxidation behavior of SiCN–ZrO_2 fiber prepared from alkoxide-modified silazane. *J Am Ceram Soc* 2004;**87**: 1556–8.
9. Riedel R, Ruwisch LM, An L, Raj R. Amorphous silicoboron carbonitride ceramic with anomalously high resistance to creep. *J Am Ceram Soc* 1998;**81**:3341–4.
10. An L, Riedel R, Konetschny C, Kleebe HJ, Raj R. Newtonian viscosity of amorphous silicon carbonitride at high temperature. *J Am Ceram Soc* 1998;**81**:1349–52.
11. Schempp S, Dürr J, Lamparter P, Bill J, Aldinger F. Study of the atomic structure and phase separation in amorphous Si–C–N ceramics by X-ray and neutron diffraction. *Z Naturforsch* 1998;**53a**:127–33.
12. Uhlig H, Frieß M, Dürr J, Bellissent R, Lamparter HP, Aldinger F, Steeb S. A diffraction study of $Si_{0.40}C_{0.24}N_{0.36}$. *Z Naturforsch* 1996;**51a**: 1179–84.
13. Uhlig H, Frieß M, Lamparter P, Steeb S. Local order of polymer derived amorphous $Si_xC_yN_z$. *J Appl Phys* 1998;**83**:5714–8.
14. Mera G, Tamayo A, Nguyen H, Sen S, Riedel R. Nanodomain structure of carbon-rich silicon carbonitride polymer-derived ceramics. *J Am Ceram Soc* 2010;**93**:1169–75.
15. Kleebe HJ. Microstructure and stability of polymer-derived ceramics: the Si–C–N system. *Phys Stat Sol A* 1998;**166**:297–312.
16. Kleebe HJ, Störmer H. TEM study of SiCN glasses: polymer architecture versus ceramic microstructure. *Key Eng Mater* 2009;**403**:153–6.
17. Seitz J, Bill J, Egger N, Aldinger F. Structural investigation of SiCN-ceramics from polysilazane precursors by nuclear magnetic resonance. *J Eur Ceram Soc* 1996;**16**:885–91.
18. Matsunaga K, Iwamoto Y, Fisher CAJ, Matsubara H. Molecular dynamics study of atomic structures in amorphous Si–C–N Ceramics. *J Ceram Soc Jpn* 1999;**107**:1025.
19. Resta N, Kohler C, Trebin HR. Molecular dynamics simulations of amorphous Si–C–N ceramics: composition dependence of the atomic structure. *J Am Ceram Soc* 2003;**86**:1409–14.
20. Dürr J, Lamparter P, Bill J, Steeb S, Aldinger F. An X-ray and neutron scattering investigation of precursor derived $Si_{24}C_{43}N_{33}$ ceramics. *J Non-Cryst Solids* 1998;**223–234**:155–61.
21. Amkreutz M, Frauenheim T. Understanding precursor-derived amorphous Si–C–N ceramics on the atomic scale. *Phys Rev B* 2002;**65**:134113 (8 pp.).
22. Toyoda R, Kitaoka S, Sugahara Y. Modification of perhydropolysilazane with aluminium hydride: preparation of poly(aluminasilazane)s and their conversion into Si–Al–C–N ceramics. *J Eur Ceram Soc* 2008;**28**: 271–7.
23. Papendorf B, Nonnenmacher K, Ionescu E, Kleebe HJ, Riedel R. Strong influence of polymer architecture on the microstructural evolution of hafnium-alkoxide-modified silazanes upon ceramization. *Small* 2011;**7**:970–8.
24. Bradley DC. Metal alkoxides as precursors for electronic and ceramic materials. *Chem Rev* 1989;**89**:1317–22.
25. Gerardin C, Taulelle F, Bahloul D. Pyrolysis chemistry of polysilazane precursors to silicon carbonitride. Part 2. Solid state NMR of the pyrolytic residues. *J Mater Chem* 1997;**7**:117–26.
26. Bill J, Seitz J, Thurn G, Dürr J, Canel J, Janos BZ, Jalowiecki A, Sauter D, Schempp S, Lamparter HP, Mayer J, Aldinger F. Structure analysis and properties of Si–C–N-ceramics derived from polysilazanes. *Phys Stat Sol* 1998;**166**:269–96.
27. Oestrike R, Yang WH, Kirckpartrick RJ, Hervig RL, Navrotsky A, Montez B. High-resolution ^{23}Na, ^{27}Al and ^{29}Si NMR spectroscopy of framework aluminosilicate glasses. *Geochim Cosmochim Acta* 1987;**51**:2199–209.
28. Hartman JS, Millard RL, Vance ER. A ^{29}Si magic angle spinning NMR and DTA study of thermal crystallization of sphene and zircon gels. *J Mater Sci* 1990;**25**:2785–90.
29. Ionescu E, Papendorf P, Kleebe HJ, Poli F, Müller K, Riedel R. Polymer-derived silicon oxycarbide/hafnia ceramic nanocomposites. Part I: Phase and microstructure evolution during the ceramization process. *J Am Ceram Soc* 2010;**93**:1774–82.
30. Dirè S, Ceccato R, Gialanella S, Babonneau F. Thermal evolution of polydimethylsiloxane–zirconia nanocomposites prepared by the sol–gel method. *J Eur Ceram Soc* 1999;**19**:2849–58.

31. Iwamoto Y, Vögler W, Kroke E, Riedel R. Crystallization behavior of amorphous silicon carbonitride ceramics derived from organometallic precursors. *J Am Ceram Soc* 2001;**84**:2170–8.
32. Brodie N, Majoral JP, Disson JP. An NMR study of the step by step pyrolysis of a polysilazane precursor of silicon nitride. *Inorg Chem* 1993;**32**:4646–9.
33. Schuhmacher J, Weinmann M, Bill J, Aldinger F, Müller K. Solid-state NMR studies of the preparation of Si–C–N ceramics from polysilylcarbodiimide polymers. *Chem Mater* 1998;**10**:3913–22.
34. Berger F, Weinmann M, Aldinger F, Müller K. Solid-state NMR studies of the preparation of Si–Al–C–N ceramics from aluminum-modified polysilazanes and polysilylcarbodiimides. *Chem Mater* 2004;**16**: 919–29.
35. Bill J, Kamphowe TW, Müller A, Wichmann T, Zern A, Weinmann M, Schuhmacher J, Müller K, Peng J, Seifert HJ, Aldinger F. Precursor-derived Si–(B–)C–N ceramics: thermolysis, amorphous state and crystallization. *Appl Organomet Chem* 2001;**15**:777–93.