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Submicro Structure of Silicon Carbide Derived from Poly(methylchlorosilane)

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Abstract

Poly(methylchlorosilane) characterized by silicon domains in the macromolecules is pyrolysed at 165°C. The resulting structure is investigated by Raman-spectroscopy. Silicon carbide, silicon, and carbon areas of nanoscale dimensions are detected. The silicon carbide and carbon particles are strong disordered and small in particle size which was proved by spreaded signals and an additional Raman-band in the spectra. Additionally, a remarkable amount of silicon was found in the material. The silicon and carbon domains are extremely fine dispersed and properly originated from the molecule structure of the polysilane. An estimation of the particle dimensions is performed. Furthermore a description of the relation between molecular structure of the poly(methylchlorosilane) and the silicon carbide is given in the paper. © 1997 Elsevier Science Limited.

1 Introduction

Polysilanes and polycarbosilanes are widely investigated as precursor for silicon carbide materials. Special interest is focused on their application as precursor for ceramic fiber manufacture.

The structure of the ceramic materials which were derived from precursors was investigated by a number of authors.[1–4] The conversion from polymeric to ceramic material is characterized by gas evolution, cleavage of chemical bonds, crosslinking of molecules and crystallization of the ceramic. A design of the polymeric structure is strongly desired because a controlled structural built up of the ceramic material would allow to tailor properties like chemical and thermal resistance, mechanical strength, toughness and electrical behavior.

Results with regard to polymer and ceramic structure design were already published by other authors.[5–7] The aim was to obtain stoichiometric silicon carbide by exactly designed polycarbosilane with alternating silicon-carbon bonds and fitted silicon–carbon ratio. Subsequently a homogeneous material is desired which is resistant against oxidation and possess high mechanical strength. Those properties would be very valuable for the manufacture of high temperature and high strength silicon carbide fibers. Generally silicon carbide which is derived from polymeric precursors shows inhomogeneities in the nanometer range. Some authors found carbon or silica domains in fiber materials. Especially a local concentration of carbon decreases the oxidation resistance of the material.[8] Carbon domains are enlarged and concentrated with crystallization of the amorphous silicon carbide as already described.[9,10]

Compared to carbonrich silicon carbide excess silicon is rarely observed.[10–12] Seyferth *et al.*[11] described polysilanes which generate silicon carbide with a silicon/carbon ratio > 1. Poly(methylchlorosilane), as used in this investigation, also enables the manufacture of siliconrich silicon carbide depending on the polymer structure and the composition of the precursor. But generally poly(methylchlorosilane) is, with regard to SiC, a nearly stoichiometric precursor with silicon/carbon ratios ~1. This silicon/carbon ratio is achieved as consequence of the chlorine content which allows an adjustment of the carbon content in the precursor molecules in contrast to silicon polymers with alkyl or aryl groups. The finally resulting silicon carbide is regularly stoichiometric with a small amount of excess carbon. The structure during the conversion

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process has to change drastically if a homogenous silicon carbide ceramic will be realized.

Inhomogeneities of the polymer corresponding to the element distribution are regularly found on poly(methylchlorosilane). The dimensions of inhomogeneities of the pyrolysed ceramic are in the range of the previous molecular inhomogeneities of the precursor. This is a very interesting point because it shows the potential of molecular structuring by polymer design.

2 Experimental

Poly(methylchlorosilane) was prepared at the Institute of Inorganic Chemistry, Freiberg University of Mining and Technology. The synthesis was described in detail by Richter *et al.*,[13,14] but in contrast, the basic reaction for the polymerization is a homogeneous catalytic redistribution of methylchlorodisilanes in the case of this paper. This type of synthesis can be described as follows. After 0·5% of the catalyst was added to the disilanefraction, the mixture was heated up to 230°C in a three-necked flask under an argon atmosphere. The formed methylchlorosilanes were continuously removed form the pot residue by destillation. Within 1 h the reaction was completed giving a powder-like polysilane.

Characterization of the polysilanes was performed by NMR-spectroscopy. In this paper spectra of ^{29}Si and ^{13}C CP MAS NMR-spectra are shown. The spectra were recorded on a Bruker MSL 300 spectrometer. Additionally X-ray diffraction was applied using a gas tight chamber and Cu K_α radiation in the $2\,\theta$ range of 20 to 80° with 20 s per 0·05° step.

The obtained polysilane was pyrolysed under argon atmosphere in an alumina tube furnace (HTM-Reetz GmbH, Berlin) which allows high heating rates. The heating rate was 30 K min^{-1}. The argon flush was 5 litre h^{-1}. The maximum temperature of the samples was 1650°C. The dwell time at maximum temperature was varied with 5, 10, 15, 30 and 60 min. After pyrolysis the samples were powdered in a mortar to prepare them for further investigations.

The powdered samples were investigated by X-ray diffraction and Raman spectroscopy.

X-ray investigation was performed using Cu K_α-radiation in the $2\,\theta$ range of 20 to 80° with 20 s per 0·05° step.

The Raman spectra were exicited with the 514·5 nm line of an Ar$^+$ laser. The scattered light was analyzed with a triple monochromator (Jobin Yvon T64000) and detected with a cooled CCD (charge coupled device) camera. A laser beam power < 1 mW was used to avoid sample heating.

3 Results and Discussion

3.1 Polymer structure

The structure of the poly(methylchlorosilane) was extensively investigated by Richter and Babonneau.[13,15,16] Prefered methods were solid state CP MAS NMR- and MAS NMR-spectroscopy for ^{29}Si and ^{13}C nucleus to characterize the polymer architecture.

The ^{29}Si and ^{13}C CP MAS NMR-spectra of the used polysilane are given in Fig. 1. Typical signals are found at 35, 25, 14 and −64 ppm in the ^{29}Si spectra. These signals correspond to the units which are shown in Fig. 2 with regard to Richter.[13] Characteristic entities of the used poly(methylchlorosilane) are Si–Cl$_x$ (x = 1, 2) and Si–Si$_z$ (z = 3, 4) surroundings. The dimensions of these entities are not exactly defined. During the formation of the

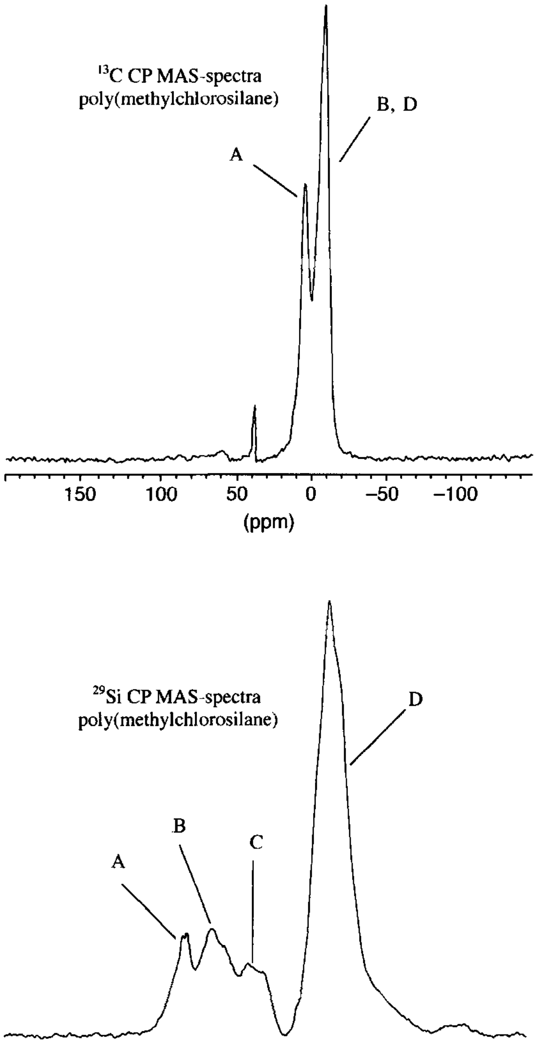

Fig. 1. CP MAS NMR-spectra of poly(methylchlorosilane).

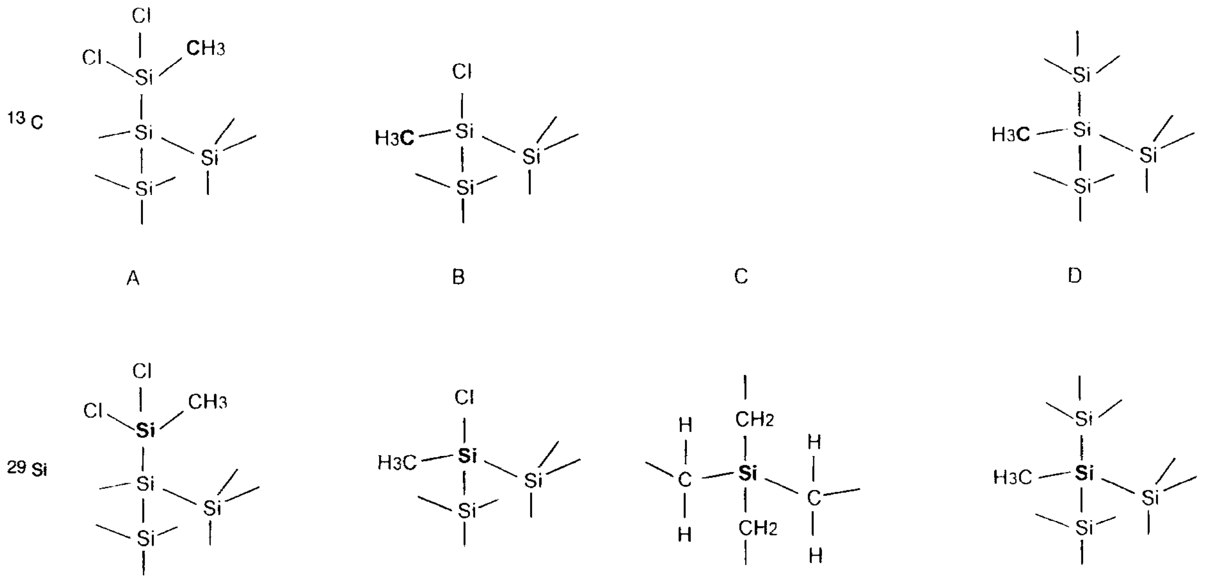

Fig. 2. Entities of poly(methylchlorosilane).

polysilane Si-oligomers are found which properly combine to the polymer. Furthermore the rather broad NMR-peak at −65 ppm implies a variety of such Si–Si$_x$ surroundings in the second order. The dimension of such silicon clusters can reach about one or two nanometers, if the structural units, which are described in Ref. 16, combine to the polymer skeleton.

The signals around 0 ppm in the spectra show that carbosilane units already exist in the polymer which is in contrast to those polymers which were characterized by Richter *et al.*[13,14] where a heterogeneous catalysis was used for polymer synthesis. The existence of carbosilane units is obviously an effect of the homogeneous catalysis of the polymer investigated in this paper. The catalyst is not seperated from the polymer so that the reaction can not be stoped at a certain level as for the heterogeneous catalysis.

The ^{13}C MAS NMR peaks of the polymer are typically found around 0 ppm situated at 11, 4 and −9 ppm for $MeCl_2Si$-, $MeClSi<$ and $MeSi(Si)_3$, respectively.[13] The dimensions of the carbon containing domains are rather small compared with the silicon domains. These groups may generate a polysilane structure similar to that shown in Fig. 3.

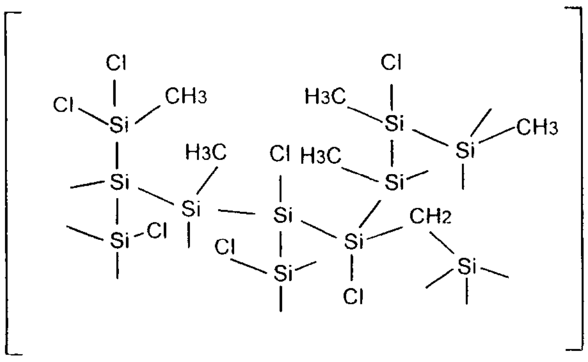

Fig. 3. Principle structure of poly(methylchlorosilane).

Additionally, the polysilane was investigated by X-ray diffraction. The polymer was completely X-ray amorphous, no distinct or spreaded reflex was found. This shows that the molecular structure is disordered and no crystallographic structure is preformed during the polymerization despite of crosslinking of the molecules. The conversion of the precursor to the silicon carbide is already described more precisely in Ref. 17 for similar poly(methylchlorosilane)s. It was additionally found that the resulting structure strongly depends on the heating rate and the pyrolysis time. Rapid heating enables a preservation of the molecular structure of the polymer.

3.2 Ceramic structure

The ceramic residue of the pyrolysed polysilane was investigated by X-ray diffraction and Raman-spectroscopy. The X-ray diffraction patterns are shown in Fig. 4. The patterns correspond with the β-SiC polytype. The detected peaks are broadened what demonstrates the small crystallite dimensions. A calculation of the crystallite size by means of the Scherrer formula gives results between 20 and 30 nm for SiC. Additionally silicon peaks are detected by diffraction. The dimensions of the silicon regions which are also estimated by Scherrer calculation are about 40 nm. The peak broadening was not corrected of the experimental broadening.

Raman spectra of the samples depending on dwell time are shown in Fig. 5. The observed Raman-bands can be assigned to silicon carbide, carbon and silicon. All bands show broadening and frequency shift in comparison with the corresponding phonon lines in large crystals of β-SiC (transversal

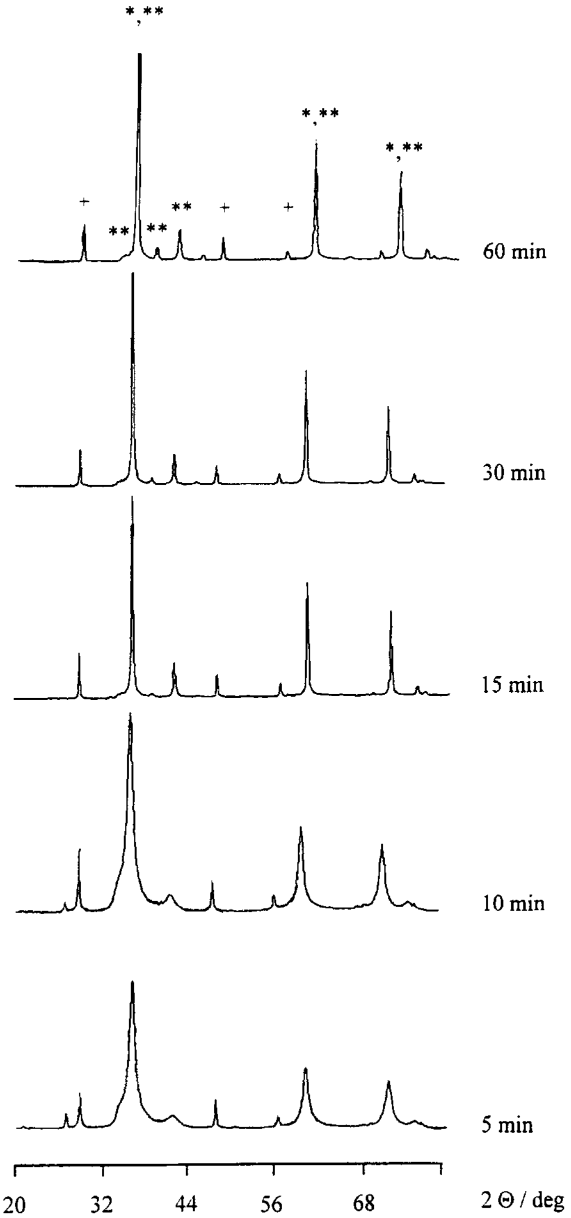

Fig. 4. X-ray diffraction patterns of poly(methylchlorosilane). after heating to 1650°C and varied dwell time. *β-SiC, **α-SiC, +Si.

optical (TO)-phonon → 790 cm^{-1}, longitudinal optical (LO)-phonon → 930 cm^{-1}), Si (516 cm^{-1}) and C (1360, 1610 cm^{-1}). In the spectra we found no indications of phonon lines appearing in α-SiC polytypes, the SiC is assumed to be of β-type.

Further bands are found for SiC (1520 cm^{-1}) and Si (500–507 cm^{-1}). The band at 1520 cm^{-1} can be assigned to a second order Raman-scattering process in SiC which is weak in bulk material compared with the first order scattering, but in our spectra enhanced in intensity, induced by disorder. At 1520 cm^{-1} the two-phonon density of states has a pronounced maximium.[18]

A small size of the SiC particles is already expected with respect to the X-ray results. This is confirmed by Raman-spectra in Fig. 5, which show very broad bands below the TO- and LO-phonon frequencies of bulk SiC. Their shape can be attributed to small particle effects in different ways. First, due to the uncertainty of the wavevector q transferred in the Raman scattering process in particles of some nm in size, phonons from the whole Brillouin zone with $q \neq 0$ take part in the scattering and a downshifting and broadening occurs. Second, in small particles of crystals like SiC surface related phonon modes between the TO- and LO-phonon are observed.[19] From calculations based on the first effect, a particle size of ~2 nm was estimated for the beginning of the dwell time at 1650°C. With increased dwell time a distinct TO-phonon appears at about 790 cm^{-1} and a distinct LO-phonon appears at about 960 cm^{-1} too. This shows the existence of larger well ordered β-SiC crystallites. The already existing silicon carbide particles go to more perfect crystallites and new silicon carbide particles are built up from the silicon and carbon inclusions.This assumption is suppported by the disappearing carbon bands, which is surely caused by consumption of carbon due to reaction with silicon. The discrepancy of the X-ray and Raman calculations for the particle size may result from the different sensibility of the methods to crystallite defects. A concentration of stacking faults may influence the Raman scattering more than the diffraction of X-rays so that we find a smaller size by Raman spectroscopy.

For the two shortest dwell times two bands for silicon exist, which are labeled as A and B in Fig. 5. With increasing dwell time the broader band A is shifted to higher frequencies, somewhat narrowed and disappears for the dwell times 30 and 60 min. Bands with similar shifts of the frequency and bandwidth in comparison with crystalline bulk silicon were observed as well in thin polycrystalline silicon films prepared by low-pressure chemical vapor deposition[20] as in porous silicon.[21–23] From data in the literature[22] and own calculations[19] we estimated the particle sizes corresponding to the bands A and B to be 3 nm and 7 nm, respectively. The discrepancy to the X-ray results is derived for the same reason as already mentioned above. The disappearing of band B and narrowing of band A with increased dwell time could be interpreted as a growing of the larger particles. Another interpretation was given in,[20] where also two bands were observed. With increasing annealing temperature band B decreased in intensity and became narrower. A model of nanosized silicon crystalline grains (band A) surrounded by a surface layer of disordered Si was proposed by those authors. However, we did not observe the broad peak at 480 cm^{-1} characteristic of amorphous silicon.[24] Therefore, we conclude that the observed nanosized silicon is crystalline ordered.

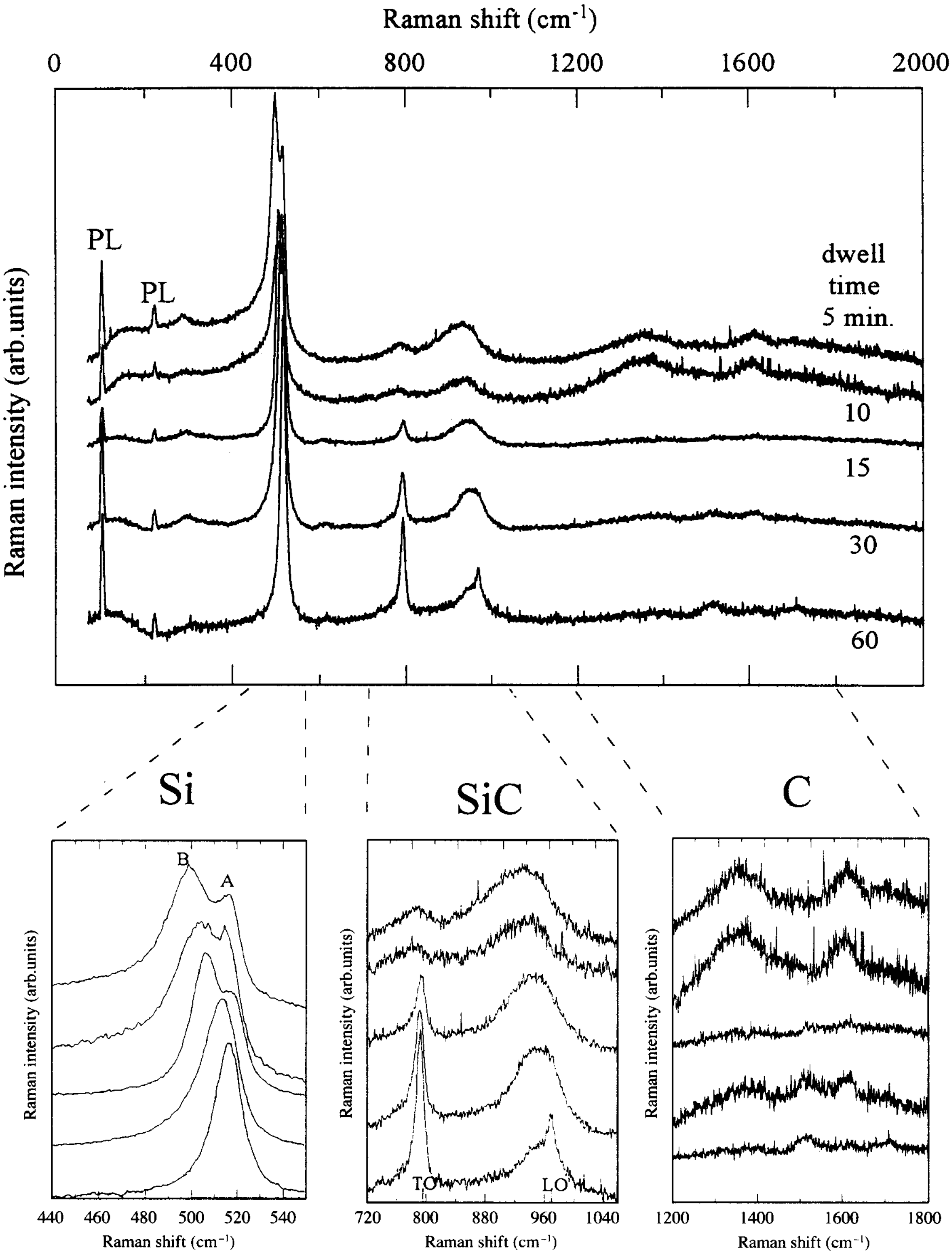

Fig. 5. Raman spectra of SiC samples after 1650°C depending on dwell time.

The silicon particles occur in a remarkable amount and can regarded as characteristic feature of the samples. This component is generally not expected in polymer derived SiC, but it is sometimes observed as already mentioned.[11] A very interesting aspect is that the silicon is of outstanding fine dimenensions. The calculated size for the silicon particles lies in a range of about 100 elementary cells [$a_0 = 0{\cdot}54$ nm (diamond structure)]. This fact implies the estimation that these structures are built up from residuals of the original polymer which serve as nucleus for crystallite grow. Probably the smallest silicon particles form with the carbon silicon carbide and additionally there is a diffusion of silicon to more agglomerated particles with dwell time.

The carbon component seems to be not really dominating in the material. Some weak bands are detected around 1360 and 1610 cm^{-1}. The occurrence of both bands confirms the existence of small amorphous carbon particles. The structure of that carbon is identical to that already described in Refs 10 and 25. An empirical formula derived in Ref. 26 relates the intensity ratio of the two carbon bands at $1355\,cm^{-1}$ and $1575\,cm^{-1}$ to the particle size. The results were found in good agreement with data from X-ray diffraction by other authors.[27]

4 Conclusions

Controlling a ceramic material structure by design of precursor molecules through chemical methods is an ambitious aim for the future. The behavior of the polysilane after a certain pyrolysis step to preserve its structure should be a first step on this way.

A comparison of the polysilane structure and the ceramic structure demonstrates the resembling architecture of both materials:

polysilane:

- silicon rich polymer ($Si/C > 1$)
- Si units of about 1 nm size, (assumed from molecular data)
- carbon units of 0·4 nm size, (assumed from molecular data)
- partly Si-C skeleton

ceramic (after pyrolysis):

- Si (metallic) 45 nm homogeneously distributed
- carbon small amount, amorphous, 5 nm
- β-SiC nanocrystalline 30 nm and amorphous

Also more complex structures can be obtained depending on the pyrolysis conditions and the precursor structure. Rapid firing and stable precursor molecules seems to be a good tool to gain designed microstructures of ceramics.

Acknowledgements

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