

# The microstructure of polymer-derived amorphous silicon carbide layers

A. Hilbig<sup>a,\*</sup>, E. Müller<sup>a</sup>, R. Wenzel<sup>b</sup>, G. Roewer<sup>b</sup>, E. Brendler<sup>c</sup>, G. Irmer<sup>d</sup>, G. Schreiber<sup>e</sup>

<sup>a</sup> Institute of Ceramic Materials, Gustav-Zeuner-Str. 3, Freiberg University of Mining and Technology, D-09596 Freiberg, Germany

<sup>b</sup> Institute of Inorganic Chemistry, Leipziger Str. 29, Freiberg University of Mining and Technology, D-09596 Freiberg, Germany

<sup>c</sup> Institute of Analytical Chemistry, Leipziger Str. 29, Freiberg University of Mining and Technology, D-09596 Freiberg, Germany

<sup>d</sup> Institute of Theoretical Physics, Bernhard-von-Cotta-Str. 4, Freiberg University of Mining and Technology, D-09596 Freiberg, Germany

<sup>e</sup> Institute of Physical Metallurgy, Gustav-Zeuner-Str. 5, Freiberg University of Mining and Technology, D-09596 Freiberg, Germany

Available online 11 September 2004

## Abstract

In order to achieve thin amorphous silicon carbide layers a two-stage process was applied. The deposition of thin layers from liquid chlorovinylsilanes was carried out under argon flow using a spin-coating-system. Afterwards, the samples were pyrolysed in a temperature range between 800 °C and 1200 °C with different hydrogen concentrations in the atmosphere. Additionally, bulk material was pyrolysed in order to characterise structural changes by transition oligomer to a-SiC:H.

In this work we present studies on the structure of the layers and of bulk material, which were carried out by XRD, MAS NMR and Raman spectroscopy, depending on pyrolysis conditions. Following results were obtained: Both, silicon carbide layers and bulk material, pyrolysed at 800 °C, were amorphous. Increase of the temperature to 1200 °C leads to a partial amorphous-to-crystalline transition forming  $\beta$ -SiC. Moreover, derivations from stoichiometric SiC were observed: Free silicon was found in thin layers, whereas crystallites of graphite were detected in the bulk material. The amount of excess carbon can be influenced by addition of hydrogen to the pyrolysis atmosphere.

© 2004 Elsevier Ltd. All rights reserved.

**Keywords:** Silicon carbide; Amorphous; Polymeric route

## 1. Introduction

Silicon carbide (SiC), due to its excellent properties such as very high hardness, high abrasive wear resistance and very high thermal conductivity, has been successfully used in quite different forms in many industrial applications.<sup>1</sup> In case of SiC layers, two functional aims are to distinguish: very thin layers for electronic devices and wear or oxidation resistant coatings for constructive applications. The most popular way to obtain such layers – the deposition from the gas phase – is relatively expensive. Therefore, we obtained silicon carbide from a liquid phase by the conversion of organosilicon compounds into ceramic materials. The polymeric route is cheaper than CVD or PVD processes and also the deposition system is uncomplicated and its usage very simple. A particular reason for trying such an approach is as follows: For applications of SiC layers in the field of opto-electronics the

amorphous state of silicon carbide is of special interest.<sup>2</sup> This state can be stabilised by hydrogen occupying dangling bonds within the amorphous network of silicon carbide. During the transformation of a preceramic oligomer into polycrystalline SiC ceramics during thermal treatment, the material is passing through such an amorphous state.<sup>3</sup>

In our work thin amorphous hydrogenated silicon carbide layers were obtained from oligomers using a spin-coating-system and then pyrolysed to amorphous and partially crystalline structures. The starting precursors were derived by a catalytic heterogeneous disproportionation reaction.<sup>4</sup> The polymerisation process and optimisation of the deposition and pyrolysis processes are described in detail in Refs. <sup>5,6</sup>. Additionally, we pyrolysed bulk material in order to compare the results with these of the layers and also to apply investigation methods, which are not suitable for thin layers. The aim of this paper is a characterisation of the microstructure of such amorphous or semi-crystalline layers using various experimental techniques: Raman spectroscopy, solid state NMR and XRD.

\* Corresponding author. Tel.: +49 3731 392388; fax: +49 3731 393662.  
E-mail address: [hilbig@ikw.tu-freiberg.de](mailto:hilbig@ikw.tu-freiberg.de) (A. Hilbig).

## 2. Experimental

The layers were deposited from the liquid chlorovinylsilanes using a spin-coating-system, B.L.E. Laboratory Equipment GmbH. The deposition was carried out under inert gas conditions on different substrates like silicon wafers or silica. In order to obtain homogeneous layers with a thickness smaller than 1  $\mu\text{m}$ , the oligomers were dissolved in  $\text{CH}_2\text{Cl}_2$  (dichloromethane). After deposition, some layers were heated at 800 °C under argon flow (presented in this article are samples 38, 61 and 62) or in a gas mixture containing 10% hydrogen in argon (samples 78, 81, 87 and 102) by heating rates of 1–2 °C/min. Layers 61 and 87 were also annealed in 10% hydrogen in argon at 1200 °C to investigate the beginning of crystallisation. Heating rates of 3 °C/min were applied in this case. Bulk material was pyrolysed under the same conditions as the layers and annealed under different hydrogen concentrations. The optimisation of the deposition process and pyrolysis conditions are described in Ref. 5.

The XRD measurements were carried out using a diffractometer TUR-M-62 HZG 4. Due to small thickness of the layers, analyses were carried out under grazing incident (about 1°). For Raman measurements a spectrometer LABRAM 800 HR [Laser: Nd:YAG, doubled frequency ( $\lambda = 532 \text{ nm}$ )] was used. The MAS-NMR-measurements were carried out at a Bruker MSL 300 at a spinning speed of 5 kHz and resonance frequencies of 75.47 MHz ( $^{13}\text{C}$ ) and 56.627 MHz ( $^{29}\text{Si}$ ).

## 3. Results and discussion

Layers obtained at 800 °C were amorphous, which was confirmed by XRD measurements (see Fig. 1a). Character-

istic peaks of polycrystalline silicon carbide are not observable in this case. After pyrolysis of the bulk material at the same temperature (Fig. 2a) we also did not find any indication for a real crystallisation process, but a smeared intensity “hump” is already observable in the  $2\theta$  region between 30° and 36°, where the strongest peak of  $\beta\text{-SiC}$  (1 1 1) will occur after crystallisation ( $2\theta = 35.6^\circ$ ). If we interpret this hump as a pre-form of that reflex we are able to use the Scherrer equation for estimating the dimension of the pre-formed coherent – but still disturbed – structure units from the “broadening” of this “peak”. This would give a value of about 0.9 nm. This is about 20% larger than the diameter of one cubic unit cell of SiC. Such a unit cell contains four  $[\text{SiC}_4]$  tetrahedra connected by sharing corners. Thus, we can get a rough idea of the cluster sizes of tetrahedra, which represent already structure units similar to the final crystal structure within the amorphous network.

The Raman spectra of the layers after pyrolysis at 800 °C in pure argon show the existence of an excess carbon with a graphite-like structure in our materials, which was indicated by the presence of the G- and D-peaks (Fig. 3a). A band at 1598  $\text{cm}^{-1}$  is assigned to ordered graphite structure (G-peak), while the band at 1345  $\text{cm}^{-1}$  – mostly called “disordered carbon” – (D-peak), originated from breathing vibrations of aromatic rings in carbon clusters. The absence of these bands after pyrolysis in 10% hydrogen in argon (layer 102, see Fig. 3b) indicates that already at this temperature hydrogen is able to reduce the graphitic excess carbon resulting from the decomposition of the precursors (very small graphite cluster sizes below 2 nm are not visible in Raman spectra).

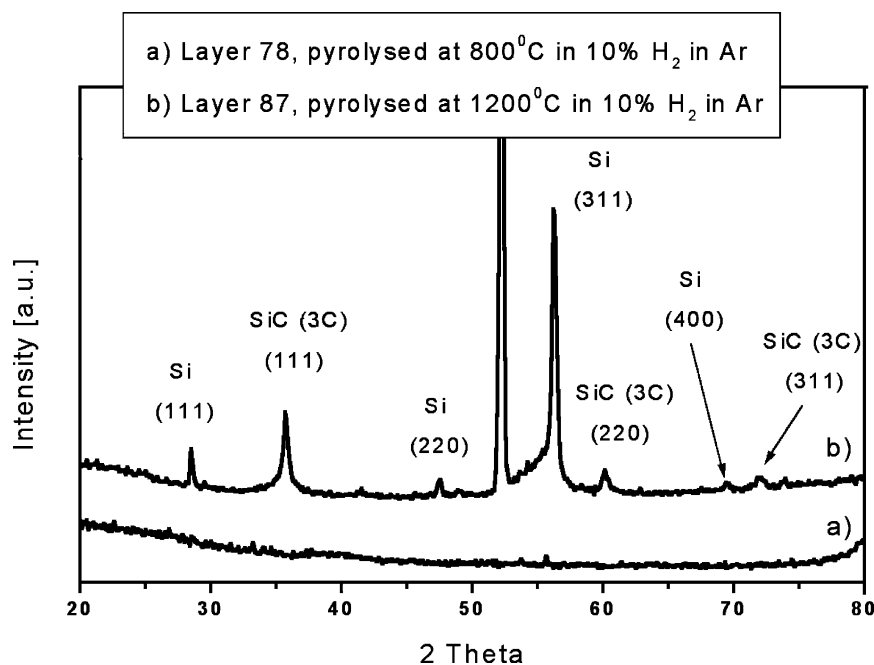


Fig. 1. Diffraction pattern of two SiC:H layers: (a) obtained after a treatment at 800 °C; (b) after pyrolysis at 1200 °C.

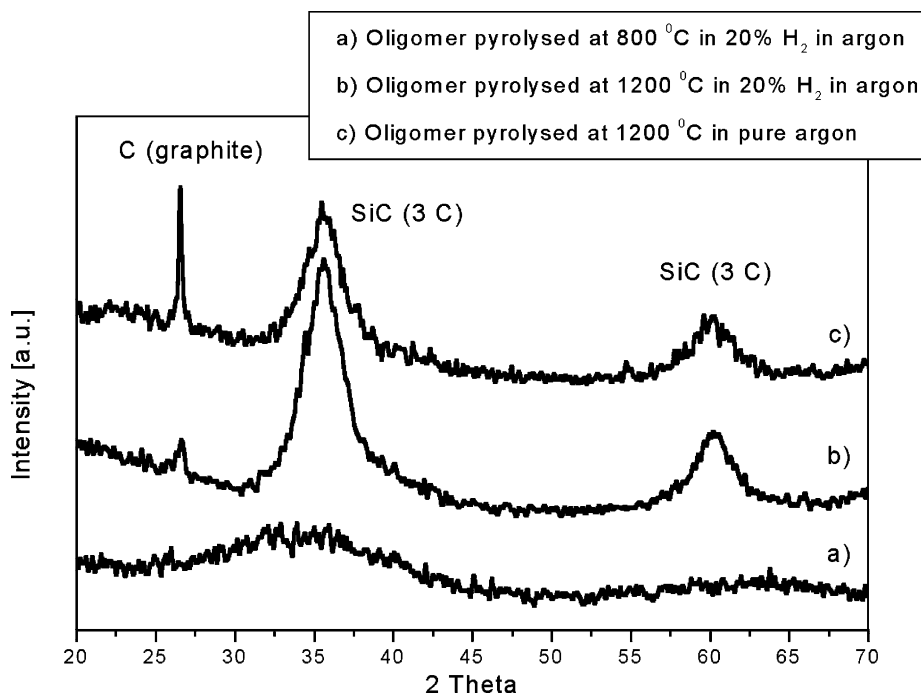


Fig. 2. Diffraction pattern of bulk material after pyrolysis: (a) at 800 °C in a gas mixture containing hydrogen; (b) at 1200 °C in the same atmosphere; (c) at 1200 °C in pure argon.

The existence of an amount of excess carbon was also found in the <sup>13</sup>C single pulse- and cross-polarisation-MAS-NMR-spectra of the bulk material. Fig. 4 shows two spectra of the precursor after pyrolysis at 800 °C under argon with 10% hydrogen. Several carbon environments can be observed. The signal at about 17 ppm can be assigned to carbon surrounded

by silicon. The signals between 100 and 150 ppm are related to aromatic carbon structures. The remaining hydrogen is localised in the CSi<sub>4</sub> environments and in the aromatic region giving rise to the signal at 135 ppm. This signal can be due to aromatic graphite-like structures with remaining hydrogen or connected with C–H bonds. In this case they should correlate

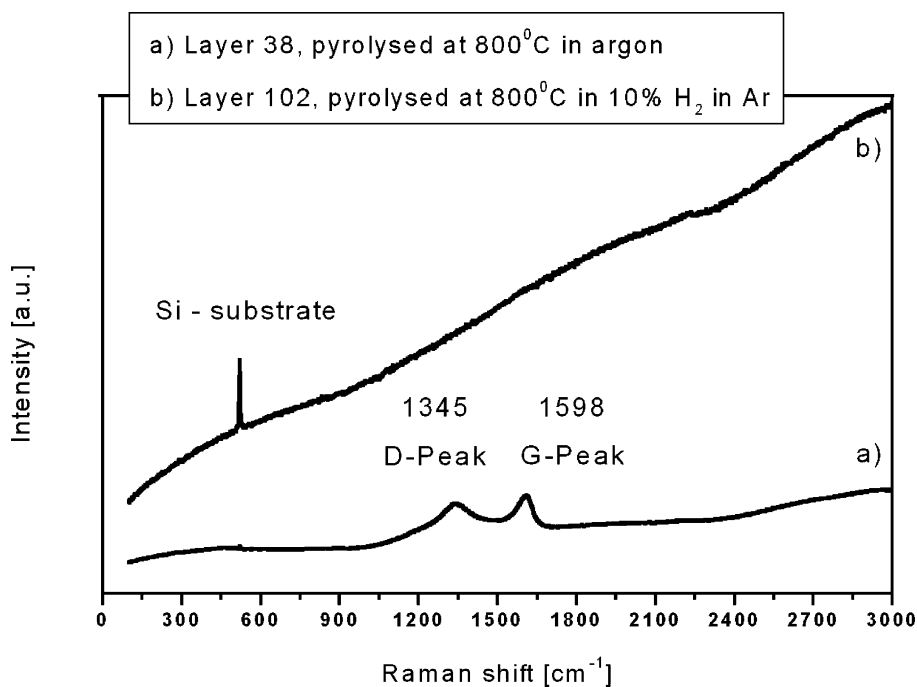


Fig. 3. Raman spectra of two SiC:H layers pyrolysed at 800 °C: (a) in argon; (b) in a gas mixture containing hydrogen.

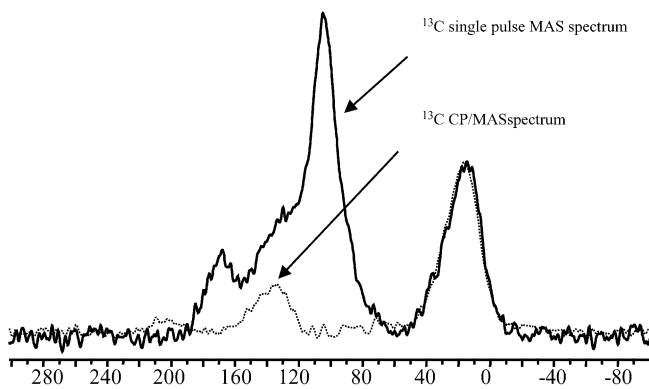


Fig. 4.  $^{13}\text{C}$  CP/MAS- and  $^{13}\text{C}$  single pulse MAS spectra of the oligomer after pyrolysis at  $800^\circ\text{C}$  in argon + 10% hydrogen.

with the D-peak of the Raman spectra. However, the dominating carbon signal at 105 ppm represents a hydrogen free structure and is assigned to free carbon. It correlates clearly to the graphite structure (G-peak) already observed in the Raman spectra.

The MAS NMR spectra of the bulk material after pyrolysis are strongly different from those of the precursors. In Fig. 5, the  $^{13}\text{C}$  CP/MAS NMR spectrum of the starting oligomer is shown. In the spectral region from  $-10$  to  $10$  ppm methyl- and  $\text{CH}_2$ - or  $\text{CH}$ -groups connected to silicon were found. The signal around  $30$  ppm is related to  $\text{CH}_2/\text{CH}$ -groups, not connected to silicon, which are formed during the reaction of vinyl groups with each other. The low intensity signal around  $135$  ppm is assigned to residual double bonds originating from the reaction of the vinyl groups.

In the  $^{29}\text{Si}$  CP/MAS NMR spectrum (Fig. 6) three main peaks around  $20$  ppm are related to silicon atoms connected to a methyl-group and two chlorine atoms or to methyl, one chlorine and an alkyl/alkene bridge to another silicon atom. The low intensity peak at about  $-40$  ppm is typical for linear polysilane structures ( $\text{MeSiSi}_2\text{C}$ ) and that one around  $-65$  ppm for silicon atoms bonded to three other silicon atoms ( $\text{MeSiSi}_3$ ). From the  $^{13}\text{C}$  and  $^{29}\text{Si}$  spectra, it can be

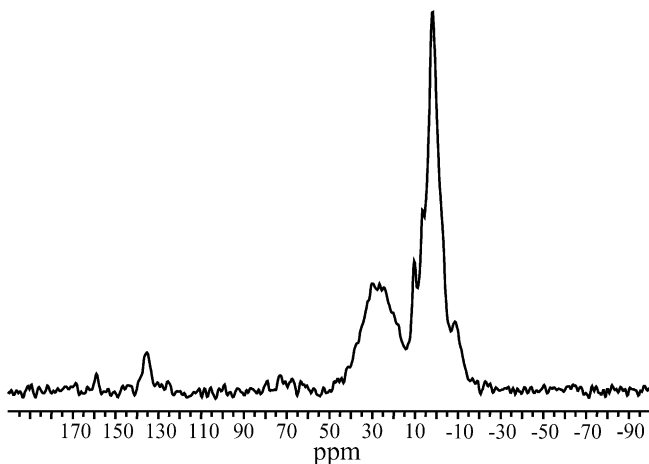


Fig. 5.  $^{13}\text{C}$  CP/MAS NMR spectrum of starting oligomer.

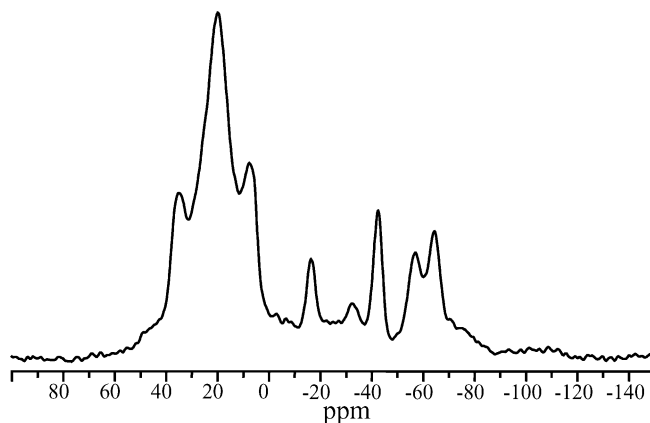


Fig. 6.  $^{29}\text{Si}$  CP/MAS NMR spectrum of starting precursor.

concluded that the oligomerisation process is dominated here by the reaction of the vinyl groups with each other.

Pyrolysis at  $1200^\circ\text{C}$  leads to a partial crystallisation of the materials, which indicates the presence of the peaks at  $2\theta_1 = 35,7^\circ$  and  $2\theta_2 = 60^\circ$  assigned to the cubic polytype 3 C of silicon carbide ( $\beta\text{-SiC}$ ) (Fig. 1b and Fig. 2b, c). The reflexes are broadened due to still relatively small sizes of the SiC crystallites (about  $3$  nm). Diffraction pattern of layer 87 after pyrolysis at  $1200^\circ\text{C}$  shows also the presence of peaks correlated with silicon. The strongest peak at  $2\theta = 52,1^\circ$  arises from the monocrystalline silicon substrate and is excited accidentally, under the geometric diffraction conditions chosen here (W  $\text{L}\alpha$  radiation), due to W impurities in the Cu anode of the X-ray tube, which pass the monochromator after the sample [ $\text{Si}(3\ 1\ 1)$ ,  $\lambda = \text{W L}\alpha$ ]. The smaller Si peaks arise from the Cu  $\text{K}\alpha$  radiation applied here and are due to polycrystalline silicon which was formed beside SiC during the pyrolysis within the layer (Fig. 1b).

The occurrence of polycrystalline silicon within the layers exhibits a significant difference to the results obtained from bulk material under the same pyrolysis conditions (Fig. 2). Here we can detect free carbon (graphite) beside silicon car-

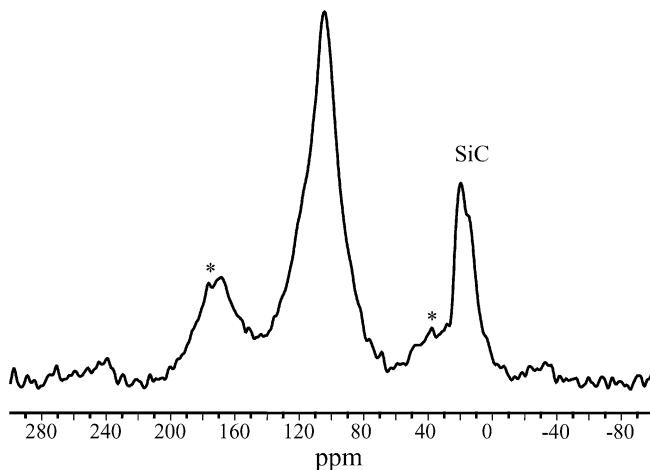


Fig. 7.  $^{13}\text{C}$  single pulse MAS spectrum of the oligomer after pyrolysis at  $1200^\circ\text{C}$  under argon flow.

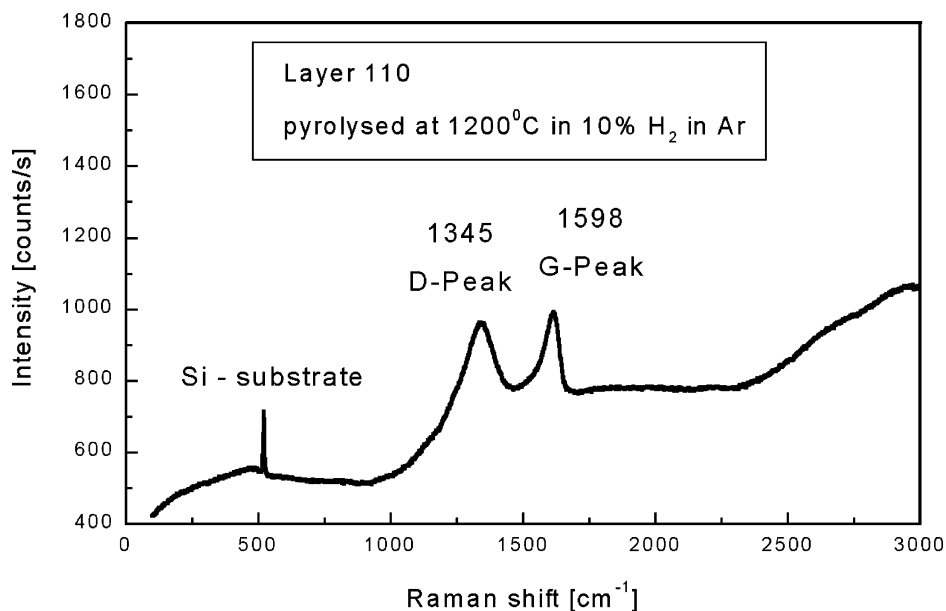


Fig. 8. Raman spectrum of a SiC:H layer after pyrolysis at 1200 °C in 10% hydrogen in argon.

bide, but no indication of the existence of free silicon was found. We have to discuss two aspects responsible for these differences. On the one hand, we must consider possible differences in the C/Si ratio developing during the pyrolysis of layers and bulk. Due to the small thickness of the layers, residual monomers as well as cleaved organic side groups may escape more quickly from the layers structure than from bulk material during heating. It is possible, that we obtain an amorphous Si–C–H network after pyrolysis, which is poorer in carbon than the corresponding network of the bulk material. On the other hand, we know from our own investigations<sup>7</sup> that depending on the heating conditions NMR and Raman spectra of polymers pyrolysed in different ways show differences, especially with respect to the transformation degree of polysilanes into polycarbosilanes in the temperature range between 300 °C and 400 °C. In case of an incomplete transformation due to a high heating rate, NMR signals of [SiSi<sub>4</sub>] or [SiSi<sub>3</sub>C] units are still detectable in the pyrolysed material. In such cases the XRD pattern reveals also diffraction peaks of silicon beside that ones of SiC after further annealing up to 1650 °C. Obviously, the crystallisation mechanisms are significantly influenced by such units, which can act as nuclei for a crystallisation of silicon. We suppose that in the layers, due to the quickly escaping of the organic groups, the so-called Kumada-rearrangement takes place similar incompletely like in case of the bulk material, which was pyrolysed by high heating rates. The silicon peaks are disappearing during a longer high temperature treatment due to a progressing reaction of silicon with excess carbon which is also detectable by Raman spectroscopy.

A reflex at  $2\theta = 26.5^\circ$  in Fig. 2c of the sample pyrolysed in pure argon at 1200 °C is related to graphite. It is remarkable that this reflex is not detectable in case of materials pyrolysed in the gas mixture containing hydrogen, which suggests that

hydrogen is able to reduce the amount of excess carbon in those materials (Fig. 2b and c).

Fig. 7 shows a <sup>13</sup>C single pulse MAS NMR spectrum of a sample pyrolysed at 1200 °C under argon flow. The line narrowing for the CSi<sub>4</sub> peak (in comparison with the same signal in Fig. 4) is connected with the beginning of crystallisation of SiC, which is in agreement with the XRD results. The intensity of the SiC-signal is lower than that of free carbon, which is related to the very long relaxation time of carbon in crystalline SiC, especially of β-SiC.

The last figure shows a comparison of the Raman spectra of layer 102 and layer 110 (Fig. 8). Layer 110 was pyrolysed in the same atmosphere as layer 102, but at a higher temperature of 1200 °C. Although after the treatment up to 800 °C, free carbon was not detectable in layer 102, we find the D- and G-peaks after treatment at 1200 °C, which can be interpreted by the growth of carbon clusters at higher temperature, using excess carbon, which was distributed within the amorphous network, and was released only at higher temperatures due to the crystallisation of SiC.

Expected Raman bands of silicon carbide at 795 cm<sup>-1</sup> are not observable, but we know from former investigations<sup>7,8</sup> that the sizes of SiC crystallites, which are detectable by Raman spectroscopy, required higher annealing temperatures than applied here, above 1500 °C. Non characteristic Raman band is known for amorphous SiC:H.

#### 4. Conclusions

Amorphous silicon carbide layers and bulk material stabilised by hydrogen (a-SiC:H) were obtain by polymer route. After pyrolysis at 800 °C, both layers and bulk material were amorphous, which was confirmed by X-ray diffraction

and MAS NMR spectroscopy. The materials contain also an amount of excess carbon which can be influenced by an addition of hydrogen to the pyrolysis atmosphere and is depending on the geometric dimensions of the sample. Therefrom, drastic differences of the content of free carbon in the amorphous networks of thin layers in comparison to bulk material result. Annealing at 1200 °C leads to partial crystallisation processes by forming  $\beta$ -SiC in all materials. Additionally, free silicon was found in thin layers, whereas the crystallites of graphite were detected in the bulk material.

### Acknowledgement

The authors thank Deutsche Forschungsgemeinschaft (DFG) for financial support of this work.

### References

1. Müller, E. and Martin, H. P., *J. Prakt. Chem.*, 1997, **339**, 401.
2. Krause, M., Topic, M., Stiebig, H. and Wagner, H., *Phys. Stat. Sol. (a)*, 2001, **185**(1), 121.
3. Roewer, R., Herzog, U., Trommer, K., Müller, E. and Frühauf, S., *High-Performance Non-Oxide Ceramics. I, Vol 101*, ed. M. Jansen. Springer, Berlin, Heidelberg, New York, 2002, p. 92.
4. Richter, R., Roewer, G., Böhme, U., Busch, K., Babonneau, F., Martin, H.-P. et al., *Appl. Organomet. Chem.*, 1997, **11**, 71.
5. Müller, E., Hilbig, A., Wenzel, R., Trommer, K., Roewer, G., Sciuropa, O. et al., *Adv. Eng. Mater.*, 2002, **4**, 880.
6. Trommer, K., Herzog, U., Schulze, N. and Roewer, G., *Main Group Metal Chem.*, 2001, **24**, 425.
7. Martin, H.-P., Irmer, G. and Müller, E., *J. Eur. Ceram. Soc.*, 1998, **18**, 193.
8. Martin, H.-P., Thesis, TU Freiberg, 1994.