Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of the European Ceramic Society 32 (2012) 627–632

www.elsevier.com/locate/jeurceramsoc

On the shrinkage during pyrolysis of thin films and bulk components: The case of a hybrid silica gel precursor for SiOC glasses

Gian Domenico Sorarù [a,*], Aylin Karakuscu [a], Cédric Boissiere [b], Florence Babonneau [b]

[a] *Dipartimento di Ingegneria dei Materiali e Tecnologie Industriali, Via Mesaino 77, 38123 Trento, Italy*
[b] *Laboratoire de Chimie de la Matière Condensee de Paris, Université Pierre et Marie Curie, 75005 Paris, France*

Received 23 June 2011; received in revised form 22 September 2011; accepted 1 October 2011
Available online 21 October 2011

Abstract

This paper compares the shrinkage during pyrolysis of a gel precursor as thin film and as bulk sample. The hybrid silica gel, precursor for SiOC glasses, contains $Si–CH_3$ and Si–H moieties. The shrinkage of bulk samples has been measured with conventional dilatometry. Shrinkage of thin films has been studied for the first time with in situ dilatometry allowing to measure the thickness and the refractive index during pyrolysis. Thin films shrink more compared to bulk samples and the pyrolytic transformation occurs at lower temperature (100–150 °C) compared to the bulk samples.

Keywords: Films; Sol–Gel processes; Precursors-organic

1. Introduction

Silicon oxycarbide (SiOC) is a ceramic material belonging to the wider Polymer Derived Ceramics (PDCs) family[1] which has attracted much attention in recent years for its high thermal stability,[2] creep resistance[3] and interesting electrical and optical properties.[4–6] Processing of SiOCs via polymer pyrolysis starts with the shaping and cross-linking of the polymer precursor followed by pyrolysis at 800–1000 °C. The polymer-to-ceramic transformation occurs via solid-state reactions with the release of gaseous products such as H_2, hydrocarbons (CH_4 or $CH_2{=}CH_2$) and Si-containing molecules (silanes or siloxanes), which are responsible for the weight loss and for the shrinkage of the component.[7] Weight losses around 20–30% and volumetric shrinkage around 50% are common for many SiCN and SiOC PDCs.[8] The gaseous species produced during pyrolysis, must diffuse through the network to the surface of the component. Accordingly the "diffusion distance" could affect the polymer-to-ceramic transformation, its ceramic yield and eventually the composition and the structure of the final ceramic material. In principle, ultra-thin structures such as thin films with thickness lower than ~1–2 μm or 1D/2D nanostructure could allow a higher escape of pyrolysis gases compared to thicker samples such as rods[3,8] or powders[7] with a length-scale of ~ 0.1–1 mm in the shortest dimension. Differences in weight loss could in turn affect the shrinkage and the composition/properties of the final PDC components compared to those obtained on thicker structures. Among the various papers reported in the literature dealing with PDC thin films[1] only one study mentions a difference in the pyrolitic transformation between thin films and coarse powders.[9] In this work,[9] the synthesis of thin SiC films from polycarbosilane is studied and it showed that standard grade Ar (99%) led to a complete oxidation of the polycarbosilane thin film to SiO_2, whereas corresponding coarse SiC powders were produced without any problem. More interestingly, thin films exhibited an enhanced crystallization of β-SiC compared to powder sample. These results seem to point out the importance of the samples's dimensions (film thickness or powder size) when processing a PDC. However, perhaps due to the experimental difficulties in characterizing the pyrolitic transformation of thin films, no information are available in the literature to compare the weight loss and/or the shrinkage of thin films and bulk samples.

To get insights into this problem, in the present study we compare the pyrolysis behavior of a hybrid silica gel, precursor for SiOC glass, as thin film and as bulk sample. The shrinkage of

* Corresponding author.
E-mail address: soraru@ing.unitn.it (G.D. Sorarù).

0955-2219/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2011.10.004

the bulk sample has been recorded using conventional dilatometry while the shrinkage of the corresponding thin film has been studied by in situ ellipsometry. To the best of our knowledge these are the first in situ ellipsometry measurements obtained during the pyrolysis of a preceramic precursor. This technique allows measuring the thickness and the refractive index of the thin film. Since the refractive index is also related to the porosity of the material, in situ ellipsometry gives also information on the development of porosity during the pyrolytic conversion.

The precursor for the present study is a hybrid silica gel containing Si–CH_3 and Si–H groups.[10] This precursor has been chosen since: (i) it has been extensively studied and its pyrolysis mechanism is well known,[7] and (ii) it can be easily pyrolyzed to SiOC glass either as millimeter-sized crack-free components (in the form of thin disks of 5–10 mm in diameter and around 1–1.5 mm thick)[11] and as thin films.[12]

2. Experimental

2.1. Synthesis of the samples

Bulk SiOC samples were produced by the polymer pyrolysis method from sol–gel derived precursors. The sol–gel solution was prepared from triethoxysilane (TH), $HSi(OEt)_3$, and methyldiethoxysilane (DH), $HCH_3Si(OEt)_2$ with a TH:DH = 2:1 molar ratio and using ethanol as solvent with a Si:EtOH = 1:2 (molar ratio). The hydrolysis was induced by adding acidic water (HCl, pH 4.5). After stirring for 20 min, the solution was cast into test tube and left open at room temperature for gelation. Xerogels were obtained after drying the gel by increasing the temperature slowly up to 110 °C for 10 days. Accordingly, crack formation due to fast release of solvent was prevented and xerogel rods were obtained with 7–8 mm in diameter and 30–40 mm in length.

A sol–gel solution, with the same molar ratio of the two Si alkoxides, was used and spin coated on ultrasonically cleaned SiO_2 (Heraeus – HSQ300) at 3000 rpm for 1 min. For the FT-IR characterization in transmission mode the sol–gel solution was spun on Si wafers. The gel films were dried at 80 °C for 24 h before pyrolysis. Typical thickness of the gel films is below 1 μm. Details of this preparation are reported elsewhere.[12]

2.2. Sample characterization

FT-IR (Nicolet Avatar 330) in transmission mode is used to analyze bonding structure of bulk samples. The bulk sample was milled in an agata mortar and the powders were mixed with KBr to get a pellet for FT-IR analysis. Similar to bulk samples, bonding structure of the dried film is analyzed by FT-IR in transmittance mode without further preparation. The FT-IR spectra were collected from 4000 to 400 cm^{-1} recording 256 scans for each analysis.

2.3. Characterization of the pyrolysis process

2.3.1. Weight loss

Weight loss of the powdered sample (80 μm ≤ d_p ≤ 224 μm) was followed by thermo gravimetric analysis (TGA) using a STA 409 Netzsch apparatus. The experiment was performed under Ar flow of 100 ml/min with a heating rate of 10 °C/min up to 1400 °C.

2.3.2. Shrinkage

The shrinkage of the bulk gel samples during pyrolysis was followed by dilatometric experiments up to 1400 °C. Disc sample having approximately 1.5 mm thickness and 7.7 mm diameter was obtained by cutting and polishing a dried gel rod. The sample was loaded into Netzsch 402/E dilatometer and the expansion and/or contraction along its diameter was recorded as a function of temperature. Experiment was performed under Ar flow (100 ml/min) with a heating rate of 5 °C/min. The sample survived the dilatometric test without breaking – or even developing cracks – allowing for ex-post measurement of its dimensions at room temperature. Measuring the shrinkage along the disc diameter and thickness provides a means to assess if the volume contraction is isotropic.

Shrinkage of the films during pyrolysis was followed up to 700 °C by measuring its thickness using in situ thermal ellipsometric analysis. Ellipsometry measurements were performed on a UV–vis variable-angle spectroscopic ellipsometer (VASE) from Woollam, and data analysis was performed with the WVase32 software. Measurements were fitted over the transparent range (550–1000 nm). A single Cauchy layer was used to model the deposited films, asymmetric optical properties emanating from unidirectional contraction were not observed, and therefore, no correction was applied. For in situ ellipsometric analysis, the ellipsometer was fitted with a home-built covered heating unit connected to a programmable temperature regulator (developed in conjunction with SOPRA). Small holes were present to allow a thermocouple and beam access to the sample as well as gas flow. The pyrolysis environment was adjusted by flowing Ar (ca 2.5 L min^{-1}) on top of the sample.[13]

For pyrolysis temperature above 700 °C the film shrinkage was followed by ex-post measurements by standard ellipsometry. Accordingly, the films were pyrolyzed in a C-furnace under Ar flow (100 ml/min) with a heating rate of 5 °C/min at different temperatures, in the range 800–1200 °C with 1 h holding time at the maximum temperature. Both in situ and standard ellipsometer are used to calculate refractive indexes of the films allowing following its evolution during pyrolysis.

3. Results and discussion

3.1. Characterization of the samples

Since the aim of this study is to compare the shrinking behavior during pyrolysis of thin coatings and bulk monoliths it is important to characterize the starting precursors to make sure that the two different processing techniques, i.e. spin coating for the films and casting for the bulk components, did not result in

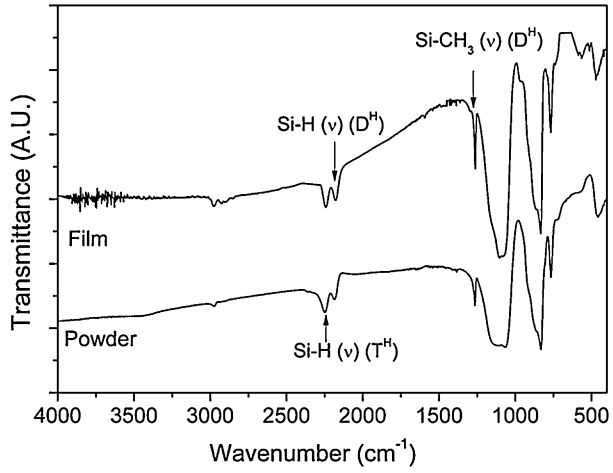

Fig. 1. FT-IR spectra of gel film and powder. Relevant bands used to have a semi-quantitative comparison of the two samples are indicated with arrows.

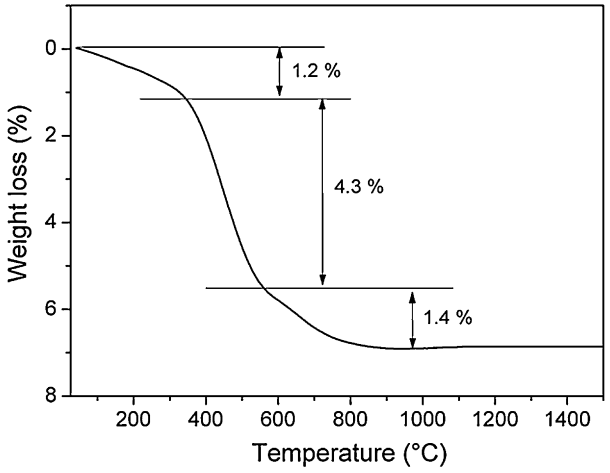

Fig. 2. TGA curve of the gel powders (80 μm ≤ d_p ≤ 224 μm) with corresponding weight losses.

different chemical composition or gel structure. For example, a preferential evaporation of one of the two silicon precursors could occur at different extent from the thin films compared to the thick monolithic gels. Accordingly, the bonding structure of the bulk and films in the gel state is studied by FT-IR analysis (Fig. 1). Both spectra showed similar features: C–H (ν) bond are visible at 2900–3000 cm^{-1}, Si–H bonds gave rise to peaks at 2250 cm^{-1} (ν_{Si-H} in TH units), 2180 cm^{-1} (ν_{Si-H} in DH units) and 830 cm^{-1} (δ), Si–CH_3 vibrations at 1265 cm^{-1} (ν) and 760 cm^{-1} (rocking). Si–O (ν) peaks lead a broad peak at 1140–1065 cm^{-1}. These results indicate that in both samples peaks related to the presence of Si–CH_3 and Si–H moieties of the DH and TH precursors are present with similar intensities suggesting that no major compositional differences exist between the two set of samples (see Fig. 1).

3.2. Characterization of the pyrolysis process

3.2.1. TGA

The organic-to-inorganic transformation was followed by TGA and the result is reported in Fig. 2. The precursor gel shows a very small weight loss up to 350 °C (1.2 wt%) due to the removal of residual OH and/or OEt groups,[7] a 4.3 wt% loss between 350 and 550 associated with the evolution of silanes/siloxanes formed through redistribution reactions between Si–H, Si–O and Si–C bonds and a final ceramization step (1.4 wt%) with evolution of CH_4 and H_2.[7] Above 800 °C the TGA does not show any further weight loss and the pyrolysis may be considered complete. The overall weight loss is small, ~6.9 wt%, in agreement with published data[7] and with our previous experience.[14]

3.2.2. Shrinkage behavior

The dimensional changes of the bulk sample after the dilatometric study are reported in Table 1. It can be seen that the linear shrinkage is isotropic and reaches 22% from RT up to 1400 °C while the volume shrinkage is ~53%.

The shrinkage behavior of 3D bulk samples and thin films cannot be studied by comparing the linear shrinkage measured by dilatometry on bulk gels and the shrinkage of the film thickness. Indeed, it should be noted that the shrinkage of 3D samples is isotropic (see Table 1) while the volume shrinkage of the film is accommodated only in the z direction being the shrinkage in the plane constrained by the bonding with the substrate. Therefore, what we need to compare is the *volumetric* shrinkage rather than the *linear* one. Accordingly, the raw data have been used to calculate the volume shrinkage using the following relationships:

$$\left(\frac{\Delta V}{V_0}\right)_{\text{film}} = \frac{\Delta h}{h_0} \quad (1)$$

$$\left(\frac{\Delta V}{V_0}\right)_{\text{bulk}} = 3\frac{\Delta l}{l_0} + 3\left(\frac{\Delta l}{l_0}\right)^2 + \left(\frac{\Delta l}{l_0}\right)^3 \quad (2)$$

with h being the thickness of the film and l the linear dimension of the bulk gel.

The volumetric changes of the film and bulk sample are compared in Fig. 3. The shrinkage of the film is measured up to

Table 1
Dimensions, weight and density of bulk sample in the gel state and after the dilatometric test up to 1400 °C.

Sample and % of change	Dimensions (mm)		Volume (mm^3)	Weight (mg)	Density (g/cc)
	Thickness	Diameter			
Precursor gel	1.53	7.69	71.1	91.1	1.26
SiOC pyrolyzed at 1400 °C	1.19	5.99	33.5	83.5	2.53
Variation from RT and 1400 °C (%)	22.2	22.1	52.8	8.3	100

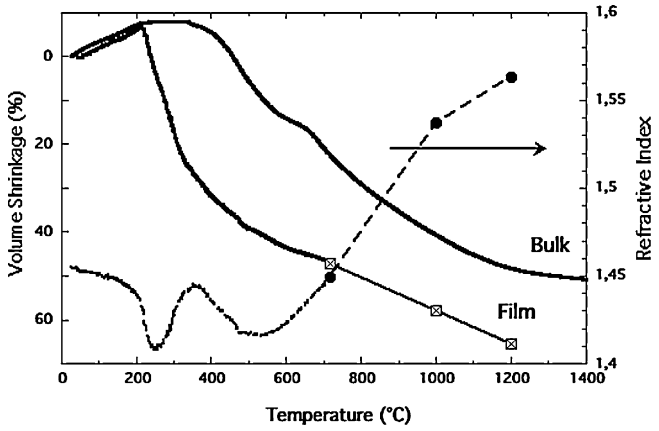

Fig. 3. Volumetric changes of bulk sample, calculated from dilatometer and of film measured by in situ ellipsometer up to 700 °C. Volumetric shrinkage measured at 700 °C, 1000 °C and 1200 °C are measured ex-post by standard ellipsometer. Similarly, the refractive index of film is measured by in situ ellipsometer up to 700 °C and ex-post for pyrolysis temperature of 700 °C, 1000 °C and 1200 °C.

700 °C with in situ ellipsometry and above that temperature, at 700, 1000 and 1200 °C, the thickness is measured after the pyrolysis with standard ellipsometry technique.

Both bulk and film samples show an initial expansion, that reach a maximum and then start to shrink. For the bulk sample the inversion is gradual and spans over a temperature range of 100–150 °C. The maximum temperature can be estimated at around 300–350 °C. Above 350 °C the bulk sample shows a first shrinkage step up to ~600 °C and a second step up to ~1200 °C. By comparing this dilatometric behavior with the corresponding TGA curve (see Fig. 2) recorded on coarse powders ($80\,\mu m \leq d_p \leq 224\,\mu m$) the following information can be obtained: (i) the temperature at which the sample starts to shrink corresponds to the temperature at which the gel starts to decompose (after the removal of the residual OH and/or OEt group); (ii) the main weight loss step, from ~350 to ~550 °C, where there is the evolution of silanes and siloxanes, is associated with the first shrinkage step up to 550–600 °C, (iii) the last weight loss step above 600 °C leads to an extended continuous shrinkage from 600 up to ~1200 °C, well beyond the temperature at which the pyrolysis can be considered complete from the TGA curve, ~800 °C. The shrinkage measured in the temperature range where the TGA shows no weigh loss, i.e. from ~800 to ~1200 °C, could be correlated either to the escape of very low amount of H_2, below the resolution of the TG instrument or to a structural rearrangement occurring without any compositional change.

The evolution of the thickness of the film with the pyrolysis temperature (Fig. 3) shows an initial expansion up to 200 °C. The curve matches perfectly the one recorded for the bulk sample providing a further support, beyond the results of the FT-IR characterization previously discussed, that no major compositional and structural differences exist between the two set of samples.

Interestingly the film suddenly inverts its expansion trend and, above 200 °C, begins to shrink. The shrinkage of the film continues up to 1200 °C. The volume shrinkage of the film is very rapid from 200 up to 400–500 °C and then, from 500 up to 1200 °C, the shrinkage continues with a constant and lower rate. Above 1200 °C we do not have data points since the film becomes unstable and starts to react with the substrate.

The evolution of refractive index with the pyrolysis temperature is also shown in Fig. 3. At room temperature the as-prepared film shows a refractive index of 1455 which is consistent with the known value of hybrid silica-based gels.[15] By increasing the temperature, the refractive index shows two distinct decreases: a well defined one centered at ~250 °C and a second one at ~500 °C which is much broader. Each peak shows a decrease of refractive index to a minimum value and then it increases again. After the 2nd peak the refractive index increases monotonically up to the maximum pyrolysis temperature (1200 °C). At 1200 °C the refractive index reaches the value of 1.563. The transformation occurring in the film during pyrolysis and densification, such as evolution of residual water and alcohol, CH_4, H_2, etc., they all promote an increase in the refractive index of the film. Therefore the observed decrease of refractive index has to be associated with the formation of porosity. Accordingly, each peak in the curve can be associated with the development of porosity, which is then re-adsorbed by further increasing the temperature. The formation of "transient porosity" is well documented for the pyrolysis of preceramic polymers as powder or bulk and the results obtained in this study on thin film agree well with this model.[16] In particular, the porosity formed between 200 and 300 °C is related with the first shrinkage step which could be assigned to the evolution of silanes/siloxanes while the porosity formed between ca 400 and ca 700 °C can be related to the evolution of H_2/CH_4 from the mineralization reactions. Thus, the refractive index data suggest that even for the thin film the pyrolysis occurs with two distinct processes as for the bulk samples. Finally, the increases in refractive index from 700 to 1200 °C indicate a densification of the glass. At 1200 °C the refractive index at 700 nm is 1.563, higher than the value for fused silica ($n_{700nm} = 1456$) as can be expected if C is inserted in to siloxane structure via the formation of Si–C bonds.

By assuming that films prepared at 1200 °C are dense, we can estimate the volume fraction of SiC, and consequently the molar fraction of SiC in the pyrolyzed film. According to the literature, amorphous SiC is significantly less dense than crystalline SiC. In particular, Heera et al.[17] showed that amorphous SiC can be from 10 to 30% less dense than crystalline SiC–4H. By using an effective medium approximation of Bruggemann[18,19] mixing amorphous SiC and silica optical properties, the estimated molar fraction of SiC in the film was between 23 and 25% (for amorphous SiC density equal to 90 and 70% that of dense SiC–4H respectively).

The SiC molar fraction in this film has also been measured by XPS analysis and was found to be 35%.[12] The difference between theoretical and experimental fraction of SiC can be due to a residual porosity of the film that decreases the refractive index of the film. Indeed, based on network models obtained using density functional theory, Kroll suggested the presence, in the glassy SiOC networks, of substantial fractions of open space which could be associated with closed porosity.[20]

4. Discussion

The volume shrinkage data reported in Fig. 3 show that the pyrolytic conversion of bulk and thin film samples is different: thin film shrinks 15–20% more than bulk samples. This is an important result since a different shrinkage may also imply a different chemical composition of the resulting SiOC material and suggests that we need to be very cautious in conveying experimental data obtained on coarse powders or bulk samples to thin films, thin fibers or fine powders.

As a general trend, the shrinkage curves show two common decomposition stages: a first one (low temperature stage) which show a rapid reduction of the volume and a second stage (high temperature stage) which goes on up to 1200 °C. The presence of two distinct stages is clear from the shrinkage curve of bulk sample while for thin film this feature is suggested only from the refractive index study more than from the measured shrinkage from ellipsometry.

The data reported in Fig. 3 also show the following main differences between the two type of samples: (i) the onset temperature of first stage for the thin film ($T_{onset,\ film}$ ∼200 °C) is shifted 100–150 °C to lower temperatures compared to the bulk sample ($T_{onset,\ bulk}$ = 300–350 °C), (ii) the peak present in the refractive index curve at around 500–550 °C suggests that even the second decomposition step is shifted to lower temperatures compared to the bulk gel and (iii) the first decomposition stage of the film results into a higher volumetric shrinkage and the difference is maintained up to the maximum temperature.

The reason why we observe, in the low temperature regime of the pyrolysis process, a higher shrinkage for the film compared to the bulk gel is not straightforward. Indeed, while for the high temperature regime, i.e. from ∼800 to ∼1200 °C, the shrinkage could be due to either the escape of very low amount of H_2, below the resolution of the TG instrument and/or to a structural rearrangement occurring without any compositional change, in the low temperature regime, i.e. up to ∼800 °C, the shrinkage is clearly associated with the weight losses. Weight loss is the result of two consecutive steps: (i) the formation of molecular species through the pyrolysis reactions and (ii) their diffusion through the solid network to the surface of the sample.

Bearing in mind that no compositional and structural differences are detected between starting film and bulk samples, we can suggest that the chemical reaction forming the gaseous species should be similar in terms of amount and rate of the reaction products. Therefore, the observed difference in the volumetric shrinkage must be related to the diffusion process.

The chemical reactions involved in the first decomposition step are the so called "redistribution reactions" between Si–O, Si–H and Si–C bonds which lead to the formation of silanes and siloxanes molecules such as: SiH_4, CH_3SiH_3, or even $R_3Si–O–SiR_3$, R=H, CH_3.[7,14,21] These reactions are known to be very fast[21] with low activation energies around 80–100 kJ/mol[22] and therefore the overall process could well be diffusion-controlled, especially for the bulk sample. Accordingly, for the bulk sample, the longer diffusion distance compared to thin film decreases the decomposition rate shifting the temperature onset toward higher values and limiting the amount of by-products, which can be released.

On the other hand, the second decomposition process, the so-called ceramization or mineralization process, involves the homolytic cleavage of Si–C and C–H bonds with a very high activation energy and the formation of H_2 and CH_4. The shrinkage curve of the bulk sample indicates that the ceramization step starts at ∼600 °C. The refractive index curve shows that the same process for the thin film is shifted to lower temperatures and has its peak at ∼500 °C. Again, we observe a low temperature shift for the thin film but in this case this difference does not result into a major difference of volumetric shrinkage for the two types of samples. The reason for this is not known at the moment.

5. Conclusion

The shrinkage during pyrolysis of a hybrid silica gel, precursor for SiOC glass, has been studied with conventional dilatometry (for bulk samples) and, for the first time, with in situ ellipsometry (for thin films). Both type of samples continue to shrink well above the temperature (800 °C) at which the TGA analysis suggests that the weight losses are complete. Compared to bulk samples thin films: (i) show a higher shrinkage (15–20 vol%) and (ii) the onset of the pyrolytic transformation is shifted 100–150 °C toward lower temperatures.

Acknowledgement

This Research was partially supported by European Community FP6 through MCRTN-019601, PolyCerNet.

References

1. Colombo P, Mera G, Riedel R, Soraru GD. Polymer-derived ceramics: 40 years of research and innovation in advanced ceramics. *J Am Ceram Soc* 2010;**93**:1–32.
2. Blum YD, MacQueen DB, Kleebe H-J. Synthesis and characterization of carbon-enriched silicon oxycarbides. *J Eur Ceram Soc* 2005;**25**:143–9.
3. Rouxel T, Soraru GD, Vicens J. Creep viscosity and stress relaxation of gel-derived oxycarbide glasses. *J Am Ceram Soc* 2001;**84**:1052–8.
4. Cordelair J, Greil P. Electrical conductivity measurements as a microprobe for structure transitions in polysiloxane derived Si–O–C ceramics. *J Eur Ceram Soc* 2000;**20**:1947–57.
5. Riedel R, Toma L, Janssen E, Nuffer J, Melz T, Hanselka H. Piezoresistive effect in SiOC ceramics for integrated pressure sensors. *J Am Ceram Soc* 2010;**93**:920–4.
6. Zhang Y, Quaranta A, Soraru GD. Synthesis and luminescent properties of novel Eu2+-doped silicon oxycarbide glasses. *Opt Mater* 2004;**24**:601–5.
7. Bahloul-Hourlier D, Latournerie J, Dempsey P. Reaction pathways during the thermal conversion of polysiloxane precursors into oxycarbide ceramics. *J Eur Ceram Soc* 2005;**25**:979–85.
8. Sorarù GD, D'Andrea G, Campostrini R, Babonneau F. Characterization of methyl-substituted silica gels with Si–H functionalities. *J Mater Chem* 1995;**5**:1363–74.
9. Colombo P, Paulson TE, Pantano CG. Synthesis of silicon carbide thin films with polycarbosilane (PCS). *J Am Ceram Soc* 1997;**80**:2333–40.
10. Babonneau F, Sorarù GD, D'Andrea G, Dirè S, Bois L. Silicon-oxycarbide glasses from sol–gel precursors. *Mater Res Soc Symp Proc* 1992;**271**:789–94.
11. Modena S, Soraru GD, Blum Y, Raj R. Passive oxidation of an effluent system: the case of a polymer derived SiOC. *J Am Ceram Soc* 2005;**88**:339–45.

12. Karakuscu A, Guider R, Pavesi L, Sorarù GD. White luminescence from sol–gel derived SiOC thin films. *J Am Ceram Soc* 2009;**92**:2969–74.
13. Boissiere C, Grosso D, Lepoutre S, Nicole L, Bruneau AB, Sanchez C. Porosity and mechanical properties of mesoporous thin films assessed by environmental ellipsometric porosimetry. *Langmuir* 2005;**21**:12362–71.
14. Campostrini R, D'Andrea G, Carturan G, Ceccato R, Sorarù GD. Pyrolysis study of methyl-substituted Si–H containing gels as precursors for oxycarbide glasses, by combined thermogravimetric, gas chromatographic and mass spectrometric analysis. *J Mater Chem* 1996;**6**:585–94.
15. Su K, Degroot Jr JV, Norris AW, Lo PY. Siloxane materials for optical applications. In: *Proceedings of SPIE – The International Society for Optical Engineering, vol. 6029*. 2006 [art. no. 60291 C].
16. Schmidt H, Koch D, Grathwohl G, Colombo P. Micro-/macroporous ceramics from preceramic precursors. *J Am Ceram Soc* 2001;**84**:2252–5.
17. Heera V, Prokert F, Schell N, Seifarth H, Fukarek W, Voelskow M, et al. Density and structural changes in SiC after amorphization and annealing. *Appl Phys Lett* 1997;**70**:3531–3.
18. Stroud D. The effective medium approximations: some recent developments. *Superlattices Microstruct* 1998;**23**:567–73.
19. Tinga WR, Voss WAG, Blossey DF. Generalized approach to multiphase dielectric mixture theory. *J Appl Phys* 1973;**44**:3897–902.
20. Kroll P. Modelling and simulation of amorphous silicon oxycarbide. *J Mater Chem* 2003;**13**:1657–68.
21. Mutin PH. Role of redistribution reactions in the polymer route to silicon–carbon–oxygen ceramics. *J Am Ceram Soc* 2002;**85**:1185–9.
22. Campostrini R, Sicurelli A, Ischia M, Carturan G. Pyrolysis study of a hydride–sol–gel silica. Part II. Kinetic aspects. *J Therm Anal Calorim* 2007;**90**:179–84.