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SiC ceramic micropatterns from polycarbosilanes

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Abstract

Micropatterned SiC ceramics were fabricated from polycarbosilanes applying a softlithographic replication technique. A polydimethylsiloxane mould replicated from a photolithographic microstructured silicon wafer was used as master structure. The polydimethylsiloxane mould was coated with a solution containing a mixture of two different polycarbosilanes in n-octane. After treatment at 200–400 °C the cross-linked polycarbosilane films were debonded and pyrolysed at 900 °C in nitrogen and subsequently crystallised at temperatures up to 1500 °C in argon. The cross-linking and thermal degradation behaviour of the polycarbosilanes was investigated by Fourier-transform infrared spectroscopy, differential scanning calorimetry and thermogravimetric analysis. X-ray diffractrometry showed the expected development of a nanocrystalline β-SiC (3 nm) as the main phase with increasing temperature. However, traces of α-SiO_2 derived from the polycarbosilane precursors were also detected by X-ray analysis. Removal of the α-SiO_2 dioxide with hydrofluoric acid in the pyrolysed samples and subsequent increased the crystallite size to 7 nm. The Young's modulus determined by nanoindentation was increased from 3 GPa after cross-linking to 110 GPa after crystallisation. Scanning electron microscopy revealed, that the initial micropatterns were fully retained in the pyrolysed and crystallised SiC ceramics. The micropatterned cross-linked and crystallised β-SiC based substrates exhibited light scattering characteristics, which qualify them as promising candidates for diffractive optical elements in microoptical applications.

Keywords: Microstructure-final; SiC; Precursors-organic; Optical properties; Softlithography

1. Introduction

Polymer-derived SiC based ceramics offer attractive polymer forming capabilities and materials properties such high temperature stability, high strength and corrosion resistance.[1,2] Polycarbosilane compounds were used for the production of SiC fibres,[3–5] thin films,[1,6,7] membranes[8,9] and ceramic matrix composite.[10] Micropatterning of ceramics using polymeric ceramic precursors has gained particular interest due to facile shaping processes and their applications in mechanical devices, energy systems, bioengineering, biomedical science or as catalyst supports.[11–14] Conventional techniques for micropatterning of SiC, Si_3N_4 and SiBNC using reactive ion etching[15] are time consuming and cost intensive. Liquid polymeric ceramic precursors are suitable candidates to generate complex ceramic features applying soft lithographic techniques without the need for etching procedures.[13,16] The fabrication of microelectromechanical systems made from oxidation resistant SiBNC ceramics using soft lithographic techniques was recently reported.[14] Nanoscale SiCN ceramic were obtained from a polyvinylsilazane on silicon substrates by combining imprinting lithographic and a modified "micromoulding in capillaries" technique.[13] A major challenge for the application of preceramic polymers in ceramic manufacturing is the reduction of extensive cracking and pore formation, which generally occurs when the structural changes in the polymer-derived phase cannot be relaxed by viscous flow or diffusion based material transport. Thus, direct conversion of a polymer compact into dense ceramic compacts appears to be difficult whereas defect free low dimensional products such as fibres or coatings can be readily

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fabricated.[17] Herein, we report on the fabrication of freestanding SiC substrates from polycarbosilane precursors with an ordered microstructure applying a modified softlithographic process. First a microstructured polydimethylsiloxane (PDMS) mould was manufactured from a conventionally patterned silicon wafer. The conversion of the PCS into SiC and the microstructural formation was investigated. The presented method will be of specific benefit for the production of large areas of microstructured ceramics due to the utilisation of inexpensive raw materials (polymeric precursors). The applied softlithographic technique is a highly versatile method, which allows the flexible formation of non-planar ceramic parts, which are readily accessible by conventional lithographic approaches. Furthermore, the developed process exhibits an interesting potential for three-dimensional fabrication for large-scale functional and structural ceramic microdevices and low-cost generation of microelectromechanical systems (MEMS).

2. Experimental

2.1. Materials and methods

The microstructured PDMS master mould was manufactured by pouring the precursor liquid (Sylgard 184, Dow-Corning, USA) onto a photolithographic microstructured silicon wafer with a diameter 15 cm, followed by drying and cross-linking at room temperature for 1–2 days, Fig. 1. The PDMS mould was carefully peeled from the Si-wafer master after cross-linking. The PDMS was cut into smaller specimens (1.8 cm × 2 cm) and cleaned for 10 min in ethanol by ultrasonic treatment. Two liquid allyl-substituted hybridopolycarbosilanes (PCS, SMP-10 and RD-518, Starfire Systems, USA), which give near-stoichiometric SiC ceramics,[18] were used as ceramic SiC precursors. The PCS have a general chemical formula of $[Si(CH_2CH{=}CH_2)_2CH_3]_{0.1}[SiHCH_3]_{0.9}$. The PCS and given PCS mixtures were dissolved in n-octane with a concentration of 50 wt.% PCS. All PCS samples and PCS mixtures investigated are given in Table 1. The prepared PCS solutions were poured on the PDMS master mould and subsequently cross-linked between 200 and 400 °C for 1 h with a heating rate of 0.3 °C/min in a nitrogen atmosphere. Pyrolysis of cross-linked PCS films was carried out in nitrogen in an Al_2O_3 tube furnace (Hereaus, K1251, Germany) with a heating rate of 0.5 °C/min up to 900 °C and a holding stage for 1 h each at 400, 600 and 900 °C. Finally, the pyrolysed PCS films were crystallised with a heating rate of 2 °C/min at 1500 °C for 1 h in argon atmosphere (Astro, Thermal Technology, USA). The applied processing scheme is summarised in Fig. 1.

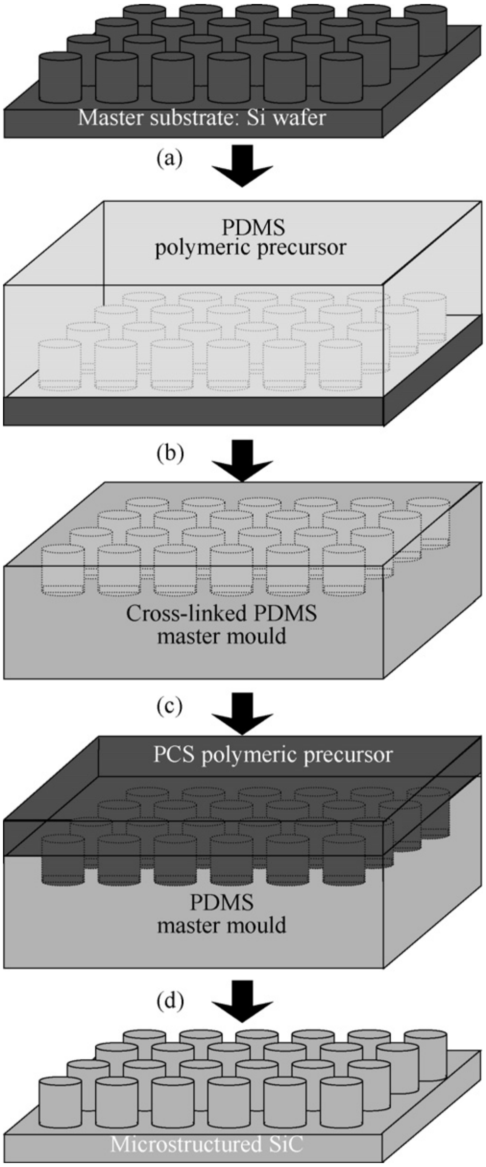

Fig. 1. Scheme for the fabrication of PCS-derived microstructured SiC ceramics: (a) Replication of a photolithographically microstructured silicon wafer by casting of a PDMS polymeric precursor and subsequent cross-linking, (b) debonding of the cross-linked PDMS polymer, (c) casting of the PCS precursor and cross-linking at temperature from 200 to 400 °C and (d) pyrolysis at 900 °C and crystallisation at 1500 °C finally yield the microstructures silicon carbide ceramic.

2.2. Characterisation

Cross-linking and pyrolytic conversion of the two PCS and their mixtures were analysed by thermogravimetric analysis

Table 1
Sample codes, prepared mixtures and conditions for temperature treatment.

Sample code	PCS (wt.%)	Solvent (wt.%)	Cross-linking/pyrolysis (N_2-atmosphere)	Crystallisation (Ar-atmosphere)
A	100 SMP-10	50 n-octane	200–400 °C (1 h)/900 °C (1 h)	1500 °C (1 h)
B	100 RD-518			
C	50 SMP-10/50 RD-518			
D	20 SMP-10/80 RD-518			

(TGA, Netzsch 409, Netzsch Selb, Germany) and differential scanning calorimetry (DSC, Netzsch Selb, Germany). A heating rate of 5 °C/min was applied up to 1400 °C in argon atmosphere. FT-IR spectra were recorded between 4000 and 400 cm^{-1} (Impact 420T, Nicolet, Madison, USA) with a resolution of 2 cm^{-1} using an attenuated total reflection sampling unit (ATR, Dura Sample IR II, Smiths detection, USA). The crystallisation behaviour of the pyrolysed SiC products was monitored by X-ray diffraction (XRD, D500, Siemens, Germany) using monochromatic Cu-Kα radiation. Intensity data were collected by the step counting method (step 0.02 and time 1 s) in the range $2\theta = 5$–$70°$. The crystallite sizes of β-SiC phase were estimated applying the Scherrer formula for the (1 1 1) peak: $L_{1\,1\,1} = 0.89\lambda/(D\cos\theta)$, where $\lambda = 0.154$ nm, D represents the full width at medium height of the (1 1 1) reflection of β-SiC and $\theta = 17.88°$.[19] The microstructures of the PDMS master, the cross-linked PCS, the pyrolysed and crystallised PCS specimens were investigated by scanning electron microscopy (SEM, Quanta 200, FEI, Czech Republic) operated at 20 kV. The samples were embedded in epoxy resin and polished for mechanical analyses. The polished PCS cross-sections were investigated by nanoindentation (Nanoindenter XP, MTS Nanoinstruments, Oak Ridge, TN, USA) using a three-sided pyramidal Berkovich tip and the continuous stiffness method (CSM). Tip shape calibration was performed according to the so-called Oliver/Pharr method and machine compliance was taken into account.[20] Using the CSM method, the indentation stiffness is determined continuously and the reduced modulus and indentation hardness is obtained as a function of indentation depth. Using the elastic constants of the diamond indenter with an assumed Poisson number of 0.17 for SiC, Young's modulus was derived from the reduced modulus. The reported values of hardness and modulus are determined as the average values in a indentation depth range between 400 and 900 nm. The hardness and modulus values were averaged from at least six indentations.

3. Results and discussion

The TGA curve of as-received PCS A showed a weight loss of 27 wt.% up to 1400 °C, Fig. 2. The TGA curve of PCS B (not shown) was similar to PCS A. The determined weight loss for PCS B was 33 wt.%. Both TGA curves could be separated into three regions: (1) 50–450 °C: the major weight loss occurred due to thermal degradation of the PCS and evaporation of the low molecular weight components,[5] (2) 450–800 °C: the weight loss of 5 wt.% is attributed to the cleavage of the side chains (dehydrogenation and demethanation) of the PCS. The conversion of the polymeric PCS is into inorganic structure with a three-dimensional network structure also occurs in this region,[5] (3) >800 °C: a minor weight loss of only 2 wt.% indicated loss of residual hydrogen. The corresponding DSC showed a small exothermic peak at 220 °C, which is derived for the melting of the PCS. A large and broad exothermic peak at 450 °C is associated with the gradual weight loss and decomposition of polymer. A broad peak the region at 800–1400 °C indicates the transition from amorphous SiC to crystalline β-SiC. The exothermic behaviour above 1000 °C might be due to crystallisation of the amorphous parts.[21] Since thin PCS films appear to be sensitive to pyrolysis conditions (development of cracks),[1] heating of the samples during pyrolysis should be very slow. It was observed that the samples fragmented into small pieces when heating rates above 2 °C/min up to 900 °C were applied. Therefore, the pyrolysis of the bulk PCS substrates was carried out according to the findings from the TGA. Stable, crack-free microstructured SiC ceramics could be obtained when slow heating rates (0.5 K/min) and a 1 h holding time at 400, 600 and 900 °C were applied.

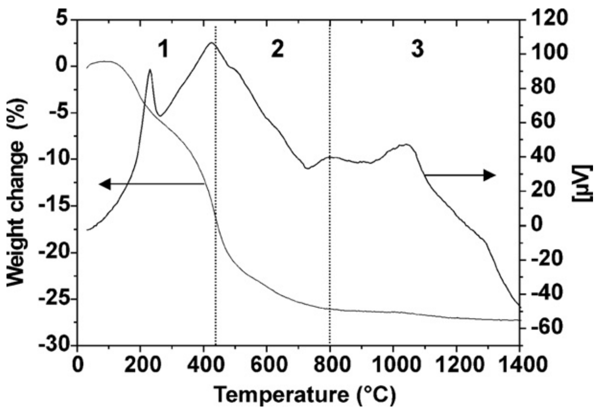

Fig. 2. TGA-DSC diagram of PCS A up to 1400 °C under argon atmosphere.

FT-IR spectroscopy was used to identify the functional groups of the pure PCS compounds and to monitor the cross-linking reaction, Fig. 3. The FT-IR spectra of as-received PCS A and B were similar,[22–24] except for the content of the Si–H function (strong stretching vibration of ν(Si–H) at 2100 cm^{-1}), which appears to be higher in PCS A. Additional peaks in the FT-IR spectra of the PCS are ν_s(C–H) stretching mode and the symmetric deformation δ_s(C–H) in Si–CH$_3$ at 2880–2950 cm^{-1}, whereas the peaks at 1420 and at 1250 cm^{-1} are assigned to the asymmetric deformation δ_{as}(C–H) in Si–CH$_3$. The vibrations at 1355 cm^{-1} and at 1020 cm^{-1} are derived from the Si–CH$_2$–Si wagging vibration and the δ(C–H) deformation vibration in then methylene group (–CH$_2$–). The peaks located at 800–950 cm^{-1} are assigned to the Si–CH$_3$ rocking and the vibrations at 700–850 cm^{-1} are due to stretching Si–C bonds. The vibration found at 3060 cm^{-1} is assigned to the ν(C–H) stretching mode of the carbon double bond (CH=CH$_2$) of the allyl function. The corresponding ν(C–C) stretching mode of the C=C bond was found at 1630 cm^{-1} for the PCS A. However, the C=C stretching vibration in PCS B are weak indicating a low concentration of allyl functions. To compare as-received and cross-linked PCS materials FT-IR spectra were recorded from room temperature up to 400 °C, Fig. 3a. During the cross-linking reaction (hydrosilylation of the allyl function) the peak intensity from the silane groups located at 2100 cm^{-1} were gradually reduced with increasing temperature. H$_2$O and Si–OH groups related absorptions often described in literature could not be observed.[23–26] However, undesired side reactions from condensation products (hydroxylation) are not likely to occur since the cross-linking reaction is based on an addition reaction (hydrosilylation).[27] The polymer to ceramic transition was studied at temperatures from 400 to 900 °C, Fig. 3b. It was shown that the ν(C–H)

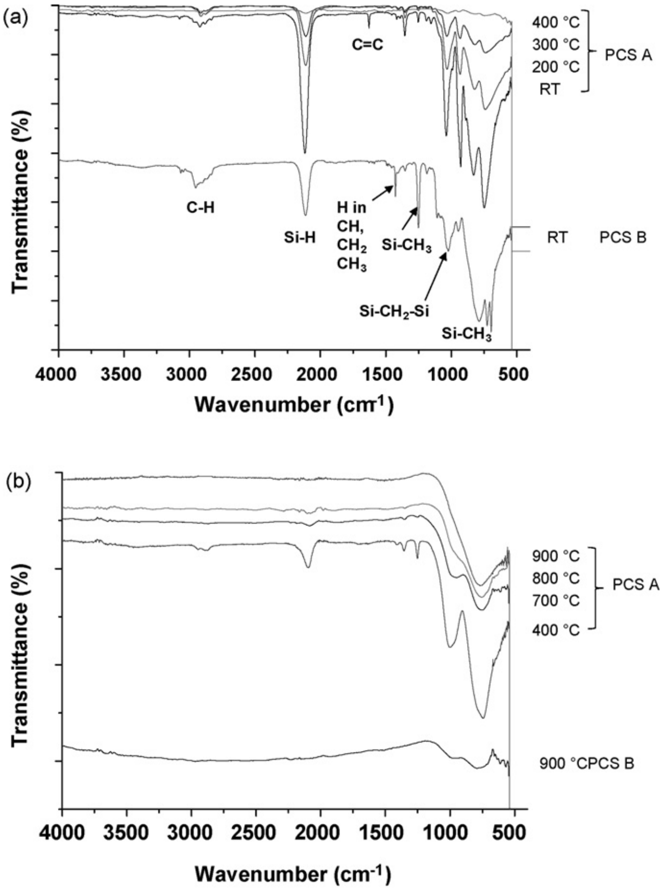

Fig. 3. FT-IR spectroscopy of PCS A of (a) from room temperature to 400 °C and PCS B at room temperature, (b) pyrolysed PCS A from 400 to 900 °C and pyrolysed PCS B at 900 °C.

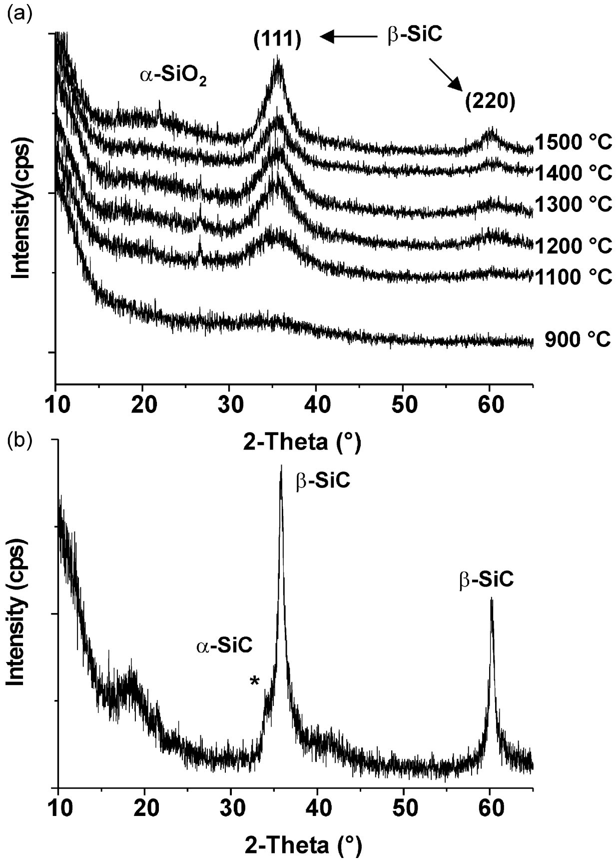

Fig. 4. XRD diagrams of (a) PCS D derived SiC ceramic products from 800 to 1500 °C, and (b) PCS D pyrolysed at 900 °C, treated with HF and subsequently crystallised at 1500 °C.

and the ν(Si–H) related absorption bands decreased with increasing temperature due to cleavage and degradation of the organic side chains and reactions of the silane groups.[28] After pyrolysis at 900 °C almost all of the adsorption bands for PCS A derived from Si–H and C–H vibrations disappeared leaving a strong adsorption at 900 cm^{-1} attributable to the SiC solid network.[29] However, in PCS B still some Si–CH$_2$–Si related vibrations at 1020 cm^{-1} were observed, which suggests that dehydrogenation was not complete for PCS B.[30]

Preliminary experiments showed, that it was not possible to obtain stable PCS films by direct replication of microstructured silicon wafers. Attempts to directly replicate the PCS on the silicon wafers resulted in cracking and fragmentation during cross-linking. Therefore, a microstructured PDMS mould was first fabricated. Furthermore, pure PCS A and PCS B yielded fractured and porous specimens, which could not be debonded from the PDMS master. The films prepared from mixtures PCS C and D could be easily lifted off after cross-linking. However, mixture PCS C showed segregation and the formation of polymeric particle knobs. Solely, the mixture PCS D was suitable for the fabrication of stable cross-linked PCS films with reduced shrinkage, no fragmentation and the same dimensions as PDMS pattern (1.8 cm × 2 cm). It was suggested that the formation of the ceramic surface patterns depends on the immiscibility of the polymers, polymer ratio, the evaporation rate of the solvent in addition to the film thickness.[12] If PCS films were too thin (<30 μm), they are difficult to peel off from the PDMS master. In the present work a cross-linking temperature of 200 °C yielded PCS specimens with an undamaged microstructure and as an intact film compared to a cross-linking temperature of 400 °C. Cross-linking at 400 °C resulted in considerably hard PCS films, which strongly adhered to the PDMS and showed defects in the replication of the microstructure. For this reason all samples referred to hereafter were cross-linked at 200 °C.

X-ray diffraction analysis showed a very broad peak at $2\theta = 36°$ corresponding to the (1 1 1) peak of β-SiC for the sample PCS D pyrolysed at 800 °C, Fig. 4a. With increasing temperature the (1 1 1) peak gradually developed and the (2 2 0) peak of β-SiC was visible at temperatures higher than 1200 °C. The peak shapes indicated an amorphous to nanocrystalline transition of the SiC with increasing temperature.[1,24,31] The crystallite size calculated from the Scherrer equation was 3 nm at 1500 °C and was considerably smaller compared to others, who reported 33 nm at 1600 °C.[24] It was shown that the β-SiC peaks in vacuum pyrolysed samples were sharper than specimens pyrolysed in argon due to oxygen contamination in the argon, which leads to the formation amorphous SiOC residues.[1] This is supported by the occurrence of sharp reflections located at $2\theta = 23°$ and 27° indicating the presence of α-SiO$_2$. Cross-linking and pyrol-

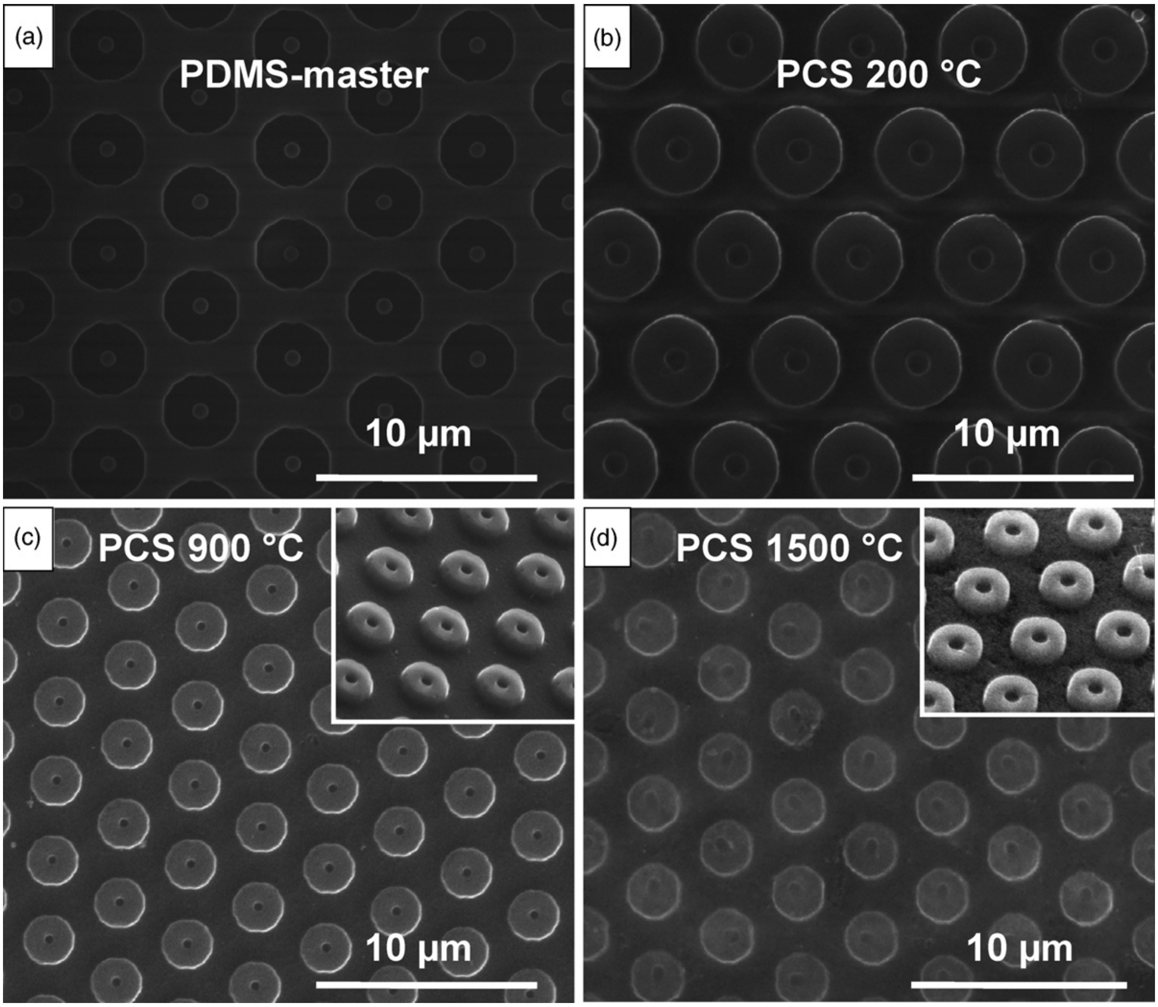

Fig. 5. SEM micrographs of (a) the PDMS master, (b) the cross-linked, (c) the pyrolysed and (d) the crystallised microstructured PCS films; the insets in (c) and (d) show the same structure viewed under an inclination angle.

ysis in this study was performed in nitrogen atmosphere and SiO_2 formation was already observed at 900 °C. This suggests that chemically bound oxygen was already present in the PCS starting material. Absorption of oxygen or moisture during processing might also lead to a higher oxygen content than expected. In order to reduce SiO_2 content prior to crystallisation of the SiC, the specimens were subjected to a hydrofluoric acid treatment.[5] After dissolution of the SiO_2 with hydrofluoric acid the SiC derived peaks exhibited a sharper appearance and the crystallite size was increased to 7 nm, Fig. 4b. It can be assumed, that the residual SiO_2 inhibited to crystallisation. Due to the high crystallisation temperature a small peak assigned to α-SiC was present in the XRD diagram.[21]

The microstructure of the PDMS master was successfully transferred into a patterned SiC substrate and the structural features were fully retained up to 1500 °C, Fig. 5. The quality of the replicated microstructured amorphous SiC ceramic up to 900 °C is comparable to the initial cross-linked PCS structure. After crystallisation at 1500 °C some flaws within the microstructure were visible. The edges of the poles became irregular. Shrinkage of 23% was calculated after pyrolysis at 900 °C from the photographic images and SEM micrographs. The dimensions of the pyrolysed specimens hardly changed after crystallisation. The successful replication of the initial microstructure was clearly demonstrated. The height of the SiC poles was approximately 1 μm (see insets in Fig. 5c and d). The light interference capabilities and the formation of structural colours of the fabricated samples are illustrated in Fig. 6. Prior to pyrolysis, the microstructured PCS films are yellow, optically transparent and flexible. As a consequence the light interference showed pastel like colours. Additionally, variation of the colours could be observed due to the fact that the samples were not fully planar. The microstructure of the pyrolysed amorphous SiC exhibited bright colours suitable for microoptical applications.[16] Due to some microstructural flaws after crystallisation at 1500 °C, the observed structural colours from the surface were less brilliant.

The mechanical properties of the microstructured PCS ceramics were investigated by nanoindentation, Fig. 7. The average Young's modulus of the cross-linked PCS films was 2.5 GPa and indentation hardness values of around 0.1 GPa were determined. However, after pyrolysis at 900 °C the Young's modulus increased to 122 GPa and the hardness to 14 GPa.

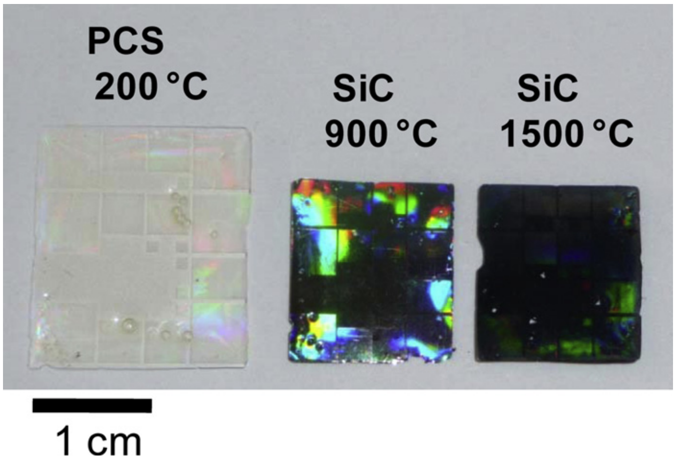

Fig. 6. Photographic image of microstructured substrates of the cross-linked PCS film at 200 °C, the pyrolysed amorphous SiC ceramic at 900 °C and the crystallised β-SiC at 1500 °C, respectively.

These values were considerably higher than the ones obtained for polymer-derived ceramic compacts (not fibres) which were 30 GPa after pyrolysis at 800 °C.[13] The Young's modulus and the corresponding hardness for the PCS films are highest at 900 °C and decreased with the increasing temperature. The weight loss of 1 wt.% in the TGA curve above 900 °C indicated structural rearrangement derived from the evaporation of CH_4 and H_2,[24] which might be responsible for the development of porosity in the PCS films.[17] Porosity might be also due to the decomposition of the oxycarbide phase after the polymer conversion to SiC.[32] The oxycarbide phase was found to be unstable at temperature higher than >1450 °C and tend to decompose into SiO and CO gas, which might form pores. In order to control shrinkage and porosity during pyrolysis addition inert powder fillers might be beneficial.[33] However, in our case, the SiC substrates were fabricated without filler only by a mixture of two different PCS.

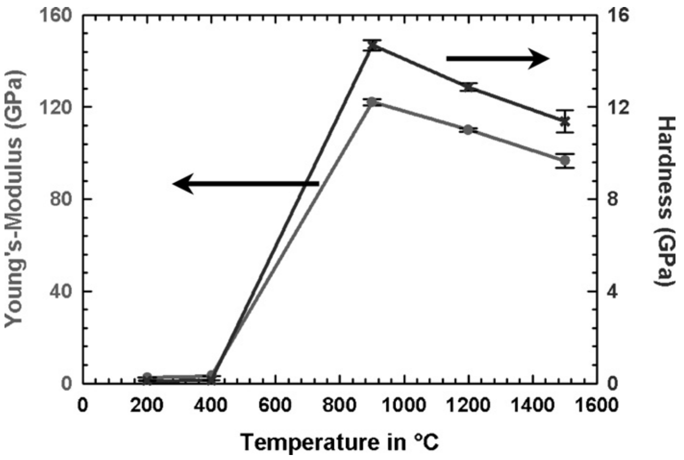

Fig. 7. Young's modulus and hardness of pyrolysed SiC ceramic at 900, 1200 and 1500 °C temperatures.

4. Conclusions

In this work, polymer-derived microstructured SiC ceramic films were fabricated applying a softlithographic technique. The microstructure was generated by replication of PDMS mould, which was obtained by soft lithographic techniques from a microstructured silicon wafer. After pyrolysis of the cross-linked PCS films at 900 °C, a micropatterned amorphous SiC was obtained, which subsequently was crystallised at 1500 °C into microstructured nanoscale β-SiC. The microstructural features of the PDMS master substrate were fully replicated in the SiC ceramic. The light diffraction ability of the PCS-derived ceramic substrates was demonstrated. The resulting structural colours from the surface of the substrates established their potential in applications as diffractive optical elements. The developed replication technique for PCS-derived SiC ceramic substrate from PDMS master structures provides a general low-cost and facile method for shaping and diffraction of light.

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