

Polymer-Derived SiOC Nanotubes and Nanorods via a Template Approach

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The synthesis of silicon-based ceramic nanowires and nanotubes produced by liquid infiltration of commercially available silicon-based polymers, namely polysilazane (Cera-setTM, polyureasilazane), polysilazane VL20 (Kion Coop.) and polycarbosilane (Starfire Systems SP-MatrixTM) in alumina templates with defined pore channels is reported. After polymer infiltration, pyrolysis of the preceramic polymer at 1000–1100 °C in Ar atmosphere followed by dissolution of the alumina templates, ceramic nanowires and nanotubes were obtained. In the case of the polymeric ceramic precursor polysilazane, nanorods were formed only if an oligomeric fraction was distilled off from the polymer precursor prior to infiltration of the template. In contrast, the formation of nanotubes was found after infiltration of the untreated (crude) preceramic polymer. Despite the fact that the preceramic polymers contain silicon, carbon and nitrogen and *no* oxygen as constituting elements, the final ceramic nanostructures ob-

tained were analysed consistently by various techniques to contain oxygen and only limited amounts of carbon and nitrogen after pyrolysis consistent with a composition as silicon oxycarbide (SiOC). This behaviour strongly indicates that the porous alumina template may significantly influence the pyrolysis process of the precursors thus affecting the chemical composition of the final ceramic products. It is a central result of our study that the alumina templates are not inert under the reaction conditions employed instead acting as a reaction partner at the high temperatures employed during pyrolysis. Taking this into account, reaction of otherwise inert amorphous alumina with inorganic polymers at elevated temperatures could lead to a directed synthesis of new ceramic compositions.

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Introduction

There has been an enormous interest in the syntheses of ceramic nanorods and nanotubes over the past years.^[1,2] Besides their synthesis the alignment of such nanostructures has become a further important topic for technological applications.^[3,4] In particular, SiCN-based systems can be applied at high temperatures and in harsh environments and do not tend to deform even under mechanical load up to 1000 °C.

Silicon-based ceramic nanorods and nanotubes were synthesized by a variety of different methods such as chemical vapour deposition (CVD),^[5] carbothermal reduction,^[6,7] sol-gel,^[1,8] catalytic growth on metal particles^[9] as well as

via infiltration of silicon containing polymers in templates.^[2,10] Porous aluminium oxide (PAOX) has been frequently used as a hard template for the preparation of rod-like nanoscale materials from liquid precursors.^[11–16] The control of anodization conditions,^[17–19] combined with chemical etching methods, can be used to control the size and the ordering of parallel channel arrays in amorphous PAOX as well as the final 1D-structures derived therefrom.

Molecular precursors to SiC-based ceramics are available as stable, low viscosity liquids, and have significantly low transition temperature into ceramic components (800–1100 °C). Due to the low surface tension, those liquid precursors are also good candidates for coating and capillary driven infiltration of porous materials, thus offering the possibility of forming 1D-structures.

It has been claimed that the specific composition of the pore walls in PAOX make them active participants in different reactions, rather than being just an inert matrix. This might be quite unusual since bulk metal oxide powders are often used as passive fillers during the thermal decomposition of preceramic polymers without any evidence of chemical interaction.^[20] Nevertheless an inner PAOX surface is covered with extra Lewis acid sites, which are indeed efficient host centres for Lewis bases, e. g. unsaturated organic compounds. Such Lewis acid sites have indeed played

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an important role during the pyrolytic conversion of organic precursors into carbon-like 1D-composite materials.^[21] The fabrication of hollow SiC tubes from organosilicon polymers in commercial PAOX templates has been reported.^[22–24] In case of reports on polymer-derived SiC nanostructures within porous alumina templates, the true composition of the resulting ceramic materials was not clarified so far.^[25] It would thus be interesting to produce 1D-ceramic structures with small diameters in order to explore possible size effects on the properties of such materials and to clarify the chemical reaction pathway to silicon-based ceramics from molecular and polymeric precursors in porous alumina in more depth.

In the present work we report on a detailed study of template assisted formation of aligned ceramic nanowires and nanotubes starting from commercially available nitrogen containing silicon-based polymers. The template-based synthesis was carried out i) in home made porous alumina membranes (PAOX membranes) with pore diameters of 20 and 40 nm, obtained by anodic oxidation of aluminium metal sheets in oxalic or sulfuric acid solutions and ii) in commercially available anodic aluminium oxide with sub micron sized pore diameters (200 nm).

Results and Discussion

Ceramic Nanowires Derived from 40 V PAOX Templates

The pores diameter of the PAOX templates employed (0.3 M oxalic acid) was 41 ± 3 nm (Figure 1) which showed a good correlation with BET-measurements which yielded 41.75 nm and a surface area of 156.7 m²/g for calcined samples. The thickness of the membranes used depends on the anodization time and was around 60 µm. The front side of the pores increased after removal of the barrier layer to approximately 75–80 nm (Figure 1).

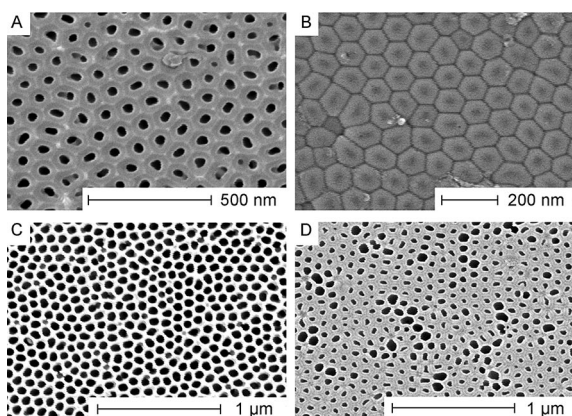


Figure 1. SEM pictures of front (A) and backside (B) of PAOX. Pore widening effect (C) and the backside after the barrier layer removal (D).

Thermogravimetric analysis (TGA) of PAOX membranes suggests that the amount of anion impurities is reduced after the wet etching step. The comparison of the TG curves reveals a mass loss event due to the oxalate anion decompo-

sition between 880–980 °C for both the unetched and etched membranes, but the quantitative characteristics are clearly different (Figure 2). The amount of oxalate anion impurities is reduced due to the predominant dissolution of the electrolyte-rich inner area of the individual PAOX cells.^[26] The following reaction takes place between dichromate and oxalate anions in the acid medium:

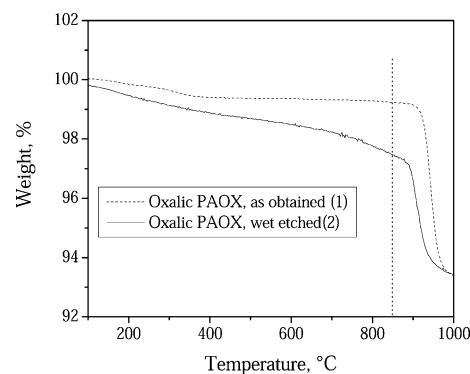
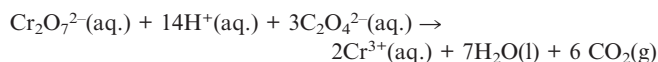


Figure 2. TG traces of: (1) unetched PAOX membranes (oxalic acid); (2) the same PAOX membranes after the barrier layer removal in the etching mixture.

The diameter of the KiON Cereset-derived ceramic wires after dissolution of the PAOX template was about 70 nm [see Figures 3 (SEM) and 4 (TEM)], which is approximately 20% smaller, than the nominal pore diameter of the templates used for this series of experiments. This decrease in volume obviously results from a polymer shrinkage during the thermal processing step. The length of the wires was about 45 µm after dissolving the template with a concentrated H₃PO₄ solution, but only 13 µm after treatment with HF. This observation suggests that concentrated hydrofluoric acid destroys the resulting 1D-ceramic wires formed during the ceramisation process.

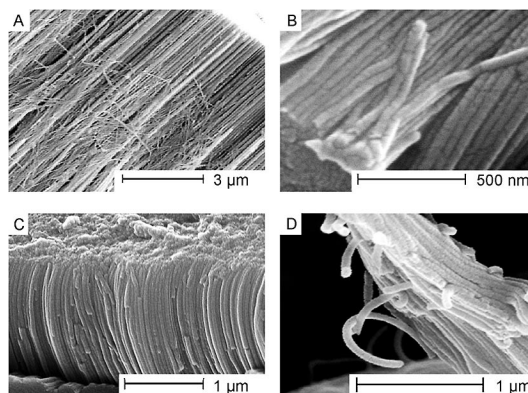


Figure 3. SEM micrograph alongside the template pores after infiltration and pyrolysis step, but before dissolution of the template (A). Resulting KiON Cereset-derived wires (B, C, D) after dissolution of the template.

In this context it is also important to note, that silicon nitride is etchable at room temperature in concentrated or buffered HF and in a boiling H₃PO₄ solution.^[27] This be-

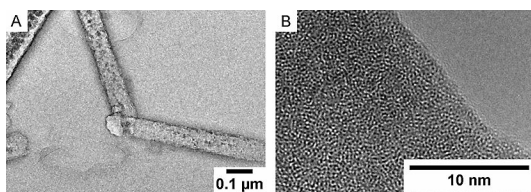


Figure 4. TEM micrographs of KION Ceraset-derived nanowires. The high resolution TEM micrograph B shows the amorphous nature of the wire composition.

haviour would certainly affect a possible product formed via pyrolysis of the nitrogen-containing organosilicon polymer. Indeed and according to the Energy Dispersive X-ray analysis (EDS) data, no presence of nitrogen could be detected in the resulting material.

The resulting dimensions of the SP Matrix polymer-derived wires can be estimated from the SEM micrographs to be 25–40 μm . They exhibit a wire diameter of about 43 nm (Figures 5 and 6).

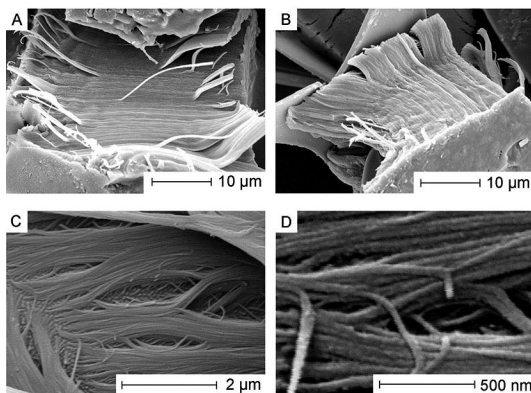


Figure 5. SEM micrographs (A, B) and close-up SEM micrographs (C, D) of the SP matrix polymer-derived wires after dissolution of the template.

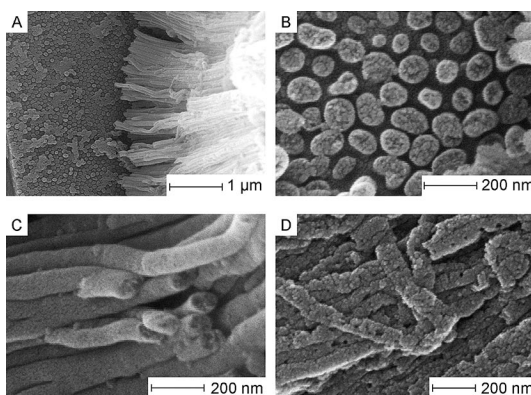


Figure 6. SEM micrographs (A–D) with close up views of the nanorods of the SP matrix polymer-derived wires after dissolution of the template. (A) aligned rods together with rod stubs [left side of (A)] from which the rods have been broken off. (B) Rod stubs and outer rod surface with higher magnification (C) showing the particulate nature of the rods. (D) particulate nature of the rods with higher magnification.

Attempts to obtain TEM micrographs of the ceramic wires obtained from the SP matrix polymer were hampered due to the structure of the rods. Sample preparation by dispersing the nanorods under vigorous stirring in ethanol or ultrasonic agitation in different solvents often destroys the rods completely. We attribute this finding to the particulate nature of the nanorods being composed of particle agglomerates rather than having a compact homogeneous structure as can be seen from Figure 7.

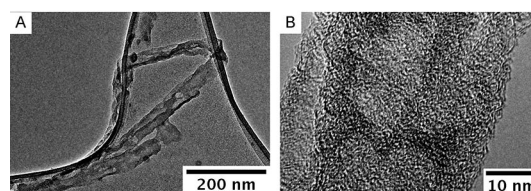


Figure 7. TEM micrographs of isolated nanorods of the SP matrix polymer at different magnifications obtained by ultrasonification of a suspension of calcined ceramic material after dissolution of the alumina template.

The good wettability of the pore walls of the PAOX templates could be predicted from earlier studies on nanotubes prepared from polycarbosilanes. If adhesion between the pore walls and the filling material is very strong, or the solidification of the preceramic precursor starts at the interface pore wall/precursor and proceeds to the inside of the pores. The formation of hollow nanotubes is thus preferred over formation of solid rod like material when taking a massive shrinkage of the material due to the ceramization process into account.^[28]

To follow the chemical changes in the polymer-derived nanomaterials, their composition was studied by means of FTIR spectroscopy. The infrared spectra of (i) the liquid KiON Ceraset polyureasilazane precursor, (ii) the polymer cured within the PAOX template at 700 $^{\circ}\text{C}$ (the temperature below the transition of the bulk cross-linked product into ceramic components) and (iii) cured within the template at 1000 $^{\circ}\text{C}$ are compared in Figure 8.

The intense band at 3450–3200 cm^{-1} in the liquid polymer spectra can be attributed to N–H stretching vibrations. The signal at 3045 cm^{-1} corresponds to C–H stretching vibrations of the vinyl groups, methyl and methylene vibrations are presented at 2965 cm^{-1} (CH_3 asymmetric, 2975–2950 cm^{-1}), 2920 cm^{-1} (CH_2 asymmetric, 2940–2915 cm^{-1}) and 2850 cm^{-1} (CH_2 symmetrical, visible only at high resolution around 2870 cm^{-1}). The broad intense band at 2127 cm^{-1} is characteristic of Si–H (2140 cm^{-1}). The strong band at 1260 cm^{-1} corresponds to the absorption of Si–CH₃ (1280–1255 cm^{-1}) and is assisted by the deformation vibration at 760–790 cm^{-1} . Possibly Si–N vibrations are presented at 1170–1175 cm^{-1} and around 900 cm^{-1} which are, however, significantly weakened at the higher curing temperature of 1000 $^{\circ}\text{C}$ compared to 700 $^{\circ}\text{C}$.

The appearance of the spectra of the KiON Ceraset polyureasilazane polymer precursor (Figure 8) cured within the PAOX template at 700 $^{\circ}\text{C}$ shows significant similarities

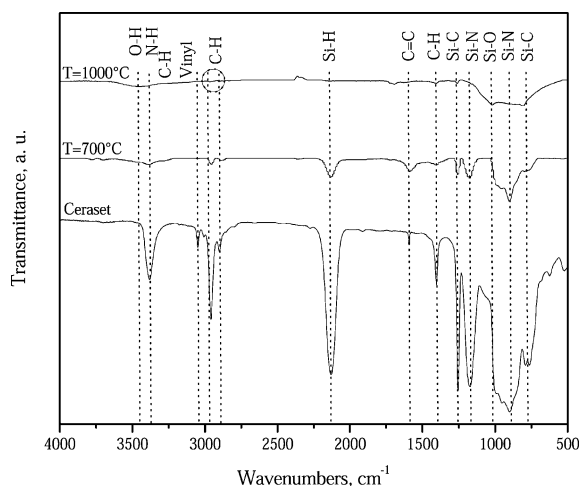


Figure 8. FTIR spectra of the KiON Ceraset polyureasilazane (ceramic polymer precursor) as received (below), and cured within the PAOX template at 700 °C (middle) and at 1000 °C (above) together with reasonable band assignment.

with the appearance of the spectrum of bulk ceramic samples obtained from the precursor under no confinement conditions in the characteristic fingerprint region (temperature range 450–600 °C).^[29] The broad but intense absorption at 3700–3100 cm^{−1} with the maximal absorption at 3450–3440 cm^{−1} can be attributed to an O–H (3650–3200 cm^{−1}) stretch. However, $\nu\delta$ of the hydroxy absorption at 1450–1250 cm^{−1} and 750–650 cm^{−1} is either absent or too weak to be considered as significant. The intensity of vibrations in the C–H region is low possibly due to the vinyl cross-linking. The appearance of a free carbon phase could be confirmed in the spectra at that temperature. The band envelope at 1650–1580 cm^{−1} can be assigned to the stretching mode of the conjugated C=C framework of graphite. Furthermore, the aromatic C_{sp2} stretching vibrations are present at 1630 cm^{−1}.

Ceramic material finally synthesized at 1000 °C in not dehydrated PAOX templates showed two additional intense bands at 1100 and 1030 cm^{−1}, which are characteristic of Si–O–Si (1125–1010 cm^{−1}) and Si–O–R (1100–1000 cm^{−1}) bending modes, respectively.^[30] This finding can be attributed to a hydrolysis reaction of the KiON Ceraset precursor with adsorbed hydroxy groups still present on the template's pore surface. When the alumina films were thus first calcinated at 700 °C to remove this hydroxy layer, the intensity of those two bands decreased significantly (see Figure 8, middle).

The spectra of the liquid SP Matrix Polymer precursor, of its bulk thermolysis product (at 1000 °C) and of the nanowires derived from the SP Matrix Polymer are depicted in Figure 9. The most intensive bands are: C=C stretching vibrations mode around 3070–3080 cm^{−1} and deformation vibration modes at 1630 cm^{−1}, the band system between 2860–2975 cm^{−1} is due to the C–H stretching modes, a characteristic absorption Si–H absorption is centred around 2100–2170 cm^{−1}. Absorptions with maximal intensities

at 1360, 1059 and 955 cm^{−1} are present due to the Si–CH₂–Si fragments, the peaks at 255, 865 and 780 cm^{−1} are due to Si–C stretching vibrations of the Si–CH₃ groups.

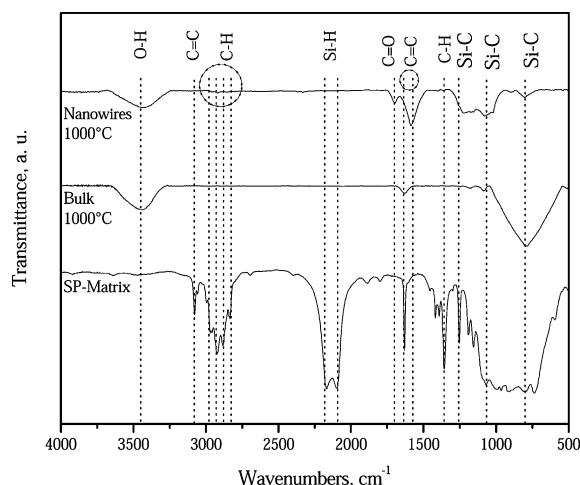


Figure 9. FTIR spectra of the SP matrix polymer as received (below), bulk pyrolysis product at 1000 °C (middle) and cured within the PAOX template at 1000 °C (above) together with reasonable signal assignments.

The PAOX template-based nanowire species cured at 1000 °C exhibit a significant absorption around 1700 cm^{−1}. The appearance of this band might be due to the release of decomposition products derived from oxalate anions which are incorporated into the PAOX template due to the anodic oxidation process which is performed in oxalic acid. The thermal behaviour of PAOX templates derived from sulfuric and oxalic acid solution is clearly different to that obtained from phosphoric acid solution.^[31] The thermal analysis displayed a unique mass-loss event around 800–1150 °C for oxalic and sulfuric alumina-derived PAOX templates due to the decomposition of anion impurities (oxalate or sulfate, respectively).

Depending on pyrolysis conditions and a precursor used, the amorphous polymer-derived ceramic material usually contains silicon, carbon and other minor doping atoms in variable nonstoichiometric proportions (excess carbon, see Figure 10), however phonon modes corresponding to SiC at around 800 and 973 cm^{−1} were not observed. This corresponds with the results from the X-ray diffraction experiments (see following discussion).

In entirely amorphous carbon specimens, G and D bands merge into one broad signal with the maximal intensity value around 1500 cm^{−1}. The observation of two separated, however broad phonon bands which correspond to the D and G modes (signals at around 1300 and 1600 cm^{−1}) denote the partial ordering of the carbon phase present in the ceramic into a graphitic layered structure. Comparison of the spectra suggests that the KiON Ceraset polyureasilazane-derived ceramics has a more developed graphite framework than the SP Matrix polymer derivative.

The broad D band resonance at 1290–1300 cm^{−1} results from Raman scattering at the crystallite edges of graphitic structures and is a disorder-induced mode. Its intensity is

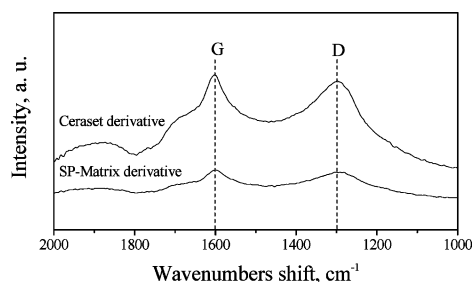


Figure 10. Raman spectra of the KiON Cereset polyureasilazane-derived template-based nanowires (above) and SP matrix polymer-derived wires (below).

inversely proportional to the crystallite size of the graphitic structures.^[32,33]

The G band signal at 1600 cm^{-1} is caused by the E_{2g} optical mode of ordered graphite forms.^[33] Its appearance is always around 1580 cm^{-1} , and a slight shift toward higher wavenumbers is found only in some samples with extremely small crystallite sizes. The high-energy shoulder of this band normally appears in the presence of disordered phase which are in the focus of the laser beam.

X-ray diffraction patterns of the nanowires confirmed a difference in phase composition (Figure 11). Both materials are entirely amorphous, but the prominent signals corresponding to the carbon phases are clearly presented in the case of the KiON Cereset polyureasilazane-derived ceramics whereas they are not seen in the SP Matrix polymer-derived product. The growth of the graphite phase in bulk polymer-derived ceramics occurs already at $800\text{ }^{\circ}\text{C}$, but the size of the domains is normally too small to be detected as a separate phase up to $1100\text{ }^{\circ}\text{C}$.^[34] The phase separation and formation of turbostratic graphite takes place at approximately $1200\text{ }^{\circ}\text{C}$, whereas formation of nanocrystalline SiC is observed only at temperatures from $1300\text{ }^{\circ}\text{C}$ onwards.

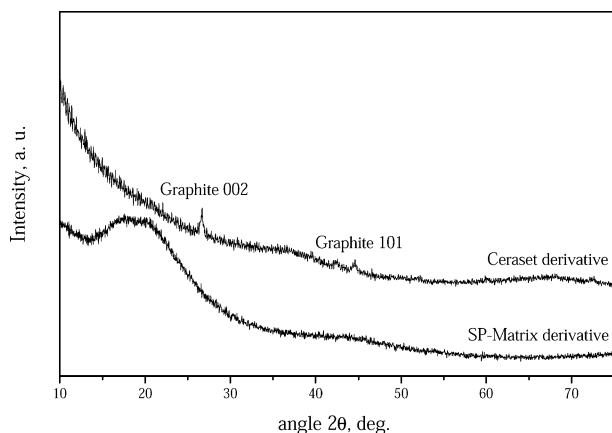


Figure 11. XRD-patterns of the KiON Cereset polyureasilazane-derived template-based nanowires (above) and SP matrix polymer-derived wires (below).

Ceramic Nanowires Derived from 20 V PAOX Templates

The SP Matrix polymer was chosen for studying the influence of smaller pore diameters ($23 \pm 3\text{ nm}$) of PAOX templates with respect to formation of 1D ceramic structures. When switching to a template obtained from a sulfuric acid solution, like the one with 23 nm pores one should expect a greater reactivity of the pore walls during the pyrolysis step. In comparison to PAOX prepared from oxalic acid sulfuric acid-derived PAOX templates are known to incorporate a significantly higher concentration of dopant species derived from the electrolyte during their formation process and thus the surface of the pore walls show a higher hydrophilic character due to more surface hydroxy groups as well as adsorbed water.^[31]

The synthesis of ceramic wires of a smaller diameter was performed in the same way as described in the experimental part, except longer infiltration times (membranes were fully immersed in the precursor for three days) and the use of a 90 wt.-% mixture of the ceramic precursor in *n*-hexane (to decrease its viscosity). After pyrolysis of the precursor the template was removed in 48% HF solution. As deduced from SEM micrographs a dense arrangement of ceramic wires was obtained (Figure 12). The diameter of the wires was uniform and averaged 26 nm (HRSEM, not shown). As with the larger sized template pores we met difficulties to obtain free nanorod structures with 23 nm alumina templates for TEM analysis of the ceramic nanowires derived from the SP matrix precursor. In the future we are aiming to encapsulate the ceramic wires within a stable shell which would stabilize the ceramic 1D structures thus allowing to disperse them in a more sufficient manner e. g. by ultrasonification.

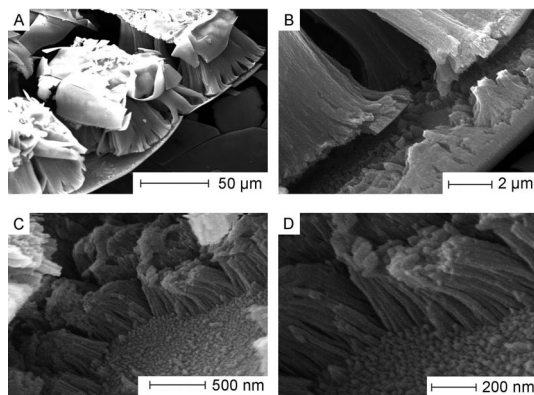


Figure 12. SEM micrographs (A, B) (C, D, higher magnification of A and B) of the SP matrix polymer-derived wires after complete dissolution of the from PAOX templates.

Based on X-ray photoelectron studies (XPS) the ceramic wires contain some sulfur contamination due to pyrolysis of sulfate anion content present in the PAOX template due to the usage of sulfur acid as electrolyte (Figure 13).

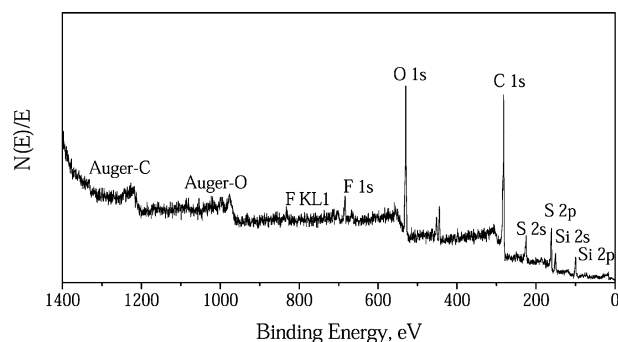


Figure 13. XPS of the SP matrix polymer-derived wires, derived from PAOX templates.

When comparing the XPS data for pure Si, the measured Si 2s and Si 2p binding energies (150.9 and 99.9 eV respectively) of the ceramic nanowires are slightly shifted towards higher values. This effect results from the electrons charge displacement from silicon atoms to the neighbouring more electronegative oxygen and suggests the existence of covalent Si–O bonds in the material.

For the accurate quantitative analysis the photoelectron emission from the sample has to be isotropic. This implies a high flatness, homogeneity and purity of the sample surface. In addition to that, XPS is a surface analysis method, and the electrons output depth is only a couple of nanometers. At the same time, there is always a naturally occurring oxide layer on the ceramic samples, and the composition in the bulk may significantly differ from that on the surface. The calculated atomic percentage of the elements (65.9% C, 7.11% Si, 26.9% O) shows a large excess of carbon and

oxygen. This suggests the prevailing dissolution of surface silica fragments in HF during the PAOX template removal, whereas the carbon phase remains intact.

Ceramic 1D Nanotubes and Wires Derived from Anodisc 13 (Whatman Inc.)

It is known that commercially available polysilazanes contain a significant amount of oligomers. Low volatile oligomers can be distilled off at temperatures below the cross-linking temperature of the KiON VL20 polyvinylsilazane (260 °C).^[29] In the case of cross-linking of the infiltrated polymer in the cylindrical pores of Anodisc 13 PAOX templates the oligomers are able to displace the liquid precursor from the pore surface. Thus, under these conditions ceramic nanotubes are formed. The evaporation of volatile fragments in the nano channels can be avoided by the removal of the oligomeric fraction from the precursor before infiltration into the nanopores and additional cross-linking at 150 °C after infiltration. This procedure results in an increase in the degree of pore filling of the Anodisc 13 PAOX and compact nanowires are obtained (see prior studies on PAOX templates with 20 and 40 nm nominal pore diameters).

The influence of the above described different cross-linking conditions on the morphology of the synthesized nanowires becomes apparent by SEM investigations. Figure 14 (A) shows the top view of a Anodisc 13 PAOX template after infiltration with as-received KiON VL20 polyvinylsilazane followed cross-linking within the nano channels at 260 °C for 2 h. All tubes exhibit diameters below

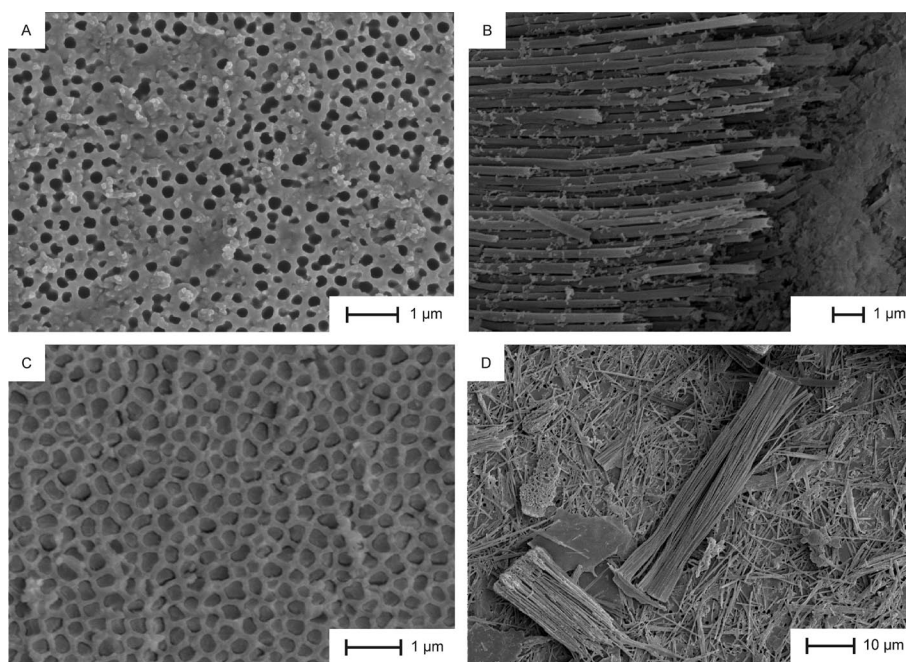


Figure 14. Filling grade of Anodisc 13 PAOX A) KiON VL20 polyvinylsilazane infiltrated as-received and cross-linked in the template at 260 °C (2 h), B) corresponding nanotubes after pyrolysis at 1100 °C and template dissolving, C) pre-treated KiON VL20 polyvinylsilazane after infiltration and further cross-linking between 150 and 260 °C in the template and D) nanowires of second series of experiments after dissolving of template.

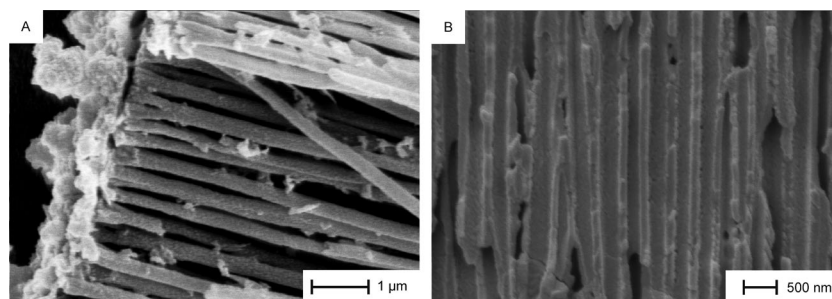


Figure 15. Morphology and surface condition after annealing at 1100 °C (2 h) A) SiOC-nanowires and B) Anodisc 13 PAOX.

that of the nominal pore diameter of the native Anodisc 13 PAOX template after pyrolysis. Ceramic nanotubes after pyrolysis at 1100 °C and etching of the template are depicted in Figure 14 (B).

In the second series of experiments with pre-treated KiON VL20 polyvinylsilazane and optimized cross-linking conditions, nanotubes were no longer observed. Figure 14 (C, D) show a completely filled Anodisc 13 PAOX template and dense nanorods obtained therefrom after etching of the template. From Figure 14 (D) it is also obvious that the template is completely removed. The nanowires occur as single nanowires or as bundles. The nanowire bundles are kept together by a thin ceramic coating that was generated on both sites of the Anodisc 13 PAOX template. The synthesized nanowires are 60 µm long (according to the thickness of the template used) and had an external diameter in the range between 200 and 300 nm (according to the average diameter of the pores). Figure 15 (A) depicts a SEM image of the produced nanowires. It can be seen that the surface of the wires is smooth corresponding to the surface structure of the uninfiltrated pores after annealing at 1100 °C [Figure 15 (B)].

More detailed information on the morphology and composition of the nanowires are obtained by analytical TEM studies.^[35,36] To determine the chemical composition of the nanowires, energy dispersive X-ray spectroscopy (EDS) as well as electron energy-loss spectroscopy (EELS) is performed on the nanowire sample and bulk SiCN ceramic obtained by pyrolysis of pure KiON VL20 polyvinylsilazane.

The TEM image in Figure 16 shows the morphology of a single nanowire. The investigated nanowires have a smooth surface and their diameter averaged to 200 nm. It should be noted that it was not possible to clearly identify hollow regions within the nanostructures, however some might appear as visible by the distinct contrast differences at both ends of the tubes. The relatively short length of the fiber could be an artefact of the treatment in an ultrasonic bath to disperse the fibers in ethanol for TEM sample preparation. No crystalline phases, as already observed for the smaller diameter tubes (Figure 4) derived from Ceraset could be detected by selected area electron diffraction (SAED). The area where the EELS and EDS measurements were performed is indicated by the white circle.

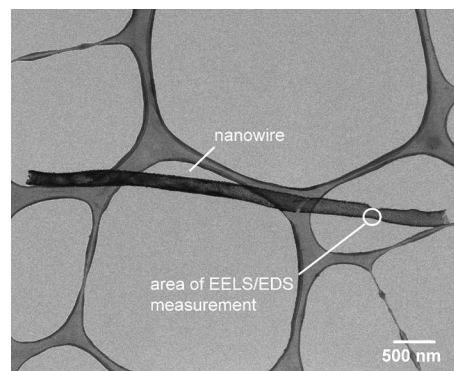


Figure 16. TEM bright field image of a single SiOC nanowire obtained by pyrolysis of pretreated KiON VL20 polyvinylsilazane and subsequent etching of the Anodisc 13 PAOX template. The area of the corresponding EELS analysis is indicated (see also Figure 15).

The EDS spectrum for the nanowire shown in Figure 17 (top) reveals peaks which can be assigned according to their energies to carbon, oxygen, copper, sodium, silicon and phosphor. Nitrogen and aluminium is below the detection limit of the EDS system. The strongest peaks are for carbon, oxygen and silicon. The copper signal is from the use of a copper grid as support for the TEM samples. The absence of aluminium in the EDX spectrum proves that the alumina template was completely dissolved. Phosphorous and sodium contamination can be attributed to the phosphoric acid treatment. For the bulk sample obtained by pyrolysis [see Figure 17 (bottom)], an additional peak at 0.4 keV can be observed which is assigned to nitrogen. The intensity ratio for the carbon and silicon peak is similar to the spectrum from the nanowire. The oxygen peak is only weak in intensity as compared to the spectrum taken of the nanowire. The peaks of sodium and phosphor were not detected in the bulk SiCN sample, indicating that these peaks recorded in the nanowire indeed represents an artefact as a result of the etching process.

The C, N, and O k-edge of the SiCN bulk sample and the etched nanowire were also measured with EELS. The background corrected spectra are depicted in Figure 18. The C k-edge can be detected in both samples.

The nitrogen k-edge is only present in the spectra of the bulk SiCN sample, whereas in the etched nanowire sample

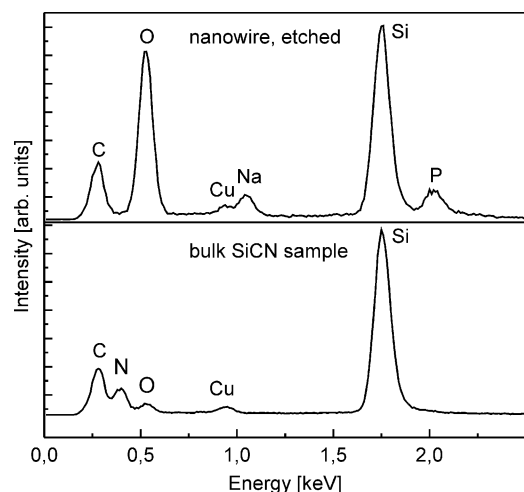


Figure 17. EDS spectra of the SiOC nanowire (top) and a bulk SiCN sample (bottom). Both materials were processed with the KiON VL20 polyvinylsilazane. Peaks are labeled according to their energies.

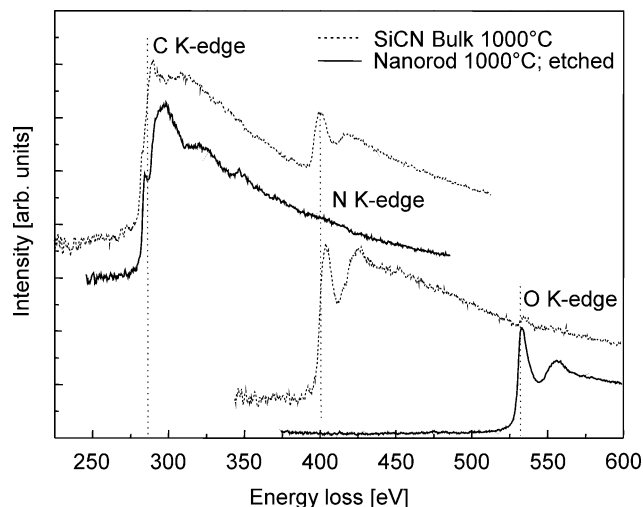


Figure 18. EELS measurements on pyrolyzed SiCN bulk material (dotted) and nanowire (solid) after etching to remove the PAOX template. The carbon, nitrogen and oxygen k-edge are given.

the nitrogen content is below the detection limit of the EELS system. This result is consistent with the EDS data. The picture for the oxygen k-edge is different. There, a small peak is also visible in the bulk SiCN sample, while the etched nanowire sample reveals a strong signal of the O k-edge, which is in agreement with the EDS analysis (Figure 18), where the peak assigned to oxygen is also strong in intensity.

The chemical composition of the bulk SiCN ceramic obtained by pyrolysis of pure KiON VL20 is determined by hot gas extraction and combustions analysis, respectively. The SiCN ceramic is composed of 56.1 wt.-% Si, 19.8 wt.-% C, 21.6 wt.-% N and 2.5 wt.-% O and correspond to a molecular formula of $\text{Si}_1\text{C}_{0.82}\text{N}_{0.77}\text{O}_{0.08}$ which is in accordance with our previous study^[29] and the EELS analysis. A quantitative examination of the EDS spectra reveals a com-

position of $\text{Si}_1\text{O}_{1.36}\text{C}_{0.31}$ for the investigated nanowire (see Figure 19). This different result of the elemental composition of the ceramic obtained by pyrolysis of infiltrated and non infiltrated KiON VL20 polyvinylsilazane clearly indicates a strong influence of the membrane material and/or the etching process on the pyrolysis behaviour of KiON VL20 as has been described before for the lower pore diameter PAOX templates.

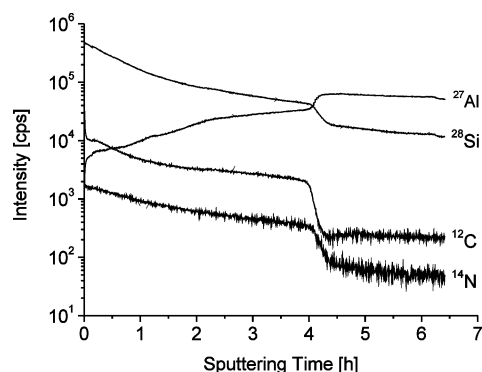


Figure 19. SIMS depth profile of SiONC nanowires within Anodisc 13 PAOX.

Comparing the EDS and EELS results with data obtained by SIMS analysis, where nitrogen is detected in the nanowires before etching to remove the PAOX, one can conclude that the residual nitrogen in the nanowire sample is lost during the etching process.

The chemical composition of the nanowires within the Anodisc 13 PAOX before the PAOX was removed by etching was determined by a SIMS depth profile measurement. Figure 19 shows the detected masses of the infiltrated Anodisc 13 PAOX after pyrolysis at 1100 °C. Within the sputtering time of 4 h the investigated SiCN layer on the bottom of the template has the same composition as that of the KiON VL20-derived bulk SiCN ceramic and was used as reference. Towards a sputtering time of 4 h the transition of the SiCN layer to the infiltrated template was observed. The atomic ratios C/Si and N/Si after the transition are lower than those of the bulk SiCN ceramic and it is evident that during the pyrolysis the carbon and nitrogen content decrease due to hydrolysis of the SiCN precursor by release of residual water of the template. Semi-quantitative examination of the synthesized nanowires derived from SIMS depth profiles revealed a composition of $\text{Si}_1\text{O}_{0.8}\text{N}_{0.4}\text{C}_{0.3}$ corresponding formally to $4\text{SiO}_2 + 3\text{SiC} + 1\text{Si}_3\text{N}_4$.

XRD measurements were performed in order to investigate the crystallinity of the nanowires within PAOX. The observed XRD pattern from the infiltrated sample differs not from the pattern of the native Anodisc 13 PAOX template which was annealed at 1025 °C for formation of $\theta\text{-Al}_2\text{O}_3$.^[37] The patterns of the different samples comprise the same signals which are attributed to the $\theta\text{-Al}_2\text{O}_3$ polymorph. The formation of any crystalline silicon containing phase is not found in the XRD pattern.

To explain the high content of oxygen in the nanowires measured by SIMS and TEM, an empty Anodisc 13 PAOX membrane is investigated by thermal gravimetric analysis. A mass loss in the amount of 1 wt.-% is found between 100 and 1100 °C as shown in Figure 20. No decomposition products are identified by in situ mass spectrometry between 350 and 980 °C. However, as already described before, it is well known that alumina templates release chemically physisorbed water from their surface and the amount of the released water cannot be distinguished from the baseline of the mass spectrum in our case. In the temperature range between 980 and 1000 °C carbon dioxide is clearly detected as released gas species, exclusively. The release of CO₂ can be attributed to the decomposition of oxalate anions from the electrolyte and is coupled with an exothermal peak at 1005 °C in the differential thermal analysis (DTA) curve.^[35] In addition, an exothermal peak at 865 °C is found in the DTA suggesting the formation of γ -Al₂O₃ which transforms to θ -Al₂O₃ at 1025 °C (Figure 17).^[38]

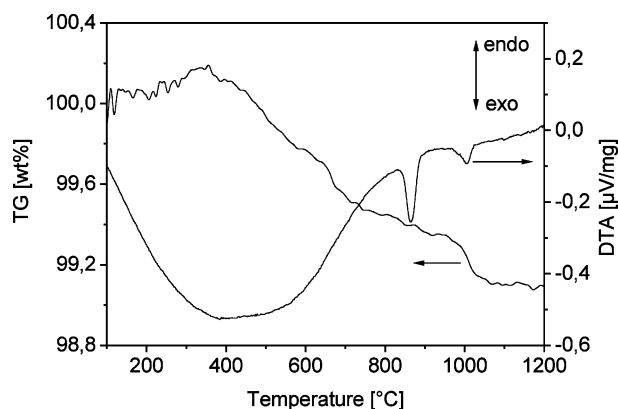


Figure 20. TG and DTA characteristics of an as-received Anopore 13 PAOX.

Thus, the occurrence of gaseous oxygen containing decomposition products, namely H₂O and CO₂, formed directly from the Anodisc 13 PAOX membrane upon heating indicates possible reactions of the released gases with the polymeric infiltrate and can explain the loss of nitrogen during the annealing process of the preceramic polymer material.

Thus commercial Anodisc 13 PAOX exhibits a high thermal stability with respect to morphology and allows their application as high temperature templates for the fabrication of tailored nanostructures. Furthermore, the sensitivity of the infiltrated system with respect to its oxidation behaviour has to be taken into account in order to successfully apply alumina templates for the synthesis of non-oxidic nanostructures. The unavoidable release of water at high temperature as well as the phase transitions of alumina restricts the utilization of alumina templates in the fabrication of non-oxide systems. In the case of our experiments the ceramization of the precursor occurs at 1000 °C and in the temperature range below 1000 °C the precursor is prone to hydrolysis and other reactions with oxygen containing species. Consequently, SiO(N)C nanowires with a high oxygen

content are fabricated from PAOX templates during pyrolysis of the infiltrated polyvinylsilazane under the applied conditions studied here.

Conclusions

A successful attempt to alter the geometry of silicon-based ceramic nanowires by means of PAOX pore size tailoring has been made. However, diverse optical, spectral and structural characterization methods confirm the active participation of the PAOX matrix in reactions with the Si ceramic precursors within the nano channels and the influence on the chemical composition of the nanostructures synthesized therein.

Aluminium oxide obtained from electrolytic anodic oxidation of aluminium metal usually display a complex composition formulated as AlO(OH)·(H₂O)_n. Water-free surfaces are accessible via calcination at 300–400 °C, but still this process leaves up to 10% of the porous surface covered with hydroxy groups. At the same time, many organosilicon polymers are hydrolytically sensitive substances. Our results show that alumina templates composed of such a nonstoichiometric composition AlO(OH)·(H₂O)_n do react at higher temperatures with all three precursors employed in this study (KiON Ceraset polyureasilazane, KiON VL20 polyvinylsilazane and polycarbosilane SP Matrix Polymer) to form one dimensional SiO(N)C materials. Under high temperature conditions PAOX templates are even further reactive towards these Si-based ceramic precursors.

The results of our investigations will have a practical importance for the design of further PAOX template-based experiments and shed new light on the chemical reactivity of widely used PAOX templates as structure directing matrix and as reaction partner in solid state reactions. The sensitivity of the infiltrated molecules with respect to its oxidation behavior has thus to be taken into account in order to successfully apply alumina templates, for the synthesis of non-oxide nanostructures. The release of water at high temperatures, the reactivity of residual hydroxy groups as well as the phase transitions of alumina restricts the utilization of alumina templates in the fabrication of non-oxide systems. In the case of our experiments the ceramization of the precursor occurs at 1000 °C and in the common temperature range up to 1000 °C the precursor is oxidation sensitive. We have shown that oxygen was inserted at low temperature in the SiCN and SiC precursor and SiO(N)C nanowires are formed in PAOX templates during pyrolysis. Thus, it can be concluded that PAOX is no innocent, just structure directing template under high temperature conditions, however it has significant impact on the reaction chemistry under such conditions.

Experimental Section

Preparation of PAOX: The two-step anodization of aluminium sheets (PURALUX®, purity 99.93%, thickness 1 mm) was performed in a 0.3 M oxalic acid or in a 10 wt.-% sulfuric acid solution as described elsewhere (pore diameter approx. around 40 and 20 nm respectively).^[18,19] Voltage reversal^[26] was employed to separate freestanding PAOX films from the aluminium substrate. Large membranes (surface area of several square centimeters) with the backside closed were obtained by this method. To open the backside of PAOX films, the barrier layer was removed in an etching aqueous solution (0.16 M K₂Cr₂O₇ and 1.5 M H₃PO₄). At this stage, the pores become widened and their diameter increases. The barrier

oxide layer dissolves in an etching solution slower than the porous layer,^[39] which may lead to the complete inter-pore walls dissolution even before the channels are completely open from both sides.

Synthesis of 1D-SiOC Nanostructures in PAOX Templates of 20 and 40 nm Nominal Pore Diameter: Two commercially available thermo-setting resins, KiON Ceraset polyureasilazane (SiCN precursor^[40]) and Starfire Systems SP Matrix polymer (SiC precursor) (Figure 21), were used for the infiltration procedure in an argon glove box.

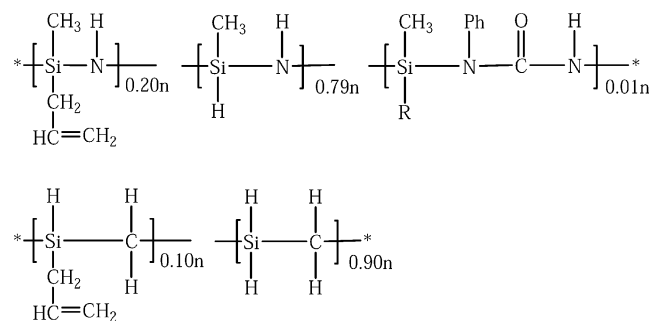


Figure 21. Structural formula of the KiON Ceraset polyureasilazane (top) and of the SP matrix polymer (bottom).

The precursor was placed on a glass slide, and then a PAOX membrane is placed on top of a liquid. The increasing transparency of the membrane indicates filling of the pores by capillary force infiltration. The ceramization reaction was performed in a quartz tube in an argon flow. After a cross-linking step at 260 °C for 2 h the temperature was increased and hold for 2 h at 1000 °C to achieve the transition of the precursor to the final ceramic material.

To dissolve the alumina template, the samples were placed either in a 48 wt.-% HF solution at ambient temperature or in 85 wt.-% H₃PO₄ solution at 110 °C (the etching time varied from 20 to 48 h). The resulting material was thoroughly rinsed with distilled water and dried at 130 °C. A summary of the processing steps is schematically depicted in Figure 22.

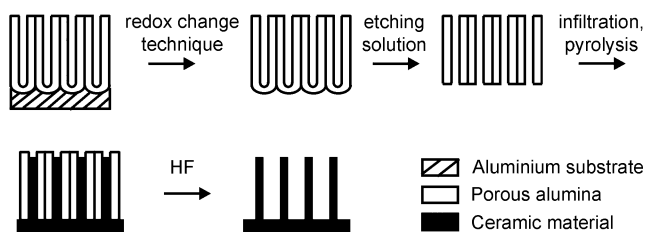


Figure 22. Schematics of the template-based approach to polymer-derived ceramic wires.

Preparation of 1D-SiOC Nanostructures in Anodisc™ Membranes (Whatman Inc.): Anodic aluminium oxide (Anodisc 13, Whatman Inc.) with an average pore size of 250 nm and a membrane thickness of 60 µm was used for the infiltration experiments. The templates were dried at 700 °C for 2 h under argon and then they were stored in a glove box also under argon. Polyvinylsilazane KiON VL20 (Figure 23) was used as the nitrogen-containing preceramic polymer.

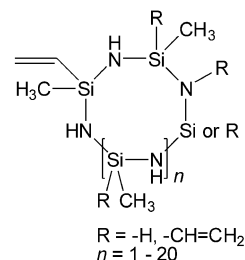


Figure 23. Structural formula of the KiON VL20 polyvinylsilazane.^[41]

Two series of experiments have been carried out. First, KiON VL20 was infiltrated as-received and the cross-linking step was conducted at 260 °C for 2 h. Second, the oligomers of KiON VL20 were removed at 50 °C under vacuum for 5 h before infiltration into the porous alumina membrane. Cross-linking was conducted in the temperature range between 150 and 260 °C with a heating rate of 0.5 °C/min. In these experiments the temperature was kept constant at 150, 200 and 260 °C for 1, 2 and 1 h, respectively. PAOX templates were placed on top of a piece of glass with a thin film of KiON VL20 for 5 min. The infiltration occurred at room temperature under argon atmosphere. After infiltration, the samples were transferred into an alumina boat and then pyrolyzed in a quartz-tube furnace under a flow of argon (4 l/h) at 1100 °C with a heating rate of 2 °C/min and held at the final temperature for 2 h. In order to obtain free standing nanostructures the PAOX template was subsequently treated with 5 M KOH/ethylene glycol solution at 110 °C for 20 h and after that aluminium oxide was dissolved with 85% wt H₃PO₄ at 110 °C. The received nanowires were filtered and washed with distilled water.

Characterisation Techniques: Scanning electron microscopy (SEM) studies were done using a Philips XL-30 FEG or a JEOL JSM-6300F SEM. The morphology and the chemical composition of single nanowires were determined using a FEI CM12 transmission electron microscope (TEM) operating at a nominal acceleration voltage of 120 kV equipped with energy dispersive X-ray spectroscopy (EDS; EDAX Genesis 2000, Ametek GmbH) and electron energy-loss spectroscopy (EELS; Gatan DigiPeels 766 parallel electron spectrometer).

Silicon, carbon, and nitrogen contents of the infiltrated PAOX templates were determined by secondary ion mass spectrometry (SIMS) using a Cameca ims 5f instrument. The depth profiling was performed with oxygen primary ions (O⁻) and an accelerating voltage of 17 kV. The sputtered area was (150 µm)² and for measurement the inner area of 60 µm diameter was used. Semi quantitative evaluation of the SIMS data was performed by using SiCN bulk material as reference, which is present at the top of the template. The oxygen content of the nanowires was estimated by balancing to 100%.

To follow the structural changes after the thermal treatment, qualitative X-ray analysis (XRD) of the species was carried out on a STOE STADI 4 4-circle-diffractometer using Cu-K_{α1} radiation (λ = 1.541 Å) or with a STOE STADI-P in Debye-Scherrer geometry equipped with a Mo-K_{α1} radiation (λ = 0.709 Å). The specific surface area of the PAOX templates (BET-measurements) was determined on a Nova 3000e surface area and pore size analyser. Fourier transform infrared spectra (FTIR, Nicolet Impact 400) of solid species were taken by a standard KBr discs method. Raman spectra were obtained on a Bruker FRA-106 Fourier transform spectrometer. To eliminate the thermal sensitivity effect, the samples were

grinded with KBr in mortar, and then pressed onto a metal sample holder.^[42] An unfocused beam has been employed. The thermogravimetric analysis (TGA) was performed on a Netzsch TG 209 F1 Iris analyser in an argon flow at a 10 °C/min heating rate or by a simultaneous thermal analysis using a Netzsch STA 429 coupled with a Balzers QMA 400 quadrupole mass spectrometer (STA-MS) for identification of the decomposition products by TGA-MS. Chemical element analysis was performed on an Escalab 250 Spectrometer with a monochromatized Al anode.

Acknowledgments

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After publication in Early View, Figure 10 was replaced by the correct Raman spectra.