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# Multiscale microshaping of functionally graded polymer-derived SiCN ceramics

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to mom and dad and my sister...

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A few weeks ago, a major German newspaper published an article about the meaning and value of a PhD in today's society which contained the following phrase: "Those who successfully complete a doctoral thesis have good stamina, a high tolerance for frustration, are team players, and know how to develop new things."<sup>1</sup> Here, I want to emphasize the importance of the *team* aspect and try to acknowledge the people who mostly contributed to this work and helped me to cope with the occasional frustration.

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<sup>&</sup>lt;sup>1</sup>A.-L. Scholz, "Was ist der Doktor noch wert?", *DIE ZEIT*, Nr. 22, 25.05.2022; quote by Karsten Danielmeier

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Lorenz Hagelüken

## Abstract

Polymer-derived ceramics (PDCs) exhibit excellent properties and are compatible with many shaping techniques due to the liquid character of the preceramic polymers (PCPs). Furthermore, their properties are adjustable by modifying the precursor composition and controlling the processing conditions. In this thesis, poly(methylvinylsilazane) (PMVSz) is chosen as the precursor basis and varied amounts of divinylbenzene (DVB) are added to increase the carbon content, which significantly increases the electrical conductivity of the silicon carbonitride (SiCN) obtained after pyrolysis. Based on molding and pressureless processing, samples are manufactured with varied homogeneous composition and functional properties as well as with engineered property contrasts, so-called functionally graded ceramics.

Starting with shaping aspects, several mold materials, mold fabrication techniques, and the casting and thermal processing are discussed in the first part. The liquid precursor formulation is directly pipetted into the molds, either CNC-machined PTFE for bulk samples or anisotropically etched Si for microsized parts. Thermally cured bulk green bodies (GBs) are removed from the PTFE molds before pyrolysis whereas the monolithic and resilient character of Si allows for an in-mold pyrolysis which eliminates the need for mold release of fragile GBs. While the Si molds define the parts' general shape, sacrificial 3D microstructures are optionally added onto the mold bottom by two-photon polymerization (2PP). After pyrolysis, the PDC parts are obtained loose in the mold with sub-µm resolution features replicated as imprints.

The second part focuses on the processing conditions and the tuning of the PDCs' bulk properties. Thanks to a thermal initiator, the PMVSz-based precursors are cured without pressurization within 30 min at 200°C. The pore-free GBs, filled with 0–60 wt.% DVB, are converted to SiCN with varied carbon (C) concentration by pyrolysis at 800–1400°C under Ar atmosphere. Dense and defect-free PDCs are obtained whose free carbon content is adjusted in the range 15–25 wt.%. The influence of the pyrolysis temperature on the ceramics' microstructure is analyzed and correlated to the electrical conductivity, tunable across 10 orders of magnitude up to 0.4 S/cm. Very high characteristic flexural strength of up to 1.65 GPa is observed and the SiCNs' cytocompatibility demonstrated.

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Thirdly, PCPs with and without DVB-filling are combined by consecutive casting to fabricate functionally graded SiCN parts. The dissimilar precursors are joined in vertical or lateral arrangement in dedicated PTFE molds, typically with an intermediate thermal curing step. Monolithic and defect-free property-contrast PDC parts are obtained after pyrolysis which exhibit seamless transitions and no signs of delamination at the interface. The casting order and extent of intermediate curing are varied, showing that composition gradients are adjustable from sub-µm to mm-range transition lengths. Significant contrasts in C-concentration and consequently electrical conductivity are observed within monolithic samples entirely consisting of SiCN. Finally, a cm-scale plate with two seamlessly integrated contrast regions is designed and fabricated. The all-SiCN parts have an insulating matrix and two conductive feedthroughs. An LED connected to the areas with higher C-concentration is powered through the ceramic and lit up.

**Keywords:** Polymer-derived ceramics, Functionally graded materials, Molding, Additive Manufacturing, Microfabrication, Bioceramics

## Zusammenfassung

Polymerabgeleitete Keramiken (PDCs) weisen hervorragende Eigenschaften auf und sind aufgrund des flüssigen Charakters der präkeramischen Polymere (PCPs) mit vielen Formgebungsverfahren kompatibel. Darüber hinaus lassen sich ihre Eigenschaften durch Änderung der Zusammensetzung des Präkursors und durch Anpassung der Prozessbedingungen einstellen. In dieser Arbeit werden Poly(methylvinylsilazan) (PMVSz) als Präkursorbasis gewählt und unterschiedliche Mengen Divinylbenzol (DVB) zugesetzt, um den Kohlenstoffgehalt zu erhöhen, was die elektrische Leitfähigkeit des nach der Pyrolyse erhaltenen Siliciumcarbonitrids (SiCN) deutlich erhöht. Mittels Formgießen und druckloser Verarbeitung werden Proben mit unterschiedlicher homogener Zusammensetzung und funktionalen Eigenschaften sowie mit gezielten Eigenschaftskontrasten, sogenannte funktional abgestufte Keramiken, hergestellt.

Beginnend mit Formgebungsaspekten werden im ersten Teil verschiedene Formmaterialien, Formherstellungstechniken sowie die gießtechnische und thermische Verarbeitung diskutiert. Die flüssige Präkursorformulierung wird direkt in die Formen pipettiert, entweder CNC-gefrästes PTFE für mm-große oder anisotrop geätztes Si für µm-kleine Teile. Thermisch ausgehärtete Grünkörper (GBs) werden vor der Pyrolyse aus den PTFE-Formen entnommen, während die monolithische und robuste Beschaffenheit von Si eine Pyrolyse in der Form ermöglicht, sodass Entformung der zerbrechlichen GBs nicht erforderlich ist. Während die Si-Formen die generelle Form der Teile bestimmen, werden optional 3D-Mikrostrukturen durch Zwei-Photonen-Polymerisation (2PP) auf dem Formboden aufgetragen. Nach der Pyrolyse liegen die PDC-Teile lose in der Form und weisen Strukturen mit einer Auflösung im Submikrometerbereich auf, die als Abdrücke reproduziert sind.

Der zweite Teil befasst sich mit den Verarbeitungsbedingungen und der Einstellung der Eigenschaften der PDCs. Dank eines thermischen Initiators werden die PMVSz-basierten Präkursoren ohne Überdruck innerhalb von 30 min bei 200°C ausgehärtet. Die porenfreien GBs, die mit 0–60 Gew% DVB gefüllt sind, werden durch Pyrolyse bei 800–1400°C unter Ar-Atmosphäre in SiCN mit unterschiedlichen Kohlenstoffkonzentrationen umgewandelt. Es werden dichte und defektfreie PDCs erhalten, deren freier Kohlenstoffgehalt im Bereich

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von 15-25 Gew% eingestellt wird. Der Einfluss der Pyrolysetemperatur auf die Mikrostruktur der Keramiken wird analysiert und mit der elektrischen Leitfähigkeit korreliert, die über 10 Größenordnungen bis zu 0,4 S/cm einstellbar ist. Es wird eine sehr hohe charakteristische Biegefestigkeit von bis zu 1,65 GPa beobachtet und die Zytokompatibilität der SiCNs nachgewiesen.

Drittens werden PCPs mit und ohne DVB-Füllung durch konsekutives Gießen kombiniert, um funktional abgestufte SiCN-Teile herzustellen. Die unterschiedlichen Präkursorformulierungen werden in vertikaler oder lateraler Anordnung in speziellen PTFE-Formen zusammengefügt, typischerweise mit einem zwischengeschalteten thermischen Aushärtungsschritt. Nach der Pyrolyse erhält man monolithische und defektfreie PDC-Teile mit Eigenschaftskontrasten, die nahtlose Übergänge und keinerlei Anzeichen von Delamination an der Grenzfläche aufweisen. Die Reihenfolge des Gießens und das Ausmaß der Zwischenaushärtung werden variiert, was zeigt, dass die Zusammensetzungsgradienten von Submikrometer- bis mm-Übergangslängen einstellbar sind. Innerhalb monolithischer Proben, die vollständig aus SiCN bestehen, werden signifikante Unterschiede in der C-Konzentration und folglich der elektrischen Leitfähigkeit beobachtet. Schließlich wird eine cm-große Platte mit zwei nahtlos integrierten Kontrastbereichen entworfen und hergestellt. Die vollständig aus SiCN bestehenden Teile haben eine isolierende Matrix und zwei elektrisch leitende Durchführungen. Eine LED, die mit den Bereichen mit höherer C-Konzentration verbunden ist, wird durch die Keramik mit Strom versorgt und zum Leuchten gebracht.

**Stichwörter:** Polymerabgeleitete Keramiken, Funktional gradierte Werkstoffe, Abformung, Additive Fertigung, Mikrofabrikation, Biokeramiken

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# List of abbreviations, elements, and chemicals

2PP	two-photon polymerization	vii
ACC	amorphous covalent ceramic	8
Ag	silver	1
Al <sub>2</sub> O <sub>3</sub>	alumina	24
AM	additive manufacturing	11
Ar	argon	22
ARDE	aspect ratio dependent etching	28
Au	gold	74
B3B	ball on 3 balls	44
BFT	bi-feedthrough	2
BSU	basic structural unit	15
С	carbon	vii
C <sub>4</sub> F <sub>8</sub>	octafluorocyclobutane	27
CAM	computer-aided manufacturing	23
CIP	cold isostatic pressing	11
CLIP	continuous liquid interface production	13
CMC	ceramic matrix composite	13
CNC	computer numerical control	22
CNT	carbon nanotube	16
СТЕ	coefficient of thermal expansion	1
Cu	copper	14
CVD	chemical vapor deposition	11
CY	ceramic yield	8
DCP	dicumyl peroxide	7
DLP	digital light processing	13
DRIE	deep reactive ion etching	22
DSC	differential scanning calorimetry	43
DVB	divinylbenzene	vii
DIW	direct ink writing	13
DLW	direct laser writing	13
DTG	derivative thermogravimetry	71
Dz18	Durazane <sup>®</sup> 1800	42
EA	elemental analysis	43
EDX	energy-dispersive X-ray spectroscopy	14
EOL	end of life	24
FDM	fused deposition modeling	12
FGC	functionally graded ceramic	17

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FGM	functionally graded material 17
FIB	focused ion beam
FTIR	Fourier-transform infrared spectroscopy
FWHM	full width at half maximum
GB	green body
GBL	$\gamma$ -butyrolacton
GC	glassy carbon
HF	hydrofluoric acid
HIP	hot isostatic pressing
HMDS	hexamethyldisilazane
HRTEM	high-resolution transmission electron microscopy 67
HT	high-temperature
HTCC	high temperature co-fired ceramic
IPA	isopropyl alcohol
IR	infrared
КОН	potassium hydroxide
LED	light-emitting diode 17
LTCC	low temperature co-fired ceramic 1
MEMS	microelectromechanical systems
MWCNT	multi-walled carbon nanotube
Ν	nitrogen
NHDF	normal human dermal fibroblast
NTC	negative temperature coefficient
ОМ	optical microscopy
OPSZ	organopolysilazane
PAN	polyacrylonitrile
PCP	preceramic polymer
PDC	polymer-derived ceramic vii
PDMS	poly(dimethylsiloxane)
PGMEA	propylene glycol methyl ether acetate
PHPS	perhydropolysilazane 4
PLA	polylactic acid
PIXE	ENAC Interdisciplinary Platform for X-ray micro-tomography 43
PMMA	poly(methyl methacrylate) 8
PMVSz	poly(methylvinylsilazane)
PSI	Paul Scherrer Institute 67
Pt	platinum
PTFE	polytetrafluoroethylene 12
PU	polyurethane
QR	quick response
ROI	region of interest
RT	room temperature
SAED	selected area electron diffraction
SEM	scanning electron microscopy 27
SF <sub>6</sub>	sulfur hexafluoride
Si	silicon
$Si_3N_4$	silicon nitride
SiC	silicon carbide
SiCN	silicon carbonitride
0.00	siliaan awaarbida

a <del>.</del> .		
SLA	stereolithography	12
SLS	Swiss Light Source	67
STA	simultaneous thermal analysis	43
TEM	transmission electron microscopy	14
TGA	thermogravimetric analysis	43
Ti	titanium	17
TMCS	trimethylsilyl chloride	29
TOMCAT	TOmographic Microscopy and Coherent rAdiology experimentTs	67
TPU	thermoplastic polyurethane	12
UHT	ultra-high temperature	17
UHTC	ultra-high temperature ceramic	10
UV	ultraviolet	4
V-UV	vacuum ultraviolet	13
XRD	X-ray diffraction	43
YSZ	yttria-stabilized zirconia	8

## **1** Introduction

#### 1.1 Motivation

Due to their high strength, low coefficient of thermal expansion (CTE), and chemical stability at high temperatures, technical ceramics are the material class of choice for demanding applications such as in the fields of energy conversion, aerospace, industrial manufacturing, brakes, and engine systems [1]. The major challenge is that at some point almost every ceramic part requires connection to a dissimilar material, typically metals [2, 3], either for mechanical fixation or electric / electronic functionality. This fact is concomitant with mainly two considerations which are the atomic bonding difference (ionic or covalent in ceramics vs. metallic bonds) and the mismatch of CTEs (~factor 3 smaller for common engineering ceramics compared to typical alloys) [3]. In order to prevent failure and potentially catastrophic consequences in service, extensive research has been conducted on ceramic-metal and ceramic-ceramic joining over the past 25 years. The latter combination will be described in more detail in Section 1.3. An approach for robust monolithic devices partially coping with some of the above-mentioned challenges is co-fired ceramics. In a laminated layer procedure, green tapes are patterned and filled with metallic pastes. Applied materials are subdivided into two adequate firing temperature ranges. Processing above 1000°C is required in case of high temperature co-fired ceramics (HTCCs) in order to sinter the ceramic matrix so that high-melting metals like platinum (Pt) are necessary. In contrast, addition of a glassy phase allows for sintering below 1000°C, called low temperature co-fired ceramics (LTCCs), involving more conductive metals such as silver (Ag) [4]. However, involved noble metals are expensive, co-fired ceramics are also constraint by mismatched CTEs [5] and especially LTCCs have limited operating temperatures.

Overcoming those limitations, a new concept for structural parts and functional devices suitable for harsh environments is presented in this work. Based on the PDC route and exploiting the liquid nature of the precursors as well as the ability to tune various properties

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across a wide range by partial addition of fillers [6], property-contrast PDCs with an engineered heterogeneity and functionality integration are introduced. As the schematic of a rather simple demonstration object in Figure 1.1 illustrates, monolithic parts are fabricated fully composed of the very same ternary ceramic system. Based on an organopolysilazane (OPSZ) as PCP, high strength ceramics of the SiCN system are obtained after inert gas pyrolysis whose carbon content and consequently electrical conductivity are adjustable through the addition of organic fillers such as DVB. Spatially defined combination of these dissimilar PCP formulations in an early stage of the processing route followed by joint thermal treatment yields all-ceramic parts or devices, for instance exhibiting two electrically conducting feedthroughs seamlessly integrated into an insulating matrix. A slight lateral contrast in atomic composition and microstructure causes a conductivity contrast of 5–10 orders of magnitude while otherwise behaving very similarly. This way, required joining and assembly as well as risk of failure are reduced drastically. Considering the excellent properties of PDCs and the PDC route's compatibility with several advanced shaping techniques, which are both going to be presented in the following sections, functionally graded PDCs are a promising approach for applications in chemical engineering, energy conversion, and biomedical implants.



**Figure 1.1: Sketch of a monolithic all-ceramic plate with seamless functionality integration**: proposed bi-feedthrough (BFT) design based on the PDC route exhibiting two conducting electrical feedthroughs with locally higher C concentration serving as transmission of electricity for harsh environment applications.

#### 1.2 Polymer-derived ceramics

*Ceramics* are generally known for outstanding chemical and physical material properties, such as high hardness, chemical and corrosion resistance, high working temperatures, good electrical insulation, and high compressive strength [7]. Originating from the Greek word "keramos", meaning "burntstuff" or "pottery", this material class is defined as "all manmade non-metallic and inorganic solids" [8] and hence covering both clay-derived bricks, earthenware, and porcelain as well as modern (advanced) technical / engineering ceramics such as carbides, nitrides, or oxides. Their fabrication is typically based on conventional powder processing methods, followed by thermal treatment up to 2100°C involving addition of sintering aids for improved densification [7].

#### 1.2.1 Brief historical introduction

The very first steps of an alternative ceramic synthesis route requiring significantly lower processing temperatures were set in 1956 when Fritz and Raabe converted tetramethylsilane and tetraethylsilane to silicon carbide (SiC) [9]. Some progress was made in the 1960s [10, 11] but it took another ten years until the work of Verbeek et al. [12] and Yajima et al. [13, 14] attracted big attention. Pyrolysis of certain silicon (Si)-containing organometallic polymers yielded advanced ceramics such as silicon nitride  $(Si_3N_4)/SiC$  and SiC fibers with promising properties. The nowadays established term for materials produced by this route is "polymer-derived ceramics (PDCs)". As **Figure 1.2** illustrates, they enjoyed greater popularity in academic research from year to year. This success is related to a couple of advantages compared to classical powder synthesis (sintering) which Mera and Ionescu summarize as follows [15]:

- "pure starting compounds (precursors)
- possibility to modify the molecular structure of the precursors by a variety of chemical reactions
- application of shaping technologies well known from plastic forming
- easy machining of the green body
- relatively low synthesis temperatures in comparison with classical ceramic powder processing technology
- ternary SiCN and SiCO ceramics cannot be produced by sintering methods"

#### 1.2.2 Silicon-containing preceramic polymers

Si-based polymers are a versatile class of polymeric materials which among other purposes serve as precursors for PDCs. Polysilanes, polycarbosilanes, polysiloxanes, polysilazanes, and



Figure 1.2: Number of publications on the topic "polymer derived ceramics" per year from *Web of Science* (all databases).

polysilylcarbodiimides consist of a backbone of Si and except for polysilane another element or group (–C–, –O–, –N–, or –N=C=N–, respectively) as the (simplified) molecule structures in **Figure 1.3** illustrate. Depending on the polymer type, there are 2–4 bonds available per monomer unit which can be either hydrogen atoms (e.g. inorganic perhydropolysilazane (PHPS)) or organic functional groups ( $R_1$ – $R_4$ ) such as methyl or vinyl. Backbone structure and presence of functional groups strongly affect both the polymer's physico-chemical behavior (e.g. stability, solubility, electronic, optical, rheological, polymer-to-ceramic transformation and yield) as well as the resulting ceramics composition, i.e. the Si:C ratio [15]. For successful PDC fabrication, used PCPs should exhibit the following three characteristics: 1) Sufficiently high molecular weight in order to avoid volatilization which would reduce ceramic yield and increase risk of pore and crack formation, 2) Rheological and solubility properties compatible with intended shaping technique, 3) Presence of suited functional groups for latent reactivity enabling curing and crosslinking [6].

The simplest one of the five PCPs, polysilanes (**Figure 1.3a**), became popular through the previously mentioned Yajima process [13], however, exhibit a number of disadvantages such as sensitivity to air, moisture and ultraviolet (UV) radiation, as well as insolubility and non-meltability [16]. At 400°C, polydimethylsilane converts into polycarbosilane (**Figure 1.3b**), a radical-induced methylene migration called Kumada rearrangement (**Figure 1.4**) [15, 17]. Further methods for polycarbosilane synthesis exist and are applied for commercial production. The allylhydridopolycarbosilane *SMP10*<sup>®</sup> by *Starfire*<sup>®</sup> *Systems, Inc.* is a popular example used as (near stoichiometric) SiC precursor.



Figure 1.3: Schematic polymeric structures of the five classes of Si-containing PCPs and the corresponding PDC systems pyrolysis converts them to, adapted from [6].



Figure 1.4: Overview of the synthesis routes of silicon-containing PCPs and corresponding ceramic systems they convert to by pyrolysis [18].

Polycarbodiimides (**Figure 1.3e**) were introduced in the 1960's along with the discovery of several synthesis methods [19]. In 1997, Riedel et al. used this PCP class for the first synthesis of crystalline solids in the ternary SiCN system [20]. Since then, polycarbodiimides serve as SiCN precursors, especially for carbon-rich compositions [21].

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Polysiloxanes are the best-known Si-containing PCP, using the synonym "silicones" their application reaches from everyday materials (e.g. pot seals) to highly engineered fields in medicine and microengineering [22]. The backbone's strong –Si–O– bonds (**Figure 1.3c**) lead to excellent chemical, physical, and electrical properties, especially oxidation resistance up to 250°C [23, 24]. The most important industrial polysiloxane is poly(dimethylsiloxane) (PDMS) in its linear form. In addition to applications in its crosslinked organic state (e.g. as soft micromolds presented in Section 2.3), poylsiloxanes are the typical precursor for silicon oxycarbide (SiOC) fabrication. Although SiOC ceramics are less oxidation resistant than SiCN, preceramic polysiloxanes offer a number of benefits such as commercial availability in large quantities, processing compatibility in air, and use of fillers for property tuning [25].

An organopolysilazane (OPSZ) serves a the basis for all PCP formulations used in this work which is why only the class of polysilazanes is introduced in more detail. With their –Si–N– backbone (**Figure 1.3d**), they act as precursor for both silicon nitride and SiCN, depending on the functional groups  $R_1-R_3$  [26]. In the absence of organic functional groups (as it is the case for PHPS),  $Si_3N_4$  is obtained after pyrolysis in nitrogen atmosphere [27]. Poly<u>carbo</u>silazanes are synthesized by ammonolysis or aminolysis of functionalized halogeno silanes ( $R_xSiCl_{4-x}$ ). The Si–N–Si links are then formed by a replacement of a chlorine unit by a NH<sub>2</sub> group and condensation reactions (**Figure 1.4**). The number of the chlorine as well as nature and size of organic substituents in the initial halogeno silane determine the type of silazane obtained. For linear polysilazanes,  $R_2SiCl_2$  is typically used [15].

The probably most used and best investigated OPSZ is the PMVSz commercially known as *Durazane*<sup>®</sup> *1800* (Merck KGaA, Germany). It was previously called *HTT1800* and is synthesized by coammonolysis of dichloromethylvinysilane and dichloromethylsilane [28]. The polymer chain which is shown in **Figure 1.5** in a simplified way is composed of 80% methyl-substituted and 20% vinyl-methyl-substituted units. This structure with presence of both N–H and Si–H bonds, vinyl and methyl groups is particularly beneficial for the crosslinking behavior as well as carbon integration which will both be discussed in the following subsections. Blending of PHPS and *Durazane*<sup>®</sup> *1800* allows for a variation of the carbon content in the derived SiCN(O) material [29].



Figure 1.5: Simplified structure of the commercially available OPSZ *Durazane 1800* which is 80% methyl- and 20% methyl-vinyl-substituted.

#### 1.2.3 Crosslinking

In the PDC route, crosslinking is an important step in the temperature range below 500°C. The liquid organic precursor transforms into an infusible organic/inorganic state, called GB, which conserves its shape during following pyrolysis. Extensive crosslinking prevents volatilization of lower molecular weight components and hence increases the ceramic yield [15]. For each PCP class different mechanisms occur, depending on the presence of certain functional groups. Polysilazanes can crosslink through UV irradiation in the presence of oxygen [30] or photoinitiators [31], by moisture [32], and additive-free by thermal treatment in inert atmosphere [26].

The mechanisms for thermal crosslinking of pure polysilazanes are presented schematically in **Figure 1.6**. Occurring in the temperature range 200–400°C, transamination causes mass loss and reduced nitrogen and silicon contents due to evolving species such as ammonia or silazane(oligo)fragments [15]. Vinyl polymerization occurs above 300°C and is mass conservative because no small molecules are generated. In OPSZs containing both Si–H and vinyl groups, fast hydrosilylation reactions occur at temperatures as low as 100–120°C. Formation of the Si–C–(C–)Si bonds strengthen the polymeric network because they don't depolymerize later on. This behavior raises carbon content and ceramic yield. Under the influence of suited catalysts, the reaction rate increases [15, 33, 34]. The fourth crosslinking mechanism is called dehydrocoupling due to the involved hydrogen evolution at temperatures around 300°C. A pair of Si–H/N–H or Si–H/Si–H thereby forms a Si–N or Si–Si bond [15]. For a PMVSz at 120°C, hydrosilylation has been found to be the predominant mechanism occurring, followed by dehydrocoupling, transamination, and vinyl polymerization to decreasing extent [26, 34].

Transamination			Vinyl polymerization	ו	
3 –Śi–NH–Śi–	> 2	$2 - \dot{S}i - \dot{N} - \dot{S}i - + NH_3$	n –Si–CH=CH₂	> -	Ғ-сн-сн₂ <mark></mark> –сн–сн₂
					_Śi−
Hydrosilylation	a-addition	, CH₃ ,	Dehydrocoupling		Si
  -\$i–H + -\$i–CH=CH		-Și-CH-Și-	-Şi-H + -Şi-NH-Şi-	$\longrightarrow$	$-S_{i}^{i}-N-S_{i}^{i}-+H_{2}$
	β-addition	-\$¦i-CH <sub>2</sub> -CH <sub>2</sub> -\$¦i-	2 –Ši–H	$\longrightarrow$	-Si-Si- + H <sub>2</sub>

Figure 1.6: Polysilazane thermal crosslinking mechanisms, based on [15, 33].

For inert gas processing, required temperatures for thermal curing can be significantly reduced by appropriate catalysts or initiators such as peroxides. Among others [35], dicumyl peroxide (DCP) is commonly used with PMVSz. At concentrations in the range of 0.01–5%, polysilazanes' thermosetting is reduced to 120–150°C by promotion of the vinyl polymerization and hydrosilylation reactions. Long crosslinking times have shown to be beneficial for maximized ceramic yield [36–42].

#### 1.2.4 Polymer-to-ceramic transformation

A high-temperature (HT) thermal treatment, in the following referred to as pyrolysis, of the PCPs in the temperature range of 600–1000°C causes thermolysis and volatilization of certain organic species. This organic/inorganic transformation is a highly complex process via several intermediates forming amorphous covalent ceramics (ACCs) [43]. Processes differ for every class of PCP, are influenced by the atmosphere, and are not well understood. In the case of PMVSz, a decrease of Si–H, Si–CH<sub>3</sub>, and N–H bonds was monitored in the range of 600–800°C, indicating ongoing dehydrocoupling reactions and methane formation [40,43]. Carbon chains formed by vinyl polymerization during the crosslinking step convert into sp<sup>2</sup>-hybridized carbon in the final SiCN material [15].

Chemical reactions along the entire PDC processing route typically lead to a mass loss and densification of the material. Consequently, volume shrinkage of 20-30% is typical [6] and mass / ceramic yield (CY) strongly depends on the PCP nature, potential additives, and processing parameters. Figure 1.7a shows the accompanying densification with increasing pyrolysis temperature for an OPSZ. Stress and gas formation typically create defects such as cracks and pores, especially for fully dense geometries larger than a few hundreds of micrometers in all three dimensions [6]. Since such defects are detrimental for mechanical and functional properties, a lot of effort has been invested in order to avoid them. For part design, shrinkage is ideally kept to a minimum (near-net shape). Both aims can be addressed by process parameter optimization. Additionally, dedicated filler strategies have been developed, as summarized in Figure 1.7b. Polymeric, ceramic, glass, or metal particles in the range of few nanometers to few micrometers are added to the PCP formulation, serving different purposes [44]. Passive fillers are inert, typically ceramics such as yttria-stabilized zirconia (YSZ), and reduce the total shrinkage by not altering the volume of their volume fraction [45]. In contrast, active (metallic or intermetallic such as B, Si, Al, CrSi<sub>2</sub>, MoSi<sub>2</sub>) fillers expand during pyrolysis by reaction with the polymer's decomposition products and compensate for the PCP shrinkage in order to achieve overall near-net shape [46, 47]. Glasses serve as common meltable filler type, their melting or softening at elevated temperatures seals porosity and densifies the material [48]. Sacrificial fillers, mostly organic compounds such as poly(methyl methacrylate) (PMMA), decompose during pyrolysis or can be dissolved chemically afterwards and allow controlled porosity creation [49].



**Figure 1.7: Polymer-to-ceramic transformation effects**: **a)** Typical densification of an OPSZ during inert gas pyrolysis, **b)** Characteristics of obtained PDCs depending on potential filler type [44].

#### 1.2.5 PDC properties

Depending on the class of PCP, binary (Si<sub>3</sub>N<sub>4</sub>, SiC, BN, AlN), ternary (SiCN, SiOC, BCN), or quaternary (SiCNO, SiBCN, SiBCO, SiAlCN, SiAlCO) systems are obtained after pyrolysis (**Figure 1.4**) [6]. Mera and Ionescu summarize PDCs' unique features as follows [15]:

- · "remarkable thermal stability
- presence of nanodomains of 1-3 nm in size
- · high oxidation and thermal shock resistance
- · near-zero steady-state creep behavior up to very high temperatures
- low thermal conductivity
- functional properties depending on their composition, for example, semiconduction, photoluminescence, piezoresistivity, piezoelectricity, and lithium-storage capability"

Among these points, the microstructure with its intrinsically complex nanodomains is responsible for some aspects of PDCs' outstanding behavior. Thermal treatment at T>1000°C (annealing) generally causes profound microstructural changes in PDCs but they remain amorphous until ~1300°C (oxidic PDCs) or 1500°C (nonoxidic systems) [6, 15]. Incorporation of excess / free carbon was found to render the ceramics both more chemically durable and thermally stable against crystallization [15, 21, 43]. Within the SiCN system, actual microstructure differs depending on the class of PCP. Polysilazanes convert to a single-phase amorphous SiCN phase where tetrahedrally coordinated Si is present in mixed bond situation, Si–N and Si–C. Polysilylcarbodiimide-derived SiCN does not exhibit such mixed bonds but is rather composed of separate amorphous phases, mainly Si<sub>3</sub>N<sub>4</sub> and C clusters plus some SiC [6,21,50]. Investigations on the processing route influence on the stability against crystallization have shown that monolithic bulk samples directly derived from the liquid precursor are more stable than samples produced from compacted powders [15,51]. Occurring processes in SiCN above

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1000°C include loss of residual hydrogen and starting devitrification, leading to nucleation and growth of nanocrystals and phase-separation above 1484°C accompanied by carbothermal reaction with nitrogen release (Si<sub>3</sub>N<sub>4</sub> + 3C  $\rightarrow$  3SiC + 2N<sub>2</sub>). Silicon nitride finally decomposes at temperatures above 1841°C. In brief, PDCs' exceptional thermal stability results from a combination of kinetic stabilization due to the microstructure as well as thermodynamic stabilization [43]. A strategy to further increase their thermal stability is the incorporation of metals or transition metals such as boron, zirconium, or hafnium forming nanocomposites. These ultra-high temperature ceramics (UHTCs) are thermally stable against crystallization up to 2000/2200°C due to encapsulation of the Si<sub>3</sub>N<sub>4</sub> in a BC<sub>x</sub>N phase retarding the carbothermal reaction [7, 21, 52–54]. Within the SiBCN system, Hf and Zr both significantly improve the oxidation resistance [55].

Properties of polymer-derived ceramics vary across wide ranges, strongly depending on the precursor class, fillers, and processing parameters. The approximate ranges of SiOC and SiCN reported property values such as density, free carbon content, coefficient of thermal expansion, and mechanical key figures for bulk material are provided in Table 1.1. Mechanical values for corresponding materials in fiber geometry are typically higher [6]. Generally, mechanical testing of PDCs is challenging due to the difficulties in the fabrication of suitable bulk test specimens [6]. Significant disparity exists between results on the same material from different reports which is mainly due to dissimilar inherent porosity and microstructures nearly impossible to repeatably produce [56]. Contradicting observations and conclusions show that the relationships are not fully understood but some general trends can be stated: Existing heterogeneities at various length scales (atomistic to macroscopic) govern the mechanical behavior of PDCs [56]. Elastic modulus and density are lower than those of crystalline SiC and Si<sub>3</sub>N<sub>4</sub> due the open structure of their networks. Stripping of residual hydrogen with increasing pyrolysis temperature increases the network connectivity and hence increases elastic modulus and density. Hardness of SiCN is higher compared to SiOC due to a higher crosslinking degree in the covalent network. Increasing pyrolysis temperature and carbon content tend to yield harder materials. SiOC and SiCN system exhibit similar fracture toughness, values obtained from powder route samples were higher than liquid route ones [6].

PDCs do exhibit several interesting functional properties, among which some have been barely investigated, others comprehensively. In short, they generally exhibit low thermal conductivity ( $K_{RT} \approx 1.2 \text{ W/(m K)}$ ) and CTEs (~  $3 \times 10^{-6} \text{ K}^{-1}$ ). Photoluminescent behavior has been reported for all major PDC systems [18]. Biocompatibility has been shown for some PDCs, mostly for the SiOC system [57–60]. Iron- or cobalt-incorporation has shown to modify the magnetic properties of some SiCN and SiOC ceramics. Also, excellent piezoresistive behavior was demonstrated, commonly in quaternary systems such as SiBCN [61]. Possibly most intriguing and application relevant is the intrinsic room temperature (RT) electrical

**Table 1.1: Basic and mechanical property ranges of bulk main PDC systems**: literature reported low- and high-end values of density, free carbon content, Vickers hardness, fracture strength, Young's modulus, fracture / crack tip toughness, Poisson's ratio, and coefficient of thermal expansion; values in same row do not correlate to each other. Summarized from [6, 18].

System		ρ (g/cm <sup>3</sup> )	C <sub>free</sub> (wt.%)	H <sub>v</sub> (GPa)	$\sigma_F$ (MPa)	E (GPa)	K <sub>I</sub> (MPa m <sup>1/2</sup> )	ν	CTE (10 <sup>-6</sup> K <sup>-1</sup> )
SIOC	min	1.6	<1	4.7	70	57	0.57	0.11	1.84
SIUC	max	2.35	61	11	900	113	1.8	0.17	5.29
SICN	min	1.85	6.86	6.1	80	82	0.56	0.21	3.08
SIGN	max	2.49	52.5	26	1100	155	2.1	0.25	3.96

conductivity ranging across up to 15 orders of magnitude (typically  $\sim 10^{-10}$ –1 S/cm). Mostly related to the carbon concentration and its arrangement, PDCs' electrical behavior can be tuned by proper selection of PCP and fillers and processing parameters [18]. These aspects will be described and discussed in more detail in the upcoming Section 1.4 and Chapter 3.

#### 1.3 PDC shaping

One of the PDC route main advantages is the liquid nature of the PCP formulations at RT, allowing them to be shaped by a large number forming techniques. Colombo et al. list 20 forming methods: "(freeze) casting, impregnation / infiltration, tape casting, coating (spray, dip, spin, chemical vapor deposition (CVD)), pressing, injection molding, extrusion, fiber drawing, blowing / foaming, machining, joining, rapid prototyping / additive manufacturing (AM), ink jetting, electro-hydrodynamic spraying / spinning, aerosol spraying, self-assembly, photolithography, microfluidics processing, emulsion processing, formation of nanostructures" [6]. Conventional ceramic powders or slurries in contrast are incompatible or less suited for many of these techniques. In order not to exceed the length of this section, only techniques relevant to this work, i.e. pressing, molding, AM, photolithography, and joining, will be discussed here.

#### 1.3.1 Molding

20–30 years ago, in the early stage of SiCN and SiOC fabrication based on the PDC route, the thermally partially crosslinked PCPs were typically ball-milled to fine powders at first (powder route). These were then pressed into green compacts under pressures up to 980 MPa, either at RT (cold isostatic pressing (CIP)) [62–64], elevated temperature (warm pressing) [65, 66], or high temperature (hot isostatic pressing (HIP)) [67, 68]. This route is suited for simple shape monolithic bulk samples, is less prone to crack formation but typically does not yield fully dense material.

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Fully exploiting the PDC route's advantages is the liquid route. In this case, the precursor formulation (PCP with potential initiators and fillers) is pyrolyzed after crosslinking, without an intermediate milling and pressing step. Molding can be conducted from the micrometer to the centimeter scale, typically using photolithography-manufactured Si [57], SU-8 [41, 69], or PDMS [70-72] molds for smaller dimensions and CNC-machined polytetrafluoroethylene (PTFE) [73–76] molds, possibly lined with sheets like mylar [77], for larger geometries. Micromolds or masters are manufactured by a series of processes, typically conducted in a cleanroom. A photoresin is spin coated on a (e.g. Si) substrate, photolithography defines a pattern by local photoreactions in the resin, and selective dissolution or etching processes then transfer the pattern to the actual mold material. PDMS (micro)molds or stamps [78] are replicated from Si or SU-8 masters. The liquid PCP formulation is then cast (poured / pipetted / injected with a syringe into the molds) and typically thermally crosslinked with an applied pressure, reducing volatilization and increasing density. These pressure-assisted approaches often require special pressure vessels and long curing times of several hours at elevated temperatures [73, 79, 80]. Only few results on entirely pressureless bulk PDC processing have been reported, mainly UV-photocrosslinking of polysiloxanes or polysilazanes mixed with photoinitiators [31, 74, 81, 82]. For microsized parts, dedicated strategies have been developed for precise mold filling [70]. Releasing the parts undamaged from the mold can be challenging, especially for small samples in more fragile GB state. This issue has been addressed by using flexible / soft PDMS molds [70], sacrificial layers [69], or even sacrificial ("lost") mold material [41].

A recent example of PDC shaping which rather falls into the category of indirect shaping is impregnation AM. This approach is inspired by earlier work, the replica technique, where bulk polymeric foams (often polyurethane (PU)) are impregnated with the PCP formulation yielding PDC foams after pyrolysis [83,84]. Instead of simple geometry bulk foams, 3D printed polymeric structures can be PCP impregnated. Relying on established and low-cost AM techniques and materials such as stereolithography (SLA) [85] or fused deposition modeling (FDM) [86–88] and acrylic resins, thermoplastic polyurethane (TPU) or polylactic acid (PLA) ceramic freeform structures are obtained in a cost-efficient way. The scaffold polymer which is soaked with polysilazanes for instance mostly decomposes during pyrolysis, yielding SiCN or SiOC structures.

#### 1.3.2 Direct shaping

Photocrosslinking of preceramic polymers allows for direct shaping of polymer-derived ceramics. Categorized in 2D or 3D techniques, i.e. photolithography or additive manufacturing, these techniques don't require forming tools and offer higher resolution and shape complexity. Photoinitiator-free photocuring of PCPs is possible in some cases, for example for polysilazanes. Si–N bond scission and reaction require, however, vacuum ultraviolet (V-UV) irradiation ( $\lambda \leq 220$  nm) and presence of oxygen for radical formation [30, 89]. For this reason, application of suited photoinitiators is the preferred strategy for both photolithography and SLA. Relying on conventional photoinitiators such as *Irgacure 651* which form crosslinking radicals if excited by common UV-wavelengths of  $\lambda = 365$  nm for instance, 2D or multilayer 2.5D structures can be formed by mask or maskless (laser writer) photolithography. Unexposed polymer is selectively dissolved (development), sacrificial layers such as SiO<sub>2</sub> between substrate and structure may serve for part release before pyrolysis [71,90–92].

Starting in 2015/2016 with two high-impact publications by Colombo group [93] and Eckel et al. [94], a lot of attention was paid to AM of PDCs. In a typical approach, the PCP is mixed with a solvent, a photoinitiator, a photoabsorber, and optionally fillers such as acrylates [95–97]. Polysiloxanes are used more often as polysilazanes due their stability in air. Selective curing by light-exposure is mostly performed in commercial vat photopolymerization systems, either by SLA or digital light processing (DLP). SiOC or SiCN structures are obtained after pyrolysis, exhibiting a shrinkage ranging from 3-70% compared to the initial design [98,99]. Due to facilitated outgassing, scaffolds with thin struts are much less prone to cracking than bulk samples which is why even ultrafast polymer-to-ceramic transformation in 10 s at 1200°C is possible [100]. Ceramic matrix composite (CMC) structures have been printed by DLP using PCPs loaded with glass [101] or ceramic [102] powders, or metal nitrates [103], reducing shrinkage and improving properties. Already in 2005, selective laser curing (similar to selective laser sintering (SLS)) of a polysiloxane filled with SiC was performed based on laser-induced local curing [104]. Also material extrusion (MEX), i.e. direct ink writing (DIW) [105–108]/FDM [109], has been demonstrated for PDC fabrication, FDM PCP-filament production, however, is very challenging. Another technique, ejecting the preceramic precursor from a nozzle into a thixotropic support bath, allows for overhang structures and scalability [38, 110, 111]. Recently, new processes, continuous liquid interface production (CLIP) [112] and volumetric printing / xolography [113, 114], have been demonstrated which reduce the manufacturing times significantly. Highest resolutions with feature sizes of  $<1 \,\mu m$  are achieved by  $2PP^1$  [115–117] which has also been combined with DLP in order to obtain multiscale / hierarchical PDC 3D-structures [118].

#### 1.3.3 Joining

Joining of ceramics is essential in order to successfully integrate them into applications. Traditionally, brazing and diffusion bonding techniques were used which may suffer from poor thermomechanical properties [2]. Starting in the end of the 1990's, Si-containing PCPs were

<sup>&</sup>lt;sup>1</sup>The terms two-photon polymerization (2PP or TPP / 2PL) and (2PP-)direct laser writing (DLW) are sometimes used as synonyms, the abbreviation 2PP is used in the following only.

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used as liquid adhesive. Colombo et al. joined SiC with a thin layer of a methyl-hydroxylsiloxane-based solution and obtained a  $\sim$  500 nm thin SiOC joining layer after 1200°C pyrolysis. As shown in the images and energy-dispersive X-ray spectroscopy (EDX) linescan in Figure 1.8a a sharp interface is formed with no reactions between the two dissimilar materials [119]. Theoretical considerations recommend the use of low heating rates in order to keep PCP shrinkage rate low during viscosity increase (reducing stress) and allow for evolving gas to escape so that crack formation is avoided [120]. Further examples using polysiloxanes [1], polycarbosilanes [121], or polysilazanes [122] as adhesive have been demonstrated for SiAlCN, SiC, or copper (Cu) plus epoxy material to be joined. For conducting ceramics, high currents (360<j<1020 A/cm<sup>2</sup>) could serve for rapid processing within 10 s ("flash joining") [123]. Strength of the obtained joints is in the order of other joining techniques and often is more temperature resistant. Compared to the bulk material, however, joints typically are the weak point. This problem is overcome by the "polymer-based bonding" technique, presented by Cross, An, Liew et al. in 2000/2001 [41, 79, 124]. Joining the parts in the still organic GB state before pyrolysis, using the same liquid PCP (formulation) the GB were derived from, establishes crosslinking across the parts. This process, shown schematically in Figure 1.8b, yields neither noticeable defects nor any noticeable interface after pyrolysis.



**Figure 1.8: Two examples of ceramic joining using liquid PCP as adhesive:** a) methyl-hydroxylsiloxane in ethanol to join reaction-bonded SiC: i) optical micrograph of a 1200°C pyrolyzed joint, ii) transmission electron microscopy (TEM) image of the joint, iii) HREM image of the SiC–RBSiC interface, iv) EDX linescans across the interface; b) polymer-based bonding of SiCN creating 3D structures using a polysilazane as adhesive between two GBs derived from the same PCP, followed by joint pyrolysis, yielding a monolithic PDC part with no noticeable interface(s) [41,119].

#### 1.4 Property tuning and contrast creation

#### 1.4.1 Property tuning of PDCs

Properties of PDCs depend on the system (e.g. ternary SiCN) and microstructure which depend on the PCP class and are strongly influenced by addition of fillers, processing route, and thermal as well as atmospheric processing parameters. In addition to this previously described processing influence on mechanical properties, some attempts to improve the mechanical behavior of PDCs have been made. PCPs are elegant precursors as matrix material for CMCs (e.g. [125]) which will be introduced briefly in Section 1.5. In contrast to infiltration of aligned or woven fibers, smaller scale fillers with no predefined orientation were added as mechanical reinforcement to PCP formulations. Multi-walled carbon nanotubes (MWCNTs) added at 6.4 vol.% to an OPSZ homogeneously distributed retained their integrity during pyrolysis and significantly increased elastic modulus and hardness [126]. Reinforcement fibers in the form of chopped carbon fibers (l=100  $\mu$ m, d=7.5 $\mu$ m) were added to a polysiloxane-based formulation for DIW AM. Shear stress in the nozzle during extrusion aligns the fibers which after pyrolysis lead to increased strength and graceful failure [105, 106].

Tuning of PDCs' electrical conductivity across up to 15 orders of magnitude is primarily performed through control of the (free) carbon phase. Due to the hydrocarbon functional groups of the organopolysilazanes or organopolysiloxanes, in situ formation of carbon occurs during the polymer-to-ceramic transformation. The amount of this free carbon<sup>1</sup> is higher for unsaturated side groups (e.g. vinyl or phenyl) compared to saturated ones (e.g. methyl or ethyl). The temperature influence on the microstructural evolution of PDCs is shown in Figure 1.9 using the example of SiCN. Starting from a temperature of T~600°C, aromatic hydrocarbons decompose and convert into hydrogenated amorphous excess carbon which is mostly sp<sup>3</sup>hybridized. For an OPSZ-derived SiCN, the matrix is present in mixed-bond situation (Si-N and some Si–C) with some residual hydrogen. At higher temperatures (T>800°C), so-called basic structural units (BSUs) nucleate which consist of 2–3 sp<sup>2</sup>-hybridized aromatic carbon layers with hydrogenated  $sp^3$ -hybridized peripheral C atoms. In the third phase (T>1000°C), most residual hydrogen escapes as H<sub>2</sub>, allowing for an edge-to-edge linkage of BSUs and formation of 3–4 nm long mostly sp<sup>2</sup>-hybridized carbon stacks. Finally, at T>1400°C, nanodomains with graphitic C nanocrystallites as well as an entangled free carbon network are obtained [18].

The phases present in PDCs differ strongly in their electrical behavior.  $SiO_2$  and  $Si_3N_4$  are insulators ( $10^{-14}-10^{-12}$  S/cm), SiC,  $SiO_xC_y$ ,  $SiC_xN_y$ , and amorphous C are semiconductors ( $10^{-4}-10^{-2}$  S/cm), and segregated (turbostratic or graphitic) carbon is conducting ( $1-10^5$  S/cm). The nature of the carbon phase dominates the overall material's conductivity. Referring to

<sup>&</sup>lt;sup>1</sup>also called segregated carbon, sp<sup>2</sup>-carbon, or excess carbon [18]



Figure 1.9: Structural evolution of free carbon during pyrolysis of preceramic polymers (i.e. OPSZs). Adapted from [18].

the four evolution steps from Figure 1.9, low-temperature pyrolyzed PDCs exhibit insulating properties ( $\sigma$ <10<sup>-10</sup> S/cm) as the present carbon domains are fully separated from each other. In the medium temperature range of 800<T<sub>pyro</sub><1200°C, electrical conductivity is temperature dependent, typical for an amorphous semiconductor. In this semiconducting regime, it is not entirely clear whether a variable-range or band tail hopping mechanism is responsible for the behavior. Approaching the establishment of a carbon percolation network, which depends on the amount of carbon and the aspect ratio of the carbon features, the mechanism then switches to the tunneling percolation regime. This means that individual carbon ribbons are not interconnected but close enough for a temperature-activated tunneling. In the fourth (high pyrolysis / annealing temperature) state exceeding the percolation threshold and establishing a graphitic free carbon network (percolation regime), direct transportation of free electrons causes the metallic-like electrical conductivity [6, 18].

Therefore, strategies for electrical conductivity tuning can be based on choice and chemical modification of preceramic organosilicon polymers [21] and pyrolysis atmosphere and temperature control [127–129]. Furthermore, fillers can be added to the PCP. The most common carbon-filler is divinylbenzene (DVB) which is cost-efficient and conveniently mixes and cross-polymerizes with the PCP [73, 130–132]. Several carbon allotropes such as carbon nanotubes (CNTs) and graphene have been demonstrated to significantly increase the PDC's electrical conductivity by added amounts smaller than 1 vol.% of CNTs for instance [133–137], however, require more effort to ensure homogeneous dispersion. In addition to carbon-based conduction, several metals were used as conducting phase, introduced into the PDC in the form of metal salts or complexes. These include for example titanium [138, 139], or copper, nickel, and cobalt [103, 140]. In contrast, detrimental effects on the effective electrical conductivity of PDCs are created by appearance or creation of porosity [66].
## 1.4.2 Property contrasts

Homogeneously adapting the PDC's property may provide an excellent material perfectly suited for a certain application. The PDC route, however, also has an immense potential for more advanced applications by creation of contrasts or gradients within a monolithic sample. Some of the phenomena and characteristics occurring along the process route described in the previous sections allow for a functionality integration by self-forming or engineered spatially defined inhomogeneities within the material. The general term for this strategy is "functionally graded materials (FGMs)", more specifically "functionally graded ceramics (FGCs)". Outside the PDC field, there is a multitude of established material class combinations (metal-metal, metal-ceramic, ceramic-ceramic, ceramic-polymer), recently especially AM techniques facilitated new arrangements and applications [141]. Locally different composition, microstructure, or porosity variations for instance cause dissimilar mechanical and functional behavior within the same part. As one very recent example, copper has been integrated into a kaolin ceramic matrix by a multi-vat DLP technique. This way, 3D freeform electrical paths were spatially defined within the otherwise insulating part, supplying power for a light-emitting diode (LED) for instance [142].

Focusing on the PDC field, number and variety of examples related to such FGMs is more limited. The most common case is a porosity gradient within the PDC part. In order to obtain such ceramic foams, either bubble nucleation and viscosity increase dynamics are optimized and exploited or a temperature gradient in the PCP formulation is applied during thermal curing [143–146]. An example for a self-forming gradient has recently been demonstrated. Titanium-filled polysiloxane exhibited a 3-layer structure in the SiTiOC state after pyrolysis with significantly higher titanium (Ti) concentrations in the outer layers compared to the core [139]. As the Ti-filling creates an electrical conductivity, this contrast could be exploited for HT electronic applications. Certain types of PDCs are well suited as ultra-high temperature (UHT) semiconducting material. Diode functionality based on a p-n-junction has been demonstrated by combining two of them, a p-type SiCNO and an n-type SiBCNO [147, 148]. A continuous ceramic-to-polymer gradient composite has been shown, manufactured by dissimilar thermal processing of a 92 mm long carbon fiber reinforced PMVSz GB bar. In a custom-designed heating and cooling system, one end of the bar remained at T<350°C in GB state while the opposite end at T>1000°C converts to SiCN. In between, a 55 mm continuous organic-inorganic gradient was obtained [149]. A PDC-based double-layer thermistor has been developed by combination of a DVB-doped SiCN sensing element onto an undoped SiCN serving as substrate. This 100 µm thin structure showed a repeatable and sensitive negative temperature coefficient (NTC) behavior suited for HT sensor applications [150]. As a final intriguing example of reported FG-PDCs, Greil group laminated several partially crosslinked PCP tapes adhesive-free in different orders. The polysiloxane-silane-based tapes

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were filled with small or large SiC particles. After stacking of the dissimilar sheets, pressureassisted thermal processing bonded the layers together and formed multilayer-CMCs whose mechanical properties depend on the stacking sequence [151].

## 1.5 Applications

Despite five decades of academic research, advantageous shaping capabilities, and excellent or even unique properties, the number of polymer-derived ceramics real world applications is humble till this day. Riedel group recently summarized applications, listing ten categories visualized in **Figure 1.10**. In all of them, HT and chemical stability are of particular interest.



Figure 1.10: Selected PDC applications summarized by Wen, Yu, and Riedel: "a) Nicalon silicon carbide continuous fibers; b) Ceramic matrix composites; c) SEM image of the 100  $\mu$ m thick polysilazane-derived coatings with boron silicate-barium silicate glass filler particle mixture on a 1.7335 steel substrate; d) SEM image of a micro-cellular open cell foam obtained by pyrolysis of a silicone resin; e) SiCO based ceramic glow plug; f) Polymer-derived engineering ceramics: high precision shaping of complex components with a thermal expansion similar to steel for vacuum pump devices; g) Additive manufactured SiOC ceramics; h) Lithium ion batteries in which the SiOC and SiCN ceramics can be used for anode materials; i) SiOC ceramic microstructures on silicon wafer (with dimensions down to 20  $\mu$ m) fabricated by photolithography approach; j) Polymer-derived C/C/SiC ceramic brake disk Starblade<sup>TM</sup> produced for motorbikes; k) A ball and stick model of a preceramic polymer. The inset in k) is a picture of a commercially available allylhydridopolycarbosilane (SMP10, Starfire systems)" [18].

Firstly, there are a number of HT structural applications where the precursors' liquid nature and comparably lower processing temperatures are particularly advantageous from a manufacturing point of view. These include fibers [152], CMCs [125, 153], environmental or thermal barrier coatings [48, 154], foams [155], and more which mostly have been mentioned previously. PDCs' electromagnetic wave absorbing and shielding behavior has been investigated and materials were optimized for this purpose, e.g. by adding graphene oxide and CNTs to a PMVSz and achieving outstanding 67 dB shielding in a 2 mm thin sample [156]. Benefiting from excellent tribological properties [157], PDCs (typically polycarbosilane-derived CMCs with SiC fillers) are used in transportation for demanding or high-end motorsport brake rotors [6]. Outperforming traditionally used metallic materials, PDCs are used as heaters, glow plugs in engines [25], and heat exchangers [158] where the HT oxidation resistance is of great importance. A few PDCs have been tested for their biocompatibility, performing at least as well as currently used standard materials [57]. In combination with metal-filler-modified properties, application as biomedical implants such as heart pacemaker electrodes [60, 159] or load-bearing bioactive glasses [160] can be considered. In the field of energy and environmental applications, primary research interest went into optimization of PDCs as anode material for lithium-ion batteries [161, 162]. The semiconductive, piezoresistive, and gas adsorbing properties of PDCs make them suitable material for harsh environment sensing applications, e.g. temperature [132, 163], pressure [61], or gas detection [68, 164, 165]. Lastly, due to the liquid molding and photocrosslinking ability, PDC-microelectromechanical systems (MEMS) have been researched for 20 years. High-resolution structural part such as microgears [79, 166], high aspect ratio structures [90, 124], micro-glow plugs [167], and micro-actuators, reactors, or manipulators [91] have been demonstrated.

# **2** Shaping approaches

**Disclaimer:** This chapter (2) is partially adapted from the following article with permissions of all co-authors:

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**My contribution:** conceptualization, design, fabrication, experiments, data processing, figures, coordination, and writing.

## 2.1 Introduction

As introduced in the previous chapter, the liquid polymer-derived ceramic route is compatible with a large number of shaping techniques. For the purpose of cost-efficiency and upscalability, this work focuses on molding and micromolding where the liquid PCP is cast into the mold and thermally cured so that it adopts and retains the mold's shape. Additionally, some microfluidics and bonding are involved for which dedicated molds are used. This chapter describes the three main activities on bulk casting, microcasting, and submicrometer to centimeter multiscale shaping by replication of 2PP enhanced micromolds. Considerations for mold material choice, design, manufacturing, and characterization are explained as well as the PCP casting, curing, and transformation process, related challenges, and methods of resolution. Actual PDC processing and material aspects will be mentioned to a minimum extent only here and discussed in detail in Chapter 3.

## 2.2 Bulk casting

A cylindrical geometry of 7 mm diameter and 500 µm thickness was chosen for bulk sample fabrication. The thickness is limited by the outgassing of reaction products during crosslinking and pyrolysis and the mold diameter is chosen to yield approximately 5 mm sample diameter after pyrolysis which is a size well suited for most characterization techniques. For the fabrication of such bulk molds, there are several material and process options, such as deep reactive ion etching (DRIE) of silicon [57], computer numerical control (CNC) machining of metals (e.g. steel, aluminum, brass), or CNC machining of PTFE. An ideal PCP mold exhibits the following characteristics:

- · high dimensional accuracy
- very smooth surfaces (bottom and sidewalls)
- · reasonable fabrication effort and cost
- good PCP wetting / filling behavior
- chemical inertness
- · sufficient thermal conductivity and low CTE
- thermal stability up to  $\gg$ 200°C for thermal PCP curing
- low adhesion for undamaged GB release
- · handling robustness and reusability

Commonly known under *DuPont*'s commercial brand name *Teflon*<sup>TM</sup>, PTFE has been chosen mainly for its easy machinability, beneficial mold releasing behavior, and handling robustness. Figure 2.1 shows two different custom mold designs consisting of 18 or 16 identical cavities each to facilitate the fabrication of large sample numbers. The CNC-machined PTFE pieces have a 2 or 1 mm high outer rim and central pillar which facilitate the mold release. The typical PDC bulk / disc sample fabrication process is outlined in Figure 2.2. The PTFE molds are thoroughly cleaned in acetone and isopropyl alcohol (IPA), dried and thermally dehydrated in an oven, and transferred into an argon (Ar) atmosphere (>99.9999% purity,  $c_{0,2}$ <0.5 ppm,  $c_{H2O}$  < 0.5 ppm) glovebox through a vacuum antechamber. The low viscosity PCP formulation (PMVSz, DCP, varied amounts of DVB) is prepared in the glovebox. Details on the processing optimization to yield defect-free material and tuning of mechanical and functional properties are discussed in detail in Chapter 3. Up to three molds are placed on a level hotplate in the glovebox and the precise amount of PCP formulation is then poured into each mold<sup>1</sup> with an air displacement micropipette (Figure 2.3a). Normally, the precursor fully wets the PTFE cavities. However, in some cases, careful lateral movement of the pipette tip is needed to wet the sidewalls without spilling liquid. A thermally isolated volume is created with glass

<sup>&</sup>lt;sup>1</sup>up to 3x18=54 samples in one batch

Petri dishes and thermal curing of the PCP is achieved within 30 min at 200°C maximum<sup>1</sup> (**Figure 2.3b,c**). The thermoset GBs are released from the mold by flipping it upside down (**Figure 2.3d**). Gentle tapping is required in some cases. The mold's rim and central pillar act as spacers and therefore support the release procedure by creating a gap to the table surface allowing the green parts to come off the molds. Application of fine spatulas or needles for mold release must be avoided because they damage both the mold and the sample, even when done carefully. Due to the non-negligible CTE of PTFE ( $100 \cdot 10^{-6} \text{ K}^{-1}$  [169]), GB release at elevated temperatures around  $100^{\circ}$ C generally works better because a mold diameter reduction of >100 µm from 200°C to RT may clamp the samples otherwise.



Figure 2.1: PTFE disc molds: Two design versions, CNC-machined with a) 18 or b) 16 cylindrical cavities of 7 mm diameter and 500  $\mu$ m depth each.



Ar glove box



The quality of the PTFE molds is essential for the successful fabrication of cast PDCs, especially for high throughput. The same mold designs were sent to three different machining workshops, each using different CNC machines, tooling, and computer-aided manufacturing (CAM) toolpaths. The performance in sample release varied significantly between the suppliers and degree of usage of the molds. Typically, the sample release was more difficult during the first 2–3 casting batches, then improved for 20–30 more runs until the behavior worsened again,

<sup>&</sup>lt;sup>1</sup>PTFE starts to deteriorate at 250°C and creates toxic fluorocarbon gases [169]



**Figure 2.3:** Photos of the PCP casting and thermal crosslinking in an Ar glovebox: a) Precise pipetting of the liquid PCP into molds; b) thermal crosslinking on a hotplate with two upside-down glass Petri dishes for thermal insulation; c) crosslinked PCP inside the molds; d) demolded green parts.

reaching its end of life (EOL). The initial difficulties are believed to be caused by cusps and burrs formed during CNC machining of soft materials such as PTFE. During the first few times of usage, the GBs get caught on the cusps. These casting and subsequent mold cleaning processes help remove the artifacts, reduce the surface roughness, and improve the mold release. In order to understand the difference between the molds from different suppliers, optical profilometry was performed on pristine molds are given in **Figure 2.4**. The molds from supplier A exhibit a severe curvature and Sq (quadratic average) and Sa (arithmetic average) areal roughness values ~3.5 times higher compared to the other two. The curvature apparently results from a drilling (with a 7 mm tool) rather than a conventional machining approach (with a smaller tool). The molds from suppliers B and C do not show such global curvature and are generally very similar. Circular traces from the cutting tool are slightly visible and areal roughness values are very close. While the molds from supplier C were best on paper, both B and C worked well after running-in usage with no noticeable difference in casting and sample release behavior. Only molds from supplier A were disregarded.

The 7 mm diameter disc GB samples which come off the (supplier B and C) molds easily and undamaged by flipping or tapping were grouped by amount of DVB added and pyrolysis temperature they are intended for. Pyrolysis temperatures of 800, 1000, 1200, and 1400°C were chosen in order to cover the most relevant range of the microstructural transformations as described in Section 1.4. For a typical pyrolysis run, several tens of GB samples of different compositions were placed into separate alumina (Al<sub>2</sub>O<sub>3</sub>) crucibles in the glovebox. Crucibles with samples (**Figure 2.5a,c,e,g**) were stacked (2×2 or 2×3), covered with an extra empty crucible, and quickly transferred into the tube furnace which was instantly purged with Ar ( $\geq$  99.9999% purity). After pyrolysis (details in Chapter 3), crucibles were transferred back into the glovebox with the samples converted into black PDC lying loose in the crucibles



**Figure 2.4: Optical profilometry surface roughness comparison of CNC-machined PTFE molds: a)** supplier A: radial curvature and highest areal roughness; **b)** supplier B: no curvature, low roughness; **c)** supplier C: no curvature, lowest roughness.

(**Figure 2.5b,d,f,h**). Nearly 800 homogeneous SiCN disc samples have been fabricated this way with much less than 1% failure rate (cracking or scattering).



**Figure 2.5:** Photos of GB and PDC disc samples in Al<sub>2</sub>O<sub>3</sub> crucibles before and after Ar pyrolysis. A scrap rate of <1% was achieved during fabrication of nearly 800 homogeneous samples of this geometry. a) GBs for 800°C pyrolysis; b) PDCs after 800°C pyrolysis; c) GBs for 1000°C pyrolysis; d) PDCs after 1000°C pyrolysis; e) GBs for 1200°C pyrolysis; f) PDCs after 1200°C pyrolysis; g) GBs for 1400°C pyrolysis; h) PDCs after 1400°C pyrolysis.

# 2.3 Micromolding

The molding process can be downscaled for fabrication of microsized PDC parts which requires, however, two major changes. Firstly, micromolds are typically obtained from cleanroom microfabrication processes rather than CNC machining to achieve smaller feature sizes. Secondly, the reduction in volume requires a revised mold filling strategy. Different mold materials, manufacturing processes, designs, casting techniques, and processing strategies were applied in this work. Some experiments were conducted by semester project students, details on the topics of their projects such as characterization and optimization of SU-8 processing, Bosch process, or potassium hydroxide (KOH) etching of Si for PDC micromolds can be found in the respective reports [170–173]. This section briefly summarizes the activities and findings.

#### 2.3.1 Micromold fabrication

As introduced in Section 1.3, micromolds can be classified, based on their rigidity, into hard molds or (flexible) soft molds. A schematic overview of the different types and fabrication approaches is shown in **Figure 2.6**. There are two established options for hard molds which are anisotropic etching (DRIE / Bosch process or KOH) of silicon (a) or patterning of (thick) SU-8 (b). Soft molds are made of PDMS (e,f), replicated from an inverted hard master, also fabricated by Si etching or SU-8 processing (c,d). This section is structured by the key process step responsible for the mold or master fabrication, i.e. SU-8 processing, DRIE of silicon, and KOH etching of Si.



**Figure 2.6: Comparison of micromold types and fabrication approaches**: **a)** Si hard mold; **b)** SU-8 on Si hard mold; **c)** Si negative master for PDMS replication; **d)** SU-8 on Si negative for PDMS replication; **e)** PDMS soft mold replicated from Si negative; **f)** PDMS soft mold replicated from SU-8 on Si negative.

#### SU-8 micromolds

SU-8 is a negative-tone near-UV photoresist, well established for high-aspect-ratio microstructures [174]. The viscous epoxy-based resin is typically spin coated on wafer substrates, allowing for ultrathick layers up to 500  $\mu$ m. A series of thermal treatments and i-line ( $\lambda \approx 365$  nm) UVphotolithography crosslinks the exposed parts whereas the unexposed material is selectively dissolved afterwards.

In this work, SU-8 layers of typically 300  $\mu m$  thickness were manufactured.  $\langle 100\rangle$  Si wafers (100 mm / 4 in diameter, 525  $\mu m$  thickness) were used as substrate / mold material for

all processes described in this section. The process flow for SU-8 processing is provided in **Figure A.1**, applied wafer designs in **Figure A.6a-e**. In brief, SU-8 (GM1075, Gersteltec, Switzerland) was spin coated onto the oxygen plasma cleaned Si wafer. Levelled overnight relaxation in a closed space (to enclose the contained solvent  $\gamma$ -butyrolacton (GBL)) yields a more homogeneous layer thickness. After solvent evaporation in the 130°C soft bake step on a hotplate, the wafers were exposed to UV (i-line) in a mask aligner (soft contact mode). This step triggers photo-activated crosslinking which is completed in the subsequent 90°C postexposure bake. Development in propylene glycol methyl ether acetate (PGMEA) selectively dissolved the unexposed SU-8. Finally, IPA rinsing cleaned the substrate. Optionally, a 200 nm– 2 µm Parylene-C layer<sup>1</sup> can be applied by CVD and 10–20 nm of carbon sputtered on top which is generally known to improve mold release behavior and has previously been shown to increase PCP wetting [70], respectively.

Four examples of SU-8-on-Si wafers are shown in **Figure 2.7a-d**. The SU-8 layers are  $\approx$  300 µm thick. The first three (a-c) serve as hard molds, the designs contain different large shapes for direct filling and special patterns for characterization. Small geometries with volumes <10 µL such as the 1 mm diameter disc mold in Figure 2.7e (V= $0.24 \,\mu$ L) are arranged around a filling pot, connected with a zigzag filling channel. This capillary-driven mold filling strategy has been proposed by Grossenbacher et al. [70] and allows precise filling of the entire mold array's volume to the central area. The zigzag shape of the channel avoids a distorting pulling force by shrinkage during thermal processing after casting. In contrast to designs a-c where cavities were created in the SU-8 to form molds, the fourth example exhibits protruded geometries, this wafer type serves as master for a later PDMS soft mold replication. General advantages of the SU-8 approach are very large possible thicknesses up to 1200 µm by sequential spin coating and joint exposure and development [174]. SU-8 sidewalls are smooth and the mold bottoms represented by the Si wafer surface even smoother. Sidewall verticality can be challenging but angles very close to 90° are achievable with optimized exposure and thermal processing parameters, as shown in the cross-sectional scanning electron microscopy (SEM) image in Figure 2.7f.

## Silicon micromolds

Alternatively to SU-8, hard micromolds can be fabricated by vertical etching of silicon. The Bosch process is a well-established DRIE technique in which sequential alternation of isotropic plasma etching (e.g. sulfur hexafluoride (SF<sub>6</sub>)) and passivation (e.g. octafluorocyclobutane  $(C_4F_8)$ ) are performed for a few seconds each. An applied bias voltage creates directional ions, bombarding preferentially the bottom passivation layer. With the sidewalls still being

<sup>&</sup>lt;sup>1</sup>causing the Si coloring (e.g. purple or green), depending on layer thickness



Figure 2.7: Images of  $\approx$ 300 µm SU-8 on 100 mm Si wafers: a) large molds, micromolds connected to filling pots, and test structures, Parylene-C coated; b) large molds, micromolds connected to filling pots, and test structures; c) large molds, micromolds connected to filling pots, and test structures; d) individual discs and gears of various sizes, Parylene-C coated, master for PDMS replication; e) optical microscopy (OM) image of a 1 mm diameter disc mold with a filling channel, Si is Parylene-C coated; f) cross-sectional SEM image of a smooth SU-8 sidewall angled 89.3° with respect to the Si surface.

passivated, this effectively leads to anisotropic etching, developing undulating sidewalls (scallops) of a few hundreds of nanometers [175].

For PDC micromold fabrication, Si wafers were spin coated with a standard positive photoresist (e.g. AZ9260, Microchemicals, Germany) first. As summarized schematically in the process flow in **Figure A.2**, the resist was then patterned by UV-exposure (mask aligner or laser writer) and development. The 10 µm photoresist layer served as a mask during the DRIE process (AMS 200 SE, Adixen) in which a Si etch depth of  $\approx$ 300 µm was achieved in 80 min process time. Afterwards, the remaining photoresist was dissolved (wet stripping), the wafers were rinsed, and optionally coated with Parylene-C and carbon.

Among the wafer designs summarized in **Figure A.6**, b,c, and f were fabricated this way. They are shown in **Figure 2.8a-c**. Designs are identical or similar to the ones described for SU-8 above. One of the designs (**Figure 2.8b**) was intended for dicing so that individual mold arrays can be handled separately. The undulating sidewalls visible in **Figure 2.8d** are a detrimental artifact of the Bosch process which leads to rough surfaces but can be addressed by shortening of the pulse durations or subsequent treatment [176–178]. Generally recommended for the Bosch process, thorough process control should be exerted in order to avoid unintended feature appearance such as sidewall mouse bites, bottom micrograss formation or nonuniform etch depths due to aspect ratio dependent etching (ARDE) [178]. Advantages of this technique



as compared to SU-8 processing are the obtainable vertical sidewalls (**Figure 2.8e**) and creation of molds with higher temperature resistance and monolithic character.

Figure 2.8: Images of Si hard mold wafers fabricated by  $\approx$ 300 µm deep DRIE: a) large molds, micromolds connected to filling pots, and test structures, Parylene-C coated; b) micromolds connected to filling pots and test structures, cut into 20x20 mm<sup>2</sup> dices; c) large molds, micromolds connected to filling pots, and test structures; d) SEM image of a sidewall with typical scallops of 230 nm in this case; e) cross-sectional OM image of a 100 µm wide and 320 µm deep trench with vertical sidewalls.

For more complex 2.5D multilayer parts, several photolithography and etching steps can be performed consecutively, either with several SU-8 layers, several DRIE steps, or a combination of both. The latter has been done in the case of the design **Figure A.6a**, first performing Bosch process on a Si wafer and then applying and patterning an SU-8 layer on top, following the process flow in **Figure A.3**. The fabricated wafer after Parylene-C coating and carbon sputtering is shown in **Figure 2.9a**, an example of one of the bilayer molds in **Figure 2.9b**. This mold for a watch part consists of a 338  $\mu$ m deep cylindrical cavity etched into the Si and a 247  $\mu$ m deep second layer formed by SU-8 (**Figure 2.9c**). These depths as well as the lateral dimensions are upscaled to 130% with respect to the final desired dimensions in order to compensate for shrinkage during the polymer-to-ceramic transformation.

Soft micromolds consisting of PDMS are replicated from a hard master, typically either SU-8 (**Figure 2.7d**) or Si. The replication process, according to the process flow in **Figure A.4**, is illustrated in **Figure 2.10**. The Si master (design **Figure A.6b**) was fabricated by photolithography and Bosch process. After photoresist stripping, silanization of the Si with trimethylsilyl chloride (TMCS) was performed. The wafer was then placed in a plastic Petri dish and degassed PDMS (Sylgard 184, 10:1 ratio with curing agent) was poured on top and thermally cured during 75 min at 80°C. The soft mold has finally been obtained by peeling it off the Si master which then could be used for several more replication processes.



Figure 2.9: Bilayer micromold wafer combining DRIE in Si and SU-8 processing: a) wafer with small geometries connected to filling pots and large geometries, Parylene-C and C coated; b) OM image of a bilayer mold for a watch part; c) mechanical profilometry across a bilayer mold showing SU-8 thickness of 247  $\mu$ m and Si etch depth of 338  $\mu$ m, sidewall slopes are a tool artifact.



Figure 2.10: PDMS soft mold replication process from a Si master: a) Si master fabricated by Bosch process; b) degassed viscous PDMS poured onto Si master; c) cured PDMS soft mold after release.

Especially in the case of high-aspect ratio molds (e.g. deep and narrow trenches) the Bosch process's characteristic sidewall roughness may make the undamaged green part release from the mold impossible. Smooth mold surfaces are generally desired in PDC fabrication by micromolding. While vertical sidewalls are desired in many designs sloped sidewalls opening to the mold top are tolerable in some cases and facilitate the part release significantly. Anisotropic KOH etching of silicon is a technique which can fabricate such geometries. Single-crystal Si immersed in diluted KOH dissolves much faster along the  $\langle 100 \rangle$  direction compared to the (111) plane (factor 200–400). The selectivity of this anisotropic wet etchant yields the characteristic 54.7° Si sidewall angles and flat and smooth bottom for geometries with high width-to-depth ratio. Mold shapes, however, need to be aligned to the crystallographic orientation of the wafer which can typically be done using the primary flat [179].

Two wafer designs, **Figure A.6g,h**, have been prepared specifically for KOH etching of Si. They primarily contain large rectangular mold shapes with their borders aligned to the wafer's crystallographic orientation. The actual result of misaligned mask openings or more complex freeform shapes is difficult to predict. Dedicated simulation tools can help and furthermore generate corner compensation patterns [172]. The fabrication of KOH Si mold wafers has been

realized according to the process flow shown in **Figure A.5**. First, a 2 µm thick SiO<sub>2</sub> layer was thermally grown on 100 mm  $\langle 100 \rangle$  Si wafers and subsequently patterned by photolithography and plasma etching, typically with rectangular shapes ranging from 1–20 mm in lateral size aligned to the primary flat. The patterned SiO<sub>2</sub> layer serving as a mask, Si molds were etched for 180–240 minutes in KOH (23%, 80°C), until a depth of ~300 or 400 µm was reached. Removal of the SiO<sub>2</sub> was performed by hydrofluoric acid (HF) etching. For easier and separate handling, the Si wafers were cut into 25×25 mm<sup>2</sup> dices, each containing 1–15 molds. Some of these mold dices are presented in **Figure 2.11a,b**, the SEM images (**Figure 2.11c,d**) bring out this method's outstanding contour accuracy and surface smoothness.



**Figure 2.11: KOH etched Si micromolds: a,b)** Si chips with 300 and 400  $\mu$ m deep molds of various sizes and aligned shapes; **c)** SEM image of a 2×2 mm<sup>2</sup> square mold showing the smooth surfaces obtained by this method; **d)** tilted SEM image of two smaller rectangles forming inverted pyramids.

## 2.3.2 Casting and thermal processing

A number of PCP casting and curing experiments were conducted with the different kinds of micromolds introduced above. Two major problems have been encountered thereby. Firstly, all molds made from SU-8 on a Si substrate exhibited poor thermal behavior during thermal crosslinking of the PCP at 150–200°C. With a glass transition temperature of  $T_g>200°C$  [174] it is not the peak temperature which causes the problems but the more than a factor of 10 higher CTE of SU-8 compared to Si [180]. This generates stress during the heating and cooling phase of the cast PCP curing and causes the SU-8 to crack or delaminate from the Si substrate. When using a hotplate as heat supply (generating more heat inhomogeneity than an oven)

and aiming for high heating and cooling rates in the range of 10–100 K/min in order to achieve fast overall process times, defects occurred rapidly in most cases. The number of GB parts obtained in good condition was very limited and most molds were so damaged that they could not be reused for a second molding run. For this reason, SU-8 micromolds may serve better for photocrosslinking of PCP formulations or if no reuse is intended (lost mold approach [41]). The second difficulty which was encountered was the release of the parts from the molds after thermal crosslinking (GB state). With no significant lateral shrinkage occurring during the thermal curing, green parts often were clamped in the molds, impaired by the undulating sidewall roughness in case of Bosch process Si molds. Furthermore, microsized parts' mass and inertia were so low that flipping and tapping of the molds remained unsuccessful.

For these reasons, a novel PDC microfabrication process has been introduced: in-mold pyrolysis. Unlike SU-8 or PDMS, no alteration of silicon occurs at a temperature of 1000°C ( $T_m$ =1414°C [181]). SU-8 and PDMS would decompose at such pyrolysis temperatures and samples are therefore typically released from the molds in the GB state. Relying on monolithic Si molds, obtainable by Bosch process and KOH etching, however, allows the green state material to remain in the molds for subsequent pyrolysis. This way, the shrinkage occurring during the polymer-to-ceramic transformation process self-releases the parts which are then obtained loose in the PDC state.

Firstly, Si micromolds with vertical sidewalls, fabricated by Bosch process, were used. Micromold array chips (Figure 2.8b) were coated with 2  $\mu$ m Parylene-C and 20 nm carbon (**Figure 2.12a,b**). Inside the glovebox, the chips were placed on the level hotplate and the PCP formulation (3 wt.% DCP, no DVB) was pipetted into the central filling pot (100% of the array's total volume). Capillary driven, the polymer flows along the filling channels into the actual micromolds. Due to the increased wettability by C sputtering the liquid partially wet the silicon around the molds. With two upside-down glass Petri dishes placed on top, the PCP cured thermally during a sequence of 3×10 min at 100, 150, 200°C. High initial heating rates did not damage the Si mold. After turning off the hotplate after 30 min, molds remained there for slower cool down in order to reduce the cracking risk of the thermoset GB samples. At RT, green parts did not come off the mold by flipping or gentle tapping. Therefore, molds with the green parts inside were then quickly transferred into the Ar flow tube furnace (STF 15/450, Carbolite Gero, Germany). Pyrolysis was performed at 1000°C peak temperature (1 h dwell time at 300°C and 1000°C, 300 K/h heating and cooling rate).

Due to the PDCs' shrinkage of ~30%, the approach of in-mold pyrolysis is unsuited for complex and laterally constraint structures such as rings. During the transformation process, tensile stress builds up in the PDC part and results in cracking. This is visible using the example of a  $2\times2 \text{ mm}^2$  Swiss flag mold shown in **Figure 2.12c**. The Si cross insert does not allow the surrounding ceramic to shrink freely which is therefore obtained broken into several

#### 2.3 Micromolding



**Figure 2.12: Vertical sidewall PDC microfabrication by in-mold pyrolysis in Bosch process Si molds**: **a)** micromold array, Parylene-C and C coated; **b)** magnification of the area highlighted in a: 1 mm square and circular mold with filling channel; **c)** after in-mold pyrolysis: example of a laterally constraint mold where the Si cross inset causes the shrinking PDC around to crack; **d)** 1 mm circular mold from b after pyrolysis with the PDC part loose inside, some Parylene and PDC thin film pieces on the surrounding Si; **e)** PDC microdisc released from the circular mold with part of the filling channel still attached, lateral shrinkage of 28.5%; **f)** top side of the disc after breaking off the filling nipple (lower right side); **g)** side view on the microdisc; **h)** bottom view exhibiting a ring area with texture affected by the Parylene decomposition; **i)** bottom view on the edge area of another microdisc cast in a mold with was silanized instead of Parylene coated and exhibits a homogeneously smooth texture on the bottom surface.

pieces after pyrolysis. However, simpler shapes such as squares and circles, allow the part to shrink and hence yielded intact micro-PDC parts lying loose in the mold after pyrolysis (**Figure 2.12d**). Remains of the Parylene coating and overflowing PCP form scattered thin parts on the top surface of the surrounding Si, not impairing the molding itself. PDC microparts shrank in the range of 26.1–28.5% in this case, the filling nipple remained attached to some

parts (**Figure 2.12e**). Fabricated parts are crack-free and dense, their surfaces are flat and smooth. A microdisc's top surface and sidewall are shown in **Figures 2.12f,g**. Filling nipples could be removed easily but left some asperity. Bottom surfaces exhibited a texture apparently resulting from the inhomogeneous Parylene coating and its decomposition during pyrolysis (**Figure 2.12h**). For this reason, the entire process was repeated with Si micromold chips which were silanized (TMCS) instead of Parylene-C coated. The bottom side edge of another PDC microdisc fabricated this way is presented in **Figure 2.12i** and is free of such defects.

Secondly, Si micromolds obtained from KOH etching were applied. The process was mostly identical to the procedure described above for Bosch process Si micromolding. The Si chips (**Figure 2.13a**) were coated with 1 µm Parylene-C but no carbon was sputtered in this case. Chips were placed onto the hotplate in the glovebox and the PCP formulation (3 wt.% DCP, no DVB) was pipetted into the molds. Curing was performed during 30 min at 200°C, followed by a slow cool down to RT. The thermoset PCP remained inside the molds (**Figure 2.13b**) for 1000°C Ar pyrolysis with the same conditions as before. As **Figure 2.13c** displays, a majority of parts was obtained intact, lying loose inside the molds. Photographs, OM images, and SEM images of several PDC parts (**Figure 2.13d-f**) show that no cracking occurred and that top surfaces are mirror-like smooth with very few small defects. Due to some volatilization in the early stage of the PCP's curing, samples exhibit a minor circumferential rim. Bottom and sidewall corners are well defined, bottom surfaces exhibit again artifacts resulting from the Parylene-C decomposition.

These two examples of PDC micromolding have shown that Si is an excellent hard mold material. Availability and compatibility with well-established cleanroom microfabrication techniques allow scalable mold fabrication with vertical or sloped sidewalls. Si is a robust material suited for high-temperature processing and reuse. The liquid PDC route is ideal for microcasting. By performing the entire (liquid) polymer-to-ceramic transformation process (curing and pyrolysis) in the molds green part release and the risk of damaging the parts in this fragile state are avoided. Crack-free microsized PDC parts of various shapes have been fabricated successfully. With a melting temperature of  $T_m=1414$ °C [181] in-Si-mold pyrolysis at temperatures above 1000°C is possible. For annealing of the ceramics approaching or exceeding temperatures of 1400°C, however, a separate annealing treatment of the PDC parts should be considered in order not to damage the Si molds. In order to overcome the PDC-shrinkage related geometrical constraints, sacrificial photoresin insets could be added into the molds, either 2D by means of photolithography (SU-8) or 3D by 2PP.



Figure 2.13: Sloped sidewall PDC microfabrication by in-mold pyrolysis in KOH etched Si molds: a) 300  $\mu$ m deep molds of 5×5, 10×10, and 20×20 mm<sup>2</sup> lateral size; b) chip with thermally cured PCP in the molds; c) photographs of chips after 1000°C Ar in-mold pyrolysis with shrunk PDC parts loose in the molds, arrows indicate parts shown in e; d) photographs of PDC parts removed from the molds; e) OM images of two parts: mirror-like top surface, texture from mold and Parylene replicated onto bottom surfaces; f) SEM images of a PDC square's bottom side. Scale bars: a-c: 5 mm, d: 1 mm.

# 2.4 Submicrometer to centimeter multiscale shaping

Silicon micromolds, fabricated by Bosch process or KOH etching, were shown to be well suited for fabrication of simple geometry 2.5D PDC microparts. Multiple Si etching steps could be performed consecutively (Bosch process, KOH, or a combination) in order to achieve more complex multilayer structures. This approach, however, would increase mold fabrication cost significantly without allowing for real freeform geometries. Furthermore, designs must

respect the PCPs' shrinkage so that the parts do not crack when being constraint by insets, for instance, as shown above.

In order to overcome these limitations, a novel multiscale shaping technique, combining micromolding and sacrificial additive manufacturing, is proposed. The parts' general shape is defined by a silicon mold whereas freeform microfeatures are implemented through the addition of custom sacrificial photoresin microstructures onto the mold. Two-photon polymerization (2PP) is a type of SLA where simultaneous absorption of two (or more) photons is required to excite the photoinitiator and trigger the resin's crosslinking reaction. Thanks to a squared dependency on the laser intensity, a significant probability for such an excitation and reaction is only given in a very small focal volume, called a voxel. Typically directed by galvo mirrors, this laser voxel scans through the resin in a line-by-line, layer-by-layer path. The technique was introduced for AM in the 1990's [182] and has been commercialized and established by the company Nanoscribe GmbH & Co. KG (Germany) during the past 15 years. Several proprietary 2PP-photoresins are offered, the standard ones IP-Dip, IP-S, and IP-Q are acrylic-based and optimized for different length scales [183]. Moreover, direct fabrication of ceramic microparts by means of 2PP has been demonstrated [98, 117], however, would be very time-consuming and costly for large number fabrication of high-resolution mm-sized parts.

Among the micromold types introduced in Section 2.3, KOH etched silicon is best suited for this hierarchical shaping approach. The characteristic flat and smooth bottom surfaces serve as substrate and allow to be detected for focusing and writing of the first layer ensuring good adhesion. Due to the molds' monolithic nature and silicon's thermal resistance, the full thermal conversion process, including the decomposition of the photoresin, can be conducted without damaging the mold. Furthermore, depending on the printing configuration and mold aspect ratio, the tilted sidewalls of KOH Si molds may grant better access of the printer's conical microscope lens.

Chips of  $25 \times 25 \text{ mm}^2$  were cut from the 100 mm KOH etched Si mold wafer so that they could be handled conveniently with the commercial 2PP-system (Photonic Professional GT+, Nanoscribe). Each chip contained several molds of  $5 \times 5$ ,  $10 \times 10$ , or  $20 \times 20 \text{ mm}^2$  lateral size and depths of 300 or 400 µm, such as the one shown in Figure 2.11a. A droplet of the IP-S photoresin which is dedicated for smooth surfaces at the micro- and mesoscale was placed into the mold and the printer's  $25 \times$  lens was immersed (DiLL configuration). In this medium printing configuration, 3D structures of a volume up to 1 mm<sup>3</sup> can be written with a voxel size of <600 nm laterally (x/y) and <2 µm vertically (z) in a reasonable print time of a few hours<sup>1</sup>. A schematic of the printing setup is shown in **Figure 2.14a**. The Nanoscribe 25× lens's working distance is 360 µm which means that writing could be performed close to the edge or

 $<sup>^1</sup>Writing$  of a solid cube of  $(1000\,\mu\text{m})^3$  would take ~7 h but could be reduced to ~1 h with a shell & scaffold approach

in narrow Bosch processed trenches as long as the mold depth is  $\ll$ 360 µm. Deeper molds can be patterned, too, but a safety distance from the edge is required in order not to crash the lens and damage both lens and mold. Writing of structures and patterns of different shapes and sizes was conducted at center regions of separate molds. Unexposed resin was selectively dissolved by development in PGMEA, followed by rinsing in IPA. In order to complete the photocrosslinking and increase mechanical strength, a UV post-curing was performed for 5 min ( $\lambda = 375$  nm). As done in case of unpatterned micromolds, a 1 µm Parylene-C coating was applied afterwards by CVD.



**Figure 2.14:** Process flow for freeform microfeature enhanced multiscale part fabrication: a) 2PP writing of 3D microstructures onto the bottom of KOH etched Si mold; b) casting of the PCP formulation; c) thermal crosslinking to GB state; d) shrunk PDC sample with feature imprint, obtained loose after in-mold pyrolysis.

The actual PCP casting process and thermal conversion were conducted similarly to the procedure described in the previous section. Micropatterned and Parylene coated mold chips were placed on a level hotplate inside an Ar glovebox and the PCP formulation (3wt.% DCP, no DVB) was pipetted into the mold (**Figure 2.14b**). To compensate for partial volatilization during curing and avoid the circumferential rim, 120% of the molds' volume were used this time. A short 20 min heating at 200°C was found to be sufficient to give infusible material, free of cracks and bubbles (**Figure 2.14c**) which could safely be transferred into the furnace for pyrolysis. Similar to the previous case, the samples were not demolded before pyrolysis, but remained inside the mold for polymer-to-ceramic transformation. While the Si mold survived the thermal treatment at 1000°C undamaged, only the IP-S 3D structure decomposed. Due to the Parylene-C separation layer and the GB's lateral shrinkage of ~27% the PDC parts were obtained loose and mostly undamaged in the mold after process completion (**Figure 2.14d**).

Several 2PP microstructures have been realized including test patterns, bioinspired hydrophobicity patterns, or 3D quick response (QR) codes. An example of the latter is presented in **Figure 2.15a**. It is the negative of  $50 \times 50 \ \mu\text{m}^2$  sized square mesa pixels with a height of 12.5  $\mu$ m and lateral total dimensions of  $1.65 \times 1.65 \ \text{mm}^2$ , written in 49 visible stitching blocks of  $250 \times 250 \ \mu\text{m}^2$  each. The QR code represents the URL of our lab website. Due to the transparency of DVB-free PCP after curing, this and two other printed structures remain visible on the Si chip, see **Figure 2.15b**. Among the seven filled molds of this chip, one sample cracked already during thermal curing on the hotplate. The other three conventional cast samples with no 2PP features broke during pyrolysis (**Figure 2.15c**). This observation could hint an improved sample detachment from the mold caused by the photoresin structures. In the furnace, both the Parylene-C layer and acrylic-based IP-S structure decompose with the majority

of the products volatilizing. According to literature, a very small amount of glassy carbon (GC) remains, 2–10% for the photoresin and ~35% of the Parylene-C [41, 184–186]. Positioned at the PDC parts' outer faces, these potential GC traces could theoretically be burned away in a subsequent HT treatment in an oxidizing atmosphere. As a decomposition control experiment, the same 3D QR code and a  $(250 \,\mu\text{m})^3$  cube were printed onto Si, UV post-cured, coated with 1  $\mu$ m Parylene, and pyrolyzed under the same conditions but with no PCP cast on top. The summary in **Figure A.7** revealed, however, that the IP-S decomposed and volatilized, entirely free of residues, and only a negligible thin film remained, consisting of gold (used for SEM inspection) and presumably carbon resulting from the Parylene decomposition.



**Figure 2.15: 2PP-enhanced PDC Si micromolding**: **a)** OM image of the  $1583 \times 1583 \ \mu\text{m}^2$  3D QR code, 2PP-written in IP-S onto the Si mold bottom; **b)** 300  $\mu$ m deep, 5 and 10 mm large Si molds, three of them with 3D micropatterns, Parylene-C coated, PCP filled and thermally cured; **c)** same mold chip after 1000°C Ar pyrolysis; **d)** pyrolyzed PDC part with the QR code imprinted on the bottom side; **e)** SEM close-up view at the PDC QR code pixels.

In case of preceramic polymer casting, the infusible green part adopts the respective mold and 3D microstructure shape, which is conserved during the polymer-to-ceramic transformation occurring shortly after the decomposition of the other two materials. As a result, the 2PP 3D structure is imprinted mirror-inverted on the bottom side of the PDC part (**Figure 2.15d**). The cavity pixels from the print correspond to the mesa pixels protruded from the new recessed base level. The PDC part is free of cracks and pores but as a consequence of the decomposition outgassing, radially oriented traces are visible. **Figure 2.15e** shows an SEM image of the region highlighted in red in Figure 2.15a,d. The replication of the 2PP structure is very

precise. The liquid precursor formulation filled the mold conformally and no bubbles were trapped or formed, showing that neither vacuum degassing nor pressure-assisted curing are necessary. Even printing artifacts such as stitching and hatching lines (~750 nm) are clearly visible, showcasing the submicrometer PDC-replication capability which has been demonstrated for simpler tip-geometries before [72]. The PDC mesa pixel top surfaces which were in direct contact with the Parylene-C coated silicon area are noticeably smoother than the now recessed bottom area. No contamination from the IP-S photoresin derivatives in the form of glassy carbon particles remains after rinsing the sample with IPA. Occurring shrinkage during the polymer-to-ceramic transformation can either be exploited for higher resolution or compensated in the design phase.

This example shows the feasibility of the hierarchical PDC shaping technique. Molds with lateral dimensions ranging from hundreds of micrometers up to centimeter scale can be applied as substrate. Also, 2.5D multilayer molds with angled (KOH) or vertical (Bosch) sidewalls or a combination of them can be achieved by consecutive etching steps. Alternatively to the used IP-S/25× Nanoscribe configuration, three times smaller features as well as 2–3 times larger voxels can be written in IP-Dip/63× or IP-Q/10× configuration, respectively. This way, structures could be imprinted with either much finer features or much larger total size up to millimeter scale while keeping printing time low. When reusing the Si molds, effective part fabrication cost can be kept at a reasonable level due to the fast and reliable character of the process and reduced need of special hardware. Definition of the general shape by the mold and application of 2PP only where needed shortens the printing time and hence reduces cost further compared to 2PP-writing of the entire (pre)ceramic part. In addition to any kind of part labelling, protection against forgery, surface patterning and functionalization (e.g. altering hydrophobicity), or 2D and 3D microfluidic structures can be realized this way in ceramic.

## 2.5 Summary and conclusion

This chapter has presented the molding capabilities of the liquid PDC route. Large numbers of millimeter-sized, disc-shaped polymer-derived ceramic parts have been fabricated using CNC-machined PTFE molds. Experiments have shown that for a successful demolding of the green parts after thermal curing, a good surface finish of the molds is essential. Pyrolysis of GB material was conducted in Al<sub>2</sub>O<sub>3</sub> crucibles. Several types of micromolds for PCP casting and their microfabrication processes have been presented as well. SU-8 processing and anisotropic etching of silicon are the key steps for hard micromold creation or fabrication of masters for PDMS soft mold replication. SU-8 micromolds exhibit smooth near vertical sidewalls but are prone to thermally induced cracking or delamination. Monolithic silicon molds are more resilient, however, are limited by possible artifacts such as undulating rough sidewalls in case of the Bosch process or design restrictions in case of KOH etching due to the crystallographic

relations. Green body mold release is generally challenging for microparts which is why the in-mold pyrolysis approach has been tested with Si micromolds. Using the example of several simple shapes such as circles, squares, and bars, PDC microparts have been manufactured successfully by pyrolysis inside the Bosch or KOH Si molds. Polymer-to-ceramic conversion and shrinkage cause the part release while the mold remains unaffected.

In order to address some of the design restrictions inherent to the above-mentioned microfabrication processes, a novel multiscale PDC shaping technique has been introduced. Mesoscale KOH etched silicon molds with smooth surfaces were refined by addition of sacrificial custom freeform microfeatures through 2PP. In a fast and pressureless PCP casting process, the shapes defined by the multiscale mold have been successfully replicated into PDC parts with the 2PP features resulting as imprinted cavities with submicrometer resolution. Due to a target-oriented application of 2PP and the option to reuse the Si mold, the part fabrication cost can be reduced.

Further research would be required to expand the possibilities of sacrificial 2PP or additive manufacturing in general. Additional optimization of the process would enable more complex shaped PDC (micro)parts. For example, cutouts could be included by sacrificial insets written into Si molds which decompose and allow the surrounding PDC to shrink freely. One step further would be the printing of entire molds onto a thermally stable substrate. At least for highly customized parts, this lost mold approach would allow for very complex geometries and would eliminate the risk of mold trapping or substrate adhesion.

# **3** SiCN property tuning

**Disclaimer:** This chapter (3) is partially adapted from the following article with permissions of all co-authors:

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**My contribution:** conceptualization, design, fabrication, experiments, data processing, figures, coordination, and writing.

## 3.1 Introduction

This chapter focuses on the fabrication of ternary silicon carbonitride (SiCN) ceramics, derived from a commercially available poly(methylvinylsilazane) (PMVSz). Using a suited thermal initiator and varied amounts of the organic carbon-filler divinylbenzene (DVB), the preceramic polymer formulation is cast in millimeter-sized disc shaped PTFE molds. The thermal crosslinking parameters are optimized in order to yield fully dense and crack-free samples starting with a fast and pressureless curing step. The bulk green parts are demolded and pyrolyzed in argon (Ar) atmosphere with peak temperatures of 800–1400°C for ceramic transformation and annealing. Integrity, composition, microstructure, mechanical behavior, electrical conductivity, and cytocompatibility of the obtained SiCN material are analyzed and correlated to C-filler addition and processing parameters. These relations form the basis for application specific property tuning of the PDCs or creation of contrasts in composition, microstructure, and properties introduced in Chapter 4.

# 3.2 Materials and methods

## 3.2.1 Synthesis of SiCN ceramics

PDC-precursor formulation was performed in an Ar atmosphere glovebox as illustrated previously in Figure 2.2. The PMVSz *Durazane*<sup>®</sup> *1800 (Dz18)* has been provided by Merck KGaA, Germany. In each formulation, 3 wt.% of the radical initiator dicumyl peroxide (DCP) (99%, Acros, United Kingdom) were added and dissolved. Subsequently, 0, 20, 40, or 60 wt.% DVB (80%, Sigma-Aldrich) were added. **Table 3.1** lists the typical amounts and concentrations for preparation of 1 g PCP formulation, for larger batches a multiple thereof was prepared. Formulations were used directly or stored in an inert, dark, and refrigerated place until casting, not later than 14 days after preparation.

Name	m <sub>Dz18</sub> (mg)	m <sub>DVB</sub> (mg)	m <sub>DCP</sub> (mg)	c <sub>Dz18</sub> (wt.%)	c <sub>DVB</sub> (wt.%)	c <sub>DCP</sub> (wt.%)
DVB00	970	0	30	97.00	0	3
DVB20	770.5	199.5	30	77.05	19.95	3
DVB40	570.3	399.7	30	57.03	39.97	3
DVB60	370.2	599.8	30	37.02	59.98	3

Table 3.1: Nomenclature and composition of main Dz18-based PCP formulations.

PTFE molds with 18 or 16 identical cylindrical cavities of 7 mm diameter and 500 µm depth (Figure 2.1) were placed on a level hot plate inside the glovebox. To compensate for partial volatilization, 23.1 µL of the precursor formulation (corresponding to 120% of a molds' volume) were pipetted into each mold (Figure 2.3a), temporarily forming a convex liquid surface. Two upside-down glass Petri dishes of different sizes were placed on top to create an oven-like thermally insulated chamber (Figure 2.3b). Thermal crosslinking was performed during 30 min at 200°C for 0% DVB formulations and in a 3-step process (10 min each at 100, 150, 200°C) for the DVB-containing samples (**Figure A.8**). Obtained green body (GB) material was released from the PTFE molds undamaged by upside-down tapping, typically at a mold temperature of 60–80°C. PTFE molds were immersed in acetone, brushed, rinsed with IPA, and dried before reuse.

Pyrolysis was conducted in a tube furnace (STF 15/450, Carbolite Gero, Germany) with a constant Ar flow. Green state discs were placed in alumina  $(Al_2O_3)$  crucibles which were positioned in the furnace center. Heating and cooling rates of typically 100 K/h were applied, with a 1 h crosslinking dwell time at 300°C and 1 h dwell time at the maximum temperature of 800, 1000, 1200, or 1400°C. This standard temperature sequence is shown in **Figure 3.1** in solid lines.



**Figure 3.1: Pyrolysis temperature profiles**: Fast cycle (300 K/h, dashed lines), standard cycle (100 K/h, solid), and optimized cycle (300, 60, 100 K/h, dotted), temperature values measured in the tube furnace center. 1 h holding time at 300°C for extended crosslinking and 1 h holding time at peak temperatures of 800, 1000, 1200, or 1400°C were applied.

#### 3.2.2 Characterization

Cross sections of some samples were prepared by means of diamond-wire sawing. Part inspection and imaging were performed by OM (M80, Leica, Germany) and SEM (Merlin, Zeiss, Germany). At EPFL's ENAC Interdisciplinary Platform for X-ray micro-tomography (PIXE), a selection of 13 PDC disc samples was imaged by X-ray micro computer tomography (Ultratom  $\mu$ CT system, RX-SOLUTIONS, France; 110 kV LaB<sub>6</sub> cathode). Fourier-transform infrared spectroscopy (FTIR) spectra of green parts were recorded with a Tensor 27 (Bruker, United States), using a Golden Gate ATR and applying a constant pressure during measurements. Simultaneous thermal analysis (STA), combining thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), was carried out using a STA449 F3 Jupiter (Netzsch, Germany) under an Ar atmosphere. Confocal Raman laser spectroscopy ( $\lambda$ =488 nm; inVia, Renishaw, United Kingdom) was performed on pyrolyzed SiCN disc samples. Selected PDC samples were manually ground to a fine powder for X-ray diffraction (XRD) (D8, Discover Vario, Bruker, United States). For elemental analysis (EA), up to three samples were manually ground to a fine powder and split into two fractions of approximately 5 mg for each of the five different sample types. One fraction was used in CHN(S) mode and the other one for oxygen analysis (Unicube, Elementar Analysensysteme, Germany). Si concentration was calculated as the difference to 100%.

Flexural strength of SiCN disc samples was measured in a ball on 3 balls (B3B) test setup which is visualized in **Figure 3.2**. Ceramic samples were placed between four steel balls and an increasing load was applied until the sample broke. The flexural strength was then calculated based on the following formula:

$$\sigma_{fl} = f_{\alpha,\beta,\nu} \frac{F}{t^2} \tag{3.1}$$

with  $\sigma_{fl}$  the flexural strength in MPa, *F* the applied force in N, and *t* the thickness of the tested disc in mm. *f* is a dimensionless factor which depends on the ratio of thickness to the radius of the disc ( $\alpha = t/R$ ), the ratio of the support radius of the three balls to the disc radius ( $\beta = R_a/R$ ), and the Poisson's ratio of the ceramic, which was defined as v = 0.22. The balls' radii were 1.9 mm and the crosshead displacement was set to 5 mm/min [76, 187, 188].



Figure 3.2: Experimental setup for B3B flexural strength measurements: a) cross-sectional schematic setup; b) photo of the setup with sample installed before loading; c) example of a weak sample breaking into few pieces; d) example of a strong sample scattering in many very small pieces.

Room temperature electrical conductivity of ceramic disc samples was measured in two ways. Firstly, in a sheet resistivity approach, a collinear four-point probe head (SP4, Microworld, France) and a Keithley 2450 source meter (Tektronix, United Kingdom) were used on pristine SiCN samples. The pins had a spacing of 1.26 mm each. Measurements were performed under a current bias technique where a current of 1  $\mu$ A was applied at the outer probes and the corresponding voltage between inner probes was measured. From the obtained resistance, conductivity is calculated using the following formulae 3.2 & 3.3:

$$R = R_{mean}f \tag{3.2}$$

with f the geometric correction factor, which is a ratio of the disc diameter (*d*) to probe pin spacing (*s*). In the case of the present ratio  $d/s \approx 4$ , f = 2.9289. 50 resistance values were acquired from each sample. Typically, only one sample per type was measured but in some cases several measurements were performed of the identical sample, e.g. at a different position

or on the other side. With the sample's thickness *t*, the conductivity was finally calculated from the obtained resistance using the following equation [76, 189]:

$$\sigma_{dc} = \frac{1}{Rt} \tag{3.3}$$

In the second electrical conductivity measurement approach, the disc samples' bulk resistivity was measured in transition. For this, a custom two-probe setup was built which is shown and explained in **Figure 3.3**. Probes were connected to a Keithley 2400 source meter. In order to ensure a good electrical contact, the Cu probe tips were polished and conductive two-component Ag epoxy glue (Epo-Tek<sup>®</sup> H20E, Epoxy Technology, United States) was applied on both sides of the PDC discs to be measured. The Ag glue was placed centered and spread to cover a circular area with 80% of the sample's diameter. Samples were clamped between the probes for measurement and then flipped and recontacted for a second measurement. Resistance R was obtained as the inverse of the IV-curve linear regression line, IV ranges were adapted depending on the samples' conductivity and kept well below values which would cause heat induced effects. Conductivity was finally calculated based on the basic correlation in Equation 3.4 which leads to Equation 3.5 in good approximation:

$$R = \rho \frac{t}{A} \tag{3.4}$$

$$\sigma_{dc} = \rho^{-1} = \frac{t}{RA} = \frac{t}{R\pi \left(\frac{d_{eff}}{2}\right)^2} = \frac{4t}{R\pi (0.8d_{disc})^2}$$
(3.5)



Figure 3.3: Experimental setup for electrical resistance measurement in transition: a) probe fixation and wiring overview; b,c) closeup views on a sample clamped between the polished Cu probes; d) cross-sectional schematic illustrating the dimensional relations.

Cytocompatibility of the PDCs was evaluated with normal human dermal fibroblasts (NHDFs) (PromoCell, cat. C12302, Lot 410Z037.5). Cells were cultured and maintained under standard cell culture conditions (37°C, 5% CO2, >95% humidity, in Dulbecco's Modified Minimal Medium (DMEM) with high glucose, supplemented with 10% fetal calf serum (FCS), 1% penicillin-streptomycin-neomycin (PSN), and 1% L-glutamine). PDC disc samples filled with 20% and 40% DVB, each pyrolyzed at 1000°C and 1200°C, were sterilized by steam autoclaving (121°C, 2 bar for 30 min). They were then placed upside-down in a 96-well plate and seeded with cells in 200  $\mu$ L medium at ~15500 cells/cm<sup>2</sup> on top. PDCs prepared without addition of DVB were used as reference. At days 1 and 4, metabolic activity of the cells was assessed with an MTS assay (Promega), according to the manufacturer's instructions. Absorbance was measured at 490 nm (Mithras2 plate reader, Berthold Technologies) with three technical repeats from triplicate samples per condition and time point. Cell attachment and spreading was observed by staining for the nuclei and cell cytoskeleton at day 1 and 4 after fixing and permeabilizing the cells with 4% paraformaldehyde and 0.1% Triton X-100 in PBS, respectively. After washing in PBS (3 times), cells were stained with Alexa Fluor 488 labelled phalloidin (Invitrogen, A12379) at a dilution of 1:200 (in 1X PBS) and DAPI (4,6-diamidino-2-phenylindole, Sigma, D9542) at a dilution of 1:1000 (in 1X PBS) for 1 h. After washing with PBS, cells were imaged using a confocal laser scanning microscope (LSM 780, Carl Zeiss). Statistical analyses were performed using IBM SPSS statistics software (version 25). Error bars represent standard deviation. Data was analyzed using a Welch test with post-hoc Games Howell test when homogeneity of variances was not obeyed, with statistical significance defined at p<0.05.

## 3.3 Results and discussion

## 3.3.1 Precursor system and polymer-to-ceramic transformation

An overview of the pressureless fabrication process of millimeter-sized SiCN discs was presented in Figure 2.2. The PMVSz *Durazane*<sup>®</sup> *1800* (Dz18) can be crosslinked thermally without catalysts or initiators. The occurrence of the four crosslinking mechanisms which were shown in Figure 1.6 is well known in theory. Hydrosilylation is reported to occur above 100–120°C, transamination in the range 200–400°C, dehydrogenation above 300°C, and vinyl polymerization at higher temperatures [15]. One of the main goals of this work was to find a new combination of precursor system and processing parameters in order to result in high-yield and high-quality samples in a short time, with a reduced need for large and expensive equipment such as presses or pressure vessels. Rapid and extensive crosslinking is targeted, to be achieved by the appropriate type and concentration of initiator as well as curing conditions. At the same time, mold damage, sample cracking, excessive mass loss, and pore formation caused by PTFE thermal decomposition, thermal stress, oligomer volatilization, and volatile trapping, respectively need to be avoided. For this reason, the radical initiator DCP was introduced at a comparably high concentration of 3 wt.%. DCP reportedly lowers the curing temperature of polyvinylsilazanes to 50–150°C through promotion of the vinyl polymerization and hydrosilylation reactions [36–38]. In contrast to transamination and dehydrocoupling, vinyl polymerization and hydrosilylation are mass-conservative mechanisms and hence beneficial for achieving higher ceramic yields.

In order to tune the properties while staying within the SiCN system, the carbon-filler DVB was added to the preceramic polymer (PCP) at four different concentrations of 0, 20, 40, and 60 wt.%. The thermally formed DCP radicals not only activate the Dz18's vinyl groups but also the DVB molecules. Therefore, DVB polymerization (**Figure 3.4**) is initiated which leads to integration of DVB monomers and formed oligomers into the polysilazane network by cross-polymerization.



**Figure 3.4: DVB polymerization reaction**: formation of DVB oligomer units which can also cross-polymerize with the PMVSz's vinyl groups and thereby integrate into the crosslinked GB network.

Without DVB addition, a 30 min heat treatment at 200°C resulted in an adequate degree of thermosetting and absence of trapped bubble formation. For DVB-filled precursors, in order to reduce the DVB volatilization, a 3-step sequence of 10 min each at 100, 150, and 200°C was applied (Figure A.8), also leading to bubble-free disc green bodies as shown in **Figure 3.5**. Obtained green body samples are colorless and transparent in the absence of DVB and become gradually more yellow and opaque with increasing DVB concentration. In case of the maximum DVB concentration of 60 wt.%, slight warping is observed already in the GB state.

FTIR data of thermally cured green state material of the four compositions shown in **Figure 3.6** does not exhibit bands related to the vinyl group stretching ( $v_{C-H}$  at 3053 cm<sup>-1</sup>,  $v_{C=C}$  at 1592 cm<sup>-1</sup> and 1402 cm<sup>-1</sup>) [190], confirming their complete consumption. Various bands of the polysilazane's other functional groups such as N–H at 3378 cm<sup>-1</sup> and Si–H at 2118 cm<sup>-1</sup> persist, indicating overall incomplete crosslinking of the system after the first thermal treatment. For this reason, a 1 h dwell time at 300°C was included in the subsequent pyrolysis process under Ar atmosphere, allowing transamination and dehydrocoupling to proceed.

TGA of the same samples in **Figure 3.7** illustrates the polymer-to-ceramic transformation process. All compositions behaved very similarly up to 440°C where the organic-inorganic conversion sets in and the 60% DVB formulation exhibits a severe mass loss. This extra mass loss of 10% indicates an excess amount of DVB, unable to integrate into the polymeric network and hence decomposing and volatilizing. For DVB concentrations of 20 and 40 wt.%, however,



**Figure 3.5: Green state and ceramic sample overview**: Photographs of green body (GB) discs with four different DVB concentrations (in wt.%) and corresponding SiCN ceramic discs after pyrolysis at four different peak temperatures under argon atmosphere. Representation to scale visualizes the trend of lateral shrinkage increasing from 24% in case of DVB00, 800°C up to 36% for DVB60, 1400°C with higher DVB concentration and higher pyrolysis temperature.

the filler is mostly incorporated into the network. Therefore, high ceramic yields of 77% and 75% were acquired at 1400°C, which is only slightly below the value of 79% for the DVB-free material.

Pyrolysis of the green parts was conducted in a tube furnace with a constant Ar flow. While high heating and cooling rates (300 K/h is the maximum allowed value for the used furnace) are generally favorable with regard to process efficiency, ceramic samples often crack due to thermal stress. Therefore, reduced heating and cooling rates of 100 K/h were chosen as a tradeoff. **Figure 3.5** shows one example of each obtained PDC sample type after thermal treatment. Relative shrinkage ranged from 24% to 36% laterally (diameter) and 7% to 48% vertically (thickness). As a general trend, increasing shrinkage was observed with higher DVB concentrations and higher pyrolysis temperatures. This can be explained with the partial DVB volatilization and ongoing material densification, mainly through hydrogen stripping in remaining C–H bonds [6].



**Figure 3.6: FTIR spectra for each GB type** exhibiting the identical characteristic bands with decreasing intensity for increasing DVB amount.



**Figure 3.7: Simultaneous thermal analysis of each GB type**: TGA (solid) and DSC (dashed lines) performed in Ar: 0–40 wt.% DVB: slightly decreasing ceramic yields (79–75 wt.%) with increasing DVB concentration, 60 wt.% DVB: significantly lower value of 65 wt.% indicates reduced degree of crosslinking. DSC curves' minima show some exothermic reactions.

Defects such as unintentional pore formation, cracking or severe warping are common problems in PDC fabrication. Our optimized precursor system and processing parameters, as described above, in contrast allow for a very reliable and predictable sample fabrication. Among nearly 800 PDC disc samples produced, less than 1% exhibited visible pores or cracks. SEM images in **Figure 3.8** show the samples' bottom surfaces as received (unpolished, uncoated) which are defect-free at higher magnification as well. The topography of the PTFE molds is replicated, including some signs of wear. DVB-free SiCN appears very homogeneous, whereas 20 and 40% DVB-filled material exhibits a grayscale contrast pattern presumably caused by phase separation and formation of carbon-rich areas. In the case of the highest C-filling, no such contrast is present, but a regular fine surface roughness exists instead. The ceramics' top surfaces are generally very similar, however, do not exhibit topographical unevenness from the molds. Hence, 0% DVB SiCN shows extremely smooth surfaces (Figure 3.9a). A major difference occurs for 40% DVB samples which form a particular microporosity layer (Figure 3.9b), unique to this composition and the top surface. Cross-sectional SEM in Figure 3.9c-e reveals the thickness of approximately 5  $\mu$ m of this microporosity layer. It is possibly caused by a DVB and carbon enrichment leading to decomposition processes limited to the top layer with access to traces of oxygen. The unpolished SEM cross sections exhibit roughness and breakouts from the diamond-wire sawing. Locally, for the center of this sample, the SEM images confirm the absence of cracking and pore formation in the bulk volume.

In order to non-destructively reveal potential subsurface defects in the entire volumes, Xray microtomography scans of 13 samples were performed. In Figure 3.10, two examples are shown where the DCP concentration was only 2 wt.% and a higher temperature curing sequence (200–250°C) and faster pyrolysis (300 K/h, Figure 3.1: dashed lines) were applied. A large number of trapped bubbles is present in both samples a and b, that already formed during the first thermal treatment step and were conserved during the subsequent thermal processing. Tearing cracks may already occur in the green state but, similar to the full fracture in sample a, they are typically the consequence of rapid heating and cooling (300 K/h) during the pyrolysis. Due to overpressure formed in enclosed pores or thermal stress related to temperature gradients in the material, cracks are formed, in particular along pores. Our process modifications reliably allowed avoidance of such defects as samples c and d in Figure 3.10 show, as well as b-i in Figure A.9. The obtained ceramic material is free of cracks and pores down to  $\sim 1 \,\mu m$  size. However, some artifacts are present. Due to the liquid precursor casting approach and minor volatilization during crosslinking, samples tend to form a meniscus at the top side edge which is more pronounced at higher DVB concentrations (Figure A.9g-i). In case of 40% DVB filling, some micro edge porosity formed (Figures 3.10d and A.9g,h), probably caused by pinning of evolving gas at the mold sidewall. The maximum DVB concentration of 60 wt.% causes the green body to warp, an effect which becomes even more pronounced after pyrolysis (Figure A.9c).

## 3.3 Results and discussion



**Figure 3.8: SEM images of 1000°C pyrolyzed SiCN discs' bottom surfaces**, unpolished, uncoated, mixed in-lens and secondary electron detector signals to accentuate density contrast and topography features: a,c,e,g) overview; b,d,f,h) closeup of highlighted regions. **a,b)** 0% DVB: very smooth, no inhomogeneities, some mold scratches replicated; **c,d)** 20% DVB smooth, mold scratch replicated, darker spots represent C-rich areas; **e,f)** 40% DVB, nearly identical to 20% DVB; **g,h)** 60% DVB: very regular fine surface roughness.

## Chapter 3. SiCN property tuning



Figure 3.9: SEM images of selected 1000°C pyrolyzed SiCN discs top surfaces and cross sections, unpolished, uncoated: a) 0% DVB top: extremely smooth; b) 40% DVB top: open microporosity layer; c-e) 45° tilt cross-sectional views on 40% DVB sample with a total thickness of 264  $\mu$ m in the center and a porosity layer thickness of  $\approx 5 \mu$ m.



**Figure 3.10:** Microtomography images of four PDC disc samples with cracks and pores highlighted in red: **a,b)** 0% DVB 1000°C before process optimization suffering from severe pore and crack formation; **c)** 20% DVB 1200°C with optimized processing leads to best results, fully dense samples without any noticeable pore or cracks; **d)** optimized 40% DVB 800°C exhibits no enclosed pores or cracks but some minor edge porosity.
#### 3.3.2 SiCN composition and microstructure

Polysilazanes are precursors for silicon carbonitride (SiCN) which is obtained as a so-called amorphous covalent ceramic (ACC) with mixed bonds after pyrolysis in an inert atmosphere [43, 191]. The amorphous character of the obtained PDCs has been verified by XRD. No incipient crystallization was observed during 1 h at 1400°C. This thermal stability against crystallization is caused by the particular nanodomains and free carbon content [18]. In order to determine the PDCs' composition, five sample types were selected and respective disc samples were ground to a fine powder and analyzed by elemental analysis (EA). 1000°C pyrolyzed samples of all four precursor compositions were chosen as well as a second 20% DVB sample but pyrolyzed at 1400°C. This way, both DVB concentration and temperature influence can be seen. The resulting carbon (C), nitrogen (N), hydrogen (H), and oxygen (O) concentrations for each sample type are listed in Table 3.2, where the silicon (Si) concentration was calculated as the difference to 100%. Conversion to the empirical formulae normalized to  $Si_1$  shows that the oxygen contamination from the glovebox-to-furnace transfer or inert gas impurities is negligible (<0.006 mol). Neglecting the hydrogen contents, the samples' composition is also visualized in the ternary Si-C-N diagram in Figure 3.11 where all five compositions are centrally positioned in the 3-field region of  $Si_3N_4$ , SiC, and C.

Due to the organic character of the used PMVSz, resulting ceramic material contains a significant inherent carbon concentration of 21 wt.%. This value is in good agreement with a similarly prepared PDC from the literature [192]. The samples' free carbon content was calculated based on a set of atomic bonding assumptions according to the literature [131, 193, 194]:

- residual hydrogen is bonded to carbon (C-H)
- all nitrogen is bonded to silicon (Si<sub>3</sub>N<sub>4</sub>)
- all oxygen is bonded to silicon (SiO<sub>2</sub>)
- all other silicon is bonded to carbon (SiC)
- all remaining carbon is free (sp<sup>2</sup>)

which can be summarized and represented in the form of the following equation, taking stoichiometries into account:

$$wt.\% C_{free} = M_C \left( \frac{c_C}{M_C} - \frac{c_{Si}}{M_{Si}} - \frac{c_H}{4M_H} - \frac{3c_N}{4M_N} - \frac{c_O}{2M_O} \right)$$
(3.6)

The approximate fraction of "free" sp<sup>2</sup>-hybridized carbon therefore is 15 wt.% in the case of 1000°C pyrolyzed DVB-free Dz18. In general, free-carbon incorporation is of interest because of positive influences on the PDCs' properties such as improved thermal stability and a metallic-like electron conduction [6]. The addition of 20 and 40 wt.% DVB to the precursor

was proven to be effective as the corresponding free carbon values in the resulting ceramic increased by 5 wt.% each, to a maximum of 25 wt.%. Higher values of up to 55 wt.% have been reported for the SiCN system but required more complex or time-consuming processing [131, 195]. In agreement with the observations on 60 wt.% DVB addition described before, such a high filler concentration gives inferior results with a free carbon concentration of only 21 wt.%, similar to the value of 20% DVB. Comparing the two elemental analysis measurements of 20% DVB confirms the expected trend of mainly hydrogen stripping occurring in the temperature range of 1000–1400°C.

Table 3.2: Selected PDC samples' elemental composition, empirical formulae normalized to Si<sub>1</sub>, and calculated free carbon content: a maximum free carbon content of 24.9% is observed for 40% DVB.

	c <sub>DVB</sub>	Tpyro	Elemental content (wt.%)					Empirical	Free carbon
#	(wt.%)	(°C)	Si	С	Ν	Н	0	formula	(wt.%)
1	0	1000	56.5	21.3	20.8	1.3	0.12	SiC <sub>0.88</sub> N <sub>0.74</sub> H <sub>0.64</sub>	14.5
2	20	1000	52.1	27.1	19.9	0.90	0.06	SiC <sub>1.22</sub> N <sub>0.77</sub> H <sub>0.48</sub>	20.3
3	20	1400	53.1	27.8	18.8	0.26	0.05	SiC <sub>1.23</sub> N <sub>0.71</sub> H <sub>0.14</sub>	18.0
4	40	1000	48.5	30.8	20.0	0.67	0.03	SiC <sub>1.48</sub> N <sub>0.83</sub> H <sub>0.38</sub>	24.9
5	60	1000	52.1	31.4	15.8	0.48	0.17	SiC <sub>1.41</sub> N <sub>0.61</sub> H <sub>0.25</sub>	20.8



**Figure 3.11: Ternary Si-C-N diagram** visualizing the molar composition of five samples analyzed by elemental analysis, neglecting hydrogen and oxygen.

Raman spectroscopy is a powerful non-destructive method for carbonaceous materials structural analysis. Measured spectra of all 16 PDC sample types presented in **Figure 3.12** exhibit two bands at ~1350 cm<sup>-1</sup> and 1600 cm<sup>-1</sup>, called D and G band, respectively. The D band is caused by the free carbon's disorder-induced vibration mode of graphene-like sp<sup>2</sup>-rings (see inset in Figure 3.12). In-plane bond stretching of sp<sup>2</sup>-hybridized carbon atoms is responsible for the G band [192, 196]. Lorentzian peak fitting of the baseline-subtracted spectra was performed in order to determine both bands' intensities, peak position, and full width at half maximum (FWHM). The increasing  $I_D/I_G$  intensity ratio of all four compositions with increasing pyrolysis temperature as well as the D band width decrease indicate a carbon ordering towards aromatic graphene layers proceeding in the temperature range of 800– 1400°C [192, 196]. Peak fitting and key figures are shown in **Figure A.10** using the example of 20% DVB containing samples.



Figure 3.12: Raman spectroscopy of all 16 homogeneous SiCN sample types where the free carbon D and G band intensity ratio indicates the ordering. Lorentzian peak fitting and calculated values are given for the set of 20% DVB samples in Figure A.10. Inset with D mode  $A_{1g}$ -symmetry and G mode  $A_{2g}$ -symmetry from [18].

## 3.3.3 Tuning of functional and mechanical properties

The carbon presence and its ordering process are the main reason for the observed large range in electrical conductivity of up to 10 orders of magnitude. Conductivity data obtained by the

two different measurement approaches described in Section 3.2 deviate from each other, due to the differing measurement principles, possible detrimental effects, and simplifying assumptions. Nevertheless, they do confirm the most important trends and relations. Values from four-probe sheet resistivity measurements listed in **Table A.1** and visualized in **Figure 3.13a** are generally higher than those from 2-probe transition measurements provided in **Table A.2** and **Figure 3.13b**.



Figure 3.13: Contour plots of SiCN's RT electrical conductivity depending on DVB filling and pyrolysis temperature, same arrangement as in figure 3.5: data obtained from **a**) collinear four-probe measurements ranging from  $5 \cdot 10^{-11}$  to  $4 \cdot 10^{-1}$  S/cm for DVB00 1200°C pyrolyzed and DVB40 1400°C pyrolyzed, respectively; **b**) two-probe transition measurements ranging from  $2 \cdot 10^{-12}$ to  $3 \cdot 10^{-3}$  S/cm for DVB00 800°C pyrolyzed and DVB40 1400°C pyrolyzed, respectively.

In the sheet resistivity approach, samples with 0% and 20% DVB added were found to be insulating with  $4.6 \cdot 10^{-11}$  and  $3.7 \cdot 10^{-9}$  S cm<sup>-1</sup> as the lowest and highest conductivity values measured, respectively. A maximum free carbon content of 20 wt.% in these samples appears to be insufficient for establishing a carbon percolation network which is reported to be mainly responsible for electrical conductivity in SiCN [6]. A major conductivity increase is observed in Figure 3.13a when increasing the amount of added DVB to 40%, resulting in approximately 25 wt.% of free carbon in the obtained ceramic, which appears to be above the threshold concentration. 40% DVB samples pyrolyzed at 800°C exhibit a conductivity of ~ $8.4 \cdot 10^{-7}$  S cm<sup>-1</sup>. With an increasing pyrolysis temperature samples of this composition become progressively more conductive up to metallic-like  $0.4 \,\mathrm{S}\,\mathrm{cm}^{-1}$ , with a maximum measured value of  $1.3 \,\mathrm{S}\,\mathrm{cm}^{-1}$ . This trend is in line with previous investigations [73, 76] and is caused by hydrogen stripping and the sp<sup>3</sup>-to-sp<sup>2</sup> transition described before [6]. Data acquired for 60% DVB samples is less reproducible and has larger variation, which is another sign of this composition's poor qualities. The sheet resistivity technique, however, is susceptible to potential surface oxide layers, curved surfaces, and local microdefects, especially surface cracks perpendicular to the line of the four probes.

Due to the large contacting areas on both sample sides achieved by the silver glue, the applied 2-probe transition technique should yield more representative bulk data. The respective contour plot in Figure 3.13b clearly visualizes the general trend of increasing electrical conductivity with both increasing carbon content and increasing pyrolysis temperature. The lowest conductivity of  $\sigma_{\rm DC} \ll 1 \cdot 10^{-9}$  S/cm was observed for 800°C pyrolyzed unfilled SiCN. Exact quantification, however, is not possible in this approach due to the tool's limited sensitivity for resistances of R>210 M $\Omega^1$ . This data, in contrast to the sheet resistivity data, suggests that medium conductivity in the range of 10<sup>-6</sup>–10<sup>-4</sup> S/cm results from either HT-pyrolysis of unfilled material or high DVB filling concentrations at low pyrolysis temperature. In both cases, some basic structural units (BSUs) have presumably formed and caused this behavior. The highest conductivity, possibly with an established graphitic free carbon network, was again found for 40% DVB PDCs pyrolyzed at 1400°C. The values of  $\sigma_{DC}$  = 2.9 · 10<sup>-3</sup> S/cm are, however, significantly lower compared to the previous measurement approach. Reasons for this shift to lower conductivity values could be the fact that not one but two potential surface layers may affect the bulk measurement and that the chance for the presence of defects is higher in a larger analyzed volume. For elimination of the first detrimental influence, all samples would need to be polished on both sides, for the second, samples would need to undergo comprehensive high-resolution microtomography for detection of potential internal defects.

Mechanical performance of twelve sample types (0–40% DVB, 800°C<T<sub>pyro</sub><1400°C) was investigated by means of ball on 3 balls (B3B) testing of SiCN discs. 60% DVB samples were excluded due to shrinkage and excessive warpage, making them incompatible with the measurement setup. Calculated flexural strength values of three tested samples each are summarized in **Table 3.3**. Typical for ceramics, hidden defects may cause large variation of results such as in the case of 0% DVB 1200°C ranging from 77 MPa up to 1350 MPa.

$\sigma_{fl}$ (MPa)	800°C			1000°C			1200°C			1400°C		
DVB00	712	920	1115	1187	1328	1363	77	119	1350	69	74	83
DVB20	780	889	1387	533	1511	2209	749	1116	1908	363	650	862
DVB40	583	823	839	516	682	695	491	540	804	176	260	615
DVB60	not measured due to excessive warping											

Table 3.3: Flexural strength prescreening: B3B testing of three PDC discs each of twelve different types, values sorted smallest to largest.

Hence, based on this data set, the two sample types with the highest measured values have been chosen for repeated testing with 12–16 samples each. The results of 1000°C pyrolyzed samples with 20 and 40% DVB added to the precursor formulation are presented in **Figure 3.14** as a Weibull plot. The derived characteristic flexural strength value of 988 MPa for the 40%

<sup>&</sup>lt;sup>1</sup>Refer to Figure A.11 and Table A.2 for IV-curve examples explaining the measurement limits.

DVB composition is comparable to results which have been obtained recently for similarly measured DVB-modified SiOC [76]. In contrast, the characteristic flexural strength of 20% DVB modified SiCN of 1.65 GPa outperformed previously published results for PDC with a maximum value of 1.1 GPa [6,56,80]. Considering the Weibull modulus also being significantly higher for 20% DVB than 40%, the lower DVB addition is clearly favorable for mechanically demanding applications. The high level of strength affirms a generally low defect concentration and suggests fully dense character of the SiCN material. The differing behavior of the two sample types may be explained by the 20% DVB samples' naturally smoother top surface, absence of edge microporosity, and possibly lower internal micro flaw concentration, [56] rather than by the actual composition. Fabrication of dedicated test specimens by grinding and polishing would be required to entirely eliminate this influence.



**Figure 3.14: Weibull diagram of two sample types: 1000°C pyrolyzed DVB20 and DVB40** exhibiting characteristic flexural strength values of 1.65 GPa and 988 MPa, respectively.

## 3.3.4 Cytocompatibility of SiCN

In order to evaluate the PDCs' suitability for biomedical applications such as material for heart pacemaker electrodes, their cytocompatibility was assessed. As a major component of cardiac tissue, fibroblasts, commonly used in cytocompability tests, were selected. To mimic human physiology, normal human dermal fibroblasts (NHDFs) were cultured for 1 and 4 days on the bottom surface of the disc samples and metabolic activity as well as cell attachment and spreading on the substrate were investigated for samples with 0, 20, and 40% DVB added (pyrolyzed at 1000°C and 1200°C). Confocal microscopy shows well spread cells with no obvious differences in all PDC groups at day 1 (**Figure 3.15a**). After 4 days of culture, a cell layer was observed on PDCs pyrolyzed at 1000°C, while less cells were visible on PDCs pyrolyzed at 1200°C. Quantification of the cells' metabolic activity (**Figure 3.15b**) did not show significant differences between the conditions at day 1, reflecting the observation in the images. At day 4, the metabolic activity of cells on PDCs pyrolyzed at 1200°C showed slightly lower levels than cells grown on substrates pyrolyzed at 1000°C, but differences are not statistically significant. While this indicates that elevated pyrolysis temperatures might alter surface properties, which in turn affects cell attachment and proliferation, further research would be needed. Importantly however, the increased carbon concentrations to improve



Figure 3.15: Cytocompatibility of four different SiCN sample types: a) representative confocal images of cells on the surface of PDCs, stained for actin (green) and nucleus (blue) at day 1 and 4, scale bar: 100  $\mu$ m; b) NHDF on the surface of PDCs with metabolic activity quantified by an MTS assay (N=3).

the mechanical and electrical properties do not affect cell attachment nor their metabolic activity, which is in agreement with previous reports where DVB was used in a similar way [57]. Collectively, the data presented here shows the cytocompatibility and thus the suitability of DVB as an additive that improves the mechanical and electrical properties of PDCs for biomedical applications.

# 3.4 Summary and conclusion

This chapter described a facilitated process for the high-yield fabrication of very dense poly(methylvinylsilazane)-derived silicon carbonitride (SiCN). Due to the thermal initiator dicumyl peroxide, the preceramic polymer was thermally cured at a moderate temperature of 200°C at ambient pressure in only 30 min. The addition of the carbon-filler divinylbenzene modified the composition of the PDC obtained after pyrolysis, i.e., the free carbon content in the range 15–25 wt.%, which was verified by means of elemental analysis. Crosslinking behavior was monitored by FTIR spectroscopy and ceramic yields up to 79% were observed in TGA measurements. As analyzed by SEM and  $\mu$ -tomography, defect-free samples were fabricated, whose structure, mechanical, and electrical behavior have been investigated. DVB additions of 20 and 40 wt.% were found to be beneficial for achieving ceramics with very high flexural strength up to 1.65 GPa and maintained cytocompatibility. Metallic-like electrical conductivity up to 0.4 S cm<sup>-1</sup> was observed in 40% DVB materials due to the increased free carbon content. In combination with these ceramics' versatile formability and demonstrated cytocompatibility, carbon-rich SiCN is of interest for implant applications, particularly heart pacemaker electrodes.

# **4** Property-contrast ceramics

# 4.1 Introduction

The previous chapter has demonstrated the liquid PDC route's ability to modify the resulting SiCN's composition and properties by the addition of the carbon-filler DVB. Instead of manufacturing separate parts with dissimilar carbon concentration, this chapter explores the possibility to create those composition and property contrasts within single monolithic parts with different geometries. Spatially defined property contrasts, e.g. in electrical conductivity, in functionally graded ceramic parts entirely composed of SiCN would allow for an integration of functionality such as the example of the plate with electrical feedthroughs shown in Figure 1.1.

There are three main material states along the PDC route which are the liquid (L) organic preceramic polymer (PCP), the solidified (infusible) still organic green body (GB), and the solid inorganic polymer-derived ceramic (PDC). They are typically transformed from one state to the following by thermal treatment, in the present system at T≈200°C and T≥800°C for the first and second transformation, respectively. Based on these three states, there are six theoretical combination options for joining which are illustrated in Figure 4.1a-f. In addition to these direct combination options, there are three more possible cases (Figure 4.1g-i), where the liquid PCP would serve as an adhesive to bond two solid GB / PDC parts. Two of them, both bonding two parts of the same material, have been reported in the literature and were introduced in section 1.3 (Figure 1.8): the polymer-based bonding of GBs (g) [41, 79, 124] and the bonding of SiC parts with a polysiloxane (i) [119]. Compared to the few reports on PDC related bonding, direct joining of dissimilar PCP states has barely been researched. Thermal crosslinking and consolidation of the first component before contacting the second part (Figure 4.1b: GB–PCP/L) is the straightforward approach because of a defined interface geometry and conformal contacting. Therefore, the majority of the following experiments will be based on this GB-L combination. High concentrations (30-60 wt.%) of the carbon-filler

divinylbenzene (DVB) will be added to one of the two PCP formulations for the purpose of achieving the composition and property contrasts in the PDC obtained after pyrolysis. The casting order and the extent of the thermal pre-curing of the first component will be varied in order to evaluate the influence on the interface nature. Secondly, the PCP formulations with a high contrast in DVB loading will also be directly combined in liquid state (**Figure 4.1a**: PCP–PCP / L–L) and the resulting composition gradient will be compared to the different results from the GB–L case. The remaining direct combination options (**Figure 4.1c-f**) would require significantly more preparation and processing efforts while the chances of successful joining would be low. Therefore, they have not been included to the scope of this work.



Figure 4.1: Theoretical combination options of the three material states along the PDC processing route: a-f) direct combination liquid-liquid, liquid-solid, or solid-solid; g-i) indirect with liquid PCP "gluing" of solids. The blue background highlights the discussed cases a,b.

# 4.2 Materials and methods

## 4.2.1 Synthesis of heterogeneous SiCN ceramics

All heterogeneous ceramic samples presented in this chapter were fabricated by molding in CNC-machined PTFE. For successful green part mold release, the same requirements on mold surface finish as introduced in Section 2.2 apply, especially important for larger and complex designs such as the bi-feedthrough (BFT) plate. For standard heterogeneous samples, dissimilar PCP formulations were sequentially cast, normally with an intermediate thermal (pre-)curing step (Figure 4.1b). The mold geometry for the first type of standard samples is shown in **Figure 4.2a**. These molds consist of two cylindrical layers with diameters of 6 and 8 mm and a depth of 500  $\mu$ m each. Eight of them are combined in one mold array. Similar to the casting process of homogeneous disc samples described in Section 2.2 and Section 3.2, one or several of these PTFE mold arrays were placed on the level hotplate inside the Ar



Figure 4.2: PTFE molds for joining of dissimilar PCPs: a) Eight bilayer disc molds with 6 and 8 mm diameter and 500  $\mu$ m layer height; b) eight rectangular bar molds of 500  $\mu$ m depth and lateral dimensions ranging  $2 \times 8 - 8 \times 26$  mm<sup>2</sup>.

glovebox. The fabrication process is outlined in Figure 4.3a. Starting with the DVB-filled PCP formulation (3% DCP, typically 60% DVB), 19.8  $\mu$ L (=140%<sup>1</sup> of the layer's volume) were pipetted into each molds' lower layer and thermally cured, typically during 15 min at 100°C. When cooled down to RT,  $30.2 \,\mu\text{L}$  (=120% of the upper layer's volume) of the DVB-unfilled PCP were cast in each mold and jointly crosslinked during 30 min at 200°C. Nomenclature of the heterogeneous samples is based on the casting order, these samples will therefore be referred to as DVB60|00 bilayer in the following. In case of the opposite casting order (DVB00|60), 19.8 µL of the DVB-free PCP were cast into the molds' lower layers and thermally cured during 30 min at 200°C. The DVB containing PCP (typically 60%) was then pipetted on top (25.1 µL  $\equiv 100\%^1$  of the layer's volume) and cured in a 3-step sequence of 10 min each at 100, 150, and 200°C. Dedicated to microtomography, one set of thinner DVB30|00 bilayer samples was fabricated in single-layer molds with 8 mm diameter and 500 µm depth by a sequence of 25.1 µL DVB30 PCP casting, thermal pre-curing (10 min at 200°C), 12.6 µL DVB00 casting, and joint 30 min at 200°C curing. For demolding, molds were generally flipped upside down and gently tapped. PTFE molds were immersed in acetone, brushed, rinsed with IPA, and dried before reuse.

The second standard sample type are rectangular bars with aspect ratios of  $3.25 \le AR \le 4$  in which the dissimilar PCPs were arranged laterally. Eight molds are combined in one array in PTFE, shown in **Figure 4.2b**. They are 500 µm deep and have six different sizes with lateral dimensions of 8×2, 9.5×2.5, 11×3, 14×4, 20×6 and 26×8 mm<sup>2</sup>, each with corner radii of 1 mm. As illustrated in the **Figure 4.3B**, the first PCP formulation was pipetted into one end of the cavity. For DVB40|00 order, 77.7 µL ( $\equiv$ 150% of the mold's half volume) of DVB-filled PCP were pipetted in the largest type and the equivalents of 140% into the smaller ones (41.7–5.3 µL). Volumes of 68.4–4.09 µL of the DVB-free PCP were cast into the molds' other half. Information

<sup>&</sup>lt;sup>1</sup>PCP overfilling compensates for partial volatilization during thermal crosslinking and contributes to a more planar interface in DVB60|00 casting order. In the opposite DVB00|60 casting order, it was not done in case of the upper layer to prevent DVB60 overflow.



**Figure 4.3:** Process flows for basic composition-contrast ceramic sample fabrication: A) bilayer disc arrangement; B) laterally arranged bars. a) casting of first PCP formulation; b) extensive or mild thermal crosslinking to GB state (pre-curing); c) casting of second PCP; d) final joint thermal crosslinking to GB state; e) GB release from the mold; f) composition-contrast PDC sample obtained after pyrolysis.

on the intermediate and final thermal curing processing is provided in **Table 4.1**, line standard (Std) / type 0 (T0). Inverse casting sequence (DVB00|40) was performed with volumes of 120–140% of the molds' half volume for DVB-free PCP and 120% for DVB40. Liquid polymers were thermally cured right after casting according to the parameters in Table 4.1, type 1. In addition to these two cases where the firstly cast PCP was extensively crosslinked and solidified (GB) before contacting with the dissimilar liquid (L) PCP, five more sample types in lateral bar geometry were fabricated with decreasing degree of pre-curing. For types 2–4, DVB00 PCP was cast first and pre-cured thermally for 5 min at 200°C, 1 min and 200°C, or 1 min at 175°C. 40% DVB PCP was added and joint curing performed in the 3-step (3S) 100–200°C process. Finally, both PCP formulations were also combined in liquid states with no intermediate pre-curing step. One was cast right after the other in both orders (types 5 and 6).

Table 4.1: Nomenclature and fabrication parameters of laterally heterogeneous ceramic bar series with extensive (T0,1), partial (T2–4), or no (T5,6) pre-curing. *3S* abbreviates the standard 3-step curing sequence established for DVB-filled precursors (10 min  $@ 100^{\circ}C + 10 min @ 150^{\circ}C + 10 min @ 200^{\circ}C)$ .

Туре	State	1 <sup>st</sup> casting	Thermal pre-curing	2 <sup>nd</sup> casting	Final curing
Std (0)	GB-L	DVB40	35	DVB00	30 min @ 200°C
1	GB-L	DVB00	30 min @ 200°C	DVB40	3S
2	GB-L	DVB00	5 min @ 200°C	DVB40	38
3	GB-L	DVB00	1 min @ 200°C	DVB40	3S
4	L/GB-L	DVB00	1 min @ 175°C	DVB40	3S
5	L-L	DVB40	none	DVB00	20 min @ 150°C + 10 min @ 200°C
6	L-L	DVB00	none	DVB40	20 min @ 150°C + 10 min @ 200°C

Composition-contrast ceramic BFT plates were fabricated using two types of dedicated CNCmachined PTFE molds which are shown in **Figure 4.4**. The first one (**a**) consists of a 1 mm deep, 25 mm diameter circular matrix cavity with two central 50  $\mu$ m recessed areas with circular geometry, 5 mm diameter each, and 5 mm spacing. The second BFT PTFE mold geometry has a square matrix of 20×20 mm<sup>2</sup> with a depth of 1 mm and corner radii of 2 mm. The two 100  $\mu$ m recessed circular areas of 4 mm diameter and 4 mm spacing either serve as a positioning aid



for the 4 mm diameter placeholder PTFE rods (**Figure 4.4b**) or for placing the liquid inset PCP (**Figure 4.4c**).

**Figure 4.4: PTFE molds for BFT fabrication**: **a)** Cylindrical matrix of 25 mm diameter and 1 mm depth with two 5 mm spaced, 50  $\mu$ m recessed circular areas of 5 mm diameter for feedthrough droplet placement; **b)** square matrix of 1 mm depth, 20 mm width, and 2 mm corner radius with two placeholder PTFE rods of 4 mm diameter for cavity creation; **c)** same square mold as b) but without rods, revealing the two 4 mm spaced, 100  $\mu$ m recessed circular areas of 4 mm diameter.

With these molds, two main bi-material casting strategies, both based on the GB–L combination, were applied. Firstly, the square mold with the placeholder rods positioned on the recessed areas was placed onto the level hotplate inside the Ar glovebox. In this placeholder approach schematically summarized in **Figure 4.5A**, the liquid matrix PCP formulation (mostly DVB00 but also DVB40/60) was pipetted into the mold (around the rods) and thermally crosslinked following the typical temperature sequences for DVB-filled or unfilled precursors. The rods then needed to be extracted without damaging or demolding the cured matrix green part. Afterwards, the two cavities were filled with the dissimilar PCP, thermally cured, and the part finally demolded.



Figure 4.5: Process flows for BFT ceramic plate fabrication: A) placeholder and cavity filling approach: a) positioning of PTFE rods, b) casting of matrix PCP formulation, c) rod removal after matrix crosslinking, d) casting of the inset PCP into the cavities, e) removal of the crosslinked bi-material GB from the mold, f) BFT-PDC plate obtained after pyrolysis; B) inset droplet approach: a) inset PCP formulation droplet placing, b) thermal crosslinking of insets, c) casting of the matrix PCP, d) matrix filling height slightly lower than droplet peak, e) removal of the crosslinked bi-material GB from the mold, f) BFT-PDC plate obtained after pyrolysis.

Alternatively, one large droplet of the PCP (typically DVB40/60 but also DVB00) was placed onto each recessed area as illustrated in **Figure 4.5B**. Volumes of 18  $\mu$ L were chosen, in order to achieve the maximum material height with no or minimal lateral spreading exceeding the predefined area. To render the PCP droplets stable, they were thermally pre-cured before the dissimilar matrix PCP (mostly DVB00) was cast around. The matrix volume, e.g. 275  $\mu$ L for the square mold, was selected to not bury the green parts but leave the insets' top exposed. After joint thermal curing and thermosetting of the matrix, BFT green parts were released from the mold by upside down tapping at elevated temperatures around 100°C.

The composition-contrast green parts were placed in Al<sub>2</sub>O<sub>3</sub> crucibles for Ar atmosphere pyrolysis. Most bilayer samples were processed with the homogeneous discs (Figure 2.5) at all four pyrolysis temperatures of 800–1400°C and standard heating and cooling rates of 100 K/h. The seven types of laterally heterogeneous bars and BFT plates were pyrolyzed together at 1000 and 1400°C only as shown in **Figure 4.6a,c**. In this case, pyrolysis parameters were optimized with a reduced heating rate of 60 K/h in the temperature range of 300–800°C (**Figure 3.1**: dotted lines), resulting in low scrap rates of 0% for 1000°C and 14% for 1400°C pyrolysis (**Figure 4.6b,d**).



**Figure 4.6:** Pyrolysis of laterally heterogeneous bars and BFT plates: Photos of samples placed in Al<sub>2</sub>O<sub>3</sub> crucibles before and after pyrolysis. **a)** GBs for 1000°C pyrolysis, grouped into the 7 types of bars (Table 4.1) plus DVB40|00 BFTs, grouping and positioning are maintained for b-d; **b)** PDCs after 1000°C pyrolysis, no sample was damaged during polymer-to-ceramic transformation; **c)** GBs for 1400°C pyrolysis; **d)** PDCs after 1400°C pyrolysis, 14% of samples broke.

# 4.2.2 Characterization

The cross sections of some samples were prepared by means of cleaving or diamond-wire sawing. Part inspection and imaging were performed by OM (M80, Leica, Germany; Eclipse L200, Nikon, Japan) and SEM (Merlin, Zeiss, Germany). The latter was also used for EDX

analysis. Electrical conductivity was measured in the 2-probe bulk approach introduced in Section 3.2, using the same silver epoxy contact pads. Thermal imaging was performed with a PI 640i infrared (IR) camera (Optris, Germany).

Preparation for TEM analysis of a DVB60|00 1400°C pyrolyzed bilayer sample (intermediate curing: 10 min at 100°C, 10 min at 150°C), involving 1 µm carbon sputtering and gallium (Ga+) focused ion beam (FIB) lamella cutting, was performed with a NVision 40 (Zeiss, Germany). This process is illustrated in the SEM images in **Figure 4.7**. TEM, high-resolution transmission electron microscopy (HRTEM), and EDX were then conducted on a Tecnai Osiris (FEI, United States).



Figure 4.7: SEM images of (Ga+) FIB lamella cutting for TEM investigations of a 1400°C pyrolyzed DVB60|00 bilayer sample, interface indicated in red: a) interface region with clear contrast; b) sputtering of support carbon (C) bar perpendicular to the interface line; c) trench cut around the lamella; d) lamella after transfer onto Cu grid; e) lamella after final FIB thinning.

Several bilayer and laterally heterogeneous SiCN samples were analyzed by means of X-ray absorption contrast tomographic microscopy. To achieve sufficient phase contrast, specimen dimensions needed to be in the range of few hundreds of micrometers in two dimensions. For this reason, bilayer samples were typically cleaved into small pieces. In case of the lateral composition-gradient bar samples, the region of interest (ROI), a sharp angle triangular center piece, was cut out of each sample (sized ~8.2×2.2 mm<sup>2</sup> resulting from 11×3 mm<sup>2</sup> molds) by diamond wire sawing (**Figure 4.8a**). Microtomography was performed at Paul Scherrer Institute (PSI) Swiss Light Source (SLS) TOmographic Microscopy and Coherent rAdiology experimentTs (TOMCAT) beamline [197] which is shown in **Figure 4.8b**. Typically, the vertically mounted PDC sample was placed into the 15 or 20 keV X-ray beam and rotated by 180° around its long axis. Data was acquired with a 100 µm thick LuAG:Ce scintillator, a

 $10 \times$  or  $20 \times$  microscope lens, and an sCMOS camera. These configurations result in a field of view of  $1.66 \times 1.4 \text{ mm}^2$  or  $830 \times 700 \mu \text{m}^2$  and pixel sizes of 0.65 or  $0.325 \mu \text{m}$  for  $10 \times$  or  $20 \times$ magnification, respectively. A Gridrec algorithm reconstructed tomographic volumes from the X-ray projections which were then visualized and segmented using Avizo software (Thermo Fischer, United States). In the case of T4, three adjacent scans were stitched.



**Figure 4.8: Synchrotron microtomography scanning of laterally heterogeneous bars**: **a)** diamond-wire saw cutting of samples' ROI center piece with 3 cutting lines indicated; **b)** PSI SLS TOMCAT setup.

# 4.3 Results and discussion

# 4.3.1 Carbon-contrast SiCN

Monolithic silicon carbonitride (SiCN) samples with an integrated carbon-contrast have been manufactured by sequential casting of DVB-filled and unfilled preceramic polymer formulations. Therefore, the experience from the homogeneous PDC fabrication and characterization described in Chapter 3 served as the basis for the work described in the following section. The 6|8 mm bilayer arrangement allows for convenient casting and its circular step helps to locate the interface. On these grounds, it was chosen as the main specimen geometry for the investigation of the heterogeneous PDCs.

**Figure 4.9** shows a set of DVB60|00 and DVB00|60 bilayer green parts and the corresponding Ccontrast PDC parts they converted to after 1400°C pyrolysis under argon atmosphere. In order to obtain visually intact GBs and finally defect-free bilayer SiCN, a number of aspects needed to be considered during processing. Firstly, the PCPs' partial volatilization during thermal crosslinking was partially compensated by casting PCP volumes corresponding to 120–140% of the molds' volumes. This approach reduced the effect of inhomogeneous layer thickness formation, the obtained surfaces and interfaces exhibited less distinct curvature. Secondly, to achieve accurate material arrangement, the lower layer PCP should not shrink laterally and detach from the mold during thermal pre-curing. Any potential gap forming between the pre-cured GB and PTFE mold material would be filled with the second dissimilar PCP formulation pipetted on top in liquid state. Hence, the thermal treatment of DVB containing PCPs cast as lower layer was reduced (typically to 15 min at 100°C) because it is more prone to shrinkage than DVB free PCP. In this way, the material was just sufficiently solidified to conserve its shape. The precursor system and final (entirely pressureless) joint curing at 200°C, established before, then successfully yielded bubble- and crack-free bilayer green parts with good demolding behavior. DVB00 lower layers were pre-cured in the normal manner (30 min at 200°C), resulting in a partial DVB60 thin film coverage of the lower edges (visible in **Figure 4.9c**). Lastly, due to the differing shrinkage in the two layers coming along with the DVB-filling contrast, reduction of heating and cooling rates during pyrolysis became necessary to reduce thermal stress. While the vast majority of bilayer samples broke when pyrolyzed with rates of 300 K/h, high yields were observed for processing with a rate of 100 K/h, even in case of 1400°C peak temperature.



**Figure 4.9: OM images of bilayer samples with DVB-contrast**, bottom view, representation to scale for size and shrinkage comparison: **a)** 6/8 mm DVB60/00 GB; **b)** DVB60/00 PDC, 1400°C pyrolyzed; **c)** DVB00/60 GB; **d)** DVB00/60 PDC, 1400°C pyrolyzed.

While the visual contrast of the colorless transparent DVB-free and the yellow opaque DVB-filled material is clear in the green state, the all-black character of the final SiCN, independent of the carbon-filling level, makes the layer and interface visualization and characterization challenging. Due to the ceramics' strong but brittle character, cleaving of bilayer samples has yielded pieces of undefined shapes and uneven sidewalls. An example which was pyrolyzed at 1400°C (100 K/h) is presented in **Figure 4.10a-c**. No clear cleavage could be initiated by scratching one sample side with a sharp diamond tip. Instead, fractured pieces exhibited steps and facets rendering them challenging for optical inspection. The examples of an OM and SEM image in **Figure 4.10b,c** allowed for a distinction of the DVB30 and DVB00 layers under certain imaging settings but were not suited for measurements and analysis.

The cross-sectional microscopy inspection of sample pieces which were obtained broken after pyrolysis with high heating and cooling rates of 300 K/h revealed more even sidewalls which facilitated imaging and focusing. The OM images in **Figure 4.10d-f** showed severe



Figure 4.10: Cross-sectional microscopy of cleaved and broken 1400°C pyrolyzed bilayer samples with DVB-contrast: a) cleaved 6|8 mm DVB30|00 PDC; b) OM image of an unevenly cleaved cross section; c) low-magnification cross-sectional SEM of the same cleaved sample piece as in b, interface highlighted; d) 6|8 mm DVB30|00 PDC which split during pyrolysis; e) cross-sectional OM of the left piece in d; f) cross-sectional OM of a thin DVB30|00 bilayer PDC; g) cross-sectional OM of a cleaved DVB60|00 bilayer PDC, interface highlighted.

cracking but allowed for better focusing. Under strong illumination, false coloring appeared which differed for the DVB-filled and unfilled layers. Furthermore, DVB-free fracture surfaces showed to be smoother and the cracking behavior seemed to be influenced by the composition as well. The interface line is curved towards the layer's edges due to a meniscus forming at the mold sidewall (**Figure 4.10e**) but runs fairly horizontal towards the sample center region (**Figure 4.10f**). In both examples, the interface was very sharp and the transition length below 3 µm, close to the limit of resolution. In another case, cleaving of a DVB60|00 bilayer sample has resulted in an even fracture surface (**Figure 4.10g**) but could not be pictured well by OM.

To obtain clearly defined vertical profiles, some bilayer SiCN samples were cut by means of diamond wire sawing. The ultrasonically cleaned parts were imaged by SEM without further preparation. The example in **Figure 4.11** shows the cross section of a 1400°C pyrolyzed DVB60|00 bilayer. The layer steps in **Figure 4.11a,c** served as reference points for the interface location. However, independently of the electron beam parameters and detector choice, no layered phase contrast could be identified due to the cutting-induced sidewall roughness. The intact condition and monolithic character of the sample were indicated by the absence of signs of pore formation, cracking, or delamination.

The geometry of laterally arranged heterogeneous bars was introduced to eliminate the need for sample cross sectioning and polishing. With areas of dissimilar composition next to each other, the interface became directly accessible and characterization of the DVB-filled and unfilled regions was facilitated by exhibiting larger regions allowing for localized measurements.



Figure 4.11: SEM cross-sectional images of a 1400°C pyrolyzed DVB60|00 bilayer SiCN sample, cut by diamond-wire sawing, unpolished, uncoated, 45° tilt, mixed in-lens and secondary electron detector signals to accentuate density contrast and topography features: a) left step; b) center; c) right step. The interface between the 60% DVB-filled and the unfilled layer is not visible. Cross section exhibits roughness and breakouts from the sawing but shows neither cracks nor pores.

Based on the findings on the effectiveness of DVB PCP filling at concentrations of 40 and 60% described in Chapter 3, the lower DVB40 composition was chosen to contrast with unfilled DVB00 precursor.

A comprehensive overview of the manufactured samples is provided in Figure 4.12. The PCP formulation of one composition was cast into one half of the rectangular PTFE mold, pre-cured to different extents, joint with the dissimilar precursor in liquid state, and commonly thermally cured (Figure 4.3B). That way, green parts with a 0/40% DVB-contrast have been obtained free of pores or cracks, in rectangular geometry ranging from 8×2 to 26×8 mm<sup>2</sup> and a thickness of approximately 500 µm. Again, thanks to the yellow opaque and colorless transparent appearance of filled and unfilled PCPs, respectively, the composition-contrast was clearly visible in the green state (Figure 4.12a). Therefore, a first visual impression of the influence of casting and thermal processing on the interface character could be gained. Sharp interfaces were achieved by extensive pre-curing of the PCP cast at first which was the case for types 0 (DVB40|00) and 1 (DVB00|40) (refer to Table 4.1 for processing details). When reducing the degree of pre-curing by shortening the thermal treatment time and lowering the temperature (as it was the case for T2–4), material transitions started to exhibit a gradient character. Finally, liquid-liquid joining of the dissimilar precursors (T5: DVB40|00), T6: DVB00|40) with no intermediate curing but immediate joint thermal crosslinking was performed. This approach yielded long range gradients but no complete intermixing.

The pyrolysis of the laterally arranged heterogeneous bars was conducted at peak temperatures of 1000 and 1400°C with a further reduced heating rate. Examination of the involved DVB00 and DVB40 precursor formulations' TGA (**Figure 3.7**) and derivative thermogravimetry (DTG) (**Figure A.12**) showed highest mass loss rates in the temperature range of 300–800°C. Therefore, the heating rate was reduced from 100 K/h down to 60 K/h in this critical range to further reduce the risk of cracking. Thanks to an accelerated heating from RT to 300°C and maintained heating and cooling rates of 100 K/h for the rest of the process, overall processing time of this



Figure 4.12: DVB40|00 and DVB00|40 laterally heterogeneous bars of type 0–6 (Table 4.1): a) top and bottom view on fully cured green parts in glovebox; b) view on top side after  $1000^{\circ}$ C polymer-to-ceramic transformation; c) view on top side after  $1400^{\circ}$ C pyrolysis; d) cartesian top view on  $1000^{\circ}$ C pyrolyzed T5 samples of all six sizes; e) view on bottom sides of  $1400^{\circ}$ C pyrolyzed samples of T0 and T5; f) OM images of  $1000^{\circ}$ C pyrolyzed T2 and T4 samples diamond wire sawn center pieces for microtomography; g) OM image of a T0 sample bottom side; h) SEM image of the same T0 sample's center region; i) example of electrical conductivity transition measurements of the dissimilar regions.

optimized cycle increased by 1 h only (Figure 3.1). Resulting samples in PDC state shown in **Figure 4.12b-d** were mostly intact with minor bending in case of T0–T4 larger geometries.

The SiCN's characteristic glossy and mat top surfaces for DVB00 and DVB 40 composition, respectively, allow for a material distinction and approximate evaluation of the transition gradient. Regardless of the pyrolysis temperature, sharp contrasts were obtained for sample types 0–3 whereas a graded change occurred in case of T4–6. Interestingly, dissimilar shrinkage of the two compositions did not cause any failure in case of 1000°C pyrolysis. Particularly in type 2 (well visible for the larger geometries), kinks have formed at the interface's ends due to width reductions of 25.1% in the DVB00 and 27.1% in the DVB40 part. The higher conversion temperature of 1400°C goes along with a higher difference in shrinkage, which is why some samples partially or fully cracked (e.g. T2 in Figure 4.12c or the bottom side of large T0 sample in **Figure 4.12e**).

The visibility of the interface lines on the samples' surfaces was beneficial for further investigations. Sharp tip (~15°) triangular center pieces were cut from four different sample types by a diamond wire saw (**Figure 4.12f**), aiming to position the interface centrally. The actual interface shape is curved in two dimensions. Firstly, in top view it formed a v/u-shape for T0-T4 due to the sidewall wetting of the first precursor. This could be observed clearer on the samples' bottom surfaces (**Figure 4.12e,g,h**) where the texture was homogeneously replicating the mold bottom (CNC machining traces), irrespective of the DVB filling concentration. The second curvature (side-face) resulted from the shape which the first cast liquid PCP formed with respect to the mold bottom, refer to Figure 4.3B. Microtomography of the triangular specimens of four different types was later performed to reconstruct the interface in 3D.

Sample arrangement and size allowed for electrical conductivity measurements of the dissimilar composition regions within the same monolithic sample in a transition approach. In a manner analogous to the measurement of the homogeneous disc samples described in Section 3.2, conductive silver epoxy contact pads were applied at selected samples' both ends on top and bottom side. The measurement setup with two polished copper probes is shown in **Figure 4.12i**. Resistance values were derived from linear IV-curves and approximate conductivity calculated using the local sample thickness and Ag contact area. Obtained values are reported in **Table 4.2**.

With only a few sample types measured and one sample per type only, no comprehensive conclusions can be drawn from this data. However, some observations should be pointed out. In comparison to the results on the respective homogeneous materials measured by the same method (repeated here from Table A.2), obtained electrical conductivity values were generally higher in the laterally heterogeneous bars. Slight deviations could result from the simplifying assumptions in the calculations, but the present difference must have further reasons. This could for instance be the slower heating during pyrolysis possibly leading to less

Туре	T <sub>pyro</sub> (°C)	σ <sub>DVB40</sub> (S/cm)	$\sigma_{ m DVB00}$ (S/cm)	$rac{\sigma_{DVB40}}{\sigma_{DVB00}}$
0	1400	0.20	$2.3 \cdot 10^{-3}$	84
1	1400	0.32	$4.9 \cdot 10^{-2}$	6.5
5	1400	0.15	$2.4 \cdot 10^{-2}$	6.3
5	1000	$2.6 \cdot 10^{-3}$	$3.1 \cdot 10^{-4}$	8.5
homogeneous homogeneous	1400 1000	$2.9 \cdot 10^{-3} \\ 1.4 \cdot 10^{-5}$	$4.3 \cdot 10^{-4} \\ 2.6 \cdot 10^{-11}$	$6.6 \\ 5.3 \cdot 10^5$

Table 4.2: Electrical conductivity of DVB40-filled and unfilled SiCN and their ratio in composition-contrast monolithic bar samples, values averaged from two measurements of the identical sample. For comparison, values of respective homogeneous samples from Table A.2 are repeated here.

volatilization of C-containing species<sup>1</sup> or promoted C ordering. In all four cases, significant contrasts in electrical conductivity were observed across the sample length, confirming the functionally graded character achieved by the presented method. When comparing DVB40 and DVB00 material processed at the same temperature, the conductivity ratios (6.5 and 6.3) in case of 1400°C pyrolyzed heterogeneous T1 and T5 samples were nearly identical to the ratio of the corresponding homogeneous samples (6.6). This relation hints that the joining of the two dissimilar precursors did not result in significant influence on each other's composition which would cause averaging of composition and conductivity across the entire sample in these cases. In contrast, for 1000°C pyrolyzed T5, the ratio of 8.5 is much lower than the one from homogeneous material  $(5.3 \cdot 10^5)$ , indicating the existence of such a joining influence despite being based on the same type of green part as the previous case pyrolyzed at 1400°C. The highest electrical conductivity contrast within monolithic laterally graded SiCN bars was observed for 1400°C pyrolyzed type 0, where the filled part was 84 times more conducting than the unfilled opposite end of the sample. The discrepancy compared to the respective homogeneous ceramics could have the same reasons as described above. For possible applications of carbon-contrast monolithic SiCN, type 0 (DVB-filled PCP cast and extensively crosslinked at first) and 1400°C pyrolysis appear to be the best suited approach.

Based on the more vertical character of the interface and thanks to its visibility in some cases (e.g. Figure 4.12g,h), the bottom side of the laterally heterogeneous bars was expected to be well suited for further composition transition analysis by means of EDX. Several samples were coated with a conductive gold (Au) layer (10 nm) and investigated by combined SEM and EDX. Line scans perpendicular to the interface were recorded at different lengths and acquisition times. EDX mapping was performed with differently sized squared regions cover-

<sup>&</sup>lt;sup>1</sup>However, overall mass loss of DVB40|00 BFT plates processed at 1400°C (60 K/h) together with the laterally heterogeneous bars was 27%, in line with 26% and 29% for 1400°C (100 K/h) pyrolyzed homogeneous 0% and 40% DVB disc samples.

ing the interface. However, neither technique could resolve significant contrasts of carbon concentration and quantify the concentration gradient this way. Explanations could be the small carbon concentration difference (13 at.% or less<sup>1</sup>) and the light atomic character of the element rendering it more challenging for EDX detection than heavier elements. Furthermore, carbon may generally deposit on surfaces in the SEM chamber, for instance originating from electron beam impact on the conductive tape or other organic material. The difference in concentration of the other contained elements such as the heavier silicon is much smaller (~3 at.%) and therefore not serving for gradient quantification either. EDX signals averaged from large areas of the sample's both ends (**Figure 4.13a,b**) exhibited a significant difference between DVB40-filled and unfilled regions. The spectra in **Figure 4.13c** proof a significantly higher carbon concentration in the left DVB40 region. The Si signal was slightly reduced and the occurrence of an oxygen peak suggests the formation of a thin surface oxide layer. Without a suited standard, no reliable quantification of the respective concentrations was possible.



**Figure 4.13: EDX analysis of a laterally heterogeneous bar** (T0, 1000°C-pyrolyzed, bottom side, Au coated): **a)** SEM image of DVB40 end with marked scanning area; **b)** SEM image of DVB00 end with marked scanning area; **c)** EDX spectra of both marked areas exhibiting a significant difference in carbon signal intensity.

In order to obtain comprehensive compositional and microstructure information at much higher resolution, one prototype<sup>2</sup> DVB60|00 bilayer sample (1400°C pyrolyzed) was prepared for SEM, EDX, and TEM. The sample preparation process was illustrated previously in Figure 4.7. On the polished surface of a cleaved sample piece (Figure 4.7a), a material contrast was clearly visible in SEM and the interface appeared sharp and straight. A first EDX analysis before lamella cutting gave atomic concentration ratios  $c_C:c_{Si}$  changing from 1:1 on the DVB60-filled to 2:3 on the unfilled side. Due to a non-perpendicular orientation of the surface with respect to the interface into the volume, a diagonal interface line was then obtained on the lamella cut by FIB. Even after final thinning down, it is still visible in the SEM image in **Figure 4.14a**. Thanks to a more sensitive EDX detector and a higher DVB-filling contrast

<sup>&</sup>lt;sup>1</sup>In EA of respective homogeneous material (Table 3.2), atomic carbon concentrations were 27.0 and 40.0% for DVB00 and DVB40 SiCN, respectively.

<sup>&</sup>lt;sup>2</sup>The lower DVB60 layer was pre-cured during 10 min at 100°C and 10 min at 150°C instead of the typical 15 min at 100°C.

(60|00 instead of 40|00), EDX mapping (**Figure 4.14b**) was able to visualize a significant difference of carbon concentration between the (upper) filled and (lower) unfilled SiCN in this case. An EDX line scan was performed perpendicular to the interface. The carbon and silicon concentration profiles shown in **Figure 4.14c** allow for an approximate quantification of the compositional transition length which is approximately 0.5 µm in this case with extended lower layer pre-curing.



**Figure 4.14: EDX analysis of DVB60**|00 bilayer sample FIB-cut into lamella: a) SEM image with interface position highlighted in red; b) C and Si EDX map with line scan positioning highlighted in green, perpendicular to interface line; c) line scan EDX data showing a transition length of ~500 nm.

The same DVB60|00-contrast lamella was then imaged by TEM. Several HRTEM images were recorded in the interface region but within the field of view of  $100 \times 65 \text{ nm}^2$ , no obvious change or trend in microstructure could be observed in single images. Two examples of HRTEM images from homogeneous regions are shown in Figure 4.15a,b. They originate from locations approximately 2.5 µm away from the interface and exhibit features typical for silicon carbonitride processed at high temperatures of 1400°C. Both the unfilled (Figure 4.15a) and DVB60-filled (Figure 4.15b) material contain dark crystallites with an interplanar distance of 0.25  $\mu$ m, corresponding to  $\beta$ -SiC's (111) d-spacing [73]. The planes of the  $\beta$ -SiC cause the two diffraction rings with the relative high intensity in the selected area electron diffraction (SAED) patterns<sup>1</sup> in Figure 4.15c,d [75]. Both HRTEM images also show ribbon-like features with interlayer spacings ranging from 0.34 up to 0.42 nm. These features are turbostratic graphitic phases, also called basic structural units (BSUs). Comparing their occurrence and structure between DVB00 and DVB60 SiCN, there are noticeably more and longer BSUs in the DVB-filled material, which furthermore consist of more stacked layers. The selective addition of DVB as a carbon-filler to the PCP therefore effectively altered the obtained SiCN's composition and microstructure, with spatial control in a monolithic sample. While the two SAED patterns in Figure 4.15c,d appear similar, the subtraction of both (Figure 4.15e) emphasizes the microstructural differences. Primarily, rings at  $\sim$ 4,  $\sim$ 6.5, and  $\sim$ 7.5 nm<sup>-1</sup> result, caused by the  $\beta$ -SiC's (111), (220), and (311) planes [75], indicating the presence of more  $\beta$ -SiC crystallites in the DVB-filled PDC.

<sup>&</sup>lt;sup>1</sup>recorded in thicker lamella regions in order not to be impaired by possible beam amorphization effects

#### 4.3 Results and discussion



**Figure 4.15: HRTEM analysis of 1400°C pyrolyzed DVB60**|00 bilayer lamella: a) characteristic TEM image of DVB00 region with SiC precipitate and few C BSUs highlighted in green and yellow, respectively; b) characteristic TEM image of DVB60 region with SiC precipitates and overall more C BSUs; c,d) SAED patterns of DVB00 and DVB60 region; e) subtraction of d-c highlighting the differences in periodic small features.

#### 3D interface analysis by tomographic microscopy

In contrast to the previous 2D investigations of surfaces and cross sections of the heterogeneous ceramics, microtomography allows for 3D reconstruction of entire volumes. However, a laboratory scale-tool like the PIXE which was used for the scanning of the homogeneous PDC discs in Chapter 3, does not allow for resolving a phase contrast between the DVB-filled and unfilled ceramic regions. On the contrary, synchrotron radiation's monochromatic character and high photon flux reduce noise and increase the contrast. The high brilliance improves the resolution to feature sizes of ~1  $\mu$ m. In three beamtime sessions, a total of eight compositioncontrast samples was analyzed at PSI SLS TOMCAT beamline. The results will be presented and discussed in the following paragraphs.

The first set of scanned samples was fabricated in a bilayer arrangement in 500 µm deep 8 mm diameter PTFE molds. Following the GB-L approach, the DVB30 lower layer was thermally cured (10 min at 200°C) to consolidate the top surface before the DVB00 second layer was cast on top. Fast pyrolysis (300 K/h heating and cooling rate) was performed with peak temperatures of 1000 and 1400°C. **Figure 4.16a** shows the reconstructed scan of a large volume of 1000°C pyrolyzed material which is free of cracks and pores. Due to the moderate carbon contrast and the large size of the scanned sample, the phase contrast is very weak, but the curved interface line is well visible by assigning a color map to the X-ray attenuation coefficient. The partial volatilization of DVB30 PCP causes the concave shape which then was seamlessly adopted by the upper DVB00 layer. Slightly lower lateral shrinkage of the DVB-free layer resulted in the circumferential fillet on the bottom left.



Figure 4.16: Microtomography of DVB30|00-contrast bilayer SiCN and transition length determination: a) 3D reconstruction of a 1000°C pyrolyzed piece with a very weak phase contrast, a color map was therefore chosen for the attenuation coefficient to uncover the interface. b) 3D grayscale reconstruction of a 1400°C pyrolyzed piece with clear layer contrast and some cracks; c) phase segmentation and semi-transparent and colorized representation revealing that cracks are superficial and the interface is seamless; d) bottom view showing superficial cracks and replicated PTFE mold texture; e) side view showing layers and crack extent; f) 2D view on interface region and averaged grayscale intensity profile perpendicular to the interface, exhibiting a transition length of <2  $\mu$ m for this DVB30|00 bilayer sample.

Pyrolysis of the same bilayer GB type at 1400°C, followed by manual cleavage into small pieces yielded a higher phase contrast in the microtomography scan. The reconstructed volume of the respective piece shown in **Figure 4.16b** exhibits cracking but a clear layered contrast

in grayscale representation of the attenuation. The addition of 30 wt.% DVB to the PCP formulation therefore effectively results in a SiCN composition with lower X-ray absorbance. The in average lower atomic density is caused by the higher concentration of carbon going along with a reduced concentration of the heavier silicon. Phase segmentation and semi-transparent visualization (**Figure 4.16c**) reveals the absence of pores as well as the seamless, smooth, and planar character of the interface in the sample's central area. The two layers of similar thickness in the order of 200  $\mu$ m exhibit no signs of delamination. Bottom and side view (in **Figure 4.16d,e**) show the replicated texture from the CNC machining traces in the PTFE molds and the seamless sharp character of the straight interface, respectively. A central 2D slice of the scan was used to approximate the interface transition length based on the grayscale contrast. **Figure 4.16f** shows the profile measured perpendicular to the interface and averaged from the ~60  $\mu$ m wide yellow rectangle. A clear jump from one gray level to the other within less than 2  $\mu$ m indicates the sharp character of the interface.

Secondly, bilayer samples with a higher DVB-filling contrast, higher pyrolysis temperature, and lower heating and cooling rates were analyzed. Fabricated in the 6/8 mm bilayer PTFE molds, both casting orders were compared. In case of DVB60|00 order, the lower DVB60 layer was mildly pre-cured during 15 min at 100°C. In the opposite DVB00|60 arrangement, the lower DVB00 layer was extensively pre-cured during 30 min at 200°C. The 3D reconstructed microtomography images of both sample types, cleaved into smaller pieces, are presented in Figure 4.17. For both casting orders (Figure 4.17a,d), the volumes are entirely free of cracks and pores, despite the high DVB-filling contrast and high pyrolysis temperature of 1400°C. This indicates the suitability of the pressureless thermal crosslinking conditions and the positive effect of the reduced heating and cooling rates (100 K/h) during pyrolysis. Layered phase contrasts are clearly visible. The interfaces are seamless and curved, concave in case of DVB60|00 due to partial PCP volatilization and convex in case of DVB00|60 due to lower layer overfilling and less volatilization. In order to quantify and compare the SiCN composition gradients resulting from the sequential casting of DVB-filled and unfilled precursor, intensity profiles perpendicular to the interface were again created on 2D cross-sectional slices (Figure 4.17b,c,e,f). The grayscale profile lines confirm the visual impression from the 3D and 2D views that the DVB6000 order exhibits a smoother transition in this case. There are two possible reasons contributing to the ~25 μm long transition range. Firstly, DVB60 PCP typically forms a rougher top surface compared to DVB00 which results in signal intensity mixing and grayscale averaging in the interface area on the 2D plane. Secondly, compared to the bilayer sample analyzed by TEM, the lower DVB60 layer was pre-cured very mildly only. Thermal treatment during 15 min at 100°C (compared to 10 min each at 100 and 150°C) was apparently sufficient to consolidate the global shape (curved interface line) but possibly still allowed for interlayer mixing or DVB diffusion processes on the micro-scale. Comparison to the previous DVB30|00 bilayer sample (Figure 4.16b-f) which was pre-cured to a much higher

extent (10 min at 200°C instead of 15 min at 100°C) suggests that the composition gradient in bilayer SiCN is adjustable by variation of the pre-curing degree. Despite extensive thermal crosslinking (30 min at 200°C) of the lower layer in the DVB00|60 arrangement (**Figure 4.17e,f**), an intermediate transition length of ~5  $\mu$ m was obtained. In this case, the DVB molecules contained in the upper liquid precursor formulation potentially diffused into the DVB-free GB layer below before the second thermal curing step immobilized them by integration into the upper layer crosslinked network.



Figure 4.17: Microtomography of 1400°C pyrolyzed 60% DVB contrast bilayer SiCN and transition length determination: a) 3D reconstruction of a DVB60|00 piece; b) 2D view on interface region serving for grayscale intensity profile measurements; c) several intensity profiles perpendicular to the interface, featuring a transition length of 25  $\mu$ m for DVB60|00 casting order; d) 3D reconstruction of a cleaved DVB00|60 piece; e) 2D view on interface region; f) several intensity profiles perpendicular to the interface, featuring a transition length of 5  $\mu$ m for DVB00|60 casting order.

With the objectives to increase the segment lengths perpendicular to the interface and reduce influencing factors, a set of four different types of laterally heterogeneous SiCN bars was investigated where only the degree of pre-curing from extensive to none and the casting order were varied. Types 0, 2, 4, and 5 (Table 4.1) were selected which were all fabricated in the same molds (11×3 mm<sup>2</sup>), with the same DVB00/40 filling contrast, identical pyrolysis conditions (60 K/h heating rate in the critical range, 1000°C peak temperature), and same cut triangular geometry (Figure 4.12f) for scanning. T0 represents the GB–L approach where the first part was solidified by extensive thermal curing before addition of the second part. No intermediate curing was performed in case of T5, both dissimilar PCPs were directly pipetted in liquid state (L–L). With T2 and T4, two examples with pre-curing to slightly and significantly reduced extent were included.

The four prepared specimens, shown in **Figure A.13**, have lengths ranging from 3.4–4.4 mm while the microtomography setup's field of view covers only 700 µm in this dimension. Even when the top surfaces exhibited signs of an interface line as it was the case for T2 and T5 (**Figure A.13c,g,i,j**), capturing of the interface region in a single scan remained very challenging due to its non-vertical character. The 3D reconstructed data of a T0 (DVB40|00) scan in **Figure 4.18a,c** shows the smooth top surface entirely consisting of DVB00 SiCN. Below, a darker layer is clearly distinguishable with a decreasing thickness from the wider DVB40 to the narrower DVB00 end. The interface shape and orientation are a consequence of the casting process as Figure 4.3B illustrated previously. A closer look at the cross section, when rotated bottom side up, reveals the presence of three distinct layers (**Figure 4.18b**), suggesting that the cured DVB40 tip partially lifted from the PTFE mold bottom. The liquid DVB00 PCP then both filled this gap and covered the sloped top surface. The captured volume is crack-free and the



**Figure 4.18:** Microtomography of the triangular center piece of a 1000°C pyrolyzed laterally heterogeneous T0 bar. The DVB40 PCP was cast first and extensively pre-cured before casting of the DVB00 PCP. a) 3D reconstruction with smooth upside up, crack- and pore-free volume; b) bottom side up with CNC machining traces replicated from the PTFE mold: cross section perpendicular to the long axis reveals 3 planar layers with high contrasts; c) two-plane cross sections showing the interface positioning and seamless nature; d) segmentation and partial highlighting of the DVB00 layer in blue to bring out the interface roughness.

more central cross sections in **Figure 4.18c** show no porosity or interface delamination. The rough top surface which DVB40 typically forms was conformally adopted by the DVB00 layer above. Segmentation and partial blue coloring of the latter in **Figure 4.18d** bring out the rough but sharp interface character in this DVB40|00 T0 sample with extensive pre-curing. While the brighter unfilled layer appears homogeneous and fully dense, the generally darker DVB-filled region seems inhomogeneous. With an increasing occurrence towards the bottom surface, these darker features exhibit a lower atomic density causing reduced X-ray absorption.

The same kind of low-density features was also obtained in the type 2 sample where DVB-free PCP was cast first and partially crosslinked during 5 min at 200°C. They occurred exclusively in the DVB40 region and are visible on the entire cross section in **Figure 4.19a**. Segmentation and yellow highlighting within the transparent matrix (**Figure 4.19c-e**) demonstrates their distribution and hence the two-phase arrangement in 3D. The zone within the sample where the two dissimilar PCPs overlap is exactly captured in the field of view of this scan. Clearly visible in the side view in **Figure 4.19d**, the reduced extent of thermal pre-curing did not



Figure 4.19: Microtomography of the triangular center piece of a 1000°C pyrolyzed laterally heterogeneous T2 bar. The DVB00 PCP was cast first and shorter-time pre-cured before casting of the DVB40 PCP. a) 3D reconstruction with upside up, crack-free volume; b) view on bottom side with CNC machining traces replicated from the PTFE mold: cross section perpendicular to the long axis reveals 3 planar layers with high contrasts; c) volume transparency and yellow segmentation of single-digit µm-sized volumes with much lower density which only occur in the DVB40 region; d) side view showing exactly the region where the two dissimilar PCPs overlap, curved and smooth interface; e) top view showing the thinning of the DVB40 layer from left to right.

significantly alter the interface characteristics. The interface line is clearly defined and due to the DVB00|40 casting order smoother in this case.

Neither in the case of the scanned homogeneous DVB40 discs (Figure 3.10d, Figure A.9g-i) nor the bilayer samples' DVB30 and DVB60 layers (Figure 4.16 and Figure 4.17), such lowdensity features were observed before. While the lab scale microtomography system used for the homogeneous samples lacks both the required resolution and phase contrast, the bilayer samples were scanned at PSI TOMCAT with the 10× lens for a larger field of view. Consequently, voxels were  $2^3$ =8 times larger compared to the 20× lens setup applied in case of the laterally heterogeneous bars, therefore possibly not resolving the features before. Furthermore, it is also possible that the inhomogeneity with light features only occurs in DVB40 material and not in case of lower or higher DVB-filling concentrations. The microtomography data alone does not allow the clear identification of the low-density features. They could either be a light solid element (e.g. graphitic carbon) or porosity (gaseous). For this reason, all four laterally arranged specimens were cleaved approximately in the middle and their cross sections were inspected by SEM. The images in Figure A.14 show the fracture surfaces but no evidence of any porosity, suggesting fully dense character of the SiCN material. The smooth and dense T4 cross section (Figure A.14h,i) resembles DVB00 SiCN at this position but T2 or T5 (Figure A.14d-g,j-k) exhibit dark features which do not appear like pores. In agreement with previous findings (Figure 3.8), these observations suggest that phase separation occurs and micrometer-sized graphitic carbon forms in DVB40-filled SiCN. This possibly results from the decomposition of locally enriched polymerized DVB which did not cross-polymerize with the PMVSz.

With decreasing extent of pre-curing, longer composition (i.e., carbon concentration) gradients are expected. In case of the PCP-joining type 4 (DVB00 partially pre-cured during 1 min at 175°C), three vertically shifted microtomography scans were recorded. By stitching of the adjacent data, a nearly 2 mm long continuous segment of the specimen could be reconstructed in 3D. The grayscale images in **Figure 4.20a,b** show a crack-free volume with a smooth top surface, rough side walls (from the diamond wire sawing), and replicated mold machining traces on the bottom surface. Both the top and bottom surface exhibit aligned c-shaped grayscale contrasts, indicated by the red arrows. In the typical concave shape of the firstly cast PCP (DVB00 in this case), this suggests a partial material consolidation resulting from the mild pre-curing avoiding extensive mixing of the two dissimilar PCPs. In the bulk volume, the same low-density features as observed in the previous two cases are present. These features, which again are possibly graphitic carbon, were segmented and highlighted in **Figure 4.20c-e** in yellow. They occurred across the entire captured specimen length. Especially the side view in **Figure 4.20e** visualizes a high concentration in the direction towards the sample's DVB40 end. From right to left, the concentration decreases continuously with a noticeable drop at the



**Figure 4.20:** Microtomography of the triangular center piece of a 1000°C pyrolyzed laterally heterogeneous T4 bar. The DVB00 PCP was cast first and pre-cured to low extent before casting of the DVB40 PCP. a) 3D reconstruction stitched from three scans, upside up, crack-free volume with a c-shaped surface contrast; b) view on bottom side with replicated machining traces and c-shaped surface contrast; c) volume transparency and yellow segmentation of single-digit µm-sized volumes with much lower density which occur more towards the DVB40 end; d) top view; e) side view showing low-density features at high concentration on the right and decreasing occurrence towards the left.

position of the superficial grayscale contrasts. At the left end of the captured volume (DVB00 direction), almost no more low-density features are present. This example of mild pre-curing (T4) suggests that composition contrasts in polymer-derived SiCN can be tailored to yield gradients ranging from the submicrometer to the millimeter range, probably ~2.5 mm in this case. For an exact quantification, more scans would be required to cover an even longer part of the specimen.

Lastly, the liquid-liquid approach with no pre-curing was analyzed using the example of T5 (DVB40|00). The processed microtomography data from one scan is presented in **Figure 4.21**. The grayscale 3D images (**Figure 4.21a-c**) show typical bottom and sidewall texture and a rough top surface. Cross sections exhibit no lateral material contrast or interface but the inhomogeneously distributed dark features observed in DVB40 material before. The segmentation in **Figure 4.21d,e** reveals predominant occurrence in proximity to the bottom and top surface, more expressed to the top left. Localization of the captured volume on the OM images in Figure A.13g,j suggests that the transition is centered a bit further in the DVB00 direction and



Figure 4.21: Microtomography of the triangular center piece of a 1000°C pyrolyzed laterally heterogeneous T5 bar. The DVB40 PCP was cast first and DVB00 added with no intermediate pre-curing. a) 3D reconstruction, upside up; b) two-plane cross sections showing no cracks and no apparent contrast; c) view on bottom side with replicated machining traces; d) yellow segmentation of single-digit  $\mu$ m-sized volumes with much lower density; e) side view with transparent volume showing tendency of low-density feature presence being higher close to the bottom and top surface and to the left.

therefore not captured in this scan. The composition gradient in this L-L approach is expected to be longer than in the previous T4 type, therefore no significant trend of the low-density feature concentration can be identified within the covered range of less than 700  $\mu$ m on the DVB40 side of the interface. However, above-mentioned observations, such as the visible contrast in the GB state (Figure 4.12a) or the significant difference in both ends' electrical conductivity in PDC state (Table 4.2), have confirmed that there is a long-range composition-and property-contrast also in case of type 5.

## 4.3.2 Towards all-ceramic devices

The previous sections have demonstrated the versatility and outstanding properties of polymerderived silicon carbonitride ceramics. The liquid nature of the polymeric precursor allows for efficient fabrication of parts ranging from the micrometer to centimeter scale by casting. The electrical conductivity of the material is tunable across several orders of magnitude by carbon-filler addition and processing parameter choice while maintaining high mechanical strength. Dissimilar precursors can be joined to form seamless functionally graded monolithic ceramics with integrated conductivity contrast. This is achieved by spatially controlling the carbon content and the microstructure in parts entirely consisting of the same ternary ceramic system: SiCN. These properties make the material an intriguing candidate for applications where resistance to harsh environments, thanks to the all-ceramic character, as well as electric or electronic functionality integration are required. As a demonstration object, the bi-feedthrough (BFT) plate introduced in Figure 1.1 was chosen. The manufacturing and assembly as well as its testing are described in this section.

#### Fabrication of SiCN bi-feedthrough plates

Based on the findings of the previous Section 4.3.1, PCP combination in the states green body–liquid (GB–L) was chosen for the fabrication of the bi-feedthrough (BFT) plate. Two similar versions were designed for which the two types of dedicated CNC-machined PTFE molds introduced in Section 4.2 were used (Figure 4.4). Among the two main bi-material casting strategies detailed previously (Figure 4.5), first fabrication attempts were based on the placeholder and cavity filling approach.

The fabrication process inside the argon glovebox is documented in Figure 4.22 in a series of photos. Firstly, the square matrix PTFE mold was placed onto the hotplate, the placeholder PTFE rods were positioned vertically, and the DVB-free precursor pipetted into the mold and extensively crosslinked at 200°C (Figure 4.22a). Occurrence of bubbles, especially around the placeholders, cracking due to mold sidewall adhesion as well as cracks formed during the rod extraction were commonly encountered problems (Figure 4.22b). Furthermore, the PTFE rod removal caused the cured matrix green part to detach from the mold bottom. In the subsequent cavity filling step, the liquid DVB60 PCP actually flowed into the gap between matrix and mold before thermosetting, resulting in the failure shown in **Figure 4.22c**. Thanks to an improved rod removal technique, where the green part was fixed in place (with a metallic stick placed horizontally across the sample center) and the PTFE rods were pulled in a rotational movement, nearly perfect DVB00 matrix parts could be obtained (Figure 4.22d). However, the matrix material always detached from the mold, so that an alternative way for sealing of the cavity bottom was required. Adhesive copper tape as a thermally stable material was then tested. In this manner, casting and crosslinking of the DVB60 PCP inside the cylindrical cutouts succeeded but the subsequent removal of the Cu tape damaged the sample and left significant amounts of adhesive residues (Figure 4.22e,f). For these reasons, the placeholder and cavity filling approach was abandoned.

Inversion of the casting order, as it was performed in the inset droplet approach (Figure 4.5B), eliminates the placeholder removal step and reduces the risk of unintended green part detachment from the mold. Due to frequently occurring cracking of the cured polymer matrix's corners in case of the square geometry, the alternative round matrix design was introduced.

## 4.3 Results and discussion



**Figure 4.22:** Unsuccessful BFT fabrication process based on the placeholder and cavity filling approach: a) thermal curing of the DVB00 PCP cast around the placeholder rods into the square PTFE mold; b) matrix GB after rod extraction exhibiting pores and cracks; c) DVB60 PCP pipetted into the cavities flowing in between mold and matrix before thermosetting; d) significantly improved matrix GB; e) filling approach with cavities sealed off by adhesive Cu tape; f) obtained fully cured GB with DVB60-filled cavities, marked by cracks, warping and adhesive residues.

The rotation-symmetric shape was expected to reduce sample cracking risk by eliminating the weak points. The DVB filling concentration was reduced from 60 to 40 wt.% due to the latter composition's superior behavior. The round PTFE molds were placed onto the level hotplate inside the glovebox and the DVB40 precursor was pipetted onto each circular re-



Figure 4.23: Unsuccessful BFT fabrication process based on the inset droplet approach in round molds: a) thermal curing of the two DVB40 PCP droplets placed onto the recessed areas; b) DVB40 GB insets; c) pore- and crack-free fully cured round BFT plate with DVB00 matrix in PTFE mold; d) sample cracked from cooling and demolding attempts.

cessed area. They primarily served for precision positioning whereas lateral overflow was avoided by exact casting volume determination. Inset volumes were maximized for largest possible height in order not to be buried in the subsequent matrix casting step. After thermal crosslinking and consolidation of the insets (**Figure 4.23a,b**), DVB-free PCP was cast as matrix and thermally cured. Defect-free BFT green parts resulted at the end of the 30 min curing at 200°C (**Figure 4.23c**) but the cooling process and mold release attempts typically lead to severe cracking as shown in **Figure 4.23d**. This behavior is expected to be related to the round geometry and the associated lack of preferential mold detachment points. Instead of initiating detachment from the squared molds at four points and further propagating from there, stress builds up homogeneously and causes the round matrix to crack rather than demold.

Since no sound BFT green parts could be fabricated with the circular matrix design, the inset droplet approach was finally applied to the initial square matrix molds. The casting and curing procedure was generally the same as for the round molds. Less cracking was observed, due to the fact that compared to the placeholder approach, the more critical matrix part experiences one heating and cooling cycle only. Repeated fabrication experiments have finally shown that an extended inset pre-curing (10 min at 100°C, 10 min at 150°C, and *20 min* at 200°C) reduced subsequent outgassing and therefore bubble formation. Furthermore, the introduction of two-step matrix thermal curing (20 min at 180°C, 10 min at 200°C) was found to eliminate cracking. **Figure 4.24a-d** shows an example of an entirely crack-free DVB40|00



**Figure 4.24:** Successful BFT fabrication process based on the inset droplet approach in square molds: a) two thermally cured DVB40 PCP droplet insets; b) fully cured BFT plate with DVB00 matrix in PTFE mold; c) upside of a demolded green state BFT plate; d) bottom side of a demolded green state BFT plate. e) Inverted fabrication with cured DVB00 PCP droplet insets; f) cured BFT plate with DVB60 matrix in PTFE mold; g) upside of a demolded green state inverted BFT plate; h) bottom side.
BFT plate in green state exhibiting very few small bubbles only. Due to the insets' droplet shape, the matrix partially covers the inset, but it is visible in **Figure 4.24c** that a small central area of the inset remains exposed to the top surface. The DVB40|00 arrangement is relevant for the foreseen application as plate for transmission of electricity (Figure 1.1). The opposite DVB00|60 arrangement has been fabricated as well for completeness of this proof of concept. A respective sample is shown in **Figure 4.24e-h**. Thanks to the optical contrast of unfilled and DVB-filled material, the insets' stretching across the entire sample thickness is visible better in this case.

The polymer-to-ceramic transformation is a process becoming increasingly challenging with increasing sample size, geometry complexity, and degree of heterogeneous material composition. Therefore, among all samples of this work, the BFT geometry represents the highest risk of failure during pyrolysis. The application of standard heating and cooling rates of 100 K/h (Figure 3.1) indeed often resulted in severe sample cracking such as the examples of DVB00/60 arrangement in **Figure A.15** show. This problem was overcome by process adaptation with the optimized cycle (reduced heating rate of 60 K/h in the most critical temperature range). One example each of 1000 and 1400°C pyrolyzed BFT plates in PDC state is presented in Figure 4.25. Intact samples were obtained after pyrolysis, however, exhibiting some superficial cracks. Main drawback of the inset droplet approach is the geometrically less defined character of the feedthroughs. For testing and application functionality, stretching of the insets from the sample bottom to the top surface is essential. As it was the case in the GB state, even in pyrolyzed state, a DVB-filling induced surface texture influence allows the material distinction with the naked eye. The effective surface-exposed circular inset areas are highlighted in Figure 4.25. On the samples' upsides (Figure 4.25a,c), the surface-exposed diameter was typically ~1.5 mm, smaller compared to the design of ~3 mm<sup>1</sup>. On the bottom sides (Figure 4.25b,d), due to some lateral spreading at the beginning of the insets' thermal

<sup>&</sup>lt;sup>1</sup>The circular recessed area in the PTFE mold and hence the insets in GB state were designed with a diameter of 4 mm, resulting in ~2.9 mm diameter after lateral shrinkage of ~28% during 1400°C pyrolysis.



**Figure 4.25:** OM images of DVB40|00 BFT ceramic plates with feedthroughs by design highlighted in red, feedthrough area visually exposed to the top surface highlighted in green, and feedthrough area on bottom side highlighted in blue: a) 1000°C pyrolyzed top side; b) 1000°C pyrolyzed bottom side; c) 1400°C pyrolyzed top side; d) 1400°C pyrolyzed bottom side.

pre-curing, diameters were larger (~3.8 mm). Based on the measured electrical conductivity of the 1400°C pyrolyzed T0 bar's DVB40 part of 0.2 S/cm (Table 4.2), the effective resistance of the droplet shaped feedthroughs is estimated to R≈10  $\Omega$  each. A total serial resistance in the order of 20  $\Omega$  would be acceptable for the foreseen proof of concept device assembly documented in the upcoming paragraphs.

### Proof of concept device assembly and testing

The fabrication of entirely ceramic electronic devices is a vision becoming increasingly realistic, for which recent progress such as functionally graded PDC sensors for harsh environments [132] and the above-mentioned findings contribute. Additionally, more complex electronics in the form of conventional circuit boards or LTCC / HTCC could be enclosed in a hermetic housing entirely made from PDCs. As a first step, the bi-feedthrough (BFT) plate introduced in the previous paragraphs is intended to act as one sidewall of such a housing. The two DVB-filled and conductive feedthroughs serve for transmission of electricity, as power supply or data transfer. For the proof of concept, a simple red LED has been selected as an electronic component with visual feedback in case of successful power supply. The concept of this demonstration assembly aims for mechanical fixation of the LED on one side of the BFT plate. Electric contact of the LED's cathode and anode leads to the conductive SiCN feedthroughs needs to be established as well as wiring of the opposite side's ceramic contacts to the power source.

Several options for electric contacting were evaluated and tested on homogeneous 1400°C DVB40 discs first. Neither conventional tin-solder with a soldering iron nor soldering paste applied with a spatula and processed with a hot-air gun allowed satisfying wetting behavior on both sides of the PDC discs. Experiments with liquid metal (gallium–indium eutectic) showed better wetting and electrical contact, however, did not mechanically fix the electrodes and wires. The above-mentioned conductive Ag epoxy adhesive was therefore chosen which requires a thermal curing. An intact DVB40|00 BFT plate, pyrolyzed at 1400°C, was selected for assembly and placed on an Al<sub>2</sub>O<sub>3</sub> plate upside up. The process is summarized in **Figure 4.26** in a series of photos. The ends of two copper wires were bared, polished, and positioned onto the BFT plate's feedthrough areas (**Figure 4.26a**). The Ag paste was applied and the assembly then carefully transferred into an oven for curing during 15 min at 120°C (**Figure 4.26b**). The plate was flipped, again fixed with tape, and the bent LED<sup>1</sup> leads were positioned onto the feedthrough areas of the ceramic's bottom side (**Figure 4.26c**). A metallic fastening structure was used to temporarily lock the LED in place. The Ag paste was applied and cured in an oven

 $<sup>^{1}</sup>d = 5 \text{ mm}, \lambda = 655 \text{ nm}$  (L-7113SRD-D, Kingbright, Taiwan) [198]

during 45 min at 80°C<sup>1</sup>. Once thermally cured, a strong mechanical bond between the LED leads and PDC plate was established by the conductive adhesive (**Figure 4.26d**).

**Figure 4.26: FGC demo device assembly process:** a) positioning of Cu wires on the ceramic plate's top side feedthrough regions, b) Ag epoxy applied for electrical contact and mechanical fixation, c) positioning of the LED electrodes on the bottom side feedthrough regions, d) Ag epoxy applied, e) power supplied through the ceramic lighting up the LED.

The opposite ends of the two copper wires were connected to a source meter and a current of 30 mA was applied. While forward operating currents are specified to 30–155 mA in the LED's technical data sheet [198], it did not light up when 30 mA were applied. The current was increased stepwise until the LED lit up, emitting bright red light (**Figure 4.26e**). Therefore, powering an electronic component through a carbon-rich silicon carbonitride plate was demonstrated to be possible. However, currents in the range of 150–175 mA were required, corresponding to voltages of ~15 V.

A schematic cross section of the assembled setup is shown in **Figure 4.27a**. Ideally, the DVB-filled feedthroughs exhibit a low resistance whereas the unfilled PDC matrix behaves as insulator. This ideal situation is depicted by the circuit model in **Figure 4.27b** where  $R_f$  represents the LED and  $R_i$  and  $R_{ii}$  the DVB40 feedthroughs' resistance in the order of 10  $\Omega$ . To investigate the above-mentioned unexpected electrical behavior of the system, the resistances of all four accessible contact points (A–D) were measured. The obtained resistance values for all six access point combinations are listed below (4.1):

$$R_{AC} = 5200 \ \Omega, \quad R_{AD} = 4130 \ \Omega, \quad R_{AB} = 140 \ \Omega$$

$$R_{BD} = 4060 \ \Omega, \quad R_{BC} = 5270 \ \Omega, \quad R_{CD} = 9260 \ \Omega$$
(4.1)

<sup>&</sup>lt;sup>1</sup>The curing temperature was reduced (and time increased accordingly) in order to stay below the LED's maximum storage temperature specified to 85°C in its technical data sheet [198].



Figure 4.27: Schematics of the transmission of electricity in the C-contrast BFT SiCN plate: a) To scale cross-sectional sketch illustrating ceramic plate setting, wiring, connections, and measuring points A–D; b) ideal electrical circuit model with the two C-rich (C+) feedthroughs as  $R_i$  and  $R_{ii}$ and insulating SiCN (C-) in between; c) electrical circuit model reflecting the real current paths with significant leakage current.

The measurements revealed that the ceramic feedthroughs' resistances  $R_{AC}$  and  $R_{BD}$  were much larger than expected. Furthermore, the total assembly's resistance measured at the Cu wires ( $R_{AB}$ ) was only 140  $\Omega$ , significantly lower than expected. Therefore, a second electrical circuit model was introduced which is shown in **Figure 4.27c**. It takes the apparent leakage current between the two feedthroughs into account, represented by the resistance  $R_e$ . Due to the unknown vertical position of this path, the previous resistances  $R_i$  and  $R_{ii}$  were divided into  $R_a+R_c$  and  $R_b+R_d$ , respectively. Then, approximating the LED's resistance (in the cut-off regime) of  $R_f \approx 1.5 M\Omega$  as infinite, the following (over-determined) system of linear equations was established (4.2):

$$R_{AC} = R_{a} + R_{c} = 5200 \Omega$$

$$R_{BD} = R_{b} + R_{d} = 4060 \Omega$$

$$R_{AD} = R_{a} + R_{e} + R_{d} = 4130 \Omega$$

$$R_{BC} = R_{b} + R_{e} + R_{c} = 5270 \Omega$$

$$R_{AB} = R_{a} + R_{e} + R_{b} = 140 \Omega$$

$$R_{CD} = R_{c} + R_{e} + R_{d} = 9260 \Omega$$
(4.2)

Its solution yielded the following five resistance values  $R_{a-e}$  (4.3):

$$R_{\rm a} = 35 \,\Omega, \quad R_{\rm c} = 5165 \,\Omega, \quad R_{\rm e} = 70 \,\Omega$$
  
 $R_{\rm b} = 35 \,\Omega, \quad R_{\rm d} = 4025 \,\Omega,$ 
(4.3)

The resulting values reveal that the two DVB40 feedthroughs are actually not electrically insulated from each other but short-circuited by  $R_e=70 \Omega$ . Secondly, the fact that the model's  $R_a$  and  $R_b$  are much smaller than  $R_c$  and  $R_d$  indicates that this current path is located on

the BFT plate's wired side or inside the ceramic very close to the surface with the Cu wires (Figure 4.28A). Cross-sectional OM of a similar DVB40|00 BFT sample which broke during 1400°C pyrolysis revealed that the conductive feedthroughs in fact might be fully buried in the unfilled matrix material (Figure A.16). Due to the uncontrolled sample cracking, the surfaces are uneven and difficult to focus but a material contrast is clearly visible both on the bottom and top side. The situation is expected to vary significantly from one sample to another, but the imaged example has a DVB00 layer of a thickness in the order of 30 µm on the feedthroughs bottom side (Figure A.16a) which indicates a previously unnoticed mold detachment after pre-curing and liquid matrix PCP-filling the created gap. Due to the droplet nature, the insets' top surface is curved (Figure A.16b). Therefore, the DVB00 layer thickness decreases from the circumferential area (on the left) towards the center (on the right). The present cross-sectional plane does not intersect the feedthroughs center but a DVB-free layer of up to 19 µm could also cover the inset on the top side. Therefore, instead of the feedthroughs extending from the bottom to the top surface as targeted (Figure 4.28B:a), they may actually be buried within the matrix and fully covered by an insulating layer (Figure 4.28B:b). These observations, in case they apply to the assembled BFT plate in a similar way, would explain the high resistances of the two feedthroughs. A possible way to overcome the occurrence of the insulating thin film on the top side is further increasing the inset droplet heights with respect to the matrix filling height. On the bottom side, modification of the insets' pre-curing process or grinding off the thin layer, preferentially in the softer green state, should be considered.



**Figure 4.28: Hypotheses for actual current flow and BFT plate arrangement**: Cross-sectional sketches of **A**) assembly with schematic leakage current indication: only a small fraction of the 150 mA applied lights up the LED, the rest generates heat in the ceramic. **B**) feedthrough areas: **a**) ideal setup with 40% DVB feedthroughs extending from bottom surface to top surface; **b**) approximate representation of the possibly actual composition with the 40% DVB-filled parts buried within the 0% DVB matrix.

Regarding the unexpectedly low resistance  $R_{AB}$  between the two feedthroughs, no clear signs of cause could be found. The Ag paste appears well separated from one contact to the other (Figure 4.26b). Therefore, the conduction is more likely occurring in the PDC. This assumption is supported by the observed semiconducting behavior of the system which is shown in **Figure 4.29**. When a constant high current (**Figure 4.29a**) or constant high voltage (**Figure 4.29b**) is applied to the assembled system, the resistance decreases instantly from ~140  $\Omega$  to ~110  $\Omega$ and then reduces further to the asymptotic value of ~90  $\Omega$  after 1 min.



Figure 4.29: Semiconducting behavior of SiCN in demo device: a) development of voltage, resistance, and power over time at constant current; b) development of current, resistance, and power over time at constant voltage.

The majority of the more than 2 W of applied power cause Joule heating of the ceramic plate while only a small current fraction lights up the LED. The value of  $R_e$  reduces during constant current / voltage supply. Consequently, the LED's brightness decreases. The BFT plate's heating was measured and imaged by means of an IR camera, presented in **Figure 4.30**. The temperature at the sample center increases from RT to approximately 130°C within less than 40 s when a constant current of 150 mA is applied. The plate's corners reach a temperature of ~75°C in the same time. Unintentionally serving as a heating element, no material degradation such as crack formation was observed during several tens of rapid heating and cooling cycles.

Owing to their attractive properties, polymer-derived ceramics have been reported as dedicated material for heating applications such as micro or macro glow plugs [18, 199]. The observed semiconducting behavior is typical for amorphous SiCN with hydrogenated BSUs and disordered turbostratic free carbon (Figure 1.9) [6, 18]. Based on variable-range or band tail hopping mechanism, the negative temperature coefficient (NTC) behavior has been exploited for temperature sensing applications [132, 163]. In the present case of the BFT ceramic plate for transmission of electricity, the leakage current Joule heating is a detrimental effect rendering this specific assembled system unusable for the targeted purpose. The findings reported here as well as previously for the homogeneous discs and laterally heterogeneous bars (Table 4.2) show that achievement of an electrical conductivity contrast of several orders of

#### 4.4 Summary and conclusion



Figure 4.30: IR camera thermal monitoring of powered demo device: a) approximate temperature development of the ceramic plate with constant I=150 mA applied; b) thermal image at t=37 s with approximately 130°C temperature in the plate center.

magnitude within a monolithic SiCN part processed at a uniform temperature is challenging. Further studies are required in order to maximize the (free) carbon concentration contrast as well as expand the understanding of composition gradients resulting from different joining approaches. Furthermore, enhanced electrical conductivity contrasts should be obtainable by dissimilar HT treatment in addition to the filling level contrast. Strategies such as rapid sintering by Joule heating between carbon strips [100] or flash spark plasma sintering [123] might allow for selectively applied annealing temperatures. This way, combining an 800°C pyrolyzed DVB00 matrix with  $\geq$ 1400°C flash sintered DVB40 insets should potentially allow for conductivity contrasts of ~9 orders of magnitude (Tables A.1 and A.2).

### 4.4 Summary and conclusion

In this chapter, the development and characterization of functionally graded polymer-derived silicon carbonitride was introduced. Based on the pressureless thermal processing of the preceramic PMVSz *Durazane*<sup>®</sup> *1800* and the composition- and property-tuning by DVB addition presented in Chapter 3, monolithic ceramic parts with engineered property-contrasts were fabricated by consecutive casting of dissimilar precursor formulations. DVB-filled and unfilled PCPs were joined in PTFE molds in vertical bilayer or lateral arrangement. The degree of the intermediate thermal treatment was varied, i.e., liquid precursor of one composition was combined with cured, partially cured, or liquid precursor of the dissimilar composition. DVB-contrast green parts were transformed into carbon-contrast SiCN by pyrolysis under Ar atmosphere with peak temperatures of 1000 and 1400°C and reduced heating and cooling rates. Obtained ceramic parts, their phases, and the interface characteristics were analyzed

by cross-sectional microscopy, electrical conductivity measurements, EDX, TEM, and synchrotron tomographic microscopy. Furthermore, different approaches for the fabrication of the geometrically more complex design of a (low-carbon concentration) insulating SiCN plate with seamlessly integrated (higher carbon concentration) conductive feedthroughs were tested. One of these bi-feedthrough (BFT) plates was assembled to a demonstration device with Cu wiring and an LED electrically connected and tested.

Pore-free composition-contrast green parts were fabricated in short time by consecutive casting of the PMVSz-based precursor system with DCP and DVB and pressureless thermal curing at maximum temperatures of 200°C. Low heating and cooling rates in the order of 60-100 K/h during the inert atmosphere pyrolysis have shown to be essential for the conversion to crack-free carbon-contrast PDCs. Cross-sectional microscopy and 3D microtomography have demonstrated the dense and defect-free character of millimeter-sized parts in different geometries and arrangements. The same techniques have also shown that seamless interfaces with no signs of delamination were formed irrespective of the PCP joining states. The character of the interface between ceramic regions derived from unfilled PCP and PCP filled with DVB at concentrations of 30-60 wt.% was analyzed and correlated to the casting order and extent of intermediate thermal curing. If DVB-filled precursor was cast first and thermally pre-cured before being brought into contact with the unfilled liquid counterpart, partial volatilization altered the interface shape (e.g. forming curvature) which was typically rough. The inverted casting order yielded geometries more accurate to shape and smoother interface planes. The sharpest material contrast with an interface transition length below 1 µm was observed by EDX in case of DVB60|00 bilayer arrangement with extensive intermediate curing. Several steps of longer gradients (5  $\mu$ m, 25  $\mu$ m, and >1.9 mm) were visualized by microtomography, resulting from varied casting order and reduced intermediate thermal curing. Even when the dissimilar PCPs were joined both in liquid state (laterally) with no intermediate curing, long range composition contrasts were obtained as electrical conductivity measurements of the monolithic SiCN material suggested. Electrical conductivity contrasts within monolithic samples up to a factor of 84 were observed. Localized differences in carbon concentration were identified in such samples by EDX and TEM microstructure analysis. Microtomography of Ccontrast SiCN exhibited micrometer-sized low-density features in regions derived from DVB40 precursor which could be graphitic carbon. While the liquid PDC route is well compatible with molding, shape forming of the interface remained challenging, due to gravitational and mold surface wetting influences. An approach to fabricate 14×14×0.6 mm<sup>3</sup> large SiCN plates with laterally defined contrasts in carbon concentration and therefore electrical conductivity was introduced and tested. Mechanically stable electrical contacts were established by a silver epoxy and an LED as a simple example of an electronic component was powered and lit up through the monolithic BFT SiCN plate. However, further fabrication optimization and extended testing are required in order to ensure precise spatial definition of the conductive and insulating ceramic areas allowing for efficient and safe application. Ultimately, complexity in geometry and functionality would be increased and functionally graded all-ceramic reactor chambers or housings for electronics realized. Instead of the assembled BFT plate fitted into a non-ceramic case (**Figure A.17**), two or more parts will be joined in green state by the polymer-based bonding technique and yield full ceramic bodies after pyrolysis.

# **5** Conclusion and outlook

## 5.1 Conclusion

- Based on the liquid PDC route, defect-free, dense SiCN parts were fabricated by a fast and entirely pressureless molding process at moderate temperatures
- Optional sacrificial 2PP 3D structures on Si and in-mold pyrolysis of the PCP yielded a new level of submicrometer freeform features in PDCs
- The addition of 0–60 wt.% DVB to the preceramic PMVSz and adjustment of the pyrolysis temperature (800–1400°C) allowed for a tuning of the ceramic's electrical conductivity across 10 orders of magnitude (up to 0.4 S/cm) while exhibiting flexural strength of up to 1.65 GPa
- Intact monolithic SiCN parts with spatially defined contrasts in C-concentration and electrical conductivity were fabricated
- Composition gradients were tailored from submicrometer to millimeter transition length
- An LED was supplied with power through a functionally graded SiCN plate

This thesis investigated the fabrication of organopolysilazane-derived silicon carbonitride with focuses on the aspects of pressureless processing, high-resolution shaping, tuning of composition and properties, and engineering of functionally graded ceramics thereby. The work exploited the advantages of the liquid PDC route which were essential for the shaping by molding, property tuning by filler addition, and joining activities.

Starting with shaping aspects, several mold materials, mold fabrication techniques, and the casting and thermal processing were discussed first. For millimeter-sized bulk PDC sample fabrication, CNC-machined PTFE molds were used. The liquid PCP was directly pipetted into the molds and thermally cured. Geometry, shape complexity, and surface finish may impair the GB mold release behavior, which is why simple disc shapes with smooth surfaces  $(Sq/Sa \approx 5 \,\mu m)$  were used primarily. Smaller scale micromolds with more complex 2D/2.5D geometries were fabricated by means of photolithography and microfabrication processes. Several options, including thick SU-8 hard molds, silicon molds made by DRIE or KOH etching, and PDMS soft molds replicated from Si, were compared. Due to its monolithic and resilient character, Si was chosen as preferred material for PCP micromolding. Use of the molds made by KOH anisotropic etching, which typically exhibit very smooth surfaces, and an in-mold pyrolysis of the cast PCPs showed to yield defect-free SiCN parts obtained loose inside the molds. While these molds defined the parts' general shape, a method to add individual freeform microfeatures was introduced. Sacrificial photoresin 3D microstructures, such as a 3D micro QR-code, added by two-photon polymerization onto the Si mold bottom were successfully replicated as (inverted) imprint on SiCN parts with submicrometer resolution. This multiscale shaping technique allows for a high degree of (customizable) shape complexity at comparably low cost due to a target-oriented application of 2PP and the option to reuse the Si mold.

The second part focused on the processing conditions and the tuning of the PDCs' bulk properties. The PMVSz Durazane<sup>®</sup> 1800 was selected as the PCP, DCP as an efficient thermal initiator (3 wt.%), and 0-60 wt.% DVB as an organic carbon filler. In an entirely pressureless process, the precursor formulations were cured inside PTFE molds within 30 min at 200°C and converted to dense and defect-free SiCN by pyrolysis under Ar atmosphere with peak temperatures of 800–1400°C and 100 K/h heating and cooling rates. The polymer-to-ceramic transformation process was monitored by FTIR and TGA. The obtained SiCN samples were analyzed by SEM and microtomography, visualizing their shape and confirming their integrity. The influence of the DVB addition concentration and pyrolysis temperature on the ceramics' composition, microstructure, mechanical strength, and electrical conductivity was investigated by means of elemental analysis, Raman spectroscopy, B3B testing, and resistance measurements. The addition of 40% DVB to the PCP was found to effectively increase the SiCN's free carbon concentration from 15 to 25 wt.%. When pyrolyzed at 1400°C, this free carbon transformed from amorphous towards turbostratic or graphitic ordering, which caused an electrical conductivity 10 orders of magnitude higher (up to 0.4 S/cm) compared to the DVB-free insulating counterpart processed at 800–1000°C. Good mechanical properties were observed for most combinations of DVB-filling concentration and pyrolysis temperature, with characteristic flexural strengths of up to 990 MPa and 1.65 GPa for 1000°C pyrolyzed DVB40 and DVB20 composition, respectively. Furthermore, also the cytocompatibility of the different SiCN compositions and pyrolysis temperatures was demonstrated with NHDF, showing that the DVB addition did not impair the materials' cell attachment or metabolic activity.

Finally, functionally graded monolithic SiCN parts were fabricated by consecutive casting of precursors of dissimilar composition. The established PCP system of the PMVSz, DCP, and no (0%) or a significant (30–60 wt.%) amount of DVB added served as the basis to create property contrasts within parts consisting entirely of SiCN. Dedicated PTFE molds were used for shaping and the thermal conditions of the pressureless processing were slightly modified. In this way, pore-free green parts with a contrast in DVB-filling were obtained and converted into crack-free carbon contrast SiCN in various geometries and arrangements. Cross-sectional microscopy, EDX, TEM, and synchrotron tomographic microscopy of the ceramic parts with engineered heterogeneity were performed in order to visualize the interface between the contrasting regions in 2D and 3D. The samples' interface regions generally showed seamless transitions with no signs of delamination. However, depending on the PCP casting order and the extent of thermal curing of the PCP cast at first, the interface shape and nature varied significantly. Gradients with transition lengths ranging from the order of 500 nm to millimeters were obtained resulting from PCP joining after extensive curing (GB-liquid joining) or very mild to no intermediate curing (liquid-liquid joining), respectively. The observations suggest that application specific precise tailoring of the property gradients is possible. In consequence of the compositional contrasts within the ceramics, significant differences in electrical conductivity up to a factor of 84 were measured.

As a showcase, a cm-scale plate was designed in square geometry with two property contrast regions seamlessly integrated. Using custom PTFE molds, several PCP casting approaches were compared. Best results were obtained by the inset droplet approach, where the PCP with high DVB-filling was placed and thermally cured on predefined areas in the mold and subsequently surrounded by the liquid DVB-free precursor. A second thermal curing step followed by pyrolysis yielded intact all-SiCN plates with spatially defined contrasts in C-concentration and electrical conductivity. An LED was electrically connected to the two ceramic feedthroughs and lit up by applying a voltage to the respective areas on the plate's opposite side. The used exemplar, however, showed parasitic Joule heating which rendered it inefficient as a passive element and requires further process optimization.

In conclusion, the outstanding properties of carbon-enriched polysilazane-derived silicon carbonitride such as high-temperature stability, chemical inertness, high strength, tunable electrical conductivity, and cytocompatibility make this versatile material a valuable candidate for potential applications in various fields. The concept of functionally graded PDCs with spatial control allows for a new level of all-ceramic functionality integration. In combination with the design freedom and resolution of the demonstrated multiscale microshaping technique,

the use as reactors or sensors in chemical engineering and energy conversion and especially as biomedical implants such as heart pacemaker electrodes should be considered.

## 5.2 Outlook

This work demonstrated the molding, property tuning, and property contrast creation in PDC parts. Each of the three main aspects leaves room for improvement and further research. Regarding the shaping by PCP molding, PTFE molds were reused dozens of times which is beneficial from economic and ecological perspectives. On the contrary, the longevity and reusability of Si micromolds were not tested. Due to higher initial manufacturing cost compared to PTFE, reusability is more important. Even for the demanding in-mold pyrolysis at 1000°C, reusability is expected due to the monolithic character and high melting temperature of silicon (1414°C [181]), but requires verification. A few sacrificial 2PP photoresin structures were successfully replicated as imprints onto SiCN parts. Using higher  $(63\times)$  or smaller  $(10\times)$ magnification lenses and the corresponding resins (IP-Dip / IP-Q) in the 2PP system, smaller features down to the lower range of hundreds of nanometers or overall larger structures, respectively, could be replicated into PDCs. Furthermore, 2PP printing of entire lost molds (using Si chips as substrate only) would allow for very complex shapes with no lateral shrinkage constraints. Finally, sacrificial free-standing structures such as arches or scaffolds could create 3D hollow channel network structures within PDC parts, particularly interesting for microfluidic applications.

The processing of the PMVSz and the property tuning with DVB focused on the rapidity and facility of the molding and curing, i.e., prioritized doing without bulky and time-consuming pressure vessels. Therefore, the present ceramic yields in the range 64–76% are acceptable. Minor modifications of the precursor compositions and thermal processing sequence may allow for a generally desirable increase in ceramic yield while maintaining the pressureless and rapid character. The presented PCP system and process conditions reliably provided defect-free SiCN samples. Major deviations from the composition and sample geometry, especially when increasing sample size, most probably will require slight adaptations of the process. Warping is a detrimental effect which occurred to increasing extent in case of higher DVB-filling. Further work on the precursor composition in the range of 40–60 wt.% DVB and the temperature sequence is required to reduce distortion to a minimum. In this work, DVB was used as a carbon filler in order to adjust the PDC composition and electrical conductivity. The suitability and effectivity of further organic (e.g. polyacrylonitrile (PAN) [195, 200]) or metallic fillers, as well as the use of transition metal precursors (e.g. Cu [201], iron, cobalt, or nickel [202]) to catalyze the crystallization of graphite, should be studied to achieve higher maximum values of electrical conductivity.

Functionally graded SiCN was fabricated with contrasts in both composition and electrical conductivity. With a focus on the GB-liquid joining, problems related to volatilization, shrinkage, and mold detachment were encountered which impaired the spatial accuracy of the dissimilar areas. Especially in the case of the BFT plates, the functionality was compromised. Therefore, further optimization of the processing conditions and general revisiting of the casting strategies are required. A promising approach to improve shape definition (by increasing the PCP viscosity and reducing volatilization) and reduce cracking risk without changing the ceramic's composition or properties would be the addition of crosslinked precursor particles to the PCP formulation, as demonstrated by Pierin et al. [203]. Also, resorting to the theoretical joining and bonding combinations along the PDC route (Figure 4.1), many more options remain to be explored with regard to feasibility and potential interface characteristics. Among the measured composition contrast PDC samples, a maximum electrical conductivity contrast of a factor of 84 was observed. For efficient and safe electronic application, a difference of several orders of magnitude is required. Improvements in this regard can be carried out in two ways. Firstly, increasing the conducting phase's conductivity leads back to considering further filling materials or graphite crystallization catalyzing transition metal precursors. Secondly, more insulating contrasting material could be introduced, for instance low-carbon SiCN or SiOC derived from PHPS or polysiloxanes, respectively. Furthermore, the possibility to perform selective annealing could be investigated, for instance by the previously mentioned flash spark plasma sintering approach. In addition to the demonstrated contrast in electrical conductivity, further property contrasts could be created, e.g. in magnetic properties or porosity. For instance, by addition of PMMA particles [49] to one of the PCP formulations to be combined, a spatially defined open porosity could potentially be seamlessly integrated in a fully dense matrix part, a promising scenario for filtering or catalytic applications. Finally, the presented BFT plate with lateral contrasts in carbon concentration and electrical conductivity served as a first proof-of-concept. Further research on the polymer-based bonding technique would allow for higher degrees of geometry and property-contrast complexity. In this way, even hermetically sealed full-ceramic shells seem feasible, e.g. serving as reaction chambers or shielding housing for electronics.

## A Experimental details



Figure A.1: Detailed process flow for SU-8 hard micromold manufacturing: a) oxygen plasma cleaning of 525  $\mu$ m 100 mm Si wafer; b) spin coating of  $\approx$ 300  $\mu$ m SU-8; c) GBL atmosphere relaxation (thickness homogenization); d) 130°C soft bake; e) UV-exposure; f) 90°C post-exposure bake and relaxation; g) PGMEA development and IPA rinse; h) optional CVD of Parylene-C and sputtering of  $\approx$ 15 nm C.



Figure A.2: Process flow for Si hard micromold manufacturing by DRIE (Bosch process): a) dehydration and hexamethyldisilazane (HMDS) coating of 525  $\mu$ m 100 mm Si wafer; b) spin coating of 10  $\mu$ m photoresist and UV-exposure; c) development and rinse; d)  $\approx$ 300  $\mu$ m DRIE (Bosch process); e) wet photoresist stripping, rinse, oxygen plasma; f) optional CVD of Parylene-C and sputtering of  $\approx$ 15 nm C.



Figure A.3: Process flow for Si and SU-8 bilayer hard micromold manufacturing: a) dehydration and HMDS coating of 525  $\mu$ m 100 mm Si wafer; b) spin coating of 10  $\mu$ m photoresist and UV-exposure; c) development and rinse; d)  $\approx$ 340  $\mu$ m DRIE (Bosch process); e) wet photoresist stripping, rinse, oxygen plasma; f) spin coating of  $\approx$ 300  $\mu$ m SU-8 and soft bake; g) UV-exposure, post-exposure bake, relaxation and PGMEA development and IPA rinse; h) optional CVD of Parylene-C and sputtering of  $\approx$ 15 nm C.



Figure A.4: Process flow for PDMS soft micromold manufacturing using a Si master: a) dehydration and HMDS coating of 525  $\mu$ m 100 mm Si wafer; b) spin coating of 10  $\mu$ m photoresist and UV-exposure; c) development and rinse; d)  $\approx$ 300  $\mu$ m DRIE (Bosch process); e) wet photoresist stripping, rinse, oxygen plasma; f) silanization; g) liquid PDMS pouring and thermal curing; h) peeled off PDMS mold.



Figure A.5: Process flow for Si hard micromold manufacturing by KOH etching: a) 525  $\mu$ m 100 mm  $\langle 100 \rangle$  Si wafer; b) wet oxidation for 2  $\mu$ m SiO<sub>2</sub> layers; c) dehydration, HMDS coating, spin coating of 2  $\mu$ m photoresist, and UV-exposure; d) development and rinse; e) plasma dry etching of SiO<sub>2</sub>; f) plasma photoresist stripping and rinse; g)  $\approx$ 300  $\mu$ m KOH etching (23%, 80°C); h) HF SiO<sub>2</sub> removal; i) dicing; j) optional CVD of Parylene-C.



Figure A.6: Eight micromold designs for 100 mm wafer: a-c) micromolds with filling pot and channels, large basic shapes, and test patterns; d) SU-8 master for PDMS replication; e) for SU-8 characterization; f) for Bosch process characterization; g,h) shapes for Si KOH etching. For close examination, the reader is referred to the digital version of this document.





**Figure A.7: IP-S and Parylene-C pyrolysis control experiment: a)** SEM image of 2PP-written IP-S 3D QR code (1593x1593x12.5  $\mu$ m<sup>3</sup>) on Si substrate, Au coated; **b)** SEM image of 2PP-written solid cube (250x250x250  $\mu$ m<sup>3</sup>) on Si, Au coated; **c)** OM image of the IP-S 3D QR code after deposition of 1  $\mu$ m Parylene-C; **d)** OM image of the cube after deposition of 1  $\mu$ m Parylene-C; **e,f)** results after 1000°C Ar pyrolysis with IP-S completely volatilized and only traces of Parylene-C decomposition products and Au spheres remaining.



**Figure A.8: Schematic temperature sequences of thermal PCP curing**: 30 min at 200°C for DVB00 PCP and stepwise 10 min each at 100, 150, and 200°C for DVB-filled PCPs.



**Figure A.9: Microtomography images of 9 additional homogeneous SiCN disc samples**, defects highlighted in red: **a)** 0% DVB 1000°C with one central pore, **b)** 0% DVB 800°C, **c)** 60% DVB 1400°C severely warped, **d)** 20% DVB 800°C, **e)** 20% DVB 1000°C, **f)** 20% DVB 1400°C, **g)** 40% DVB 1000°C with edge porosity, **h)** 40% DVB 1200°C, **i)** 40% DVB 1400°C.



Figure A.10: Raman spectra of 20% DVB samples with Lorentzian peak fitting of the D and G bands, the obtained FWHM of the D bands, and the calculated  $I_D/I_G$  ratios. With increasing pyrolysis temperature, the D band width decreases and  $I_D/I_G$  increases, indicating an ongoing carbon ordering.



Figure A.11: Selected examples of IV-curves from bulk (transition) conductivity measurements:
a) DVB00 800°C pyrolyzed: resistance too high for measurement setup, therefore non-linear behavior;
b) DVB20 1000°C pyrolyzed: measurement with maximum possible resistance of R≈210 MΩ;
c) DVB40 1400°C pyrolyzed: linear behavior;
d) DVB60 1400°C pyrolyzed: linear behavior.

**Table A.1: Electrical conductivity values in S cm<sup>-1</sup> calculated from the sheet resistance measurements** of 16 samples. Where two or three values per sample type are provided, measurements were performed on the identical sample but on different sides or after reestablished probe contacting. Average (AVG) and where applicable standard deviation (SD) are given. Large variations may arise from contacting problems or local microdefects in the samples.

$\sigma_{\rm DC}$	800°C	AVG SD	1000°C	AVG SD	1200°C	AVG SD	1400°C	AVG SD
DVB00	$3.1 \cdot 10^{-10}$	3.1·10 <sup>−10</sup> n/a	$2.8 \cdot 10^{-10}$	2.8·10 <sup>−10</sup> n/a	$4.6 \cdot 10^{-11}$	4.6·10 <sup>−11</sup> n/a	$3.6 \cdot 10^{-10}$	3.6·10 <sup>−10</sup> n/a
DVB20	$4.4 \cdot 10^{-10}$	4.4·10 <sup>−10</sup> n/a	1.8·10 <sup>-10</sup>	1.8·10 <sup>−10</sup> n/a	$\frac{1.0 \cdot 10^{-9}}{6.4 \cdot 10^{-9}}$	$3.7 \cdot 10^{-9}$ $3.8 \cdot 10^{-9}$	$1.4 \cdot 10^{-10}$	1.4·10 <sup>−10</sup> n/a
DVB40	$1.4 \cdot 10^{-6}$ $2.7 \cdot 10^{-7}$	8.4·10 <sup>-7</sup> 8.1·10 <sup>-7</sup>	$2.5 \cdot 10^{-3}$	2.5·10 <sup>-3</sup> n/a	$1.8 \cdot 10^{-9}$ 0.19	9.6·10 <sup>-2</sup> 0.14	$     \begin{array}{r}       1.1 \cdot 10^{-8} \\       1.3 \\       2.0 \cdot 10^{-5}     \end{array} $	0.43 0.75
DVB60	$1.7 \cdot 10^{-5}$ $4.2 \cdot 10^{-5}$	$3.0 \cdot 10^{-5}$ $1.8 \cdot 10^{-5}$	$ \begin{array}{r} 1.7 \cdot 10^{-2} \\ 1.9 \cdot 10^{-2} \\ 1.9 \cdot 10^{-2} \end{array} $	$\frac{1.8 \cdot 10^{-2}}{9.5 \cdot 10^{-4}}$	$2.0 \cdot 10^{-8}$ $3.9 \cdot 10^{-9}$	$1.2 \cdot 10^{-8}$ $1.2 \cdot 10^{-8}$	$1.7 \cdot 10^{-10}$	1.7·10 <sup>-10</sup> n/a

**Table A.2: Electrical conductivity values in S cm<sup>-1</sup> calculated from the bulk (transition) measurements** of 16 samples. Every sample was flipped for second measurement. Average (AVG) and standard deviation (SD) are given. Values in gray are only indicative because sensitivity of used electrical equipment was insufficient for related low currents, consequently leading to non-linear IV-curves (refer to figure A.11).

$\sigma_{\rm DC}$	800°C	AVG SD	1000°C	AVG SD	1200°C	AVG SD	1400°C	AVG SD
DVB00	$\frac{1.7 \cdot 10^{-12}}{1.6 \cdot 10^{-12}}$	$\frac{1.7 \cdot 10^{-12}}{7.4 \cdot 10^{-14}}$	$2.8 \cdot 10^{-11} \\ 2.4 \cdot 10^{-11}$	$2.6 \cdot 10^{-11} \\ 2.8 \cdot 10^{-12}$	$\frac{1.4 \cdot 10^{-10}}{1.4 \cdot 10^{-10}}$	$\frac{1.4 \cdot 10^{-10}}{1.3 \cdot 10^{-12}}$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$4.3 \cdot 10^{-4}$ $4.5 \cdot 10^{-6}$
DVB20	$5.3 \cdot 10^{-12} \\ 5.5 \cdot 10^{-12}$	$5.4 \cdot 10^{-12} \\ 1.4 \cdot 10^{-13}$	$\frac{1.4 \cdot 10^{-9}}{1.4 \cdot 10^{-9}}$	$\frac{1.4 \cdot 10^{-9}}{3.1 \cdot 10^{-11}}$	$8.1 \cdot 10^{-5}$ $8.2 \cdot 10^{-5}$	$8.2 \cdot 10^{-5}$ $9.0 \cdot 10^{-7}$	$\begin{array}{c} 4.1 \cdot 10^{-4} \\ 3.4 \cdot 10^{-4} \end{array}$	$3.8 \cdot 10^{-4}$ $4.8 \cdot 10^{-5}$
DVB40	$\frac{1.5 \cdot 10^{-8}}{1.5 \cdot 10^{-8}}$	$\frac{1.5 \cdot 10^{-8}}{2.8 \cdot 10^{-10}}$	$\frac{1.4 \cdot 10^{-5}}{1.4 \cdot 10^{-5}}$	$1.4 \cdot 10^{-5}$ $6.5 \cdot 10^{-8}$	$4.5 \cdot 10^{-5} \\ 4.6 \cdot 10^{-5}$	$4.5 \cdot 10^{-5}$ $3.4 \cdot 10^{-7}$	$\begin{array}{c} 2.9 \cdot 10^{-3} \\ 2.9 \cdot 10^{-3} \end{array}$	$2.9 \cdot 10^{-3}$ $1.9 \cdot 10^{-5}$
DVB60	$\frac{1.6 \cdot 10^{-6}}{1.6 \cdot 10^{-6}}$	$1.6 \cdot 10^{-6}$ $3.3 \cdot 10^{-8}$	$ \begin{array}{c} 1.1 \cdot 10^{-4} \\ 2.0 \cdot 10^{-4} \end{array} $	$1.5 \cdot 10^{-4}$ $6.5 \cdot 10^{-5}$	$ \begin{array}{c} 1.1 \cdot 10^{-3} \\ 9.2 \cdot 10^{-4} \end{array} $	$1.0 \cdot 10^{-3}$ $1.2 \cdot 10^{-4}$	$ \begin{array}{c} 1.1 \cdot 10^{-3} \\ 1.1 \cdot 10^{-3} \end{array} $	$1.1 \cdot 10^{-3}$ $2.1 \cdot 10^{-5}$



Figure A.12: Mass loss rate of GB material: TGA (dashed) and DTG (solid), range  $300^{\circ}C < T < 800^{\circ}C$  highlighted where mass loss rate is highest.



Figure A.13: OM images of diamond wire sawn triangular center pieces for microtomography, areas marked in blue are captured in the microtomography scans (Figures 4.18–4.21): a) Type 0 top side with no visible interface, b) T0 bottom side; c) T2 top side with clear topography contrast, d) T2 bottom side; e) T4 top side with long range topography change, f) T4 bottom side; g) T5 top side with no clear topography contrast, h) T5 bottom side; i) higher magnification of T2 top side with interface line indicated; j) higher magnification of T5 top side with possible interface line indicated.



**Figure A.14: Cross-sectional SEM images of cleaved triangular center pieces of bars analyzed by microtomography: a-c)** Type 0: faceted fracture surface, crack- and pore-free; **d-g)** T2: crack-free fracture surface with dark features appearing rather like material contrast than pores; **h,i)** T4: smooth fracture surface, fully dense; **j,k)** T5: faceted fracture surface with some particles attached, crack- and pore-free.



Figure A.15: Two examples of DVB00|60 BFT plates broken during 1000°C Ar pyrolysis: a) upside of a broken piece; b) bottom side of same piece; c) upside of a partially cracked sample, d bottom side of same sample.



**Figure A.16: Cross-sectional OM images of a broken BFT plate's feedthrough area**: **a)** DVB00 layer of homogeneous thickness covering the DVB40 feedthrough's surface on the bottom side; **b)** feedthrough's top side covered with a DVB00 layer of up to 19 µm thickness.



**Figure A.17: Demonstration of a housing with the assembled BFT plate fitted into an additively manufactured (FDM) hollow and translucent cube**. Ultimately, different / more electronic components would be involved and the housing would consist of two or more functionally graded PCP elements to be hermetically joined by the polymer-based bonding technique: **a)** fitted BFT plate with the two feedthrough regions wired; **b)** side view showing the LED positioning; **c,d)** red shining LED inside the translucent cube, powered through the BFT plate.

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Curriculum Vitae

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# **EDUCATION AND TRAINING**

### Ph.D. Materials Science and Engineering

#### École polytechnique fédérale de Lausanne (EPFL), EDMX

07/2017 - 07/2022

- Lausanne, Switzerland
- Thesis: Multiscale microshaping of functionally graded polymer-derived SiCN ceramics Supervisor: Prof. Dr. Jürgen Brugger

### M.Sc. Materials Science

### **Technical University of Darmstadt**

**i** 10/2014 - 12/2016

- Darmstadt, Germany
- Thesis: Structural Characterization and Ceramization of Preceramic Polysilazanes Supervisors: PD Dr. Emanuel Ionescu & Prof. Dr. Ralf Riedel
- 01/2016 03/2016: Research project at University of New South Wales, Sydney, Australia
- 08/2015 12/2015: Semester abroad at University of Wisonsin Milwaukee, Milwaukee, U.S.

### **B.Sc. Materials Science**

### **Technical University of Darmstadt**

10/2011 - 08/2014

- Darmstadt, Germany
- Thesis: Electroless Deposition of 1D Gold-Nanostructures on 3D Macrostructures Supervisors: Dr. Sandra Schäfer & Prof. Dr. Wolfgang Ensinger

# WORK EXPERIENCE

### **Doctoral Researcher**

### École polytechnique fédérale de Lausanne (EPFL), Microsystems Laboratory

- **i** 07/2017 07/2022
- Lausanne, Switzerland
- Research in the frame of the Swiss federal project SFA AM Ceramic X.0
- Teaching assistant for Master courses: Introduction to additive manufacturing
  - Advanced additive manufacturing technologies - MEMS practicals I
- Project supervision of 5 Master students

# Teaching Assistant

# **Technical University of Darmstadt**

- 04/2014 07/2016
- Lab course instructor
- Exercise group tutor

### Intern

### Vacuumschmelze GmbH & Co. KG

**i** 09/2013

- R&D Rapid Solidification
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# LANGUAGES

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German: Native proficiency

English: Full professional proficiency

French: Limited working proficiency

# MEMBERSHIPS

- American Ceramic Society (ACerS)
- European Ceramic Society (ECERS)
- Schweizerischer Verband f
  ür Materialwissenschaft und Technologie (SVMT)
- Verein Deutscher Ingenieure e.V. (VDI)

# AWARDS

- Scholarship from the state of Hesse for a semester abroad at the University of Wisconsin - Milwaukee (U.S.)
- DAAD Promos scholarship from TU Darmstadt
- ECERS travel grant to attend ICACC 2018

# INTERESTS

- Road biking
- Running
- Rock climbing
- Skiing
- Hiking



### Student assistant Umicore AG & Co. KG 08/2013 - 09/2013 Hanau, Germany Analytical Competence Center Intern Vacuumschmelze GmbH & Co. KG **i** 08/2011 - 09/2011 Hanau, Germany R&D Rapid Solidification Intern Umicore AG & Co. KG **i** 03/2010 Hanau, Germany Test Center Automotive Catalysts Intern Öko-Institut e.V. **i** 10/2008 Darmstadt, Germany • Critical metals for future sustainable technologies and their recycling potential Intern Umicore AG & Co. KG **i** 07/2008 🗣 Hanau, Germany • Precious Metals Refining

# PUBLICATIONS

#### Journal papers

- L. Hagelüken, P.V.W. Sasikumar, H.-Y. Lee, D. di Stadio, Y. Chandorkar, M. Rottmar, K. Maniura-Weber, G. Blugan, and J. Brugger, "Multiscale 2D/3D microshaping and property tuning of polymer-derived SiCN ceramics," *Journal of the European Ceramic Society*, vol. 42, no. 5, pp. 1963–1970, 2022.
- M. Groeb, L. Hagelüken, J. Groeb, and W. Ensinger, "Experimental analysis of ductile cutting regime in face milling of sintered silicon carbide," *Materials*, vol. 15, no. 7, p. 2409, 2022.
- M. Kollep, G. Konstantinou, J. Madrid-Wolff, A. Boniface, L. Hagelüken, P.V.W. Sasikumar, G. Blugan, P. Delrot, D. Loterie, J. Brugger, and C. Moser, "Tomographic volumetric additive manufacturing of silicon oxycarbide ceramics," *Advanced Engineering Materials*, p. 2101345, 2022.
- J. Jang, P.V.W. Sasikumar, F. Navaee, L. Hagelüken, G. Blugan, and J. Brugger, "Electrochemical performance of polymer-derived SiOC and SiTiOC ceramic electrodes for artificial cardiac pacemaker applications," *Ceramics International*, vol. 47, no. 6, pp. 7593–7601, 2021.
- M. Makowska, P.V.W. Sasikumar, <u>L. Hagelüken</u>, D. F. Sanchez, N. Casati, F. Marone, G. Blugan, J. Brugger, and H.v. Swygenhoven, "Cracks, porosity and microstructure of Ti modified polymer-derived SiOC revealed by absorption-, XRD- and XRF-contrast 2D and 3D imaging," *Acta Materialia*, vol. 198, pp. 134–144, 2020.
- G. Konstantinou, E. Kakkava, L. Hagelüken, P.V.W. Sasikumar, J. Wang, M.G. Makowska, G. Blugan, N. Nianias, F. Marone, H.v. Swygenhoven, J. Brugger, D. Psaltis, and C. Moser, "Additive micro-manufacturing of crack-free PDCs by two-photon polymerization of a single, low-shrinkage preceramic resin," *Additive Manufacturing*, vol. 35, p. 101343, 2020.
- F. Muench, S. Schaefer, L. Hagelüken, L. Molina-Luna, M. Duerrschnabel, H.-J. Kleebe, J. Brötz, A. Vaskevich, I. Rubinstein, and W. Ensinger, "Template-free electroless plating of gold nanowires: Direct surface functionalization with shape-selective nanostructures for electrochemical applications," ACS Applied Materials & Interfaces, vol. 9, no. 36, pp. 31142–31152, 2017.

#### Conference contributions (1<sup>st</sup> author only)

- L. Hagelüken, M. Makowska, and J. Brugger, "Multiscale 2D/3D microshaping of property-contrast polymer-derived SiCN," *Ceramics in Europe 2022*, 2022. Krakow, Poland. (Oral)
- L. Hagelüken, M. Makowska, and J. Brugger, "Multiscale 2D/3D microshaping of property-contrast polymer-derived SiCN," 46<sup>th</sup> International Conference and Expo on Advanced Ceramics and Composites, 2022. Daytona Beach, U.S. (Oral)
- L. Hagelüken, H.-Y. Lee, D. di Stadio, and J. Brugger, "Freeform microstructuring of cast polymer-derived ceramics by sacrificial direct laser writing," 47<sup>th</sup> International Conference on Micro and Nano Engineering, 2021. Turin, Italy. (Oral)
- L. Hagelüken, P.V.W. Sasikumar, G. Blugan, and J. Brugger, "Electrical conductivity tuning of polysilazane-derived silicon carbonitride ceramics," *Electroceramics XVII*, 2020. Darmstadt, Germany. (Poster)