Polymer Derived Ceramics in MEMS/NEMS – A Review on Production Processes and Application

Michael Schulz, Dr.-Ing.

Forschungszentrum Karlsruhe GmbH
Institut für Materialforschung III
Material- und Prozessentwicklung
P.O. Box 3640
76021 Karlsruhe
Tel.: +49 (0)7247 / 82-6462
Fax : +49 (0)7247 / 82-2095
email: Michael.Schulz@imf.fzk.de

Abstract
The availability of Micro- and Nanoelectromechanical systems (MEMS/NEMS) made from non-oxide ceramics containing the elements Si, C, N and B opens up new areas of applications in various branches of technology. By using Polymer Derived Ceramics (PDC) the application of MEMS/NEMS in harsh environments with high temperature under oxidizing conditions becomes possible. Smallest features below one micron have already been realized. Two main approaches to the fabrication of PDC containing MEMS/NEMS are presented in this review. In so called nano-imprint- (NIL) or soft-lithography methods the microstructures are initially prepared on a duroplastic master for derivative moulding or printing processes. A direct method is the structuring and cross linking of preceramic polymers using lithographic energy sources like UV, X-ray, E-beam and laser.

Keywords
Polymer Derived Ceramics, Preceramic Polymers, MEMS, NEMS, Lithography

Polymer Derived Ceramics in MEMS/NEMS – A Review on Production Processes and Application

Introduction

In Micro and Nano-Electromechanical Systems (MEMS/NEMS) the combination and interaction of different materials and the accurate mounting of several parts is of major importance. Routes to shape ceramic materials are needed that fit common MEMS-processes like different lithographic methods or printing techniques because the manufacturing of miniaturized ceramic components using the powder route, i.e. pressing or micro powder injection moulding is limited. In general, producing original moulds needed to shape micro parts is very complex and therefore expensive.

The direct shaping of sintered ceramics using mechanical methods like milling, cutting or grinding is critical since the machining tools suffer from the hardness of the material. Shaping micro parts in the green state before sintering is of no avail when it comes to smallest features because it is difficult to produce tools with dimensions smaller then 0.1 mm [1]. Moreover, strong efforts are necessary in order to accomplish the accuracy requirements of Microsystem Technologies.

Amorphous bulk ceramics derived from the thermal pyrolysis of liquid organic precursors, known as polymer-derived ceramics (PDCs) containing the elements Si, C, N and sometimes B, O provide interesting material properties[2]. Favourable creep, thermal shock and high oxidation resistance have been reported [3, 4, 5, 6]. The nanostructure of the SiCN PDCs can be adjusted by tailoring the ceramic precursor polymer and their processing to alter specific properties [4, 7]. For example the formation of nanocarbon during pyrolysis allow the use in electronic devices [8, 9].

Two innovative approaches to the fabrication of MEMS/NEMS using ceramic precursor polymers are presented. The direct structuring and cross linking of preceramic polymers using lithographic energy sources like UV, X-ray, E-beam or laser and the nano-imprint- (NIL) or soft-lithography methods. In the latter case the microstructures are initially prepared on a duroplastic (not a PDC) master for use in derivative moulding or printing processes.

MEMS/NEMS production processes

Lithography

Lithographic methods in general selectively remove parts of a thin film using different kinds of radiation like visible and UV-light, X-ray and E-beam. In Fig. 1 (left) a schematic of an UV exposure unit is illustrated. A geometric pattern is transferred to a radiation sensitive chemical (so called resist, possibly a precursor for PDC) from a mask or by deflection of an exposure beam, respectively. Tab. 1 gives a partial overview of the mechanisms used to transfer the pattern to the resist in common lithographic methods.

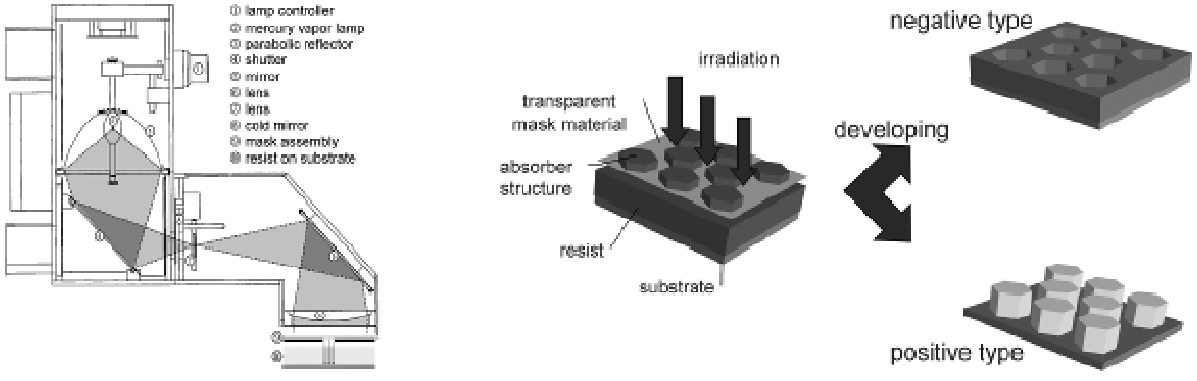

Fig. 1: Schematic of an UV exposure unit (left). Schematic view of the different behaviour of negative and positive type resists in mask based microlithography processes (right).

The first step in lithography is to apply the resist on a substrate e.g. by spin-coating or casting. To get highest precision in the lithographic processes, the resist materials must be solid or at least provide high viscosity. Although the successful application of liquid ceramic precursors was demonstrated in scientific publications it will probably not be a feasible approach in commercial processes [10, 11]. Contact with liquid resist will damage the highly expensive lithographic mask. In X-ray lithography the assembly of the substrate, resist and mask has to be mounted vertically, therefore the use of liquid resist materials is impossible.

Tab. 1: Pattern transfer mechanism overview of common lithographic methods.

process	radiation type	pattern transfer	exposure type	light source
photolithography	visible or UV-light	mask or dynamic pattern generator	surface, possibly rastered beam	arc lamp or UV-laser
stereolithography (SLA)	UV	beam deflection	laser spot	UV-laser system
selective laser sintering (SLS)	IR	beam deflection	laser spot	CO_2-laser
X-ray-lithography	X-ray	mask	surface	synchrotron
E-beam-lithography	electrons	beam deflection	electron beam	electron source
EUV-lithography	extreme UV (120 - 10 nm)	mask	surface	plasma
Two photon stereolithography	extreme UV	beam deflection	laser spot	Eximer-laser

Additionally, the test chamber in X-ray or E-beam-lithography has to be evacuated before exposure starts to make sure that no side reactions with the ionizing radiation occur. Resist materials therefore must not emit solvent or low molecular weight species. After application on the substrate the solvents used to coat the resist have to be completely removed.
Depending on whether the resist reacts by cross linking (negative type) or chain crack (positive type) the exposed areas become soluble in the developing solvent or remain on the substrate after developing (Fig. 1, right)
Ceramic precursor polymers used for direct lithographic microfabrication of MEMS/NEMS mostly act as negative type resists because they often carry vinyl side chains that can be easily activated as can be seen in Fig. 2 on the left for the common Ceraset precursor (KiON Corp.). Furthermore, using high energy radiation like X-ray or extreme UV causes elimination of hydrogen and other side chains followed by recombination with other polymer chains leading to a cross linking of the precursor as it has been shown by Schulz et al. for the ABSE precursor (Fig. 2, right) [4, 12].

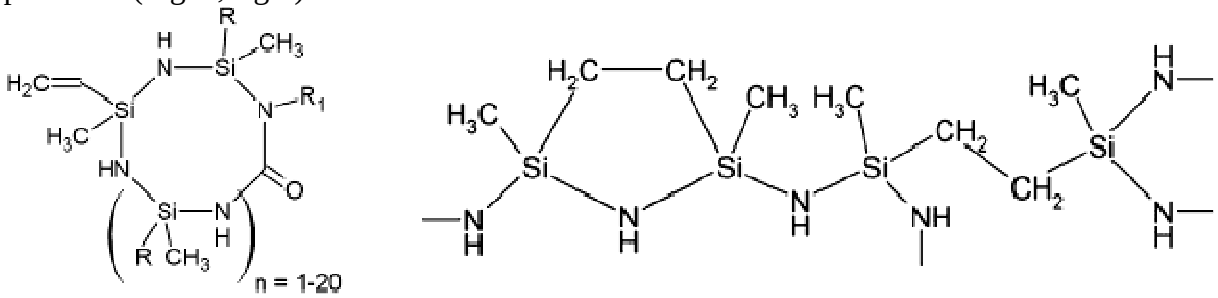

Fig. 2: Molecular structure of the Ceraset® Polyureasilazane[2] and the ammonolysed bis(dichlorosilyl)ethane ABSE[4].

Besides the exposure the developing of the transferred pattern is crucial. Normally a specific developer solution has to be found for each resist to optimize developing time and microstructure quality. Depending on the resist type the solvent used as a developer should selectively dilute the exposed or unexposed areas. Standard developers tend to influence the

materials properties by contamination with oxygen. This affects the properties for high temperature application in a negative way.
Common microfabrication is carried out in clean rooms under well defined ambient conditions, i.e. air moisture (40% relative humidity) and temperature (21°C). Because most ceramic precursor polymers are air and especially moisture sensitive this ambience is not adequate. On the other hand, new materials in MEMS/NEMS technology should match the existing processes to have high potential[13]. Therefore only preceramic polymers with low sensitivity to moisture and air can be used in standard MEMS/NEMS processes.
Lithographic microfabrication usually ends after the developing step when the designated pattern is free-standing on the substrate and possibly can be processed to the MEMS. To obtain a PDC containing MEMS/NEMS it is necessary to pyrolyse the preceramic resist to the concluding ceramic. As in bulk bodies, the shrinkage upon pyrolysis significantly influences the quality of the remaining component. In case of the substrate bonded lithographically manufactured structures this shrinkage can lead to delaminating and partial destruction due to thermal expansion mismatch. It has been shown that structures with diameter smaller than 50 µm and thickness of 20 µm could be pyrolysed on the substrate without cracking and delaminating [12].
Different approaches using ceramic powder fillers can be found in literature to control the shrinkage and reduce the tendency of crack formation and delaminating. Microfabrication has to be adapted since the filler particles induce scattering and therefore cause unwanted absorption in the direct lithographic processes. Typically, the exposure doses raise and surface quality and edge precision of the fabricated MEMS and NEMS are extremely influenced by the particle size of the filler used. It has also been shown that native substrates that were thermally cross-linked before the resists were applied effectively inhibited the formation of cracks and warping [14].
Nano-Stereo-Lithography
A special type of lithographic method is the **N**ano- or two-photon **S**tereo**l**ithography (NSL). In NSL the energy of the incident photons from a femto second laser source is below the absorption threshold of the resist. Hence the resist material is transparent for the laser light used. However, by focusing the laser beam the probability of multi-photon absorption increases in the focal volume, i.e. the UV-sensitive material absorbs two NIR-photons at 790nm, which is energetically equivalent to one UV-photon at 395 nm [15, 16]. Photocuring therefore takes place selectively in a small focal volume of about 120 nm.
Soft lithography / nanoimprinting
Other popular tools to pattern polymers, metals and ceramics with micro- and nano-structures are soft-lithography [9] and nano-imprint-lithography (NIL) [17]. The common feature of both techniques is that a lithographically patterned master is either used as a mould to impart patterns via physical confinement of a fluid precursor that dries to form the final structured thin film or as a stamp to directly transfer the material to the target substrate. In NIL high resolution stamps are usually made by E-beam lithography and dry etching of Silicon or SiO_2. In soft-lithography the master is structured using UV-lithography and standard resists like the epoxy based SU-8. An elastomeric material, most commonly polydimethylsiloxane (PDMS), is used to obtain a negative of the lithographic master (in the center of Fig. 3). Schematic drawings of the techniques mentioned are provided in Fig. 3. Varieties of derivative processes like micro transfer moulding (µTM, Fig. 3, A), embossing (B) and micro moulding in capillaries (MIMIC, E) have been developed and successfully adopted with ceramic precursor polymers [18, 19, 20, 21, 9, 22]. Micro contact printing (µCP, F) requires self assembling molecules. Microchannel molding (D) uses the same capillary filling principle as MIMIC, whereby a pool of liquid precursor is placed at the entrance region of channels formed by the patterned substrate and a flat PDMS membrane. The membrane can be peeled off after the fluid is drawn into the channels by capillary suction and dried or cured respectively.

In the microcasting (Fig. 3, C) approach the lithographically produced pattern master itself is used as a mould for microcasting of liquid precursor polymer[23, 24]. The preceramic structured parts are separated from the substrate before pyrolysis and sintering. For example a sharp blade can be used to remove the structures from weakly adhering Teflon or even a silicon substrate [11]. Another innovative way is the usage of a bulk NaCl crystal as a sacrificial substrate, which is readily dissolved in water after exposure and development[11].
Liquid ceramic precursors are well suited for NIL and soft-lithography and it is easy to accomplish these processes in inert atmosphere. Hence, the number of appropriate preceramic polymers is higher compared to direct lithographic microfabrication and even boron containing compounds have been successfully used [25, 26, 22].

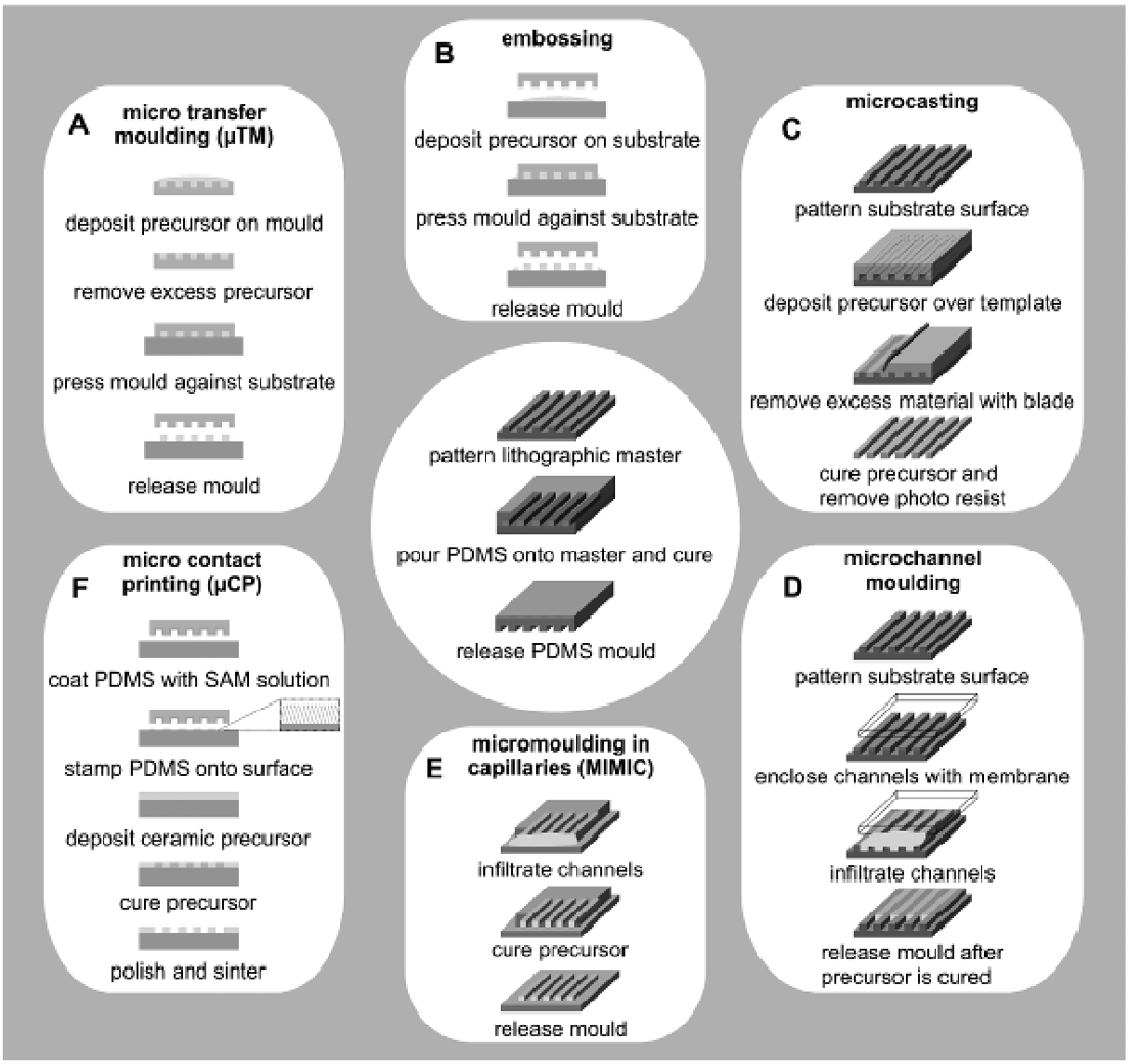

Fig. 3: Schematic illustration of PDMS mould preparation and soft lithography techniques used to pattern ceramic materials.

Applications

Actuators

A demonstrator for a vertical piston electrostatic actuator was assembled applying the four-flexured structure shown in Fig. 4 after pyrolysis by Liew et al. [27, 23]. The authors used the lithographically shaped SU-8 master in the microcasting process. In an optimized process potential reactions between the Ceraset based resist and the mould material were avoided by

using the SU-8 master to emboss a thin aluminum foil as separator before filling with the ceramic precursor
The actuator is being developed for experimental temperatures up to 1600°C so that the internal friction behaviour and the glass transition of the SiCN ceramic as a function of frequency and temperature can be determined. For example the Youngs Modulus of 150 GPa obtained by using the voltage-deflection data closely agrees with that obtained using indentation techniques[11].
Another possible application mentioned by the authors is the use as a micro mirror for high-power laser systems where polysilicon surface-micromachined mirrors have failed, provided that a suitable metal is applied to the SiCN plate in order to make the surface reflective.

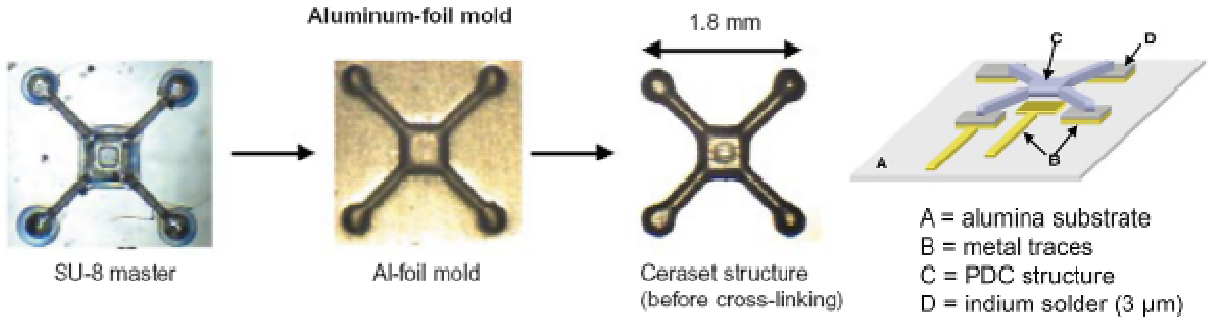

Fig. 4: Left: The SU-8 mould cavity is embossed into aluminum foil that is peeled away after casting and solidifying the precursor[23]. Right: Schematic of the electrostatic actuator MEMS. Reprinted from [23], with permission from the American Ceramic Society.

By combining two thermal actuators made from polymer derived SiCN the same authors assembled a micro-gripper for manipulating chip-size objects (Fig. 5, right) [28]. The thermal actuators were patterned using microcasting followed by thermal (up to 1400°C) and pressure (up to 425 psi) treatment in a hot isostatic press. The initial resistance measured between the contact pads was 400-500 Ω. By applying a d.c. current of 30 mA the small blade of the actuator starts to glow with yellow colour causing a deflection of several microns (Fig. 5, left).
Compared with surface-micromachined grippers, the SiCN grippers are capable of supporting larger masses. The low thermal conductivity of SiCN inhibits the heating of the objects that are manipulated by the gripper compared to metal devices.

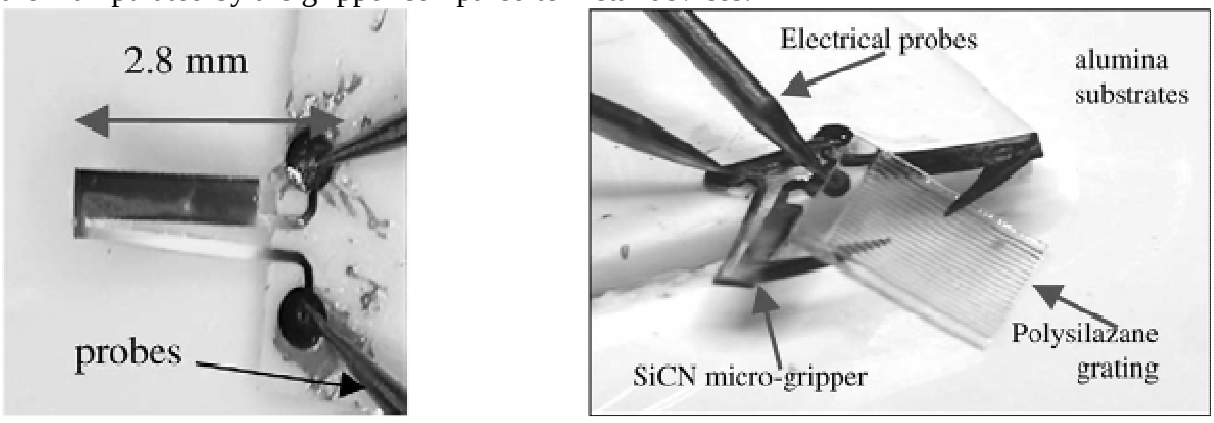

Fig. 5: Photographs of a polymer derived SiCN thermal *a* actuator and *b* microgripper, tilting 3 x 3 mm grating made from Ceraset precursor. Reprinted from [28], Copyright 2003, with permission from Elsevier.

Photonics
A method similar to the MIMIC process is presented by Feiertag et al. to produce so called "three cylinder" structures for application as photonic crystal [29]. It consists of using deep X-

ray lithography of PMMA positive resist and filling the remaining structures after developing with liquid ceramic precursor. By repeated exposure of the tilted stack of mask and resist, the 3D-master structure providing a lattice constant of 114 µm was fabricated. After developing, the microchannels were filled with a polyvinylsilazane from Hoechst with a molecular composition of $SiN_{1.5}C_{2.0}H_{5.0}$ diluted in THF [30]. After evaporation of the solvent and cross-linking of the ceramic precursor by air exposure the PMMA was removed during pyrolysis up to 1100 °C. The lattice constant of the obtained photonic crystal was 85 µm and the rods diameter was 22 µm (Fig. 6).

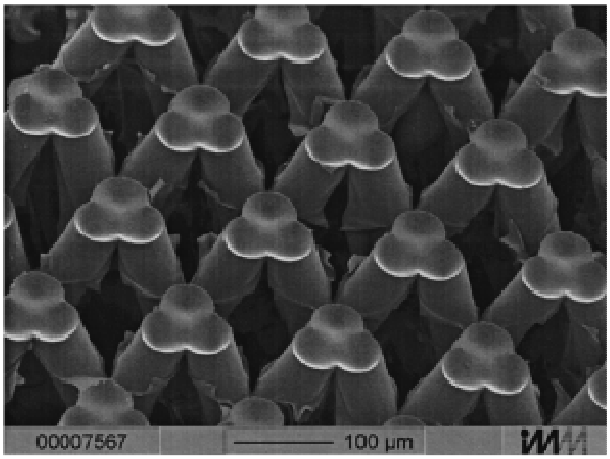

Fig. 6: Photonic crystal made of siliconcarbonitride ceramic. Reprinted from [29], Copyright 1997, with permission from the American Institute of Physics.

Recently Pham et al. presented the production of real 3D ceramic microstructures by NSL using a newly developed functionalized VL20 (KiON Corp.) based resist[31, 32]. Quite impressive are the realization of a woodpile structure (edge length of only 9 µm, Fig. 7 a-f), a spiral microtube and a microcruciform (Fig. 7 g,h) with nanometer resolution [32]. Comparable microstructures have been reported before from polysiloxane based resist materials [33]. Nevertheless, the shrinkage during pyrolysis causes deformation of these structures, too (Fig. 7 c-e). Thus, the authors added up to 40 wt % of silica filler (10 nm diameter) to support the geometry (Fig. 7f) [32]. This ceramic precursor was demonstrated to be a highly sensitive resist for conventional UV-lithography [31].

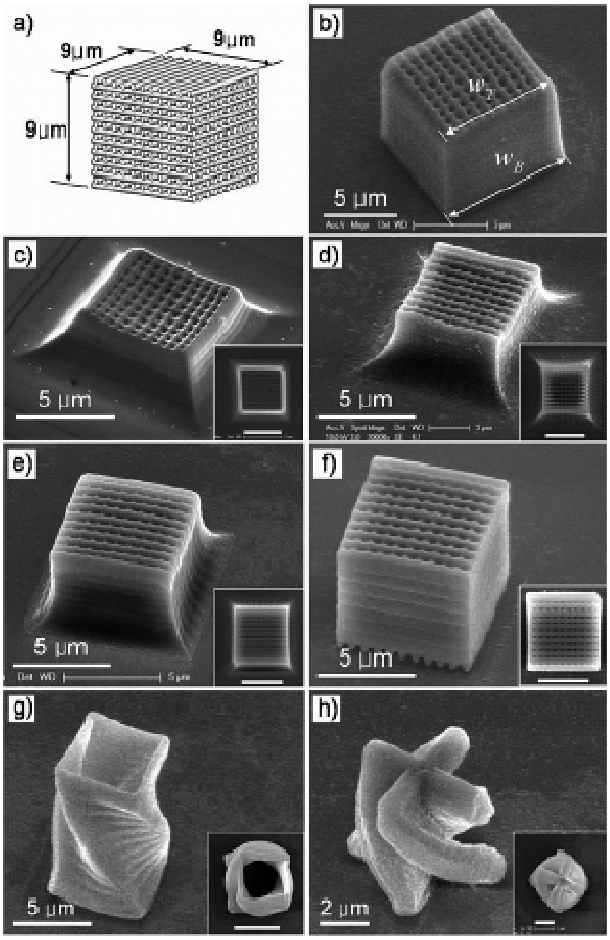

Fig. 7: Three-dimensional ceramic microstructures fabricated by nanostereolithography or/and subsequent pyrolysis at 600 °C; a) schematically designed woodpile structure and b) polymeric structure with no filler. c) Ceramic woodpile structure with no filler. d–f) Ceramic woodpile structures obtained from the mixed resin containing various amount of silica filler for reduced shrinkage: d) 20 wt% silica, e) 30 wt %, and f) 40 wt %. Other 3D ceramic microstructures of spiral g) microtube and h) microcruciform with a twisting angle of 90° between their bottom and top; they are fabricated using the resin containing 40 wt% silica particles. (Each inset is the top-view of the structure.) Reprinted from [32], copyright 2006, with permission of Wiley VCh.

Electrical heating applications

The application and successful testing of Ceraset based ceramic micro igniters or glow plugs manufactured using both, photopolymerization and microcasting has been described by Liew et al.[34] (Fig. 8). The micro igniter is suited for applications in harsh environments e.g. in diesel engines. It was demonstrated, that the thermite reaction (resulting temperature exceeding 2000 °C) can be ignited using this glow plug. Compared to conventional glow plugs the power consumption (PDC derived: 3 W) and response time (PDC derived: 0.5 s) and probably the manufacturing costs are extremely lower. Temperatures up to 1450 °C in air have been measured using this electrical heating circuit. Additionally the samples have been used for *in situ* measurement of high-temperature properties like resistivity and oxidation activation energy in the MEMS processed PDCs. More than 1000 glow cycles have been achieved applying 40 mA of dc current before the specimen failed due to oxidation.

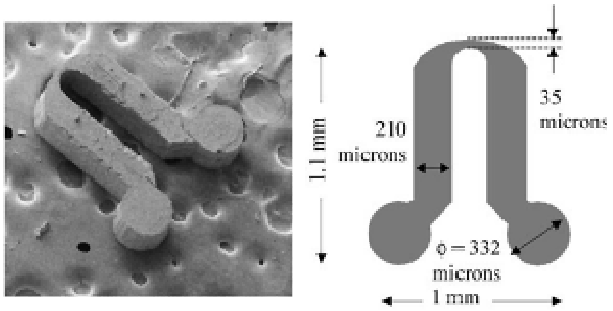

Fig. 8: Scanning electron micrograph and geometrical data of a PDC-SiCN micro glow plug and conducting tape. At the glow tip aspect ratios between one and ten were realized. Reprinted from [34], Copyright 2003, with permission from Elsevier.

Micro fluidics

The embossing of microchannels has been reported by Lee et al. [21]. The polyvinylsilazane (Ultra II from KiON Corp. USA) in combination with thermal (dicumyl peroxide) and photo initiator (Irgacure 369) was cured after embossing using UV and heating but the subsequent pyrolysis was passed. Therefore the ceramic precursor was used in its polymeric state to form a microfluidic structure for use as a capillary system (Fig. 9). In the cross-linked state the precursor provides high optical transparency as well as excellent thermal stability and chemical inertness. Hence, unpyrolysed preceramic polymers provide high potential in micro total analysis systems and photochemical reactors. Smallest channels produced provided a depth and width of 20 µm. To test the boundaries of the process a digital versatile disc (DVD) was utilized as an economic nano-sized master with an approximate with of 500 nm and a height of 140 nm [19, 21]. A comparable technique using a SiCBN precursor (borazine modified allylhydridopolycarbosilane) that was thermally cured while the DVD mould was pressed against the substrate was reported by Nghiem et al. [26]. Due to the high ceramic yield of 92 %wt after annealing up to 1200 °C crack free high oxidation resistant ceramic nanostructured components become available.

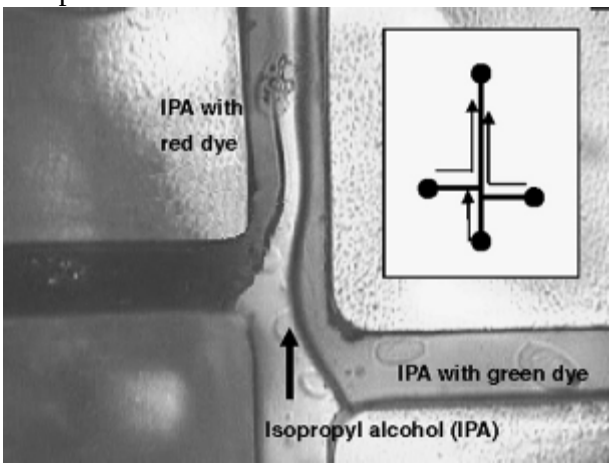

Fig. 9: Microfluidics in the cross-linked polymeric polyvinylsilazane channel structure. A green and a red dye were used to visualise the flow. Reprinted from [21], Copyright 2007, with permission from Elsevier.

Summary and Conclusion

Various efficient microfabrication techniques for polymer derived ceramic MEMS/NEMS were demonstrated. The electrical properties of the PDC can be tailored and enables the use in electrical actuators and efficient heaters. Due to the outstanding thermo mechanical properties and the chemical resistance of PDC the application of MEMS/NEMS in harsh environments with high temperature under oxidizing conditions becomes possible. Micro grippers, photonic crystals and micro fluidic components have been tested and are a promising origin to new

applications. Smallest features below one micron have already been realized. One challenge is to adapt the processes and materials to common MEMS technologies. For direct lithographic applications air and moisture stable precursor polymers are needed that provide side chains that can be photochemically activated. The methods presented are also applicable to precursor polymers for a variety of ceramics like, among others, lead zirconate titanate [35].

References

1. F. Fang, K. Liu, T. Kurfess, and G. Lim: 'Tool-based Micro Machining and Applications in MEMS', in 'MEMS/NEMS', (ed. edn, 678-740; 2006.
2. R. Riedel, G. Mera, R. Hauser, and A. Klonczynski: *Journal of the Ceramic Society of Japan*, 2006, **114**, 425-444.
3. T. Cross and R. Raj: *Journal of the American Ceramic Society*, 2006, **89**, 3706-3714.
4. M. Günthner, T. Kraus, A. Dierdorf, D. Decker, W. Krenkel, and G. Motz: *Journal of the European Ceramic Society*, 2009, **10**, 2061-2068.
5. R. Raj, L. N. An, S. Shah, R. Riedel, C. Fasel, and H. J. Kleebe: *Journal of the American Ceramic Society*, 2001, **84**, 1803-1810.
6. S. R. Shah and R. Raj: *Journal of the American Ceramic Society*, 2001, **84**, 2208-2212.
7. L. G. Zhang, Y. S. Wang, Y. Wei, W. X. Xu, D. J. Fang, L. Zhai, K. C. Lin, and L. N. An: *Journal of the American Ceramic Society*, 2008, **91**, 1346-1349.
8. S. Traßl, D. Suttor, G. Motz, E. Rössler, and G. Ziegler: *Journal of the European Ceramic Society*, 2000, **20**, 215-225.
9. Y. Xia and G. M. Whitesides: *Angewandte Chemie International Edition*, 1998, **37**, 550-575.
10. T. Hanemann, M. Ade, M. Borner, G. Motz, M. Schulz, and J. Hausselt: *Advanced Engineering Materials*, 2002, **4**, 869-873.
11. L.-A. Liew, Y. Liu, R. Luo, T. Cross, L. An, V. M. Bright, M. L. Dunn, J. W. Daily, and R. Raj: *Sensors and Actuators A: Physical*, 2002, **95**, 120-134.
12. M. Schulz, M. Borner, J. Gottert, T. Hanemann, J. Hausselt, and G. Motz: *Advanced Engineering Materials*, 2004, **6**, 676-680.
13. D.-P. Kim, T.-H. Yoon, H.-J. Lee, and J. Yan: *Journal of the Ceramic Society of Japan*, 2006, **114**, 473-479.
14. M. Schulz, M. Börner, J. Hausselt, and R. Heldele: *Journal of the European Ceramic Society*, 2005, **25**, 199-204.
15. T. Hanemann, W. Bauer, R. Knitter, and P. Woias: 'Rapid Prototyping and Rapid Tooling Techniques for the Manufacturing of Silicon, Polymer, Metal and Ceramic Microdevices', in 'MEMS/NEMS', (ed. edn, 801-869; 2006.
16. S. Maruo, O. Nakamura, and S. Kawata: *Optics Letters*, 1997, **22**, 132-134.
17. S. Y. Chou, P. R. Krauss, and P. J. Renstrom: *Science*, 1996, **272**, 85-87.
18. G.-S. Chung: *Microelectronics Journal*, 2007, **38**, 888-893.
19. D. P. Kim, A. Asthana, Y. Asthana, and I. K. Sung: *Lab on a Chip*, 2006, **6**, 1200-1204.
20. D. P. Kim, I. K. Sung, Q. D. Nghiem, and A. Asthana: *Eco-Materials Processing & Design Vii*, 2006, **510-511**, 1030-1033.
21. H.-J. Lee, T.-H. Yoon, and D.-P. Kim: *Microelectronic Engineering*, 2007, **84**, 2892-2895.
22. H. Yang, P. Deschatelets, S. T. Brittain, and G. M. Whitesides: *Advanced Materials*, 2001, **13**, 54-+.

23. L. A. Liew, W. G. Zhang, L. N. An, S. Shah, R. L. Luo, Y. P. Liu, T. Cross, M. L. Dunn, V. Bright, J. W. Daily, R. Raj, and K. Anseth: *American Ceramic Society Bulletin*, 2001, **80**, 25-30.
24. C. R. Martin and I. A. Aksay: *Journal of Electroceramics*, 2004, **12**, 53-68.
25. J. Kong, G. B. Zhang, and Q. Liu: *Progress in Chemistry*, 2007, **19**, 1791-1799.
26. Q. D. Nghiem, A. T. Pham, and D. P. Kim: *Eco-Materials Processing & Design Vii*, 2006, **510-511**, 774-777.
27. L.-A. Liew, L. Ruiling, L. Yiping, W. Zhang, L. An, V. M. Bright, M. L. Dunn, J. W. Daily, and R. Raj: 'Fabrication of multi-layered SiCN ceramic MEMS using photo-polymerization of precursor', Micro Electro Mechanical Systems, 2001. MEMS 2001. The 14th IEEE International Conference on, 86-89.
28. L. A. Liew, R. A. Saravanan, V. M. Bright, M. L. Dunn, J. W. Daily, and R. Raj: *Sensors and Actuators a-Physical*, 2003, **103**, 171-181.
29. G. Feiertag, W. Ehrfeld, H. Freimuth, H. Kolle, H. Lehr, M. Schmidt, M. M. Sigalas, C. M. Soukoulis, G. Kiriakidis, T. Pedersen, J. Kuhl, and W. Koenig: *Applied Physics Letters*, 1997, **71**, 1441-1443.
30. H. Freimuth, V. Hessel, H. Kolle, M. Lacher, W. Ehrfeld, T. Vaahs, and M. Bruck: *Journal of the American Ceramic Society*, 1996, **79**, 1457-1465.
31. D. P. Kim, T. A. Pham, P. Kim, M. Kwak, and K. Y. Suh: *Chemical Communications*, 2007 4021-4023.
32. D. Y. Yang, T. A. Pham, D. P. Kim, T. W. Lim, S. H. Park, and K. S. Lee: *Advanced Functional Materials*, 2006, **16**, 1235-1241.
33. M. Straub, L. H. Nguyen, A. Fazlic, and M. Gu: *Optical Materials*, 2004, **27**, 359-364.
34. L.-A. Liew, V. M. Bright, and R. Raj: *Sensors and Actuators A: Physical*, 2003, **104**, 246-262.
35. C. R. Martin and I. A. Aksay: *Journal of Materials Research*, 2005, **20**, 1995-2003.