

Cross linking behavior of preceramic polymers effected by UV- and synchrotron radiation

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The fabrication of micro components made from ceramic materials is becoming more and more important in micro system technology (MST). The pronounced chemical stability and the outstanding mechanical properties like the reduced thermal expansion coefficient and the high mechanical strength allow for the use of those materials. Different replication methods like slip casting, tape casting, stamping, low or high pressure ceramic injection molding a.o. using micro structured mold inserts as master have been established, but in all cases the organic binder amount in the used feedstock has to be eliminated by debinding and sintering procedures to achieve a dimensionally stable micro structured part [1-3]. A further post processing after sintering is almost impossible in the structural region of interest around a few micrometers.

Various lithographic methods are being widely used for the direct fabrication of very precise plastic or metal micro structured surfaces [4-6]. Mass production of computing processors is based on these processes. Furthermore it is well known, that high temperature stable ceramics can be achieved from preceramic polymers using relatively low pyrolysis temperatures [7-9].

The aim of this work was to develop a direct lithographic process to produce ceramic microstructures. Based on preceramic polymers new resist materials for the UV- and deep X-ray lithography should be developed.

The developed process starts with the mixing of a preceramic polymer with a specific amount of an aprotic solvent. Where applicable some ceramic powder is added as a filler. By using spin coating, casting or tape casting techniques the resist is deposited on a substrate. Exposure with UV- or synchrotron radiation transfer a mask pattern into the resist. After development of the exposed structure the material can be ceramised by pyrolysis (Figure 1).

From the described process the specification for an appropriate ceramic precursor polymer can be derived [10].

- solid aggregate state under ambient conditions, in case of UV-lithography an adjustable highly viscous liquid state is possible,
- improved chemical stability against cross linking through reactions with moisture and oxygen, necessary for
- processability in (dry) air for several hours,
- soluble in or miscible with standard aprotic solvents,
- formation of stable films on substrate surfaces (e.g. silicon or alumina wafers),
- small molecular weight distribution with respect to the development step,
- high sensitivity for photochemical cross linking e.g. by formation of radicals with photo electrons (X-ray) or addition reactions with existing vinyl substituents (UV).

The actual research is focused on two available preceramic polymers. The commercial liquid Ceraset polymer, achieved from KiON Corp. and the soluble solid ABSE [11] (ammonolyzed bis(dichlorosilyl)ethane) from the Institute of Materials Research, IMA Bayreuth. While the Ceraset polymer can easily be cross linked e.g. by hydrosilylation [12-15], the necessary vinyl and Si-H groups are missing in the ABSE polymer (Figure 2).

To investigate the photochemical cross linking behavior a small glass reactor using a UV-light source was deployed. For detailed description of the reactor system see [10]. The change of the polymer properties can be examined by continuous sample extraction. For the ABSE polymer the molecular weight distribution was observed by gel permeation chromatography (Figure 3). It could be shown, that with increasing exposure time the rate of low weight molecules decrease, while fractions with high molecular weight are formed, although typical chromophore groups are missing.

UV spectroscopy allows for the analyzation of absorption behavior in the range of visible light down to 190 nm. The Ceraset polymer absorbs significantly from 350 nm down to lower

wavelengths. The absorption can induce cross linking by activation of vinyl groups. The ABSE polymer in comparison shows a considerably smaller absorption range (Figure 4).

Using deep X-ray lithography a value for the *contrast* of the ABSE material was calculated. The contrast describes the sensitivity of a resist material in X-ray lithography. The remaining resist thickness after exposure and development, standardized to the starting thickness is plotted against the incident dose (Figure 5) [4]. The ascertained value is extremely depending on the process, e.g. radiation source, solvent or drying time. For contrast determination samples with a resist thickness up to 500 µm were prepared and exposed using a perforated aluminum plate with different carbon filters. By linear regression in the transition range between the dose where no effect on the resist is observable (D_0) and the dose where the material gets insoluble over the whole thickness (D_{100}) the slope can be calculated. For the

ABSE material a contrast value of $\gamma = \frac{1}{\log \frac{D_{100}}{D_0}} \cong 0.8$ was determined. The contrast curve shows the typical characteristics for a negative resist.

For UV lithography resist films with thickness up to 20 µm were produced by spin coating. With the deployed low resolution UV exposure system using a standard chromium on glass test mask aspect ratios of one with exposure time around ten minutes were achieved.

Figure 6 shows the 2D view of the topography of the exposed and developed test structure generated with contactless measuring white light interferometrie. The sharpness of edges is limited among other things by the optical properties of the imaging system as can be seen from the extracted height profile. It is obvious that the roughness of the resists surface and the substrate correspond.

In deep X-ray lithography resist layers up to 200 µm were manufactured by casting and tape casting. Thicker layers are achievable with this method. Using a bottom minimal dose of $1.5 \text{ kJ} \cdot \text{cm}^{-3}$ aspect ratios up to 20 were realized. The test mask layout and the resulting

3D-surface topography of a sector of the exposed and developed structure based on ABSE polymer, recorded using multi layer optical microscopy have been presented in [10] (Figure 7). By improving the process the thickness of the structured layers was increased compared to earlier publications [10, 16]. The sharpness of edges is lower than 1° as can be seen on the profile of a bar structure (Figure 8) from the middle of the mapped sample. The topographic view shows a star structure from the rear of the picture with a height of $100\text{ }\mu\text{m}$.

To increase the ceramic yield after pyrolysis ceramic powder where dispersed in the preceramic polymer. The used silicon nitride powder with particle size $d_{50} < 0.5\text{ }\mu\text{m}$ absorbs the synchrotron radiation to a minor degree. The mass absorption coefficient of the elements contained in the ceramic is small, that means that the powder is transparent for the used X-rays [17]. Aspect ratios up to ten were achieved based on resist thickness up to $100\text{ }\mu\text{m}$.

Agglomeration of the powder particles affects the sharpness of edges, which is obvious when microscopic views of identical structures are compared (Figure 9). The figure shows a star structure made from pure ABSE polymer (darker areas in this picture mark the surface of the substrate). The same structure made from powder filled resist exhibit particles on the edges (darker areas represent the resist surface in this picture).

The mass reduction during pyrolysis leads to volume shrinkage. In case of the substrate bonded lithographically manufactured structures this shrinkage leads to delamination and partial destruction (Figure 10). After pyrolysis the original structure size emerge on the substrate. For clarification this was highlighted with the small dotted ring. Structures with diameter smaller than $50\text{ }\mu\text{m}$ could be pyrolysed on the substrate without crack formation. Investigations in using substrates made from preceramic polymer that can shrink with the microstructure in the pyrolysis step are focus of actual research.

Conclusion:

Aim of this work was to develop a direct lithographic process to manufacture ceramic microstructures. It has been shown that the photochemical cross linking of preceramic polymers at ambient conditions is controllable. Using UV-lithography aspect ratios of one with minimal structure width of 10 μm were produced. In deep X-ray lithography aspect ratios up to 20 with structural details of 5 μm using filled and unfilled materials were realized. In case of structures with diameter smaller than 50 μm the shape could be retained after ceramisation. It could be shown that preceramic polymers are suitable as new resist materials for the UV- and deep X-ray lithography.

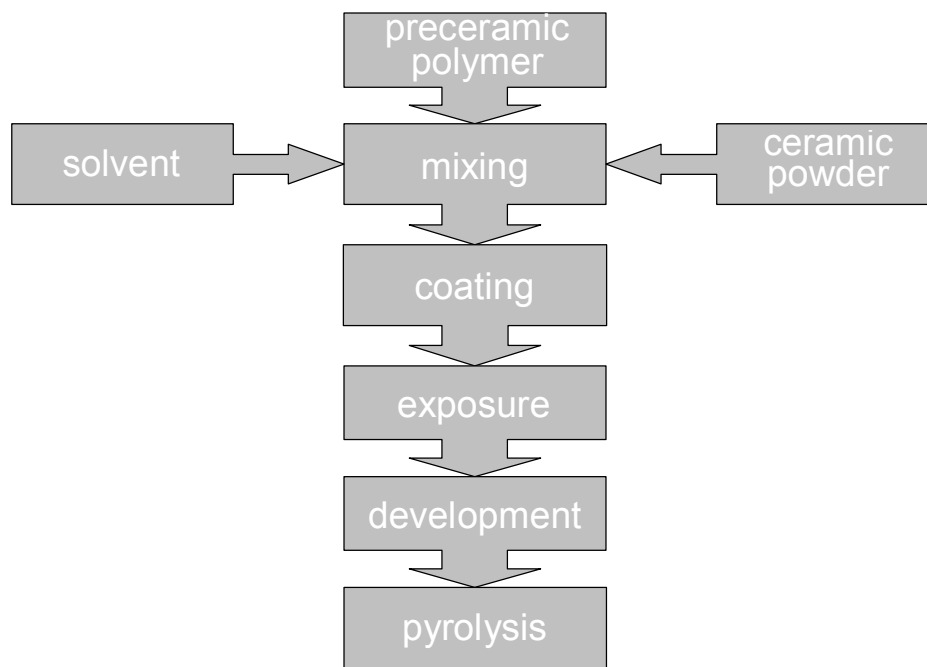


Figure 1: Scheme of the direct lithographic process to produce ceramic microstructures.

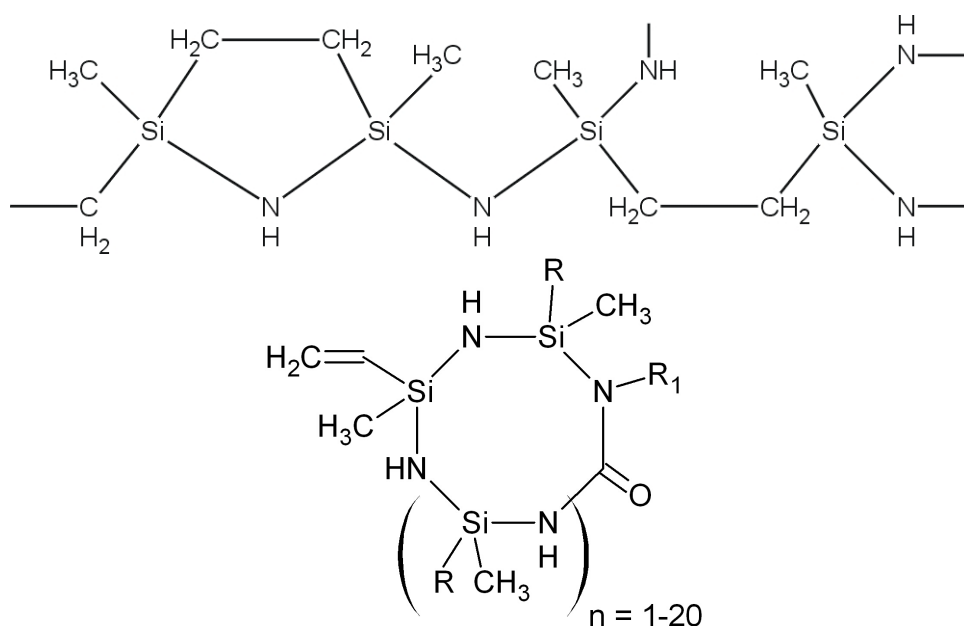


Figure 2: Chemical structures of the investigated preceramic polymers ABSE and Ceraset. For the Ceraset Polymer the rest R is vinyl or hydrogen, the rest R_1 is not further specified.

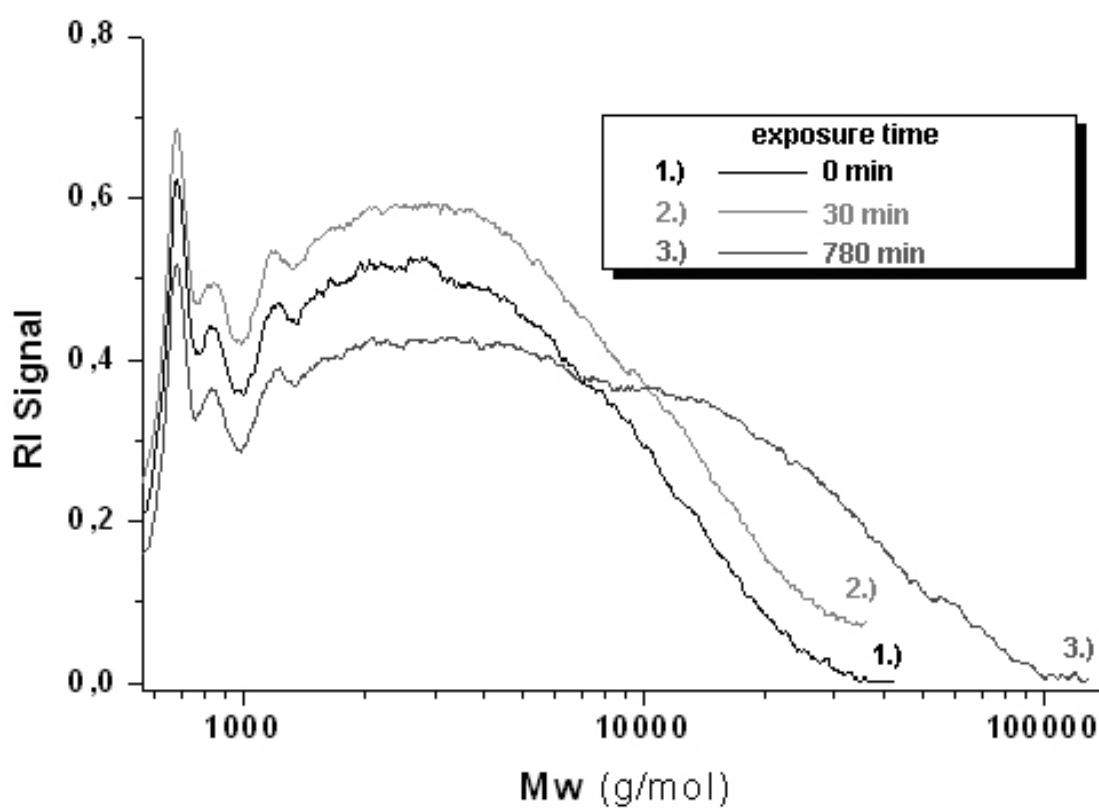


Figure 3: Exposure time dependent molecular weight distribution from gel permeation chromatography.

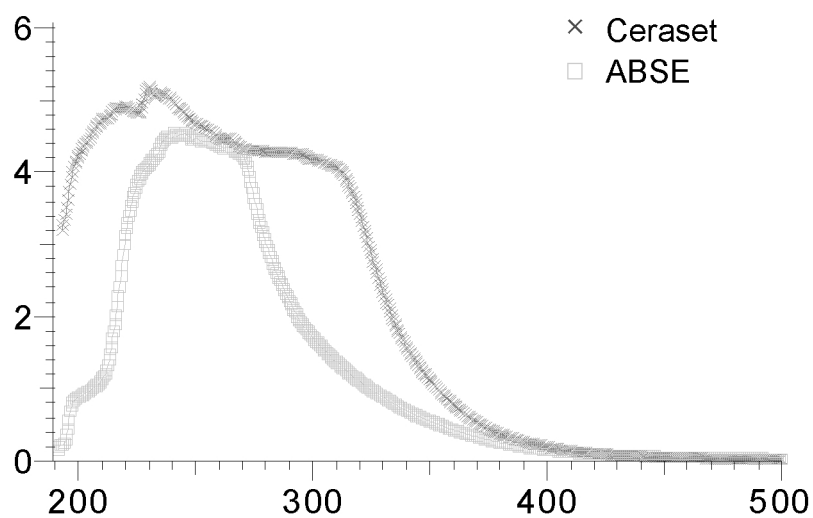


Figure 4: UV-spectra of the investigated preceramic polymers.

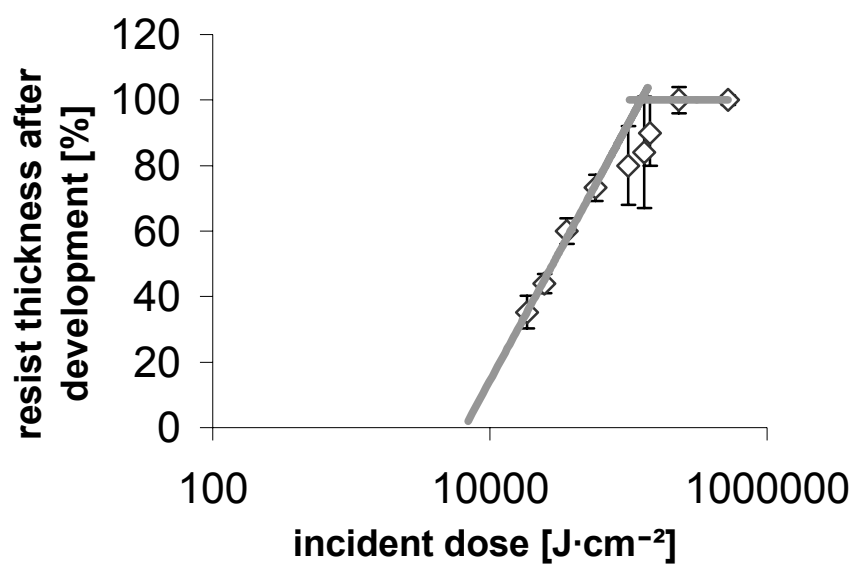


Figure 5: Contrast curve of the ABSE polymer determined at CAMD synchrotron facility, (beamline XRLM2, solvent octane).

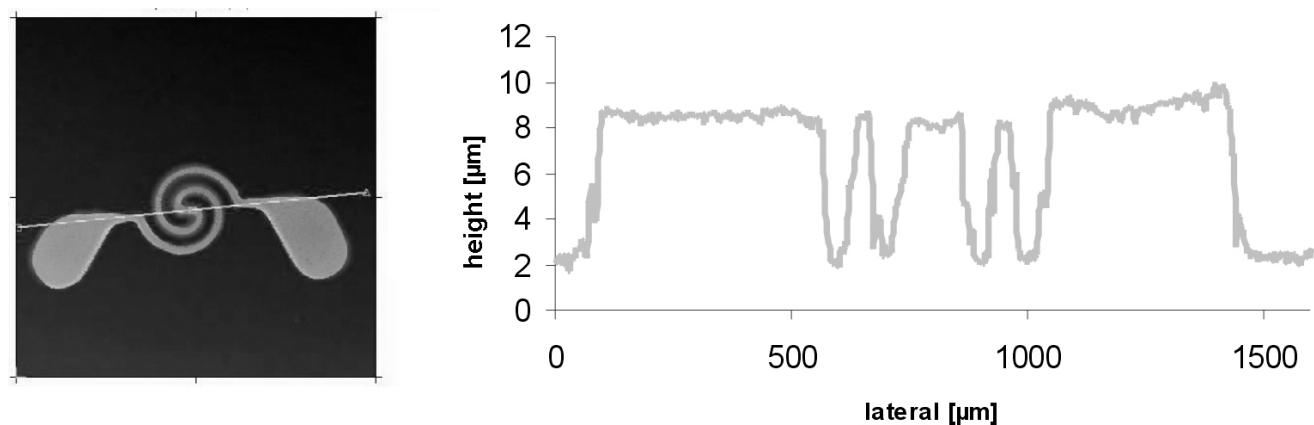


Figure 6: 3D-topographical view of a test structure produced by UV-lithography and height profile.

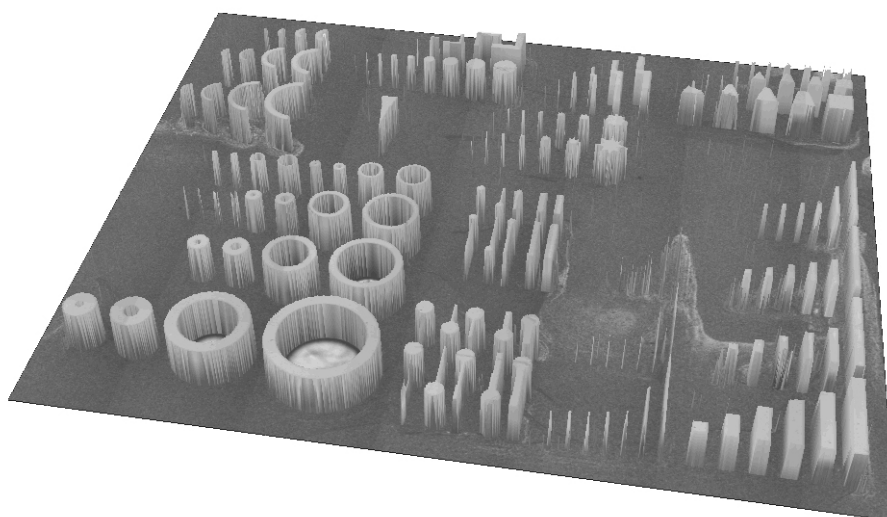


Figure 7: 3D-surface topography of the test structure for X-ray lithography made from ABSE polymer using multi layer optical microscopy.

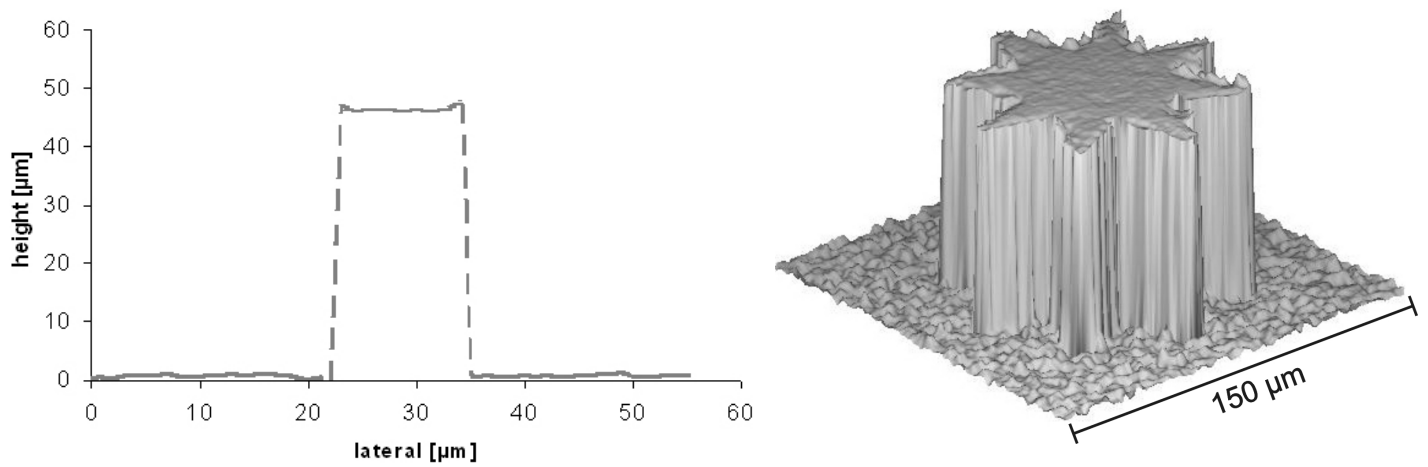


Figure 8: Height profile and topography of structural details of a X-ray lithographically produced sample (ABSE polymer).

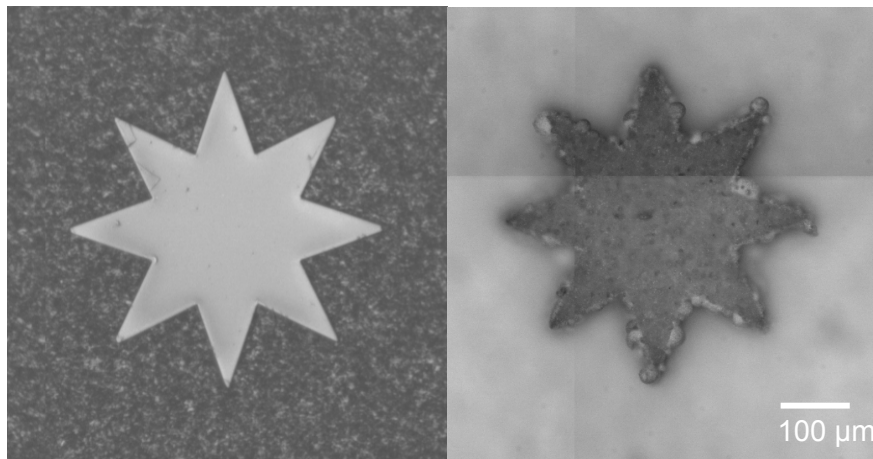


Figure 9: Structural detail of the developed structure using unfilled (left) and Si₃N₄ filled (right) ABSE polymer, made by X-ray lithography.

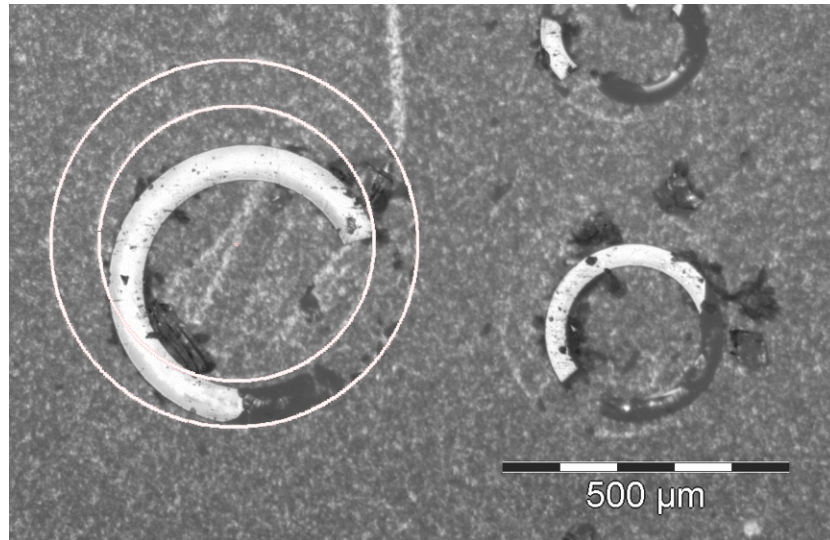


Figure 10: Delamination and destroying effects caused by volume shrinkage of the substrate fixed lithographically manufactured structures during pyrolysis.

- [1] W. Bauer, H.-J. Ritzhaupt-Kleissl, J. H. Haußelt, *Ceramics International* **1999**, 25, 201.
- [2] T. Hanemann, M. Hecke, V. Piotter, *Polymer News* **2000**, 25, 224.
- [3] V. Piotter, T. Benzler, T. Gietzelt, R. Ruprecht, J. H. Haußelt, *Adv. Eng. Mater.* **2000**, 2, 639.
- [4] W. Menz, J. Mohr, O. Paul, *Microsystem Technology*, Wiley-VCH, Weinheim, **2001**.
- [5] R. Brück, N. Rizvi, A. Schmidt, *Applied Microtechnology: LIGA-Laser-Micro Precision Engineering*, Carl Hanser Verlag, München, **2001**.
- [6] W.-J. Fischer, *Mikrosystemtechnik*, Vogel Verlag, Würzburg, **2000**.
- [7] F. Aldinger, W.D.G. Böcker, *Keramische Zeitschrift* **1992**, 44, 164 and 236.
- [8] P. Greil, *J. Am. Ceram. Soc.* **1995**, 78, 835.
- [9] E. Kroke, Y.-L. Li, C. Konetschny, E. Lecomte, C. Fasel, R. Riedel, *Mater. Sci. Eng.* **2000**, R26(4-6), 97.
- [10] T. Hanemann, M. Ade, M. Börner, G. Motz, M. Schulz, J. Haußelt, *Adv. Eng. Mat.*, **2002**, 4, 869.

- [11] G. Motz, J. Hacker, G. Ziegler, *Ceramic Engineering & Science Proceeding* **2000**, 21 [4], 307
- [12] N. S. Choong Kwet Yive, R. Corriu, D. Leclercq, P. H. Mutin, A. Vioux, *New. J. Chem.* **1991**, 15, 85.
- [13] Y.-L. Li, E. Kroke, R. Riedel, C. Fasel, C. Gervais, F. Babonneau, *Appl. Organomet. Chem.* **2001**, 15, 820.
- [14] Y.L. Li, R. Riedel, J. Steiger, H.v. Seggern, *Adv. Eng. Mat.*, **2000**, 2, 290.
- [15] S. Traßl, D. Suttor, G. Motz, E. Rößler, G. Ziegler, *J. Europ. Ceram. Soc.* **2000**, 20, 215
- [16] T. Hanemann, M. Schulz, M. Ade, *Proc. Materials Week* **2001**, München, Germany.
- [17] B. Maid, W. Ehrfeld, J. Hormes, J. Mohr, D. Münchmeyer, *KfK Bericht 4579*, **1989**.