Polymer derived ceramic microparts from X-ray lithography—cross-linking behavior and process optimization

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Abstract

The fabrication of micro components made from ceramic materials is becoming more and more important because of their outstanding chemical stability. Different replication methods like low or high-pressure injection molding of ceramic feedstocks have been established. Various lithographic methods are being widely used for the direct fabrication of very precise plastic or metal micro structured surfaces.

The presented work deals with the direct manufacturing of microstructures by using ceramic precursors in combination with X-ray lithography. This allows for a rapid fabrication of micro structured plastic components that are stable at high temperatures (400 °C), chemically resistant and transparent. Pyrolysis of these parts yields amorphous Si−C−N or Si_3N_4 ceramics.

The applicability of different preceramic polymers based on polysilazane for direct structuring with synchrotron radiation was investigated.

X-ray exposures of polysilazane polymer filled with Si_3N_4 ceramic powders were carried out, showing that it is possible to microstructure those composites. By inserting ceramic fillers, a reduction of the shrinkage during pyrolysis was possible. Further investigations were made to determine the maximum filler content, the required exposure dose and the cross-linking mechanism using IR- and NMR-spectroscopy. As established in the LIGA technique with PMMA, resist layers up to 1 mm should be possible by deep X-ray lithography on preceramic polymers. Admittedly for the pyrolytic conversion into the amorphous SiCN ceramic, film thickness should be limited as crack formation is deteriorating with increasing dimensions.
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1. Introduction

The main range of application for preceramic polymers at present are the production of ceramic fibers and the protective coating against oxidation and/or pollution.[1–3] Furthermore, ceramic precursors can be used as low loss binder for different replication techniques.[2,3] Silazanes are expensive to produce and are mainly used for niche products, so that their sales potential is small. Therefore, companies within the chemical industry have almost completely abandoned their production in recent years. The adaptation of polymer characteristics in order to meet specific demands is not offered. Smaller, highly specialized corporations like KiON and scientific workgroups like IMA Bayreuth can meet the current demand. Their existing installations for synthesis in the range of several kilograms per week are sufficient. For the use in micro system technologies, especially for lithographic processes, the needed material amounts are small.[5] The pyrolysis of bulk samples from preceramic polymers often leads to high porous material because of the formed volatile products. Thin layers from preceramic polymers can be pyrolysed and sintered into dense ceramics.[3,4]

By using lithographic methods, the direct micro structuring of preceramic polymers is possible.[5,6,10] The cross-linking mechanism under irradiation conditions was investigated and a process to achieve native substrates that shrink homogeneously during pyrolysis was developed. Microstructures were replicated using a test mask in lithographic processes on such substrates. X-ray lithography on powder filled resist materials was successfully used to produce ceramic microstructures.

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2. Experimental

The cross-linking mechanism under X-ray irradiation of the ABSE material from IMA Bayreuth, Germany was explored using FT-IR and NMR-spectroscopy. Material samples with a diameter of 10 mm and a thickness of 300 μm were produced using uniaxial dry pressing. For separation stearic acid was added. A number of ABSE samples were put in a kapton© foil to protect them from oxidation and to prevent the X-ray beamline from damage by possibly developing decomposition products. Absorption of the incident X-rays in the top layer causes a decrease of the deposited dose from the top to the bottom of the sample. After the first half of irradiation time specimens were turned around to minimize the dose gradient and a middle dose was deposited in the specimen. Fig. 1 shows the dose distribution over the thickness of the specimen calculated concerning the absorption coefficient of the ABSE material.[7]

To make sure that differences in the subsequently measured spectra are caused by irradiation effects and not by hydroxylation or oxidation, the unexposed samples were treated identically except from irradiation.

Before the FT-IR and NMR-spectra were measured, the samples were milled in an agate mortar (in case of FT-IR KBr 1:100 was added).

To achieve substrates made from preceramic polymer, a tape casting process was established that allows for the production of substrates with a thickness around 500 μm. By filling the polymer solutions with Si_3N_4 powder a higher ceramic yield should be feasible. Solutions of preceramic polymer as well as suspensions with different Si_3N_4 filler content were coated on the thermally cross-linked substrates. After

evaporation of the solvent the samples were exposed using X-ray lithography with a micro structured test mask. The primary particles of the ceramic powder ($d_{50} = 0.5$ μm, manufacturers data) are smaller than 1/10 of the dimensions of the replicated structures. To achieve high resolution in the lithographic process it is necessary to deagglomerate the powder as well as possible. Deagglomeration of the α-Si_3N_4 powder was reached using both, an ultrasound disintegrator and a dissolving stirrer. Rheological behavior was determined using a Bohlin CVO cone–plate viscosimeter (cone radius: 40 mm, angle: 4°).

Substrates made from powder filled preceramic polymer material using the mentioned tape casting process were coated either with pure preceramic polymer or with suspensions containing silicon nitride. Samples were exposed at the ANKA synchrotron facility (beamline Litho2 @ 2.5 GeV) settled at the Research Center Karlsruhe and the CAMD (beamline XRLM2 @ 1.3 GeV) facility of the Louisiana State University, Baton Rouge. The microstructures were converted into ceramics after the patterning and development steps at temperatures up to 1500 °C. Further information on the process used for the micro structuring can be found in previous publications.[6]

3. Results

3.1. IR spectroscopy

There was no significant difference between the spectra of unexposed ABSE and the sample irradiated with a middle dose of 2 kJ cm^{-3} (Fig. 2). To detect a significant change in
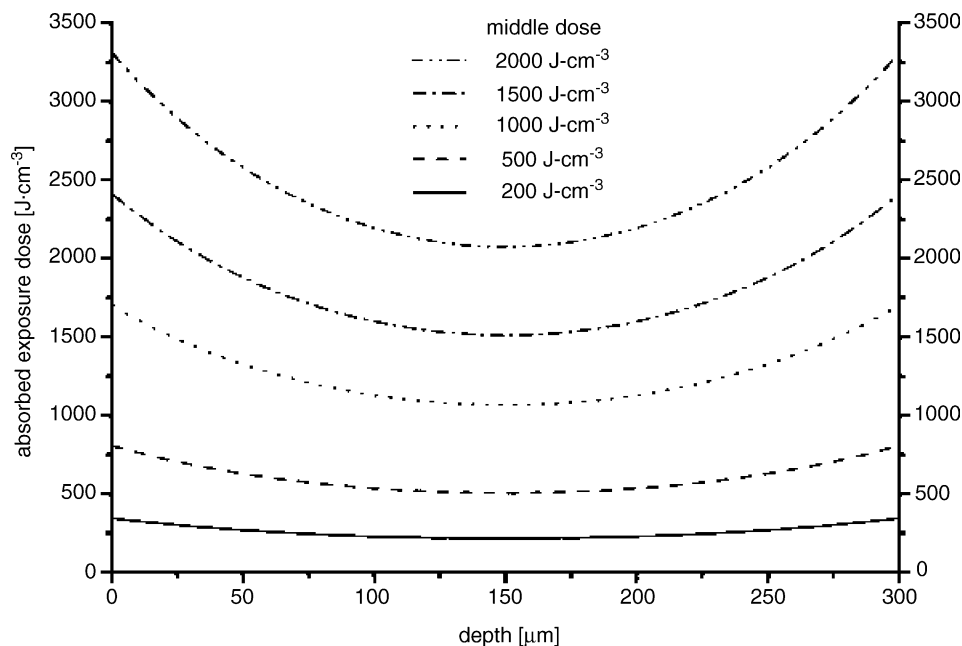

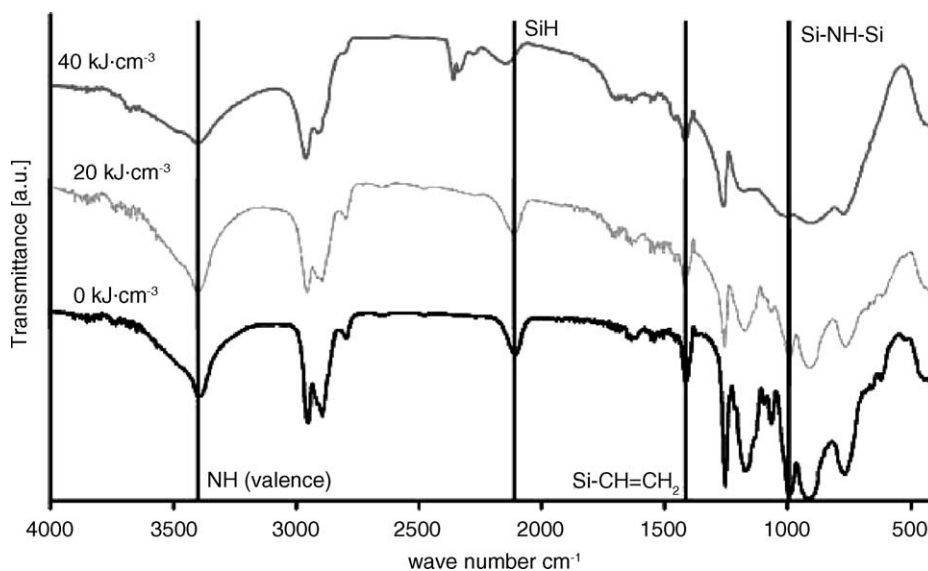Fig. 1. Dose distribution in the X-ray irradiated ABSE samples calculated concerning the absorption behavior.[7]

Fig. 2. Comparison of the IR-spectra of differently exposed ABSE samples (exposure dose from top to bottom of the chart: 40 kJ cm^{-3}, 2 kJ cm^{-3}, unexposed).

the absorption spectra a considerably higher exposure dose was necessary. Three main effects in the spectrum for the sample exposed with 40 kJ cm^{-3} should be mentioned here. A broadening of the NH-valence vibration with its maximum at 3400 cm^{-1}, the decrease of absorption of the Si–H vibration at 2107 cm^{-1} accompanied by a small shift to higher wave numbers and the increase in the range between 1240 and 670 cm^{-1} where a distinction of specific peaks is not possible anymore.

3.2. NMR spectroscopy

^{13}C-, ^{29}Si- and ^{15}N- solid-state MAS NMR spectra were measured at the TU Bergakademie Freiberg using a Bruker Avance^{TM} 400 MHz WB spectrometer at 5 kHz rotation frequency. The ^{13}C NMR spectrum of the unexposed specimen shows signals corresponding to the ethylene (11 ppm) and the methylene groups (3 ppm) connected to the Si-atoms[11,12] (Fig. 3). For the specimen that was exposed to highest extend (middle dose of 40 kJ cm^{-3}) the maximum of the signals shifts to 6 ppm and the peaks merge, the ratio between the two signals changes.

In the ^{29}Si-spectra the signals for Si–H (-15 to -25 ppm) and the ethylene bridge (Si–CH$_2$–CH$_2$–Si, $+4$ and -4 ppm) can be differentiated (Fig. 4).[12,13] The ethylene bridge is represented by two maxima because it appears in a ring as well as in a linear structure. The exposed sample shows an increase of the peak around -22 ppm.
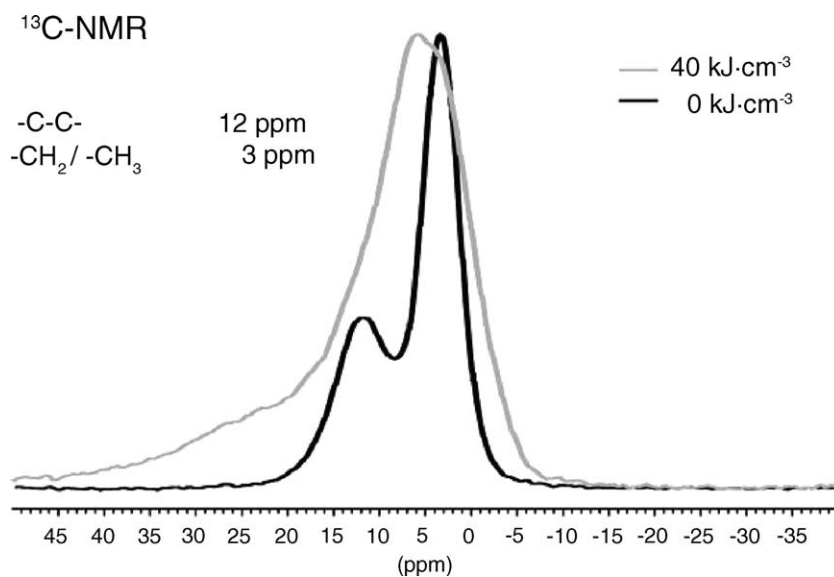

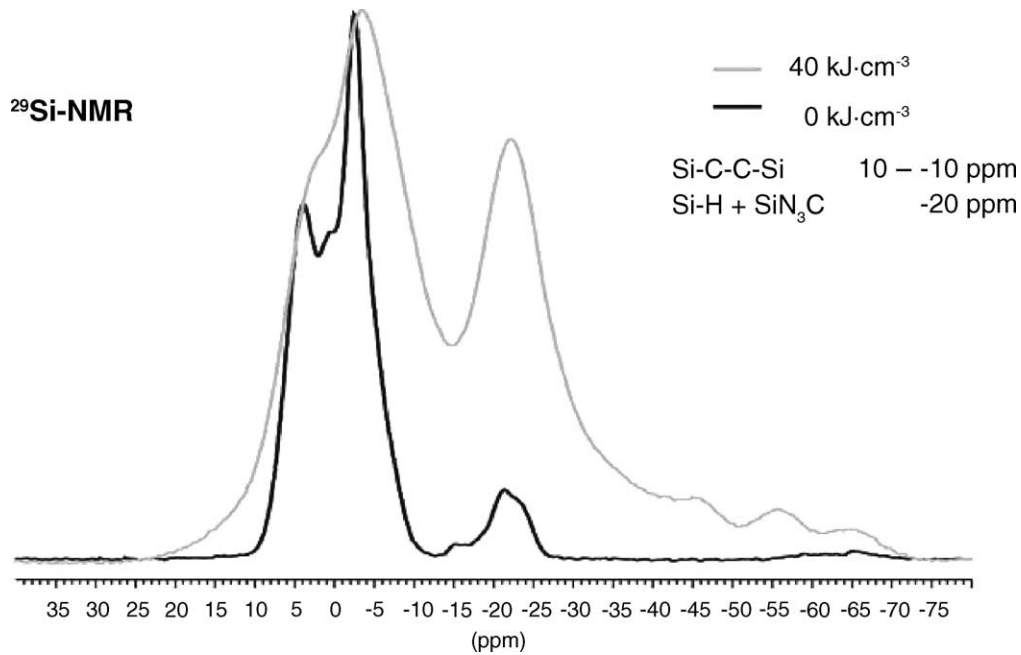Fig. 3. ^{13}C-MAS NMR spectra of ABSE before and after exposure.

Fig. 4. ^{29}Si-MAS NMR spectra of ABSE before and after exposure.

The ^{15}N-spectrum of the unexposed sample is dominated by a NSi_2H environment (-340 ppm). The signal at -325 ppm is assigned to the NSi_3 environment and a peak corresponding to the $NSiH_2$ group (ca. -360 ppm) is detectable.[14] After the exposure the intensity around -320 ppm is rising (Fig. 5). The ^{15}N-spectra were calibrated relatively to nitro-methane.

3.3. Processing behavior of dispersions

Disintegration of the powder agglomerates by using ultrasound decreases the viscosity (Fig. 6). The shear thickening behavior of the dispersions disappears after the ultrasonic treatment. In Fig. 7 the surfaces of the pyrolysed substrates are shown in SEM pictures. By treating the tape casting suspension with ultrasound the surface roughness was lowered and the highly agglomerated particles could be destroyed (powder content in both cases 50 wt.% concerning the ABSE content).

3.4. Microteststructures on native substrates

Best results for the structuring of the ABSE polymer could be found using a bottom dose of 500–1500 J cm^{-3}. The required dose for polymer/ceramic composites were calculated before the exposure concerning the content of Si_3N_4. Although the mass absorption coefficient of the Si and N atoms is low, for samples filled with powder the desired dose is rising steadily with filler content.[7] Microstructures with smallest details of 5 μm could be produced after pyrolysis without cracking or delaminating.
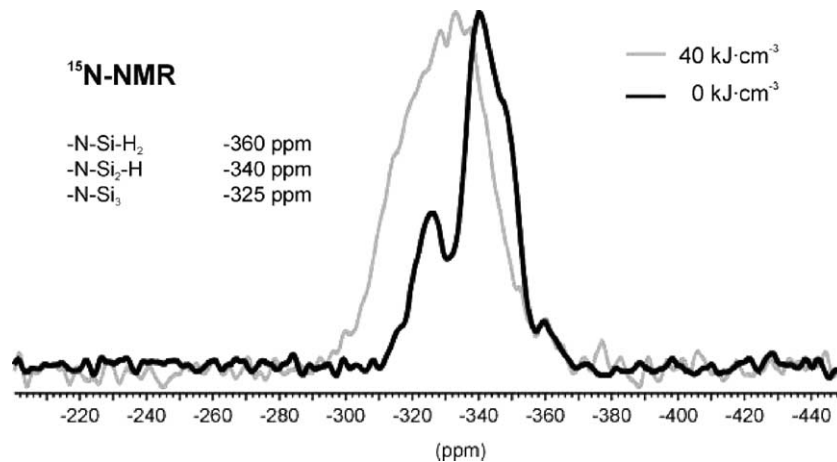

Fig. 5. ^{15}N-MAS NMR spectra of ABSE before and after exposure.
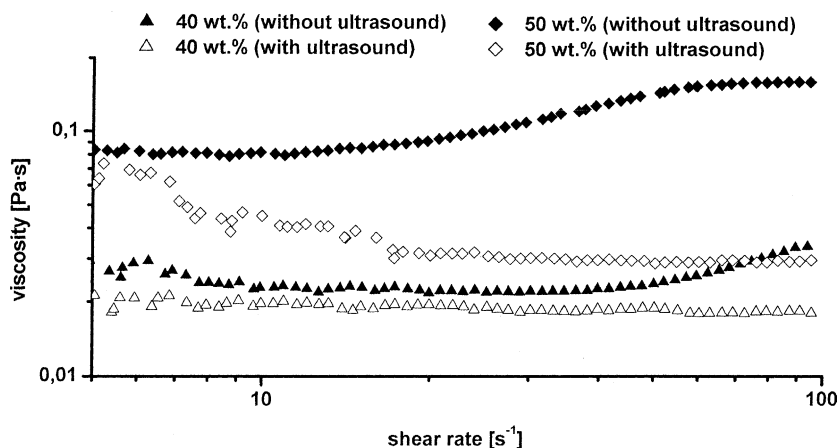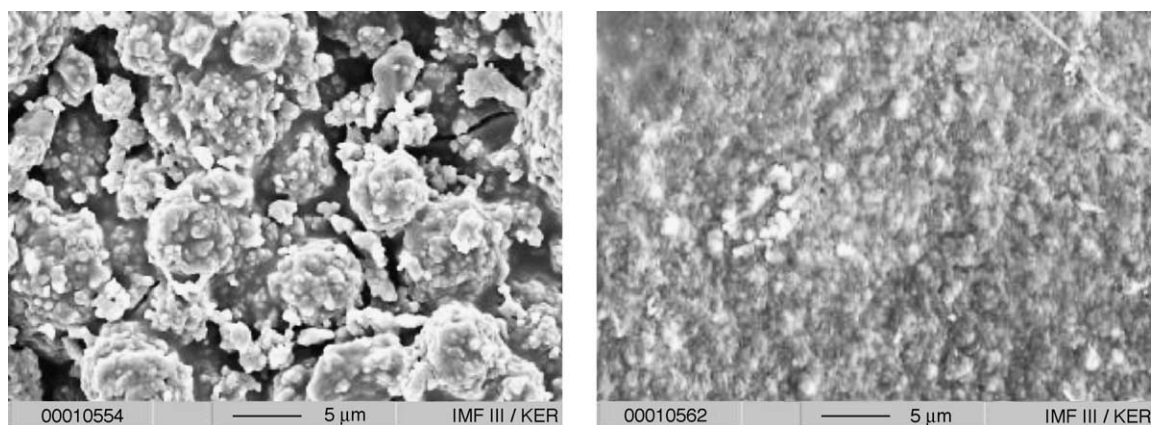
Fig. 6. Influence of ultrasound on the rheology.

Fig. 7. SEM picture of the pyrolysed substrate. Tape casting suspensions treated without (left) and with ultrasound (right).

4. Discussion

4.1. Cross-linking mechanism

In contrast to the molecule structure given by the manufacturer[1] from the IR- and NMR spectra of the unexposed samples, it is obvious that the ABSE polymer used carries Si–H groups. Since the polymer was received in an uncleaned condition this may be explainable by remaining educts of the preparation process because no further cleaning process was carried out before exposure. It is noticeable that the exposure dose needed to measure an effect in the IR- and NMR-spectroscopy was more than 20 times higher than the dose needed for the micro structuring of the polymer using X-ray lithography. Obviously a considerably lower dose is necessary to cross-link the material to an insoluble state.

The results of the ^{13}C-spectra in combination with the spectra of the other cores and the IR spectroscopy allow for the conclusion that the cross-linking occurs mainly including the N-atoms. The increase of the −22 ppm signal in the ^{15}N-spectra can be interpreted by a cross-linking during X-ray irradiation leading to a SiN_3C environment. A rise of the SiH signal is unlikely because the cross polarization behavior of

the signal should distinguish the silicon bonded protons, but this effect was not detectable in appropriate measurements.

4.2. Conditioning of suspensions

Generally the viscosity of a suspension should increase with decreasing particle size,[8,9] but a contrary effect was observed by disintegrating powder agglomerates using ultrasound. One of the essential basics for the theory is the fact, that the form of the different sized particles is the same. In reality the form of particle agglomerates is far away from being identical with the primary particles. On the other hand the specific surface of the powder agglomerates is comparable to the primary particles. Therefore, a decrease in viscosity occurs during ultrasound disintegration leading to a smoother surface that is considerably more homogeneous.

4.3. Rating of microstructures

At the top of Fig. 8 a test structure field is shown before and after pyrolysis. While the unfilled resist material except from smallest features cracked upon pyrolysis the powder filled structures remained undestroyed. The surface roughness of
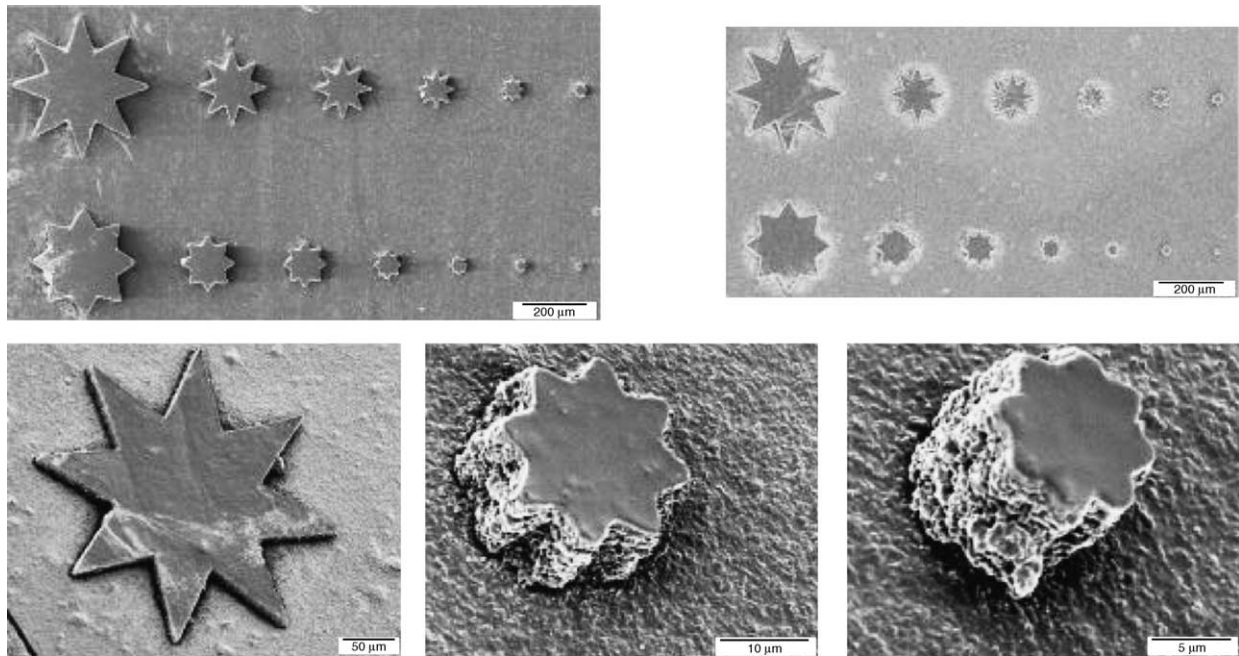
Fig. 8. SEM pictures of some test structures made by X-ray lithography of powder filled preceramic polymer and subsequent pyrolysis.

the samples filled with powder is low compared to the sidewall roughness as can be seen from the SEM pictures at the bottom of Fig. 8. When the dimensions of the microstructure meet the powder particle size the quality of reproduction decreases (bottom left of Fig. 8). The edge precision of unfilled polymer is excellent, sidewalls are perpendicular to the surface of the substrate and the pattern.

5. Conclusions

The influence of synchrotron radiation on the crosslinking behavior of ABSE material was investigated. The sensitivity of this ceramic precursor as a resist material for X-ray lithography can be arranged between the two established resists SU-8 (negative resist, minimun exposure dose $15 \, J \, cm^{-3}$) and PMMA (positive resist, minimun exposure dose $4000 \, J \, cm^{-3}$)[15]. By application of preceramic polymers as resist materials in X-ray lithography microstructures with aspect ratio up to 60 and structural details $<5 \, \mu m$ were realized. The use of native substrates manufactured by a tape casting process of suspensions of preceramic polymer and ceramic filler allows for crack free conversion of the micro structured parts into the ceramic state. Particle size and processing of the suspensions is of great influence on the achievable feature size.

Acknowledgments

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