Doctoral Thesis

Microfabrication of ceramics

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Microfabrication of Ceramics

A dissertation submitted to the

SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZÜRICH

for the degree of
Doctor of Technical Science

presented by
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Prof. Dr. N. D. Spencer, co-examiner

Zürich, 2000
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# I Microfabrication of Ceramics

Summary ................................................................. 1
Zusammenfassung .................................................... 2

# II General Introduction ........................................... 5

# III Aim of this Study ............................................... 9

# IV State of the Art in Ceramic Microfabrication

1 Introduction .......................................................... 11

2 Methods without Mold ............................................ 14
   2.1 Rapid Prototyping Techniques ................................... 14
   2.2 Direct Ceramic Machining ....................................... 19
   2.3 Extrusion ....................................................... 20

3 Methods with 2-Dimensional Molds ........................... 21
   3.1 Etching .......................................................... 21
   3.2 Screen Printing ................................................ 24
   3.3 Stamping Methods .............................................. 25

4 Methods with 3-Dimensional Molds ........................... 27
   4.1 Slip Casting ................................................... 28
   4.2 Centrifugal Casting ............................................ 28
   4.3 Filter Pressing ................................................ 29
   4.4 Injection Molding .............................................. 30
   4.5 Tape Embossing ............................................... 31

5 Summary ............................................................. 32

6 References .......................................................... 34

# V Process Development ........................................... 37

A: Generation of Patterned Ceramic Surfaces

1 Introduction .......................................................... 38

2 General Experimental Procedure ................................ 38
   2.1 Mold Fabrication ................................................ 39
   2.2 Suspension Preparation ....................................... 42
   2.3 Casting ........................................................ 42
   2.4 Demolding and Sintering ...................................... 42
   2.5 Characterization ............................................... 43

3 Investigated Issues ................................................ 43
   3.1 Influence of Powder Particle Size ............................ 43
   3.2 Increase of Suspension Solids Loading ....................... 48
   3.3 Surface Chemistry of PDMS ................................... 59
   3.4 Conclusions .................................................... 61
I Microfabrication of Ceramics

Summary

To date, ceramic materials have almost been excluded from the general trend of miniaturization of functional devices, which goes on in other fields of materials science. Especially in the semiconductor industry the feature sizes of the generated structures decreased constantly in the last years. Today, submicron structures with a feature size of 0.2 μm are already produced in semiconductor pilot plants. On the other hand, the smallest ceramic features produced in industry so far are almost three orders of magnitude larger. Piezoceramic rods for the fabrication of ultrasonic transducers have diameters in the range of 100 μm. Other techniques which allow the production of features with a size of 50 μm and slightly below, are in a research state but not applied on a large scale. Smaller surface structures on ceramics have not been generated up to now. In the present work we therefore attempted to develop powder-based ceramic forming techniques which allow the generation of ceramic features with dimensions of a few micrometers.

In the first part of the study, bulk samples with a patterned surface are generated by slip casting of water-based suspensions into nonporous elastomeric molds made of poly(dimethyl siloxane) (PDMS). Surface structures of excellent quality with dimensions as small as 1 μm are feasible. It was found that a suspension with a high solids loading has to be used in order to reduce drying shrinkage and a hydrophobic surface of the mold material is essential for defect-free demolding. The slip casting process is applicable to various ceramic materials. Also polymers other than PDMS can be used as molds, however, PDMS offers the simplest mold generation process.

In the second part of the work, three fabrication methods for the generation of ceramic surface patterns on arbitrary substrates are investigated. In the first method, micromolding in capillaries, a PDMS structure forms three walls of a capillary, the surface of the substrate acts as the fourth wall. A liquid is then dragged into these capillaries and solidified, leaving a three dimensional structure after removing the PDMS. The process was developed for solutions and could not be successfully adapted to dense ceramic suspensions, as the ceramic structures could not be obtained in a reproducible manner. The second technique uses selective wetting of an aqueous suspension on gold surfaces functionalized with hydrophilic and hydrophobic self-assembled monolayers. It produced promising results, but sintering of the ceramic features on the gold surface as well as the transfer of the process to other than gold substrates could not be achieved. Finally, filling of surface molds made of patterned photoresist yielded the most reproducible structures with a feature size of 5 μm. Matching coefficients of thermal expansion is crucial in order to get a crack-free structure after sintering. The process can be applied to various substrates and ceramic suspensions.
Zusammenfassung


flächen war nicht möglich. Die dritte und vielversprechendste Methode benutzt dreidi-
mensionale Strukturen aus Photolack auf der Substratoberfläche als verlorene Form für
Schlickerguss. Mit dieser Technik konnten keramische Muster mit einer Auflösung von
bis zu 5 \( \mu \text{m} \) reproduzierbar hergestellt werden.
II General Introduction

Microfabrication is becoming more and more important in modern science and technology. The ability to fabricate new types of microstructures or to produce existing structures in down-sized versions offer a large potential in cost reduction. The most obvious examples are sensors, actuators and microelectronic devices. Miniaturization of electronic elements has made terrific progress in the last decades and is still going on. Components with micrometer or even nanometer dimensions can also open up the opportunity to study basic scientific phenomena that occur at small dimensions. One example is quantum confinement observed in nanostructures [1]. Although most research on microfabrication is silicon-based and has been focused on microelectronic devices [2], applications in other areas are rapidly emerging. These include sensor systems for microanalysis [3–6], micro-volume reactors [7–9] combinatorial synthesis [10], micro-electromechanical systems (MEMS) [11,12], optical components (for example photonic band gap materials) [13–15] and systems for non-magnetic data storage [16].

One promising use for microanalytical devices is in the separation and analysis of chemical and biological substances [3–6]. These devices require only small quantities of reagents, have relatively short analysis times and can show efficiencies in separation and detection that are better than those of larger analysis systems. In the last years, several miniaturized total chemical analysis systems [17,18], sometimes also referred to as ‘labs on a chip’, have been developed that perform all sample-handling steps on their own. An array of chemical tools on a chip makes it possible to analyze extremely small amounts of a product. These systems will be useful for the parallel screening of a large number of compounds. For example an artificial nose can be realized with a large number of single sensors of which each one is tuned to detect a different ‘flavor’ [19]. Structures in the micrometer range allow the integration of a large number of single elements on a small area. Even though the selectivity of a single element might by mediocre, their large number compensates this disadvantage by far.

Miniaturization of sensor elements has not only the advantage that more data can be collected in the same amount of space, but also that the sensing devices may be integrated directly on the electronic chip along with monitoring, actuating and controlling devices. With such an integration, a sensor element can directly generate a digital output signal. In the past years, the scope of fabrication techniques has widened and the number of devices has increased [11,12,20]. Most are fabricated from silicon using standard microlithographic techniques [21,22]. With these methods, thousands of mechanical elements, for example cantilevered beams, springs, linkages, mass elements and joints, can be batch-fabricated on a single silicon substrate [10,12]. Microactuators, micromotors and microengines [22] have been fabricated for optical switches, fluid pumps [23], sys-
tems for drug delivery and microchemical analysis [24–27]. More recently, surface micromachining techniques have been used to fabricate miniaturized optical components which are attractive for applications in spectrometers, display devices, sensors, optoelectronic packages and data storage systems [13–15].

Most of the devices mentioned above are made using silicon based microfabrication techniques. Up to now, not much has been done to fabricate miniaturized parts of ceramic materials. Sensors with ceramic detection materials are still built in the classical manner. A macroscopic ceramic part detects the signal which is fed to the evaluating electronics by electric connectors. For a possible integration of ceramic materials into the length scale of microelectronic components no suitable fabrication techniques have been developed yet, although ceramic materials are operating in numerous types of sensors, as summarized in Table IV-1.

<table>
<thead>
<tr>
<th>Type of Sensor</th>
<th>Output Signal</th>
<th>Effect</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature sensor</td>
<td>Change in the resistance</td>
<td>Thermistor effect (PTC or NTC)</td>
<td>NiMn$_2$O$_4$, CoFe$_2$O$_4$, BaTiO$_3$</td>
</tr>
<tr>
<td>Oxygen sensor</td>
<td>Electromotive force</td>
<td>Conductivity of oxygen ions</td>
<td>ZrO$_2$</td>
</tr>
<tr>
<td>Gas Sensor</td>
<td>Change in the resistance</td>
<td>Semiconducting behavior</td>
<td>SnO$_2$</td>
</tr>
<tr>
<td>Optical sensor</td>
<td>Electromotive force</td>
<td>Pyroelectric effect</td>
<td>SrTiO$_3$, PZT, PbTiO$_3$, PbZrO$_3$</td>
</tr>
<tr>
<td>Ultrasonic sensor</td>
<td>Phase difference of emitted and detected waves</td>
<td>Piezoelectric effect</td>
<td>PZT, PbTiO$_3$, PbZrO$_3$</td>
</tr>
<tr>
<td>Sensors for measuring force, pressure, acceleration</td>
<td>Change in output voltage</td>
<td>Piezoelectric effect</td>
<td>PZT, PbTiO$_3$, PbZrO$_3$</td>
</tr>
</tbody>
</table>

Table IV-1: Ceramic sensor materials [28,29].

One of the most crucial issues towards the integration of ceramic materials into micro-scale devices, is the development of suitable forming methods. When features with dimensions below 100 μm are required, a simple downscaling of established ceramic processing techniques is not suitable. In the present thesis, principles of colloidal chemistry with ceramic powders were combined with new approaches for mold fabrication.
References


III Aim of this Study

The goal of the present work was to find and apply new processing routes for the fabrication of well defined ceramic surface components in the micrometer range, one order of magnitude smaller than the structures feasible today.

This miniaturization of ceramic components may lead to advances in sensor technology, possibly being integrated on the same silicon chip used for data processing. This would allow the production of ceramic-containing devices of similar dimensions as polymeric and metallic structures which are already available today. However, it is not the goal of this work to fabricate a fully functional sensor, rather appropriate methods for the production of such sensors are evaluated.

In order to narrow the broad focus and also with regard to potential industrial applicability of these processes, additional boundary conditions for the new processing method had to be formulated:

- The processing method should be versatile and be able to use commercially available powders of various compositions as raw materials
- The process should enable the production of ceramic microcomponents on various substrate materials
- The molds should be reusable in order to be cost effective
- Expensive machinery should be avoided.
IV State of the Art in Ceramic Microfabrication

Processing techniques that are suitable for producing ceramic parts with a minimal feature size smaller than 500 μm are described and compared based on the specific requirements of this study. In conclusion of this overview, a strategy for the first approach of the present investigation is developed.

1 Introduction

The first efforts in ceramic microtechnology have been made by downscaling elaborated macroscale forming technologies. This was also the case for the most widely used ceramic microsystem, the piezoelectric ultrasonic transducer. These transducers are made of small piezoceramic rods embedded in a polymer matrix (Figure IV-1).

![Figure IV-1: Schematic of a composite ultrasonic transducer.](image)

This composite setup avoids losses of ultrasonic energy at the transducer–tissue interface in medical imaging [1]. The rods have to be long and slender in order to ensure a noise–free signal [2]. The first generation of such rods was made by cutting perpendicular grooves into a sintered PZT plate (Figure IV-2) [3] that leads to individual posts with small dimensions. The width of the grooves is determined by the width of the dice and the width of the rods is limited by the mechanical stability of the material. The high stresses involved in this technique lead to breaking of small rods during manufacturing. Both the width of the trenches and of the rods are in the range of 200 μm, the aspect ratio (Figure IV-3) is in the order of 1. The described limitations of the downscaled technique gave rise to the demand for other approaches for the production of such ceramic rod structures. Molds made with methods developed in semiconductor manufacturing were combined with traditional suspension–based ceramic forming techniques. Today, rods as narrow as 20 μm with an aspect ratio of 10 are produced [4,5].
In different fields, as for example in sensor technology [6] or rapid prototyping [7], special techniques of forming small-scale ceramic structures have been developed to date. An overview of processing techniques and some examples of their applications is given in Table IV-1. For each of these applications the ceramic parts have to fulfill certain requirements. Therefore, several processing methods have been developed, each one with its special focus on a certain application.
<table>
<thead>
<tr>
<th>Method</th>
<th>Examples</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rapid prototyping</td>
<td>Prototypes, casting molds for metals</td>
<td>[7–17]</td>
</tr>
<tr>
<td>Direct ceramic machining</td>
<td>Dental implants</td>
<td>[18]</td>
</tr>
<tr>
<td>Co-extrusion</td>
<td>Polycrystalline fiber composite material</td>
<td>[19–21]</td>
</tr>
<tr>
<td>Etching</td>
<td>Superconducting connectors</td>
<td>[22–27]</td>
</tr>
<tr>
<td>Screen printing</td>
<td>Electrolytes for solid oxide fuel cells</td>
<td>[28–31]</td>
</tr>
<tr>
<td>Stamping methods</td>
<td>Conductor lines</td>
<td>[32–35]</td>
</tr>
<tr>
<td>Slip casting</td>
<td>Piezoelectric array</td>
<td>[37–38]</td>
</tr>
<tr>
<td>Centrifugal casting</td>
<td>Piezoelectric array</td>
<td>[39]</td>
</tr>
<tr>
<td>Filterpressing</td>
<td>Piezoelectric array, nozzle</td>
<td>[39–40]</td>
</tr>
<tr>
<td>Injection molding</td>
<td>Piezoelectric array</td>
<td>[41]</td>
</tr>
<tr>
<td>Tape embossing</td>
<td>Piezoelectric array</td>
<td>[42–44]</td>
</tr>
</tbody>
</table>

Table IV-1: Applications for microfabricated ceramic parts produced by the forming methods discussed in this chapter. For references see the respective sections.

It would not be very informative to compare the different processing methods directly with each other. What is an advantage for one application might be a disadvantage for another. Therefore, the advantages and disadvantages listed in the following subsections are specified with regard to an 'ideal processing method', which was already described in the aim of this work. Such a method does not (yet) exist, it serves only as common reference to judge the single processes more objectively. The criteria for the comparison were chosen to allow a statement about the suitability of the processing method for the fabrication of the small features required in this study.

The ideal processing technique has the following characteristics:
- The smallest lateral dimension is below 10 micrometers
- An aspect ratio larger than 1 is possible
- Dense polycrystalline ceramic bodies can be produced.

The fulfillment of one or all of these requirements is listed as an advantage in the process characteristics table of each section. If the technique does not fulfill these requirements, it is listed as a disadvantage. The smallest lateral feature size and the largest achievable aspect ratio are listed and visualized for each of the processes in the characteristics table at the end of the respective sections. Their determination is based on the
processes, not on the properties of the materials that are used. With techniques that can make structures with high aspect ratios, the strength of the ceramic material becomes the limiting factor for the structure height, but this is of no concern here.

The smallest lateral feature size is the width of the smallest feature that has been achieved using the respective process. The aspect ratio is a dimensionless number that is calculated by dividing the maximal height of a structure by its width. Long, slender structures have a high aspect ratio; broad, flat structures have a low one.

![High Aspect Ratio, Low Aspect Ratio](image)

*Figure IV-3: Structures with high and low aspect ratios.*

In the following section the discussed processes are grouped according to the kind of molds that are employed. Some methods do not require a mold at all. In this case the ceramic part is built in all three dimensions from a powder bed or a blank on a computer controlled machine. Methods that use 2-dimensional molds are strongly related to methods used on a larger length scale in the traditional printing industry. In these methods the third dimension is generated directly during the process. When 3-dimensional molds are used, the processes are related to traditional casting methods where ceramic materials are usually processed as suspensions.

## 2 Methods without Mold

### 2.1 Rapid Prototyping Techniques

Rapid prototyping techniques, sometimes also referred to as solid freeform fabrication techniques, were developed in order to generate parts directly from a computer model to avoid the costs and time involved in mold fabrication for the production of single prototypes or of small series of a functional part [7].

The parts are built layer by layer in order to realize even complex geometries. The 2-dimensional geometrical information for each layer is generated by a slicing algorithm applied to a CAD model of the part. Rapid prototyping systems therefore have two critical dimensions: The smallest lateral feature size and the thickness of a solidified layer. A smaller feature size and a thinner layer thickness lead to a better resolution, but also to significantly longer process times for the produced parts. A compromise has to be made between resolution and processing time. In general, a minimal cure depth and minimal
cure width of 200 μm are desired. The aspect ratios of the produced parts are only limited by the geometry of the machine. Theoretically an infinite number of layers could be stacked.

Figure IV-4: Principle of layered object fabrication.

Because of the wish to generate exact 1:1 prototypes, the ceramic powders used in Rapid Prototyping are usually tailored to avoid shrinkage during sintering. This leads to porous ceramic microstructures of low strength and modulus. Most of the ceramic parts made by rapid prototyping are made of refractory grade powders and are used as molds for metal casting of prototypes or small scale serial production.

Different methods for rapid prototyping of ceramics have been developed, but they can all be grouped into three fields:
1. Selective addition of material to an existing surface.
2. Chemical alteration of a liquid or solid using directed light energy.
3. Sintering of a powder using directed light energy.

In the following subchapters techniques for each of these field are described. Three Dimensional Printing and Suspension Printing representing the first group, Stereolithography the second and Selective Laser Sintering the third.

The suitability of all the described rapid prototyping techniques for ceramic microfabrication is summarized at the end of this section.

Three Dimensional Printing

In Three Dimensional Printing (3DP) the single layers of the ceramic part are solidified by spraying a binder suspension with an inkjet printer head into a ceramic powder bed [8]. Structures with a minimal feature size of 430 μm are reported. The parts are made using an alumina powder with an average grain size of 40 μm. The powder is solidified via a glass phase during heat treatment at 800 °C, practically no shrinkage occurs. The parts can be used as casting molds for small series in metal production where 3DP is cheaper than creating molds for lost wax models [9]. Investigations to use the produced parts as drug delivery devices have also been reported [10].

3DP is performed using both available systems of inkjet printers: drop-on-demand and continuous-jet technology. The latter is favored because of the higher printing speed.
Applying a layer of loose powder on top of solidified part

Printing step. Binder is selectively printed into the powder bed.

Printing step is terminated, next layer of powder can be applied

Figure IV-5: Process of 3DP.

<table>
<thead>
<tr>
<th>Three Dimensional Printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
</tr>
<tr>
<td>430 µm</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>only limited by machine geometry</td>
</tr>
</tbody>
</table>

Table IV-2: Process characteristics of 3DP.

Suspension Printing

This technique is related to 3DP, but instead of printing a binder into a powder bed, a ceramic suspension is printed onto a substrate. The suspension is deposited with either a continuous \([11,12]\) or a drop-on-demand ink jet printer \([13]\). As the viscosity of the printing suspensions is limited to about 10 mPa-s, the reported solids loadings of the suspensions are only 5–10 vol %. The vast amount of solvent that has to be evaporated limits the printing speed. Therefore, only porous substrates, that support drying, are used. Due to the low solids loading the layer thickness for each printing cycle is about 1 µm; much thinner than with the other layered fabrication techniques. This technique is still in the experimental stage, no applications have been reported so far.
Figure IV-6: Pattern created by suspension printing [12].

### Table IV-3: Process characteristics of Suspension Printing.

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
<td>300 μm</td>
</tr>
</tbody>
</table>

**Advantages:**
- dense structures

**Disadvantages:**
- low resolution
- low aspect ratio
- very slow speed

**Remarks:**
- Only porous substrates can be coated

**Stereolothography**

In ceramic stereolithography a suspension of ceramic particles in a photopolymerizable monomer is solidified by crosslinking the molecules with an ultraviolet laser directed by a mirror system. In the following heat treatment the polymer matrix is pyrolyzed and the ceramic part is sintered. Parts made of silica, alumina and silicon nitride have been reported [14].

Compared to stereolothography with pure monomer solutions, as used in rapid prototyping of polymeric parts, the dispersed ceramic particles lower the cure depth and increase the cure width of the laser beam, even if the ceramic material is transparent to UV. For example a laser beam with a diameter of 210 μm is widened in the suspension and cures an area of 300 μm in diameter [15].

Figure IV-7: Experimental setup for stereolothography [14].
**Stereolithography**

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>300 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>aspect ratio</td>
<td>only limited by machine geometry</td>
</tr>
</tbody>
</table>

**Advantages:**
- high aspect ratio

**Disadvantages:**
- low resolution
- no dense microstructure

**Remarks:**
Scattering effects lower lateral resolution

*Table IV-4: Process characteristics of stereolithography.*

**Selective Laser Sintering (SLS)**

A laser beam melts the low melting component of a two component inorganic powder system. The liquid phase wets the solid ceramic powder and joins it during the solidification. After shaping, the low melting phase is no longer beneficial, it limits the thermal stability of the part. Therefore, a following heat treatment step is used to increase the thermal stability of the microstructure. Examples of SLS powder systems are alumina with a low melting phosphate binder forming a glass phase during heat treatment [16] or alumina with metallic aluminum as melting phase which is subsequently oxidized [17]. After sintering, the microstructure reaches about 50% of the theoretical density [17]. The speed of the laser beam relative to the powder surface is determined by the thermal conductivity of the powder material to be compacted. A high thermal conductivity leads to dissipation of large amounts of energy into the powder bed, requiring longer irradiation

*Figure IV-8: Ceramic parts produced via SLS [16].*
times to melt the binder phase. On the other hand, a low thermal conductivity can lead to thermal shock failures in the produced part.

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>500 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspect Ratio</td>
<td>only limited by machine geometry</td>
</tr>
</tbody>
</table>

Advantages: - high aspect ratio

Disadvantages: - low resolution - no dense microstructure

Remarks: Limited speed due to heat transfer limitations, needs liquid phase sintering

Table IV-5: Process characteristics of Selective Laser Sintering.

The described rapid prototyping techniques have two major advantages. First, parts can be generated in very short time without the need for a mold, second, structures with high aspect ratios can be made. However, the lateral resolution of the techniques is quite low. This also leads to a rather rough surface. The effects responsible for this low resolution are the physical limitations of these techniques. It is not likely that with these techniques feature sizes much smaller than 150–200 μm can be realized in the future.

The main limitations are

- size of the generated droplets and spread of liquid droplets in a porous substrate for the ink-jet related techniques,
- scattering effects in stereolithography,
- heat conduction in Selective Laser Sintering.

In addition, some of the processes need powder systems with liquid phase sintering. This limits the high temperature stability of the produced parts.

2.2 Direct Ceramic Machining (DCM)

An isostatically pressed and presintered ceramic blank is shaped on a computer controlled milling machine. After the shaping process, the ceramic bodies are sintered to full density and exhibit excellent mechanical behavior [18]. As this is not a layered fabrication technique, even round shapes can be made with good accuracy. The resolution is determined by the positioning accuracy of the milling machine and the diameter of the milling cutter. The aspect ratio is also limited by the available milling cutters. Rounded structures inside the part are not feasible because of the ‘one dimensional’ geometry of the milling cutter. By compensating the sintering shrinkage of the ceramic material, net-
shaped sintered parts can be made. An image of the milling process is shown later in Figure V.A-33.

DCM is a very powerful technique for the fabrication of parts in the size range of 400 μm. The ceramic structures can be shaped fast and sintered to full density. One application of this technique is the fabrication of ceramic tooth bridges which exhibit very high mechanical strength.

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>400 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspect Ratio</td>
<td>8</td>
</tr>
</tbody>
</table>

**Advantages:**
- high aspect ratio
- dense microstructure

**Disadvantages:**
- low resolution
- geometrical limitations

**Remarks:**
Net-shape method

**Table IV-6: Process characteristics of direct ceramic machining.**

2.3 Extrusion

Elongated fine-scaled ceramic parts are fabricated by extruding a thermoplastic polymer filled with ceramic particles through a size-reducing die. The feedrod used for extrusion consists of several powder-filled polymer compounds. During extrusion, the shape in which the different compounds are assembled is maintained. The feedstock is only reduced in its dimensions perpendicular to the extrusion direction. After each extrusion step the extrudates are reassembled and extruded again until the desired size reduction is achieved. Objects with complex shapes can be fabricated by assembling an extrusion feedrod from several shaped ceramic compounds. With a space-filling carbon black compound that can be pyrolyzed, even free-standing or hollow structures are possible. Objects in the size range of 10 μm were produced [19,20]. Polycrystalline fiber composites with defined fiber geometries and orientations can be made also [21].

With this method, no micromachined parts are necessary to generate microscopic features, they are generated by the uniform size reduction of macroscopic assemblies. Although very small structures with high aspect ratios can be made, this method suffers from important restrictions. The shape of the structures is limited to quasi-3D shapes due to the one dimensional extrusion process. In addition, the generated patterns get slightly distorted during the extrusion.
### Extrusion

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 μm</td>
<td>- very high aspect ratio</td>
</tr>
<tr>
<td></td>
<td>- good resolution</td>
</tr>
</tbody>
</table>

Aspect Ratio

<table>
<thead>
<tr>
<th>almost infinite</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- only quasi-3D structures</td>
</tr>
</tbody>
</table>

Remarks:

Objects get slightly distorted with increasing number of extrusion steps

Table IV-7: Process characteristics of extrusion.

![Process schematic and micrograph of an extruded part. The initial size of the feedrod was in the range of 4 mm [20].](image)

3 Methods with 2-Dimensional Molds

In the processes described in this section the mold has to be defined in two dimensions, the third dimension is directly generated in the process.

3.1 Etching

Etching processes are not very widespread in ceramics manufacturing because ceramics are among the hardest and most inert materials known. Especially wet etching processes are generally not suitable for patterning ceramics which are usually very inert to aggressive liquid media. However, this method is used for niche applications with a well matched pair of etchant and material to be etched. In dry etching processes the material is removed either by sputtering or in a highly reactive plasma. This process has less problems with the chemical inertness of ceramics. As the standard polymeric resist
materials are often removed faster than the ceramic material, mechanical aperture masks are needed to direct the etching plasma.

**Wet Etching**

Patterning by wet etching is carried out similar to silicon–based techniques in microelectronic manufacturing [22]. A ceramic surface is coated with a photoresist film. This resist film is exposed through a photomask and developed, the irradiated area of the resist is dissolved. Through the blank spaces in the resist the ceramic material can be etched with an appropriate liquid etchant. Most of the research in wet etching of ceramics is done in the field of ceramic high-T<sub>c</sub> superconductors. For the fabrication of small-scale coils or other superconducting circuits epitaxially deposited cuprate films have been etched with a variety of chemicals, such as hydrofluoric acid, EDTA, nitric acid or phosphoric acid [23]. The application of wet etching is limited to some special ceramics and is often isotropic. Underetching of the template structures may occur, thus limiting the achievable feature size and aspect ratio.

![Figure IV-10: Wet etched superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> coil on a SrTiO<sub>3</sub> substrate [23].](image)

<table>
<thead>
<tr>
<th>Wet Etching</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
<td>- good resolution</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>- low aspect ratio</td>
</tr>
<tr>
<td>2 µm</td>
<td>- not generally applicable</td>
</tr>
<tr>
<td>0.3</td>
<td>Remarks:</td>
</tr>
<tr>
<td>0.1</td>
<td>Only isotropic etching possible</td>
</tr>
</tbody>
</table>

*Table IV-8: Process characteristics of wet etching of ceramics.*
Dry Etching

In dry etching processes the material is patterned either by exposing it to a reactive plasma which forms volatile compounds with the material to be removed or by removing the undesired part mechanically with an ion beam [22]. The main parameter of a dry etching process is the energy of the incorporated plasma. At low ion energies the process is chemically controlled, not all components in a multi material mixture form volatile components with a certain plasma. Therefore, these processes exhibit a high selectivity. For example, if layers of different materials are stacked, the etching reaction stops at the interface between two materials, because only one material is removed by the plasma. The etching process is more or less isotropic in all directions, no structures with high aspect ratios can be made. In physical plasma processes the material is removed by sputtering. These processes allow a stronger anisotropy; structures with a higher aspect ratio can be produced. However, the larger anisotropy results in a smaller selectivity of the etching process, as illustrated in Figure IV-11.

![Figure IV-11: Dry etching processes [22].](image)

Several binary metal oxides such as CuO, ZnO and PbO have been plasma etched with hexafluoroacetylacetone at temperatures above 200 °C [24], also binary nitrides can be etched [25]. Etching of PZT has been done with excimer laser radiation in a reducing atmosphere [26] and also with SF$_6$ [27].

Like in wet etching, also dry etching of ceramics can only be applied to materials that form volatile components with the etchant. This greatly limits the applicability of this technique.
Table IV-9: Process characteristics of dry etching.

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 μm</td>
<td>- high aspect ratio</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>- low resolution</td>
</tr>
<tr>
<td></td>
<td>- not generally applicable</td>
</tr>
</tbody>
</table>

Remarks: Volatile components have to be formed.

3.2 Screen Printing

A paste of ceramic powder, plasticizer and binder is placed on a patterned screen of metal wires. The pattern is generated by sealing some of the meshes of the screen with a polymer. The paste is then forced through the remaining openings in the screen by using a rubber squeegee which depresses the screen to contact the substrate as it traverses the pattern. The thickness of the deposited layer is determined by the thickness of a polymer spacer film attached to the lower side of the mesh. Patterning of the screen is done by coating it with a photoreactive polymer and dissolving the latter selectively after exposure [28].

To overcome the limitation that only flat substrates can be patterned by screen printing, transfer printing has been developed [29]. The ceramic layer is printed onto a sheet of coated paper and can later be transferred onto tubular or corrugated surfaces.

Screen printing is a simple process, but only low aspect ratios with low resolutions can be made. The resolution is limited by the viscosity of the ceramic paste that is used. The crosswise arranged metal wires form isolated openings, separated by the width of the wires. In order to form a continuous pattern, the paste has to flow laterally to connect the isolated portions of the paste that are pressed through the mesh. This causes blurring of the structure.

Screen printing is mostly used for unpatterned layers, for example for electrodes or electrolytes in solid oxide fuel cells [30], but also the formation of an array of more than one hundred single sensor dots (1.5 x 1.5 mm²) has been reported [31].
The screen printing paste is deposited on the patterned mesh. With a squeegee the mesh is pressed onto the substrate and the paste is squeezed through the openings. The pattern is transferred to the substrate and the excess paste remains on the mesh.

**Figure IV-12**: Screen printing process.

### Screen Printing

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 μm</td>
<td>- generally applicable</td>
</tr>
<tr>
<td></td>
<td>- dense microstructure</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
</tr>
</tbody>
</table>

Disadvantages:
- low resolution
- small aspect ratio

Remarks:
- Good control of layer thickness

**Table IV-10**: Process characteristics of screen printing.

3.3 Stamping Methods

**Gravure Offset Printing**

This procedure is similar to the offset printing process in the printing industry and is described in [32] for the fabrication of conductive line patterns. The desired pattern, which is etched into a metallic gravure plate, is first covered with a screen printing paste and then scraped clean so that the paste remains only in the engraved pattern. Subsequently the paste in the pattern is picked up and transferred from the plate to the desired substrate by a flexible silicon rubber pad which is pressed onto the substrate. Structures made by Gravure Offset Printing have smoother surfaces than those made by screen printing because the screen printing mesh leads to a superstructure grid on the surface of the deposited layer when high viscosity pastes are used. Screen printing on the other hand allows a better control of the layer thickness.

In literature only pattern transfer with metal–filled screen printing pastes has been reported. However, this method is listed here, because enough recipes for ceramic–filled
pastes are also available. As in screen printing only low aspect ratio structures can be achieved.

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Aspect Ratio</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 µm</td>
<td>0.1</td>
<td>- generally applicable</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- dense microstructure</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Print</th>
<th>Rubber Pad</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ink</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure IV-13: Schematic of Gravure Offset Printing. By means of a rubber pad ink is transferred from a printing plate to a substrate [32].

**Microcontact Printing (µCP)**

This technique uses well defined patterns of self assembling monolayers for pattern formation. They are transferred to a substrate by means of a soft polymer stamp made of poly(dimethylsiloxane) (PDMS). The process has proven to be very versatile in generating micron- and nanoscale monolayer patterns [33]. By using the stamped monolayer as resist material for an etching process, defined gold features as narrow as 30 nm can be obtained [34].

Patterning a substrate with ceramics uses selective wetting of an aqueous suspension on the hydrophilic part of a partially hydrophilic and hydrophobic surface [35]. When the substrate is dipped for example into an aqueous suspension of a colloidal iron oxide, small suspension droplets are formed on the hydrophilic parts of the substrate. Then, the solvent is evaporated and the solid particles remain on the substrate as a thin coating. Feature sizes of 1 µm have been made with this process.

The self assembling monolayer that determines the pattern can be made with an excellent lateral resolution. But, due to the low solids loading of the colloidal suspension,
only thin layers in the range of 100 nm can be achieved. In addition, appropriate colloidal particles are required in a homogeneous dispersion. A diagram of the process is depicted in the experimental section in Figure V.B-16.

<table>
<thead>
<tr>
<th>Microcontact Printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
</tr>
</tbody>
</table>

| Advantages: |
| - excellent resolution |
| - generally applicable |

| Disadvantages: |
| - small aspect ratio |

| Remarks: |
| Deposition is controlled by the wetting behavior of the ceramic suspension. |

**Table IV-12: Process characteristics of microcontact printing.**

4 Methods with 3-Dimensional Molds

Many of these methods require a separate mold for every part produced. After shaping, the molds are destroyed during the process, in most cases by pyrolysis. The feature size of the parts can become as small as 10 μm. However, the techniques involved in fabricating such molds from scratch are quite costly, because microfabrication techniques have to be used for their production. Therefore, it is desirable to make a positive master mold of durable material and high accuracy. The single lost molds are replicated from this master with macro-scale technology, for example by injection molding [36]. In the case where each mold has to be microfabricated separately, the fabrication process becomes more costly, as a cleanroom environment with very expensive machinery is generally needed. Ideally, reusable molds are employed. But demolding becomes increasingly difficult with higher aspect ratios and smaller feature sizes because of the increasing contact areas parallel to the demolding direction and the incorporated surface friction during demolding.

**Figure IV-14: Two fabrication strategies with lost molds. Creating a master structure with microtechnology and replicating it with macro-technology is preferred.**
4.1 Slip Casting

In the traditional slip casting process the suspension agent of a slip is dragged into the porous mold by capillary flow which leads to the formation of a ceramic green body at the surface of the mold. Either plaster or porous polymers are used as mold materials. These mold materials are not suited for the generation of miniaturized parts, as the required surface quality cannot be achieved due to their porosity. Hence, nonporous mold materials have to be used and the solidification of the suspensions is achieved by evaporating the solvent through the sample surface and not through the mold.

Molds made by X-ray lithography have been filled with a 23 vol % slurry of lead zirconate titanate (PZT) for the formation of an array of piezoelectric rods [37]. A honeycomb structure with a wall thickness of 10 µm and an aspect ratio of 20 was also produced. As the solids loading is relatively low, drying cracks occurred. Defect-free structures have been made by a combination of cold isostatic pressing after drying of slip cast green bodies and subsequent hot isostatic pressing [38].

<table>
<thead>
<tr>
<th>Slip Casting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
</tr>
<tr>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>Advantages:</td>
</tr>
<tr>
<td>Disadvantages:</td>
</tr>
<tr>
<td>Remarks:</td>
</tr>
</tbody>
</table>

Table IV-13: Process characteristics of slip casting.

4.2 Centrifugal Casting

The damage during drying of the green body can be reduced by increasing the wet green density of the ceramic bodies mechanically. One method to achieve this is by sedimentation of the ceramic particles in a centrifuge. The centrifugal forces are relatively low compared to pressing techniques, therefore wax molds can be used [39]. A PZT array with an aspect ratio of 10 has been produced this way. Because the centrifugal force acts uniformly on every particle, the produced green bodies have a better homogeneity than those produced by filter pressing (see below).
Microfabrication of Ceramics

A dissertation submitted to the

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ZÜRICH

for the degree of
Doctor of Technical Science

presented by
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Dipl. Werkstoffing. ETH

born on June 21, 1969
citizen of Lützelflüh, BE

accepted on the recommendation of
Prof. Dr. L. J. Gauckler, examiner
Prof. Dr. N. D. Spencer, co-examiner

Zürich, 2000
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- Natalie Stutzmann for her contributions on micropatterned polymers and for many interdisciplinary events,

and all the people sharing my office for creating a motivating atmosphere.

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## Microfabrication of Ceramics

### Summary

To date, ceramic materials have almost been excluded from the general trend of miniaturization of functional devices, which goes on in other fields of materials science. Especially in the semiconductor industry the feature sizes of the generated structures decreased constantly in the last years. Today, submicron structures with a feature size of 0.2 μm are already produced in semiconductor pilot plants. On the other hand, the smallest ceramic features produced in industry so far are almost three orders of magnitude larger. Piezoceramic rods for the fabrication of ultrasonic transducers have diameters in the range of 100 μm. Other techniques which allow the production of features with a size of 50 μm and slightly below, are in a research state but not applied on a large scale. Smaller surface structures on ceramics have not been generated up to now. In the present work we therefore attempted to develop powder-based ceramic forming techniques which allow the generation of ceramic features with dimensions of a few micrometers.

In the first part of the study, bulk samples with a patterned surface are generated by slip casting of water-based suspensions into nonporous elastomeric molds made of poly(dimethyl siloxane) (PDMS). Surface structures of excellent quality with dimensions as small as 1 μm are feasible. It was found that a suspension with a high solids loading has to be used in order to reduce drying shrinkage and a hydrophobic surface of the mold material is essential for defect-free demolding. The slip casting process is applicable to various ceramic materials. Also polymers other than PDMS can be used as molds, however, PDMS offers the simplest mold generation process.

In the second part of the work, three fabrication methods for the generation of ceramic surface patterns on arbitrary substrates are investigated. In the first method, micromolding in capillaries, a PDMS structure forms three walls of a capillary, the surface of the substrate acts as the fourth wall. A liquid is then dragged into these capillaries and solidified, leaving a three dimensional structure after removing the PDMS. The process was developed for solutions and could not be successfully adapted to dense ceramic suspensions, as the ceramic structures could not be obtained in a reproducible manner. The second technique uses selective wetting of an aqueous suspension on gold surfaces functionalized with hydrophilic and hydrophobic self-assembled monolayers. It produced promising results, but sintering of the ceramic features on the gold surface as well as the transfer of the process to other than gold substrates could not be achieved. Finally, filling of surface molds made of patterned photoresist yielded the most reproducible structures with a feature size of 5 μm. Matching coefficients of thermal expansion is crucial in order to get a crack-free structure after sintering. The process can be applied to various substrates and ceramic suspensions.
Zusammenfassung


flächen war nicht möglich. Die dritte und vielversprechendste Methode benutzt dreidimensionale Strukturen aus Photolack auf der Substratoberfläche als verlorene Form für Schlickerguss. Mit dieser Technik konnten keramische Muster mit einer Auflösung von bis zu 5 μm reproduzierbar hergestellt werden.
II General Introduction

Microfabrication is becoming more and more important in modern science and technology. The ability to fabricate new types of microstructures or to produce existing structures in down-sized versions offer a large potential in cost reduction. The most obvious examples are sensors, actuators and microelectronic devices. Miniaturization of electronic elements has made terrific progress in the last decades and is still going on. Components with micrometer or even nanometer dimensions can also open up the opportunity to study basic scientific phenomena that occur at small dimensions. One example is quantum confinement observed in nanostructures [1]. Although most research on microfabrication is silicon-based and has been focused on microelectronic devices [2], applications in other areas are rapidly emerging. These include sensor systems for microanalysis [3–6], micro-volume reactors [7–9] combinatorial synthesis [10], micro-electromechanical systems (MEMS) [11,12], optical components (for example photonic band gap materials) [13–15] and systems for non-magnetic data storage [16].

One promising use for microanalytical devices is in the separation and analysis of chemical and biological substances [3–6]. These devices require only small quantities of reagents, have relatively short analysis times and can show efficiencies in separation and detection that are better than those of larger analysis systems. In the last years, several miniaturized total chemical analysis systems [17,18], sometimes also referred to as ‘labs on a chip’, have been developed that perform all sample-handling steps on their own. An array of chemical tools on a chip makes it possible to analyze extremely small amounts of a product. These systems will be useful for the parallel screening of a large number of compounds. For example an artificial nose can be realized with a large number of single sensors of which each one is tuned to detect a different ‘flavor’ [19]. Structures in the micrometer range allow the integration of a large number of single elements on a small area. Even though the selectivity of a single element might by mediocre, their large number compensates this disadvantage by far.

Miniaturization of sensor elements has not only the advantage that more data can be collected in the same amount of space, but also that the sensing devices may be integrated directly on the electronic chip along with monitoring, actuating and controlling devices. With such an integration, a sensor element can directly generate a digital output signal. In the past years, the scope of fabrication techniques has widened and the number of devices has increased [11,12,20]. Most are fabricated from silicon using standard microlithographic techniques [21,22]. With these methods, thousands of mechanical elements, for example cantilevered beams, springs, linkages, mass elements and joints, can be batch-fabricated on a single silicon substrate [10,12]. Microactuators, micromotors and microengines [22] have been fabricated for optical switches, fluid pumps [23], sys-
tems for drug delivery and microchemical analysis [24–27]. More recently, surface micromachining techniques have been used to fabricate miniaturized optical components which are attractive for applications in spectrometers, display devices, sensors, optoelectronic packages and data storage systems [13–15].

Most of the devices mentioned above are made using silicon based microfabrication techniques. Up to now, not much has been done to fabricate miniaturized parts of ceramic materials. Sensors with ceramic detection materials are still built in the classical manner. A macroscopic ceramic part detects the signal which is fed to the evaluating electronics by electric connectors. For a possible integration of ceramic materials into the length scale of microelectronic components no suitable fabrication techniques have been developed yet, although ceramic materials are operating in numerous types of sensors, as summarized in Table IV-1.

<table>
<thead>
<tr>
<th>Type of Sensor</th>
<th>Output Signal</th>
<th>Effect</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature sensor</td>
<td>Change in the resistance</td>
<td>Thermistor effect (PTC or NTC)</td>
<td>NiMn$_2$O$_4$, CoFe$_2$O$_4$, BaTiO$_3$</td>
</tr>
<tr>
<td>Oxygen sensor</td>
<td>Electromotive force</td>
<td>Conductivity of oxygen ions</td>
<td>ZrO$_2$</td>
</tr>
<tr>
<td>Gas Sensor</td>
<td>Change in the resistance</td>
<td>Semiconducting behavior</td>
<td>SnO$_2$</td>
</tr>
<tr>
<td>Optical sensor</td>
<td>Electromotive force</td>
<td>Pyroelectric effect</td>
<td>SrTiO$_3$, PZT, PbTiO$_3$</td>
</tr>
<tr>
<td>Ultrasonic sensor</td>
<td>Phase difference of emitted and detected waves</td>
<td>Piezoelectric effect</td>
<td>PZT, PbTiO$_3$, PbZrO$_3$</td>
</tr>
<tr>
<td>Sensors for measuring force, pressure, acceleration</td>
<td>Change in output voltage</td>
<td>Piezoelectric effect</td>
<td>PZT, PbTiO$_3$, PbZrO$_3$</td>
</tr>
</tbody>
</table>

Table IV-1: Ceramic sensor materials [28,29].

One of the most crucial issues towards the integration of ceramic materials into micro-scale devices, is the development of suitable forming methods. When features with dimensions below 100 μm are required, a simple downscaling of established ceramic processing techniques is not suitable. In the present thesis, principles of colloidal chemistry with ceramic powders were combined with new approaches for mold fabrication.
References


(28) N. Ichinohe, Introduction to fine ceramics; Ch. 3.14, pp. 100–102. John Wiley & Sons, 1983.
III Aim of this Study

The goal of the present work was to find and apply new processing routes for the fabrication of well defined ceramic surface components in the micrometer range, one order of magnitude smaller than the structures feasible today.

This miniaturization of ceramic components may lead to advances in sensor technology, possibly being integrated on the same silicon chip used for data processing. This would allow the production of ceramic–containing devices of similar dimensions as polymeric and metallic structures which are already available today. However, it is not the goal of this work to fabricate a fully functional sensor, rather appropriate methods for the production of such sensors are evaluated.

In order to narrow the broad focus and also with regard to potential industrial applicability of these processes, additional boundary conditions for the new processing method had to be formulated:

• The processing method should be versatile and be able to use commercially available powders of various compositions as raw materials
• The process should enable the production of ceramic microcomponents on various substrate materials
• The molds should be reusable in order to be cost effective
• Expensive machinery should be avoided.
IV State of the Art in Ceramic Microfabrication

Processing techniques that are suitable for producing ceramic parts with a minimal feature size smaller than 500 μm are described and compared based on the specific requirements of this study. In conclusion of this overview, a strategy for the first approach of the present investigation is developed.

1 Introduction

The first efforts in ceramic microtechnology have been made by downscaling elaborated macroscale forming technologies. This was also the case for the most widely used ceramic microsystem, the piezoelectric ultrasonic transducer. These transducers are made of small piezoceramic rods embedded in a polymer matrix (Figure IV-1).

![Figure IV-1: Schematic of a composite ultrasonic transducer.](image)

This composite setup avoids losses of ultrasonic energy at the transducer–tissue interface in medical imaging [1]. The rods have to be long and slender in order to ensure a noise-free signal [2]. The first generation of such rods was made by cutting perpendicular grooves into a sintered PZT plate (Figure IV-2) [3] that leads to individual posts with small dimensions. The width of the grooves is determined by the width of the dice and the width of the rods is limited by the mechanical stability of the material. The high stresses involved in this technique lead to breaking of small rods during manufacturing. Both the width of the trenches and of the rods are in the range of 200 μm, the aspect ratio (Figure IV-3) is in the order of 1. The described limitations of the downscaled technique gave rise to the demand for other approaches for the production of such ceramic rod structures. Molds made with methods developed in semiconductor manufacturing were combined with traditional suspension-based ceramic forming techniques. Today, rods as narrow as 20 μm with an aspect ratio of 10 are produced [4,5].
In different fields, as for example in sensor technology [6] or rapid prototyping [7], special techniques of forming small-scale ceramic structures have been developed to date. An overview of processing techniques and some examples of their applications is given in Table IV-1. For each of these applications the ceramic parts have to fulfill certain requirements. Therefore, several processing methods have been developed, each one with its special focus on a certain application.
### Method Examples Literature

<table>
<thead>
<tr>
<th>Method</th>
<th>Examples</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rapid prototyping</td>
<td>Prototypes, casting molds for metals</td>
<td>[7–17]</td>
</tr>
<tr>
<td>Direct ceramic machining</td>
<td>Dental implants</td>
<td>[18]</td>
</tr>
<tr>
<td>Co–extrusion</td>
<td>Polycrystalline fiber composite material</td>
<td>[19–21]</td>
</tr>
<tr>
<td>Etching</td>
<td>Superconducting connectors</td>
<td>[22–27]</td>
</tr>
<tr>
<td>Screen printing</td>
<td>Electrolytes for solid oxide fuel cells</td>
<td>[28–31]</td>
</tr>
<tr>
<td>Stamping methods</td>
<td>Conductor lines</td>
<td>[32–35]</td>
</tr>
<tr>
<td>Slip casting</td>
<td>Piezoelectric array</td>
<td>[37–38]</td>
</tr>
<tr>
<td>Centrifugal casting</td>
<td>Piezoelectric array</td>
<td>[39]</td>
</tr>
<tr>
<td>Filterpressing</td>
<td>Piezoelectric array, nozzle</td>
<td>[39–40]</td>
</tr>
<tr>
<td>Injection molding</td>
<td>Piezoelectric array</td>
<td>[41]</td>
</tr>
<tr>
<td>Tape embossing</td>
<td>Piezoelectric array</td>
<td>[42–44]</td>
</tr>
</tbody>
</table>

*Table IV-1: Applications for microfabricated ceramic parts produced by the forming methods discussed in this chapter. For references see the respective sections.*

It would not be very informative to compare the different processing methods directly with each other. What is an advantage for one application might be a disadvantage for another. Therefore, the advantages and disadvantages listed in the following subsections are specified with regard to an ‘ideal processing method’, which was already described in the aim of this work. Such a method does not (yet) exist, it serves only as common reference to judge the single processes more objectively. The criteria for the comparison were chosen to allow a statement about the suitability of the processing method for the fabrication of the small features required in this study.

The ideal processing technique has the following characteristics:

- The smallest lateral dimension is below 10 micrometers
- An aspect ratio larger than 1 is possible
- Dense polycrystalline ceramic bodies can be produced.

The fulfillment of one or all of these requirements is listed as an advantage in the process characteristics table of each section. If the technique does not fulfill these requirements, it is listed as a disadvantage. The smallest lateral feature size and the largest achievable aspect ratio are listed and visualized for each of the processes in the characteristics table at the end of the respective sections. Their determination is based on the
processes, not on the properties of the materials that are used. With techniques that can make structures with high aspect ratios, the strength of the ceramic material becomes the limiting factor for the structure height, but this is of no concern here.

The smallest lateral feature size is the width of the smallest feature that has been achieved using the respective process. The aspect ratio is a dimensionless number that is calculated by dividing the maximal height of a structure by its width. Long, slender structures have a high aspect ratio; broad, flat structures have a low one.

![High Aspect Ratio Low Aspect Ratio](image)

*Figure IV-3: Structures with high and low aspect ratios.*

In the following section the discussed processes are grouped according to the kind of molds that are employed. Some methods do not require a mold at all. In this case the ceramic part is built in all three dimensions from a powder bed or a blank on a computer controlled machine. Methods that use 2-dimensional molds are strongly related to methods used on a larger length scale in the traditional printing industry. In these methods the third dimension is generated directly during the process. When 3-dimensional molds are used, the processes are related to traditional casting methods where ceramic materials are usually processed as suspensions.

2 Methods without Mold

2.1 Rapid Prototyping Techniques

Rapid prototyping techniques, sometimes also referred to as solid freeform fabrication techniques, were developed in order to generate parts directly from a computer model to avoid the costs and time involved in mold fabrication for the production of single prototypes or of small series of a functional part [7].

The parts are built layer by layer in order to realize even complex geometries. The 2-dimensional geometrical information for each layer is generated by a slicing algorithm applied to a CAD model of the part. Rapid prototyping systems therefore have two critical dimensions: The smallest lateral feature size and the thickness of a solidified layer. A smaller feature size and a thinner layer thickness lead to a better resolution, but also to significantly longer process times for the produced parts. A compromise has to be made between resolution and processing time. In general, a minimal cure depth and minimal
cure width of 200 μm are desired. The aspect ratios of the produced parts are only limited by the geometry of the machine. Theoretically an infinite number of layers could be stacked.

![Diagram](image)

**Figure IV-4: Principle of layered object fabrication.**

Because of the wish to generate exact 1:1 prototypes, the ceramic powders used in Rapid Prototyping are usually tailored to avoid shrinkage during sintering. This leads to porous ceramic microstructures of low strength and modulus. Most of the ceramic parts made by rapid prototyping are made of refractory grade powders and are used as molds for metal casting of prototypes or small scale serial production.

Different methods for rapid prototyping of ceramics have been developed, but they can all be grouped into three fields:
1. Selective addition of material to an existing surface.
2. Chemical alteration of a liquid or solid using directed light energy.
3. Sintering of a powder using directed light energy.

In the following subchapters techniques for each of these field are described. *Three Dimensional Printing* and *Suspension Printing* representing the first group, *Stereolithography* the second and *Selective Laser Sintering* the third.

The suitability of all the described rapid prototyping techniques for ceramic microfabrication is summarized at the end of this section.

*Three Dimensional Printing*

In Three Dimensional Printing (3DP) the single layers of the ceramic part are solidified by spraying a binder suspension with an inkjet printer head into a ceramic powder bed [8]. Structures with a minimal feature size of 430 μm are reported. The parts are made using an alumina powder with an average grain size of 40 μm. The powder is solidified via a glass phase during heat treatment at 800 °C, practically no shrinkage occurs. The parts can be used as casting molds for small series in metal production where 3DP is cheaper than creating molds for lost wax models [9]. Investigations to use the produced parts as drug delivery devices have also been reported [10].

3DP is performed using both available systems of inkjet printers: drop–on–demand and continuous–jet technology. The latter is favored because of the higher printing speed.
Applying a layer of loose powder on top of solidified part

Printing step. Binder is selectively printed into the powder bed.

Printing step is terminated, next layer of powder can be applied

Figure IV-5: Process of 3DP.

<table>
<thead>
<tr>
<th>Three Dimensional Printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
</tr>
<tr>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>Advantages:</td>
</tr>
<tr>
<td>Disadvantages:</td>
</tr>
<tr>
<td>Remarks:</td>
</tr>
</tbody>
</table>

Table IV-2: Process characteristics of 3DP.

Suspension Printing

This technique is related to 3DP, but instead of printing a binder into a powder bed, a ceramic suspension is printed onto a substrate. The suspension is deposited with either a continuous [11,12] or a drop-on-demand ink jet printer [13]. As the viscosity of the printing suspensions is limited to about 10 mPa-s, the reported solids loadings of the suspensions are only 5–10 vol %. The vast amount of solvent that has to be evaporated limits the printing speed. Therefore, only porous substrates, that support drying, are used. Due to the low solids loading the layer thickness for each printing cycle is about 1 μm; much thinner than with the other layered fabrication techniques. This technique is still in the experimental stage, no applications have been reported so far.
Figure IV-6: Pattern created by suspension printing [12].

Table IV-3: Process characteristics of Suspension Printing.

<table>
<thead>
<tr>
<th>Suspension Printing</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
<td>dense structures</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>Disadvantages:</td>
</tr>
<tr>
<td>0.05</td>
<td>low resolution</td>
</tr>
<tr>
<td>0.1</td>
<td>low aspect ratio</td>
</tr>
<tr>
<td>1</td>
<td>very slow speed</td>
</tr>
<tr>
<td>100</td>
<td>Remarks:</td>
</tr>
<tr>
<td>100</td>
<td>Only porous substrates can be coated</td>
</tr>
</tbody>
</table>

Stereolithography

In ceramic stereolithography a suspension of ceramic particles in a photopolymerizable monomer is solidified by crosslinking the molecules with an ultraviolet laser directed by a mirror system. In the following heat treatment the polymer matrix is pyrolyzed and the ceramic part is sintered. Parts made of silica, alumina and silicon nitride have been reported [14].

Compared to stereolithography with pure monomer solutions, as used in rapid prototyping of polymeric parts, the dispersed ceramic particles lower the cure depth and increase the cure width of the laser beam, even if the ceramic material is transparent to UV. For example a laser beam with a diameter of 210 μm is widened in the suspension and cures an area of 300 μm in diameter [15].

Figure IV-7: Experimental setup for stereolithography [14].
Stereolithography

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 µm</td>
<td>- high aspect ratio</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>only limited by machine geometry</td>
<td>- low resolution</td>
</tr>
<tr>
<td></td>
<td>- no dense microstructure</td>
</tr>
</tbody>
</table>

Remarks:
Scattering effects lower lateral resolution

Table IV-4: Process characteristics of stereolithography.

Selective Laser Sintering (SLS)

A laser beam melts the low melting component of a two component inorganic powder system. The liquid phase wets the solid ceramic powder and joins it during the solidification. After shaping, the low melting phase is no longer beneficial, it limits the thermal stability of the part. Therefore, a following heat treatment step is used to increase the thermal stability of the microstructure. Examples of SLS powder systems are alumina with a low melting phosphate binder forming a glass phase during heat treatment [16] or alumina with metallic aluminum as melting phase which is subsequently oxidized [17]. After sintering, the microstructure reaches about 50% of the theoretical density [17]. The speed of the laser beam relative to the powder surface is determined by the thermal conductivity of the powder material to be compacted. A high thermal conductivity leads to dissipation of large amounts of energy into the powder bed, requiring longer irradiation.

Figure IV-8: Ceramic parts produced via SLS [16].
times to melt the binder phase. On the other hand, a low thermal conductivity can lead to thermal shock failures in the produced part.

### Selective Laser Sintering

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>500 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspect Ratio</td>
<td>only limited by machine geometry</td>
</tr>
</tbody>
</table>

| Advantages: |
| - high aspect ratio |

| Disadvantages: |
| - low resolution |
| - no dense microstructure |

| Remarks: |
| Limited speed due to heat transfer limitations, needs liquid phase sintering |

**Table IV-5: Process characteristics of Selective Laser Sintering.**

The described rapid prototyping techniques have two major advantages. First, parts can be generated in very short time without the need for a mold, second, structures with high aspect ratios can be made. However, the lateral resolution of the techniques is quite low. This also leads to a rather rough surface. The effects responsible for this low resolution are the physical limitations of these techniques. It is not likely that with these techniques feature sizes much smaller than 150–200 µm can be realized in the future.

The main limitations are

- size of the generated droplets and spread of liquid droplets in a porous substrate for the ink-jet related techniques,
- scattering effects in stereolithography,
- heat conduction in Selective Laser Sintering.

In addition, some of the processes need powder systems with liquid phase sintering. This limits the high temperature stability of the produced parts.

2.2 Direct Ceramic Machining (DCM)

An isostatically pressed and presintered ceramic blank is shaped on a computer controlled milling machine. After the shaping process, the ceramic bodies are sintered to full density and exhibit excellent mechanical behavior [18]. As this is not a layered fabrication technique, even round shapes can be made with good accuracy. The resolution is determined by the positioning accuracy of the milling machine and the diameter of the milling cutter. The aspect ratio is also limited by the available milling cutters. Rounded structures inside the part are not feasible because of the ‘one dimensional’ geometry of the milling cutter. By compensating the sintering shrinkage of the ceramic material, net-
shaped sintered parts can be made. An image of the milling process is shown later in Figure V.A-33.

DCM is a very powerful technique for the fabrication of parts in the size range of 400 μm. The ceramic structures can be shaped fast and sintered to full density. One application of this technique is the fabrication of ceramic tooth bridges which exhibit very high mechanical strength.

<table>
<thead>
<tr>
<th>Direct Ceramic Machining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
</tr>
<tr>
<td>Aspect Ratio</td>
</tr>
</tbody>
</table>

Advantages:
- high aspect ratio
- dense microstructure

Disadvantages:
- low resolution
- geometrical limitations

Remarks:
Net-shape method

Table IV-6: Process characteristics of direct ceramic machining.

2.3 Extrusion

Elongated fine-scaled ceramic parts are fabricated by extruding a thermoplastic polymer filled with ceramic particles through a size-reducing die. The feedrod used for extrusion consists of several powder-filled polymer compounds. During extrusion, the shape in which the different compounds are assembled is maintained. The feedstock is only reduced in its dimensions perpendicular to the extrusion direction. After each extrusion step the extrudates are reassembled and extruded again until the desired size reduction is achieved. Objects with complex shapes can be fabricated by assembling an extrusion feedrod from several shaped ceramic compounds. With a space-filling carbon black compound that can be pyrolyzed, even free-standing or hollow structures are possible. Objects in the size range of 10 μm were produced [19,20]. Polycrystalline fiber composites with defined fiber geometries and orientations can be made also [21].

With this method, no micromachined parts are necessary to generate microscopic features, they are generated by the uniform size reduction of macroscopic assemblies. Although very small structures with high aspect ratios can be made, this method suffers from important restrictions. The shape of the structures is limited to quasi-3D shapes due to the one dimensional extrusion process. In addition, the generated patterns get slightly distorted during the extrusion.
3 Methods with 2-Dimensional Molds

In the processes described in this section the mold has to be defined in two dimensions, the third dimension is directly generated in the process.

3.1 Etching

Etching processes are not very widespread in ceramics manufacturing because ceramics are among the hardest and most inert materials known. Especially wet etching processes are generally not suitable for patterning ceramics which are usually very inert to aggressive liquid media. However, this method is used for niche applications with a well matched pair of etchant and material to be etched. In dry etching processes the material is removed either by sputtering or in a highly reactive plasma. This process has less problems with the chemical inertness of ceramics. As the standard polymeric resist
State of the Art

materials are often removed faster than the ceramic material, mechanical aperture masks are needed to direct the etching plasma.

Wet Etching

Patterning by wet etching is carried out similar to silicon–based techniques in microelectronic manufacturing [22]. A ceramic surface is coated with a photoresist film. This resist film is exposed through a photomask and developed, the irradiated area of the resist is dissolved. Through the blank spaces in the resist the ceramic material can be etched with an appropriate liquid etchant. Most of the research in wet etching of ceramics is done in the field of ceramic high–Tc superconductors. For the fabrication of small-scale coils or other superconducting circuits epitaxially deposited cuprate films have been etched with a variety of chemicals, such as hydrofluoric acid, EDTA, nitric acid or phosphoric acid [23]. The application of wet etching is limited to some special ceramics and is often isotropic. Underetching of the template structures may occur, thus limiting the achievable feature size and aspect ratio.

![Figure IV-10: Wet etched superconducting YBa$_2$Cu$_3$O$_7$ coil on a SrTiO$_3$ substrate [23].](image)

<table>
<thead>
<tr>
<th>Wet Etching</th>
<th>Advantages:</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension 2 µm</td>
<td>- good resolution</td>
<td>- low aspect ratio</td>
</tr>
<tr>
<td>Aspect Ratio 0.3</td>
<td></td>
<td>- not generally applicable</td>
</tr>
<tr>
<td></td>
<td>Remarks:</td>
<td>Only isotropic etching</td>
</tr>
<tr>
<td></td>
<td>Only isotropic etching possible</td>
<td></td>
</tr>
</tbody>
</table>
Dry Etching

In dry etching processes the material is patterned either by exposing it to a reactive plasma which forms volatile compounds with the material to be removed or by removing the undesired part mechanically with an ion beam [22]. The main parameter of a dry etching process is the energy of the incorporated plasma. At low ion energies the process is chemically controlled, not all components in a multi material mixture form volatile components with a certain plasma. Therefore, these processes exhibit a high selectivity. For example, if layers of different materials are stacked, the etching reaction stops at the interface between two materials, because only one material is removed by the plasma. The etching process is more or less isotropic in all directions, no structures with high aspect ratios can be made. In physical plasma processes the material is removed by sputtering. These processes allow a stronger anisotropy; structures with a higher aspect ratio can be produced. However, the larger anisotropy results in a smaller selectivity of the etching process, as illustrated in Figure IV-11.

Figure IV-11: Dry etching processes [22].

Several binary metal oxides such as CuO, ZnO and PbO have been plasma etched with hexafluoroacetylacetone at temperatures above 200 °C [24], also binary nitrides can be etched [25]. Etching of PZT has been done with excimer laser radiation in a reducing atmosphere [26] and also with SF₆ [27].

Like in wet etching, also dry etching of ceramics can only be applied to materials that form volatile components with the etchant. This greatly limits the applicability of this technique.
## Dry Etching

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 μm</td>
<td>- high aspect ratio</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>- low resolution - not generally applicable</td>
</tr>
</tbody>
</table>

Remarks:
Volatile components have to be formed

**Table IV-9: Process characteristics of dry etching.**

### 3.2 Screen Printing

A paste of ceramic powder, plasticizer and binder is placed on a patterned screen of metal wires. The pattern is generated by sealing some of the meshes of the screen with a polymer. The paste is then forced through the remaining openings in the screen by using a rubber squeegee which depresses the screen to contact the substrate as it traverses the pattern. The thickness of the deposited layer is determined by the thickness of a polymer spacer film attached to the lower side of the mesh. Patterning of the screen is done by coating it with a photoreactive polymer and dissolving the latter selectively after exposure [28].

To overcome the limitation that only flat substrates can be patterned by screen printing, transfer printing has been developed [29]. The ceramic layer is printed onto a sheet of coated paper and can later be transferred onto tubular or corrugated surfaces.

Screen printing is a simple process, but only low aspect ratios with low resolutions can be made. The resolution is limited by the viscosity of the ceramic paste that is used. The crosswise arranged metal wires form isolated openings, separated by the width of the wires. In order to form a continuous pattern, the paste has to flow laterally to connect the isolated portions of the paste that are pressed through the mesh. This causes blurring of the structure.

Screen printing is mostly used for unpatterned layers, for example for electrodes or electrolytes in solid oxide fuel cells [30], but also the formation of an array of more than one hundred single sensor dots (1.5 x 1.5 mm²) has been reported [31].
Patterned Mesh
Ceramic Paste
Substrate

Polymer Squeegee

Superfluent Paste

The screen printing paste is deposited on the patterned mesh.

With a squeegee the mesh is pressed onto the substrate and the paste is squeezed through the openings.

The pattern is transferred to the substrate and the excess paste remains on the mesh.

Figure IV-12: Screen printing process.

<table>
<thead>
<tr>
<th>Screen Printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
</tr>
<tr>
<td>Aspect Ratio</td>
</tr>
</tbody>
</table>

Advantages:
- generally applicable
- dense microstructure

Disadvantages:
- low resolution
- small aspect ratio

Remarks:
Good control of layer thickness

Table IV-10: Process characteristics of screen printing.

3.3 Stamping Methods

Gravure Offset Printing

This procedure is similar to the offset printing process in the printing industry and is described in [32] for the fabrication of conductive line patterns. The desired pattern, which is etched into a metallic gravure plate, is first covered with a screen printing paste and then scraped clean so that the paste remains only in the engraved pattern. Subsequently the paste in the pattern is picked up and transferred from the plate to the desired substrate by a flexible silicon rubber pad which is pressed onto the substrate. Structures made by Gravure Offset Printing have smoother surfaces than those made by screen printing because the screen printing mesh leads to a superstructure grid on the surface of the deposited layer when high viscosity pastes are used. Screen printing on the other hand allows a better control of the layer thickness.

In literature only pattern transfer with metal-filled screen printing pastes has been reported. However, this method is listed here, because enough recipes for ceramic-filled
pastes are also available. As in screen printing only low aspect ratio structures can be achieved.

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 μm</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**Advantages:**
- generally applicable
- dense microstructure

**Disadvantages:**
- low resolution
- small aspect ratio

**Remarks:**
Less control over layer thickness.

*Table IV-11: Process characteristics of Gravure Offset Printing.*

*Figure IV-13: Schematic of Gravure Offset Printing. By means of a rubber pad ink is transferred from a printing plate to a substrate [32].*

**Microcontact Printing (μCP)**

This technique uses well defined patterns of self assembling monolayers for pattern formation. They are transferred to a substrate by means of a soft polymer stamp made of poly(dimethylsiloxane) (PDMS). The process has proven to be very versatile in generating micron- and nanoscale monolayer patterns [33]. By using the stamped monolayer as resist material for an etching process, defined gold features as narrow as 30 nm can be obtained [34].

Patterning a substrate with ceramics uses selective wetting of an aqueous suspension on the hydrophilic part of a partially hydrophilic and hydrophobic surface [35]. When the substrate is dipped for example into an aqueous suspension of a colloidal iron oxide, small suspension droplets are formed on the hydrophilic parts of the substrate. Then, the solvent is evaporated and the solid particles remain on the substrate as a thin coating. Feature sizes of 1 μm have been made with this process.

The self assembling monolayer that determines the pattern can be made with an excellent lateral resolution. But, due to the low solids loading of the colloidal suspension,
only thin layers in the range of 100 nm can be achieved. In addition, appropriate colloidal particles are required in a homogeneous dispersion. A diagram of the process is depicted in the experimental section in Figure V.B-16.

![Table](https://via.placeholder.com/150)

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- excellent resolution</td>
</tr>
<tr>
<td></td>
<td>- generally applicable</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- small aspect ratio</td>
</tr>
</tbody>
</table>

Remarks:
Deposition is controlled by the wetting behavior of the ceramic suspension.

Table IV-12: Process characteristics of microcontact printing.

4 Methods with 3-Dimensional Molds

Many of these methods require a separate mold for every part produced. After shaping, the molds are destroyed during the process, in most cases by pyrolysis. The feature size of the parts can become as small as 10 μm. However, the techniques involved in fabricating such molds from scratch are quite costly, because microfabrication techniques have to be used for their production. Therefore, it is desirable to make a positive master mold of durable material and high accuracy. The single lost molds are replicated from this master with macro-scale technology, for example by injection molding [36]. In the case where each mold has to be microfabricated separately, the fabrication process becomes more costly, as a cleanroom environment with very expensive machinery is generally needed. Ideally, reusable molds are employed. But demolding becomes increasingly difficult with higher aspect ratios and smaller feature sizes because of the increasing contact areas parallel to the demolding direction and the incorporated surface friction during demolding.

![Figure](https://via.placeholder.com/150)

Figure IV-14: Two fabrication strategies with lost molds. Creating a master structure with microtechnology and replicating it with macro-technology is preferred.
4.1 Slip Casting

In the traditional slip casting process the suspension agent of a slip is dragged into the porous mold by capillary flow which leads to the formation of a ceramic green body at the surface of the mold. Either plaster or porous polymers are used as mold materials. These mold materials are not suited for the generation of miniaturized parts, as the required surface quality cannot be achieved due to their porosity. Hence, nonporous mold materials have to be used and the solidification of the suspensions is achieved by evaporating the solvent through the sample surface and not through the mold.

Molds made by X-ray lithography have been filled with a 23 vol% slurry of lead zirconate titanate (PZT) for the formation of an array of piezoelectric rods [37]. A honeycomb structure with a wall thickness of 10 μm and an aspect ratio of 20 was also produced. As the solids loading is relatively low, drying cracks occurred. Defect-free structures have been made by a combination of cold isostatic pressing after drying of slip cast green bodies and subsequent hot isostatic pressing [38].

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 μm</td>
<td>- high aspect ratio</td>
</tr>
<tr>
<td></td>
<td>- good resolution</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>- drying cracks possible</td>
</tr>
</tbody>
</table>

Remarks: Defects can be removed by isostatic pressing

Table IV-13: Process characteristics of slip casting.

4.2 Centrifugal Casting

The damage during drying of the green body can be reduced by increasing the wet green density of the ceramic bodies mechanically. One method to achieve this is by sedimentation of the ceramic particles in a centrifuge. The centrifugal forces are relatively low compared to pressing techniques, therefore wax molds can be used [39]. A PZT array with an aspect ratio of 10 has been produced this way. Because the centrifugal force acts uniformly on every particle, the produced green bodies have a better homogeneity than those produced by filter pressing (see below).
Microfabrication of Ceramics

A dissertation submitted to the

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ZÜRICH

for the degree of
Doctor of Technical Science

presented by
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citizen of Lützelflüh, BE

accepted on the recommendation of
Prof. Dr. L. J. Gauckler, examiner
Prof. Dr. N. D. Spencer, co-examiner

Zürich, 2000
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and all the people sharing my office for creating a motivating atmosphere.

I wish to thank my mother for always believing in me and Myriam Schefer for her constant support throughout my studies.

The present work substantially benefited from the following acronyms: CD, FM, PDF, G & T, SMTP.

Financial support from the Jubiläumsfonds of ETH Zürich under the TEMA project is gratefully acknowledged.
# Microfabrication of Ceramics

## Summary

Zusammenfassung

## General Introduction

## Aim of this Study

## State of the Art in Ceramic Microfabrication

1. Introduction
2. Methods without Mold
   2.1 Rapid Prototyping Techniques
   2.2 Direct Ceramic Machining
   2.3 Extrusion
3. Methods with 2-Dimensional Molds
   3.1 Etching
   3.2 Screen Printing
   3.3 Stamping Methods
4. Methods with 3-Dimensional Molds
   4.1 Slip Casting
   4.2 Centrifugal Casting
   4.3 Filter Pressing
   4.4 Injection Molding
   4.5 Tape Embossing
5. Summary
6. References

## Process Development

### A: Generation of Patterned Ceramic Surfaces

1. Introduction
2. General Experimental Procedure
   2.1 Mold Fabrication
   2.2 Suspension Preparation
   2.3 Casting
   2.4 Demolding and Sintering
   2.5 Characterization
3. Investigated Issues
   3.1 Influence of Powder Particle Size
   3.2 Increase of Suspension Solids Loading
   3.3 Surface Chemistry of PDMS
   3.4 Conclusions
4 Applicability of the Process .......................................................... 62
  4.1 Maximal Aspect Ratio ............................................................. 62
  4.2 Smallest Replicable Feature Size .............................................. 63
  4.3 Applicability of Various Ceramic Powders ............................... 64
  4.4 Applicability of Various Polymeric Mold Materials .................. 67
  4.5 Conclusions ........................................................................... 70
5 Feature Quality Comparison ......................................................... 70
  5.1 Experimental ......................................................................... 71
  5.2 Results and Discussion ........................................................... 73
  5.3 Conclusions ........................................................................... 75
6 Summary ...................................................................................... 77
7 References .................................................................................... 78

B: Pattern Application to Flat Substrates

1 Introduction .................................................................................. 79
2 Micromolding in Capillaries with Ceramic Suspensions ............... 80
  2.1 General Procedure ................................................................. 81
  2.2 Alumina Suspensions ............................................................... 81
  2.3 Alignment of Vanadium Oxide Nanotubes ............................... 91
3 Selective Wetting on Self Assembled Monolayers ........................ 94
4 Filling of Photoresist Molds on Substrates .................................. 100
5 Summary and Conclusions ........................................................... 108
6 References .................................................................................... 110

VI General Conclusions.................................................................. 113

VII Outlook ..................................................................................... 115

Appendix .......................................................................................... 119

1 Composite Ultrasonic Transducer ................................................. 120
2 Anodic Etching of Aluminum ....................................................... 122
3 Fabrication Methods for Lost Molds ............................................. 123
  3.1 Pattern Generation ................................................................. 123
  3.2 Mold Replication ................................................................. 125
4 Powder Data ................................................................................. 127
5 References ..................................................................................... 133

List of Abbreviations ...................................................................... 135

Curriculum Vitae ............................................................................. 137
I Microfabrication of Ceramics

Summary

To date, ceramic materials have almost been excluded from the general trend of miniaturization of functional devices, which goes on in other fields of materials science. Especially in the semiconductor industry the feature sizes of the generated structures decreased constantly in the last years. Today, submicron structures with a feature size of 0.2 μm are already produced in semiconductor pilot plants. On the other hand, the smallest ceramic features produced in industry so far are almost three orders of magnitude larger. Piezoceramic rods for the fabrication of ultrasonic transducers have diameters in the range of 100 μm. Other techniques which allow the production of features with a size of 50 μm and slightly below, are in a research state but not applied on a large scale. Smaller surface structures on ceramics have not been generated up to now. In the present work we therefore attempted to develop powder-based ceramic forming techniques which allow the generation of ceramic features with dimensions of a few micrometers.

In the first part of the study, bulk samples with a patterned surface are generated by slip casting of water-based suspensions into nonporous elastomeric molds made of poly(dimethyl siloxane) (PDMS). Surface structures of excellent quality with dimensions as small as 1 μm are feasible. It was found that a suspension with a high solids loading has to be used in order to reduce drying shrinkage and a hydrophobic surface of the mold material is essential for defect-free demolding. The slip casting process is applicable to various ceramic materials. Also polymers other than PDMS can be used as molds, however, PDMS offers the simplest mold generation process.

In the second part of the work, three fabrication methods for the generation of ceramic surface patterns on arbitrary substrates are investigated. In the first method, micromolding in capillaries, a PDMS structure forms three walls of a capillary, the surface of the substrate acts as the fourth wall. A liquid is then dragged into these capillaries and solidified, leaving a three dimensional structure after removing the PDMS. The process was developed for solutions and could not be successfully adapted to dense ceramic suspensions, as the ceramic structures could not be obtained in a reproducible manner. The second technique uses selective wetting of an aqueous suspension on gold surfaces functionalized with hydrophilic and hydrophobic self-assembled monolayers. It produced promising results, but sintering of the ceramic features on the gold surface as well as the transfer of the process to other than gold substrates could not be achieved. Finally, filling of surface molds made of patterned photoresist yielded the most reproducible structures with a feature size of 5 μm. Matching coefficients of thermal expansion is crucial in order to get a crack-free structure after sintering. The process can be applied to various substrates and ceramic suspensions.
Zusammenfassung


flächen war nicht möglich. Die dritte und vielversprechendste Methode benutzt dreidimensionale Strukturen aus Photolack auf der Substratoberfläche als verlorene Form für Schlickerguss. Mit dieser Technik konnten keramische Muster mit einer Auflösung von bis zu 5 μm reproduzierbar hergestellt werden.
II  General Introduction

Microfabrication is becoming more and more important in modern science and technology. The ability to fabricate new types of microstructures or to produce existing structures in down-sized versions offer a large potential in cost reduction. The most obvious examples are sensors, actuators and microelectronic devices. Miniaturization of electronic elements has made terrific progress in the last decades and is still going on. Components with micrometer or even nanometer dimensions can also open up the opportunity to study basic scientific phenomena that occur at small dimensions. One example is quantum confinement observed in nanostructures [1]. Although most research on microfabrication is silicon-based and has been focused on microelectronic devices [2], applications in other areas are rapidly emerging. These include sensor systems for microanalysis [3–6], micro-volume reactors [7–9] combinatorial synthesis [10], micro-electromechanical systems (MEMS) [11,12], optical components (for example photonic band gap materials) [13–15] and systems for non-magnetic data storage [16].

One promising use for microanalytical devices is in the separation and analysis of chemical and biological substances [3–6]. These devices require only small quantities of reagents, have relatively short analysis times and can show efficiencies in separation and detection that are better than those of larger analysis systems. In the last years, several miniaturized total chemical analysis systems [17,18], sometimes also referred to as ‘labs on a chip’, have been developed that perform all sample-handling steps on their own. An array of chemical tools on a chip makes it possible to analyze extremely small amounts of a product. These systems will be useful for the parallel screening of a large number of compounds. For example an artificial nose can be realized with a large number of single sensors of which each one is tuned to detect a different ‘flavor’ [19]. Structures in the micrometer range allow the integration of a large number of single elements on a small area. Even though the selectivity of a single element might by mediocre, their large number compensates this disadvantage by far.

Miniaturization of sensor elements has not only the advantage that more data can be collected in the same amount of space, but also that the sensing devices may be integrated directly on the electronic chip along with monitoring, actuating and controlling devices. With such an integration, a sensor element can directly generate a digital output signal. In the past years, the scope of fabrication techniques has widened and the number of devices has increased [11,12,20]. Most are fabricated from silicon using standard microlithographic techniques [21,22]. With these methods, thousands of mechanical elements, for example cantilevered beams, springs, linkages, mass elements and joints, can be batch-fabricated on a single silicon substrate [10,12]. Microactuators, micromotors and microengines [22] have been fabricated for optical switches, fluid pumps [23], sys-
tems for drug delivery and microchemical analysis [24–27]. More recently, surface micromachining techniques have been used to fabricate miniaturized optical components which are attractive for applications in spectrometers, display devices, sensors, optoelectronic packages and data storage systems [13–15].

Most of the devices mentioned above are made using silicon based microfabrication techniques. Up to now, not much has been done to fabricate miniaturized parts of ceramic materials. Sensors with ceramic detection materials are still built in the classical manner. A macroscopic ceramic part detects the signal which is fed to the evaluating electronics by electric connectors. For a possible integration of ceramic materials into the length scale of microelectronic components no suitable fabrication techniques have been developed yet, although ceramic materials are operating in numerous types of sensors, as summarized in Table IV-1.

<table>
<thead>
<tr>
<th>Type of Sensor</th>
<th>Output Signal</th>
<th>Effect</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature sensor</td>
<td>Change in the resistance</td>
<td>Thermistor effect (PTC or NTC)</td>
<td>NiMn2O4, CoFe2O4, BaTiO3</td>
</tr>
<tr>
<td>Oxygen sensor</td>
<td>Electromotive force</td>
<td>Conductivity of oxygen ions</td>
<td>ZrO2</td>
</tr>
<tr>
<td>Gas Sensor</td>
<td>Change in the resistance</td>
<td>Semiconducting behavior</td>
<td>SnO2</td>
</tr>
<tr>
<td>Optical sensor</td>
<td>Electromotive force</td>
<td>Pyroelectric effect</td>
<td>SrTiO3, PZT, PbTiO3, PbZrO3</td>
</tr>
<tr>
<td>Ultrasonic sensor</td>
<td>Phase difference of emitted and detected waves</td>
<td>Piezoelectric effect</td>
<td>PZT, PbTiO3, PbZrO3</td>
</tr>
<tr>
<td>Sensors for measuring force, pressure, acceleration</td>
<td>Change in output voltage</td>
<td>Piezoelectric effect</td>
<td>PZT, PbTiO3, PbZrO3</td>
</tr>
</tbody>
</table>

*Table IV-1: Ceramic sensor materials [28,29].*

One of the most crucial issues towards the integration of ceramic materials into micro-scale devices, is the development of suitable forming methods. When features with dimensions below 100 μm are required, a simple downscaling of established ceramic processing techniques is not suitable. In the present thesis, principles of colloidal chemistry with ceramic powders were combined with new approaches for mold fabrication.
References


III  Aim of this Study

The goal of the present work was to find and apply new processing routes for the fabrication of well defined ceramic surface components in the micrometer range, one order of magnitude smaller than the structures feasible today.

This miniaturization of ceramic components may lead to advances in sensor technology, possibly being integrated on the same silicon chip used for data processing. This would allow the production of ceramic-containing devices of similar dimensions as polymeric and metallic structures which are already available today. However, it is not the goal of this work to fabricate a fully functional sensor, rather appropriate methods for the production of such sensors are evaluated.

In order to narrow the broad focus and also with regard to potential industrial applicability of these processes, additional boundary conditions for the new processing method had to be formulated:

- The processing method should be versatile and be able to use commercially available powders of various compositions as raw materials
- The process should enable the production of ceramic microcomponents on various substrate materials
- The molds should be reusable in order to be cost effective
- Expensive machinery should be avoided.
IV State of the Art in Ceramic Microfabrication

Processing techniques that are suitable for producing ceramic parts with a minimal feature size smaller than 500 μm are described and compared based on the specific requirements of this study. In conclusion of this overview, a strategy for the first approach of the present investigation is developed.

1 Introduction

The first efforts in ceramic microtechnology have been made by downscaling elaborated macroscale forming technologies. This was also the case for the most widely used ceramic microsystem, the piezoelectric ultrasonic transducer. These transducers are made of small piezoceramic rods embedded in a polymer matrix (Figure IV-1).

![Figure IV-1: Schematic of a composite ultrasonic transducer.](image)

This composite setup avoids losses of ultrasonic energy at the transducer–tissue interface in medical imaging [1]. The rods have to be long and slender in order to ensure a noise–free signal [2]. The first generation of such rods was made by cutting perpendicular grooves into a sintered PZT plate (Figure IV-2) [3] that leads to individual posts with small dimensions. The width of the grooves is determined by the width of the dice and the width of the rods is limited by the mechanical stability of the material. The high stresses involved in this technique lead to breaking of small rods during manufacturing. Both the width of the trenches and of the rods are in the range of 200 μm, the aspect ratio (Figure IV-3) is in the order of 1. The described limitations of the downscaled technique gave rise to the demand for other approaches for the production of such ceramic rod structures. Molds made with methods developed in semiconductor manufacturing were combined with traditional suspension–based ceramic forming techniques. Today, rods as narrow as 20 μm with an aspect ratio of 10 are produced [4,5].
In different fields, as for example in sensor technology [6] or rapid prototyping [7], special techniques of forming small-scale ceramic structures have been developed to date. An overview of processing techniques and some examples of their applications is given in Table IV-1. For each of these applications the ceramic parts have to fulfill certain requirements. Therefore, several processing methods have been developed, each one with its special focus on a certain application.
<table>
<thead>
<tr>
<th>Method</th>
<th>Examples</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rapid prototyping</td>
<td>Prototypes, casting molds for metals</td>
<td>[7–17]</td>
</tr>
<tr>
<td>Direct ceramic machining</td>
<td>Dental implants</td>
<td>[18]</td>
</tr>
<tr>
<td>Co-extrusion</td>
<td>Polycrystalline fiber composite material</td>
<td>[19–21]</td>
</tr>
<tr>
<td>Etching</td>
<td>Superconducting connectors</td>
<td>[22–27]</td>
</tr>
<tr>
<td>Screen printing</td>
<td>Electrolytes for solid oxide fuel cells</td>
<td>[28–31]</td>
</tr>
<tr>
<td>Stamping methods</td>
<td>Conductor lines</td>
<td>[32–35]</td>
</tr>
<tr>
<td>Slip casting</td>
<td>Piezoelectric array</td>
<td>[37–38]</td>
</tr>
<tr>
<td>Centrifugal casting</td>
<td>Piezoelectric array</td>
<td>[39]</td>
</tr>
<tr>
<td>Filterpressing</td>
<td>Piezoelectric array, nozzle</td>
<td>[39–40]</td>
</tr>
<tr>
<td>Injection molding</td>
<td>Piezoelectric array</td>
<td>[41]</td>
</tr>
<tr>
<td>Tape embossing</td>
<td>Piezoelectric array</td>
<td>[42–44]</td>
</tr>
</tbody>
</table>

*Table IV-1: Applications for microfabricated ceramic parts produced by the forming methods discussed in this chapter. For references see the respective sections.*

It would not be very informative to compare the different processing methods directly with each other. What is an advantage for one application might be a disadvantage for another. Therefore, the advantages and disadvantages listed in the following subsections are specified with regard to an ‘ideal processing method’, which was already described in the aim of this work. Such a method does not (yet) exist, it serves only as common reference to judge the single processes more objectively. The criteria for the comparison were chosen to allow a statement about the suitability of the processing method for the fabrication of the small features required in this study.

The ideal processing technique has the following characteristics:

- The smallest lateral dimension is below 10 micrometers
- An aspect ratio larger than 1 is possible
- Dense polycrystalline ceramic bodies can be produced.

The fulfillment of one or all of these requirements is listed as an advantage in the process characteristics table of each section. If the technique does not fulfill these requirements, it is listed as a disadvantage. The smallest lateral feature size and the largest achievable aspect ratio are listed and visualized for each of the processes in the characteristics table at the end of the respective sections. Their determination is based on the
processes, not on the properties of the materials that are used. With techniques that can
make structures with high aspect ratios, the strength of the ceramic material becomes the
limiting factor for the structure height, but this is of no concern here.

The smallest lateral feature size is the width of the smallest feature that has been
achieved using the respective process. The aspect ratio is a dimensionless number that is
calculated by dividing the maximal height of a structure by its width. Long, slender
structures have a high aspect ratio; broad, flat structures have a low one.

![High Aspect Ratio](image1.png) ![Low Aspect Ratio](image2.png)

*Figure IV-3: Structures with high and low aspect ratios.*

In the following section the discussed processes are grouped according to the kind
of molds that are employed. Some methods do not require a mold at all. In this case the
ceramic part is built in all three dimensions from a powder bed or a blank on a computer
controlled machine. Methods that use 2-dimensional molds are strongly related to meth¬
ods used on a larger length scale in the traditional printing industry. In these methods the
third dimension is generated directly during the process. When 3-dimensional molds are
used, the processes are related to traditional casting methods where ceramic materials are
usually processed as suspensions.

2 Methods without Mold

2.1 Rapid Prototyping Techniques

Rapid prototyping techniques, sometimes also referred to as solid freeform fabrication
techniques, were developed in order to generate parts directly from a computer
model to avoid the costs and time involved in mold fabrication for the production of sin¬
gle prototypes or of small series of a functional part [7].

The parts are built layer by layer in order to realize even complex geometries. The
2-dimensional geometrical information for each layer is generated by a slicing algorithm
applied to a CAD model of the part. Rapid prototyping systems therefore have two criti¬
cal dimensions: The smallest lateral feature size and the thickness of a solidified layer. A
smaller feature size and a thinner layer thickness lead to a better resolution, but also to
significantly longer process times for the produced parts. A compromise has to be made
between resolution and processing time. In general, a minimal cure depth and minimal
cure width of 200 μm are desired. The aspect ratios of the produced parts are only limited by the geometry of the machine. Theoretically an infinite number of layers could be stacked.

![Diagram](image)

**Figure IV-4:** Principle of layered object fabrication.

Because of the wish to generate exact 1:1 prototypes, the ceramic powders used in Rapid Prototyping are usually tailored to avoid shrinkage during sintering. This leads to porous ceramic microstructures of low strength and modulus. Most of the ceramic parts made by rapid prototyping are made of refractory grade powders and are used as molds for metal casting of prototypes or small scale serial production.

Different methods for rapid prototyping of ceramics have been developed, but they can all be grouped into three fields:

1. Selective addition of material to an existing surface.
2. Chemical alteration of a liquid or solid using directed light energy.
3. Sintering of a powder using directed light energy.

In the following subchapters techniques for each of these field are described. *Three Dimensional Printing* and *Suspension Printing* representing the first group, *Stereolithography* the second and *Selective Laser Sintering* the third.

The suitability of all the described rapid prototyping techniques for ceramic microfabrication is summarized at the end of this section.

*Three Dimensional Printing*

In Three Dimensional Printing (3DP) the single layers of the ceramic part are solidified by spraying a binder suspension with an inkjet printer head into a ceramic powder bed [8]. Structures with a minimal feature size of 430 μm are reported. The parts are made using an alumina powder with an average grain size of 40 μm. The powder is solidified via a glass phase during heat treatment at 800 °C, practically no shrinkage occurs. The parts can be used as casting molds for small series in metal production where 3DP is cheaper than creating molds for lost wax models [9]. Investigations to use the produced parts as drug delivery devices have also been reported [10].

3DP is performed using both available systems of ink jet printers: drop-on-demand and continuous–jet technology. The latter is favored because of the higher printing speed.
Applying a layer of loose powder on top of solidified part

Printing step. Binder is selectively printed into the powder bed.

Printing step is terminated, next layer of powder can be applied

**Figure IV-5:** Process of 3DP.

<table>
<thead>
<tr>
<th>Three Dimensional Printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
</tr>
<tr>
<td>430 μm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>only limited by machine geometry</td>
<td>- low resolution</td>
</tr>
<tr>
<td></td>
<td>- no dense microstructure</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Remarks:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic parts are solidified with a glass phase in liquid phase sintering</td>
</tr>
</tbody>
</table>

**Table IV-2:** Process characteristics of 3DP.

**Suspension Printing**

This technique is related to 3DP, but instead of printing a binder into a powder bed, a ceramic suspension is printed onto a substrate. The suspension is deposited with either a continuous [11,12] or a drop-on-demand ink jet printer [13]. As the viscosity of the printing suspensions is limited to about 10 mPa-s, the reported solids loadings of the suspensions are only 5–10 vol %. The vast amount of solvent that has to be evaporated limits the printing speed. Therefore, only porous substrates, that support drying, are used. Due to the low solids loading the layer thickness for each printing cycle is about 1 μm; much thinner than with the other layered fabrication techniques. This technique is still in the experimental stage, no applications have been reported so far.
Stereolithography

In ceramic stereolithography a suspension of ceramic particles in a photopolymerizable monomer is solidified by crosslinking the molecules with an ultraviolet laser directed by a mirror system. In the following heat treatment the polymer matrix is pyrolyzed and the ceramic part is sintered. Parts made of silica, alumina and silicon nitride have been reported [14].

Compared to stereolithography with pure monomer solutions, as used in rapid prototyping of polymeric parts, the dispersed ceramic particles lower the cure depth and increase the cure width of the laser beam, even if the ceramic material is transparent to UV. For example a laser beam with a diameter of 210 µm is widened in the suspension and cures an area of 300 µm in diameter [15].
Stereolithography

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 µm</td>
<td>- high aspect ratio</td>
</tr>
<tr>
<td></td>
<td>Disadvantages:</td>
</tr>
<tr>
<td></td>
<td>- low resolution</td>
</tr>
<tr>
<td></td>
<td>- no dense microstructure</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>Remarks:</td>
</tr>
<tr>
<td>only limited by machine geometry</td>
<td>Scattering effects lower lateral resolution</td>
</tr>
</tbody>
</table>

Table IV-4: Process characteristics of stereolithography.

Selective Laser Sintering (SLS)

A laser beam melts the low melting component of a two component inorganic powder system. The liquid phase wets the solid ceramic powder and joins it during the solidification. After shaping, the low melting phase is no longer beneficial, it limits the thermal stability of the part. Therefore, a following heat treatment step is used to increase the thermal stability of the microstructure. Examples of SLS powder systems are alumina with a low melting phosphate binder forming a glass phase during heat treatment [16] or alumina with metallic aluminum as melting phase which is subsequently oxidized [17]. After sintering, the microstructure reaches about 50% of the theoretical density [17]. The speed of the laser beam relative to the powder surface is determined by the thermal conductivity of the powder material to be compacted. A high thermal conductivity leads to dissipation of large amounts of energy into the powder bed, requiring longer irradiation.

Figure IV-8: Ceramic parts produced via SLS [16].
times to melt the binder phase. On the other hand, a low thermal conductivity can lead to thermal shock failures in the produced part.

<table>
<thead>
<tr>
<th>Selective Laser Sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
</tr>
</tbody>
</table>

| Advantages: |
| - high aspect ratio |
| Disadvantages: |
| - low resolution |
| - no dense microstructure |
| Remarks: |
| Limited speed due to heat transfer limitations, needs liquid phase sintering |

Table IV-5: Process characteristics of Selective Laser Sintering.

The described rapid prototyping techniques have two major advantages. First, parts can be generated in very short time without the need for a mold, second, structures with high aspect ratios can be made. However, the lateral resolution of the techniques is quite low. This also leads to a rather rough surface. The effects responsible for this low resolution are the physical limitations of these techniques. It is not likely that with these techniques feature sizes much smaller than 150–200 μm can be realized in the future.

The main limitations are
- size of the generated droplets and spread of liquid droplets in a porous substrate for the ink-jet related techniques,
- scattering effects in stereolithography,
- heat conduction in Selective Laser Sintering.

In addition, some of the processes need powder systems with liquid phase sintering. This limits the high temperature stability of the produced parts.

2.2 Direct Ceramic Machining (DCM)

An isostatically pressed and presintered ceramic blank is shaped on a computer controlled milling machine. After the shaping process, the ceramic bodies are sintered to full density and exhibit excellent mechanical behavior [18]. As this is not a layered fabrication technique, even round shapes can be made with good accuracy. The resolution is determined by the positioning accuracy of the milling machine and the diameter of the milling cutter. The aspect ratio is also limited by the available milling cutters. Rounded structures inside the part are not feasible because of the ‘one dimensional’ geometry of the milling cutter. By compensating the sintering shrinkage of the ceramic material, net-
shaped sintered parts can be made. An image of the milling process is shown later in Figure V.A-33.

DCM is a very powerful technique for the fabrication of parts in the size range of 400 μm. The ceramic structures can be shaped fast and sintered to full density. One application of this technique is the fabrication of ceramic tooth bridges which exhibit very high mechanical strength.

<table>
<thead>
<tr>
<th>Direct Ceramic Machining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
</tr>
<tr>
<td>Aspect Ratio</td>
</tr>
</tbody>
</table>

Advantages:  
- high aspect ratio  
- dense microstructure

Disadvantages:  
- low resolution  
- geometrical limitations

Remarks:  
Net-shape method

Table IV-6:  Process characteristics of direct ceramic machining.

2.3 Extrusion

Elongated fine-scaled ceramic parts are fabricated by extruding a thermoplastic polymer filled with ceramic particles through a size-reducing die. The feedrod used for extrusion consists of several powder-filled polymer compounds. During extrusion, the shape in which the different compounds are assembled is maintained. The feedstock is only reduced in its dimensions perpendicular to the extrusion direction. After each extrusion step the extrudates are reassembled and extruded again until the desired size reduction is achieved. Objects with complex shapes can be fabricated by assembling an extrusion feedrod from several shaped ceramic compounds. With a space-filling carbon black compound that can be pyrolyzed, even free-standing or hollow structures are possible. Objects in the size range of 10 μm were produced [19,20]. Polycrystalline fiber composites with defined fiber geometries and orientations can be made also [21].

With this method, no micromachined parts are necessary to generate microscopic features, they are generated by the uniform size reduction of macroscopic assemblies. Although very small structures with high aspect ratios can be made, this method suffers from important restrictions. The shape of the structures is limited to quasi-3D shapes due to the one dimensional extrusion process. In addition, the generated patterns get slightly distorted during the extrusion.
21 State of the Art

Extrusion

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 μm</td>
<td>- very high aspect ratio</td>
</tr>
<tr>
<td>100</td>
<td>- good resolution</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>almost infinite</td>
<td>- only quasi-3D structures</td>
</tr>
<tr>
<td>100</td>
<td>Remarks:</td>
</tr>
<tr>
<td>0.1</td>
<td>Objects get slightly distorted with increasing number of extrusion steps</td>
</tr>
</tbody>
</table>

Table IV-7: Process characteristics of extrusion.

Figure IV-9: Process schematic and micrograph of an extruded part. The initial size of the feedrod was in the range of 4 mm [20].

3 Methods with 2-Dimensional Molds

In the processes described in this section the mold has to be defined in two dimensions, the third dimension is directly generated in the process.

3.1 Etching

Etching processes are not very widespread in ceramics manufacturing because ceramics are among the hardest and most inert materials known. Especially wet etching processes are generally not suitable for patterning ceramics which are usually very inert to aggressive liquid media. However, this method is used for niche applications with a well matched pair of etchant and material to be etched. In dry etching processes the material is removed either by sputtering or in a highly reactive plasma. This process has less problems with the chemical inertness of ceramics. As the standard polymeric resist
materials are often removed faster than the ceramic material, mechanical aperture masks are needed to direct the etching plasma.

**Wet Etching**

Patterning by wet etching is carried out similar to silicon–based techniques in microelectronic manufacturing [22]. A ceramic surface is coated with a photoresist film. This resist film is exposed through a photomask and developed, the irradiated area of the resist is dissolved. Through the blank spaces in the resist the ceramic material can be etched with an appropriate liquid etchant. Most of the research in wet etching of ceramics is done in the field of ceramic high-Tc superconductors. For the fabrication of small-scale coils or other superconducting circuits epitaxially deposited cuprate films have been etched with a variety of chemicals, such as hydrofluoric acid, EDTA, nitric acid or phosphoric acid [23]. The application of wet etching is limited to some special ceramics and is often isotropic. Underetching of the template structures may occur, thus limiting the achievable feature size and aspect ratio.

*Figure IV-10: Wet etched superconducting YBa$_2$Cu$_3$O$_7$ coil on a SrTiO$_3$ substrate [23].*

<table>
<thead>
<tr>
<th>Wet Etching</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
<td><img src="image" alt="Graph" /></td>
<td>2 (\mu)m</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td><img src="image" alt="Graph" /></td>
<td>0.3</td>
</tr>
<tr>
<td>Advantages:</td>
<td></td>
<td>- good resolution</td>
</tr>
<tr>
<td>Disadvantages:</td>
<td></td>
<td>- low aspect ratio</td>
</tr>
<tr>
<td>Remarks:</td>
<td></td>
<td>Only isotropic etching possible</td>
</tr>
</tbody>
</table>

*Table IV-8: Process characteristics of wet etching of ceramics.*
Dry Etching

In dry etching processes the material is patterned either by exposing it to a reactive plasma which forms volatile compounds with the material to be removed or by removing the undesired part mechanically with an ion beam [22]. The main parameter of a dry etching process is the energy of the incorporated plasma. At low ion energies the process is chemically controlled, not all components in a multi material mixture form volatile components with a certain plasma. Therefore, these processes exhibit a high selectivity. For example, if layers of different materials are stacked, the etching reaction stops at the interface between two materials, because only one material is removed by the plasma. The etching process is more or less isotropic in all directions, no structures with high aspect ratios can be made. In physical plasma processes the material is removed by sputtering. These processes allow a stronger anisotropy; structures with a higher aspect ratio can be produced. However, the larger anisotropy results in a smaller selectivity of the etching process, as illustrated in Figure IV-11.

Several binary metal oxides such as CuO, ZnO and PbO have been plasma etched with hexafluoroacetylacetone at temperatures above 200 °C [24], also binary nitrides can be etched [25]. Etching of PZT has been done with excimer laser radiation in a reducing atmosphere [26] and also with SF6 [27].

Like in wet etching, also dry etching of ceramics can only be applied to materials that form volatile components with the etchant. This greatly limits the applicability of this technique.
Dry Etching

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 μm</td>
<td>- high aspect ratio</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>- low resolution</td>
</tr>
<tr>
<td></td>
<td>- not generally applicable</td>
</tr>
</tbody>
</table>

Remarks:
Volatile components have to be formed

Table IV-9: Process characteristics of dry etching.

3.2 Screen Printing

A paste of ceramic powder, plasticizer and binder is placed on a patterned screen of metal wires. The pattern is generated by sealing some of the meshes of the screen with a polymer. The paste is then forced through the remaining openings in the screen by using a rubber squeegee which depresses the screen to contact the substrate as it traverses the pattern. The thickness of the deposited layer is determined by the thickness of a polymer spacer film attached to the lower side of the mesh. Patterning of the screen is done by coating it with a photoreactive polymer and dissolving the latter selectively after exposure [28].

To overcome the limitation that only flat substrates can be patterned by screen printing, transfer printing has been developed [29]. The ceramic layer is printed onto a sheet of coated paper and can later be transferred onto tubular or corrugated surfaces.

Screen printing is a simple process, but only low aspect ratios with low resolutions can be made. The resolution is limited by the viscosity of the ceramic paste that is used. The crosswise arranged metal wires form isolated openings, separated by the width of the wires. In order to form a continuous pattern, the paste has to flow laterally to connect the isolated portions of the paste that are pressed through the mesh. This causes blurring of the structure.

Screen printing is mostly used for unpatterned layers, for example for electrodes or electrolytes in solid oxide fuel cells [30], but also the formation of an array of more than one hundred single sensor dots (1.5 x 1.5 mm²) has been reported [31].
3.3 Stamping Methods

*Gravure Offset Printing*

This procedure is similar to the offset printing process in the printing industry and is described in [32] for the fabrication of conductive line patterns. The desired pattern, which is etched into a metallic gravure plate, is first covered with a screen printing paste and then scraped clean so that the paste remains only in the engraved pattern. Subsequently the paste in the pattern is picked up and transferred from the plate to the desired substrate by a flexible silicon rubber pad which is pressed onto the substrate. Structures made by Gravure Offset Printing have smoother surfaces than those made by screen printing because the screen printing mesh leads to a superstructure grid on the surface of the deposited layer when high viscosity pastes are used. Screen printing on the other hand allows a better control of the layer thickness.

In literature only pattern transfer with metal–filled screen printing pastes has been reported. However, this method is listed here, because enough recipes for ceramic–filled
pastes are also available. As in screen printing only low aspect ratio structures can be achieved.

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 µm</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**Table IV-11: Process characteristics of Gravure Offset Printing.**

**Figure IV-13:** Schematic of Gravure Offset Printing. By means of a rubber pad ink is transferred from a printing plate to a substrate [32].

**Microcontact Printing (µCP)**

This technique uses well defined patterns of self assembling monolayers for pattern formation. They are transferred to a substrate by means of a soft polymer stamp made of poly(dimethylsiloxane) (PDMS). The process has proven to be very versatile in generating micron- and nanoscale monolayer patterns [33]. By using the stamped monolayer as resist material for an etching process, defined gold features as narrow as 30 nm can be obtained [34].

Patterning a substrate with ceramics uses selective wetting of an aqueous suspension on the hydrophilic part of a partially hydrophilic and hydrophobic surface [35]. When the substrate is dipped for example into an aqueous suspension of a colloidal iron oxide, small suspension droplets are formed on the hydrophilic parts of the substrate. Then, the solvent is evaporated and the solid particles remain on the substrate as a thin coating. Feature sizes of 1 µm have been made with this process.

The self assembling monolayer that determines the pattern can be made with an excellent lateral resolution. But, due to the low solids loading of the colloidal suspension,
only thin layers in the range of 100 nm can be achieved. In addition, appropriate colloidal particles are required in a homogeneous dispersion. A diagram of the process is depicted in the experimental section in Figure V.B-16.

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- excellent resolution</td>
</tr>
<tr>
<td></td>
<td>- generally applicable</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>Disadvantages:</td>
</tr>
<tr>
<td></td>
<td>- small aspect ratio</td>
</tr>
<tr>
<td></td>
<td>Remarks:</td>
</tr>
<tr>
<td></td>
<td>Deposition is controlled by the wetting behavior of the ceramic suspension.</td>
</tr>
</tbody>
</table>

Table IV-12: Process characteristics of microcontact printing.

4 Methods with 3-Dimensional Molds

Many of these methods require a separate mold for every part produced. After shaping, the molds are destroyed during the process, in most cases by pyrolysis. The feature size of the parts can become as small as 10 µm. However, the techniques involved in fabricating such molds from scratch are quite costly, because microfabrication techniques have to be used for their production. Therefore, it is desirable to make a positive master mold of durable material and high accuracy. The single lost molds are replicated from this master with macro-scale technology, for example by injection molding [36]. In the case where each mold has to be microfabricated separately, the fabrication process becomes more costly, as a cleanroom environment with very expensive machinery is generally needed. Ideally, reusable molds are employed. But demolding becomes increasingly difficult with higher aspect ratios and smaller feature sizes because of the increasing contact areas parallel to the demolding direction and the incorporated surface friction during demolding.

Figure IV-14: Two fabrication strategies with lost molds. Creating a master structure with microtechnology and replicating it with macro-technology is preferred.
4.1 Slip Casting

In the traditional slip casting process the suspension agent of a slip is dragged into the porous mold by capillary flow which leads to the formation of a ceramic green body at the surface of the mold. Either plaster or porous polymers are used as mold materials. These mold materials are not suited for the generation of miniaturized parts, as the required surface quality cannot be achieved due to their porosity. Hence, nonporous mold materials have to be used and the solidification of the suspensions is achieved by evaporating the solvent through the sample surface and not through the mold.

Molds made by X-ray lithography have been filled with a 23 vol % slurry of lead zirconate titanate (PZT) for the formation of an array of piezoelectric rods [37]. A honeycomb structure with a wall thickness of 10 µm and an aspect ratio of 20 was also produced. As the solids loading is relatively low, drying cracks occurred. Defect-free structures have been made by a combination of cold isostatic pressing after drying of slip cast green bodies and subsequent hot isostatic pressing [38].

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 µm</td>
<td>- high aspect ratio</td>
</tr>
<tr>
<td></td>
<td>- good resolution</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>- drying cracks possible</td>
</tr>
</tbody>
</table>

Remarks: Defects can be removed by isostatic pressing

Table IV-13: Process characteristics of slip casting.

4.2 Centrifugal Casting

The damage during drying of the green body can be reduced by increasing the wet green density of the ceramic bodies mechanically. One method to achieve this is by sedimentation of the ceramic particles in a centrifuge. The centrifugal forces are relatively low compared to pressing techniques, therefore wax molds can be used [39]. A PZT array with an aspect ratio of 10 has been produced this way. Because the centrifugal force acts uniformly on every particle, the produced green bodies have a better homogeneity than those produced by filter pressing (see below).
Microfabrication of Ceramics

A dissertation submitted to the
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Prof. Dr. N. D. Spencer, co-examiner

Zürich, 2000
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I  Microfabrication of Ceramics

Summary ............................................................................................................. 1
Zusammenfassung ............................................................................................... 2

II  General Introduction ..................................................................................... 5

III  Aim of this Study .......................................................................................... 9

IV  State of the Art in Ceramic Microfabrication

1  Introduction ................................................................................................... 11

2  Methods without Mold .................................................................................. 14
   2.1  Rapid Prototyping Techniques ................................................................. 14
   2.2  Direct Ceramic Machining ....................................................................... 19
   2.3  Extrusion .................................................................................................. 20

3  Methods with 2-Dimensional Molds ............................................................. 21
   3.1  Etching ................................................................................................... 21
   3.2  Screen Printing ....................................................................................... 24
   3.3  Stamping Methods .................................................................................. 25

4  Methods with 3-Dimensional Molds ............................................................. 27
   4.1  Slip Casting ............................................................................................. 28
   4.2  Centrifugal Casting ................................................................................ 28
   4.3  Filter Pressing ......................................................................................... 29
   4.4  Injection Molding ................................................................................... 30
   4.5  Tape Embossing ....................................................................................... 31

5  Summary ....................................................................................................... 32

6  References .................................................................................................... 34

V  Process Development ..................................................................................... 37

A: Generation of Patterned Ceramic Surfaces

1  Introduction ................................................................................................... 38

2  General Experimental Procedure ................................................................. 38
   2.1  Mold Fabrication ..................................................................................... 39
   2.2  Suspension Preparation ......................................................................... 42
   2.3  Casting .................................................................................................... 42
   2.4  Demolding and Sintering ...................................................................... 42
   2.5  Characterization ..................................................................................... 43

3  Investigated Issues ......................................................................................... 43
   3.1  Influence of Powder Particle Size ......................................................... 43
   3.2  Increase of Suspension Solids Loading ................................................. 48
   3.3  Surface Chemistry of PDMS .................................................................. 59
   3.4  Conclusions ............................................................................................ 61
I Microfabrication of Ceramics

Summary

To date, ceramic materials have almost been excluded from the general trend of miniaturization of functional devices, which goes on in other fields of materials science. Especially in the semiconductor industry the feature sizes of the generated structures decreased constantly in the last years. Today, submicron structures with a feature size of 0.2 μm are already produced in semiconductor pilot plants. On the other hand, the smallest ceramic features produced in industry so far are almost three orders of magnitude larger. Piezoceramic rods for the fabrication of ultrasonic transducers have diameters in the range of 100 μm. Other techniques which allow the production of features with a size of 50 μm and slightly below, are in a research state but not applied on a large scale. Smaller surface structures on ceramics have not been generated up to now. In the present work we therefore attempted to develop powder-based ceramic forming techniques which allow the generation of ceramic features with dimensions of a few micrometers.

In the first part of the study, bulk samples with a patterned surface are generated by slip casting of water-based suspensions into nonporous elastomeric molds made of poly(dimethyl siloxane) (PDMS). Surface structures of excellent quality with dimensions as small as 1 μm are feasible. It was found that a suspension with a high solids loading has to be used in order to reduce drying shrinkage and a hydrophobic surface of the mold material is essential for defect-free demolding. The slip casting process is applicable to various ceramic materials. Also polymers other than PDMS can be used as molds, however, PDMS offers the simplest mold generation process.

In the second part of the work, three fabrication methods for the generation of ceramic surface patterns on arbitrary substrates are investigated. In the first method, micromolding in capillaries, a PDMS structure forms three walls of a capillary, the surface of the substrate acts as the fourth wall. A liquid is then dragged into these capillaries and solidified, leaving a three dimensional structure after removing the PDMS. The process was developed for solutions and could not be successfully adapted to dense ceramic suspensions, as the ceramic structures could not be obtained in a reproducible manner. The second technique uses selective wetting of an aqueous suspension on gold surfaces functionalized with hydrophilic and hydrophobic self-assembled monolayers. It produced promising results, but sintering of the ceramic features on the gold surface as well as the transfer of the process to other than gold substrates could not be achieved. Finally, filling of surface molds made of patterned photoresist yielded the most reproducible structures with a feature size of 5 μm. Matching coefficients of thermal expansion is crucial in order to get a crack-free structure after sintering. The process can be applied to various substrates and ceramic suspensions.
Zusammenfassung


flächen war nicht möglich. Die dritte und vielversprechendste Methode benutzt dreidimensionale Strukturen aus Photolack auf der Substratoberfläche als verlorene Form für Schlickerguss. Mit dieser Technik konnten keramische Muster mit einer Auflösung von bis zu 5 μm reproduzierbar hergestellt werden.
II General Introduction

Microfabrication is becoming more and more important in modern science and technology. The ability to fabricate new types of microstructures or to produce existing structures in down-sized versions offer a large potential in cost reduction. The most obvious examples are sensors, actuators and microelectronic devices. Miniaturization of electronic elements has made terrific progress in the last decades and is still going on. Components with micrometer or even nanometer dimensions can also open up the opportunity to study basic scientific phenomena that occur at small dimensions. One example is quantum confinement observed in nanostructures [1]. Although most research on microfabrication is silicon-based and has been focused on microelectronic devices [2], applications in other areas are rapidly emerging. These include sensor systems for microanalysis [3–6], micro-volume reactors [7–9] combinatorial synthesis [10], microelectromechanical systems (MEMS) [11,12], optical components (for example photonic band gap materials) [13–15] and systems for non-magnetic data storage [16].

One promising use for microanalytical devices is in the separation and analysis of chemical and biological substances [3–6]. These devices require only small quantities of reagents, have relatively short analysis times and can show efficiencies in separation and detection that are better than those of larger analysis systems. In the last years, several miniaturized total chemical analysis systems [17,18], sometimes also referred to as ‘labs on a chip’, have been developed that perform all sample-handling steps on their own. An array of chemical tools on a chip makes it possible to analyze extremely small amounts of a product. These systems will be useful for the parallel screening of a large number of compounds. For example an artificial nose can be realized with a large number of single sensors of which each one is tuned to detect a different ‘flavor’ [19]. Structures in the micrometer range allow the integration of a large number of single elements on a small area. Even though the selectivity of a single element might be mediocre, their large number compensates this disadvantage by far.

Miniaturization of sensor elements has not only the advantage that more data can be collected in the same amount of space, but also that the sensing devices may be integrated directly on the electronic chip along with monitoring, actuating and controlling devices. With such an integration, a sensor element can directly generate a digital output signal. In the past years, the scope of fabrication techniques has widened and the number of devices has increased [11,12,20]. Most are fabricated from silicon using standard microlithographic techniques [21,22]. With these methods, thousands of mechanical elements, for example cantilevered beams, springs, linkages, mass elements and joints, can be batch-fabricated on a single silicon substrate [10,12]. Microactuators, micromotors and microengines [22] have been fabricated for optical switches, fluid pumps [23], sys-
tems for drug delivery and microchemical analysis [24–27]. More recently, surface micromachining techniques have been used to fabricate miniaturized optical components which are attractive for applications in spectrometers, display devices, sensors, optoelectronic packages and data storage systems [13–15].

Most of the devices mentioned above are made using silicon based microfabrication techniques. Up to now, not much has been done to fabricate miniaturized parts of ceramic materials. Sensors with ceramic detection materials are still built in the classical manner. A macroscopic ceramic part detects the signal which is fed to the evaluating electronics by electric connectors. For a possible integration of ceramic materials into the length scale of microelectronic components no suitable fabrication techniques have been developed yet, although ceramic materials are operating in numerous types of sensors, as summarized in Table IV-1.

<table>
<thead>
<tr>
<th>Type of Sensor</th>
<th>Output Signal</th>
<th>Effect</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature sensor</td>
<td>Change in the resistance</td>
<td>Thermistor effect (PTC or NTC)</td>
<td>NiMn$_2$O$_4$, CoFe$_2$O$_4$, BaTiO$_3$</td>
</tr>
<tr>
<td>Oxygen sensor</td>
<td>Electromotive force</td>
<td>Conductivity of oxygen ions</td>
<td>ZrO$_2$</td>
</tr>
<tr>
<td>Gas Sensor</td>
<td>Change in the resistance</td>
<td>Semiconducting behavior</td>
<td>SnO$_2$</td>
</tr>
<tr>
<td>Optical sensor</td>
<td>Electromotive force</td>
<td>Pyroelectric effect</td>
<td>SrTiO$_3$, PZT, PbTiO$_3$, PbZrO$_3$</td>
</tr>
<tr>
<td>Ultrasonic sensor</td>
<td>Phase difference of emitted and detected waves</td>
<td>Piezoelectric effect</td>
<td>PZT, PbTiO$_3$, PbZrO$_3$</td>
</tr>
<tr>
<td>Sensors for measuring force, pressure, acceleration</td>
<td>Change in output voltage</td>
<td>Piezoelectric effect</td>
<td>PZT, PbTiO$_3$, PbZrO$_3$</td>
</tr>
</tbody>
</table>

*Table IV-1: Ceramic sensor materials [28,29].*

One of the most crucial issues towards the integration of ceramic materials into micro-scale devices, is the development of suitable forming methods. When features with dimensions below 100 μm are required, a simple downscaling of established ceramic processing techniques is not suitable. In the present thesis, principles of colloidal chemistry with ceramic powders were combined with new approaches for mold fabrication.
References


III  Aim of this Study

The goal of the present work was to find and apply new processing routes for the fabrication of well defined ceramic surface components in the micrometer range, one order of magnitude smaller than the structures feasible today.

This miniaturization of ceramic components may lead to advances in sensor technology, possibly being integrated on the same silicon chip used for data processing. This would allow the production of ceramic-containing devices of similar dimensions as polymeric and metallic structures which are already available today. However, it is not the goal of this work to fabricate a fully functional sensor, rather appropriate methods for the production of such sensors are evaluated.

In order to narrow the broad focus and also with regard to potential industrial applicability of these processes, additional boundary conditions for the new processing method had to be formulated:

- The processing method should be versatile and be able to use commercially available powders of various compositions as raw materials
- The process should enable the production of ceramic microcomponents on various substrate materials
- The molds should be reusable in order to be cost effective
- Expensive machinery should be avoided.
IV State of the Art in Ceramic Microfabrication

Processing techniques that are suitable for producing ceramic parts with a minimal feature size smaller than 500 μm are described and compared based on the specific requirements of this study. In conclusion of this overview, a strategy for the first approach of the present investigation is developed.

1 Introduction

The first efforts in ceramic microtechnology have been made by downscaling elaborated macroscale forming technologies. This was also the case for the most widely used ceramic microsystem, the piezoelectric ultrasonic transducer. These transducers are made of small piezoceramic rods embedded in a polymer matrix (Figure IV-1).

![Figure IV-1: Schematic of a composite ultrasonic transducer.](image)

This composite setup avoids losses of ultrasonic energy at the transducer–tissue interface in medical imaging [1]. The rods have to be long and slender in order to ensure a noise-free signal [2]. The first generation of such rods was made by cutting perpendicular grooves into a sintered PZT plate (Figure IV-2) [3] that leads to individual posts with small dimensions. The width of the grooves is determined by the width of the dice and the width of the rods is limited by the mechanical stability of the material. The high stresses involved in this technique lead to breaking of small rods during manufacturing. Both the width of the trenches and of the rods are in the range of 200 μm, the aspect ratio (Figure IV-3) is in the order of 1. The described limitations of the downscaled technique gave rise to the demand for other approaches for the production of such ceramic rod structures. Molds made with methods developed in semiconductor manufacturing were combined with traditional suspension-based ceramic forming techniques. Today, rods as narrow as 20 μm with an aspect ratio of 10 are produced [4,5].
In different fields, as for example in sensor technology [6] or rapid prototyping [7], special techniques of forming small-scale ceramic structures have been developed to date. An overview of processing techniques and some examples of their applications is given in Table IV-1. For each of these applications the ceramic parts have to fulfill certain requirements. Therefore, several processing methods have been developed, each one with its special focus on a certain application.
Table IV-1: Applications for microfabricated ceramic parts produced by the forming methods discussed in this chapter. For references see the respective sections.

It would not be very informative to compare the different processing methods directly with each other. What is an advantage for one application might be a disadvantage for another. Therefore, the advantages and disadvantages listed in the following subsections are specified with regard to an ‘ideal processing method’, which was already described in the aim of this work. Such a method does not (yet) exist, it serves only as common reference to judge the single processes more objectively. The criteria for the comparison were chosen to allow a statement about the suitability of the processing method for the fabrication of the small features required in this study.

The ideal processing technique has the following characteristics:

- The smallest lateral dimension is below 10 micrometers
- An aspect ratio larger than 1 is possible
- Dense polycrystalline ceramic bodies can be produced.

The fulfillment of one or all of these requirements is listed as an advantage in the process characteristics table of each section. If the technique does not fulfill these requirements, it is listed as a disadvantage. The smallest lateral feature size and the largest achievable aspect ratio are listed and visualized for each of the processes in the characteristics table at the end of the respective sections. Their determination is based on the
processes, not on the properties of the materials that are used. With techniques that can make structures with high aspect ratios, the strength of the ceramic material becomes the limiting factor for the structure height, but this is of no concern here.

The smallest lateral feature size is the width of the smallest feature that has been achieved using the respective process. The aspect ratio is a dimensionless number that is calculated by dividing the maximal height of a structure by its width. Long, slender structures have a high aspect ratio; broad, flat structures have a low one.

![Figure IV-3: Structures with high and low aspect ratios.](image)

In the following section the discussed processes are grouped according to the kind of molds that are employed. Some methods do not require a mold at all. In this case the ceramic part is built in all three dimensions from a powder bed or a blank on a computer controlled machine. Methods that use 2-dimensional molds are strongly related to methods used on a larger length scale in the traditional printing industry. In these methods the third dimension is generated directly during the process. When 3-dimensional molds are used, the processes are related to traditional casting methods where ceramic materials are usually processed as suspensions.

2 Methods without Mold

2.1 Rapid Prototyping Techniques

Rapid prototyping techniques, sometimes also referred to as solid freeform fabrication techniques, were developed in order to generate parts directly from a computer model to avoid the costs and time involved in mold fabrication for the production of single prototypes or of small series of a functional part [7].

The parts are built layer by layer in order to realize even complex geometries. The 2-dimensional geometrical information for each layer is generated by a slicing algorithm applied to a CAD model of the part. Rapid prototyping systems therefore have two critical dimensions: The smallest lateral feature size and the thickness of a solidified layer. A smaller feature size and a thinner layer thickness lead to a better resolution, but also to significantly longer process times for the produced parts. A compromise has to be made between resolution and processing time. In general, a minimal cure depth and minimal
cure width of 200 \textmu m are desired. The aspect ratios of the produced parts are only limited by the geometry of the machine. Theoretically an infinite number of layers could be stacked.


curvature width of 200 \textmu m are desired. The aspect ratios of the produced parts are only limited by the geometry of the machine. Theoretically an infinite number of layers could be stacked.

![Desired Structure Layered Object](image)

*Figure IV-4: Principle of layered object fabrication.*

Because of the wish to generate exact 1:1 prototypes, the ceramic powders used in Rapid Prototyping are usually tailored to avoid shrinkage during sintering. This leads to porous ceramic microstructures of low strength and modulus. Most of the ceramic parts made by rapid prototyping are made of refractory grade powders and are used as molds for metal casting of prototypes or small scale serial production.

Different methods for rapid prototyping of ceramics have been developed, but they can all be grouped into three fields:
1. Selective addition of material to an existing surface.
2. Chemical alteration of a liquid or solid using directed light energy.
3. Sintering of a powder using directed light energy.

In the following subchapters techniques for each of these field are described. *Three Dimensional Printing* and *Suspension Printing* representing the first group, *Stereolithography* the second and *Selective Laser Sintering* the third.

The suitability of all the described rapid prototyping techniques for ceramic microfabrication is summarized at the end of this section.

*Three Dimensional Printing*

In Three Dimensional Printing (3DP) the single layers of the ceramic part are solidified by spraying a binder suspension with an inkjet printer head into a ceramic powder bed [8]. Structures with a minimal feature size of 430 \textmu m are reported. The parts are made using an alumina powder with an average grain size of 40 \textmu m. The powder is solidified via a glass phase during heat treatment at 800 °C, practically no shrinkage occurs. The parts can be used as casting molds for small series in metal production where 3DP is cheaper than creating molds for lost wax models [9]. Investigations to use the produced parts as drug delivery devices have also been reported [10].

3DP is performed using both available systems of inkjet printers: drop-on-demand and continuous-jet technology. The latter is favored because of the higher printing speed.
Applying a layer of loose powder on top of solidified part

Printing step. Binder is selectively printed into the powder bed.

Printing step is terminated, next layer of powder can be applied

Figure IV-5: Process of 3DP.

Table IV-2: Process characteristics of 3DP.

<table>
<thead>
<tr>
<th>Three Dimensional Printing</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
<td>- high aspect ratio</td>
</tr>
<tr>
<td>430 µm</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>only limited by machine geometry</td>
<td>- low resolution</td>
</tr>
<tr>
<td></td>
<td>- no dense microstructure</td>
</tr>
</tbody>
</table>

| Remarks: Ceramic parts are solidified with a glass phase in liquid phase sintering |

Suspension Printing

This technique is related to 3DP, but instead of printing a binder into a powder bed, a ceramic suspension is printed onto a substrate. The suspension is deposited with either a continuous [11,12] or a drop-on-demand inkjet printer [13]. As the viscosity of the printing suspensions is limited to about 10 mPa·s, the reported solids loadings of the suspensions are only 5–10 vol %. The vast amount of solvent that has to be evaporated limits the printing speed. Therefore, only porous substrates, that support drying, are used. Due to the low solids loading the layer thickness for each printing cycle is about 1 µm; much thinner than with the other layered fabrication techniques. This technique is still in the experimental stage, no applications have been reported so far.
Figure IV-6: Pattern created by suspension printing [12].

<table>
<thead>
<tr>
<th>Suspension Printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
</tr>
<tr>
<td>Aspect Ratio</td>
</tr>
</tbody>
</table>

Advantages:
- dense structures

Disadvantages:
- low resolution
- low aspect ratio
- very slow speed

Remarks:
Only porous substrates can be coated

Table IV-3: Process characteristics of Suspension Printing.

Stereolithography

In ceramic stereolithography a suspension of ceramic particles in a photopolymerizable monomer is solidified by crosslinking the molecules with an ultraviolet laser directed by a mirror system. In the following heat treatment the polymer matrix is pyrolyzed and the ceramic part is sintered. Parts made of silica, alumina and silicon nitride have been reported [14].

Compared to stereolithography with pure monomer solutions, as used in rapid prototyping of polymeric parts, the dispersed ceramic particles lower the cure depth and increase the cure width of the laser beam, even if the ceramic material is transparent to UV. For example a laser beam with a diameter of 210 μm is widened in the suspension and cures an area of 300 μm in diameter [15].

Figure IV-7: Experimental setup for stereolithography [14].
Stereolithography

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 μm</td>
<td>- high aspect ratio</td>
</tr>
</tbody>
</table>

only limited by machine geometry

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>only limited by machine geometry</td>
<td>- low resolution - no dense microstructure</td>
</tr>
</tbody>
</table>

Remarks:
Scattering effects lower lateral resolution

Table IV-4:  Process characteristics of stereolithography.

Selective Laser Sintering (SLS)

A laser beam melts the low melting component of a two component inorganic powder system. The liquid phase wets the solid ceramic powder and joins it during the solidification. After shaping, the low melting phase is no longer beneficial, it limits the thermal stability of the part. Therefore, a following heat treatment step is used to increase the thermal stability of the microstructure. Examples of SLS powder systems are alumina with a low melting phosphate binder forming a glass phase during heat treatment [16] or alumina with metallic aluminum as melting phase which is subsequently oxidized [17]. After sintering, the microstructure reaches about 50% of the theoretical density [17]. The speed of the laser beam relative to the powder surface is determined by the thermal conductivity of the powder material to be compacted. A high thermal conductivity leads to dissipation of large amounts of energy into the powder bed, requiring longer irradiation.

Figure IV-8: Ceramic parts produced via SLS [16].
times to melt the binder phase. On the other hand, a low thermal conductivity can lead to thermal shock failures in the produced part.

<table>
<thead>
<tr>
<th>Selective Laser Sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
</tr>
<tr>
<td>500 μm</td>
</tr>
<tr>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>only limited by machine geometry</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>- high aspect ratio</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>- low resolution</td>
</tr>
<tr>
<td>- no dense microstructure</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Remarks:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limited speed due to heat transfer limitations, needs liquid phase sintering</td>
</tr>
</tbody>
</table>

Table IV-5: Process characteristics of Selective Laser Sintering.

The described rapid prototyping techniques have two major advantages. First, parts can be generated in very short time without the need for a mold, second, structures with high aspect ratios can be made. However, the lateral resolution of the techniques is quite low. This also leads to a rather rough surface. The effects responsible for this low resolution are the physical limitations of these techniques. It is not likely that with these techniques feature sizes much smaller than 150–200 μm can be realized in the future.

The main limitations are:

- size of the generated droplets and spread of liquid droplets in a porous substrate for the ink-jet related techniques,
- scattering effects in stereolithography,
- heat conduction in Selective Laser Sintering.

In addition, some of the processes need powder systems with liquid phase sintering. This limits the high temperature stability of the produced parts.

2.2 Direct Ceramic Machining (DCM)

An isostatically pressed and presintered ceramic blank is shaped on a computer controlled milling machine. After the shaping process, the ceramic bodies are sintered to full density and exhibit excellent mechanical behavior [18]. As this is not a layered fabrication technique, even round shapes can be made with good accuracy. The resolution is determined by the positioning accuracy of the milling machine and the diameter of the milling cutter. The aspect ratio is also limited by the available milling cutters. Rounded structures inside the part are not feasible because of the 'one dimensional' geometry of the milling cutter. By compensating the sintering shrinkage of the ceramic material, net-
shaped sintered parts can be made. An image of the milling process is shown later in Figure V.A-33.

DCM is a very powerful technique for the fabrication of parts in the size range of 400 µm. The ceramic structures can be shaped fast and sintered to full density. One application of this technique is the fabrication of ceramic tooth bridges which exhibit very high mechanical strength.

<table>
<thead>
<tr>
<th>Direct Ceramic Machining</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
<td>- high aspect ratio</td>
</tr>
<tr>
<td></td>
<td>- dense microstructure</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>Disadvantages:</td>
</tr>
<tr>
<td></td>
<td>- low resolution</td>
</tr>
<tr>
<td></td>
<td>- geometrical limitations</td>
</tr>
<tr>
<td></td>
<td>Remarks:</td>
</tr>
<tr>
<td></td>
<td>Net-shape method</td>
</tr>
</tbody>
</table>

Table IV-6: Process characteristics of direct ceramic machining.

2.3 Extrusion

Elongated fine-scaled ceramic parts are fabricated by extruding a thermoplastic polymer filled with ceramic particles through a size-reducing die. The feedrod used for extrusion consists of several powder-filled polymer compounds. During extrusion, the shape in which the different compounds are assembled is maintained. The feedstock is only reduced in its dimensions perpendicular to the extrusion direction. After each extrusion step the extrudates are reassembled and extruded again until the desired size reduction is achieved. Objects with complex shapes can be fabricated by assembling an extrusion feedrod from several shaped ceramic compounds. With a space-filling carbon black compound that can be pyrolyzed, even free-standing or hollow structures are possible. Objects in the size range of 10 µm were produced [19,20]. Polycrystalline fiber composites with defined fiber geometries and orientations can be made also [21].

With this method, no micromachined parts are necessary to generate microscopic features, they are generated by the uniform size reduction of macroscopic assemblies. Although very small structures with high aspect ratios can be made, this method suffers from important restrictions. The shape of the structures is limited to quasi-3D shapes due to the one dimensional extrusion process. In addition, the generated patterns get slightly distorted during the extrusion.
Extrusion

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 µm</td>
<td>- very high aspect ratio</td>
</tr>
<tr>
<td></td>
<td>- good resolution</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>almost infinite</td>
<td>- only quasi-3D structures</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Objects get slightly dis-torted with increasing number of extrusion steps</td>
</tr>
</tbody>
</table>

**Table IV-7:** Process characteristics of extrusion.

**Figure IV-9:** Process schematic and micrograph of an extruded part. The initial size of the feedrod was in the range of 4 mm [20].

### 3 Methods with 2-Dimensional Molds

In the processes described in this section the mold has to be defined in two dimensions, the third dimension is directly generated in the process.

#### 3.1 Etching

Etching processes are not very widespread in ceramics manufacturing because ceramics are among the hardest and most inert materials known. Especially wet etching processes are generally not suitable for patterning ceramics which are usually very inert to aggressive liquid media. However, this method is used for niche applications with a well matched pair of etchant and material to be etched. In dry etching processes the material is removed either by sputtering or in a highly reactive plasma. This process has less problems with the chemical inertness of ceramics. As the standard polymeric resist
materials are often removed faster than the ceramic material, mechanical aperture masks are needed to direct the etching plasma.

**Wet Etching**

Patterning by wet etching is carried out similar to silicon–based techniques in microelectronic manufacturing [22]. A ceramic surface is coated with a photoresist film. This resist film is exposed through a photomask and developed, the irradiated area of the resist is dissolved. Through the blank spaces in the resist the ceramic material can be etched with an appropriate liquid etchant. Most of the research in wet etching of ceramics is done in the field of ceramic high–T_c superconductors. For the fabrication of small–scale coils or other superconducting circuits epitaxially deposited cuprate films have been etched with a variety of chemicals, such as hydrofluoric acid, EDTA, nitric acid or phosphoric acid [23]. The application of wet etching is limited to some special ceramics and is often isotropic. Underetching of the template structures may occur, thus limiting the achievable feature size and aspect ratio.

![Figure IV-10: Wet etched superconducting YBa2Cu3O7 coil on a SrTiO3 substrate [23].](image)

<table>
<thead>
<tr>
<th>Wet Etching</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Smallest Lateral Dimension</strong></td>
</tr>
<tr>
<td><strong>Aspect Ratio</strong></td>
</tr>
</tbody>
</table>

**Advantages:**
- Good resolution

**Disadvantages:**
- Low aspect ratio
- Not generally applicable

**Remarks:**
- Only isotropic etching possible

**Table IV-8:** Process characteristics of wet etching of ceramics.
Dry Etching

In dry etching processes the material is patterned either by exposing it to a reactive plasma which forms volatile compounds with the material to be removed or by removing the undesired part mechanically with an ion beam [22]. The main parameter of a dry etching process is the energy of the incorporated plasma. At low ion energies the process is chemically controlled, not all components in a multi material mixture form volatile components with a certain plasma. Therefore, these processes exhibit a high selectivity. For example, if layers of different materials are stacked, the etching reaction stops at the interface between two materials, because only one material is removed by the plasma. The etching process is more or less isotropic in all directions, no structures with high aspect ratios can be made. In physical plasma processes the material is removed by sputtering. These processes allow a stronger anisotropy; structures with a higher aspect ratio can be produced. However, the larger anisotropy results in a smaller selectivity of the etching process, as illustrated in Figure IV-11.

![Figure IV-11: Dry etching processes][22].

Several binary metal oxides such as CuO, ZnO and PbO have been plasma etched with hexafluoroacetylacetone at temperatures above 200 °C [24], also binary nitrides can be etched [25]. Etching of PZT has been done with excimer laser radiation in a reducing atmosphere [26] and also with SF$_6$ [27].

Like in wet etching, also dry etching of ceramics can only be applied to materials that form volatile components with the etchant. This greatly limits the applicability of this technique.
Dry Etching

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 μm</td>
<td>- high aspect ratio</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>- low resolution</td>
</tr>
<tr>
<td></td>
<td>- not generally applicable</td>
</tr>
</tbody>
</table>

Remarks:
- Volatile components have to be formed

**Table IV-9:** Process characteristics of dry etching.

### 3.2 Screen Printing

A paste of ceramic powder, plasticizer and binder is placed on a patterned screen of metal wires. The pattern is generated by sealing some of the meshes of the screen with a polymer. The paste is then forced through the remaining openings in the screen by using a rubber squeegee which depresses the screen to contact the substrate as it traverses the pattern. The thickness of the deposited layer is determined by the thickness of a polymer spacer film attached to the lower side of the mesh. Patterning of the screen is done by coating it with a photoreactive polymer and dissolving the latter selectively after exposure [28].

To overcome the limitation that only flat substrates can be patterned by screen printing, transfer printing has been developed [29]. The ceramic layer is printed onto a sheet of coated paper and can later be transferred onto tubular or corrugated surfaces.

Screen printing is a simple process, but only low aspect ratios with low resolutions can be made. The resolution is limited by the viscosity of the ceramic paste that is used. The crosswise arranged metal wires form isolated openings, separated by the width of the wires. In order to form a continuous pattern, the paste has to flow laterally to connect the isolated portions of the paste that are pressed through the mesh. This causes blurring of the structure.

Screen printing is mostly used for unpatterned layers, for example for electrodes or electrolytes in solid oxide fuel cells [30], but also the formation of an array of more than one hundred single sensor dots (1.5 x 1.5 mm²) has been reported [31].
The screen printing paste is deposited on the patterned mesh.

With a squeegee the mesh is pressed onto the substrate and the paste is squeezed through the openings.

The pattern is transferred to the substrate and the excess paste remains on the mesh.

**Figure IV-12:** Screen printing process.

<table>
<thead>
<tr>
<th>Screen Printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
</tr>
<tr>
<td>Aspect Ratio</td>
</tr>
</tbody>
</table>
| Advantages: | - generally applicable
- dense microstructure |
| Disadvantages: | - low resolution
- small aspect ratio |
| Remarks: | Good control of layer thickness |

**Table IV-10:** Process characteristics of screen printing.

### 3.3 Stamping Methods

**Gravure Offset Printing**

This procedure is similar to the offset printing process in the printing industry and is described in [32] for the fabrication of conductive line patterns. The desired pattern, which is etched into a metallic gravure plate, is first covered with a screen printing paste and then scraped clean so that the paste remains only in the engraved pattern. Subsequently the paste in the pattern is picked up and transferred from the plate to the desired substrate by a flexible silicon rubber pad which is pressed onto the substrate. Structures made by Gravure Offset Printing have smoother surfaces than those made by screen printing because the screen printing mesh leads to a superstructure grid on the surface of the deposited layer when high viscosity pastes are used. Screen printing on the other hand allows a better control of the layer thickness.

In literature only pattern transfer with metal–filled screen printing pastes has been reported. However, this method is listed here, because enough recipes for ceramic–filled
State of the Art 26

pastes are also available. As in screen printing only low aspect ratio structures can be achieved.

<table>
<thead>
<tr>
<th>Gravure Offset Printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
</tr>
<tr>
<td>Aspect Ratio</td>
</tr>
</tbody>
</table>

| Advantages: |
| - generally applicable |
| - dense microstructure |

| Disadvantages: |
| - low resolution |
| - small aspect ratio |

| Remarks: |
| Less control over layer thickness. |

**Table IV-11:** Process characteristics of Gravure Offset Printing.

**Figure IV-13:** Schematic of Gravure Offset Printing. By means of a rubber pad ink is transferred from a printing plate to a substrate [32].

**Microcontact Printing (µCP)**

This technique uses well defined patterns of self assembling monolayers for pattern formation. They are transferred to a substrate by means of a soft polymer stamp made of poly(dimethylsiloxane) (PDMS). The process has proven to be very versatile in generating micron- and nanoscale monolayer patterns [33]. By using the stamped monolayer as resist material for an etching process, defined gold features as narrow as 30 nm can be obtained [34].

Patterning a substrate with ceramics uses selective wetting of an aqueous suspension on the hydrophilic part of a partially hydrophilic and hydrophobic surface [35]. When the substrate is dipped for example into an aqueous suspension of a colloidal iron oxide, small suspension droplets are formed on the hydrophilic parts of the substrate. Then, the solvent is evaporated and the solid particles remain on the substrate as a thin coating. Feature sizes of 1 µm have been made with this process.

The self assembling monolayer that determines the pattern can be made with an excellent lateral resolution. But, due to the low solids loading of the colloidal suspension,
only thin layers in the range of 100 nm can be achieved. In addition, appropriate colloidal particles are required in a homogeneous dispersion. A diagram of the process is depicted in the experimental section in Figure V.B-16.

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>1 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspect Ratio</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**Advantages:**
- excellent resolution
- generally applicable

**Disadvantages:**
- small aspect ratio

**Remarks:**
Deposition is controlled by the wetting behavior of the ceramic suspension.

*Table IV-12: Process characteristics of microcontact printing.*

4 Methods with 3-Dimensional Molds

Many of these methods require a separate mold for every part produced. After shaping, the molds are destroyed during the process, in most cases by pyrolysis. The feature size of the parts can become as small as 10 µm. However, the techniques involved in fabricating such molds from scratch are quite costly, because microfabrication techniques have to be used for their production. Therefore, it is desirable to make a positive master mold of durable material and high accuracy. The single lost molds are replicated from this master with macro-scale technology, for example by injection molding [36]. In the case where each mold has to be microfabricated separately, the fabrication process becomes more costly, as a cleanroom environment with very expensive machinery is generally needed. Ideally, reusable molds are employed. But demolding becomes increasingly difficult with higher aspect ratios and smaller feature sizes because of the increasing contact areas parallel to the demolding direction and the incorporated surface friction during demolding.

*Figure IV-14: Two fabrication strategies with lost molds. Creating a master structure with microtechnology and replicating it with macro-technology is preferred.*
4.1 Slip Casting

In the traditional slip casting process the suspension agent of a slip is dragged into the porous mold by capillary flow which leads to the formation of a ceramic green body at the surface of the mold. Either plaster or porous polymers are used as mold materials. These mold materials are not suited for the generation of miniaturized parts, as the required surface quality cannot be achieved due to their porosity. Hence, nonporous mold materials have to be used and the solidification of the suspensions is achieved by evaporating the solvent through the sample surface and not through the mold.

Molds made by X-ray lithography have been filled with a 23 vol % slurry of lead zirconate titanate (PZT) for the formation of an array of piezoelectric rods [37]. A honeycomb structure with a wall thickness of 10 μm and an aspect ratio of 20 was also produced. As the solids loading is relatively low, drying cracks occurred. Defect-free structures have been made by a combination of cold isostatic pressing after drying of slip cast green bodies and subsequent hot isostatic pressing [38].

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 μm</td>
<td>20</td>
</tr>
</tbody>
</table>

Table IV-13: Process characteristics of slip casting.

4.2 Centrifugal Casting

The damage during drying of the green body can be reduced by increasing the wet green density of the ceramic bodies mechanically. One method to achieve this is by sedimentation of the ceramic particles in a centrifuge. The centrifugal forces are relatively low compared to pressing techniques, therefore wax molds can be used [39]. A PZT array with an aspect ratio of 10 has been produced this way. Because the centrifugal force acts uniformly on every particle, the produced green bodies have a better homogeneity than those produced by filter pressing (see below).
Microfabrication of Ceramics

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Prof. Dr. N. D. Spencer, co-examiner

Zürich, 2000
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## I Microfabrication of Ceramics

Summary ................................................................. 1
Zusammenfassung ..................................................... 2

## II General Introduction ............................................ 5

## III Aim of this Study ............................................... 9

## IV State of the Art in Ceramic Microfabrication

1 Introduction .......................................................... 11
2 Methods without Mold ............................................... 14
   2.1 Rapid Prototyping Techniques ................................. 14
   2.2 Direct Ceramic Machining ..................................... 19
   2.3 Extrusion .......................................................... 20
3 Methods with 2-Dimensional Molds ............................... 21
   3.1 Etching ............................................................ 21
   3.2 Screen Printing .................................................. 24
   3.3 Stamping Methods .............................................. 25
4 Methods with 3-Dimensional Molds ............................... 27
   4.1 Slip Casting ...................................................... 28
   4.2 Centrifugal Casting ............................................ 28
   4.3 Filter Pressing .................................................. 29
   4.4 Injection Molding .............................................. 30
   4.5 Tape Embossing ................................................ 31
5 Summary .............................................................. 32
6 References ........................................................... 34

## V Process Development ............................................. 37

A: Generation of Patterned Ceramic Surfaces

1 Introduction .......................................................... 38
2 General Experimental Procedure .................................. 38
   2.1 Mold Fabrication ................................................. 39
   2.2 Suspension Preparation ........................................ 42
   2.3 Casting ........................................................... 42
   2.4 Demolding and Sintering ....................................... 42
   2.5 Characterization ................................................ 43
3 Investigated Issues ................................................... 43
   3.1 Influence of Powder Particle Size ........................... 43
   3.2 Increase of Suspension Solids Loading ..................... 48
   3.3 Surface Chemistry of PDMS .................................... 59
   3.4 Conclusions ..................................................... 61
I Microfabrication of Ceramics

Summary

To date, ceramic materials have almost been excluded from the general trend of miniaturization of functional devices, which goes on in other fields of materials science. Especially in the semiconductor industry the feature sizes of the generated structures decreased constantly in the last years. Today, submicron structures with a feature size of 0.2 μm are already produced in semiconductor pilot plants. On the other hand, the smallest ceramic features produced in industry so far are almost three orders of magnitude larger. Piezoceramic rods for the fabrication of ultrasonic transducers have diameters in the range of 100 μm. Other techniques which allow the production of features with a size of 50 μm and slightly below, are in a research state but not applied on a large scale. Smaller surface structures on ceramics have not been generated up to now. In the present work we therefore attempted to develop powder-based ceramic forming techniques which allow the generation of ceramic features with dimensions of a few micrometers.

In the first part of the study, bulk samples with a patterned surface are generated by slip casting of water-based suspensions into nonporous elastomeric molds made of poly(dimethyl siloxane) (PDMS). Surface structures of excellent quality with dimensions as small as 1 μm are feasible. It was found that a suspension with a high solids loading has to be used in order to reduce drying shrinkage and a hydrophobic surface of the mold material is essential for defect-free demolding. The slip casting process is applicable to various ceramic materials. Also polymers other than PDMS can be used as molds, however, PDMS offers the simplest mold generation process.

In the second part of the work, three fabrication methods for the generation of ceramic surface patterns on arbitrary substrates are investigated. In the first method, micromolding in capillaries, a PDMS structure forms three walls of a capillary, the surface of the substrate acts as the fourth wall. A liquid is then dragged into these capillaries and solidified, leaving a three dimensional structure after removing the PDMS. The process was developed for solutions and could not be successfully adapted to dense ceramic suspensions, as the ceramic structures could not be obtained in a reproducible manner. The second technique uses selective wetting of an aqueous suspension on gold surfaces functionalized with hydrophilic and hydrophobic self-assembled monolayers. It produced promising results, but sintering of the ceramic features on the gold surface as well as the transfer of the process to other than gold substrates could not be achieved. Finally, filling of surface molds made of patterned photoresist yielded the most reproducible structures with a feature size of 5 μm. Matching coefficients of thermal expansion is crucial in order to get a crack-free structure after sintering. The process can be applied to various substrates and ceramic suspensions.
Zusammenfassung


flächen war nicht möglich. Die dritte und vielversprechendste Methode benutzt dreidi-
mensionale Strukturen aus Photolack auf der Substratoberfläche als verlorene Form für
Schlickerguss. Mit dieser Technik konnten keramische Muster mit einer Auflösung von
bis zu 5 \( \mu \text{m} \) reproduzierbar hergestellt werden.
II General Introduction

Microfabrication is becoming more and more important in modern science and technology. The ability to fabricate new types of microstructures or to produce existing structures in downsized versions offer a large potential in cost reduction. The most obvious examples are sensors, actuators and microelectronic devices. Miniaturization of electronic elements has made terrific progress in the last decades and is still going on. Components with micrometer or even nanometer dimensions can also open up the opportunity to study basic scientific phenomena that occur at small dimensions. One example is quantum confinement observed in nanostructures [1,2]. Although most research on microfabrication is silicon-based and has been focused on microelectronic devices [2], applications in other areas are rapidly emerging. These include sensor systems for microanalysis [3–6], micro-volume reactors [7–9] combinatorial synthesis [10], micro-electromechanical systems (MEMS) [11,12], optical components (for example photonic band gap materials) [13–15] and systems for non-magnetic data storage [16].

One promising use for microanalytical devices is in the separation and analysis of chemical and biological substances [3–6]. These devices require only small quantities of reagents, have relatively short analysis times and can show efficiencies in separation and detection that are better than those of larger analysis systems. In the last years, several miniaturized total chemical analysis systems [17,18] sometimes also referred to as ‘labs on a chip’, have been developed that perform all sample-handling steps on their own. An array of chemical tools on a chip makes it possible to analyze extremely small amounts of a product. These systems will be useful for the parallel screening of a large number of compounds. For example an artificial nose can be realized with a large number of single sensors of which each one is tuned to detect a different ‘flavor’ [19]. Structures in the micrometer range allow the integration of a large number of single elements on a small area. Even though the selectivity of a single element might by mediocre, their large number compensates this disadvantage by far.

Miniaturization of sensor elements has not only the advantage that more data can be collected in the same amount of space, but also that the sensing devices may be integrated directly on the electronic chip along with monitoring, actuating and controlling devices. With such an integration, a sensor element can directly generate a digital output signal. In the past years, the scope of fabrication techniques has widened and the number of devices has increased [11,12,20]. Most are fabricated from silicon using standard microlithographic techniques [21,22]. With these methods, thousands of mechanical elements, for example cantilevered beams, springs, linkages, mass elements and joints, can be batch-fabricated on a single silicon substrate [10,12]. Microactuators, micromotors and microengines [22] have been fabricated for optical switches, fluid pumps [23], sys-
tems for drug delivery and microchemical analysis [24–27]. More recently, surface micromachining techniques have been used to fabricate miniaturized optical components which are attractive for applications in spectrometers, display devices, sensors, optoelectronic packages and data storage systems [13–15].

Most of the devices mentioned above are made using silicon based microfabrication techniques. Up to now, not much has been done to fabricate miniaturized parts of ceramic materials. Sensors with ceramic detection materials are still built in the classical manner. A macroscopic ceramic part detects the signal which is fed to the evaluating electronics by electric connectors. For a possible integration of ceramic materials into the length scale of microelectronic components no suitable fabrication techniques have been developed yet, although ceramic materials are operating in numerous types of sensors, as summarized in Table IV-1.

<table>
<thead>
<tr>
<th>Type of Sensor</th>
<th>Output Signal</th>
<th>Effect</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature sensor</td>
<td>Change in the resistance</td>
<td>Thermistor effect (PTC or NTC)</td>
<td>NiMn$_2$O$_4$, CoFe$_2$O$_4$, BaTiO$_3$</td>
</tr>
<tr>
<td>Oxygen sensor</td>
<td>Electromotive force</td>
<td>Conductivity of oxygen ions</td>
<td>ZrO$_2$</td>
</tr>
<tr>
<td>Gas Sensor</td>
<td>Change in the resistance</td>
<td>Semiconducting behavior</td>
<td>SnO$_2$</td>
</tr>
<tr>
<td>Optical sensor</td>
<td>Electromotive force</td>
<td>Pyroelectric effect</td>
<td>SrTiO$_3$, PZT, PbTiO$_3$</td>
</tr>
<tr>
<td>Ultrasonic sensor</td>
<td>Phase difference of emitted and detected waves</td>
<td>Piezoelectric effect</td>
<td>PZT, PbTiO$_3$, PbZrO$_3$</td>
</tr>
<tr>
<td>Sensors for measuring force, pressure, acceleration</td>
<td>Change in output voltage</td>
<td>Piezoelectric effect</td>
<td>PZT, PbTiO$_3$, PbZrO$_3$</td>
</tr>
</tbody>
</table>

*Table IV-1: Ceramic sensor materials [28,29].*

One of the most crucial issues towards the integration of ceramic materials into micro-scale devices, is the development of suitable forming methods. When features with dimensions below 100 μm are required, a simple downscaling of established ceramic processing techniques is not suitable. In the present thesis, principles of colloidal chemistry with ceramic powders were combined with new approaches for mold fabrication.
References


III Aim of this Study

The goal of the present work was to find and apply new processing routes for the fabrication of well defined ceramic surface components in the micrometer range, one order of magnitude smaller than the structures feasible today.

This miniaturization of ceramic components may lead to advances in sensor technology, possibly being integrated on the same silicon chip used for data processing. This would allow the production of ceramic-containing devices of similar dimensions as polymeric and metallic structures which are already available today. However, it is not the goal of this work to fabricate a fully functional sensor, rather appropriate methods for the production of such sensors are evaluated.

In order to narrow the broad focus and also with regard to potential industrial applicability of these processes, additional boundary conditions for the new processing method had to be formulated:

• The processing method should be versatile and be able to use commercially available powders of various compositions as raw materials
• The process should enable the production of ceramic microcomponents on various substrate materials
• The molds should be reusable in order to be cost effective
• Expensive machinery should be avoided.
Seite Leer /
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IV State of the Art in Ceramic Microfabrication

Processing techniques that are suitable for producing ceramic parts with a minimal feature size smaller than 500 \( \mu \text{m} \) are described and compared based on the specific requirements of this study. In conclusion of this overview, a strategy for the first approach of the present investigation is developed.

1 Introduction

The first efforts in ceramic microtechnology have been made by downscaling elaborated macroscale forming technologies. This was also the case for the most widely used ceramic microsystem, the piezoelectric ultrasonic transducer. These transducers are made of small piezoceramic rods embedded in a polymer matrix (Figure IV-1).

![Figure IV-1: Schematic of a composite ultrasonic transducer.](image)

This composite setup avoids losses of ultrasonic energy at the transducer–tissue interface in medical imaging [1]. The rods have to be long and slender in order to ensure a noise–free signal [2]. The first generation of such rods was made by cutting perpendicular grooves into a sintered PZT plate (Figure IV-2) [3] that leads to individual posts with small dimensions. The width of the grooves is determined by the width of the dice and the width of the rods is limited by the mechanical stability of the material. The high stresses involved in this technique lead to breaking of small rods during manufacturing. Both the width of the trenches and of the rods are in the range of 200 \( \mu \text{m} \), the aspect ratio (Figure IV-3) is in the order of 1. The described limitations of the downscaled technique gave rise to the demand for other approaches for the production of such ceramic rod structures. Molds made with methods developed in semiconductor manufacturing were combined with traditional suspension–based ceramic forming techniques. Today, rods as narrow as 20 \( \mu \text{m} \) with an aspect ratio of 10 are produced [4,5].
In different fields, as for example in sensor technology [6] or rapid prototyping [7], special techniques of forming small-scale ceramic structures have been developed to date. An overview of processing techniques and some examples of their applications is given in Table IV-1. For each of these applications the ceramic parts have to fulfill certain requirements. Therefore, several processing methods have been developed, each one with its special focus on a certain application.

**Figure IV-2: Fabrication processes for ultrasonic transducers embedded in a polymer matrix [5].**
<table>
<thead>
<tr>
<th>Method</th>
<th>Examples</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rapid prototyping</td>
<td>Prototypes, casting molds for metals</td>
<td>[7–17]</td>
</tr>
<tr>
<td>Direct ceramic machining</td>
<td>Dental implants</td>
<td>[18]</td>
</tr>
<tr>
<td>Co–extrusion</td>
<td>Polycrystalline fiber composite material</td>
<td>[19–21]</td>
</tr>
<tr>
<td>Etching</td>
<td>Superconducting connectors</td>
<td>[22–27]</td>
</tr>
<tr>
<td>Screen printing</td>
<td>Electrolytes for solid oxide fuel cells</td>
<td>[28–31]</td>
</tr>
<tr>
<td>Stamping methods</td>
<td>Conductor lines</td>
<td>[32–35]</td>
</tr>
<tr>
<td>Slip casting</td>
<td>Piezoelectric array</td>
<td>[37–38]</td>
</tr>
<tr>
<td>Centrifugal casting</td>
<td>Piezoelectric array</td>
<td>[39]</td>
</tr>
<tr>
<td>Filterpressing</td>
<td>Piezoelectric array, nozzle</td>
<td>[39–40]</td>
</tr>
<tr>
<td>Injection molding</td>
<td>Piezoelectric array</td>
<td>[41]</td>
</tr>
<tr>
<td>Tape embossing</td>
<td>Piezoelectric array</td>
<td>[42–44]</td>
</tr>
</tbody>
</table>

*Table IV-1: Applications for microfabricated ceramic parts produced by the forming methods discussed in this chapter. For references see the respective sections.*

It would not be very informative to compare the different processing methods directly with each other. What is an advantage for one application might be a disadvantage for another. Therefore, the advantages and disadvantages listed in the following subsections are specified with regard to an 'ideal processing method', which was already described in the aim of this work. Such a method does not (yet) exist, it serves only as common reference to judge the single processes more objectively. The criteria for the comparison were chosen to allow a statement about the suitability of the processing method for the fabrication of the small features required in this study.

The ideal processing technique has the following characteristics:

- The smallest lateral dimension is below 10 micrometers
- An aspect ratio larger than 1 is possible
- Dense polycrystalline ceramic bodies can be produced.

The fulfillment of one or all of these requirements is listed as an advantage in the process characteristics table of each section. If the technique does not fulfill these requirements, it is listed as a disadvantage. The smallest lateral feature size and the largest achievable aspect ratio are listed and visualized for each of the processes in the characteristics table at the end of the respective sections. Their determination is based on the
processes, not on the properties of the materials that are used. With techniques that can make structures with high aspect ratios, the strength of the ceramic material becomes the limiting factor for the structure height, but this is of no concern here.

The smallest lateral feature size is the width of the smallest feature that has been achieved using the respective process. The aspect ratio is a dimensionless number that is calculated by dividing the maximal height of a structure by its width. Long, slender structures have a high aspect ratio; broad, flat structures have a low one.

![High Aspect Ratio](image1.png) ![Low Aspect Ratio](image2.png)

*Figure IV-3: Structures with high and low aspect ratios.*

In the following section the discussed processes are grouped according to the kind of molds that are employed. Some methods do not require a mold at all. In this case the ceramic part is built in all three dimensions from a powder bed or a blank on a computer controlled machine. Methods that use 2-dimensional molds are strongly related to methods used on a larger length scale in the traditional printing industry. In these methods the third dimension is generated directly during the process. When 3-dimensional molds are used, the processes are related to traditional casting methods where ceramic materials are usually processed as suspensions.

2 Methods without Mold

2.1 Rapid Prototyping Techniques

Rapid prototyping techniques, sometimes also referred to as solid freeform fabrication techniques, were developed in order to generate parts directly from a computer model to avoid the costs and time involved in mold fabrication for the production of single prototypes or of small series of a functional part [7].

The parts are built layer by layer in order to realize even complex geometries. The 2-dimensional geometrical information for each layer is generated by a slicing algorithm applied to a CAD model of the part. Rapid prototyping systems therefore have two critical dimensions: The smallest lateral feature size and the thickness of a solidified layer. A smaller feature size and a thinner layer thickness lead to a better resolution, but also to significantly longer process times for the produced parts. A compromise has to be made between resolution and processing time. In general, a minimal cure depth and minimal
cure width of 200 μm are desired. The aspect ratios of the produced parts are only limited by the geometry of the machine. Theoretically an infinite number of layers could be stacked.

![Desired Structure](image1)  ![Layered Object](image2)

*Figure IV-4: Principle of layered object fabrication.*

Because of the wish to generate exact 1:1 prototypes, the ceramic powders used in Rapid Prototyping are usually tailored to avoid shrinkage during sintering. This leads to porous ceramic microstructures of low strength and modulus. Most of the ceramic parts made by rapid prototyping are made of refractory grade powders and are used as molds for metal casting of prototypes or small scale serial production.

Different methods for rapid prototyping of ceramics have been developed, but they can all be grouped into three fields:

1. Selective addition of material to an existing surface.
2. Chemical alteration of a liquid or solid using directed light energy.
3. Sintering of a powder using directed light energy.

In the following subchapters techniques for each of these fields are described. *Three Dimensional Printing* and *Suspension Printing* representing the first group, *Stereolithography* the second and *Selective Laser Sintering* the third.

The suitability of all the described rapid prototyping techniques for ceramic microfabrication is summarized at the end of this section.

**Three Dimensional Printing**

In Three Dimensional Printing (3DP) the single layers of the ceramic part are solidified by spraying a binder suspension with an ink jet printer head into a ceramic powder bed [8]. Structures with a minimal feature size of 430 μm are reported. The parts are made using an alumina powder with an average grain size of 40 μm. The powder is solidified via a glass phase during heat treatment at 800 °C, practically no shrinkage occurs. The parts can be used as casting molds for small series in metal production where 3DP is cheaper than creating molds for lost wax models [9]. Investigations to use the produced parts as drug delivery devices have also been reported [10].

3DP is performed using both available systems of ink jet printers: drop–on–demand and continuous–jet technology. The latter is favored because of the higher printing speed.
Applying a layer of loose powder on top of solidified part

Printing step. Binder is selectively printed into the powder bed.

Printing step is terminated, next layer of powder can be applied

Figure IV-5: Process of 3DP.

<table>
<thead>
<tr>
<th>Three Dimensional Printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
</tr>
<tr>
<td>Advantages:</td>
</tr>
<tr>
<td>Disadvantages:</td>
</tr>
<tr>
<td>Remarks:</td>
</tr>
</tbody>
</table>

Table IV-2: Process characteristics of 3DP.

Suspension Printing

This technique is related to 3DP, but instead of printing a binder into a powder bed, a ceramic suspension is printed onto a substrate. The suspension is deposited with either a continuous [11,12] or a drop-on-demand ink jet printer [13]. As the viscosity of the printing suspensions is limited to about 10 mPa·s, the reported solids loadings of the suspensions are only 5–10 vol %. The vast amount of solvent that has to be evaporated limits the printing speed. Therefore, only porous substrates, that support drying, are used. Due to the low solids loading the layer thickness for each printing cycle is about 1 \mu m; much thinner than with the other layered fabrication techniques. This technique is still in the experimental stage, no applications have been reported so far.
Figure IV-6: Pattern created by suspension printing [12].

<table>
<thead>
<tr>
<th>Suspension Printing</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Smallest Lateral Dimension</strong></td>
</tr>
<tr>
<td>Aspect Ratio</td>
</tr>
</tbody>
</table>

**Disadvantages:**
- low resolution
- low aspect ratio
- very slow speed

**Remarks:**
Only porous substrates can be coated

**Table IV-3:** Process characteristics of Suspension Printing.

**Stereolithography**

In ceramic stereolithography a suspension of ceramic particles in a photopolymerizable monomer is solidified by crosslinking the molecules with an ultraviolet laser directed by a mirror system. In the following heat treatment the polymer matrix is pyrolyzed and the ceramic part is sintered. Parts made of silica, alumina and silicon nitride have been reported [14].

Compared to stereolithography with pure monomer solutions, as used in rapid prototyping of polymeric parts, the dispersed ceramic particles lower the cure depth and increase the cure width of the laser beam, even if the ceramic material is transparent to UV. For example a laser beam with a diameter of 210 μm is widened in the suspension and cures an area of 300 μm in diameter [15].

**Figure IV-7:** Experimental setup for stereolithography [14].
Stereolithography

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 μm</td>
<td>- high aspect ratio</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>only limited by machine geometry</td>
<td>- low resolution</td>
</tr>
<tr>
<td></td>
<td>- no dense microstructure</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Remarks:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scattering effects lower lateral resolution</td>
</tr>
</tbody>
</table>

*Table IV-4: Process characteristics of stereolithography.*

**Selective Laser Sintering (SLS)**

A laser beam melts the low melting component of a two component inorganic powder system. The liquid phase wets the solid ceramic powder and joins it during the solidification. After shaping, the low melting phase is no longer beneficial, it limits the thermal stability of the part. Therefore, a following heat treatment step is used to increase the thermal stability of the microstructure. Examples of SLS powder systems are alumina with a low melting phosphate binder forming a glass phase during heat treatment [16] or alumina with metallic aluminum as melting phase which is subsequently oxidized [17]. After sintering, the microstructure reaches about 50% of the theoretical density [17]. The speed of the laser beam relative to the powder surface is determined by the thermal conductivity of the powder material to be compacted. A high thermal conductivity leads to dissipation of large amounts of energy into the powder bed, requiring longer irradiation.

*Figure IV-8: Ceramic parts produced via SLS [16].*
times to melt the binder phase. On the other hand, a low thermal conductivity can lead to thermal shock failures in the produced part.

### Table IV-5: Process characteristics of Selective Laser Sintering.

<table>
<thead>
<tr>
<th>Selective Laser Sintering</th>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500 μm</td>
<td>- high aspect ratio</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>only limited by machine geometry</td>
<td>- low resolution</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- no dense microstructure</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Remarks:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Limited speed due to heat transfer limitations, needs liquid phase sintering</td>
<td></td>
</tr>
</tbody>
</table>

The described rapid prototyping techniques have two major advantages. First, parts can be generated in very short time without the need for a mold, second, structures with high aspect ratios can be made. However, the lateral resolution of the techniques is quite low. This also leads to a rather rough surface. The effects responsible for this low resolution are the physical limitations of these techniques. It is not likely that with these techniques feature sizes much smaller than 150–200 μm can be realized in the future.

The main limitations are

- size of the generated droplets and spread of liquid droplets in a porous substrate for the ink–jet related techniques,
- scattering effects in stereolithography,
- heat conduction in Selective Laser Sintering.

In addition, some of the processes need powder systems with liquid phase sintering. This limits the high temperature stability of the produced parts.

### 2.2 Direct Ceramic Machining (DCM)

An isostatically pressed and presintered ceramic blank is shaped on a computer controlled milling machine. After the shaping process, the ceramic bodies are sintered to full density and exhibit excellent mechanical behavior [18]. As this is not a layered fabrication technique, even round shapes can be made with good accuracy. The resolution is determined by the positioning accuracy of the milling machine and the diameter of the milling cutter. The aspect ratio is also limited by the available milling cutters. Rounded structures inside the part are not feasible because of the ‘one dimensional’ geometry of the milling cutter. By compensating the sintering shrinkage of the ceramic material, net-
shaped sintered parts can be made. An image of the milling process is shown later in Figure V.A-33.

DCM is a very powerful technique for the fabrication of parts in the size range of 400 μm. The ceramic structures can be shaped fast and sintered to full density. One application of this technique is the fabrication of ceramic tooth bridges which exhibit very high mechanical strength.

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 μm</td>
<td>- high aspect ratio</td>
</tr>
<tr>
<td></td>
<td>- dense microstructure</td>
</tr>
<tr>
<td></td>
<td>Disadvantages:</td>
</tr>
<tr>
<td></td>
<td>- low resolution</td>
</tr>
<tr>
<td></td>
<td>- geometrical limitations</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>Remarks:</td>
</tr>
<tr>
<td>8</td>
<td>Net-shape method</td>
</tr>
</tbody>
</table>

*Table IV-6: Process characteristics of direct ceramic machining.*

2.3 Extrusion

Elongated fine-scaled ceramic parts are fabricated by extruding a thermoplastic polymer filled with ceramic particles through a size-reducing die. The feedrod used for extrusion consists of several powder-filled polymer compounds. During extrusion, the shape in which the different compounds are assembled is maintained. The feedstock is only reduced in its dimensions perpendicular to the extrusion direction. After each extrusion step the extrudates are reassembled and extruded again until the desired size reduction is achieved. Objects with complex shapes can be fabricated by assembling an extrusion feedrod from several shaped ceramic compounds. With a space-filling carbon black compound that can be pyrolyzed, even free-standing or hollow structures are possible. Objects in the size range of 10 μm were produced [19,20]. Polycrystalline fiber composites with defined fiber geometries and orientations can be made also [21].

With this method, no micromachined parts are necessary to generate microscopic features, they are generated by the uniform size reduction of macroscopic assemblies. Although very small structures with high aspect ratios can be made, this method suffers from important restrictions. The shape of the structures is limited to quasi-3D shapes due to the one dimensional extrusion process. In addition, the generated patterns get slightly distorted during the extrusion.
Table IV-7: Process characteristics of extrusion.

3 Methods with 2-Dimensional Molds

In the processes described in this section the mold has to be defined in two dimensions, the third dimension is directly generated in the process.

3.1 Etching

Etching processes are not very widespread in ceramics manufacturing because ceramics are among the hardest and most inert materials known. Especially wet etching processes are generally not suitable for patterning ceramics which are usually very inert to aggressive liquid media. However, this method is used for niche applications with a well matched pair of etchant and material to be etched. In dry etching processes the material is removed either by sputtering or in a highly reactive plasma. This process has less problems with the chemical inertness of ceramics. As the standard polymeric resist
materials are often removed faster than the ceramic material, mechanical aperture masks are needed to direct the etching plasma.

**Wet Etching**

Patterning by wet etching is carried out similar to silicon–based techniques in microelectronic manufacturing [22]. A ceramic surface is coated with a photoresist film. This resist film is exposed through a photomask and developed, the irradiated area of the resist is dissolved. Through the blank spaces in the resist the ceramic material can be etched with an appropriate liquid etchant. Most of the research in wet etching of ceramics is done in the field of ceramic high-T$_c$ superconductors. For the fabrication of small-scale coils or other superconducting circuits epitaxially deposited cuprate films have been etched with a variety of chemicals, such as hydrofluoric acid, EDTA, nitric acid or phosphoric acid [23]. The application of wet etching is limited to some special ceramics and is often isotropic. Underetching of the template structures may occur, thus limiting the achievable feature size and aspect ratio.

![Figure IV-10: Wet etched superconducting YBa$_2$Cu$_3$O$_7$ coil on a SrTiO$_3$ substrate [23].](image)

<table>
<thead>
<tr>
<th>Wet Etching</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smallest Lateral Dimension</td>
<td>good resolution</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>low aspect ratio</td>
</tr>
<tr>
<td>Remarks:</td>
<td>not generally applicable</td>
</tr>
</tbody>
</table>

**Table IV-8:** Process characteristics of wet etching of ceramics.
Dry Etching

In dry etching processes the material is patterned either by exposing it to a reactive plasma which forms volatile compounds with the material to be removed or by removing the undesired part mechanically with an ion beam [22]. The main parameter of a dry etching process is the energy of the incorporated plasma. At low ion energies the process is chemically controlled, not all components in a multi material mixture form volatile components with a certain plasma. Therefore, these processes exhibit a high selectivity. For example, if layers of different materials are stacked, the etching reaction stops at the interface between two materials, because only one material is removed by the plasma. The etching process is more or less isotropic in all directions, no structures with high aspect ratios can be made. In physical plasma processes the material is removed by sputtering. These processes allow a stronger anisotropy; structures with a higher aspect ratio can be produced. However, the larger anisotropy results in a smaller selectivity of the etching process, as illustrated in Figure IV-11.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Ion Energy</th>
<th>Anisotropy</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Physical Plasma Process: Sputter Etching</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Balanced Process: Reactive Ion Etching</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chemical Plasma Process: Plasma Etching</td>
<td></td>
</tr>
<tr>
<td>High</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>

*Figure IV-11: Dry etching processes [22].*

Several binary metal oxides such as CuO, ZnO and PbO have been plasma etched with hexafluoroacetylacetone at temperatures above 200 °C [24], also binary nitrides can be etched [25]. Etching of PZT has been done with excimer laser radiation in a reducing atmosphere [26] and also with SF₆ [27].

Like in wet etching, also dry etching of ceramics can only be applied to materials that form volatile components with the etchant. This greatly limits the applicability of this technique.
TABLE IV-9: Process characteristics of dry etching.

3.2 Screen Printing

A paste of ceramic powder, plasticizer and binder is placed on a patterned screen of metal wires. The pattern is generated by sealing some of the meshes of the screen with a polymer. The paste is then forced through the remaining openings in the screen by using a rubber squeegee which depresses the screen to contact the substrate as it traverses the pattern. The thickness of the deposited layer is determined by the thickness of a polymer spacer film attached to the lower side of the mesh. Patterning of the screen is done by coating it with a photoreactive polymer and dissolving the latter selectively after exposure [28].

To overcome the limitation that only flat substrates can be patterned by screen printing, transfer printing has been developed [29]. The ceramic layer is printed onto a sheet of coated paper and can later be transferred onto tubular or corrugated surfaces.

Screen printing is a simple process, but only low aspect ratios with low resolutions can be made. The resolution is limited by the viscosity of the ceramic paste that is used. The crosswise arranged metal wires form isolated openings, separated by the width of the wires. In order to form a continuous pattern, the paste has to flow laterally to connect the isolated portions of the paste that are pressed through the mesh. This causes blurring of the structure.

Screen printing is mostly used for unpatterned layers, for example for electrodes or electrolytes in solid oxide fuel cells [30], but also the formation of an array of more than one hundred single sensor dots (1.5 x 1.5 mm²) has been reported [31].
The screen printing paste is deposited on the patterned mesh. With a squeegee the mesh is pressed onto the substrate and the paste is squeezed through the openings. The pattern is transferred to the substrate and the excess paste remains on the mesh.

Figure IV-12: Screen printing process.

<table>
<thead>
<tr>
<th>Screen Printing</th>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50 µm</td>
<td>- generally applicable</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>0.1</td>
<td>- dense microstructure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Disadvantages:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- low resolution</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- small aspect ratio</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Remarks:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Good control of layer thickness</td>
</tr>
</tbody>
</table>

Table IV-10: Process characteristics of screen printing.

3.3 Stamping Methods

*Gravure Offset Printing*

This procedure is similar to the offset printing process in the printing industry and is described in [32] for the fabrication of conductive line patterns. The desired pattern, which is etched into a metallic gravure plate, is first covered with a screen printing paste and then scraped clean so that the paste remains only in the engraved pattern. Subsequently the paste in the pattern is picked up and transferred from the plate to the desired substrate by a flexible silicon rubber pad which is pressed onto the substrate. Structures made by Gravure Offset Printing have smoother surfaces than those made by screen printing because the screen printing mesh leads to a superstructure grid on the surface of the deposited layer when high viscosity pastes are used. Screen printing on the other hand allows a better control of the layer thickness.

In literature only pattern transfer with metal–filled screen printing pastes has been reported. However, this method is listed here, because enough recipes for ceramic–filled
pastes are also available. As in screen printing only low aspect ratio structures can be achieved.

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 μm</td>
<td>- generally applicable</td>
</tr>
<tr>
<td>0.1</td>
<td>- dense microstructure</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>- low resolution</td>
</tr>
<tr>
<td></td>
<td>- small aspect ratio</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Remarks:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less control over layer thickness.</td>
</tr>
</tbody>
</table>

Table IV-11: Process characteristics of Gravure Offset Printing.

![Diagram of Gravure Offset Printing]

Figure IV-13: Schematic of Gravure Offset Printing. By means of a rubber pad ink is transferred from a printing plate to a substrate [32].

Microcontact Printing (μCP)

This technique uses well defined patterns of self assembling monolayers for pattern formation. They are transferred to a substrate by means of a soft polymer stamp made of poly(dimethylsiloxane) (PDMS). The process has proven to be very versatile in generating micron- and nanoscale monolayer patterns [33]. By using the stamped monolayer as resist material for an etching process, defined gold features as narrow as 30 nm can be obtained [34].

Patterning a substrate with ceramics uses selective wetting of an aqueous suspension on the hydrophilic part of a partially hydrophilic and hydrophobic surface [35]. When the substrate is dipped for example into an aqueous suspension of a colloidal iron oxide, small suspension droplets are formed on the hydrophilic parts of the substrate. Then, the solvent is evaporated and the solid particles remain on the substrate as a thin coating. Feature sizes of 1 μm have been made with this process.

The self assembling monolayer that determines the pattern can be made with an excellent lateral resolution. But, due to the low solids loading of the colloidal suspension,
only thin layers in the range of 100 nm can be achieved. In addition, appropriate colloidal particles are required in a homogeneous dispersion. A diagram of the process is depicted in the experimental section in Figure V.B-16.

![Table IV-12: Process characteristics of microcontact printing.](attachment:image)

**Table IV-12:** Process characteristics of microcontact printing.

4 Methods with 3-Dimensional Molds

Many of these methods require a separate mold for every part produced. After shaping, the molds are destroyed during the process, in most cases by pyrolysis. The feature size of the parts can become as small as 10 μm. However, the techniques involved in fabricating such molds from scratch are quite costly, because microfabrication techniques have to be used for their production. Therefore, it is desirable to make a positive master mold of durable material and high accuracy. The single lost molds are replicated from this master with macro-scale technology, for example by injection molding [36]. In the case where each mold has to be microfabricated separately, the fabrication process becomes more costly, as a cleanroom environment with very expensive machinery is generally needed. Ideally, reusable molds are employed. But demolding becomes increasingly difficult with higher aspect ratios and smaller feature sizes because of the increasing contact areas parallel to the demolding direction and the incorporated surface friction during demolding.

![Figure IV-14: Two fabrication strategies with lost molds. Creating a master structure with microtechnology and replicating it with macro-technology is preferred.](attachment:image)
4.1 Slip Casting

In the traditional slip casting process the suspension agent of a slip is dragged into the porous mold by capillary flow which leads to the formation of a ceramic green body at the surface of the mold. Either plaster or porous polymers are used as mold materials. These mold materials are not suited for the generation of miniaturized parts, as the required surface quality cannot be achieved due to their porosity. Hence, nonporous mold materials have to be used and the solidification of the suspensions is achieved by evaporating the solvent through the sample surface and not through the mold.

Molds made by X-ray lithography have been filled with a 23 vol % slurry of lead zirconate titanate (PZT) for the formation of an array of piezoelectric rods [37]. A honeycomb structure with a wall thickness of 10 μm and an aspect ratio of 20 was also produced. As the solids loading is relatively low, drying cracks occurred. Defect-free structures have been made by a combination of cold isostatic pressing after drying of slip cast green bodies and subsequent hot isostatic pressing [38].

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>10 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspect Ratio</td>
<td>20</td>
</tr>
</tbody>
</table>

Table IV-13: Process characteristics of slip casting.

4.2 Centrifugal Casting

The damage during drying of the green body can be reduced by increasing the wet green density of the ceramic bodies mechanically. One method to achieve this is by sedimentation of the ceramic particles in a centrifuge. The centrifugal forces are relatively low compared to pressing techniques, therefore wax molds can be used [39]. A PZT array with an aspect ratio of 10 has been produced this way. Because the centrifugal force acts uniformly on every particle, the produced green bodies have a better homogeneity than those produced by filter pressing (see below).
29 State of the Art

### Centrifugal Casting

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
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<tbody>
<tr>
<td>20 µm</td>
<td>- high aspect ratio</td>
</tr>
<tr>
<td></td>
<td>- good resolution</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>- no dense microstructure</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Remarks:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Better homogeneity than in filterpressing</td>
</tr>
</tbody>
</table>

*Table IV-14: Process characteristics of centrifugal casting.*

![Image of Centrifugal Casting](image)

*Figure IV-15: Centrifugal casting in lost molds.*

4.3 Filter Pressing

In this method the ceramic suspension is compacted with a porous piston in a non-porous die. The piston simultaneously presses the ceramic particles into the mold at the bottom of the die and removes the water from the suspension [39]. The parts produced exhibit no drying shrinkage.

The molds for this process need to have high strength, because high pressures of up to 20 MPa are applied [40]. The total absence of drying shrinkage is not only an advantage. Usually shrinkage promotes the separation of the part from the mold. The PMMA molds used in the described filter pressing process have either to be pyrolyzed, which can cause problems due to the strongly exothermal reaction, or they have to be dissolved. Similar to parts produced by dry pressing, pressure gradients and with that density gradients are introduced. They lead to differences in sintering shrinkage especially in parts with high aspect ratios. Sintering densities of 90% are reported for piezoceramic arrays and of 98% for alumina nozzles [40].
### Filter Pressing

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>10 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspect Ratio</td>
<td>5</td>
</tr>
</tbody>
</table>

**Advantages:**
- high aspect ratio
- good resolution

**Disadvantages:**
- mold removal

**Remarks:**
Density gradients limit the aspect ratio

*Table IV-15: Process characteristics of filter pressing.*

*Figure IV-16: Filterpressing with a porous piston.*

#### 4.4 Injection Molding

An injection molding process with lost photoresist molds for the fabrication of PZT rods is described in [41]. Deep etched photoresist structures fabricated by X-ray lithography are placed in an injection molding machine. The injection chamber is evacuated to avoid entrapment of air. After injection molding the mold is removed by plasma etching in order to avoid distortions caused by dissolving or melting of the resist material.
4.5 Tape Embossing

In this technique a ceramic slurry is tape cast and the dry tape is subsequently shaped by embossing with a metal stamp [42] or with a plasma-etched polyimide pattern [43,44]. The stamp is removed from the green tape and can be reused. Structures with an aspect ratio of up to 4 can be demolded. To realize thick structures, up to four tapes of 500 µm thickness can be stacked before embossing. Piezoceramic arrays and a small heat exchanger with an edge length of about 20 mm have been produced. In this technique, drying in contact with the mold can be avoided.
5 Summary

From the process characteristics of all the different techniques, it becomes evident that only four of them meet the requirements of a minimal lateral feature size below 10 μm and an aspect ratio of at least 1. These techniques are

- co-extrusion (Section 2.3),
- dry etching (Section 3.1),
- slip casting (Section 4.1),
- filter-pressing (Section 4.3).

All the other techniques fail to fulfill at least one of these two main criteria. With respect to our further requirements, such as the use of commercial powders, the ability to coat substrates, high density of the produced parts, the use of reusable molds and the simplicity of the process, these four methods can be qualified as follows:

With co-extrusion no ceramic surface patterns can be made. The boundary regions of the extruded feedrod are deformed during the extrusion process due to wall friction in the extruding die. For this reason the structures produced by co-extrusion are encapsulated in sacrifice material to protect the surface. Coating of substrates is also not possible and the produced features are slightly distorted. Dry etching is not pursued in this study.
because of its limitation to certain ceramic materials. The two remaining techniques, slip casting and filterpressing, use a similar approach for the formation of microstructures: A ceramic suspension is consolidated in a three dimensional mold. This approach seems promising to solve our need for a simple method suitable for the processing of a variety of ceramic powders. In the search for suitable molds, microcontact printing, excluded up to now from this summary, seems attractive. The excellent resolutions achievable with the elastomeric molds looked most promising for the present investigation. The results of this approach are reported in the following section.

6 References


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V Process Development

It is obvious, that with the method of casting suspensions into elastomeric molds (as described in the summary of the previous chapter), coating of arbitrary substrates with ceramic structures is not possible. The bulk material is always the same as the material forming the surface structure (Figure V-1). However, the proposed method seemed very promising to achieve the small feature sizes demanded in this study. As it was not clear whether such small structures can be produced with ceramic powders as raw material, it was decided to split the experimental work into two parts. First, the method with the elastomeric molds was chosen to investigate the patterning accuracy achievable with ceramic powder suspensions. This is described in part A of this chapter. Methods for patterning arbitrary substrates are described in part B.

Figure V-1: The two variations of micropatterned ceramics.
V.A: Generation of Patterned Ceramic Surfaces

The influence of powder particle size, of suspension properties and of the mold material on the quality of micropatterned ceramic surfaces will be reported below. To illustrate the potential of the method, properties of parts fabricated with the elaborated process will be compared to those of parts produced with known methods.

1 Introduction

The subject of this chapter is the identification of the main processing parameters for patterning ceramic surfaces using powder-based techniques.

The experimental procedure is described in Section 2. In Section 3 the influences of several processing parameters that were identified to be essential for this work are reported. These separate issues are presented in individual subchapters, each one with an experimental part, results and conclusions.

All described experiments were conducted with alumina powders as model material because of its availability in a wide variety of grain sizes and its controllable rheology in suspension. The experimental procedure does not use or depend on special properties of alumina. This was verified by processing powders of other materials with the developed method. However, not all the experiments were repeated with different ceramic powders, it was assumed that the general conclusions are mutually applicable.

Parts of this chapter have been published in Advanced Materials 11 (8) 630-632 (1999) and are reproduced with permission of the publisher.

2 General Experimental Procedure

The patterned structures were all produced with the method depicted in Figure V.A-1. A ceramic suspension of high solids loading is cast into an elastomeric mold made of poly(dimethylsiloxane) (PDMS). The solvent is evaporated and after demolding the rigid ceramic parts are sintered. Thereafter, the produced parts were characterized, mainly by using different microscopic techniques. The detailed experimental procedure is listed in this subsection for each processing step.
2.1 Mold Fabrication

*Mold Material*

PDMS was chosen as mold material because it exhibits a variety of positive properties for this purpose. It has an excellent replication accuracy, features as small as 50 nm have been reproduced [1]. With the two component system used in this study (Sylgard 184, Dow Corning, La Hulpe, Belgium) mold-making is simple. The mixture of the two viscous precursor parts is poured over a template structure and a crosslinking reaction cures the oligomer precursors. Neither pressure nor vacuum has to be applied to ensure a proper filling of the template structures. The low surface energy of the polymer mixture ensures a very good bubble-free spreading on almost any surface. After curing, the elas-
tic nature of the PDMS facilitates the separation of the mold from the reproduced template.

Figure VA-2: Chemical structure of linear PDMS.

The employed two-component system does not produce linear PDMS as shown in Figure VA-2. The two precursor polymers get crosslinked by a hydrosilylation reaction, which involves the addition of a Si–H bond to a carbon–carbon double bond, catalyzed by a platinum containing catalyst [2]. One oligomer of the two component system is therefore functionalised with hydrosilane groups and the other with silicon vinyl groups (Figure VA-3). Of each of these reactive groups at least three have to be present per molecule to ensure a crosslinked polymer structure. The chloroplatinic acid catalyst, also referred to as Speier catalyst, is shipped mixed with the vinyl–functionalized oligomer. This is more favorable in terms of product stability than mixing it with the hydrosilane–functionalized oligomer. Some important physical properties of PDMS are listed in Table V.A-1.

Hydrosilane-functional Oligomer:

Vinyl-functional Oligomer:

Catalyst: $\text{H}_2\text{PtCl}_6$

Figure VA-3: Composition of the 2–component PDMS precursor. The catalyst is supplied mixed with the vinyl–functional oligomer.
Table VA-1: Physical properties of PDMS. The surface energy has a very low value for polymeric materials.

Mold Fabrication

The two components of the PDMS prepolymer mixture are weighed and mixed with a glass stick in a disposable polystyrene dish. During mixing many bubbles are introduced into the viscous polymer mixture. The dish is then left for an hour. During this time the gas bubbles rise in the liquid and burst at the surface. The mixture is subsequently cast onto a template structure which is placed in another disposable dish. The template was a photoresist structure on a silicon wafer. The templates are left for another hour at room temperature to allow the removal of gas bubbles formed during casting. The

Figure VA-4: Mold fabrication process with PDMS. The template structure of photoresist on a silicon wafer (a) is covered with the PDMS prepolymer mixture which is subsequently cured (b) and thereafter removed from the template structure (c). The template structure can be reused.
dishes are then covered with a polymer foil to avoid contamination and placed in a fur-
nace at 50 °C for two hours to accelerate curing. After this the PDMS is rigid and can
easily be peeled off the master template (Figure V.A-4). To avoid contamination by dust
particles the processing steps are carried out in a laminar flow box (Aura–V–190 (class
100), Ehret GmbH, Emmendingen, Germany). Even after several reproduction cycles
from the same template no wear can be observed.

Lithographical Template Generation

Silicon wafers were cut into pieces of 3x3 cm². After mounting on a spin coater they
were cleaned with pressurized nitrogen and acetone (puriss, Fluka, Buchs, Switzerland)
and spun dry. Subsequently, they were coated at 200 rpm with photoresist (AZ 4562,
Clariant, Wiesbaden, Germany). The photoresist was subsequently hardened for two
minutes on a hotplate at 120 °C. For pattern generation, the resist was exposed through a
lithographic mask for 30 seconds to UV light in a maskaligner (MJB 3, Karl Süss AG,
Munich, Germany). The exposed parts of the photoresist were dissolved (MF–319
Developer, Shipley, Berlin, Germany) to form the three dimensional pattern. A schematic
representation of the process is given in the Appendix in Figure A-2.

2.2 Suspension Preparation

The ceramic suspensions were prepared by adding powder to distilled water
(18 MΩ·cm) under constant stirring. The pH was always kept between 4 and 5 by drop-
wise addition of a 2 M solution of hydrochloric acid (Titrisol, Merck, Darmstadt, Ger-
many). The typical batch size was 50 ml. The suspensions were ball milled with alumina
balls for 18 hours. After separating the suspensions from the milling balls two drops of
1–Octanol (puriss, Fluka, Buchs, Switzerland) were added to reduce the surface tension
of the suspension followed by degassing for 15 minutes at 90 mbar under constant rota-
tion in a rotavap (Rotavapor, Büchi, Flawil, Switzerland).

2.3 Casting

For the formation of the ceramic samples a few drops of the degassed particle sus-
pension were poured onto the PDMS mold and dried in a laminar flow box at room tem-
perature. No separating agent was applied to the mold. The suspension layer on the
template structure was kept relatively thin (about 1 mm) with respect to its diameter
(about 5 mm) to get quasi uniaxial shrinkage in the thickness direction and to prevent
high lateral shrinking rates during drying.

2.4 Demolding and Sintering

After drying, the ceramic parts were carefully separated from the molds by bending
the latter and removing the green bodies with tweezers. The PDMS templates were
cleaned in an ultrasonic bath after processing and were reused. Sintering was done in various high temperature furnaces. The detailed sintering programs are reported later.

2.5 Characterization

The produced parts were mainly characterized with different microscopic techniques:

- Light Microscopy (Wild M10, Leica, Heerbrugg, Switzerland; Polyvar MET, Reichert-Jung, Vienna, Austria)
- Scanning Electron Microscopy (JSM-6400, Jeol, Tokyo, Japan)
- Atomic Force Microscopy (Explorer TMX 1010 and Discoverer TMX 2010, Thermo Microscopes, Sunnyvale, CA, USA)

SEM samples were coated with a gold layer of 30–50 nm thickness before imaging (SCD 040, Balzers, Liechtenstein). All microscopes were equipped with digital image acquisition devices. Techniques other than microscopy are described in the respective subsections.

3 Investigated Issues

Several issues which are not directly related to each other were investigated to improve the quality of the produced micropatterned parts. The experimental methods, results and conclusions regarding the consideration of these problems are reported in this chapter.

3.1 Influence of Powder Particle Size

The influence of the powder particle size on the shape accuracy of the sintered microstructures was investigated by producing parts using three powders with different particle sizes and investigating the resulting structures in the SEM. The accuracy was determined by comparing a pattern consisting of an array of 12 round cavities reproduced with the three powders. Both, the concave pits and the convex walls separating the pits have a size of about 2 μm in width and depth.

Experimental

Two α-alumina powders with average grain sizes of 0.5 and 0.2 μm respectively and a boehmite (γ-AlOOH) powder with an average grain size of 50 nm were used. The powder characteristics are summarized in Table V.A-2.

Sample parts were prepared using these three powders according to the general procedure described in Section 2. The solids loadings of the suspensions were adjusted to achieve a viscosity of about 0.5 Pa·s. This viscosity limit ensures a proper filling of the molds.
The sintering programs had to be adapted to the different powders. The alumina samples were heated with 300 K/h to 1550 °C and held there for 3 hours. The boehmite samples were heated with 300 K/h to 300 °C, then with 60 K/h to 600 °C to allow the phase transition of boehmite to γ-Al₂O₃ to take place and then with 300 K/h to 1250 °C with a dwell time of 4 hours. All the samples were furnace cooled.

The lateral shrinkage was measured by comparing the length of a specific feature in SEM micrographs on the template and on the samples in the green and in the sintered state. The densities were measured by the Archimedes method in water.

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Manufacturer</th>
<th>Crystal Structure</th>
<th>d₅₀ [μm]ᵃ</th>
<th>BET [m²/g]ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPA 0.5</td>
<td>Ceralox (Tucson, AZ, USA)</td>
<td>α-Al₂O₃</td>
<td>0.49</td>
<td>8.9</td>
</tr>
<tr>
<td>Taimicron TM-DAR</td>
<td>Taimei (Tokyo, Japan)</td>
<td>α-Al₂O₃</td>
<td>0.19</td>
<td>14.2</td>
</tr>
<tr>
<td>Disperal S</td>
<td>Condea (Hamburg, Germany)</td>
<td>γ-AlOOH</td>
<td>0.05</td>
<td>233</td>
</tr>
</tbody>
</table>

ᵃ. Microtrac UPA, Leeds & Northrup, St. Petersburg, FL, USA.
b. BET, Ströhlein Instruments, Kaarst, Germany.

*Table V.A-2: Characteristics of the investigated powders.*

**Results and Discussion**

With the viscosity-criterion given, solids loadings of 55, 45 and 10 vol % were reached for the powders having average particle sizes of 0.5, 0.2 and 0.05 μm respectively. The decrease in solids loading at a fixed viscosity value with decreasing particle diameter was expected. It originates from the increasing volume percentage that is occupied by the stabilizing double layer for smaller particles [5].

Figure V.A-5 shows the influence of the initial particle size of the powders on the quality of the replicated patterns. The pattern in image a), made from the coarsest of the three powders with an average particle size of 0.5 μm, shows very poor edge resolution. The concave dots are not clearly separated from each other. Reduction of the initial particle size to 0.2 μm in b) leads to a much better pattern resolution. The edges of the single dots are now very steep and the planarity of the sample surface is maintained between the single dots. The edge resolution of the dots is further improved in c) with the nanoscale boehmite powder. Clearly visible is also the increasing total shrinkage of the sample with decreasing solids loading of the cast slurry. The total width of the sintered dot pattern (measured from the left edge of the leftmost dot to the right edge of the rightmost dot) in a) is 27 μm, in b) 25 μm and in c) 22 μm.
Figure VA-5: SEM images of cavities of 2 µm in diameter and depth replicated with ceramic powders of different particle sizes. The quality of the replicated patterns depends strongly on the particle size of the ceramic powders. In a) a sintered alumina part with an initial average particle size of 0.5 µm is shown. The edge resolution is quite poor. Better results were achieved in b) with a particle diameter of 0.2 µm. Very sharp edges could be produced in c) with a boehmite powder of an average particle size of 50 nm.
Table V.A-3: Shrinkage data of the investigated samples.

Only small lateral shrinkage occurs for samples made of the coarsest powder, as can be seen in Table V.A-3. The other powders shrink in the thickness direction but also laterally. Unexpectedly none of the samples that exhibited shrinkage cracked during drying. Because the drying shrinkage of the parts occurs while they are in mechanical contact with the mold, the lateral movement of the parts is hindered by this mechanical contact and crack formation was expected to occur as shown in Figure V.A-6.

Figure V.A-6: Uniform shrinkage in all directions can lead to crack formation when the shrinkage is hindered by the mold. This mechanism was not found when using PDMS molds.

However, no cracks occurred on samples made from the Taimicron powder despite a lateral shrinkage of 10%. The quality of the replicated patterns is good over the whole sample area which has a diameter of about 5 mm. The explanation for this is, that the mold gets compressed by the green body as much as the part shrinks and this buffers the shrinkage. In case of the boehmite powder the samples exhibited a lateral shrinkage of 20% due to the very low suspension solids loading of 10 vol %. This can no longer be buffered by the elastic PDMS but also here no cracks are formed. Instead the shrinkage causes the ceramic part to slide over the mold surface which leads to destruction of some of the surface patterns, as shown in Figure V.A-7. Apparently the height of the features on the mold was not high enough to lead to a strong interlocking between mold and sample that could have caused the sample to crack. The undestroyed area with good pattern replication was about 20% of the surface area of the samples. The exact location of this
zone of good pattern replication on the sample could not be predicted. Therefore, sometimes several attempts had to be made in order to obtain defect-free boehmite microstructures.

Figure V.A-7: Schematic representation and SEM images of the shrinkage area for boehmite samples.

Figure V.A-8: Micrograph of a boehmite sample. The zone of good pattern quality appears darker due to a smoother surface.
The samples of the two α-alumina powders sintered to full density without grain coarsening. The boehmite samples reached only 95% of the theoretical density due to the very low solids loading of the slurry and the inherent high shrinkage rates.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>0.5</td>
<td>55</td>
<td>0.6</td>
<td>100</td>
</tr>
<tr>
<td>0.2</td>
<td>45</td>
<td>0.4</td>
<td>100</td>
</tr>
<tr>
<td>0.05</td>
<td>10</td>
<td>0.1</td>
<td>95</td>
</tr>
</tbody>
</table>

*Table V.A-4: Solids loading of the suspensions and microstructure data of the sintered powders.*

**Conclusions**

The results show that the initial particle size of the powders used for the replication of microstructures plays a crucial role. The smaller the particle size, the better the accuracy of the patterns. However, the partial destruction of the surface patterns due to the high lateral shrinkage rate of the boehmite suspension makes this powder unsuitable. Therefore, the Taimicron powder with an average particle size of 0.2 μm was chosen for further experiments.

A clearly unexpected result of this particle size study is that the PDMS molds buffered lateral drying shrinkages of up to 10% by elastic deformation. As the produced parts investigated here had a diameter of about 5 mm, the involved absolute shrinkages were in the range of 500 μm. It is expected that higher absolute shrinkages lead to damaged parts. Bigger parts (55 mm in diameter) made of 45 vol % Taimicron suspensions indeed showed cracks upon drying. It is concluded that drying shrinkage limits the sample size. Suspensions with a higher solids loading at the same viscosity and a lower drying shrinkage are therefore desirable.

**3.2 Increase of Suspension Solids Loading**

With solids loadings of more than 45 vol % the viscosity of the suspensions raises dramatically and casting is no longer possible. At first sight it might be surprising that with the coarser powder of 0.5 μm solid loads of 55 vol % were reached at the same viscosity (Table V.A-4). The origin of this effect is due to the interparticle interactions. In aqueous suspension, the particles build up an electrostatic double layer that prevents coagulation of the suspension. However, this double layer occupies volume that can no longer be filled with particles which leads to the increase in viscosity.
As mentioned above, an increased solids loading of the Taimicron powder with a 
d_50 of 0.2 μm is desired. In the present section two approaches for such an increase are 
presented. First, it is attempted to change the double layer thickness in order to reduce 
the volume that each particle occupies. Second, the effect of various particle size distribu-
tions on the packing density of a suspension is investigated.

Variation of Double Layer Thickness

The total free energy of interaction of two colloid particles is determined by the 
combination of an attractive and a repulsive term according to the DLVO theory [6].

\[ V_{tot} = V_{repulsive} + V_{attractive} \]

The repulsive term originates from the electrostatic double layer repulsion of the 
particles. For spherical particles of diameter \( a \), with a surface potential \( \Psi_0 \), in a medium 
with dielectric constant \( \varepsilon \), with a double layer thickness \( \kappa \), this term can be written as a 
function of the surface-to-surface distance \( H_0 \)

\[ V_{repulsive} = \frac{\varepsilon a \Psi_0^2}{2} \ln(1 + e^{-\kappa H_0}) \]

\[ \kappa = \frac{1}{\kappa} = \frac{1}{\sqrt{\frac{4 \pi \varepsilon^2 \sum n_i z_i^2}{\eta \varepsilon_0 k_B T}}} \]

Van der Waals forces are responsible for the attractive contribution to the total free 
ergy. With the Hamaker constant \( A \) this leads to

\[ V_{attractive} = -\frac{A a}{12 H_0} \]

The minimal distance between two particles and subsequently the solids loading of 
the suspension is determined by these two contributions. The double layer thickness 
enters as a fixed length in the repulsive term and is therefore of main influence. The 
thickness of this buffer layer around the particles is independent of the particle size in the 
DLVO approximation. The smaller the particles are, the bigger the relative amount of 
volume excluded by the double layer becomes, as schematically shown in Figure V.A-9. 
For the large particles the double layer thickness is one-tenth of the particle diameter; for 
the small ones the double layer thickness is equal to the particle diameter. In the latter
case the excluded volume is therefore much larger. This explains the strongly decreasing solids loading of suspensions with smaller particles.

Figure V.A-9: Close-packed planes of colloidal particles with identical double layer thickness. The solids loading decreases if the particle radius becomes smaller. The numeric values for the two-dimensional discs shown here are 64%, 51% and 10% from left to right.

The effect can also be illustrated with a thought experiment. We imagine to be able to build three dimensional structures of crystalline order out of spherical colloidal particles of uniform size surrounded by an electrostatic double layer (in analogy to the two dimensional planes shown in Figure V.A-9). In a face centered cubic assembly the volume of a unit cell of this colloidal crystal is \( \sqrt{2} \cdot \left( \frac{a}{2} + \frac{1}{\sqrt{2}} \right)^3 \). The volume occupied by solid particles in the unit cell is \( 4 \cdot \left( \frac{a}{2} \right)^3 \). The solids loading of such a crystal (the relation of particle volume divided by the unit cell volume) in function of the particle diameter is plotted in Figure V.A-10. For small particle sizes the achieved volume loading drops dramatically and for large particle sizes the solids loading approaches the value of a densely packed crystal, which is 0.74.

The purpose of the double layer is to prevent the coagulation of particles. However, when the attraction of smaller particles decreases a narrower double layer can prevent the suspension from coagulation. By compressing the double layer higher solid loads can be reached. This is also illustrated in Figure V.A-10. When the double layer thickness is lowered from 5 to 3 nm with particle sizes of up to 0.2 \( \mu \)m significantly higher solids loadings can be achieved. The only parameter for varying the double layer thickness of alumina particles in aqueous suspensions is the ionic strength \( I \) in the solvent \( \left( \frac{1}{\kappa} = \frac{1}{d} \right) \).
Figure V.A-10: Solids loading of colloidal crystals formed by close packed spherical particles of identical size with fixed double layer thickness of 3 and 5 nm respectively.

The double layer can not be compressed infinitely because too small double layers do not stabilize suspensions and coagulation can occur. This effect is also used in ceramic forming technology [7]. Hence an optimal salt concentration must be found resulting in a low viscosity. This concentration is determined experimentally in this section for the Taimicron powder with an average particle size of 0.2 μm.

- Optimal Salt Concentration for a Suspension with a High Solids Loading

The salt used to adjust the ionic strength needs to consist of components that are removed during sintering and do not contain undesired elements, such as for example Sodium.

(NH₄)₂CO₃ would be an ideal choice as it consists only of volatile compounds. However, this salt can not be used in the acidic regime because CO₂ evaporates upon the addition of the salt. Therefore, NH₄Cl (puriss p.a., Fluka, Buchs, Switzerland) was chosen for the experiments.

The suspensions were prepared according to the general procedure (Section 2) with the difference that instead of deionized water, NH₄Cl solutions with fixed salt concentration were used as suspension agent. Before each viscosity measurement the pH was adjusted to 4.5.

Viscosity was measured with a rotational viscosimeter (Rheomat 115, Contraves, Zürich, Switzerland). A cylindrical measurement tool with a rotating cylinder of 8 mm in
diameter and a slit width of 0.25 mm was used. Data was collected at 100 1/s for 5 s. Averages from 5 measurements were calculated.

Viscosities of 55 vol % suspensions with different salt concentrations were measured with a rheometer (Rheometer CS–50, Bohlin, Mühlacker, Germany), using a vane tool. Viscosities at a shear rate of 100 1/s were read from flow curves.

Solids loadings of the suspensions were determined by heating a suspension sample for two hours at 150 °C and measuring its weight loss.

Two arbitrary salt concentrations (0.03 M and 0.3 M) were chosen for initial measurements to determine the concentration regime that has to be investigated closer.

- Results and Discussion

The results of these initial experiments are plotted in Figure V.A-11. The viscosity of the suspension with 0.03 M salt is lower than that without salt. A salt concentration of 0.3 M already leads to higher a viscosity. Obviously the coagulation of the suspension has already started. The suitable concentration must be in the order of 0.03 M. For further investigation of the exact concentration with the lowest viscosity, suspensions with 55 vol % and different salt concentrations were compared.

![Figure V.A-11: Viscosity of suspensions with added salt with raising solid load measured at 100 1/s. Error bars are smaller than the symbols. The lines are drawn as visual guide.](image-url)
Figure V.A-12: Viscosity of 55 vol % slurries with varying NH₄Cl concentrations measured at 100 l/s. Error bars are smaller than the symbols. The data point at a concentration of 0.30 M illustrates the increase of viscosity at higher salt concentrations.

The results in Figure V.A-12 show that a plateau in viscosity is established at a NH₄Cl concentration of 0.05 M and above. This is in accordance with results obtained with different salts and different powders [5,8]. As the salt is present in the suspension and the water is evaporated upon drying, the salt crystallizes inside the green body. These salt crystals are embedded in the ceramic compact. For introducing as little defects as possible into the green body, as little salt as necessary was added to establish a low viscosity suspension. Salt concentrations between 0.05 and 0.07 M were chosen for further experiments.

With such a suspension, even large parts with a diameter of 55 mm could be fabricated without drying cracks.

Increasing the solids loading of boehmite suspensions by adding ions was also tried [8]. But the results were not as successful as with the Taimicron powder. The solid load could only be increased from 10 to about 15 vol % before the significant increase of viscosity occurred. This was attributed to the needle-like grain shape of the boehmite particles that strongly influences the suspension rheology.
Variation of Particle Size Distribution

Another method for increasing the solids loading of a suspension, besides the variation of the double layer thickness, is the variation of the particle size distribution. Under certain circumstances, small particles can fill voids that are present in a random packing of coarser ones and increase the overall density of the suspension. For understanding the principle of the effect, suspensions of spherical particles are discussed in the following. Three different cases are listed: Monosized particles, particles with a size distribution and bimodal particle mixtures.

- Monosized Particles

A colloidal crystal, a perfectly ordered structure of spherical particles of identical size, fills 74% of the available volume. When the particles are no longer ordered, but randomly packed, the packing density is lowered to 63.7% [9]. Additional voids are generated by breaking the long-range order of the particles and this leads to the decrease in packing density.
Log-normal distributed particles

Ceramic powders always have a particle size distribution, they are not monosized. A good approximation for the shape of the size distribution is a log-normal distribution of particle sizes [10]. The log-normal distribution is described in terms of the mean particle size $\bar{d}$ and the geometric standard deviation as follows:

$$P(x) = \frac{1}{\sqrt{2\pi} \cdot \sigma} \cdot \exp \left[ -\frac{\left( \ln d - \ln \bar{d} \right)^2}{2\sigma^2} \right]$$

where $P(x)$ is the probability of finding a particle with size $d$. The mean particle size is $\bar{d}$. The distribution spread parameter is defined as

$$\sigma = \ln \left( \frac{d_{84}}{d_{50}} \right)$$

where $d$ is the particle size and the subscripts indicate the respective percentage points in the cumulative particle size distribution.

The fractional density of randomly packed log-normal distributed powders increases with the distribution spread as shown in Figure V.A-15 [11]. For spreads of around 0.5 as they are commonly found in ceramic powders the packing density lies around 65%, slightly above the value for random packing of monosized particles.

Ceramic powders rarely have distribution spreads of more than 0.5. For example, the Taimicron powder with a $d_{50}$ of 0.2 $\mu$m has a spread of 0.2 when its particle size distribution is approximated with a log-normal distribution. With this spread, the maximal packing density is only slightly improved compared to a monomodal distribution. Just for illustration: if a distribution with a $d_{50}$ of 0.2 $\mu$m has a $\sigma$ of 5, the $d_{84}$ would be
30 μm. Such large particles (30 μm is only d₈₄, the d₉₉ is even higher) are clearly not feasible for the formation of micropatterns. Therefore, a change of the particle size distribution of the powder was not considered for experimental investigation.

![Random packing density of a log-normal distributed powder versus the standard deviation σ of the distribution](image)

*Figure V.A-15: Random packing density of a log–normal distributed powder versus the standard deviation σ of the distribution [11].*

- **Bimodal particle mixtures**

  A way for significantly increasing the packing density of particles is the use of a bimodal particle size distribution. This is obvious, when one imagines a dense packed structure of monospherical particles and then introduces a second particle family of reduced size which fits into the voids of such a structure. In order to lead to an increase in packing density the difference in particle size of the two powders have to be large enough.

  In Figure V.A-16 experimental results show the increase in fractional density with increasing particle size ratio [12]. From the density of 64% for random packing of monosized particles an increase in size difference leads to a steep increase of density up to 80% at a size ratio of about 8. At larger size ratios the curve starts leveling off and remains at 83% for particle size ratios larger than 20. This seems promising for our purpose and it was tried to reproduce this results with ceramic powders feasible for micropatterning.
Figure VA-16: Experimental results demonstrating the effect of particle size ratio on the packing density of bimodal powder mixtures (73 wt % large particles) [12].

A commercial powder generally used for slip casting is supplied with a bimodal particle size distribution. The two peaks of the distribution are at 0.8 and at 8 μm. Indeed, with the powder a very high solids loading of 63% can be achieved at a viscosity of 0.5 Pa·s at pH 4.5 without addition of any salt or other liquefier. However, for the purposes of the present work the powder particle size is too coarse.

Figure VA-17: Random packing of a bimodal mixture of spheres.

In order to achieve an increased solids loading with an identical feature quality the Taimicron powder with an average particle size 0.2 μm chosen in the previous chapter has to be blended with a powder which has a grain size smaller than these 0.2 μm. No α-alumina powder is available in this grain size regime. Therefore, only the boehmite powder with an average particle diameter of 50 nm is feasible. The Taimei powder and the boehmite thus have a particle ratio of 4:1. In the monodisperse case of Figure VA-16 this leads to an increase in solids loading of roughly 10% (from 0.64 to ~0.70), if the two
Pattee ned Surfaces 58

powders are mixed with a weight fraction of 73% large particles. The same was expected to happen with the suspension of Taimei and boehmite. However, this is less than the increase achieved by salt addition where the solids loading of the suspension was increased by 20%. The experiment reveals that no additional boehmite powder could be dispersed in a Taimicron suspension of 45 vol %, the viscosity of the suspension instantaneously increased to more than 1 Pa·s upon addition of boehmite.

In a more detailed study of the effect of boehmite addition to alumina suspensions, the nanoscale powder was added to suspensions of a powder with a d50 of 0.5 μm [8]. Here, the ratio of the average particle sizes is 1:10. Referring to the spherical particles of Figure V.A-16, this leads to an increase in particle packing density of over 25% from 0.64 to more than 0.8. However, the experimental results of the cited study demonstrate that even the smallest addition of boehmite leads to an increase in viscosity of the alumina suspension. In the experiments the overall solids loading of the suspension is held constant which means that the alumina content is decreased upon addition of boehmite. Also in this case the viscosity increases constantly with boehmite addition. Even when the strongly anisotropic particle shape of boehmite is taken into account an increase in packing density should be possible, however, to a smaller extent than in the case of a bimodal mixture of spherical particles. In Figure V.A-18 the packing efficiency of spheres and rods with an aspect ratio of 10 is shown [13]. The diameter of the spheres is 10 times larger than the diameter of the fibers. The packing density increases with fiber addition and has a peak at slightly over 20 vol %.

![Figure V.A-18: Packing density variation with composition for fiber-sphere mixtures with a fiber aspect ratio of 10 and a ratio of sphere diameter to fiber diameter of 10 [13].](image)

It is concluded that the double layer surrounding the boehmite particles greatly expands their volume in suspension and therefore lowers the maximal packing density upon boehmite addition. The increase in packing density predicted in theory can not be reproduced with the powder. Hence, the desired increase in solids loading at a fixed vis-
cosity (with all particle sizes smaller than 0.5 μm) could not be achieved by blending two different ceramic powders.

Conclusions

Compression of the electrostatic double layer of ceramic particles in aqueous suspensions diminishes their viscosity and therefore higher solids loadings can be achieved at a fixed viscosity. This is an effective way to produce defect-free micropatterned parts because the negative influence of shrinkage in contact with the mold is substantially reduced. An increase in solids loading by using a bimodal particle size distribution could not be achieved with powders of particle sizes suitable for the present investigation.

3.3 Surface Chemistry of PDMS

The surface of PDMS is hydrophobic, as the material has only methyl groups on its surface. Water exhibits a large contact angle of 120° on the mold surface. The question was if the quality of the produced micropatterns might be even better if the aqueous suspension wets the mold surface and spreads out on it. Therefore, parts made with hydrophilic and hydrophobic mold surfaces were produced and are compared below.

Experimental

PDMS molds were made hydrophilic by exposing them for two minutes to a 100 W oxygen plasma in a plasma sterilizer apparatus (PDC-32G Plasma Cleaner Sterilizer, Harrich Scientific, Ossining, NY, USA). The surface methyl groups of the polymer are partially transformed into hydroxyl groups during the process [14]. Water wetted readily on the PDMS surface after this treatment as shown in the contact angle measurements (NRL C. A. Goniometer, Ramé-Hart Inc., Mountain Lakes, NY, USA) in Table V.A-5.

<table>
<thead>
<tr>
<th>PDMS Surface</th>
<th>Water Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>120°</td>
</tr>
<tr>
<td>Oxygen Plasma Treated</td>
<td>2°</td>
</tr>
</tbody>
</table>

Table V.A-5: Contact angles of deionized water on PDMS before and after plasma treatment.
Figure VA-19: Mold and shaped ceramic part in case of hydrophilic (top) and hydrophobic (bottom) PDMS surface. The part shaped with the hydrophilic mold exhibits a poor surface quality because the powder particles adhered strongly to the mold and broke off upon demolding. A hydrophobic mold leads to good pattern quality, no residues remain on the mold. Cracks and distortions in the pictures of the molds are due to heating effects caused by the electron beam during imaging.

Results and Discussion

In Figure VA-19 the resulting ceramic structures and the respective molds used for shaping are shown. The part from the hydrophilic mold shows a poor pattern quality. By looking at the mold the reason for the bad quality is obvious: It is still covered with ceramic powder. The hydrophilic mold surface leads to a strong adhesion of the ceramic particles and this causes the layer of ceramic particles in direct contact with the mold to break off from the rest of the green body and to remain in contact with the mold. In case the PDMS is left in the native hydrophobic state there are no such strong adhesive forces. The green body can be demolded without leaving residues on the mold and the pattern quality is good.
Figure VA-20: Sintered samples reproduced with a PDMS mold. The right image with lower magnification shows the large area of good pattern homogeneity.

Conclusions

From the described experiment it can be concluded that a hydrophobic and there-with a water repelling mold surface is a necessary condition for the formation of high quality micropatterns from suspensions. The same result has been found in a study on polymer and metallo–organic solutions [15].

It would have been interesting to see if pattern replication is also possible in the reverse cast of repelling interactions, with a hydrophilic mold and a hydrophobic suspension. Unfortunately, PDMS easily swells in apolar solvents making pattern replication with a hydrophobic suspension impossible.

3.4 Conclusions

It has been shown in this chapter that defined alumina surface patterns in the micron range are feasible with a suspension based ceramic processing method. After optimizing the powder particle size, the solids loading of the suspension and the surface of the mold, the structures of Figure V.A-20 with a periodicity of 2.8 μm and a height of about 1 μm have been fabricated. The sample shows an excellent pattern quality over the whole surface area of 3 x 3 mm². The right image in Figure V.A-20 shows an area of lower magnification. The initial particle size of the alumina powder was 0.2 μm and it was processed as suspension of 55 vol % in water at pH 4.5 with a NH₄Cl concentration of 0.07 mol/l.
4 Applicability of the Process

After small surface structures have been realized with alumina, the question arises, what aspect ratios and smallest feature sizes are feasible using process. It has also to be shown, whether the process is transferable to ceramic powders other than alumina and whether mold materials other than PDMS can be used. Experiments regarding these four questions are reported in this section.

One general problem that arose during all the experiments was the availability of template structures. Custom patterns can be designed as lithography masks which can then be transformed into three dimensional template structures. However, the process of mask writing is costly and time consuming, but it is the only way to get custom made template structures. Cheaper templates are calibration grids for various microscopic techniques, but the designs of available templates is strongly limited.

4.1 Maximal Aspect Ratio

The maximal aspect ratio of the periodic structures used as templates is limited by the elastic properties of PDMS and not by the process itself. This flexibility on the other hand is beneficial for demolding the elastic stamp from the silicon master template and for demolding the green ceramic body from the PDMS mold after casting. However, the low elastic modulus of the material also causes limitations in mold design. Structures with an aspect ratio larger than about 1.5 tend to bend and adjacent structures stick to each other as illustrated schematically in Figure V.A-21 and shown in Figure V.A-22. This behavior was also found by other groups working with PDMS molds [16].

![Figure V.A-21: Bending and sticking of adjacent PDMS structures with high aspect ratio.](image)
4.2 Smallest Replicable Feature Size

The minimal feature size that is feasible with the process was determined by replicating a pattern of cone-shaped spikes. These structures were 1.5 μm in height with an aperture of 20°. The base of the cones has a diameter of 0.5 μm (Figure V.A-23). The alumina suspension used for replication had a solids loading of 55 vol % and was stabilized at pH 4.5 with a NH₄Cl concentration of 0.07 mol/l. The initial average particle size of the alumina powder was 0.2 μm.

The sintered alumina sample is shown in Figure V.A-24. The elevated tips of the replicated cones appear bright in the SEM. It can be seen that most of the structures are present in the image but they are not uniformly shaped. Some are more pronounced than others. The feature diameter of 0.5 μm is a little too small for a perfect replication with the alumina powder used. Therefore, considering also the good quality of the structures
in Figure V.A-20 it is concluded, that the minimal feasible feature size for the process
with this powder is 1 \( \mu m \).

What also strikes the eye is that the spikes have a much smaller size than the rest of
the microstructure. The bright spots have a diameter of about 0.5 \( \mu m \) while the underly-
ing dense alumina body has a grain size of 1–2 \( \mu m \).

![Image of microstructure](image)

*Figure V.A-24: Sintered alumina replica of the cone structure.*

4.3 Applicability of Various Ceramic Powders

The process was developed by using exclusively alumina suspensions as model sys-
tem. But it is not limited to alumina; it was only used because it is readily available in a
wide range of particle size distributions. In this section it is shown that powders other
than alumina can be patterned successfully with PDMS molds.

For the powders investigated below, not the whole suspension optimization process
was performed as it was for alumina. The solids loading of the suspensions was not tuned
to high values by the addition of salt. Therefore, some shrinkage defects occurred with
the samples shown below. Only about 80% of the 3 x 3 mm\(^2\) area of the samples was
defect–free.

**Zirconia**

With zirconia powder (TZ-3Y, Tosoh, Tokyo, Japan; \( d_{50} = 0.23 \mu m \)), doped with
3 mol % yttria, a 45 vol % suspension stabilized at pH 4.5 with hydrochloric acid
(Tritisol, Merck, Darmstadt, Germany) was used. The suspension was ball milled with
zirconia milling balls for 18 hours and subsequently degassed at 90 mbar after adding a
drop of 1–Octanol (puriss, Fluka, Buchs, Switzerland). Then, the suspension was cast
into the PDMS mold. After drying, sintering was performed with the following program:
Heating with 60 K/h to 850 °C, holding for 1 h at 850 °C, heating with 600 K/h to 1500 °C, holding 2 h at 1500 °C, cooling with 240 K/h to room temperature.

The resulting surface structure is depicted in Figure V.A-25. The pattern reproduction is good and the average grain size lies below 0.5 µm. However, the surface of the zirconia part appears slightly rougher than the one of the very smooth alumina part of Figure V.A-20.

![Image](image.jpg)

*Figure V.A-25: Sintered zirconia surface.*

*Cerium Gadolinium Oxide (CGO)*

This material is used as ion-conducting electrolyte in solid oxide fuel cells. The powder stoichiometry is Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$.

A 30 vol % suspension in water was prepared with a commercial CGO powder (Rhodia, Courbevoie, France; specific surface area 23 m$^2$/g). To 3 ml of water 0.2 ml of a 32 vol % solution of polyacrylic acid (Aldrich, Steinheim, Germany; molecular weight 2000 g/mol, adjusted to pH 8.4 with NH$_3$) were added as dispersion agent. The suspension was dispersed for 3 minutes with an ultrasonic horn (UP 200s, Dr. Hielscher GmbH, Berlin, Germany). After casting and drying, burnout of the organic additives was performed at 400 °C for 180 minutes. Then, the samples were doped with a Cobalt-containing solution (Co(II) nitrate hydrate in ethanol). Sintering was carried out at 1000 °C for one hour. The heating rate was 300 K/h in both cases.

The CGO surface of Figure V.A-26 shows the three dimensional surface structure with a nanocrystalline grain size below 0.1 µm. Also with this powder, the pattern was successfully transferred to the ceramic surface.
Tin Oxide

Tin oxide was chosen because the material is widely used in gas-sensing applications [17]. Microfabrication of such sensors is desirable for the integration of sensing elements directly into microelectronic circuits.

Figure VA-26: Sintered CGO surface.

Figure VA-27: Sintered tin oxide surface.

A 34 vol % suspension was prepared by adding SnO$_2$ powder (Cerac, Milwaukee, MI, USA; d$_{50}$ = 0.25 μm) to a mixture of 6 ml of deionized water and 0.1 ml of the same polyacrylic acid (PAA) solution, the same one as used for the CGO suspension. After all the powder was added, the suspension was ball milled for four hours. During milling, twice 0.05 ml of PAA solution were added. Then, the suspension was further dispersed for 10 min in an ultrasonic horn and subsequently degassed at 90 mbar after adding a
drop of 1-Octanol. After casting and drying, the part was sintered for two hours at 1200 °C.

In Figure V.A-27 the tin oxide surface is shown. The pattern is clearly resolved and of very good quality. The residual porosity in the body is intended. Gas detection with tin oxide sensors is based on the change of resistivity of the material when it is exposed to various gas atmospheres. The response time of such sensors is faster if residual porosity supports gas diffusion into the body.

4.4 Applicability of Various Polymeric Mold Materials

In order to determine if successful pattern replication is also possible with other mold materials an identical pattern was replicated with molds made of PDMS, high density polyethylene (HDPE), poly(tetrafluoroethylene–co–hexafluoropropylene) (FEP) and an epoxy system. The resulting ceramic parts were then compared.

*Experimental*

The mold fabrication process with the viscous PDMS prepolymer mixture is very simple and requires no polymer processing equipment, as described in Section 2.1. For other than crosslinked polymers such easily applicable prepolymer mixtures do not exist. Moldmaking has thus to be made with mechanical shaping technology. Molds of HDPE (Stamylan HD7048, DSM, Geleen, Holland) and FEP (Teflon FEP 100, DuPont Fluoro-products, Geneva, Switzerland) were produced by embossing polymer films at elevated temperatures and pressures with etched silicon template structures (TGG01, Paul Bucher AG, Basel, Switzerland) as described in Figure V.A-28 [18]. Epoxy (41.3 wt % Epon

*Figure V.A-28: Process schematic of embossing of polymer films at elevated temperatures and pressures.*
812, 54 wt % Dibutylphthalate, 4.7 wt % Durcupan ACM, all of Fluka, Buchs, Switzerland) molds were made by curing an epoxy system on embossed HDPE samples. For the exact processing details refer to [9]. The PDMS molds and the fabrication of the ceramic patterns for all molds were made according to the general procedure for alumina with a suspension of 55 vol % and a NH₄Cl concentration of 0.07 M.

**Results and Discussion**

The parts resulting from the different molds are pictured in Figure V.A-20 (PDMS) and Figure V.A-29 to Figure V.A-31 (Epoxy, FEP and HDPE). The samples show a good homogeneity over the whole patterned area of 3 x 3 mm². The structures replicated with PDMS, FEP and HDPE show almost an identical pattern quality. The single lines are clearly separated. With the epoxy mold the reproduction was not successful, the pattern shows a lower quality than the other ones. The reason for this is the hydrophilic nature of the mold that causes adhesion of powder particles.

The different grain shapes of the samples (which were all sintered simultaneously) were noticed but not further investigated in this study.

*Figure V.A-29: Sample reproduced with epoxy molds. Poor pattern reproduction is caused by particles remaining in contact with the mold upon demolding.*
Figure VA-30: Sample reproduced with FEP molds.

Figure VA-31: Sample reproduced with PE molds.

Conclusions

The micrographs show that good pattern replication is possible not only with PDMS but also with other mold materials for the investigated sample size of 3 x 3 mm$^2$. However, the fabrication of such molds is not as simple as for PDMS and it was not tried whether also larger molds can be made. With this aspect and based on the results of the previous section in mind, it can be concluded that a hydrophobic surface of the mold material is essential for successful pattern formation.
4.5 Conclusions

It has been demonstrated in this section that with the described process of slip casting into nonporous PDMS molds a very good pattern resolution of 1 μm can be achieved and that the results obtained with alumina can be transferred to other ceramic powders. Other mold materials than PDMS can also be used. However, these polymers do not offer as simple mold fabrication processes as PDMS does.

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>1 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspect Ratio</td>
<td>1</td>
</tr>
</tbody>
</table>

**Table VA-6: Process characteristics of the developed method.**

5 Feature Quality Comparison

In this subsection it will be shown that an increased microscopic accuracy also leads to beneficial results in the production of macroscopic parts. This was done by comparing the surface feature qualities of zirconia medals which were replicated with three different forming techniques from a metallic original, depicted in Figure VA-32. The first method is Direct Ceramic Machining (DCM, already mentioned in Chapter IV) in which the

![Figure VA-32: Metallic medal which was replicated in zirconia.](image)
parts are produced on a computer controlled milling machine. The second is slip casting, as it is widely used in manufacturing of traditional ceramics, and the third method is slip casting into nonporous polymer molds, as described in Section 2 of this chapter. It was expected that the use of PDMS molds, which is beneficial for microscopic feature sizes will also give the best results with a macroscopic part.

5.1 Experimental

Direct Ceramic Machining

In DCM the shape of the desired product is first digitized with a 3D sensor resulting in a digital representation of the surface. This data can be numerically enlarged in order to compensate the sintering shrinkage before milling. Then, a presintered ceramic blank is machined and subsequently sintered to full density. With this operation ceramic copies of identical size can be made from an original template [19].

In order to get the numerical data for the positioning of the machine the metallic template was mounted on the milling machine (Kern, Aarau, Switzerland) and the relief was digitized by scanning the surface line by line using a sapphire crystal with a spherical tip (0.5 mm in diameter) attached to a digitizing unit. The spacing of the lines in digitizing was 10 μm. The relief was subsequently milled into an uniaxially pressed and presintered disk (thickness: 8 mm, diameter: 110 mm) of zirconia powder (TZ-3YB, Tosoh, Tokyo, Japan). The density of the green body after pressing was 44% of the theoretical density. Presintering increases this value to 50%. The milling tool had a diameter of 0.5 mm and its tip was of spherical geometry. During milling, the incremental step width of scanning was also 10 μm. Sintering was performed with the following program: Heating with 60 K/h to 850 °C, holding for 1 h at 850 °C, heating with 600 K/h to 1500 °C, holding 2 h at 1500 °C, cooling with 240 K/h to room temperature. This program was chosen to take care of the burnout of the binder present in the powder used for DCM.
**Slip Casting**

In slip casting a suspension is cast into a porous mold, usually made of gypsum. The ceramic green body is solidified by removal of the water from the suspension due to capillary forces. For the fabrication of the mold, gypsum powder (Modellgips 0, Gipsunion, Holderbank, Switzerland) was mixed with water in a weight ratio of 2:3 and cast over the metallic medal. The latter was coated with a thin film of a separating agent (coconut grease and vaseline mixed 4:1 by weight) which was applied with a brush, removing excess material with a stream of hot air. The use of a separating agent was necessary in order to ensure a good demoldability of the metal template from the solidified gypsum. The diameter of the mold was chosen to be only slightly larger than the diameter of the medal. This geometry inhibits an extensive contraction in the plane of the medal and therewith limits the lateral shrinkage (Figure V.A-34). It is desired that the ceramic green body solidifies from the relief side towards its backside in order to ensure a defect-free filling of the mold. After removing the metal template the gypsum molds were dried first in ambient air for three days and then in a furnace at 50 °C for one day. Thereafter, a previously ball milled and degassed aqueous zirconia suspension (TZ–3Y, Tosoh, Tokyo, Japan) of 45 vol %, stabilized at pH 5 with nitric acid, was cast into the mold which was subsequently vibrated for two minutes (Vibro, Schierz & Hauenstein, Arlesheim, Switzerland) to ensure a proper filling of the mold. After careful drying for three days in laboratory atmosphere the ceramic medal was demolded, dried at 50 °C for three days and thereafter sintered according to the program mentioned above.
Slip Casting Into PDMS Molds

For casting into PDMS molds the identical zirconia suspension as for slip casting was used. The suspension was poured into the PDMS mold. After vibrating for two minutes to ensure a proper filling of the mold the samples were placed in a desiccator (volume ~2 liters) with water saturated air atmosphere. In the desiccator only a small opening of about 1 mm was present. With this setup, drying was extremely careful but also very slow, the process lasted about two weeks. After drying, the PDMS mold was peeled away from the dry green bodies and the parts were sintered according to the temperature program mentioned above.

5.2 Results and Discussion

The main criteria for comparison of the three fabrication methods, was the quality of the produced relief on the medal. For all methods the same region of the medal was enlarged and depicted. The respective area in the original medal, showing windows of the main building of the ETH is shown in Figure V.A-36. Besides the feature quality, also the speed and the applicability of the processes are discussed. Even though the compensation of the sintering shrinkage would have been possible with DCM, we intentionally retrained from doing it because a direct comparison of the three techniques was intended.

Direct Ceramic Machining

With DCM, all features of the windows are replicated in Figure V.A-36, but with low resolution. The balcony below the windows shows no details at all. With the process a lower sintering shrinkage is achieved because the blank ceramic part is already presintered and shrunk during this operation.

Both scanning and milling, the two mechanical processing steps limit the resolution of DCM. In each of the steps the part is scanned line by line. The radius of the sapphire tip used for scanning determines the quality of the digitized data and the diameter of the...
millng cutter used for machining the green body determines the resolution of the part. Tip diameters smaller than 0.5 mm could not be used because the force applied by the machine led to plastic deformation of the template during scanning. The stripe pattern generated by milling the ceramic material line by line is shown in Figure V.A-35. In areas containing many features, such as the window area in Figure V.A-36, this scanning pattern is not as obvious as in flat areas of the medal. However, this rather low resolution is the only limitation of DCM. The process offers several unique advantages. The most striking one is, that the copies and the original have identical sizes. By enlarging the scanned data before milling, the sintering shrinkage of the ceramic material can be compensated. Demolding is no issue, as the presintered blank is mounted mechanically onto the milling machine. Additionally, by reversing the blank after milling the front side of the medal, double-sided patterns can be produced. A drawback of DCM is the large investment that has to be made for buying the necessary equipment. The technique is fast, time consumption for milling and digitizing is about eight hours for each step. However, the ceramic parts need to be presintered before milling which requires an additional day.

![Figure V.A-35: Optical micrograph showing the line pattern generated by the milling cutter.](image)

**Slip Casting**

In the medal replicated with slip casting, the main features can be seen but fragile details of the windows can not be distinguished. It can also be seen that the surface is rougher than with the other methods.

The relatively poor pattern quality is caused by two resolution-limiting factors. First, the pattern of the original medal is slightly blurred by the application of a separating agent during mold preparation. The separating agent is needed for the removal of the template medal from solidified plaster mold. Second, the porous plaster material itself limits the achievable resolution, because of its finite particle size.

Regarding the production process, slip casting is a simple method. Drying of the parts can be done in laboratory atmosphere, no special drying rates are necessary. The
molds are very cheap and once they are available, a large number of parts can be produced in a short time. A problem that occurred with the medal was the absence of lateral shrinkage. Regarding the feature quality this effect is desirable, but it led to problems in demolding. Normally, in slip casting lateral shrinkage separates the green body from the mold. Then, the green body simply falls out of the mold when the latter is reversed. In the present case, the absence of lateral shrinkage leads to strong adhesion of the parts to the molds. For demolding, the parts had to be broken loose from the molds with a thin blade. If this is not done very carefully, either the green body or the mold can be damaged.

*Slip Casting Into PDMS Molds*

The best replication quality was obtained by using PDMS molds. All features of the metallic original are clearly present in the zirconia medal. Even the slightly patterned structure of the flat areas are replicated.

Because the solidification of the suspension is achieved by evaporation of the solvent, a careful drying process is crucial. In traditional slip casting with porous molds the particles get compacted at the interface to the mold and are already coagulated before the network starts to loose water. In the PDMS molds, the coagulation of the particles happens during drying. In this case continuous particle rearrangement occurs during drying as the particles are still stabilized in the beginning of drying. This can lead to crack formation if the rearrangement happens too fast. Besides the excellent pattern replication, another advantage of the use of PDMS molds with regard to plaster molds is the ease of demolding. The elastomeric PDMS can be simply peeled away from the green bodies and even complex geometries are left undamaged.

5.3 Conclusions

As expected, the best pattern quality was obtained by using PDMS molds. All details of the metallic template are clearly resolved. A drawback of the process is its need for very long drying times. The two other methods show significantly lower pattern resolution. They do, however, have their respective advantages: Slip casting is very fast and cheap, as the plaster molds can be reused with a short cycle time. With DCM shrinkage compensation is feasible and no mold has to be generated, however, expensive equipment is required.
Figure VA-36: Original medal and the three zirconia replicas. The linear sintering shrinkage for the ceramic medals is 7% for DCM and 20% for the two suspension-based processes.
6 Summary

It has been shown in this chapter that ceramic surface patterns of excellent quality with a resolution of 1 μm and an aspect ratio of 1 can be produced with a slip casting process using nonporous elastomeric molds. Several factors are crucial for the process. First, the average particle size of the powder has to be about one order of magnitude smaller than the features to be reproduced. Coarser powders lead to a significantly lower pattern quality. Second, a high solids loading of the suspension is essential to prevent drying shrinkage. As shrinking would occur in contact with the mold the fragile surface relief is destroyed during shrinking. In the present investigation the solids loading of alumina suspensions was increased by raising the ionic strength and therewith lowering the interaction of the particles. Third, a hydrophobic mold surface is necessary for a defect-free demolding of the cast ceramic parts. Hydrophilic molds lead to adhesion of powder particles to the mold and to an unsatisfactory pattern quality. The described process is not only suited for the formation of micropatterned ceramic surfaces, also macroscopic parts can benefit from the excellent surface quality.

The shaping process is applicable to different ceramic powders, not only to alumina which was successfully used for process development. Furthermore, various hydrophobic polymer mold materials are applicable, however, the primarily used two component poly(dimethyl siloxane) system offers the most convenient mold generation process.
7 References


V.B: Pattern Application to Flat Substrates

In this chapter, three different methods for the generation of micron-scale ceramic features on different flat substrate materials are investigated and their main issues are discussed.

1 Introduction

The aim of the work presented in this chapter was to find a processing technique suitable for the fabrication of micron-scale ceramic structures on arbitrary substrates, as already illustrated in the introduction of Chapter V. Possible applications are ceramic patterns in sensor technology. In this field a combination of two different materials is required: The sensing part has to be insulated at least electrically from the rest of the device in order to get a noise-free signal for detection.

In search of a suitable processing technique for micron-scale feature application we first look through the methods reviewed in Chapter IV:

- Screen printing is suited for the fabrication of coatings of various materials but the process lacks resolution, the desired few micrometers in structure width are not realizable.
- Etching techniques can provide small structures when a coating deposited with thin film techniques is patterned on an inert substrate, but the process is not applicable to all ceramic materials.
- The processes which include lost molds require mostly processing steps after sintering in order to achieve composite structures (for example a grinding step is required to place the second electrode in the fabrication process of the piezoelectric transducer with lost molds, as shown in Figure IV-2). However, such processing steps after sintering have to be avoided.

Hence, the only method mentioned in Chapter IV that can fulfill the requirements in lateral resolution is microcontact printing (Section 3.3 in Chapter IV).

Microcontact printing is one of several techniques developed in recent years and summarized under the expression 'soft lithography'. All these techniques have in common that micrometer scale structures are replicated without standard lithographic exposure techniques using a PDMS template in different ways. For a complete survey of the varieties of these techniques the reader is referred to the respective review literature [1,2,3]. In this investigation it was tried to adapt two soft lithography techniques to dense ceramic suspensions: Micromolding in capillaries (MIMIC) and microcontact printing (μCP). Besides these two techniques, presented in Sections 2 and 3, also a newly devel-
oped own technique, which uses photoresist structures as lost molds, was investigated (Section 4). Alumina was used as model material and the results were later transferred to other ceramic powders.

2 Micromolding in Capillaries with Ceramic Suspensions

In this technique substrates are patterned by capillary flow at the substrate surface. A PDMS mold forms three of the four capillary walls, the substrate itself being the fourth. Then a drop of liquid is placed at the open end of the capillaries and the liquid is dragged into the mold by capillary forces forming a pattern on the substrate surface (Figure V.B-1) [4]. Silicon wafers are normally used as substrates. In order to be able to demold the micropatterns the suspension has to be solidified after it has filled the capillaries entirely. According to literature prepolymers are often used to fill the capillaries [4]. Before removing the mold they can be easily crosslinked either thermally or photochemically. Drying of latex monosphere suspensions inside the capillaries is also reported [5].

In this section efforts to transfer these procedures for prepolymers and polymer suspensions to ceramic suspensions are reported.

Figure V.B-1: Process of micromolding in capillaries [4].
2.1 General Procedure

PDMS molds with straight capillaries were prepared by reproducing master structures made either by bookprinting lithography in magnesium sheets (capillary width ~50 μm) or by photolithography as photoresist structures on silicon wafers (capillary width ~5 μm). Before placing them on the substrates, the stamps were cut on both sides of the capillaries in order to get open ends. The suspension was then placed at one end of the capillaries and got dragged in gradually. Sooner or later the flow in the capillaries stopped and after a drying time of about an hour the stamps were removed and the ceramic patterns could be inspected. All experiments were carried out on glass substrates.

2.2 Alumina Suspensions

The main parameter for capillary flow is the wetting behavior of the capillary and the liquid medium. A contact angle smaller than 90° is needed. Without wetting, no capillary flow is observed. Water does not wet PDMS, the contact angle is 120°. Therefore pure water does not flow into a capillary of PDMS, even when the mold is placed on a hydrophilic substrate, as for example glass. For this reason, water based alumina suspensions can not be patterned in native PDMS molds. There are two possibilities to establish capillary flow: Either the suspension has to be made hydrophobic or the molds have to be adapted to aqueous suspensions by making them hydrophilic. Both cases have been investigated and shall now be discussed in detail.

Considering the many processing varieties discussed in the following, it might be helpful to refer to Figure V.B-12 which gives a condensed schematic overview.

**Hydrophobic Suspensions**

Various hydrophobic suspensions were made by dispersing alumina powder (HPA 0.5, Ceralox, Tucson, AZ, USA) in 50 ml of 2:1 mixtures of different alkane solvents and isopropanol adding one drop of dispersant (Beycostat, CeCa SA, Paris, France). This recipe was taken from literature [6]. The capillaries had a cross section of about 50 x 50 μm².

In first experiments, heptane (puriss, Fluka, Buchs, Switzerland) was used as dispersion medium in combination with isopropanol (puriss, Fluka, Buchs, Switzerland). The alumina suspensions of 30 vol % had an apparent viscosity of 0.05 Pa·s at 300 s⁻¹. They did not flow into the capillaries, however. This could be attributed to the relatively high evaporation rate (bp: 99°C) of heptane. As soon as a drop of suspension was placed at the end of the capillaries, the surface of the droplet dried, a rigid shell of powder particles was formed and no flow occurred. Subsequent experiments were made with two mixtures of different alkanes of higher boiling points: terpenalin (purum, Fluka, Buchs,
Switzerland; bp: 150–190 °C) and petrol (purum, Fluka, Buchs, Switzerland; bp: 180–220 °C). But also with suspensions based on these solvents the capillary flow was unsatisfactory; it stopped after a few seconds. Even though the suspension reservoir remained liquid after deposition at the PDMS mold the capillaries were only filled to a very small extent. Viscosity measurements revealed that all the suspensions showed shear thinning and a thixotropic hysteresis in their flow curve. A schematic representation of a typical flow curve is shown in Figure V.B-2. With this information, the behavior of the suspension can be explained: initially it has a low viscosity because the particle interactions are broken when depositing the suspension with a pipette at the end of the capillaries. In the flow curve of Figure V.B-2 this is the reversal point at high shear rates. But during the flow into the capillary, at the small shear rates induced by the capillary force, the viscosity increases again and further flow is inhibited.

![Flow curve of a shear thinning suspension with thixotropic hysteresis.](image)

It was also observed during the experiments that the alkanes caused swelling of the PDMS stamps. This is a normal reaction when crosslinked PDMS is in contact with apolar solvents [7]. In our process, this effect leads to a relative movement of the swelling stamp over the substrate surface which destroys the micropattern formed.

Because of the discouraging results with hydrophobic suspensions, aqueous suspensions were used for further experiments. Several possibilities to establish capillary flow with aqueous suspensions in PDMS molds were tried.

**Aqueous Suspensions**

Establishing capillary flow of aqueous suspensions into capillaries of PDMS was tried using various methods:

a) Change of the surface tension of the suspension by adding ethanol to water

b) Forcing capillary flow by applying vacuum

c) Plasma treatment of the PDMS to get a hydrophilic surface

d) Coating of the PDMS surface with surfactants.
The capillaries had a cross section of approximately 5x5 µm² and a length of approximately 10 mm. All experiments were carried out with an alumina powder with an average particle diameter of 0.2 µm (Taimicron TM–DAR, Taimei, Tokyo, Japan). Deionized water was used as suspension agent. The procedure of suspension preparation is described in Section 2.2 of Chapter V.A.

a) Alteration of the surface tension

The strongly repelling behavior of PDMS against water can be lowered by adding a less polar solvent, for example ethanol. This promotes the flow into capillaries [8]. An amount of 5 vol % (ethanol in water) was found to be sufficient.

We prepared suspensions with different ethanol contents (puriss, Fluka, Buchs, Switzerland), but even with a volume fraction of 30 % of the total amount of solvent no capillary flow was observed. With higher ethanol volume fractions the dispersion of the alumina powder was unsatisfactory.

Unlike in the experiments described in literature, this method was not successful for filling the capillaries with alumina suspensions. A reason for this discrepancy is not obvious and was not investigated any further. It may be that the suspension described in literature contained surfactants which were not explicitly mentioned.

b) Forcing capillary flow by applying vacuum

For this method slightly altered stamps had to be constructed. Only the end of the capillaries facing the suspension drop was left open. The other end of the capillaries led into a closed reservoir in the stamp. A needle of a syringe was stabbed through the PDMS into this reservoir and through this needle the vacuum was applied. A schematic of the setup is shown in Figure V.B-3.

![Figure V.B-3: Vacuum setup. A hollow needle is used to apply the vacuum to the capillaries.](image-url)
By applying vacuum the capillaries were readily filled. But in most cases the end of the stamp where the suspension entered into the capillaries was lifted off the substrate leading to a continuous ceramic layer between the stamp and the substrate.

The vacuum had to be left until the suspension had dried completely otherwise the filled capillaries emptied again.

c) Plasma treatment of the PDMS Surface

The PDMS surface can be made hydrophilic by an oxygen plasma treatment [9]. The presence of the reactive oxygen atoms leads to the replacement of the surface methyl groups by silanol groups. The treatment was done in a plasma cleaner (PDC-32G Plasma Cleaner Sterilizer, Harrick Scientific, Ossining, NY, USA) for two minutes at 100 W. Typically, the contact angle of water at the PDMS surface is 120° in the native state and only 2° after the plasma treatment. Such PDMS stamps could be filled over the whole length of about 10 mm. An area of perfect pattern replication is depicted in Figure V.B-4.

![Figure V.B-4: Region of perfect filling of the capillaries (unsintered, on glass substrate, alumina suspension of 30 vol %).](image)

The combination of an entirely hydrophilic stamp with a likewise hydrophilic substrate was problematic. Since the suspension wetted not only the inside of the capillaries but also the regions where the stamp was in contact with the substrate the stamp was partially lifted off from the underlying substrate. This led to the formation of a continuous layer of ceramic particles on the substrate, as illustrated schematically in Figure V.B-5.
Completely hydrophilic stamp in contact with a hydrophilic glass substrate.

When the capillaries are filled with the suspension, the latter is dragged into the contact areas of stamp and substrate.

The stamp is entirely lifted off the substrate and is floating on the suspension.

Figure V.B-5: Lift-off of a plasma treated stamp because the suspension is wetting the interface between the substrate and the PDMS.

To lower this effect it was tried to make only the walls of the stamp hydrophilic and to leave the area in contact with the substrate hydrophobic. For this purpose the native stamp which was already in contact with the substrate was put into the plasma chamber. The plasma should thus penetrate the capillaries and make them hydrophilic without affecting the PDMS areas in contact with the substrate (Figure V.B-6).

Figure V.B-6: Hydrophilic capillary walls and hydrophobic contact areas.

The suspension flow into these capillaries however stopped after about one millimeter. Obviously the plasma did not penetrate further into the narrow capillaries and the rest of the length remained hydrophobic. For further experiments a wet chemical method was chosen to make the capillaries hydrophilic.

d) Coating of the PDMS surface

In the first approach, a surfactant solution was dragged through the capillaries which were subsequently dried before starting the suspension flow. The surfactants remain on the capillary walls and make sure that there is capillary action. The stamps could not sim-
ply be immersed into a surfactant solution and afterwards be dried because by this treatment the entire PDMS surface would be changed.

Four surfactant solutions were tested:

- Stearic acid (purum, Carl Roth KG, Karlsruhe, Germany) in ethanol (puriss, Fluka, Buchs, Switzerland),
- Stearate in ethanol (stearate was made by dissolving stearic acid in 25% NH₃ solution and subsequent solvent evaporation),
- Triton X–45 (Polyethylene glycol 4–tert-octylphenyl ether) (Fluka, Buchs Switzerland) in water,
- Octadecyltrimethylammoniumchloride (purum, Fluka, Buchs Switzerland) in water.

Only with Octadecyltrimethylammoniumchloride was the suspension partially dragged into the capillaries, the three other surfactants showed no positive effect.

A possible reason for this is that the bifunctional molecules are not well ordered on the PDMS surface. It is a necessary condition, however, in order to achieve an alteration of the PDMS surface that all the molecules adsorb with their hydrophobic part on the PDMS and that all the hydrophilic groups stick into the capillary. Otherwise, the surfactants do not turn the PDMS completely hydrophilic.

Figure VB-7: Process schematic for the functionalization of PDMS with a self assembling monolayer.
As a second possibility, experiments with surfactants which form self assembled monolayers (SAM) were conducted. In microcontact printing, SAMs that formed on PDMS template structures are transferred onto different substrates [10,11,12]. A common system for this process is hexadecanethiol which is transferred onto a gold surface. The homogeneity of the SAMs on gold is very good, because the molecules have to be already well ordered on the PDMS before transferring them to the gold. After lifting the stamp off the gold surface, the areas of the PDMS which were in contact with the gold are no longer covered with hexadecanethiol. When the stamp is now placed on a glass substrate, the areas in contact with the glass are blank but on the walls of the capillaries there surfactant molecules are still present, as shown in Figure V.B-7.

With such stamps very good results were achieved in terms of capillary flow. Unfortunately, the affinity of the ceramic particles to the surfactant molecules was so high, that often parts of the ceramic lines were lifted off the substrate upon demolding, as can be seen in the central region of Figure V.B-8.

![Figure V.B-8](image)

*Figure V.B-8: In the central region of this image the alumina lines remained in the stamp upon demolding (unsintered, on glass substrate, alumina suspension of 30 vol %).*

**General considerations**

Besides the necessity to adjust the wetting behavior three other effects were observed during the investigation of MIMIC. Firstly, not all capillary dimensions are feasible, secondly, the flow into capillaries on glass substrates suddenly stopped after a few millimeters and thirdly, the occurrence of unusual flow patterns in the capillaries. These points are described and discussed below.
• Geometry of Capillaries

In Chapter V.A the limitations of PDMS for the generation of structures with high aspect ratio were discussed. High, slender structures tend to bend and to stick to each other which leads to flaws. The maximal aspect ratio is about 2. There is, however, also a limitation regarding small aspect ratios. When a very flat and wide capillary shall be generated, the soft PDMS bends and as soon as it touches the substrate the 'wetting' of the PDMS causes the capillary to close, as illustrated in Figure V.B-9. This effect was found to occur at aspect ratios lower than 0.5.

![Figure V.B-9: Instability of capillaries with low aspect ratios.](image)

• Reduced Flow on Glass Substrates

It was observed that the suspension flow in capillaries on glass substrates (microscope slides) was worse than on silicon wafers. The flow in capillaries on glass substrates stopped before they were entirely filled. A first possible explanation is that drying effects at the front of the suspension flowing through the capillary are responsible for the insufficient filling. Evaporation of water would lead to an increase of the concentrations of both the alumina powder and the salt added to reduce the viscosity of the suspension. Both effects, an increase of the solids load and an increase of the ionic strength, would lead to an increase of viscosity which can stop the capillary flow. However, experiments at 100% relative humidity revealed that drying is not the reason for the different behavior on the two substrates.

The real reason was an ion exchange reaction of the suspension with the underlying glass. Protons of the acidic suspension are exchanged with the alkali ions of the glass, the known acidic attack of sodium lime glass. The exchange reaction causes the proton concentration in the suspension to decrease, the pH increases. This also increases the viscosity of the suspension. However, on glass substrates which were immersed in concentrated hydrochloric acid overnight the capillaries were filled just as well as they were on silicon wafers.

• Flow in Rectangular Capillaries

In many experiments only a small amount of ceramic particles was found on the substrate after demolding. Either only the bottom of the capillary was covered with
ceramic particles or two narrow lines of particles were found on the edges of the capillary. The pattern as shown in Figure V.B-10 looks different from these regions where the ceramic line was broken away from the substrate (compare to Figure V.B-8).

![Figure V.B-10: Anomalous flow in capillaries (unsintered, on glass substrate, alumina suspension of 20 vol %).](image)

The transition regions from entirely filled capillaries to the two narrow lines at the edges of the capillary looks the same in all samples. At the end of the continuously filled capillary a concave meniscus is formed (Figure V.B-10). Behind this meniscus the suspension flows only at the bottom and at the edges of the capillary and no longer at all four walls.

Such a behavior has also been observed with other fluids, such as prepolymer [13]. The driving force is the different wetting of the PDMS and of the substrate material which form the capillary walls. It has been found that the described flow behavior in the capillary, schematically shown in Figure V.B-11, is characteristic for filling rectangular capillaries on hydrophilic substrates.

Material is also transported through the thin lines at the capillary walls. Towards the end of the capillaries, they are filled again totally. Very small powder particles get dragged along with the flow through the thin lines and are deposited at the opening of the capillaries when the water evaporates. The salt in the suspension crystallizes at the end of the capillaries.

![Figure V.B-11: Representation of the flow in rectangular capillaries on a hydrophilic substrate [13].](image)

In the present investigation the size of the spikes at the capillary boundaries depends on the solids content of the suspension. The higher the solids content, the less pronounced are the spikes and the more homogeneously the capillaries are filled. But with
increasing solids load also the viscosity of the suspension increases which slows down the capillary flow. The optimal solids content for suspensions with the investigated alumina powder having an average particle size of 0.2 μm was found to be 30 vol %. The flow was still sufficient and any irregularities were not too pronounced.

**Conclusions**

Although in literature very promising results were reported with micromolding in capillaries, the adaptation of the technique to alumina suspensions has not been successful. The reasons are, first, that no ideal surface treatment has been found to establish capillary flow without causing problems in demolding. Secondly, that the suspensions of alumina powders with a particle size distribution were negatively affected by the special flow pattern in the rectangular capillaries. A summary of the different modifications that were investigated and of the results that were observed is given in Figure V.B-12.

To bring it to a point, for the adaptation of micromolding in capillaries to alumina suspensions too many parameters play an important role in the behavior of the suspension. It might be possible to find a parameter set that allows the reproducible formation of alumina structures, but many more experiments with variations of all these parameters are needed. This would go beyond the scope of this dissertation.

![Figure V.B-12: Summary of the results obtained with different variations of micromolding in capillaries.](image)
2.3 Alignment of Vanadium Oxide Nanotubes

Introduction

Another scope we wanted to solve with micromolding in capillaries was the generation of order in a suspension of needle-shaped particles. The flow field in the capillaries should force these particles to align with their long dimension parallel to the capillary, like in the nematic phase of a liquid crystal [14]. As particle system, vanadium oxide nanotubes from a collaborating group were used.

Bulk measurements on pressed pills of such nanotubes have revealed a semiconducting behavior with a resistivity of 600 $\Omega$-cm at room temperature. In order to establish a link between these bulk measurements and measurements on single nanotubes, it was desirable to study the behavior of assemblies of oriented and aligned nanotubes. The intention was to make a four-point resistivity measurement on a line of consecutively oriented nanotubes. In this work the alignment of the nanotubes for such experiments was made by micromolding in capillaries.

Multi-walled vanadium oxide nanotubes are obtained as the main product in a sol-gel reaction followed by hydrothermal treatment from vanadium(V)alkoxide precursors and primary amines ($\text{C}_n\text{H}_{2n+1}\text{NH}_2$ with $4 \leq n \leq 22$). The alkylamines act as structure-directing templates and are intercalated in between the vanadium oxide layers [15,16,17]. The nanotubes typically have lengths of 2 to 5 $\mu$m, diameters of 20 to 200 nm and the single layers of the rolled structures are separated by 1.5 to 4 nm, depending on the length of the alkane chain of the alkylamine template which was used in the synthesis (Figure V.B-13).
Experimental

The capillaries in the PDMS stamps had a cross section of about 5 x 5 μm² and a length of about 10 mm, they were prepared according to the general procedure described in Section 2.2. All stamps were plasma treated to make them hydrophilic. The ideal dispersant for the suspensions of the nanotubes in terms of long time stability was chloroform. But as this solvent causes swelling of the PDMS, 1-octanol (puriss, Fluka, Buchs, Switzerland) was used as dispersant instead. After about one week on the shelf, the tubes were decomposed in octanol. But for the time ranges in the alignment experiments the stability of the octanolic suspensions was sufficient.

The suspensions were prepared by immersing the desired amount of nanotubes into octanol. A typical concentration was 1.5 wt %. The homogenization of the suspension was done in an ultrasonic bath for half an hour. After the ultrasonic treatment the suspension was centrifuged at 3000 rpm during 10 min to achieve the sedimentation of agglomerates. Roughly 5 vol % of the nanotubes sedimented. The supernatant suspension was thereafter decanted and used for the capillary experiments. Different nanotube batches of varying size and with different template molecules were used throughout the duration of the experiments. The exact properties of the different batches are listed in the respective figure captions.

As substrates for the capillary experiments glass slides were used. They were cleaned in chromosulfuric acid to remove organic impurities at the surface. After rinsing with deionized water and ethanol (puriss, Fluka, Buchs, Switzerland) the substrates were blown dry with nitrogen. Thereafter, the stamps were put onto the substrates and the suspension was placed at the open end of the capillaries with a pipette. All experiments were conducted in a laminar flow box in order to avoid dust contamination. After the capillar-
Patterning Coatings

ies were filled with the suspensions, the samples were left for at least three days to allow the evaporation of octanol. Afterwards the stamps were removed and the samples were examined by light and electron microscopy.

Results and Discussion

In some experiments good results were obtained, as can be seen in Figure V.B-14 for a concentrated suspension of 1.5 wt % in octanol. The single tubes are well ordered and the whole lines have a rather uniform geometry.

The width of the lines is easily controllable with the concentration of the suspension immersed in to the capillaries. In the more diluted case of 0.5 wt % in Figure V.B-15 much narrower lines were obtained, however, the concentration of nanotubes was too low to form continuously connected lines.

![Figure V.B-14: Wide lines of well aligned vanadium oxide nanotubes (template molecule C_{16}H_{33}NH_3; initial concentration of suspension 1.5 wt % in octanol).](image)

It is remarkable that the width of the lines of assembled tubes (1.5 μm) is much smaller than the width of the capillaries in the employed PDMS template (5 μm). During the evaporation of the octanol the tube assembly contracts only perpendicularly to its axis and not in longitudinal direction. The latter would cause gaps in the assembled lines, but none are observed in Figure V.B-14.

Unfortunately, the general reproducibility of the experiments was poor. When several identical samples were prepared simultaneously, it could not be predicted which sample showed good alignment and which did not. The most frequent failures were either partial liftoff of the stamp from the glass substrate due to insufficient adhesion of
the PDMS or inhibited flow due to numerous unaligned and interlocked nanotubes at the entrances of the capillaries.

![Patterned Coatings](image)

**Figure V.B-15**: Discontinuous narrow lines from a diluted suspension (template molecule $C_{12}H_{25}NH_2$; initial concentration of suspension 0.5 wt % in octanol).

**Conclusions**

The alignment of the needle-shaped vanadium oxide nanotubes in capillaries is feasible. However, before the desired resistivity measurements become possible, the reliability of the alignment process has to be improved; long, regularly shaped lines need to be made in a reproducible manner. One future effort to make the process more stable will be to build funnel-like structures at the opening of the capillaries to promote a narrowing linear flow. Thereby the nanotubes are automatically aligned and pile ups, which happened occasionally at the front side of the capillaries, is prevented.

3 Selective Wetting on Self Assembled Monolayers

In microcontact printing (μCP) self-assembled monolayers (SAM) of surfactants are transferred onto a surface by means of a patterned PDMS stamp (Figure V.B-16 a–c) [10,11,12]. A frequently used system is hexadecanethiol on gold surfaces. The surfactant layer that is transferred to the substrate can be used for example as mask for etching the underlying gold [10,11,12] or for selective additive reactions, as electroless deposition [18,19]. The alkane tail of hexadecanethiol that sticks away from the gold surface makes it strongly hydrophobic. If such a gold substrate, which is partially covered with the SAM of hexadecanethiol and partially blank, is immersed into a solution of a hydrophilic
thiol, the latter adsorbs on the blank parts of the substrate, leading to a partially hydrophilic and partially hydrophobic substrate (Figure V.B-16 d). Such substrates can be used for various purposes. Water and aqueous solutions only adsorb on the hydrophilic parts of the surface. When a patterned substrate is withdrawn from an aqueous solution, small droplets are formed on the hydrophilic part of the surface (Figure V.B-16 e). By evaporating the water or by initiating a precipitation reaction, for example by shifting the pH with ammonia vapor, the substrate can be coated with a precipitated salt [18]. When a functionalized substrate is selectively wetted with a monomer, the latter can be cured and patterned polymer structures are formed [20,21]. Even biological structures are sensitive to different surface chemistries, for example self-assembly of proteins [22] and cells [23] on patterned substrates has been reported.

Figure V.B-16: Schematic diagram of the selective wetting process. A substrate coated with a thin gold layer is functionalized with a hydrophilic and a hydrophobic self-assembled monolayer (see text for processing details). By dipcoating in an aqueous suspension, a ceramic pattern is formed on the hydrophilic part of the surface.

In this study we tried to transfer the reported work on selective wetting of aqueous solutions to dense aqueous suspensions. For the fabrication of ceramic structures, dense suspensions are required. If the wetting experiments would be done with precursor salt solutions, the large shrinkage during calcining of the precipitated metal hydroxides would make it impossible to form continuous structures, for example lines. Using the
precipitation process only discontinuous dot-structures are reported in literature [18]. Another reason for a powder based processing method is that suitable salt precursors cannot be found for all materials.

**Experimental**

The substrates were prepared by sputtering a gold layer of 100 nm thickness onto silicon wafers. In between the gold and the wafer a 10 nm thick chromium layer was deposited as adhesion promoter. The PDMS stamp was inked for 30 minutes in a 5 mM solution of hexadecanethiol (pract., Fluka, Buchs Switzerland) in ethanol. Then, the stamp was removed from the solution, rinsed with pure ethanol and dried with a stream of nitrogen. Subsequently, it was placed on the surface of the substrate for 20 seconds. After removing the stamp, the substrate was immersed into a 5 mM ethanolic solution of a thiol with a hydrophilic endgroup for 30 minutes. The substrate was then removed from the solution, rinsed with ethanol and dried with a stream of nitrogen. The functionalized substrates were then coated with the ceramic suspension by dipping them into alumina suspensions by hand.

The following parameters were varied:

- **Suspension:**
  Alumina suspensions of 37 and 45 vol % were prepared in 0.05 M NH₄Cl and in pure water.

- **Surfactant molecules of the hydrophilic SAM [18]:**
  - Potassium thioacetate, CH₃COSK, (purum, Fluka, Buchs, Switzerland)
  - Cysteamine hydrochloride, HSCH₂CH₂NH₂HCl, (MicroSelect, Fluka, Buchs, Switzerland)
  - Sodium 2-mercaptopoethanesulfonate, HSCH₂CH₂SO₃Na, (>98%, Fluka, Buchs, Switzerland)
  All surfactant molecules were used as 5 mM solutions in ethanol.

- **Structure width of the stamped line pattern:**
  Line patterns of 5 and 20 μm in width and spacing were used.
  However, not all parameter combinations were investigated, it was assumed that the general conclusions are mutually applicable.

**Results and Discussion**

Regarding the suitable linewidth it was found that the pattern with a line width and a line spacing of 5 μm was not feasible. The suspension was not repelled by such narrow hydrophobic lines, the substrates behaved like they were totally hydrophilic and were entirely covered with alumina particles upon removal from the suspension. Obviously,
the 5 \( \mu \)m wide lines were too narrow for a selective adsorption of the suspension. On the substrates patterned with 20 \( \mu \)m wide lines and spaces good results were obtained. The failure of the experiments with a resolution of 5 \( \mu \)m is in contrast to results reported in literature where structure sizes of some micrometers were achieved with selective wetting [18]. Probably the higher viscosity of the suspensions used in our study is responsible for this discrepancy. Water has a viscosity of 0.01 Pa·s at room temperature [24]. The viscosity of diluted solutions (as used in the reported literature) might be slightly higher than for pure water but still around the same value. However, the viscosity of the alumina suspensions is more than one order of magnitude larger.

The addition of \( \text{NH}_4\text{Cl} \) to the suspension was crucial. Without salt, the suspension did not selectively wet the patterned substrate, only a dense, continuous layer was formed. The change of viscosity by the addition of salt can not explain this behavior. In the investigated concentration regime below 50 vol \% the salt causes only a minor reduction of the viscosity (compare to Figure V.A-11). However, not only the viscosity but also the surface tension is affected by the salt. When added to pure water, salt increases the surface tension of the solution [25,26].

In order to get a rough estimate of the change of the surface tension of the suspension by the salt addition, the weight of suspension droplets generated with a pipette was measured. The surface tension \( \sigma \) of a liquid is related to the weight of a droplet \( W_D \) and the radius of the capillary \( r_C \) in the following way [27,28]:

\[
W_D = 2\pi r_C \sigma
\]

The surface tension of distilled water at room temperature is \( 7.275 \times 10^{-2} \) N/m [24]. With the described method a value of \( 10.0 \times 10^{-2} \) N/m was obtained. For the comparison of several liquids measured in the same way the accuracy of the method is sufficient.

The surface tension of the suspension is significantly lowered by the salt addition as can be seen in Table V.B-2. With the other solid loads also a decrease in surface tension has been observed. It seems that a lower surface tension is favorable for the wetting process.

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>37 vol % alumina suspension</th>
</tr>
</thead>
<tbody>
<tr>
<td>no salt added</td>
<td>10.0 ( \times ) 10^{-2} N/m</td>
<td>8.81 ( \times ) 10^{-2} N/m</td>
</tr>
<tr>
<td>0.05 M ( \text{NH}_4\text{Cl} )</td>
<td>10.4 ( \times ) 10^{-2} N/m</td>
<td>3.87 ( \times ) 10^{-2} N/m</td>
</tr>
</tbody>
</table>

*Table V.B-2: Change of surface tension of water and of an alumina suspension by the addition of ammonium chloride. The initial value of water is slightly increased, that of the suspension is signifi-
lightly lowered by the salt addition.
Radius of capillary $r_c$: 0.535 mm.

Regarding the volume content of the suspensions the one with the highest solids loading of 45 vol % showed the best resolution. The reason for this is the reduced drying shrinkage compared to the other suspensions. Probably a even higher solids loading would be favorable. The upper limit of 45 vol % in the experiments was caused by the parallel investigation of suspensions with and without salt addition. In the latter case only suspensions with a solid load of 45 vol % can be processed because of the viscosity increase with increasing solids loading.

Of the investigated SAM molecules, with cysteamine hydrochloride and sodium 2-mercaptopoethanesulfonate as hydrophilic layer good results were achieved. The patterns made with cysteamine hydrochloride even exhibited a slightly better quality than the ones of sodium 2-mercaptopoethanesulfonate, as can be seen in Figure V.B-17. The ends of the ceramic lines, dark in the microscope image, show better resolution in the right image, in the left image these regions are slightly blurred.

![Figure V.B-17: Unsintered alumina lines (dark) on a gold surface. In the left image sodium 2-mercaptopoethanesulfonate was used as hydrophilic SAM, in the right one a layer of cysteamine hydrochloride was present. With the latter a slightly better edge resolution was achieved.](image)

With a SAM of potassium thioacetate no pattern transfer was possible. It seemed like the thioacetate removed all the hexadecanethiol from the gold surface. The whole substrate was hydrophilic after immersing it partially covered with hexadecanethiol into the thioacetate solution.

The morphology of the ceramic lines formed by selective wetting is governed by the contact angle and the surface tension of the suspension. The ceramic micropattern has a
characteristic rounded shape which is illustrated in a cross section of a sample (Figure V.B-18), recorded with an atomic force microscope. This leads to a limited aspect ratio of 0.1–0.2 for the structures produced with this method.

Figure V.B-18: AFM cross section of deposited alumina lines revealing their rounded shape (note the different scaling of the axes).

The gold layer in between the silicon wafer and the ceramic features melts upon sintering of the alumina. This causes delamination of the ceramic structures, as shown in Figure V.B-19. The gold coalesces into small droplets of 3–5 μm in diameter. Although chemical removal of the gold before sintering is possible [29] we wanted to use no gold layer at all and use a different monolayer/substrate system. A first approach was to use carboxylic acids on sapphire single crystals. These molecules have been found to self-assemble on oxidized aluminum single crystals [30,31,32]. Unfortunately, these results could not be transferred to the polished sapphire single crystals used in this work. The
carboxylic acids did not self-assemble on sapphire as revealed in UV spectra. The reason for this behavior was not obvious and was not further investigated.

**Conclusions**

Microcontact printing and subsequent selective wetting is a simple method which is feasible for the generation of ceramic microstructures in the range of 20 μm. However, the aspect ratio as well as the rounded geometry of the structures is implicated by the process and can not be altered. In order to be suitable for sensor applications a SAM/substrate combination that avoids the use of a gold layer has to be found. Furthermore, also the solids loading of the suspensions should be increased further and a more uniform deposition technique than dip coating has to be found, for example spin coating would be a possible method.

<table>
<thead>
<tr>
<th>Selective Wetting of Ceramic Suspensions</th>
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<tbody>
<tr>
<td><strong>Smallest Lateral Dimension</strong></td>
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<tr>
<td><strong>Aspect Ratio</strong></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>- simple technique</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Disadvantages:</th>
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</thead>
<tbody>
<tr>
<td>- average resolution</td>
</tr>
<tr>
<td>- limited aspect ratio</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Remarks:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Results must be transferred to different SAM/substrate systems.</td>
</tr>
</tbody>
</table>

**Table V.B-3: Process characteristics of selective wetting.**

4 **Filling of Photoresist Molds on Substrates (FPM)**

The method presented in this chapter is new. It combines the accuracy and the versatility of lost mold techniques with the possibility to use arbitrary substrates for coating. Unlike the two methods presented before, it does not use self-assembly of any kind. The pattern is transferred mechanically.

The idea for the process was developed by working with the silicon wafers and the photoresist that was used in the template fabrication for replicating PDMS molds. If a flat substrate is patterned with photoresist, a three dimensional structure is generated at its surface. This structure can be used as a mold by itself. The bottom of the mold is made of the ceramic substrate and the walls consist of photoresist (Figure V.B-20). The suspension is cast into this mold and the excess suspension that covers the entire substrate is removed. The thin layer of ceramic material dries instantaneously. Thereafter, the photo-
resist is removed, the part is sintered and the substrate is covered with the ceramic structure.

![Diagram](image)

**Figure V.B-20: Schematic of pattern formation by FPM using photoresist structures as lost molds.**

**Experimental**

Photoresist structures on silicon wafers and on glass slides were used, sintered samples were prepared on silicon and on sapphire single crystals.

The photoresist pattern was applied by standard ultraviolet lithography techniques. After mounting on a spin coater, the substrates were cleaned with pressurized nitrogen and acetone (puriss, Fluka, Buchs, Switzerland) and spun dry. Then they were coated at 200 rpm with photoresist (AZ 4562, Clariant, Wiesbaden, Germany). The resist was exposed for 30 seconds to UV light in a maskaligner (MJB 3, Karl Süss AG, Munich, Germany) through a chromium pattern on a glass substrate. The resist pattern was subsequently developed (MF-319, Shipley, Berlin, Germany). The lithographic patterns had a height of approximately 5 μm and a width of 5 and 20 μm respectively.

Alumina suspensions (TM–DAR, Taimei, Tokyo, Japan) of 50 vol % and zirconia suspensions (TZ–8Y, Tosoh, Tokyo, Japan) of 45 vol % were used. The preparation of the alumina suspensions is described in Section 2.2 of Chapter V.A. Zirconia suspensions were prepared using the same processing steps as described for alumina. However, the suspensions were stabilized at pH 5 and zirconia milling balls were used. The
cubic coating was applied to the substrates with the photoresist structures by pouring some of the suspension over the mold and subsequently removing the excess material with a polymer blade as it is used in screen printing. However, by simply scraping over the photoresist not all particles were removed from the top of it. The resist was still covered with a thin ceramic layer. In order to remove also these particles, an adhesive tape was put onto the ceramic pattern, gently pressed to the sample and subsequently peeled off again. This procedure was repeated until the photoresist appeared clean upon inspection under the light microscope. Thereafter, some of the samples were either put directly into the sintering furnace where the photoresist was pyrolyzed during heating. From other samples, the resist was removed before sintering by cautiously dipping the substrate into a beaker of acetone to dissolve the photoresist. Then, these samples were sintered. After sintering the adhesion of the ceramic structure to the substrate was tested by putting an adhesive tape on the ceramics and pulling it off again [33].

Results and Discussion

A typical sample on which the photoresist structures were pyrolyzed before sintering is shown in Figure V.B-21. The ceramic structures broke along the photoresist and continuous parts of the ceramic became stuck to the substrate. The effect also occurred when the samples were sintered upside down. The parts that broke off also sintered onto the substrate when they had to move against gravity.

![Image of Alumina structure on silicon wafer](image)

*Figure V.B-21: Alumina structure on a silicon wafer, sintered at 1350 °C. The photoresist was pyrolyzed before sintering. At all photore sist–ceramic interfaces a continuous part of the ceramic material broke off and sintered to the substrate.*
A thermogravimetry (STA 501, Bähr, Hüllhorst, Germany) experiment in air revealed that the photoresist is pyrolyzed in the range between 400 and 500 °C. To investigate the cause of the cracking, several samples were put into a furnace which was heated to 500 °C. At different temperatures a sample was taken out of the furnace and investigated in the SEM. The results are depicted in Figure V.B-22. It can be seen that already at 300 °C, hundred degrees below the start of the decomposition reaction, small cracks can be found near the interface of ceramic and photoresist. At 400 °C these cracks become wider. Continuous parts of ceramic material are adhering to the photoresist. At 450 °C the decomposition of the photoresist can be seen which is finished at 500 °C. During the reaction the ceramic material moves closer to the substrate as shown in Figure V.B-22: SEM images of different stages of the pyrolysis process. 

Figure V.B-22: SEM images of different stages of the pyrolysis process. Already at 300 °C cracks are formed, as can be seen on the inset. At 400 °C these cracks have become larger. Then the pyrolysis of the photoresist starts. At 500 °C the polymer is removed and the edges of the ceramic lines broke off and are lie on the substrate.
Figure V.B-23. The sample now looks like the sintered one of Figure V.B-21, without the cracks perpendicular to the lines. These cracks are formed during sintering and caused by flaws generated from the breakoff of the edges of the ceramic lines.

The crack pattern along the interface of photoresist and alumina is most probably generated by a shrinkage process in either one of the materials. A possible cause for shrinkage of the photoresist may be that residual solvent, which was still present in the polymer after the softbake process, evaporates. Another possibility is that the alumina shrinks because of water evaporation. To determine whether the cracks are caused by an evaporation process, a sample was annealed for 5 hours at 200 °C. At this temperature the solvent in the photoresist as well as the water in the alumina should evaporate. After this heat treatment the sample exhibited no cracks. Hence, the cracks in the ceramic samples must have another origin. One might also consider the possibility that an internal reaction in the photoresist above 200 °C causes the volume shrinkage. Such reactions could be a rearrangement in the polymer or a crosslinking reaction that leads to shrinkage. A differential scanning calorimetry experiment (DSC 200, Netzsch, Selb, Germany) revealed that no crystallization occurs in the polymer during heating to 400 °C. As photoresist materials are not designed for treatment at high temperatures this behavior is undocumented.

![Diagram of flaw formation during pyrolysis of the photoresist.](image)

*Figure V.B-23: Schematic of the flaw formation during pyrolysis of the photoresist.*

By dissolving the photoresist in acetone before sintering, defect-free samples as the one shown in Figure V.B-24 were obtained. The slight blurrings at the corners of the structure are caused by incomplete removal of the excess suspension with the polymer blade and the adhesive tape.

After process development with the 20 μm wide pattern shown in the previous figures the resolution was increased and also 5 μm wide lines were made, as shown in Figure V.B-25. The process we used for generating the lithography masks does not allow
the generation of features narrower than 5 µm. Therefore, this was the smallest feature size that was produced.

Figure V.B-24: Alumina structure on a silicon wafer, sintered at 1350 °C.
The photoresist was dissolved in acetone before sintering.
Ceramic structures of good quality are obtained.

Figure V.B-25: Alumina structure on a silicon wafer, sintered at 1350 °C.

Zirconia lines on a silicon wafer are shown in Figure V.B-26. In this case, it was not possible to achieve defect-free samples. The zirconia lines show cracks perpendicular to the lines. This was caused by the different thermal expansion coefficients of zirconia and the silicon substrate, as seen in Table V.B-4. The fact, that the lines cracked and did not
delaminate from the substrate shows the good adhesion between the ceramic structure and the substrate.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\alpha \times 10^6$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>3</td>
</tr>
<tr>
<td>Alumina</td>
<td>5.5</td>
</tr>
<tr>
<td>Zirconia</td>
<td>9</td>
</tr>
</tbody>
</table>

*Table V.B-4: Linear thermal expansion coefficients at room temperature [24].*

*Figure V.B-26: Zirconia structure on a silicon wafer; sintered at 1350 °C. Cracking occurred perpendicular to the long dimension due to a mismatch in thermal expansion coefficients. No delamination occurred.*

**Conclusions**

Very promising results were achieved with the described method. The dimensions of the structures shown is limited by the photoresist templates that were used. As the templates were only available with a resolution of 5 μm and an aspect ratio of 1, no other features were produced. Even though in the process the excess suspension was removed by hand with the polymer blade a very good feature quality was obtained and the results
were reproducible. A drawback of the technique is, that it is necessary to process every substrate in a cleanroom.

<table>
<thead>
<tr>
<th>Smallest Lateral Dimension</th>
<th>5 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspect Ratio</td>
<td>1</td>
</tr>
</tbody>
</table>

**Advantages:**
- simple technique
- good resolution

**Disadvantages:**
- limited aspect ratio

**Remarks:**
Every substrate needs to be processed separately in a cleanroom.

*Table V.B-5: Process characteristics of FPM.*
5 Summary and Conclusions

In the following, the methods investigated in this chapter are compared regarding the following criteria:

Resolution and Aspect Ratio

The resolution of micromolding in capillaries (MIMIC) and of filling of photoresist molds (FPM) is 5 μm or lower, this is in accordance with the aim of the study. With selective wetting, only structures with a width of 20 μm were feasible. Unfortunately none of the techniques is capable of producing structures with an aspect ratio larger than 1. With MIMIC and FPM an aspect ratio of 1 can be obtained, selective wetting achieves 0.1.

Reproducibility

MIMIC suffers from a poor reproducibility. The capillaries are not filled uniformly with the suspensions. This strongly limits the applicability of the technique. The two other methods have significantly better reproducibilities.

Simplicity of the Process

The biggest disadvantage of FPM is the complexity of the process. Every substrate has to be processed in a cleanroom. For the two other techniques conventional processing techniques can be used once the master template structure for the PDMS stamps is available. Especially selective wetting is a very elegant and simple technique, as the ceramic structures are generated by self-assembly on the substrate and no mechanical molds are in contact with the ceramic suspension.

Transferability

A very important criterion for further applications is the transferability of the techniques to systems other than the suspension / substrate systems investigated in the process development. Here, selective wetting is the most challenging, because a molecule that forms self-assembling monolayers has to be found for every substrate. Especially for polycrystalline materials this is a major limitation. In MIMIC not the substrate but the ceramic suspension is the problem. It needs to be adapted to the PDMS molds which was not easy even for alumina. The only restriction for the use of photoresist molds is that water based suspensions must be used because organic solvents dissolve the photoresist.

Possible Pattern Geometries

All the processes have limitations regarding the geometries of the patterns which are feasible. MIMIC only allows the production of interconnected structures, dot-patterns can not be produced. The use of PDMS as material for creating the surface capillaries also implies limitations on the aspect ratio of the produced structures. The aspect ratios that can be produced are in the range of 0.5–2. Only the aspect ratio of the structures pro-
duced by selective wetting is limited, in principle all two dimensional patterns can be produced. In FPM, the limitations are due to the lithography process. Like in selective wetting, all pattern geometries are feasible, but with this process aspect ratios of up to 1 are feasible.

<table>
<thead>
<tr>
<th></th>
<th>MIMIC</th>
<th>Selective Wetting</th>
<th>FPM</th>
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<tbody>
<tr>
<td>Resolution</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Reproducibility</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Simple Process</td>
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<td>-</td>
</tr>
<tr>
<td>Transferability</td>
<td>0</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Pattern Geometry</td>
<td>-</td>
<td>0</td>
<td>+</td>
</tr>
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</table>

*Table V.B-6: Comparison of the three processing methods.*

Considering all the advantages and disadvantages of the various techniques, the photoresist mold is the most promising to be developed further. In spite of the relatively complicated mold generation process it is preferred to the other methods because the limited reproducibility of MIMIC and the limited transferability of selective wetting are regarded as more severe drawbacks.
6 References


VI General Conclusions

Two different strategies to miniaturize ceramic surface structures were explored. The formation of bulk parts with a micropatterned surface and the formation of ceramic structures on a substrate of different material. For both pathways a fabrication method was developed which is compared in the following to the requirements listed in the aim of the study:

- A resolution of a few micrometers should be feasible
- The processing method should be versatile and should be able to use commercially available powders of different composition as raw materials
- The process should enable the production of ceramic microcomponents on various substrate materials
- The molds should be reusable in order to be cost effective
- Expensive machinery should be avoided.

For surface structured bulk samples, slip casting into nonporous elastomeric molds, is very suitable, as can be seen in Table VI-1.

<table>
<thead>
<tr>
<th>Slip casting into nonporous polymer molds</th>
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<tbody>
<tr>
<td>Resolution</td>
</tr>
<tr>
<td>Various powders applicable</td>
</tr>
<tr>
<td>Coating of substrates possible</td>
</tr>
<tr>
<td>Reusable molds</td>
</tr>
<tr>
<td>No machinery needed</td>
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</tbody>
</table>

Table VI-1: Fabrication method for patterned surfaces.

For applying surface structures on various substrates, slip casting into photoresist molds is preferred. With this method, arbitrary substrates can be coated with ceramic structures, however, it suffers from certain limitations, as shown in Table VI-2. Lost molds have to be used, which in addition need to be made with a costly cleanroom process. Nevertheless, also with this technique, the goals in resolution and in transferability to other powders are achieved.
General Conclusions 114

Filling of photoresist molds

<table>
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<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Resolution</td>
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<tr>
<td>Various powders applicable</td>
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<td>Coating of substrates possible</td>
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<td>Reusable molds</td>
<td></td>
</tr>
<tr>
<td>No machinery needed</td>
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</table>

Table VI-2: Fabrication method for patterned coatings.

In general, it can be said that with both processes the demands in terms of resolution, which are the most important ones in this work, are fulfilled. It should now be possible to integrate these features of 5 μm and below into microchip-based devices. One particularly promising application is described in the outlook below.
VII Outlook

It has been shown in this work that ceramic structures with dimensions of 5 µm can be produced with powder-based techniques. The next step now is to make a functional device by using the developed techniques. One particularly interesting application is the fabrication of a so-called 'electronic nose' for gas detection. Such sensors are used for monitoring the concentrations of different gases, the most common applications of gas detection are leakage detection for gas pipes in houses and the lambda–sensor in automotive exhausts. Unfortunately, most of the materials used in gas detection show a relatively poor selectivity. This means that an identical signal is generated by various gaseous species. To overcome this problem, several different single sensors can be combined in an array, which results in a much better selectivity of the entire device [1,2]. Various possible designs of electronic noses have been proposed [3,4]. Most of the microfabricated multi–sensor arrays investigated use polymers as sensing materials [5,6], however, arrays using oxide sensor materials are also produced [7]. The advantage of oxide sensor materials in contrast to polymers is their feasibility for detection of hot gases, for example in exhaust streams.

![Diagram of proposed sensor array](image)

Figure VII-1: Design of the proposed sensor array using microfabricated tin oxide dots with different dopant concentrations as sensing elements.

In continuation of the present work it is planned to use the methods developed to fabricate a miniaturized sensor array of many single sensor pads of oxide ceramics. The design of the proposed microfabricated sensor is shown in Figure VII-1. The single sensor pads, in the size range of 10 µm, are doped with perpendicular gradients of two dif-
different elements. These dopants slightly change the selectivities of the single sensors which leads to an increased selectivity range of the whole array. With a wiring of perpendicular continuous contacts it is possible to read the signal of every single sensor individually without the need for applying separate electrical contacts to every pad. By continuously switching between the contacts, the response of the whole sensor is recorded and can be processed by a computer.

Tin oxide is going to be used as sensing material. This material is quite common in sensors for gas detection [8]. It has a good sensitivity and selectivity, especially if it is used with a nanocrystalline microstructure [9,10]. The selectivity of tin oxide can be changed by doping with palladium, platinum or silver [11,12]. Current tin oxide sensors are microfabricated mostly by using thin film technologies such as sputtering and evaporation [13]. On the other hand, suspension-based methods, as for example screen printing [7], have the advantage of a better microstructural control, as the final grains are not generated by deposition from the vapor phase but by sintering of a ceramic powder. Regarding the work already performed on tin oxide suspensions, the adaptation of this ceramic material to the processing methods developed in the present work seems feasible.
References


Appendix

Further details concerning applications of micropatterned ceramics, mold fabrication and ceramic powder data will be given in the following sections.

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Appendix to</th>
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<tbody>
<tr>
<td>1</td>
<td>Composite Ultrasonic Transducer</td>
<td>Chapter IV</td>
</tr>
<tr>
<td>2</td>
<td>Anodic Etching of Aluminum</td>
<td>Section IV.2</td>
</tr>
<tr>
<td>3</td>
<td>Fabrication Methods for Lost Molds</td>
<td>Section IV.4</td>
</tr>
<tr>
<td>4</td>
<td>Ceramic Powder Data</td>
<td>Chapter V</td>
</tr>
</tbody>
</table>
1 Composite Ultrasonic Transducer

The most widely produced and applied microfabricated ceramic device is the ultrasonic transducer used in medicine, for sonar applications and in nondestructive testing of materials. The theoretical considerations why these transducers are built of rod-like shaped ceramic structures are given below.

The pulse-echo modality in which a piezoelectric transducer acts both as acoustic source and as detector of ultrasound is the most common technique used for ultrasonic imaging. In this method the transducer is excited by an electrical signal to emit acoustic waves of short duration into the medium to be investigated. When the emitted wave encounters a discontinuity in acoustic impedance, which is the product of the density and the speed of sound in a medium, some of the energy is reflected and this is detected by the transducer. The period of time between the emission and the detection of the signal is proportional to the distance from the transducer to the echo generating interface [1].

The desired resolutions for medical applications range from 1 mm for abdominal examinations to 50 μm for intravascular imaging. As no objects can be detected that are smaller than the wavelength employed, the corresponding frequencies to these resolutions are 1.5–30 MHz. This is determined with $\lambda \cdot f = v_{\text{sound}}$, whereby $v_{\text{sound}}$ is the velocity of sound in the human body, which is approximately 1500 m/s.

The use of composite material as transducer instead of a solid piezoceramic plate has two reasons: Matching of the acoustic impedance and avoiding of lateral standing waves. Human tissue has an acoustic impedance of 1.3–1.7 $\frac{kg}{m^2 \cdot s}$, bones have one of 3.8–7.4 $\frac{kg}{m^2 \cdot s}$. The refractive index is the analogon to the acoustic impedance for electromagnetic waves. When considering that solid piezoceramics have an impedance of about 30'000 $\frac{kg}{m^2 \cdot s}$, it can be seen that at the boundary between the solid transducer and the human tissue to be examined most of the acoustic energy is reflected and does not penetrate the tissue. In a composite material the acoustic impedances of the two materials can be superimposed. In this way the impedance of the composite can be tailored to about 10 $\frac{kg}{m^2 \cdot s}$ which reduces the interfacial energy loss dramatically. Therefore, about 25% of the composite transducer consists of ceramic and 75% of polymer material. The second reason for the use of 1–3 composites (see Figure IV-1 for a schematic drawing of such a composite) is the occurrence of transversal resonant standing waves in the solid piezoceramic when the transducer is operated at its longitudinal resonance frequency. These transversal standing waves lead to noise and energy loss during the measurement. To prevent these transversal resonances, discrete rods are used instead of a continuous piezoceramic phase. The periodicity of these rods must be made small enough, and hence the resonance wavelength short enough, that the transversal resonance frequency lies above the transducer’s operating longitudinal frequency band [2,3].
In summary, the rod design of a piezocomposite transducer is subject to the following conditions:

- The rod height is determined by the operating frequency, hence the composite is operated at its longitudinal resonance mode.
  shorter rods → higher operating frequency
- The width of the rods is determined by matching the impedance of the composite and the investigated material and the avoiding of standing transversal waves.
  thinner rods → better match of impedance and less noise

Several methods for the fabrication of such 1–3 composite materials exist and are compared in overview articles [2–5]. Some of the techniques are also discussed in Chapter IV of this work. In principle, all methods can be divided into two groups: The methods where shaping of the rods is done after sintering and those where shaping is done in the green state. With the latter, smaller structures with bigger aspect ratios are feasible. The two groups of methods are illustrated in Figure IV–2.
2 Anodic Etching of Aluminum

Alumina structures with nanoscale cylindrical pores are fabricated by anodic etching of aluminum foils. As the exact location of the pores can not be controlled it is not possible to generate exactly defined pore geometries and pore patterns. Therefore, this method was not listed in the literature overview of Chapter IV.

When an aluminum foil is anodized in an acid electrolyte, submicrometer pores grow hexagonally, arranged perpendicularly to the macroscopic foil surface [6]. Depending on the process characteristics, pore diameters from 15 to 200 nm can be achieved. During pore growth the remaining aluminum in the pore walls is oxidized to alumina. These nanoporous membranes can be used as filters [7] or as templates for growing nanowires of various materials [8–10]. Of course only porous alumina structures can be produced with this process, no other porous ceramic membranes can be formed.

<table>
<thead>
<tr>
<th>Anodic Etching of Aluminum</th>
<th>Smallest Lateral Dimension</th>
<th>Advantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.1 μm</td>
<td></td>
<td>- very high aspect ratio</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- very good resolution</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>&gt;100</th>
<th>Disadvantages:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>- only irregularly distributed pores</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- works only with alumina</td>
</tr>
</tbody>
</table>

Remarks: Pore width and pore density are controlled by etching conditions.

Table A-1: Process characteristics of anodic etching of aluminum.

![SEM image of a commercial alumina membrane (Anodisc 25, Merck, Darmstadt, Germany) produced by anodic etching. The nominal pore width is 0.2 μm.](image)
3 Fabrication Methods for Lost Molds

Several methods are employed to replicate structures which later are used as lost molds from microfabricated templates with macro-scale techniques. Here, an overview of these methods and of the materials used for this purpose is given.

3.1 Pattern Generation

All of the described techniques are lithographic processes. A radiation sensitive resist layer is partially exposed to radiation by shading some parts of the layer with a mask or by moving a radiation beam over the substrate. The radiation changes the chemical structure of the resist. In a subsequent development process the irradiated parts (or the not irradiated parts, depending on the resist) are removed and the two-dimensional pattern on the mask becomes a three-dimensional pattern in the photoresist.

Optical Lithography

Optical lithography with ultraviolet light is the most common technique in semiconductor manufacturing (Figure 2). Metal structures (chromium or iron) on transparent glass or glass ceramic wafers act as masks. The equipment used today in industry can provide a resolution of 0.35 μm, devices with a resolution of 0.19 μm are currently under development [11]. Topographic features on the wafer surface can either be generated by etching a continuous layer of deposited material through a resist mask or by depositing material onto a patterned substrate and subsequent liftoff of the resist with the excess material. Although in standard semiconductor processing only low aspect ratios are required, also aspect ratios of up to 10 are realizable with UV lithography using special processing steps [12].

X-Ray Lithography

The short wavelength and the high energy of X-rays is used for two purposes in lithography: For the exposure of thick resist layers or for the generation of very narrow features.

In the LIGA process [13] optical lithography with high aspect ratios is possible. A PMMA resist film on a metal substrate is patterned with X-ray synchrotron radiation through a mask with an absorbing pattern of gold and copper on a beryllium carrier foil. The PMMA structure is subsequently filled with a metal by electrodeposition [13,14]. After dissolving the polymer, the metal structure is used as master for the mass production of lost molds, for example by injection molding [15]. With LIGA aspect ratios of 500 and minimal structure widths of 1 μm can be achieved [16]. X-rays are also used for exposing thin resist layers with much better resolutions than in UV lithography. Due to the shorter wavelength of the radiation, structures as narrow as 50 nm are feasible [17].
Such small structures, however, do not have the high aspect ratios, the ones created by LIGA have.

![Diagram of UV lithography processing steps]

**Figure A-2:** Processing steps in UV lithography.

**Electron Beam Lithography**

An electron beam, for example in an electron microscope, can be directed to create a pattern into a resist film. This is no exposure technique like the two mentioned above where the latent image in the resist is generated by a single exposure through a mask, here the pattern is literally written into the resist [18,19]. Therefore, process times are much longer for electron beam lithography. The advantage is that no mask is needed, the electron beam moves computer controlled over the sample surface. This makes the technique very suitable for the fabrication of single samples with high resolution. The most important application for electron beam lithography is the generation of masks for UV lithography, but also for research purposes the flexibility of the process is of interest [20]. Features as small as 50 nm can be generated [21].
Scanning Probe Lithography

Another possibility to irradiate resist films with electrons is by applying a current flow between the tip and the sample in a scanning probe microscope [22–24]. The advantage of this method is, that no vacuum is required during exposure. However, not only photoresist can be applied as resist material for further processing steps. Selectively altered self-assembled monolayers [25] or selectively oxidized silicon surfaces [26,27] have also been used as resist structures for subsequent etching.

3.2 Mold Replication

The methods for the generation of patterns on a micron scale are generally expensive. In order to reduce the overall processing costs it is desirable that the structures made by micro-scale technology can be used as templates for repeated replication with macro-scale technologies to create the molds which are destroyed thereafter. A common process for this is injection molding, for example metal structures generated by LIGA are replicated with polymers by injection molding [28]. As mold materials either thermoplastic polymers or, in reaction molding, duromers are used. In the latter process pre-polymers are injected and crosslinked inside the mold. Another process for the generation of lost molds is embossing of thermoplastic polymers [29].

Waxes can also be used as mold material. This offers several advantages compared to polymers [30]:

- Wax molds can be produced easily by casting,
- after shaping the ceramic green body the molds can be removed by melting,
- the wax remaining in the pores of the green body improves its green strength.

However, the limited mechanical stability of the waxes imposes limitations on the shaping process of the ceramics.

When lost molds can not be generated by replication, for whatever reason, the mold material is already defined by the previous processing steps. For example for lithographic techniques the photoresist material has to be used as mold and the rest of the process has to be adapted to it. The molds are either pyrolyzed during sintering [31] or removed chemically beforehand [32].
4 Powder Data

Alumina Powders

<table>
<thead>
<tr>
<th>Powder Name</th>
<th>Taimicron TM–DAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Taimei Chemicals, Tokyo, Japan</td>
</tr>
<tr>
<td>Composition</td>
<td>$\alpha$-Al$_2$O$_3$</td>
</tr>
<tr>
<td>Lot No.</td>
<td>2831</td>
</tr>
<tr>
<td>BET [m$^2$/g]</td>
<td>14.2</td>
</tr>
<tr>
<td>$d_{10}$ [µm]</td>
<td>0.15</td>
</tr>
<tr>
<td>$d_{50}$ [µm]</td>
<td>0.19</td>
</tr>
<tr>
<td>$d_{90}$ [µm]</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Figure A-3: Particle size distribution of TM–DAR.
<table>
<thead>
<tr>
<th>Powder Name</th>
<th>HPA 0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Ceralox, Tucson, AZ, USA</td>
</tr>
<tr>
<td>Composition</td>
<td>$\alpha$-Al$_2$O$_3$, with 0.5 wt% MgO</td>
</tr>
<tr>
<td>Lot No.</td>
<td>C 65142</td>
</tr>
<tr>
<td>BET $[\text{m}^2/\text{g}]$</td>
<td>8.9</td>
</tr>
<tr>
<td>$d_{10}$ $[\mu\text{m}]$</td>
<td>0.22</td>
</tr>
<tr>
<td>$d_{50}$ $[\mu\text{m}]$</td>
<td>0.49</td>
</tr>
<tr>
<td>$d_{90}$ $[\mu\text{m}]$</td>
<td>1.3</td>
</tr>
</tbody>
</table>

*Figure A-4: Particle size distribution of HPA 0.5.*
**Boehmite**

<table>
<thead>
<tr>
<th>Powder Name</th>
<th>Disperal S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Condea, Hamburg, Germany</td>
</tr>
<tr>
<td>Composition</td>
<td>γ-AlOOH (boehmite)</td>
</tr>
<tr>
<td>Lot No.</td>
<td>57949</td>
</tr>
<tr>
<td>BET [m²/g]</td>
<td>233</td>
</tr>
<tr>
<td>$d_{10}$ [µm]</td>
<td>0.03</td>
</tr>
<tr>
<td>$d_{50}$ [µm]</td>
<td>0.05</td>
</tr>
<tr>
<td>$d_{90}$ [µm]</td>
<td>0.12</td>
</tr>
</tbody>
</table>

![Particle size distribution of Disperal S.](image)

*Figure A-5: Particle size distribution of Disperal S.*
Zirconia

<table>
<thead>
<tr>
<th>Powder Name</th>
<th>TZ-3Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Tosoh, Tokyo, Japan</td>
</tr>
<tr>
<td>Composition</td>
<td>Zirconia (TZP), doped with 3 mol % Y₂O₃</td>
</tr>
<tr>
<td>Lot No.</td>
<td>Z 306327 P</td>
</tr>
<tr>
<td>BET [m²/g]</td>
<td>17</td>
</tr>
<tr>
<td>d₁₀ [μm]</td>
<td>0.14</td>
</tr>
<tr>
<td>d₅₀ [μm]</td>
<td>0.16</td>
</tr>
<tr>
<td>d₉₀ [μm]</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Figure A-6: Particle size distribution of TZ-3Y.
Cerium Gadolinium Oxide

<table>
<thead>
<tr>
<th>Powder Name</th>
<th>Cerium Gadolinium Oxide 80/20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Rhodia, Courbevoie, France</td>
</tr>
<tr>
<td>Composition</td>
<td>Ce₀.₅Gd₀.₅O₁.₉</td>
</tr>
<tr>
<td>Lot No.</td>
<td>98189/98</td>
</tr>
<tr>
<td>BET [m²/g]</td>
<td>25</td>
</tr>
</tbody>
</table>

Because of its high density and the consequently fast sedimentation, no particle measurements in suspension were possible with the CGO powder.
Tin oxide

<table>
<thead>
<tr>
<th>Powder Name</th>
<th>Tin Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Cerac, Milwaukee, MI, USA</td>
</tr>
<tr>
<td>Composition</td>
<td>SnO₂</td>
</tr>
<tr>
<td>Lot No.</td>
<td>X 21153</td>
</tr>
<tr>
<td>BET ( \text{m}^2/\text{g} )</td>
<td>7.8</td>
</tr>
<tr>
<td>( d_{10} ) [( \mu \text{m} ) ]</td>
<td>0.14</td>
</tr>
<tr>
<td>( d_{50} ) [( \mu \text{m} ) ]</td>
<td>0.28</td>
</tr>
<tr>
<td>( d_{90} ) [( \mu \text{m} ) ]</td>
<td>0.47</td>
</tr>
</tbody>
</table>

*Figure A-7: Particle size distribution of SnO₂.*
5 References


### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3DP</td>
<td>Three Dimensional Printing</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>CGO</td>
<td>Ce$<em>{0.8}$Gd$</em>{0.2}$O$_{1.9}$</td>
</tr>
<tr>
<td>DCM</td>
<td>Direct Ceramic Machining</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>FEP</td>
<td>Poly(tetrafluoroethylene–co–hexafluoropropylene)</td>
</tr>
<tr>
<td>FPM</td>
<td>Filling of photoresist molds</td>
</tr>
<tr>
<td>HDPE</td>
<td>High density polyethylene</td>
</tr>
<tr>
<td>LIGA</td>
<td>Lithography and galvanofoming</td>
</tr>
<tr>
<td>μCP</td>
<td>Microcontact Printing</td>
</tr>
<tr>
<td>MEMS</td>
<td>Microelectromechanical systems</td>
</tr>
<tr>
<td>MIMIC</td>
<td>Micromolding in capillaries</td>
</tr>
<tr>
<td>PAA</td>
<td>Polyacrylic acid</td>
</tr>
<tr>
<td>PDMS</td>
<td>Poly(dimethyl siloxane)</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PZT</td>
<td>Lead zirconate titanate, PbZr$_{1-x}$Ti$_x$O$_3$</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-assembled monolayer</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SLS</td>
<td>Selective Laser Sintering</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet light</td>
</tr>
</tbody>
</table>
Curriculum Vitae

Personal
Name: Urs Peter Schönholzer
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Nationality: Swiss, citizen of Lützelfüh, BE

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1984 – 1989 Realgymnasium Kirchenfeld, Bern
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1990 – 1996 Student of Materials Science, Swiss Federal Institute of Technology (ETH), Zürich
1996 Diploma in Materials Science
1996 – present Research Associate and Ph. D. Student, Chair of Nonmetallic Materials, Department of Materials, ETH Zürich.

Publications

Selected Presentations
1. U.P. Schönholzer*, L.J. Gauckler, “Microfabrication of ceramics by casting colloidal suspensions onto patterned substrates”, 5. 11. 99, Annual Meeting of the American Institute of Chemical Engineers, Dallas, TX, USA.
5. U.P. Schönholzer*, L.J. Gauckler, “Preparation of ceramic surface features in the micron range”, 27. 4. 1999, 101st Annual Meeting of the American Ceramic Society, Indianapolis, IN, USA.

