The method to fabricate complex shaped micro-patterned ceramic structures has been developed. Vacuum-assisted infiltrating the suspensions to the micro channels generated by the contact of polydimethylsiloxane mold to the substrate enables simple micro patterning of ceramics with complex structures in a relatively large area in short time. The use of well-dispersed ethanol-based suspensions of solid loading ~20 vol% plays an important role in a successful pattern formation without defects. The current process, called microfluidic lithography, is applicable to the entire range of ceramic materials which can be processed to colloidal suspension with relatively low viscosity. It is demonstrated that the interdigitated ceramic structures with 50 µm in the width composed of Al₂O₃ and NiO on a Si substrate were fabricated in an area of 5 mm × 5 mm.

I. Introduction

Micro patterning of ceramic materials plays important roles in developing micro and/or highly integrated functional devices. Many attractive properties of ceramics including high temperature mechanical stability, chemical inertness, and unique electrical/magnetic effects make it suitable for microscale devices such as chemical/biological microsensor, microreactor, and microactuator. Most of these microsystems often require ceramic microstructures of high-aspect ratio rather than thin film, which are usually difficult to be produced by either physical/chemical thin-film deposition techniques or conventional powder processing for bulk ceramics.

Whitesides et al. pioneered to use a flexible elastomer (mostly polydimethylsiloxane (PDMS)) as a stamp or mold for replicating micro- and nanoscale structures. This technique, now known as soft lithography, includes microtransfer molding, microcontact printing, and micromolding in capillaries (MIMIC). In particular, MIMIC involves capillarity-induced spontaneous filling of a fluid into micro channels established by contact of the mold to a substrate. It has been successfully employed for many different applications in the fields of material science, microelectronics, biology, and chemistry.

Filling fluid used in MIMIC should wet partially either the surface of PDMS or the substrate for spontaneous filling as a result of capillary forces. Even when the filling process is thermodynamically favorable, in addition, infiltration kinetics aspect should be taken into account for surface patterning by MIMIC. The fluid that is most useful in MIMIC is powder-free chemical solution having low solid loading (<5 vol%) and low viscosity (<200 mPa·s). The powder-free filling fluid is usually a liquid prepolymer, solution of UV/thermally curable polymers, or sol–gel precursor. Only a few studies involving particulate fluids such as colloidal suspensions of latex microsphere, carbon paint, tin oxide, and carbon nanotubes (CNTs) have been reported. Most of them are still dilute suspensions of low viscosities. Heule et al. demonstrated that the MIMIC with the suspension of 40 vol% produced 10 µm wide microlines of SnO₂ ceramics in which the filling length was only ~0.5 mm. Because MIMIC relies extensively on capillary forces to fill channel arrays, its use in large area complex shape patternning with the colloidal suspension of high solid loadings likely fails.

We have introduced a microfluidic device made of PDMS to fabricate ceramic microstructures using the colloidal suspension of relatively high solid loadings (>20 vol%) as shown in Fig. 1. The large access holes to the micro channel at both its ends serve as the reservoir of the filling suspension. The microfluidic device loaded with the suspensions is then placed in a vacuum chamber to take advantage of a decreased pressure, as Monahan et al. developed a channel outgas technique (COT), for filling complex channels. The lower overall pressure allows gas contained within connected volumes of the channel networks to escape out. As the pressure is returned to atmospheric level, the suspensions from the reservoirs flow in to rapidly fill the voids left within the channels. This procedure, called vacuum-assisted microfluidic lithography (μFL), is very effective to produce complex microstructures in a relatively short period of time. It also permits simultaneous pattern generation of multiple materials on the same substrate if separate microfluidic multi-channels embedded within the molds are utilized. Furthermore the ceramic microcomponents of high-aspect ratio are easily integrated into the microsystems fabricated with silicon-based techniques, since the unfilled suspension in the reservoir is not in contact with the substrate unlikely in MIMIC. In this study, we demonstrate the use of μFL for the fabrication of interdigitated (comb-like) ceramic microstructures composed of different materials on the substrate.

II. Experimental Procedure

High purity Al₂O₃ powder (AES-11, Sumitomo Chemical Co., Tokyo, Japan) and NiO powder (J. T. Baker, Philadelphia, PA) and poly(vinylpyrrolidone) (PVP, Mₙ = 10000, Aldrich Co., St. Louis, MO), respectively. The suspension of NiO in ethanol at 20 vol% was similarly prepared using PVP.

The PDMS microfluidic device was fabricated using a master pattern of SU-8 photoresist (Microchem Corp., Newton, MA) formed by conventional photolithography. The PDMS prepolymer mixture (Sylgard 184, Dow Corning, Midland, MI) was poured over the SU-8 master to an average thickness of 3 mm, and then degassed under a vacuum environment to remove and prevent the formation of bubbles. After the polymer was cured at 85°C for 1 h, the PDMS replica mold was peeled from the master and cut into several pieces. Two reservoir holes connect ed to each channel were punched through the PDMS mold using a 16 G syringe needle.

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The PDMS devices were used as-fabricated without hydrophilic surface modification. After the sealing to the Si substrate via conformal contact, the suspensions of 200 μL were placed in each reservoir hole. The entire device was then evacuated at 10 Torr in a vacuum chamber. Upon the return to atmospheric pressure, the channels were filled with the suspensions and the samples were then left to dry at 25°C. After 24 h drying, the PDMS mold was lifted from the substrate. The patterned structures were fired at 1400°C for 2 h. The resulting structures were investigated using scanning electron microscopy (SEM, FE-SEM, S-4200, Hitachi, Tokyo, Japan) and optical microscopy (Leica DMLM, Wetzlar, Germany).

III. Results and Discussion

Aqueous and nonaqueous suspensions of alumina were used to investigate the feasibility of the μFL. Vacuum-assisted filling into long complex micro channels with multiple intersections and discontinuous branches works well for the suspensions of high solid loadings. It takes only few seconds to fill the interdigitated channels with total length of 46 cm and cross-sectional area of 650 μm².

In our μFL the flow in the microfluidic channel is dictated by the pressure gradient and fluidic resistance as described by

![Fig. 1. Schematic of the vacuum-assisted microfluidic lithography with ceramic suspension: (a) prepare polydimethylsiloxane (PDMS) mold through photolithography; (b) place PDMS mold on the Si wafer substrate; (c) apply two different suspensions at the entrances of reservoir and evacuate; (d) fill the channels by returning to atmospheric pressure; (e) remove PDMS mold after complete infiltration and drying.](image)

![Fig. 2. Scanning electron micrographs of the microstructured lines of Al₂O₃ on a silicon wafer with varying linewidths (from 10 to 100 μm) using (a) aqueous suspension and (b) ethanol-based suspension. Closeups of the circled regions present cross-section of 10 μm wide microlines with a densely packed microstructure. Arrows indicate broken microlines because of the suspension migration during the drying.](image)

![Fig. 3. Optical micrographs of complex shape patterned structures of Al₂O₃ on the Si substrate. The height of structure was 25 μm. Inserted scanning electron microscopic pictures show densely packed microstructure with a relative sharp edge definition.](image)
particles induce transportation of the suspension from the inner channel to the reservoir access holes. This makes the microlines exhibit varying lengths and gaps as shown in Fig. 2(a), leading to an imperfect pattern generation.

For the channels filled with the ethanolic suspension, the capillary-induced suspension migration was significantly reduced as shown in Fig. 2(b). Because PDMS is permeable to ethanol vapor, volumetric evaporation directly from the channels through the entire surface of PDMS microfluidic device can occur. Furthermore the capillary force that may be developed at any fast drying region is likely smaller since the surface tension of ethanol is much lower than water. These make the µFL using the ethanolic suspension allow exact control of the filling length, leading to a perfect pattern generation. Each microline was nearly a rectangular shape with well-defined sharp edges, and it exhibits densely packed microstructure of the particles. The width and the height of the narrowest microlines were 10 and 12.5 µm, respectively, which were almost the same dimension and shape as those of the channels on the PDMS mold. This indicates that close packed structures of the particles form first near at the upper surface of inside PDMS through which the solvent evaporates, and they gradually grow down to the bottom.11,18 The suspension from the reservoir must be continuously transported to growing front during drying to compensate for the volume of solvent lost by evaporation, so as to generate microstructures conformal to the PDMS mold.

Complex shape microstructures of Al2O3 were also fabricated as shown in Fig. 3. The linewidth and feature height were 30 and 25 µm, respectively. Patterned structures had a relatively sharp edge definition. Particles were densely well packed inside so that the patterned structures could be densified without cracking. Linear shrinkage after sintering at 1400°C was approximately 12.2%. Figure 4 also shows the digitigated micro patterns of 50 µm line width composed of Al2O3 and NiO on the Si substrate in the area of 5 mm × 5 mm fabricated by the vacuum-assisted µFL using the ethanolic suspensions. The use of two well-dispersed suspensions of relatively high solid loadings is required to prevent any mass segregation of particles during simultaneous filling long channels and subsequently to achieve the well-defined microstructures of two different materials.

IV. Conclusions

A simple method to fabricate complex shaped micro-patterned ceramic structures with two different materials has been presented. Micro-channels formed by contacting the mold with a substrate were simultaneously filled with two well-dispersed slurries by vacuum assisted infiltration. The slurries were solidified upon solvent evaporation through PDMS mold. Controls of suspension characteristics together with its drying behavior play an important role in the fabrication of well-defined micro-pattern structure. The current method is applicable to the entire range of ceramic materials that can be processed to the colloidal suspensions with low viscosities. Vacuum-assisted infiltrating the suspensions into the channels in the microfluidic device enables simple micro patterning of ceramics with complex structures in a relatively large area.

References


