Microfluidic Patterning of Ceramic Microstructures

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Patterned ceramic structures composed of two different materials with a feature resolution in the micrometer range have been generated by microfluidic lithography. Micro-channels made of poly(dimethylsiloxane) (PDMS) were filled with well-dispersed suspensions followed by solidification upon solvent evaporation. The cross-inserted comb-type ceramic structures with 100 μm in the width were fabricated in a relatively large area of 2 x 2 cm² for Al₂O₃ and NiO. It was found that controls of suspension characteristics and its drying play an important role in determining pattern quality. Micro-channel filling was significantly influenced by viscosity and surface tension of suspension and interfacial interaction of suspension with the surfaces of the substrate and PDMS. Once filled, a proper drying condition must be met. Otherwise, the micro-channels were disconnected due to capillary stress, resulting in an incomplete pattern generation.

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1. Introduction

For several years, there has been considerable interest and advance centered on the fabrication of micro-structures. Such microfabrication is mostly performed by the chemical and physical methods based on the silicon technology and photolithography. Although photolithography is the most successful technology in microfabrication, it is limited by its illuminating source that needs shorter wavelength for smaller micro-structures. Also, it is only applicable to two dimensional micro-patterned structures of metallic materials or photosensitive polymers.

Ceramic materials have excellent electrochemical, chemical, thermal, and mechanical functionalities. The ability to fabricate these ceramic materials into micrometer scale structures is necessary for advanced functional devices. But, it is in an early stage to micro patterning ceramic materials, and even a few possible processes are expensive or take long time.

Recently, some of cost effective and simple microfabrication methods for various materials are introduced. The most outstanding method is the use of soft lithography, especially micromolding in capillaries (MIMIC), which is developed as a low-cost route to use liquid materials in microfabrication. MIMIC makes it possible to fabricate micro-patterned structure on the curved or flat surface with various liquid materials. In fact, the use of liquid prepolymer or polymeric solution in MIMIC to fabricate field effect transistors and waveguides already has been demonstrated. In case of ceramics, several successful results are reported. But because most of these are using ceramic precursor polymer, they are merely applicable to a few restricted materials of simple continuous network structures in a small area.

We have extended MIMIC to use colloidal suspension of ceramic powders and have developed a novel method based on a vacuum-assisted filling of suspension into micro channel networks. Our process involves application of vacuum environment to the entire channel network established by contact of PDMS mold to a substrate. This procedure, called microfluidic lithography (μFL), is very effective to produce a long complex microstructure in a relatively short period of time. We demonstrate the use of μFL for fabrication of complex cross-inserted comb-type ceramic structures consisted of two different materials on a substrate.

2. Experimental

2.1 SU–8 Master

The master with a positive relief of the cross-inserted comb-type mold structures was prepared using SU–8 photore sist (Microchem Corp.) by conventional photolithography. After cleaning of the Si wafer, SU–8 50 photore sist was spin-coated onto the wafer to a thickness of 50 μm. The resist film was pre-baked at 95°C for 20 min to remove the solvent followed by exposure with a contact mask aligner (MJJ-3, Karl Süss) to i-line UV light with intensity of 16 mW/cm². Post expose bake (PEB) was performed at 95°C for 5 min to crosslink the exposed areas. The exposed film was developed in propylene glycol methyl ether acetate (PGMEA, Aldrich Co., 99%) for 6 min with agitation.

2.2 PDMS molds

The two components of the PDMS prepolymer A and B (Sylgard 184, Dow Corning) were mixed in a 10 : 1 ratio. The viscous mixture was poured over a SU–8 master structure, and then degassed under a vacuum environment to remove and prevent the formation of bubbles. The master template covered with PDMS was placed in an oven at 85°C for 1 h to accelerate curing. Thereafter, the PDMS replica mold was peeled off and cut into several pieces. Two reservoir holes connected to each micro channel were punched through the patterned PDMS mold using a steel rubber punch.

2.3 Suspension preparation

High purity Al₂O₃ powder (AES-11, Sumitomo Chemical Co.) and NiO powder (J.T Baker) were used as-received. The average particle sizes of the powders were 0.5 μm and 0.8 μm, respectively. Suspensions for the μFL were made by mixing these powders with ethanol (EtOH) and a dispersing agent (poly(vinylpyrrolidone), Mₙ=10000, Aldrich Co.), followed by ball milling for 24 h. Solid loading of Al₂O₃ and NiO suspensions was 25 vol% and 20 vol%, respectively.

2.4 Microfluidic lithography (μFL)

A schematic procedure of μFL is given in Fig. 1. The patterned PDMS mold was adhered to a silicon wafer, then a droplet of Al₂O₃ and NiO suspensions was placed in the appropriate reservoir. The sample was evacuated at 130 torr for 5 sec in a vacuum chamber. Upon the return to atmospheric pressure, two different micro channels were completely filled with each suspension.

After drying, PDMS mold was removed from substrate
Fig. 1. Schematic procedure of μFL. (a) preparation of PDMS mold through photolithography. (b) place PDMS mold on the Si wafer substrate (c) apply Al₂O₃ and NiO suspensions at the entrances of reservoir and evacuate. (d) remove PDMS mold after complete infiltration and drying.

without sticking. The resulting ceramic green structure has complex shape composed of lines with two different materials cross-inserted alternately. The sample was fired at 1400°C for 3 h, and patterned structures were observed using a field emission scanning electron microscopy (FE-SEM, S-4200, Hitachi).

3. Results and discussion

Figure 2 shows a cross-sectional view of the PDMS mold replicated against the SU-8 master. PDMS replica had complex network structures in which two different channels have cross inserted comb-type branches. The PDMS mold was also free from defects such as trapped gas bubbles or sticking with master or collapse. PDMS molding relatively well replicates the SU-8 master’s channel structure of 102 μm in the width and 53 μm in the height. The width and the height of the channel on the PDMS replica were 100 μm and 50 μm, respectively. The sizes of the micro channels were a little smaller than those of the SU-8 master, which reflects cross-linking shrinkage during curing of PDMS.

Microfluidic lithography and demolding using such a PDMS mold produced the micro channels of Al₂O₃ on the substrate as shown in Fig. 3. Each channel was a rectangular shape with well-defined sharp edges and exhibited densely packed microstructure of the particles. The width and the height of the channels were 100 μm and 48.4 μm, respectively, which were almost the same dimensions as those of the channels on the PDMS mold. High temperature heat-treatment resulted in the sintered micro channels without either delamination or cracking as presented in Fig. 4. The linear shrinkage before and after firing was measured to 12.2% in a parallel direction and 9.3% in a perpendicular direction to the substrate. Shrinkage anisotropy indicates that the solvent evaporates through the surface of the PDMS mold in the ethanol-based μFL, which makes the particles more densely consolidated in a perpendicular direction to the substrate.

Spontaneous filling of fluid into micro channel capillaries can occur when the interfacial free energies can be minimized by wetting the capillary surface. As demonstrated by Kim et al., a choice of fluid is critical for a thermodynamically driven infiltration. The fluid must have relatively low viscosity and good wetting property with the surface of PDMS. Even when the fluid penetration is thermodynamically favorable, in addition, infiltration kinetics also plays a role in the patterning by filling the micro channels. Filling long capillaries with the suspension of high viscosity requires long times. Furthermore complex capillary in which the channel has branched sub-
channels of the one end closed demands a higher pressure difference for penetration compared to simple straight capillaries. In this regard, we have used vacuum-assisted infiltration of the suspensions into the microfluidic channels for patterning complex shaped ceramic microstructures in a large area.

Once filled, the suspending liquid should be removed by means of evaporation to produce green body. Evaporation must occur through the entire surface of PDMS mold, i.e., the PDMS is permeable to liquid vapor. Otherwise, the suspension dries out only at the channel entrances, which causes a migration of the micromolded suspension due to capillary stress. Water vapor is almost impermeable through PDMS, so that the microfluidic lithography using aqueous suspension usually results in an imperfect pattern formation in which the micro channels are disconnected during drying.

Therefore, we utilize the ethanol-based suspension for µFL. The suspension based on the ethanol has a lower contact angle ($\theta = 17.8^\circ$) with PDMS than the aqueous suspension ($\theta = 86.6^\circ$), which permits a faster spontaneous infiltration. And because PDMS is permeable to ethanol vapor, volumetric evaporation from the micro channels through the mold is possible. Well-dispersed suspension is also required in the current process to prevent any mass segregation of particles during infiltration and to achieve a highly dense particle consolidated structure in the green body. It was determined that the ethanol-based suspensions of solid loading up to 25 vol% and of the viscosity less than 350 mPa·s are penetrable into the micro channels by vacuum-assisted infiltration. Under the well-controlled processing conditions, it is demonstrated that the current microfluidic lithography technique permits us to produce the complex micro-patterns composed of two different materials in the area of $2 \times 2$ cm$^2$ on a substrate as shown in Fig. 5.

4. Conclusions

Novel method to fabricate complex shaped micro-patterned structures of two different materials on a substrate was demonstrated. Microfluidic lithography is applicable to the entire range of ceramic materials which can be processed to colloidal suspension with relatively low viscosity. Vacuum-assisted infiltrating the suspensions to the micro channels generated by the contact of PDMS 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 high solid loading ~25 vol% and low viscosity (<350 mPa·s) plays an important role in a successful pattern formation by microfluidic lithography.

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References