Fabrication of PMMA Microchip of Capillary Electrophoresis by Optimized UV-LIGA Process

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Abstract. Design and fabrication of microfluidic devices on polymethylmethacrylate (PMMA) substrates for electrochemical analysis applications using improved UV-LIGA process are described. The micro-channel structures are transferred from Nickel mould into the plastic plates by hot embossing method. During the mould fabrication, the exposure process is optimized for the large ratio of exposed area to unexposed area of negative photo-resist (SU-8), then non-planar electroforming technique is used for the large line space of the SU8 photo-resist mold. Microelectrodes for electrochemical detection are fabricated on other blank PMMA plates through lift-off process. Then these substrates with microchannels are bonded to PMMA plates with microelectrodes by thermal bonding method based on surface modification. In this study, the PMMA microchips of capillary electrophoresis for electrochemical detection (CE-ECD Chips) have been demonstrated by electrophoretic separation of L-ascorbic and uric acid. The results indicate that the fabrication of CE chips by this improved UV-LIGA process has potential of mass production with low cost.

1. Introduction

MEMS technology has been applied in microfluidic devices, micrototal analysis system (µ-TAS) and lab-on-a-chip (LOC) for many years. Efforts to fabricate those microchips have been studied. In comparison to silicon or glass substrates studied in last decade[1-3], polymers[4-6] are becoming increasingly important as the alternatives for its advantages such as low cost, readily mechanical processing, wide range of chemical and surface properties, and etc.

Polymer microdevices can be produced by replication techniques such as injection molding, hot embossing, casting etc. Among these fabrication methods, the hot embossing or imprinting is the most popular due to its advantages of simple procedure, low cost and mass production. Conventional methods for fabricating the mould of microfluidic devices have focused mainly on etching quartz[2], silicon[3], stainless steel[7] etc. These templates can be successfully applied to imprint microstructures into polymer substrates. However, the Si or quartz templates readily tend to breakage due to different thermal expansion properties of the templates and polymer substrates in embossing procedures. A Si template ordinarily can only be used to imprint for tens to hundreds of devices before it has to be discarded. The stainless steel mould can obviate these problems, but the high roughness and low quality of patterns restrict its application. In comparison to these mould fabrication methods, LIGA or...
UV-LIGA process has its own advantages such as high quality of microstructures, low roughness and perfect mechanical properties. Due to the low cost of the light resource, UV-LIGA process is very suitable for the commercialization of those polymer based microfluidic devices.

It is difficult to fabricate the mould insert by conventional UV-LIGA process: 1) During the CE chip fabrication, the exposure of SU8 process has the character of large ratio of exposed area to unexposed area (defined as W) which may cause large internal stress of crosslinked SU8 layer and failure adhesion between the SU8 layer and the substrate. To avoid this, the parameters of exposure process should be optimized. 2) The large line space of the photo-resist mold prevents the back-plating from over-plating. Although sputtering a electric seed layer on the electroplated samples after over-plating may solve this problem, but this needs to take the sample out from the electrolyte and clean it before sputtering. Consequently this may affect the back-plating and the mechanical properties of the mould.

In this paper, the lithography was optimized for the large W of SU8 layer, and non-planar electroforming was used for the large line space in SU8 photo-resist mold. At last a PMMA based CE chip was made using this improved UV-LIGA process.

2. Experimental

The fabrication flowchart is shown in figure 1. Nickel mould was fabricated through the improved UV-LIGA process, and microchannel was embossed onto PMMA plates in hot embossing system, and holes were drilled as buffer reservoirs on these substrates. On other black PMMA plates, microelectrodes were fabricated through lift-off process. The two substrates with microchannel and microelectrodes were bonded using thermal bonding method based on modification PMMA surface[8], then the CE-ECD chips were fabricated.

2.1. Mould fabrication

In our study, the mask to pattern the micro-channels is shown in figure 2A. An electric seed layer (Cr/Au) was first sputtered on Si substrate, then 80 µm thickness of SU8 2075 (Micro.Chem.) was spun onto the substrate. After soft baking on hot plate, the photo-resist was exposed with the dose of 100 mJ/cm² at I-line (365 nm). After the post-baking and development, the photo-resist mould for electroforming was formed.

In order to solve the electroforming problem caused by the too large line space on the photo-resist mould, a second Au layer was sputtered on the upper surface of the cross-linked SU8 layer except the area of the patterned structure using the mask as in figure 2B. Then the substrate with photo-resist mould was electroplated on with nickel using non-planar plating method as in figure 3. Back-plating...
started when the over-plated Nickel connects to the second Au seed layer. In this study, nickel sulfamate electrolyte was used for thick electro-deposition due to its high deposition rate and low internal stress of the plated nickel. Composition of the plating solution is shown in table 1.

The deposition temperature was set to 50±1°C, and the pH value of the electrolyte was controlled between 3.7 and 4.0. Circular flow set-up was used for sufficient mass transfer of the electrolyte. The density of electroplating was about 10 mA/cm². The SEM of the mold is shown as in figure 4A.

![Figure 2](image)

**Figure 2.** (A) Micro-channel exposure mask. (B) Schematic diagram of sputtering Au as second seed layer.

![Figure 3](image)

**Figure 3.** Schematic diagram of non-planar electroplating process.

### 2.2. Chip bonding

The micro-channels were hot embossed onto PMMA substrate in HEX02 (JENOPTIK Microtechnik GmbH, Germany) with the Nickel mold. Then four holes were drilled as reservoirs in the PMMA substrate. Au microelectrodes for electrochemical detection were fabricated on other PMMA substrate through lift-off process. The bottom PMMA with micro-channels and holes was then bonded onto the cover PMMA with microelectrodes by thermal bonding method based on modification PMMA surface[8]. The bonding temperature, pressure and time was 95°C, 2MPa, 3min, respectively. A PMMA based capillary electrophoresis with electrochemical detection microchip was obtained.

### 3. Separation and detection of uric acid and L-ascorbic acid

A running buffer solution with pH value of 7.0 was prepared by mixing 0.01 M NaHPO₄ and 0.01 M H₃PO₄. The test sample of uric acid and L-ascorbic acid solution of 20 mM was prepared by using DI
water and diluted by running buffer to the required concentration. Sample separation and detection configuration is shown in Figure 5 for the end-column amperometric detection. The detection potential at the working electrode was +700 mV with respect to the reference electrode. 300V/m electrical field strength was applied to the sample separating channel. These two samples were separated in the microchannel by electrophoresis.

The detection result is shown in figure 6. Uric acid and L-ascorbic acid were completely separated within 70s. Our experimental results clearly demonstrate that the PMMA CE microchip fabrication by this improved UV-LIGA process was successful.

![Figure 4](image)

**Figure 4.** (A) SEM of the electroformed Nickel mould (B) Bonded CE chip

| Components                      | Quantity |
|---------------------------------|----------|
| Ni(SO3NH2)2 4H2O                | 330g/L   |
| NiCl2  6H2O                     | 40 g/L   |
| H3BO3                           | 50 g/L   |
| Wetting agent                   | 1-2 mL/L |

**Figure 5.** Layout of the CE-ECD chip. W: working electrode; R: reference electrode; HV: high voltage input; G: ground; B: buffer reservoir; S: Sample reservoir; BW: buffer waste reservoir; SW: sample waste reservoir. S-SW is the injection channel, B-BW is the separation channel.
Figure 6. Electropherogram of uric and L-ascorbic acid samples using the PMMA CE microchip with end-column amperometric detection system. The chip was fabricated by improved UV-LIGA process. Peaks are: (a) uric acid; (b) L-ascorbic acid. Conditions: separation field strength, +300V/cm; detection potential, +700mV; 50 μm wide Au working electrode; NaHPO₄/ H₃PO₄ buffer as running buffer.

4. Conclusion
In fabrication of capillary electrophoresis microchip using UV-LIGA process, the lithography process is optimized for the large W to avoid large internal stress and failure adhesion of the cross-linked SU-8 layer. Then non-planar electroforming was used to obviate the problem caused by the large line space in the photo-resist mold. The results indicate that the optimized and improved UV-LIGA process has potential of mass production and low-cost of micro-fluidic devices.

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