PAPER

Microcontact electrochemical etching technique for rapid fabrication of glass-based microfluidic chips†

Jiaming Ye,[a] Xiaodong Wang,[b] Jinliang Zhuang,[a] Yongliang Zhou*[a] and Zhaowu Tian[a]

A simple and rapid microfabrication method for glass-based microfluidic chips is presented. In this method, a microcontact electrochemical etching technique is used to pattern the masking metal layer. By applying an anodic potential in the presence of KCl solution, a stamp's configuration can be precisely transferred to the masking layer within 2 min. In contrast to photolithography, the new method does not require clean room facilities and a photolithography machine, and the chemical reagent used is harmless to the environment and the human body. Combined with wet etching and thermal bonding, a microfludic device was fabricated and successfully used for electrophoretic separation of FITC. We anticipate that this fabrication method will bring glass microfluidic chips within the reach of any routine laboratory with minimal facilities. This low cost and high throughput process may also be suitable for mass production of microfluidic devices.

1. Introduction

In the past two decades, the microfluidic chip has become an attractive technological platform for chemical and biological research.[1–3] Glass is an important and commonly used material for microchips due to its excellent optical transparency, thermal conductivity, surface stability, solvent compatibility, and good biological compatibility. Based on these advantages, glass microchips are particularly useful for analysis of amino acids, proteins and DNA,[4–6] organic reaction,[7,8] and synthesis of nanoparticles.[9]

Recently, much effort has been dedicated to the development of fabrication techniques for the large scale production of glass microchips.[10–13] However, a critical step in the fabrication procedure of glass microfluidic chips involves transferring the pattern by photolithography.[10,11] This process requires specialized equipment like clean-room facilities, a photolithography machine and toxic reagents, which represents a barrier to the mass production of glass microchips. Therefore it is highly desirable to simplify the photolithography fabrication process and eliminate time-consuming equipment. Campbell *et al.*[12] proposed the direct printing of

microstructures onto glass substrates by agarose stamps soaked in HF etching solution. The use of a mask and an expensive photolithography process was avoided in this simple method, but the major limitation of glass etching proposed by this author was the slow rate of 2 μm h^{-1}, therefore this time-consuming process would likely limit its usage as a production method for microfluidic chips. Hanners *et al.*[13] presented a new method for the fabrication of glass microchips, which combined microcontact printing (μCP) by use of a PDMS stamp[14–16] with wet etching. In this process, a metal film made from chromium/gold was used as the mask, and photolithography was replaced by μCP technology to obtain micro patterns on the mask. Combined with wet etching processes, microstructures could be fabricated on glass. This method reduced the manufacturing costs of glass microchips significantly, however, patterning on the metal mask *via* μCP and chemical etching required a specialized micromachining instrument and expensive reagents like alkanethiols, thiosulfate, ferrocyanide, and cerric ammonium nitrate, which are toxic and harmful. In contrast to chemical etching, electrochemical etching is a simple and inexpensive technique for fabricating micro-patterns on a metal substrate.[17] Recently an electrochemical method for the fabrication of microstructures based on agarose stamps was developed by our group,[18] using a patterned agarose stamp soaked in the appropriate electrolytes the microstructuring of a Si wafer was realized in a simple and low-cost way. This technique is promising for extending to the rapid fabrication of micro-patterns on metalized glass substrates.

Herein, we propose a rapid fabrication method for glass microchips basing on microcontact electrochemical etching

[a]*State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China. E-mail: yongliangzhou2012@gmail.com; Fax: +86-592-2183047; Tel: +86-592-2183051*

[b]*Suzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of Sciences, Suzhou, 215123, China*

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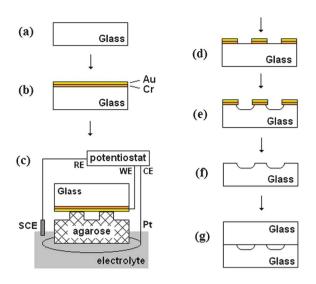
Fig. 1 Schematic illustration of the process for fabrication of a glass based microchip: (a) bare glass; (b) glass coated with Cr and Au layer; (c) μCECE; (d) exposed metal mask etched; (e) exposed glass etched; (f) metal stripped; (g) glass cover plate bonded to form microchips.

(μCECE), for the first time. In this method, a chromium/gold layer is used as the mask on which micro-patterns are formed with an agarose stamp using electrochemical etching instead of photolithography. Followed by wet etching, a micro-channel structure can be produced on the glass substrate. This method will not only bring glass-based microchips within the reach of any laboratory with minimal microfabrication equipment, but will also be a powerful tool for the mass production of glass-based microfluidic devices.

2. Experimental

The fabrication procedure is illustrated in Fig. 1. A film of Cr(100 nm)/Au(100 nm), used as the masking layer, was first sputtered onto a soda-lime glass plate (Shaoguang, Hunan, China).

μCECE was performed with a CHI-660A potentiostat (Chenhua Instruments, Shanghai, China) in a specially designed 3 electrode cell, with a platinum wire as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, a metalized glass plate as the working electrode, and an agarose stamp soaked in electrolytes as the electrolytic medium (ESI 1†). The stamp was brought into contact with the glass plate, then an anodic potential was applied to create the pattern. In all the experiments, the potentials were measured *vs.* an SCE whose potential was +0.24 V/NHE. The electrolyte used was 0.2 mol L^{-1} KCl prepared with ultrapure water (18.2 MΩ cm). The micropattern obtained on the glass plate was characterized using an optical microscope (Motic AE30, China).

The patterned glass was then etched in stirred $HF/HNO_3/H_2O$ (5 : 10 : 85 in volume ratio) at 40 °C to produce the microstructure. Once the etch was completed, the remaining

Cr/Au layer was removed by chrome etchant and gold etchant respectively. It should be noted that the same CECE technique could be used to remove the remaining Cr/Au layer. The morphology of the microstructure was characterized by scanning electron microscopy (LEO-1530, Germany).

Eventually glass-based microchips were obtained by thermally bonding the etched plate with a flat coverplate.[19]

3. Results and discussion

Electrochemical microfabrication of patterned metal mask

The glass plate was placed on top of the patterned stamp by means of a home-made substrate holder, which was designed in such a way that the metalized glass plate could be placed and removed from the stamp without mechanical deformation. The side of the Cr/Au film in contact with the stamp should be kept in air, and this configuration ensures that the electrode surface is precisely limited to the contact area.

The electrochemical dissolution potential of the Cr and Au layer was first investigated using cyclic voltammetry. The anodic potential was determined by the following procedure: a Cr layer (100 nm) was first sputtered onto the glass plate. Subsequently, a cyclic voltammogram curve was recorded in a solution containing 0.2 mol L^{-1} KCl. The procedure was repeated for an Au layer (100 nm). As shown in Fig. 2, a dissolution potential initiated at 0.6 V for Cr and 0.7 V for Au was observed during the anodic procedure, which indicated that an anodic potential of more than 0.7 V was necessary for electrochemical micromachining on a Cr/Au double layer.

Considering the processing efficiency and quality, an anodic potential of 1.0 V *vs.* SCE was applied and the chronoamperometry curve of Cr/Au/glass in 0.2 mol L^{-1} KCl solution was recorded. As shown in Fig. 3, two peaks appear, the first one corresponds to the dissolution of the Au layer, and the second
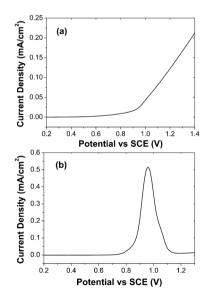

Fig. 2 Cyclic voltammogram for (a) Cr and (b) Au film deposited on glass in a solution containing 0.2 mol L^{-1} KCl (scan rate: 50 mV s^{-1}).
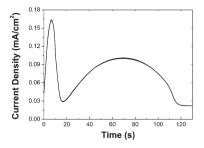
Fig. 3 Chronoamperometry curve of Au/Cr/glass in 0.2 mol L^{-1} KCl solution at 1.0 V *vs.* SCE.

one corresponds to the dissolution of the Cr layer. Electrochemical microfabrication is accomplished once the current is kept stable. The total etching time is 120 s depending on the thickness of the metallic layer used. After etching, the sample was thoroughly rinsed with DI water and dried at room temperature. The average width of the microchannel shown in Fig. 4 is 52 μm, while that of the Si mold is 50 μm. The deviation for the μCECE is approximately (52–50)/2/50 × 100% = 2%, which is due to minute distortion of the agarose stamp under the pressure of the glass substrate during the fabrication process.

Wet etching of glass-based microchannel

The procedures for the fabrication of microstructures are described in the experimental section. A microchannel with width of 102 μm and depth of 25 μm was obtained after performing a 25 min etching in HF etching solution, with an etch-rate of 1 μm min^{-1}. An RSD of 1.3% ($n = 8$) for the width was achieved. The SEM image shows that the channel surface is very smooth (Fig. 5). These results demonstrated that a glass-based microchannel with a relative high quality could be obtained by CECE combined with wet etching.

Fabrication and characterization of glass-based microfluidic chip

Based on the μCECE method, a glass microfluidic chip dedicated to electrophoretic separations was assembled and the principal characteristics of the chip like the reproducibility and stability were evaluated. The structure of the cross chip and experimental conditions used are described in ESI 2†.
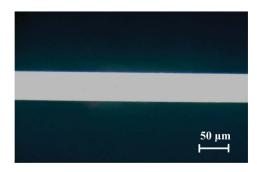

Fig. 4 Optical image of a channel fabricated by μCECE (the opaque parts are the metal mask and the transparent ones are the glass substrate).
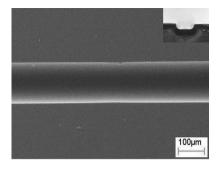

Fig. 5 Top view and cross-sectional profile (insert) of microchannel (SEM images).

As can be seen from Fig. 6, both the fluorescence signals for 10 μmol L^{-1} FITC and the migration time were almost kept constant during the measurement. The migration time and fluorescence intensity RSD ($n = 6$) for FITC were 0.42% and 4.96%, respectively. The obtained results demonstrated that the electroosmotic flow in the glass microchannel was suitable for continuous measurement.

Comparison between conventional lithography and μCECE

The features of both techniques are summarized in Table 1. Compared with conventional lithography, the features of μCECE include low cost and simple operation, thus this approach will be of interest for the development of microfluidic glass devices in a short time (less than 2 min) without the need for expensive microfabrication equipment and toxic reagents. It should be pointed out that the fabrication accuracy of μCECE is still being assessed in our laboratory, and a sub-micrometer resolution could be achieved using an agarose stamp based on a microcontact etching technique,[12] which is much less than the accuracy of photolithography (10 nm[20]). However, considering that the channel width in a glass microfluidic chip is typically about tens of micrometers with a simple structure, the proposed μCECE technique can easily fit the requirement for fabrication of glass microfluidic chips.

4. Conclusion

In summary, a localized electrochemical etching method is presented in this work. By using μCECE instead of standard UV photolithography, the pattern could be transferred to a
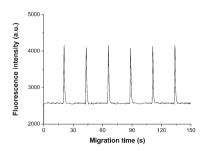

Fig. 6 Electropherograms of FITC on a microfluidic glass chip.

Table 1 Comparison between conventional lithography and CECE for the micropatterning of a mask layer on glass

	Lithography	μCECE
Operation steps	① Exposure ② Development ③ Remove Cr layer	① Microcontact electrochemical etching
Equipment (apparatus)	① Lithography tool ② Wet etching groove ③ Clean-room	① Potentiostat or power supply ② Electrolytic cell
Reagents	① Photoresist developer ② Commercial chromium etchants (ceric ammonium nitrate)	① Electrolyte (KCl)
Consuming time	Approximately 30 min	Less than 2 min
Total cost	Expensive	Low

mask layer which was deposited on glass, and the glass-based microchannel was subsequently obtained by wet etching. Finally, a microfluidic glass cross chip was assembled and the device was successfully used for electrophoretic separation of FITC. The proposed approach has the following advantages over those commonly used ones: (1) it is a non-lithographic method; (2) it does not require clean-room facilities; (3) it is low cost; (4) it is a high throughput process; (5) the reagents used in the electrochemical process are harmless to the environment and the human body; (6) combined with the room temperature bonding method,[21] it may also be appropriate for mass production of glass-based microfluidic devices. This approach should be likely to extend to the preparation of other microfluidic devices such as microelectrodes, photomasks, metal molds for polymer microchips, and so on.

Acknowledgements

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