# A toner-mediated lithographic technology for rapid prototyping of glass microchannels†

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*Received 7th March 2007, Accepted 17th May 2007*
*First published as an Advance Article on the web 5th June 2007*
**DOI: 10.1039/b702931d**



A simple, fast, and inexpensive masking technology without any photolithographic step to produce glass microchannels is proposed in this work. This innovative process is based on the use of toner layers as mask for wet chemical etching. The layouts were projected in graphic software and printed on wax paper using a laser printer. The toner layer was thermally transferred from the paper to cleaned glass surfaces (microscope slides) at 130 °C for 2 min. After thermal transference, the glass channel was etched using 25% (v/v) hydrofluoric acid (HF) solution. The toner mask was then removed by cotton soaked in acetonitrile. The etching rate was approximately $7.1 \pm 0.6$ μm $min^{-1}$. This process is economically more attractive than conventional methods because it does not require any sophisticated instrumentation and it can be implemented in any chemical/biochemical laboratory. The glass channel was thermally bonded against a flat glass cover and its analytical feasibility was investigated using capacitively coupled contactless conductivity detection ($C^4D$) and laser-induced fluorescence (LIF) detection.

## Introduction

Due to their innumerable advantages, miniaturized systems have provided a true revolution in analytical and bioanalytical sciences. An exponential increase in the number of publications has been observed[1–5] since the concept of micro total analysis systems (μTAS) was first reported in 1990s.[6–9] Since the first reports in the literature,[6–9] a large number of materials has been investigated in microfabrication sciences. Polymers have been widely employed due to their low cost and easy of processing when compared to silicon, quartz and glass substrates.[10–12] However, glass is still the most popular material for microfluidic applications presenting good mechanical and optical properties, high electrical insulation and low reactivity with all common solvents employed in analytical applications.[13]

Glass microchips are commonly fabricated by standard photolithography combined with wet chemical etching or deep reactive ion etching (DRIE) to transfer the channel patterns into the wafer surface.[13–15] The mask preparation for etching processes has a great importance, the mask determines the properties of the resulting microdevice, such as wall-channel roughness.[13] Metal masks composed by a thin layer of Cr covered by Au,[15] polysilicon[16] or amorphous silicon[14] films as well as photoresists[17–19] are often used as etching mask layers. Although the use of these conventional masks provides satisfactory results, the deposition of both thin films and photoresist layers is an expensive and time-consuming process. Furthermore, the preparation processes require sophisticated instrumentation located in expensive cleanrooms that are not always readily accessible for the researchers. For this reason, the search for alternative technologies is a constant focus for all scientific communities. In this way, Schlautmann and colleagues[20] described a technique to fabricate glass microchannels based on powder blasting. Rodriguez and co-workers[21] described an alternative process for rapid prototyping of glass microchannels. The pattern was etched on glass using PDMS channels, reversibly sealed to a glass surface, aiming to confine the etching solution. However, this process is still dependent on the photolithographic workstation for preparation of masters. A simple, fast, and inexpensive toner-mediated technology without any photolithographic step to produce glass microchannels is described in this work.

The use of toner in microfabrication technology has a short but promising history that started few years ago. Tan and co-workers[22] introduced a simple method for the fabrication of PDMS microchips by using a photocopying machine to make a high-relief master on a transparency film. Do Lago and co-workers[23] proposed a direct-printing process for the fast production of microfluidic devices at very low cost. This technology has been used to fabricate electrophoresis microchips coupled to electrochemical systems,[23–27] electrospray[23] and mixing[28] microdevices. The production of printed masters for rapid prototyping of PDMS microchips using this technique has also been reported by different groups.[29–31] This direct-printing process has also been explored for quick production of single[24,32–34] or multiple coplanar gold electrodes.[32,33] Recently, Do Lago and co-workers[35] proposed a new process to fabricate glass-toner microdevices. Microchip

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† Electronic supplementary information (ESI) available: Layout of the glass microchip; intra-chip and inter-chip reproducibility. See DOI: 10.1039/b702931d

free-flow electrophoresis fabricated in glass-toner have also been recently proposed.[36]

A toner-mediated lithographic technology for rapid prototyping of glass microchannels is presented in this paper. This technology is based on direct-printing of layouts on wax paper followed by thermal transference onto glass surface. The toner layer is then used as an etching mask. Channels were etched by using HF solution. The feasibility of the proposed low-cost glass microchips was evaluated by $C^4D$ and LIF measurements using high-mobility inorganic cations and FITC-labeled aminoacids, respectively, as model analytes. To the best of our knowledge, this is the first systematic study showing the use of toner as a mask for etching glass slides.



## Experimental

### Microfabrication process

The proposed microfabrication technology in this work can be presented by three steps: (i) preparation of toner masks by direct-printing process on wax paper and thermal transference onto glass surface; (ii) wet chemical etching by using HF solution; and (iii) bonding the glass plates by thermal process. Fig. 1 depicts the idealized technology.

The layout of the devices was drawn and laser-printed on a single A4-size wax paper sheet as previously reported.[23,24] The sheet was cut yielding several individual decals. The decal was fixed on a cleaned glass (I) microscope slide ($26 \times 75 \times 1$ mm) (Glass Tecnica, Sao Paulo-SP, Brazil) and then the first toner layer was transferred onto glass surface (II) by heating for 2 min at 130 °C under pressure (*ca.* 0.5 MPa). A commercial heating press model HT2020 (Ferragini, Sao Carlos-SP, Brazil) was used to carry out thermal transference steps. Two toner layers were aligned and sequentially transferred onto a glass surface under the same conditions. The glass with the toner mask was prebaked at 120 °C for 20 min prior to the wet chemical etching. Then, the microchannels were etched (III) in a bath containing 25% (v/v) HF solution under rigorous stirring. After the etching process (IV), the toner mask was removed (V) from the glass surface with acetonitrile. The bonding step (VI) was performed by fusing the two glass slides at 580 °C for 4 h in a conventional muffle furnace with a ramp rate of 30 °C $min^{-1}$. The glass slides were put on a polished alumina wafer to maintain the flatness. Bonding of ~80% of the area was routinely achieved. Microchips with a crossed-channel design (as shown in the ESI†) were used to evaluate their performance in electrophoretic separations. Sampling and separation channel lengths were 20 mm and 50 mm, respectively. The resultant isotropic etched channels have a trapezoid-like shape with a depth of 35 μm and a width of 200 μm.

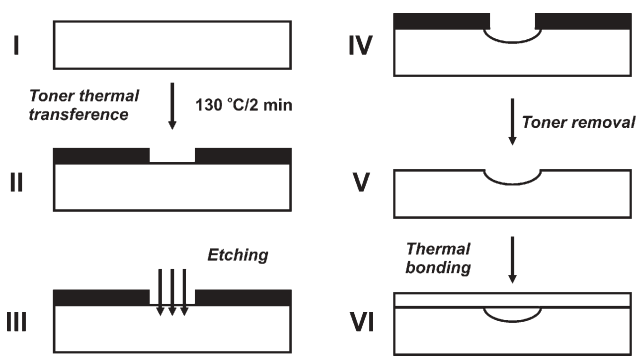


**Fig. 1** Toner-mediated microfabrication process. I, cleaned glass surface; II, toner thermal transference onto glass surface; III, wet chemical etching step; IV, channel profile before toner removal; V, etched-glass channel and; VI, thermal bonding step.

### Electrophoresis procedures

All experiments were performed at room temperature. Glass channels were preconditioned with 0.1 mol $L^{-1}$ sodium hydroxide and buffer solution for 10 min each. Injection and separation voltages were generated using a high-voltage power supply (CZE 1000R, Spellman, Hauppauge, NY, USA). A lab-made $C^4D$ system[27] was used to monitor the separations on the channel. LIF experiments were performed using a custom-made confocal system (IS BIOTECH, Porto Alegre, RS, Brazil) equipped with a 488 nm argon ion laser beam (1 to 50 mW optical output power) (LaserPhysics, Salt Lake City, UT, USA).

### Materials, reagents and samples

The following materials and chemicals were used as received: glass microscope slides ($26 \times 75 \times 1$ mm and $15 \times 50 \times 0.25$ mm) (Glass Tecnica, Sao Paulo-SP, Brazil), wax paper sheet (Ferragini, Sao Carlos-SP, Brazil), toner cartridge C4096A (Hewlett Packard, Palo Alto-CA, USA); sodium chloride, potassium chloride, lithium chloride, acetonitrile, 40% hidrofluoric acid, arginine (Arg), phenylalanine (Phe), serine (Ser), glycine (Gly), sodium hidroxyde, boric acid and sodium borate, acetone, fluorescein isothiocyanate (FITC), (Sigma, St. Louis, MO, USA); L-Histidine and 2-(*N*-morpholino ethanesulfonic acid (MES) (Fluka, Bucks, Switzerland). All buffer solutions were prepared in ultrapure water (resistivity 18 MΩ cm) and filtered through 0.45 μm membrane filters before use. The amino acids Arg, Gly, Phe, and Ser were labeled with FITC using a procedure described elsewhere.[37]

## Results and discussion

The toner layer printed on transparency film or wax paper surface has several valleys (pinholes) at the toner surface.[23–25,35,36] The low adherence on wax paper surface allows the toner to be easily transferred to other surfaces by heating. Comparing the channel features between the polyester[23, 25] and the wax paper, the toner layer transferred onto glass surface by heat and pressure has presented fewer imperfections than the polyester–toner system owing to the pressure application. The deposition of multiple layers decreases the presence of such valleys, randomly distributed at the toner surface, diminishing the probability of the lack of toner occurring in the same place in subsequent layers. The optimum temperature has been estimated to be 130 °C. Below this value, the toner transference can be incomplete. On the other hand, the use of higher temperatures can damage the resulting device. The applied pressure at toner transference has also a fundamental importance and it cannot be excessive,

 

because of the distortion on the resulting channels. The optimum pressure has been estimated to be *ca.* 0.5–1.0 MPa. The temperature and pressure were optimized according to the procedure described in ref. 35. Under the optimum conditions, the thickness for two toner layers was 17 ± 2 μm. The use of multi-layers can generate microchannels partially or completely obstructed. The obstruction is more pronounceable for channels ranging from 100 to 200 μm wide. Fig. 2A shows an optical image of one 100 μm wide channel, in which can be seen the obstructed channel due to alignment problems. Fig. 2B shows an image of a 200 μm width channel, which is the limiting useful dimension when two 600 dpi toner layers are used as the etching mask. This mask was used for all our further work. This toner-based technology can also be explored to fabricate parallel channels or curved channels considering the limiting dimensions. Parallel channels spaced by 500 μm have been successfully obtained. This complexity level requires the use of guidelines to perform the alignment of subsequent layers with the naked eye.

The toner layer exhibited good chemical resistance in an HF solution, its resistance time being directly proportional to the number of toner layers. This correlation can be explained by the fact that HF solution penetrates into the toner layer imperfections providing an undesired toner lift off. By using one toner layer, the resistance time in a 25% HF solution is less than 3 min. This time is extended to 7 min for a mask with two toner layers. The etching rate was 7.1 ± 0.6 μm $min^{-1}$ ($n$ = 10). After toner removal with acetonitrile, many pits have been observed at glass surface due to the presence of some imperfections in the toner layer or an insufficient adherence from toner layer to the glass surface. A baking step at 120 °C for 20 min prior to chemical etching was implemented and the presence of defects reduced satisfactorily. This baking step near the melting point of the toner enhanced its adherence to glass surface.

As observed in Fig. 2C and 2D, the channel wall did not present a perfect definition due to the low laser-printer resolution and the thermal transference step. The surface roughness of the glass surface protected by toner and the unprotected microchannels was, respectively, 12.5 ± 2.3 nm ($n$ = 10) and 474 ± 32 nm ($n$ = 10). The measured roughness for the area protected by toner layers indicates that the mask did not transfer its roughness (75 nm) to the glass surface, *i.e.*, the toner layers were effective as an etch mask. The high value observed on the etched channel can be related to the poor quality glass. However, the roughness found is lower than for glass microchannels fabricated by powder-blasting technique.[38]

The analytical performance of the proposed glass microchannels was demonstrated by using two detection systems. In the first one, the separation of alkaline-metal cations was monitored by $C^4D$ (Fig. 3A). The injected sample consisted of a 100 μmol $L^{-1}$ equimolar mixture of potassium, sodium, and lithium chloride dissolved in water. The sample was introduced into a separation channel using a 10 s injection at 1.0 kV. This system provided well-defined peaks for all three cations in less than 45 s under an electric field of 250 V $cm^{-1}$. At the second system, the electrophoretic feasibility was investigated by LIF measurements using FITC-labeled amino acids (Fig. 3B). An equimolar mixture containing 25 μmol $L^{-1}$ of Arg, Phe, Ser and Gly was injected into the channel using a gated injection mode. For this essay, 0.8 kV and 1.8 kV were applied to sample and buffer reservoirs, respectively, keeping both sample waste and buffer waste reservoirs grounded. To introduce sample plugs into the separation channel, the voltage applied at the buffer reservoir was floated for 1 s. The voltage was then resumed to allow simultaneous separation and sample gating. The detection was performed at 40 mm from the cross intersection. The low efficiency (400–1600 plates) obtained for FITC-labeled amino acids was expected due to the low resolution of this toner-based

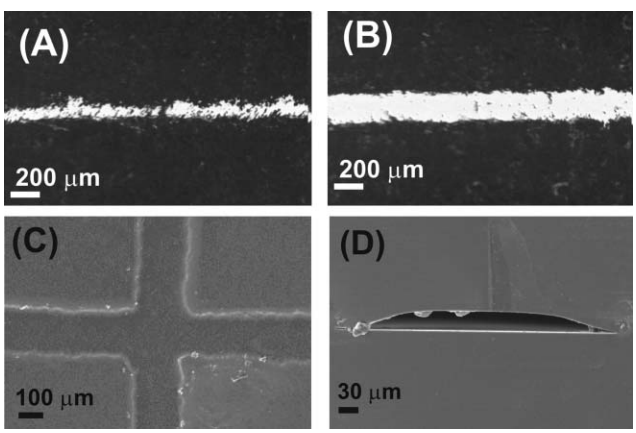


**Fig. 2** Micrographs of toner masks and etched-glass channels using the proposed technology. (A) and (B) show optical images of toner mask with 100 μm and 200 μm width microchannels, respectively. (C) and (D) show scanning electron micrographs of the cross intersection and transversal section, respectively.

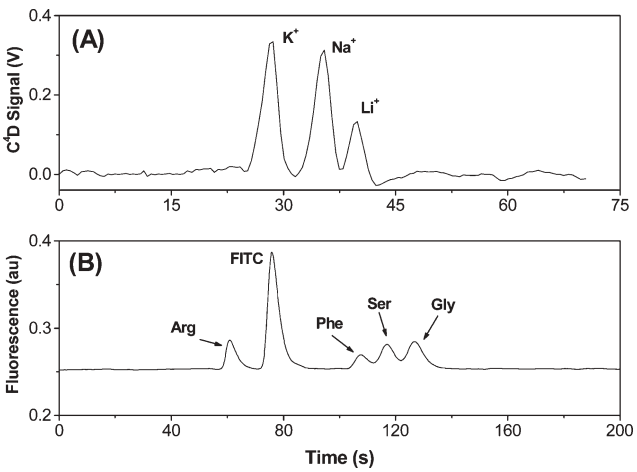


**Fig. 3** Electrophoretic separation of (A) inorganic cations (100 μmol $L^{-1}$ each) and (B) FITC-labeled amino acids (25 μmol $L^{-1}$ each). In (A), running buffer, 20 mmol $L^{-1}$ MES/His, pH 6.1; unpinched injection conditions, 1.0 kV per 10 s applied to injection microchannel; separation electric field, 250 V $cm^{-1}$; detection parameters, 500 kHz, 10 $V_{pp}$ at 30 mm from the injection channel. In (B), running buffer, 20 mmol $L^{-1}$ borate buffer, pH 9; effective length, 40 mm. The applied voltages to the sample and buffer reservoirs were 0.8 kV and 1.8 kV, respectively. Gated injection mode was performed floating the applied voltage at the buffer reservoir for 1 s.

technique, in which 200 μm width channels were projected. These electrophoretic parameters can be improved using narrower channels. Despite the low separation efficiency of these chips for the performed bioanalytical example, the low cost, simplicity and ease of construction of these glass chips suggest that they can be employed as disposable devices. In addition, the run-to-run and chip-to-chip reproducibility of these glass chips presented satisfactory results (as shown in the ESI†).

## Conclusions

A toner-mediated lithographic technology has been proposed in this work, in which toner layers can be effectively used as an etching mask to fabricate glass microchannels at very low cost. A glass microchannel can be prepared in a matter of minutes without sophisticated instrumentation. These advantageous features are suitable for inserting this low-cost technique into any chemistry or biochemistry laboratory. Besides glass microchannels fabrication, this toner-mediated lithographic technology can also be employed to produce silicon and quartz microdevices.

## Acknowledgements

This work was supported by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAFESP)—grant no. 04/01525-0—and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq)—grant no. 477982/03–05. The authors thank the Laboratory of Microfabrication (LMF) from the Brazilian Laboratory of Synchrotron Light (LNLS) for their facilities. Finally, the authors want to show their gratitude to Dr Susan M. Lunte (The University of Kansas) for her helpful contribution.



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