MICROFABRICATED PLASTIC CAPILLARY SYSTEMS WITH PHOTO-DEFINABLE HYDROPHILIC AND HYDROPHOBIC REGIONS

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ABSTRACT

In this paper we present a monolithic fabrication process for microcapillary systems that permits the formation of stable, photo-definable hydrophobic (θc ≈ 100°) and hydrophilic (θc ≈ 0°) regions on plastic channels. Using this process we have demonstrated a simple injector that uses a hydrophobic patch for cutting and transporting sample drops. Hydrophobic regions are formed by coating the inner walls with a thin parylene layer, while the hydrophilic regions are formed by selectively etching away the parylene layer followed by evaporating a thin hydrophilic silicon dioxide layer.

INTRODUCTION

Sample injection, dosing, and motion are essential functions required in miniature chemical analysis systems as samples must first be injected into the system, metered to specific volume, and properly routed to a specific reaction chamber [1]. These functions can be accomplished for example using a series of valves that control the extent and flow of the sample. Conventional diaphragm valves can fulfill this function, but their implementation is often cumbersome.

Simpler valving devices can be achieved by controlling the force that drives the wetting and wicking of the sample in these small capillary systems. Therefore these devices require localized control of the surface energy or its rate of change with respect to the amount of liquid displaced which determines thewick pressure. Two types of devices that use this scheme have been fabricated. The first type of device controls sample motion with the introduction of abrupt changes in the capillary cross-section [2, 3]. The second type uses selective texturing of hydrophilic and hydrophobic regions [4–6]. An essential requirement for both of these approaches is a wall material that holds stable surface properties. This is an intrinsic problem with plastic capillary systems which tend to be largely hydrophobic.

In this paper we present a monolithic fabrication process for microcapillary systems that permits the formation of stable, photo-definable hydrophobic (θc ≈ 95 – 100°) and hydrophilic (θc ≈ 0°) regions on plastic channels. Using this process we fabricate a simple injection device that exploit surface tension forces to perform sample stop, drop splitting and sample transport in capillary tubes without the need of any moving parts. The principle of operation is based on the pressure barrier that develops when capillaries changes from hydrophilic to hydrophobic. This type of injection device in its normal state can stop flow, but it can be electrically triggered to split and transport sample when used in combination with two electrodes. Fig. 1 shows the basic structure of a sample injector device consisting of a long capillary tube with one reservoir on one end, two TiPt electrodes, a flow restriction, and a hydrophobic patch. When a liquid sample is first introduced in the reservoir, it wicks in the channel due to its hydrophilicity and abruptly stops at the outer edge of the hydrophobic stop valve preventing any further flow. The pressure barrier provided by the valve can be overcome by external pressure. In this device the pressure is produced by an electrolytically generated O2 bubble at electrode (2) as explained in [2]. When the pressure of the electrolysis bubble exceeds the pressure barrier, the bubble pushes the liquid sample past the stop valve, and splits the liquid sample transporting the sample droplet forward as the bubble continues to grow. The hydrophobic patch is not only necessary for the establishment of the pressure barrier, but it is also required for achieving a complete separation of the sample from the main column of liquid behind and for repeating action.

In this device, the hydrophobic region is formed by coating the inner walls with a thin p-xylene (parylene-C) layer, while the rest of the hydrophilic channel is formed by selectively etching away the parylene followed by evaporation of a thin hydrophilic silicon dioxide layer. The remaining of the...
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A 2 μm-thick layer of parylene is next deposited patterned using a 300 nm-thick evaporated Au mask and subsequently etched in O₂ plasma to form the bottom of the hydrophobic patch. The Au mask is used for the etch because photoresist leaves a layer of 'resist skin' during RIE, covering the hydrophobic patch which cannot be not dissolved in acetone and making the patch surface hydrophilic. After stripping the Au mask with wet gold etchant, a 20 μm-thick layer of AZ9260 resist is spin-cast and patterned to form the sacrificial layer.

A 2 μm-thick layer of parylene is next evaporated, patterned with a 300 nm-thick Au mask, and etched in O₂ plasma at low power to form the top of the hydrophobic patch. A high plasma power deforms the sacrificial resist as well as etches it away rapidly. This top parylene layer essentially covers the top and the sidewalls of the channel, thus prevents possible any sample leakage along the sidewalls of the hydrophobic region. The gold masking layer is then removed, and the structural channel wall is then formed by evaporating a 400 nm-thick layer of evaporated oxide, and a 5 μm-thick layer of parylene. Contacts to electrodes and reservoirs are subsequently etched in O₂ plasma with a Au mask that is next removed.

**Fabrication**

Capillary systems and hydrophobic patch injectors were fabricated using a 6-mask modified version of the plastic surface micromachining process presented in [2] shown in Fig. 3. First, a 2 μm-thick layer of parylene-C is deposited on an oxidized silicon wafer. A 20:30 nm-thick TiPt layer is then deposited and patterned by liftoff to form the electrode. A second 2 μm layer of parylene and a 400 nm-thick layer of evaporated silicon dioxide is then deposited on top of the metal. Contact holes are then etched in CF₄ and CHF₃ plasma and in O₂ plasma.
resist layer in an acetone bath for 8-12 hours. The released devices were next exposed to an oxygen environment for a few days which stabilizes the surface properties of the parylene rendering the patch permanently hydrophobic. Fig. 4 shows a SEM photograph of the hydrophobic region. Fig. 5 shows the cross-section of channel with the hydrophilic and hydrophobic region.

**PRESSURE BARRIER**

In order to understand the formation of pressure barrier in the hydrophobic stop valve, one must account for the total surface energy of the system as the liquid extends near the edge of the hydrophobic region. The total interfacial energy of this system is

\[ U_T = (A_{sl} + A_{sa}) \gamma_{sa} - A_d \gamma_{ta} \cos \theta_c + A_{ta} \gamma_{ta} \]

where \( A_{sl} \) and \( A_{ta} \) are solid-liquid, and liquid-air interface areas, \( \gamma_{ta} \) is the surface energies per unit area, and \( U_o \) is constant since the sum \( A_{sl} + A_{sa} \) remains invariant. The total energy and wick pressure can be determined by examining the shape of the liquid meniscus in different regions of operation: a) wicks in, b) pivoting, and c) extending. Since the channel width \( w \) is assumed much larger than its height \( h \) hence the meniscus shape is considered as one dimensional, and the meniscus is assumed to be a circular arc of angle \( 2\alpha \) as shown in Fig. 5. In regime (a), the liquid wicks in with constant contact angle \( \theta_{\text{phobic}}(\alpha = \pi/2 - \theta_{\text{phobic}}) \) and constant meniscus cross-section due to the hydrophobicity of the channel until \( x \) reaches the edge. The total energy is a function of the injected volume \( V_i \) since as \( V_i \) increases, the wetted area changes.

\[ U_T = U_o - 2\gamma_{ta} \cos \theta_c w + \gamma_{ta} \frac{wh \alpha}{\sin \alpha} \]  

With some manipulation, it can be shown that in all regimes the pressure in the liquid is

\[ P = \frac{dU_T}{dV_i} = -2w\gamma_{ta} \cos \theta_c \frac{\cos \theta_c}{h} \]  

where \( \theta_c \) is the contact angle at the leading edge. In regime (1), \( \theta_c = \theta_{\text{phobic}} < \pi/2 \) and constant hence the negative pressure allows the liquid to wick in the channel without applying external pressure. In the pivoting regime, \( x = L \) and \( \theta_{\text{phobic}} \leq \theta_c \leq \theta_{\text{phobic}} \) smoothly changing the sign of \( P \) at the inlet of the hydrophobic patch. In regime (3), the liquid moves beyond the edge and extends into the hydrophobic region with constant contact angle \( \theta_c = \theta_{\text{phobic}} > \pi/2 \) producing a positive pressure which effectively stops the wick action. If the liquid is forced beyond the outer rim of the patch, then the a negative pressure develops again resuming the liquid wick.

Fig. 8 shows the system energy and internal liquid pressure as a function of sample volume. Initially, the energy decreases as the liquid sips into the tube (i.e. driving the wicking) with a fixed slope until the capillary stop region is reached. Beyond the stop outer edge the meniscus must expand. This expansion requires external energy therefore a pressure barrier develops that stops the flow.

The maximum pressure barrier \( \Delta P \) develops when \( x = L \) hence For \( h = 5 \mu m, \theta_c=20^\circ \), and \( \beta = 90^\circ \), the barrier is about 10 kPa or 1.4 m of water.

**EXPERIMENTS**

**Hydrophobic Stop Valves:** Hydrophobic stop valve were tested using both DI water and a red dye. Solutions were introduced from one side of the reservoir first. Figure 9 shows an example vertical stop valve.

![Figure 6: The three regimes used for calculation of barrier pressure](image6)

![Figure 7: Angle definitions](image7)

![Figure 8: Surface energy and pressure vs. sample volume](image8)
Figure 9: Photograph of vertical stop valve. The red dye stops at the outer edge of the hydrophobic stop valve.

The channel is 200 μm wide and 20 μm high. The photograph shows clearly that the liquid flow stops at the outer edge of the valve.

The pressure barrier for the vertical valves was determined experimentally by first bonding a macroscopic piece of teflon tubing to one end of a capillary containing the valve. The capillary was connected to a pressure gauge and a water reservoir. The water reservoir height was gradually raised respect to the chip while monitoring the condition of the valve until the barrier pressure is overcome. Using this method a barrier pressure of 6 kPa was recorded for 10 μm-high neck regions. Similar experiments were performed with the lateral devices, but the barrier pressures were not recorded.

**Sample Injectors:** Sample injectors were tested using hydrophobic stop valves. The actuation of an injector is illustrated in Fig. 10 showing photographs of the position of the initial meniscus, the formation and grow of the bubble, drop splitting, and the liquid motion after the valve was activated. Experimentally it was determined that the valve could only be actuated when the bubble was formed very quickly with electrode current \( I_e > 3 \mu A \) in rough agreement with our estimate. After the valve is activated, the bubble moves quickly to the leading edge of the capillary stop but it does not impede the flow completely due to the presence of capillary-induced creep flow around the bubble edge along the channel sidewalls. After the valve is activated, the liquid sample is completely broken off from the flow, since the hydrophobic patch impedes the possible capillary-induced creep flow around the bubble edge along the channel sidewalls.

Figure 11 shows a time sequence of an injector implemented with the horizontal neck valve. Unlike the previous injector, the actuation happened almost instantaneously as the current was switched to about 5 μA. In contrast to the vertical valve stop injector, the switching action did not require the formation of any visibly large bubbles. We speculate that in addition to the bubble pressure the contact angle near the electrode region may have been affected as a result of the electrolysis in a favorable manner.

**SUMMARY**

This paper presents several simple passive fluid gating devices based on the capillarity forces developed during the abrupt enlargement of channels. The devices were fabricated using micromachining of plastics. Two types of vertical and horizontal valves were tested. Asymmetric horizontal valves showed unidirectional characteristics. When used in combination with two electrodes, these valves can be used for the construction of sample injectors. These injectors are activated using an electrolytically generated bubble that creates a pressure burst that overcomes the valve pressure barrier with just a few microamps of current.

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**References**


