

A THERMALLY RESPONSIVE POLYMER MICROVALVE WITHOUT MECHANICAL PARTS PHOTO-PATTERNED IN A PARYLENE CHANNEL

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ABSTRACT

A photoresist-like thermally responsive polymer has been formulated, surface micromachined and integrated into parylene microchannels to realize an inline valve. The polymer physically swells below its lower critical solution temperature and shrinks above it. Test showed a 2.5-fold polymer volume increase by changing water temperature from 25 to 10°C. Repeated polymer swelling and shrinking were observed inside the channel with a system response time around 7 s. Pressure build-up measurements were used to demonstrate the functionality of the valve. Valve test results using DI water showed that the pressure upstream of the polymer plug increased from 15.3 to 20.3 psi with temperature change from 36°C to 15°C.

I. INTRODUCTION

Micro total analysis systems (μ TAS) require many independently operating pumps and valves to precisely control the liquid flow from one part of the system to another [1]. These pumps and valves must be simple enough to permit integration with the other components of the system [2]. Most mechanical valves actuate a diaphragm [3] separating two capillary levels as shown in Fig. 1a. This complicates the fabrication process and

makes large-scale integration difficult. Diaphragm inline valves employing a single capillary level are simpler; however, since most micro channels are rectangular, voids always exist resulting in poor sealing as shown in Fig. 1b. Due to these complexities, alternative inline valves that provide a better seal have been fabricated using working substances such as hydrogel materials. Hydrogels undergo reversible volume change (swelling) with pH [4], glucose concentration and temperature [5,6] of the liquid in which they are immersed thus plugging the microchannel.

Presently hydrogel materials are patterned by selective deposition or in-situ polymerization on (or between) pre-fabricated surfaces.

This work describes a microfabrication technique developed for a photoresist-like thermally responsive polymer and its integration into parylene microchannels to realize a surface micromachined inline valve.

II. FABRICATION

Polymer Preparation

The thermally responsive polymer material is poly(N-isopropyl acrylamide-co-allyl methacrylate). This material is formed by copolymerization of a mixture consisting of N-isopropylacrylamide (NIPAAm), allyl methacrylate and azobisisobutyronitrile (photo-initiator) triggered by UV light. This process produces polyNIPAAm copolymer with a photoresist-like film characteristic. PolyNIPAAm is one of the best-known temperature sensitive polymers. It undergoes a rapid and reversible phase transition from extended hydrated chains (swollen state) below the lower critical solution temperature (LCST) of 32°C to collapsed hydrophobic coils (shrunk state) at a temperature above LCST. Photo-patterning of a different polyNIPAAm copolymer and photo-initiator was reported previously [7].

Thin Film Formation

The thermally responsive polymer is formed by spin coating of its tetrahydrofuran (THF) solution containing a UV initiator (2,2-dimethoxy-2-phenylacetophenone

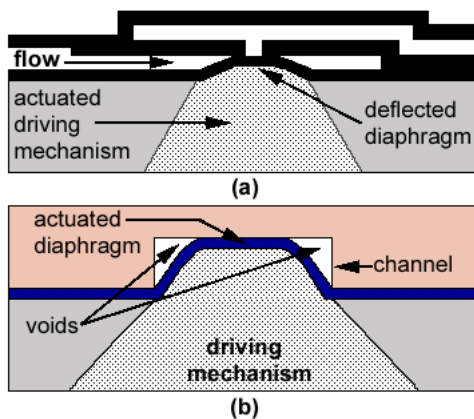


Fig. 1. Diaphragm valves using (a) two and (b) one level capillaries.

(DPAP)). The viscosity of the solution is very low. A single spin coat of 90 mg resist polymer, 2 mg DPAP in 1 ml THF solution at 300 rpm produces a film thickness of $\sim 1 \mu\text{m}$. In order to get thicker films the viscosity of the solution was increased by preparing more concentrated solution. For example, a solution of 500 mg polymer, 20 mg DPAP in 2 ml THF spun at 500 rpm provides good quality film with uniform thickness of $\sim 5 \mu\text{m}$.

Spin coating requires a large quantity of the polymer solution. Micromold casting is a more economical technique. Fig. 2 shows the fixture used for casting polyNIPAAm films. The process wafer was placed between two aluminum plates. The wafer was secured to the fixture with an o-ring in contact with the top of the wafer and screws around the top plate. Polymer solution was poured on the wafer surface through an opening in the top aluminum plate and soft baked for 10 minutes at 60°C . A film thickness of 20-30 μm was achieved. This method leaves a thicker ring of film along the wafer edge. The ring was removed with an acetone-dipped scrub to get better resolution in contact printing.



Fig. 2. Fixture used for casting polyNIPAAm films.

Adhesion of the polymer film to oxidized silicon was achieved by immersion in 7:3 mixture of acetone and 3-(trimethoxysilyl)-propyl methacrylate (AZ174 silane, Specialty Coating Systems, Inc.) for one day followed by a brief washing with acetone before spinning or casting.

The polymer was patterned using contact lithography. The film was exposed through a mask for 15 min using an EV-420 aligner with a UV light power density of 10 mW/cm^2 (365 nm wavelength). The exposed film was developed in acetone for 5 min. The resulting pattern and its response to temperature changes are shown in Fig. 3.

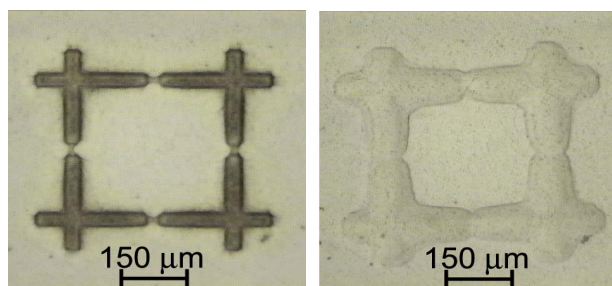


Fig. 3. Top view of UV patterned polymer immersed in water at a temperature of 40°C (left) and 15°C (right).

Volume Change Characterization

Quantification of changes in polymer volume in water at different temperatures is needed for proper design of the valve. Cross sectional views of polymer patterns in DI water at different temperatures were observed using an optical microscope with a CCD camera. Fig. 4 shows the shrinkage of the polymer with temperature. Fig. 5 shows that the film thickness increases 2.5-fold when the water temperature changes from 28°C to 5°C . Most of the volume change occurs between 10°C and 25°C . Our results also show a LCST at $20\text{-}25^\circ\text{C}$ that is somewhat lower than that of pure NIPAAm (32°C). This finding is in agreement with observations published elsewhere [7]. The size of the features also increases 3.4 and 4.2 times in acetone and IPA, respectively independent of temperature. The polymer swelling leads to problems when releasing devices.

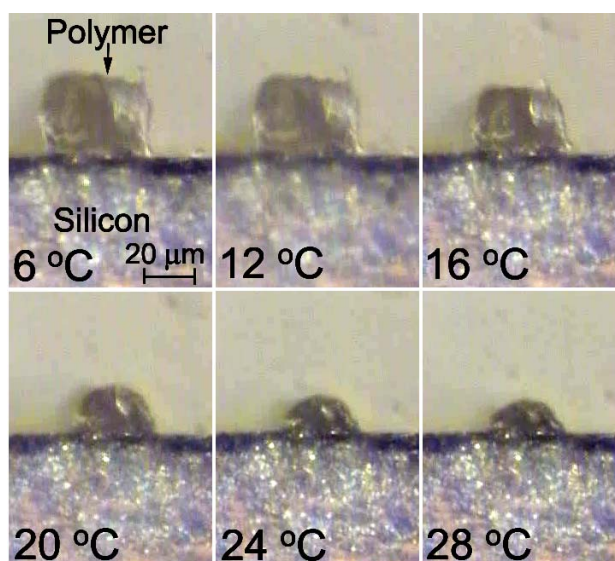


Fig. 4. Cross sectional view of patterned polymer in water at different temperatures.

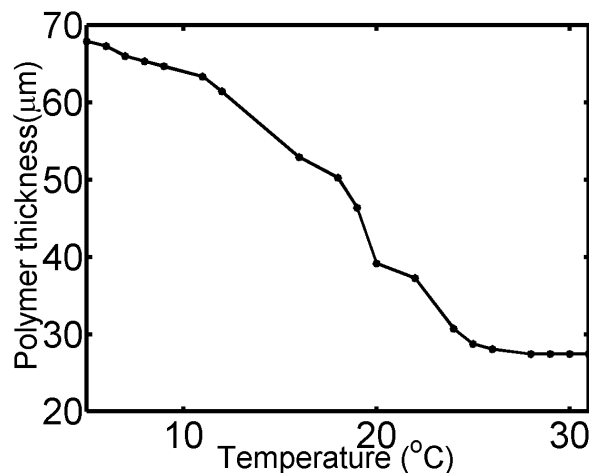


Fig. 5. Polymer thickness change with DI water temperature.

Device Fabrication

The fabrication process for a simple inline valve that utilizes this polymer is summarized in Fig. 6. First the silicon substrate is oxidized. Next, a 20 μm -thick polymer film is formed by the casting method and patterned as explained above. This is followed by patterning 20 μm thick sacrificial photoresist to form channels and reservoirs. Channel walls are formed by a 6 μm thick layer of parylene. A 20 μm thick photoresist layer is next patterned as a mask layer. Unmasked parylene is then etched in oxygen plasma to form reservoir openings. Finally, the devices are released in acetone.

The acetone release of the sacrificial photoresist is very critical since polyNIPAAm copolymer swells in acetone and hinders complete removal of the photoresist. However, once acetone evaporates, the polymer shrinks almost to its patterned size. It is found that after a day-long acetone soak, two repeated 5 min acetone soaks followed by 5 min. dry periods, result in well released devices. A picture of the released device is shown in Fig 7.

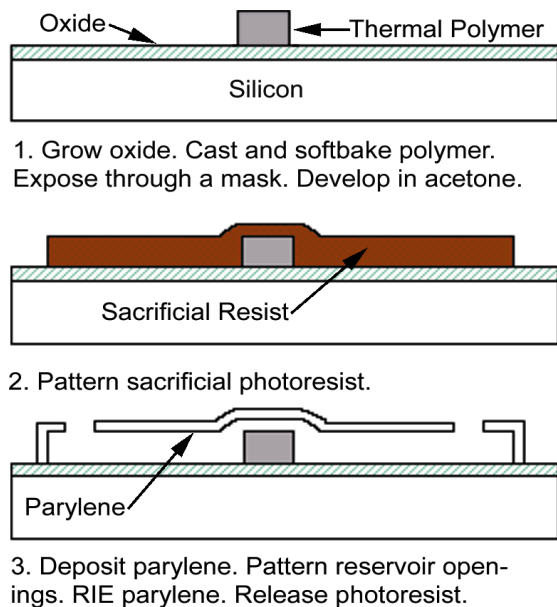


Fig. 6. Fabrication process for the valve.

In order to enhance photoresist release around the polymer, a lateral gap is left between polymer plug and channel sidewalls. Since in this design sacrificial photoresist covers both the top and sidewalls of the thermally responsive polymer, it also guarantees full protection of polymer from other chemicals in the coming process steps such as photoresist developers and strong bases, which were also found to swell the polymer. This configuration also increases the surface area that comes in contact with water during device operation. Since response time of this polymer depends on the collective diffusion of the polymer network into the surrounding medium, a larger surface area of the polymer exposed to liquid decreases the response time [4]. Further decreases can be achieved by

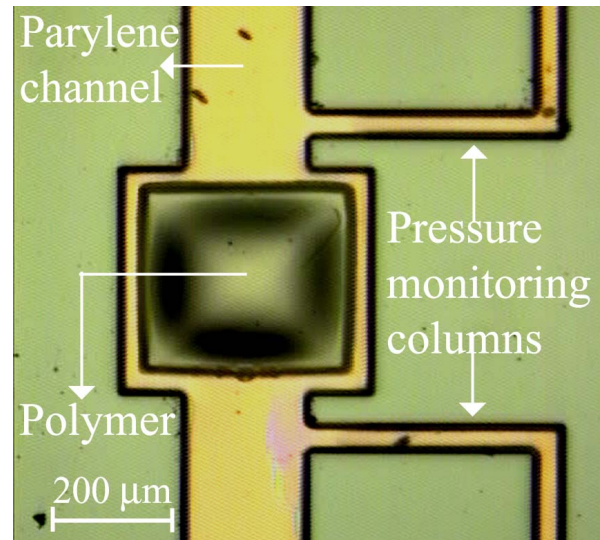


Fig. 7. Top view of inline valve.

fabricating smaller rectangular patterns in parallel instead of one large feature. Finally, the presence of the gap eliminates failures caused by bursting of the polymer during soak cycles; however, it also introduces a small leak path that determines the maximum flow resistance of the valve.

The solvent, acetone or IPA, incorporated in the polymer was a significant problem during the release of the devices. Although solvents evaporate, small residual amounts remain incorporated in the polymer network structure. This solvent cannot be released by simple rinsing with water as manifested by lack of response to temperature even after a thorough rinse.

This has been remedied using the following procedure: First, the device that has been acetone released was soaked in IPA, then it was immersed in cold DI water (4 $^{\circ}\text{C}$) for 2 hours. After this treatment, the temperature sensitivity was restored. Cold water swells the polymer and dilutes the solvent and promotes its diffusion into the surrounding liquid. Soaking devices in solutions of strong bases such as KOH and NaOH for 5 min followed by rinsing in DI water has the same effect.

III. RESULTS AND DISCUSSION

In order to test the valve performance, measurements of pressure build-up were made inside the channel upstream of the valve at different temperatures. The pressure was measured using long capillary columns patterned perpendicular to the main channel.

Once the main channel is filled with liquid, air is trapped in the columns as shown in Fig. 8. A fixed external pressure source is applied to the upstream reservoir. The local pressure upstream of the polymer plug can be calculated from the compression of the trapped air using the ideal gas law, $PV/T = \text{constant}$, where P is the pressure, V is the air volume and T is the temperature.

Prior to pressure drop measurements, shrinking and swelling of the polymer plug inside parylene channel was

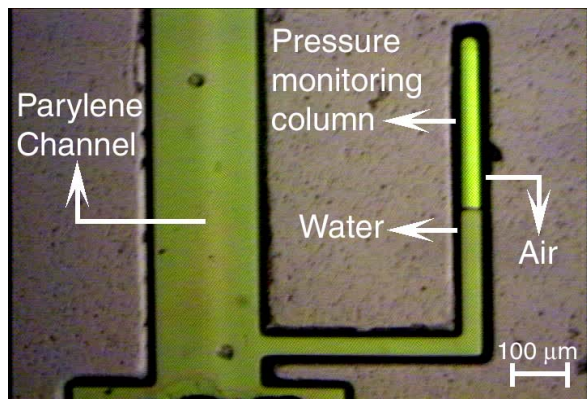


Fig. 8. Trapped air inside column is used to determine pressure inside the channel.

observed while temperature of the device was changed with an external thermoelectric (TE) cooler. Fig. 9 shows one of these observations. It shows that swollen polymer held at 10 °C shrinks rapidly after the temperature of the TE cooler is suddenly increased to 40 °C. The response time of the system was about 7 s. However response time of the polymer can be shorter than this. Fig. 10 shows the pressure at the plug interface as a function of temperature. It shows that pressure increased from 15.3 psi at 36 °C to 20.3 psi at 15 °C due to the polymer swelling.

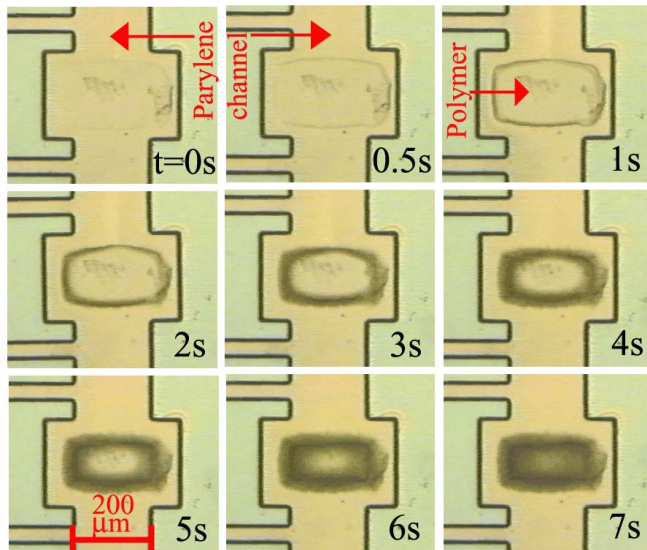


Fig. 9. Top view of thermally responsive polymer inside parylene channel shrinking with time as temperature changed from 10°C to 40 °C at time=0.

VI. SUMMARY

In this work, we presented a surface micromachined in-line valve that is fabricated by integrating a photoresist-like thermally responsive copolymer into parylene channels. Since no actuated diaphragm is used to control liquid flow, fabrication of this valve is simple. A 2.5-fold increase in polymer volume in water is observed when the water temperature changes from 25°C to 10°C. Response time of

the polymer plug inside the channel is less than 7 s. Pressure build-up measurements were used to demonstrate the functionality of the device.

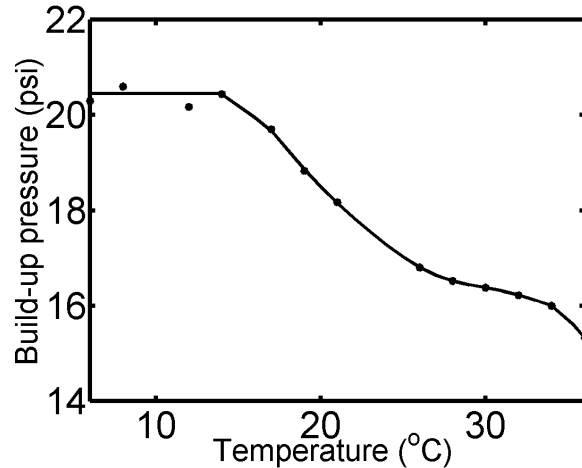


Fig. 10. Pressure build-up upstream of the polymer plug inside the channel at different temperatures.

ACKNOWLEDGEMENTS

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