Liquid as template for next generation micro devices

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Abstract: Liquids have fascinated generations of scientists and engineers. Since ancient Greece, the perfect natural shape of liquids has been used to create optical systems. Nowadays, the natural shape of liquid is used in the fabrication of microlens arrays that rely on the melting of glass or photoresist to generate high quality lenses. However shrinkage normally associated to the liquid to solid phase transition will affect the initial shape and quality of the liquid structure. In this contribution, a novel fabrication technique that enables the encapsulation and replication of liquid templates without affecting their natural shape is presented. The SOLID (SOlid on LIquid Deposition) process [1] allows for a transparent solid film to be deposited and grown onto a liquid template (droplet, film, line) in a way that the liquid shapes the overgrowing solid layer. The resulting configuration of the SOLID devices is chemically and mechanically stable and is the base of a huge variety of new micro-nano systems in the field of microfluidics, biomedical devices and micro-optics among others. The SOLID process enables in a one step process the encapsulation of liquid microlenses, fluidics channels, drug reservoir or any naturally driven liquid structure. The phenomenon and solid-liquid interface resulting from the SOLID process is new and still unexploited. The solid layer used for the SOLID process chosen in this paper is poly-para-xylylene called Parylene, a transparent biocompatible polymer with excellent mechanical and chemical properties. Moreover, as the solid layer is growing over a liquid template, atomically smooth surfaces channels can be obtained [2]. The polymerization of Parylene does not exert stress and does not change the shape of the liquid; this latter aspect is particularly interesting for manufacturing naturally driven liquid structures.

In this paper the authors explore the limits of this new method by testing different designs of SOLID encapsulated structures and their potential to deliver next generation micro devices.
1. Parylene deposition on liquids

Poly(chloro-para-xylylene) is deposited using a downstream LPCVD process known as Gorham process [3] that is carried out at typically 1-7 Pa. The dimer dichloro-para-xylylene is evaporated at typically 120 °C and cracked in a pyrolysis station at 650°C into reactive monomers. The deposition occurs in a two step reaction mechanism in a deposition chamber at room temperature. The low pressure of the standard Gorham process let water and other liquids disappear due to evaporation. The authors use in this work several liquids that have very low vapor pressures in a way that no liquid loss occurs at low pressure during deposition. Suitable liquids are e.g. glycerol, silicone oils, adipates and phthalates offering different viscosities. Other liquids such as water and aqueous solutions, have been meanwhile successfully coated by the authors [2], using APCVD parylene deposition (inert carrier gas at atmospheric pressure). For the purpose of this work a 2 µm Parylene layer was deposited over the liquid loaded substrates, following the conventional Gorham process.

2. Trapping scenarios

The first approach consisted in the encapsulation of liquids with naturally driven shapes. Drops with contact angle as high as 150° were successfully encapsulated by the SOLID process as can be seen in figure 1 below. This paper will also describe the study of the encapsulation of meniscus in capillaries and other naturally driven structures.

![Figure 1. a) SOLID encapsulated drop of glycerol on fluorinated oleophobic surface. The parylene layer of about 2 microns was deposited using the conventional Gorham process. The structure is mechanically, chemically and thermally stable (given by the intrinsic properties of the parylene film). b) Deposition of another drop on the SOLID encapsulated structure as a proof that the drop is indeed encapsulated in a stable membrane.

As shown in figure 1, the shape of the liquid features encapsulated by the SOLID process depends solely on the surface energies at the liquid – solid and gas interfaces. Therefore in order to fabricate structures for specific purposes, trapping scenarios be they physical, chemical or a combination of both were investigated. Figure 2 gives a schematic overview of the trapping scenarios.

![Figure 2. Trapping scenarios, side view: a) chemical trapping; b) physical trapping; c) chemico-physical trapping.]
Microcontact printing (µCP) or direct dispensing of self-assembled monolayers (SAMs) are good chemical traps transfer techniques for manufacturing and fast prototyping respectively. However, in order to test the limits of SOLID process in terms of feature size and feature architecture, the molecular-assembly patterning by lift-off (MAPL) process [4] was investigated thoroughly (figure 3).

Figure 3. A) Schematics of Molecular Assembly Patterning by Lift-off (MAPL). A photoresist is pre-patterned on top of SiO\textsubscript{2} grown on a silicon wafer (I); FOTS is deposited onto the surface from vapor phase (II); lift-off of the residual resist in an organic solvents (III), and finally filling of bare areas with driver liquid (IV). B) Optical microscopy of pre-patterned photoresist stripes about 4 µm in width and periodicity 10 µm. C) Optical microscopy of the same stripes on the stage IV filled with bis(2-ethylhexyl)adipate.

Moreover a series of experiments were performed using laser microstructures to create physical, chemical and physico-chemical patterns. The physical traps were obtained using UV laser bulk micromachining to generate channels on a Silicon substrate. The chemical traps were obtained by first evaporating oleophobic SAMs on quartz slides that were selectively removed by laser micro-machining to create patterns.

Test structure including lines, circles, squares and more complex forms at dimensions from a few microns to several tens of microns were designed for that purpose (figure 4).

Figure 4. SEM micrographs of complex SOLID coated structures with a 2 microns parylene layer.

3. Loading scenarios
In the case of chemical trapping, after the substrate is functionalized, liquids can be loaded by dip-coating: as the substrate is withdrawn, the liquid remains confined to the wettable areas, reproducing the structures transferred in the previous step.

This method has obvious advantages for a quick patterning of liquid networks on a flat surface. However, it provides little control for the amount of liquid loaded and the neatness of the unwettable surface, which is often spotted by satellite droplets. Both, the liquid load, and the presence of residual
droplets on the functionalized surface, are complex functions of the physicochemical properties of the liquid and of the dip-coating parameters, namely: the liquid density, viscosity and surface tension, the wetting angles on the substrate, the shape of the structures, the withdraw velocity and the tilt of the substrate. All these parameters determine the outcome of the dip-coating process in such a tangled way, that it is impossible to predict it, unless detailed numerical simulations are performed. With this aim we have carried out numerical simulations using CFD-ACE+ to test different dip-coating scenarios with different liquid properties. The results have proven their reliability and constitute an important tool for setting up new protocols of liquid patterning for SOLID applications.

**Figure 5.** Sequence of snapshots from a dip-coating simulation of a cross shaped wettable patch. The global borders of the simulation cell are represented as a box. The substrate is the back side of the box, and the colored cross is the wettable area on it. The liquid-air interface is represented in green and is gradually brought down with every time step, as the cell is drained from below. As the liquid surface passes beyond the cross, part of the liquid detaches from the main volume, thus loading the wettable structure.

An alternative to the dip-coating method for loading the substrates is by direct dispensing at predefined positions.

The advantages of this system with respect to the dip-coating process are the better control of the dispensed volume and the absence of residual droplets outside the wettable pattern. Besides, this method is better suited for filling 3D structures, since there is no risk of bubble trapping during the load. The drawbacks are the increased cost of the technology and loading time. Also, for 2D structures smaller than 100 µm, dip-coating offers a more accurate filling than dispensing. The choice of one technique or the other depends ultimately on the specific requirements of each application.

4. **Further results**

The study of the SOLID encapsulation of dynamic structures will also be presented in this publication. In this approach, standing waves are generated on a liquid during the SOLID encapsulation.

5. **Conclusions**

The fact that a solid (polymer) layer can be deposited onto a liquid substrate has the potential to contribute to next generation micro devices. The paper presents different scenarios to fabricate complex naturally driven and tailored structures using the novel SOLID technology Physical and chemical liquid patterning scenarios were investigated to test the limits of the fabrication technology with respect to feature size and layout. The possibility of dip-coating allows loading complex trap structures at high throughput and paves the way to low-cost scenarios, whereas a more expensive dispensing alternative allows a better control of the volume dispensed. A problem-adapted simulation
tool allows accurate predictions for loading of liquids on various trapping structures, whereby the quantity of trapped liquids is (predicted and experimentally confirmed) self-stabilizing.

Parylene has shown to be a suitable polymer with respect of conformal shape-replication, pinhole freeness, shape conservation due to stress-less overgrowing of the liquid template. Looking at later biomedical devices or drug delivering scenarios, parylene is particularly attractive due to its biocompatibility. In particular, the combination of SOLID technology together with MAPL technology allows complex parallel processing proved to be an extremely reliable self-stabilizing trap loading at laboratory level.

Some layouts using liquid structures are surprising indeed, and, in some cases, strictly reserved to the use of liquid templates. Generally spoken such Solid on Liquid templates contribute in a substantial way to push the potential of next generation micro and nano systems far beyond the state of the art.

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