Inkjet printed SU-8 hemispherical microcapsules and silicon chip embedding

Loïc Jacot-Descombes, Maurizio Rosario Gullo, Massimo Mastrangeli, Victor Javier Cadarso, Jürgen Brugger

Microsystems Laboratory, EPFL, 1015 Lausanne, Switzerland
E-mail: loic.jacot-descombes@epfl.ch

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Planar lithography techniques are not effective for precise fabrication of microdevices with hemispherical shapes. Drop-on-demand (DOD) inkjet printing (IJP) of photo-curable ink is a more appropriate fabrication approach as it takes advantage of the surface tension as well as of the delivery of a well-defined ink volume. Described is a DOD IJP technique onto geometrically-patterned silicon substrates enabling the controlled fabrication of SU-8 hemispherical microcapsules. Open half capsules of 100 µm in diameter with inner cavity volumes of 5, 20 and 45 pl with a printing yield above 96% are demonstrated. The same technique is directly adapted to the fabrication of microcapsules embedding silicon microchips. The reported findings open new paths for controlled encapsulation of liquids into smart microsystems.

1. Introduction: Many applications such as in-situ liquid sampling, controlled liquid handling and targeted drug delivery require microcapsules able to hold liquid volumes in the order of pico to nanolitre [1]. Usually, such systems are achieved via chemical routes such as layer-by-layer assembly, interfacial polymerisation or phase separation [2, 3]. For harsh environments, for example, liquids with extreme pH values such as gastric fluids, more robust M/NEMS capsules would be advantageous. To minimise the contact area between capsules and the surrounding surfaces, such capsules should ideally be spherical. Half microcapsules allowing the release of the embedded substance are interesting candidates for oral drug delivery [4, 5]. The additional integration of functional chips such as those provided by standard MEMS fabrication routes is a valuable additional feature. For example, the combination of mechanical and structural properties with potentially integrated electronic components of such microcapsules have attracted high interest [6]. Furthermore, a full container can be achieved by assembling two half microcapsules, for instance, by fluid-mediated self-assembly [7] or other self-assembling paths [8]. However, the micromachining of spherical shapes is not straightforward with state-of-the art MEMS technology.

Thermal reflow on photolithographically- or replica-defined resist structures allows achieving spherical profiles, such as lenses with different shapes [9]. Another approach makes use of polymer drops that are subsequently cross-linked. Having a diameter smaller than the capillary length of the polymeric solution, the drops take a spherical shape driven by surface tension [10]. Drop-on-demand (DOD) inkjet printing (IJP) [11] has shown the ability to precisely deposit drops with highly reproducible volumes [12–14]. Using epoxy-based cross-linkable composites enables the fabrication of well-controlled lens arrays [15–17]. IJP of SU-8 solution on pre-patterned pedestals induces self-alignment of the drops [18]. This approach allows, in addition, control and prediction of their radius of curvature over large arrays [19]. A pre-patterned substrate can also be used as a mould for more complex three-dimensional (3D) shapes [20].

We hereby demonstrate the use of IJP of a SU-8 solution on a two-level topographically pre-patterned silicon (Si) substrate for fabrication of 100 µm hemispherical open half capsules with sub-nanolitre cavities and their release from their fabrication substrate (Fig. 1). The potential of such an approach for fabrication and encapsulation of microsystems with embedded functionalities was also demonstrated through the successful integration and release of 100 µm Si microchips into 220 µm hemispherical SU-8 structures.

2. Experimental

2.1. Substrate fabrication processes: Half capsules with triangular cavities are fabricated by a two-step photolithography and Si deep reactive-ion etching (DRIE) to pattern the 5 µm high circular confinement pedestals and the 25 µm high central pillars (Figs. 1*a* and *b*). The circular pedestals have a diameter of 100 µm, whereas the pillars have a triangular profile with edge lengths of 20, 40 and 60 µm, respectively. The process, schematised in Fig. 1*a*, starts with an Si wafer (i) in which the triangular pillar is selectively etched by a positive photoresist (PPR) mask and DRIE (ii) and (iii). The PPR mask is then stripped by oxygen plasma (iv). A second PPR mask is deposited and the circular pedestal is then etched into the Si wafer (v) and (vi). The PPR resist is also finally stripped by oxygen plasma (vii). The Si central pillar is the negative of the capsule cavity. The fabricated confinement pedestals involving the central pillars are shown in Fig. 1*b*. The shape of the inner pillar is designed to be triangular, to reduce the risk of undesired drop confinement on top of the pillar. Indeed, the triangle is the regular convex polygon with the lowest number of edges and the lowest area which minimises the probability that a drop with a specific volume stays confined on its edges. In turn, it increases the probability that the drop overflows onto the lower circular confinement pedestal and stays confined there, as expected [21].

The two-mask fabrication process for microcapsules embedding microchips is illustrated in Fig. 1*c*. The initial stack (i) is composed by the Si substrate, a 1 µm-thick layer of SiO_2, a 5 µm-thick layer of low-pressure chemical vapour deposition (LPCVD) polycrystalline Si (polySi) and a 500 nm-thick layer of LPCVD SiO_2. The top oxide layer is lithographically patterned to define the square profile of the microchips (ii)–(iv). A second lithography step is used to define the circular profile of the pedestals (v) later engraved by DRIE (vi) and (vii). A subsequent DRIE step etches at the same time the pedestals into the Si substrate and the microchips into the polySi layer, the latter using the top oxide layer as hard mask and the bottom one as the stop layer (viii). The circular confinement pedestals and the inner microchips are shown in Fig. 1*d*.

2.2. IJP process: For both types of half capsules, the IJP process is performed as shown in Fig. 2. A software-controlled alignment procedure is first performed between the substrate and the inkjet

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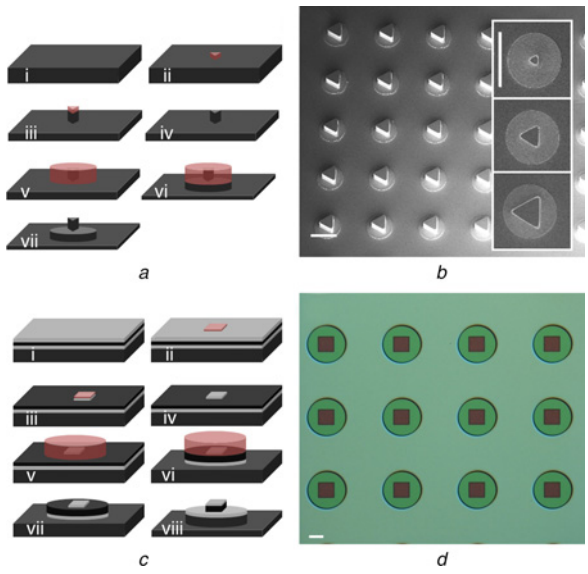


Figure 1 *Process flow for fabrication of microcapsules with triangular cavity (see text for description) (Fig. 1a). Tilted and top SEM views of 25 µm high triangular pillars with edges of 20 µm (top), 40 µm, 60 µm (bottom), centred on 100 µm in diameter and 5 µm high confinement platform (Fig. 1b). Process flow for fabrication of microcapsules embedding Si microchips (see text for description) (Fig. 1c). Top view optical image of 220 µm confinement platforms with 100 µm inner square Si chips (Fig. 1d)*

head. The IJP head and controllers are commercially available (Microdrop Technologies GmbH). A SU-8 solution (Micro Resist Technology GmbH) [15] is subsequently printed onto the pre-patterned platforms by DOD. Once the pre-calculated amount of solution is printed (Fig. 2 and 3), UV curing of the capsules is performed [22]. In the case of the open capsules, the pillar at the centre of the pedestal provides the shape for the cavity. Alternatively, the pillar can be replaced by a functional device, hereby represented by a dummy microchip as a proof of concept (Fig. 2). Depending on the type of capsules, different release chemistries are adopted. Si wet etching in KOH (1 M) at 80°C for 2 h is performed to release the open half capsules, whereas an SiO_2 wet etch in 7:1 buffered HF (BHF) is used to release the capsules embedding the Si microchips (Fig. 2*e*).

2.3. Outer shape control: The radius of the curvature of the spherical capsules is controlled by the confinement pedestal diameter, the volume of the printed ink and its shrinkage ratio upon solvent evaporation, as described earlier [19]. At microscale, that is, well below the capillary length, gravity has only a negligible effect and a sessile drop assumes a spherical

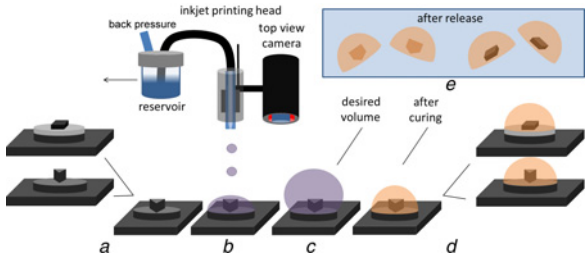


Figure 2 *Schematic illustration of IJP steps for both embedded microchip and half capsules*
a Lithography-based fabricated structures
b Deposition of SU-8 by IJP
c IJP of optimal volume
d UV exposure and cross-linking
e Release of fabricated structures

cap shape. By confining the drop on a circular pedestal with a diameter D, the drop edge angle v can be modified by increasing the drop volume. v has a minimum value equal to the ink's contact angle θ and a maximum one equal to $\theta + \phi$, where ϕ is defined as the angle of the pedestal edge. The volume needed to achieve a specific spherical cap shape, for instance a hemisphere, can thus be calculated [19]. The presence of microstructures at the centre of the circular pedestals implies the deposition of a lower solution volume as compared with our previous study to achieve the desired hemispherical profile. Described below, the number of drops N_{drops} to be printed for a specific edge angle v as a function of the pedestal diameter D and the in-flight drop radius R is given by (1), adapted from [19]. E_V is a constant for taking into account evaporation of the solvents and is defined as the initial volume divided as the final volume. V_{pillar} is the volume of the pillar or of the microchip. The nonlinear evolution of N_{drops} with respect to v, (1), is represented in Fig. 3

$$N_{\text{drops}}(D, R, v) = \left(\frac{3}{4\pi R^3}\right) E_V \left\{ \frac{\pi}{3}\left(\frac{D}{2}\right)^3 \frac{(2+\cos v)(1-\cos v)^2}{(\sin v)^3} - V_{\text{pillar}} \right\} \quad (1)$$

3. Results and discussion

3.1. Open half capsules: Hemispherical half capsules with identical diameter and three different inner cavity volumes of 45, 20 and 5 pl have been fabricated. Following the predictions of (1) and Fig. 3, hemispheres (with 90° edge angle) for three different pillar sizes were obtained by printing 30, 33 and 35 drops, respectively. These numbers have been calculated with (1), with measured R of 18 µm ± 1 µm and E_V of 3.16. As a result, Fig. 4*a* shows part of a 20 × 20 array after complete SU-8 curing. Fig. 4*b* shows platforms and pillars without polymer (left) and with printed SU-8 (right). Fig. 4*c* is a scanning electron microscope (SEM) image showing the precision of the hemispherical shape. Fig. 4*d*

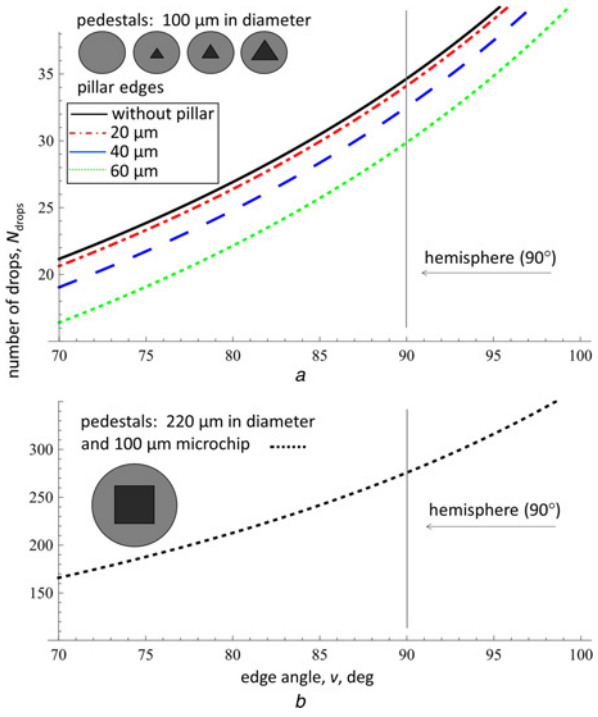


Figure 3 *Relationship of hemispherical profile of microcapsules in presence of inner pillar (Fig. 3a); plot of number of drops N_{drops} against edge angle without pillar (black line), with 20 µm pillar (red dotted dashed line), 40 µm pillar (blue dashed line), 60 µm pillar (green dotted line) with 100 µm Si chips (black dashed line). Relationship of hemispherical profile of microcapsules in presence of microchip to be embedded (Fig. 3b)*

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shows polymerised microcapsules with a 40 µm-wide inner pillars. The central pillars can be seen through the optically transparent SU-8 polymer. The 90° edge angle of hemispherical capsules is also shown. We routinely achieve fabrication yields above 96% from a total of 360 capsules, where we define the yield as the number of successfully fabricated capsules by the total number of printed capsules.

After SU-8 cross-linking, the microcapsules are successfully released from the surface by wet etching of the Si substrate in 1 M KOH aqueous solution. The SU-8 capsules do not exhibit any measurable damage because of the exposure to KOH. The capsules are subsequently transferred to a storage beaker. Fig. 5*a* shows several released capsules floating in deionised water. SU-8 has a mass density of 1.2 g/cm^3 that is approximately 1.2 times higher than water. Yet, the parts tend to float on the surface because of surface tension effects. Fig. 5 shows released capsules with a 40 µm-edge inner cavity. Top and side view zooms are shown in Figs. 5*b* and *c*, respectively. The inner concave cavity profile, resulting as the negative of the convex Si pillar, is clearly seen through the transparent SU-8 (Fig. 5*b*). The initial triangular contour of the Si pillar is precisely transferred into the SU-8 microcapsule. In Fig. 5*c*, the cavity depth of 25 µm can be seen as along with the outer hemispherical shape.

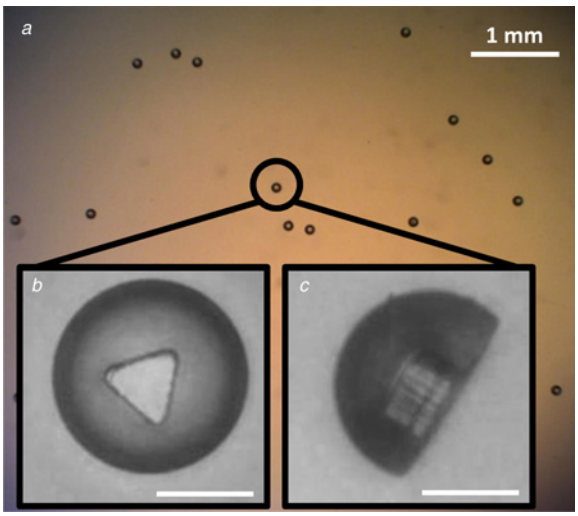


Figure 5 *Fabricated hemispherical capsules after release in water by KOH etching of silicon substrate*
a Optical view of floating microcapsules
b (detailed) top view
c (detailed) side view

3.2. Capsules with embedded silicon chips: Fig. 6*a* shows a side view of an array of polymerised SU-8 capsules embedding the Si chips before release. The edges of the chips are clearly visible through optical magnification because of transparent capsule geometry. For release of the capsules, KOH etch of the Si substrate needs to be avoided since, as shown before, it prompts separation of the SU-8 hemispheres from the entire substrate, including the pedestals, that is, the chips in this case. Hence, BHF etch of the thick SiO_2 layer is opted for. Wet release of the capsules takes about 20 h. A long etch time is expected because of the aspect ratio of the SiO_2 layer sandwiched between the Si substrate and SU-8 of the capsules. This geometrical constraint considerably slows down the native etch rate of silicon dioxide by BHF. After release from the substrate, the microcapsules are stored in water (Figs. 6*b* and *c*). Release yield is up to 50% overall. Capsules not embedding microchips are also observed. By checking the substrates after release it is apparent that delamination of SU-8 from the pedestals and chips is part of the reason for the 50% yield, as well as separation of the microchips from the capsules in liquid after release.

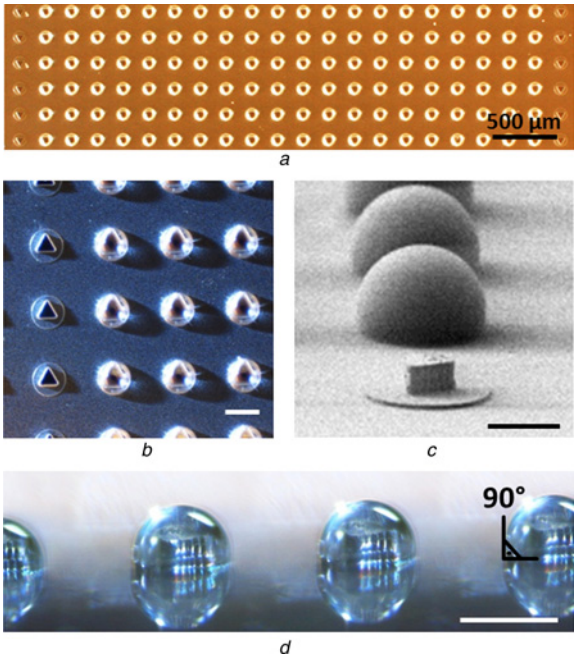


Figure 4 *Optical micrographs showing printed and polymerised microcapsules on Si substrate before release*
a Top view of large array
b Top view showing empty and filled Si platforms after curing
c SEM image showing hemispherical shape and pre-patterned Si substrate
d Optical side view of triangular shaped inner cavities with 40 µm edges showing outer hemispherical profile with 90° edge angle
Si inner pillars are seen through SU-8

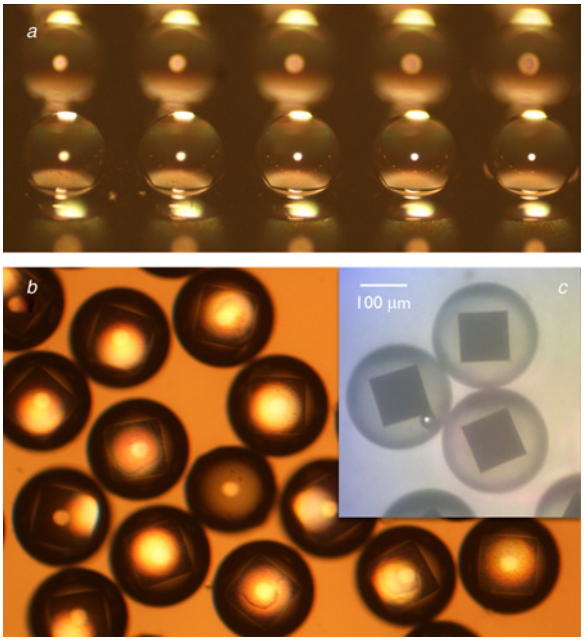


Figure 6 *IJP 220 µm hemispherical microcapsules encapsulating 100 µm wide Si microchips*
a Side view of capsules before release; embedded microchips are visible through polymerised solution
b Released capsules at water surface
c Released capsules in bulk water showing successful embedding of Si microchips

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4. Conclusions and outlook: A method based on IJP technology for flexible fabrication of SU-8 open half capsules and hemispherical capsules embedding microchips has been presented. The outer and inner profiles of the capsules are precisely controlled by a combination of lithographical surface micromachining and IJP parameters, notably the delivered ink volume. For the open capsules, inner cavities with volumes of 5, 20 and 45 pl could be fabricated on a pre-patterned Si substrate. An overall fabrication yield of 96% could be achieved. After cross-linking, the structures could be successfully released without damage by wet etching of the Si substrate. For the latter type, release in BHF severely reduced the fabrication yield because of SU-8 delamination. The novel fabrication and packaging method presented in this Letter, combined with recent results in fluidic self-assembly [7, 8], opens new avenues for liquid encapsulation within smart microsystems, targeting applications like precise liquid handling, controlled liquid release and directed drugs delivery.

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6 References

[1] Oosterbroek E., Berg A.v.d.: 'Lab-on-a-chip: miniaturized systems for (Bio) chemical analysis and synthesis' (Elsevier, 2003)
[2] Johnston A.P.R., Cortez C., Angelatos A.S., Caruso F.: 'Layer-by-layer engineered capsules and their applications', *Curr. Opin. Coll. Interface Sci.*, 2006, **11**, pp. 203–209
[3] Donath E., Sukhorukov G.B., Caruso F., Davis S.A., Mohwald H.: 'Novel hollow polymer shells by colloid-templated assembly of polyelectrolytes', *Angew. Chem., Int. Ed.*, 1998, **37**, pp. 2202–2205
[4] Nagstrup J., Keller S., Almdal K., Boisen A.: '3D microstructuring of biodegradable polymers', *Microelectron. Eng.*, 2011, **88**, pp. 2342–2344
[5] Marizza P., Keller S.S., Boisen A.: 'Inkjet printing as a technique for filling of micro-wells with biocompatible polymers', *Microelectron. Eng.*, 2013, **11**, pp. 391–395
[6] Martin F.J., Grove C.: 'Microfabricated drug delivery systems: concepts to improve clinical benefit', *Biomed. Microdevices*, 2001, **3**, pp. 97–108
[7] Terfort A., Bowden N., Whitesides G.M.: 'Three-dimensional self-assembly of millimetre-scale components', *Nature*, 1997, **386**, pp. 162–164
[8] Mastrangeli M., Abbasi S., Varel C., Hoof C.V., Celis J.P., Bohringer K.F.: 'Self-assembly from milli- to nanoscales: methods and applications', *J. Micromech. Microeng.*, 2009, **19**, pp. 083001–083038
[9] Orhan J.B., Parashar V.K., Sayah A., Gijs M.A.M.: 'Fabrication and characterization of three-dimensional microlens arrays in sol-gel glass', *J. Microelectromech. Syst.*, 2006, **15**, pp. 1159–1164
[10] Chen C.-T., Chiu C.-L., Tseng Z.-F., Chuang C.-T.: 'Dynamic evolvement and formation of refractive microlenses self-assembled from evaporative polyurethane droplets', *Sens. Actuators A, Phys.*, 2008, **147**, pp. 369–377
[11] Lee E.R.: 'Microdrop generation' (Taylor & Francis, 2010)
[12] Fakhfouri V., Mermoud G., Kim J.Y., Martinoli A., Brugger J.: 'Drop-on-demand inkjet printing of SU-8 polymer', *Micro Nanosyst.*, 2009, **1**, pp. 63–67
[13] Kim J.Y., Brauer N.B., Fakhfouri V., *ET AL.*: 'Hybrid polymer microlens arrays with high numerical apertures fabricated using simple ink-jet printing technique', *Opt. Mater. Express*, 2011, **1**, pp. 259–269
[14] Biehl S., Danzebrink R., Oliveira P., Aegerter M.A.: 'Refractive microlens fabrication by ink-jet process', *J. Sol-Gel Sci. Technol.*, 1998, **13**, pp. 177–182
[15] Voigt A., Ostrzinski U., Pfeiffer K., *ET AL.*: 'New inks for the direct drop-on-demand fabrication of polymer lenses', *Microelectron. Eng.*, 2011, **88**, pp. 2174–2179
[16] Cadarso V.J., Perera-Nùñez J., Jacot-Descombes L., *ET AL.*: 'Microlenses with defined contour shapes', *Opt. Express*, 2011, **19**, pp. 18665–18670
[17] Fakhfouri V., Cantale N., Mermoud G., *ET AL.*: 'Inkjet printing of SU-8 for polymer-based MEMS a case study for microlenses'. Proc. IEEE 21st Int. Conf. on MEMS, Tuscon, AZ, USA, 2008, pp. 407–410
[18] Kim J.Y., Martin-Olmos C., Baek N.S., Brugger J.: 'Simple and easily controllable parabolic-shaped microlenses printed on polymeric mesas', *J. Mater. Chem. C*, 2013
[19] Jacot-Descombes L., Gullo M.R., Cadarso V.J., Brugger J.: 'Fabrication of epoxy spherical microstructures by controlled drop-on-demand inkjet printing', *J. Micromech. Microeng.*, 2012, **22**, pp. 074012–074012
[20] Chen C.-T., Tu K.-Z.: 'Inkjet printing of individual polymer micro parts self-shaped with hemispherical caps', *Sens. Actuators A, Phys.*, 2012, **188**, pp. 367–373
[21] Jacot-Descombes L., Gullo M.R., Mastrangeli M., Cadarso V.J., Brugger J.: 'Polymeric hemispherical pico-liter micro cups fabricated by inkjet printing'. Int. Conf. Nano/Micro Engineered and Molecular Systems (NEMS), Suzhou, China, 2013, pp. 1119–1122
[22] Despont M., Lorenz H., Fahrni N., Brugger J., Renaud P., Vettiger P.: 'High-aspect-ratio, ultrathick, negative-tone near-uv photoresist for MEMS applications', Proc. IEEE 10th Int. Workshop on MEMS, Nagoya, Japan, 1997, pp. 518–522

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