Electronic Supplementary Information (ESI)

Leak-tight vertical membrane microvalves

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**Table S1.** Graphical overview of previous valves and this work.

<table>
<thead>
<tr>
<th>Valve type</th>
<th>Horizontal membrane microvalves</th>
<th>Previous vertical membrane microvalves</th>
<th>Vertical membrane microvalves</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non actuated state: (side view)</td>
<td><img src="Image" alt="Flow channel" /></td>
<td><img src="Image" alt="Control channel" /></td>
<td><img src="Image" alt="Flow channel" /></td>
</tr>
<tr>
<td>Actuated state: (side view)</td>
<td><img src="Image" alt="Layer 2" /></td>
<td><img src="Image" alt="Finite deformability causes leakage" /></td>
<td><img src="Image" alt="Leak tight" /></td>
</tr>
</tbody>
</table>

Number of microstructured layers: 2 layers

Problems: Limited fluidic conductance, Alignment of layers necessary
Not possible to close

**Table S2.** List of constants and parameters.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bn</td>
<td>Bell valve model n</td>
</tr>
<tr>
<td>Cn</td>
<td>Circle valve model n</td>
</tr>
<tr>
<td>$D_h$</td>
<td>Hydraulic diameter</td>
</tr>
<tr>
<td>$A$</td>
<td>Cross-sectional area</td>
</tr>
<tr>
<td>$S$</td>
<td>Cross-sectional wetted perimeter</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure</td>
</tr>
<tr>
<td>$Q$</td>
<td>Volumetric flow rate</td>
</tr>
<tr>
<td>$R$</td>
<td>Fluidic resistance ($=1/C$)</td>
</tr>
<tr>
<td>$C$</td>
<td>Fluidic conductance ($=1/R$)</td>
</tr>
<tr>
<td>$w$</td>
<td>Valve width</td>
</tr>
<tr>
<td>$h_0$</td>
<td>Valve height at zero pressure load</td>
</tr>
<tr>
<td>$h$</td>
<td>Effective valve height when pressurized</td>
</tr>
<tr>
<td>$t$</td>
<td>Membrane thickness</td>
</tr>
<tr>
<td>$L$</td>
<td>Valve length</td>
</tr>
<tr>
<td>$L_m$</td>
<td>Membrane length</td>
</tr>
<tr>
<td>$E$</td>
<td>Elastic modulus</td>
</tr>
<tr>
<td>$k$</td>
<td>Membrane spring constant</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Fluid viscosity</td>
</tr>
<tr>
<td>$l$</td>
<td>Pressurized path length</td>
</tr>
<tr>
<td>$m_r$</td>
<td>Measured feature misalignment</td>
</tr>
<tr>
<td>$r_p$</td>
<td>Resolution of photomask</td>
</tr>
<tr>
<td>$e_a$</td>
<td>Error introduced during alignment</td>
</tr>
</tbody>
</table>

Indices
at the device inlet
at the valve inlet
at the device outlet
at the valve outlet
at the control port
membrane
valve
for closed valve state
for open valve state
for vertical membrane microvalves
for horizontal membrane microvalves
Foot-print
minimum
maximum
traditional
thick beam model
thick spring model
thin spring model
for bell valve model n
for circle valve model n
Manufacturing details

The novel manufacturing process was conceptually introduced in Reference\textsuperscript{23}, but is here described in detail for the first time.

Self-aligning double-sided molds

The dual layer micromolds were fabricated using two-step spin-coating and photolithographic patterning of SU-8 2025 (MicroChem Corp, USA) on 4-inch silicon and glass wafers using an emulsion film photomask with a structure resolution of <10 µm (JD Photo, UK), with subsequent development of the SU-8 according to manufacturer protocols. The height of the first SU-8 layer defines in-plane channels and microfluidic structures, and the height of the second layer defines both guiding structures for alignment of the pairing molds and vertical interconnects. Thereafter, molds used for single-chip fabrication were saw-diced into microchip size to facilitate handling and to enable pre-alignment of the molds during the molding process.

Mold coating

The molds were first spin-coated (800 rpm, 60 s, 500 rpm/s) with a 2 % (w/w) solution of PVA (The Fishing Bag Ltd, UK) dissolved in water and thereafter dried on a hotplate (70°C, 15 min). The PVA-coated top layer molds were then immersed for 1 h into a solution of 1 % (w/w) of the Pt inhibitor aminoethylaminopropyltrimethoxysilane (AEAPS; Z-6020, Dow Corning, USA), 3 % of a silane without inhibitory function, 3-methacryloxypropyltrimethoxysilane (MEMO; Z-6030, Dow Corning, USA) in methanol. The molds were thereafter rinsed with methanol to remove unbound silanes and dried on a hotplate (70°C, 15 min). The thickness of the PVA/silane layer was measured to 75 +/- 10 nm, leading to a negligible reduction in resolution during the coating of the molds with such layer.

The two silanes used (AEAPS and MEMO), allow formation of both membranes and vias. Polymerization of PDMS relies on a freely diffusing catalyst, Pt, in the PDMS prepolymer. To prevent polymerization at via sites, AEAPS irreversibly bind and deactivates the Pt, which in sufficiently thin regions (such as the squeeze film at the via site), completely inhibits polymerization.\textsuperscript{24} Balancing the amount of AEAPS to the non-inhibiting MEMO prevents depletion for larger features (such as thin membranes).\textsuperscript{22}

Microstructured layer preparation

PDMS prepolymer (Sylgard 184, Dow Corning, USA) was mixed (1:10, curing agent:base) and degassed. The prepolymer was thereafter casted onto PVA/silane-coated micromolds and further degassed to remove any bubbles introduced during the casting process. When bubble-free PDMS prepolymer was obtained, the mold halves were folded onto each other with the pattern facing inwards and manually pre-aligned by ensuring that the external mold edges were aligned. Excess PDMS was pressed out on the sides by closing the mold, and final pressure was applied towards the guiding structures for a good fit. The paired mold halves were thereafter pressed together using a clamp pressure of 30 kPa.

Mold release, transfer and assembly

The stack composed of two mold halves enclosing a cured PDMS layer was placed in a water bath in which ultrasonication was performed 20-60 min to separate the molds by dissolving the PVA which lines the patterned side of the mold halves. The unpolymerized material at via positions was flushed away during the release, opening vertical vias in the device layer. Floatation transfer of the PDMS layer was then performed to a carrier substrate consisting of a non-sticking rough polycarbonate (PC) surface for plasma treatment (40 W, 15 s; FEMTO A, Diener electronic GmbH, Germany) using the protocol described in\textsuperscript{21}. The PDMS was thereafter easily removed from the rough carrier surface onto a methanol film on the destination substrate. The methanol prevents immediate stiction between the destination substrate and the thin PDMS layer, facilitating the final alignment. Destination substrates forming the bottom of the microchip assembly consisted either of plasma-treated glass, plasma-treated silicon (Si) or silanised polyester (PE) film. The assembly comprising a destination substrate bonded to a patterned PDMS layer was thereafter bonded to a top lid substrate using plasma bonding, resulting in a covalently bonded microfluidic device. Top substrates used were plasma-treated glass, plasma-treated PDMS, silanised PE or silanised poly(methyl methacrylate) (PMMA). Prior to bonding with PDMS devices, the PE and PMMA lids were treated with 15 min immersion in 2 % (w/w) AEAPS in isopropanol, with subsequent rinsing in isopropanol to remove unbound silanes, rinsing with water to activate silane groups, and drying using nitrogen gas. The amine group in AEAPS attacks the ester bond in PE and PMMA, forming an amide bond via chain scission of the ester group. The siloxane-functionalized PE and PMMA surfaces thereafter form covalent bonds to plasma-treated PDMS surfaces.

Yield and practical considerations

All manufacturing in this paper uses a silane inhibitor ratio of 1:3 (AEAPS:MEMO), which results in 100% yield for the valves presented in this paper and for the test-structures indicated as successfully manufactured in section 5.1. For further downscaling, it would probably be possible to optimize the ratio of the silane concentration further, as discussed in Reference\textsuperscript{22}.
Table S3. Comparison of our novel manufacturing method with standard PDMS manufacturing process for horizontal membrane microvalves\textsuperscript{11,25}. Differences in manufacturing steps are indicated with bold text font.

<table>
<thead>
<tr>
<th>Manufacturing steps</th>
<th>Horizontal membrane valves (previous work)</th>
<th>Vertical membrane valves (this work)</th>
</tr>
</thead>
</table>
| 1. Mold manufacturing | H1.1 SU-8 patterning  
H1.2 Photoresist patterning  
H1.3 Photoresist reflow | V1.1 SU-8 layer 1 patterning  
V1.2 SU-8 layer 2 patterning |
| 2. PDMS microstructuring | H2.1 Adding PMDS  
H2.2 Layer thickness definition  
H2.3 Curing  
H2.4 Demolding  
H2.5 Cutting  
H2.6 Via punching | V2.1 Mold coating  
V2.2 Adding PMDS  
V2.3 Self-aligning molds  
V2.4 Curing  
V2.5 Demolding in water  
V2.6 Cutting |
| 3. Assembly | H3.1 Plasma treat layers  
H3.2 Manually aligning elastomeric layers  
H3.3 Bond layers | V3.1 Plasma treat layers  
V3.2 Bond layers |

Manufacturing complexity comparison

Table S3 compares our novel manufacturing method with the standard PDMS manufacturing process for horizontal membrane microvalves\textsuperscript{11,25}.

The steps in vertical membrane valve fabrication that are more complex than in horizontal membrane valve fabrication relate to the molding and demolding steps: molds must be coated with silanes to allow inhibition, and demolding occurs in water to avoid rupturing of thin membranes features.

Vice versa, there are several steps that make horizontal membrane valve fabrication more cumbersome and uncontrollable than vertical membrane valve fabrication. During mold manufacturing, a resist reflow step, which has large variability, is needed to achieve rounded channel profiles. The PDMS microstructuring requires specific control of the PDMS layer thickness, because this defines the valve membrane thickness; and vertical vias must be punched in a separate step. Finally, the alignment of microfluidic layers prior to bonding is manual, hence cumbersome, and the elastomeric (deformable) nature of PDMS limits the across-device alignment precision. In comparison, the feature alignment in vertical valve fabrication occurs during molding, which is a self-aligned process with stiff (undeformable) molds.

Valve characterization

Microscopy images for determining the visual closing pressure

![Microscopy images](image)

**Figure S1.** Actuated valves. Microscopy images with inverted colors of the smallest and largest valves for both (a) bell valves and (b) circle valves, at open state and at control pressures of 100 kPa and 300 kPa.
Calculation of the valve characteristics from the experimental measurements

The pressure-flow measurement results of the experimental setup are influenced by the fluidic resistances of the connecting tubes, the on-chip flow channels, and the valve channel itself. The fluidic resistance of a flow duct, $R$, under laminar flow conditions, scales as $R \sim L/D^4_h$ (Hagen-Poiseuille equation). Compared to the resistance of the on-chip channels, $R_{ch}$, the connecting tubes have a magnitude order larger length and a magnitude order larger hydraulic diameter, which results in a three magnitude orders lower fluidic resistance. The fluidic resistance of the valve channel, $R_v$, varies from infinitely large, for a closed valve, to an open state value that can be estimated to be up to two magnitude orders below that of the on-chip channels, considering a two magnitude order shorter length and a similar open state hydraulic diameter. We can thus safely neglect the influence of the connecting tubes, whereas we must be careful to take into account the influence of the on-chip flow channels. The inlet and outlet channel flow resistances, $R_{ch, in}$ and $R_{ch, out}$, can be theoretically calculated, using the Hagen-Poiseuille equation for rectangular channels, $R_{ch} = \frac{12 \mu L \Delta P}{w d_h \eta (1 - 0.63 h_d/w_d)}$, which allows theoretically predicting $R_{ch, in} = 5.0 \text{kPa} \mu \text{m}^{-2}$, $R_{ch, out} = 7.8 \text{kPa} \mu \text{m}^{-2}$, and the sum of the resistances, $R_v = R_{ch, in} + R_{ch, out} = 12.8 \text{kPa} \mu \text{m}^{-2}$ for all valves. The value of $R_v$ can also be experimentally deduced from the B2 and B3 valve measurement data: as can be seen in Fig. 5 d and e, for small valve control pressures, the flow is almost constant, indicating that the open valve state pressure drop in the experimental setup is entirely dominated by the flow channel resistances, i.e. $R_{v,open} \ll R_{ch}$. The total flow channel resistance can thus be estimated as $P_{ch} \approx \frac{P_{in}}{L}$ at $P_{ctrl} = 0$ with resulting values $R_{ch,B2} \approx 9.4 \pm 0.6 \text{kPa} \mu \text{m}^{-2}$ and $R_{ch,B3} \approx 12.3 \pm 0.9 \text{kPa} \mu \text{m}^{-2}$. The theoretical and experimental estimations for $R_{ch,B2}$ are in accordance; the 27% lower experimental estimation for $R_{ch,B2}$ may be attributed to an 8% lower on-chip flow channel height than designed for. The valve pressure-flow characteristics can be obtained from the experimental measurements by subtracting the flow-induced pressure drop in the upstream and downstream tubings and on-chip flow channels, i.e. $P_{v, in} = P_{in} - QR_{ch, in}$, $P_{v, out} = P_{out} + QR_{ch, out}$, and $\Delta P_v = P_{v, in} - P_{v, out}$. The valve membrane pressure drop, $\Delta P_m$, is defined as the "average" pressure drop over the valve membrane, $\Delta P_m = \langle P_{ctrl} - P_{v, in} - P_{v, out} \rangle$.

Modelling calculations

Previous work suggested three models for membrane valves\textsuperscript{25,30}: the "thick beam model" (kbm) models the valve membrane in length-direction and width-direction as a pair of rigid beams joined in the middle; the "thick spring model" (ksm) models the valve membrane as a suspension bridge hanging across the channel; and the "thin spring model" (nsm) models the valve membrane as a one-dimensional spring composed of a semi-liquid slab, such that the pressure outside the slab is equal to the stress multiplied by the strain within the material. Inserting the valve dimensions and characteristics of our work, the models were used to predict the E-modulus of PDMS, $E_{PDMS}$. The concordance of the predicted and actual value of $E_{PDMS}$ indicates whether these models are suited for our novel valve design.

$E_{PDMS}$ is predicted as follows in the three models:

\[
E_{PDMS, kbm} = \frac{P_{m, close}}{4 \eta h t^3 \left(w^{-4} + L_m^{-4}\right)},
\]

\[
E_{PDMS, ksm} = \frac{P_{m, close}}{\left[ \frac{l_{m, w}}{h_w} + \frac{l_{m, l}}{l_m} \right]},
\]

\[
E_{PDMS, nsm} = \frac{P_{m, close}}{\frac{2}{L_m} \frac{h_0}{\sqrt{h_0^2 + w^2}} \left[ \frac{l_{m, w}}{h_w} + \frac{2}{w} \frac{h_0}{\sqrt{h_0^2 + l_m^2}} \frac{l_{m, l}}{l_m} \right]},
\]

where $L_m$ is the membrane length, and $l_w$ and $l_l$ are the pressurized path lengths along the length and width directions of the membrane, respectively:

\[
l_w = \frac{w^2}{6h_0} \left[ \frac{4h_0}{w} \sqrt{\frac{32h_0^2}{w^2} + 1} + \arcsinh \frac{4h_0}{w} \right]
\] and \[l_l = \frac{L_m^2}{6h_0} \left[ \frac{4h_0}{L_m} \sqrt{\frac{32h_0^2}{L_m^2} + 1} + \arcsinh \frac{4h_0}{L_m} \right].\]

Calculation of the valve channel fluidic conductance

In the case of laminar flow, the fluidic channel conductance, $C = R^{-1}$, scales roughly with the fourth power of the hydraulic diameter, $D_h$, and can be calculated as $C = \frac{\pi D_h^4}{12 \eta L}$, where $\eta$ is the fluid viscosity and $L$ the channel length. For the valves in this paper, $D_h = \frac{44}{N}$ was estimated by using images of the manufactured valves, tracing the outline of the valves in open state to vector images, extracting the area, $A$, and perimeter, $S$, from the vector. The geometry for previous horizontal microvalves,\textsuperscript{11,25} were approximated as 0.485 of an ellipse, divided parallel to the longer of its diameters $d_1$, where $d_1 \approx w$, and the shorter diameter $d_2 = h_0/0.485$. This approximation was derived from profilometry measurements of reflown photoresist in our lab. The geometry of previous vertical microvalves,\textsuperscript{12,13} are rectangles with sides $h_0$ and $w$. 

\[
C_{PDMS} = \frac{\pi D_h^4}{12 \eta L} = \frac{\pi \frac{44}{N}^4}{12 \eta L}.
\]