Lab on a Chip



PAPER

Electronic supplementary information (ESI):

Fabrication of polydimethylsiloxane (PDMS) nanofluidic chips with controllable channel size and spacing

Ran Peng, and Dongqing Li*

Department of Mechanical and Mechatronics Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G.

*E-mail: dongqing@uwaterloo.ca

Homemade alignment system for nanofluidic device bonding

Figure 1 shows the working principle of the alignment system developed on the stage of an inverted microscope (Nikon, TE-2000). There are two manipulation stages in this system, and both of them can move freely in the horizontal directions. D is an object stage of the microscope, and A is a manipulation stage with a chip holder fabricated by a 3-D printer (Dimension, Elite). The bonding can be processed in three steps. First, a PDMS slab with nanochannels is placed onto the D stage with nanochannels upwards, and these nanochannels are localized in the middle of the microscope view with the help of a 40 \times objective lens. The second step is to load the microchannel chip into the chip holder on stage A with microchannels downwards, and the microchannel sale located in the middle of the microscope view by using a 10 \times objective lens which has a longer focal length. In the third step, the PDMS nanochannel slab is lifted by a 100 \times objective lens manually from below. As the upper surface of the nanochannel touches the lower surface of the microchannel, the PDMS nanochannel and PDMS microchannel are bonded together automatically due to the properties of the plasma treated surfaces. To minimize deformation of the PDMS slabs, glass slides C are attached onto the PDMS channels to work as temporary substrates. After removing of the glass slides, a PDMS-PDMS nanofluidic chip is obtained.



Figure 1S Schematic of micro-nanochannel bonding by an alignment system.

Effects of the defect size on the number and size of nanocracks.

Figure 2S (a) and Figure 2S (b) summarize the sizes of the defects and the total number of the nanocracks recorded in the experiments. Figure 2S (a) shows that the size of the defects increases with the magnitude of the applied force, from $20\mu m$ for the 10 gF to about 210 μm for the 1000 gF. Figure 2S (b) depicts that the total number of the nanocracks generated on the defects also increases with the magnitude of the applied force. Examples of nanocracks generated on these defects created by different applied forces are showing in Figure 2S (c).



(c)	10gF	00	25gF		50gF		100gF	
	0	100µm	0.0	100µm		100µm		100µm
	200gF		300gF	0	500gF		1000gF	
		100µm		100µm		100µm		100µm

Figure 2S Defect size effects on the number of nanocracks. (a) The size of the defects increase with the applied force on the indenter; (b) The total number of cracks generated on the 7 defects increases with the applied force on the indenter. (c) Examples of nanocrack creation on polystyrene surfaces induced by defects made by different force applied ranging from 10 gF to 1000 gF.



Figure 3S (a) Size of nanocracks induced by different size of defects under the same working condition: heating 1 mL 90% ethanol for 24 hours. The force applied on the indenter is ranging from 10 gF to 500 gF and only single nanocracks are measured. (b) Effects of a defect made by 200gF on the size of single nanocrack. A is located at the tip of the defect and A, B, C, D are separated by a distance of 50 μ m. Point A: 338 nm wide and 68.8 nm deep; point B: 230 nm wide and 34.5 nm deep; Point C: 135 nm wide and 39.4 nm deep; point D: 147 nm wide and 34 nm deep; Far away: 140 wide and 28 nm deep.

Method A— UV curable soft lithography by using SU8 photoresist

Experimental details for the effects of photoresist type

The nanocracks used in this part are all about 90 nm wide and 30 nm deep, fabricated by the same working conditions. Table 1S shows the properties of the photoresists and the working parameters during the replication. The thickness of the photoresist layers and the standard UV exposure dose are obtained according to the data sheet of the SU8 2000 series photoresists, and the spin-coating time for all the cases was 60 s. The average surface roughness of the cracks and the nanochannel mold size before and after replication were measured by the AFM. For all the cases, the roughness values and the channel mold sizes were measured for at least 5 times with 5 independent samples under the same working conditions.

Table 1S Working parameters of nanochannel replication by different type of SU8 photoresist.

Types of	% Solvents	Viscosity	Density	Coating speed	l Thickness	UV dose
SU8		(cst)	(g/mL)	(rpm)	(µm)	(mJ/cm^2)
2025	31.45	4500	1.219	1200	70	200
2035	30.05	7000	1.227	1200	100	230
2050	28.35	12900	1.233	1200	150	260
2075	26.55	22000	1.236	1200	200	330
2100	25.00	45000	1.237	1500	200	330
2150	23.25	80000	1.238	3000	200	330

Nanoscale

Details for effects of spin-coating time

Nanochannel molds made by using SU8 2150 with different spin-coating time (the samples are exposed to UV light immediately after the spin-coating time) from 30 s to 120 s were examined by using AFM. The results show that the molds made by a too short spin-coating time are not consistent, i.e., the volume and the shape of such a mold vary along the length direction. On the contrary, the molds made by a longer spin-coating time are uniform in the length direction. For instance, Figure 4S (a) shows a nanochannel mold replicated by 60 s spin-coating time. It is obvious that the channel mold has a zigzag shape due to failure of SU8 material to fill the nanocrack uniformly. By contrast, the quality of nanochannel mold replicated by 120 s spin-coating time is much better, as shown in Figure 4S(b), because SU8 2150 can fully fill the nanocrack within such a longer period of time. To replicate nanochannels with high quality and smaller sizes, one has to balance the spin-coating time and the concentration of solvents in SU8 photoresist.



Figure 4S AFM 3D images of nanochannel molds replicated by using SU8 2150 with spin-coating time of (a) 60 s and (b) 120 s.

Experimental details of the effects of UV exposure dose

The thickness of the photoresist layers and the spinning coating time used in this part were about 200μ and 120 s, respectively. UV exposure dose ranging from 300 mJ/cm² to 2700 mJ/cm² was studied. For a 200 μ thick photoresist layer, the standard exposure dose is around 330 mJ/cm² according to the SU8 photoresist manual. Figure 5S (a) is an example of underexposure case (300 mJ/cm²) where the mold was peeled off too early. It is clear that the photoresist breaks and leaves some parts in the nanocrack during the peeling off process. Figure 5S (b) shows a nanochannel mold replicated also under the condition of underexposure UV exposure (300 mJ/cm²) with a longer peeling off time, the channel mold is intact, but the channel size is much larger (due to the further swelling of the nanocrack). Figure 5S (c) shows an example of a nanochannel mold made of SU8 2150 photoresist layer with an overexposure UV energy of 2700 mJ/cm². It is obvious that some parts of the SU8 nanochannel mold in this case were broken.



Figure 5S AFM images of nanochannel molds: (a) A broken SU8 mold during peeling off due to underexposure to UV light and insufficient evaporation time. (b) An example of nanochannel mold replicated by SU8 2150 with an underexposure energy of 300 mJ/cm; (c) A nanochannel mold replicated by SU8 2150 photoresist with an overexposure UV energy of 2700 mJ/cm².

Nanoscale

Details for the thickness of the photoresist layer

To examine this effect, a series of photoresist layers from $80\mu^{\mu}$ to $650\mu^{\mu}$ obtained by spin-coating SU8 2150 at different spin coating speed ranging from 1000 rpm to 8000 rpm for 120 seconds onto polystyrene surfaces with nanocracks were used to fabricate the nanochannel molds. To minimize the time of solidification, all the samples were overexposed to UV light for 1200 mJ/cm². Figure 6S (a) compares the size of nanochannel molds replicated with different thicknesses of SU8 photoresist layers. For each value of the spin-coating speed, 5 independent nanocracks were used and the sizes were measured for at least 5 times. The original nanocracks were fabricated under the same condition and the average size of the nanocracks as measured by the AFM is 215.6 nm in width and 47.7 nm in depth. Figure 6S (a) shows the average value of the channel mold size after duplication as a function of the spin-coating speed. From Figure 6S (a), one can see that both the width and the height of the nanochannel molds decrease with the spin-coating speed inversely. For example, when the spin-coating speed is 1000 rpm, the thickness of the SU8 layer is about $650\mu^{\mu m}$ and the corresponding channel mold size is about 2208 nm in width and 2388 nm in height. When the spin-coating speed increases to 8000 rpm, the thickness of the SU8 layer is only about $80\mu^{\mu m}$ and the channel mold size is approximately 541 nm in width and 134 nm in height, which is much smaller than that of the 1000 rpm case. Figure 6S (b) shows 3D images of the nanochannel molds replicated under different spin-coating speeds. It is obvious that the size of the channel molds improves with the spin-coating speed.



Figure 6S (a) Size of nanochannel molds replicated from nanocracks with an average size of 215.6 nm in width and 47.4 nm in depth for different spin-coating speeds ranging from 1000 rpm to 8000 rpm. (b) AFM 3D images of nanochannel molds replicated at different spin-coating speeds, 1000 rpm, 1500 rpm, 2000 rpm, 3000 rpm, 5000 rpm and 8000 rpm, and the corresponding channel mold sizes are 2208 × 2388 nm, 1860 × 1692 nm, 1320 × 1331 nm, 802 × 173 nm, 562 × 164nm and 541 × 134 nm, respectively.

Method B — Nanoimprint by smooth cast

Experimental details for the pre-curing time effects.

In the experiments, pre-curing time of 17 min, 20 min, 23 min, 25 min, 27 min, 30 min, 35 min and 40 min were tested to replicate nanocracks of about 300 nm in width and 60 nm in depth. For all the cases, the peeling-off time was 60 min and the pressurized time was 60 s. The pressure value for each case was different due to the difference in fluidity of the smooth cast layers. Specifically, for the 17 min and 20 min cases, no pressure was applied, because the pre-curing smooth cast layers were too soft; for the 23 min and 25 min cases, only 0.5 MPa was applied. The pressure applied on the 27 min case was 5 MPa, and for the other cases with longer pre-curing time, the pressure value was 10 MPa.

The results show that when the pre-curing time is shorter than 23 min, the surfaces of the smooth cast layers are wet and soft; as a result, the solvent from the smooth cast layer destroys the nanocracks easily. However, as the pre-curing time becomes too long, the smooth cast layers are dry and hard, therefore, higher pressure is needed during the nanoimprint, which will also trigger further cracking of the nanocracks. Figure 7S shows the examples of the the nanochannel molds replicated by pre-curing time from 17 min to 30 min. It is obvious that a longer pre-curing time contributes to a better channel mold quality. However, as the pre-curing time becomes too long (longer than 30 min), the smooth cast layer becomes too hard, and a higher pressure is needed which will likely deform or break the polystyrene nanocracks.



Figure 7S AFM 3D images of nanochannel molds replicated with different pre-curing time; (a) 17 min, (b) 20 min, (c) 23 min, (d) 25 min, (e) 27 min, (f) 30 min. For all the cases, the peeling off time is 60 min. The original nanocrack size is about 300 nm wide and 60 nm deep.

Pressure effects

Figure 8S shows the size and 3D images of the nanochannel molds. From Figure 8S (a), one can see that the width of the channel molds is almost constant when the pressure is lower than 2 MPa, about 300 nm, which is similar to that of the original nanocracks, because the nanocracks on polystyrene surfaces are stable (i.e., no further cracking is induced) when low pressure is applied. However, for the higher pressure values, 2.5 MPa and 3 MPa, the width of the channel molds increases dramatically due to further cracking of the nanocracks. In the experimental investigations, pressure as high as 5 MPa was also tested; however, it was found that a lot of new fractures were generated on the polystyrene surfaces under such a high pressure. Figure 8S (b) shows that the height of the channel molds is about 24 nm when the pressure is 0.25 MPa, and this value increases to 30 nm as the pressure increases to 0.5 MPa. This is because the cracks are partly filled with smooth cast when the pressure is smaller than 0.5 MPa. When the pressure increases from 0.75 MPa to 1.5 MPa, the height of the channels reaches about 60 nm due to fully filled smooth cast in the nanocracks. However, when the pressure is higher than 2 MPa, both the width and height of the channel molds increase dramatically due to further cracking of the nanocracks as mentioned above. For example, for the 2 MPa and 2.5 MPa cases, the channel molds become 280 nm wide and 370 nm high, and 414 nm wide and 354 nm high, respectively, which are much larger than the original crack size. For all the cases, the pre-curing time was 25 min and the pressurized time was 30 s with a peeling off time of 60 min.



Figure 8S Nanochannel molds replicated form nanocracks with an average size of 300 nm in width and 60 nm in depth by Smooth cast 305 with different pressure applied from 0.25 MPa to 3 MPa under the conditions of 25 min pre-curing time and 30 s pressurized time. (a) Width of the nanochannel molds and (b) Height of the nanochannel molds. (c) Examples of AFM 3D images of nanochannel molds under different pressures.

Examples of pressurized time effects

Figure 9S shows images of nanochannel molds replicated with (a) 10 s, (b) 1 min and (c) 5 min pressurized time, respectively. It is obvious that the nanochannel mold replicated with 10 s pressurized time is not so smooth, and the channel mold replicated with 1 min pressurized time is much better than that of the 10 s case. For the 5 min case, the channel mold is not straight due to detaching action of the smooth cast layer with the crack during the solidifying process.



Figure 9S AFM images of nanochannel molds replicated by smooth cast 305 with different pressurized time of (a) 10 s, (b) 1 min and (c) 5 min. For all the cases, the pre-curing time is 25 min, the pressure is 1 MPa and the peeling off time is 60 min.

Nanoscale

Examples of peeling off time effects

Peeling off time from 35 min to 100 min were studied experimentally. In the experiments, the pre-curing time was 25 min and the pressure value was 1 MPa with pressurized time 1 min. Figure 10S (a) and Figure 10S (b) show examples of nanochannel molds replicated by peeling off too early with peeling off time of 25 min and 40 min, respectively. It is clear that the channel mold becomes negative (should be positive) in Figure 10S (a) and zigzag-like in Figure 10S (b) due to failure of peeling off. On the other hand, when the peeling off time is too late, the contacting time between the smooth cast and the polystyrene surfaces will be longer, which will enhance the swelling of the polystyrene surface.



Figure 10S AFM 3D images of nanochannel molds replicated by smooth cast 305 with different peeling off time. (a) 25 min, (b) 40 min, (c) 100 min. For all the cases, the pre-curing time is 25 min, the pressure is 1 MPa and the pressurized time is 60 s.

Example of fabrication of nanochannel molds with optimal working parameters.



Figure 11S AFM images of a nanochannel mold of 350 nm wide and 80 nm high replicated by smooth cast by using the optimal parameters. (a) 3D image of the nanochannel mold, (b) Profiles of different cross sections along the nanochannel mold.



Figure 12S (a) AFM 3D image of a smaller PDMS nanochannel of 60 \pm 8 nm in width and 20 \pm 6 nm in depth replicated from a nanochannel mold made of Smooth cast and (b) a cross section profile of this nanochannel.



Figure 13S Nanochannel used in the electric current measurement in Figure 9(b) of the main text.



Figure 14S Enlarged version of Figure 8 of the main text. Nanofluidic chip after bonding. (a) PDMS nanofluidic chip with single nanochannel; (b) PDMS nanofluidic chip with parallel nanochannels, (c) An example of final PDMS nanofluidic chip, (d) Cross section of the bi-layer PDMS nanochannel, (e) Zoomed-in view of the cross section measured by the AFM.