Supplementary Information for

Microcontact printing using a flat metal-embedded stamp fabricated using dry peel-off process

Ikjoo Byun,[a] *Anthony W. Coleman*[b] *and Beomjoon Kim**[a]

[a] CIRMM, Institute of Industrial Science, The University of Tokyo, Tokyo, Japan.

E-mail: bjoonkim@iis.u-tokyo.ac.jp

[b] LMI-UMR 5615, CNRS, Universite Claude Bernard Lyon 1, 69622 Villeurbanne, France.

S1: Chemicals and experimental details

PDMS (Silpot 184) was obtained from Dow Corning Toray. Octadecyltrichlorosilane (OTS, $CH_3(CH_2)_{17}SiCl_3$, 90% purity), 3-mercaptopropyltrimethoxysilane (MPTMS, $HS(CH_2)_3Si(OCH_3)_3$, 95% purity), ethanol (99.5% purity), and anhydrous hexane (95% purity) were purchased from Sigma-Aldrich. Hexadecanethiol (HDT, $CH_3(CH_2)_{15}SH$, 95% purity), *1H, 1H, 2H, 2H*-perfluorodecyltrichlorosilane (FDTS, $CF_3(CF_2)_7(CH_2)_2SiCl_3$) was obtained from Wako Pure Chemical Industries, Ltd. Positive tone photoresist (PR, S1805 and S1818) was purchased from Micro Chem.

Piranha solution was prepared by 3:1 (v:v) mixture of sulfuric acid and hydrogen peroxide. Dehydration after piranha cleaning was performed on a hot plate at 200 °C for 10 min. For metal deposition, thermal evaporation was carried out (base vacuum of approximately 2.0×10^{-3} Pa and a deposition rate of less than 0.5 nm/s).

For Au etching to visualize the microcontact printing (μCP) of HDT, a freshly prepared aqueous etching solution consisting of 1 mM $K_4Fe(CN)_6$ $3H_2O$ (Wako, 99.5% purity), 10 mM $K_3Fe(CN)_6$ (Wako, 99% purity), 100 mM $Na_2S_2O_3$ $5H_2O$ (Wako, 99% purity), and 1 M KOH (Wako, 85% purity) at 42°C with gentle stirring (200 rpm) was used to etch the Au area not protected by the HDT ink [1].

To form a sparse MPTMS monolayer on a Si substrate, the Si substrate was kept in a vacuum chamber with the source (200 μl of MPTMS in a Petri dish) [2]. The substrate was mounted upside-down at a distance of 8 cm from the Petri dish. The vacuum chamber was evacuated to a pressure of ~10 Pa for 20 min to facilitate the deposition of the MPTMS on the substrate (open vial).

The roughness of Au films embedded in PDMS were measured by Stylus Profilometer (KLA-Tencor, D-120, scan speed: 0.05 mm/s, scan length: 0.5 mm, and stylus force: 0.1 mg).

S2: Au patterns embedded in thick PDMS with a glass back plate

We tried to fabricate a flat metal-embedded PDMS stamp with a thick PDMS and a glass back plate. Before the transfer of Au patterns to PDMS, Au patterns did not have any wrinkles (Fig. S1a). However, after the transfer of Au patterns to PDMS, some wrinkles on Au patterns were observed (Fig. S1b). As a result, the glass back plate could not prevent the wrinkles on Au patterns. These wrinkles of Au patterns embedded in PDMS can occur when it is peeled off from the substrate because of the large difference of elongation at rupture [2]. These wrinkles deteriorated the quality of μCP results (Fig. S1c, d). When the contact time is relatively short (10 s), HDT can be printed on areas where PDMS and the substrate have conformal contact. On the other hand, when the contact time is relatively long (20 s), vapor-phase HDT molecules can diffuse along the micro-/nano-channels generated by the voids of the metal wrinkles and the substrate surface (Fig. S2). Also, the wrinkles of Au patterns obstructed the embedment of Au patterns to PDMS (*i.e.* no flat).

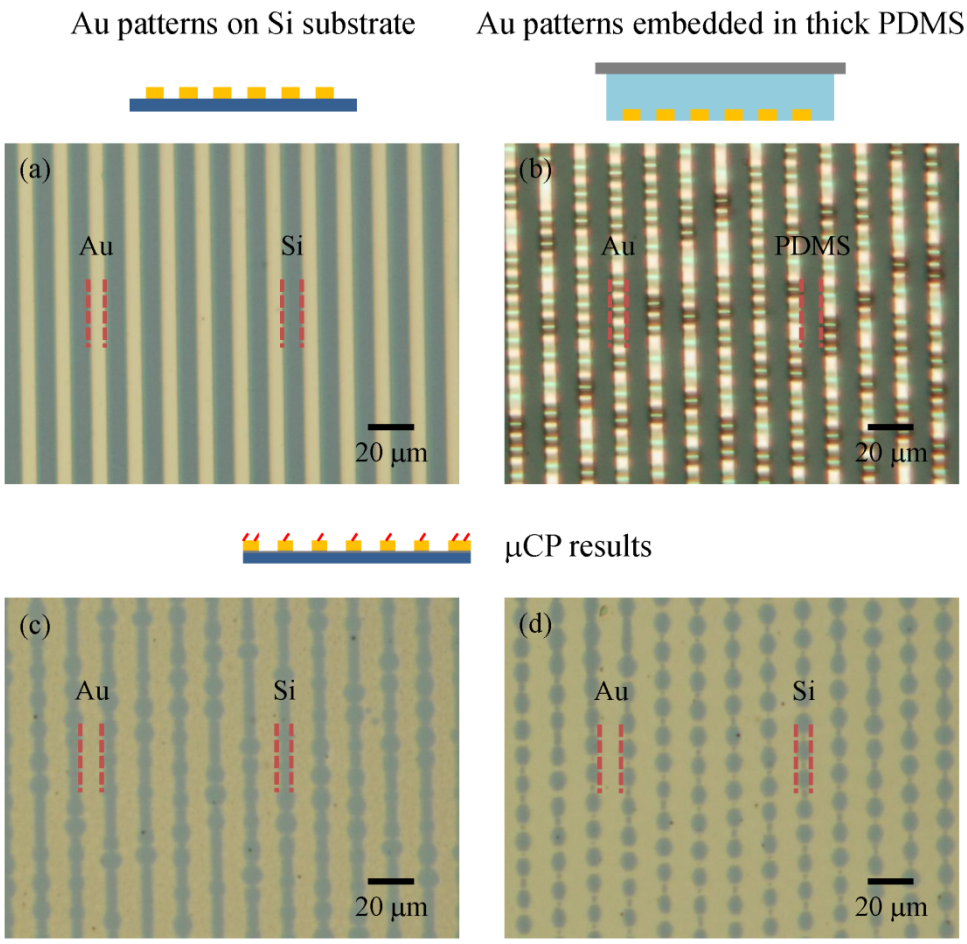

Fig. S1 Optical microscopic images of (a) original Au patterns on the Si substrate, (b) Au patterns embedded in the PDMS. (c, d) μCP results using the wrinkled stamp when the contact time was (c) 10 s and (d) 20 s.

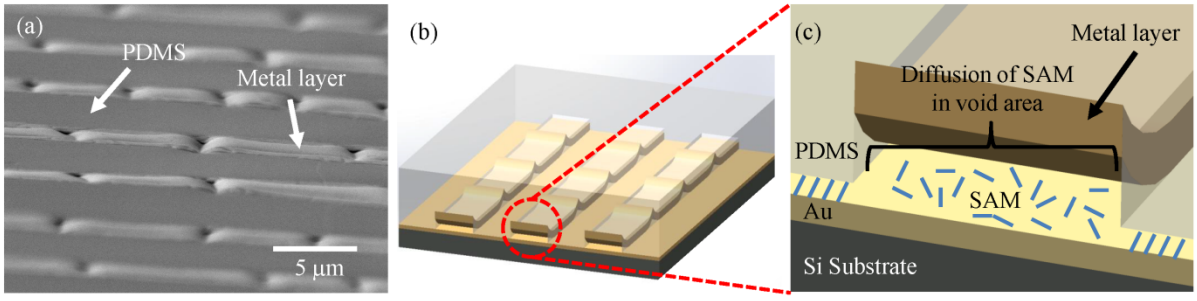

Fig. S2 (a) FE-SEM image (tilted view) showing the wrinkle of the metal layer embedded in PDMS, (b, c) exaggerated schematic illustration of flat metal-embedded PDMS stamp and voids formed during μCP. Vapor-phase SAM ink molecules can diffuse along the voids generated by the metal pattern wrinkles and the substrate surface.

S3: Fabrication of a conventional PDMS stamp for microcontact printing

For the comparison, conventional PDMS stamps with different tip heights (2 μm and 12 μm) were fabricated by replication from Si molds. For the fabrication of PDMS stamp with low aspect ratio, PDMS was replicated from photoresist patterns (thickness: 2 μm). As a result of μCP using the PDMS stamp with a tip height of 2 μm, μCP failure by a roof collapse of the PDMS stamp was observed as shown in Fig. S3a (gap between PDMS tips: 1000 μm).

To avoid the roof collapse, a PDMS stamp with moderate aspect ratio (tip height: 12 μm) was fabricated (Fig. S4). While the mold can be easily fabricated by SU-8, we choose the method that etching Si mold using RIE in order to control the height of structures precisely. Aluminum patterns (thickness: 100 nm) fabricated by conventional lithography were used as an etch mask for Si dry etching. Deep reactive ion etching (DRIE, ICP-RIE, STS) with the Bosch process was applied for 12 μm Si etching. After removal of Al layer, FDTS was treated on the surface of the Si substrate as an anti-adhesive layer. PDMS was replicated using the same experimental condition of the metal-embedded PDMS stamp, and it was manually peeled off from the Si mold. As a result of μCP using the PDMS stamp with a tip height of 12 μm, any μCP failure by a roof collapse of PDMS was not observed (Fig. S3b).

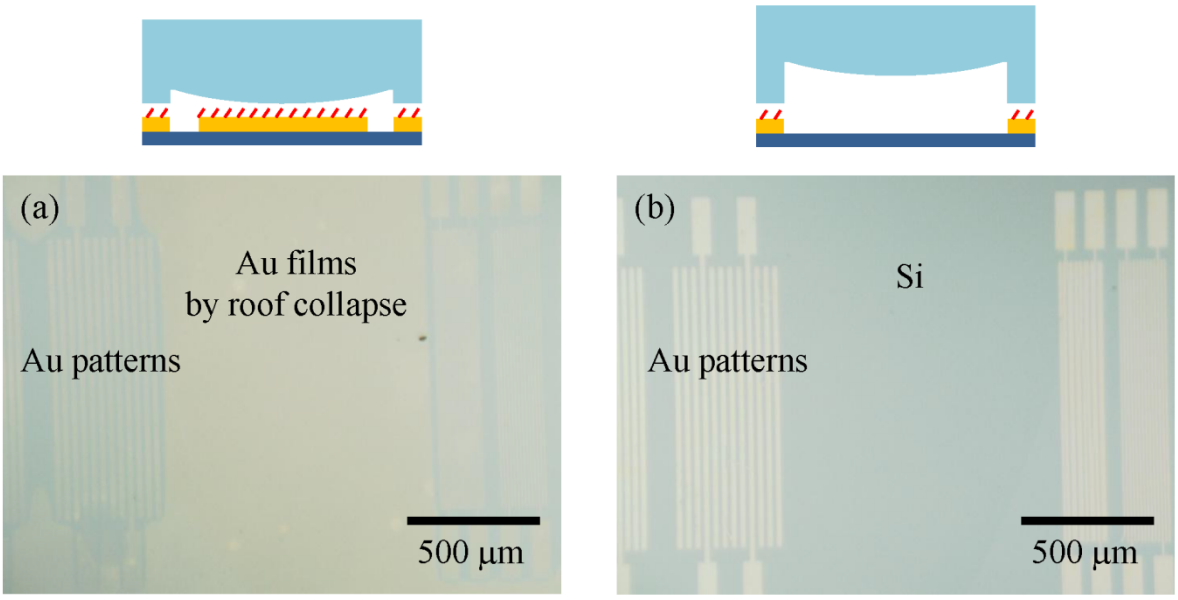

Fig. S3 Schematic illustration and optical images of Au patterns after μCP and Au etching. (a) μCP failure by roof collapse of PDMS stamp with low aspect ratio, (b) successful μCP by a PDMS stamp with moderate aspect ratio. The tip height: (a) 2 μm and (b) 12 μm.

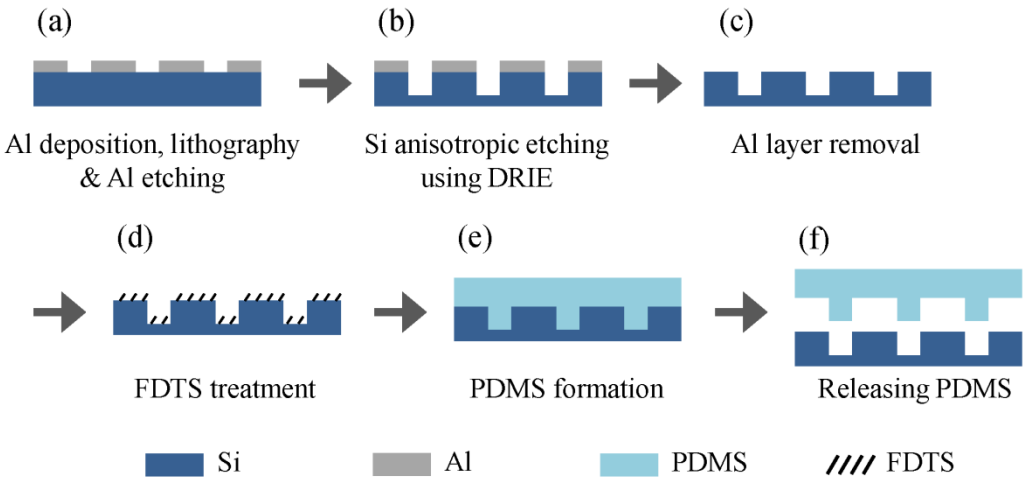

Fig. S4 Schematic illustration of fabrication process for a conventional PDMS stamp.

S4: Microcontact printing result of relatively large patterns

μCP for relatively large patterns was successful for both metal-embedded PDMS stamp (Fig. S5) and conventional PDMS stamp (Fig. S6). In case of the conventional PDMS stamp, comparably larger gaps (7~15 μm) between stamp tips were effectively prevented the lateral collapse of stamp tips. For the fabrication of both flat metal-embedded PDMS stamp and conventional PDMS stamp, the same photomask for lithography was used. However, due to the experimental condition of DRIE and wet-etching, the protruded part of the conventional PDMS stamp was 1 μm smaller than PDMS part of the metal-embedded stamp. The lateral diffusion of HDT inks was 500 nm for each direction for both types of stamps.

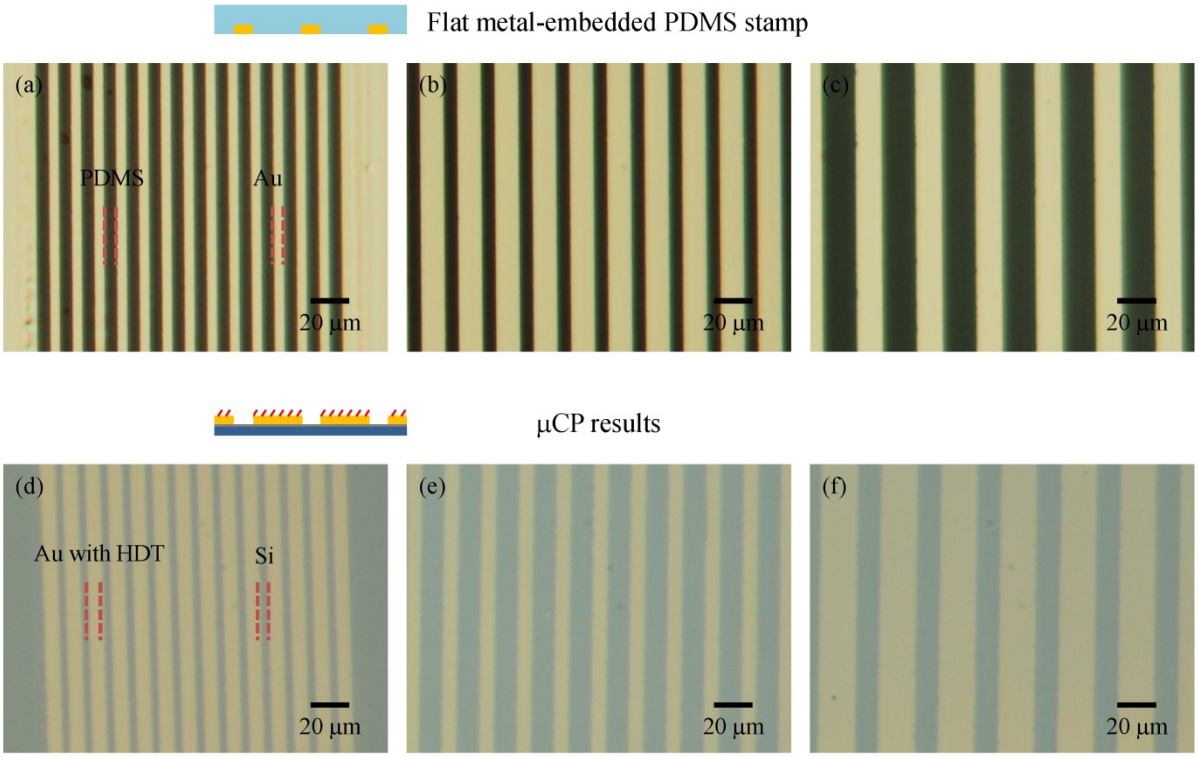

Fig. S5 Optical images of (a–c) flat metal-embedded PDMS stamps and (d–f) Au micro-patterns fabricated by μCP using the flat metal-embedded PDMS stamps after Au etching. Linewidths: (a) PDMS: 6 μm, Au: 6 μm, (b) PDMS: 6 μm, Au: 14 μm, , (c) PDMS: 18 μm, Au: 14 μm, (d) Au with HDT: 7 μm, Si: 5 μm, (e) Au with HDT: 7 μm, Si: 13 μm, and (f) Au with HDT: 19 μm, Si: 13 μm.

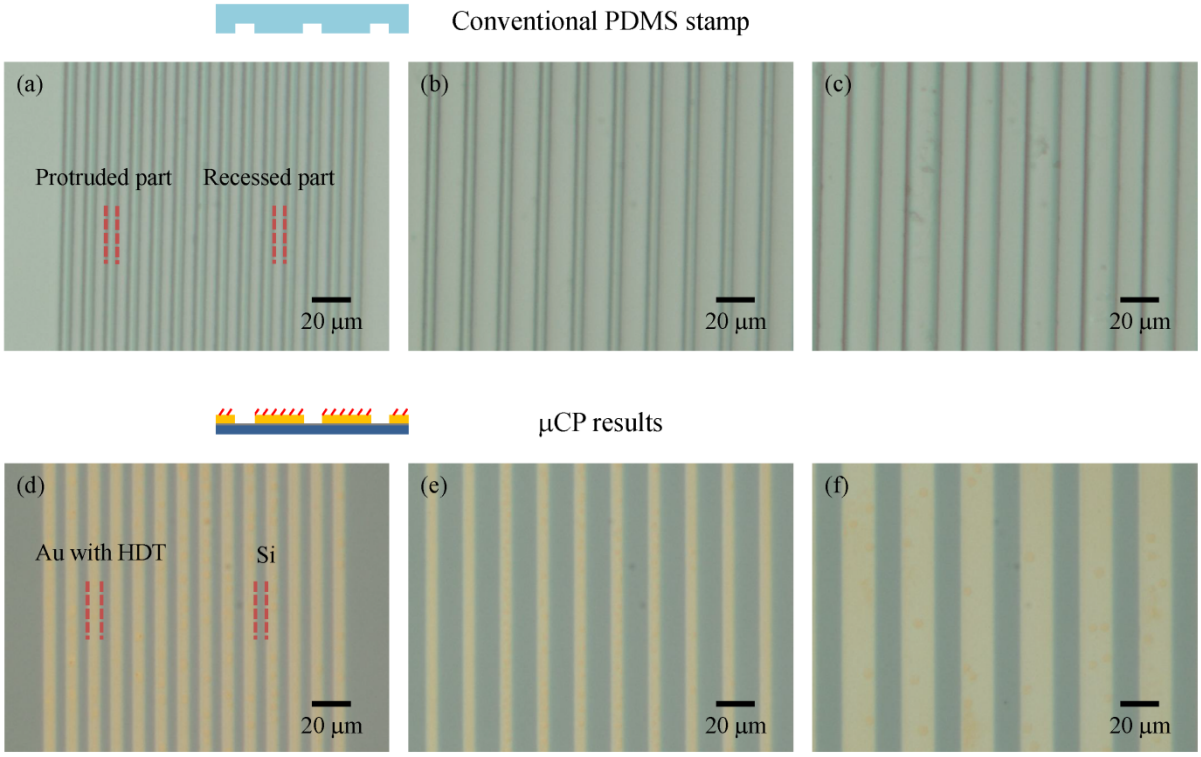

Fig. S6 Optical images of (a–c) flat metal-embedded PDMS stamp and (d–f) Au micro-patterns fabricated by μCP using the flat metal-embedded PDMS stamp. Linewidths: (a) protruded: 5 μm, recessed: 7 μm, (b) protruded: 5 μm, recessed: 15 μm, (c) protruded: 17 μm, recessed: 15 μm, (d) Au with HDT: 6 μm, Si: 6 μm, (e) Au with HDT: 6 μm, Si: 14 μm, and (f) Au with HDT: 18 μm, Si: 14 μm. The height of PDMS tip was 12 μm.

S5: Microcontact printing using a flat chromium-embedded PDMS stamp

Chromium was examined for the metal embedded in our new stamp instead of Au (Fig. S7). After cleaning with a piranha solution, a Si substrate was immersed in an OTS solution (10 mM in hexane). The self-assembled OTS monolayer functions as an anti-adhesive between the Si substrate and the chromium layer. Cr and Au were thermally deposited on the OTS-treated substrate with a thickness of 10 and 50 nm, respectively. Conventional lithography was employed to fabricate micro-metal patterns. This substrate with metal patterns was treated with an ethanolic solution of 20 mM MPTMS for strong adhesion between Au and PDMS. A PDMS prepolymer solution was prepared by mixing a silicone elastomer base and a curing agent at a weight ratio of 10:1. The PDMS mixture was degassed and poured onto the Si substrate with metal patterns. After heat curing in an oven at 60°C for 3 h and maintained at room temperature for 12 h, PDMS with Cr and Au layers was manually peeled off from the Si substrate.

The embedded metal act as a transport barrier of the SAM ink, and PDMS was used as a transporter of the SAM ink. In particular, HDT-SAM did not stain to the Cr layer. A glass back plate was not used during releasing PDMS from Si substrate, wrinkles on Cr/Au surface were observed (Fig. S8a, b). Although HDT inks were selectively soaked to PDMS and printed on Au substrate, the wrinkles deteriorated the quality of μCP (Fig. S8c, d). Vapor-phase diffusion of HDT was also observed.

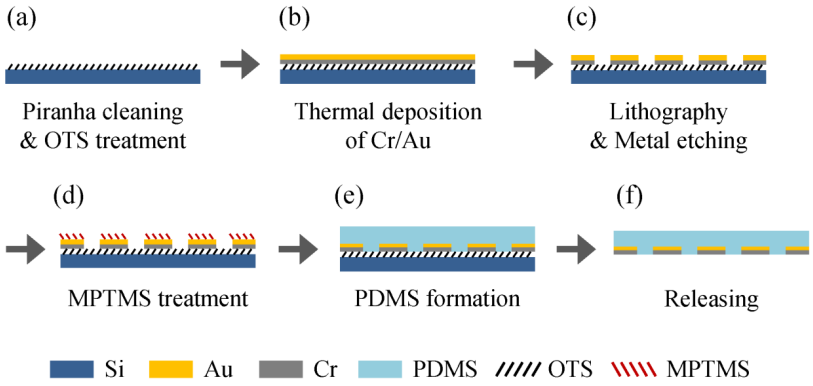

Fig. S7 Schematic illustration of fabrication process for chromium-embedded PDMS stamp.

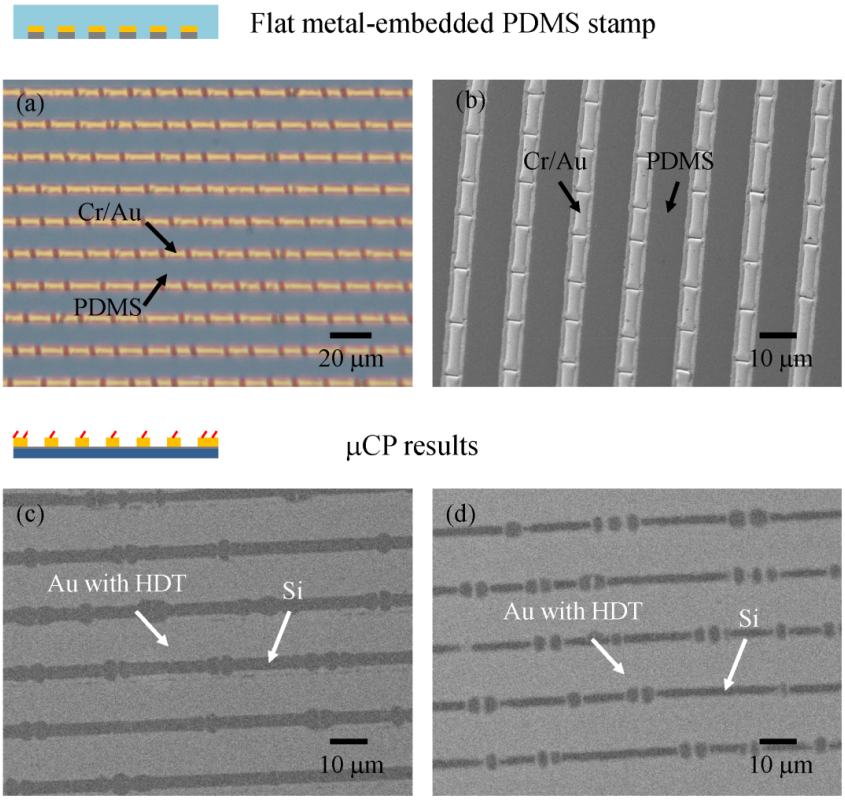

Fig. S8 (a, b) An optical image and a FE-SEM image of a flat Cr/Au embedded PDMS stamp. (c, d) μCP results after selective Au etching. μCP contact time (a): 10 s , (b): 20 s.

Supplementary References

1 Y. Xia, X. M. Zhao, E. Kim, G. M. Whitesides, *Chem. Mater.*, 1995, **7**, 2332-2337.

2 I. Byun, A. W. Coleman, B. Kim, *J. Micromech. Microeng.*, 2013, **23**, 085016.