Supporting Information

Surface Treatment-Assisted Switchable Transfer Printing on Polydimethylsiloxane Films

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S1. The change of surface-mechanical properties of PDMS induced by surface oxidation

![Diagram showing wrinkle wavelength vs. OP exposure time](image)

**Figure S1.** Wrinkle wavelength ($\lambda$) of the OP-exposed PDMS sheet as a function of OP exposure time ($t_{\text{OP}}$).

In contrary to the deposition of homogeneous film on the PDMS substrate with an obvious interface between them, the structure of the oxidized stiff layer formed by surface oxidation is much more complex and fuzzy. There have been many efforts to investigate the chemical and mechanical properties of the as-formed silica-like layer.\(^1\)\(^-\)\(^7\) Luckily, the change of modulus and thickness of the stiff skin with the exposure time of oxygen plasma ($t_{\text{OP}}$) can be indirectly yet effectively reflected via wrinkling experiments.\(^6\)\(^,\)\(^7\)

As one of mechanical instabilities, surface wrinkling in a rigid/soft bilayer is stemmed from the strain mismatch between a stiff film and a compliant substrate. When the induced compressive stress exceeds the bilayer-defined critical wrinkling stress, surface wrinkling with typically sinusoidal profiles occurs spontaneously for
minimizing the system’s free energy.\textsuperscript{8,9} There are many ways to prepare the PDMS-based film/substrate system. An efficient route is the OP/UVO oxidation of compliant PDMS elastomers, which converts the PDMS surface into a thin stiff silica-like film.\textsuperscript{10} In the in-plane compression at a small strain applied, the characteristic wrinkle wavelength ($\lambda$) is determined by\textsuperscript{8,9}

$$
\lambda = 2\pi h_t \left( \frac{E_f / (1-v_f^2)}{3E_f / (1-v_f^2)} \right)^{1/3}
$$

where $h_t$ is the thickness of the oxidized layer, $E$ is the Young’s modulus, and $v$ is the Poisson’s ratio. The subscripts “$f$” and “$s$” refer to the oxidized surface and the bulk PDMS, respectively.

Recently, Cabral \textit{et al} studied the mechanism and kinetics of OP exposure of PDMS based on the wrinkling process.\textsuperscript{6,7} A three-stage process for the vitrification of the OP-exposed PDMS surface was proposed: the silica-like layer simultaneously increases in the modulus and thickness at first (stage 1), until full oxidation of the top surface into nearly complete SiO$_2$ conversion (stage 2), and then the increase in exposure time primarily affects the film thickness (stage 3). In the highly oxidized stage, a composite PDMS system is elicited with a \textasciitilde10 nm thick silica-like outermost layer, a thick intermediate region consisting of a mixed chemical composition (intermediate species, SiO$_2$ and unreacted PDMS), and the underlying bulk PDMS layer. Although those analyses are mainly based on the OP exposure, the situation of UVO irradiation is similar in principle, except a lower conversion ratio of the outermost layer from PDMS into SiO$_x$ yet with a deeper modification depth.\textsuperscript{11}

We conducted the wrinkling experiment to investigate the oxidation process. A
cured PDMS sheet prepared by heating the base and curing agent (at the weight ratio of 10:1) at 70 °C for 4 h was cut into 5 cm × 1 cm and mounted onto a home-made tensile holder. Uniaxial strain of 10 % was exerted by mechanical stretching. Then, the pre-strained sample underwent OP treatment (Harrick PDC 32G) at a pressure of 0.02 mbar for 1 to 40 min. Finally, the pre-strain was slowly released to induce surface wrinkling. The relationship between the wrinkle wavelength \( \lambda \) and OP-treatment time \( t_{OP} \) is presented in Figure S1. The wavelength increases linearly with \( t_{OP} \) at \( t_{OP} \leq 20 \) min, and then gradually becomes constant when \( t_{OP} \) increases to 30 min. From Equation 1, the dependence of \( \lambda \) on \( t_{OP} \) can be roughly explained by assuming an increase in \( h_f \) and/or an increase in \( E_f \) for the oxide layer with \( t_{OP} \).\(^{10}\) With the further increase of \( t_{OP} \), \( \lambda \) reaches one saturated value owing to the limited oxidation depth of OP treatment.\(^{12}\)
S2. The change of interfacial adhesion strength with surface treatment

Figure S2. Changes of contact angle ($\theta$) and work of adhesion ($G_{\text{interface}}$) with $t_{\text{OP}}$ (a) and $t_{\text{UVO}}$ (b) applied on the stamp and the substrate concurrently. The inset in (a) is a zoomed plot with $t_{\text{OP}} = 0$ – 1 min. (c) Plots of $G_{\text{interface}}$ as a function of $t_{\text{OP}}$ and $t_{\text{UVO}}$ applied for the “hard” side.

In addition to the surface-stiffening process along with the increase of surface-treatment time, its effect on the surface energy of PDMS should also be considered, which would in turn affect the interfacial adhesion strength ($G_{\text{interface}}$). This adhesion under OP or UVO treatment is mainly attributed to the condensation reaction of hydroxyl groups (-OH) followed by interfacial bonding. Furthermore, the strength of covalent bonding increases with the surface -OH concentration on the contact area, which depends on $t_{\text{OP}}$ or $t_{\text{UVO}}$. Specifically, the work of adhesion at a flat PDMS/PDMS interface (simultaneous surface treatment) can be roughly calculated using the surface energy ($\gamma$) by a harmonic mean equation, which is given by

$$ G_{\text{interface}} = 4 \left( \frac{\gamma_1^d/\gamma_2^d + \gamma_1^p/\gamma_2^p}{\gamma_1^d + \gamma_2^d} \right) $$

Where subscripts 1 and 2 represent the surfaces from two different PDMS slabs, and superscripts d and p are the dispersion and polar components of the surface energy, respectively. The surface energy of flat substrates is calculated using the geometric
mean approximation from the contact angle data of two kinds of liquids.\textsuperscript{14}

\[
\gamma_{L1}(1 + \cos \theta_{L1}) = 2\left(\sqrt{\gamma_{d, L1}^d \gamma_{S}^d} + \sqrt{\gamma_{L1}^p \gamma_{S}^p}\right) \quad (3a)
\]

\[
\gamma_{L2}(1 + \cos \theta_{L2}) = 2\left(\sqrt{\gamma_{d, L2}^d \gamma_{S}^d} + \sqrt{\gamma_{L2}^p \gamma_{S}^p}\right) \quad (3b)
\]

\[
\gamma = \gamma^d + \gamma^p \quad (3c)
\]

In Equation 3a and 3b, the subscripts L1, L2 and S correspond to liquid 1, liquid 2 and solid surface, respectively. With the probe liquids of water and diiodomethane (CH\textsubscript{2}I\textsubscript{2}), contact angles of PDMS surface from various \(t_{\text{OP}}\) and \(t_{\text{UVO}}\) were measured (using a Powereach contact angle goniometer, JC2000D) to calculate surface tensions that are needed to determine the work of adhesion. For an example of treating the two PDMS slabs for the same time, the dependence of \(G_{\text{interface}}\) on a function of \(t_{\text{OP}}\) (Figure S2a) and \(t_{\text{UVO}}\) (Figure S2b) is shown in Figure S2, which demonstrates an increase of \(G_{\text{interface}}\) with \(t_{\text{OP}}\) and \(t_{\text{UVO}}\). This increase is very rapid for the OP exposure (~ 1 min arriving at the maximum value of 144 mJ m\textsuperscript{-2} from the initial 41 mJ m\textsuperscript{-2} ) and more gradual for the UVO modification (50 min arriving at the value of 104 mJ m\textsuperscript{-2}). This difference comes from a dynamic difference in the oxidation process between OP and UVO exposure.\textsuperscript{11} The modification of PDMS via OP or UVO exposure is both followed by the formation of hydroxyl groups at the expense of methyl groups, but the conversion is much more rapid for OP exposure than for UVO treatment. Moreover, OP modification can induce almost complete conversion of the surface -CH\textsubscript{3} groups, while a fraction of -CH\textsubscript{3} groups is left along with UVO modification. Thus, OP treatment usually gives rise to a much more rapid and efficient activation to establish a stronger and stable bonding between the OP-exposed PDMS sheets.
Furthermore, when the two PDMS slabs are treated with different time, i.e., only one slab is hardened with OP/UVO oxidation followed by a OP0.5min or UVO2min activation of both slabs, we roughly calculate the work of adhesion using the surface energy data with OP1–50min (UVO5–50min) and OP0.5min (UVO2min). The corresponding dependence of $G_{\text{interface}}$ on a function of $t_{\text{OP}}$ and $t_{\text{UVO}}$ for the “hard” side is shown in Figure S2c, which shows a constant value of $\sim139$ mJ m$^{-2}$ for OP treatment and a narrow range of 42–44 mJ m$^{-2}$ for UVO treatment.
S3. Switchable transfer with the cross linking-controlled cohesion difference

A well-known yet simple strategy to tailor the PDMS$_{(n:1)}$ modulus is to vary the weight ratio of the base/curing agent (i.e., n:1) in the curing process. Here n:1 = 5:1, 10:1, 20:1, and 30:1, whose elastic modulus is estimated to be 1.81 MPa, 1.41 MPa, 0.41 MPa, and 0.12 MPa, respectively, based on a Linkam TST-350 tensile stress tester (Linkam Scientific Instruments, Ltd., U.K.).

![Image](image_url)

**Figure S3.** Optical images of the resulting patterned PDMS substrates using Stamp R (a, b) or L1 (d, e) with the combination of stamp/substrate: (a, d) PDMS$_{(10:1)}$/PDMS$_{(20:1)}$, (b, e) PDMS$_{(20:1)}$/PDMS$_{(10:1)}$. The inset in the upper-right corner of each panel (a, b, d) is the corresponding three-dimensional AFM image. The inset in the upper-right corner of (e) is an optical snapshot during the drying process of 1 mM rhodamine B in ethanol on the patterned PDMS surface. (c) The plot of the transfer decal height ($h$) on the patterned substrate as a function of $E_{PDMS(n:1)}$ of the substrate in the case of the PDMS$_{(10:1)}$ Stamp R applied.

Stamp R (PDMS$_{(10:1)}$ in Figure S3a; PDMS$_{(20:1)}$ in Figure S3b) was placed promptly into contact with a flat PDMS substrate (PDMS$_{(20:1)}$ in Figure S3a; PDMS$_{(10:1)}$ in
Figure S3b) after the OP0.5min activation for both sides, followed by heating at 100 °C for 1 h. Three-dimensional AFM image inserted in Figure S3a shows the patterned substrate with uniform conical holes of (1.06±0.02) μm in the height, in which a SPm transfer occurs from the “soft” substrate to the “hard” stamp. On the contrary, the substrate presented in Figure S3b is patterned with uniform raised posts (2.11±0.05 μm in the height) and APm transfer from the “soft” stamp to the “hard” substrate happens.

The influence of the substrate modulus ($E_{\text{PDMS}(n:1)}$) (n:1=5:1, 10:1, 20:1, 30:1) on $h$ in the case of a PDMS$_{(10:1)}$ stamp employed was investigated (Figure S3c). The surface-activation treatments are OP0.5min, which ensure the same $G_{\text{interface}}$ under these conditions. As shown in Figure S3c, SPm transfer occurs in all combinations with an increasing $h$ with n:1, i.e., $h = -(0.76±0.02)$ μm, -(0.91±0.04) μm, -(1.06±0.02) μm, and -(1.24±0.04) μm for n:1 = 5:1, 10:1, 20:1, and 30:1, respectively. From the experimental conditions, we know that $G_{\text{interface}}$ and $G_{\text{stamp}}$ are constant, while $G_{\text{substrate}}$ decreases with the increase of n:1 (corresponding to the decrease of the substrate modulus), which is assumed to be responsible for the $h$ increase. In addition, the SPm transfer in all combinations indicates the stamp is “harder” than the substrate (i.e., $G_{\text{stamp}} > G_{\text{substrate}}$). This conclusion seems to be inconsistent with the combination of “soft” PDMS$_{(10:1)}$ stamp/“hard” PDMS$_{(5:1)}$ substrate as well as the combination of the same “soft” PDMS$_{(10:1)}$ stamp/PDMS$_{(10:1)}$ substrate (Figure S3c). We attribute this SPm transfer to the effect of the topography of the stamp, which will be discussed in details in Supporting Information S4.
Similar to Stamp R, switchable transfer with the cross linking-controlled cohesion difference using Stamp L1 is obtained. Figure S3d and Figure S3e represent a combination of “hard” stamp (PDMS\textsubscript{(10:1)})/“soft” substrate (PDMS\textsubscript{(20:1)}), and “soft” stamp (PDMS\textsubscript{(20:1)})/“hard” substrate (PDMS\textsubscript{(10:1)}) respectively, which leads to the corresponding SPm (Figure S3d) (indicated by the inserted three-dimensional AFM image) and APm transfer (Figure S3e) (indicated by the shape of receding triple-phase line during the drying process of 1 mM rhodamine B in ethanol), respectively.
S4. The influence of stamp structure factor on sTP

The deterministic transfer criterion in sTP can be simply formulized as follows:

SPm patterning: \( G_{\text{stamp}} > G_{\text{substrate}} \) \hfill (4a)

APm patterning: \( G_{\text{stamp}} < G_{\text{substrate}} \) \hfill (4b)

Here we define

\[ g = \frac{G_{\text{stamp}}}{G_{\text{substrate}}} \] \hfill (5)

Thus Equation 4 can be further formulized as follows:

SPm patterning: \( g > 1 \) \hfill (6a)

APm patterning: \( g < 1 \) \hfill (6b)

Considering the proportional relation between the cohesion strength and the elastic modulus, the cohesion strength of the oxidized stamp/substrate can be roughly developed as follows:

\[ G_{\text{stamp}} = G_0 \cdot f_G \cdot H_{\text{stamp}} \cdot f_{it} \] \hfill (7a)

\[ G_{\text{substrate}} = G_0 \cdot H_{\text{substrate}} \] \hfill (7b)

From Equation 5 and 7, we can have

\[ g = \frac{G_{\text{stamp}}}{G_{\text{substrate}}} = \frac{H_{\text{stamp}}}{H_{\text{substrate}}} \cdot f_G \cdot f_{it} \] \hfill (8)

Here \( g \) is composed of three parts: \( \frac{H_{\text{stamp}}}{H_{\text{substrate}}} \cdot f_G \) and \( f_{it} \). A comparison between \( \frac{H_{\text{stamp}}}{H_{\text{substrate}}} \) and 1 can be easily determined by the comparison between the surface-oxidation time for the stamp (\( t_{\text{stamp}} \)) and for the substrate (\( t_{\text{substrate}} \)). To investigate the influence of the stamp structure factor, the PDMS stamp and substrate were subjected to the same duration of surface oxidation including no surface oxidation (Figure 3), which means \( H_{\text{stamp}} = H_{\text{substrate}} \). Thus in this case, Equation 8 can be simplified to
\[ g = f_G f_H \]  \hspace{1cm} (9)

Firstly, when no surface oxidation is applied on the stamp, \( f_H \) representing the effect of the stamp structure factor on the surface oxidation-induced hardening can be assumed to be 1, and Equation 9 can be further simplified into

\[ g = f_G \]  \hspace{1cm} (10)

In this case, the patterned substrates have conical holes with a highly uniform peak height of \(-(911 \pm 43)\) nm (Figure 3a, OP surface activation) and \(-(601 \pm 19)\) nm (Figure 3b, UVO activation). That is to say, a highly uniform SPm transfer occurs with the substrate→stamp transfer in the case of no hardening processing for the substrate and stamp. This result reveals that the stamp is “harder” than the substrate (i.e., \( g > 1 \)) maybe due to the structure factor of the stamp \( (f_G) \). Therefore, from the experimental perspective, the influence of the structure factor of the stamp on the cohesion strength of the stamp should be positive (i.e., \( f_G > 1 \)). Besides, the different \( h \) for the OP and UVO activation is due to their large difference in \( G_{\text{interface}} \) (i.e., \( \sim 135 \) and \( 41 \) mJ m\(^{-2} \) respectively according to Figure 2Sa,b).

\( f_H \) is related to the surface-oxidation time, whose effect was investigated with varied oxidation time. Figure 3d shows the changes of the transfer results with \( t_{\text{OP}} \) when the stamp and the substrate are simultaneously treated with the same duration of surface oxidation. Here, no surface activation is needed. We can see that with the increase of \( t_{\text{OP}} \), four distinct stages (i, ii, iii, and iv) exist in terms of the transfer direction denoted by the plus or minus of \( h \) (Figure 3d). As for \( G_{\text{interface}} \) (Figure S2a), it increases rapidly for a short duration of OP exposure (corresponding to Figure 3d (i))
and Figure 3e) and then keeps constant with the further increase of $t_{OP}$ (corresponding to Fig. 3d (ii-iv)). Meanwhile, the transfer mode changes from the SPm (i) to the APm (iii), which means $g = f_G \cdot f_H$ decreased from a value bigger than 1 (i) to a value smaller than 1 (iii). Section (ii) is a transition zone with $g = f_G \cdot f_H \approx 1$. The unexpected anomaly occurred in section (iv) is probably because highly oxidized PDMS surface restrains the transfer process, just as the transfer between two excessively hard surfaces (e.g., between silica and silica) hardly happens. In the current case, a constant of $f_G$ is bigger than 1 from the results of Figure 3a,b, and thus we can deduce that $f_H < 1$ and decreases with $t_{OP}$. Specifically, in section (i), the negative effect on $G_{stamp}$ induced by a short-period treatment is slight, and the positive effect of $f_G$ on $G_{stamp}$ exceeds the negative effect of $f_H$, leading to $g = f_G \cdot f_H > 1$ and the final SPm transfer. With the increase of $t_{OP}$, $f_H$ further decreases and can offset the constant $f_G$, resulting in the APm transfer (iii).

When looking back at the experimental conditions in Figure 2c-①, we see it represents a combination of the untreated “soft” substrate ($H_{substrate} = 1$) and the “hard” stamp ($H_{stamp} > 1$) with a varied $t_{OP(stamp)}$. SPm transfers occur when $t_{OP(stamp)}$ increases from 1 min to 50 min. In those situations,

$$g = \frac{G_{stamp}}{G_{substrate}} = \frac{H_{stamp}}{H_{substrate}} f_G \cdot f_H = H_{stamp} \cdot f_G \cdot f_H$$  \hspace{1cm} (11)

where $f_G > 1$, $H_{stamp} > 1$ and increases with $t_{OP(stamp)}$, while $f_H < 1$ and decreases with $t_{OP(stamp)}$. From the results of SPm transfer in Figure 2c-①, $g$ should be larger than 1 all the while. That is to say, although $f_H$ has a negative effect on $G_{stamp}$, its dominative role still lies in the hardening effect ($H_{stamp}$), which guarantees that the
final $g$ is bigger than 1. On the contrary, if the substrate is hardened (i.e., $H_{\text{substrate}} > 1$) while the stamp is untreated (i.e., $H_{\text{stamp}} = 1$ and $f_{\text{II}} = 1$), the situation becomes a bit more complex. As presented in Figure 2c-②, transfer printing changes from SPm at the first ($t_{\text{OP(substrate)}} = 1$ min), to the mixed SPm/APm mode ($t_{\text{OP(substrate)}} = 5 – 10$ min), and to the final APm ($t_{\text{OP(substrate)}} = 30 – 50$ min). From Equation 8,

$$
g = \frac{G_{\text{stamp}}}{G_{\text{substrate}}} = \frac{H_{\text{stamp}}}{H_{\text{substrate}}} f_{\text{G}} f_{\text{II}} = \frac{f_{\text{G}}}{H_{\text{substrate}}} \tag{12}
$$

where $f_{\text{G}} > 1$, $H_{\text{substrate}} > 1$ and increases with $t_{\text{OP(substrate)}}$. When $t_{\text{OP(substrate)}} = 1$ min, the oxidation-hardening effect on the substrate is so small that $H_{\text{substrate}} < f_{\text{G}}$, i.e., $g > 1$, which is responsible for the SPm transfer at first. Along with the increasing of $t_{\text{OP(substrate)}}$, $H_{\text{substrate}}$ increases constantly. When $t_{\text{OP(substrate)}} = 5 – 10$ min, $H_{\text{substrate}} \approx f_{\text{G}}$ leading to a mixed mode transfer. Beyond this transition zone, $H_{\text{substrate}}$ is much greater than $f_{\text{G}}$, which brings a single APm transfer with a constant transfer height ($h = \sim 2 \, \mu m$). The similar situation exists in the case of different “soft/hard” contrast degrees with UVO treatment (Figure 2f).
S5. Transfer printing without any surface treatment of the stamp and substrate

**Figure S4.** Optical images of the patterned PDMS substrates using Stamp R (a) and Stamp L1 (b) without surface oxidation/activation processing imposed on the stamp and substrate. The inset in each panel is the corresponding three-dimensional AFM image.

A PDMS stamp with Stamp R (or L1) and a flat substrate were brought into conformal contact, followed by heating at 100 °C for 1 h. After peeling the stamp, SPm transfer with a feature height of ~80 nm (Figure S4a) or ~200 nm (Figure S4b) occurs. Note that no hardening and activation processing is imposed on the stamp and substrate. Thus this substrate→stamp transfer thoroughly indicates that the patterned stamp is “harder” than the planar counterpart. We attribute this effective transfer to the diffusion of low-molecular-weight PDMS, which is widely observed between a PDMS stamp and a solid substrate (e.g., silica) in the previous studies.\textsuperscript{15,16} Given that the diffusion process is accelerated with the rise of temperature and time, this speculation is verified through the control experiment for transfer quality (data not shown), which reveals a positive temperature/time dependence.
S6. sTP using the line-patterned PDMS sheet both as the stamp and the substrate

Figure S5. Optical images of the resulting patterns on the “hard” (a) and “soft” (b) sides in the case of the same kind of structured PDMS sheets both acting as the stamp and the substrate. The “hard” side (a) is hardened by UVO30min. The inset in (a) is an optical snapshot during drying 1 mM rhodamine B in ethanol on the PDMS surface. The inset in (b) is the corresponding three-dimensional AFM image.

A verification experiment (Figure S5) for the deterministic transfer criterion was conducted via the combination of the PDMS stamp and substrate with the same patterned structure, which thoroughly excludes the interference of the structure factor. Namely, for two pieces of identical Stamp L1, one was hardened with UVO30min while the other was without any treatment. They were brought into contact orthogonally after the surface activation of UVO2min. As shown in Figure S5, the raised lines on the “hard” side are patterned with pyramid bumps (indicated by the shape of receding triple-phase line during drying 1 mM rhodamine B in ethanol) in an APm transfer. Correspondingly, the raised lines on the “soft” side are patterned with pyramid holes (indicated by the inserted three-dimensional AFM image) in a SPm transfer. These results prove again that in our sTP, the PDMS decal inks are transferred from the “soft” side to the “hard” side.
S7. Microfluidics application of the patterned substrate

The PDMS substrate with parallel grooved patterns was sealed against a flat PDMS slab to generate enclosed microchannels L2 (using substrate as shown in Figure 5a) or L3 (using substrate as shown in Figure 5b). 10 g L\(^{-1}\) rhodamine B in water (Movie S1) and 0.1 wt% 2.5 μm-sized polystyrene colloidal microspheres in ethanol (Movie S2) are used to demonstrate the fluidic transport through microchannels L2 and L3, respectively. The results indicate that the patterned substrates have the great potentials in the related wide applications.

**Movie S1.** 10 g L\(^{-1}\) rhodamine B in water through microchannel L2.

**Movie S2.** 0.1 wt% 2.5 μm-sized polystyrene colloidal microspheres in ethanol through microchannel L3.
References:


