Stamp Collapse in Soft Lithography

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We have studied the so-called roof collapse in soft lithography. Roof collapse is due to the adhesion between the PDMS stamp and substrate, and it may affect the quality of soft lithography. Our analysis accounts for the interactions of multiple punches and the effect of elastic mismatch between the PDMS stamp and substrate. A scaling law among the stamp modulus, punch height and spacing, and work of adhesion between the stamp and substrate is established. Such a scaling law leads to a simple criterion against the unwanted roof collapse. The present study agrees well with the experimental data.

1. Introduction

Soft lithography is an important method for micro- and nanofabrication and has many applications in plastic electronics and fiber optics.1–6 Figure 1 shows a schematic diagram of an elastomeric stamp on a substrate in soft lithography. The stamp surface consists of flat punches whose width 2w is on the order of micrometers or larger. The punch height h ranges from micrometers to several hundred nanometers or even smaller, whereas punch spacing 2a also has a large variation. The ink is applied to the stamp with a pattern of surface relief shown in Figure 1, and ink is transferred to the substrate when the stamp is brought into contact with the substrate. The elastomeric stamp is usually made of poly(dimethylsiloxane) (PDMS), which is very compliant and has a low shear modulus µ of less than 1 MPa. This low stiffness makes PDMS easily deformable, which may affect the quality of soft lithography.

Hui et al.7 studied various deformation mechanisms of the stamp, such as the punch buckling, lateral collapse, and roof collapse. Here roof collapse represents the collapse of the stamp toward the substrate as shown schematically in Figure 1. Hui et al.7 obtained the critical external load (ω0)critical for roof collapse in terms of the Young’s modulus of the stamp and punch geometry (height, width, and spacing). Once the external load ω0 reaches (ω0)critical, roof collapse occurs and yields unwanted contact between the sagged surfaces of the stamp and the substrate.

Roof collapse has been observed in recent experiments of Sharp et al.8 for small punch height h (≪ punch width 2w and spacing 2a, Figure 1). Sharp et al.8 attributed roof collapse to (1) the external load that placed the sagged surfaces of the stamp in contact with the substrate and (2) the adhesion between the stamp and substrate, which kept them in contact. Recent experiments9 have shown that, for very small punch height, roof collapse may occur without any external load (i.e., ω0 = 0). Furthermore, roof collapse is not due to the self-weight of the stamp because the roof of the stamp can collapse onto the substrate (in a similar way) even when the specimen is flipped (i.e., the stamp underneath the substrate). Roof collapse without the external load is due to the adhesion between the stamp and substrate.

The purposes of this paper are to analyze roof collapse without external load and to establish a criterion against the unwanted roof collapse in soft lithography. We develop a micromechanics model for roof collapse that leads to a scaling law among the stamp modulus, punch geometry (height h, width 2w, spacing 2a), and work of adhesion between the stamp and substrate. This scaling law gives a simple criterion for roof collapse, which states that roof collapse occurs once the punch height is below a critical
value, and this critical value is given analytically in terms of the
stiffness modulus, punch spacing and width, and work of
adhesion between the stamp and substrate. This simple
criterion is useful for soft lithography against the un-
wanted roof collapse.

This paper is structured as follows. We develop the
method in section 2 to compute the total potential energy,
which consists of the deformation energy and the adhesion
density due to roof collapse. Because the punch height
is much smaller than the punch spacing 2a, the gaps
between the stamp and substrate are modeled as micro-
cracks. To illustrate this approach, we study the limit of
small punch spacing in section 3 (i.e., punch width 2w ≫
punch spacing 2a (≫ punch height h)). A scaling law
is established that involves the punch spacing 2a and height
h, stamp modulus E, and work of adhesion γ between
the stamp and substrate. The unsagged length of the stamp
during roof collapse is obtained in section 3, and it will be
used in section 6 to determine the work of adhesion from
experiments. Section 4 gives an approximate analysis for
multiple punches with width 2w and spacing 2a. The effect of
elastic mismatch between the stamp and substrate is
accounted for in section 5, and a simple design criterion
against unwanted roof collapse is also established. The
unsagged length, accounting for effects of multiple punches
and elastic mismatch between the PDMS stamp and
substrate, is compared with the experimental data in
section 6.

2. Model of Roof Collapse in Soft Lithography

The schematic diagram in Figure 2 shows roof collapse
in soft lithography due to the adhesion between the stamp
and substrate. Contrary to Figure 1, there is no external
load such that roof collapse is completely due to the
adhesion between the sagged part of the stamp and
substrate. The work of adhesion γ is given by γ = γ_PDMS
+ γ_substrate + γ_int, where γ_PDMS and γ_substrate are the surface
energy of the PDMS stamp and substrate, respectively,
and γ_int is the energy of the PDMS/substrate interfaces.

For a small punch height h ≪ punch width 2w and
spacing 2a, the roof will collapse onto the substrate if the
collapsed state has a lower state of energy. We define the
uncollapsed state as the ground state (of zero energy). The
total potential energy associated with roof collapse is
given by

\[ U_{\text{total}} = U_{\text{deformation}} - 2b\gamma \]  

(1)

where \( U_{\text{deformation}} \) is the deformation energy, γ is the work
of adhesion between the stamp and substrate, and 2b is
the collapse length (Figure 2) to be determined. Here \( U_{\text{total}} \)
and \( U_{\text{deformation}} \) are the energy per punch for the periodic
structure in Figure 2. The deformation energy \( U_{\text{deformation}} \)
scales with \( h^2 \) for linear elastic deformation and becomes
negligible for \( h \to 0 \) such that the total potential energy
becomes negative and less than that (zero) for the
uncollapsed state, which is the reason for roof collapse.

In the following, we first neglect the mismatch in the
elastic moduli between the stamp and substrate and model
them as a homogeneous material. The effect of elastic
mismatch will be accounted for in section 5. Without losing
generality, our analysis is two-dimensional (i.e., for a unit
thickness in the out-of-plane direction). The PDMS is
incompressible with the Poisson ratio \( v = 0.5 \). Let \( E \) denote
the Young’s modulus of PDMS, and its plane-strain
modulus \( E' = E(1 - v^2) = 4/3E \).

Figure 3 shows our model to calculate the deformation
energy \( U_{\text{deformation}} \) via the principle of linear superposition.
The collapsed state with collapse length 2b can be considered to be the difference
between

(i) the ground state without the collapse and
(ii) a constant opening displacement \( h \) over the length
2b around the center of each gap, as shown schematically
in Figure 3. The difference between i and ii ensures the
conditions of the collapsed state (i.e., the opening at the
center portion (of length 2b) is zero; the opening at the
ends is \( h \); and the unsagged portions remain traction-
free). The ground state (i) has zero energy (and also zero
stress and strain). Because the punch height is much
smaller than punch spacing, \( h \ll a \), we may approximate
each gap as a crack, as shown by state iii in Figure 3. In
other words, ii becomes a state of coplanar periodic cracks
with crack length (= punch spacing) 2a, crack spacing (=
punch width) 2w, and constant crack opening \( h \) over length
2b around the center of each crack. The deformation energy
is then obtained from states i and iii as

\[ U_{\text{deformation}} = -\frac{1}{2} \int_{\text{crack face}} \sigma_{yy} h \, dx = \frac{E' h^2}{4} \left[ \frac{b}{a} \right] \left[ \frac{w}{a} \right] \]  

(2)

where \( \sigma_{yy} \) is the normal stress on the crack face and \( f \) is
a nondimensional function to be determined. The total
potential energy in eq 1 becomes

\[ U_{\text{total}} = E' h^2 \left[ \frac{b}{a} \right] \left[ \frac{w}{a} \right] - \frac{8a\gamma b}{E' h^2 a} \]  

(3)

Collapse length 2b is determined by minimizing the
above total potential energy

\[ \frac{\partial U_{\text{total}}}{\partial b} = 0 \]  

(4)

which gives the normalized collapse length \( b/a \) in terms of
the punch width-spacing ratio \( w/a \) and the normalized
work of adhesion \( 8a\gamma /E' h^2 \).
3. Limit of Small Punch Spacing: $2a \ll 2w$

We first consider the limit of small punch spacing $a \ll w$ (but $a \gg h$ still holds). This limit corresponds to closely packed punches. We do not account for the effect of elastic mismatch between the PDMS stamp and substrate in this section in order to obtain a simple analytical solution that leads to a scaling law. Such an effect will be considered in section 5. Therefore, the results in section 5 should be used to compare with the experiments because PDMS and the substrate have a large elastic mismatch.

Under this limit, $2w \gg 2a \gg h$, the last figure in Figure 3 becomes a single crack of length $2a$ with a constant opening $h$ over the central portion of length $2b$ in an infinite body, as shown schematically in Figure 4. The Cartesian coordinates are set at the center of the crack.

The shear stress $\sigma_{xy}$ vanishes on the entire crack plane because of symmetry. There are three different boundary conditions on the crack plane, namely,

(i) a symmetry condition outside the crack, $u_x = 0$ for $y = 0$, $|y| > a$,

(ii) a traction-free condition away from the center of the crack $\sigma_{yy} = 0$ for $y = 0$, $a > |y| > b$, and

(iii) a constant opening condition around the center of the crack, $\Delta u_y = h$ for $y = 0$, $b > |y|$,

where $u_y$ is the displacement and $\Delta u_y = u_y^+ - u_y^-$ is the crack opening. The analytical solution for this problem can be found in Tada et al.\textsuperscript{10} In particular, the normal stress $\sigma_{yy}$ on the crack face is given by

$$\sigma_{yy}|_{y=0} = \begin{cases} -E'ha & |x| < b \\ \frac{4K}{\sqrt{1 - \frac{k^2}{a^2}}} \sqrt{(a^2 - x^2)(b^2 - x^2)} & b < |x| < a \end{cases}$$

(5)

where $E' = 4/3E$, $E$ is the Young’s modulus of the stamp, and $K$ is the complete elliptic integral of first kind given by

$$K(k) = \int_0^{\pi/2} \frac{d\phi}{\sqrt{1 - k^2 \sin^2 \phi}}$$

(6)

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The total potential energy in eq 3 is then given by

$$U_{\text{total}} = \frac{E'h}{4} \left[ \frac{K(b/a)}{\sqrt{1 - \frac{b^2}{a^2}}} - \frac{8\alpha y}{E'h^2} a \right]$$

The total potential energy, after being normalized by $E'h^2/4$, depends on the normalized collapse length $b/a$ and normalized work of adhesion $8\alpha y/E'h^2$. This nondimensional parameter $8\alpha y/E'h^2$, which has also been identified by Sharp et al., represents the ratio of the adhesion energy ($\sim 2\alpha y$) to the deformation energy ($\sim 1/E'h^2$). It suggests a scaling law among the work of adhesion, stamp modulus, and punch spacing and height. In other words, stamp collapse is controlled by this combination of material and geometry parameters, $8\alpha y/E'h^2$.

Figure 5 shows the normalized total potential energy $4U_{\text{total}}/E'h^2$ versus the normalized work of adhesion $b/a$ for the normalized work of adhesion $8\alpha y/E'h^2 = 0, 0.5, 0.83, 1.2, 1.4, 2, \text{ and } 3$, where $8\alpha y/E'h^2 = 0$ corresponds to the limit of no adhesion between the stamp and substrate and the corresponding curve increases monotonically with $b/a$. The inset in Figure 5 shows that the total potential energy $U_{\text{total}}$ is indeed zero for $b/a = 0$ (i.e., no collapse).

For the other limit $b/a \to 1$ (i.e., complete collapse), $U_{\text{total}}$ becomes unbounded.

There are several states of roof collapse that are controlled by $8\alpha y/E'h^2$. For $8\alpha y/E'h^2 < 0.83$ (weak adhesion), the curves increase monotonically with $b/a$ such that $U_{\text{total}}$ does not have a minimum. Therefore, roof collapse will not occur if the work of adhesion is low. In other words, if the roof is forced to collapse onto the substrate, then the roof will “spring back” as soon as the force is removed. For $8\alpha y/E'h^2 > 0.83$ (intermediate or strong adhesion), each curve in Figure 5 has a minimum (marked by * in Figure 5). Roof collapse may occur in order to reach this state of minimal total potential energy. In other words, if the roof is forced to collapse onto the substrate, then the roof may stay in the collapsed state after the force is removed. The corresponding collapse length at which $U_{\text{total}}$ reaches the minimum is denoted by $2b_{\text{critical}}$. The minimal total potential energy $U_{\text{total}}^{\text{min}}$ of the collapsed state is given by

$$U_{\text{total}}^{\text{min}} = \frac{E'h^2}{4} \left[ \frac{K(b_{\text{critical}}/a)}{\sqrt{1 - \frac{b_{\text{critical}}^2}{a^2}}} - \frac{8\alpha y}{E'h^2} a \right]$$

For $0.83 < 8\alpha y/E'h^2 < 1.40$ (intermediate adhesion), $U_{\text{total}}^{\text{min}}$ is positive, which gives the minimal total potential energy (marked by * in Figure 5) above the horizontal dashed line of $U_{\text{total}} = 0$ in Figure 5. The energy of the collapsed state for $0.83 < 8\alpha y/E'h^2 < 1.40$ is higher than that for the uncollapsed state $U_{\text{total}} = 0$ (ground state). Therefore, even though roof collapse may occur, it is unstable because some disturbances in the environment may reverse it back to the uncollapsed state. For $8\alpha y/E'h^2 > 1.40$ (strong adhesion), $U_{\text{total}}^{\text{min}}$ is negative, and the minimal energy (marked by * in Figure 5) is lower than the horizontal dashed line for $U_{\text{total}} = 0$ in Figure 5 such that the collapsed state is stable.

These three states of no collapse, metastable collapse, and stable collapse are further explained in Figure 6, which shows the minimal total potential energy $4U_{\text{total}}^{\text{min}}/E'h^2$ versus the normalized work of adhesion $8\alpha y/E'h^2$. These three states correspond to weak adhesion ($8\alpha y/E'h^2 < 0.83$), intermediate adhesion (0.83 < $8\alpha y/E'h^2 < 1.40$), and strong adhesion ($8\alpha y/E'h^2 > 1.40$), respectively.

Figure 7 shows the normalized collapse length, $b_{\text{critical}}/a$, versus the normalized work of adhesion $8\alpha y/E'h^2$. For $8\alpha y/E'h^2 < 0.83$, collapse does not occur, and there is no solution for $b_{\text{critical}}$. For $0.83 < 8\alpha y/E'h^2 < 1.40$, there is a solution for $b_{\text{critical}}$, but roof collapse is unstable. The collapse length ranges from $b_{\text{critical}}/a = 0.35$ (for $8\alpha y/E'h^2 = 0.83$) to 0.74 (for $8\alpha y/E'h^2 = 1.40$). This suggests that once roof collapse occurs the collapse length is at least 35% of the punch spacing. In other words, for $8\alpha y/E'h^2$ across 0.83 from 0.83 to 0.83 in $\epsilon$, $\epsilon \sim 0^+$, the collapse length jumps from zero (i.e., no collapse) to 35% of the punch spacing 2a. For $8\alpha y/E'h^2 > 1.40$, roof collapse is stable, and the collapse length is at least 74% of punch spacing 2a. For large $8\alpha y/E'h^2$, the collapse length approaches punch spacing 2a asymptotically.

As illustrated in Figure 3, the opening displacement after roof collapse is the difference between constant opening $h$ over length 2a (of the punch spacing) and that associated with constant opening $h$ over center portion.
2b. The opening displacement can be obtained from Tada et al.\textsuperscript{10} as

\[
\Delta u_g = \begin{cases} 
0, & |x| < b \\
\int_0^b F \left( \sin^{-1} \sqrt{\frac{a^2 - x^2}{a^2 - b^2}}, 1 - \frac{b^2}{a^2} \right) \, dx, & b < |x| < a 
\end{cases}
\]

which rigorously satisfies \( \Delta u_{g|x=b}=0 \) and \( \Delta u_{g|x=a}=h \), where \( F(\phi, k) = \int_0^\phi \sin \phi \sqrt{1 - k^2 \sin^2 \phi} \) is the incomplete elliptic integral of the first kind and \( F(\pi/2, k) = K(k) \).

Equation 10 can be used to compare with the experimentally measured opening displacement in the unsagged portion in order to validate the present model. The analysis of the shape of the collapsing roof will also give interesting insights into the adhesion forces.

The unsagged length in roof collapse (i.e., the length of the uncollapsed portion) is \( L = a - b_{\text{critical}} \). The unsagged length can be measured from experiments, which provide a means to determine the work of adhesion between the stamp and substrate as to be shown in section 6. Figure 8 shows the unsagged length \( L \), normalized by \( a \), versus \( 1/(8\alpha\gamma/E'h^2) \). The solid curve is obtained from Figure 7 by \( L/a = 1 - b_{\text{critical}}/a \), and it holds for arbitrary \( 8\alpha\gamma/E'h^2 \). For \( 8\alpha\gamma/E'h^2 \gg 1 \), as shown in Appendix A, the unsagged length \( L \) has the asymptotic solution

\[
L = \frac{E'h^2}{\pi} \frac{1}{8\gamma} \quad \text{if} \quad 8\alpha\gamma/E'h^2 \gg 1
\]

This asymptotic solution corresponds to the straight dashed line in Figure 8, which merges to the solid curve for \( 8\alpha\gamma/E'h^2 \gg 1 \). For \( 8\alpha\gamma/E'h^2 \) on the order of 1, the asymptotic solution underestimates unsagged length \( L \).

4. Periodic Punches: \( 2a \sim 2w \)

An approximate solution for punch width \( 2w \) comparable to punch spacing (i.e., \( 2a \sim 2w \)) is established in this section. It degenerates to the solution in section 3 in the limit \( 2a \ll 2w \). Each punch spacing is still modeled by a crack of length \( 2a \) with the center portion \( 2b \) collapsed, as shown in Figure 3. Similar to section 3, we do not account for the effect of elastic mismatch. Such an effect will be considered in section 5. Consequently, the results in section 5 can be compared with the experiments because PDMS and the substrate have a large elastic mismatch.

It is shown in Appendix B that the ratio of the deformation energy \( U_{\text{deformation}} \) for periodic cracks to the deformation energy \( U_{\text{deformation}} \) for a single crack is approximately given by

\[
\frac{U_{\text{periodic cracks}}}{U_{\text{deformation}}} \approx \frac{\pi^2}{8(1 + \frac{w^2}{a^2}) \ln \sec \left( \frac{\pi}{2} \frac{1}{1 + \frac{w}{a}} \right)}
\]

where \( \sec = 1/\cos \). The above ratio approaches 1 at the limit of small punch spacing \( w/a \rightarrow \infty \). It vanishes at the limit of small punch width \( w/a \rightarrow 0 \). The deformation energy for periodic cracks is obtained from eqs 12 and 7 as

\[
\frac{U_{\text{periodic cracks}}}{U_{\text{deformation}}} \approx \frac{E'h^2}{4} \frac{K(b)}{K(\sqrt{1 - \frac{b^2}{a^2}})} \frac{\pi^2}{8(1 + \frac{w^2}{a^2}) \ln \sec \left( \frac{\pi}{2} \frac{1}{1 + \frac{w}{a}} \right)}
\]

\[
K(\sqrt{1 - \frac{b^2}{a^2}}) \approx \frac{\pi^2}{8(1 + \frac{w^2}{a^2}) \ln \sec \left( \frac{\pi}{2} \frac{1}{1 + \frac{w}{a}} \right)}
\]
show that the normalized minimal total potential energy 

Equation 14 is identical to eq 8 except that (plane-strain) 

The total potential energy in eq 8 then becomes

where \( E'_{\text{eff}} \) is given in terms of plane-strain modulus \( E' \) of 

Equation 14 is identical to eq 8 except that (plane-strain) 

for periodic cracks. The relation between total potential 

Collapse length \( b_{\text{critical}} \), determined by minimizing \( U_{\text{total}} \) 

The normalized minimal total potential energy 

\[ U_{\text{total}} = \frac{E'_{\text{eff}}}{4E} \left[ \frac{K(b/a)}{\sqrt{1 - \left( \frac{b^2}{a^2} \right)^2}} - 8a \gamma \frac{b}{h} \right] \]

\[ E'_{\text{eff}} = E' \frac{\pi^2}{8(1 + \frac{w}{a})^2 \ln \left( \sec \left( \frac{\pi}{2} \right) \right)} \]

\[ \frac{8a \gamma}{E'_{\text{eff}} h^2} = \frac{8a \gamma}{E' h^2} \frac{8(1 + \frac{w}{a})^2 \ln \left( \sec \left( \frac{\pi}{2} \right) \right)}{\pi^2} \]

\[ K = \frac{E_1^2}{E} \]

Figure 7. Normalized collapse length \( b_{\text{critical}}/a \) vs the normalized work of adhesion \( 8a \gamma/E' h^2 \) for the limit of small punch spacing. 

Figure 10 shows the normalized collapse length \( b_{\text{critical}}/a \) 

5. Effect of Elastic Mismatch between the Stamp 

It is important to note that the analyses in sections 3 

For a crack in an elastic homogeneous material of PDMS, 

width/spacing ratio \( w/a \) decreases the curve separating collapse/no collapse shifts to the left (i.e., roof collapse becomes easier because of the interaction among punches). Furthermore, the curve for \( w/a = 5 \) is essentially the same as that for \( w/a = \infty \), which means that the interaction effect among punches disappears once the punch width is about 5 times the punch spacing. The horizontal line in Figure 9 still separates the stable and metastable collapse.

Figure 10 shows the normalized collapse length \( b_{\text{critical}}/a \) versus the normalized work of adhesion \( 8a \gamma/E' h^2 \) (not \( 8a \gamma/E'_{\text{eff}} h^2 \)) for punch width/spacing ratio \( w/a = 0.1, 0.5, 1, 5, \) and \( \infty \). Once again, the curves for \( w/a = 5 \) and \( \infty \) are essentially the same. As \( w/a \) decreases, the normalized collapse length \( b_{\text{critical}}/a \) increases (i.e., larger collapse length due to the interaction among punches). The two horizontal dashed lines in Figure 10, which correspond to \( b_{\text{critical}}/a = 0.35 \) and 0.74, still separate the collapse/no collapse and stable collapse/metastable collapse, respectively.
on the interface between PDMS and the substrate, the crack tip energy release rate becomes

\[ G = \frac{1}{2 \cosh^2(\pi \epsilon)} \left( \frac{1}{E^*} + \frac{1}{E_{\text{substrate}}^*} \right) |K|^2 \]  

(18)

where \(|K|\) is the amplitude of complex stress intensity factor \(K\) for the bimaterial interface crack tip, \(E^*\) and \(E_{\text{substrate}}^*\) are the (plane-strain) moduli of PDMS and the substrate, respectively, and bimaterial parameter \(\epsilon\) is related to shear modulus \(\mu\) and Poisson’s ratio \(\nu\) of PDMS and their counterparts \(\mu_{\text{substrate}}\) and \(\nu_{\text{substrate}}\) for

the substrate by

\[ \epsilon = \frac{1}{2\pi} \ln \left[ \frac{3 - 4v}{3 - 4v/\mu_{\text{substrate}}} \left( \frac{1}{\mu} + \frac{1}{\mu_{\text{substrate}}} \right) \right] \] (19)

The PDMS is incompressible \((v = 0.5)\), and its elastic moduli \(E\) and \(\mu\) \((\sim 1\, \text{MPa})\) are orders of magnitude smaller than the elastic moduli of the substrate \((\text{e.g., silicon or silica with moduli on the order of 100 GPa})\). These give a vanishing bimaterial parameter \(\epsilon\) in eq 19 \(\epsilon = 0\). The energy release rate in eq 18 now becomes

\[ G = \frac{1}{2E'}|K|^2 \] (20)

There exist several analytical solutions for bimaterial interface cracks.\(^{11-13}\) All of these analytical solutions show that for the vanishing bimaterial parameter, \(\epsilon = 0\), stress intensity factor \(|K|\) is the same as its counterpart \(K_1\) in homogeneous materials, \(|K| = K_1\). The energy release rate in eq 20 for an interface crack tip between PDMS and the substrate is then related to that in eq 17 for a crack tip in the homogeneous PDMS by replacing PDMS modulus \(E'\) with \(2E'\). In other words, the effect of elastic mismatch between PDMS and the substrate on the crack tip energy release rate can be accounted for if the solution for homogeneous material in sections 3 and 4 is modified by replacing \(E'\) with \(2E'\). For example, deformation energy \(U_{\text{deformation}}\) in eq 7 for the limit of small punch spacing \(2a \ll 2w\) in section 3 now becomes

\[ U_{\text{deformation}} = \frac{1}{4} \left( \frac{E' h^2}{K} \right) \left( \frac{K b}{a} \right) \] (21)

The above expression can also be obtained from a simple mechanics argument. Because the substrate is several orders of magnitude stiffer than PDMS, it hardly deforms such that the opening displacement \(h\) is completely imposed on the PDMS. This is in contrast to the analyses in sections 3 and 4 for the homogeneous material where the material on each side of the crack undergoes one-half of the opening displacement, \(h/2\). In other words, opening displacement \(h\) in sections 3 and 4 needs to be replaced by \(2h\), which gives the deformation energy as

\[ U_{\text{deformation}} = \frac{1}{2} \left( \frac{E' h^2}{K} \right) \left( \frac{K b}{a} \right) \] (22)

where the factor of 1/2 comes from half of the material (PDMS). This expression is identical to that in eq 21.

The adhesion energy \(2b\gamma\) remains the same. Therefore, the normalized work of adhesion \(8a\gamma/E'h^2\) is replaced by \(8a\gamma/(2E'h^2) = 4a\gamma/E'h^2\) after the effect of elastic mismatch is accounted for

\[ \frac{8a\gamma}{E'h^2} \rightarrow \frac{4a\gamma}{E'h^2} \] (22)

For the limit of small punch spacing \(2a \ll 2w\) in section 3, the criterion governing stamp collapse onto

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For periodic punches in section 4 (i.e., \( a \sim w \)) the criterion governing stamp collapse onto the substrate becomes

\[
\begin{align*}
\text{no collapse} & \quad \text{if} \quad \frac{4a\gamma}{E' h^2} < 0.83 \\
\text{metastable collapse} & \quad \text{if} \quad 0.83 < \frac{4a\gamma}{E' h^2} < 1.40 \\
\text{stable collapse} & \quad \text{if} \quad 1.40 < \frac{4a\gamma}{E' h^2} (23)
\end{align*}
\]

The unsagged length for the limit of \( 4a\gamma/E'h^2 \gg 1 \), accounting for the interactions among multiple punches and the elastic mismatch between the PDMS stamp and substrate, is given in Appendix A.

6. Comparison with Experiments

In this section, we compare the analytical results in section 5 with the experimental data in order to determine the work of adhesion \( \gamma \) between the stamp and substrate and to validate the present analytical models. In the following, we provide some details on processing specimen and experimental observations.

The masters used to fabricate the PDMS stamps were prepared using test-grade silicon wafers (Montco Silicon Technologies, www.silicon-wafers.com) and positive photoresist (Shipley, www.shipley.com) using conventional contact mode photolithography process. They were then coated with a nonstick fluorosilane ((tri-decafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane) self-assembled monolayer to facilitate the release of the PDMS stamps. PDMS (Sylgard 184 from Dow Corning, www.dowcorning.com) was mixed (10:1 ratio) and degassed, poured over the masters, and cured in an oven at 80 °C. For the sagging experiments, test-grade silicon wafers were cleaned with acetone, 2-propanol, and deionized water and then dried on a hot plate at 150 °C for 10 min.

The experiments were conducted by placing the patterned stamps on a substrate of silicon wafer with a native silica glass layer. The PDMS stamps have periodic, rectangular grooves and flat punches. The length of the grooves in the out-of-plane direction is a few centimeters. The grooves were observed to collapse onto the substrate. The contact part of the collapsed region always took a significant portion of the groove and did not change even if we turned the experimental setup upside down. Unsagged length \( L \) was measured in the experiments.

Figure 11 shows unsagged length \( L \) versus punch height \( h \) for several punch width/spacing ratios \( w/a \) obtained from the experiments of the PDMS stamp on a silicon wafer.

\[
\frac{a\gamma}{Eh^2} \left[ 1 + \frac{w^2}{a^2} \right] \ln \left[ \sec \left( \frac{\pi}{2} + \frac{w}{a} \right) \right] < 0.35 \tag{24a}
\]

where \( h, 2a, \) and \( 2w \) are the punch height, spacing, and width, respectively, \( E \) is the Young’s modulus (not plane-strain modulus \( E' \)) of the PDMS stamp, and \( \gamma \) is the work of adhesion between the PDMS stamp and substrate.
with a thin silica coating. The elastic modulus of PDMS is \(E = 2.8 \text{ MPa}\), which gives plane-strain modulus \(E' = 3.73 \text{ MPa}\) because PDMS is incompressible (\(v = 0.5\)). This plane-strain modulus falls into the range (3.5–4.5 MPa) reported by Sharp et al.\(^8\) The punch spacing is fixed at \(2a = 1 \text{ mm (} = 1000 \mu\text{m})\). Punch width \(2w\) ranges from 100 \(\mu\text{m}\) to 2 mm (= 2000 \(\mu\text{m})\). The work of adhesion \(\gamma\) is determined from the experimental data for \(w/a = 0.1\), which gives

\[
\frac{\gamma}{E'} = 0.0136 \mu\text{m} \quad (25)
\]

Here, unsagged length \(L\) is calculated from \(b_{\text{vertical}}/a\) in Figure 10 accounting for the effect of elastic mismatch. For \(E' = 3.73 \text{ MPa}\) of PDMS, the work of adhesion is

\[
\gamma = 50.6 \text{ mJ/m}^2 \quad (26)
\]

This value is on the same order of magnitude with that reported by Chaudhury and Whitesides.\(^{14}\)

On the basis of the work of adhesion given above, we have calculated unsagged length \(L\) versus punch height \(h\) for \(w/a = 0.2, 1, \) and 2. The results are shown in Figure 11 together with the experimental data. The analytical model agrees reasonably well with the experimental data for a wide range of \(w/a\).

In the following, we discuss the effect of gravity, which has been neglected in prior sections. Hui et al.\(^7\) provided an estimate for the maximum deflection of the punch due to uniform remote compression \(a_0\). The effect of gravity can be estimated by taking \(a_0 = \rho g H\), where \(p\) is the mass density of PDMS (≈950 kg/m\(^3\)), \(g = 9.8 \text{ m/s}^2\) is the gravity acceleration, and \(H\) is the height of the PDMS layer (not the punch). For the above representative value of punch spacing \(2a = 1 \text{ mm}\), punch width \(2w = 100 \mu\text{m}\), plane-strain modulus \(E' = 3.73 \text{ MPa}\), and a large height \(H = 10 \text{ mm}\) of the PDMS layer, the maximum displacement due to gravity is several tens of nanometer. This value is much smaller than the minimal punch height \((h = 1.34 \mu\text{m})\) such that the effect of gravity is insignificant in the present study of soft lithography.

7. Concluding Remarks and Discussion

We have studied the so-called roof collapse in soft lithography due to the adhesion between the PDMS stamp and substrate. The effects of multiple punches on the stamp, as well as the elastic mismatch between the PDMS stamp and substrate, are accounted for. It is shown that roof collapse is governed by two nondimensional parameters, \(8a \gamma/E' h^2\) and \(w/a\), where \(E' = 4/3E\) is the plane-strain modulus of the PDMS stamp \((E\) is the Young's modulus), \(\gamma\) is the work of adhesion between the stamp and substrate, \(2a\) is the punch spacing, \(h\) is the punch height, and \(2w\) is the punch width. The normalized work of adhesion \(8a \gamma/E' h^2\) suggests an important scaling law among the stamp modulus, punch height and spacing, and work of adhesion between the PDMS stamp and substrate. Three regimes of roof collapse are identified, namely, no collapse for weak adhesion, metastable collapse for intermediate adhesion, and stable collapse for strong adhesion. A simple criterion separating these three regimes is established. The present model also predicts the unsagged length in roof collapse, which agrees well with the experimental data.

It is discussed in section 2 that the work of adhesion \(\gamma\) is given by

\[
\gamma = \gamma_{\text{PDMS/air}} + \gamma_{\text{substrate/air}} - \gamma_{\text{PDMS/substrate}} \quad (27)
\]

where \(\gamma_{\text{PDMS/air}}\) and \(\gamma_{\text{substrate/air}}\) are the surface energy of PDMS and the substrate, respectively, and \(\gamma_{\text{PDMS/substrate}}\) is the interfacial energy. Once there is liquid between PDMS and the substrate, the above expression becomes \(\gamma = \gamma_{\text{PDMS/liquid}} + \gamma_{\text{substrate/liquid}} - \gamma_{\text{PDMS/substrate}}\). For rubber in air and in water, Johnson et al.’s\(^{15}\) experiments showed that \(\gamma_{\text{rubber/liquid}}\) is an order of magnitude smaller than \(\gamma_{\text{rubber/air}}\). If such properties also hold for PDMS (i.e., \(\gamma_{\text{PDMS/air}} \gg \gamma_{\text{PDMS/liquid}}\)), then the work of adhesion \(\gamma\) becomes smaller once there is liquid between PDMS and the substrate, which makes it more difficult for roof collapse in soft lithography.

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Appendix A

We consider the limit \(8a \gamma/E' h^2 \gg 1\), which corresponds to a large punch spacing (or equivalently a compliant stamp and a short punch or strong stamp/substrate adhesion). Under such a limit, collapse length \(2b\) of vertical approaches punch spacing \(2a\) (Figure 7). The total potential energy in eq 8 then takes the asymptotic form

\[
U_{\text{total}} = \frac{E' h^2}{4} \left[ 1 - \frac{a}{L} - \frac{\gamma}{E' h^2} \left( 1 - \frac{L}{a} \right) + O(1) \right] \quad (A1)
\]

where we have used the limits \(K(0) = \pi/2\) and \(K(k \rightarrow 1) = -\sqrt{2} \ln(1 - k) + O(1)\) and \(O(1)\) represents the terms that remain bounded in the limit of \(b_{\text{critical}}/a \rightarrow 1\) (or equivalently \(L/a \rightarrow 0\)).

Equation 4 can be equivalently written as \(\partial U_{\text{total}} / \partial L = 0\). Its solution is obtained analytically for \(8a \gamma/E' h^2 \gg 1\) and is given in eq 11.

For periodic punches with \(4a \gamma/E' h^2 \gg 1\), the unsagged length in eq 11 becomes

\[
L = \frac{1}{\pi} \frac{E' h^2}{4 \gamma} \left[ 1 + \frac{8a}{\pi^2} \ln \left( \sec \left( \frac{\pi}{2} \right) \left( 1 + \frac{w}{a} \right) \right) \right] \text{ if } \frac{4a \gamma}{E' h^2} \gg 1 \quad (A2)
\]

Here we have accounted for the interactions among multiple punches and the elastic mismatch between the PDMS stamp and substrate.

Appendix B

There is no analytical solution for the coplanar, periodic cracks (of length \(2a\)) shown in Figure 3 that are subject to a constant crack-opening displacement \(h\) over a central portion (of length \(2b\)) on each crack. Let \(U_{\text{periodic cracks}}\) denote the deformation energy for such a problem and \(U_{\text{single crack}}\) denote the deformation energy for a single crack subject to a constant crack-opening displacement over a central portion of the crack. We approximate their


ratio by its counterpart for periodic cracks and a single crack subject to uniform normal traction on crack faces because analytical solutions exist for the latter.

For the single crack (crack length 2a) subject to the uniform normal traction \( \sigma^{\text{single crack}} \), the crack-opening displacement is given by\(^{10} \)

\[
\Delta u_y^{\text{single crack}} = \frac{4\sigma^{\text{single crack}}}{E'} \sqrt{a^2 - x^2} \tag{B1}
\]

The deformation energy is given by

\[
\frac{1}{2} \int_{-a}^{a} \sigma^{\text{single crack}} \Delta u_y^{\text{single crack}} \, dx = \frac{(\sigma^{\text{single crack}})^2 \pi a^2}{E'} \tag{B2}
\]

For periodic cracks (crack length 2a, spacing 2w) subject to uniform traction \( \sigma^{\text{periodic cracks}} \), the opening displacement becomes\(^{10} \)

\[
\Delta u_y^{\text{periodic cracks}} = \frac{4\sigma^{\text{periodic cracks}}}{E'} \frac{2(a + w)}{\pi} \cosh^{-1} \left( \frac{\pi x}{2(a + w)} \right) \cos \left( \frac{\pi a}{2(a + w)} \right) \tag{B3}
\]

The corresponding deformation energy is given by

\[
\frac{1}{2} \int_{-a}^{a} \sigma^{\text{periodic cracks}} \Delta u_y^{\text{periodic cracks}} \, dx = \frac{(\sigma^{\text{periodic cracks}})^2 \pi a^2}{E'} \frac{8}{\pi^2 (1 + \frac{w}{a})^2} \ln \left[ \sec \left( \frac{\pi}{2} \frac{1}{1 + \frac{w}{a}} \right) \right] \tag{B4}
\]

Normal tractions \( \sigma^{\text{single crack}} \) and \( \sigma^{\text{periodic cracks}} \) are related by requiring that the periodic cracks and single crack have the same displacement in order to represent punch height \( h \). This is enforced in an average sense

\[
\frac{1}{2a} \int_{-a}^{a} \Delta u_y^{\text{single crack}} \, dx = \frac{1}{2a} \int_{-a}^{a} \Delta u_y^{\text{periodic cracks}} \, dx \tag{B5}
\]

The substitution of eqs B1 and B3 into B5 yields

\[
\frac{\sigma^{\text{periodic cracks}}}{\sigma^{\text{single crack}}} = \frac{\pi^2}{8(1 + \frac{w}{a})^2} \ln \left[ \sec \left( \frac{\pi}{2} \frac{1}{1 + \frac{w}{a}} \right) \right] \tag{B6}
\]

The ratio of deformation energy in eq B4 for periodic cracks to that in eq B2 for a single crack then leads to eq 12.