Collapse of stamps for soft lithography due to interfacial adhesion

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Collapse of elastomeric elements used for pattern transfer in soft lithography is studied through experimental measurements and theoretical modeling. The objective is to identify the driving force for such collapse. Two potential driving forces, the self-weight of the stamp and the interfacial adhesion, are investigated. An idealized configuration of periodic rectangular grooves and flat punches is considered. Experimental observations demonstrate that groove collapse occurs regardless of whether the gravitational force promotes or suppresses such collapse, indicating that self-weight is not the driving force. On the other hand, model predictions based on the postulation that interfacial adhesion is the driving force exhibit excellent agreement with the experimentally measured collapse behavior. The interfacial adhesion energy is also evaluated by matching an adhesion parameter in the model with the experimental data.
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Lithographic techniques that use elastomeric stamps, molds, and conformable photomasks are emerging as powerful low-cost tools for patterning structures in photonics, electronics, and biotechnology.[1–3] In these methods, which are collectively known as soft lithographic techniques, physical contact of the elastomeric elements with solid substrates provides the means for pattern formation. The same procedure can be used to deliver electrodes from the surface of the elastomer to an active material (e.g., semiconductors, etc.) to build devices, in a procedure known as soft contact lamination.[4,5] The low modulus and low surface energy of the elastomers that are typically used for these elements [e.g. poly(dimethylsiloxane), PDMS] allow atomic-scale conformal contacts to be established without the application of external pressure. The basic mechanisms governing this critically important contact process and the issues that can lead, in certain cases, to mechanical collapse of the relief are not well known. In order to understand this process more fully, we conducted both experimental study and modeling of an idealized structure with a simple pattern—periodic rectangular grooves and flat punches, as schematically shown in Fig. 1. The material used to fabricate the experimental specimens is PDMS (Dow Corning, Sylgard 184). The dimension of the grooves (punches) in the out-of-plane direction (z direction) is very large compared to the in-plane dimensions, w and a. In the current study, a was fixed at 500 μm, w ranged from 50 μm to 5 mm; while the dimension in the z direction, e.g., the length of grooves, is of the order of several centimeters. Such geometric arrangement usually guarantees the plane strain condition during deformation. Moreover, we choose the height of the punches h, ranging from a few hundred nanometers to a few micrometers, to be much smaller than w or a (h/a is always less than 0.01). A wide range of the a/w ratio and several values of h have been considered in the experimental measurements. The experiments were conducted by placing the patterned stamps on a substrate of a silicon wafer with a native silica glass layer. The degree of collapse was then examined and measured using optical microscopy.

In all cases, we observed that the grooves collapsed onto the substrate. A fully collapsed groove is schematically

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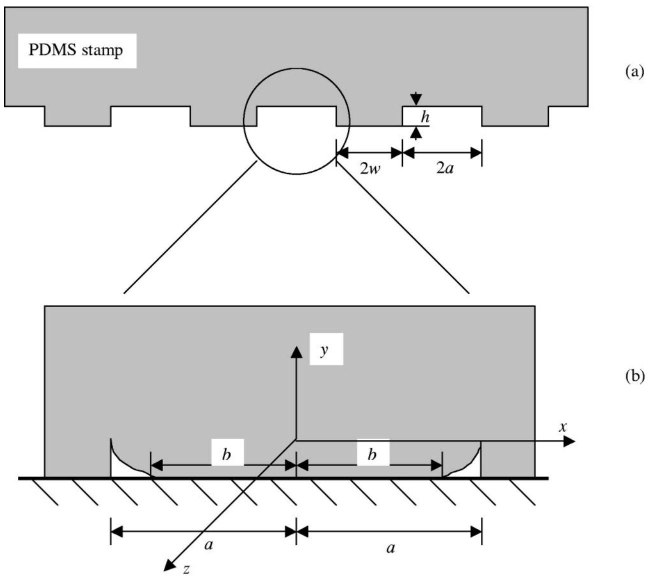

FIG. 1. (a) Schematics of the PDMS stamp specimens, and (b) details of a collapsed groove with a contact region $-b \leqslant x \leqslant b$.

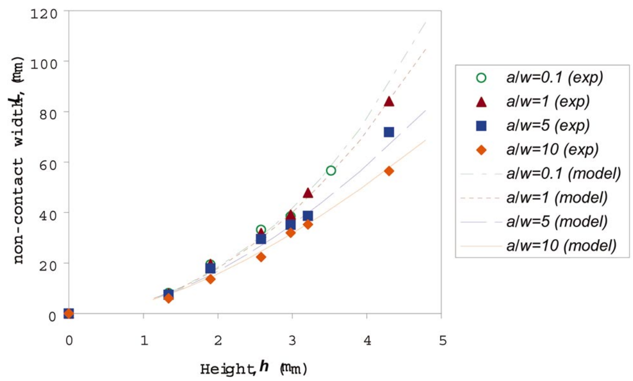

FIG. 3. (Color) Experimental measurements (individual data points) and model predictions (solid lines) of the noncontact width L of fully collapsed grooves as a function of groove height h for a wide range of a/w.

shown in Fig. 1(b). Optical microscopy videos show that once a groove collapse occurs at any location, it will progress rapidly with a front roughly normal to the long dimension [i.e., normal to z axis in Fig. 1(b)] across all grooves. An optical micrograph of a typical collapsing front of a stamp is shown in Fig. 2. Furthermore, the contact part of the collapsed region always takes a significant portion of the groove, i.e., the ratio b/a in Fig. 1(b) is always rather large (>0.7). We experimentally measured b (or the noncontact width $L=a-b$) for many different combinations of a/w and h. The measurement results are shown in Fig. 3 as discrete data points. It should be noted that similar collapse behaviors of PDMS stamps have been observed by others.[6]

One key question is what the driving force is for the groove collapse in PDMS stamps. It has been postulated that the collapse is a result of the gravitational force, i.e., the self-weight of the stamps.[7,8] Hui *et al.*[7] and Sharp *et al.*[8] provided an analysis based on this assumption to evaluate the forces needed to cause the groove collapse. However, in our experiments, we have at times turned the experimental setup up-side down, such that the gravitational force acts to prevent grooves collapse. But the grooves still collapsed with the same proportion of the contact area in the grooves. Finite

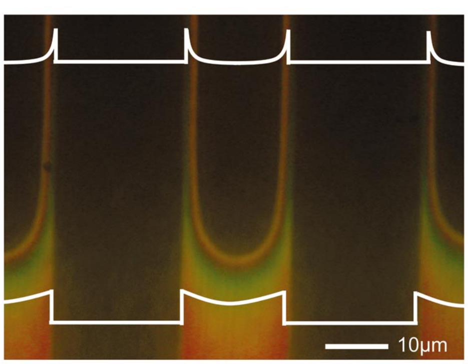

FIG. 2. (Color) Optical micrograph of a typical collapsing front in a PDMS stamp, dimension: $2a=19.5$ μm, $2w=20.5$ μm, and $h=0.5$ μm. The white contours are the displacement profiles of the stamp surface at fully collapsed and uncollapsed locations.

element analysis of the stamps also shows that the rquired “gravitational force” to collapse the stamps would be more than 30 times higher than the weight of the stamps.[9,10] These evidences indicate that the driving force for groove collapse is not the gravitational force, but is likely to be interfacial adhesion between PDMS stamp and the substrate.

We have developed a model based on the postulation that the groove collapse is caused by interfacial adhesion. The details of the model is presented elsewhere.[11] Here, the major assumptions and results of the model are briefly summarized. The driving force for stamp collapse is assumed to be the adhesion energy γ, which can be evaluated by

$$\gamma = \gamma_{\mathrm{PDMS}} + \gamma_{\mathrm{SiO_2}} - \gamma_{\mathrm{int}}, \tag{1}$$

where γ_{PDMS}, $\gamma_{\mathrm{SiO_2}}$ are the surface energy of PDMS and silica glass surfaces, respectively, and γ_{int} is the interface energy of the PDMS/glass interface. Since the depth of the grooves h is much smaller than the width a of the grooves, we model the grooves as a periodic array of cracks of length $2a$ separated by punches of width $2w$. We further assume that, within the region $-b \leqslant x \leqslant b$ [see Fig. 1(b)], the crack surface displacement remains a constant value equal to the depth of the grooves h. In order to achieve such constant crack surface displacement profile within $-b \leqslant x \leqslant b$, a certain traction distribution profile, $p(x)$, $-b \leqslant x \leqslant b$, is required. Using a fracture mechanics solution,[12] the traction distribution, $p(x)$, needed to achieve such crack surface displacement profile can be obtained by solving an integral equation.[11] Once $p(x)$ is determined, the strain energy stored in the stamp, U_{st}, can be evaluated through the work done to the system $U_{\mathrm{st}}=\int_{-b}^{b} 1/2\, p(x) h\, dx$. The total energy of the stamp, U, can then be obtained as

$$U = U_{\mathrm{st}} - 2b\gamma. \tag{2}$$

It should be noted that the magnitude of $p(x)$ is proportional to the plane strain Young’s modulus $E' = E/(1-\nu^2)$, here E is Young’s modulus and ν is Poisson’s ratio of PDMS, and to the height of the grooves h. The model identifies a dimensionless adhesion parameter that determines the strength of the adhesion force, given by

$$\Gamma = \frac{8\gamma a}{E' h^2}, \tag{3}$$

which has the physical meaning of the surface energy over the strain energy.

The model shows that, for a given value of Γ within a reasonable range, the total energy U decreases initially as the contacting width b/a increases from zero, then increases toward infinity as b/a approaches 1. Therefore, a critical value of b/a that minimizes the total energy exists for each given value of Γ. Such critical b/a versus Γ curve can be used to determine the adhesion parameter and thus the adhesion energy once the value of b is experimentally measured for a particular combination of a/w and h. On the other hand, the *only* parameter that is not known in the model is the adhesion parameter Γ. Therefore, when the value of Γ is determined, which can in principle be achieved by a single experimental measurement of b for given a/w and h, the entire collapse behavior can be predicted by the model.

The solid lines in Fig. 3 are the model predictions of the noncontact width $L=a-b$ as a function of the groove depth h for a wide range of a/w. In generating these curves, the value of Γ is determined from the experimental data for $a/w=1$, and that value is then used to plot the curves for all other a/w values. Figure 3 demonstrates that our model predictions exhibit excellent agreement with experimental measurements for a wide range of the ratio of groove width over punch width, a/w, and for all values of punch height h tested in the experiment.

It should be pointed out that if the driving force for groove collapse were the self-weight of the stamps, the noncontact width L versus groove height h curve would be linear. This assertion can be confirmed both by the formula in Hui *et al.*'s paper[7] and by finite element analysis.[9,10] However, the L versus h curve would be qualitatively different, i.e., the curve would be nonlinear if the driving force is interfacial adhesion. In fact, it can be shown from the model that L is proportional to h^2 in the limiting case of $a/w \rightarrow 0$.[11] Results presented in Fig. 3, both the experimental measurements and the model prediction, provide convincing evidence that the driving force for groove collapse is indeed interfacial adhesion.

By fitting the dimensionless adhesion parameter Γ to match the experimental results and model predictions in Fig. 3, we have obtained the value $\gamma/E' = 9.0 \times 10^{-9}$ m. Using the material property provided by the supplier, i.e., Young's modulus $E = 2.8$ MPa and Poisson's ratio $\nu = 0.5$, we can determine the value of interfacial adhesion energy $\gamma = 33.6$ mJ/m^2. This value is in general agreement with that measured by Sharp *et al.*[8]

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