

The controlled formation of ordered, sinusoidal structures by plasma oxidation of an elastomeric polymer

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(Received 6 July 1999; accepted for publication 1 September 1999)

This letter describes a technique for generating waves on polydimethylsiloxane (PDMS) patterned in bas-relief. The PDMS is heated, and its surface oxidized in an oxygen plasma; this oxidation forms a thin, stiff silicate layer on the surface. When the PDMS cools, it contracts and places the silicate layer under compressive stress. This stress is relieved by buckling to form patterns of waves with wavelengths from 0.5 to 10 μm . The waves are locally ordered near a step or edge in the PDMS. The wavelength, amplitude, and pattern of the waves can be controlled by controlling the temperature of the PDMS and the duration of the oxidation. The mechanism for the formation and order of the waves is described. © 1999 American Institute of Physics. [S0003-6951(99)01943-9]

Complex patterns can spontaneously form from simple patterns.¹⁻¹⁰ In previous work, we described the formation of ordered parallel waves [wavelength, $\lambda(m)$, $\sim 30 \mu\text{m}$] by a process that consisted of heating the polydimethylsiloxane (PDMS), depositing a thin film of gold (50 nm of gold with a 5-nm-thick titanium underlayer) by evaporation on the surface of PDMS that had been patterned in bas-relief, and cooling.¹ In this work, we describe a related, three-step method of generating ordered waves with shorter wavelength ($\lambda = 0.5\text{--}10 \mu\text{m}$) that does not require a step of metal deposition. This process involves: (i) heating the PDMS to cause it to expand; (ii) exposing it to an oxygen plasma to generate a thin surface film of silica-like material; and (iii) cooling. Starting with flat, unpatterned PDMS, these waves are locally ordered but globally disordered. By patterning the surface with bas-relief structures, it is possible to order the waves near a step or edge in these features. This method is interesting because it generates patterns of small features (the waves) from patterns of larger features (the relief structure on the surface).

We describe three methods to order the waves. (i) The waves are ordered by introducing bas-relief patterns into the PDMS. The waves align perpendicular to the steps in the surface. (ii) The waves are ordered by oxidizing a thin layer of PDMS on a cylindrical surface. The PDMS expands in one direction and the waves align parallel to the axis of the cylinder. (iii) The waves are ordered by compressing a flat slab of PDMS after it has been oxidized. The compressive stress is unidirectional and the waves align parallel to one another.

This procedure began with heating the PDMS in an oven at a chosen temperature between 50 and 250 °C for no less than 45 min to expand the polymer thermally [Fig. 1(a); the coefficient of thermal expansion of PDMS is $3.0 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ from -55 to $150 \text{ }^\circ\text{C}$]. The PDMS was taken from the oven and immediately loaded into a plasma cleaner (Anatech SP100 plasma cleaner) and placed under vacuum. The plasma cleaner was set to 100 W (other power settings

were used with similar results) and the PDMS was exposed to an oxidizing plasma for an interval from 10 s to 30 min. The temperature of the PDMS was not controlled during or after the oxidation; it began to cool as soon as it was removed from the oven. The PDMS remained warm during the oxidation because the inner tube of the plasma cleaner was heated to approximately 80 °C by energy dissipation from the plasma. After the oxidation, the PDMS was removed from the plasma cleaner and allowed to cool to room temperature. As the PDMS cooled, waves formed on the surface.

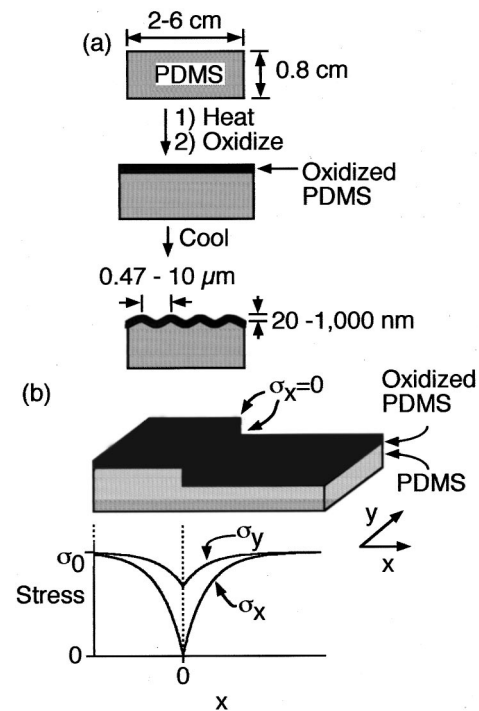


FIG. 1. (a) Formation of the waves. The PDMS was thermally expanded by heating between 50 and 250 °C in an oven; it was then placed in the plasma cleaner and oxidized at a pressure of 0.13–0.04 Torr. The sample was removed from the plasma cleaner. On cooling, the PDMS shrunk and placed the surface film in compression; this compressive force was relieved by buckling. (b) The stress prior to buckling near a step in the PDMS is modeled from equations found in Ref. 1.

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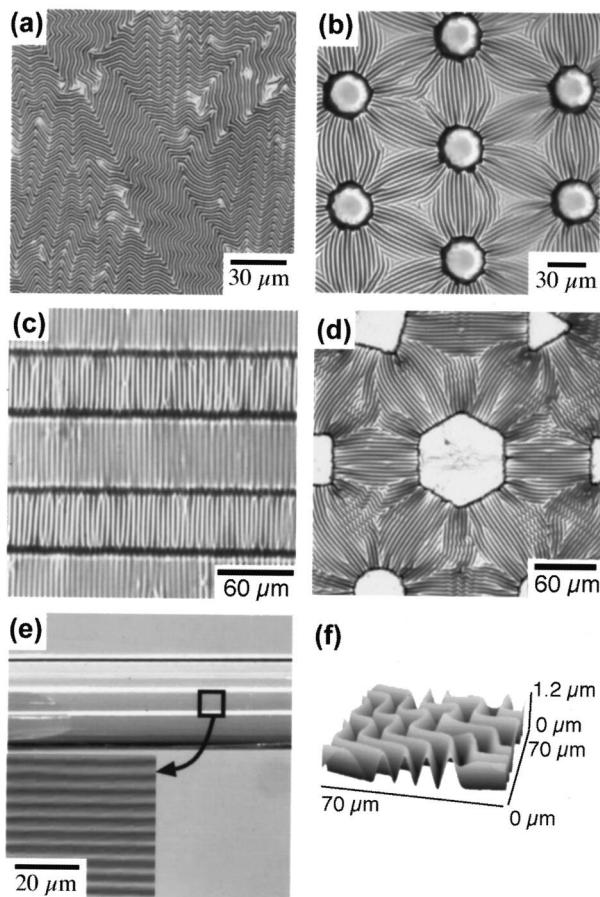


FIG. 2. (a) The surface of PDMS far from any steps or edges buckled into a pattern of waves consisting of many partially ordered domains. (b) Waves near the circles ($30\ \mu\text{m}$ in diameter; elevated by $5\ \mu\text{m}$; separated by $70\ \mu\text{m}$) were well ordered. (c) Waves near rectangular edges ($60\ \mu\text{m}$ wide; elevated by $5\ \mu\text{m}$; separated by $40\ \mu\text{m}$) were well ordered. (d) Waves near hexagons ($50\ \mu\text{m}$ on a face, elevated by $5\ \mu\text{m}$), squares ($50\ \mu\text{m}$ wide; elevated by $5\ \mu\text{m}$), circles ($50\ \mu\text{m}$ in diameter; elevated by $5\ \mu\text{m}$), and triangles ($50\ \mu\text{m}$ on a face; elevated by $5\ \mu\text{m}$) were well ordered. (e) A thin film of PDMS was cured against a glass cylinder (diameter= $1.5\ \text{mm}$). The oxidized surface buckled into waves that were aligned parallel with the cylinder (inset). (f) An AFM image of the unordered waves show the amplitudes and profiles. The images in (a), (b), (c), (d), and (e) were taken with an optical microscope. In (a), (b), (c), (d), and (e) the duration of the oxidation was 5 min, the power was 100 W, and the temperature of the samples prior to oxidation was $150\ ^\circ\text{C}$. In (f) the duration of the oxidation was 20 min.

On a flat surface, these waves formed a complex pattern consisting of globally disordered but locally ordered domains with periodicity extending perpendicular to the waves for up to thirty wavelengths [Fig. 2(a)].

We observed the formation of ordered waves near steps in the PDMS [Figs. 2(b)–2(d)], or along the axis of PDMS cast on a cylindrical surface [Fig. 2(e)]. In Figs. 2(b)–2(d) the roughness of the edges of the bas-relief pattern is due to the rapid prototyping method used to fabricate the PDMS masters and not due to the oxidation of the surface. Atomic force microscope images of the waves show the sinusoidal patterns in the surface [Fig. 2(f)].

We believe that the model used previously to describe the order of the waves in a gold film on PDMS also describes this system.¹ While the PDMS is thermally expanded, plasma oxidation forms a relatively incompressible layer of oxidized PDMS on the surface. We believe that the oxidized surface of PDMS has a lower coefficient of thermal expansion.

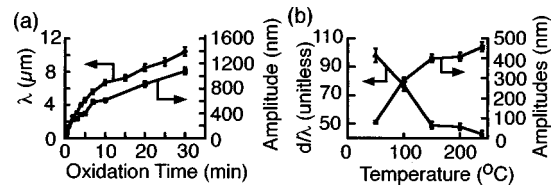


FIG. 3. (a) The wavelength, λ , and the amplitude of the waves increase with the oxidation time. All of the oxidations were carried out with the power level of the plasma cleaner set at 100 W. (b) The ratio d/λ decreases with the increasing temperature of the PDMS. The amplitudes of the waves increase with the temperature. All of the oxidations were carried out at 100 W for 5 min. The wavelengths were measured by optical microscopy or AFM (for wavelengths less than $1\ \mu\text{m}$); the error was estimated from measurements of the wavelength on at least five points on the surface. The amplitudes were measured by AFM on a replica of the waves made by UV curing a hard polymer on the surface; the error was estimated from at least ten measurements of the amplitude.

sion than the unoxidized, bulk PDMS; the surface oxide layer is placed under compressive stress when the PDMS cools and contracts. The surface buckles into a pattern of waves to relieve the stress.

The orientation of the waves on the bas-relief PDMS is determined by the pattern of stress on the surface when the PDMS is cooled. At a step or edge in the PDMS, the stress perpendicular to the step or edge is relieved by expansion. We model the stress perpendicular to a step to go to zero at the step, but the stress parallel to the step remains almost unchanged [Fig. 1(b)]. The surface buckles preferentially in one direction because of the difference in stress parallel and perpendicular to the step.

The structure of the oxidized layer is not completely characterized.^{11,12} It is believed that the oxidation introduces new crosslinks in the surface through the formation of new Si–O–Si bonds, and that the surface is terminated in Si–OH bonds (the advancing contact angle of water on PDMS is 108° and the advancing contact angle on oxidized PDMS is 30°). We have studied the oxidized PDMS by x-ray photoelectron spectroscopy (XPS); the composition of the surface is $\text{Si}_{1.00}\text{O}_{1.09}\text{C}_{1.84}$ before oxidation, $\text{Si}_{1.00}\text{O}_{2.36}\text{C}_{0.24}$ 1 h after oxidation, and $\text{Si}_{1.00}\text{O}_{1.67}\text{C}_{0.45}$ 72 h after oxidation (5 min oxidation at $150\ ^\circ\text{C}$ at 100 W). These data support the previous conclusions that the oxidized surface resembles a porous silica (SiO_2), although at long times after oxidation low molecular weight PDMS probably diffuses to the surface. We have examined the thickness of the oxide layer by viewing a cross section of the oxidized PDMS under a scanning electron microscope. The thickness of the oxide layer was approximately $0.5\ \mu\text{m}$ for a 15 min oxidation.

We can control the wavelength of the buckles by controlling the duration of the oxidation [Fig. 3(a)]. The wavelength increases rapidly in the first 5 min then the wavelength increases linearly with the oxidation time. We believe that longer oxidation times result in thicker oxidized layers on the surface; the wavelength—as predicted by equations that were developed for a thin, incompressible film on an elastomeric surface—should increase with the thickness of the oxidized layer. The following equation describes the wavelength, $\lambda(m)$, as a function of E_s , E_p , ν_s , ν_p , and t :

$$\lambda = 4.36t \left(\frac{E_s(1-\nu_p^2)}{E_p(1-\nu_s^2)} \right)^{1/3} \approx 4.4t \left(\frac{E_s}{E_p} \right)^{1/3}, \quad (1)$$

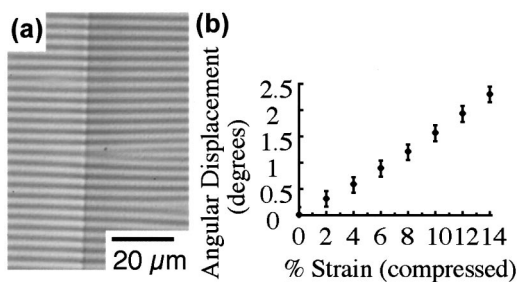


FIG. 4. (a) The waves were well ordered after oxidation of a slab of PDMS at room temperature followed by compression in one direction. The line in the middle of the optical micrograph is a crack; the cracks were perpendicular to the direction of the waves. (b) The angular displacement of the first order diffraction spot was measured as the PDMS replica was compressed in the direction parallel to the waves.

where the subscripts s and p refer to the oxidized surface and the bulk polymer, respectively, $t(m)$ is the thickness of the oxidized layer, E (Pa) is the Young's modulus, and ν (unitless) is the Poisson's ratio.¹ The values for these parameters are as follows (assuming that the oxidized surface has the same properties as glass): $E_s = 76$ GPa, $E_p = 20$ MPa, $\nu_s = 0.33$, and $\nu_p = 0.48$. Estimates of $t = 0.5 \mu\text{m}$ and $\lambda = 7.5 \mu\text{m}$ give $E_s \approx 790$ MPa, a value that is two orders of magnitude smaller than the value for glass.

This result supports the conclusion from the XPS that the oxidized surface is significantly different from SiO_2 . Because we have only a very limited knowledge about the oxidized PDMS surface layer, we cannot judge whether Eq. (1) describes the waves on the surface exactly. This equation does, however, successfully explain two general trends. (i) The dependence of the wavelength on the oxidation time can be explained by either assuming an increase in thickness or an increase in Young's modulus (E_s) for the oxide layer with increasing oxidation time. (ii) The independence of the wavelength on the temperature of the PDMS during oxidation (that is, on the magnitude of the compressive stress on the surface film) is predicted by Eq. (1). Experimentally, the wavelength was relatively constant for oxidations performed for the same length of time but at different temperatures, and the wavelength was the same near and far from the steps in the surface. We were able to generate regular structures with little temperature control because the wavelength was independent of the stress for the thermally expanded PDMS.

We can increase the amplitudes of the waves by increasing the length of the oxidation or by increasing the temperature of the PDMS [Fig. 3(b)]. As the temperature of the PDMS during oxidation is increased, the difference in area between the thermally expanded and room temperature states is increased and the compressive stress is increased. The greater the difference in area, the higher the amplitude of the waves.

One measure of the order of the waves is given by the distance, $d(m)$, from an edge or step where the waves that were parallel and straight begin to buckle in two directions. The ratio d/λ is a unitless number that relates the distance over which the compressive stress is anisotropic in the vicin-

ity of a step to the wavelength. We measured values for d and λ at the edge of a block of PDMS at various temperatures and oxidation times and made two observations. (i) The ratio d/λ is approximately constant for oxidations done at a constant temperature (for durations of 5 to 30 min). (ii) The ratio d/λ increases as the temperature of the PDMS decreases [Fig. 3(b)]. These observations demonstrate the order that is possible in this system.

We used this system to fabricate a pressure-sensitive diffraction grating. A slab of PDMS ($3 \text{ cm} \times 1 \text{ cm} \times 1 \text{ cm}$) was oxidized in the plasma cleaner for 5 min at 100 W without being heated; no waves formed on the surface. The PDMS was placed in a vise and placed under approximately 2.5% strain. Waves spontaneously formed on the surface in the direction parallel to the applied stress over the entire surface [Fig. 4(a)]; cracks formed in the direction perpendicular to the applied stress. The cracks were spaced farther apart ($>50 \times$ the wavelength) than the waves; the density of the cracks increased with increasing stress on the surface. A PDMS replica was made of the waves. We measured the change in the angle of the first order diffraction spot as a function of the strain (applied with a micromanipulator) on the PDMS [Fig. 4(b)].

This technique for fabricating ordered wavy structures on PDMS may find uses in a variety of areas including microelectromechanical systems (MEMs), biology, and nano- and microfabrication.^{13,14} Because the mechanism for the formation of the waves is described and understood, a number of methods can be used to pattern the stress, and hence the order of the waves, in the oxidized surface. Using this method, we have been able to fabricate patterns at the micron scale having sinusoidal topography on flat or nonplanar surfaces; these patterns complement the regular, square features on flat substrates that are produced by conventional photolithography.

One of the authors (N.B.) gratefully acknowledges the DOD for a Predoctoral Fellowship. This work was supported in part by funding from DARPA, Army Research Office-MURI, and NSF (Grant No. ECS-9729405).

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