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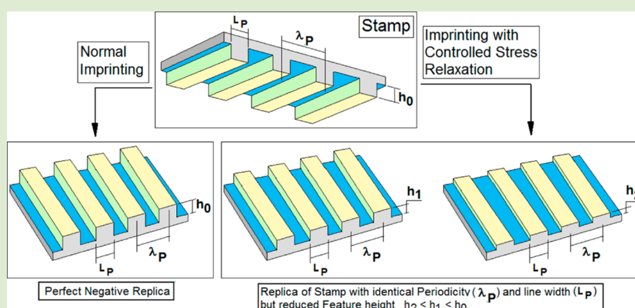
Lithographic Tuning of Polymeric Thin Film Surfaces by Stress Relaxation

Nandini Bhandaru, Sudeshna Roy, Suruchi, G. Harikrishnan, and Rabibrata Mukherjee*

Instability and Soft Petterning Laboratory, Department of Chemical Engineering, Indian Institute of Technology Kharagpur, West Bengal, 721 302, India

Supporting Information

ABSTRACT: We report a facile soft lithography (SL) technique that allows fabrication of patterned polymeric surfaces with feature height varying between 0 and h_0, using a single stamp. The method relies on the partial relaxation of the applied stress in a viscoelastic polymer thin film imprinted under a transient external load using a flexible stamp. The applicability of the technique is demonstrated for thermosetting (rubbery) as well as thermoplastic (glassy) polymers over a wide range of lateral dimensions. The lateral dimension and the periodicity of imprinted patterns remain identical to that of the original stamp. The method has potential applications in creating templates for performing combinatorial experiments related to wetting and dewetting studies, adhesion, nanotribology, microfluidics, etc.



Soft lithography (SL)[1] and nano imprint lithography (NIL)[2] groups of techniques are extensively used for creating mesoscale patterns on polymeric film surfaces, which find wide applications in areas such as fabrication of metal-oxide semiconductor field effect transistors (MOSFETs),[3] scaffolds for tissue engineering and protein immobilization,[4] patterned adhesives,[5] carbon microelectromechanical systems (C−MEMS) and microbatteries,[6] super hydrophobic surfaces, etc.[7] The success of any SL or NIL based technique depends largely on the availability of an appropriate master or mold, as most of the methods are capable of creating a perfect negative replica of the original stamp or the mold.[1,2,7] While a rigid mold is directly used for imprinting in NIL based techniques,[2] majority of the SL techniques use a soft elastomeric stamp fabricated by replica molding of cross-linked polydimethylsiloxane (PDMS) against a lithographically fabricated master.[1,7] Thus, it becomes essential to use a separate lithographically fabricated stamp or a master for every desired final pattern. This makes all NIL and SL methods indirectly dependent on photolithography or other direct write nanofabrication techniques for creating the original master mold.[7] In this communication, we present a novel imprinting technique by which it becomes possible to fabricate structures with different feature height (h_S), using a single stamp. We show that by using a single grating stamp with periodicity λ_P and feature height h_0, it becomes possible to create patterns with programmable feature height h_S that varies between 0 and h_0, though the lateral dimension of the imprinted features (λ_P) remains identical to that of the stamp. Fabrication of such a set of patterned surfaces with different feature height would require multiple lithographically fabricated masters,[8] or specially fabricated stamps with gradient topography,[9] by any existing technique. The ability to achieve the same with a single stamp makes the current technique cost effective with reduced dependence on other lithography methods for master fabrication. So far, only a few patterning methods are capable of producing patterns which are not merely a negative or a positive replica of the stamp.[10−14] For example, an ordered array of pillars can be obtained by LISA[10] and electrohydrodynamic lithography,[11] using a flat stamp. Elastic contact lithography offers the ability to create an ordered 2-D array of holes using a simple 1-D patterned grating stamp.[12] A method based on imprinting and controlled shrinkage of a hydrogel film has been utilized to obtain smaller patterns starting from a master with larger features.[13] Recently, Lee et al. have shown the possibility of varying feature periodicity by solvent-assisted swelling of the mold during embossing.[14] However, none of the techniques are capable of producing patterns with programmable feature height using a single stamp, maintaining the periodicity and the lateral dimension of the imprinted patterns the same as that of the stamp.

The method reported here relies on imprinting a polymer thin film under a transient external load while the film is in a viscoelastic state. The withdrawal of the external force while the polymer is in a nonequilibriam state causes partial relaxation of the applied stress of the deformed polymer film, resulting in a final feature height (h_S) that is lower than that of the stamp (h_0). We show that the method can be utilized for generating patterns with different h_S in both thermosetting (rubbery) and

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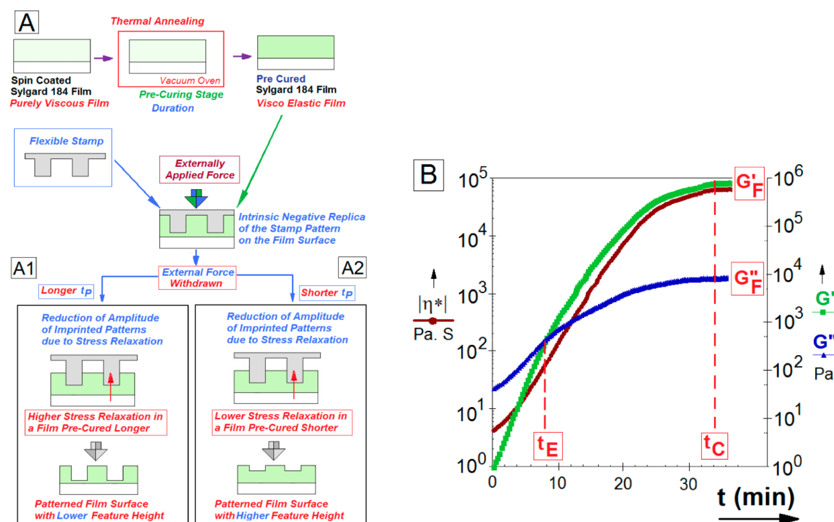

Figure 1. (A) Schematic representation of the proposed concept of creating patterns of different feature height (h_S) based on stress relaxation. (B) Rheometer data indicating the progressive change of G', G'', and η^* with time, during the early stages of cross-linking of PDMS.

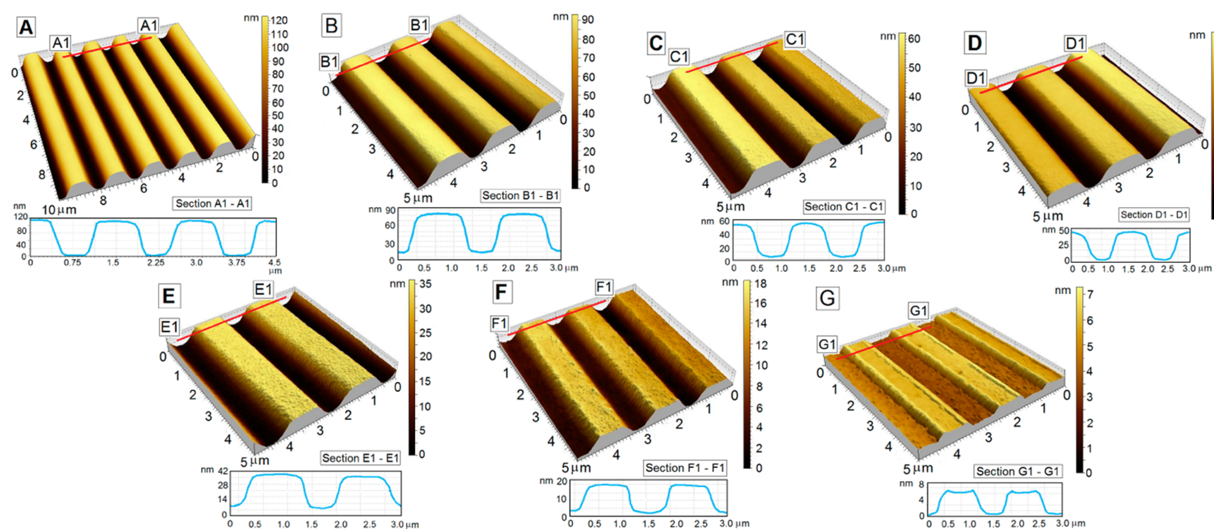

Figure 2. Structures with different feature height formed in samples precured for different durations (t_P) before imprinting. Stripe height (A) h_S = 120 nm (no precuring); (B) h_S = 95 nm for t_P = 5 min; (C) h_S = 63 nm for t_P = 10 min; (D) h_S = 50 nm for t_P = 15 min; (E) h_S = 37 nm for t_P = 20 min; (F) h_S = 22 nm for t_P = 24 min; and (G) h_S = 7 nm for t_P = 27 min. After 30 min of precuring, no pattern was seen on the film surface. In all cases, a CD foil with h_0 = 120 nm was used as the stamp.

thermoplastic (glassy) polymer thin films, which is demonstrated by imprinting Sylgard 184 (Dow Corning, USA) and polystyrene (PS, mol. wt. 280K) thin films, respectively. Though the essential concept remains the same, slightly different experimental protocol is adopted in the two cases, due to the difference in the mechanistic origin of viscoelasticity in the respective type of materials.[15−17]

We first discuss how patterns with different h_S are obtained on elastomeric (thermosetting) thin films. The spin-coated Sylgard 184 films, prior to imprinting, are thermally precured for different durations of time (t_P) at 120 °C in an air oven. After precuring, the film is cooled for 30 s before being imprinted with a flexible stamp, under a uniformly distributed applied stress of ≈2 KPa. The external force ensures a conformal contact between the film and the stamp and deforms the surface of the partially cured film at the length scale of each stamp feature, thereby forming an intrinsic perfect negative replica of the stamp on the film surface, irrespective of the duration of t_P (refer to the Supporting Information). The external force is applied for a short duration of ∼30 s and is subsequently withdrawn, leaving behind the stamp on the deformed film surface. The imprinted film, along with the stamp, is subsequently cured for 12 h at 120 °C to make the patterns permanent by complete cross-linking of Sylgard 184. The process is schematically shown in Figure 1A.

The as-cast Sylgard 184 film without any precuring is in a purely viscous state, which is evident from a higher value of loss modulus (G'') as compared to the storage modulus (G'), seen in the transient rheological behavior presented in Figure 1B. With progressive thermal annealing, gelation or cross-linking reaction proceeds. This gradually increases G', which eventually exceeds G'' at $t = t_E$ (8 min, for our system). The gelation reaction is completed at time $t = t_C$, which for our system is approximately 30 min. Beyond $t = t_C$, G' does not increase any further, and the response of the polymer film becomes predominantly elastic, which is evident from a two-order

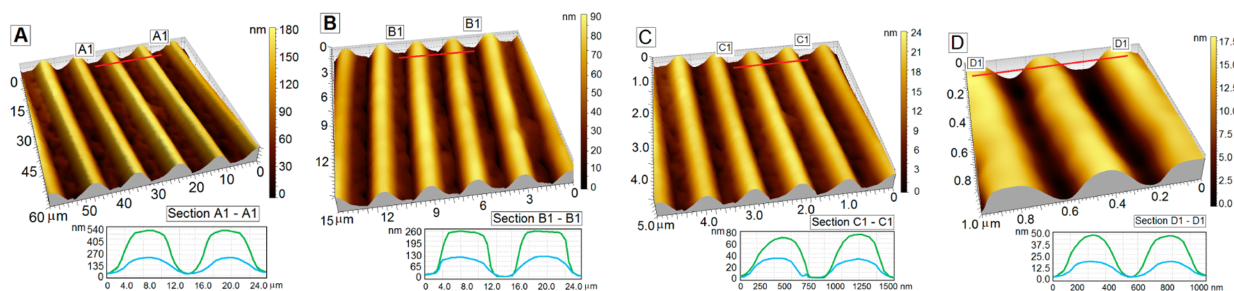

Figure 3. Patterns obtained with stamps of different periodicity and feature height. (A) Stamp used: Grating 1 (λ_P = 12.5 μm, h_0 = 530 nm), obtained feature height h_S = 176.1 nm. (B) Stamp: Grating 2 (λ_P = 3.0 μm, h_0 = 250 nm), h_S = 84.3 nm. (C) Stamp: DVD Foil (λ_P = 800 nm, h_0 = 70 nm), h_S = 22.9 nm. (D) Stamp: Blue Ray Disc Foil (λ_P = 450 nm, h_0 = 50 nm), h_S =16.9 nm. The cross-sectional line scan in each image shows both the profile of the imprinted patterns (blue line) as well as that of the original stamp (green line). In all the cases, t_P = 15 min.

higher final value of G' ($G'_F \approx 10^6$ Pa) as compared to G'' ($G''_F \approx 10^4$ Pa).

It also becomes clear from Figure 1B that before gelation is complete ($t < t_C$) a film precured longer (t_{P2}) has a higher level of elasticity in comparison to a film precured for a shorter duration (t_{P1}). This is the key concept which has been exploited for fabricating the structures with different h_S. When a partially cross-linked ($t_P < t_C$) Sylgard 184 film is imprinted, a part of the applied external energy gets stored within the film as the elastic deformation of the partially cross-linked matrix (component E_E) and the remaining portion of the energy is lost as viscous dissipation (component E_V). The relative magnitude of E_E and E_V depends on the viscoelasticity of the film and therefore on the magnitudes of G' and G'' respectively, which in turn depends on the duration of precuring. It can be clearly understood from Figure 1B that the magnitude of E_E is higher in a film precured longer than in a film precured for a shorter duration.

When the applied load is withdrawn after imprinting, the polymer chains relax, due to release of the stored elastic energy (E_E). The relaxing chains try to flatten the imprinted film surface. However, as part of the energy (E_V) is lost due to viscous dissipation, only partial flattening of the imprinted surface is achieved. This results in reduction of the amplitude of the imprinted patterns. Further, as the stamp remains in conformal contact with the film surface after the external load has been withdrawn, the imprinted stripes remain confined by the stamp stripes and do not dilate laterally. This ensures that λ_P and l_P of the imprinted structures remain unaltered. The only manifestation of the stress relaxation takes place in the form of reduction in amplitude of the imprinted patterns in the vertical direction (schematic in Figure 1A) by an amount h_{RED}, and consequently, the final height of the features as that of the stamp becomes $h_S = h_0 - h_{RED}$. The magnitude of h_{RED} depends on the extant of stress relaxation, which in turn is directly proportional to the amount of E_E stored within the film. We have already argued that E_E increases with t_P, which implies that h_{RED} also increases (and h_S decreases) with longer t_P, resulting in patterns with progressively lower h_S. Figure 2 shows patterns with different h_S obtained from a single stamp having λ_P = 1.5 μm, l_P = 750 nm, and h_0 = 120 nm. The feature height of the imprinted patterns progressively reduces from h_S = 120 nm in Figure 2A (perfect negative replica of the stamp, no precuring) to $h_S \approx 7$ nm in Figure 2G, for $t_P \approx 27$ min. Other frames of Figure 2 show patterns with intermediate h_S, depending on the duration of t_P. The cross sectional line scans given in the insets to each frame confirm that λ_P and l_P remain unaltered in all the cases. No patterns are obtained ($h_S \to 0$) once t_P exceeds 30 min, as the film becomes fully cross-linked and the deformation of the film surface under the transient external load is completely flattened by stress relaxation.

While all the structures shown in Figure 2 are obtained using a stamp with λ_P = 1.5 μm, the method works equally well with stamps having wide variation in lateral periodicity. This particular aspect can be clearly seen in Figure 3, which shows structures with λ_P varying from 450 nm to 12.5 μm. In all the cases shown in Figure 3, t_P was maintained at 15 min. From the cross-sectional line scan of the imprinted patterns superimposed on the original stamp profiles (shown in respective insets), we observe that the normalized feature height h_N (= h_S/h_0) is nearly the same (within the error bars) in all the cases. The same trend is observed for other values of t_P, where h_N is found to be nearly independent of λ_P. This is clearly seen in Figure 4, which shows the variation of h_N as a function of t_P.

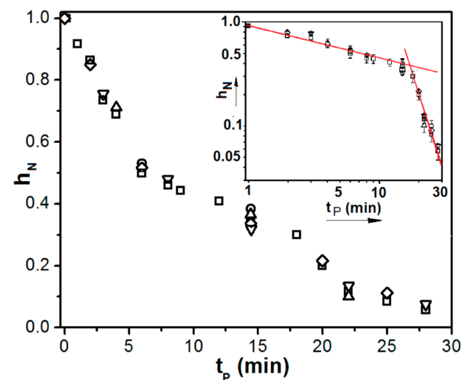

Figure 4. Plot of normalized feature height (h_N) vs precuring time (t_P) for patterns obtained with different stamps. Inset shows the same plot on a log−log plot, with clear demarcation of two regimes. Different symbols represent different stamps as follows: (Δ) Grating 1; (∇) Grating 2; (□) CD Foil; (○) DVD Foil; and (◊) Blue Ray Disc Foil.

The inset of the figure shows the same plot on a log−log scale, where we can clearly identify two distinct regimes with different rates of feature height reduction. On the basis of the best fit to the data, the exponential dependence between h_S and t_P is observed to be $h_S \approx t_P^{-0.413\pm0.027}$ for regime 1 and $h_S \approx t_P^{-4.108\pm0.553}$ for regime 2, respectively. The one order difference in the exponent of t_P across the two regimes is attributed to a change in the rheological behavior of the film. Qualitatively, regime 1 is dominated by viscous dissipation, as $G' < G''$ at lower t_P, and therefore the rate of stress relaxation is sluggish in this regime, which is reflected in the form of a low value of the exponent. In contrast, a faster relaxation in regime 2 is

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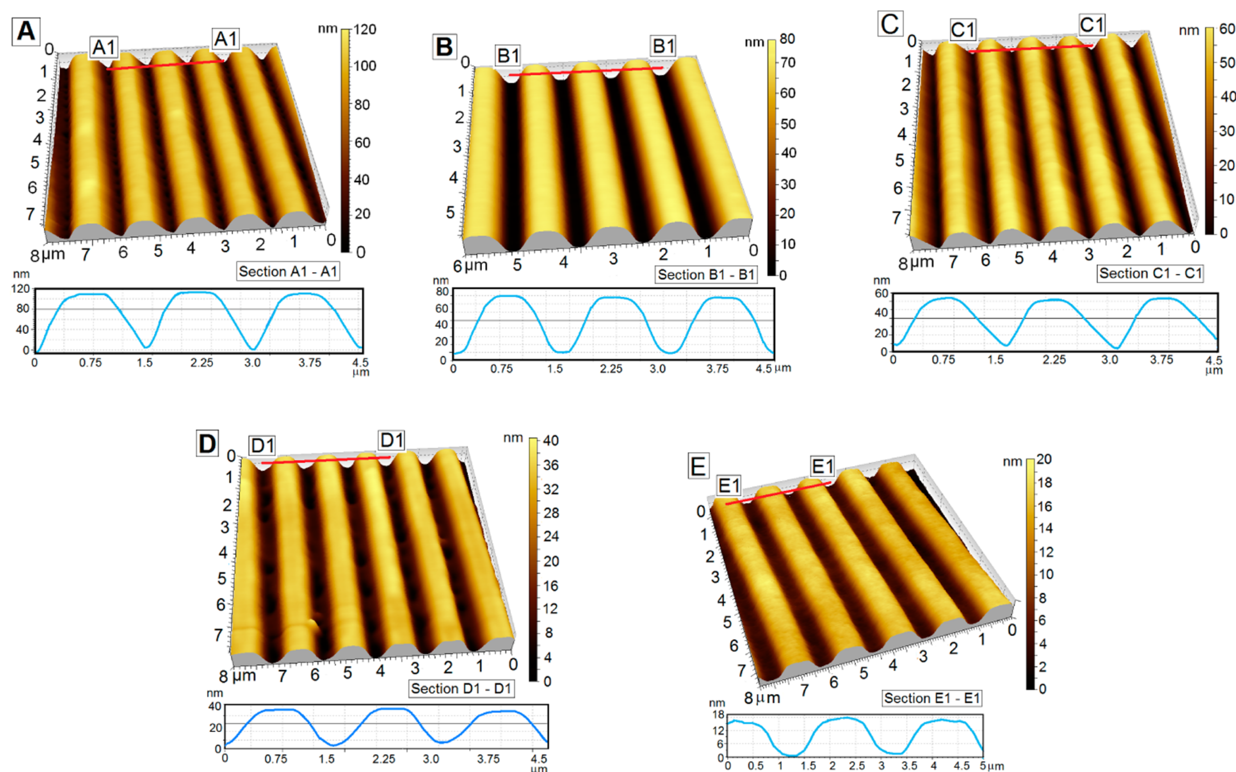

Figure 5. AFM scans of patterns obtained on a PS film with different feature height. The feature height is (A) h_S = 120 nm (no post annealing time), (B) h_S = 80 nm (2 h post annealing time), (C) h_S = 60 nm (6 h post annealing time), (D) h_S = 38 nm (12 h post annealing time), and (E) h_S = 19 nm (24 h post annealing time).

attributed to dominant elastic forces arising from significant extent of cross-linking after longer precuring. We also argue that the time at which the transition from regime 1 to regime 2 takes place in Figure 4 (t_R) qualitatively corresponds to t_E in Figure 1B. However, the magnitudes of t_R ($\approx$ 14 min) and t_C ($\approx$ 9 min) do not exactly match, which might be due to different conditions prevailing on the Rheometer stage and during imprinting. During rheological measurements, the polymer is always in contact with a hot plate, while for imprinting the films are brought out of an oven and cooled down, which attributed the rheological transformation of the film and qualitatively justifies that $t_R > t_C$. It must also be highlighted that for all the data points shown in Figure 4 the initial film thickness was approximately 5 μm. Additional experiments with different film thickness reveal a similar trend in the variation of h_N with t_P, though the rate of height reduction changes. While a rapid reduction in feature height is observed in thinner films, it becomes sluggish with an increase in the initial film thickness. On the other hand, a variation of cross-linker concentration of Sylgard also drastically alters the precuring time. No patterns can be obtained after $t_P \approx 10$ min when cross-linker concentration is increased to $\approx$15%. In contrast, for a cross-linker concentration of $\approx$5%, patterns are obtained for up to 70 min of precuring. A detailed parametric variation is beyond the scope of this paper. We have also observed that there was no variation in h_S as a function of t_P, when the magnitude of the externally applied force was varied between 1 and 8 KPa. The maximum amount of elastic energy that can be stored within the film as elastic deformation of the matrix (E_{E-max}) largely depends on the extent of cross-linking. When higher external stress is applied, the additional energy contributes to a higher value of E_V, and gets dissipated. However, the stress relaxation and associated reduction of imprinted feature height depend only on E_{E-max}, and therefore h_S remain unaltered. For very low values of external energy (<0.8 KPa), the applied force fails to fully deform the film surface and therefore results in shallower final structures. The technique can be implemented with any type of flexible patterned stamps. The use of a rigid stamp is not recommended as the weight of the stamp itself prevents the stress relaxation induced flattening of the imprinted surface and thus hinders the capability of the technique (refer to Supporting Information).

We now discuss how patterns with different h_S can be generated in a thermoplastic (glassy) thin film with minor change in the experimental protocol. A thermoplastic exhibits significant viscoelasticity when it is heated to a temperature slightly above the T_g.[18−20] At temperatures well above T_g, the chains disentangle, and the polymer flows like a predominantly viscous liquid.[19] In a linear chain polymer film which is in a viscoelastic state, the level of chain entanglement reduces with progressive annealing.[15,16] The disentanglement of the chains is associated with the release of elastic stresses confined within the entangled film matrix, particularly when the molecular weight (M_W) of the polymer is > M_{Went} (entanglement molecular weight).[17] This concept has been utilized for generating patterns with different h_S in the thermoplastic (glassy) thin PS films of polystyrene with molecular weight of 280 KDa, which is higher than the M_{Went} of PS (17 KDa). The PS thin films are imprinted at 110 °C which is slightly above the T_g ($\approx$105 °C), under a uniformly applied external load that corresponds to a stress of 2 KPa. In this case, the load is applied for 6 h, which leads to the formation of an intrinsic perfect negative replica of the stamp pattern on the PS film surface, as can be seen in Figure 5A. The external force is then withdrawn,

and the film, along with the stamp in conformal contact with it, is maintained at the same elevated temperature of 110 °C inside the oven. As the chains disentangle with progressive annealing, the elastic stresses confined within the film matrix relax and flatten the surface. As the extent of chain disentanglement is proportional to the annealing time, a film annealed longer, after the external force has been withdrawn, undergoes a higher level of stress relaxation, which leads to a higher magnitude of h_{RED} and therefore lower h_S. This can be seen in Figure 5B–E, where h_S reduces from 85 nm for a post annealing (t_A) of 2 h to $h_S \approx$ 35 nm for t_A = 12 h. However, unlike a thermosetting (rubbery) film, an imprinted PS film never becomes perfectly flat even after prolonged t_A, as the film never becomes purely elastic, unlike a cross-linked Sylgard film, and therefore there is always finite viscous dissipation. For example, we could not obtain films with h_S lower than ≈20 nm even after post annealing of more than 24 h.

In conclusion, we have presented a simple soft lithographic technique that can be used to create series of patterned surfaces which has the same lateral dimension as that of the stamp but has different feature height, using a *single* stamp. The method relies on the stress relaxation and associated self-organization of a deformed viscoelastic polymeric thin film, imprinted with a flexible stamp under a transient external load. For an elastomeric film, imprinting is performed during the pregel state while the cross-linking reaction is underway. In contrast, for a thermoplastic (glassy) film, imprinting is carried out at a temperature range that is immediately above its glass transition temperature (T_g), so that the film is in a predominantly viscoelastic state. The method is simple and can be implemented without any major instruments and is therefore ideally suited for creating meso-patterned templates, even in the absence of extensive micro- and nanofabrication facilities. The patterned substrates created by this method can find applications in areas such as nanotribology, adhesion, nano-biotechnology, microfluidics, plasmonics etc., particularly for combinatorial experiments.

■ EXPERIMENTAL SECTION

Thin films of Sylgard-184 (a two part PDMS elastomer; Dow Corning, USA), spun cast from a dilute solution in *n*-hexane, are used. The ratio of part A to part B (oligomer to cross-linker) is maintained at 10:1. The film thickness is maintained at ≈5 μm across all samples. Polystyrene (mol. wt. 280K, Sigma Aldrich, UK) films spin coated from toluene were also used. For PS films, the film thickness is maintained at ~400 nm (verified with an ellipsometer, Accuron, model SE3, Germany). In both cases, square pieces (15 mm × 15 mm) of single side polished, cleaned test grade silicon wafers (Wafer World, USA) are used as substrates. Thin metallic foils peeled from commercially available CD discs are used as stamps.[21] The CD foils have a grating geometry, with line width (l_P) = 750 nm, periodicity (λ_P) = 1.5 μm, and feature height (h_0) = 120 nm. In some experiments, foils peeled off from DVD (λ_P = 800 nm, h_0 = 70 nm) and Blue Ray disc (λ_P = 450 nm, h_0 = 45 nm), as well as foils replicated from optical gratings (grating 1: λ_P = 12.5 μm, h_0 = 530 nm and grating 2: λ_P = 3.0 μm, h_0 = 250 nm) are used as stamps. The transient rheological behavior is analyzed by using an oscillatory Rheometer with a cone and plate arrangement (cone angle 2°, Physica MCR 301, Anton Paar, Austria) at an angular frequency of 10 rad/s. The imprinted patterns are imaged using AFM (Agilent Technologies, USA, model 5100), in intermittent contact mode using silicon cantilevers. At least five samples in different batches were tested. Each sample was scanned at least at three distinct locations. The error bars shown in Figure 4 thus correspond to averaging over at least 15 values of h_S, obtained for each t_P.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Formation of transient perfect negative replica of the stamp pattern during imprinting of the precured films, use of stamps other than foils peeled from CD/DVD discs, and Figures S1–S2. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel. +91−3222 283912. E-mail: rabibrata@che.iitkgp.ernet.in.

Notes

The authors declare no competing financial interest.

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