

Electronic Supplementary Information

Bespoke Periodic Topography in Hard Polymer Films by Infrared Radiation-Assisted Evaporative Lithography

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Simple Geometric Model

The main assumption of the model is that *the whole* volume of the polymer in the latex is used to form the raised features in films patterned with IRAEL (Figure S1). In addition, it is assumed that the shape of the raised feature is that of a spherical cap, with a diameter equal to the pitch, P , of the mask.

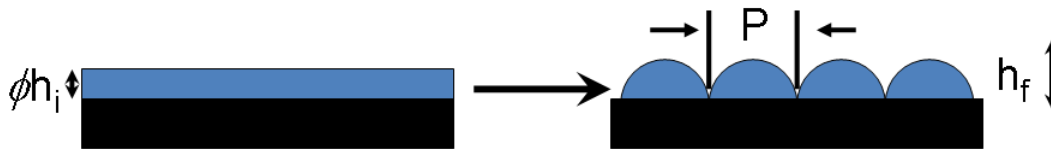


Figure S1 Schematic view of the assumption that the whole volume of the polymer is used for the formation of the raised features.

For an area of A , the volume of the polymer is equal to $V_p = h_i A \phi$ (Eq.S1), where ϕ is the volume fraction of the polymer in the latex and h_i is the initial film thickness. According to the model, the final film will be an array of spherical caps (sc). The volume of the array is $V_f = N V_{sc}$ (Eq S2), where N is the number of spherical caps per area A , and V_{sc} is the volume of one spherical cap. N is equal to the number of the holes in the mask used for the patterning. It can then be seen that $N = \frac{A f_{open}}{A_{hole}}$ (Eq. S3), where $A_{hole} = \pi \left(\frac{d_h}{2} \right)^2$ (Eq. S4) is the area of the hole in the mask and f_{open} is the fraction of the mask that is open (0.35 in our case). (The area of the mask is assumed to be equal to the area of the substrate, A). In general for a

spherical cap (Figure S2), the volume is given by $V = \frac{\pi h}{6}(3\alpha^2 + h^2)$ (Eq. S5), where α is the radius of the base of the cap, and h the height of the cap. In this simple model, it is assumed that the radius of the base is equal to one half of the pitch ($\alpha = \frac{P}{2}$) and that the final film height, h_f , is equivalent to the final peak-to-valley height (PV) of the raised feature measured by profilometry. Consequently, the volume of the spherical cap is

$$V_{sc} = \frac{\pi h_f}{6} \left(3 \left(\frac{P}{2} \right)^2 + h_f^2 \right) \quad (\text{Eq. S6}).$$

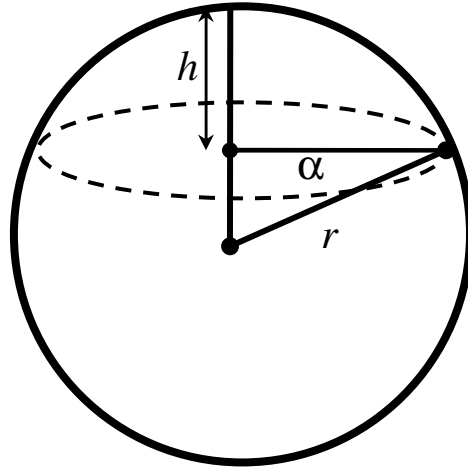


Figure S2 Diagram showing the parameters used for the calculation of the volume of a spherical cap.

From the main assumption of the model, we have $V_p = V_f$, which from Equations S1 to S6 can be written as

$$h_i A \phi = N V_{sc} = \frac{A f_{open}}{\pi \left(\frac{d_h}{2} \right)^2} \frac{\pi h_f}{6} \left(3 \left(\frac{P}{2} \right)^2 + h_f^2 \right) \quad \text{Eq. S7}$$

such that

$$h_i \phi = \frac{f_{open}}{\left(\frac{d_h}{2} \right)^2} \frac{h_f}{6} \left(3 \left(\frac{P}{2} \right)^2 + h_f^2 \right) \quad \text{Eq. S8}$$

From Eq. S8, we can make predictions of the h_f under specific conditions of IRAEL. If h_i and ϕ are kept constant and P (and hence d_h) is varied, a prediction of h_f (which is equivalent to PV) as a function of P is obtained (see Figure S3).

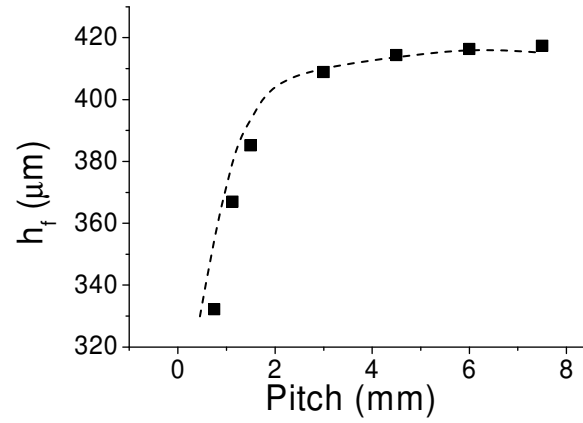


Figure S3 A prediction from a simple geometric model of the final film thickness (equivalent to the peak-to-valley height) as a function of the pitch, assuming a constant initial thickness and initial solids fraction.