Controlling the Orientation of Nanowrinkles and Nanofolds by Patterning Strain in a Thin Skin Layer on a Polymer Substrate**

Mark D. Huntington, Clifford J. Engel, and Teri W. Odom*

ange_201404483_sm_miscellaneous_information.pdf
# Table of Contents

- Calculating Wavelength of 1D Nanowrinkles ................................................................. S2
- Calculating Orientational Order for Different Strain Ratios ........................................ S3
- Model of the Evolution of Wrinkle Amplitude with Strain ........................................... S5
- Curvature of 1D Nanowrinkles ......................................................................................... S7
- Figure S6: 2D wavelength as a Function of Increased Strain ........................................... S8
- Young’s Modulus Measurements Strain ........................................................................... S9
- Figure S8: Nanowrinkle Orientation around a Single Point of Strain Relief ............... S10
- Figure S9: Alignment of Self-similar Wrinkle Orientation with 2D Strain Relief .......... S10
- Figure S10: Orientation of Nanowrinkles and Nanofolds with $\lambda < 100$ nm ........ S11
- Figure S11: Limit of Nanowrinkle Orientation ................................................................. S11
- Supplementary References ............................................................................................... S12
Calculating Wavelength of 1D Nanowrinkles

The wavelengths of the wrinkles were determined by taking the 2D fast Fourier transform (FFT) of scanning electron microscope (SEM) images (Fig. S1). Before computing the FFT, Matlab® images were converted from gray scale to binary black and white. To extract the wrinkle wavelength, we integrated the intensity of the 2D FFT radially outward.[1]

Figure S1: Representative Fast Fourier Transform (FFT) of 1D nanowrinkles. (a) Real space and (b) FFT of a SEM image of 1D nanowrinkles. The small radial spread of the transform confirms that the wrinkles were oriented in one direction. (c) Integrated FFTs used to determine the wavelengths ($\lambda \approx 160$ nm) of 1D wrinkles.
Calculating Orientational Order for Different Strain Ratios

The order parameter ($S$), which varies from 0 (completely random) to 1 (perfectly ordered), is typically used to quantify the orientational order of liquid crystals.\cite{2} To estimate $S$ of the nanowrinkled substrates, we converted wrinkled features of SEM images (Fig. S2a) into separate regions with a defined feature size by transforming the image to a black and white representation (Fig. S2b). To convert the gray scale image to calculate the orientation of the wrinkle ridges every pixel above a gray threshold scale value was converted to white and the pixels below to black. The threshold value was chosen to maximize the individual regions in the image. The order parameter can then be calculated from $S = \frac{1}{2}\langle 3\cos(\theta) - 1 \rangle$, where $\theta$ is the angle between the

Figure S2: Order parameter decreases with strain ratio. (a) Representative SEM image of nanowrinkle sample with a strain ratio of 0.16. (b) Black and white conversion of image using a threshold value of 0.44. (c) Order parameters calculated using FFT (blue) matches well with those measured by breaking the image into separate regions (red). All measurements were taken on at least 4 different SEM images. Y-error bars represent the standard deviation across measurements and x-error bars represent the uncertainty in the strain measurements.
major axis of the each region and a predefined orientation direction. **Figure S2c** (red) shows that S varies with different anisotropic strains from ca. 0.4 for 2D isotropic strain to ca. 0.98 for 1D strain. The strain ratios were calculated by measuring the change in distance between two sets of lines in the x- ($\varepsilon_x$) and y-directions ($\varepsilon_y$).

One drawback to determining S based on the orientation of the wrinkle edges in SEM images is the results can be highly dependent on the image processing. Therefore, we developed a new order parameter ($S_{FFT}$) based on the angular spread of the fast Fourier transform (FFT) of the SEM image (**Fig. S1b**). We define $S_{FFT} = (180^\circ - \delta\theta)/180^\circ$, where $\delta\theta$ is the angular spread of the FFT. To measure $\delta\theta$, we converted the FFT into polar coordinates and evaluated the full-width-at-half-maximum (fwhm) at a constant radius corresponding to the average wrinkle wavelength. **Figure S2** (blue) indicates that $S_{FFT}$ follows a trend similar to $S$ for different anisotropic strains, with ranges from ca. 0.04 for 2D isotropic strain to ca. 0.77 for 1D strain.

**Figure S3: Order parameter does not increase with strain.** Order parameters were calculated from the samples shown in figure 1. Y-error bars represent the standard deviation across measurements and x-error bars represent the uncertainty in the strain measurements.
Model of the Evolution of Wrinkle Amplitude with Strain

For the linear model, additional strain is absorbed by increasing the amplitude of the wrinkles without changing the wavelength (Fig. S4a). To understand how the wrinkle amplitude \( A \) changed with applied strain, we modeled the wrinkle as a simple sine wave and calculated the change in length (strain) of a single period of the wave as the amplitude increases. The length of the sine wave was calculated by numerically evaluating the path integral of the sine wave. The strain can be calculated by finding the change in length from zero amplitude to the max. Figure S4b shows how the amplitude changes as a function of strain. For small strain \( (\varepsilon < 0.08) \), the plot can be fit using \( A \propto \varepsilon^{1/2} \), which matches well with previous reports.\[^3\] At higher strain, the \( A-\varepsilon \)

![Linear model](image)

**Figure S4:** Linear model of how \( A \) increases with strain. (a) Scheme of increasing amplitude in the linear model. (b) Plot of \( A \) as a function of increasing \( \varepsilon \).
curve could be fit using a polynomial expansion: \( A \propto \varepsilon^{1/2}(a+b\varepsilon^2+c\varepsilon^3+\ldots) \), where \( a \), \( b \), and \( c \) are constants. For example, for strain values of \( \varepsilon < 0.36 \), the \( A-\varepsilon \) curve could be fit with three terms and matches a previous reported model for this strain regime.\(^4\) Our nanowrinkles had strain values up to \( \varepsilon > 0.6 \) which requires 4 polynomial expansion terms to fit (Fig. S4b).
**Curvature of 1D Nanowrinkles**

We measured the curvature of the 1D nanowrinkles by calculating the numerical second derivative of the line traces from the FIB cross sections in Fig. 1c. To ensure that there were no discontinuities in the derivatives both the original line trace and the first derivative were smoothed using spline interpolation. The curvature for the linear and nonlinear models were calculated from the taking the second derivatives of the linear (increasing amplitude, Fig. 2a) or nonlinear (decreasing wavelength, Fig. 2b) models.

![Curvature graph](image)

**Figure S5: Curvature increases as a function of strain.** The y-error bars represent the variation in the curvature across each cross section.
Figure S6: 2D wavelength as a function of increased strain. Plot indicated that 2D nanowrinkles wavelength decreases with increasing strain. The slope was fit to \( \lambda = (1-\alpha \varepsilon)\lambda_0 \) where \( \alpha_{2D} = 0.39 \).
Young’s Modulus Measurements Strain

To measure the Young’s Modulus of the PS substrate, a load-unload test was performed using a Hysitron TI 950 TriboIndenter equipped with a Hysitron's xSol High Temperature Stage on untreated PS films. Indentation occurred by applying a constant force of 1800 µN with a penetration depth that ranged from 400 to 600 nm. The samples were fixed to a metal stage with “Gorilla Super Glue” to ensure the sample did not move during indentation. After increasing the temperature, the sample was allowed to stabilize for 20 min prior to indentation measurement to ensure uniform heating of the sample. When the temperature \( T \) was increased beyond \( T_g \) \( (T = 110°C) \), the indentation failed because the 1800 µN could not be reached before the penetration depth exceeded the intrinsic limitations of the system (Fig. S6).

**Figure S7: Young’s modulus decreases with temperature.** For each temperature, at least 4 measurements were taken on different locations on the sample. y-error bars represent the standard deviation across measurements. Beyond \( T_g \), nanoindentation was no longer capable of determining the Young’s modulus.
Figure S8: Nanowrinkles ($\lambda \approx 70$ nm) are orientated radially around a single etched hole.

Figure S9: Self-similar wrinkles are aligned along the 2D lattice. Nanowrinkles with square arrays of strain relief features ($a_0' = 2 \mu$m, $a_f' = 866$ nm) showed oriented secondary structure.
Figure S10: Physically etched hole patterns results in oriented nanowrinkles ($\lambda \approx 70$ nm) and nanofolds. SEM images of nanowrinkles with square arrays of strain relief features: (a) $a_0 = 2000$ nm, $a_f = 1000$ nm; (b) $a_0 = 600$ nm, $a_f = 300$ nm; and (c) $a_0 = 400$ nm, $a_f = 2000$ nm.

Figure S11: Formation of directed nanowrinkles across microscale distances with etched line patterns. Physical etching after chemical treatment with CHF$_3$ resulted in directed patterns for $w = 25$ µm and $a_0 = 50$ µm. The orientation of the wrinkles was affected within ~3 µm of the line edge.
Supplementary References


