# Templating Block Copolymer Film Structure via Substrate Topography


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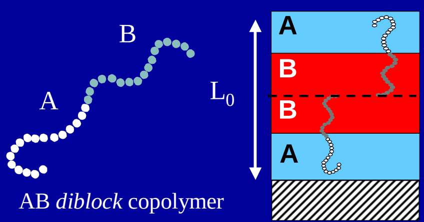
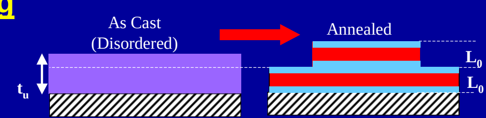
## Block Copolymer Self-Assembly and Nanoscopic Film Layering



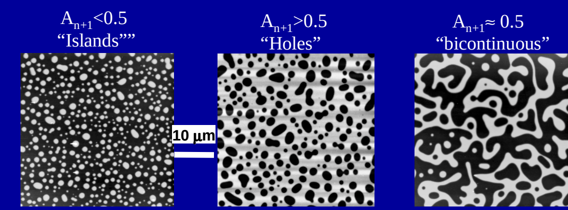

In thin films, block copolymer microphase separation is directed by surface energetics, which demands that specific polymer species reside at the air and substrate interfaces. In volume-symmetric BC systems, this typically results in lamella oriented parallel to the substrate with an equilibrium periodicity, $L_0$, in the range of 10-100nm. When the same block (e.g. A) is situated at each surface, an A-BB-A type layering develops.




Due to these effects, only films with thickness $t=nL_0$ are stable. Accordingly, films cast at an intermediate thickness ($t_u$) bifurcate, resulting in an $L_0$-high incomplete lamella on the film surface. The topology of this surface patterning is $t_u$ dependent.

### Thickness Dependent Surface Morphology

$A_{n+1}=(t_u/L_0)-n$



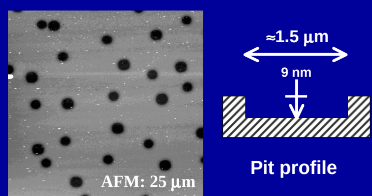

## Opportunities for Nanotechnology Applications

- Block Copolymers provide a *self-assembly* route to films with nm-scale internal layering.
- Thickness Dependent film morphology results in a range of surface relief structures with *constant* (Lo) nanometer scale amplitude.
- Topographically patterned substrates present a means to *template* block copolymer film behavior. Such films spontaneously exhibit a range of interesting architectures, which could potentially be utilized in layered opto-electronic and MEMS devices.


*Gradient high-throughput methods provide an efficient means of examining these effects.*

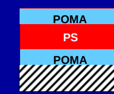
## Patterned Silicon Substrates

- 9 nm deep circular pits
- Two pit diameters chosen to reduce Airy diffraction pattern
  - Nominally 1.31 and 1.76 µm
- Pseudo-random arrangement of pits
  - 2 pits per 5 µm square
  - Suppresses pit-pit Bragg scattering

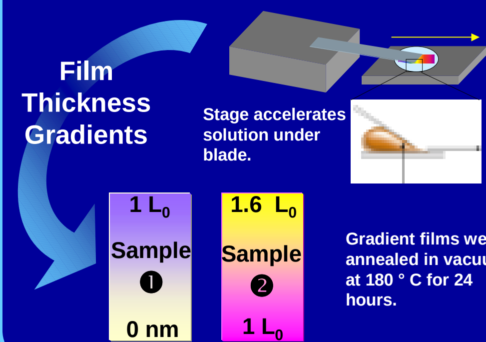



Pit profile

## Materials and Preparation

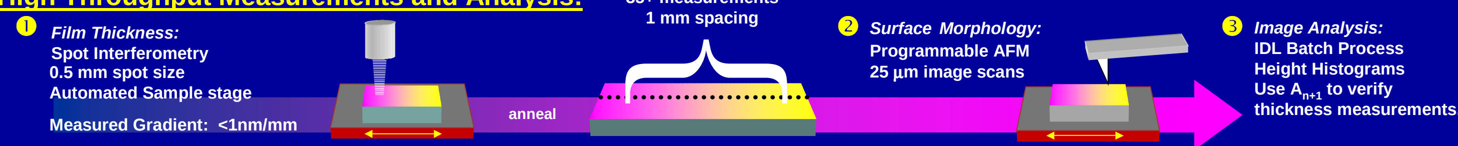


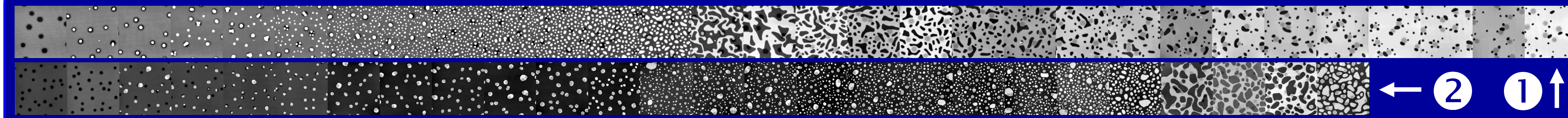

- Polystyrene-b-Poly(n-octyl methacrylate) (PS-b-POMA) block copolymer:
  - 43.5K MW, volume symmetric
  - Lamellar Motif, $L_0$=23 nm (measured by AFM)
  - POMA resides at substrate *and* air interface
- Film Thickness Gradient Libraries:
  - Films were cast from a 2 wt% toluene solution onto 40 mm long patterned substrate sections using the "Gradient Flow Coating" technique developed at NIST.



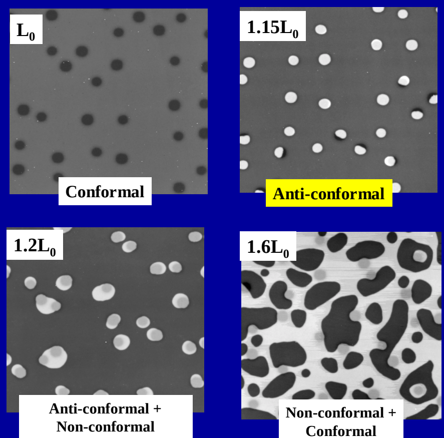

Gradient films were annealed in vacuum at 180 ° C for 24 hours.

## High Throughput Measurements and Analysis:





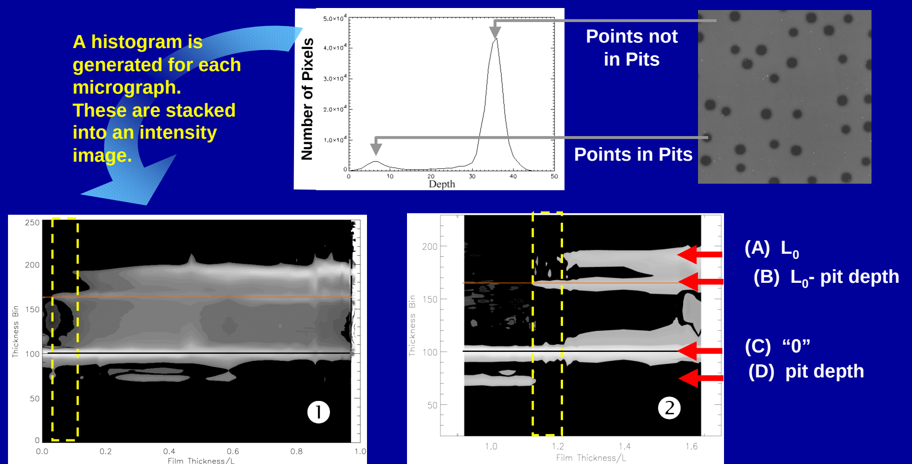
## Results and Conclusions:




The patterned substrate directly modifies the BC film surface patterns. As the film thickness increases, a range of film architectures, including the desired anti-conformal case, were observed. Because these films have well defined topography, with only a few height values relating to the pit depth and $L_0$, they are ideal candidates for testing instruments designed to measure "roughness correlations" in thin films. Indeed, anti-conformal films from this study were used to verify data analysis techniques for light scattering ellipsometry, a technique capable of characterizing the topography and roughness correlations in thin films.

## Informatics: Data Set Visualization

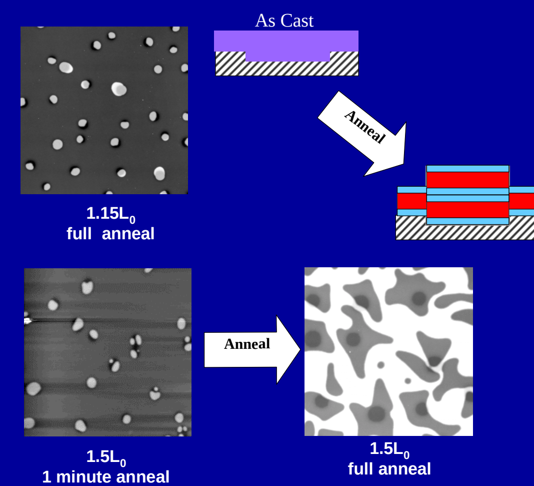
### *Height Histogram Maps*




Height Histogram Maps allow us to visualize the entire body of data and determine the thickness range over which a particular architecture is formed. These maps are constructed by generating height histograms from each AFM micrograph and assembling them as a function of film thickness into an intensity image. The horizontal bands indicate the different discrete heights formed by combining the substrate pit depth and "island height" ($L_0$).

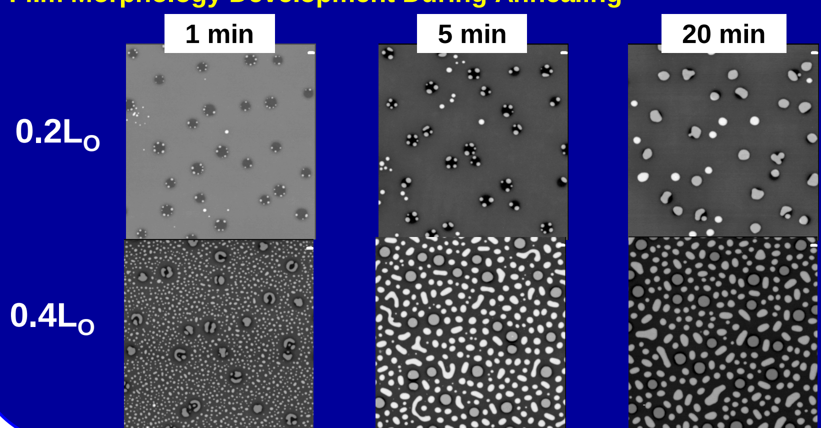
For example, pure conformal film architecture is indicated for thickness ranges over which bands *C* and *D* are exclusive. Likewise, pure anti-conformal behavior occurs for thicknesses that show only bands *C* and *D*. Anti-conformal behavior appears near $0.15L_0$ and $1.15L_0$ thicknesses. Here, the island area ($A_{n+1}$) approximately equals the pit area, i.e. 15% (highlighted in yellow).

## Substrate Topography Induced Island Nucleation

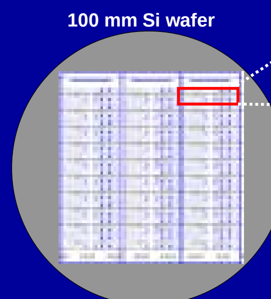


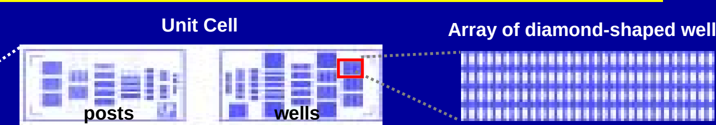

Our study indicates that these structured substrates actually nucleate island formation - the first observation (known to the authors) of its sort. Nucleation may be induced by thickness variations in the cast film caused by the substrate pits. If the film is locally thicker above a pit, upon annealing island formation may be more favorable there. Alternatively, some of our micrographs (see above right) suggest that pit edges are important in island nucleation. A more careful study of the island formation and growth kinetics will illuminate more about this process.

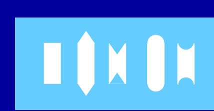
## Film Morphology Development During Annealing




## Future Directions: Substrate Topography Patterns for Combinatorial Science



Topographic Shape Primitives

- Substrate designed for combinatorial studies of topographic thin film templating.
- Unit cell is repeated 10 times along a strip, allowing a second gradient variable (film thickness, composition, surface energy) to be examined.
- Shape primitives explore geometry, corners and curvature.
- Three size scales (3, 10 and 20 µm) allow a variety of polymer thin film phenomena (wetting, self-assembly, phase separation) to be examined.

Wafer Design and fabrication by John Dagata, Precision Engineering Division