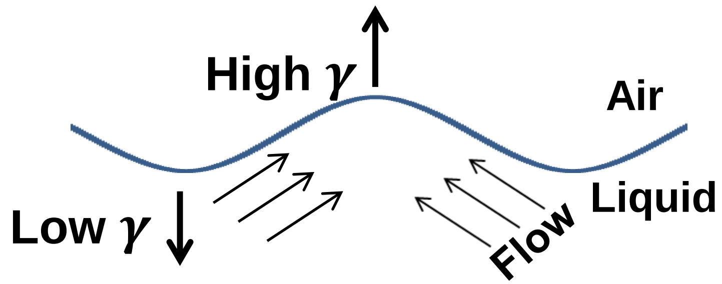
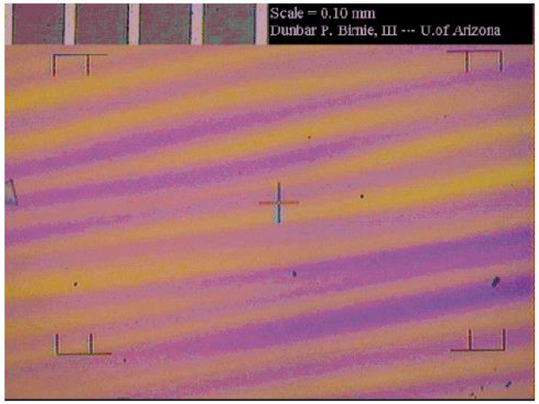
Surface Tension Gradients Can Drive Flow, …



- Surface tension gradients, thermally or chemically induced, drive convection which manifests itself in various phenomena

‘Tears’ of Wine

Striation Defects in Spin Coating



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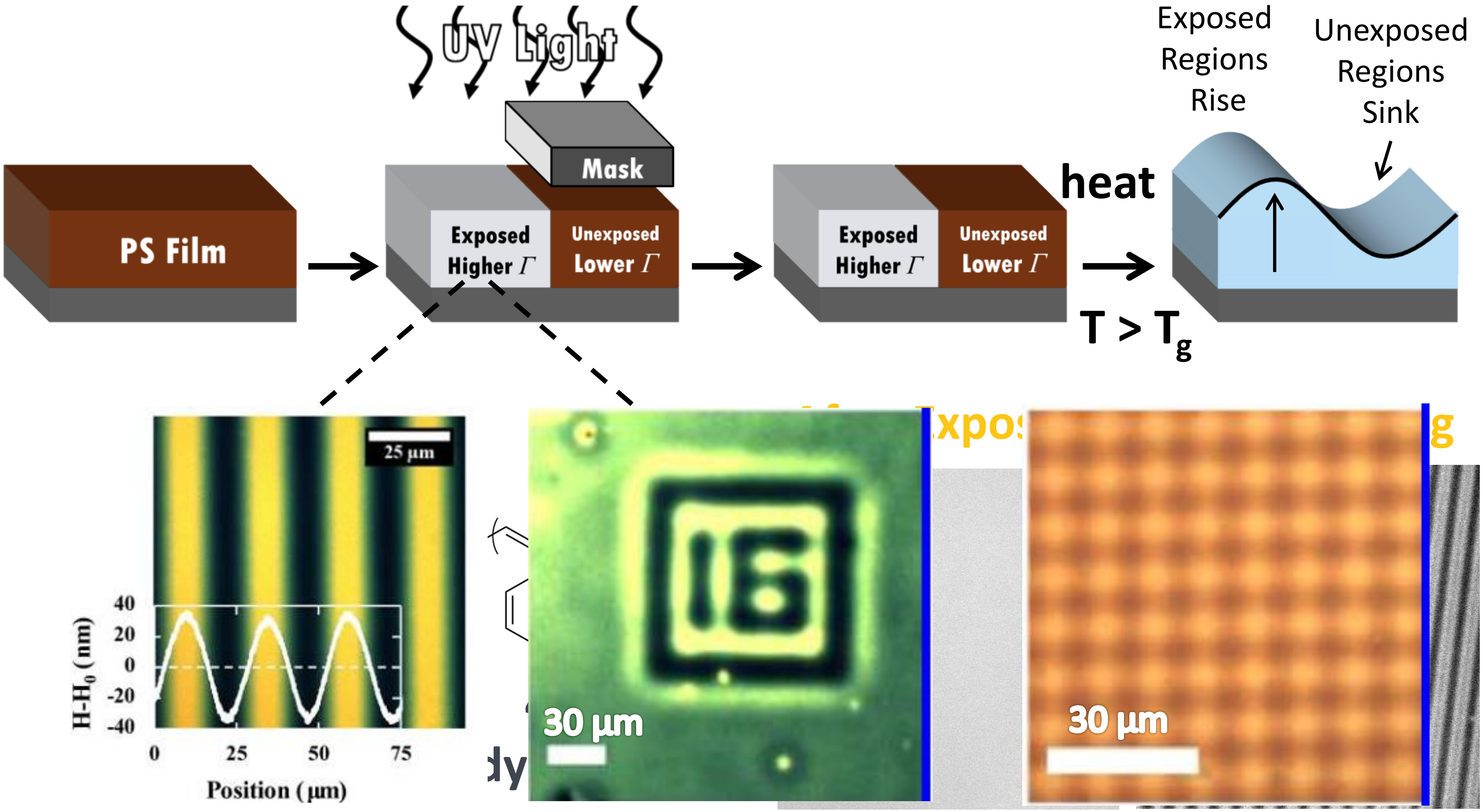
http://en.wikipedia.org/wiki/File:Wine_legs_shadow.jpg || Birnie, J. Mat. Res. 2011

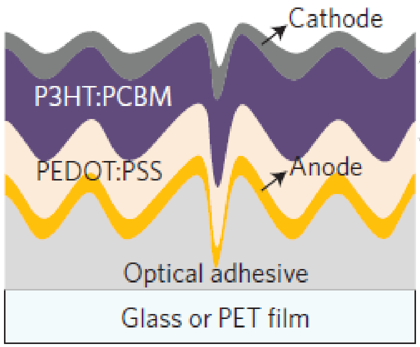
… We Can Make a Patterning Process Out of It & …

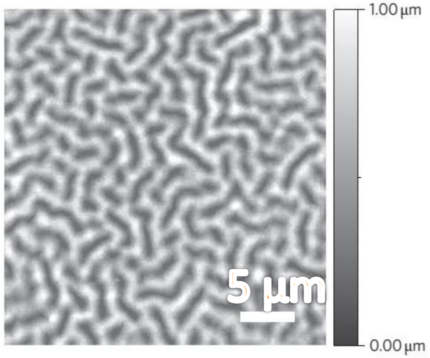


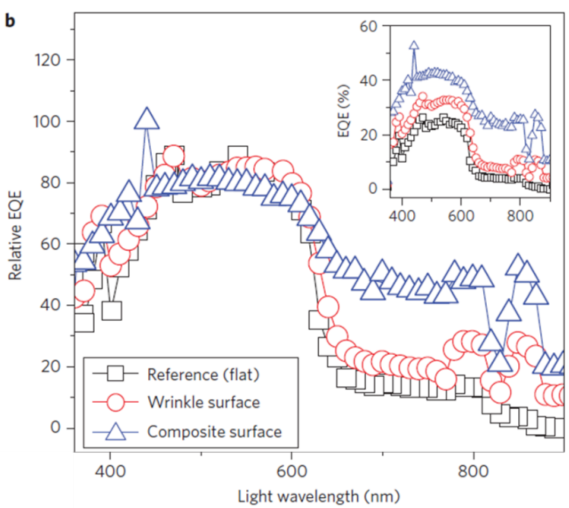
- Katzenstein *et al, ACS Macro Lett* 2012

… Such a Process Has Several Applications & Advantages

'Wrinkled' Solar Cells



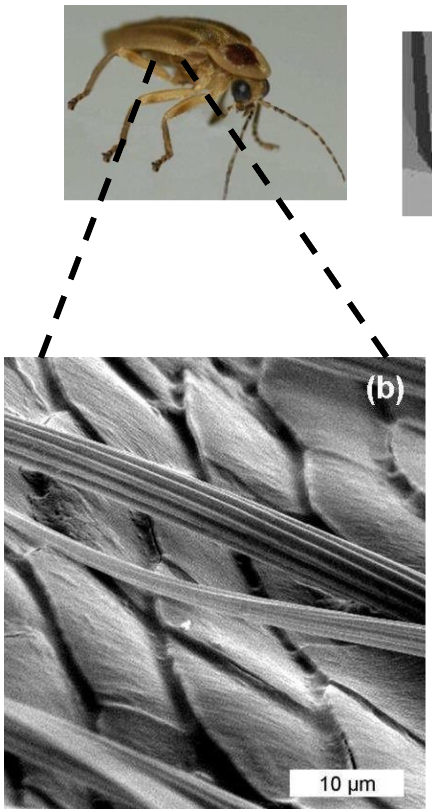


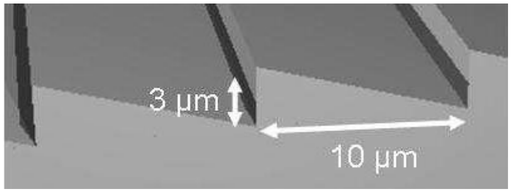


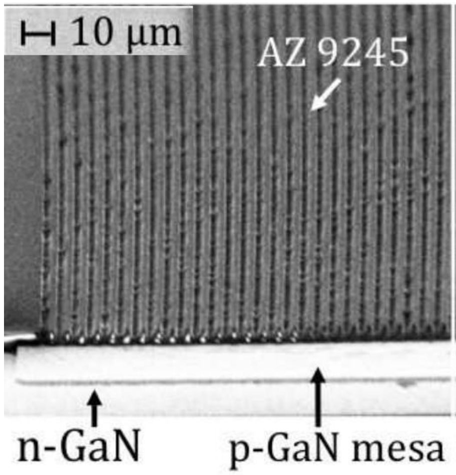
47% increase in photocurrent

- Kim *et al.*, Nature Photonics 2012.

Firefly-Inspired LEDs







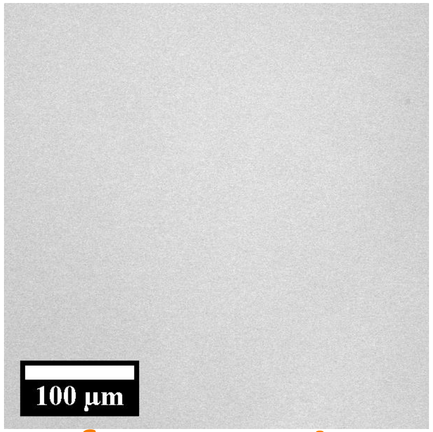
55% increase in emitted power

- Bay *et al.*, Optics Express 2013.

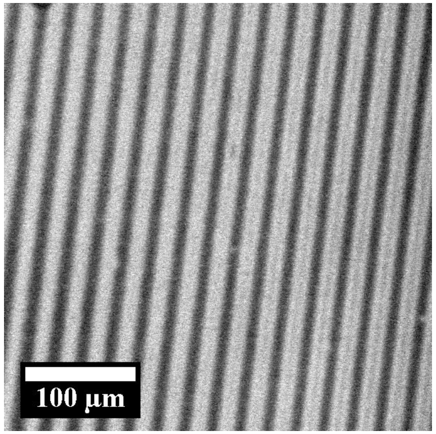
A Closer Look at the Evolution of Topography

- When heated > T_g, features rise, then decay

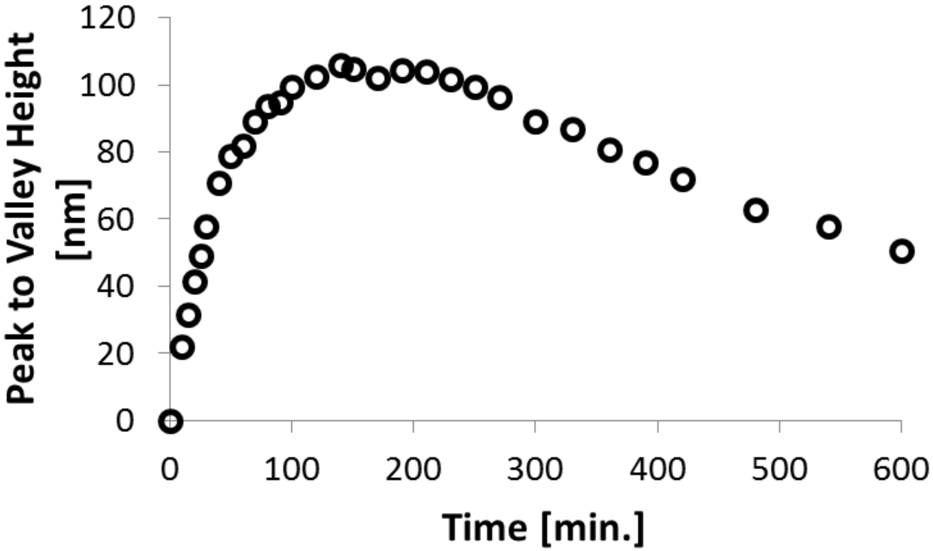
After Exposure



After Heating



Peak-to-Valley Height v.s. Heating Time

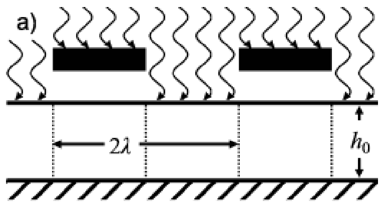


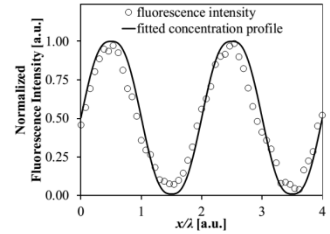
Linewidth: 12.5 µm **Film Thickness:** 145 nm
Temperature: 120°C

- Katzenstein *et al, ACS Macro Lett* 2012

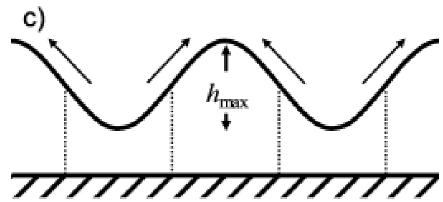
The Physics Behind the Evolution of Topography

1. Exposure generates a different species under the mask gaps

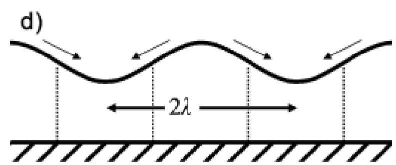




2. On heating, **Marangoni forces pull fluid** to the exposed regions; **capillary forces oppose** this flow



3. With time, the **Marangoni driving force decays** (∵ diffusion dissipates the initial concentration gradient) while the **opposing capillary force grows** (∵ features grow) . Eventually features decay



These dynamics, and hence feature height & timescale, are affected by **geometry** (h_0, λ), **material properties** (μ, D, γ) and **experimental parameters** (E, T).

Modeling the Evolution of Topography

- The **thin film equation** describes the evolution of local film height

$$\frac{\partial h}{\partial t}+\frac{\partial}{\partial x}\left[\left(\frac{1}{3A}\right)h^3\frac{\partial}{\partial x}\left\{\gamma\frac{\partial^2 h}{\partial x^2}\right\}+\left(\frac{1}{2}\right)h^2\frac{\partial \gamma}{\partial x}\right]=0$$

$\boldsymbol{A \equiv \lambda^2/{h_0}^2}$

Film height | Capillary Dissipation | Marangoni forcing

- The **convection-diffusion equation** tracks the local concentration of the photo-generated species.

$\boldsymbol{Pe \equiv h_0\gamma_0/\mu D}$

$$\frac{\partial c}{\partial t}-\left(\frac{1}{Pe}\right)\frac{\partial^2 c}{\partial x^2}+\frac{\partial}{\partial x}\left[c\left\{\left(\frac{1}{2A}\right)h^2\frac{\partial}{\partial x}\left(\gamma\frac{\partial^2 h}{\partial x^2}\right)+h\frac{\partial \gamma}{\partial x}\right\}\right]=0$$

Concentration | Diffusion | Capillary Flux | Marangoni Flux

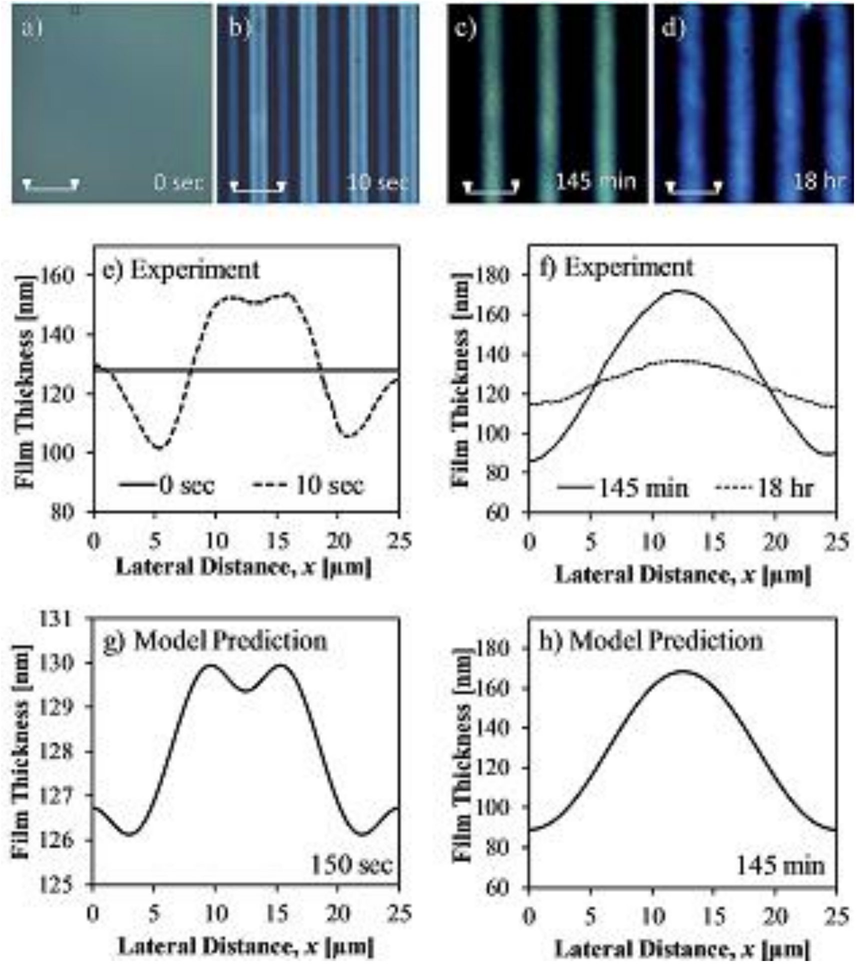
- **Model Simplifications:**
  - Thin film (i.e. film is vertically homogeneous in composition & temperature)
  - van der Waals & gravitational forces neglected
  - Surface tension assumed to be linearly related to concentration:

$\boldsymbol{(\Delta\gamma)c}$

$$\gamma = 1+(\Delta\gamma)c$$

Simulating the Evolution of Topography

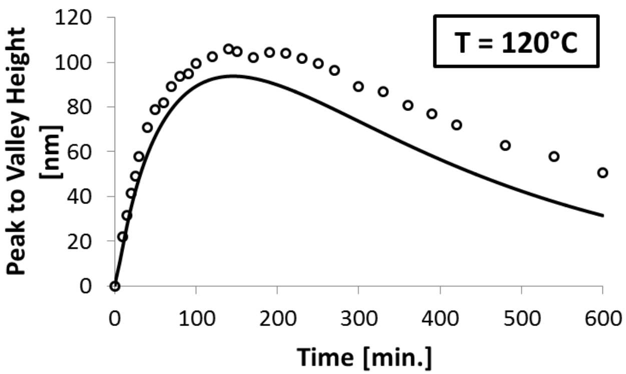
- Experimental observations v.s. Model Predictions at short and long times:

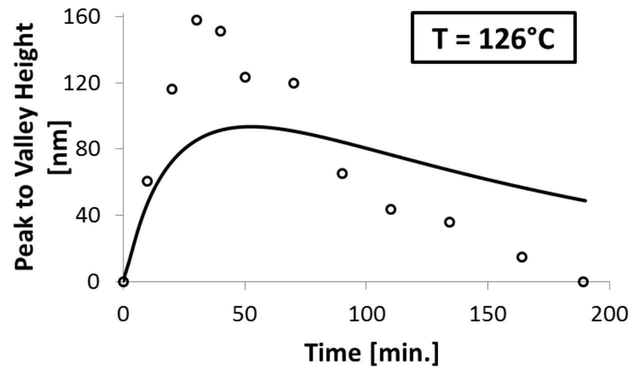


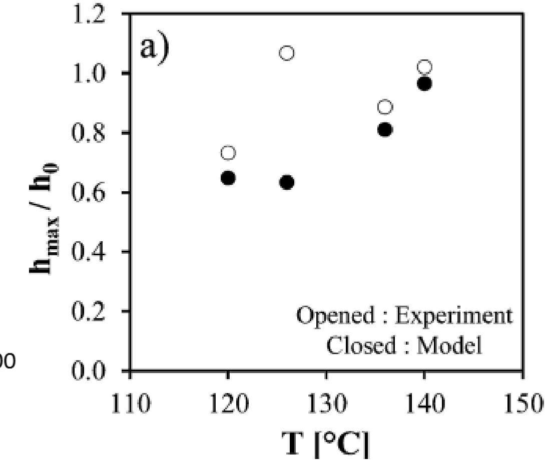
Linewidth: 12.5 µm, **Film Thickness:** 145 nm

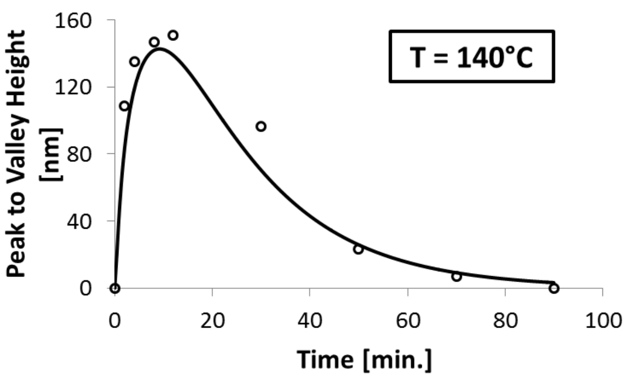
Simulating the Evolution of Topography

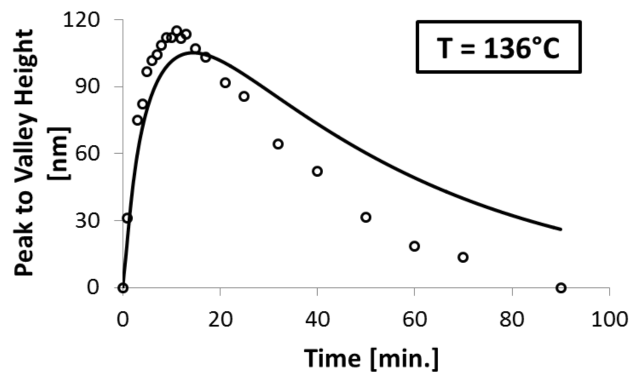
- Experimental observations v.s. Model Predictions at four different temperatures:

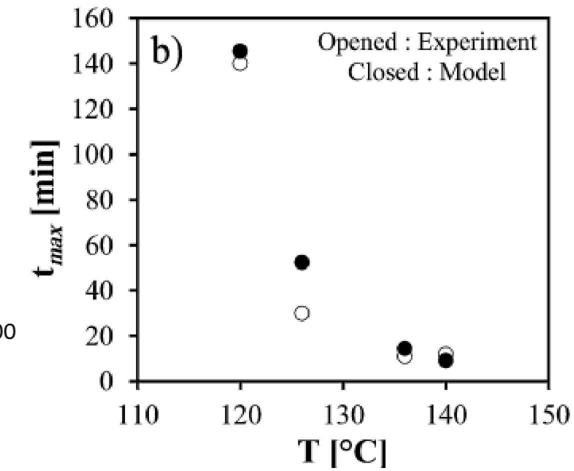












Linewidth: 12.5 µm, **Film Thickness** (in order of increasing T)**:** 145, 148, 130, 148 nm

Predicting Topography Evolution & Targeting Specific Structures Efficiently

- An **approximate analytical solution** was obtained by neglecting second (or higher) order effects

$$c = \frac{1}{2} + \xi(x,t) = \frac{1}{2} + \hat{\xi}(t)\frac{\cos(\pi x)}{2}$$

$$h = 1 + \eta(x,t) = 1 + \hat{\eta}(t)\frac{\cos(\pi x)}{2}$$

- **Maximum peak-to-valley height** attained:

$$\boxed{\hat{\eta}_{max} = \frac{\pi^2 \frac{\Delta\gamma c_0}{2}}{\psi_1 - \psi_2}\left\{\exp\left[\frac{\psi_1}{\psi_1 - \psi_2}\ln\left(\frac{\psi_2}{\psi_1}\right)\right] - \exp\left[\frac{\psi_2}{\psi_1 - \psi_2}\ln\left(\frac{\psi_2}{\psi_1}\right)\right]\right\}}$$

- **Heating time** to attain maximum height:

$$\boxed{t(\hat{\eta}_{max}) = \frac{\ln\left(\frac{\psi_2}{\psi_1}\right)}{\psi_1 - \psi_2}}$$

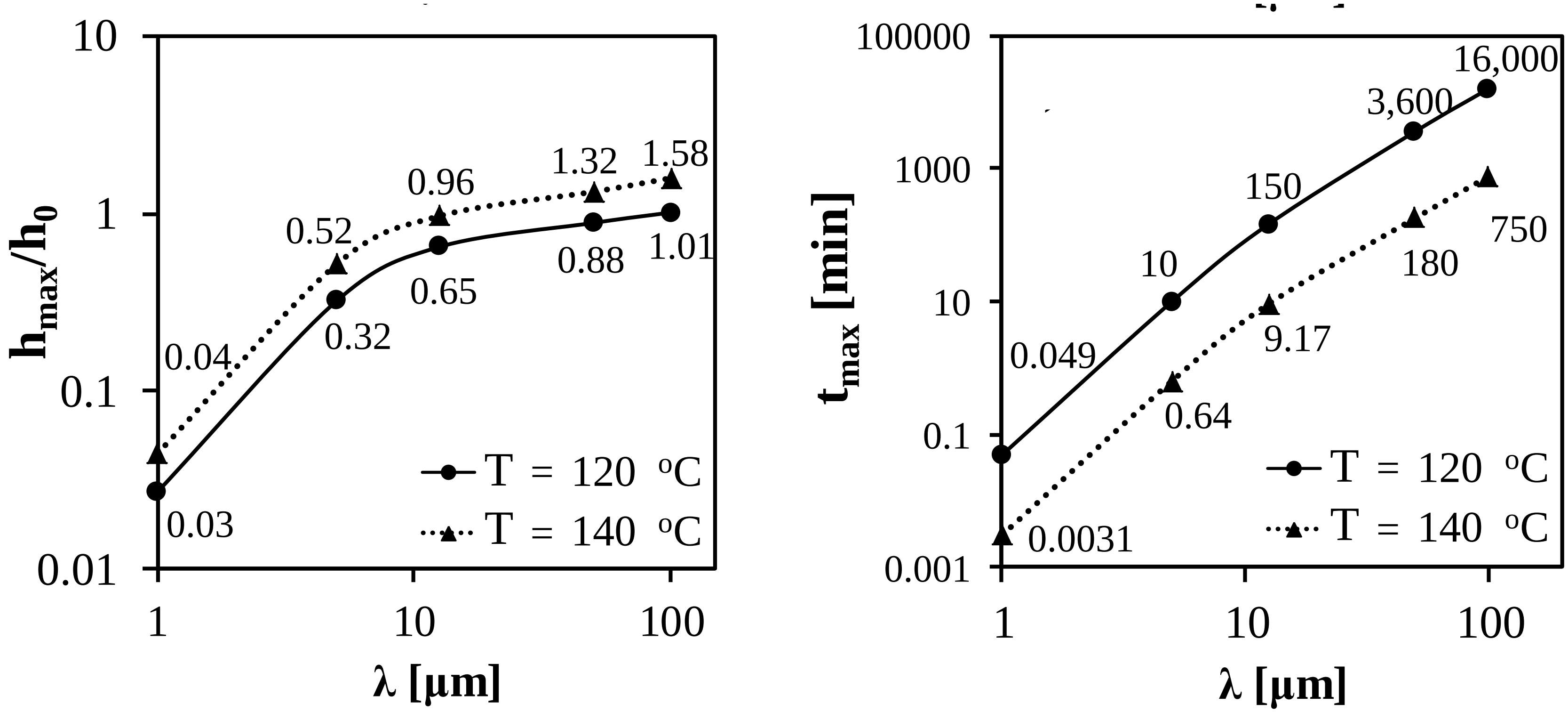
$$\psi_1, \psi_2 = \frac{\alpha \pm \sqrt{\alpha^2 - \beta}}{2}$$

$$\alpha = \left(1 - \frac{\pi^2}{3A}\right)\pi^2\frac{\Delta\gamma c_0}{2} - \pi^2\left(\frac{1}{Pe} + \frac{\pi^2}{3A}\right)$$

$$\beta = \frac{\pi^6}{3A}\left(\frac{4}{Pe} - \frac{\Delta\gamma c_0}{2}\right)\left(1 + \frac{\Delta\gamma c_0}{2}\right)$$

The Analytical Solution Yields Important Insight

- Increased resolution has a penalty in terms of the achievable feature height



- A 20°C increase in T increases feature size by ~60% while reducing annealing time by over an order of mag.

Simulating 2D Patterns

- Thin-film equation for film topography:

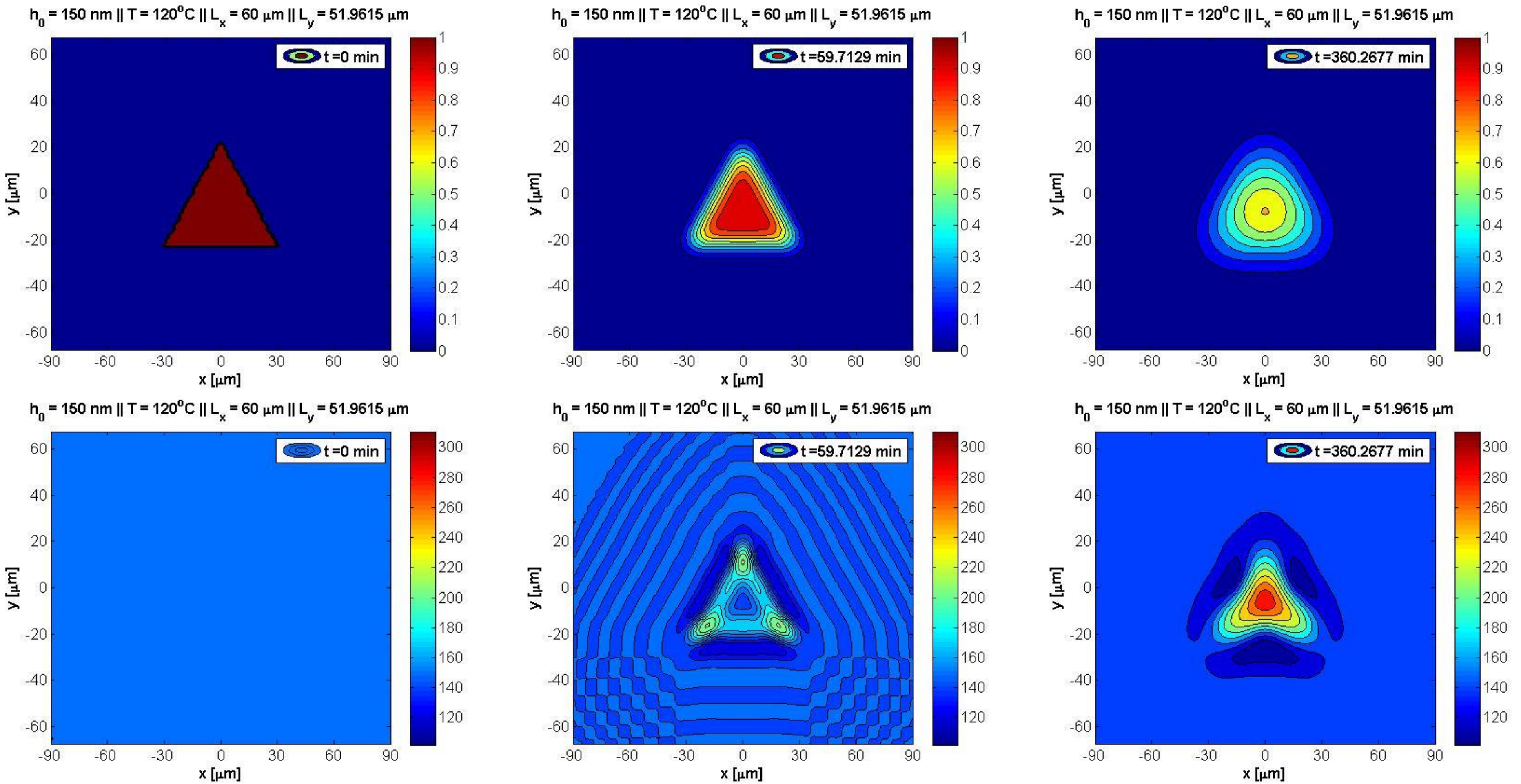
$$\frac{\partial h}{\partial t} + \nabla . \left[\left(\frac{1}{3A} \right) h^3 \nabla \{ \gamma \nabla^2 h \} + \left(\frac{1}{2} \right) h^2 \nabla \gamma \right] = 0$$

- Convection-diffusion equation for concentration profile:

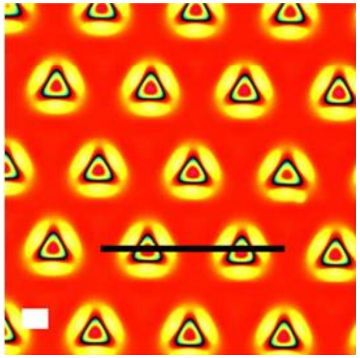
$$\frac{\partial c}{\partial t} - \left(\frac{1}{Pe} \right) \nabla^2 c + \nabla \left[c \left\{ \left(\frac{1}{2A} \right) h^2 \nabla (\gamma \nabla^2 h) + h \nabla \gamma \right\} \right] = 0$$

Simulating 2D Patterns

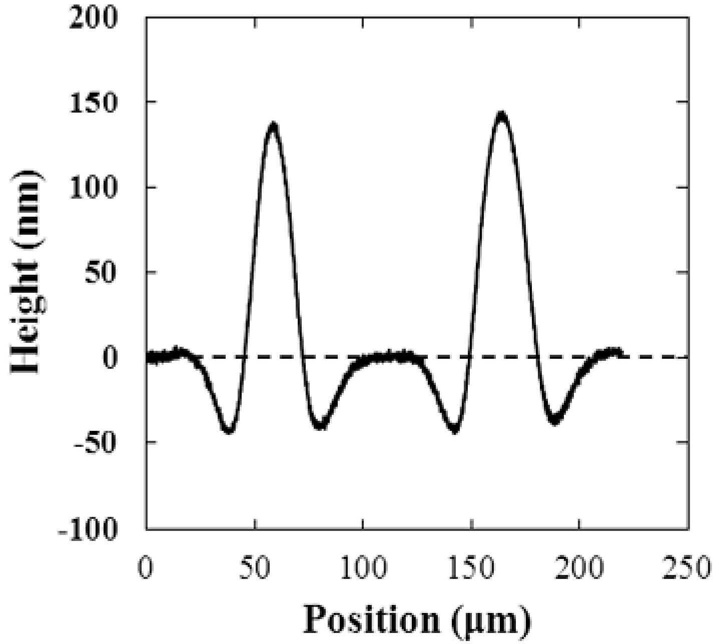
t = 0 min.	t = 1 hr.	t = 6 hrs.



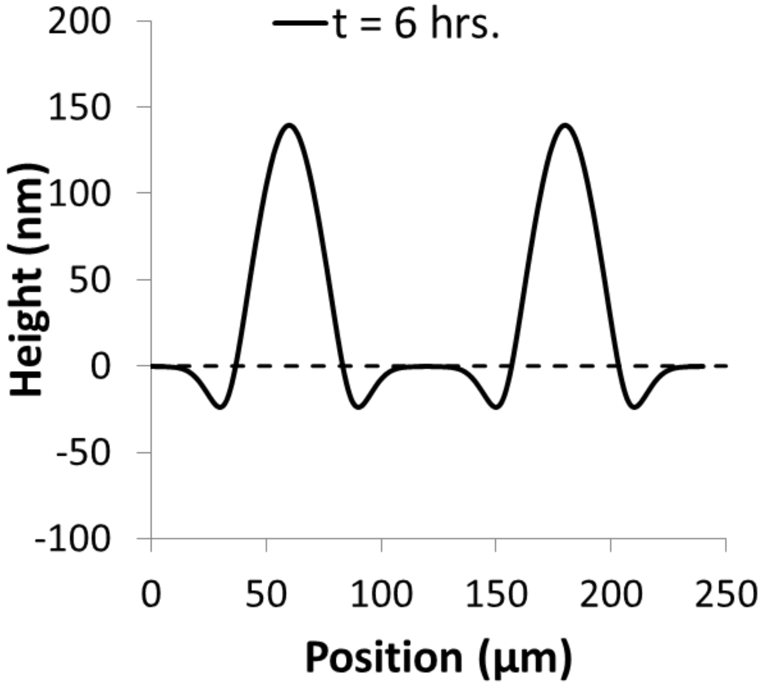
Comparison with Experiment



Experiment



Simulation



- Katzenstein *et al, ACS Macro Lett* 2012

Conclusions

Surface Tension Driven Patterning

- Film dynamics are driven by Marangoni and capillary flows as well as diffusion of the photo-generated species.

- Increased resolution incurs a cost in the height of the resulting features.

- The largest features result for large values of $\boldsymbol{Pe \equiv h_0 \gamma_0 / \mu D}$ (as well as the surface tension differential).