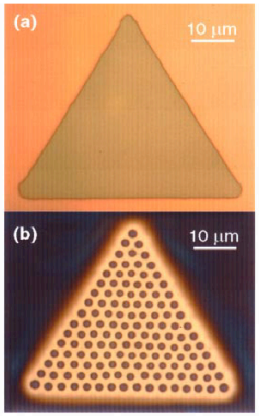
From Pillars and Rings to Infinite Arrays:
Pattern Formation in Thin Polymer Films due to Electrohydrodynamic Instabilities

Institute for Bioengineering and Nanotechnology
Singapore



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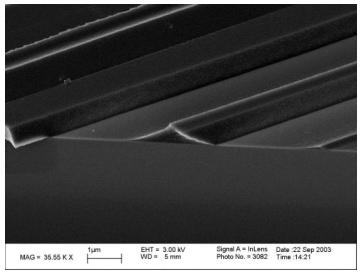
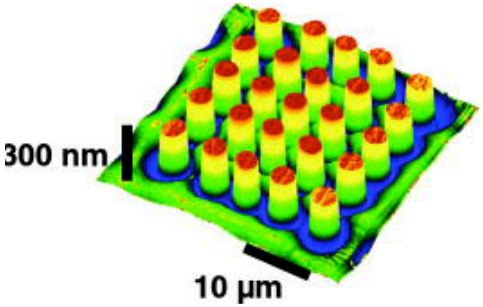
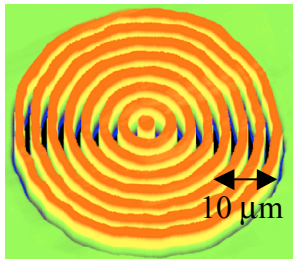
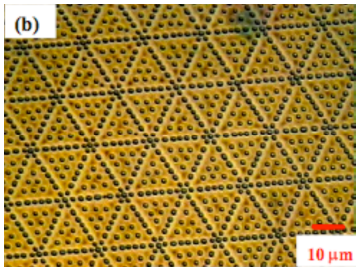


Princeton Center for Complex Materials

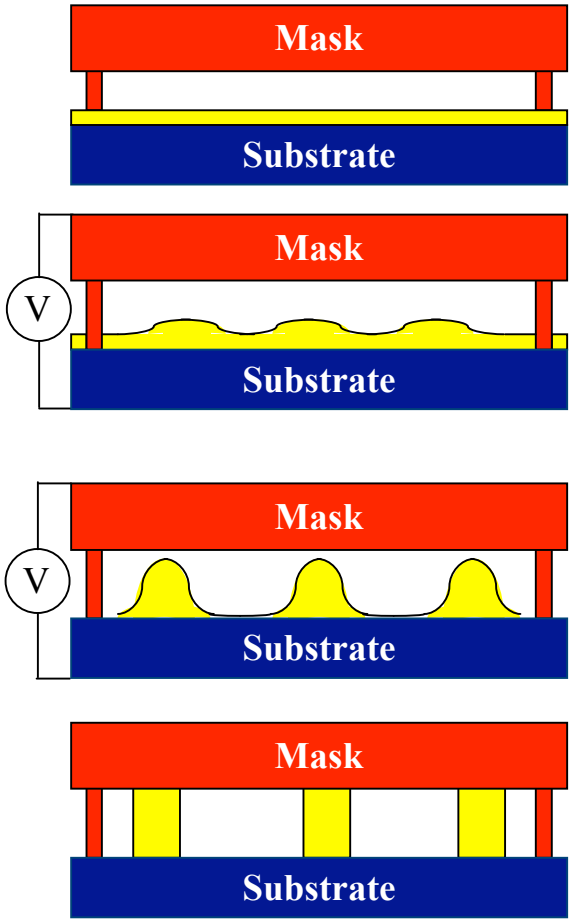
via NSF MRSEC and AFOSR

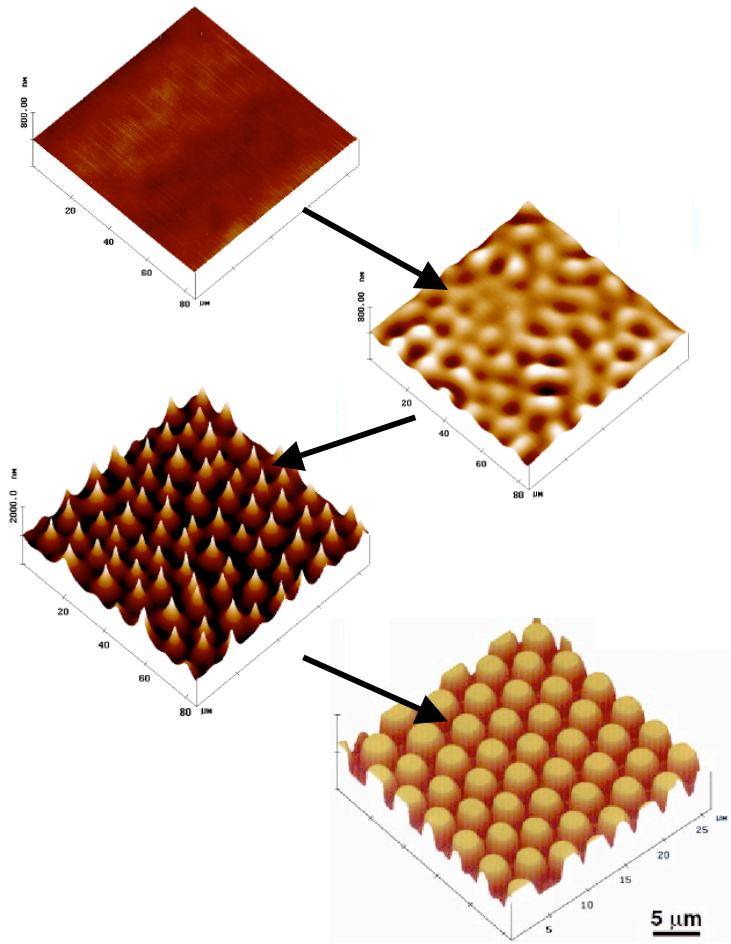






Origin of Patterns



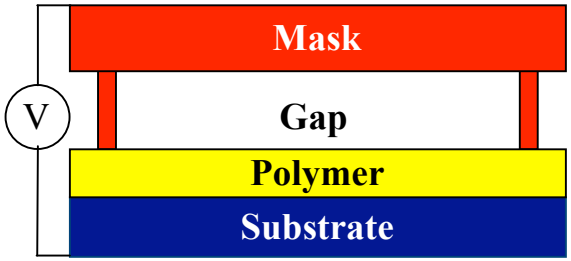


- electrostatic forces identified as driving force
- surface tension opposes increase in curvature of the interface
- later growth reminiscent of Taylor cones

➔linear stability analysis should identify fastest growing wavelength

adapted from: Chou, *et al., J. Vac. Sci. Tech. B* **17** 3197 (1999)
Schaffer, *et al.*, *Europhysics Lett.* **53** 518 (2001)
Lin, *et al.*, *Macromolecules* **35** 3971 (2002)

What We Knew—Unpatterned Mask Experiments



	S.Y. Chou (*air gap*)	T.P. Russell (*air gap*)	T.P. Russell (*filled gap*)
Mask-substrate spacing (H)	100-645 nm	236-2700 nm	705-1320 nm
Initial film thickness (h_o)	55-103 nm	93-740 nm	140-740 nm
Surface tension (γ)	33 mN/m	30-39 mN/m	1.2-6.1 mN/m
Gap dielectric constant (ε^g)	1.00	1.00	2.46-5.24
Polymer dielectric constant (ε)	3.5-4	2.5-5.5	2.5-5.24
Applied voltage ($\|V_e\|$)	0-90 V	20-60 V	19-50 V
Contact potential (V_c)*	~1 V		
Polymer conductivity (σ)*	10^{-10}-1 $C^2s/kg/m^2$		
Period (λ)	1.7-8 μm	1.0-54 μm	4.4-21 μm
Diameter (D)*	0.6-5 μm	2.2-23 μm	1.7-14 μm
Time to formation (t)*	5-80 min	1-120 h	1-24 h

* Limited information

WHY are specific patterns formed?

Broad applicability of linear analysis suggests that pattern selection should be predictable from nonlinear interactions.

HOW does the film evolve and what controls the ultimate state?

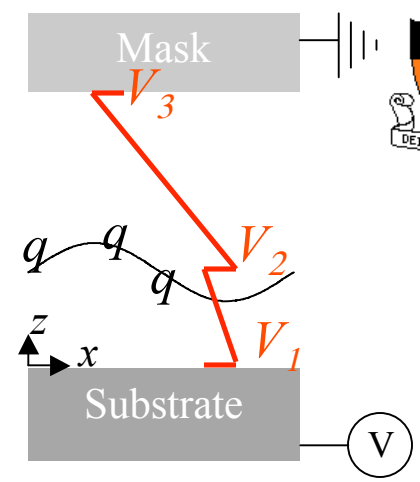
Simulations based on lubrication approximation should be able to follow the process to completion to determine whether patterns are kinetically or thermodynamically controlled.

CAN we make smaller or endlessly periodic features ?

Best route to submicron (nano?) structures is to decrease the interfacial tension with a polymer/polymer bilayer and make one component conducting.

Subtle conformal features on the mask might align large domains and suppress “polycrystallinity”.

Lubrication Theory: perfect dielectric



$$\nabla^2\psi = 0 \qquad \nabla^2\psi^g = 0$$

$$q = \left\| \varepsilon\varepsilon_o \boldsymbol{E} \right\| \cdot \boldsymbol{n} \qquad \psi - V = V_1 \qquad \psi^g - \psi = V_2 \qquad \psi^g = -V_3$$

$$-\nabla p + \mu\nabla^2\boldsymbol{u} = 0 \qquad \nabla\cdot\boldsymbol{u} = 0$$

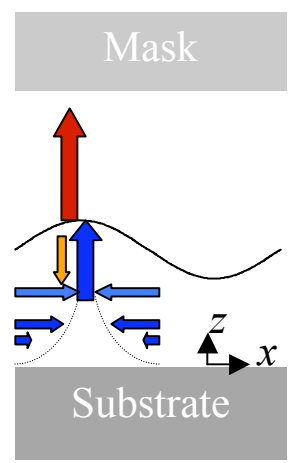
$$\frac{1}{2}\left\| \varepsilon\varepsilon_o\left[(\boldsymbol{E}\cdot\boldsymbol{n})^2 + (\boldsymbol{E}\cdot\boldsymbol{t}_x)^2 + (\boldsymbol{E}\cdot\boldsymbol{t}_y)^2\right]\right\| - \left[-p + \mu\boldsymbol{n}\cdot\left(\nabla\boldsymbol{u} + \nabla\boldsymbol{u}^t\right)\cdot\boldsymbol{n}\right] + \gamma\kappa = 0$$

Electrical Viscous Surface Tension

$$q\boldsymbol{E}\cdot\boldsymbol{t}_i - \mu\boldsymbol{t}_i\cdot\left(\nabla\boldsymbol{u} + \nabla\boldsymbol{u}^t\right)\cdot\boldsymbol{n} = 0 \qquad \boldsymbol{u} = \boldsymbol{0}$$

$$\frac{\partial h}{\partial t} = u_z - u_x h_x - u_y h_y$$

$$\frac{\partial q}{\partial t} + \boldsymbol{u}\cdot\nabla_s q = q\boldsymbol{n}\cdot(\boldsymbol{n}\cdot\nabla)\boldsymbol{u} + \sigma\boldsymbol{E}\cdot\boldsymbol{n}$$

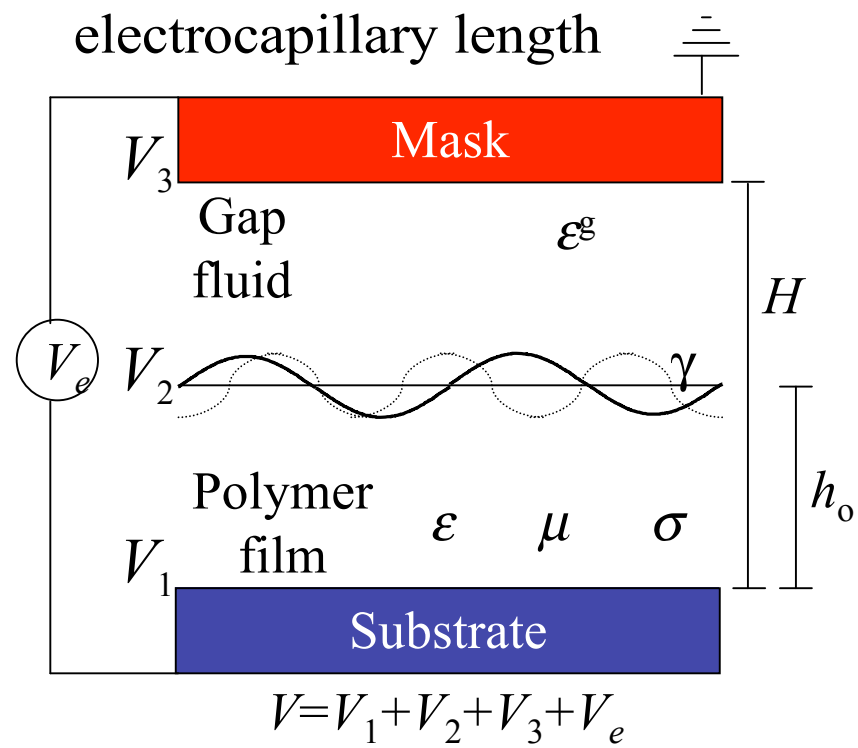


Scaling

$$\bar{z} = \frac{z}{H} \qquad \bar{x}, \bar{y} = \frac{x}{L}, \frac{y}{L} \qquad L = H\sqrt{\gamma H / \varepsilon^g \varepsilon_o V^2}$$

electrocapillary length

$\frac{H}{L} = \sqrt{\frac{\varepsilon^g \varepsilon_o V^2}{\gamma H}}$	$= 0.02 - 6.04$
$\bar{h}_o = \frac{h_o}{H}$	$= 0.07 - 0.72$
$\frac{\varepsilon}{\varepsilon^g}$	$= 0.56 - 5.5$
$S = \frac{\mu \gamma \sigma H^3}{\varepsilon^{g3} \varepsilon_o{}^3 V^4}$	$\approx 10^{-1} - 10^{16}$

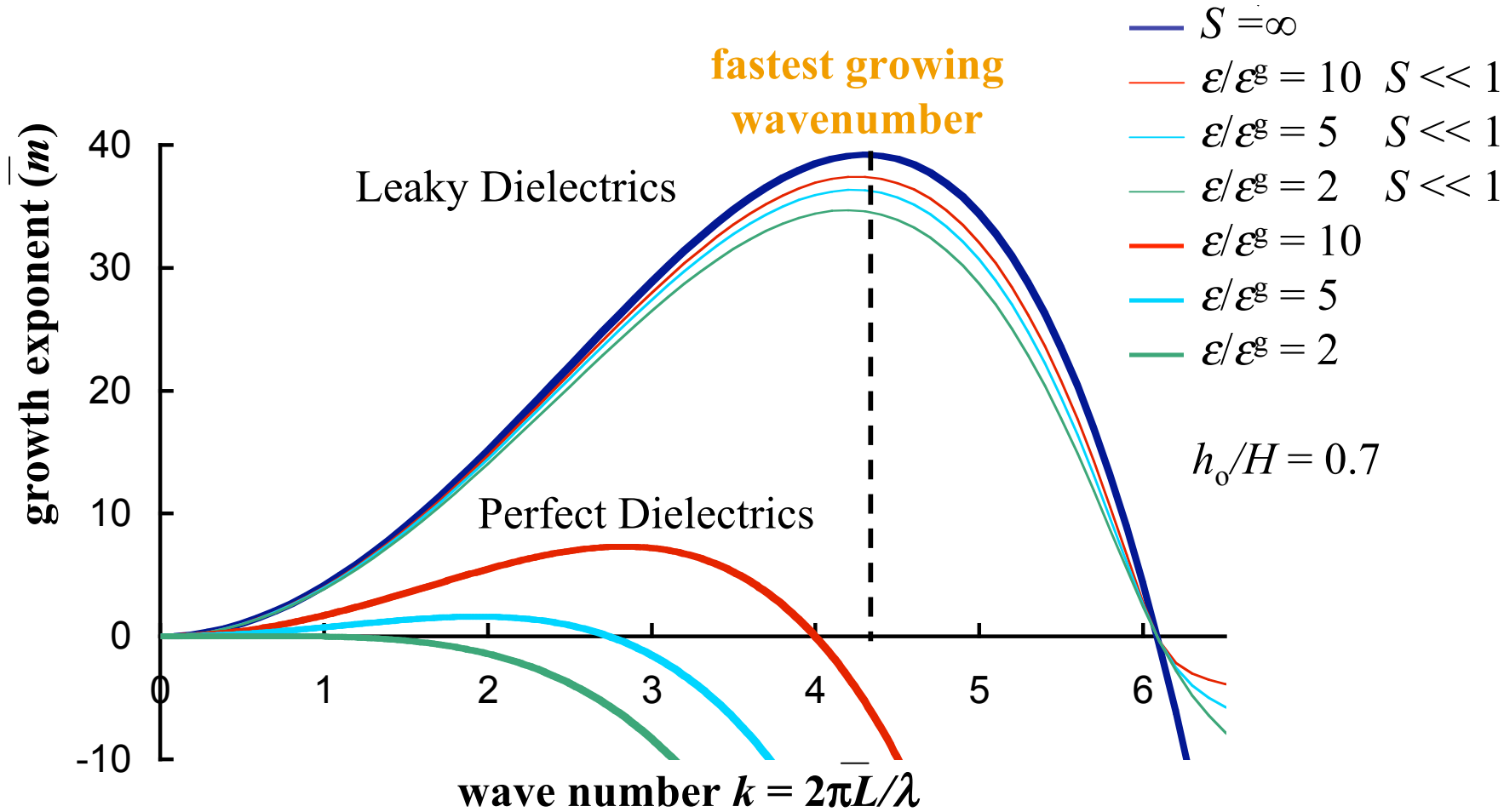


$$\lambda = \frac{2\pi L}{\bar{k}} \qquad \bar{t} = \frac{t}{\tau_p} \qquad \bar{m} = m\tau_p \qquad \tau_p = \frac{\mu \gamma H^3}{\left(\varepsilon^g \varepsilon_o V^2\right)^2}$$

Model Results

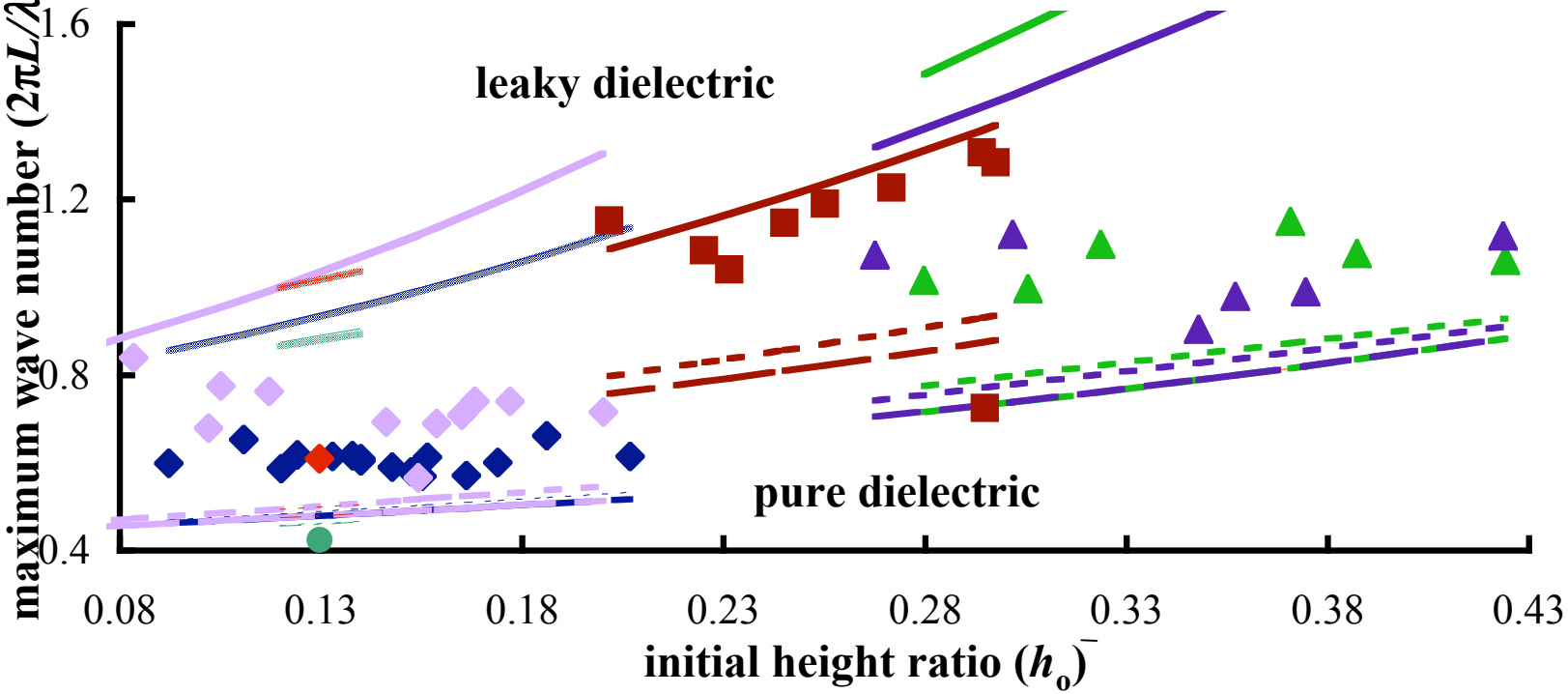
lubrication approximation $H^2/L^2 \ll 1$

$$\bar{h} = \bar{h}_o + \tilde{h}\, e^{i\bar{k}\cdot\bar{x}_s + \bar{m}\bar{t}}$$



L.F. Pease III and W.B. Russel, *JNNFM* 2002

Comparison of Fasted Growing Wavelength with Pillar-to-Pillar Spacing



Polymer	Gap	Symbol	h_o (nm)	H (nm)	γ (mN/m)	V (V)	$\varepsilon / \varepsilon^g$	H/L
PS 108K	Air		120	600-1730	30	50	2.5	0.67-1.13
PS 108K	Air		120	450-1010	30	30	2.5	0.53-0.79
PS 580	Air		140	1080	27.8	50	2.5	0.88
PMMA 98.5K	Air		100	235-380	29.7	30	3.6	0.88-1.10
PMMA 98.5K	Air		100	235-360	29.7	37	3.6	1.10-1.35
PSBr 127K	Air		125	390-620	30	30-40	5.5	0.68-1.13
PI 40K	Air		140	1080	32	20	2.4	0.34

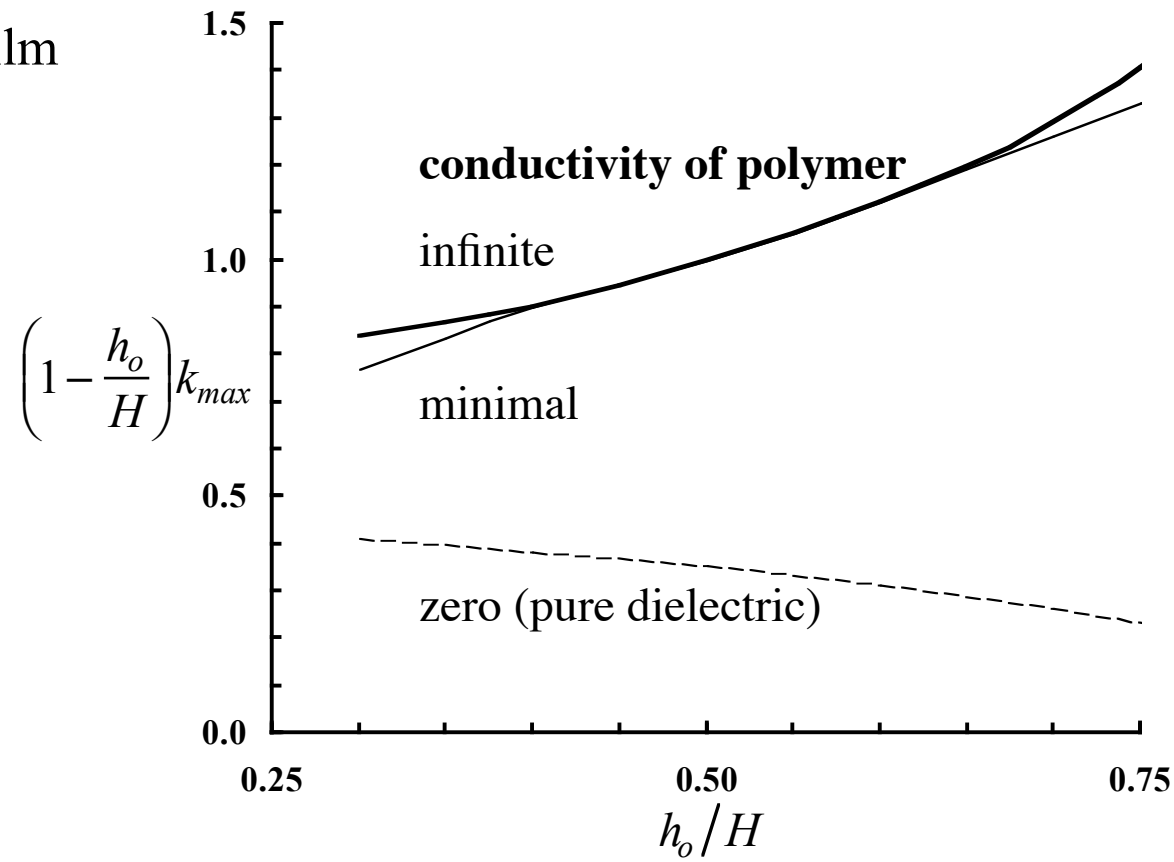
data from T.P. Russell *et al.* for air-filled gaps

L.F. Pease III and W.B. Russel *Langmuir* 2004

$$\lambda_{max} = \left(\frac{\gamma H}{\varepsilon_o V^2}\right)^{1/2} \frac{2\pi H}{k_{max}}$$

To reduce the wavelength λ_{max}

- decrease the total gap H
- increase the voltage V
- **decrease the surface tension γ**
- increase k_{max} by decreasing the air gap H-h_o
- make the polymer film conductive

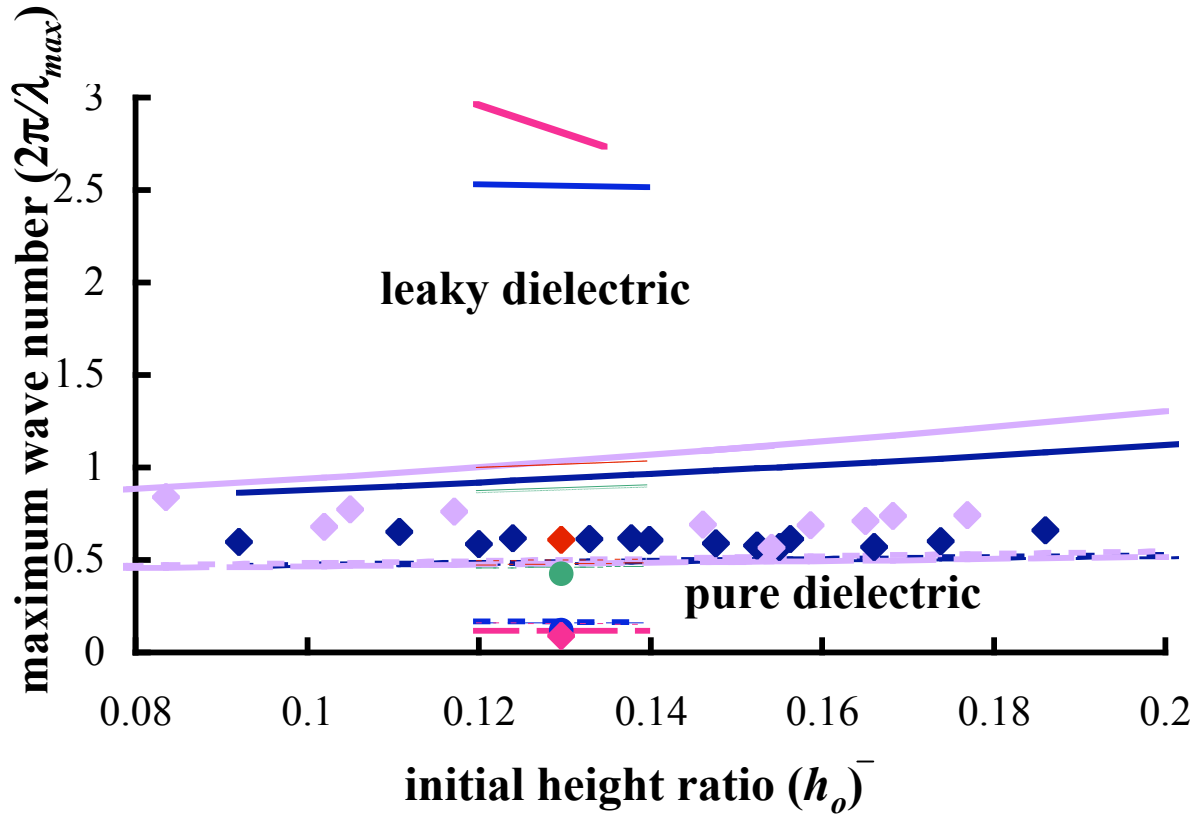


Comparison of Fasted Growing Wavelength with Spacing for Fluid-Filled Gaps

expectation: reduction in spacing due to lower interfacial tension

realization: spacing not reduced in proportion because dielectric contrast also reduced

implication: restore dielectric contrast by adding conductivity **[still trying!!]**

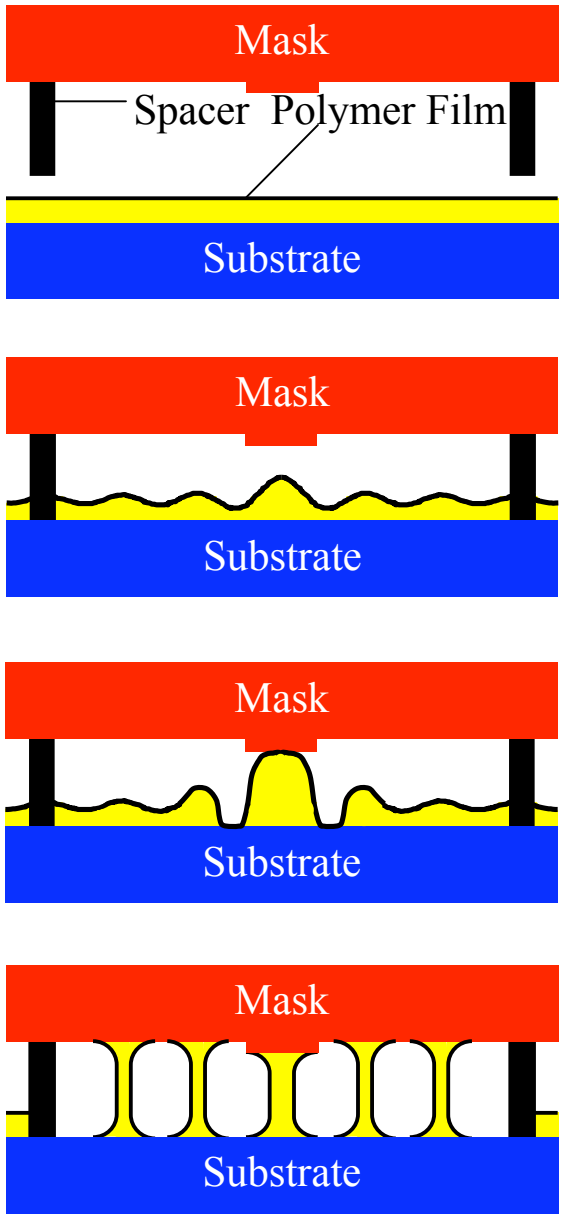


Polymer	Gap	Symbol	h_o (nm)	H (nm)	γ (mN/m)	V (V)	$\varepsilon / \varepsilon^g$	H/L
PS 580	Air	◆	140	1080	27.8	50	2.5	0.88
PS 580	ODMS	◆	140	1080	0.64	50	0.85	9.87
PI 40K	Air	●	140	1080	32	20	2.4	0.34
PI 40K	ODMS	●	140	1080	1.4	20	0.81	2.75

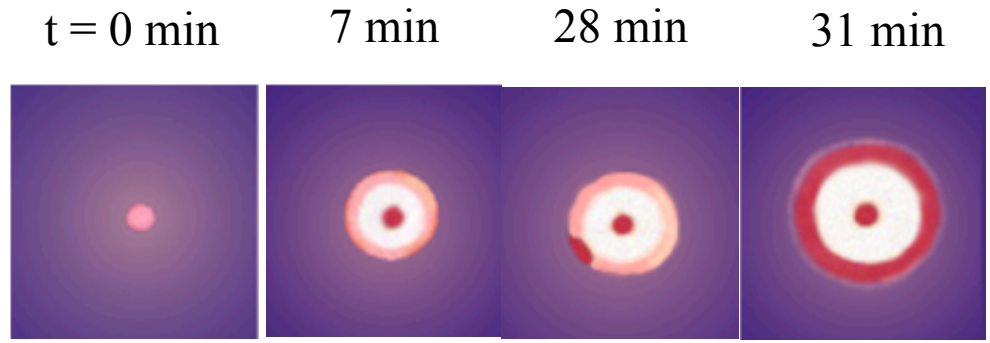
data from T.P. Russell *et al.*

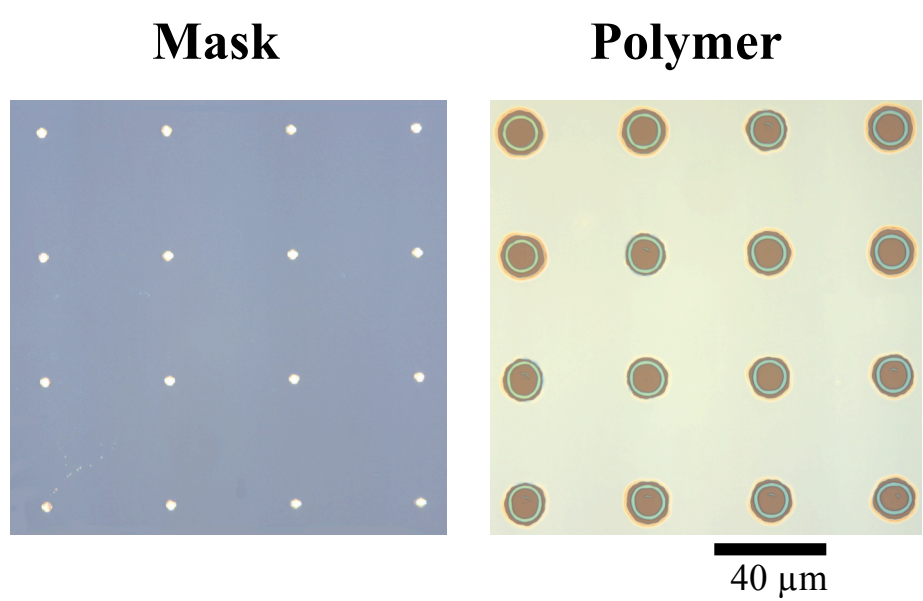
L.F. Pease III and W.B. Russel *Langmuir* 2004

Stages of Ring Growth



P. Deshpande, L.F. Pease III, L. Chen, S.Y. Chou, W.B. Russel, *Phys. Rev. E* **70** 041601 (2004)

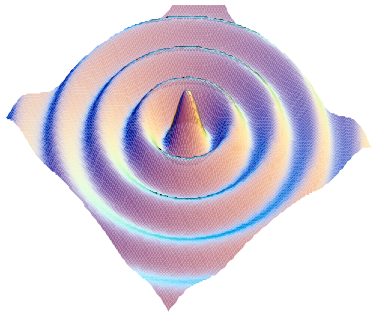


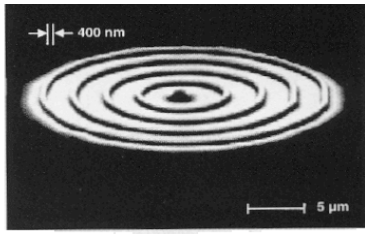


Rings

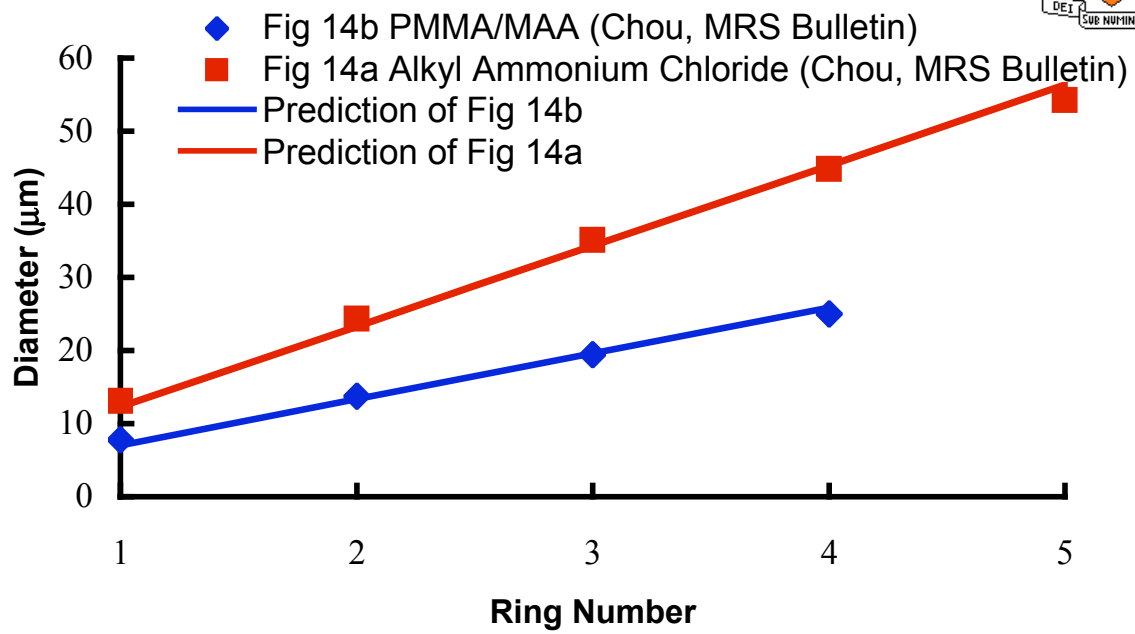
cylindrical perturbation

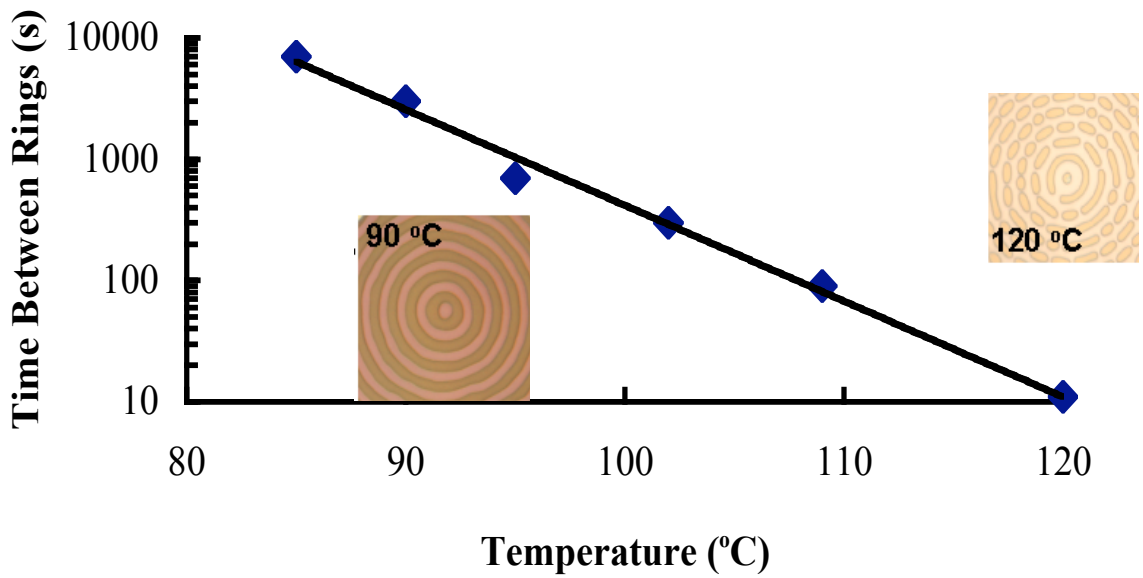
$$h = h_o + \hat{h} e^{i\nu\theta + mt} J_\nu(kr)$$





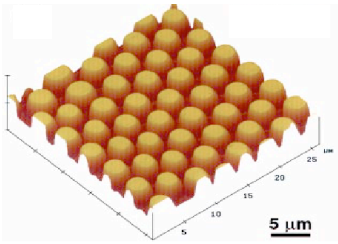
P. Deshpande, L.F. Pease III, L. Chen, S.Y. Chou, W.B. Russel, *Phys. Rev. E*, **70** 041601 (2004) figures adapted from: Chou, *MRS Bulletin*, **26** 512 (2001).

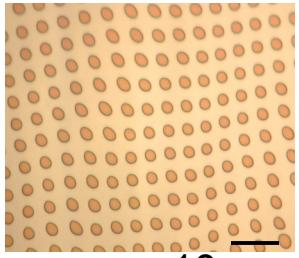


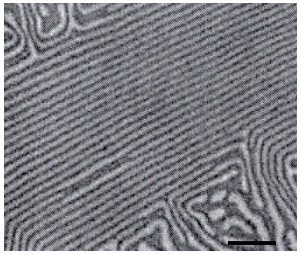


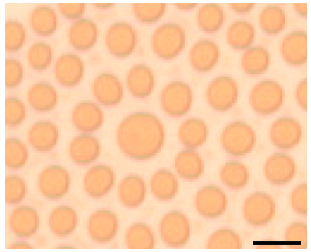
Advanced Patterning

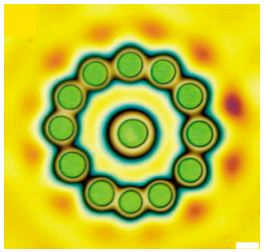
observations Chou, et al., *J. Vac. Sci. Tech. B* 17 3197 (1999); Schaffer, et al., *Nature* **403** 874 (2000); Zhuang, PhD Dissertation (2002)



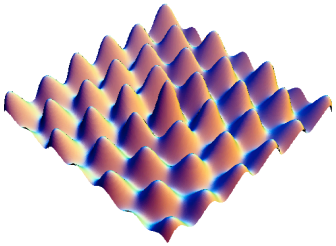


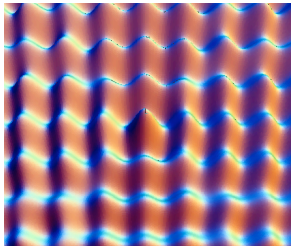


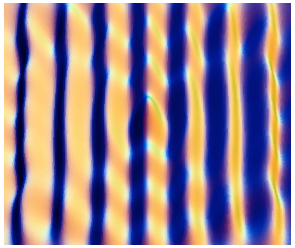


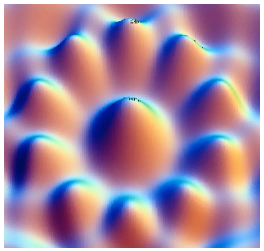


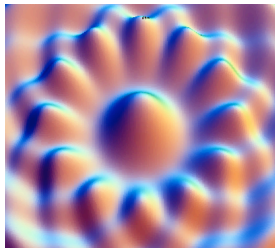
calculations











$h = h_o + h' \Sigma_\nu e^{i6\nu\theta} J_\nu(kr)$

$h = h_o + h' \Sigma_\nu e^{i4\nu\theta} J_\nu(kr)$

$h = h_o + h' \Sigma_\nu e^{i\nu\theta} J_\nu(kr)$

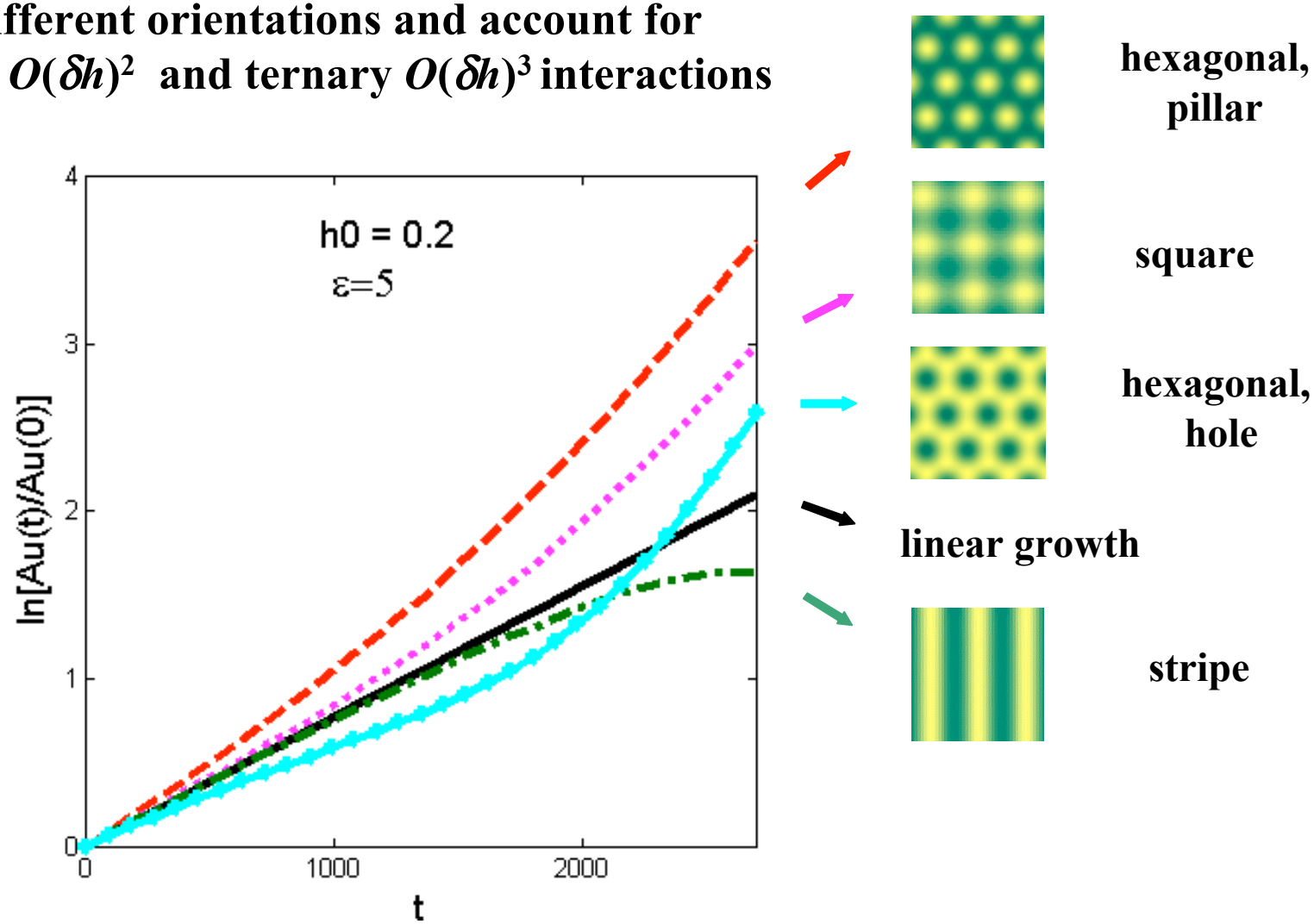
$h = h_o + h' [J_o(3kr/5) + e^{i10\theta} J_{10} kr)]$

$h = h_o + h' [J_o(kr/2) + e^{i12\theta} J_{12}(kr)]$

Unstable normal modes exist for all the patterns observed!

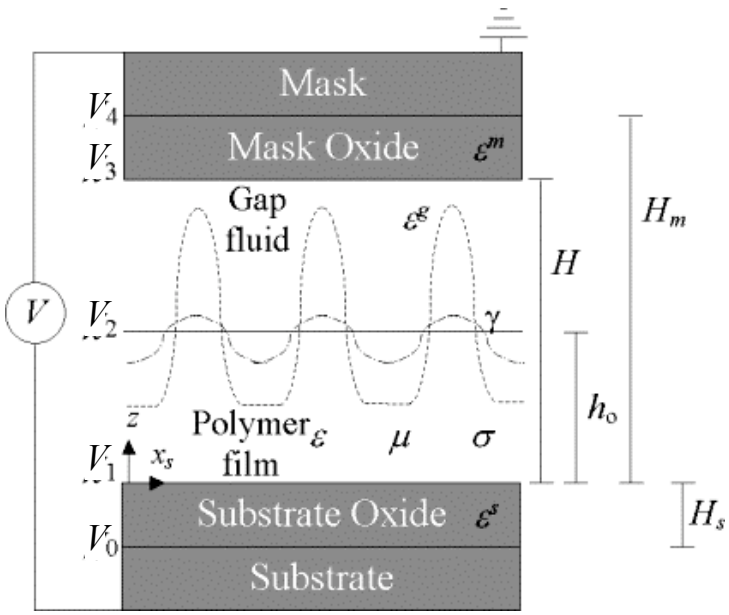
Pattern Selection: Weakly Nonlinear Theory

Superimpose fastest growing linear $O(\delta h)$ modes with different orientations and account for binary $O(\delta h)^2$ and ternary $O(\delta h)^3$ interactions



N. Wu, L. F. Pease III, and W. B. Russel, *Langmuir* 21, 12290 (2005)

Fully Nonlinear Theory: simulations



$$\frac{\partial h}{\partial t} = \nabla \cdot \left(\frac{1}{3\mu} h^3 \nabla p\right) \quad \left\{ \begin{array}{l} \text{evolution through} \\ \text{pressure driven} \\ \text{flow in film} \end{array} \right.$$

$$p - p_0 = -\frac{\varepsilon_p\left(\varepsilon_p - \varepsilon_g\right)V^2\varepsilon_0}{2\varepsilon_g\left[\varepsilon_g h + \varepsilon_p\left(H-h\right)\right]^2} \quad \left\{ \begin{array}{l} \text{tension due to} \\ \text{electrostatic} \\ \text{force on surface} \end{array} \right.$$

$$-\gamma\nabla^2 h \qquad \text{capillary pressure}$$

$$+\underbrace{\frac{A}{(H-h)^3}}_{\text{mask}} - \underbrace{\frac{A}{h^3}}_{\text{substrate}} \qquad \text{disjoining pressure}$$

dimensionless groups

$$\frac{H}{L} = \left(\frac{\varepsilon_g \varepsilon_0 V^2}{\gamma H}\right)^{1/2} << 1 \quad \text{lubrication valid}$$

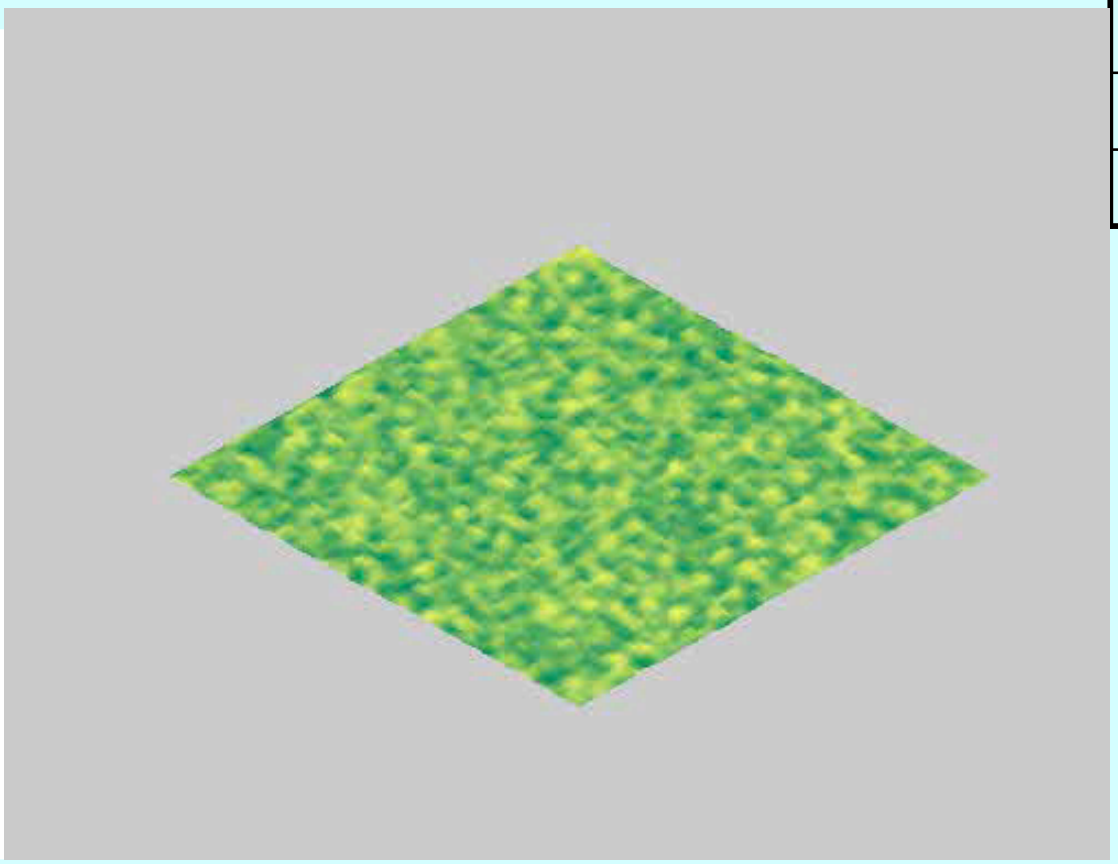
$$S = \frac{\sigma\mu\gamma H^3}{\varepsilon_g^3 \varepsilon_0^3 V^4} \quad \left\{ \begin{array}{ll} << 1 & \text{pure dielectric} \\ >> 1 & \text{leaky dielectric} \end{array} \right.$$

fastest growing wavelength

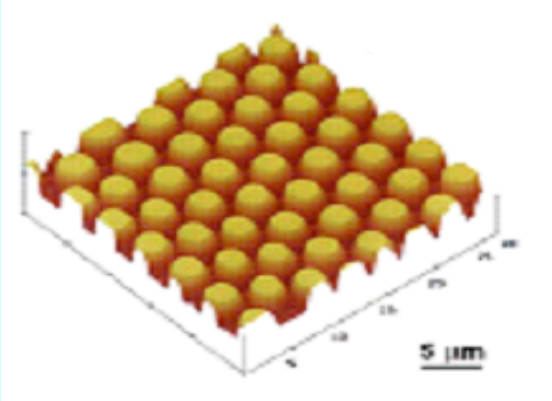
$$\lambda_{\max} = \frac{2\sqrt{2}\pi\gamma^{1/2}\left[\varepsilon_g h_0 + \varepsilon(H-h_0)\right]^{3/2}}{\left|V\right|\left(\varepsilon\varepsilon_g\varepsilon_0\right)^{1/2}\left|\varepsilon - \varepsilon_g\right|}$$

Numerical simulation

- pattern formation under a featureless mask



	period (μm)	diameter (μm)	time (min)
Exp.	3.4	2.7	~ 5
Simu.	3.44	2.79	3.10



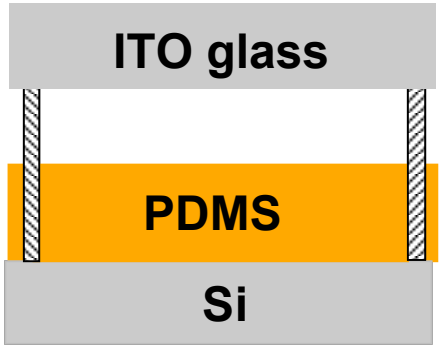
$h_0 = 95\ nm \qquad H = 260\ nm$

$\varepsilon = 5.4 \qquad \chi \approx 10\ V \quad (fitted)$

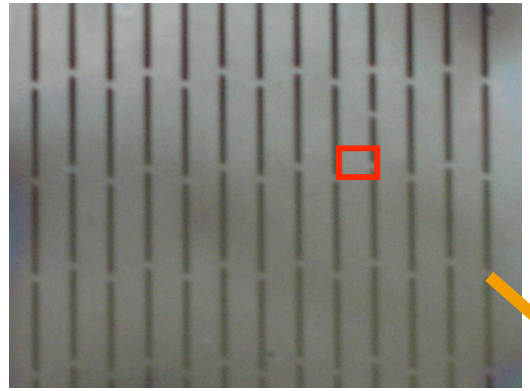
Wu & Russel, Appl. Phys. Lett. 86, 241912, (2005)

Chou & Zhuang, (1999)

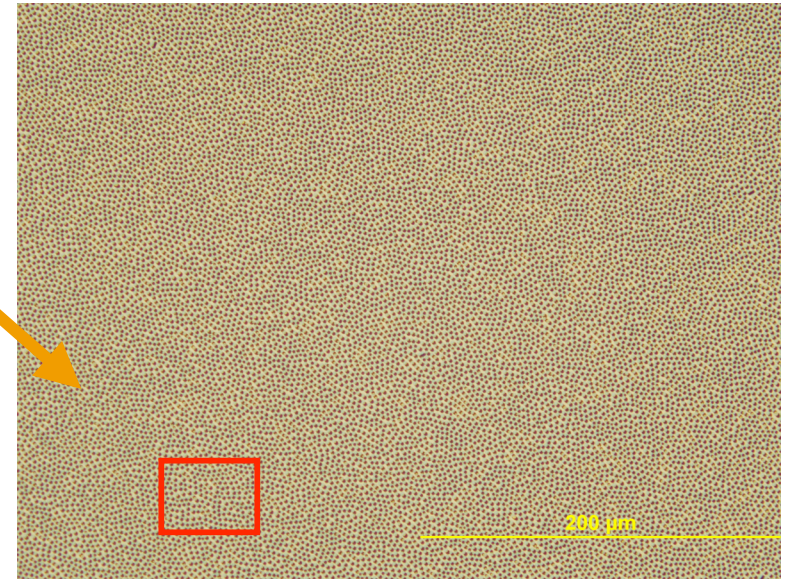
Experimental observations

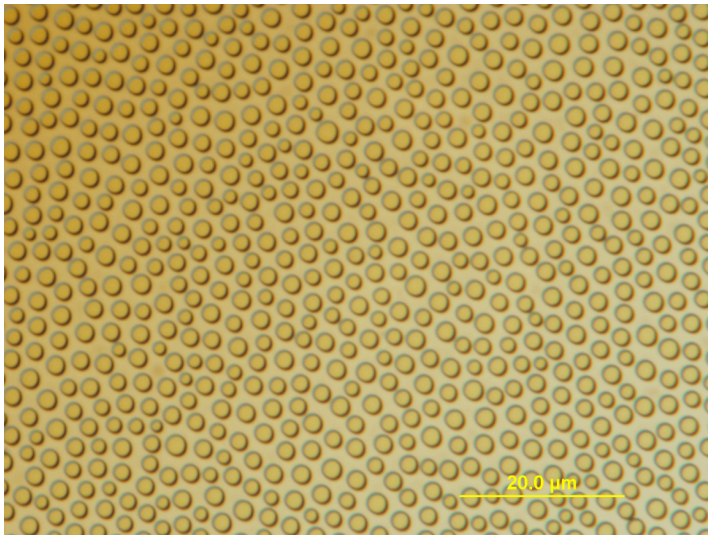


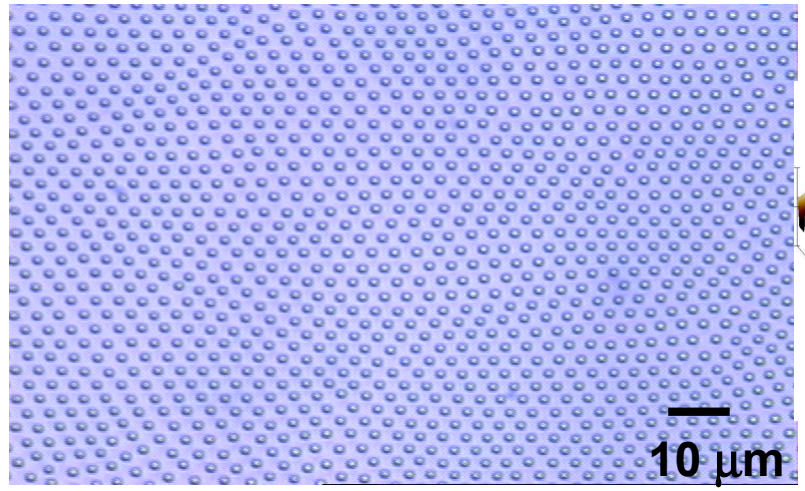
No heating is required due to low T_g of PDMS

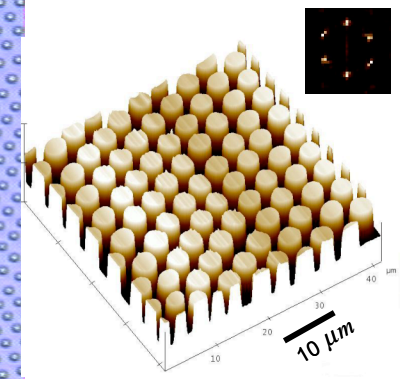


3 cm







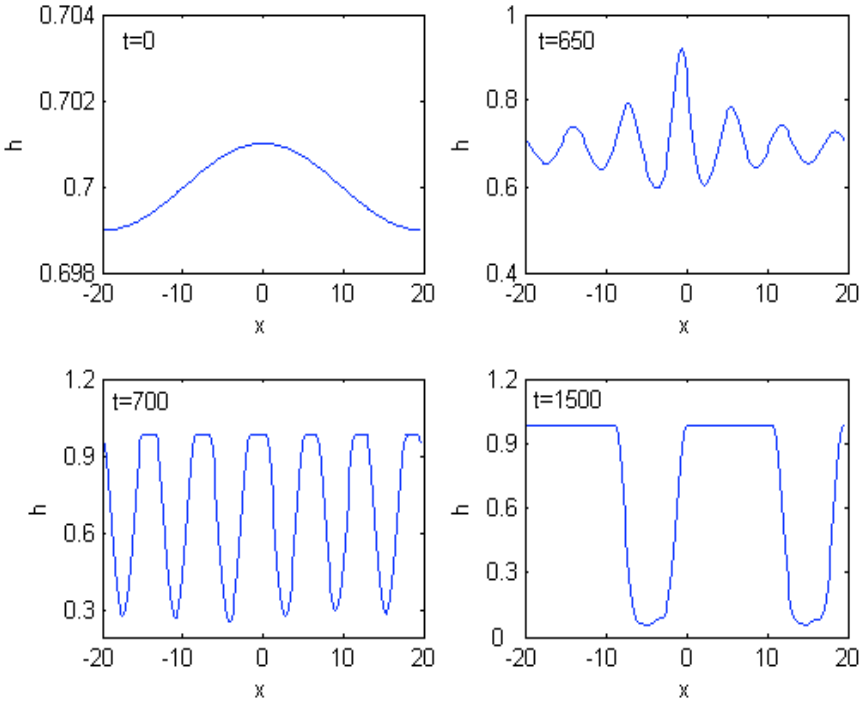


Longer times

1-dimensional growth under unpatterned mask

evolution of height $h(x,t)$

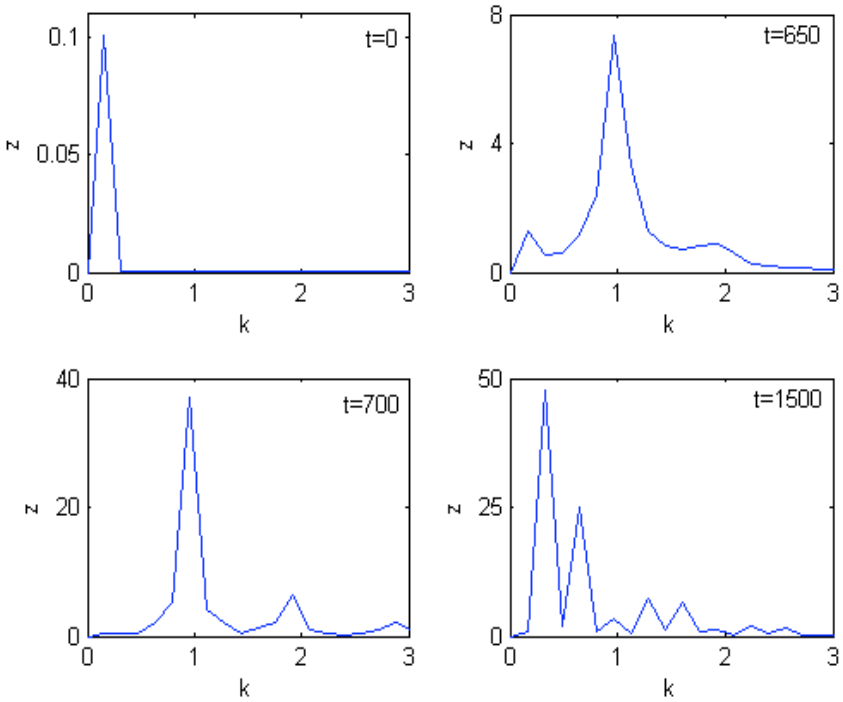
initial perturbation | weakly nonlinear



fully developed | coarsening

spectral map $\hat{h}(k,t)$

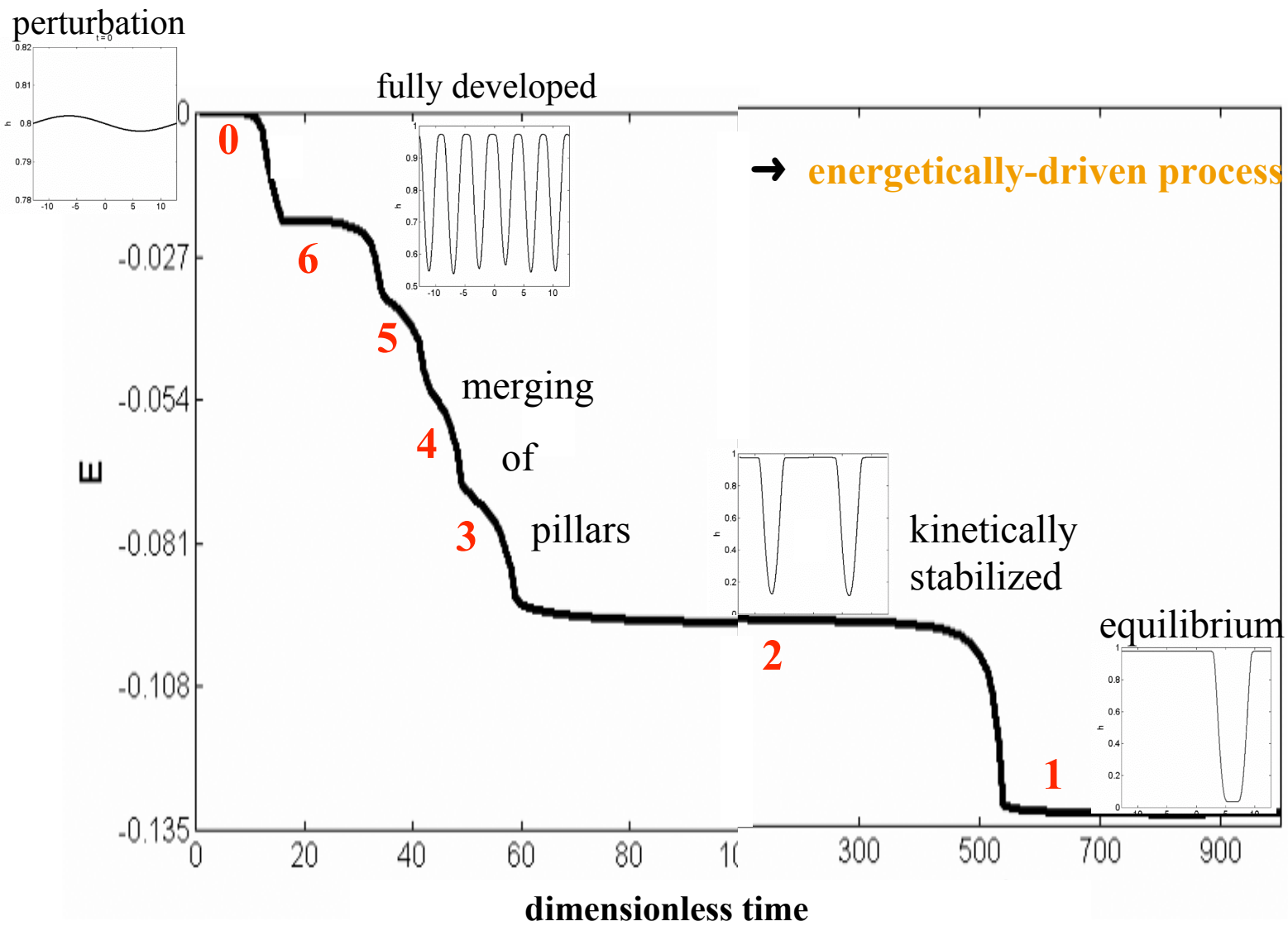
initial perturbation | weakly nonlinear



fully developed | coarsening

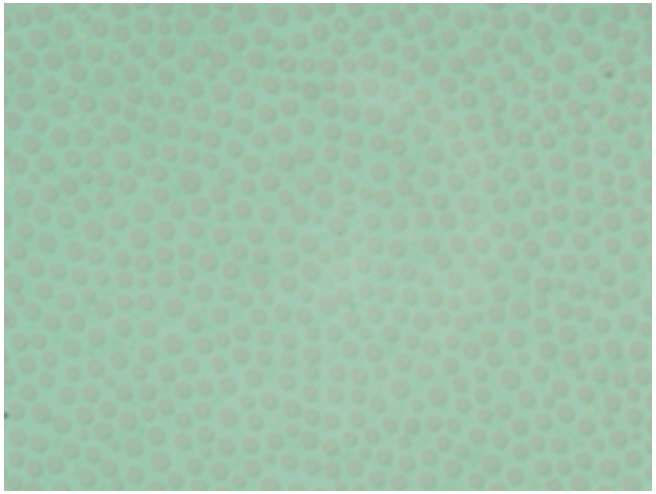
Time evolution of the total energy: electrostatic + surface + van der Waals

Wu & Russel, *Ind. Eng. Chem. Res.* (2006)

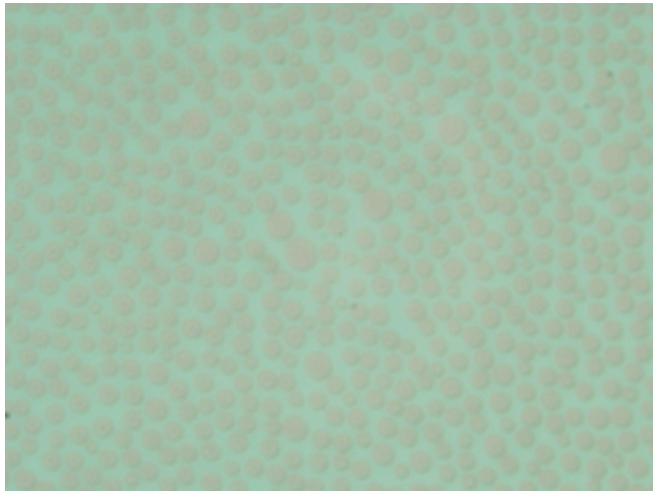


Coarsening – PDMS 2500k cst, fill ratio ~ 0.57, V ~ 50 V

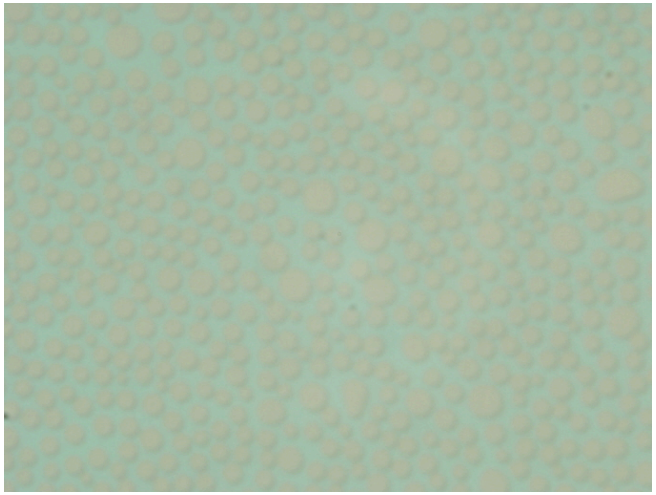
T=160s



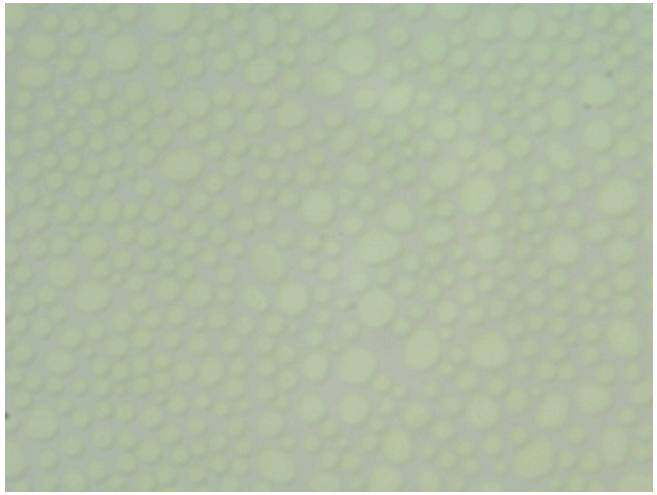
T=1000s



T=3840s



T=36720s

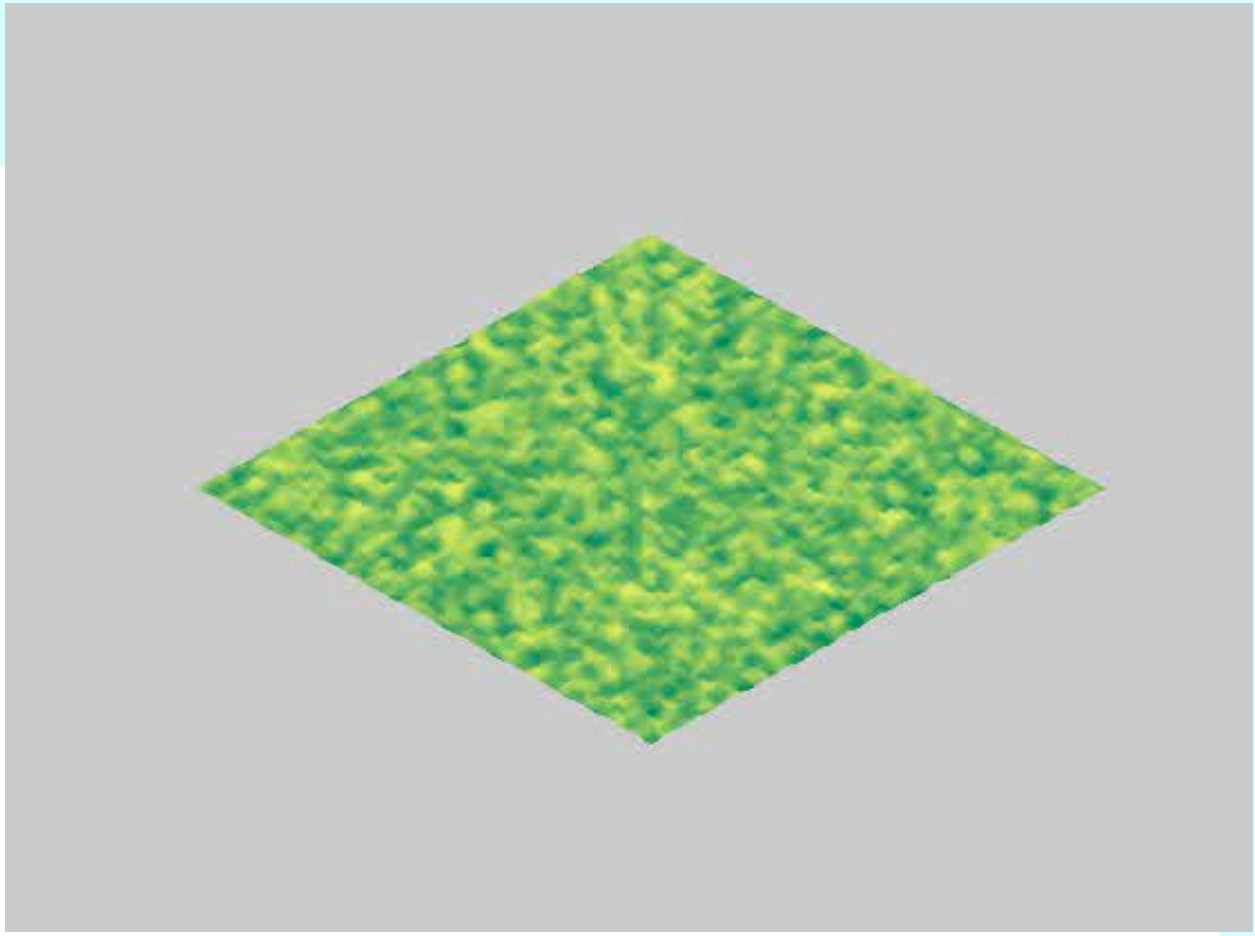


20 μm

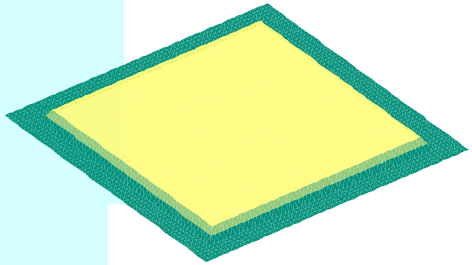
Numerical simulation

- pattern formation under a patterned mask

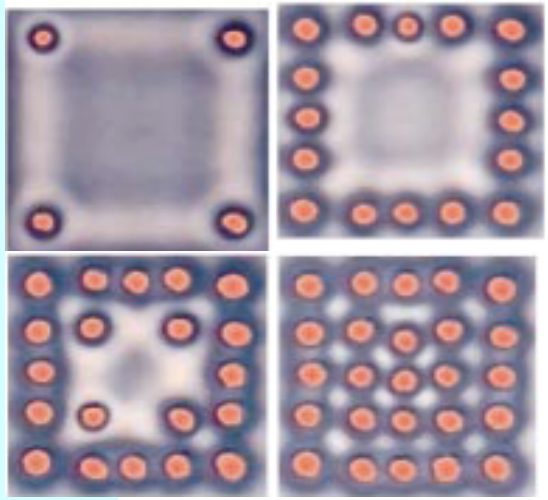
simulation



mask pattern



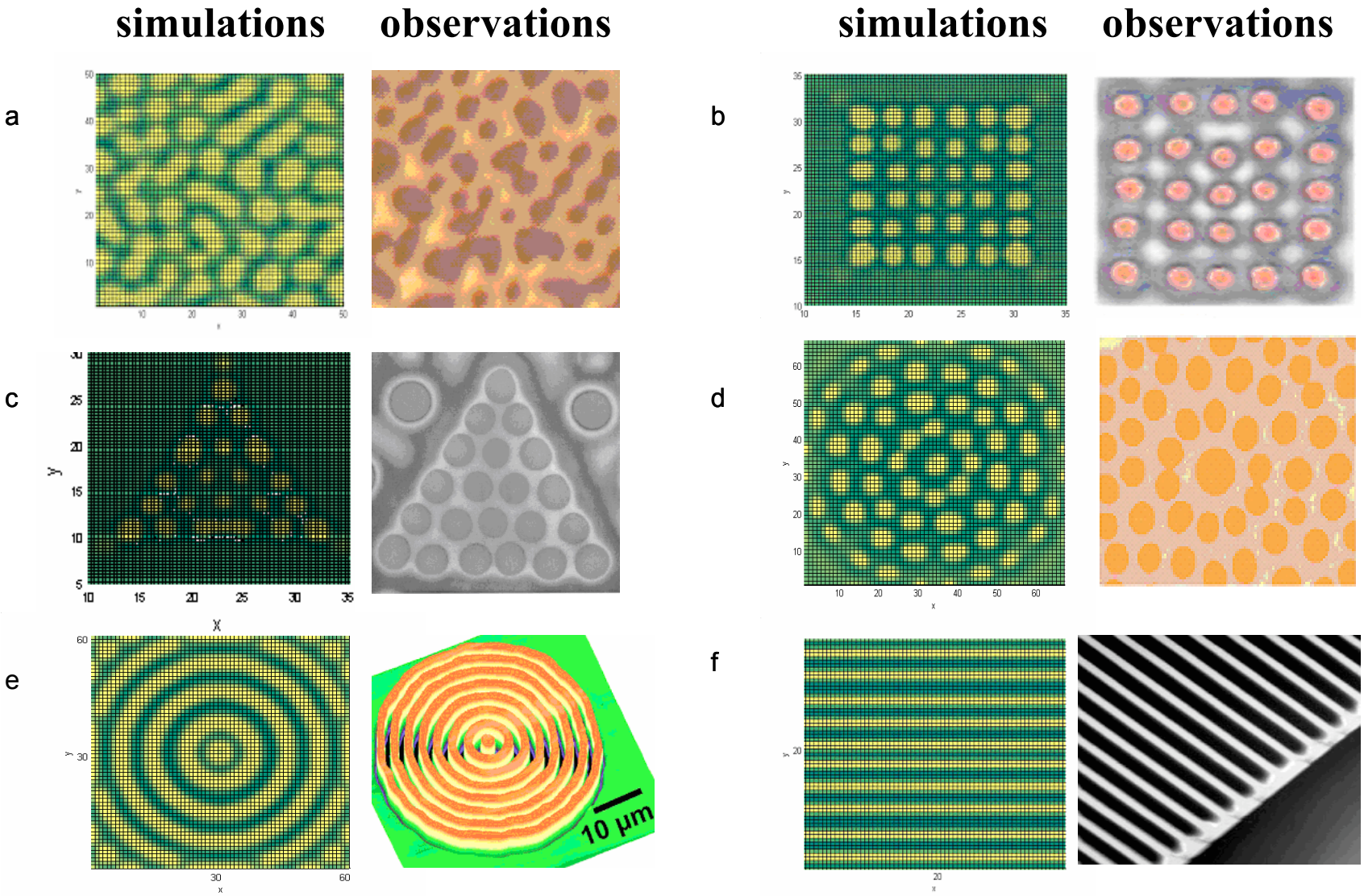
optical image



Deshpande & Chou, (2001)

Wu et. al., Langmuir 21, (2005)

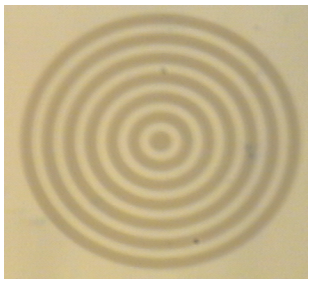
Comparison of Simulations and Observations

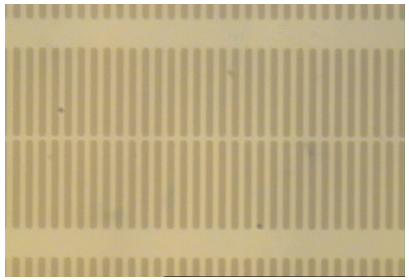


➜ faithful description of experiments

Design of masks to guide formation

- **Novel hierarchical patterns**



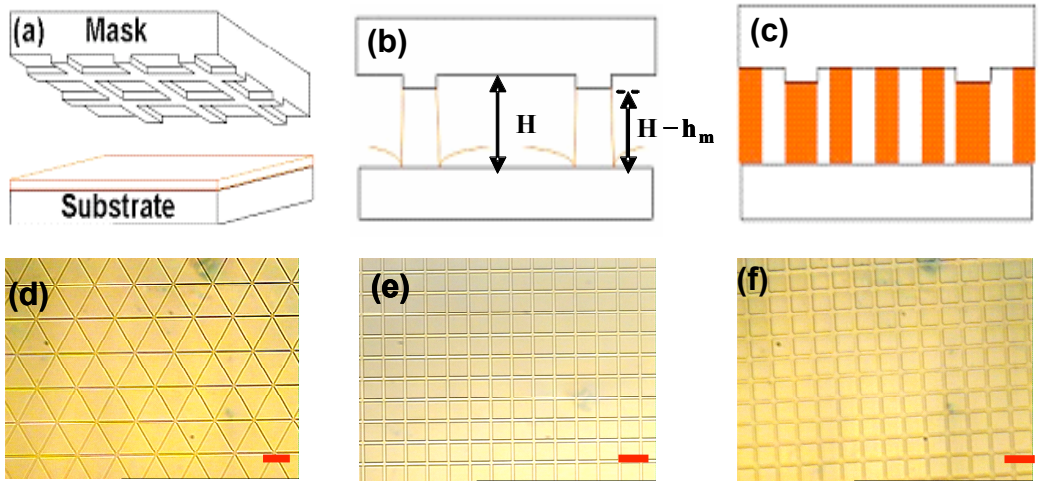


possibilities

pillars and ridges

….

- **Pillars in registry over large areas**



ridges ridges valleys

issues

shape □○△

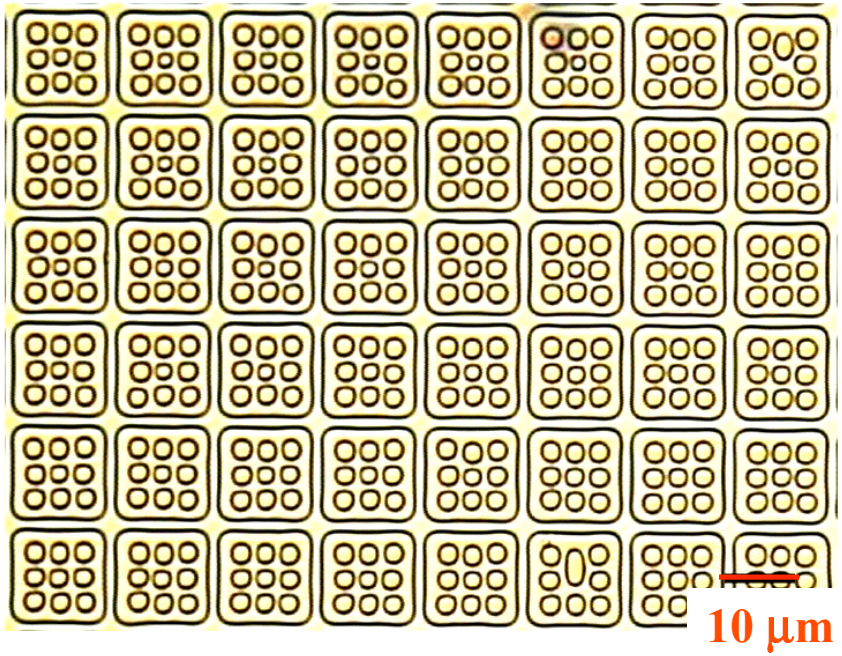
ridge $h_m > 0$

or valley $h_m < 0$

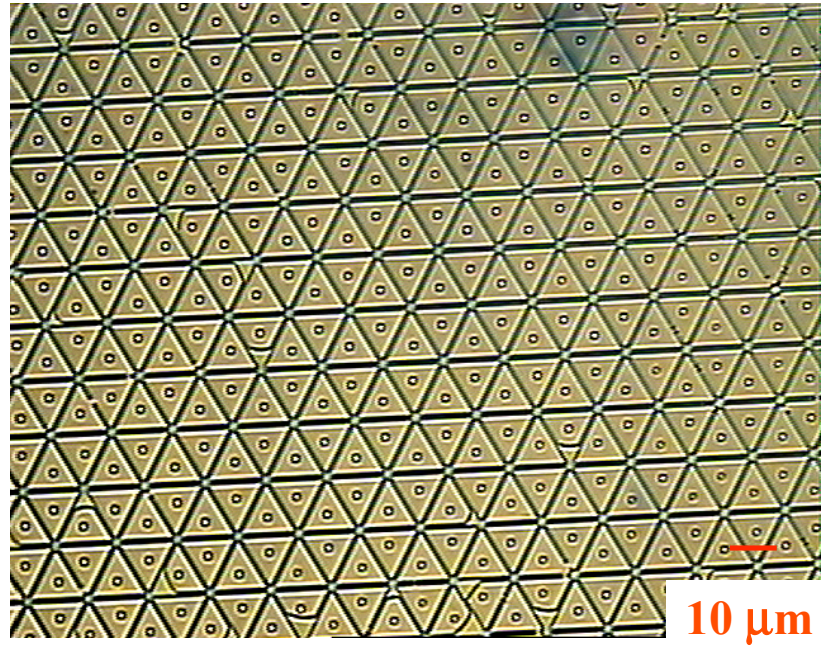
spacing L/λ

relief ratio $H\text{-}h_m/H$

Linear ridges with pillars



square array

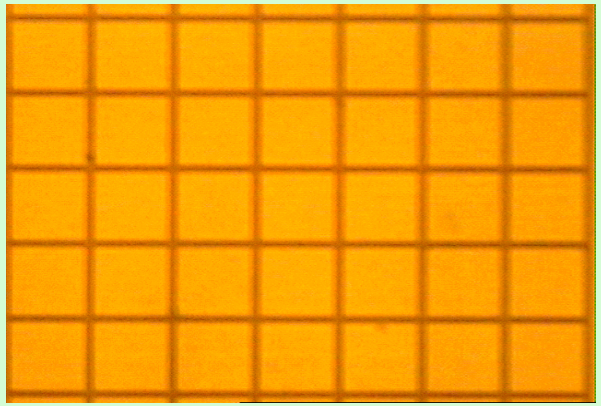


triangle array

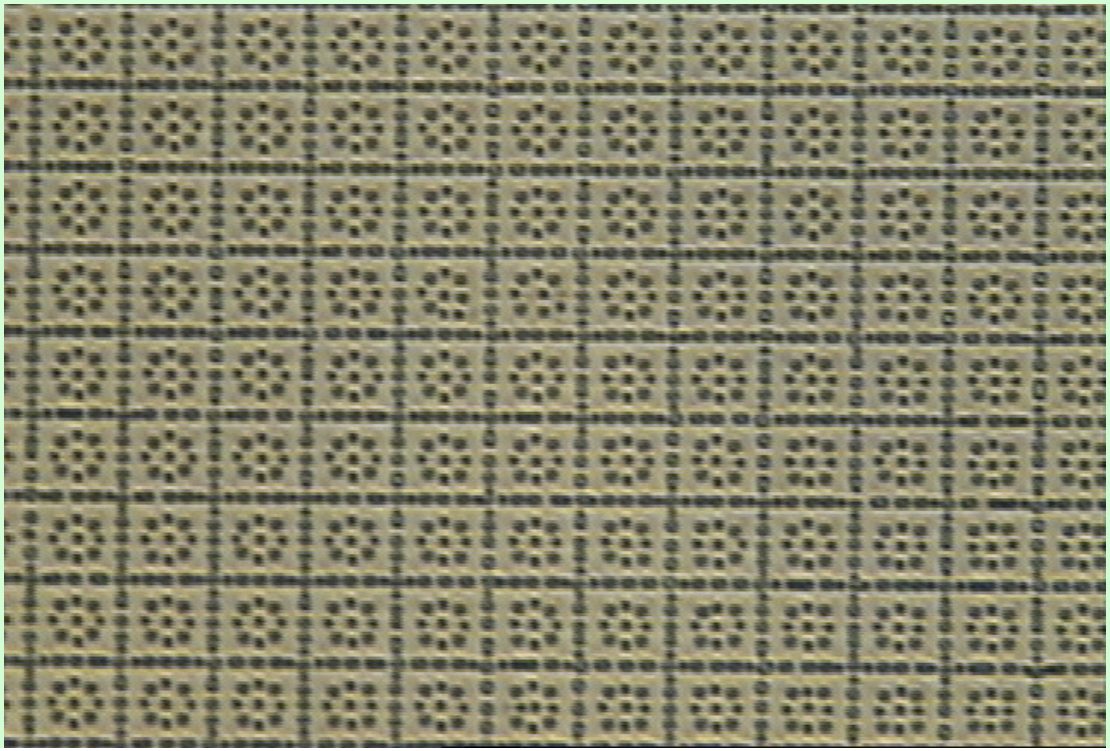
t increases

The formation of the hierarchical microstructures by an integration of self-assembly and lithography

mask



substrate



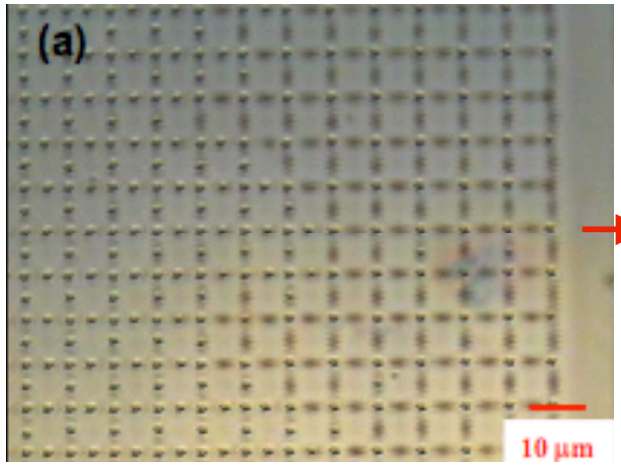
Time Evolution

square ridges L=8 µm
h_o=45 nm V_e=10 V
annealed at 130 ˚C
T = 6 hours

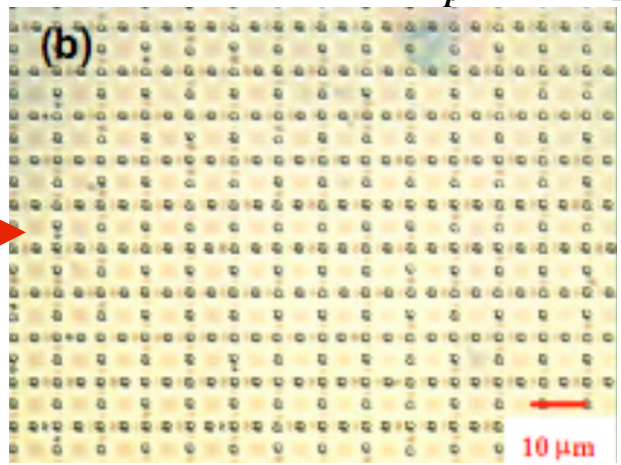
$$\bar{t} = \frac{t}{\tau_p} = \frac{\left(\varepsilon^g \varepsilon_o V^2\right)^2}{\mu \gamma H^3} t$$

→ increases with decreasing H

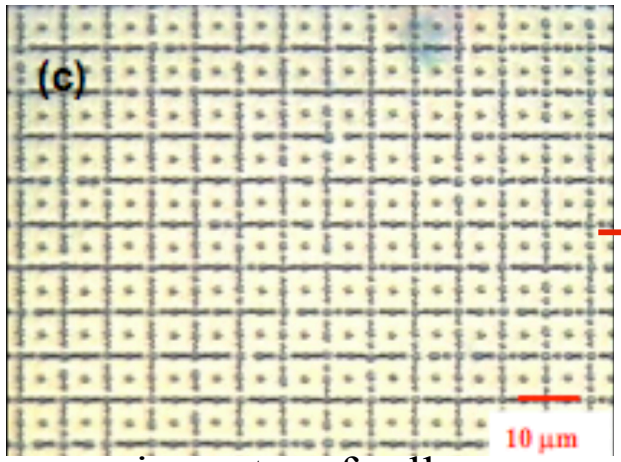
appearance of pillars with decreasing H and τ_p



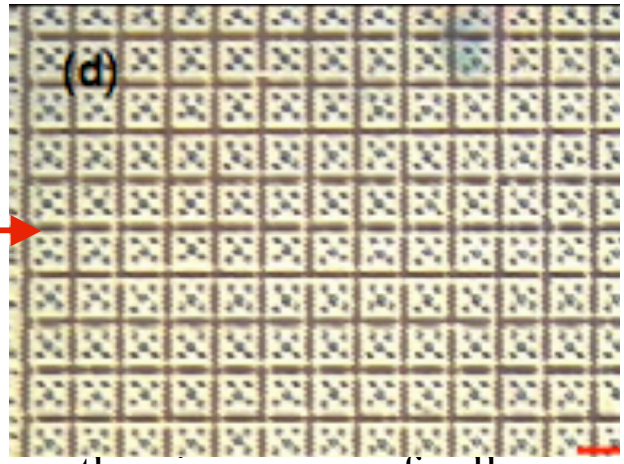
at vertices on ridges



then at midpoints on ridges



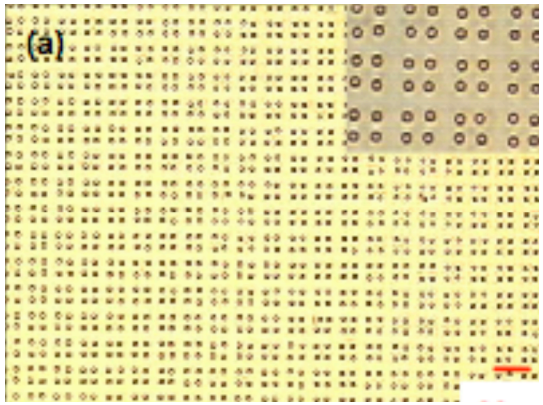
in center of cell



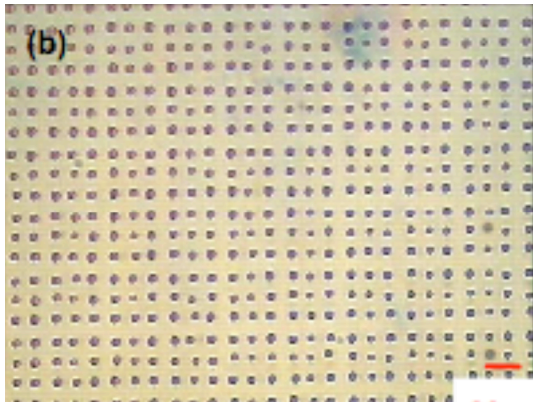
then in corners of cells
as pillars on ridges merge

relative positions on sample

Ratio of Period to Natural Wavelength

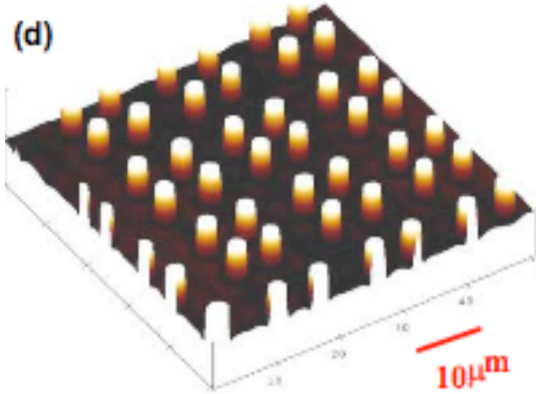


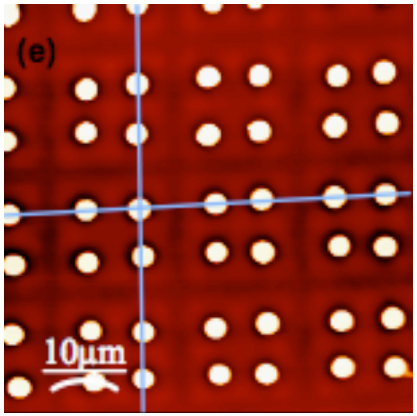
2x2 array t = 3 hrs

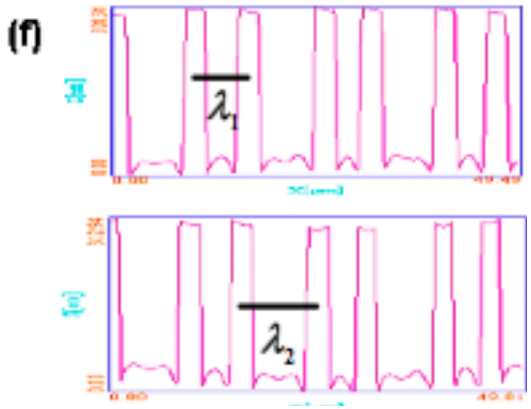


3x3 array t = 24 hrs

4x4 array t = 72 hrs







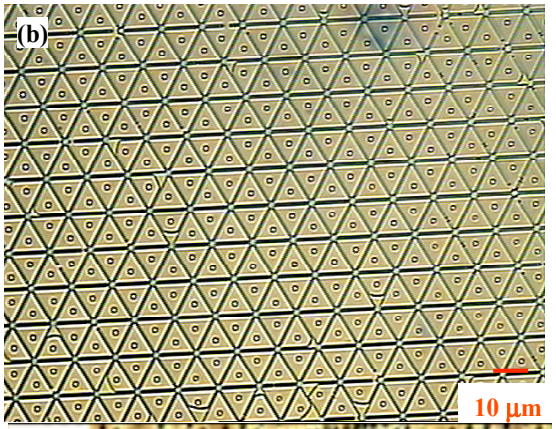
square protrusions
LxL= 12x12 μm
h_o=45 nm V_e= 10 volts

➜ **Adjusts to closest integral number of wavelengths with disorder proportional to mismatch**

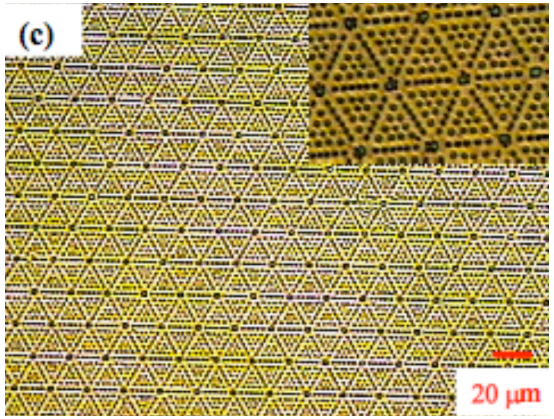
height profile 2x2 array
~ 300 nm pillars
λ_1= 6.2 μm
λ_2= 8.8 μm

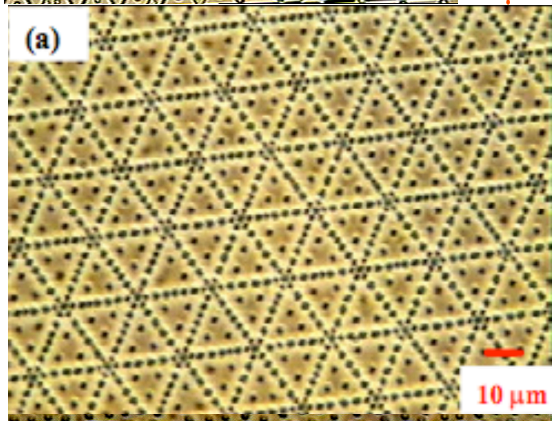
Triangular arrays of ridges

$h_o = 45$ nm $t = 3$ hours $V_e = 10$ volts.



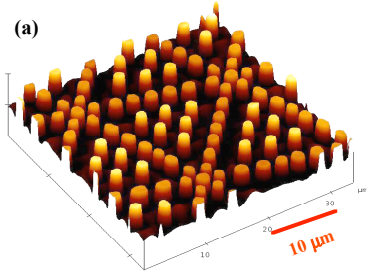
continuous ridge
one pillar in cell

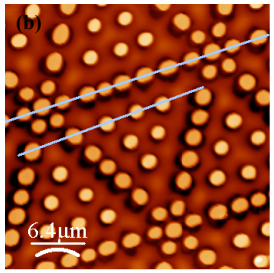


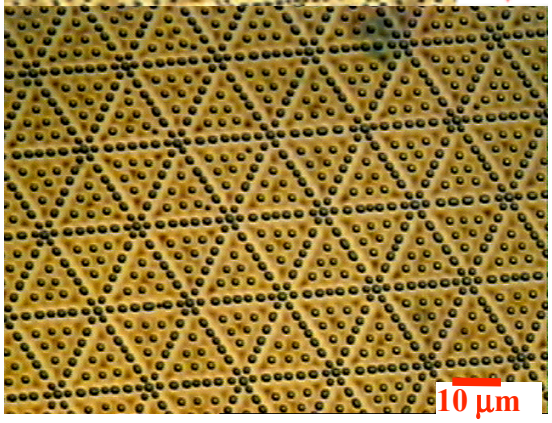


size pillars on ridge
three pillars in cell

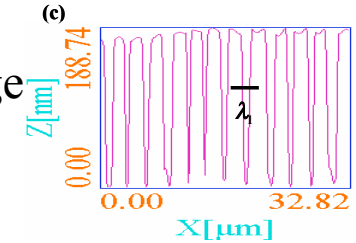
eight pillars on ridge
ten pillars in cell

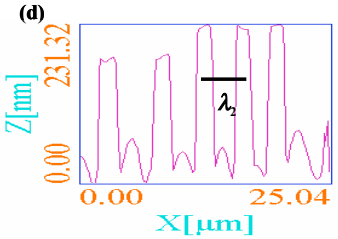






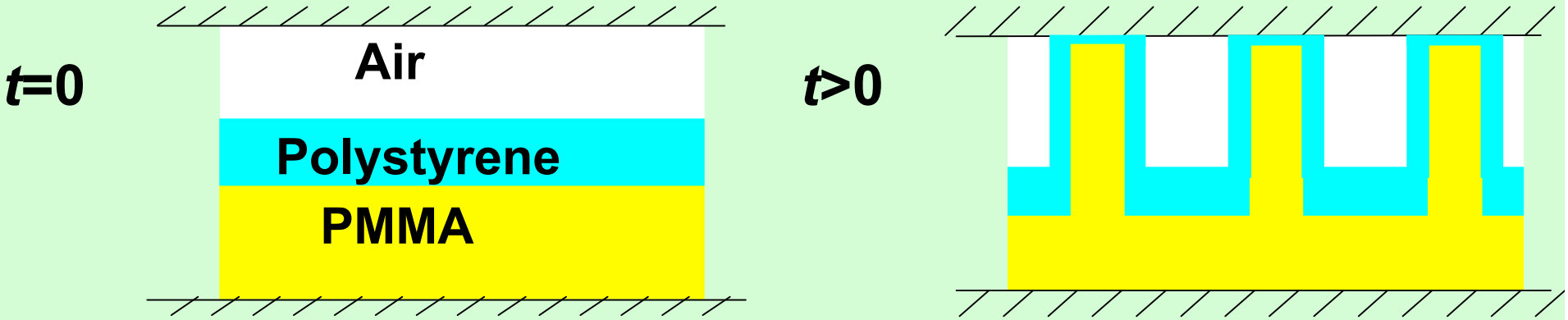
seven pillars on ridge
six pillars in cell

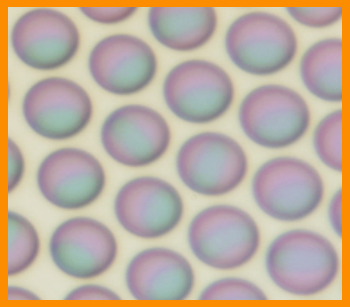




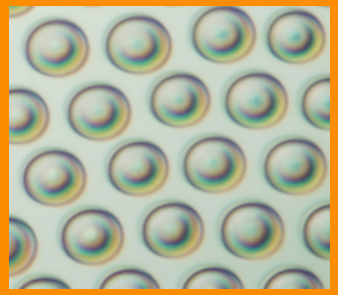
- **crowded vertices**
- **different periods between cells and ridges** ➜ **not ideal**

The formation of the hierarchical microstructures in polymer1/polymer2/air system

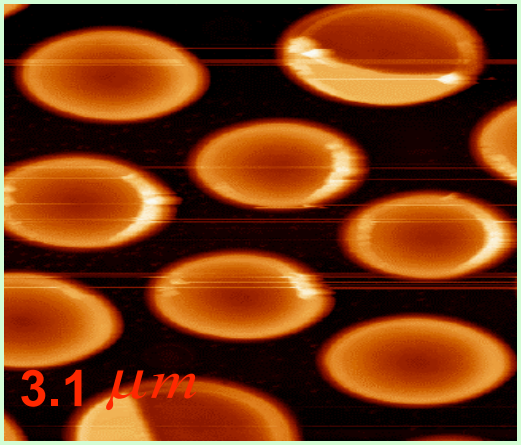


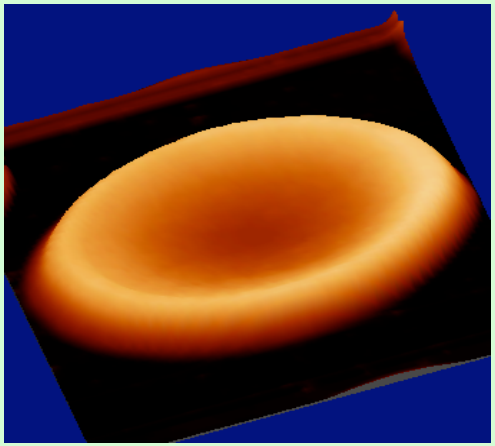


before rinsing of PS



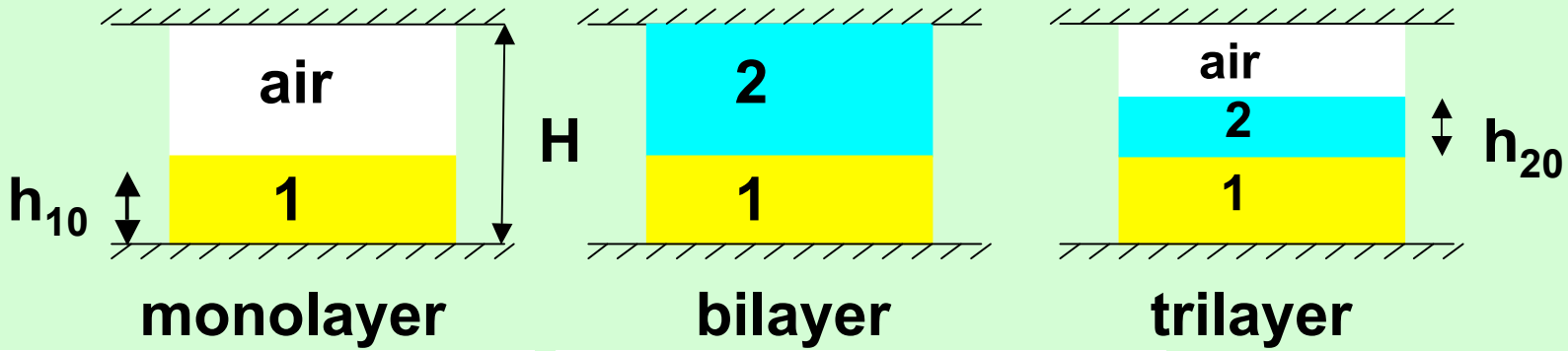
after rinsing of PS

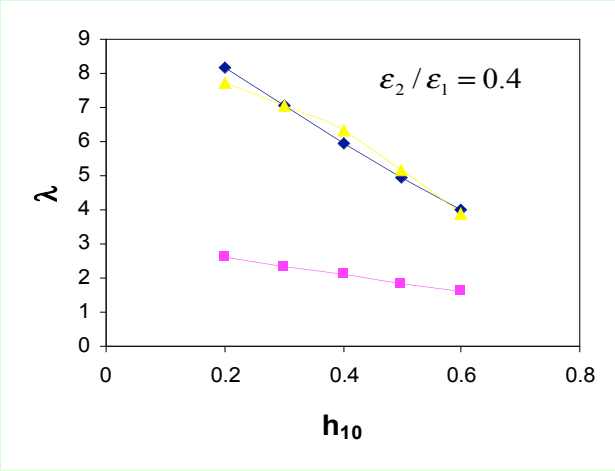


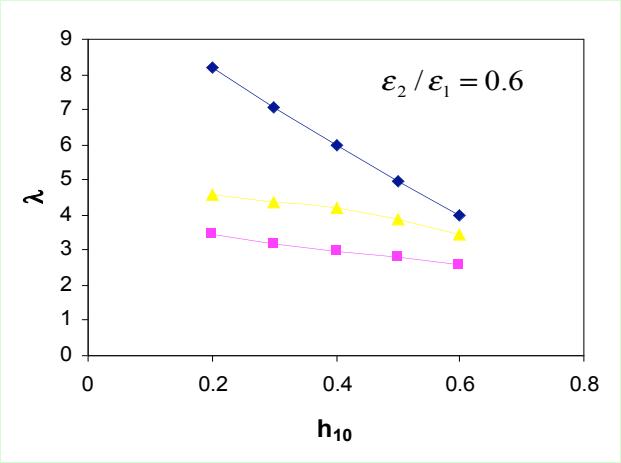


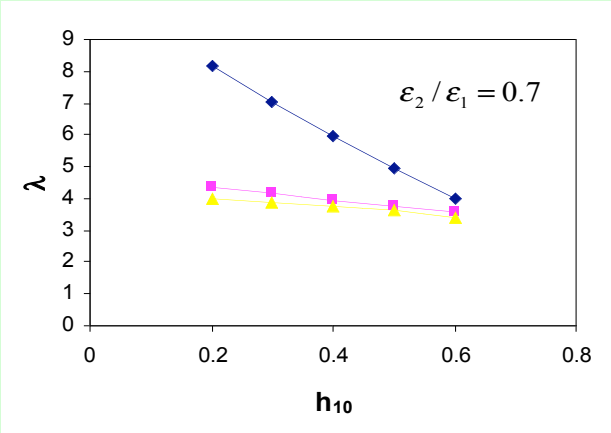
	PS/PMMA/air	PMMA/PS/air	PS/PMMA/air
H (micron)	0.5	3.0	1.7
external voltage (V)	50	136	30
period (micron) theory	2.6	15	37
period (micron) experiment	2.5	20	32

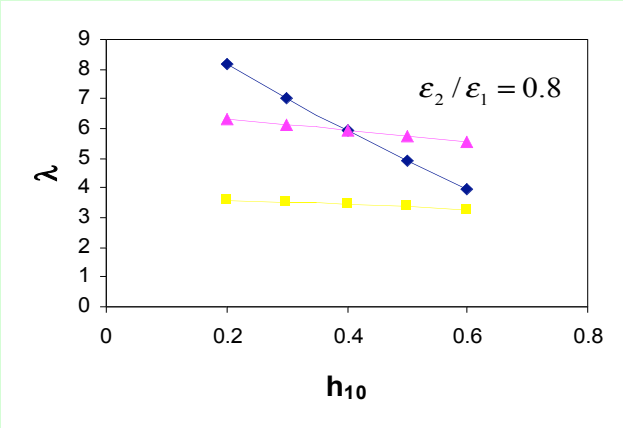
Periods for the mono-, bi-, and trilayer systems











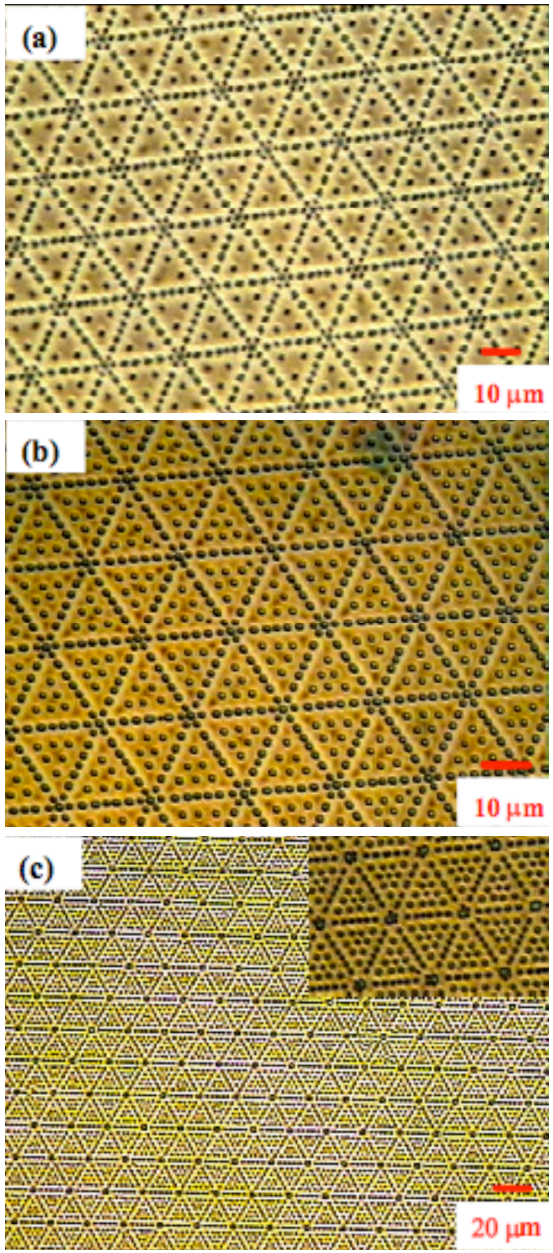
monolayer

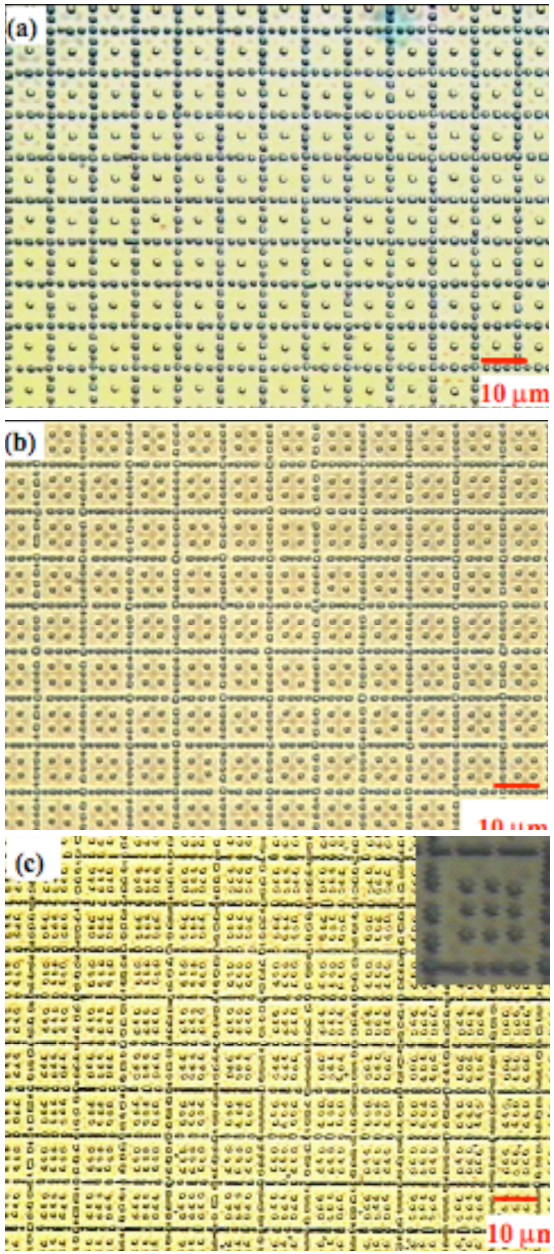
bilayer

trilayer

ε dielectric constant

λ period





Lots of fun lies ahead for patterning technologies enlightened by modelling!