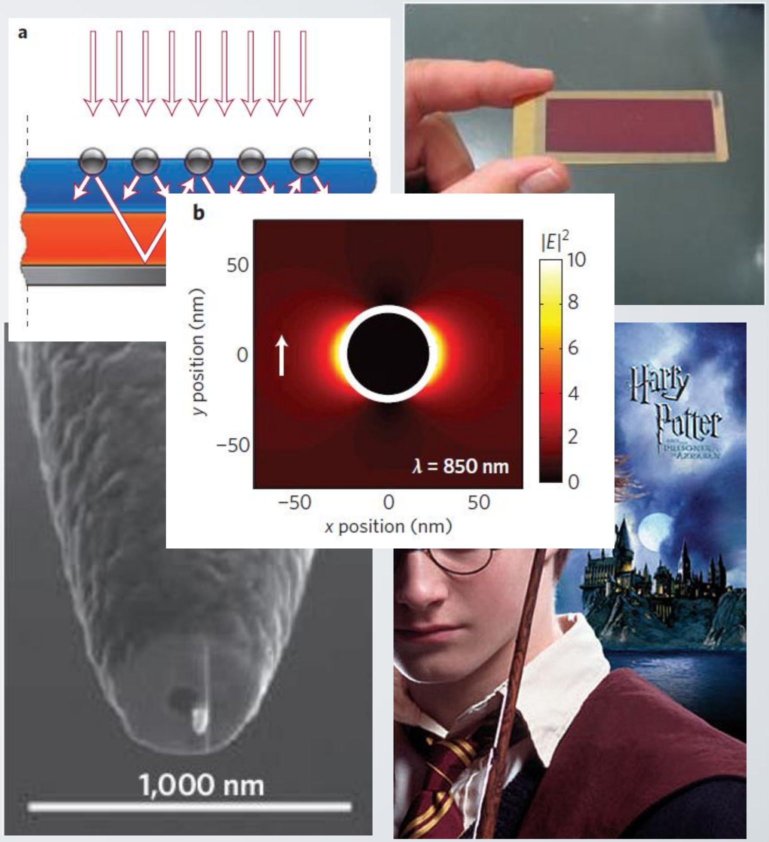
Templated Evaporative Lithography

Can ***evaporation*** be used as a driving force for **scalable** fabrication of **metallic** nanostructures?

Metallic Nanostructures

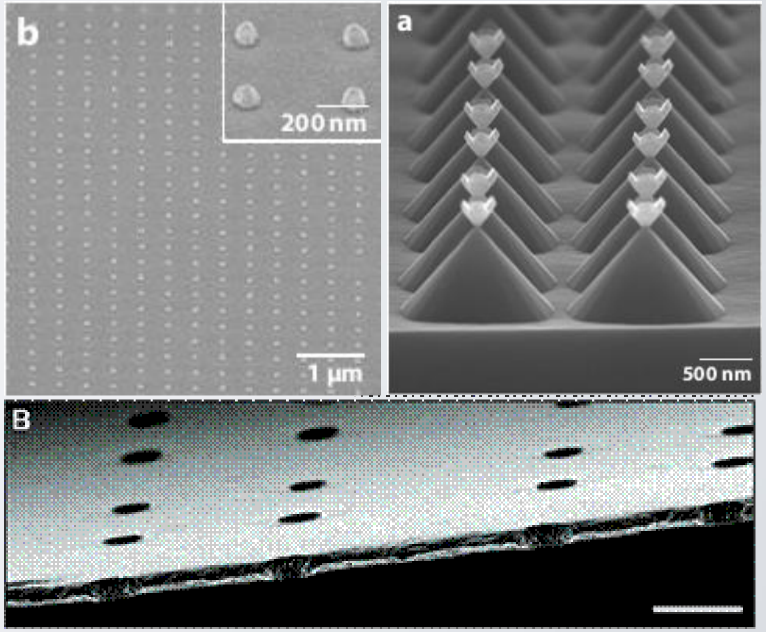
- Metallic nanostructures have special interactions with light, which gives them many applications



Schuller, J. A., E. S. Barnard, et al. (2010). "Plasmonics for extreme light concentration and manipulation." Nat Mater 9(3): 193-204.
Atwater, H. A. and A. Polman (2010). "Plasmonics for improved photovoltaic devices." Nat Mater 9(3): 205-213.
Anker, J. N., W. P. Hall, et al. (2008). "Biosensing with plasmonic nanosensors." Nat Mater 7(6): 442-453.

Metallic Nanostructures

- Metallic nanostructures have special interactions with light, which gives them many applications
- Interactions are shape-dependent; various shapes are relevant
- Traditional lithography is ill-suited to the needs of plasmonic and photonic devices

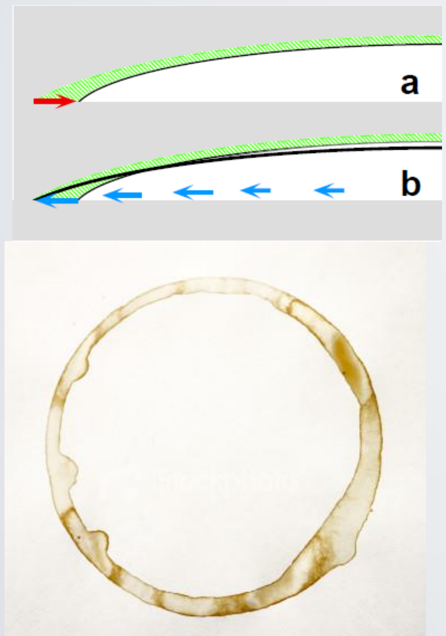


Scale bar: 500 nm

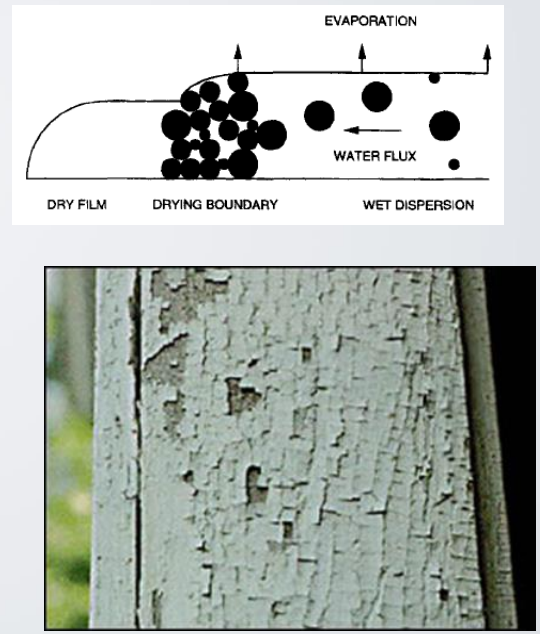
J. Henzie, J. Lee, M. H. Lee, W. Hasan and T. W. Odom, *Annual Review of Physical Chemistry, 2009, 60, 147-165.*
E.-S. Kwak, J. Henzie, S.-H. Chang, S. K. Gray, G. C. Schatz and T. W. Odom, *Nano Letters, 2005, 5, 1963-1967.*

Evaporative Self-Assembly

- Heterogeneous evaporation can drive convective transport of particles



Coffee Ring Effect

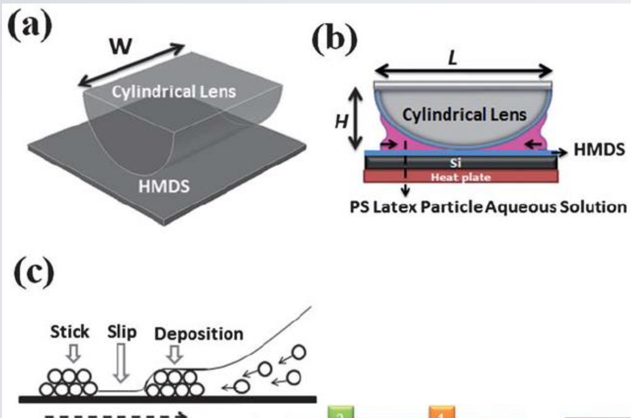


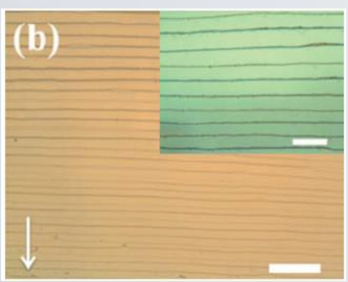
Latex Film Cracking

R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel and T. A. Witten, *Nature, 1997, 389, 827-829.*
A. F. Routh and W. B. Russel, *AIChe J, 1998, 44, 2088-2098.*

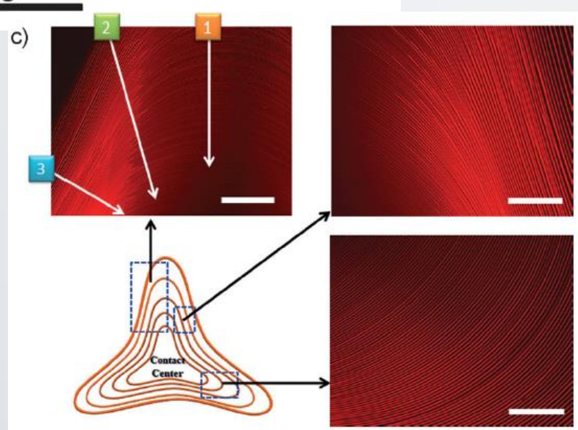
Directed Evaporative Self-Assembly

- Drying suspension bridges



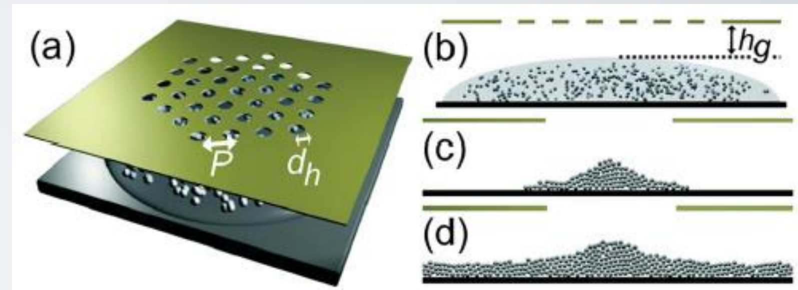


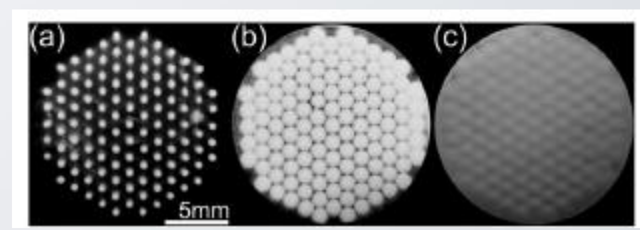
Scale bars: 200, 50 μm



Scale bars: 300, 600 μm

- Heterogeneous drying of films

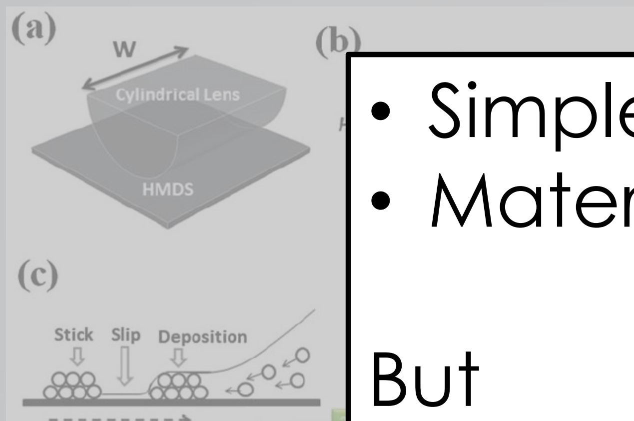


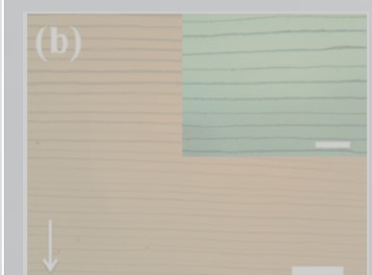


W. Han and Z. Lin, *Angewandte Chemie International Edition, 2012, 51, 1534-1546.*
W. Han, M. Byun and Z. Lin, *J Mater Chem, 2011, 21, 16968-16972.*
D. J. Harris, H. Hu, J. C. Conrad and J. A. Lewis, *Physical Review Letters, 2007, 98.*

Directed Evaporative Self-Assembly

- Drying suspension bridges





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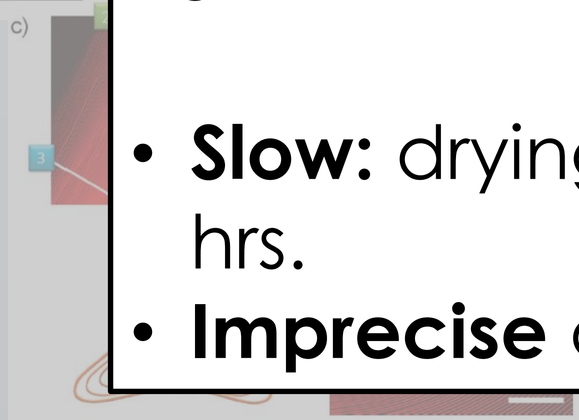

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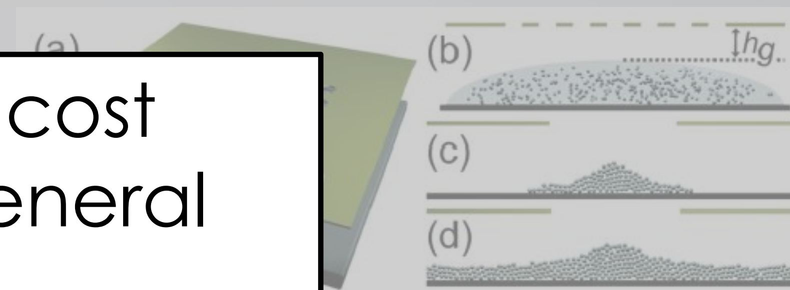
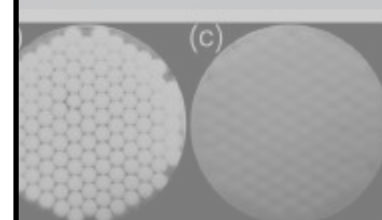
- Heterogeneous drying of films





- Simple, low cost
- Materials general

But

- **Slow:** drying time ~ hrs.
- **Imprecise** deposits

W. Han and Z. Lin, *Angewandte Chemie International Edition*, 2012, 51, 1534-1546.
W. Han, M. Byun and Z. Lin, *J Mater Chem*, 2011, 21, 16968-16972.
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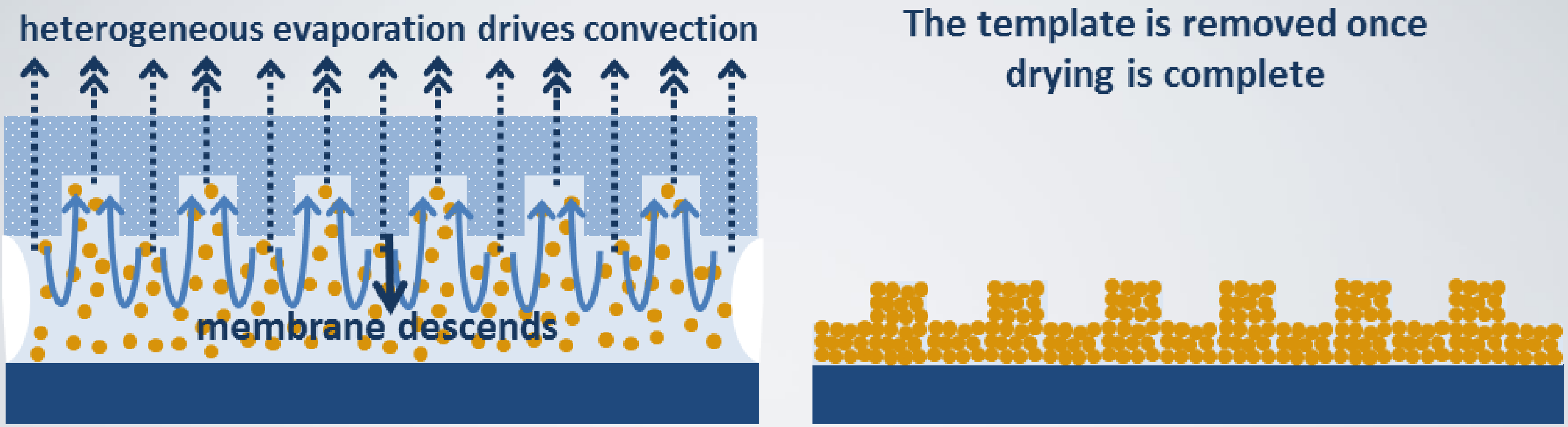
Templated Evaporative Lithography



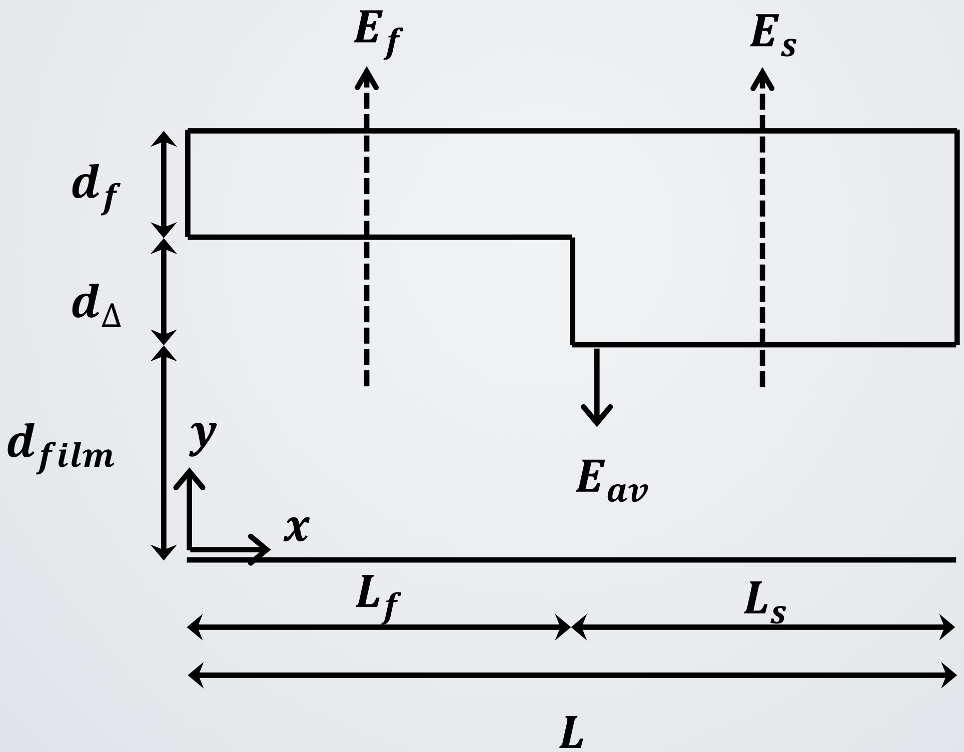
- Fast: drying time of seconds – mins.
- Well-defined deposits

T. A. Arshad and R. T. Bonnecaze, *Nanoscale*, 2013, 5, 624-633.

Dynamics

- Convection v.s. Diffusion:

$$Pe \equiv \frac{E_{av}L^2}{D_0\left(d_\Delta + d_{film}\right)}$$



Dynamics

- (scaled) Convection-diffusion equation

$$Pe\left(\frac{\partial\varphi}{\partial t}+u\frac{\partial\varphi}{\partial x}+v\frac{\partial\varphi}{\partial y}\right)=\frac{\partial}{\partial x}\left[D\frac{\partial\varphi}{\partial x}\right]+\frac{1}{A^2}\frac{\partial}{\partial y}\left[D\frac{\partial\varphi}{\partial y}\right]$$

- Constitutive relationships:

$$K(\varphi)=(1-\varphi)^{6.55}$$

$$D(\varphi)=K(\varphi)\frac{d}{d\varphi}[\varphi Z(\varphi)]$$

$$Z(\varphi)=\frac{1.85}{0.64-\varphi}$$

$$\mu=\left(1-\frac{\varphi}{0.64}\right)^{-2}$$

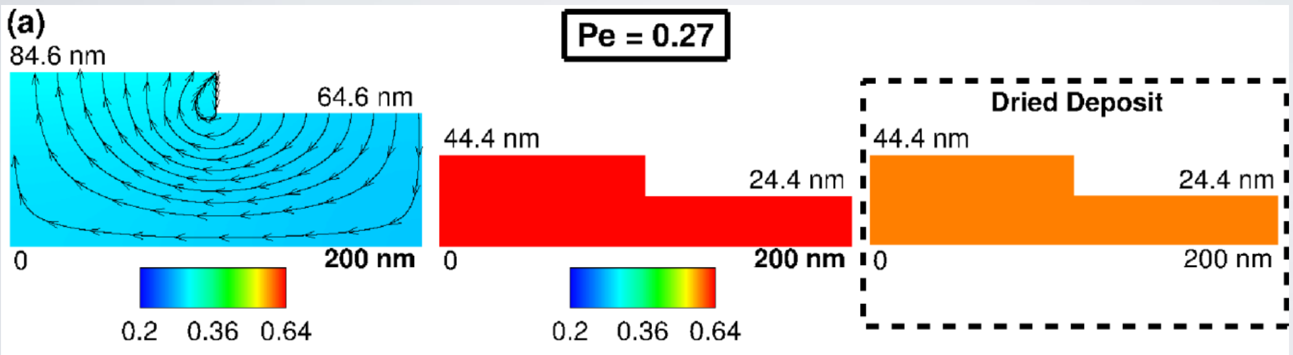
- Isolated sphere diffusivity:

$$D_0=\frac{k_B T}{3\pi\mu_0 a}$$

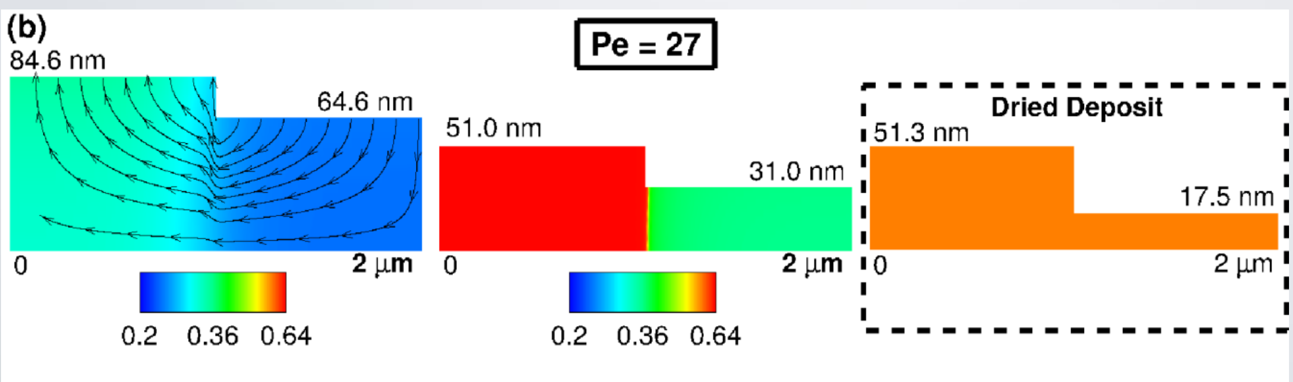
Simulation

- Convection v.s. Diffusion:

$$Pe \equiv \frac{E_{av}L^2}{D_0(d_\Delta + d_{film})}$$



$$d_f = 100\ nm$$
$$d_\Delta = 200\ nm$$
$$d_{film} = 100\ nm$$
$$\varphi_0 = 0.20$$
$$\boldsymbol{L = 200\ nm}$$



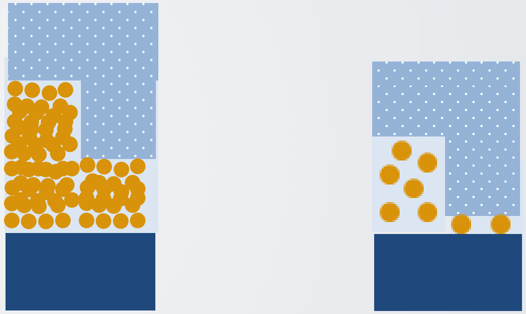
$$d_f = 100\ nm$$
$$d_\Delta = 200\ nm$$
$$d_{film} = 100\ nm$$
$$\varphi_0 = 0.20$$
$$\boldsymbol{L = 2\ \mu m}$$

- Controls: d_f, d_Δ, d_{film} & φ_0

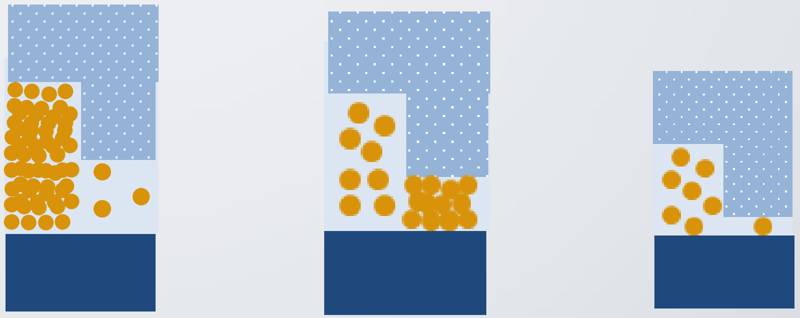
Analytical Modeling

- Convection-dominant and diffusion-dominant limits yield bounds on deposit dimensions and drying time
- The system can evolve in different ways:

Diffusive Limit (Pe→0)



Convective Limit (Pe→∞)

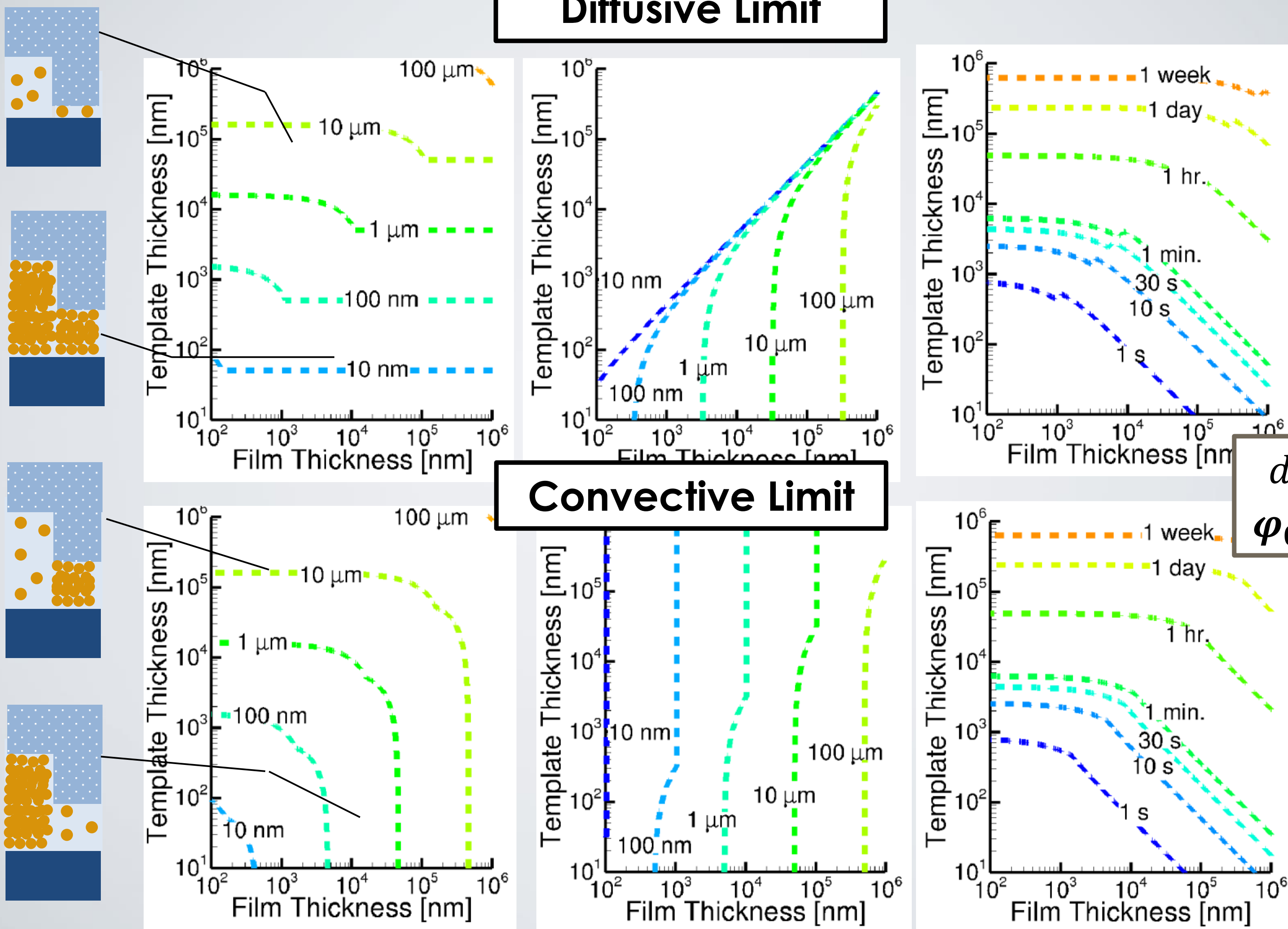


- Drying time is related to pattern *height*.

Trends

Diffusive Limit

Convective Limit



$$d_\Delta = 2d_f$$
$$\boldsymbol{\varphi_0 = 0.20}$$

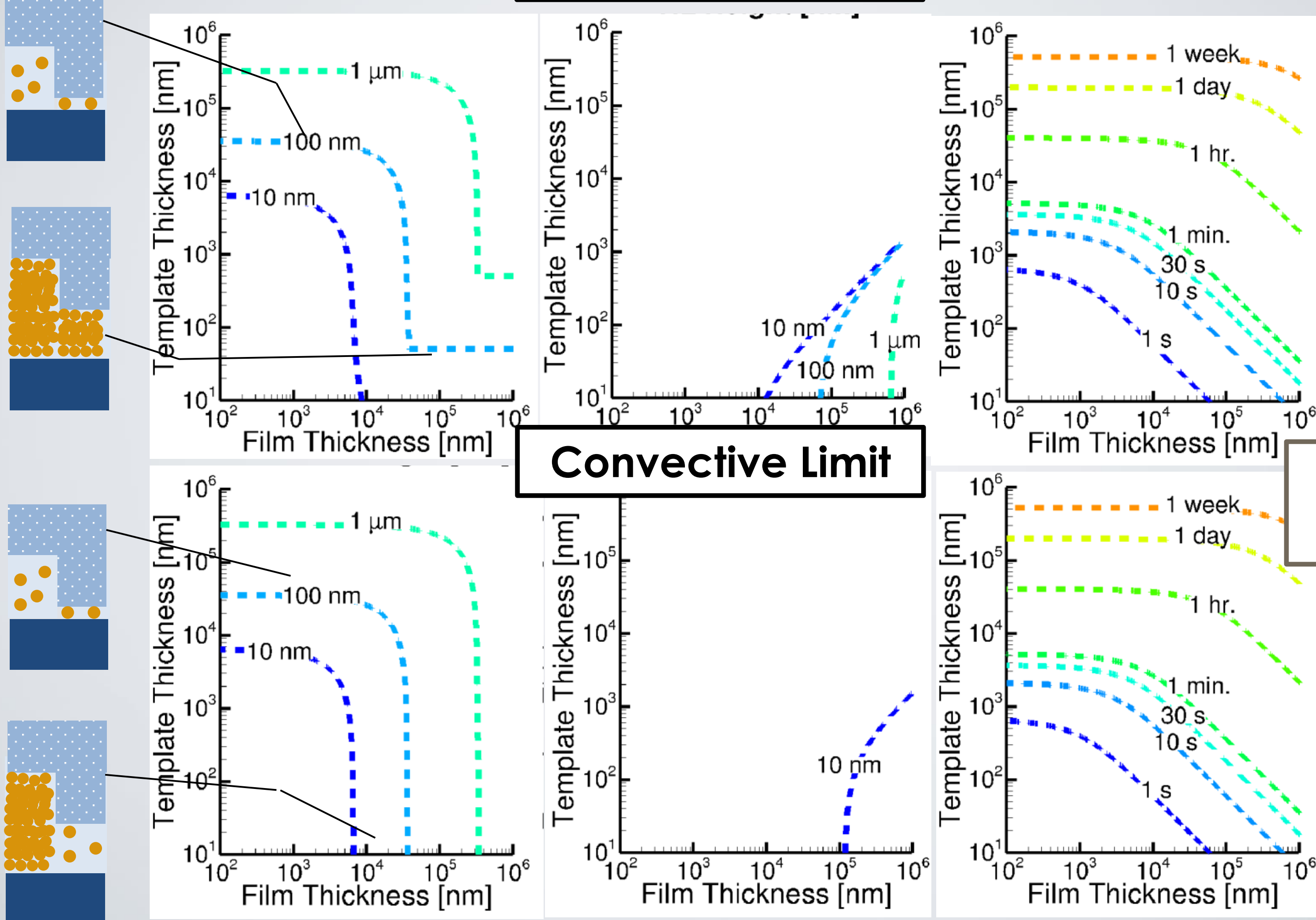
Feature – RL Thickness

RL Thickness

Drying Time

Trends

Diffusive Limit



$$d_\Delta = 2d_f$$
$$\boldsymbol{\varphi_0 = .001}$$

Feature – RL Thickness

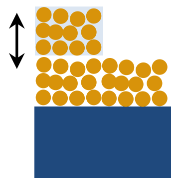
RL Thickness

Drying Time

Minimum Time for Pattern Deposition

- Fastest drying time is 1 s per 10 μm of feature height above RL.

$h_{ft} - h_{rl} = 10\ \mu m$

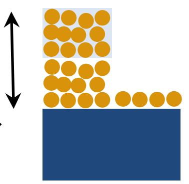


$d_f = 10\ nm$
$d_\Delta = 20\ nm$
$d_{film} = 92\ \mu m$
$\varphi_0 = 0.20$

Minimum drying time: 1 sec

- Features up to 1 micron high with mono-layered RL (10 nm) in < 2 mins.

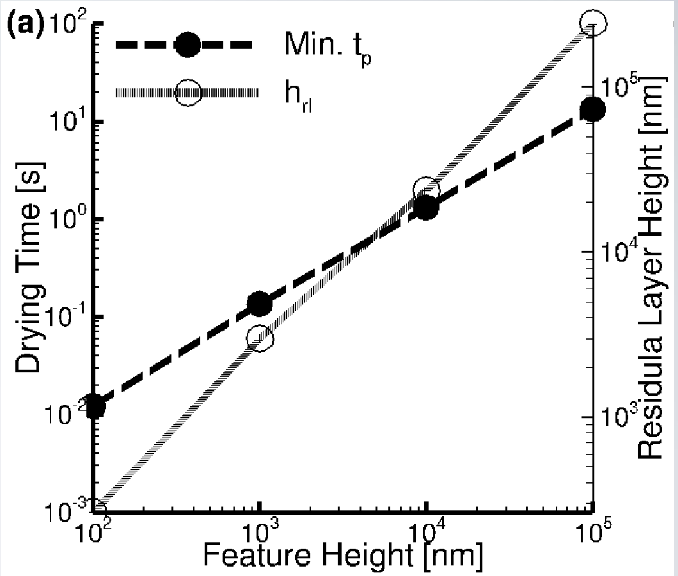
$h_{ft} = 300\ nm$

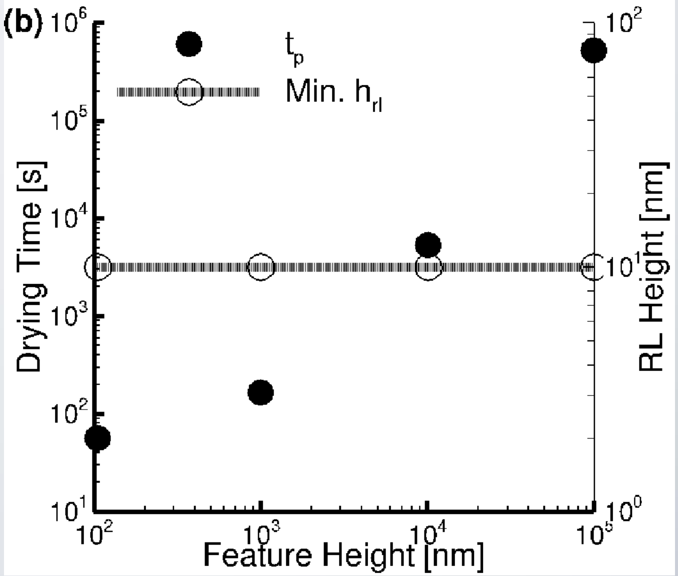


$h_{rl} = 10\ nm$

$d_f = 10\ \mu m$
$d_\Delta = 6.2\ \mu m$
$d_{film} = 1\ \mu m$
$\varphi_0 = 0.019$

Minimum drying time: 100 sec



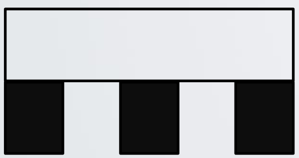


Experimental Realization

- **Deposition:**

Inkjet suspension on substrate → Cover with template → Allow to dry → Heat to sinter NPs → Strip template

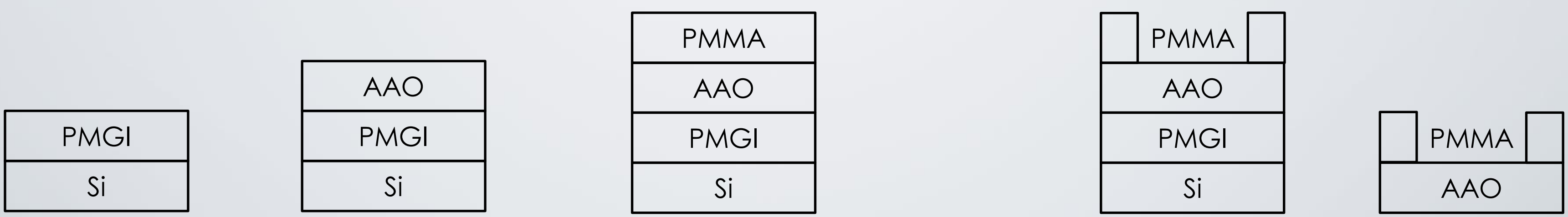
- **Template fabrication:**
  - Composite template for ease of fabrication, greater robustness and better self-assembly



Porous Alumina[1]

Photoresist

[1]Commercially available.
Porosity: 50%, Pore size: 20 nm.



Coat wafer with sacrificial layer (PMGI) → Bond Alumina membrane to wafer → Coat membrane with resist (PMMA) → Expose → Develop resist (MIBK/IPA) → Dissolve sacrificial layer (TMAH)