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Toward Scale-Up Wet Etch Process Modeling for Solar Cell Application

Kristianto Tjiptowidjojo[†], Seok Jun Han[†], Sang Eon Han[†], Sang M. Han[†], P. Randall Schunk[†,*]

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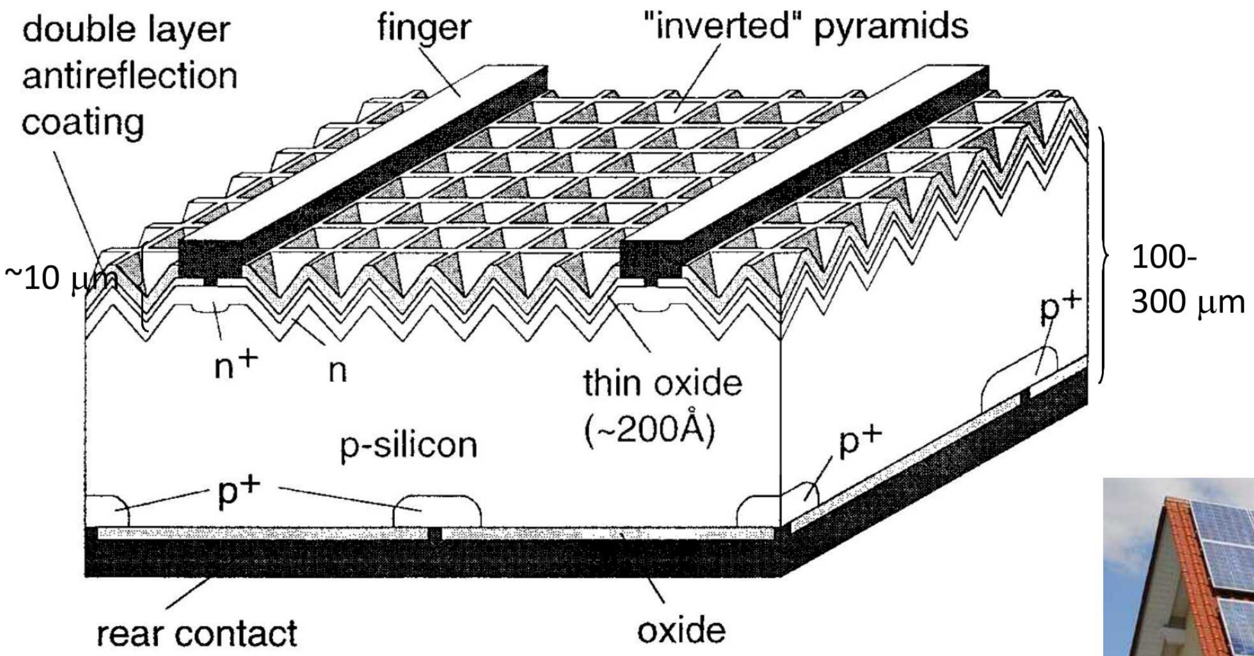
[†] UNM [*] Sandia National Laboratories

Motivation – Solar Module Material and BOS Cost



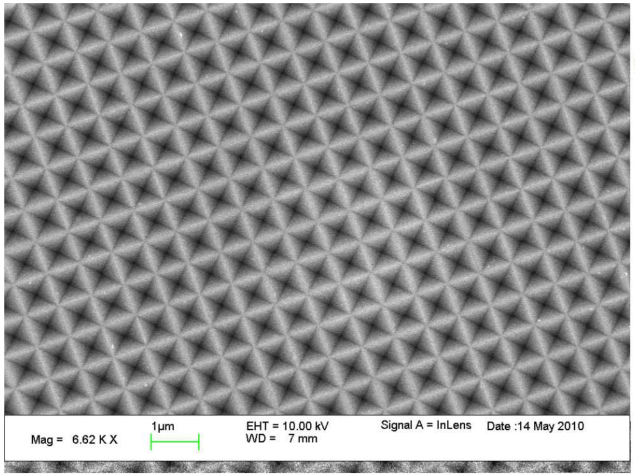
- Cost of c-Si/module
  32%(2010) → 43%(2012) → 31%(2013)
  Wafer sawing loss (kerf loss) ~50%

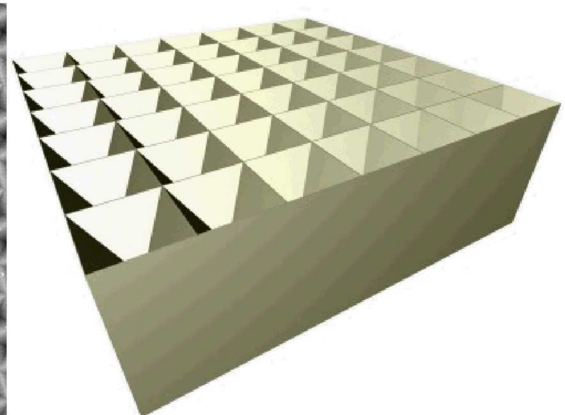
- ~40% of flattop commercial roofs cannot support the weight of conventional solar panels.

Heavy modules → Shipping & installation cost

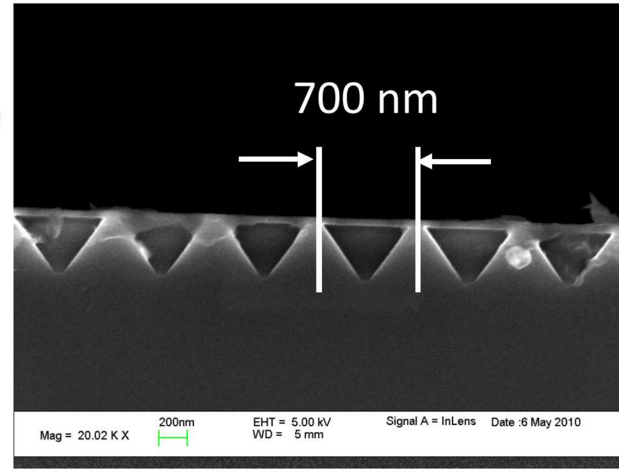
DOE workshop (2010)
Powell et al. Energy Environ Sci (2012)
Goodrich et al. Sol Energy Mat Sol Cell (2013)

Approach: Thin Nanostructured C-Si Surface

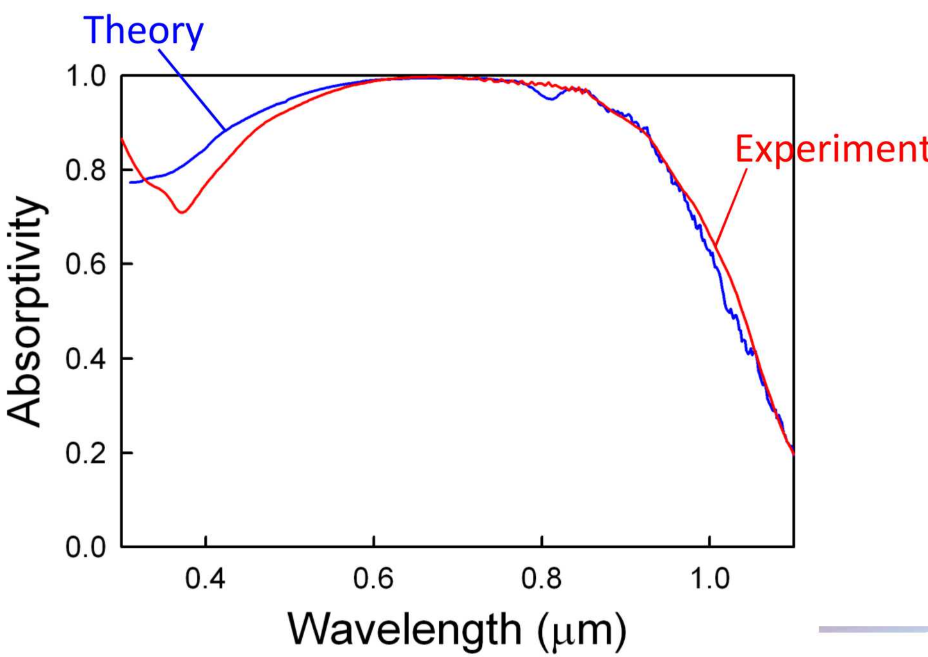




surface area increase: 1.7X



Mavrokefalos, S.E. Han, *et al*. Nano Lett (2012)
Branham *et al*. Adv Mater (2015)

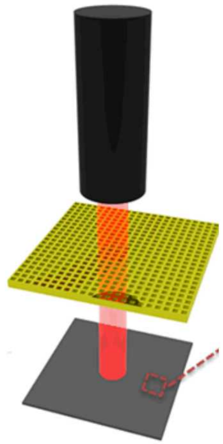


- Thin C-Si wafer saves material and installation cost
- Drawback: Loss of light absorption
- Solution: Surface corrugation with inverted nanopyramids

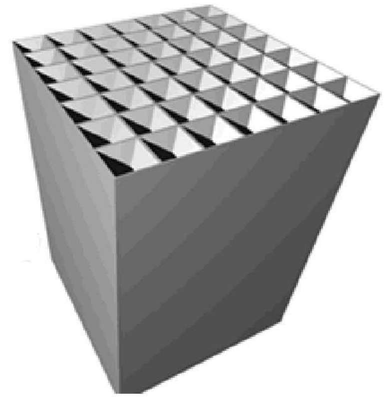
Key: Increase light absorption with less surface area increase

Fabrication Steps

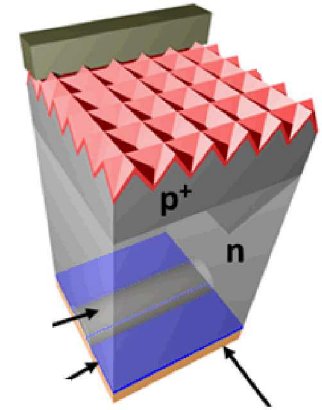
Production of thin c-Si wafer



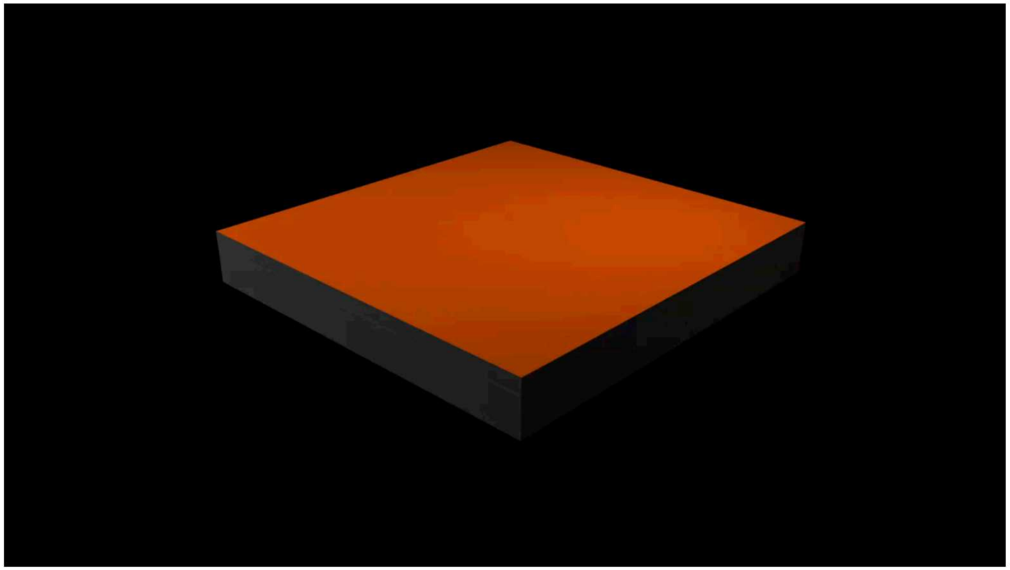
Interference lithography

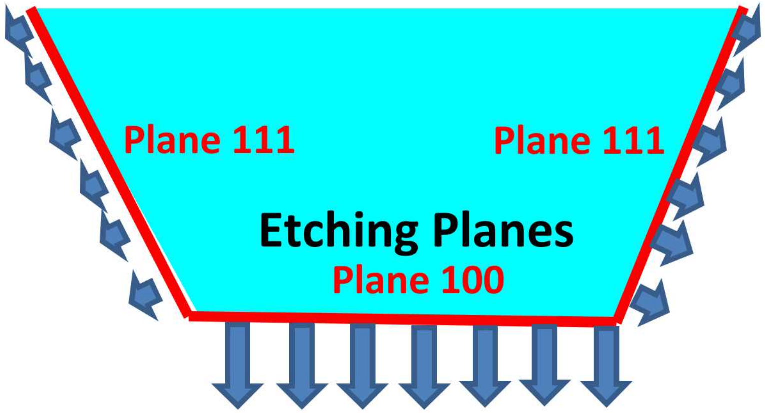


Wet etching



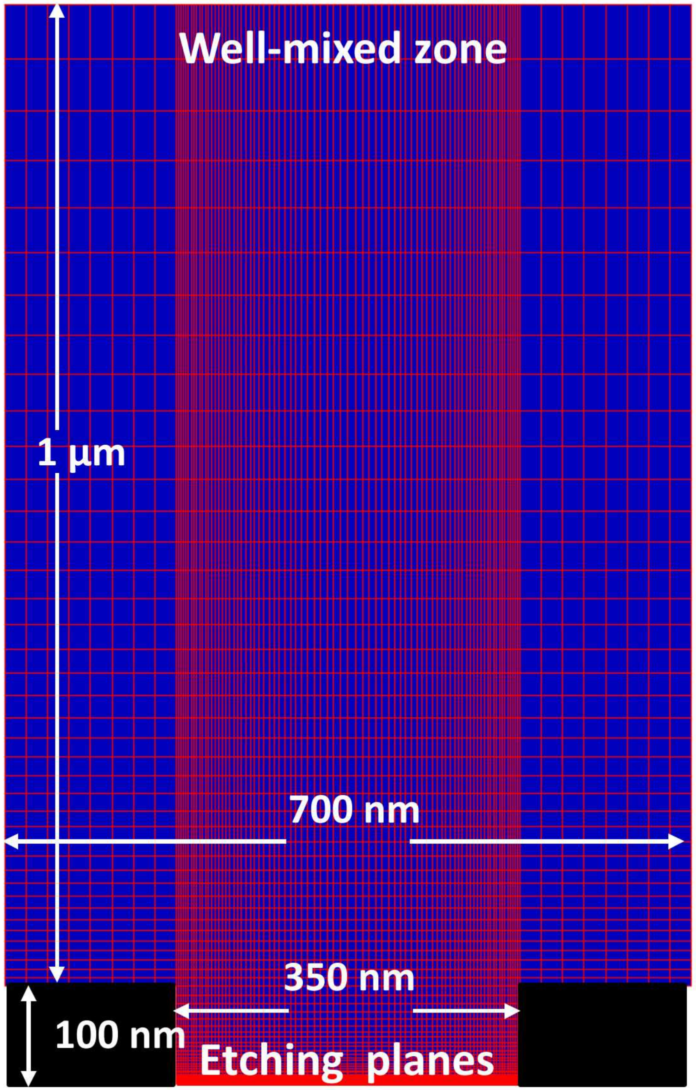
Surface passivation





Focus of this work:
Large area wet etching

Model Development – Feature Scale



Momentum and Total Mass Balance

$$\rho\left[\frac{\partial \mathbf{v}}{\partial t}+\mathbf{v}\cdot\nabla\mathbf{v}\right]=-\nabla p+\rho\mathbf{g}-\frac{\partial\rho}{\partial C_i}\left(C_i-C_{ref}\right)\mathbf{g}+\mu\nabla^2\mathbf{v}$$

$$\nabla\cdot\mathbf{v}=0$$

Boussinesq approximation

Species Transport

$$\frac{\partial C_i}{\partial t}+\mathbf{v}\cdot\nabla C_i=-\nabla\cdot\mathbf{J}_i$$

$$\mathbf{J}_i=D_i\nabla C_i$$

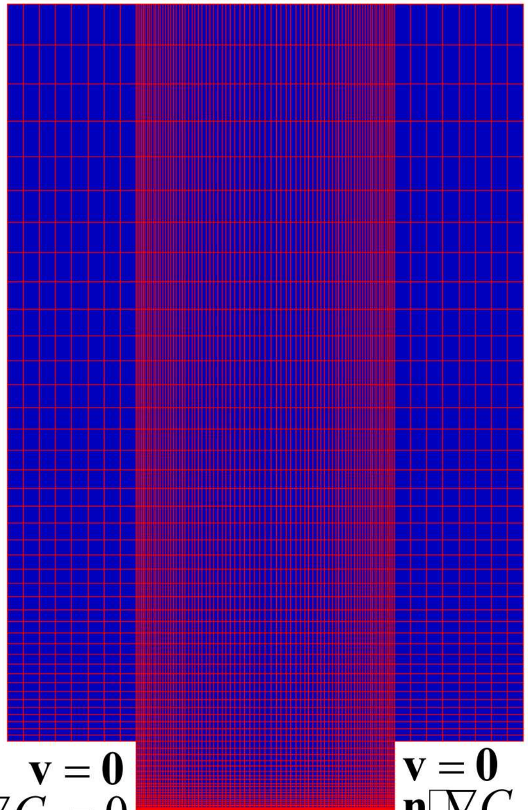
Mesh Motion – Pseudo-solid

$$\nabla\cdot\boldsymbol{\sigma}=\mathbf{0}$$

$$\boldsymbol{\sigma}=G\left[\nabla\mathbf{d}+\left(\nabla\mathbf{d}\right)^T\right]+\lambda\left[\nabla\cdot\mathbf{d}\right]\mathbf{I}$$

Boundary Conditions

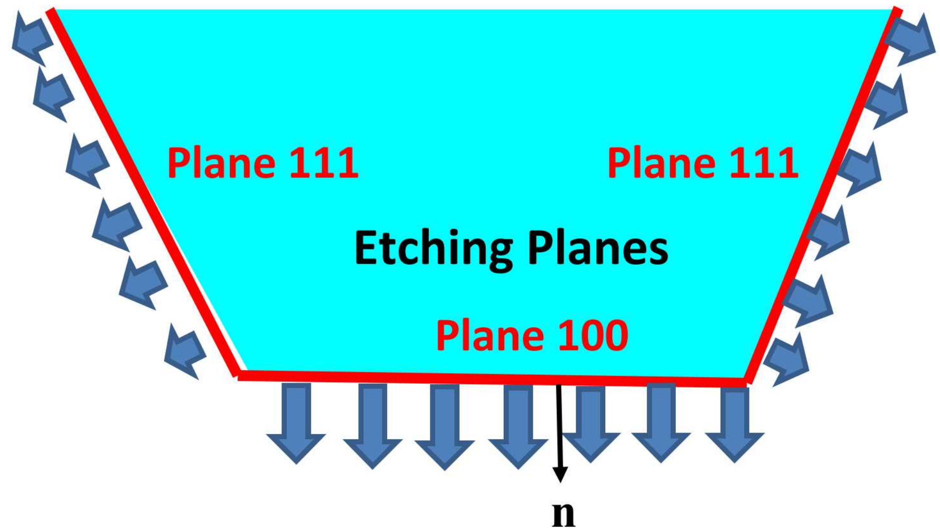
$\mathbf{n}\cdot\mathbf{T} = -\mathbf{n}p_{\text{ref}}$ $\quad C_i = C_i(t=0)$



$\mathbf{v} = \mathbf{0}$, $\mathbf{n}\cdot\nabla C_i = 0$ $\quad$ $\mathbf{v} = \mathbf{0}$, $\mathbf{n}\cdot\nabla C_i = 0$

$$Si + 2OH^- + 2H_2O \rightarrow SiO_2(OH)_2^{--} + 2H_2$$

Seidel, H., et al. *Journal of the electrochemical society* 137.11 (1990): 3612-3626.



Species BC

$$\mathbf{J}_i = \mathbf{J}_i(C_i)$$

Mass flux due to surface reaction

Mesh BC

$$\mathbf{n}\cdot\frac{\partial \mathbf{d}}{\partial t} = \text{etch rate}(C_i)$$

Etching plane movement

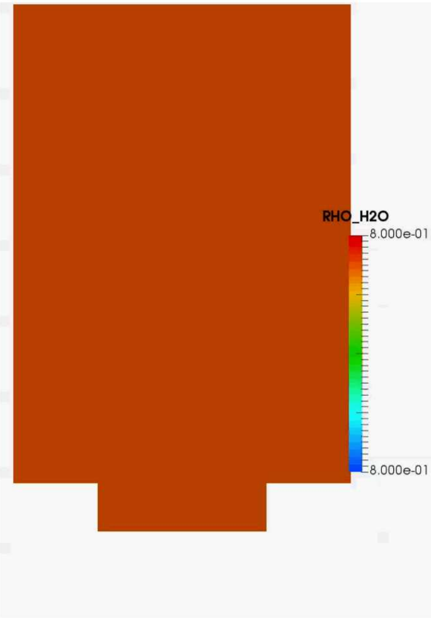
Momentum BC

Mass-averaged velocity

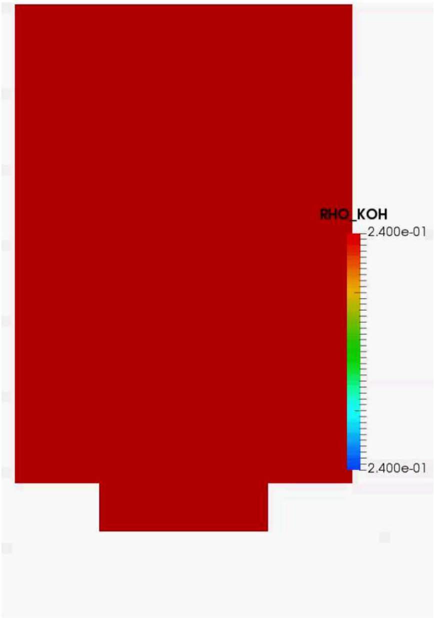
$$\mathbf{n}\cdot\left(\mathbf{v} - \frac{\partial \mathbf{d}}{\partial t}\right) = \frac{1}{\rho}\sum_i \mathbf{n}\cdot\mathbf{J}_i \qquad \mathbf{t}\cdot\mathbf{v} = 0$$

Results – Feature Scale

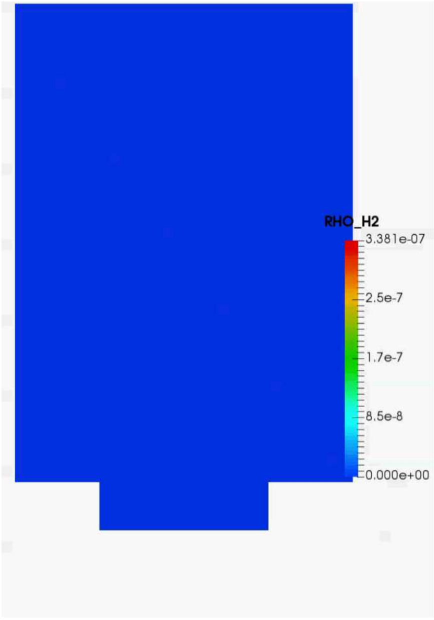
Water



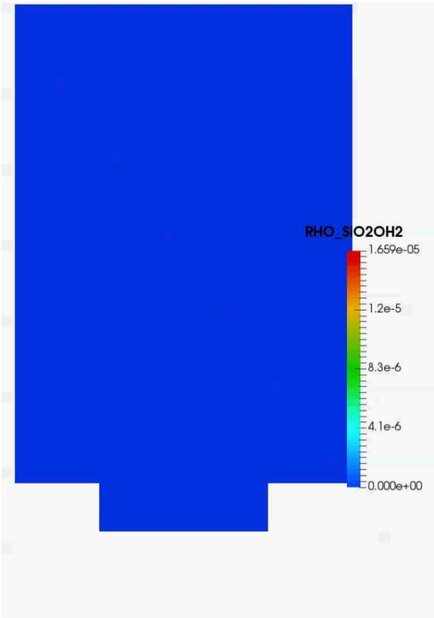
KOH

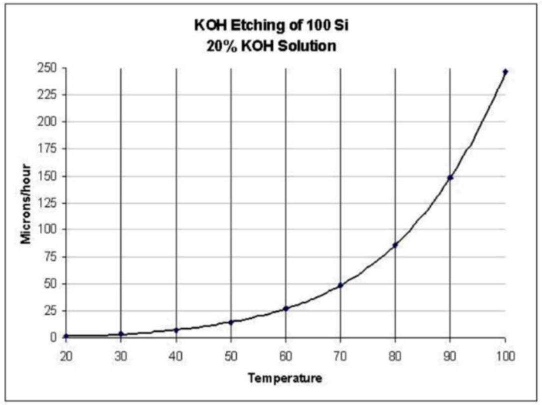


Hydrogen



$SiO_2(OH)_2$





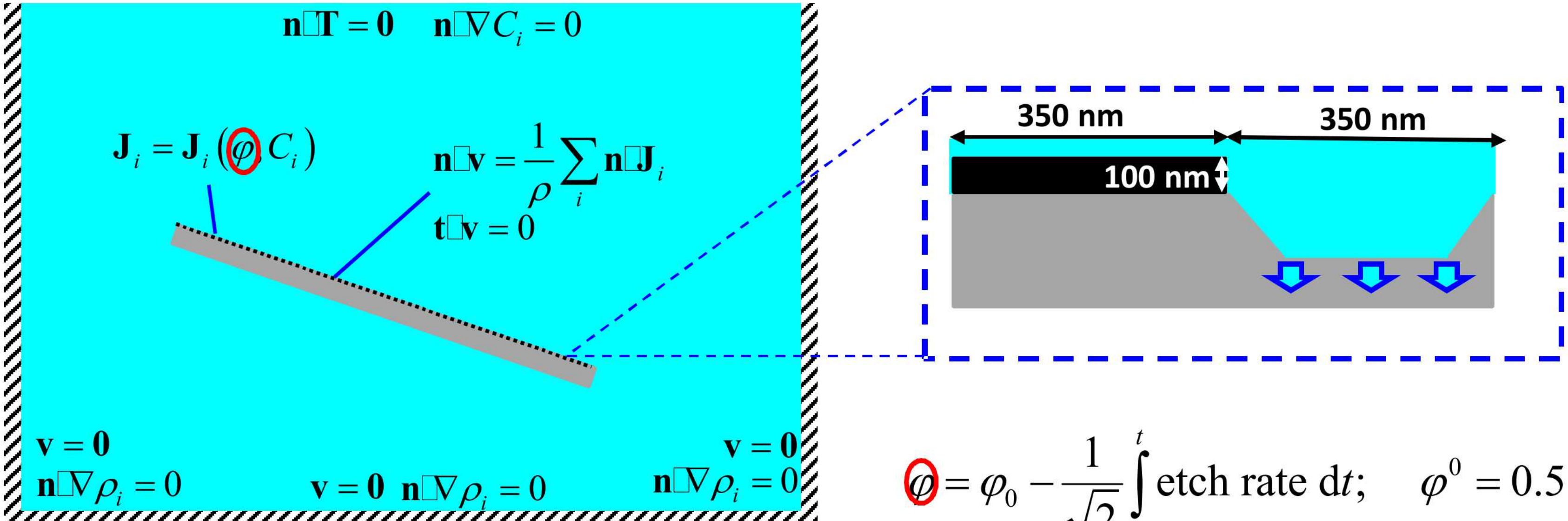
Etch rate ~ 14 µm/hour → Etch of 100 plane completed at **63.6 seconds**

Diffusion coefficient in liquid ~ 10^{-5} cm^2/s

→ Diffusion time scale is **12.8 seconds**

Negligible concentration boundary layer → Reaction is much slower than transport

Model Development – Wafer Scale



$$\varphi=\varphi_0-\frac{1}{\sqrt{2}}\int_0^t \text{etch rate } \mathrm{d}t; \quad \varphi^0=0.5$$

Momentum and Total Mass Balance

$$\rho\left[\frac{\partial\mathbf{v}}{\partial t}+\mathbf{v}\cdot\nabla\mathbf{v}\right]=-\nabla p+\rho\mathbf{g}-\frac{\partial\rho}{\partial C_i}\left(C_i-C_{\mathrm{ref}}\right)\mathbf{g}+\mu\nabla^2\mathbf{v}$$

$$\nabla\cdot\mathbf{v}=0$$

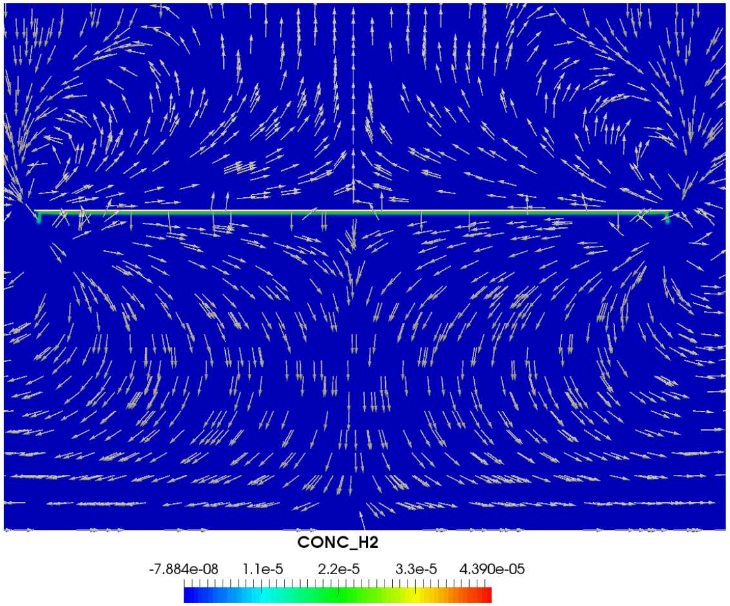
Species Transport

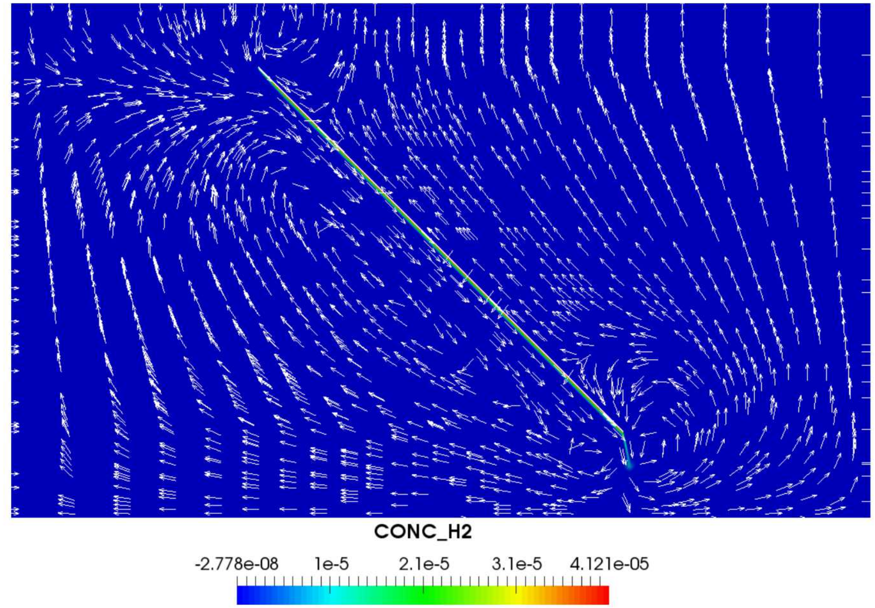
$$\frac{\partial C_i}{\partial t}+\mathbf{v}\cdot\nabla C_i=-\nabla\cdot\mathbf{J}_i$$

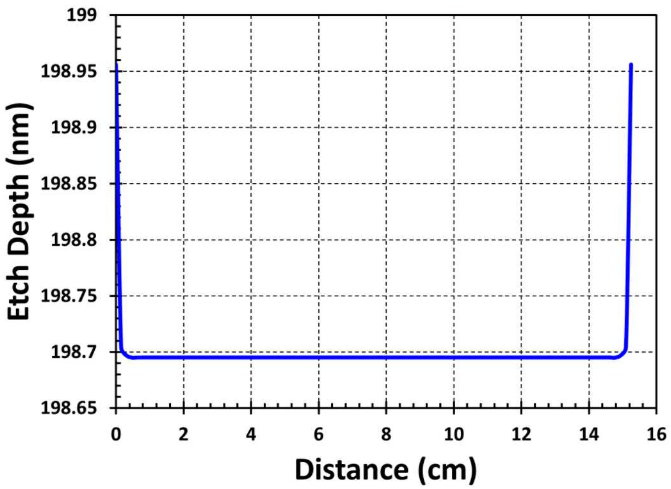
$$\mathbf{J}_i=D_i\nabla C_i$$

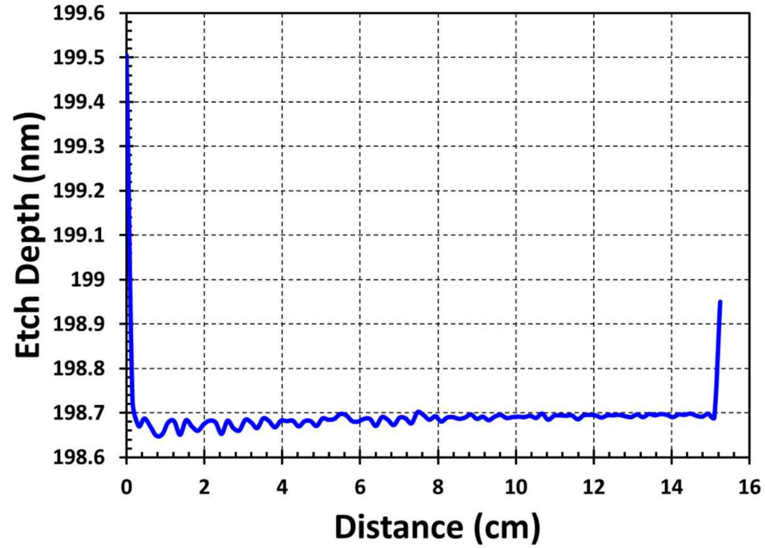
- No mesh equation – not resolving transport and surface reaction in each feature
- Feature shape is inferred from extent of ***area-averaged*** surface reaction

Results – Wafer Scale



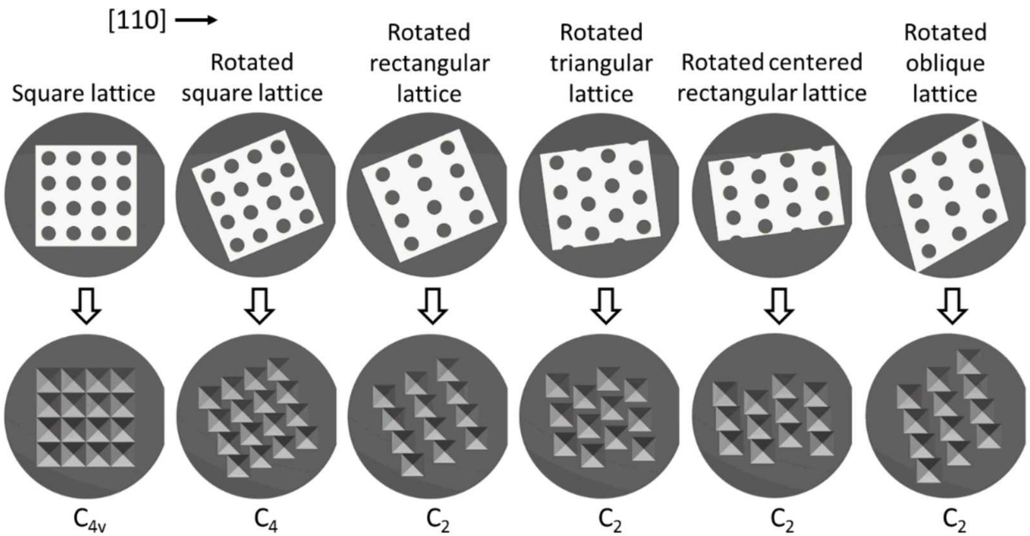






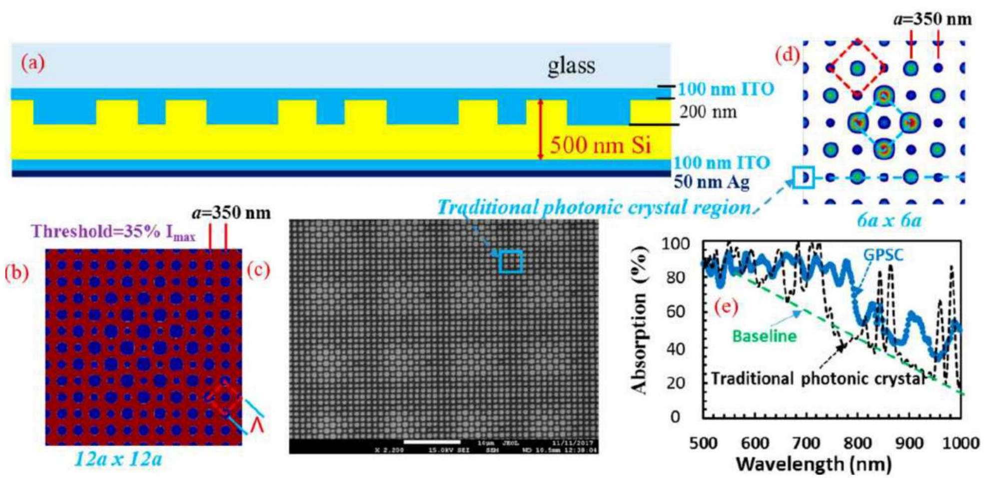
Uniform etching across the wafer – no gravity effect

Potential Further Enhancements



Symmetry Breaking

- Decrease amount of symmetry → Enhanced light trapping
- Achieved with modifying interference lithography step → modify mask and its rotation.

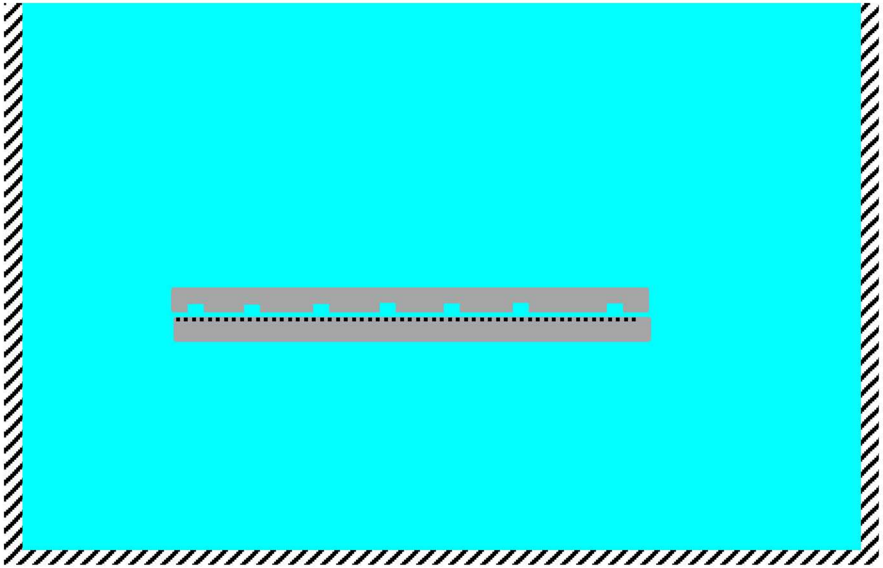


Double Periodicity

- Add more disorder into the nanostructures → Enhanced light trapping
- How to add secondary patterning in high throughput?

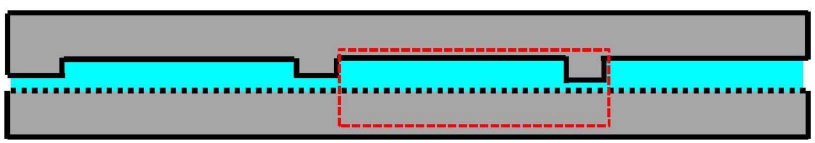
Hassan, S., et al. *Photonics* 4 (2017): 50-58.

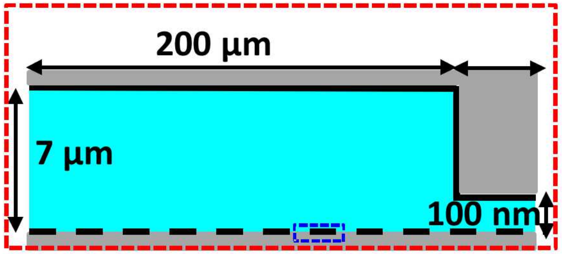
Approach to Achieve Second Periodicity

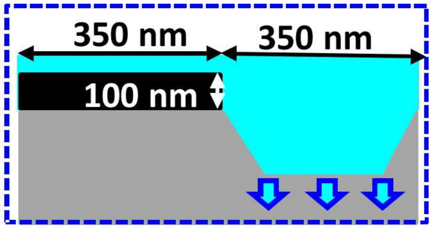


- Apply a ***confinement mask*** during wet etching step → scalable for manufacturing scale
- Slow down transport of limiting reactant: KOH
- Region with KOH depletion will have more shallow etch depth

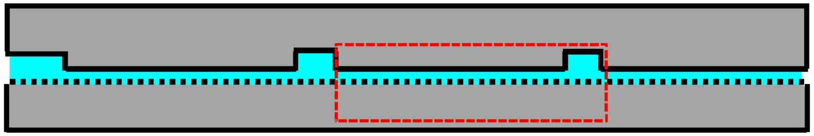
Mask 1

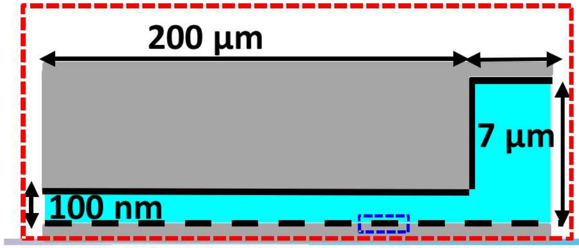




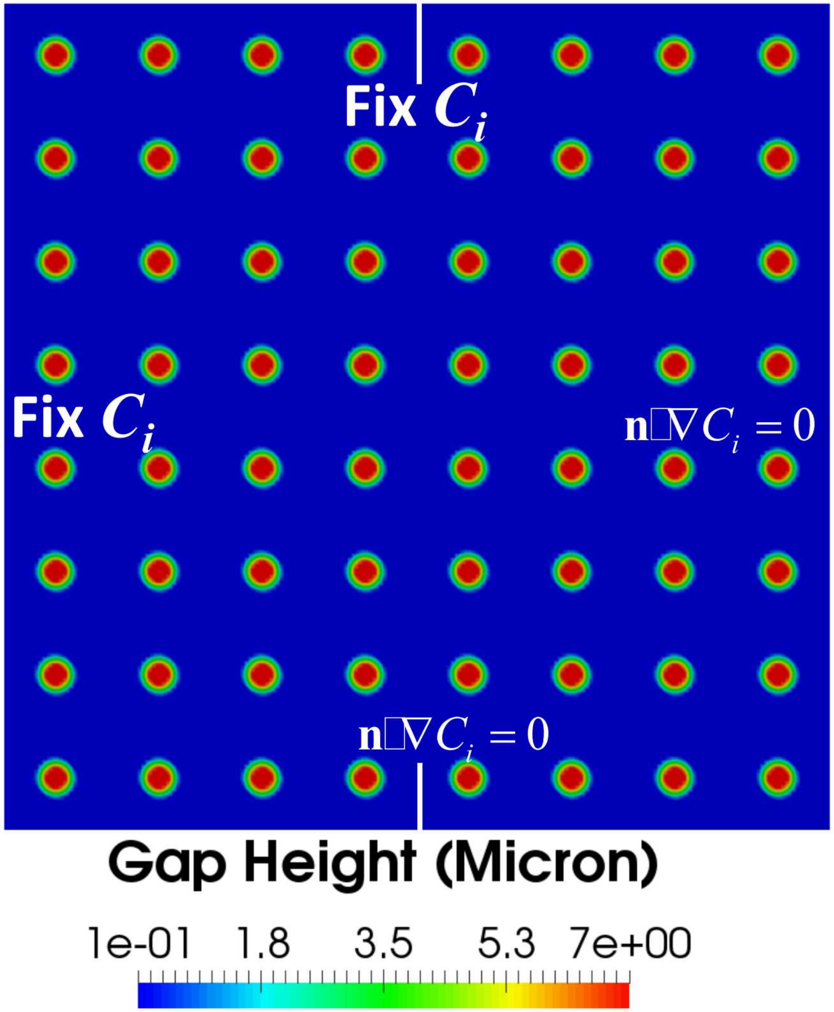


Mask 2





Model Development – Shell Balance



Species Transport

$$h\frac{\partial C_i}{\partial t} + \mathbf{v}_{\mathrm{II}}\cdot\left(h\nabla_{\mathrm{II}} C_i\right) = \nabla_{\mathrm{II}}\cdot\left(hD\nabla_{\mathrm{II}} C_i\right) + J$$

$$J = \text{etch rate}\left(\varphi, C_i\right)$$

Momentum and Total Mass Balance

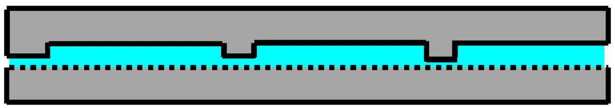
$$\mathbf{q} = \frac{h^3}{12\mu}\left[-\nabla_{\mathrm{II}} p + \rho\mathbf{g} - \frac{\partial\rho}{\partial C_i}\left(C_i - C_{\mathrm{ref}}\right)\mathbf{g}\right]$$

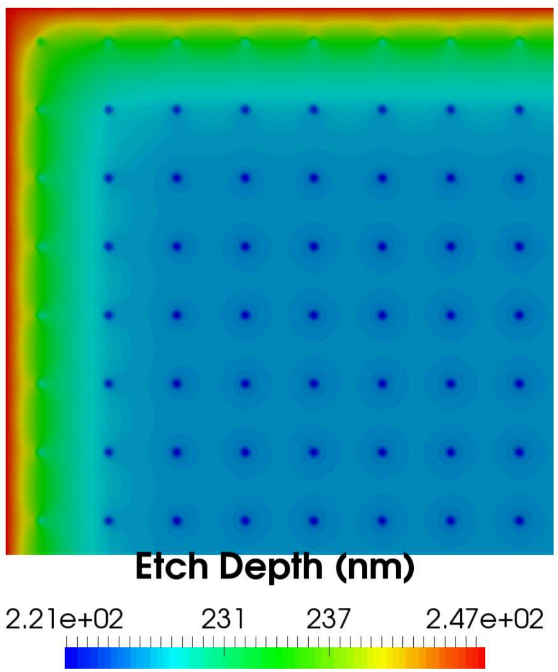
$$\nabla_{\mathrm{II}}\cdot\mathbf{q} = 0$$

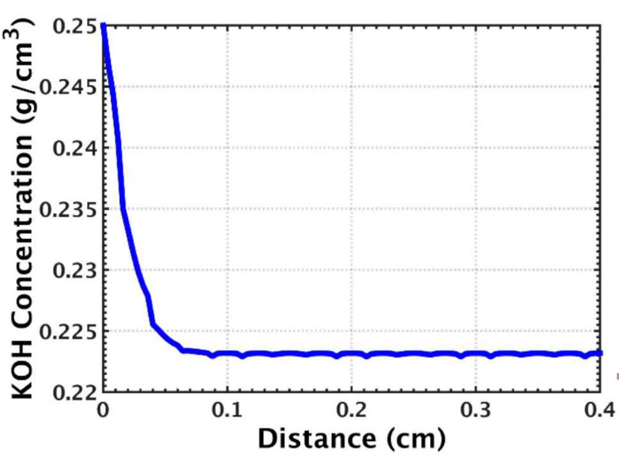
- ***Thin region – Flow and species transport are averaged in gap direction***
- ***Enable calculation at different mask patterns rapidly***

Results – After 50 s of etching

Mask 1



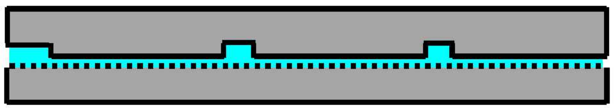


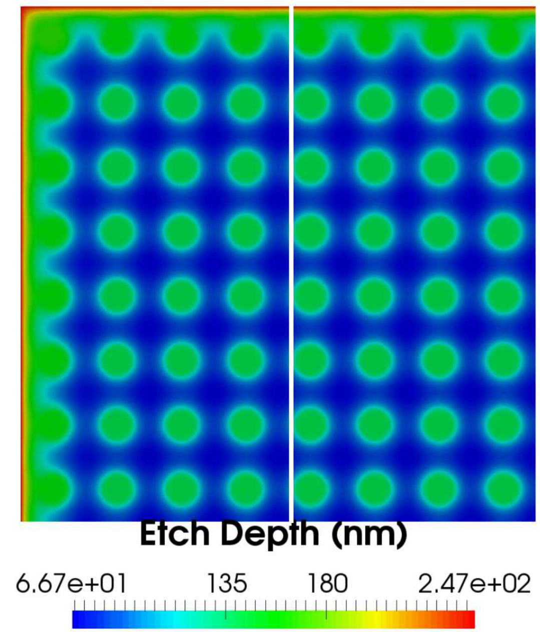


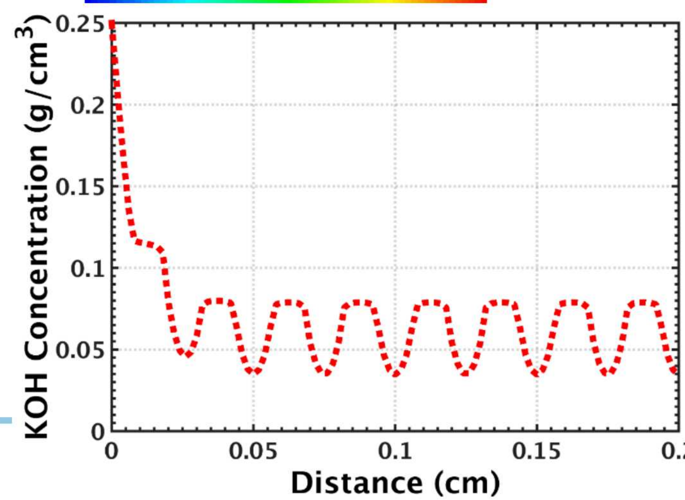
Etch depth is set by inventory of reactants at each region → ***transport limited***

Etch depth variation is more prevalent at mask 2 due to ***KOH depletion***

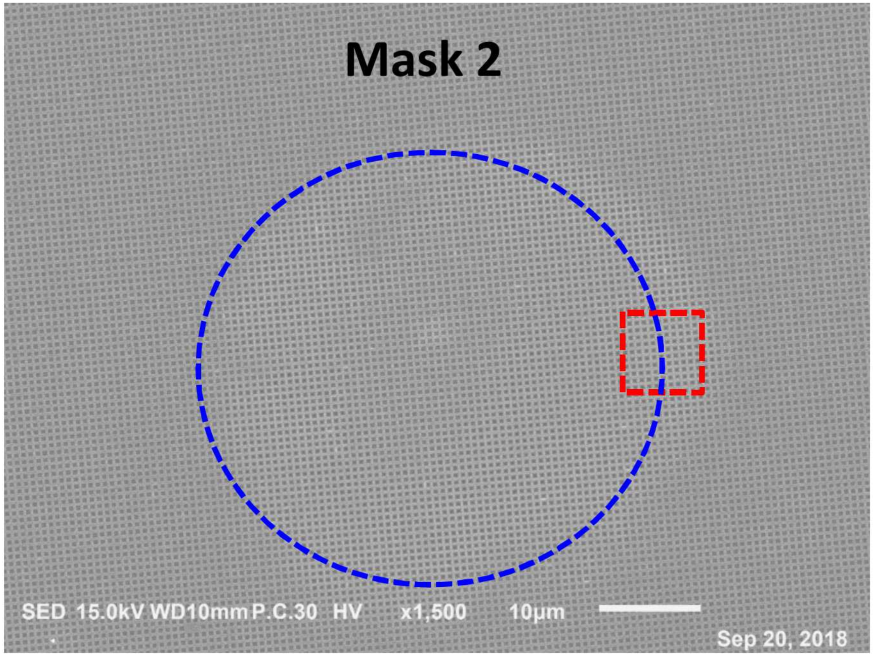
Mask 2

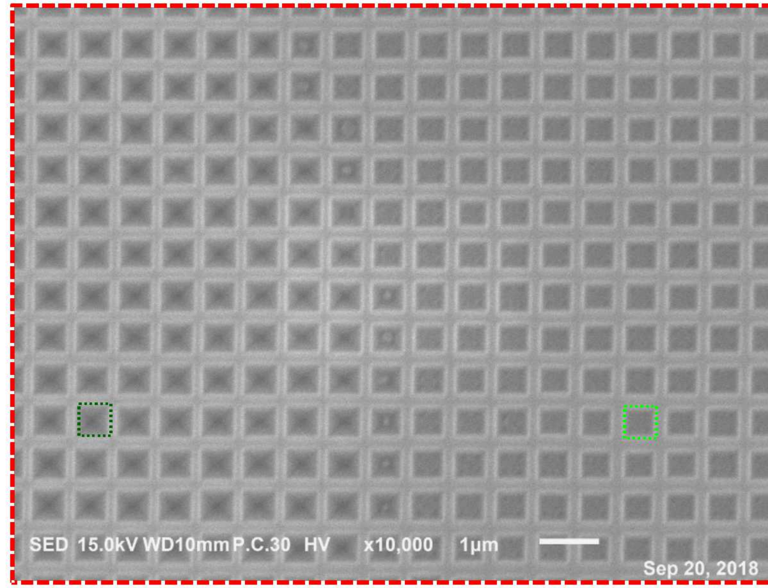


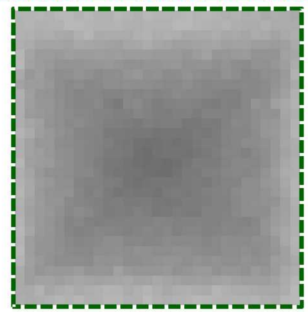


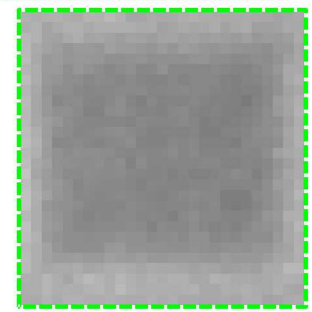


Comparison with Experiments - After 310 s of etching

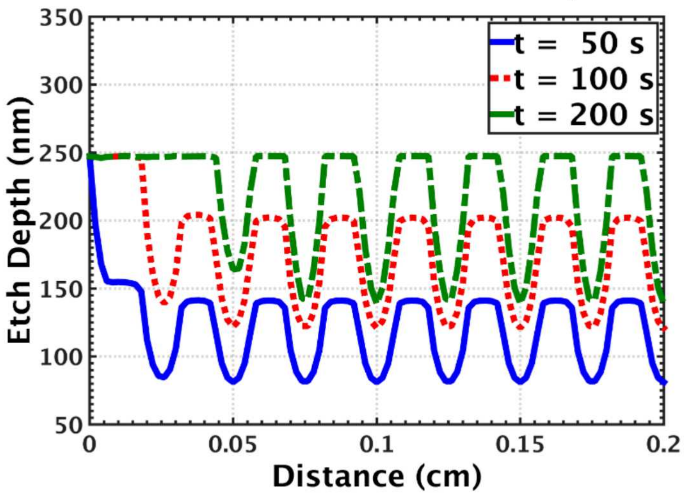








Model Prediction of Etch Depth Evolution



- *Complete inverted nanopyramids at 7 μm gap region*
- *Incomplete pyramids at 100 nm region*

Conclusions

- Performed multi-scale studies of wet etching process:
  - In feature level – reaction dominated
  - In wafer scale – reaction dominated
  - In wafer scale with confinement – transport limited

- Enable control of etch depth gradient with confinement – balance transport and etch reaction

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