ECE 444 Special Lecture

Metal-assisted chemical Etching

Wet Etch, Dry Etch, and now MacEtch

Not your ordinary etching

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http://mocvd.ece.Illinois.edu

Electrical and Computer Engineering

University of Illinois

Outline

- Background of MacEtch (Metal-assisted chemical Etching)
  - Forward MacEtch
  - Inverse MacEtch (I-MacEtch)
  - Magnetic-field MacEtch (h-MacEtch)
  - Self-anchored-catalyst (SAC-MacEtch)
  - Materials versatility and device applications
    - Si, Ge, GaAs, InGaAs, InP, Ga_2O_3, FET, PV, PD, etc.
- Summary

MacEtch

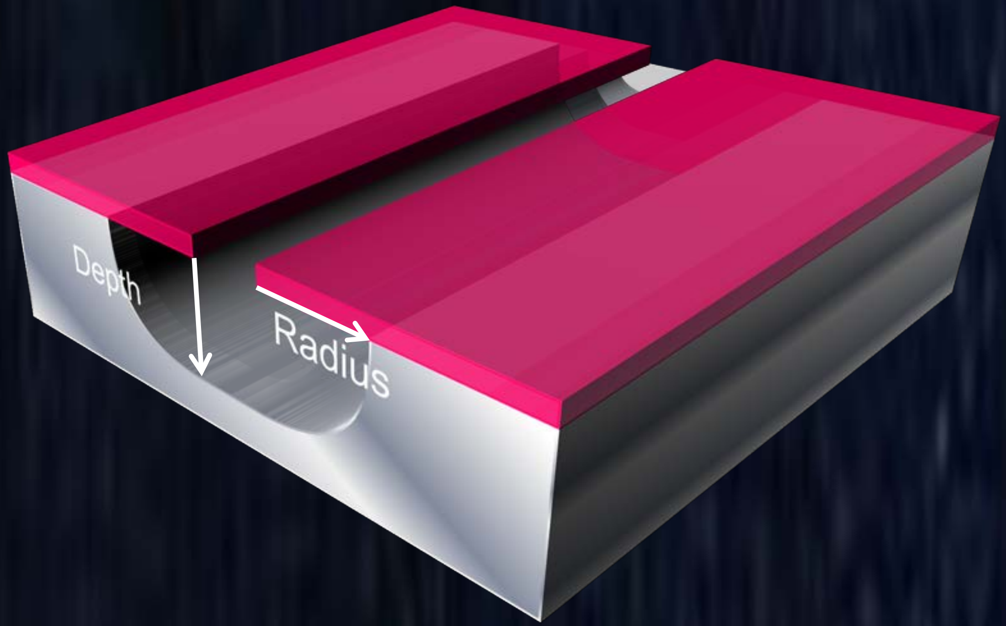
BACKGROUND AND MECHANISM

Wet Etch

http://fabweb.ece.illinois.edu

isotropic -

- most wet etches are isotropic
  i.e. they etch equally in all directions
- isotropic etches result in undercutting

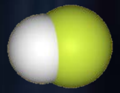


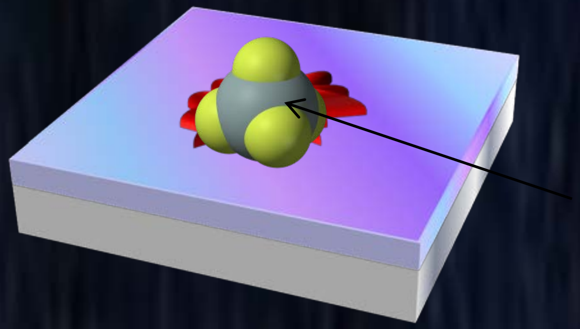
- for an isotropic etch, radius = depth
- over-etch%

Wet Etch

http://fabweb.ece.illinois.edu

rate determining steps - diffusion of reactants to the surface
reaction rate at the surface
desorption of reaction products





material removed

reaction equation mA + nB → reaction products

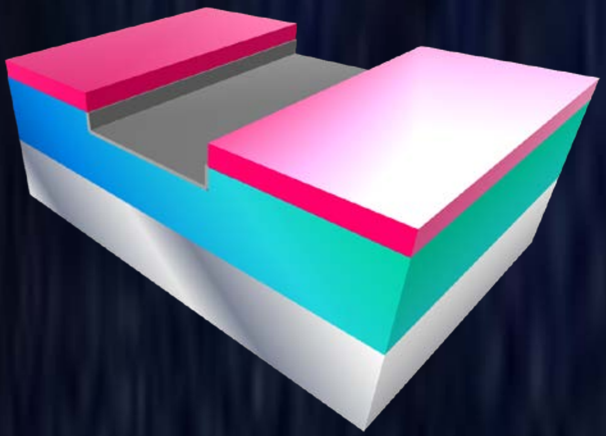
reaction rate

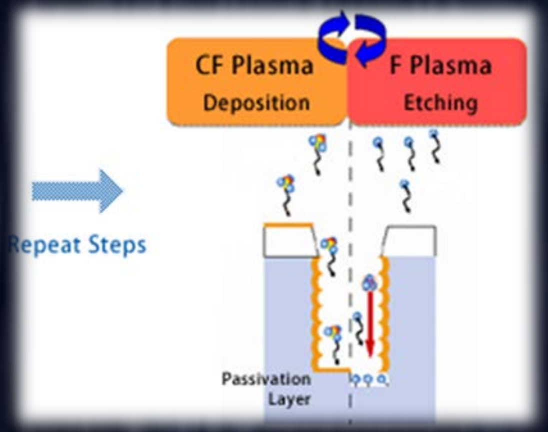
$$r = k[A]^m[B]^n e^{-\frac{E_A}{RT}}$$

Dry Etch

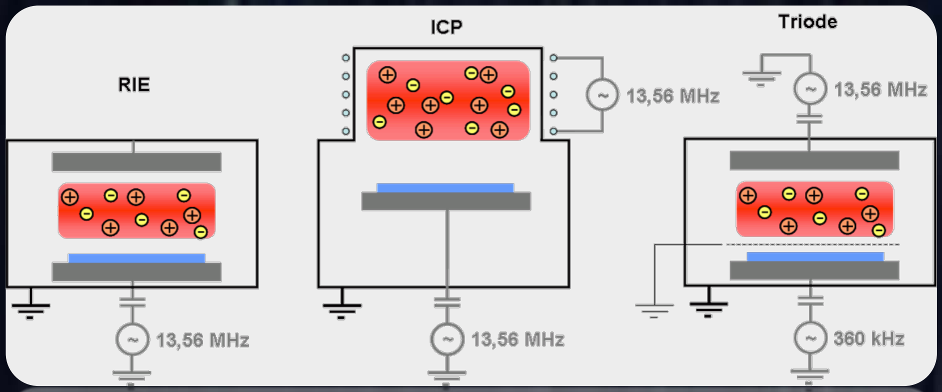
http://fabweb.ece.illinois.edu

- **Mechanism:**
  - Chemical:
    - plasma etch - small degree of anisotropy
  - Physical:
    - sputtering, directional but no selectivity
- **Goal:**
  - enhance anisotropy
    - without losing selectivity
    - without causing damage
    - maintain controllable etch rate
- **Techniques:**





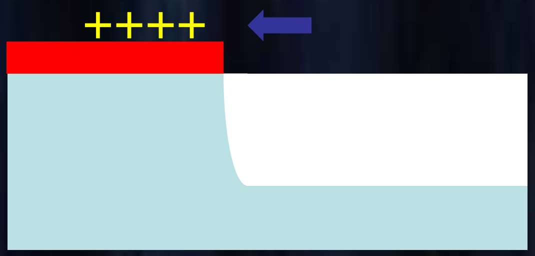
SAMCO



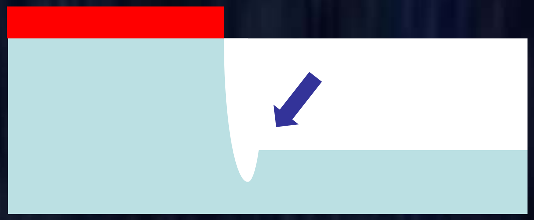
https://www.crystec.com/trietche.htm

Dry Etching Issues

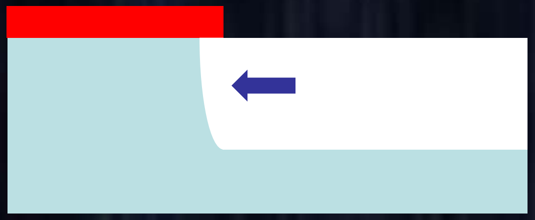
http://fabweb.ece.illinois.edu



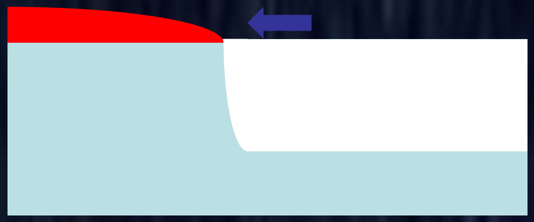
charging



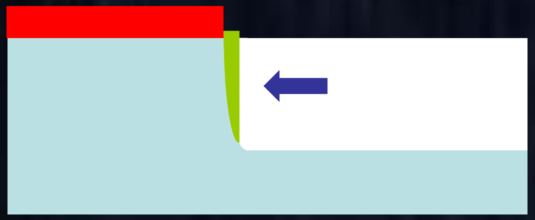
trenching



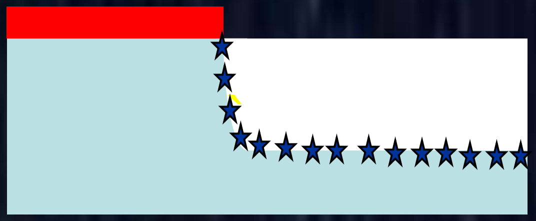
undercutting



mask erosion



sidewall residue



Surface damage

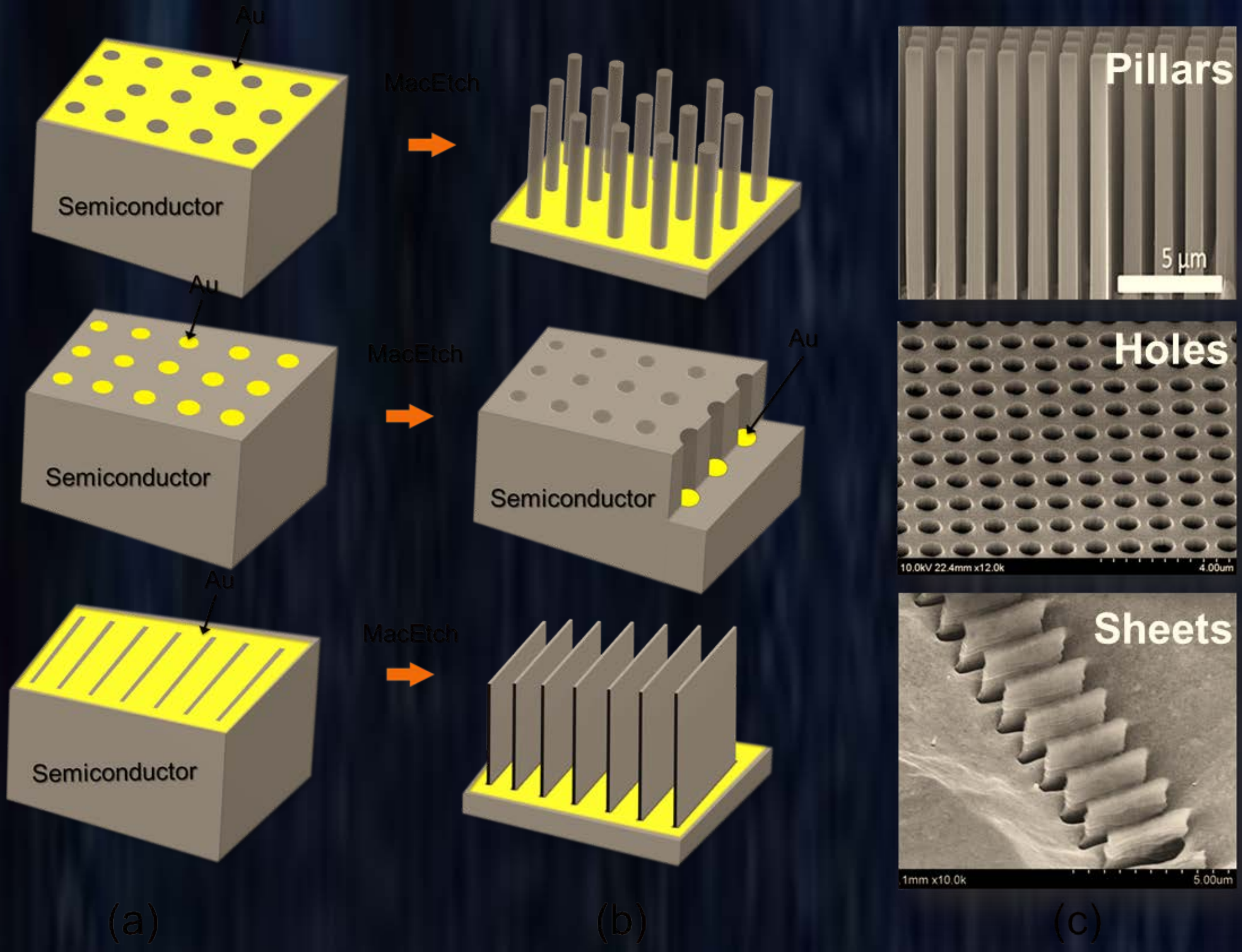
Metal-Assisted Chemical Etching (MacEtch)

Scalable, high throughput, low cost

- Process Flow
  - Pattern metal
  - Immerse in HF/H_2O_2
  - Etching takes place underneath the metal
- Contrast with
  - wet vs dry etch
  - bottom-up growth

MacEtch: wet etch but directional

Metal-Assisted Chemical Etching (MacEtch)



- X. Li and P. W. Bohn, *Appl. Phys. Lett.* 77, 2572 (2000); ~893 citation.
- Patents: 7 issued and 4+ pending

MacEtch mechanism

X. Li and P.W. Bohn, Appl. Phys. Lett.77, 2572 (2000).

Local electrochemical reaction

Cathode reaction (at metal):

$H_2O_2 + 2H^+ \rightarrow 2H_2O + 2h^+$

$2H^+ + 2e^- \rightarrow H_2 \uparrow$

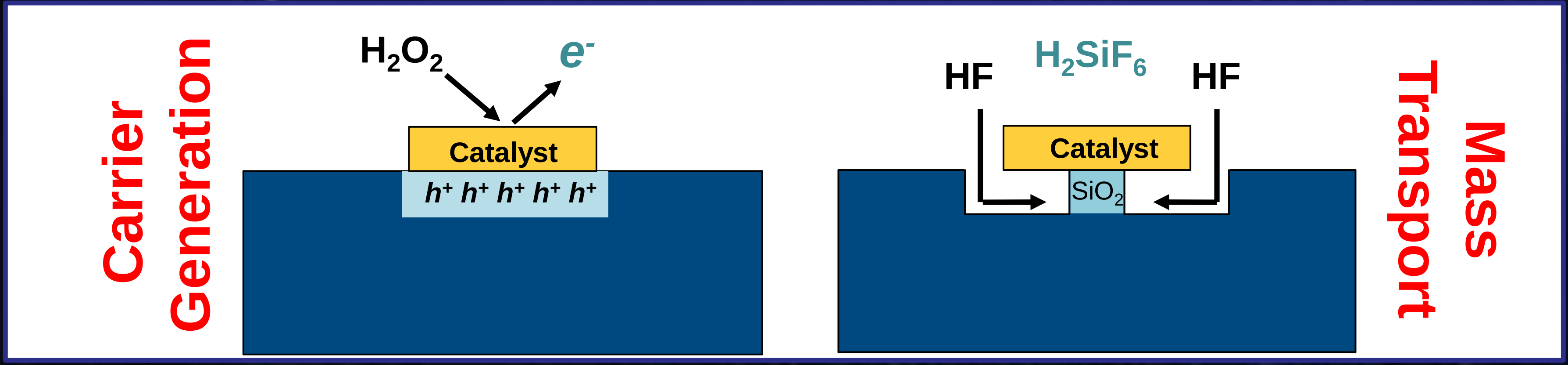
Anode reaction (at Si):

$Si + 4h^+ + 4H_2O \longrightarrow SiO_2 + 4H^+$

$SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O$

Overall reaction:

$Si + H_2O_2 + 6HF \rightarrow 2H_2O + H_2SiF_6 + H_2 \uparrow$



MacEtch

CHARACTERISTICS

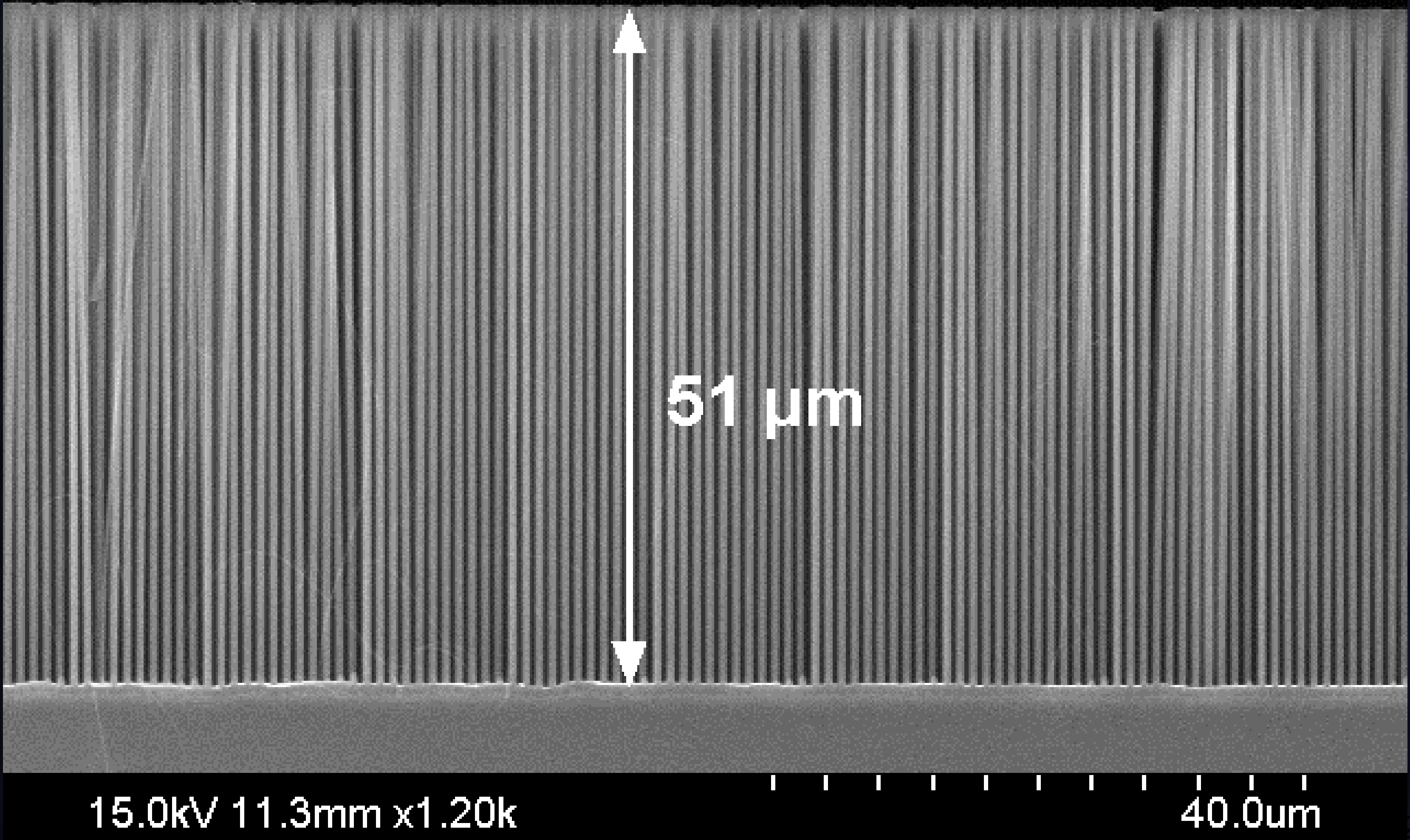
"Metal Assisted Chemical Etching for High Aspect Ratio Nanostructures: A Review of Characteristics and Applications in Photovoltaics," X. Li, Current Opinion in Solid State & Materials Science, invited review article, 16, 71-81 (2012).

"Metal-assisted chemical etching of silicon: a review," Huang Z, Geyer N, Werner P, de Boor J, Gosele U. Adv Mater 2011; 23(2):285–308.

Extremely High Aspect Ratio

Si nanowire array: 550 nm diameter, 51 µm height

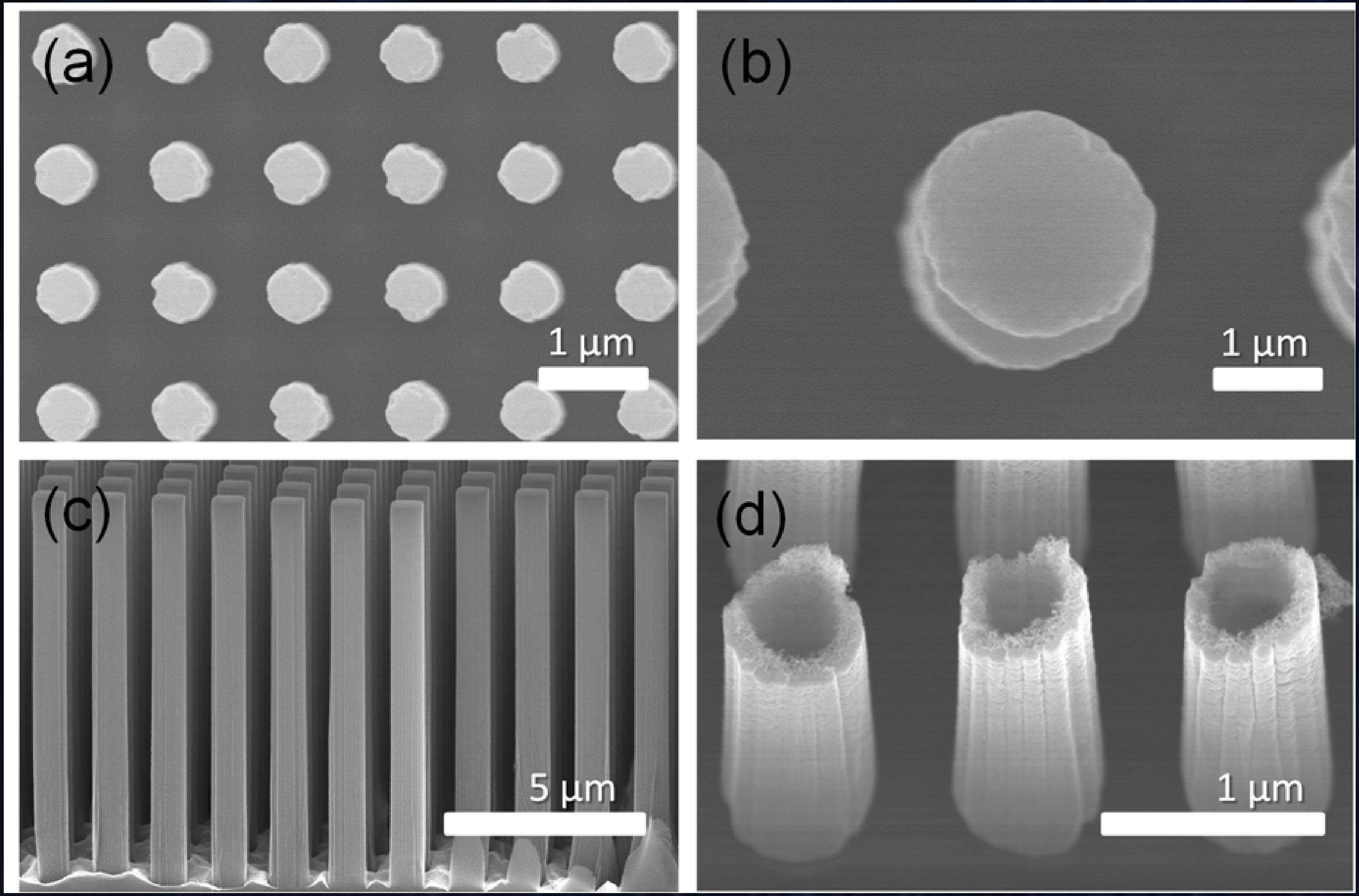
produced by Au-MacEtch in 20 mins



Nanotechnology, 23, 305304 (2012).

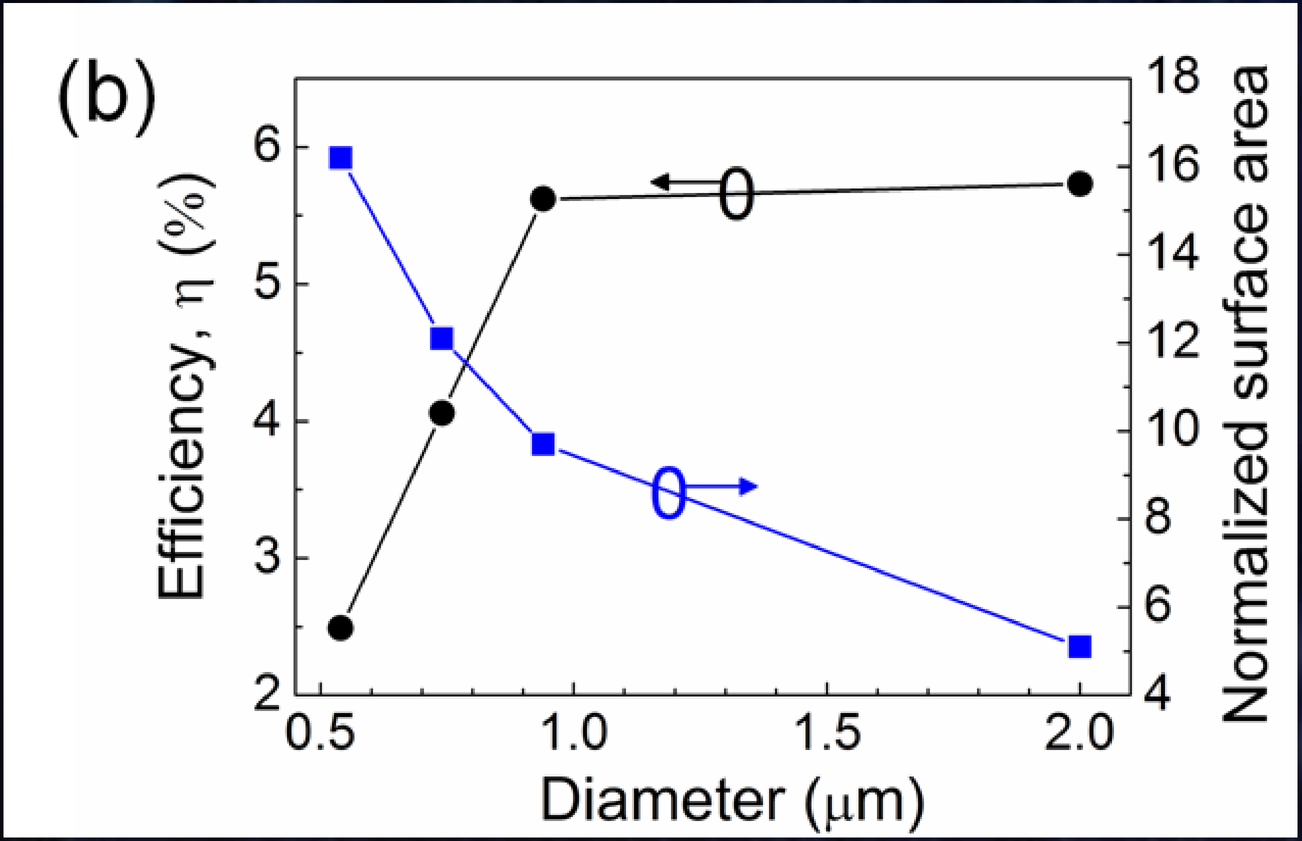
Scalability

MacEtched Si NW PV cell



Shin et al. IEEE J. Photovoltaics, 2, 129 (2012).

Efficiency limited by surface area

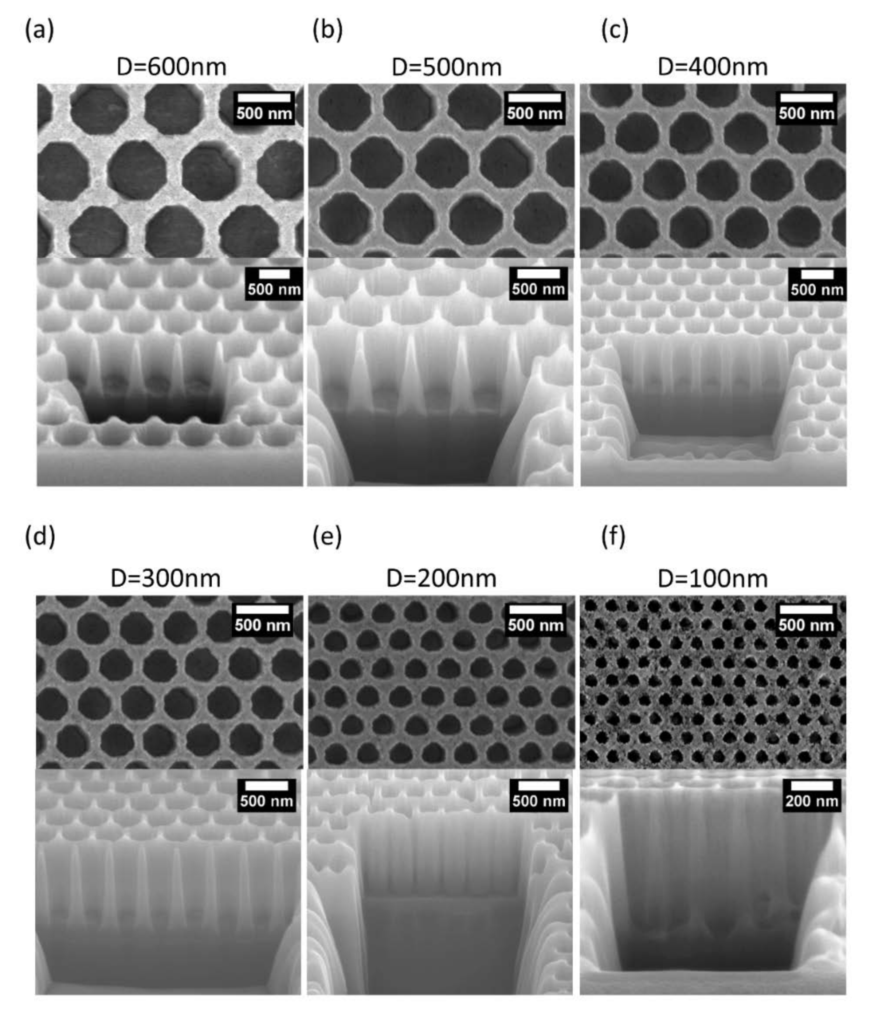


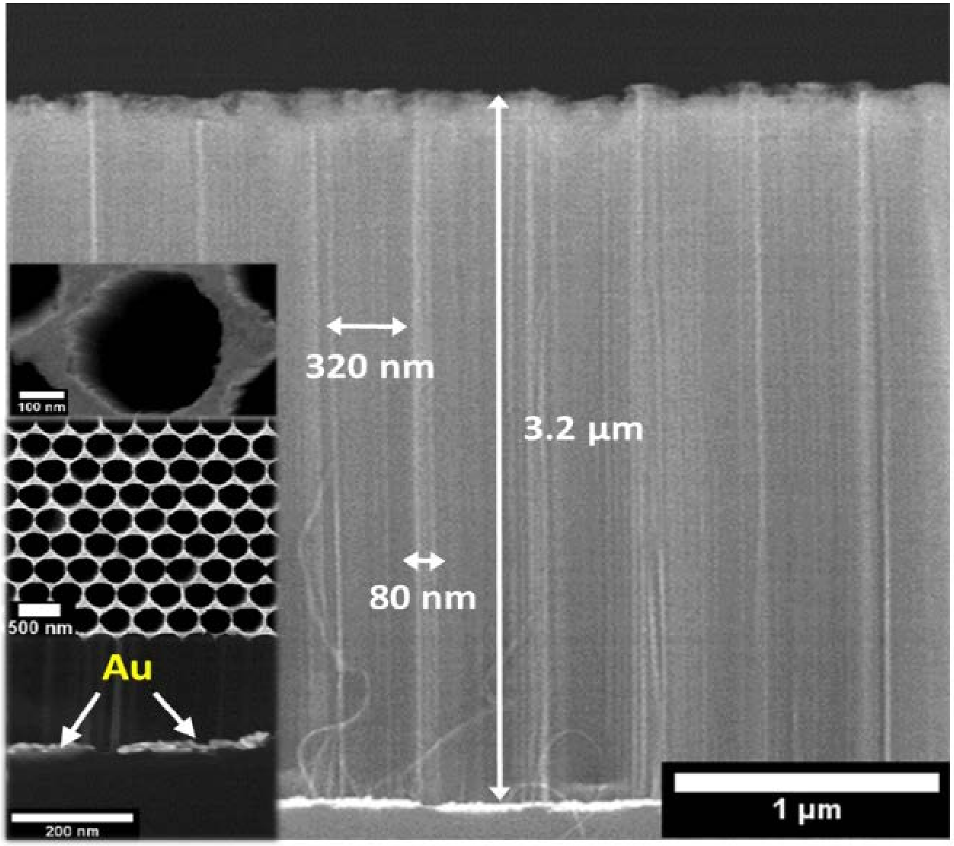
It is all about the surfaces!

Shin et al. IEEE J. Photovoltaics, 2, 129 (2012).

High Aspect Ratio sub-micron vias

- Etched the entire array over 100 µm x 100 µm patterned by EBL uniformly.
- Via dimension: Diameter = ~ 100 - 600 nm, Spacing = ~80 – 1000 nm

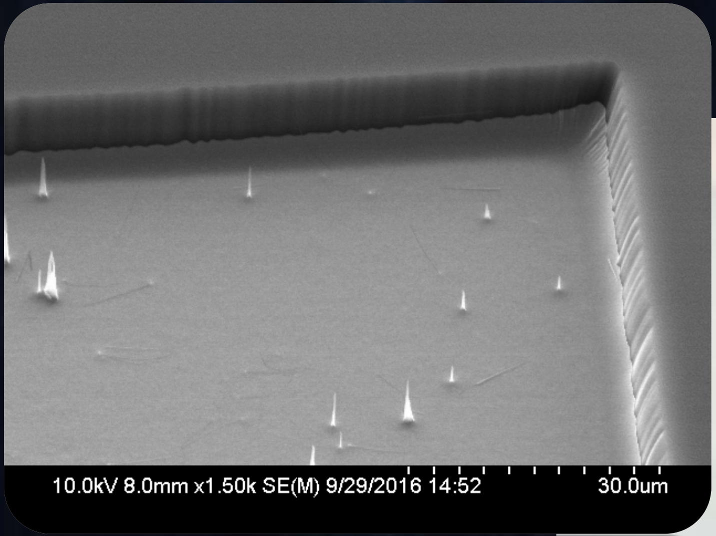


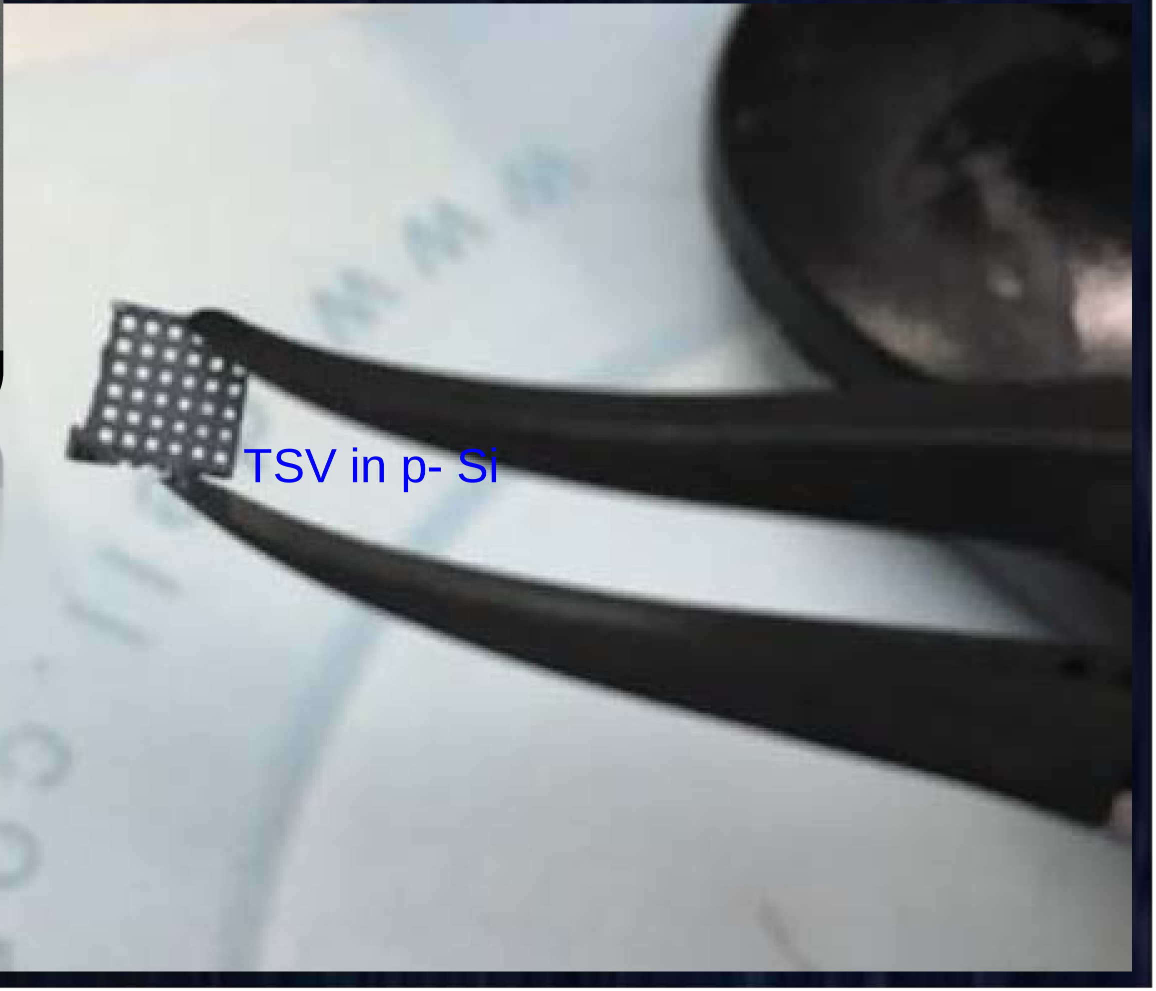


JD Kim, et al. Adv. Func. Mater. 27, 1605614 (2017).

Large Through-Si-Via (TSV) by SAC-MacEtch

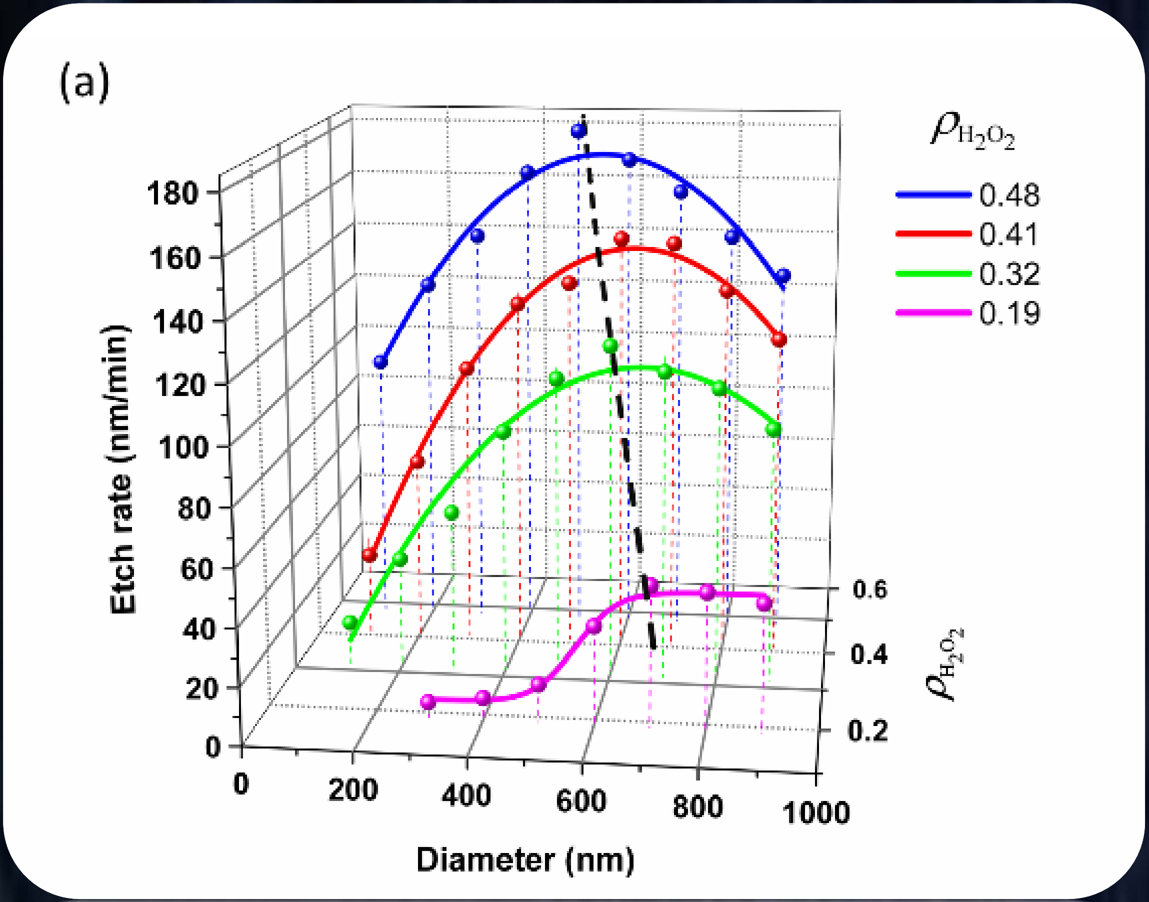
Kim et al. ACS Appl. Mater. Interfaces, 10(10) , pp 9116–9122 (2018).





Etch rate model:

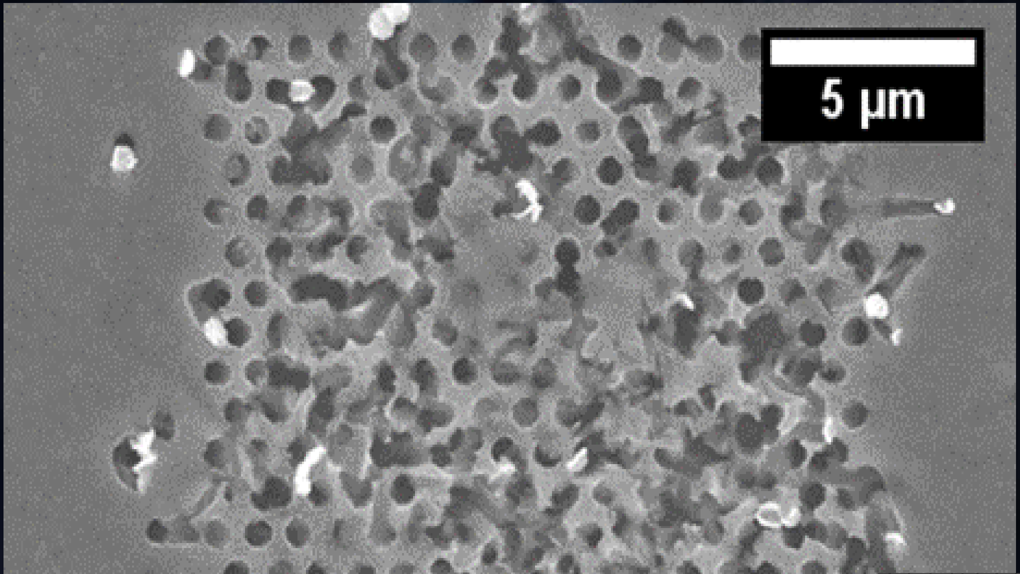
effect of carrier generation and mass transport



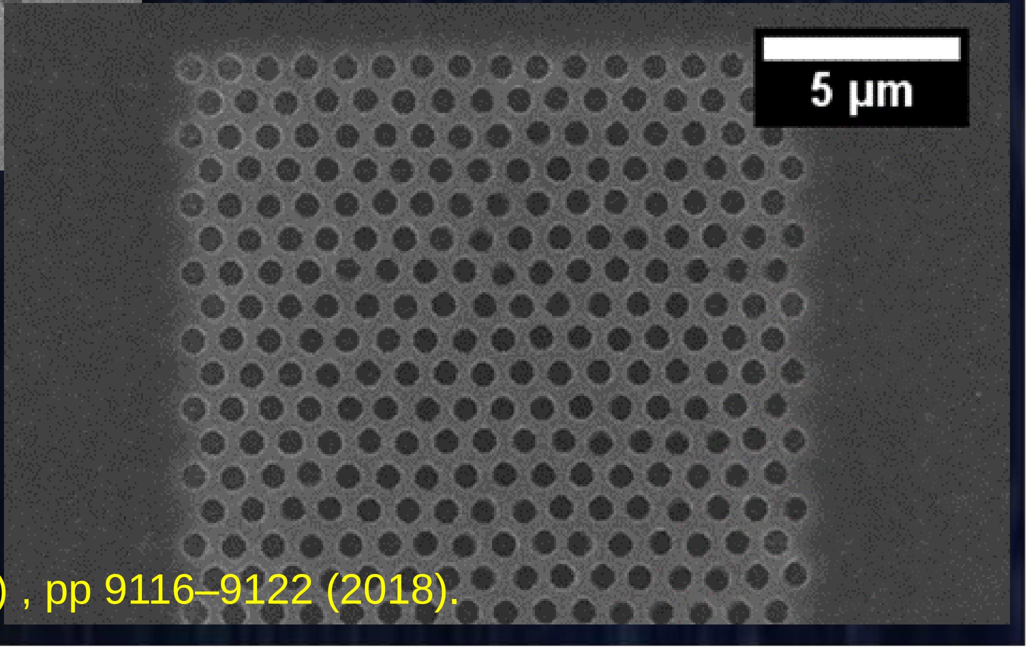
- **Parabolic vs via diameter**
- **Peak shifts wrt [H_2O_2]**

JD Kim, et al. Adv. Func. Mater. 27, 1605614 (2017).

poly Si: SAC-MacEtch

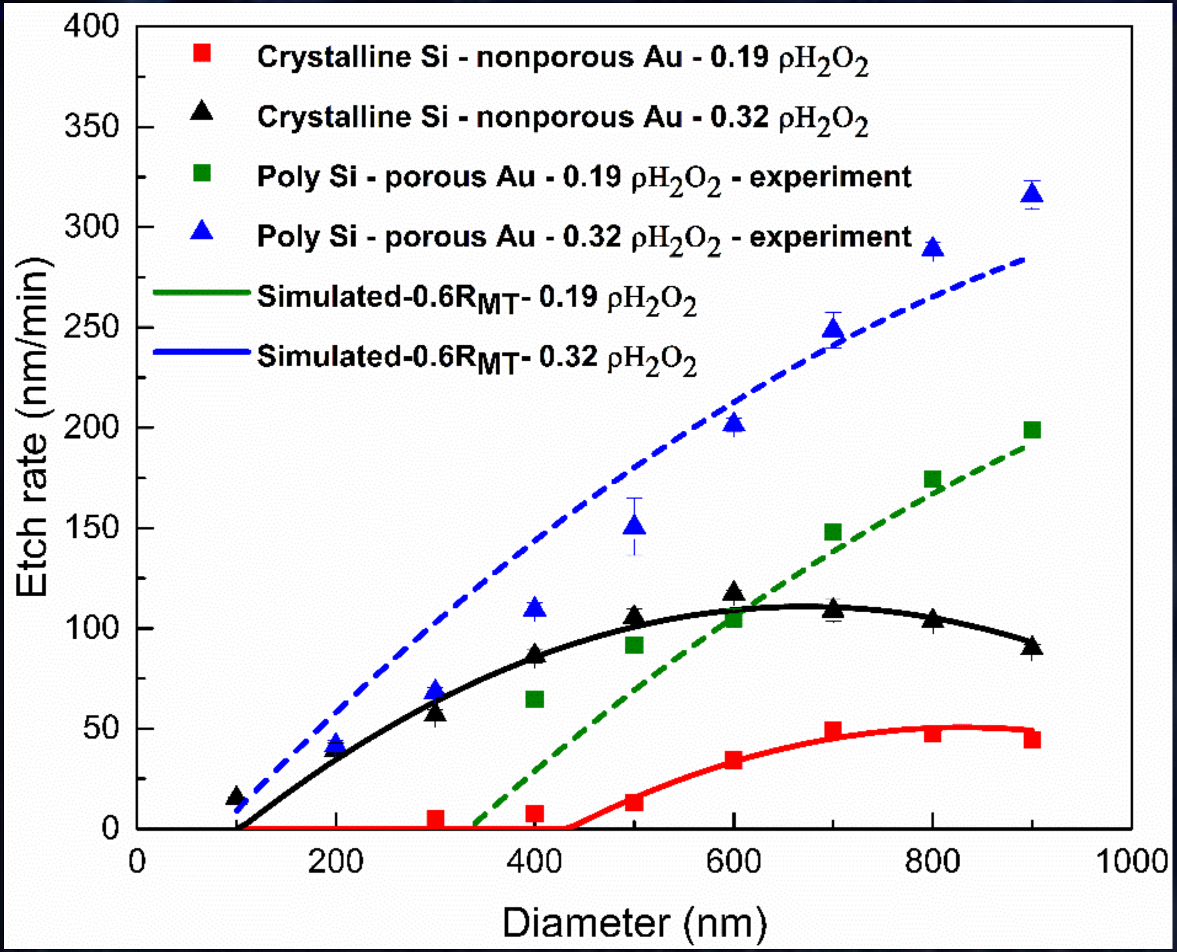


- 700 nm D and 1 µm pitch
- MacEtched in 0.32 $\rho_{H_2O_2}$ for 10 minutes



Kim et al. ACS Appl. Mater. Interfaces, 10(10) , pp 9116–9122 (2018).

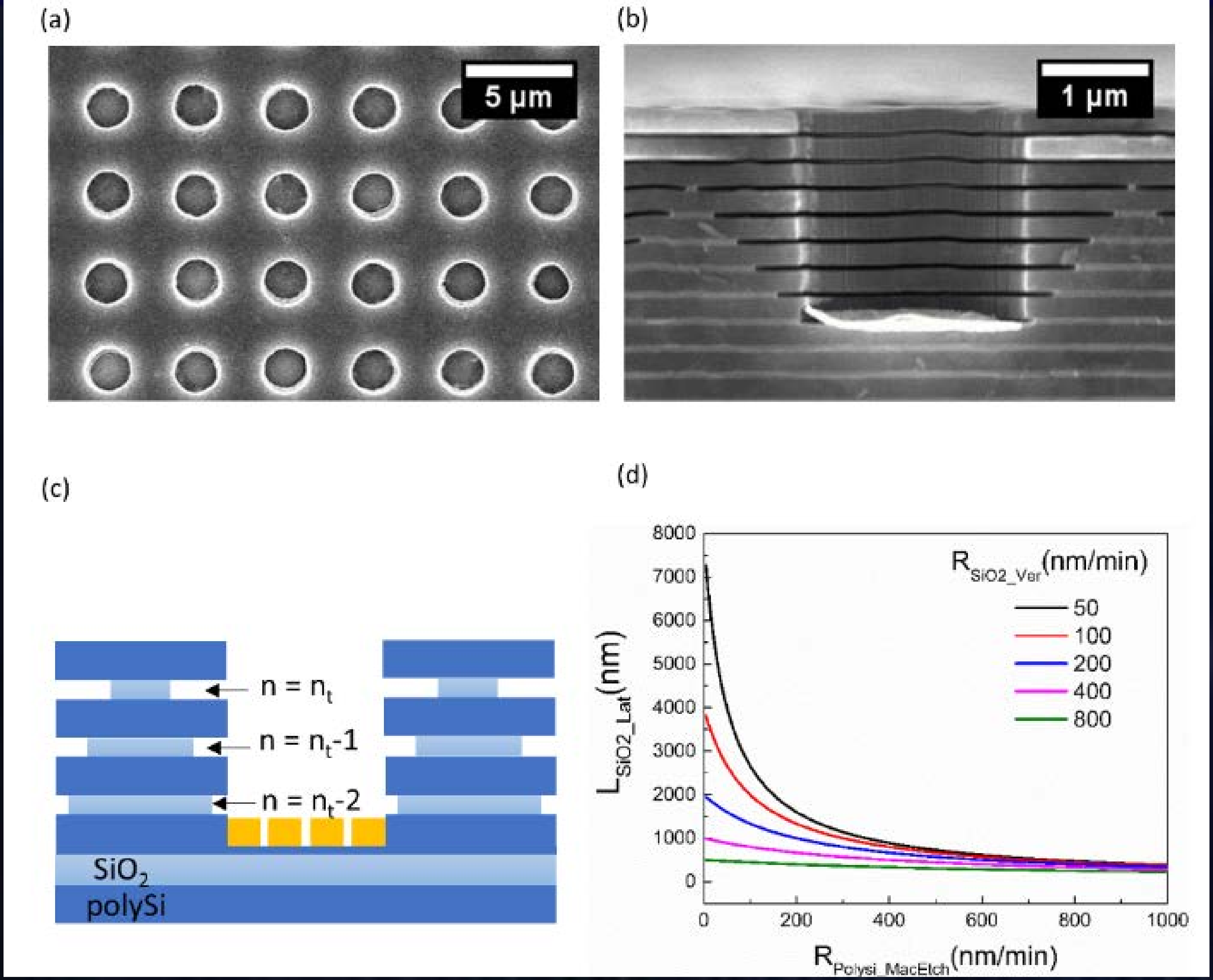
Effect of crystallinity



- **Enhanced mass transport leads to shift of parabola peak**

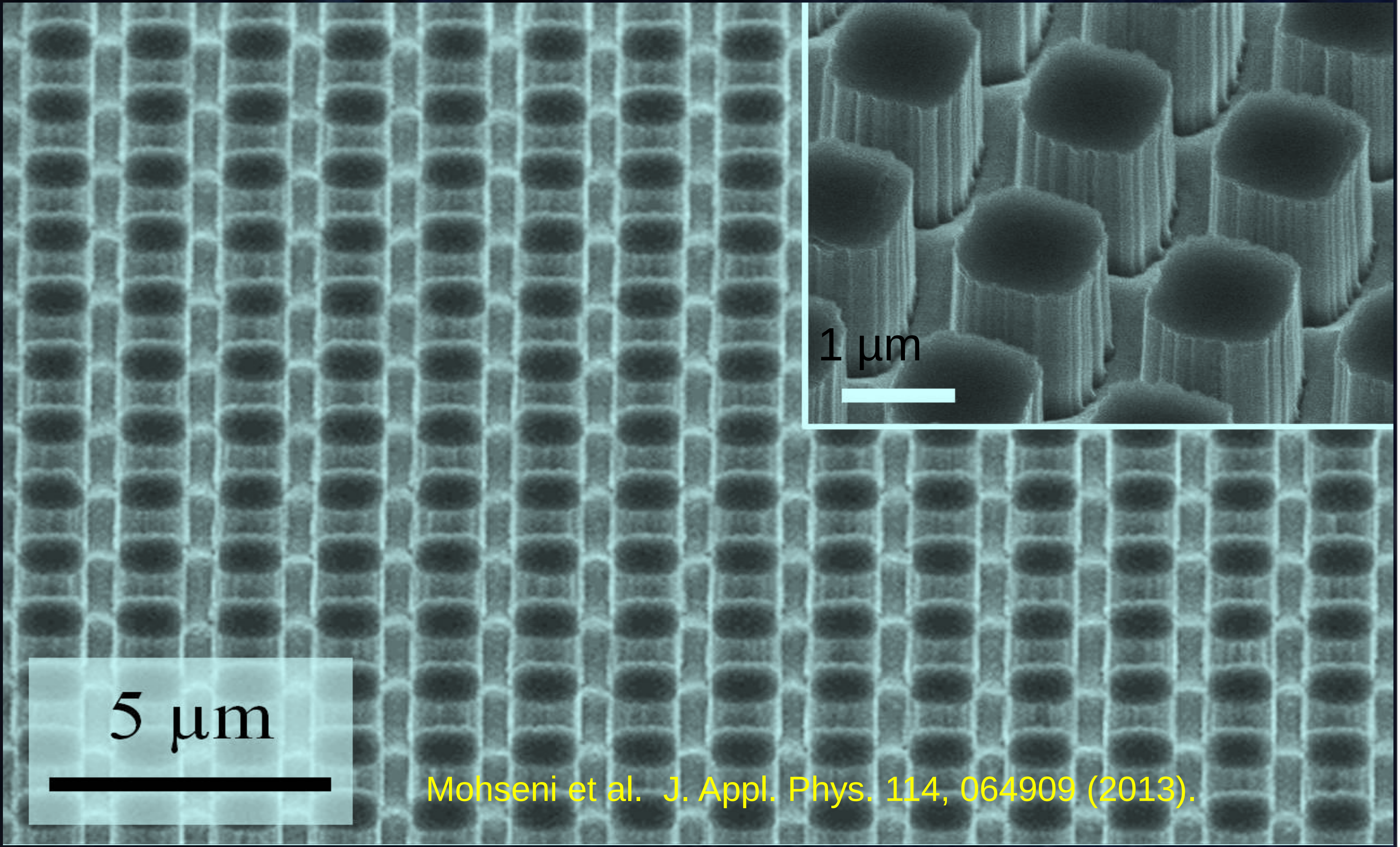
Kim et al. ACS Appl. Mater. Interfaces, 10(10) , pp 9116–9122 (2018).

Poly-Si/SiO_2 SL MacEtch



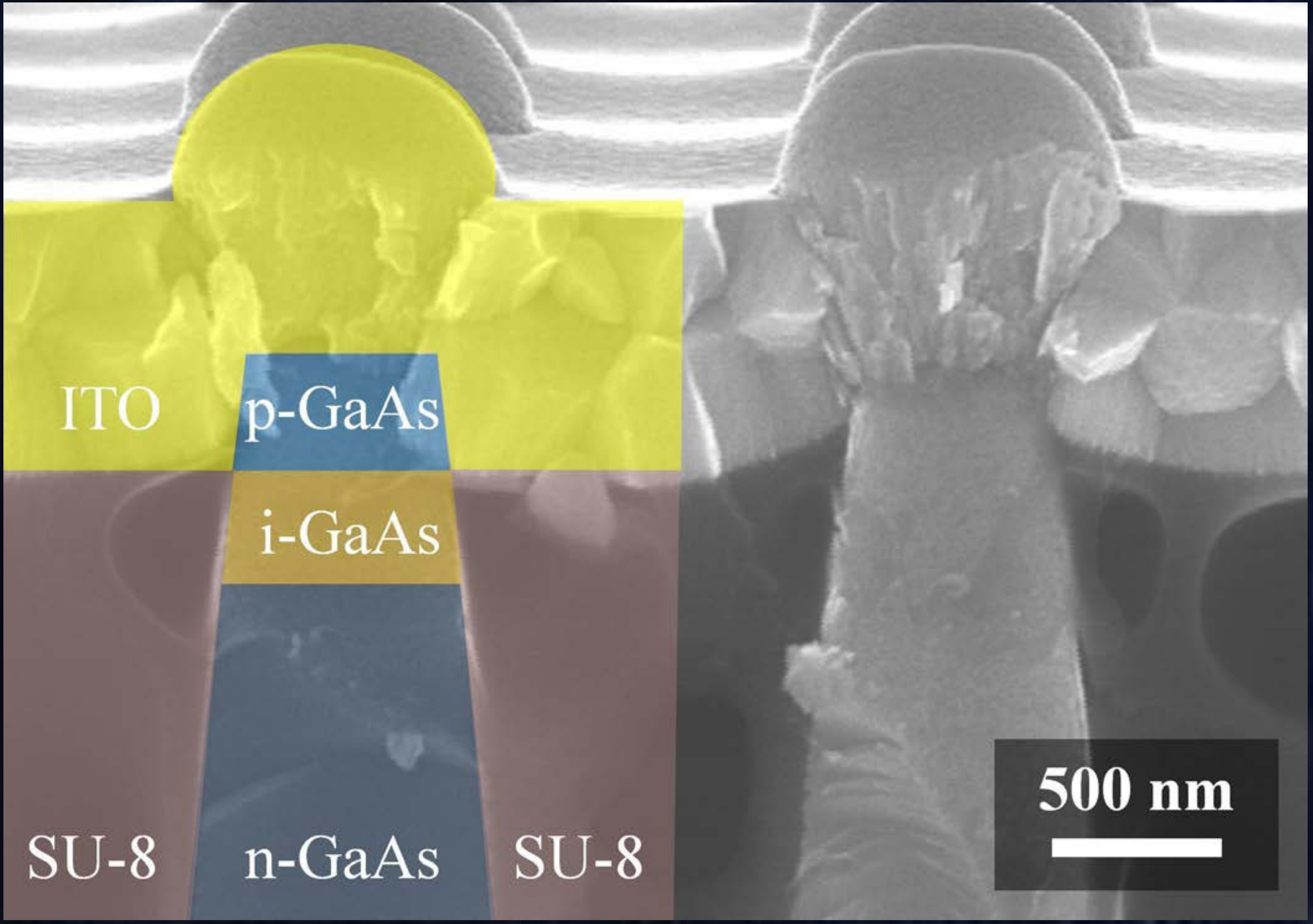
Kim et al. ACS Appl. Mater. Interfaces, 10(10) , pp 9116–9122 (2018).

GaAs p-i-n pillar based μ-LED by MacEtch



Mohseni et al. J. Appl. Phys. 114, 064909 (2013).

GaAs p-i-n Pillar Based LED by MacEtch



Mohseni et al., J. Appl. Phys. 114, 064909 (2013).

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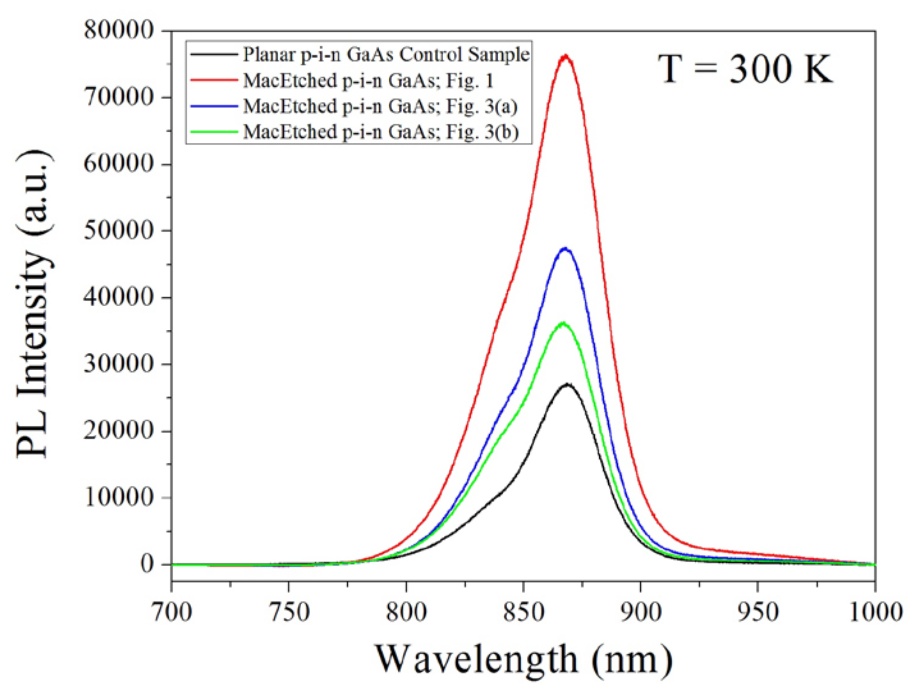
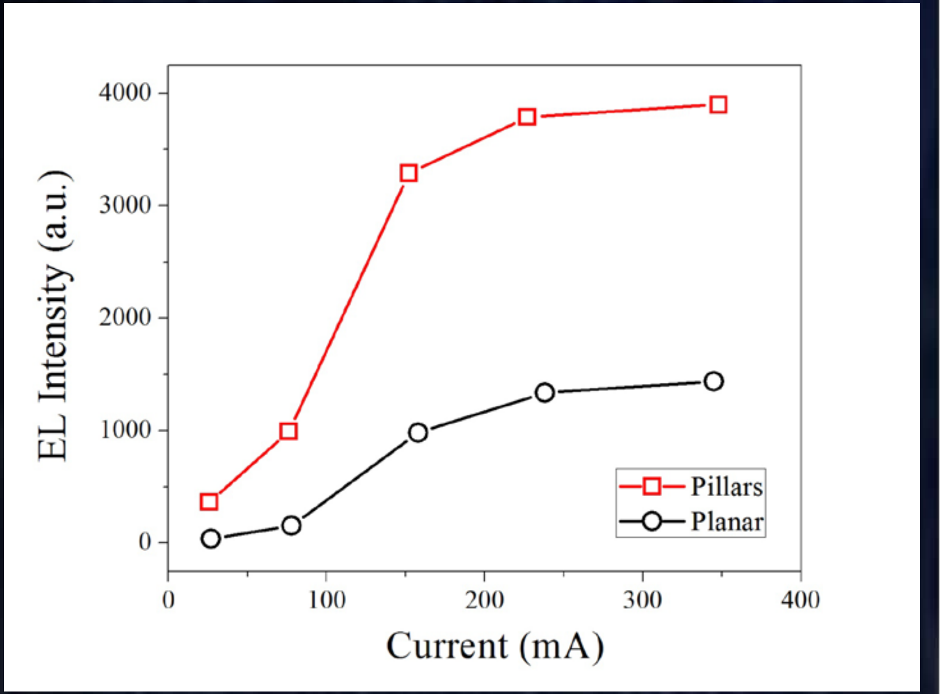
GaAs p-i-n Pillar Based μ-LED by MacEtch

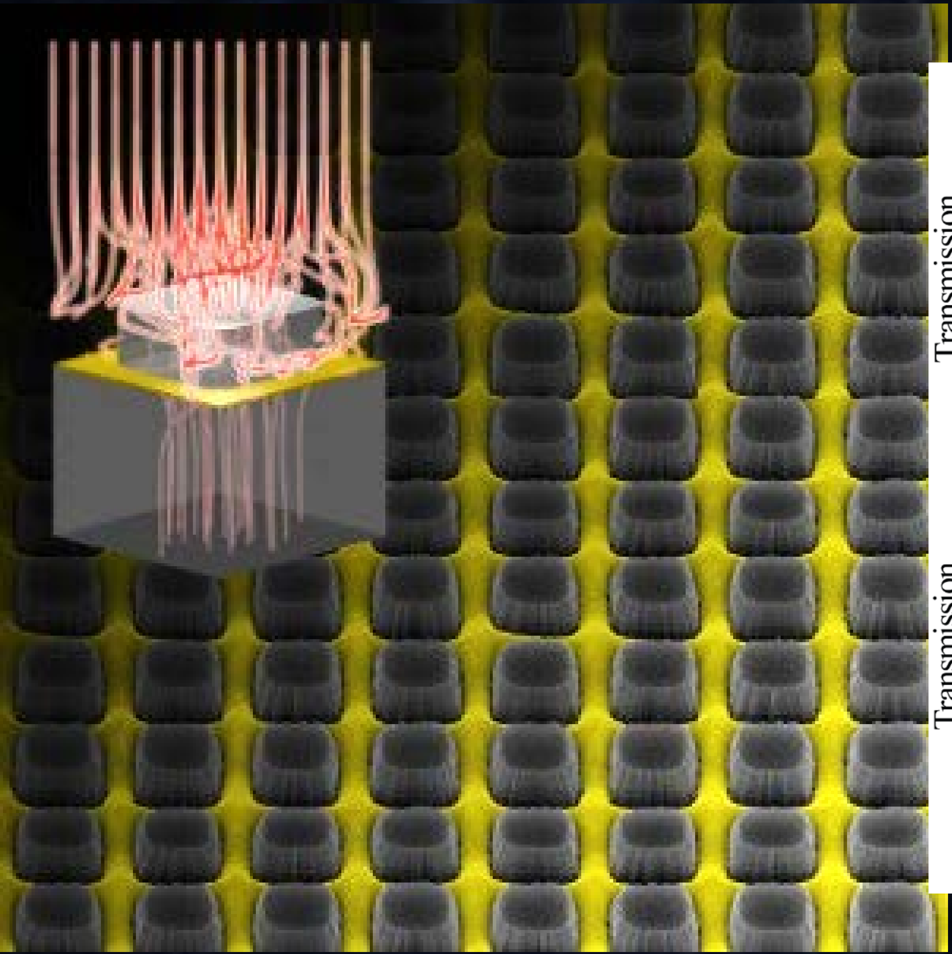




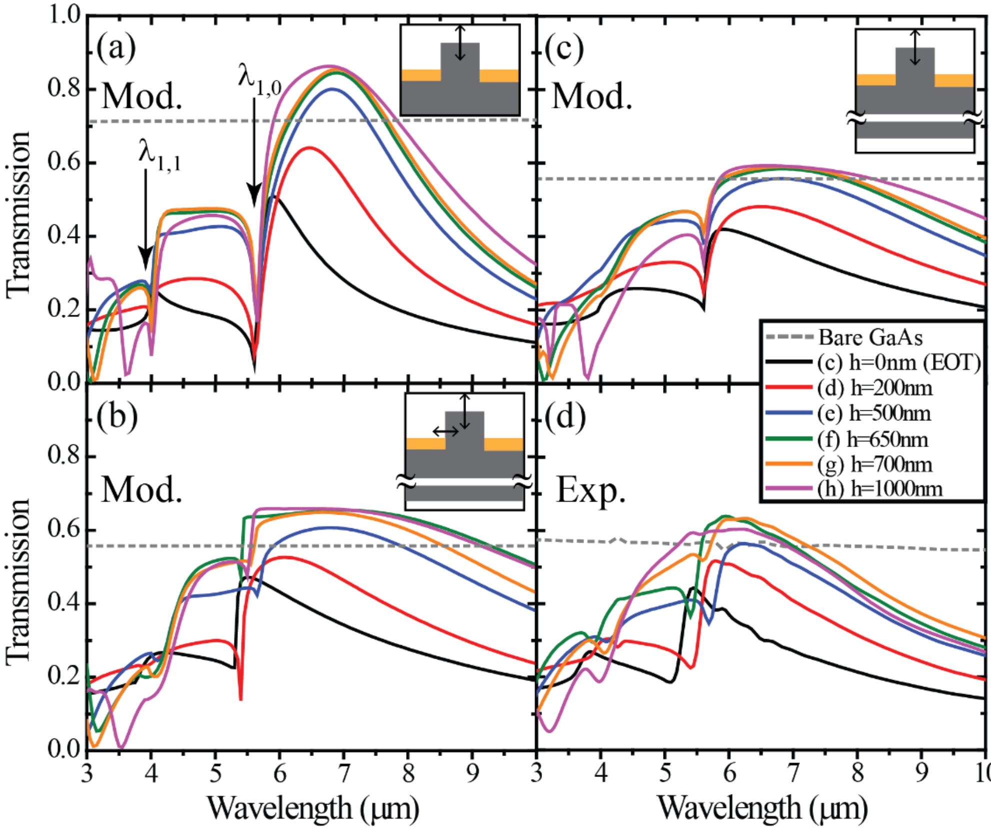
- Pillar showed stronger emission at all injection levels
- Enhancement is stronger at higher I

Mohseni et al. J. Appl. Phys. 114, 064909 (2013).

Buried Plasmonics:
Enhanced Optical Transmission



RCWA modeling and experimental results



Liu et al. Adv. Mater. 28, 1441–1448 (2016).

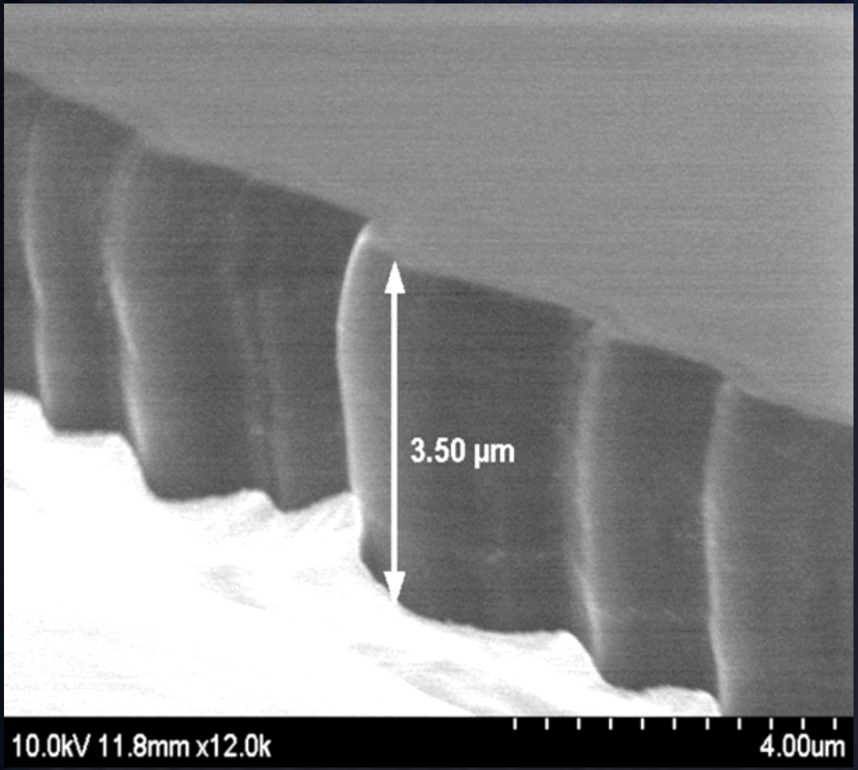
MacEtch

SIDEWALL ROUGHNESS

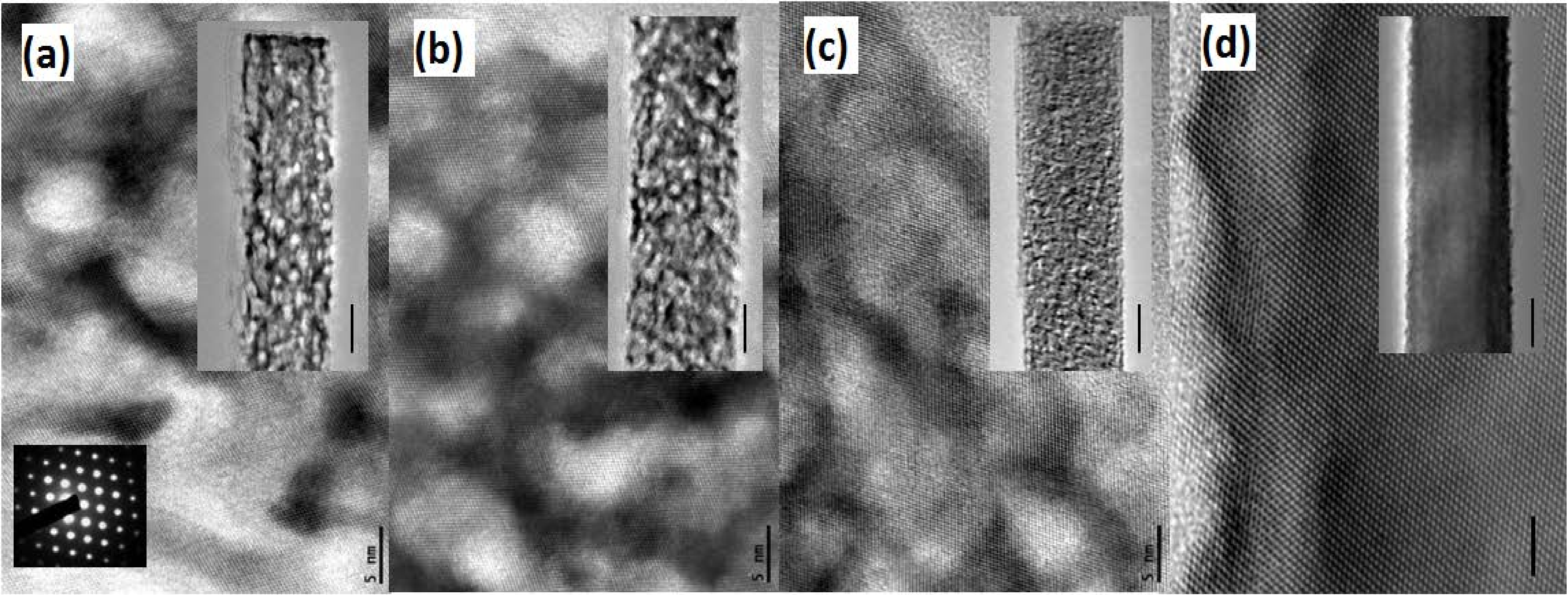
Sidewall morphology and porosity

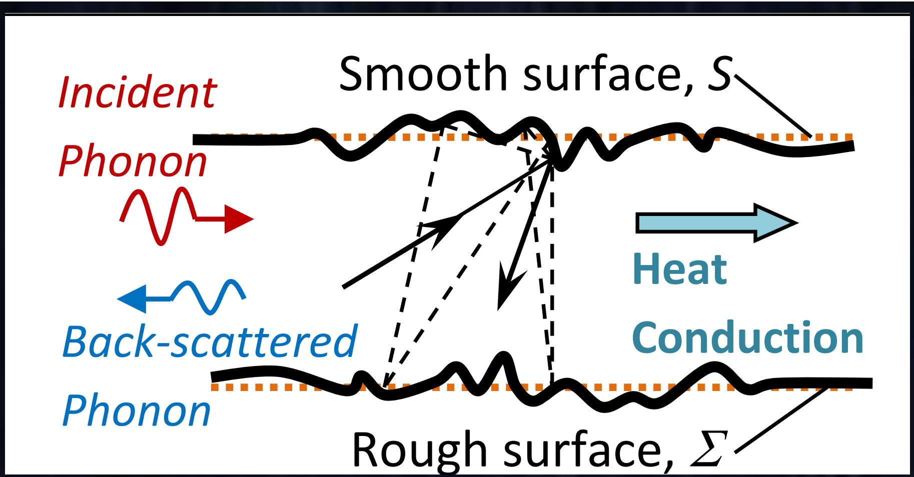
- Free of high energy ion induced damage
- Sidewall smoothness is determined by the edge roughness of the metal catalyst pattern
- Susceptible to porosity, which can be eliminated or minimized by tuning the MacEtch condition or combining with digital etch

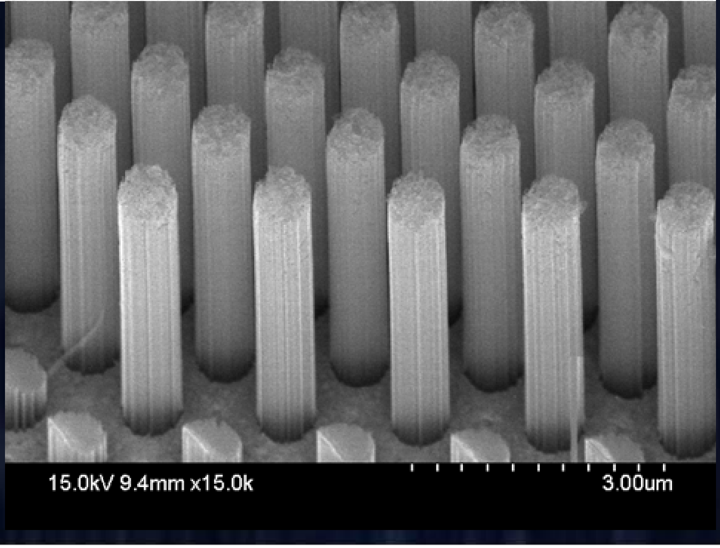
Issues: sidewall roughness



Tuning of thermal properties by porosity using MacEtch

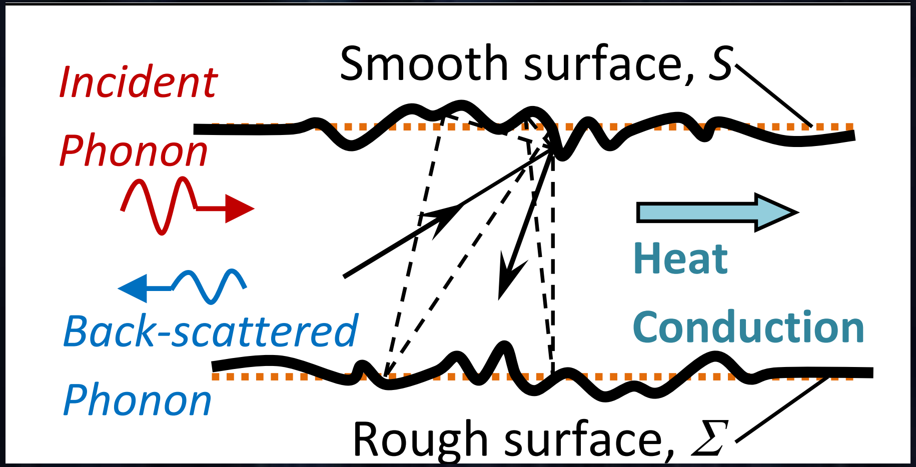




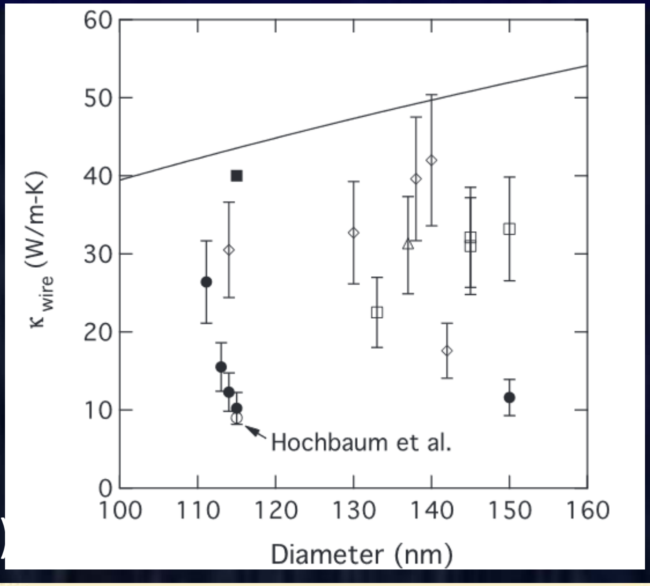


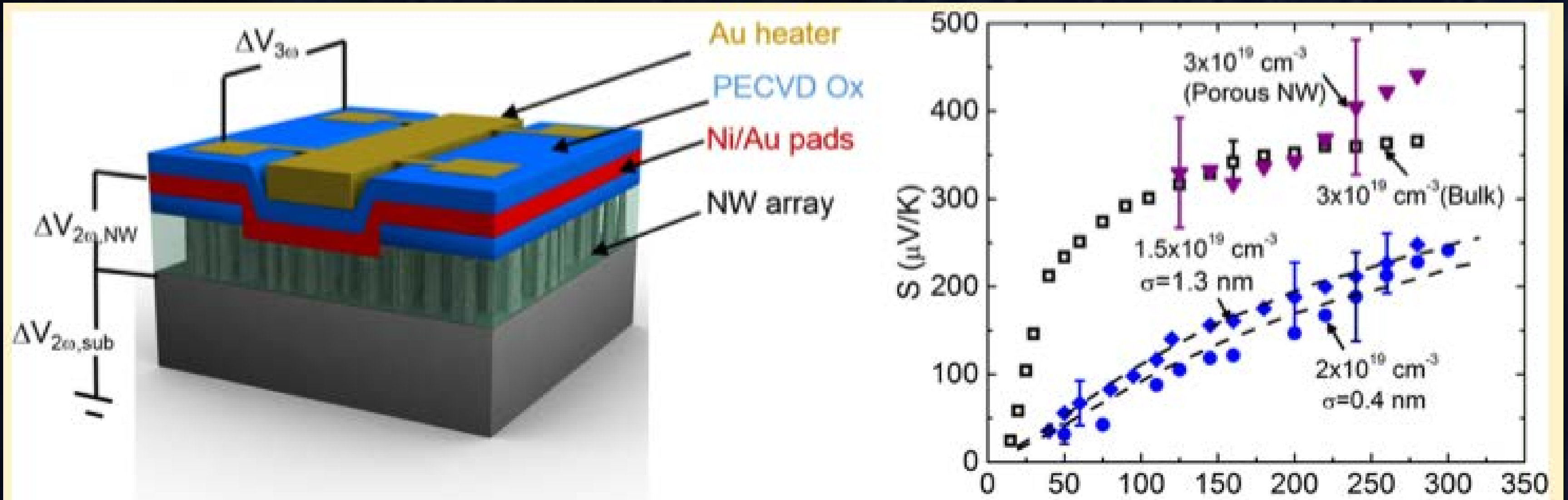
Balasundaram, et al. Nanotech. 23, 305304 (2012).

TE properties of rough Si NWs



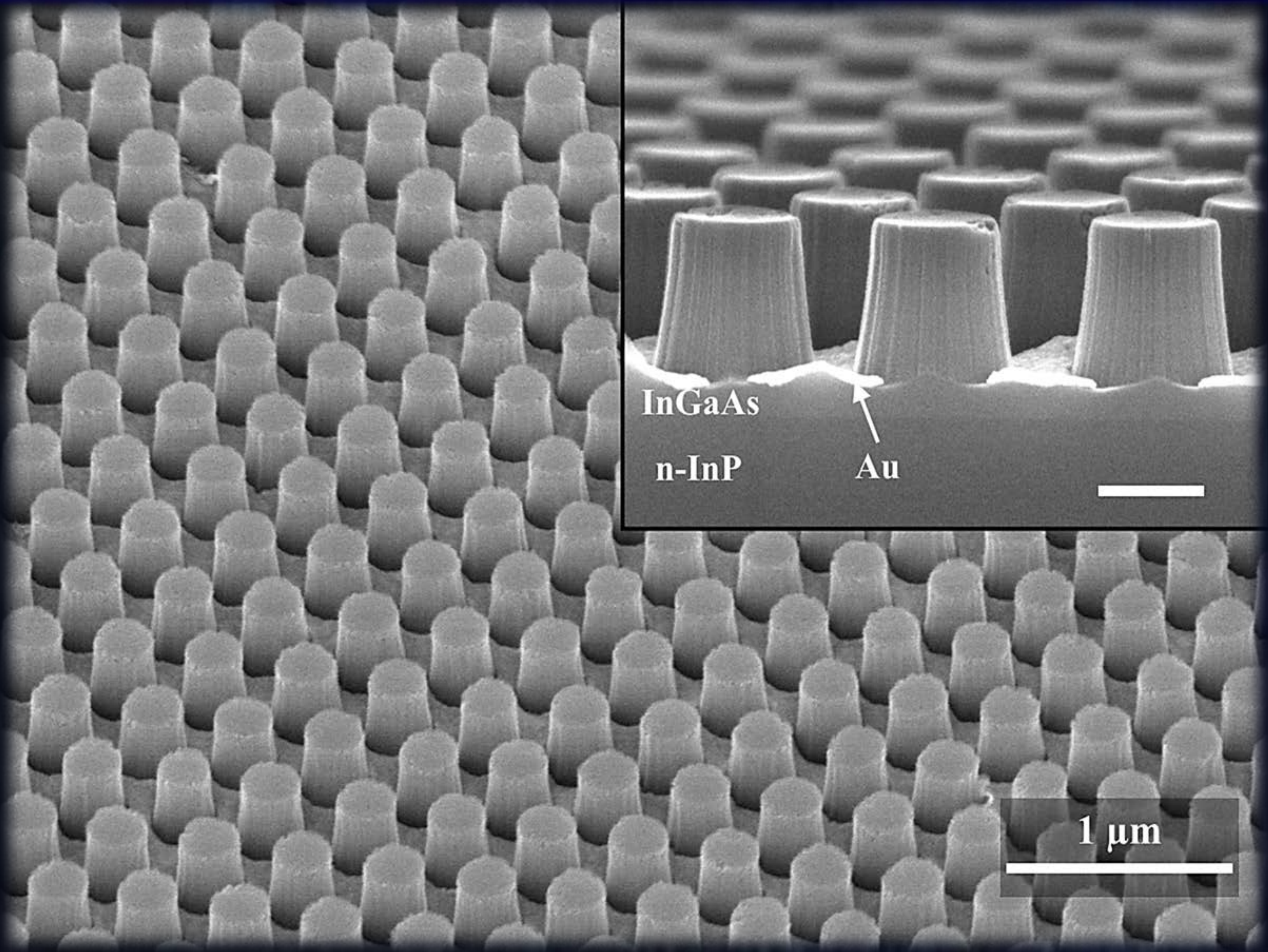
Sadhu et al. *J. Appl. Phys.* 112, 114306 (2012)





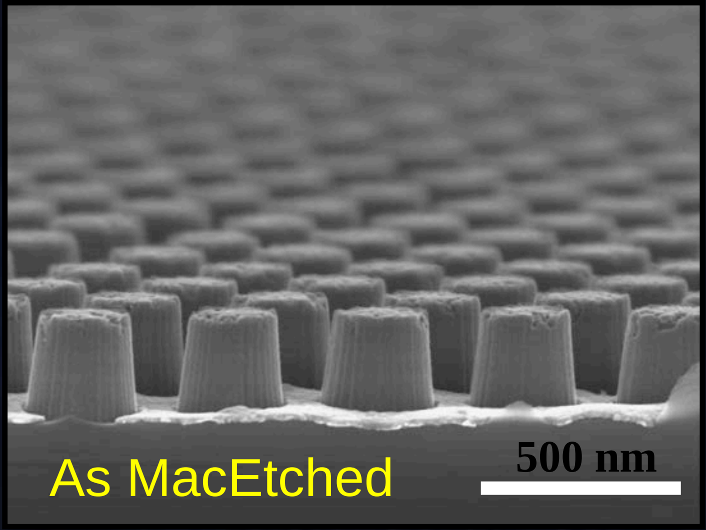
Nano Lett. 2015, 15, 3159−3165

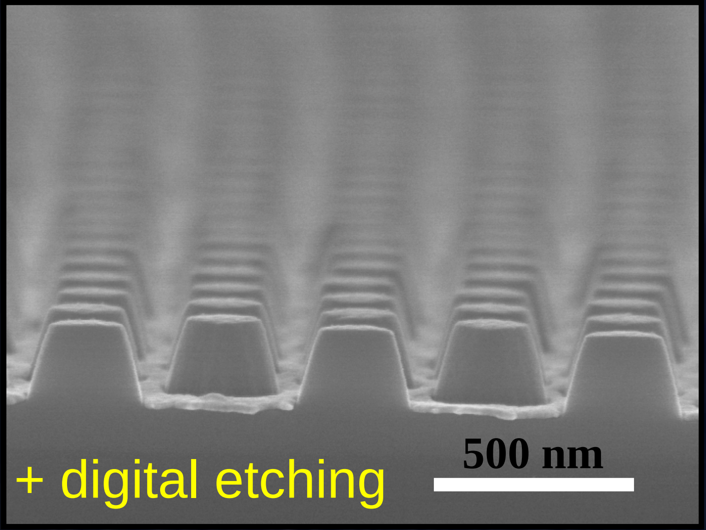
MacEtch of $In_xGa_{1-x}As$

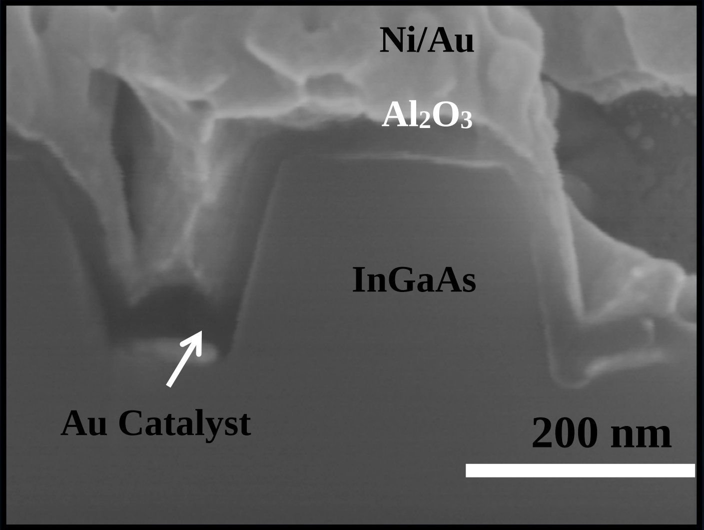


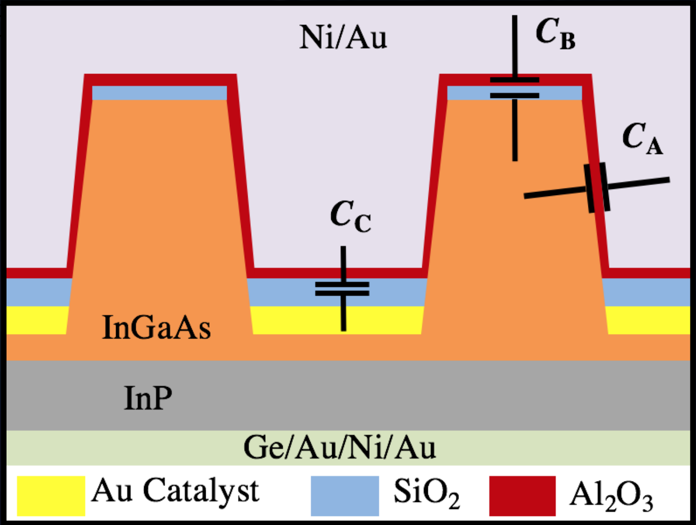
Kong et al. ACS Nano, 11 (10), pp 10193-10205 (2017).

MacEtch of $In_{0.53}Ga_{0.47}As$: porosity issue, solution, surface quality



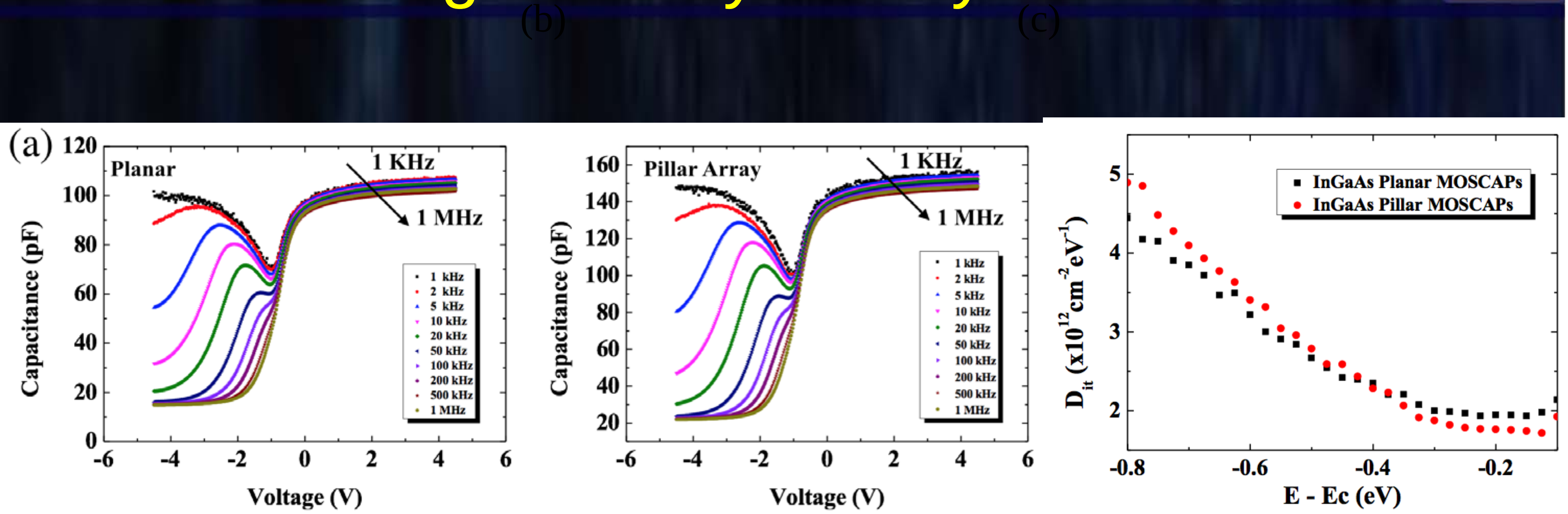


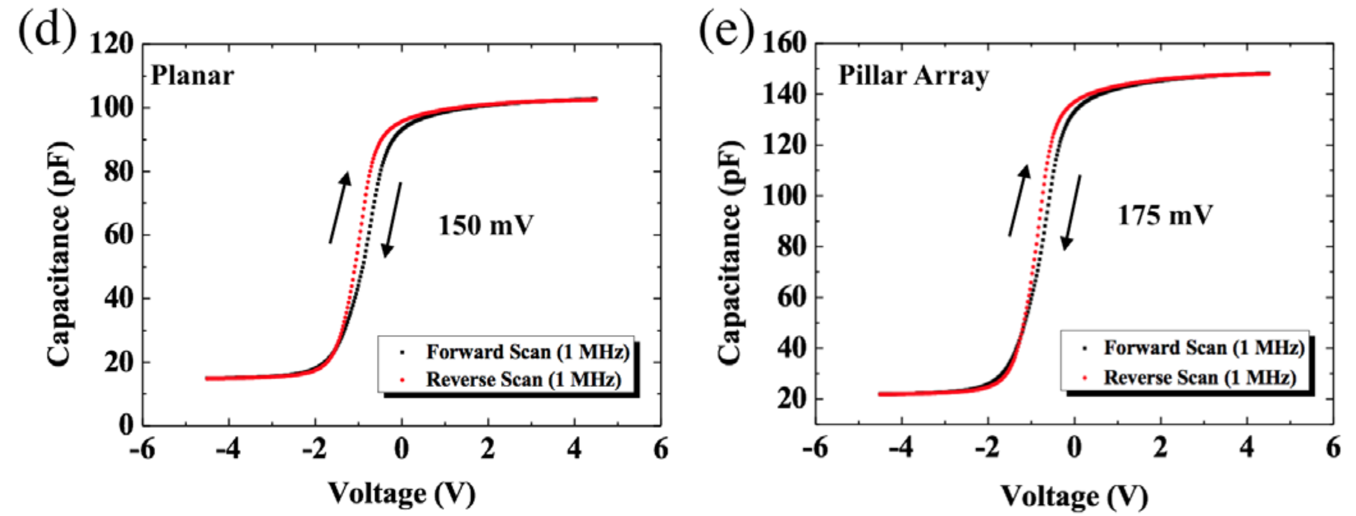




Kong et al. ACS Nano, 11 (10), pp 10193-10205 (2017).

$In_{0.53}Ga_{0.47}As$-Al_2O_3 MOSCAP: planar vs pillar
Interface charge density and hysteresis

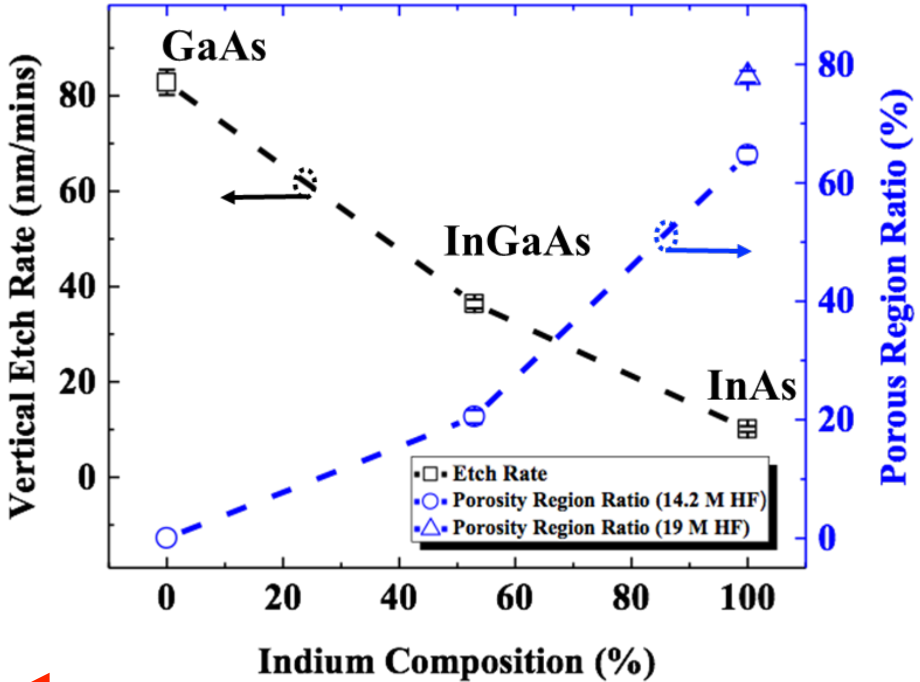


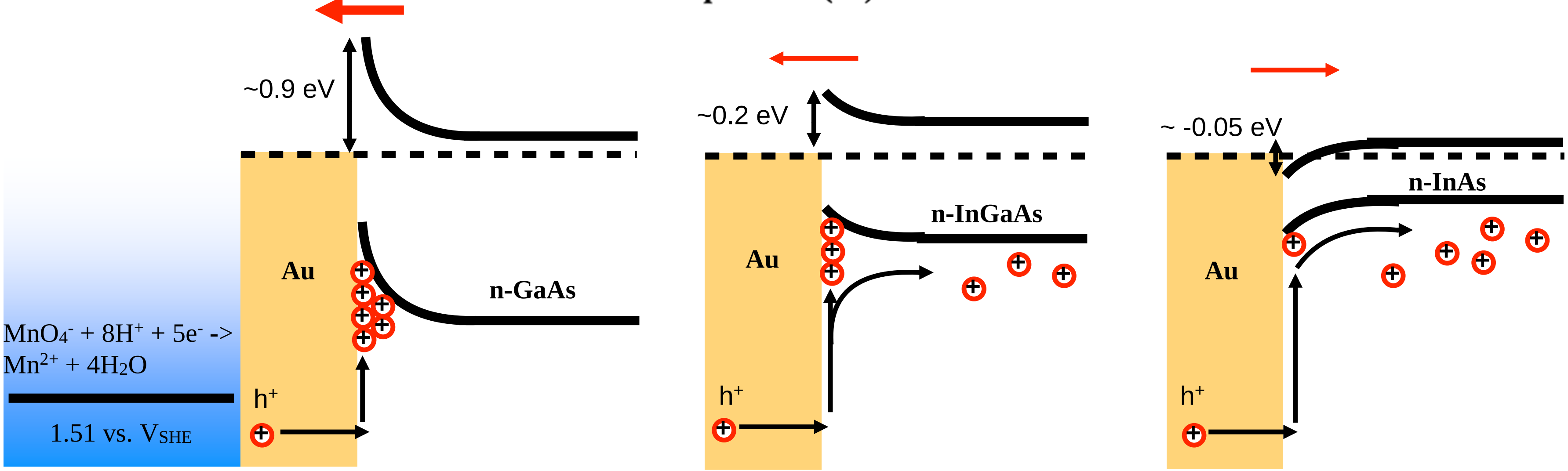


Kong et al. ACS Nano, 11 (10), pp 10193-10205 (2017).

The Schottky Barrier Model

Kong et al. ACS Nano, 11, 10193 (2017).





$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

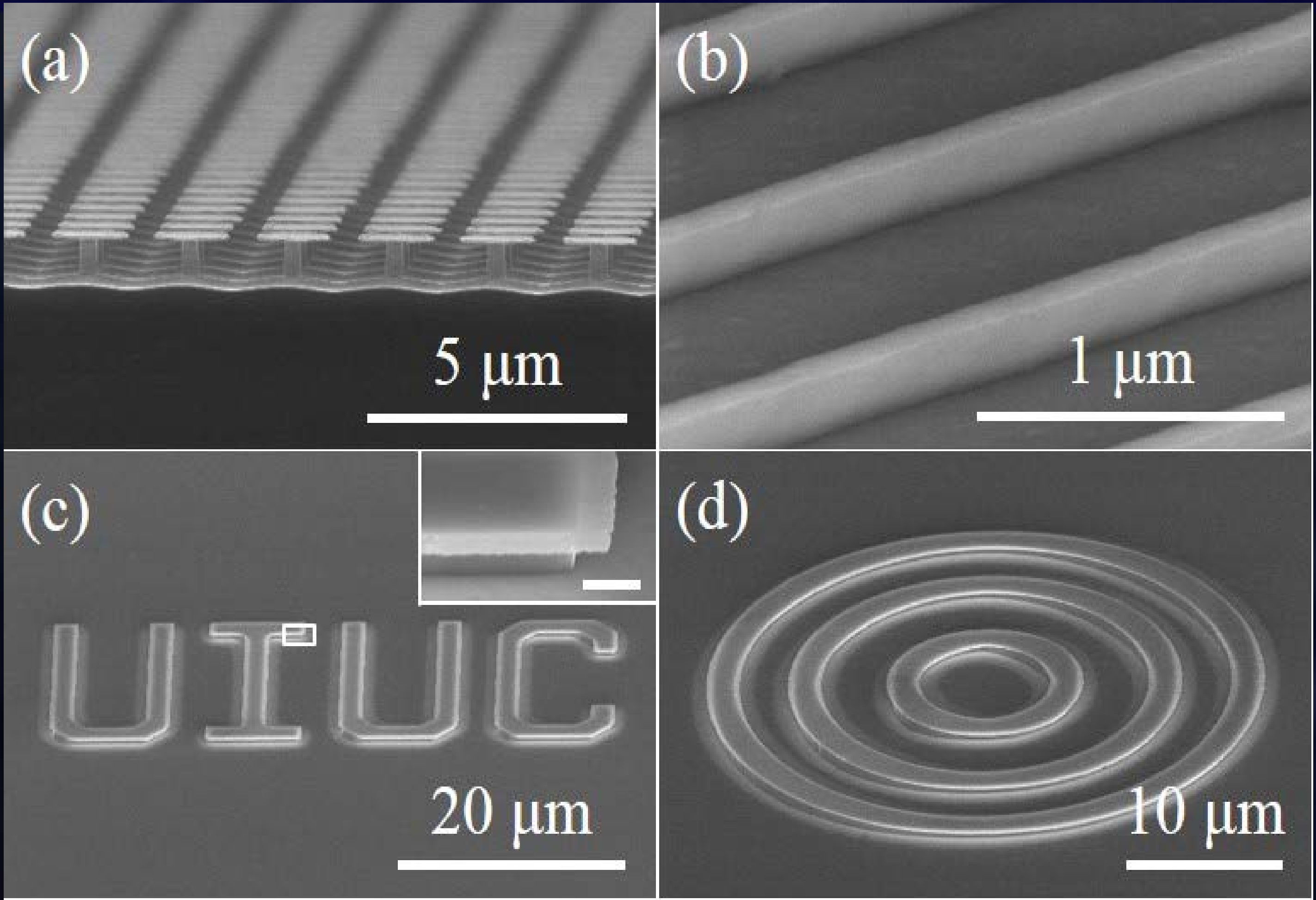
1.51 vs. V_{SHE}

Inverse-MacEtch

SMOOTH SIDEWALLS BY INVERSE-MACETCH

Inverse-MacEtch for smooth sidewalls

InP



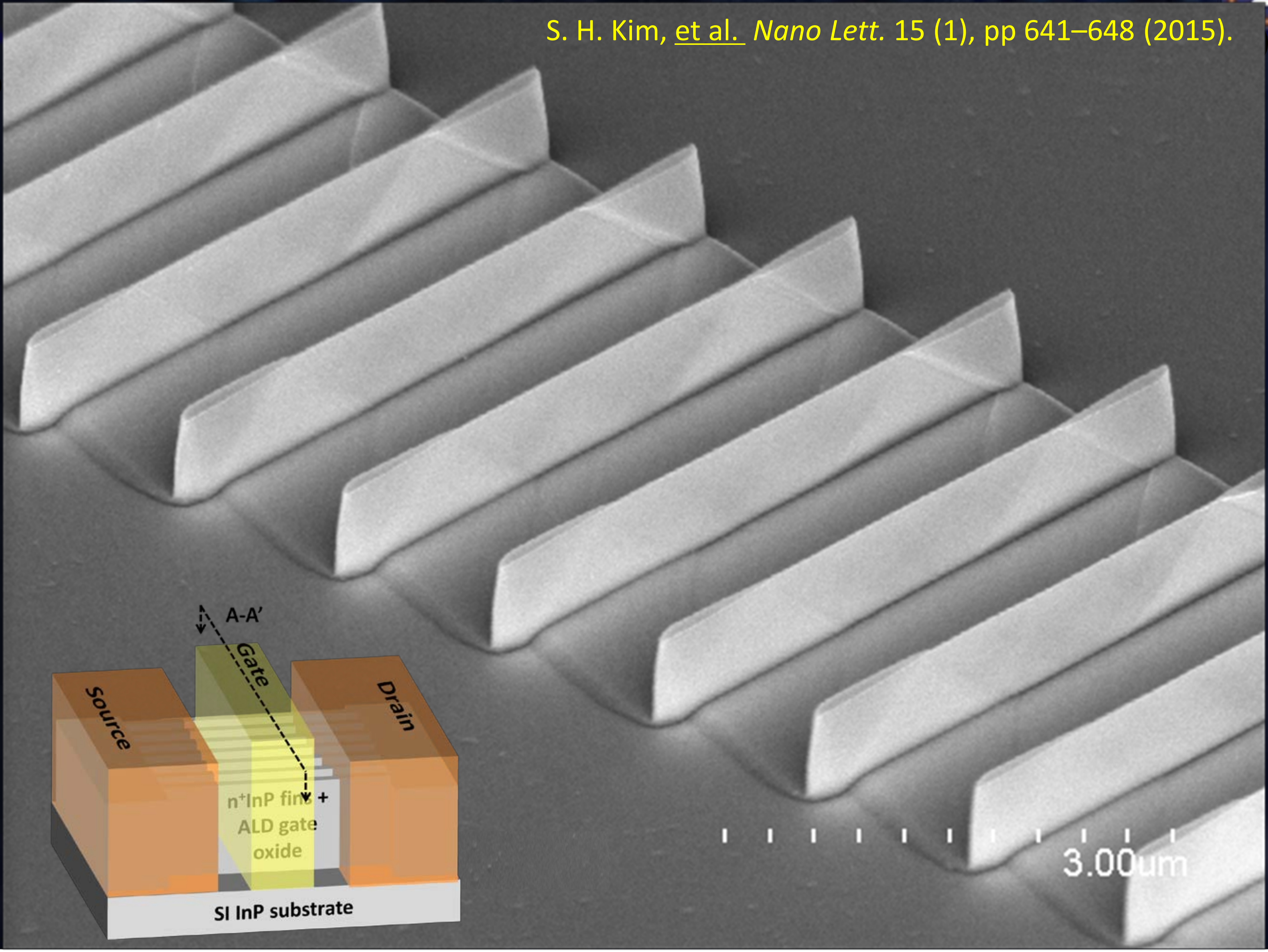
- **Metal edge roughness no longer limits sidewall smoothness**
- Limited aspect ratio (height/width) because of the inverse nature

S. H. Kim, P. K. Mohseni, Y. Song, T. Ishihara, and X. Li, *Nano Lett.* 15 (1), pp 641–648 (2015).

I-MacEtch for InP FinFET

S. H.

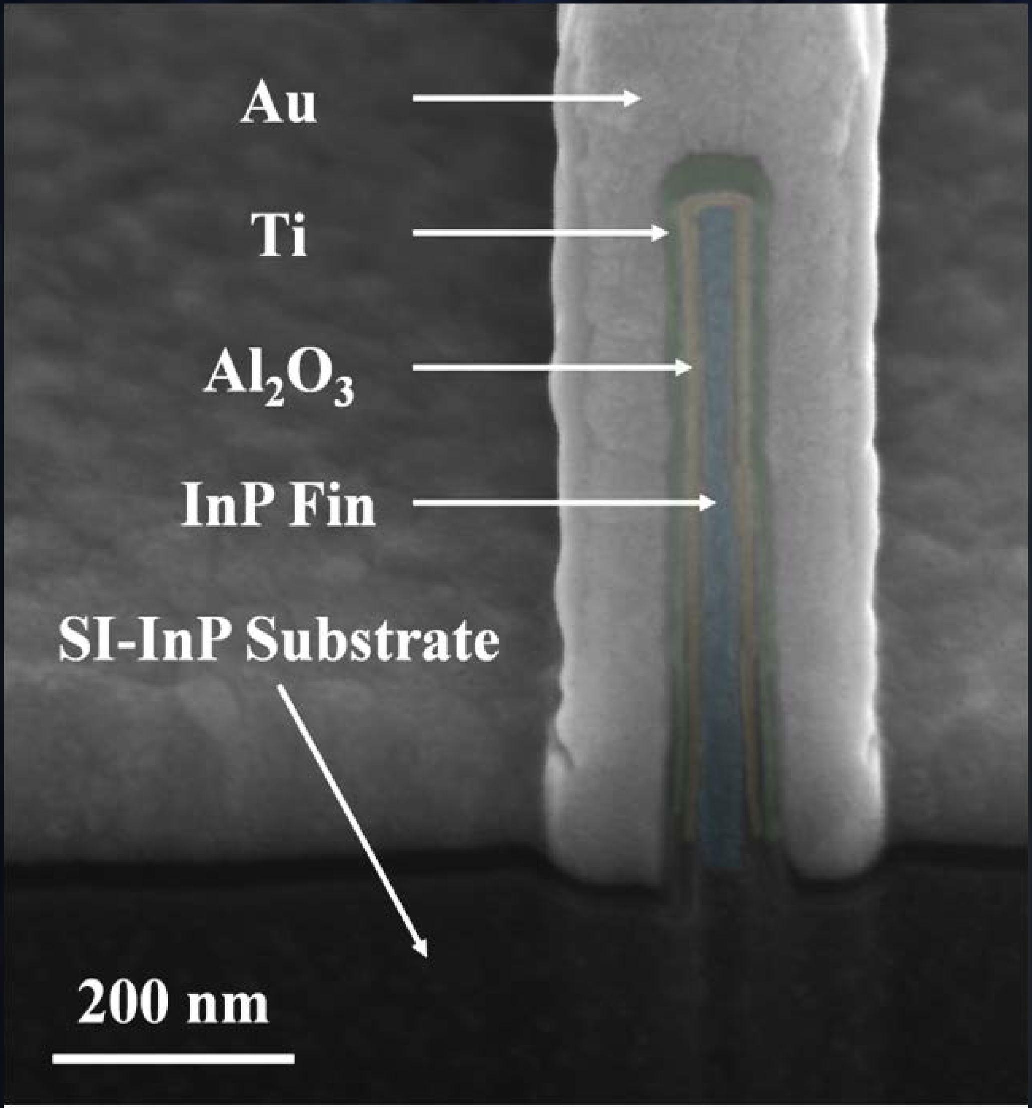
Y. So



S. H. Kim, et al. *Nano Lett.* 15 (1), pp 641–648 (2015).

HAR InP Junctionless FinFET: X-section

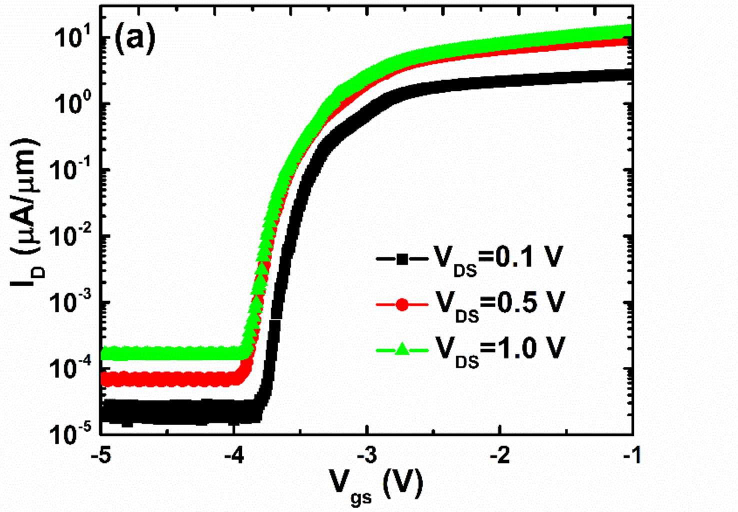
Y. Song et al. IEEE Electron Dev. Lett. 37 (8), pp 970-973 (2016)

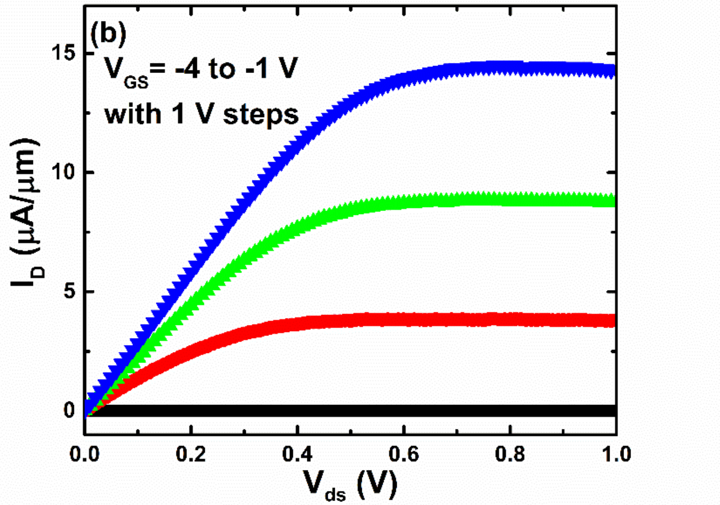


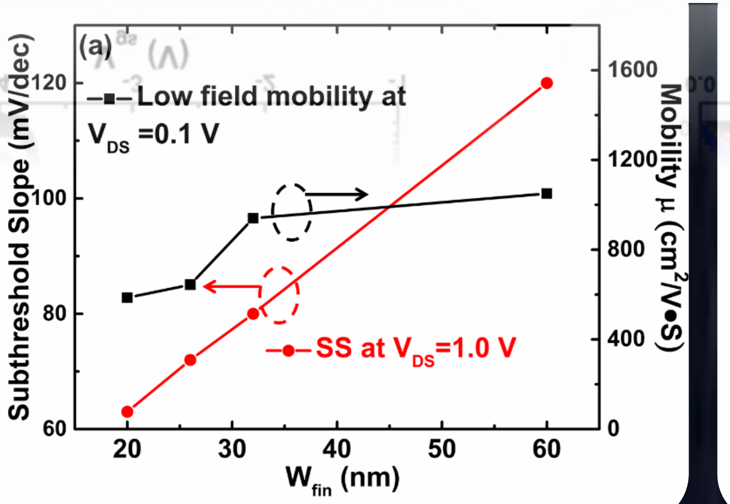
- $L_{g,\,min}$ ~ 14 nm
- AR ~ 50:1
- Atomically smooth sidewalls
- Conformal gate dielectric and metal
- SS: 63 mV/dec

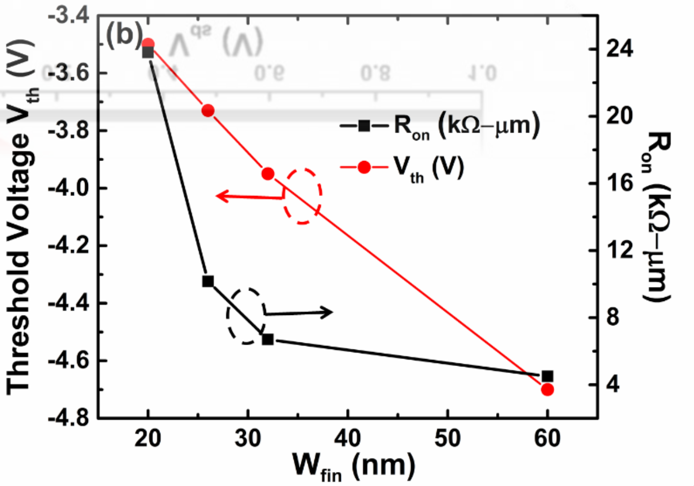
HAR InP Junctionless FinFET

Y. Song et al. IEEE Electron Dev. Lett. 37 (8), pp 970-973 (2016)





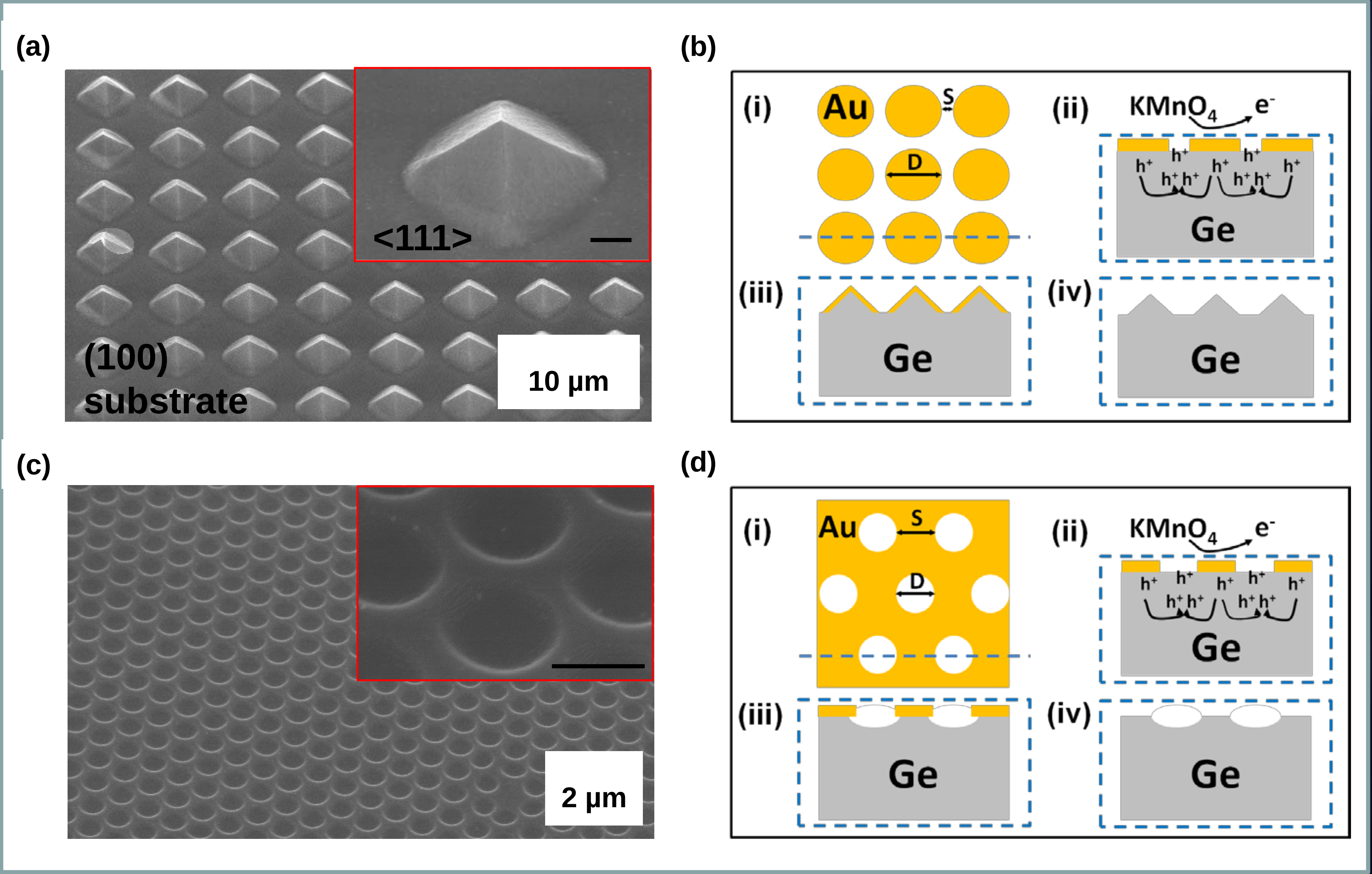




JL MOSFETs – excellent off-state and on-state performance

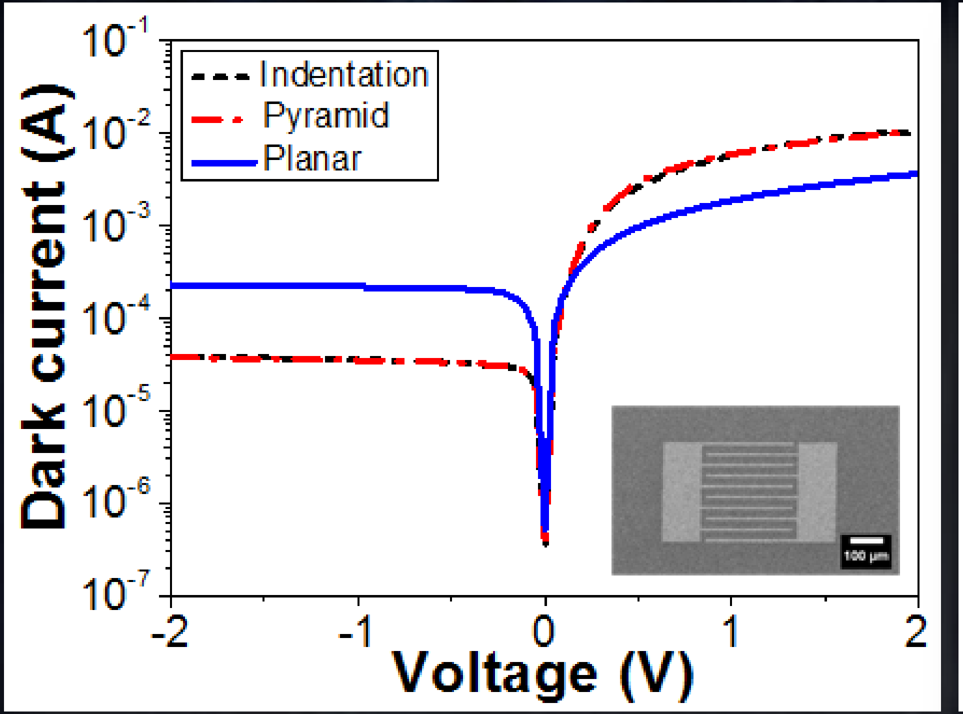
I-MacEtch for Ge

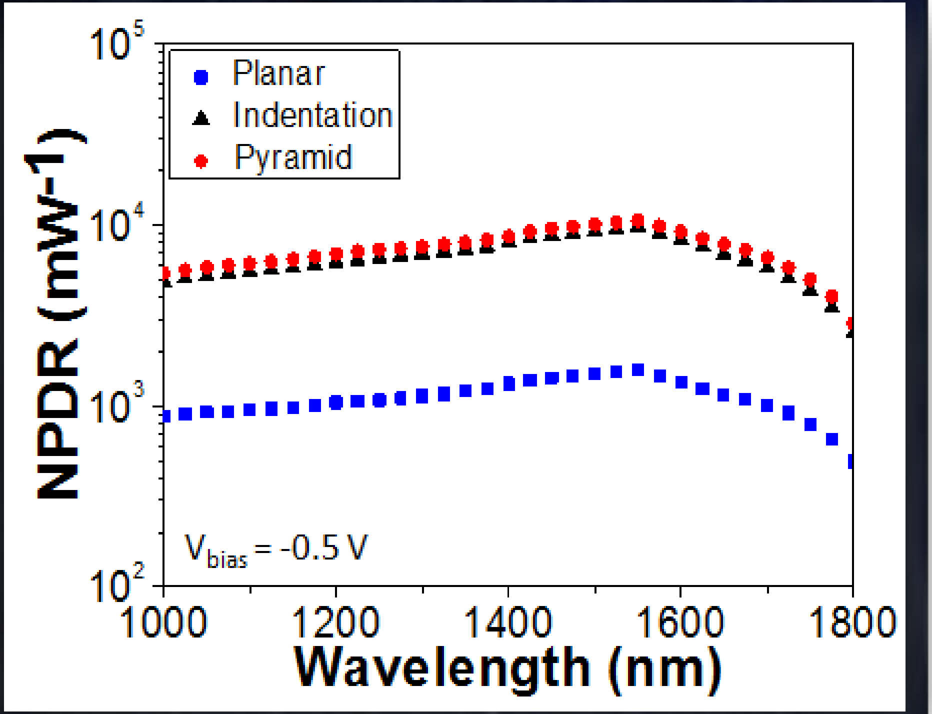
Kim et al. ACS Nano, 2018.
10.1021/acsnano.8b01848



Ge MSM PD enhanced by I-MacEtch

Kim et al. ACS Nano, 2018.
10.1021/acsnano.8b01848





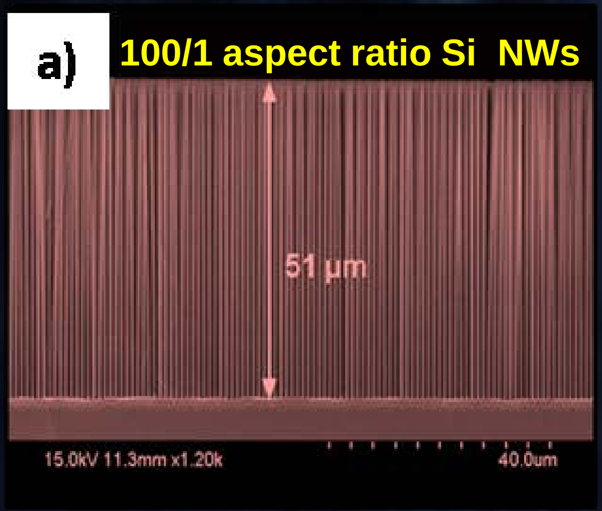
- Smooth surface by i-MacEtch w in situ α-Ge passivation
- Reduced dark current due to higher SBH by α-Ge
- Enhanced photoresponsivity due to textured surfaces

Metal Pattern Formation and resolution

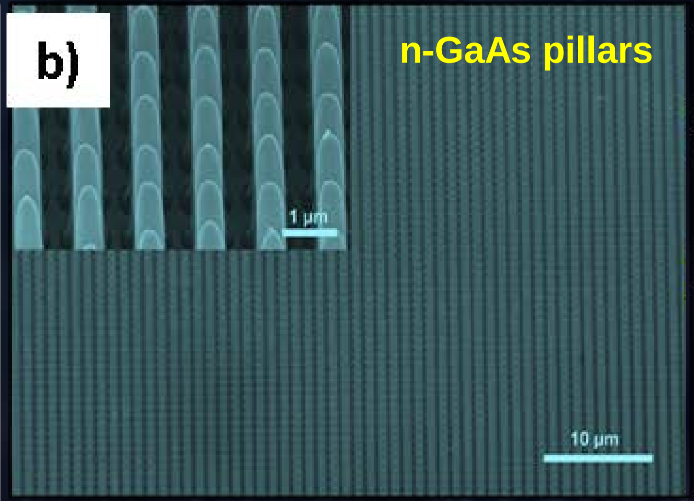
MacEtch has been realized using metal catalyst formed by the following techniques

- Electroless plating (e.g. from $AgNO_3$ solution)
- Colloidal nanoparticles
- Optical lithography
- Electron beam lithography
- Nanoimprint/soft lithography
- Superionic solid state stamping
- Nanosphere lithography
- High aspect ratio shadow mask
- Tip-based lithography (AFM, STM)

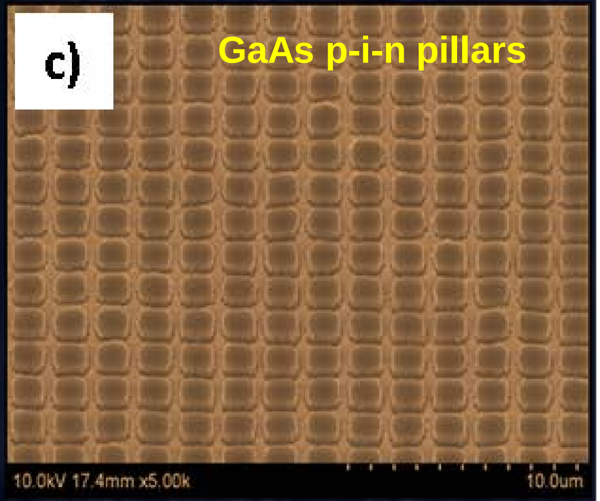
Examples of semiconductor nanostructures produced by MacEtch



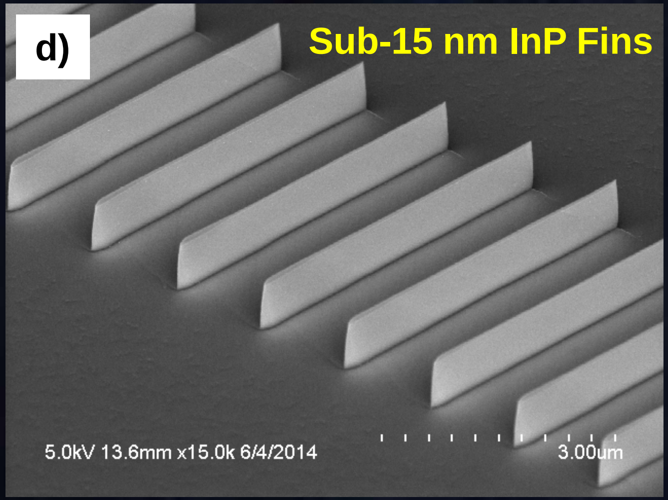
a) 100/1 aspect ratio Si NWs



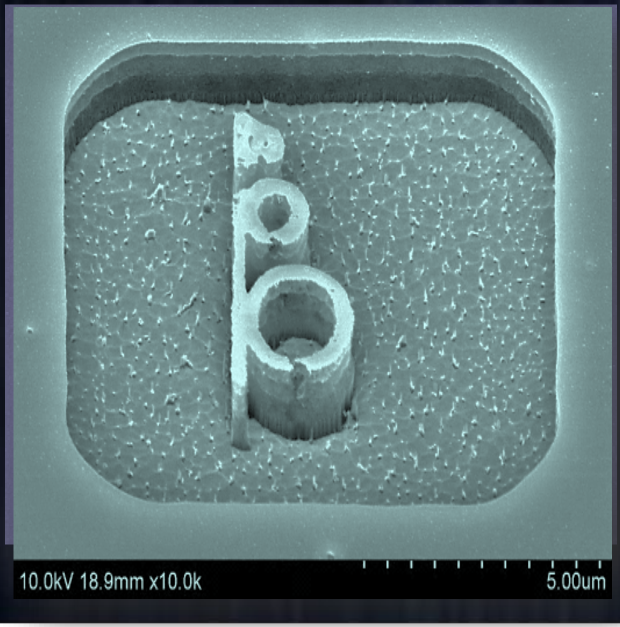
b) n-GaAs pillars

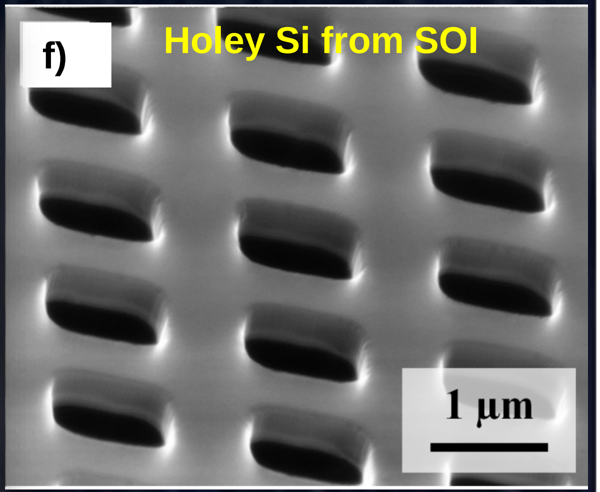


c) GaAs p-i-n pillars



d) Sub-15 nm InP Fins





f) Holey Si from SOI

MacEtch vs wet and dry etch

	Wet Etch	Dry Etch	MacEtch
Directionality	Isotropic	Anisotropic	Anisotropic
Aspect Ratio	Low	Medium	High
Ion Induced Damage	None	Mild to Severe	None
Crystal-Orientation Dependence	Some	Weak	Weak
Etch Rate	Fast	Slow	Fast
Sidewall Smoothness	Smooth	Not Smooth	Smooth or Rough
Chemical Selectivity	Good	Poor	Depends
Cost	Low	High	Low

“Metal Assisted Chemical Etching for High Aspect Ratio Nanostructures: A Review of Characteristics and Applications in Photovoltaics,” X. Li, Current Opinion in Solid State & Materials Science, 16, 71-81 (2012).

MacEtch - Not your ordinary etch

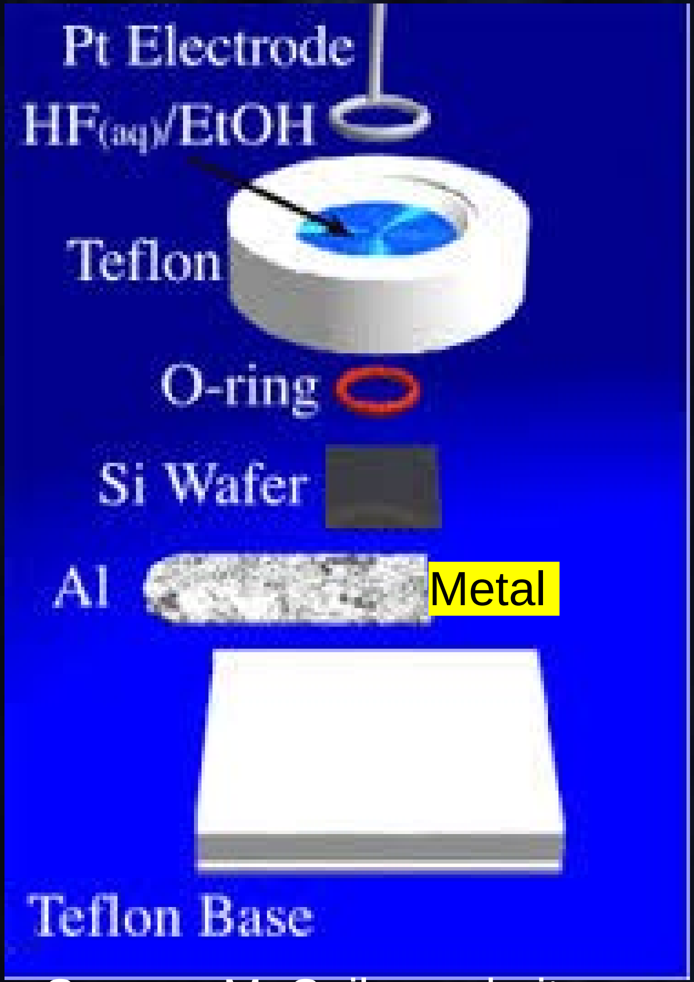
Defying text definition of wet etch, MacEtch is an anisotropic wet etching method that could potentially replace, improve dry etch for various electronics, photonics, energy, and chemical and bio-sensing applications.

- Si
- Ge
- GaAs
- InGaAs
- AlGaAs
- InP
- GaN
- SiC
- Ga_2O_3
- Single
- Poly
- Amorphous
- junctions

- MacEtch
- I-MacEtch
- H-MacEtch
- SAC-MacEtch

The Serendipity of MacEtch Discovery

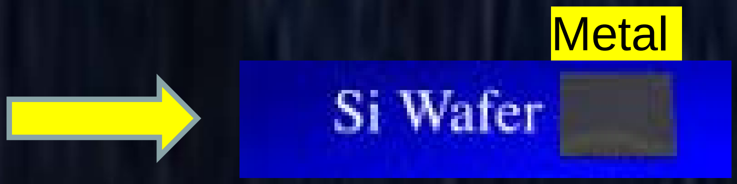
Anodic Etching for porous Si



Source: M. Sailor website

- The birth of metal-assisted chemical etch (MacEtch)
- X. Li and P. W. Bohn, *Appl. Phys. Lett.* 77, 2572 (2000); ~893 citation.

MacEtch



Selected Publications on MacEtch from Illinois

http://mocvd.ece.illinois.edu

- "Nanoscale Groove Textured beta-Ga2O3 by Room Temperature Inverse Metal-assisted Chemical Etching and Photodiodes with Enhanced Responsivity," Appl. Phys. Lett. 113, 222104 (2018).
- "Enhanced performance of Ge photodiodes via monolithic antireflection texturing and α-Ge self-passivation by inverse metal-assisted chemical etching," ACS Nano, 12 (7), 6748-6755 (2018).
- "Self-Anchored Catalyst Interface Enables Ordered Via Array Formation from Sub-micron to millimeter Scale for Poly- and Single-Crystalline Silicon," ACS Appl. Mater. Interfaces, 10 (10), pp 9116-9122 (2018).
- "Damage-Free Smooth-Sidewall InGaAs Nanopillar Array by Metal-Assisted Chemical Etching," ACS Nano, 11 (10), pp 10193-10205 (2017).
- "Scaling the Aspect Ratio of Nanoscale Closely-Packed Silicon Vias by MacEtch: Kinetics of Carrier Generation and Mass Transport," *Adv. Func. Mater.* 27, 1605614 (2017).
- "Ultra-High Aspect Ratio InP Junctionless FinFETs by a Novel Wet Etching Method," *IEEE Electron Dev. Lett.* 37, 970 (2016).
- "Inverse Metal-Assisted Chemical Etching Produces Smooth High Aspect Ratio InP Nanostructures," *Nano Lett.* 15, 641 (2015).
- "Fabrication of Arbitrarily-Shaped Silicon and Silicon Oxide Nanostructures Using Tip-based Nanofabrication," *J. Vac. Sci. Tech. B* 31, 06FJ01 (2013).
- ''Photonic crystal membrane reflectors by magnetic field-guided metal-assisted chemical etching," *Appl. Phys. Lett.* 103, 214103 (2013).
- ''GaAs pillar array-based light emitting diode fabricated by metal-assisted chemical etching'', *J. Appl. Phys.* 114, 064909 (2013).
- "Silicon nanowires with controlled sidewall profile and roughness fabricated by thin-film dewetting and metal-assisted chemical etching," *Nanotech*. 24, 225305 (2013).
- "Sub-100 nm Si nanowire and nano-sheet array formation by MacEtch using a non-lithographic InAs Nanowire Mask," *Nanotech*. 23, 305305 (2012).
- "Porosity control in metal assisted chemical etching of degenerately doped silicon," *Nanotech*. 23, 305304 (2012).
- "Metal Assisted Chemical Etching for High Aspect Ratio Nanostructures: A Review of Characteristics and Applications in Photovoltaics," *Curr. Opin. Solid State Mater. Sci.* invited review article, 16, 71 (2012).
- "Experimental Study of Design Parameters in Periodic Silicon Micropillar Array Solar Cells Produced by Soft Lithography and Metal Assisted Chemical Etching," *IEEE J. Photovoltaics* 2, 129 (2012).
- "Formation of High Aspect Ratio GaAs Nanostructures with Metal Assisted Chemical Etching," *Nano Lett.* 11, 5259 (2011).
- "Nonlithographic Patterning and Metal-Assisted Chemical Etching for Manufacturing of Tunable Light-Emitting Silicon Nanowire Arrays," *Nano Lett.* 10, 1582 (2010).
- "Nanoscale three dimensional pattern formation in light emitting porous silicon," *Appl. Phys. Lett.* 92, 191113 (2008).
- "In-plane Bandgap Control in Porous GaN through Electroless Wet Chemical Etching," *Appl. Phys. Lett.* 80, 980 (2002).
- "Metal-assisted chemical etching in HF/H_2O_2 produces porous silicon", X. Li and P.W. Bohn, *Appl. Phys. Lett.* 77, 2572 (2000); Cited for >850 times according to Google Scholar.

Patents on MacEtch from Illinois

http://mocvd.ece.illinois.edu

1. Metal-assisted chemical etching porous silicon formation method (Patent number: 6,790,785, awarded 09/14/2004). Inventors: Xiuling Li, Paul W. Bohn, Jonathan V. Sweedler
2. Metal-assisted chemical etching to produce porous group III-V materials (Patent number: 6,762,134, awarded 07/13/2004). Inventors: Paul W. Bohn, Xiuling Li, Jonathan V. Sweedler, Ilesanmi Adesida
3. Method of forming Nanoscale Three Dimensional Patterns in a Porous Material (Patent number: 8,586,843, awarded 07/16/2013). Inventors: Xiuling Li, David N. Ruzic, Ik Su Chun, Edmond K. C. Chow, Randolph E. Flauta
4. Metal-assisted chemical etching to produce III-V semiconductor nanostructures (Patent number: 8,951,430, awarded 02/10/2015). Inventors: Xiuling Li, Matthew T. Dejarld, Jae Cheol Shin, Winston Chern
5. Method of forming an array of high aspect ratio semiconductor nanostructures (Patent number: 8,980,656, awarded 03/17/2015). Inventors: Xiuling Li, Nicholas X. Fang, Placid M. Ferreira, Winston Chern, Ik Su Chun, Keng Hao Hsu
6. Apparatus and Method for Magnetic-Field Guided Metal-Assisted Chemical Etching, (Patent number 9,704,951, awarded 7/11/2017). Inventors: Xiuling Li, Weidong Zhou, Wen Huang.
7. Self-anchored Catalyst Metal-assisted chemical Etching (Patent application number: 10,134,599, awarded 07/30/2018). Inventors: Xiuling Li, Jeongdong Kim, Lingyu Kong, Munho Kim.
8. Pending 1
9. Pending 2
10. Pending 3
11. Pending 4