

Metal Etching with the Bosch Process

- Project started in 2011
- Goal was to fabricate photonic crystal (PhC) in bulk Ta
- Thermophotovoltaic applications

V. Stelmakh *et al.*, "Sputtered Tantalum Photonic Crystal Coatings for High-Temperature Energy Conversion Applications," in *IEEE Transactions on Nanotechnology*, vol. 15, no. 2, pp. 303-309 (2016).

Rinnerbauer, V.; Lausecker, E.; Schaeffler, F.; Reiningner, P.; Strasser, G.; Geil, R. D.; Joannopoulos, J. D.; Soljacic, M.; Celanovic, I. "Nanoimprinted superlattice metallic photonic crystal as ultrasensitive solar absorber", *Optica*, 2(8) (2015).

Rinnerbauer, V.; Lenert, A.; Bierman, DM; Yeng, YX; Chan, WR; Geil, R. D.; Senkevich, JJ; Joannopoulos, JD; Wang, EN; Soljacic, M.; Celanovic, I. "Metallic Photonic Crystal Absorber-Emitter for Efficient Spectral Control in High-Temperature Solar Thermophotovoltaics", *Adv. Energy Mat.* 4(12) (2014).

V. Rinnerbauer, S. Ndao, Y. X. Yeng, J. J. Senkevich, K. F. Jensen, J. D. Joannopoulos, M. Soljacic, I. Celanovic, and R. D. Geil, "Large-area fabrication of high aspect ratio tantalum photonic crystals for high-temperature selective emitters" *J. Vac. Sci. Technol. B* 31, 011802 (2013).

V. Stelmakh, V. Rinnerbauer, R. D. Geil, P.R. Aimone, J. J. Senkevich, J. D. Joannopoulos, M. Soljai, Ivan Celanovic, "High-temperature tantalum tungsten alloy photonic crystals: Stability, optical properties, and fabrication", *Appl. Phys. Lett.* 103, 123903 (2013).

Alcatel AMS100 DRIE

Specs:

- Standard Bosch process
- Wafer sizes: 4", 6" and pieces mounted on handle wafer
- Power (Source): 3000 W
- Power (Substrate holder): 300 W RF/500 W LF (50 kHz – 460 kHz)
- Gases: SF₆, C₄F₈, Ar, O₂, CH₄, He
- Temperature ranges: -10 °C to 30 °C
- Clamping: Mechanical



Project started with a question:
Do you think you can etch Ta in your DRIE?

Periodic Table of the Elements																		VIII A 8A																	
1 IA H Hydrogen 1.008																		2 He Helium 4.003																	
3 Li Lithium 6.941		4 Be Beryllium 9.012																		10 Ne Neon 20.180															
11 Na Sodium 22.990		12 Mg Magnesium 24.305																		18 Ar Argon 39.948															
19 K Potassium 39.098		20 Ca Calcium 40.078		21 Sc Scandium 44.956		22 Ti Titanium 47.867		23 V Vanadium 50.942		24 Cr Chromium 51.996		25 Mn Manganese 54.938		26 Fe Iron 55.845		27 Co Cobalt 58.933		28 Ni Nickel 58.693		29 Cu Copper 63.546		30 Zn Zinc 65.38		31 Ga Gallium 69.723		32 Ge Germanium 72.631		33 As Arsenic 74.922		34 Se Selenium 78.971		35 Br Bromine 79.904		36 Kr Krypton 84.798	
37 Rb Rubidium 84.468		38 Sr Strontium 87.62		39 Y Yttrium 88.906		40 Zr Zirconium 91.224		41 Nb Niobium 92.906		42 Mo Molybdenum 95.95		43 Tc Technetium 98.907		44 Ru Ruthenium 101.07		45 Rh Rhodium 102.906		46 Pd Palladium 106.42		47 Ag Silver 107.868		48 Cd Cadmium 112.414		49 In Indium 114.818		50 Sn Tin 118.711		51 Sb Antimony 121.760		52 Te Tellurium 127.6		53 I Iodine 126.904		54 Xe Xenon 131.294	
55 Cs Cesium 132.905		56 Ba Barium 137.328		57-71 Lanthanide Series		72 Hf Hafnium 178.49		73 Ta Tantalum 180.948		74 W Tungsten 183.84		75 Re Rhenium 186.207		76 Os Osmium 190.23		77 Ir Iridium 192.217		78 Pt Platinum 195.085		79 Au Gold 196.967		80 Hg Mercury 200.592		81 Tl Thallium 204.383		82 Pb Lead 207.2		83 Bi Bismuth 208.980		84 Po Polonium [208.982]		85 At Astatine 209.987		86 Rn Radon 222.018	
87 Fr Francium 223.020		88 Ra Radium 226.025		89-103 Actinide Series		104 Rf Rutherfordium [261]		105 Db Dubnium [262]		106 Sg Seaborgium [266]		107 Bh Bohrium [264]		108 Hs Hassium [269]		109 Mt Meitnerium [268]		110 Ds Darmstadtium [269]		111 Rg Roentgenium [272]		112 Cn Copernicium [277]		113 Uut Ununtrium unknown		114 Fl Flerovium [289]		115 Uup Ununpentium unknown		116 Lv Livermorium [298]		117 Uus Ununseptium unknown		118 Uuo Ununoctium unknown	
57 La Lanthanum 138.905		58 Ce Cerium 140.116		59 Pr Praseodymium 140.908		60 Nd Neodymium 144.243		61 Pm Promethium 144.913		62 Sm Samarium 150.36		63 Eu Europium 151.964		64 Gd Gadolinium 157.25		65 Tb Terbium 158.925		66 Dy Dysprosium 162.500		67 Ho Holmium 164.930		68 Er Erbium 167.259		69 Tm Thulium 168.934		70 Yb Ytterbium 173.055		71 Lu Lutetium 174.967							
89 Ac Actinium 227.028		90 Th Thorium 232.038		91 Pa Protactinium 231.036		92 U Uranium 238.029		93 Np Neptunium 237.048		94 Pu Plutonium 244.064		95 Am Americium 243.061		96 Cm Curium 247.070		97 Bk Berkelium 247.070		98 Cf Californium 251.080		99 Es Einsteinium [254]		100 Fm Fermium 257.095		101 Md Mendelevium 258.1		102 No Nobelium 259.101		103 Lr Lawrencium [262]							

RIE etch workshop with John Coburn

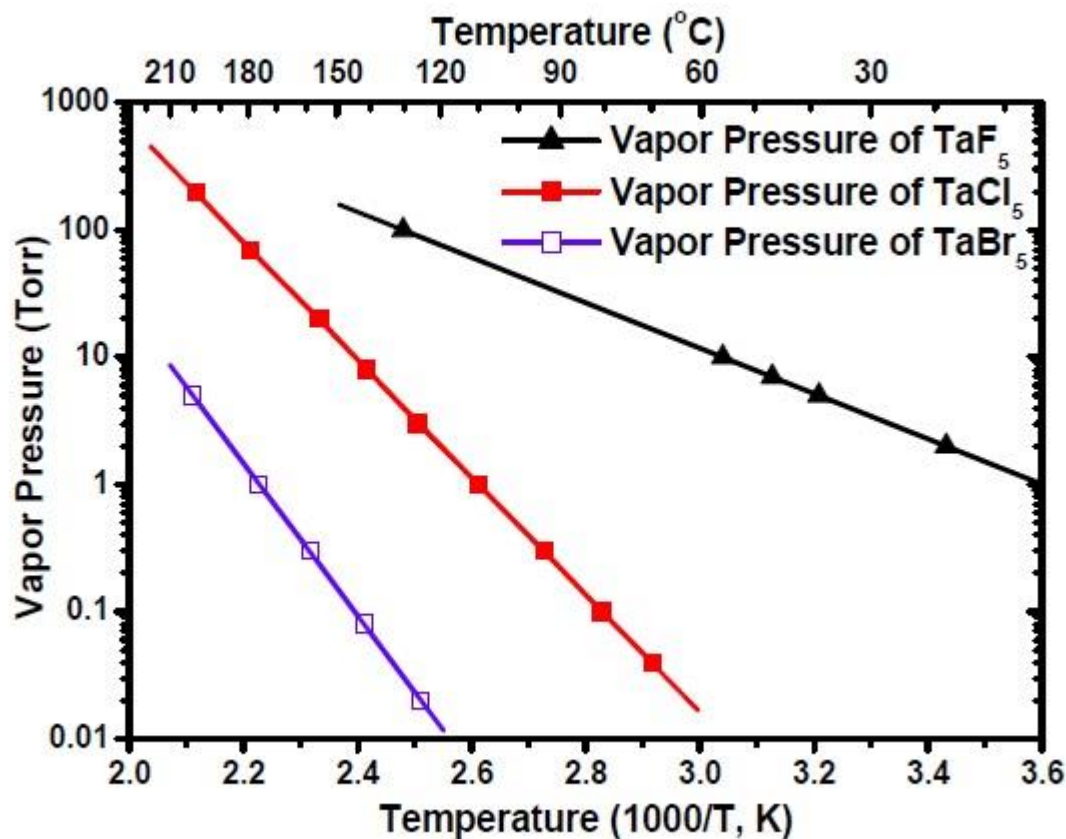
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Etchable materials that form volatile reaction products near room temp.

Etchants: CF_4 , SF_6 , Cl_2 , HBr , O_2 , H_2 , CH_4

Etchable material + Available etchant = Maybe I can etch it

Vapor pressure of Ta halides



TaF_5 significantly more volatile than TaCl_5 : ~2 Torr at 20 C

Notes about the Ta substrates

- 0.75" - 2" diameter Ta pieces lapped and polished to $\sim 1\text{nm}$ rms roughness
- Fabrication steps*:
 - Interference lithography
 - Definition of cavity by isotropic plasma ashing
 - Pattern transfer to Cr hard mask (wet and dry etching approaches)
 - Final DRIE of Ta substrate, desired results:
 - Cavity diameter $0.5 - 1.0\text{ }\mu\text{m}$
 - Aspect ratio > 2
- Ta pieces bonded to 6" Al carrier wafer with thermal paste
- Preparing Ta substrates was very time consuming: little room for optimization
- Hard to determine etch rate with out FIB milling
- Improved process through small iterations

* V. Rinnerbauer, S. Ndao, Y. X. Yeng, J. J. Senkevich, K. F. Jensen, J. D. Joannopoulos, M. Soljacic, I. Celanovic, and R. D. Geil, "Large-area fabrication of high aspect ratio tantalum photonic crystals for high-temperature selective emitters" J. Vac. Sci. Technol. B 31, 011802 (2013).

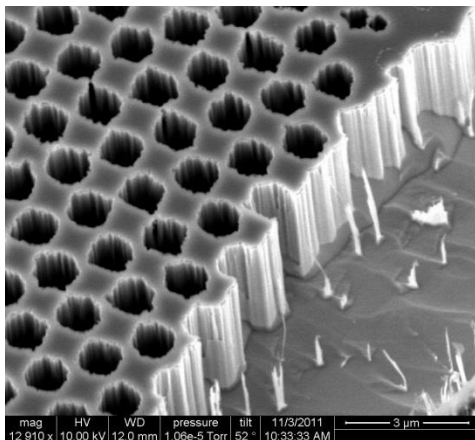
Let's just see what happens

Bosh etch process based on our “Si Low roughness” process:

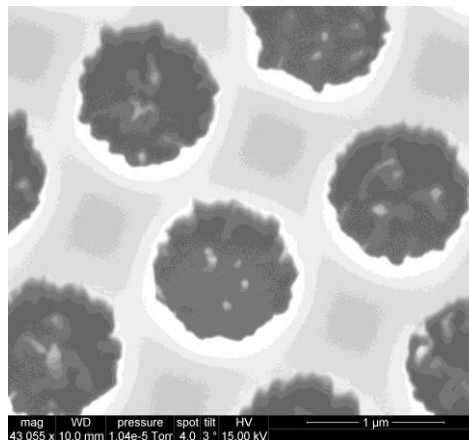
Source	SH bias	SF6/C4F8	SF6/C4F8	Valve/press	Temp
1200 W	75 W LF/10%	200/100 sccm	3/1 s	100%/~5mTorr	20 °C

Observations:

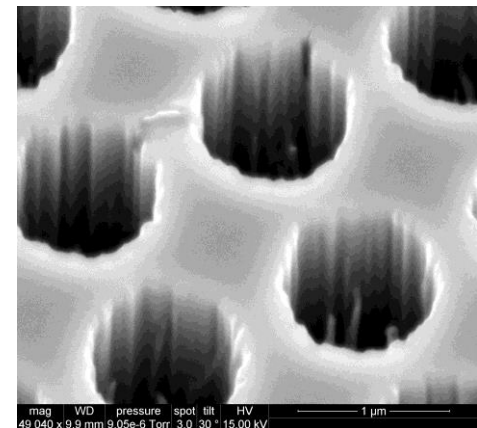
- Etch rate: 0.6 $\mu\text{m}/\text{min}$ (determined with AFM)
- Wet etching Cr is a bad idea
- Grass inside the holes
- But at least we can etch Ta! and profile is nearly vertical!



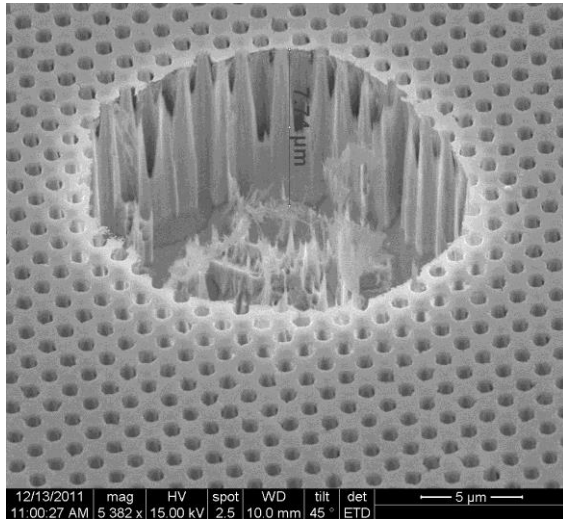
Wet etched Cr hard mask



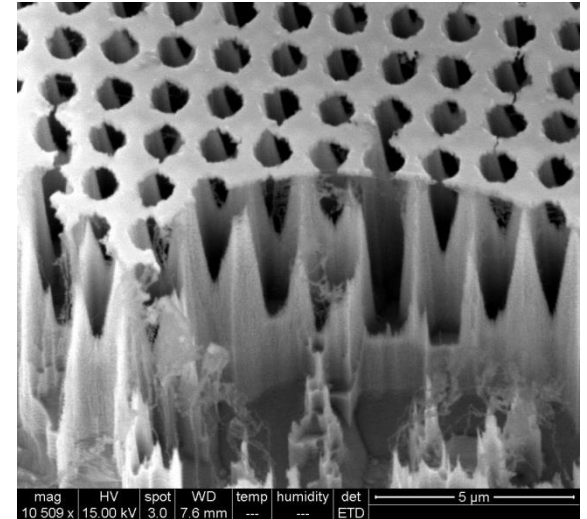
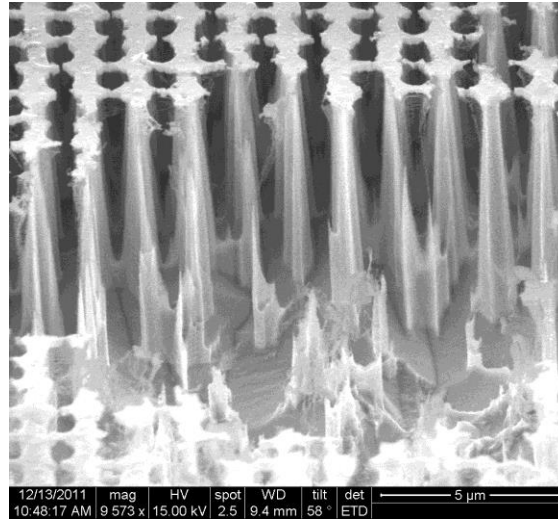
Cr hard mask on Ta etched for 5 mins



Ta Bosch etching appears to work, so let's etch a whole bunch of samples...



6 min etch, 7.7 μm deep



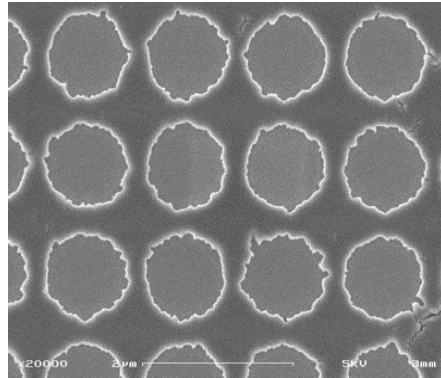
I destroyed six samples but learned two important things:

- Application of thermal grease is not trivial
- Increasing substrate temperature significantly increases Ta etch rate (1.3 μm/min)

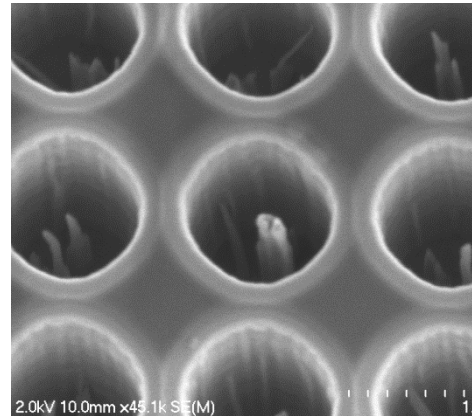
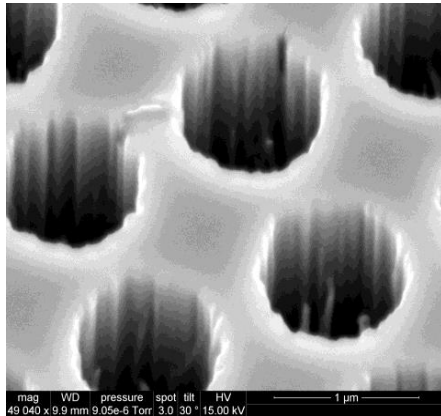
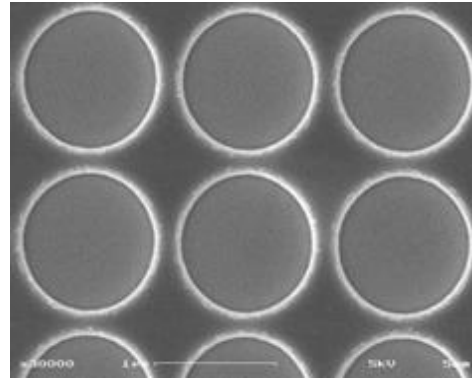
Source	SH bias	SF6/C4F8	SF6/C4F8	Valve/press	Temp
1200 W	75 W LF/10%	200/100 sccm	3/1 s	100%/~5mTorr	20 °C

Wet to dry etching of Cr hard mask

Cr wet etch



Cr dry etch

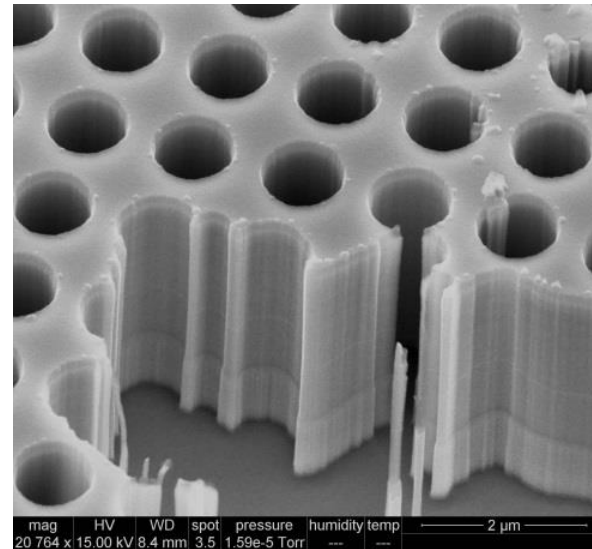
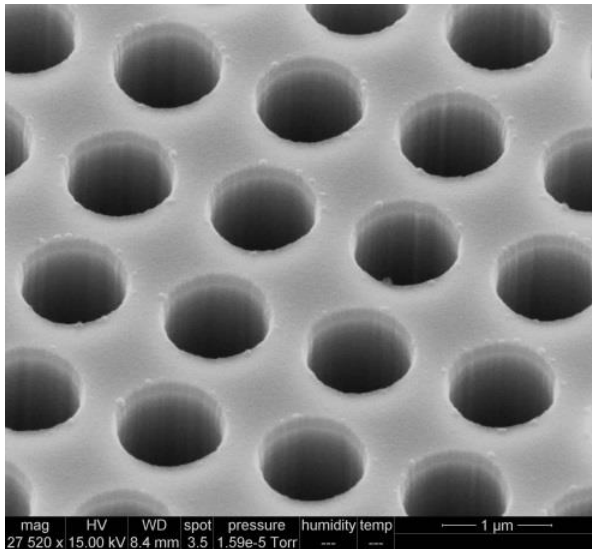


Dry etching Cr clearly the way to go but need to get rid of the grass

Source	SH bias	SF6/C4F8	SF6/C4F8	Valve/press	Temp
1200 W	75 W LF/10%	200/100 sccm	3/2 s	100%/~5mTorr	20 °C

Increased passivation time

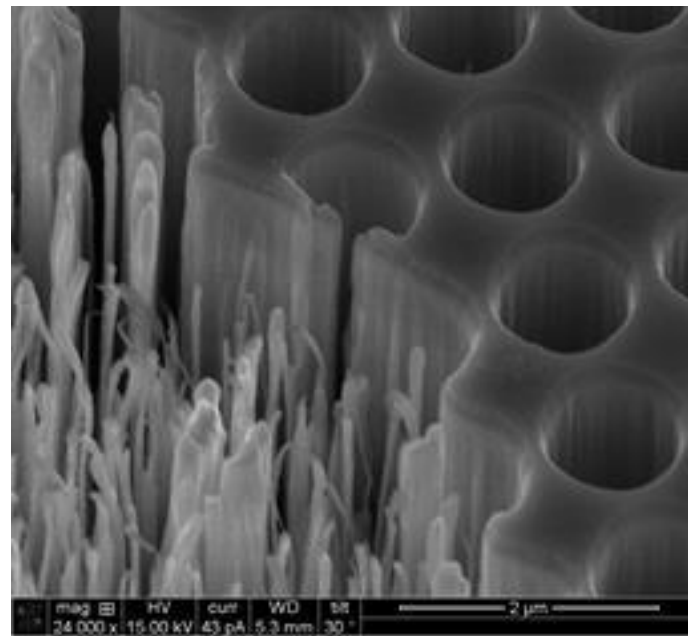
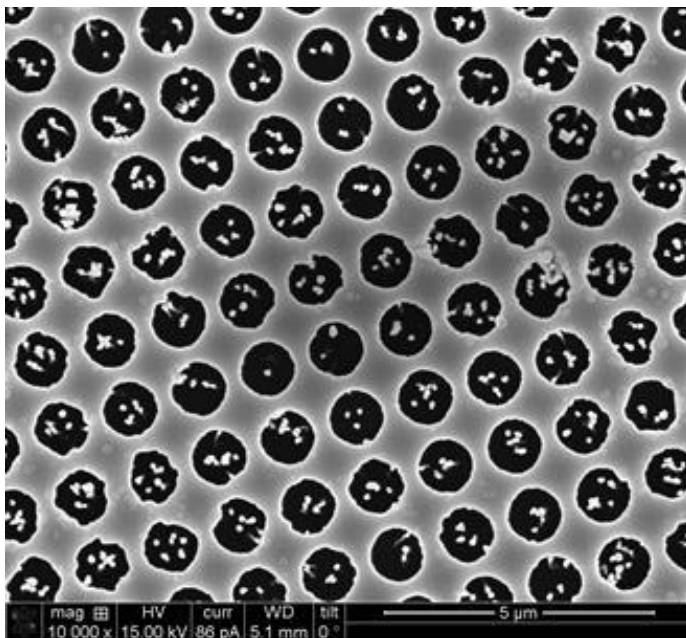
Source	SH bias	SF6/C4F8	SF6/C4F8	Valve/press	Temp
1200 W	75 W LF/10%	200/100 sccm	3/2 s	100%/~5mTorr	20 °C



- Increased passivation time from 1.0 to 2.0
- Etch intervals with cooling step
- Etch rate: ~0.57 µm/min (not significantly slower than 3/1s)
- Cr mask

Same process, different results

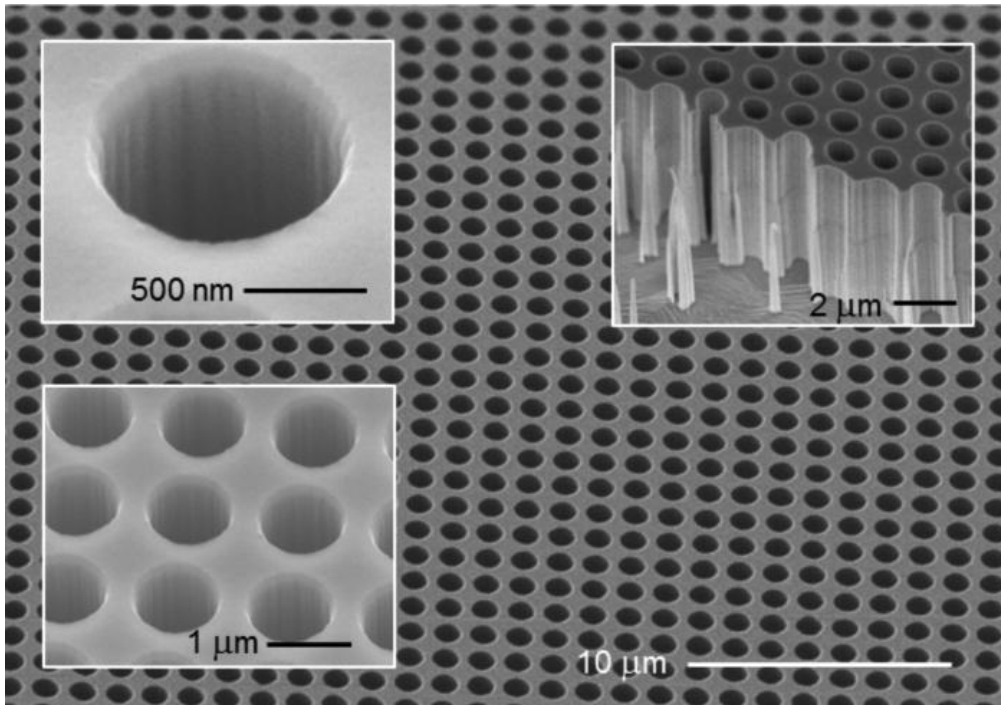
Source	SH bias	SF6/C4F8	SF6/C4F8	Valve/press	Temp
1200 W	75 W LF/10%	200/100 sccm	3/2 s	100%/~5mTorr	20 °C



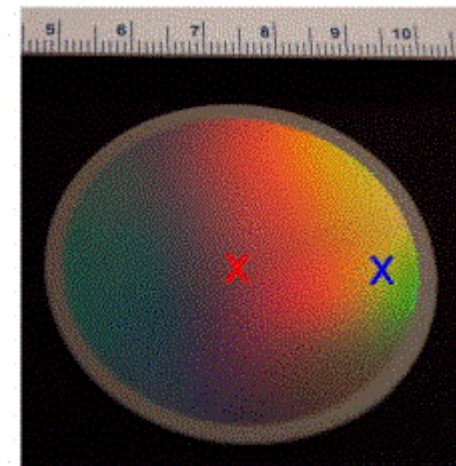
- Significant grass
- Maybe passivation time is too long?
- Possibly also an issue with prior processing (RIE, lithography)

Reduced passivation time

Source	SH bias	SF6/C4F8	SF6/C4F8	Valve/press	Temp
1200 W	75 W LF/10%	200/100 sccm	3/1.5 s	100%/~5mTorr	20 °C



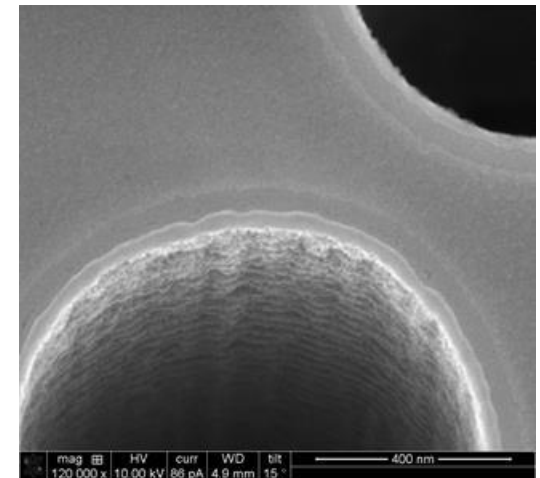
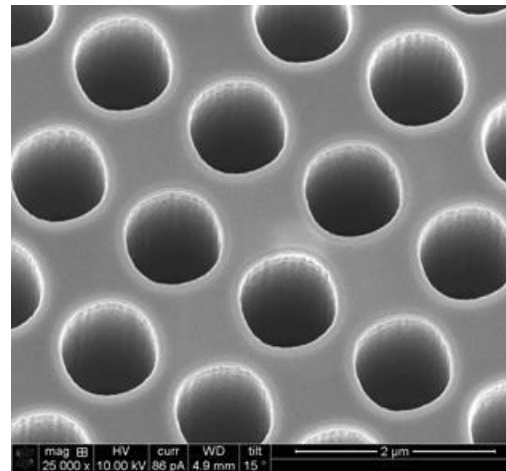
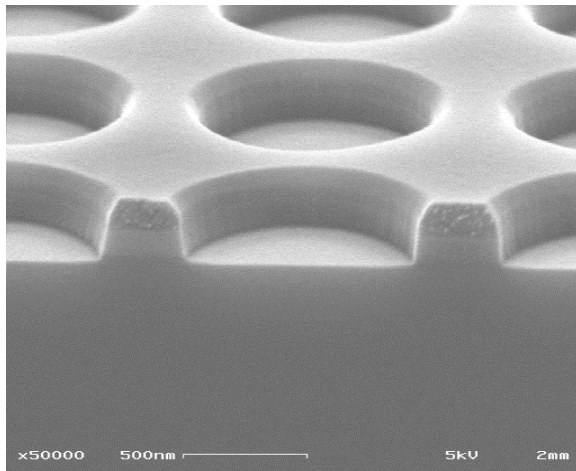
- 2" diameter Ta substrate
- Cr hard mask
- 3/1.5s passivation time



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Attempts to reduce grass

- Reduce passivation time, but not too much: 1.5 s
- Implement SiO₂ hard mask to address possible resputtering of Cr

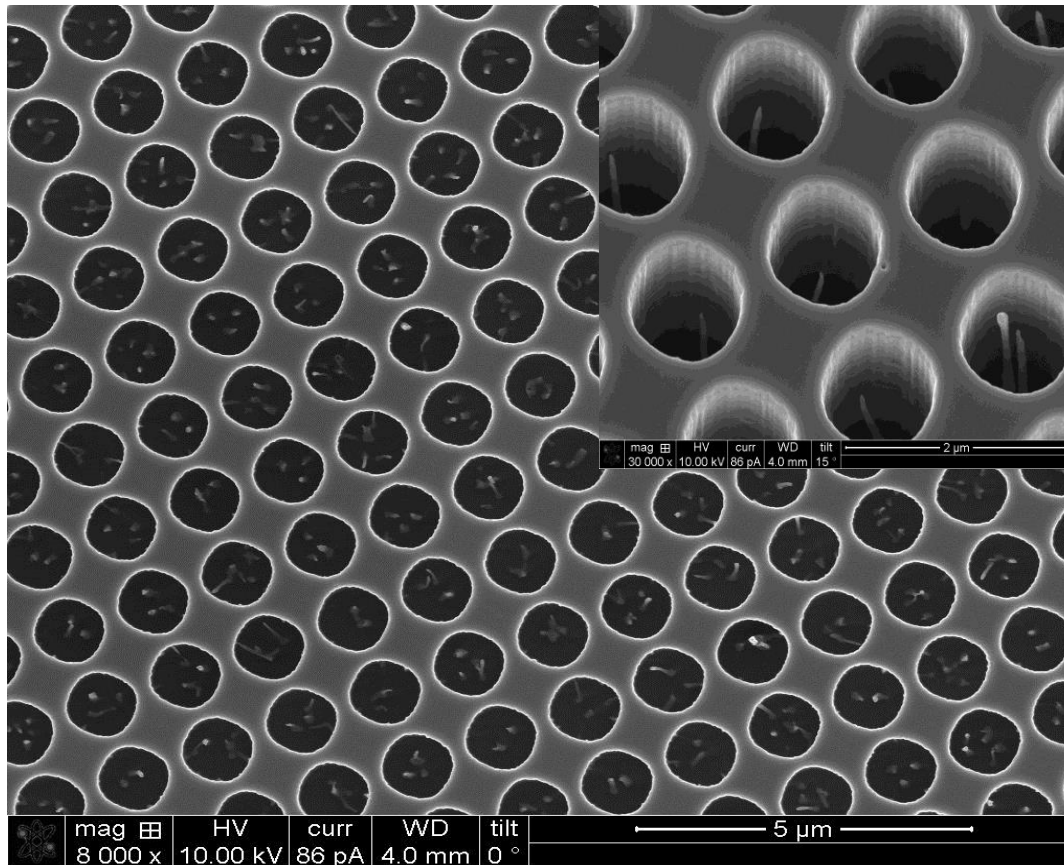


- ~100 nm SiO₂ mask (but up to 250 nm)
- Selectivity: ~25:1

Source	SH bias	SF ₆ /C ₄ F ₈	SF ₆ /C ₄ F ₈	Valve/press	Temp
1200 W	75 W LF/10%	200/100 sccm	3/1.5 s	100%/~5mTorr	20 °C

Switched to SiO₂ mask and reduced passivation time, but still some grass

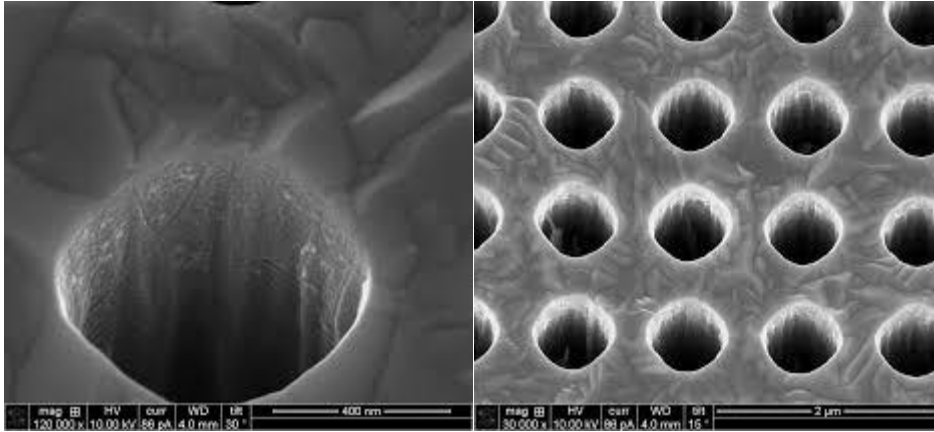
Source	SH bias	SF ₆ /C ₄ F ₈	SF ₆ /C ₄ F ₈	Valve/press	Temp
1200 W	75 W LF/10%	200/100 sccm	3/1.5 s	100%/~5mTorr	20 °C



5 min etch

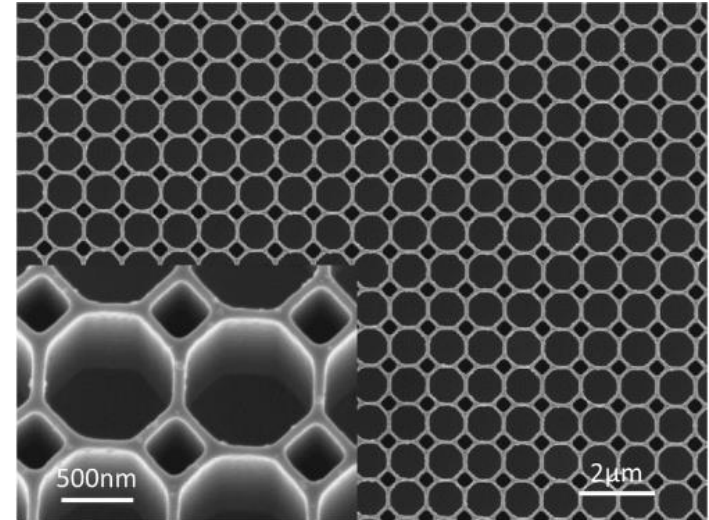
Variations in the PhC

Thick (30 μm) sputtered Ta

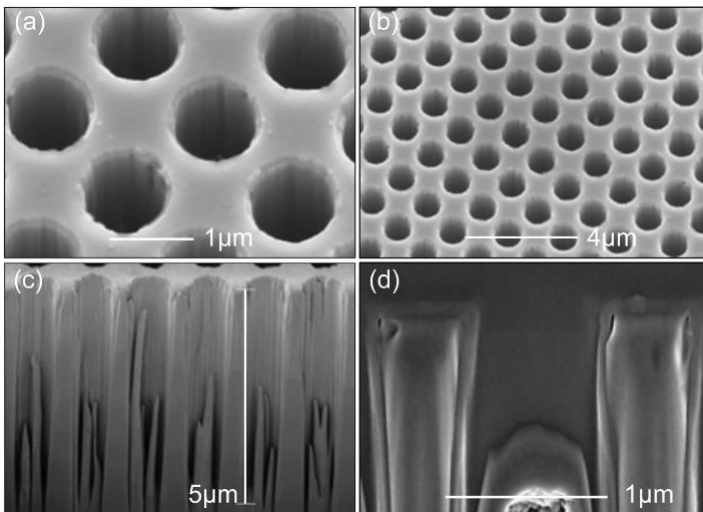


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Patterning with UV-NIL process



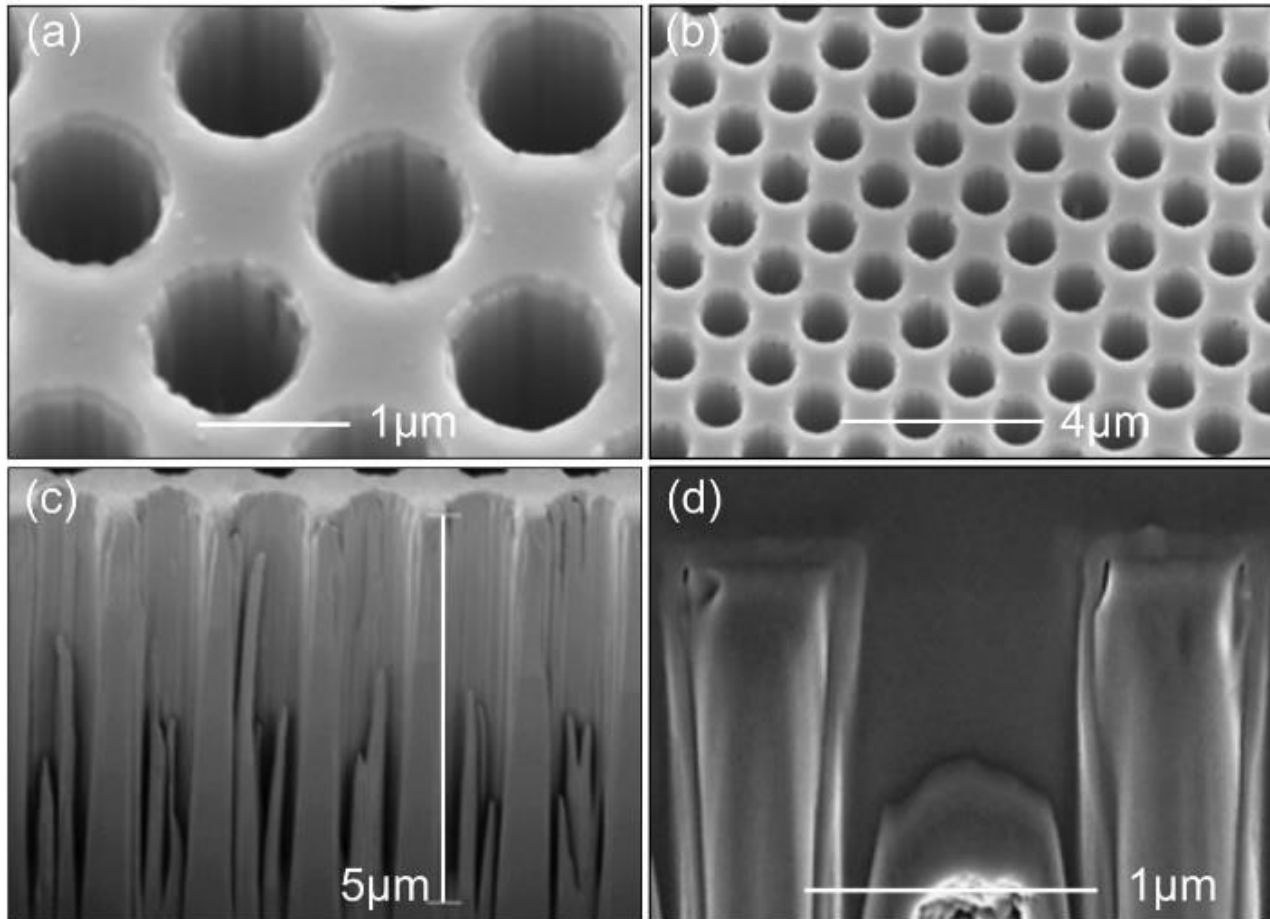
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TaW alloys

V. Stelmakh, V. Rinnerbauer, R. D. Geil, P.R. Aimone, J. J. Senkevich, J. D. Joannopoulos, M. Soljai, Ivan Celanovic, "High-temperature tantalum tungsten alloy photonic crystals: Stability, optical properties, and fabrication", *Appl. Phys. Lett.* 103, 123903 (2013).

FIB cross section of TaW PhC



Influence of grass had minimal effect on performance of emission spectrum

Where we stand

Source	SH bias	SF6/C4F8	SF6/C4F8	Valve/press	Temp
1200 W	75 W LF/10%	200/100 sccm	3/1.5 s	100%/~5mTorr	20 °C

- SiO₂ hard mask
- Aspect ratio as high as 8:1
- Etch rate > 0.6 $\mu\text{m}/\text{min}$
- In retrospect, some sort of DOE would have been good
- Chamber conditioning a likely suspect for inconsistent etch results
- After talking during breakfast with NNCl etch people: Improve substrate mounting (different bonding material?).
 - Boron-nitride is notorious for redeposition
 - Try fomblin oil, crystal bond, PMMA...