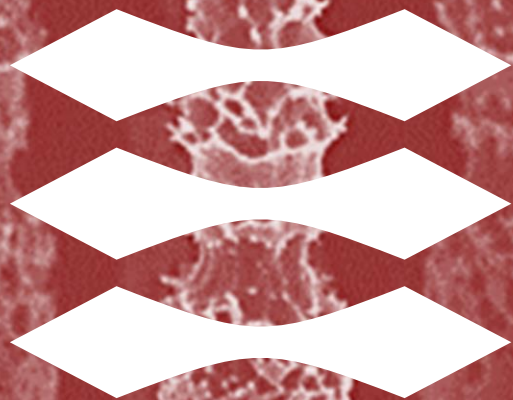


DTU



Generic build-up of silicon plasma etch processes: a practical guide to directional profiles

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Generic build-up of silicon plasma etch processes

- *What are plasmas*
- *Fundamental principles on plasmas*
- *What is plasma etching*
- *1-, 2-, and 3-steps procedures for profile control*
- *Mixed SF₆ plasma etch*
- *Switched SF₆/FC plasma etch including DREM*
- *Beyond DREM: 4-steps DREAM and 3D silicon nano-sculpturing*
- *Switched SF₆/O₂ plasma etch*

What are plasmas

Ordinarily, we hardly come into contact with plasma in our daily life.

Matter, which is normally seen, exists in the solid, liquid, or gas phase.



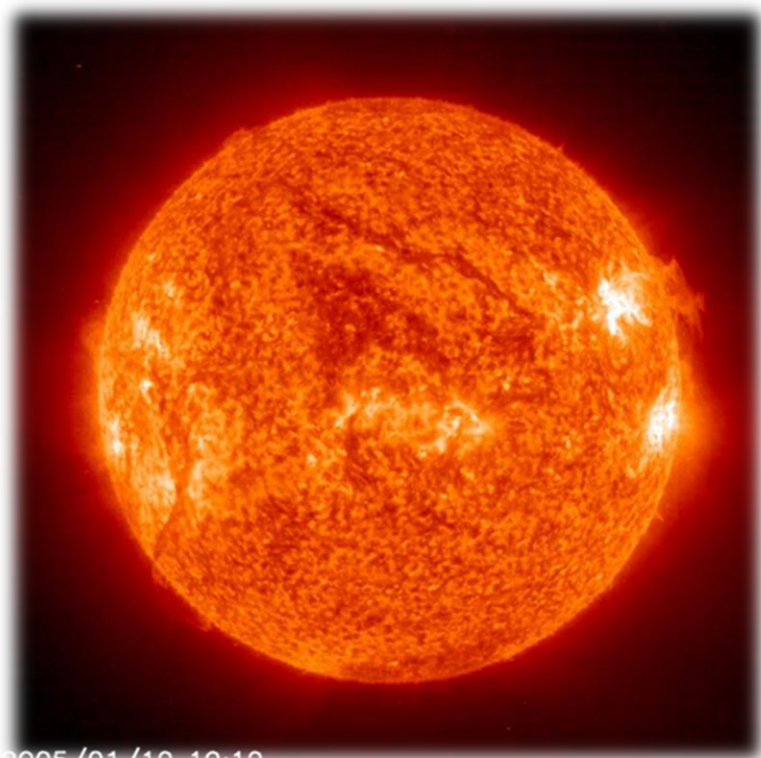
What are plasmas

But, lightning and auroras appearing in the polar regions are plasmas in nature and...

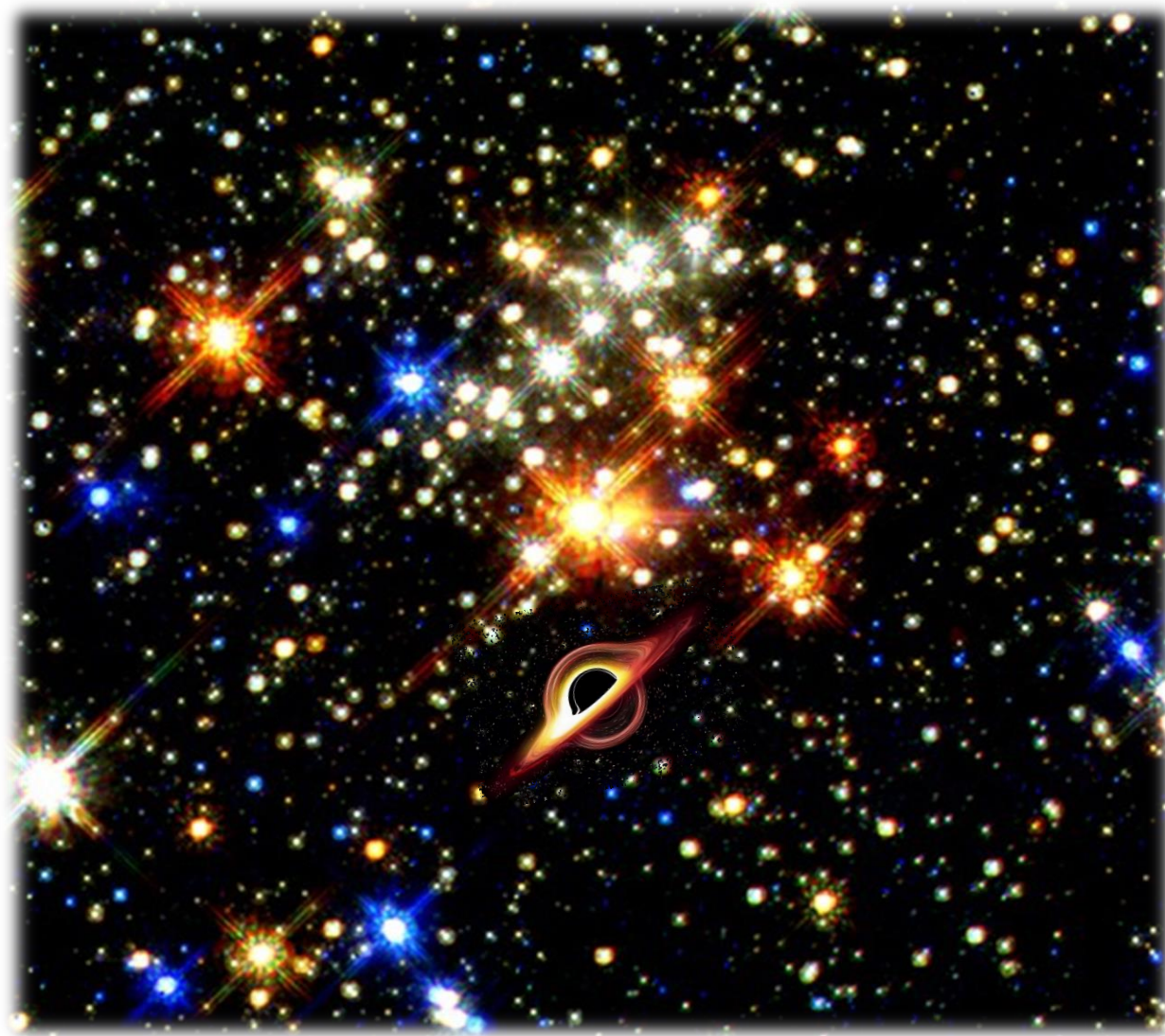


What are plasmas

... and all stars, including the sun, are masses of high-temperature plasmas.



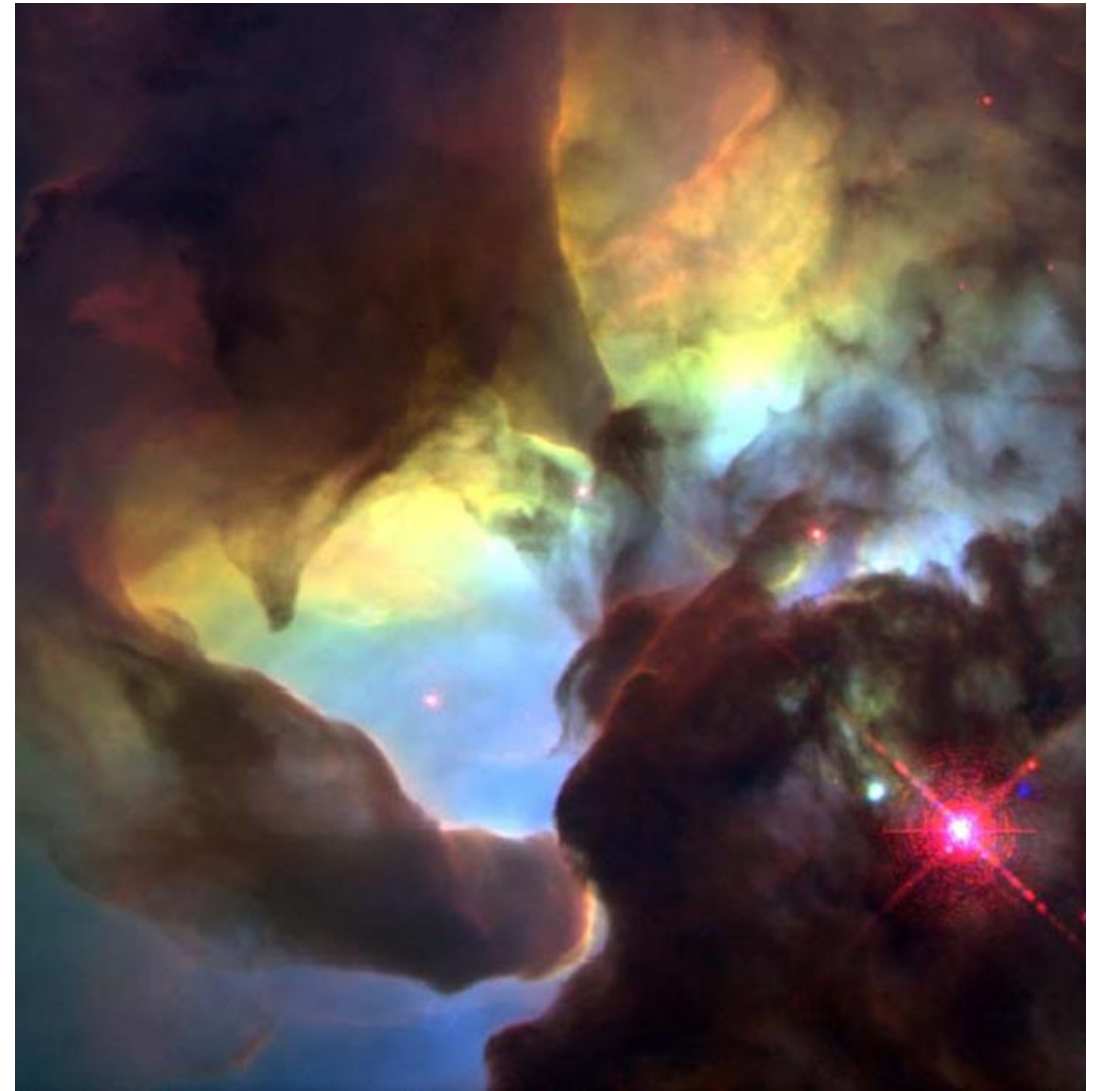
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What are plasmas

Also the interstellar matter and nebulae are in the plasma state.

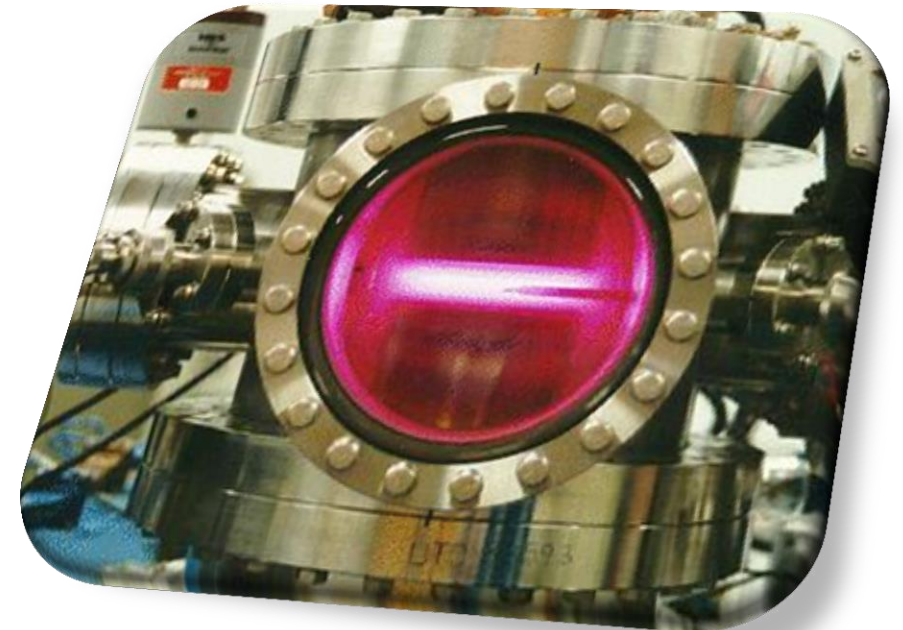
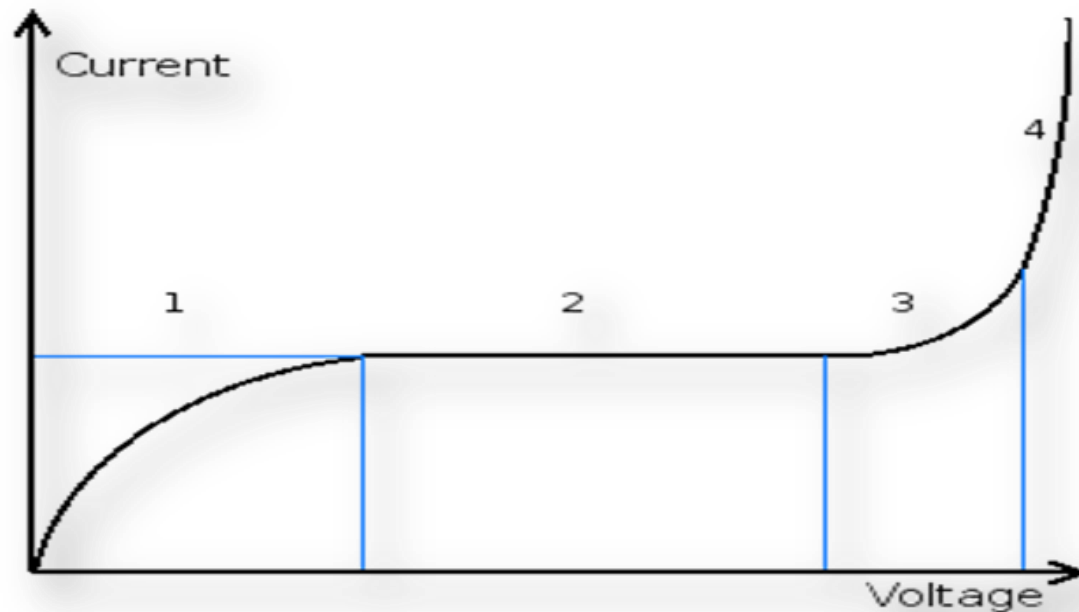
So, it has been said that the greater part of the universe is in the plasma state.



Electrical discharges: manmade plasmas

*Manmade plasmas, or electrical discharges, are accomplished by using a glass tube with two metal electrodes installed, **evacuating the tube** to a pressure between 0.1 to 1 mbar and **applying a high voltage** between the two electrodes.*

As the voltage gradually increases, only a small current flows. But when the voltage has reached a few hundred volts, current through the tube shows an abrupt increase, and the tube begins to emit visible light. A plasma is born.



Electrical discharges

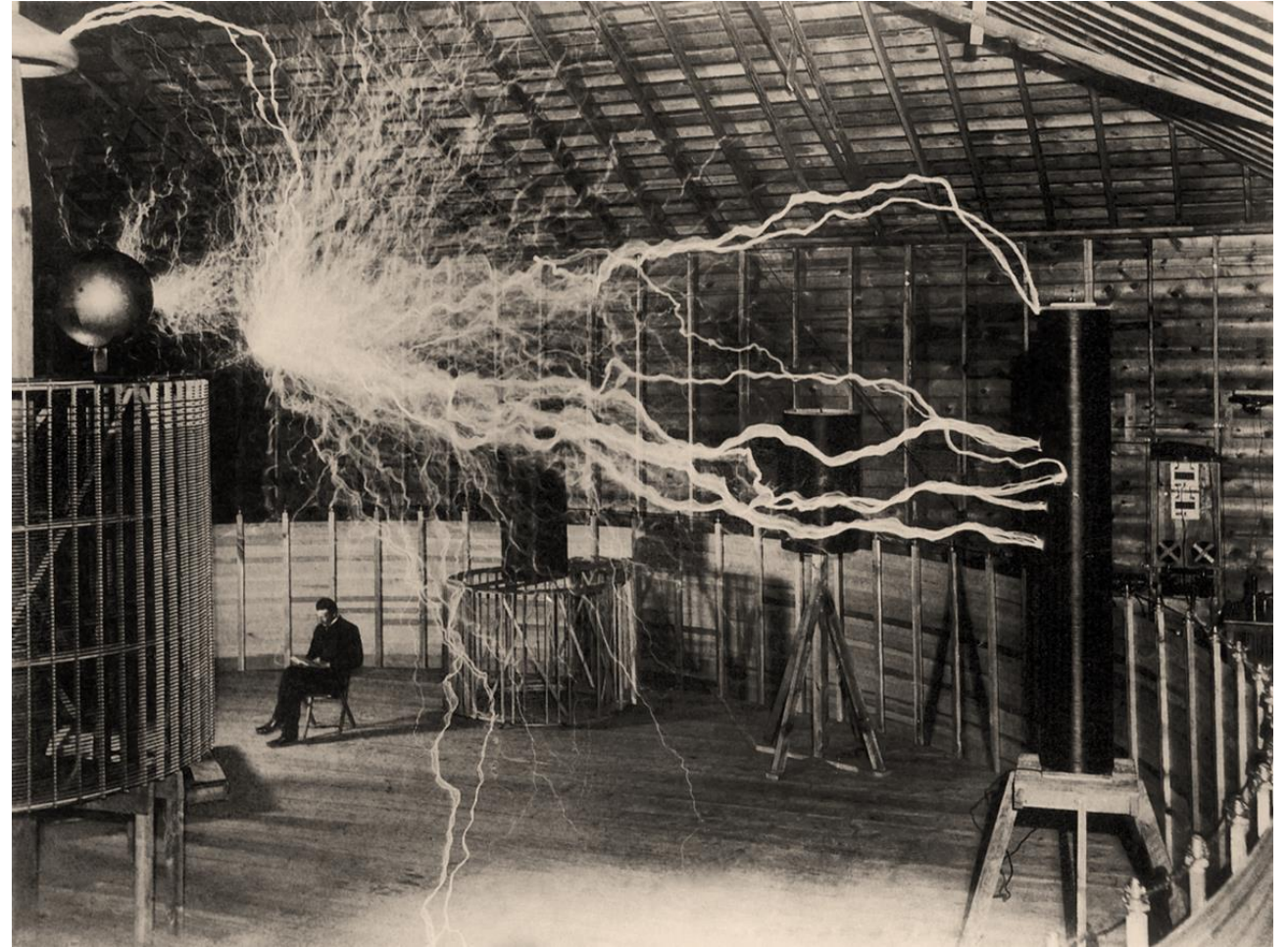


Vegas, city of fluorescent tubes and neon signs, is during the night in the plasma state.

Electrical discharges

A plasma contains a high density of charged particles and is therefore highly conductive.

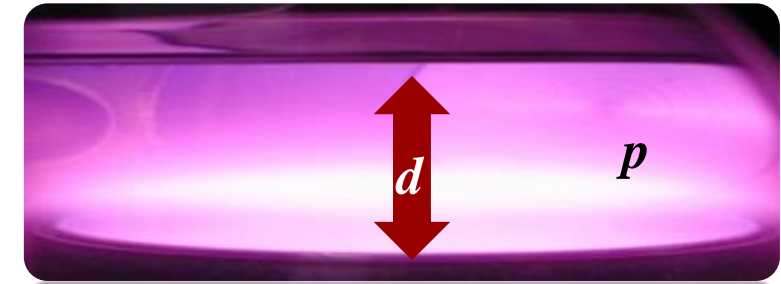
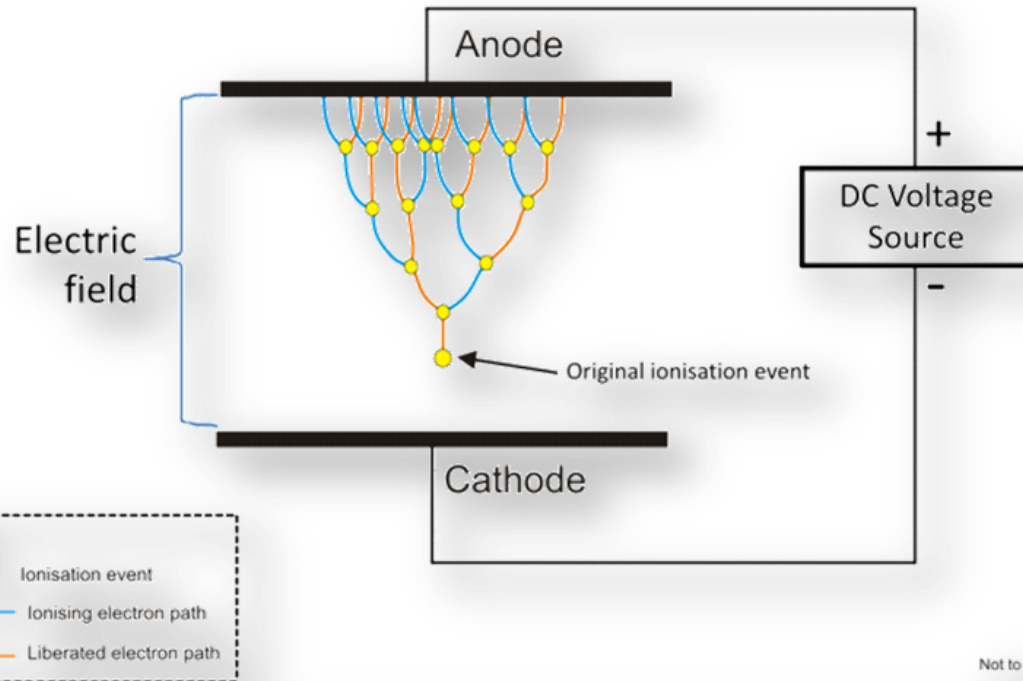
This conduction distinguishes the plasma from the normal gas and it is therefore called the forth state in which a material can exist.



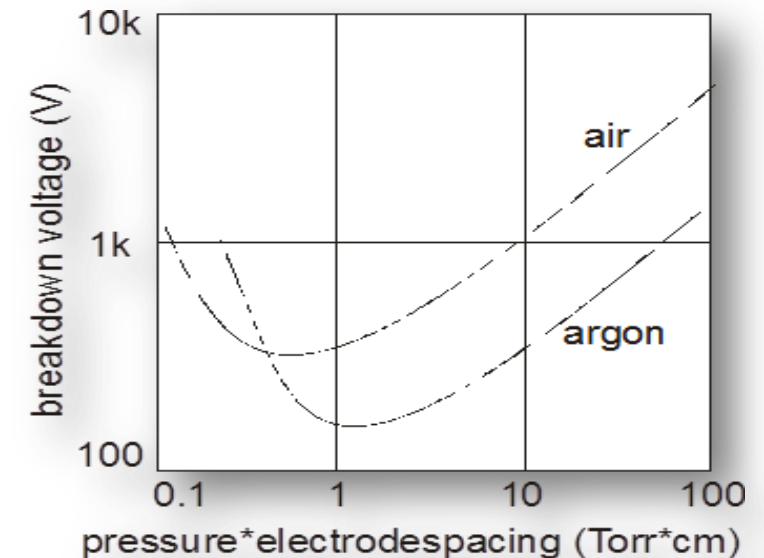
Nikola Tesla in his laboratory in 1899.

Electrical discharges

The simplest discharge uses a **direct current (dc)** source. The high electrical field creates an ever-increasing number of free electrons - due to fatal collisions that liberate additional electrons - while passing towards the positively charged anode.



An important discharge property is the **Paschen curve**. It shows the breakdown voltage of a gas between two electrodes separated by a distance d at a pressure p .



Electrical discharges

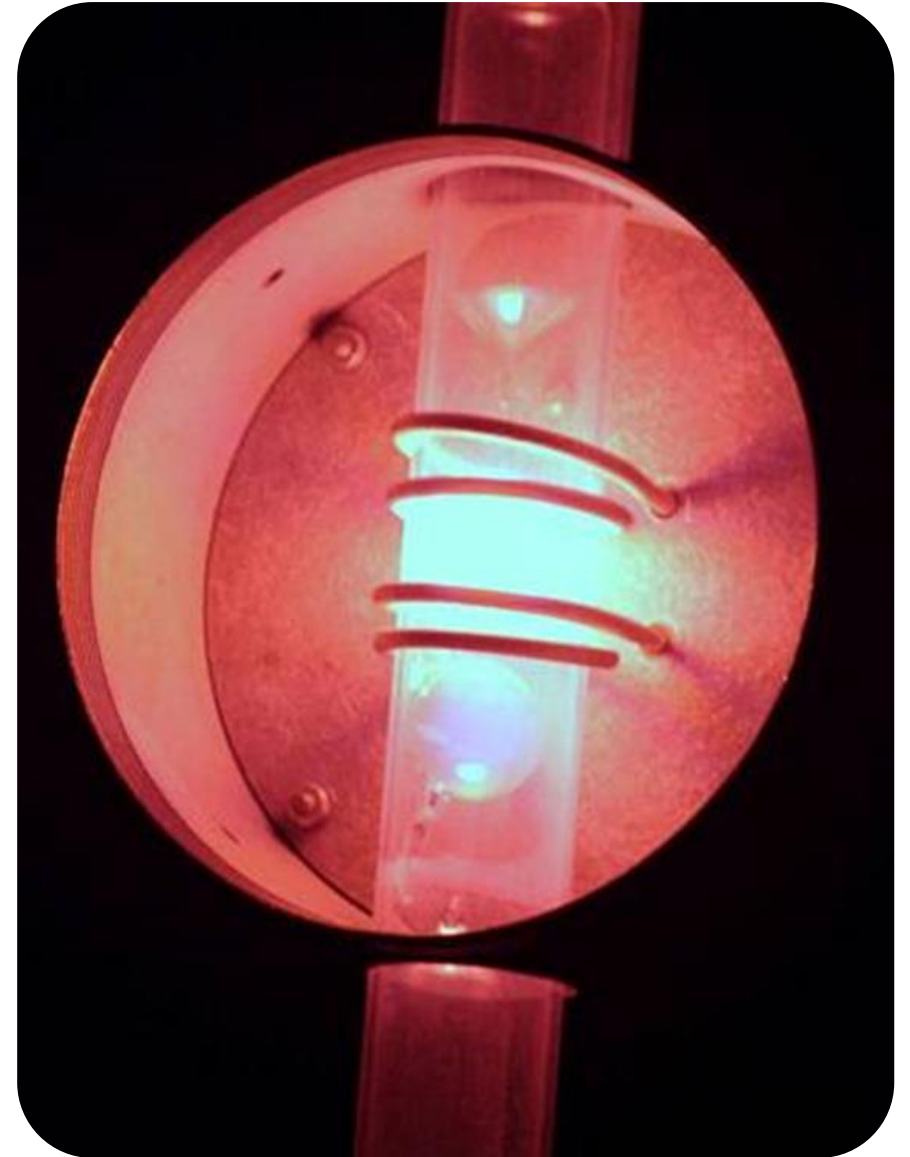
Plasma can also be generated using radio frequency (rf).

This enables us to install electrodes with insulating surfaces.

*This type is called **capacitively coupled plasma (CCP)**.*

Another possibility is to use a coil rapped around a glass tube and excite the discharge electromagnetically.

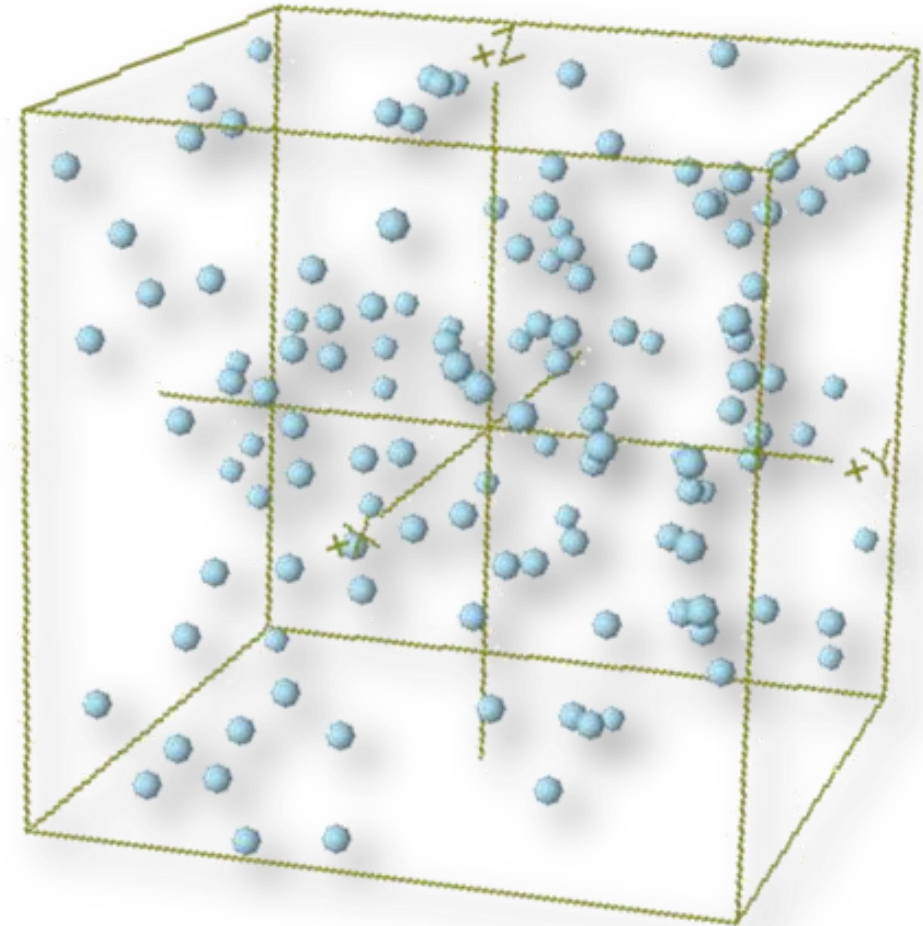
*This type is called **inductively coupled plasma (ICP)**.*



Fundamental principles

Physical model of the ideal gas

- A gas consists of **molecules** of mass m and diameter d in **ceaseless random motion**.
- **The size of the molecules is negligible** (in the sense that their diameters are much smaller than the average distance travelled between collisions).
- **The molecules do not interact**, except that they make perfectly elastic collisions when the separation of their centres is equal to d .



M-B speed distribution of the ideal gas

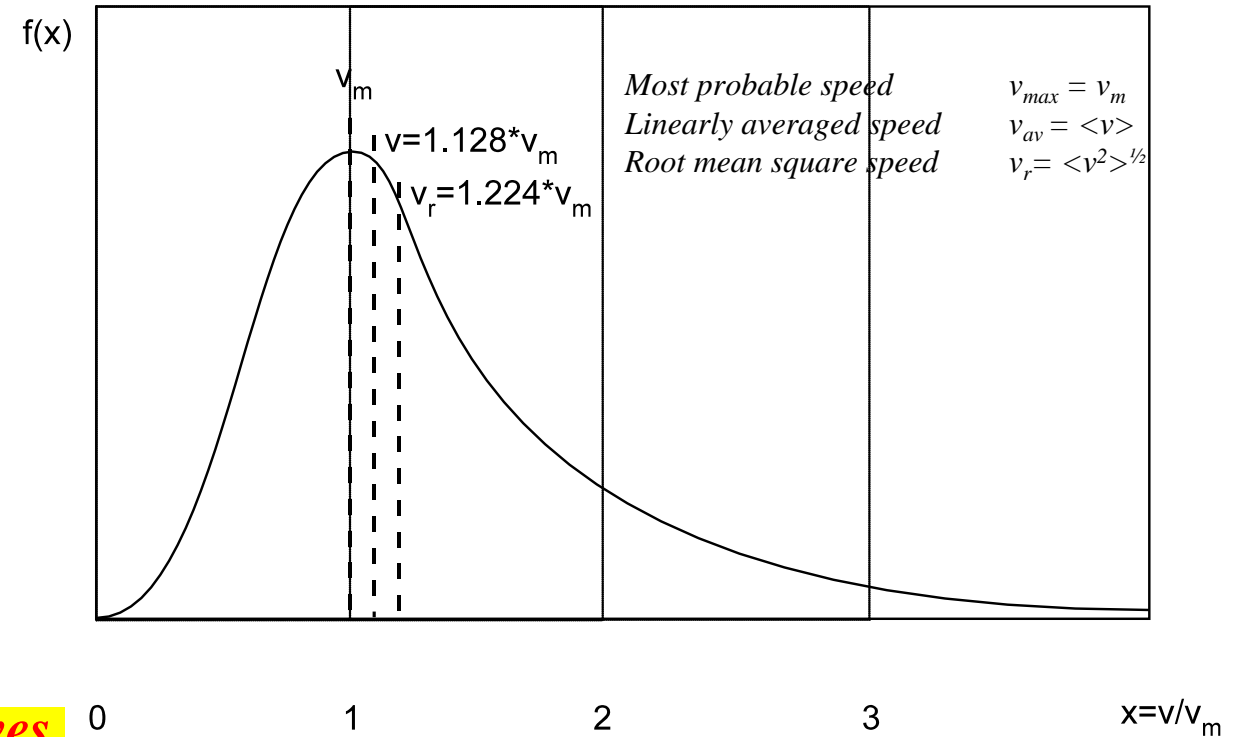
The **Maxwell–Boltzmann (M-B) distribution** describes the probability $f(v)$ of a particle's speed being near a given value as a function of the temperature T of the system, the mass m of the particle, and that speed value.

$$\frac{dN}{N} = f(v)dv = 4\pi v^2 \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mv^2}{2kT} \right) dv$$

With this we find the most probable kinetic energy per molecule:

$$\langle E_{kin} \rangle = \frac{1}{2} m v_{rms}^2 = \frac{3kT}{2}$$

$$\text{Where } v_{rms} = \left(\int_0^\infty v^2 \cdot f(v) dv \right)^{1/2} = \sqrt{\frac{3kT}{m}}$$



So, the bigger the molecule, the slower it moves.

Mean free path of the ideal gas

$$\lambda_g = \frac{v_{avg}}{f_{gg}} = \frac{1}{\sigma_g n_g 4\sqrt{2}} \quad [\text{m}]$$

$$\lambda_e = \frac{v_{ave}}{f_{eg}} = \frac{1}{\sigma_g n_g} = \frac{kT}{\sigma_g p_g} \quad [\text{m}]$$

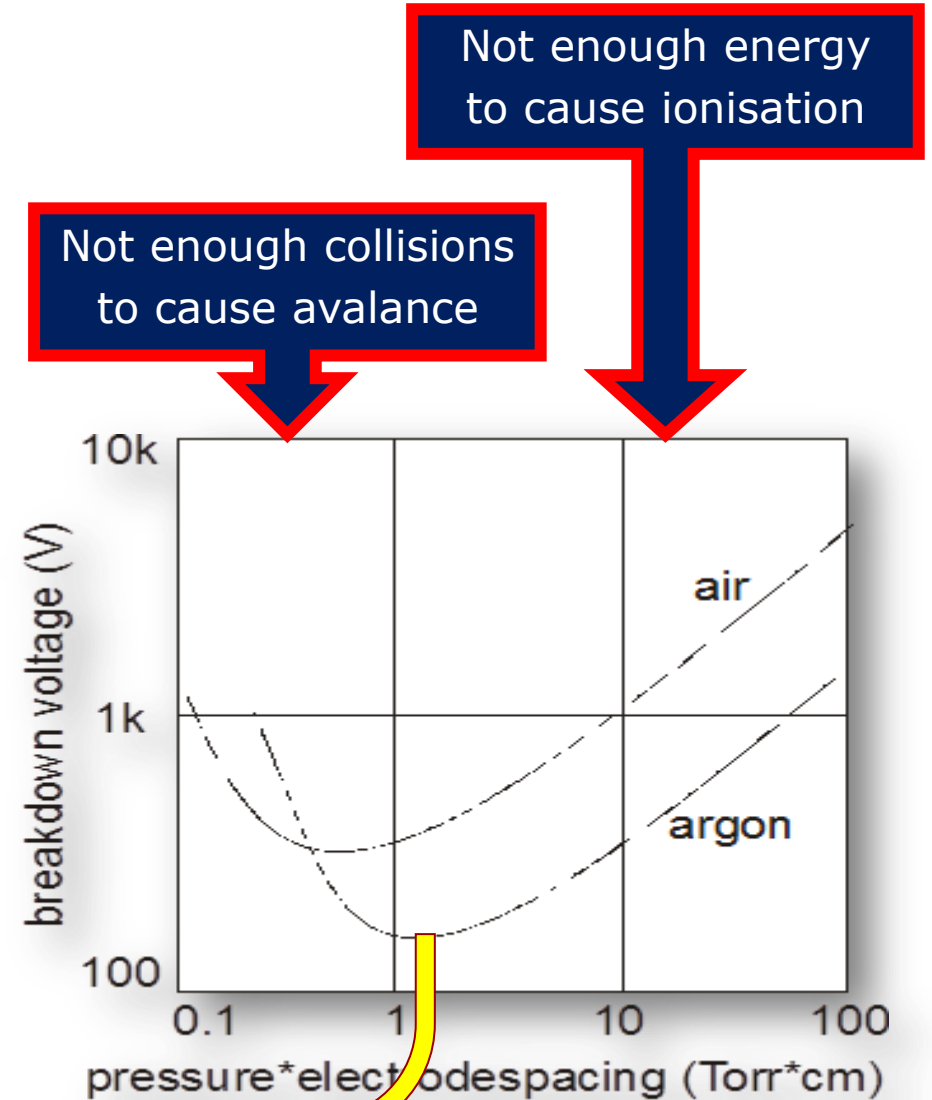
So, the mean free path of the smaller electron is ca. 6 times larger than that of the gas molecule.

For nitrogen, $\lambda_g * p_g \approx 50 \text{ mm} * \text{mTorr}$
and
 $\lambda_e * p_g \approx 300 \text{ mm} * \text{mTorr}$

Only true for
DC discharge

$10.000/300 = 33$ gap collisions
Avalanche effect = $2^{33} \approx 10^{10} = 10 \text{ billion}$ per starting electron

$10.000 \text{ mm} * \text{mTorr} = 10 \text{ mm} * \text{Torr}$

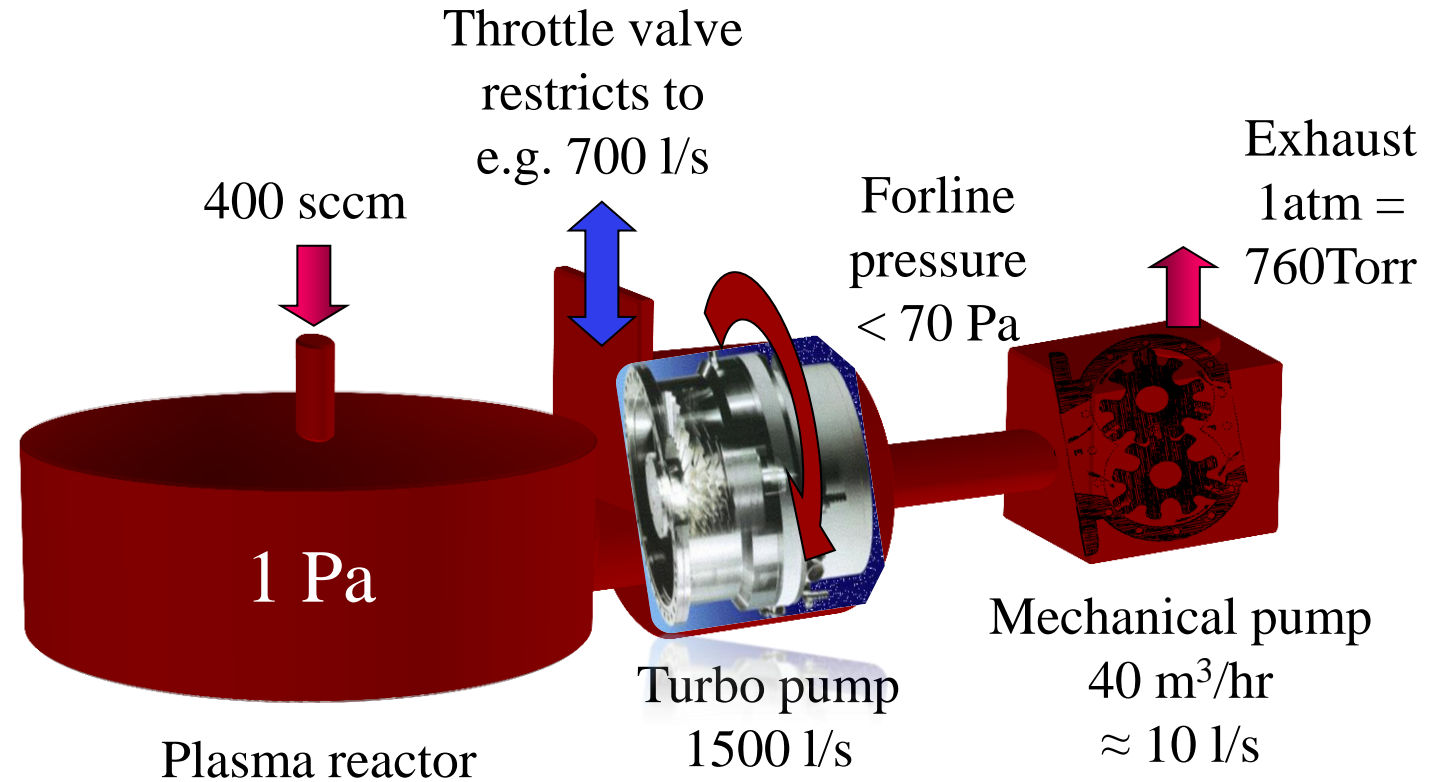


Pump system

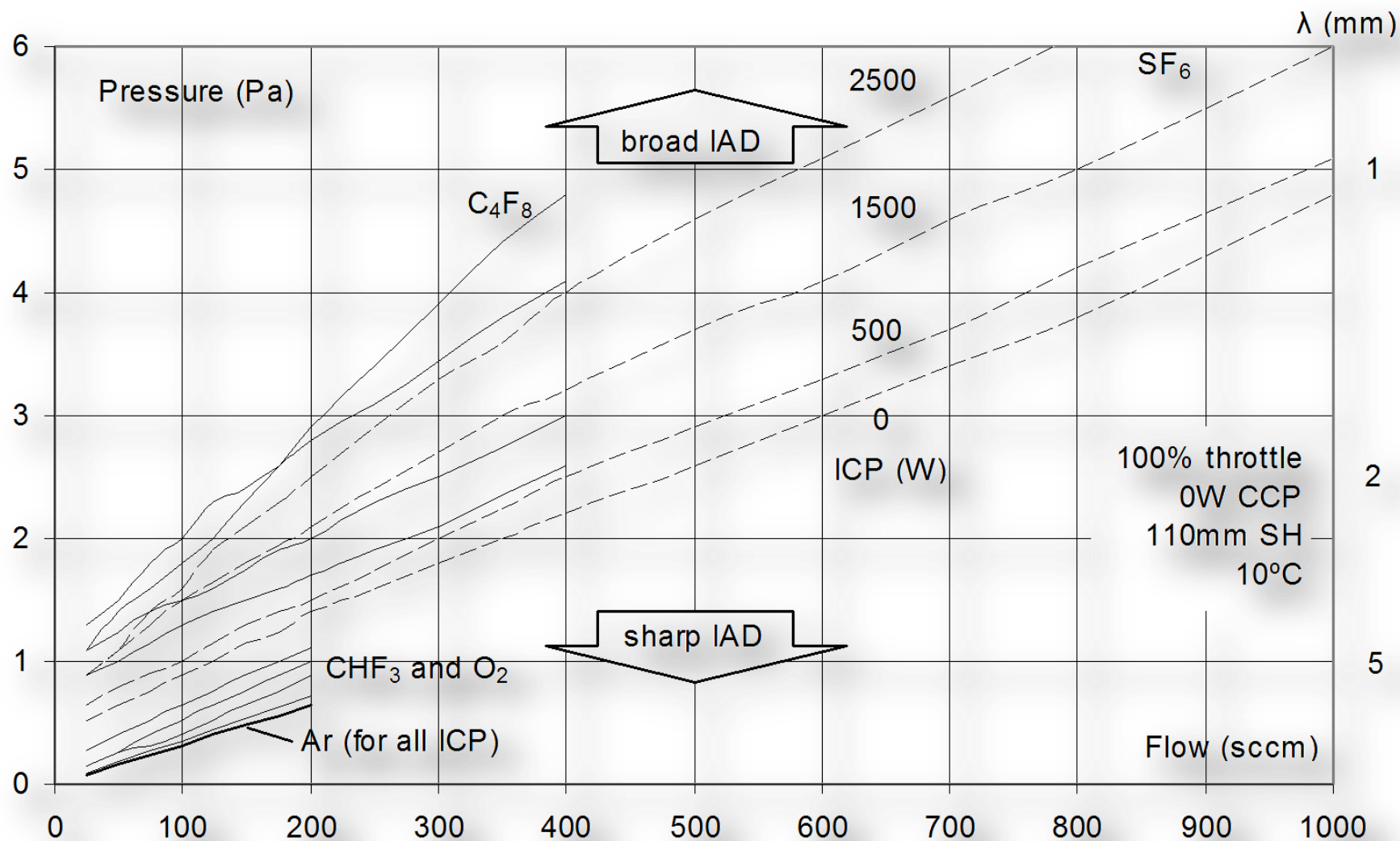
Mass Flow = 1 sccm

= 1 standard cubic cm per minute
= 1 cm³/min at 1 atm and 0 °C (=STP)
= (1 ml/min)* 101 325 Pa
= 101 Pa l/min
= 1.69 Pa l/s

⇒ 400 sccm ~ 700 Pa l/s



Pump curves

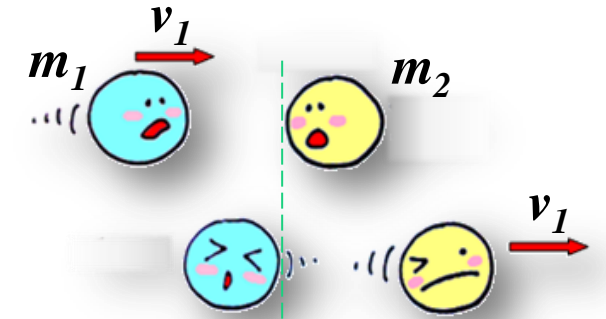
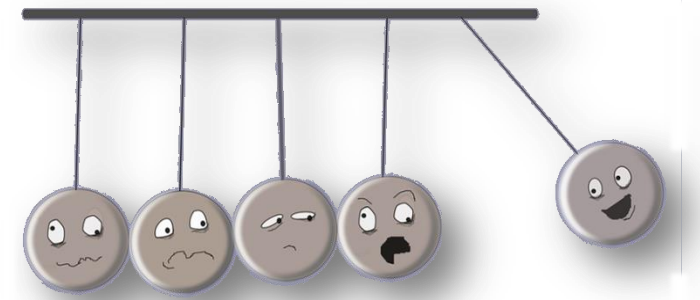


Elastic collisions

By conservation of linear momentum and energy the fractional energy E transferred from mass m_1 to mass m_2 is:

$$E_2/E_1 = \cos^2(\alpha) 4m_1m_2/(m_1 + m_2)^2 \quad [-]$$

When the collision is frontal and $m_1 = m_2$ this expression has its maximum of 1, i.e., the velocity of mass m_2 is v_1 and mass m_1 has lost all its kinetic energy. However, when an energetic electron strikes an SF_6 molecule, then the transfer function becomes just $4m_e/m_{\text{SF}_6}$. So, the function has a value of about 10^{-5} , and very little energy can be transferred from the electron to the molecule.



Inelastic collisions

Now, it is allowed for the collision to be inelastic, so that the molecule struck gains internal energy of ΔU . Then, using the same laws of conservation, we obtain:

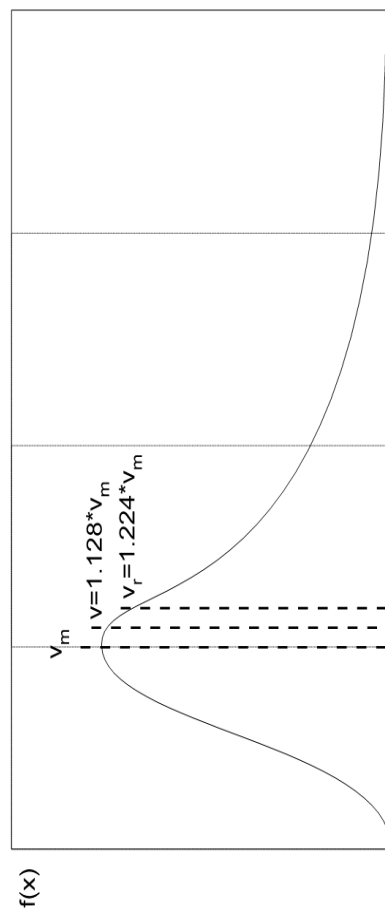
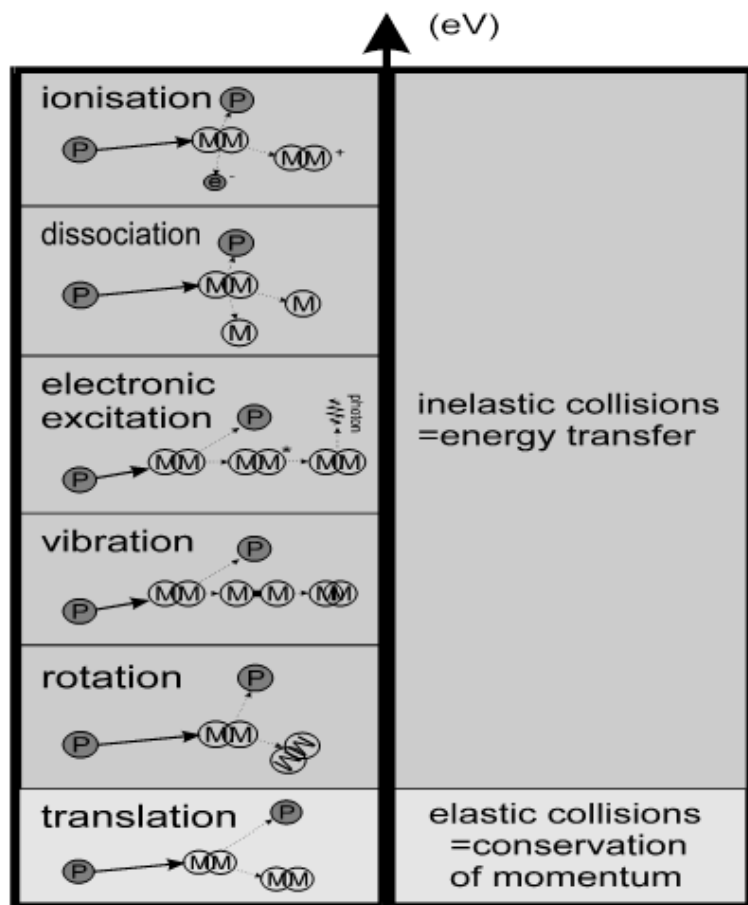
$$\Delta U / E_1 = \cos^2(\alpha) m_2 / (m_1 + m_2) \quad [-]$$



So, whereas the maximum elastic energy transfer from an electron to an SF_6 molecule was close to 0%, by inelastic means this may rise to near 100%.

Consequently, electrons driven by the RF generator will lose their kinetic energy mostly by the inelastic collisions (e.g. ionisation) and will only slightly raise the gas temperature. This is why they are frequently referred to as cold plasmas.

Excited state levels caused by particle collisions



Direct ionisation \rightarrow $\text{CF}_4 + e^- \rightarrow \text{CF}_4^+ + 2e^-$ \rightarrow \rightarrow [15.5eV]

Dissociation \rightarrow $\text{CF}_4 + e^- \rightarrow \text{CF}_3 + \text{F} + e^-$ \rightarrow \rightarrow [12.5eV]

Excitation \rightarrow $\text{CF}_4 + e^- \rightarrow \text{CF}_4^* + e^-$ \rightarrow \rightarrow [04.0eV]

Plasma-to-floating potential

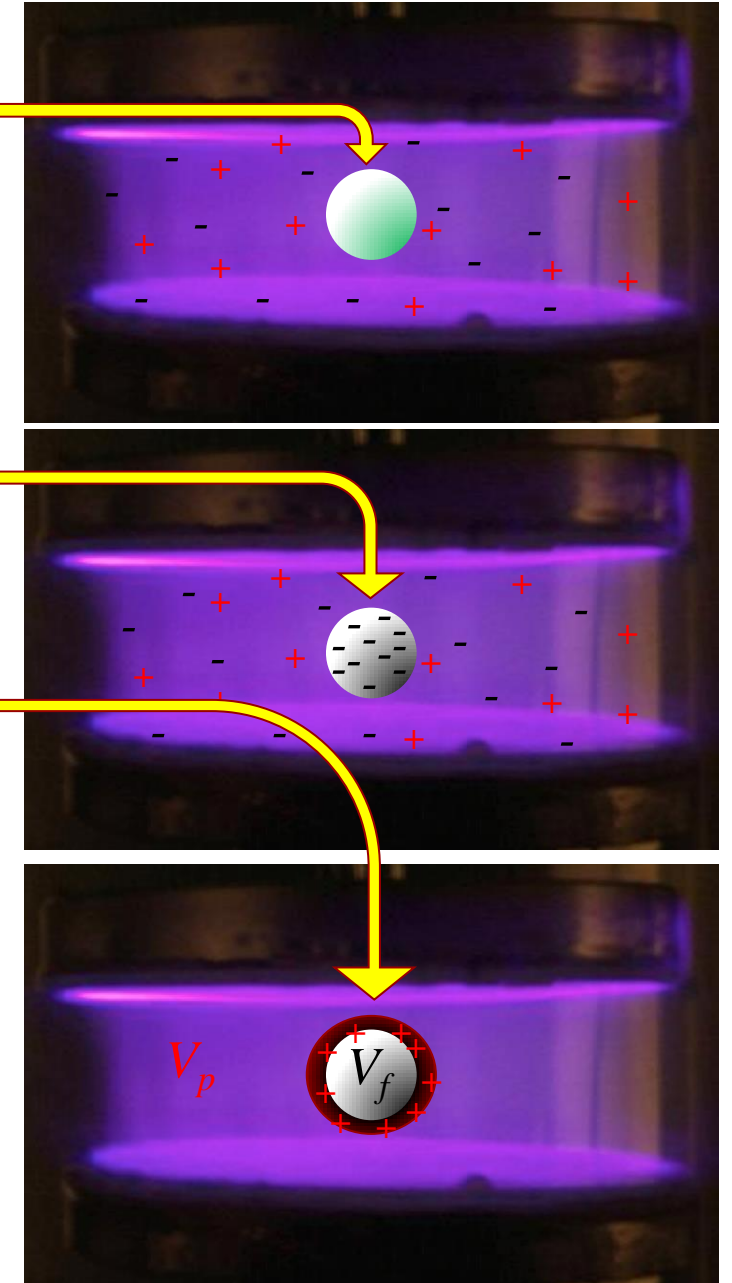
Consider an object that is emerged into a plasma. Initially much more electrons will flow into the object because electrons – driven by the RF source - move much faster than the heavier ions by at least a factor of $\sqrt{m_i/m_e}$. The object will therefore be charged negative relative to the bulk plasma.

Subsequently, positive ions will be forced to the negative object and surround it until it balances the negatively charged object: the so-called Debye shield.

Now, the plasma body is virtually electric field free (equipotential): the so-called plasma potential V_p .

Similarly, we can associate a floating potential V_f with the isolated object which is always negative with respect to V_p .

Since electrons are repelled by $V_f - V_p$, the electron density is low in the sheath and therefore doesn't glow as much: the dark space.



Plasma-to-floating potential: some algebracadabra

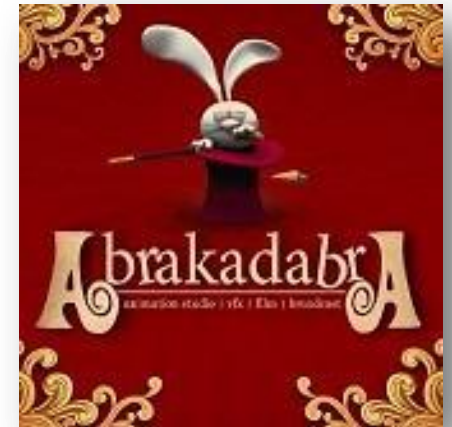
Let us now try to estimate the magnitude of $V_f - V_p$. To surmount this barrier, an electron needs $q(V_f - V_p)$ of potential energy. Hence, only electrons that enter the sheath from the plasma with kinetic energies in excess of $q(V_f - V_p)$ will reach the object. The M-B distribution function gives us the fraction that can do this:

$$V_f - V_p = \frac{kT_e}{2q} \ln \left(\frac{m_e T_i}{m_i T_e} \right) \quad [\text{V}]$$

In case of an SF_5 ion, the ion mass M_i is $127 \cdot 1836$ times the electron mass M_e and we get:

$$V_f - V_p \sim -5.2 \cdot kT_e / q$$

Thus, the ions that reach the surface will have an energy equal to what they have in the plasma plus what they have gained in passing through the pre-sheath and sheath, $(5.2 + 0.5)kT_e \sim 6kT_e$.



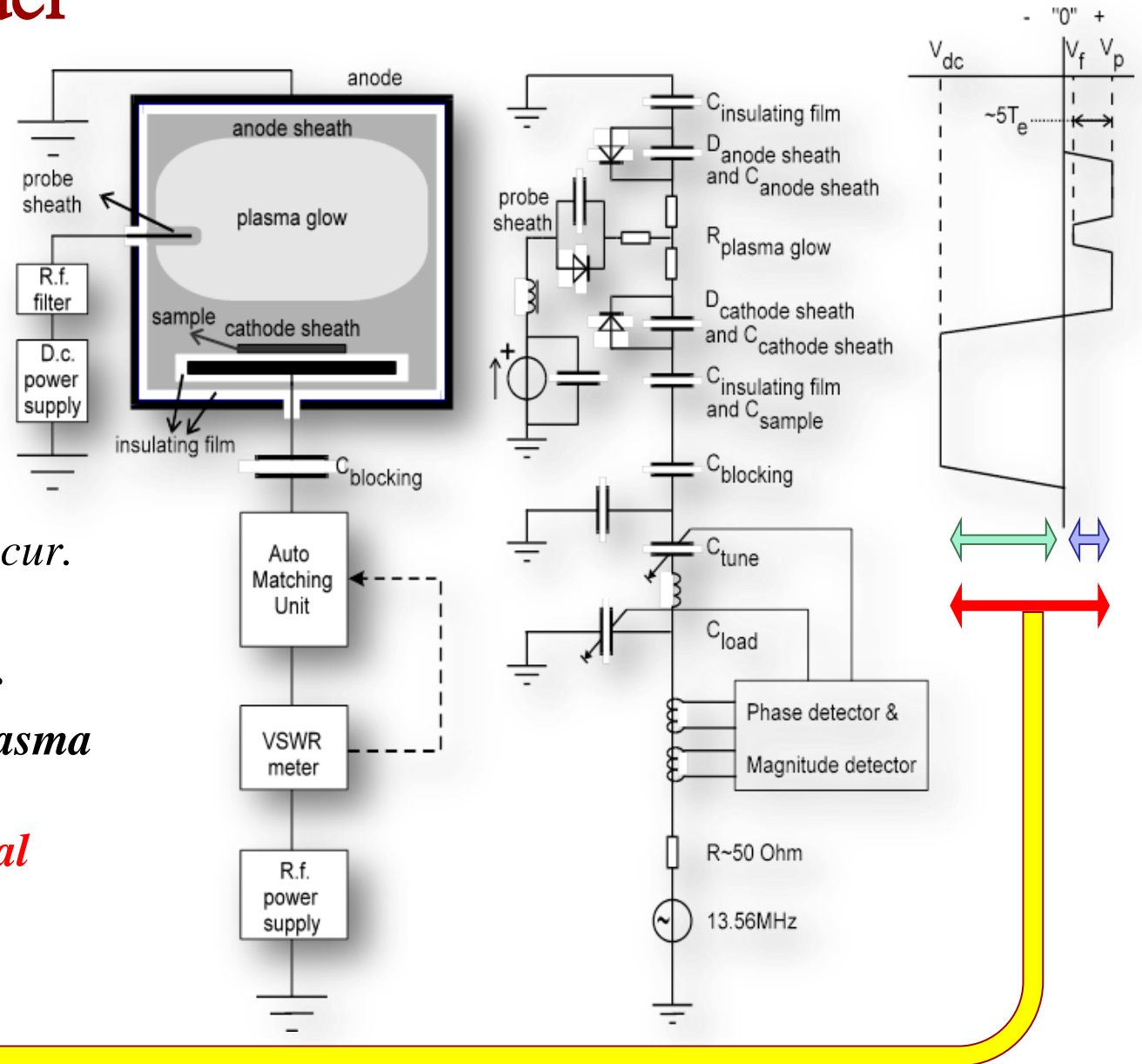
This means that ions will hit surfaces in a plasma environment severely - even when they are only floating - due to their acceleration in the plasma pre-sheath and sheath. In case of a typical electron temperature of $kT_e \sim 2\text{eV}$, the ion energy is already 12eV , which is enough to break most chemical bonds.

Electrical circuit model

The V_{dc} is caused by the difference in capacitance between the anode-plasma and cathode-plasma dark spaces.

If these areas are the same, no V_{dc} will occur.

This does not mean that there is no ionic impact as we just found out that the plasma potential can still be large enough to enhance surface reactions. **It is the total ($V_{dc} + V_p$) that depicts the impact!**

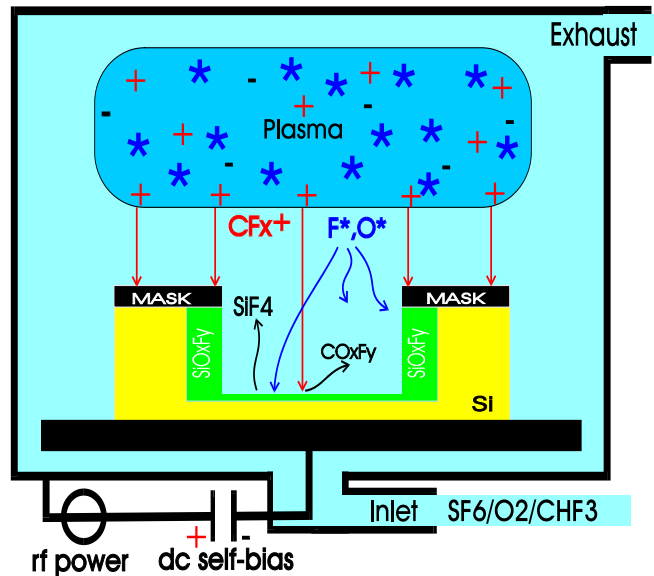


What is plasma etching

What is plasma etching

*The basis of plasma-assisted etching is simple; use a **gas glow discharge** to crack relatively stable molecules **forming chemically reactive and ionic species** and choose the chemistry such that these species **react with the solid to be etched to form volatile products**.*

Generation: *An rf power source is used to generate from a suitable feed gas (e.g. SF_6 for Si etching) by electron-impact dissociation/ionisation the gas phase etching environment which consists of neutrals, electrons, photons, radicals (F), and positive (SF_5^+) and negative (F^-) ions.*



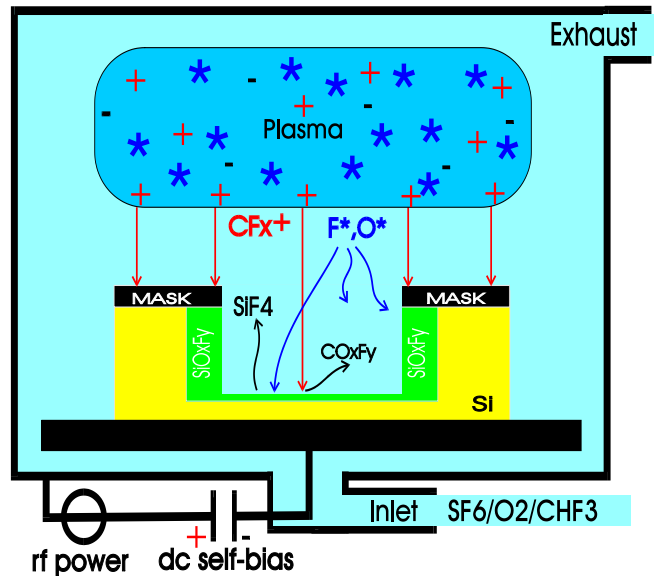
Dc bias formation: *The Si wafer is placed on an rf driven capacitively coupled electrode. Since the electron mobility is much greater than the ion mobility, after ignition of the plasma the electrode acquires a negative charge i.e. the dc self-bias voltage V_{dc} .*

Diffusion/forced convection: *The transport of reactive intermediates from the bulk of the plasma to the Si surface occurs by diffusion. Positive ions from the glow region are forced to the substrate surface by way of the V_{dc} and will assist the etching. At higher pressure, the ion path is interrupted by many collisions causing non-directional etching.*

What is plasma etching

Adsorption: Reactive radicals adsorb on the Si surface. This step can be strongly enhanced by concurrent ion bombardment which serves to produce “active sites” since it aids in the removal of e.g. an SiO_xF_y layer which otherwise passivates the Si surface.

Reaction: A reaction between the adsorbed species and the Si must take place. In the case of fluorine-based etching of Si, chemical reactions between the F-atoms and the surface produces - spontaneously- either volatile species, SiF_4 , or their precursors, SiF_x ($x < 4$).



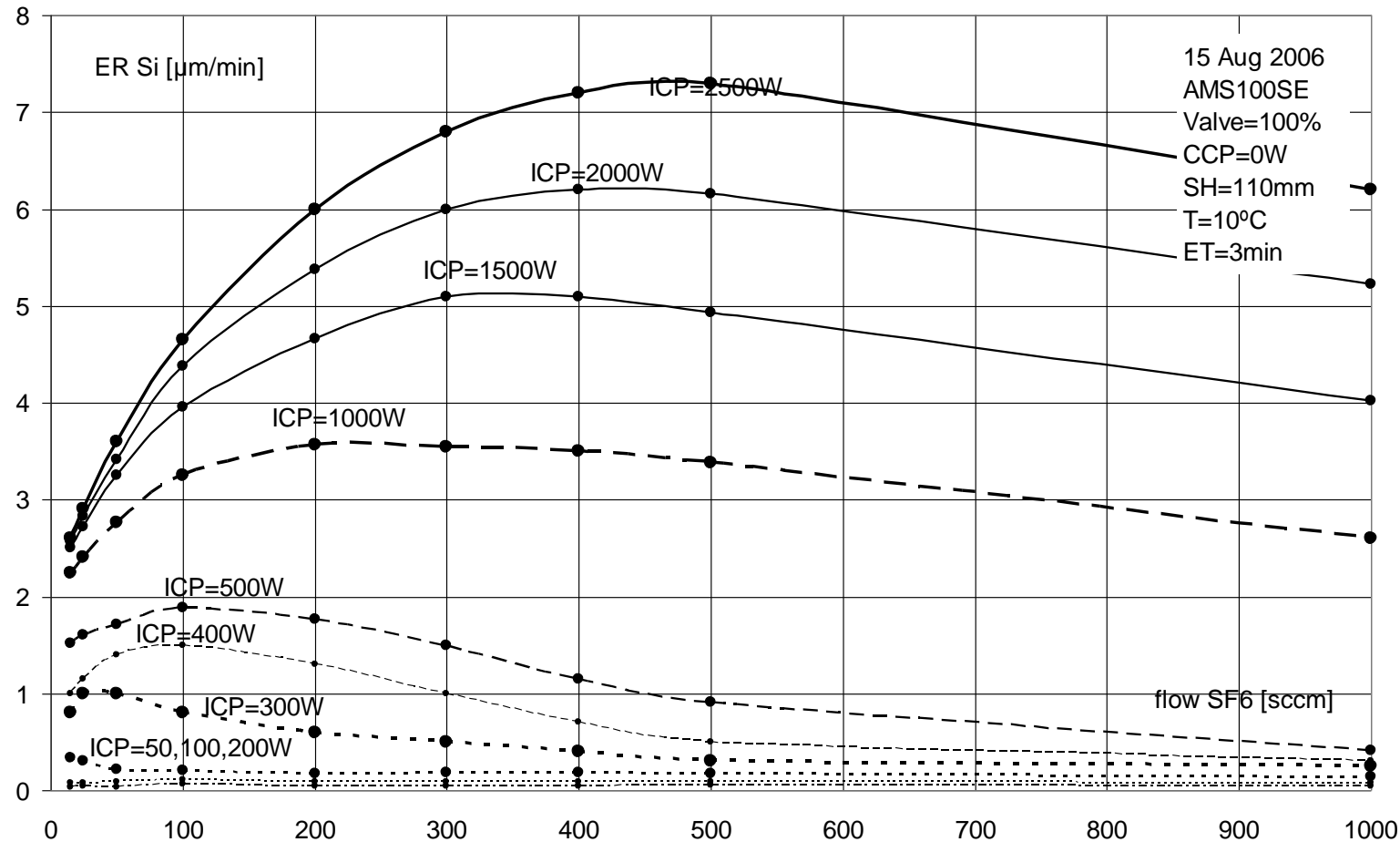
Desorption: The desorption of the reaction product into the gas phase requires that the reaction product is volatile, thus it should have a high vapour pressure at the substrate temperature. Additionally, there should be no deposited blocking film at the surface. The removal of these films can be greatly accelerated by ion bombardment via sputtering. This mechanism is known as ion-inhibitor DRIE.

Exhaust: The desorbed species diffuse from the etching surface into the bulk of the plasma and should be pumped out, otherwise plasma induced dissociation of product molecules will occur and redeposition can take place.

3 steps to find directional plasma etching recipes

1. The spontaneous etch rate of bare silicon wafers is determined for the whole spectrum of SF_6 flow and ICP power ("Spontaneous" means here the lack of any inhibiting layer which would slow down the etch rate).
 2. Oxygen -or another inhibitor- is added to inhibit etching until practically no etching is observed (say less than 5% of the spontaneous etch rate).
 3. The CCP power is increased to achieve ion-controlled directional etching until the requested etch rate is achieved.
- Finally, the wafer with the application specific resist pattern is etched with the arrived recipe and fine tuning starts.

1. Find and choose spontaneous etch rate



Maximum etch rate for 500W/100sccm = 5W/sccm

1. Find and choose spontaneous etch rate

- STP: 1 mol SF₆ gas = 22 414 cm³
- 100 sccm SF₆ = 100 cm³ SF₆/min STP
- = (100/22414) mol SF₆/min = 4.46 mmol SF₆/min

In plasma assume: SF₆ ⇒ SF₅ + F

At wafer surface: Si + 4F ⇒ SiF₄

Total: 4SF₆ + Si ⇒ 4SF₅ + SiF₄

So, 4 SF₆ molecules will remove 1 Si atom

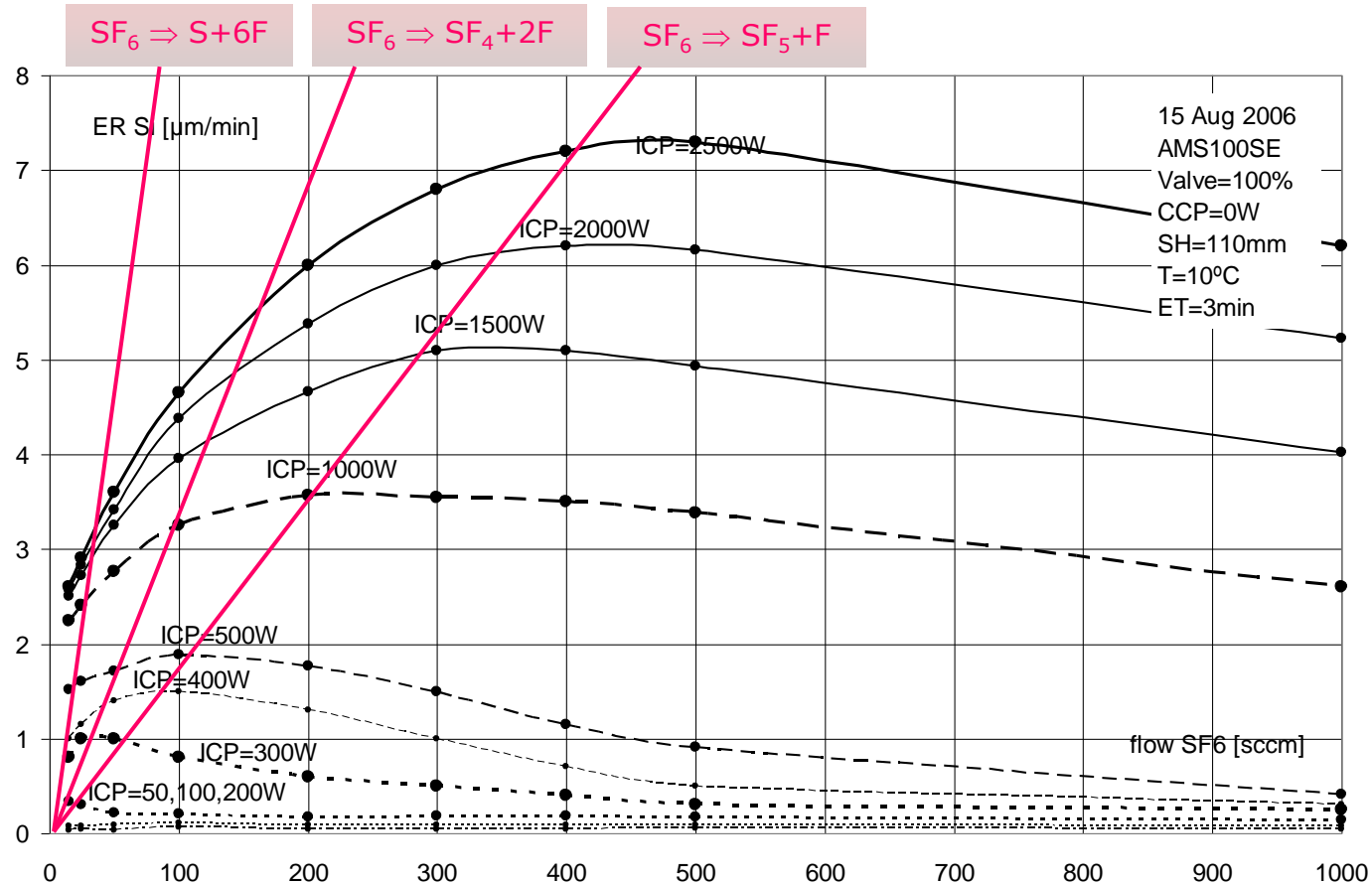
- 4 SF₆ molecules will remove 1 Si atom

- 100 sccm SF₆ etches 1/4 * 4.46 mmol Si/min
- = 1/4 * 4.46 * 28.1 mg Si/min = 31.36 mg Si/min
- 1 mg Si = 60nm Si (100mm wafer minus clamping)

1 mol Si = 28.1 gram

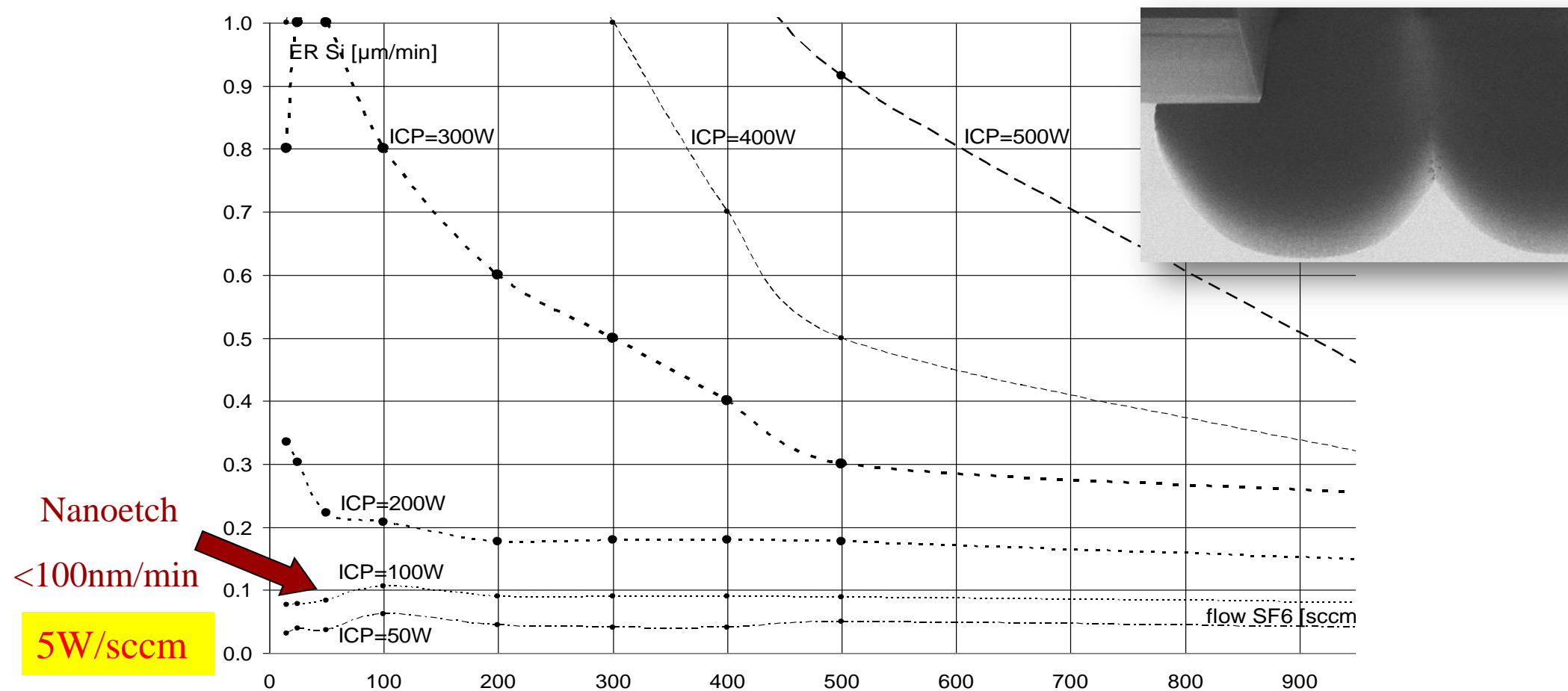
100 sccm SF₆ etches a full silicon wafer at 60*31.36 = 1882 ≈ 1900 nm/min

1. Find and choose spontaneous etch rate

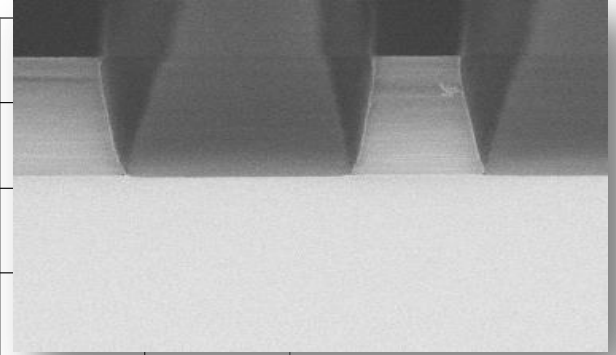
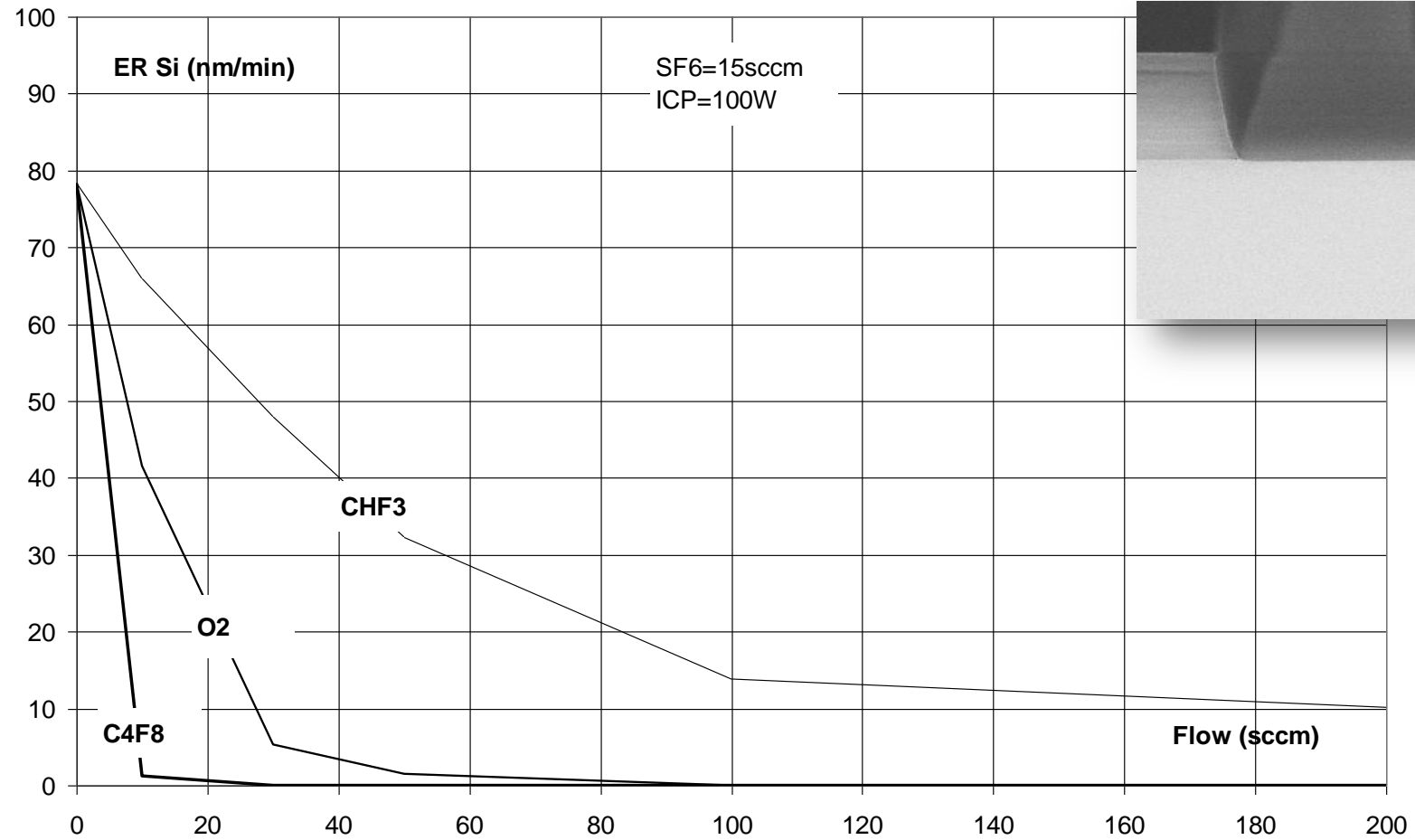


So indeed 100 sccm SF_6 etches silicon at 1900 nm/min

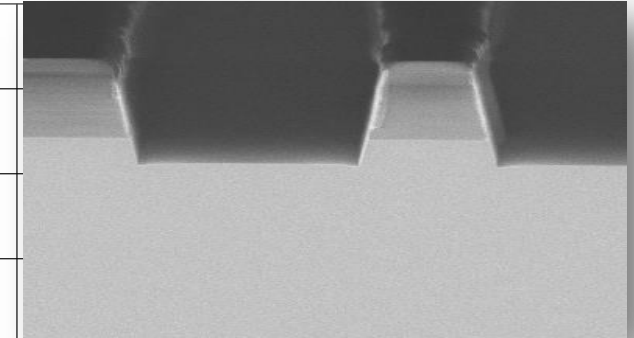
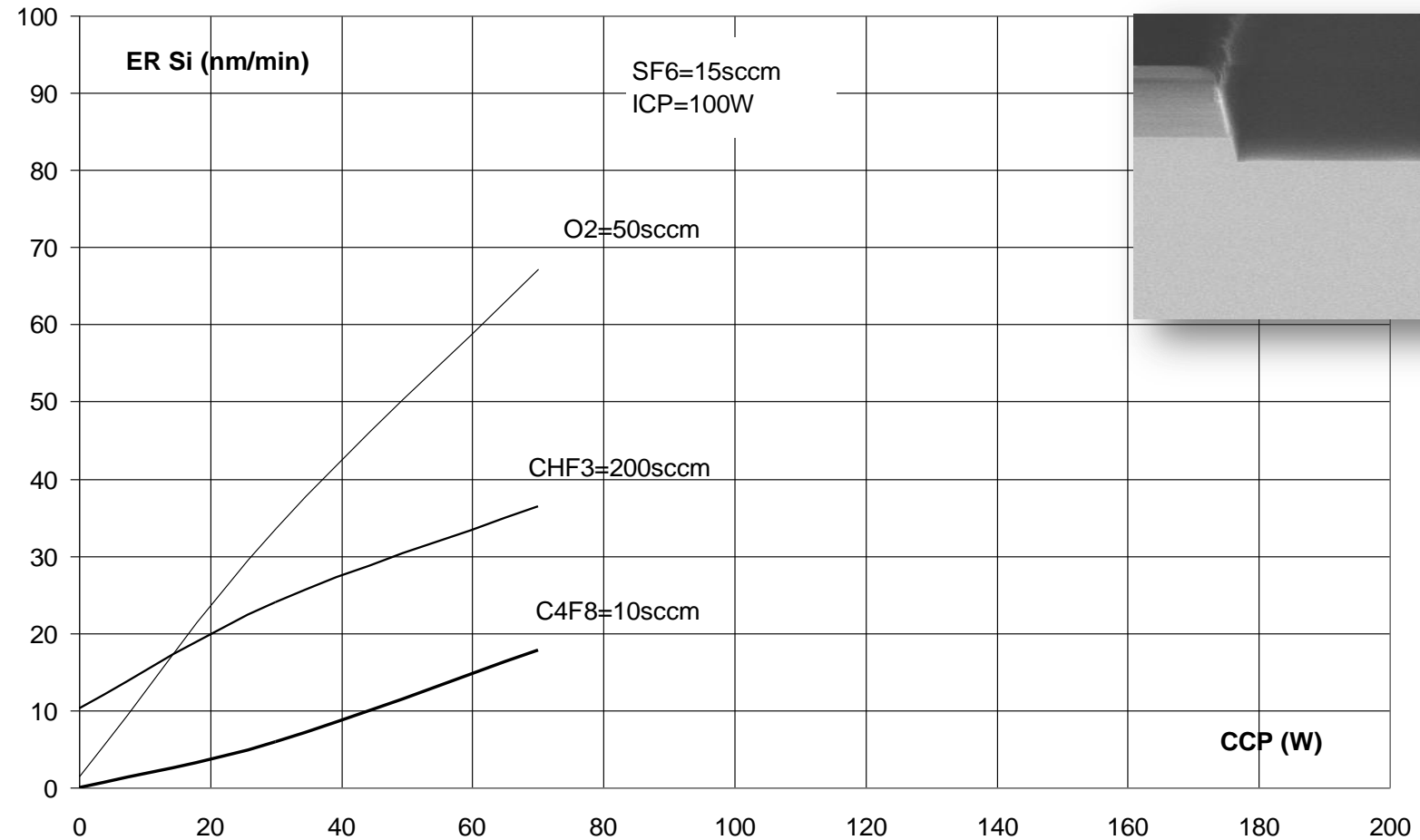
1. Find and choose spontaneous etch rate



2. Inhibit the etch using O_2 or CF_x species

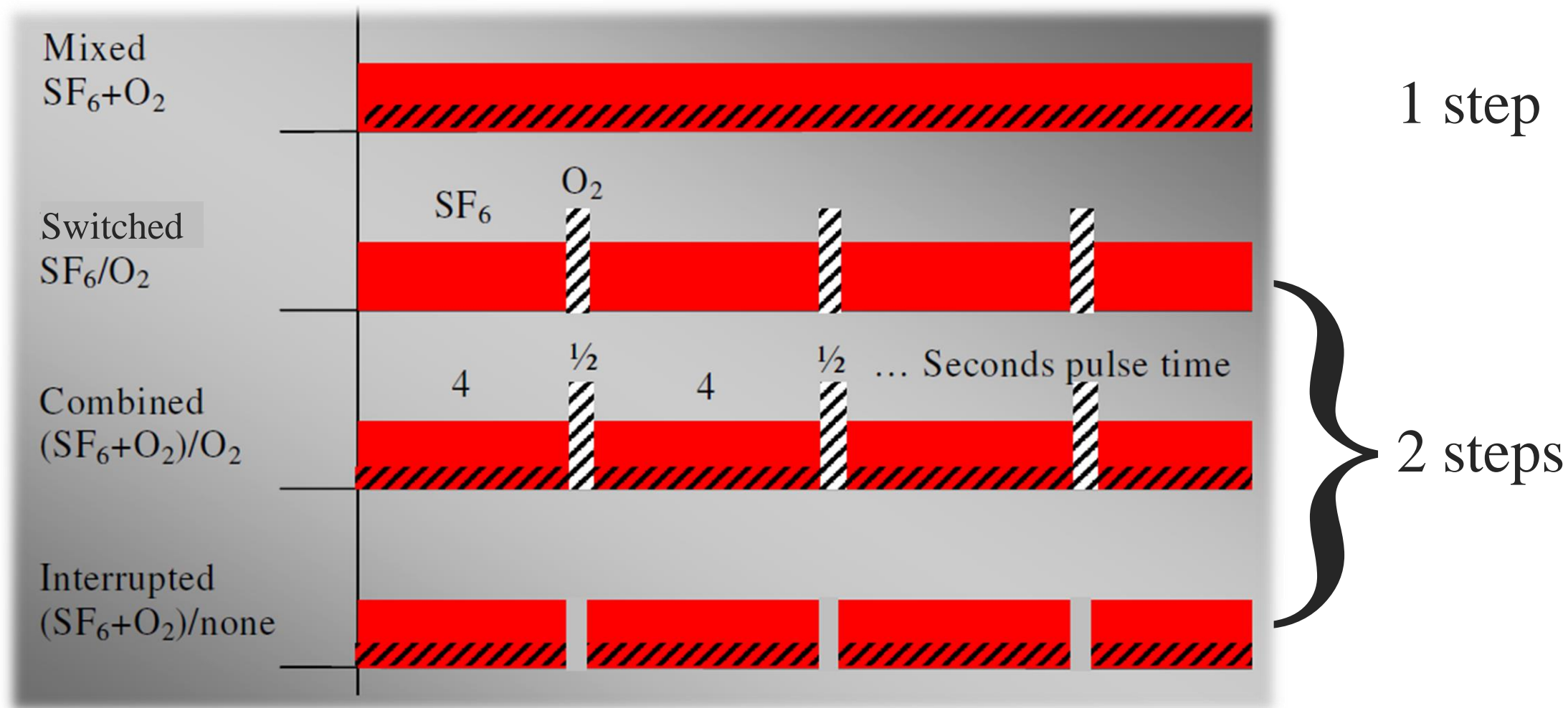


3. Increase bias for directional etch



1–, 2– and 3–steps procedures

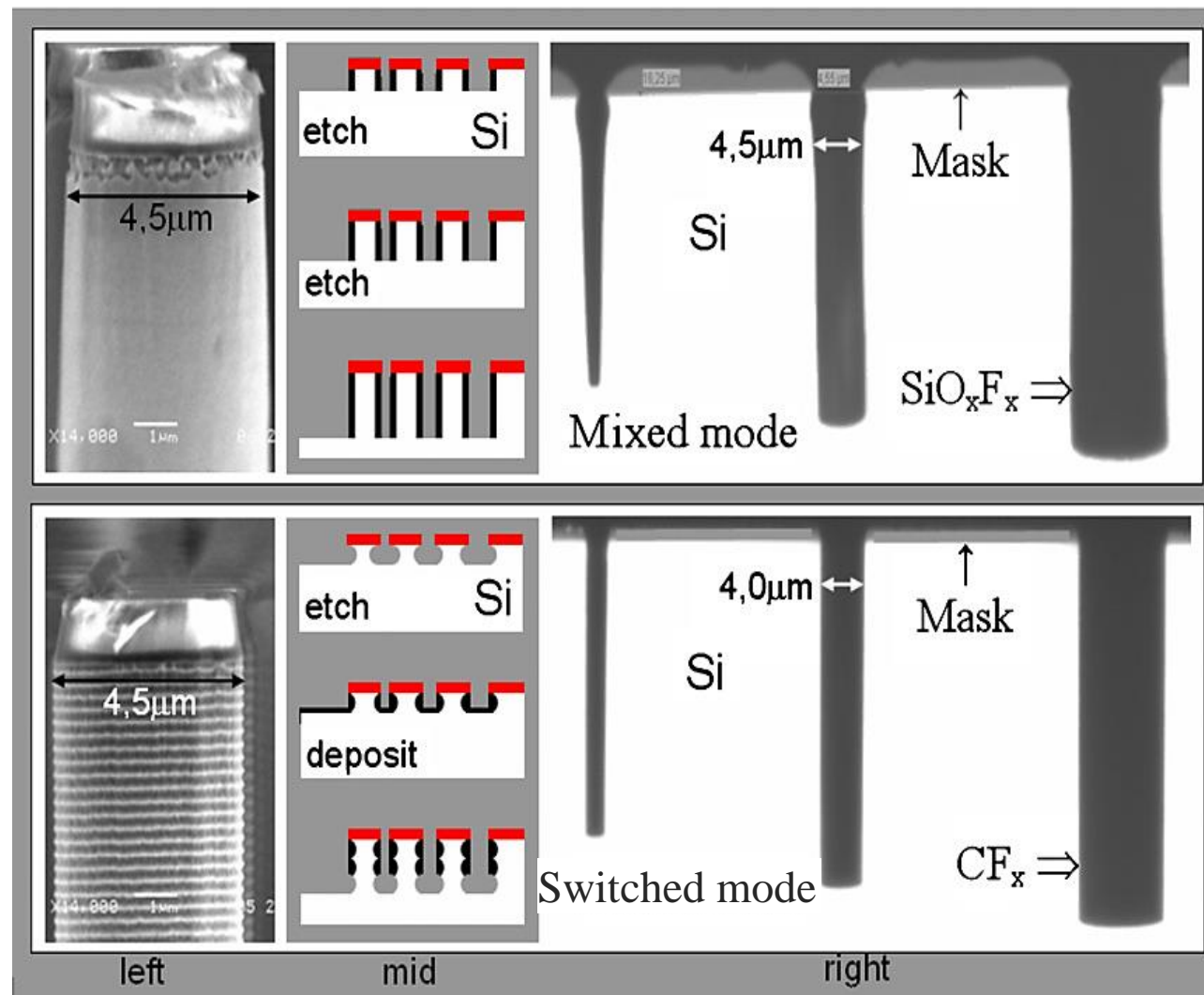
Definition of (D)RIE modes



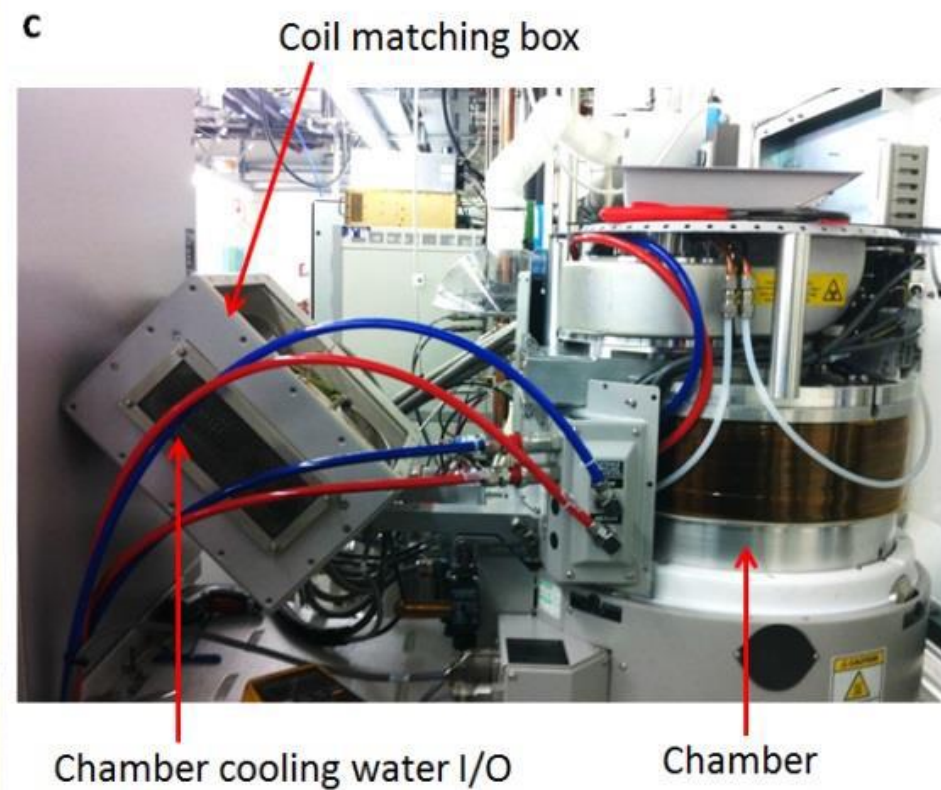
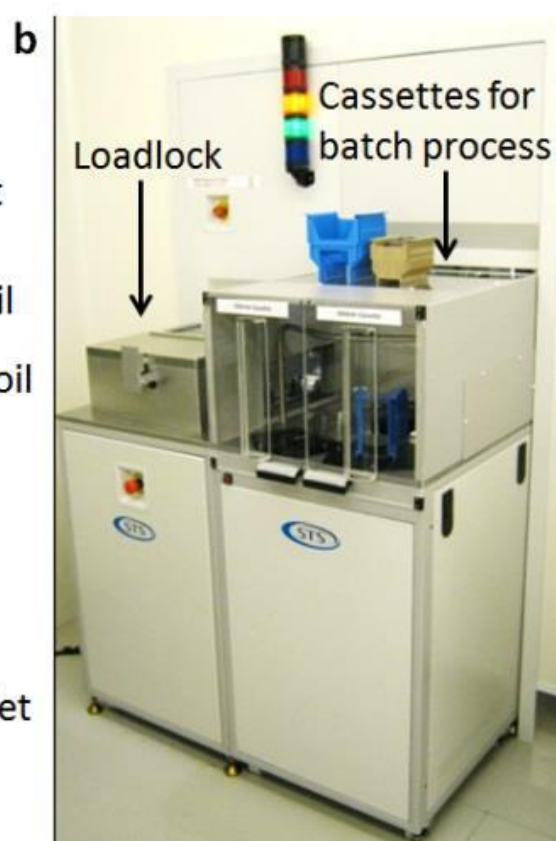
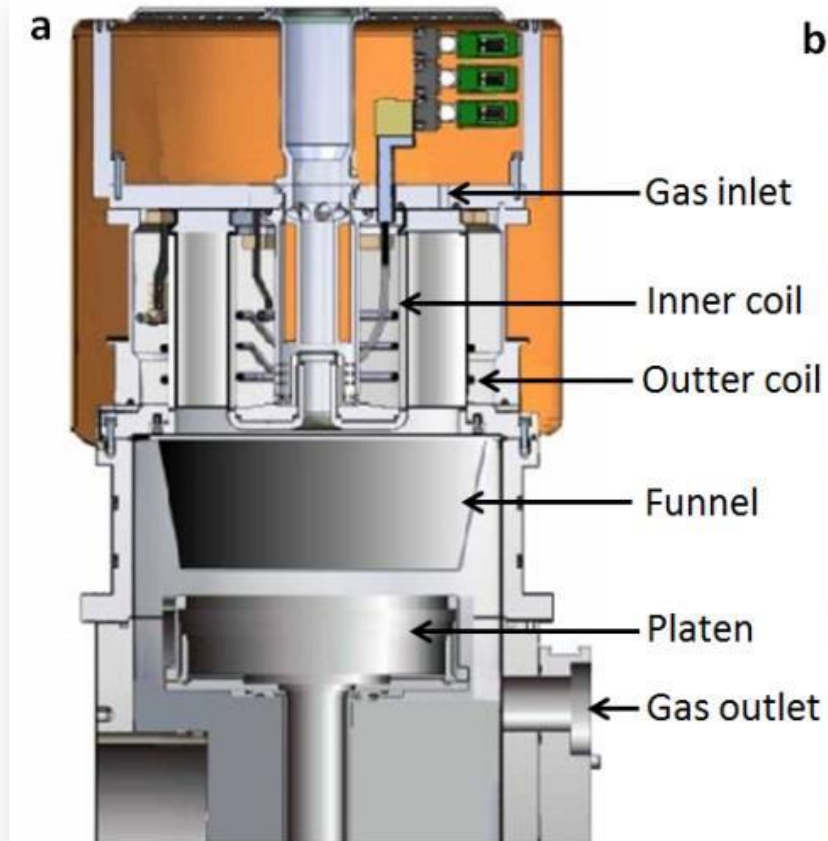
DRIE techniques for Si etch using SF_6 -based plasma

	O-inhibitor	FC-inhibitor
Mixed	Cryogenic	Nano1.42
Switched	CORE	Bosch DREM

Either oxygen or fluorocarbon-based and either mixed or switched mode



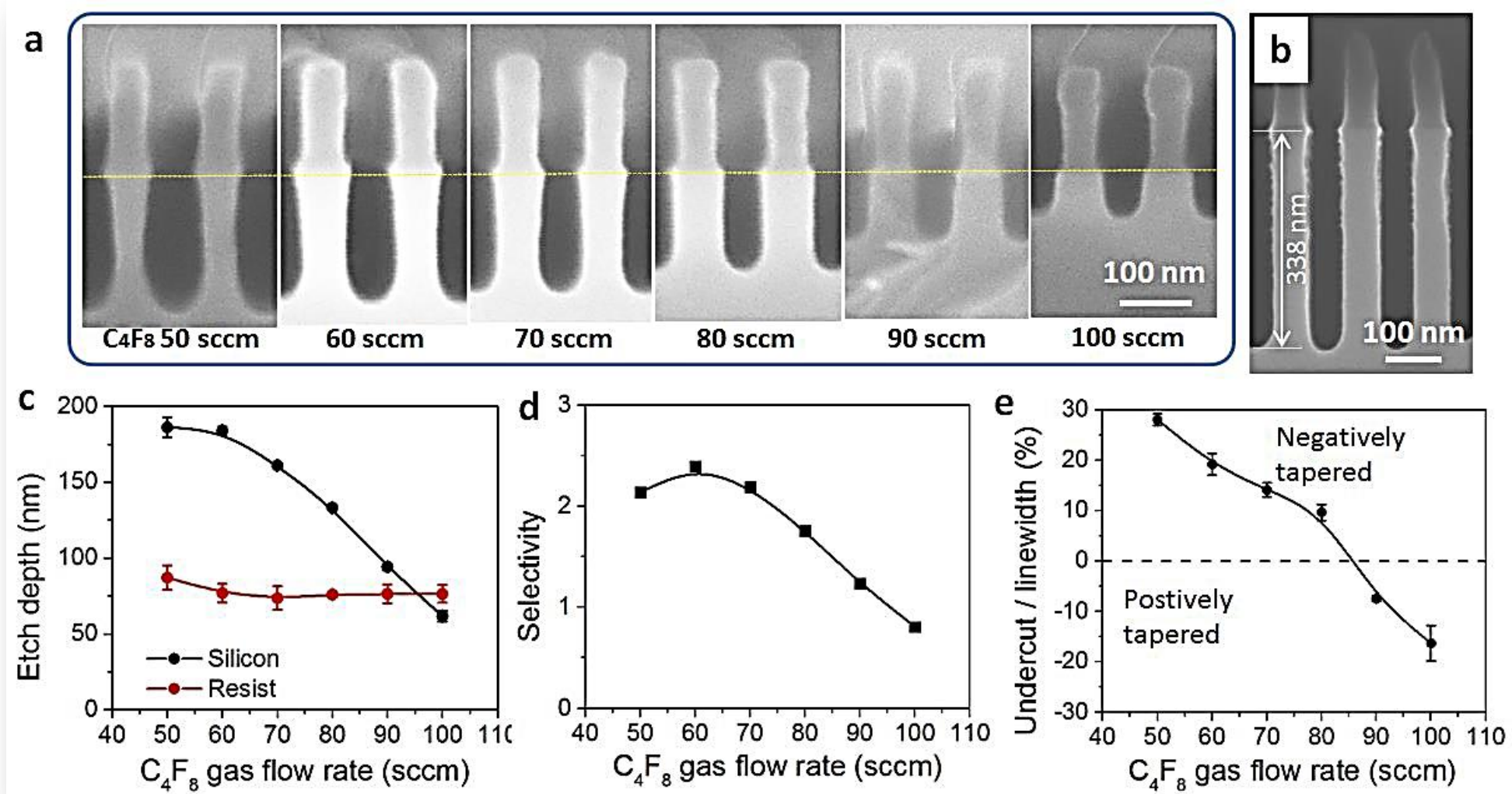
DRIE Tool: SPTS Pegasus












Mixed mode

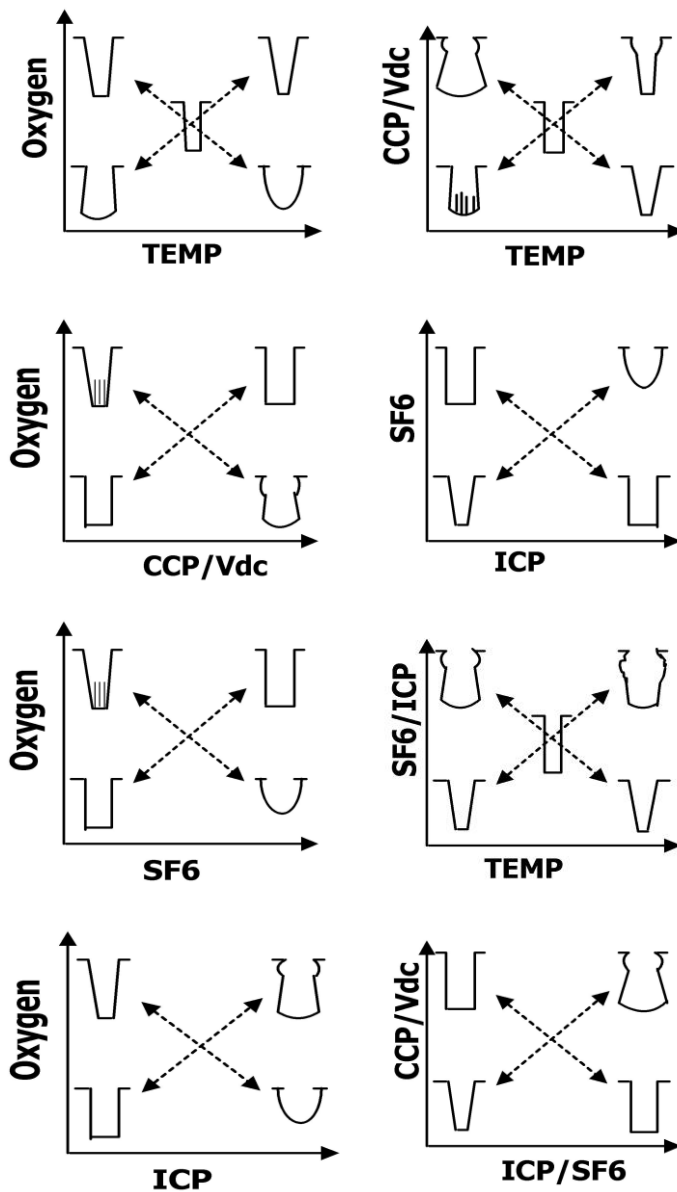
1 step

Mixed FC

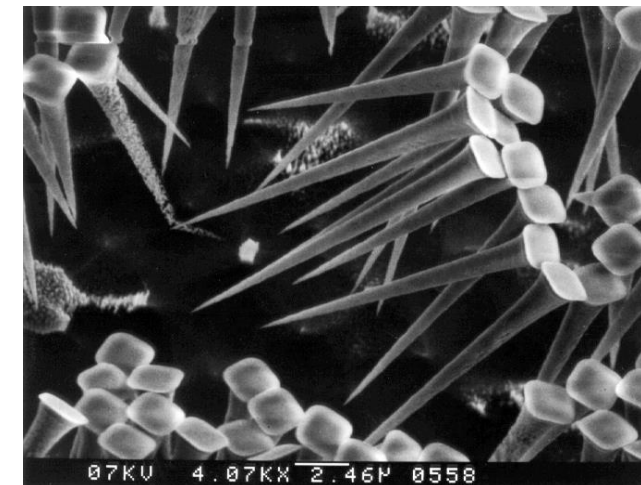
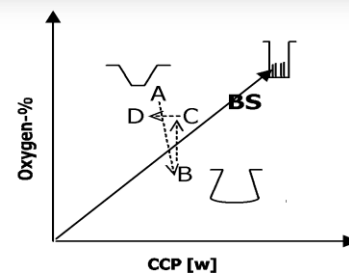
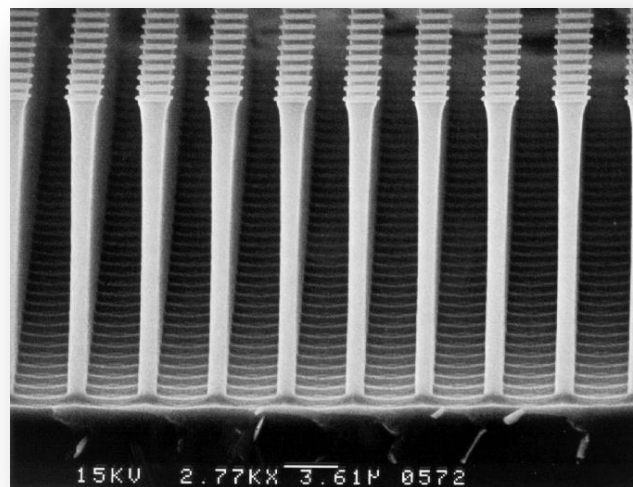
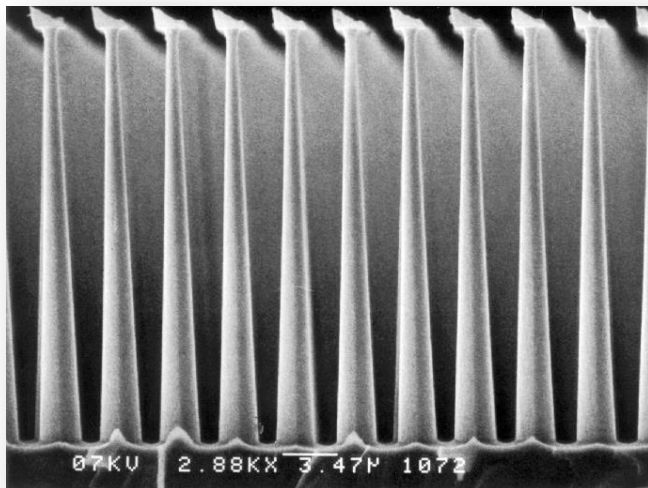


Mixed O₂: Diagrams for Profile Control

ofile/ Parameter range	 isotropic	 extr. neg	 neg. bottling	 neg. taper	 neg. + BS	 directional	 pos. bottling	 pos. taper	 pos. + BS
O2[sccm] 0-12	0	2-4	5	6		8-10		11	12
CCP[Watts] 0-32	-	-	24-32	8-24	4	2		1	0
SF6[sccm] 50-150	-	-	-	150		100		125	50-75
Electr.[°C] -80-150	-	-	-	150-140		130-120	90-80	100-110	
ICP[Watts] 750– 2000	-	-	2000-1750	1750-1050		1050-750			
He[Torr] 1.5–9.8	-	-	-	10		6.0	1.5		
P[mTorr] 7,8,9	-	-	-	-		7-8	9		
Clamp.[Bar] 0.5 – 3.0	-	-	-	-	3	1.5-0.5			
Time[min] 5- 25	-	-	-	-	-	5-25	-	-	-












Mixed O₂: Needle etching



Parameters	Recipe A	Recipe B	Recipe C	Recipe D
Pressure (mTorr)	10	10	10	10
SF ₆ (sccm)	90	90	90	90
O ₂ (sccm)	10	3	7	7
ICP (Watts)	600	600	600	600
CCP (Watts)/Vdc (Volts)	2.5/-10	3/-14	3/-14	2.5/-10
Electrode temp. (°C)	-130	-130	-130	-130
Height (µm) /time (min)	2/10	20/10	29/15	25/15
Profile sidewall	positive	negative	positive	positive

Mixed O₂: Hole etching

Exp. #	1	2	3	4	5	6	7	8	9
T [°C]	0	0	0	-40	-40	-80	-80	-120	-120
CCP LF [W]	20	20	20	20	20	20	20	20	20
CCP On-Off [ms]	10-90	10-90	20-80	20-80	20-80	20-80	20-80	20-80	20-80
CHF ₃ time [sec]	½	1	1	1	1	1	1	1	½
Etch Time [min]	3	3	3	3	15	15	20	20	15
Etch profile of a micro hole									
Etch Depth [µm]	21	22	24	26	74	76	90	58	95

Switched FC mode

2- and 3-steps

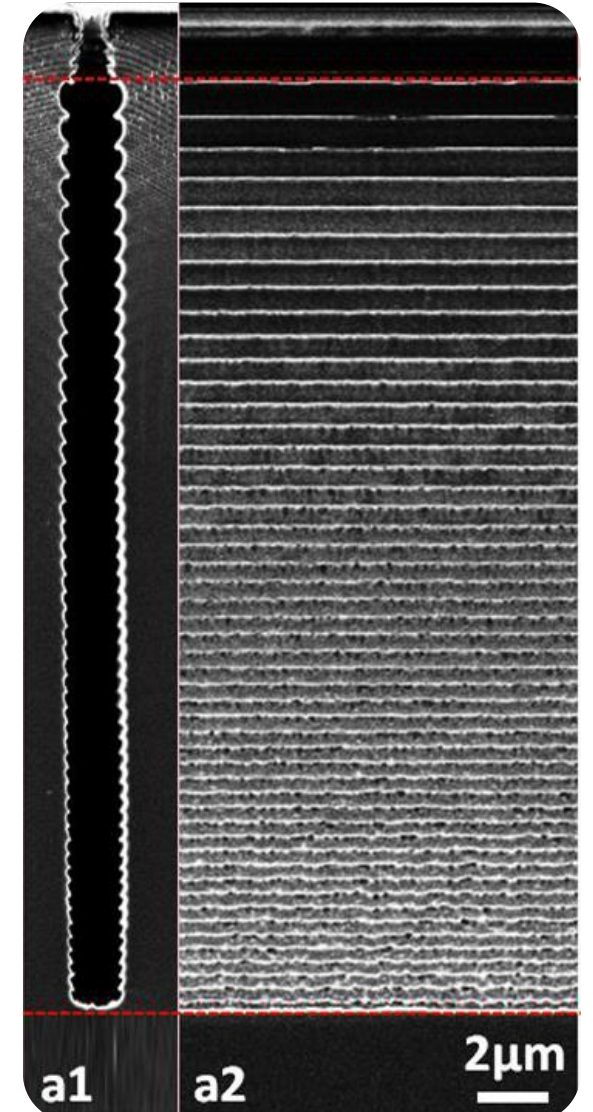
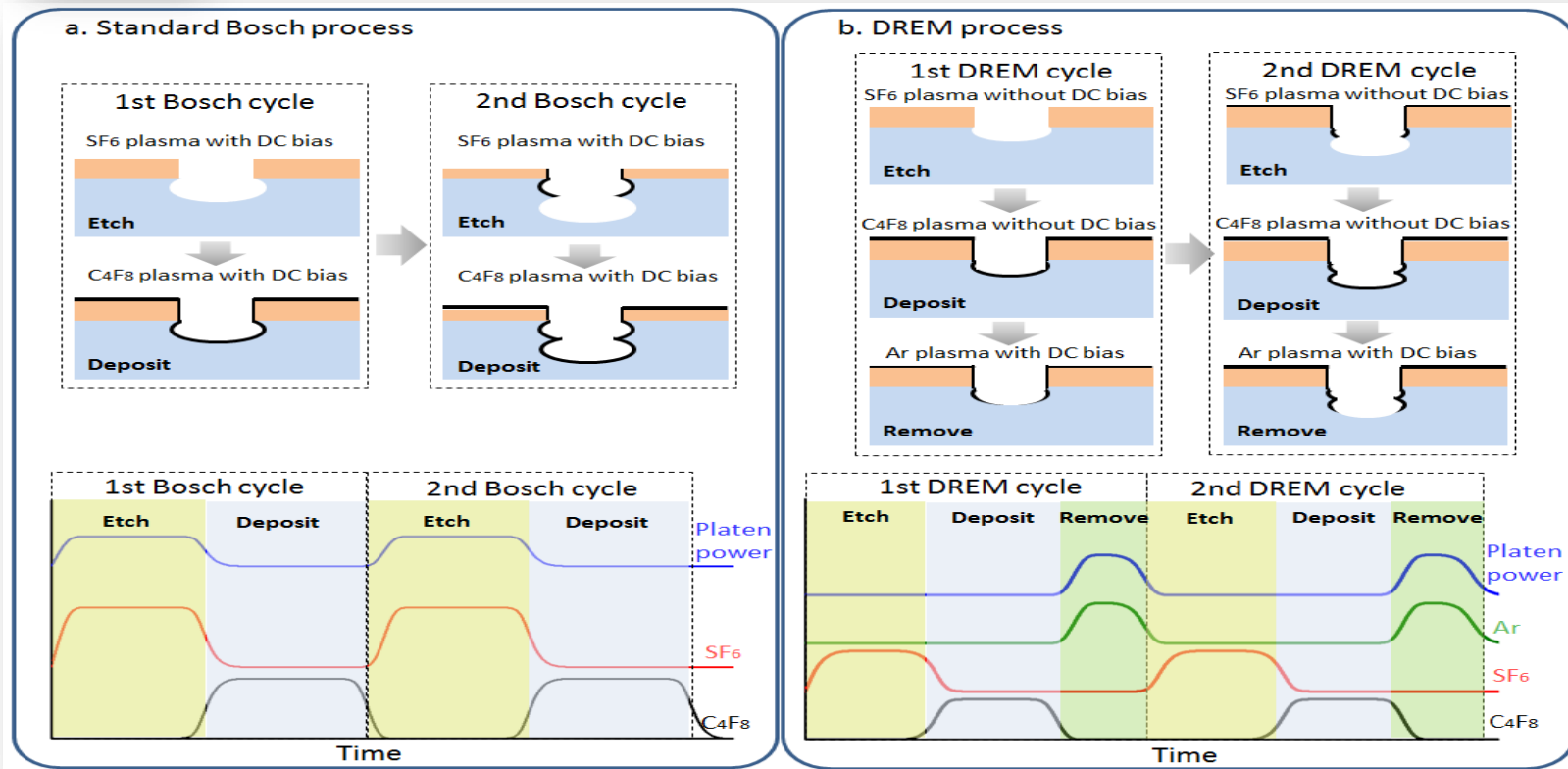
Switched FC: 2-steps versus 3-steps



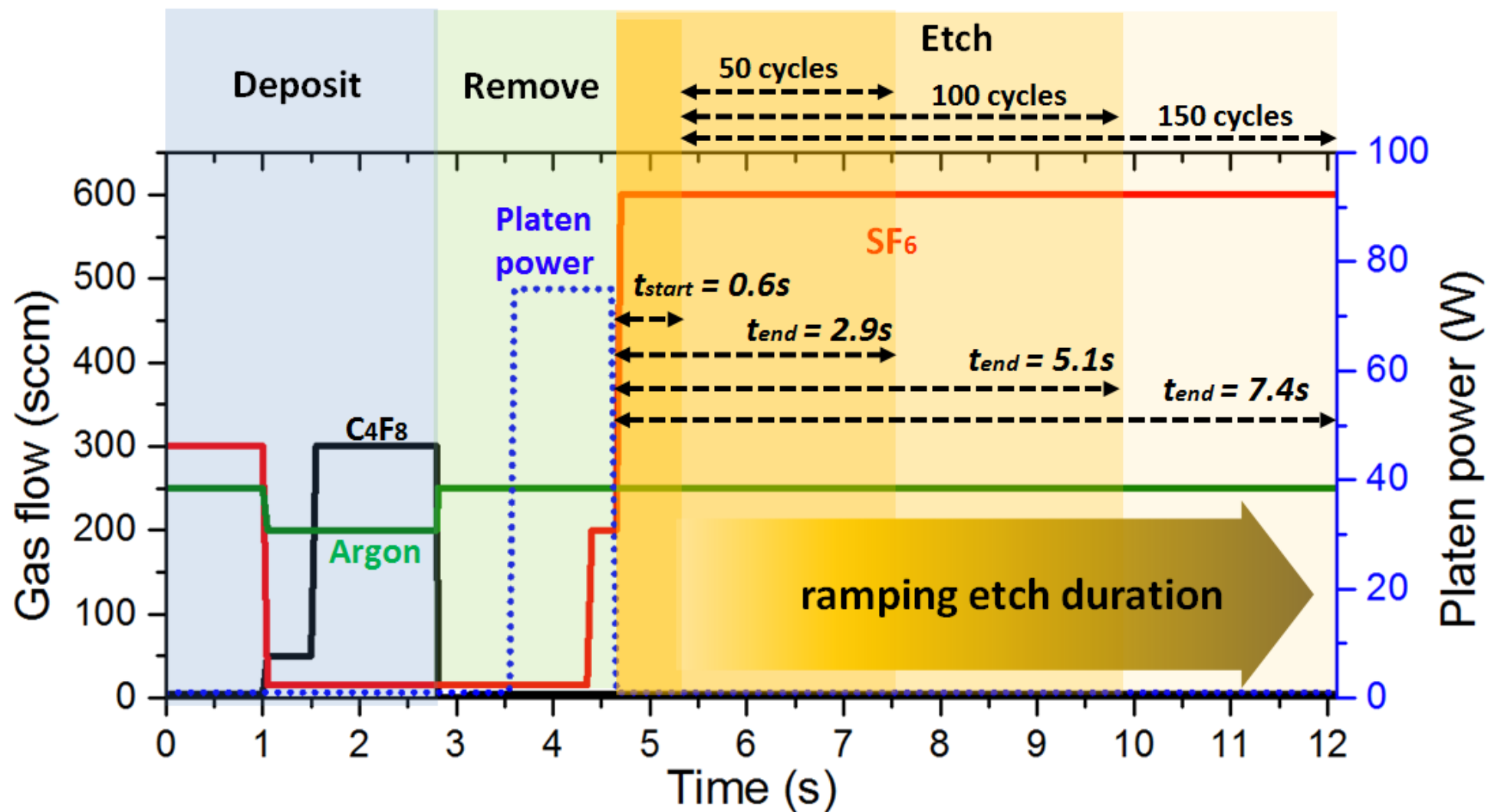
DREM process (Deposit, Remove, Etch, Multistep)

To improve process controllability and mask selectivity.

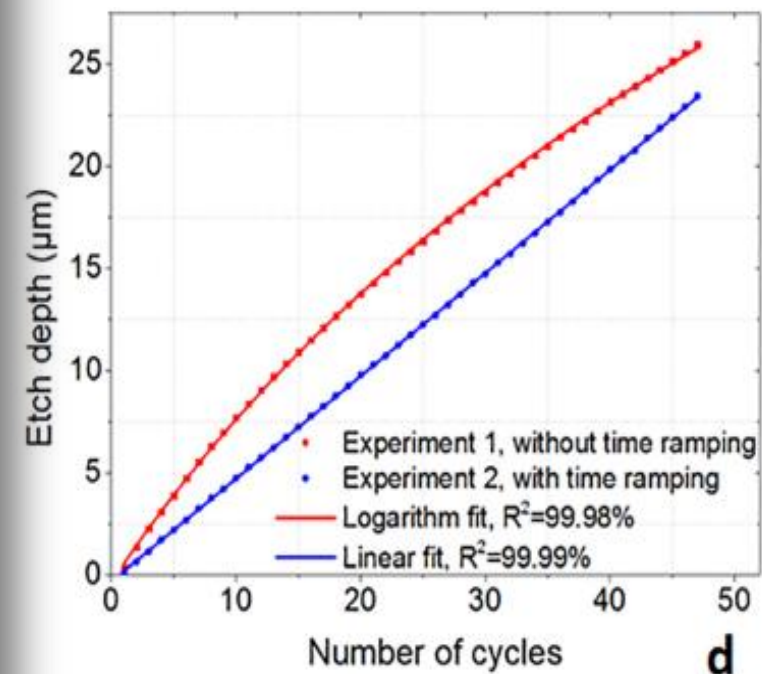
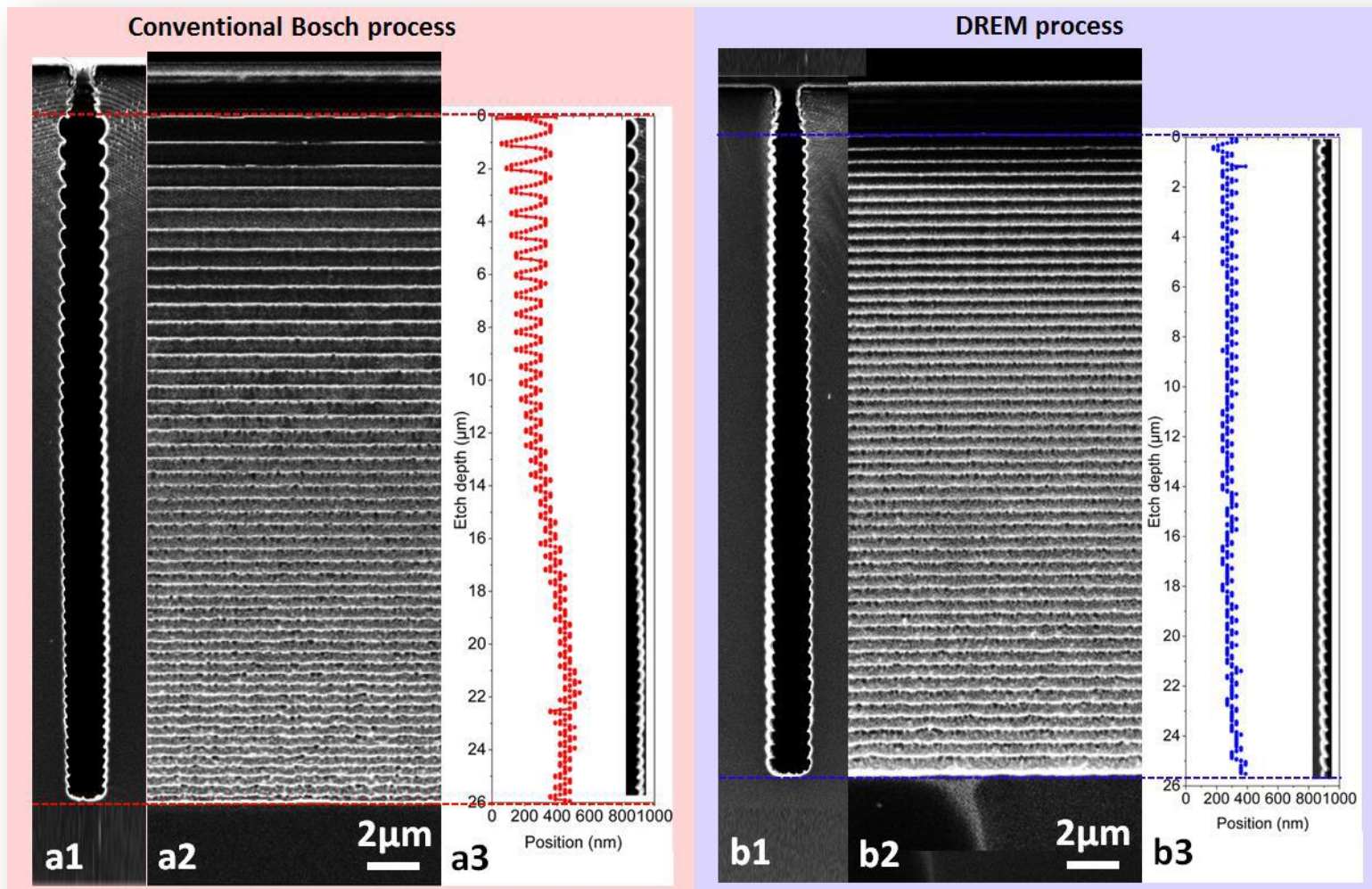
The latter due to shorter time applied platen power.



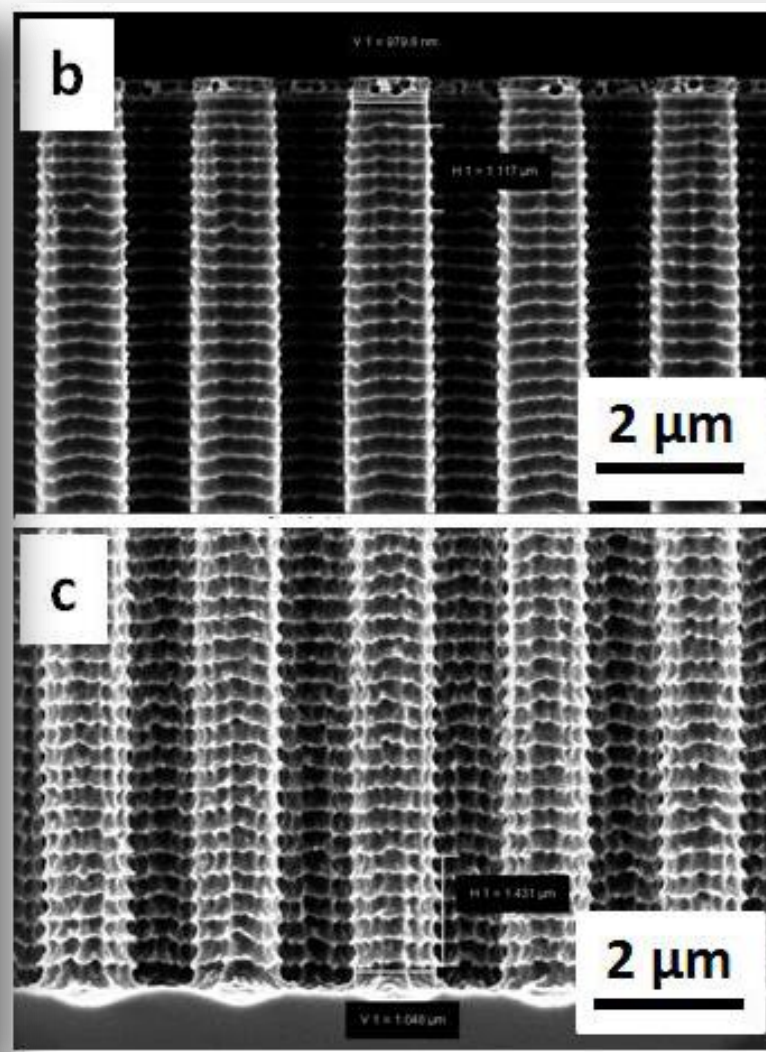
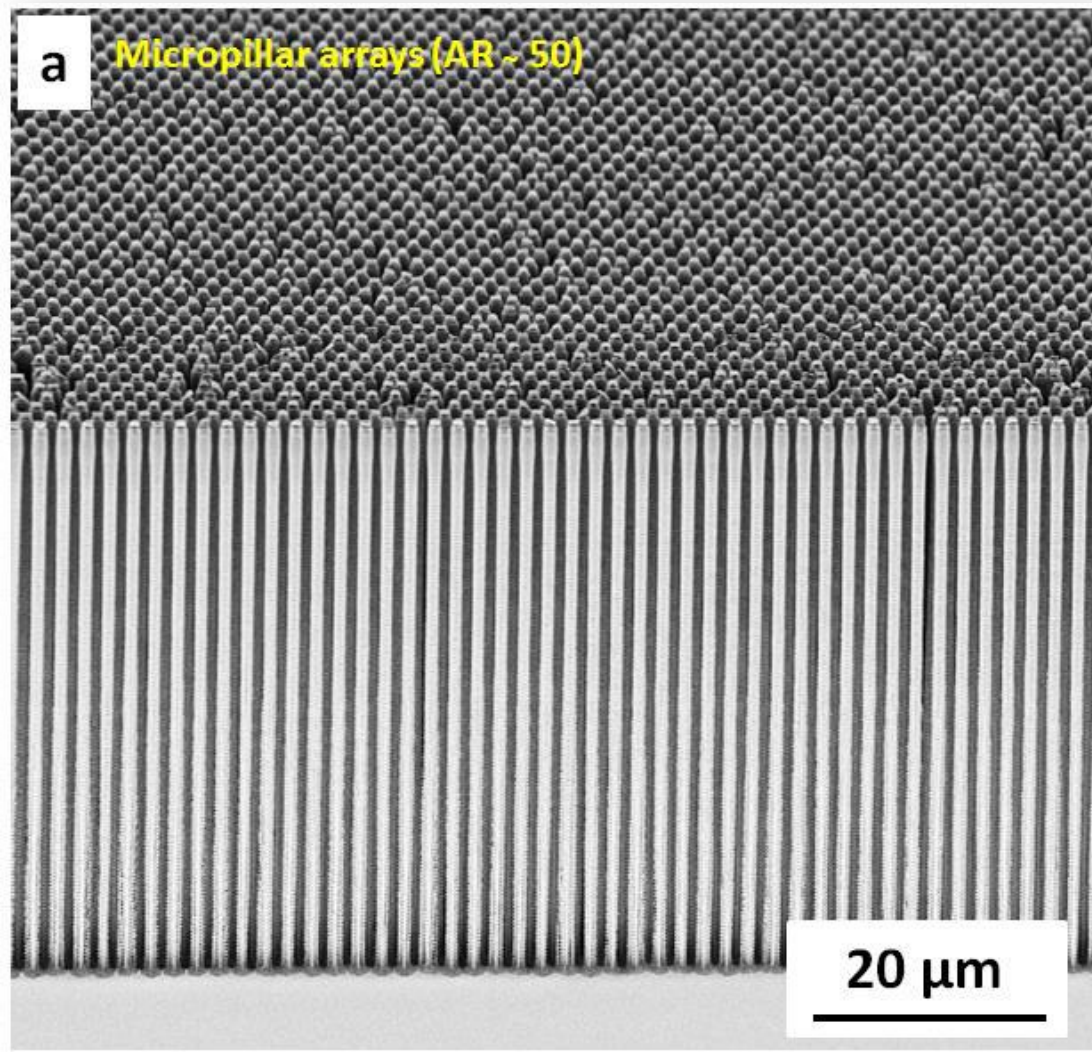
Switched FC: DREM with SF_6 etch time ramping



Switched FC: DREM with SF_6 etch time ramping



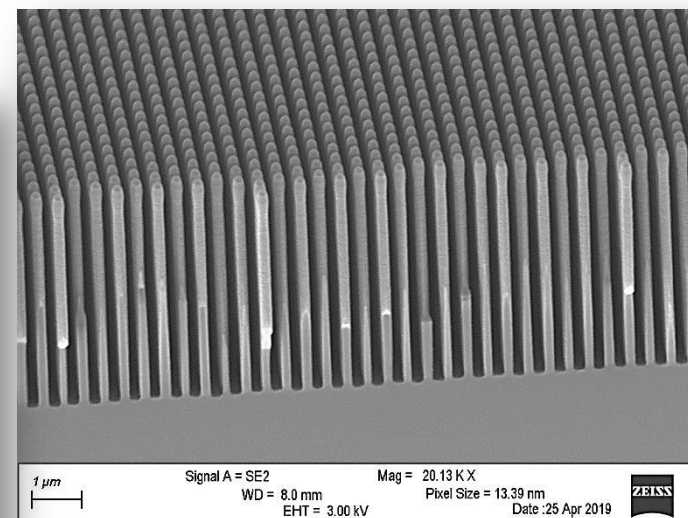
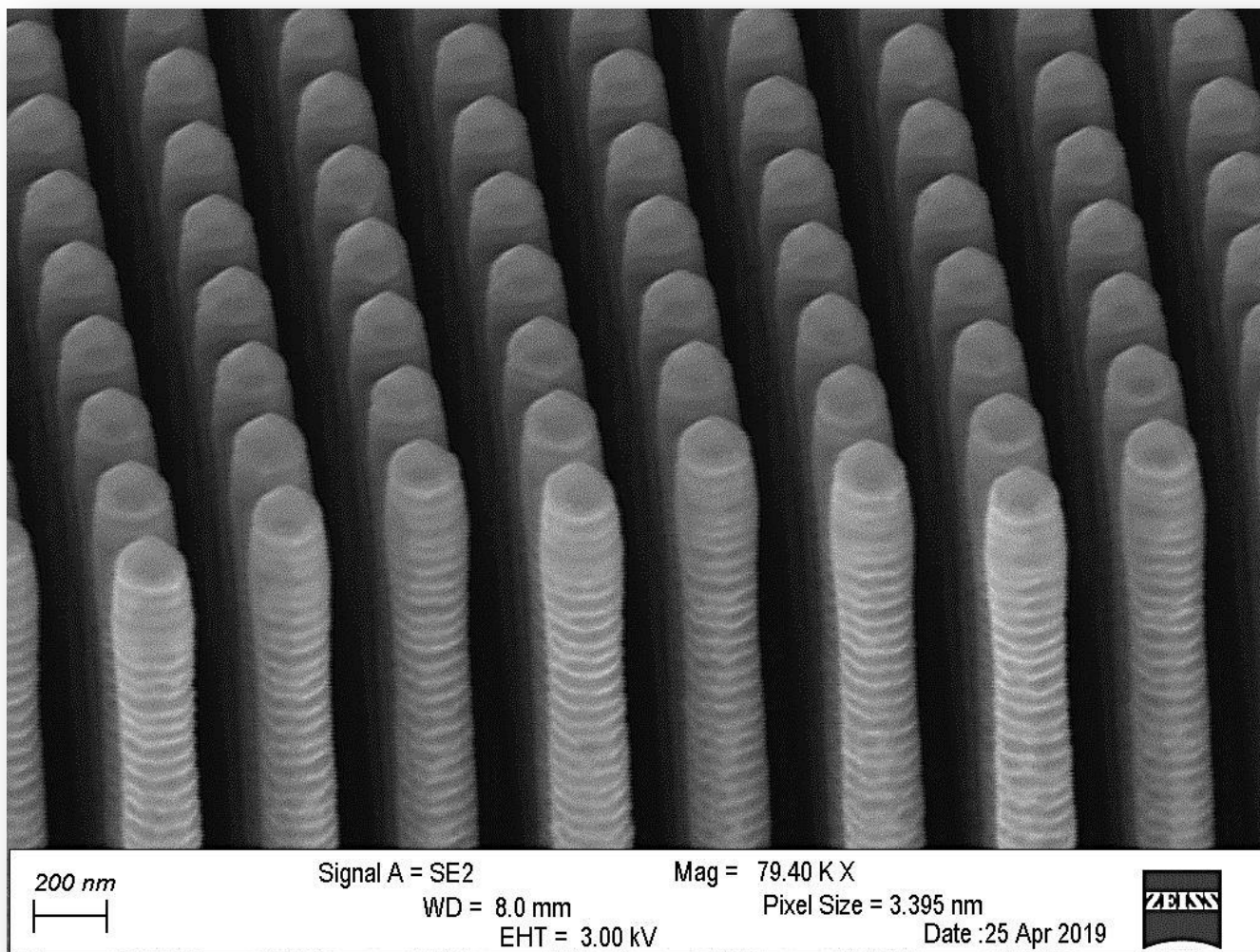
Switched FC DREM: AR=50 micropillars



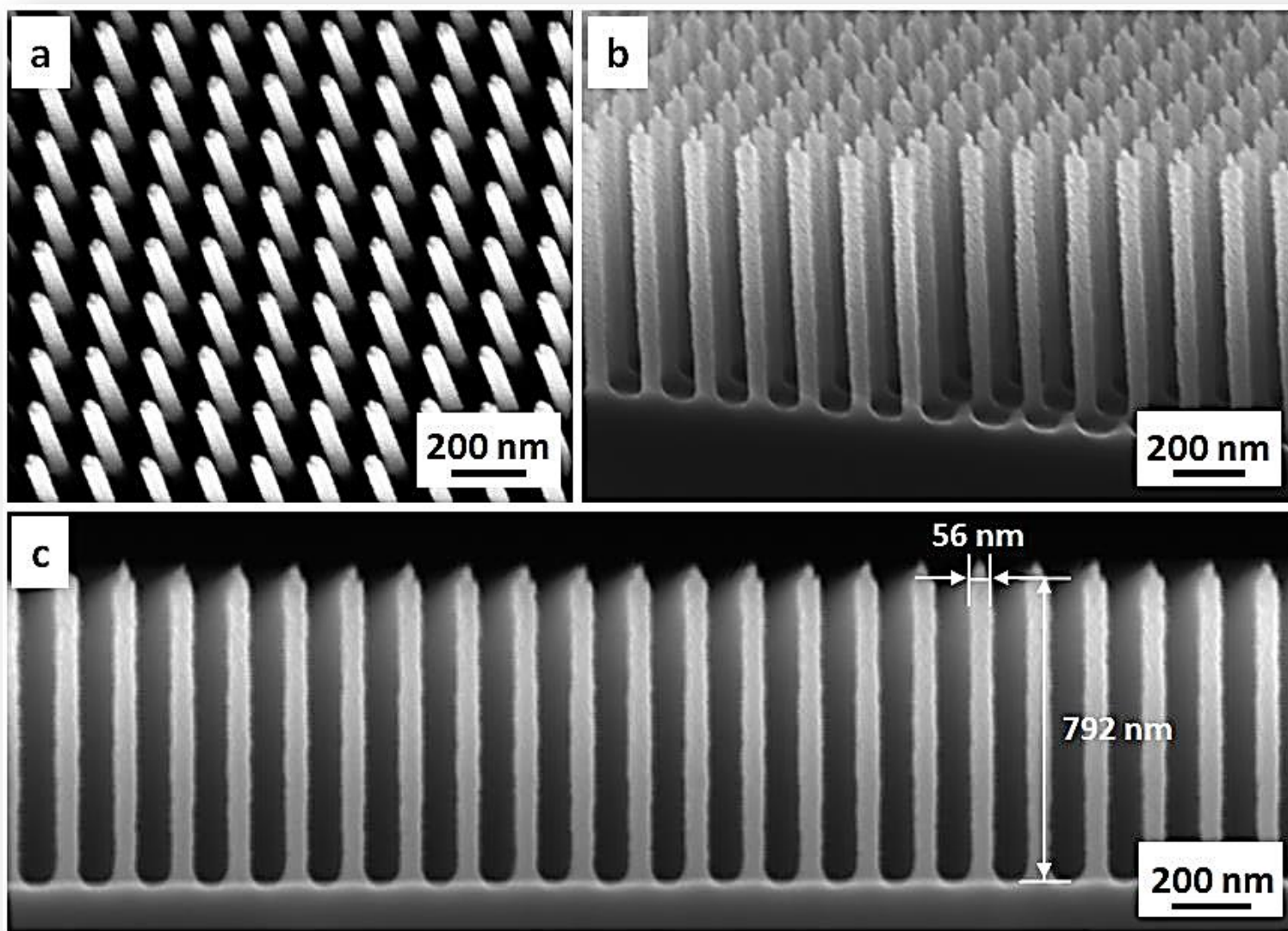
Top
of the pillars

Bottom
of the pillars

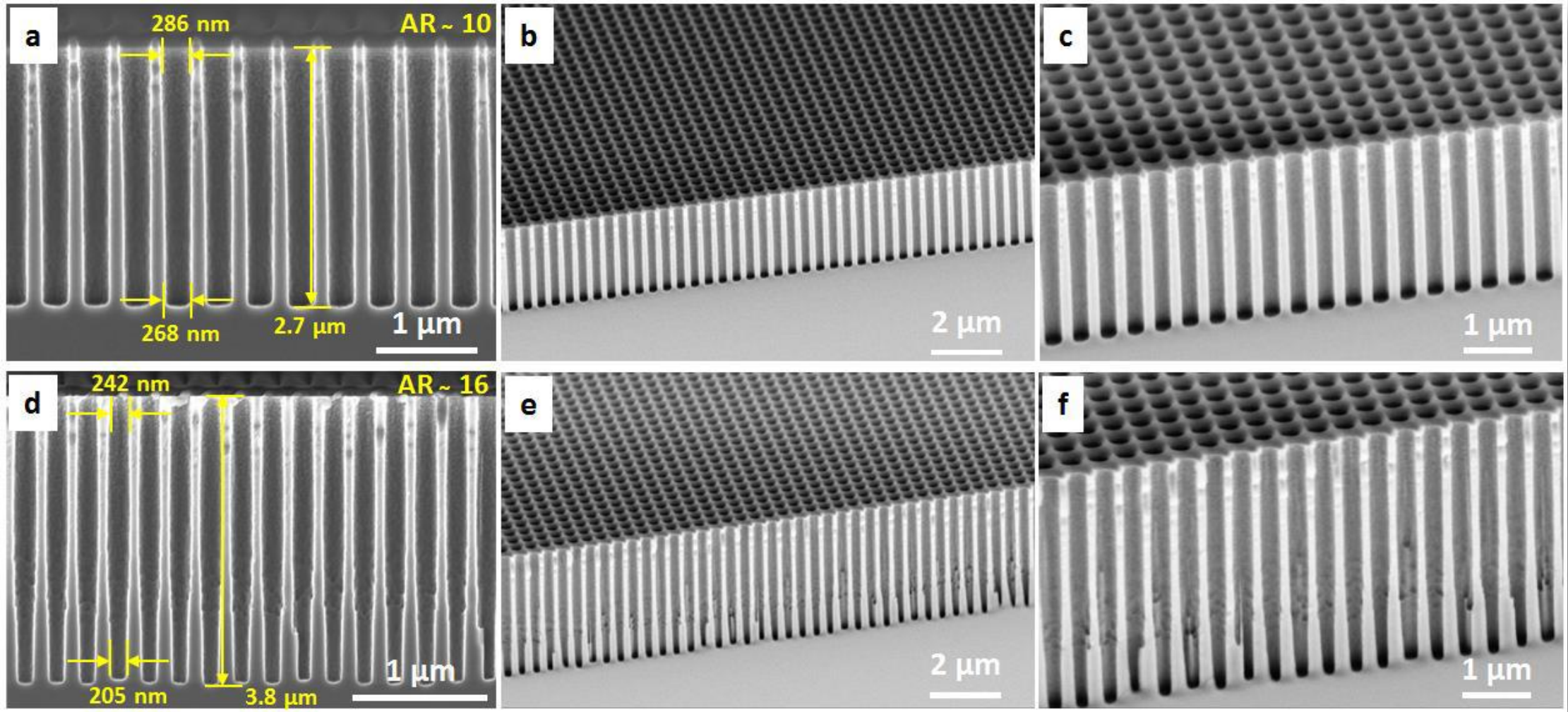
Switched FC DREM: AR=25 submicron pillars



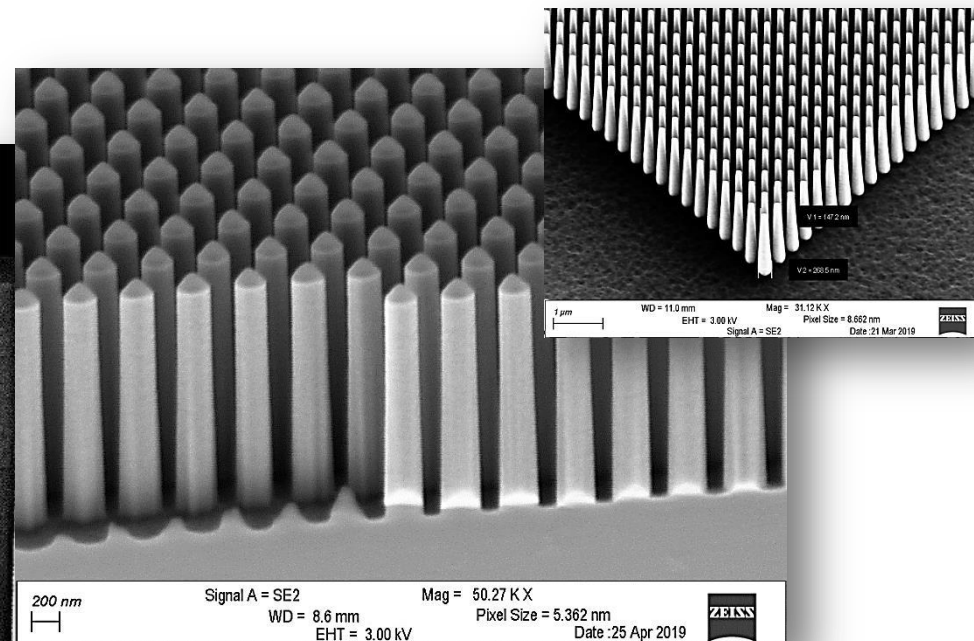
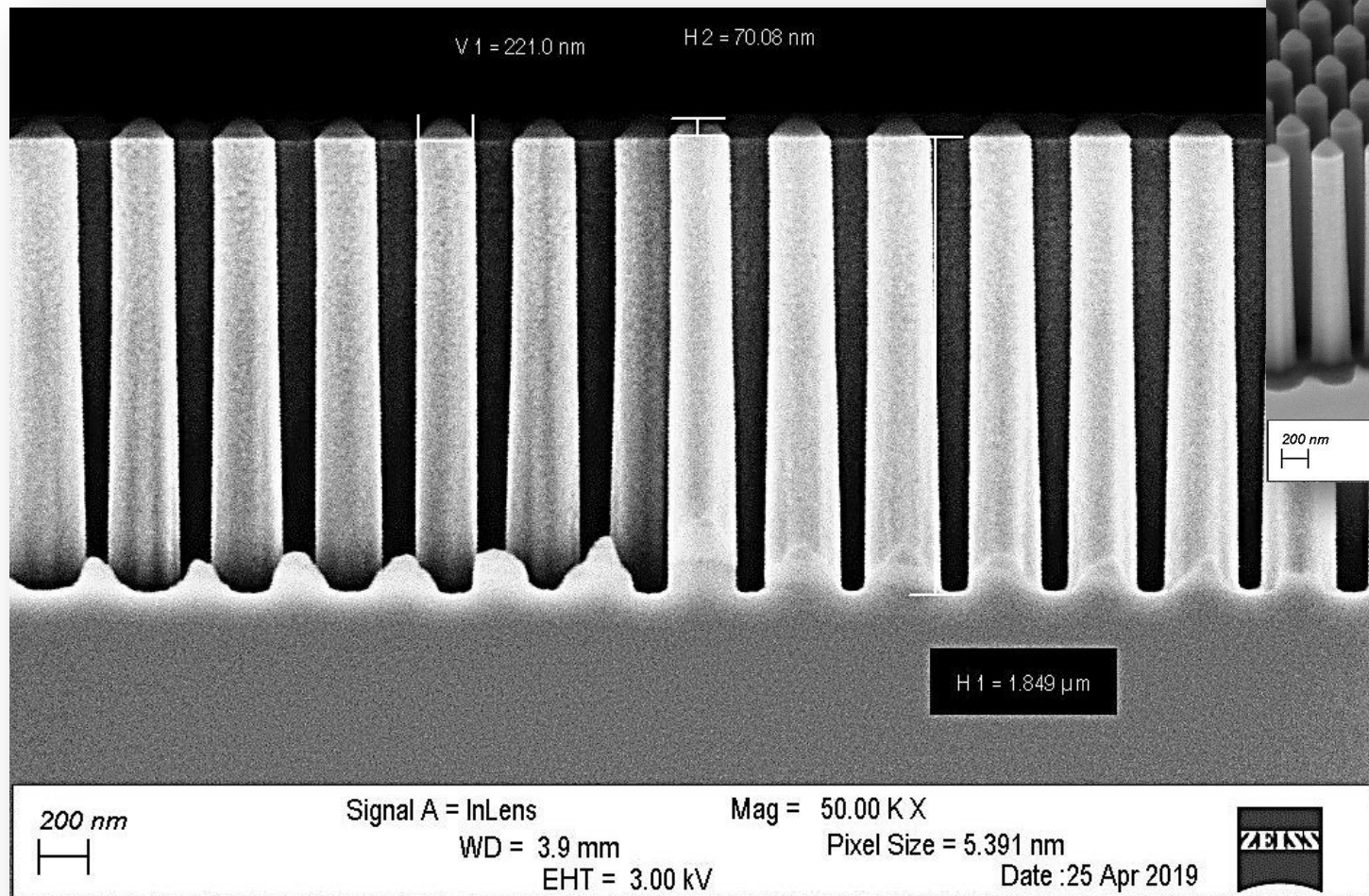
Switched FC DREM: AR=15 nanopillars



Switched FC: DREM Results: AR=10 submicron pores

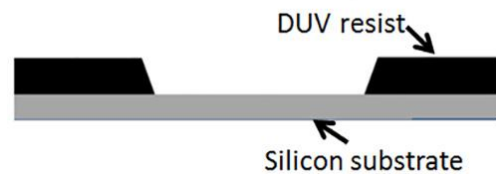


Switched FC DREM: Lower ICP power (to suppress scallops)

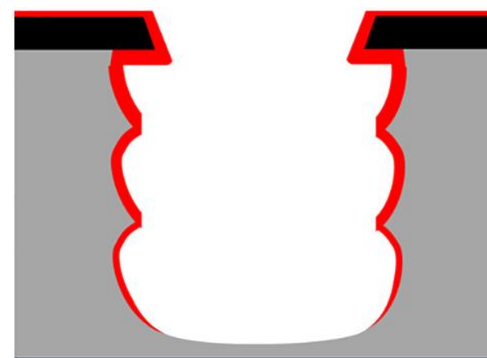
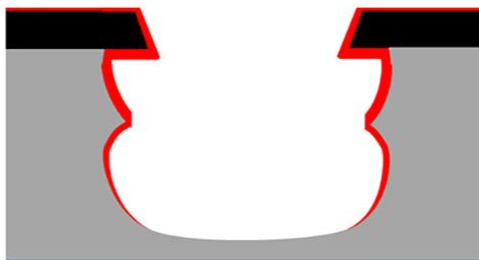


Switched FC DREM and the infinite selectivity

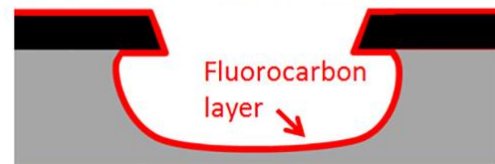
1. Patterns after DUV exposure



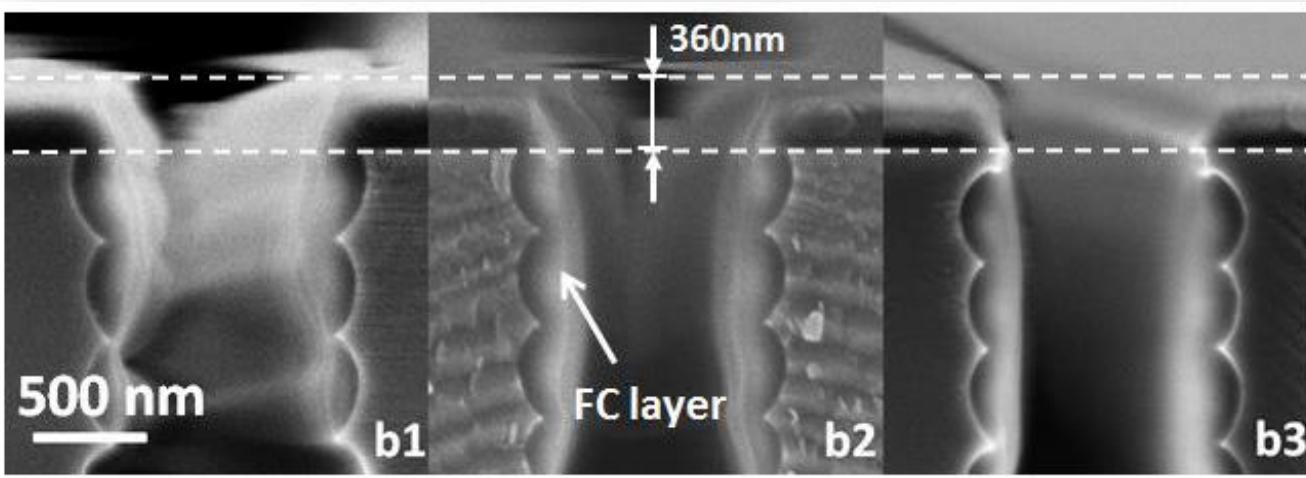
2. After first etching step



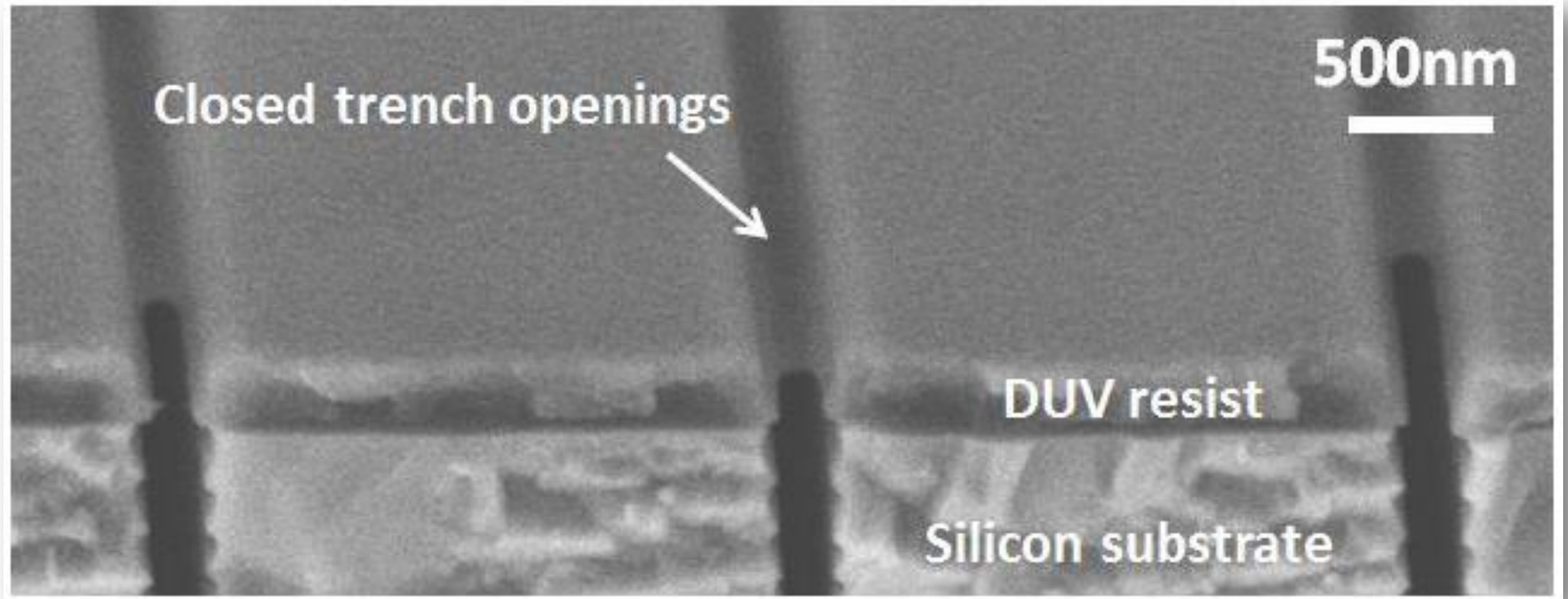
3. After first deposition step



4. After first bottom removal step



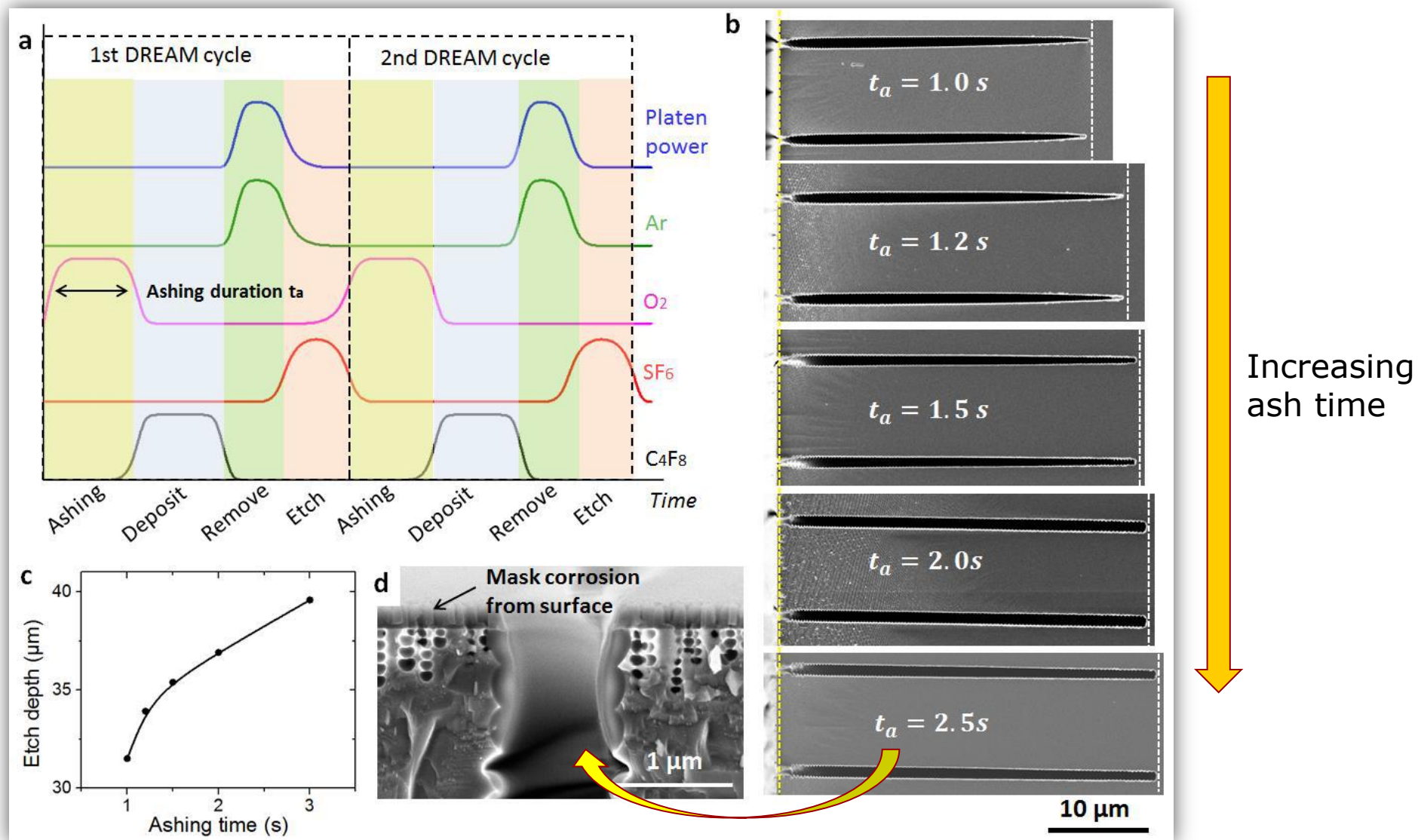
Switched FC DREM and the closing trenches



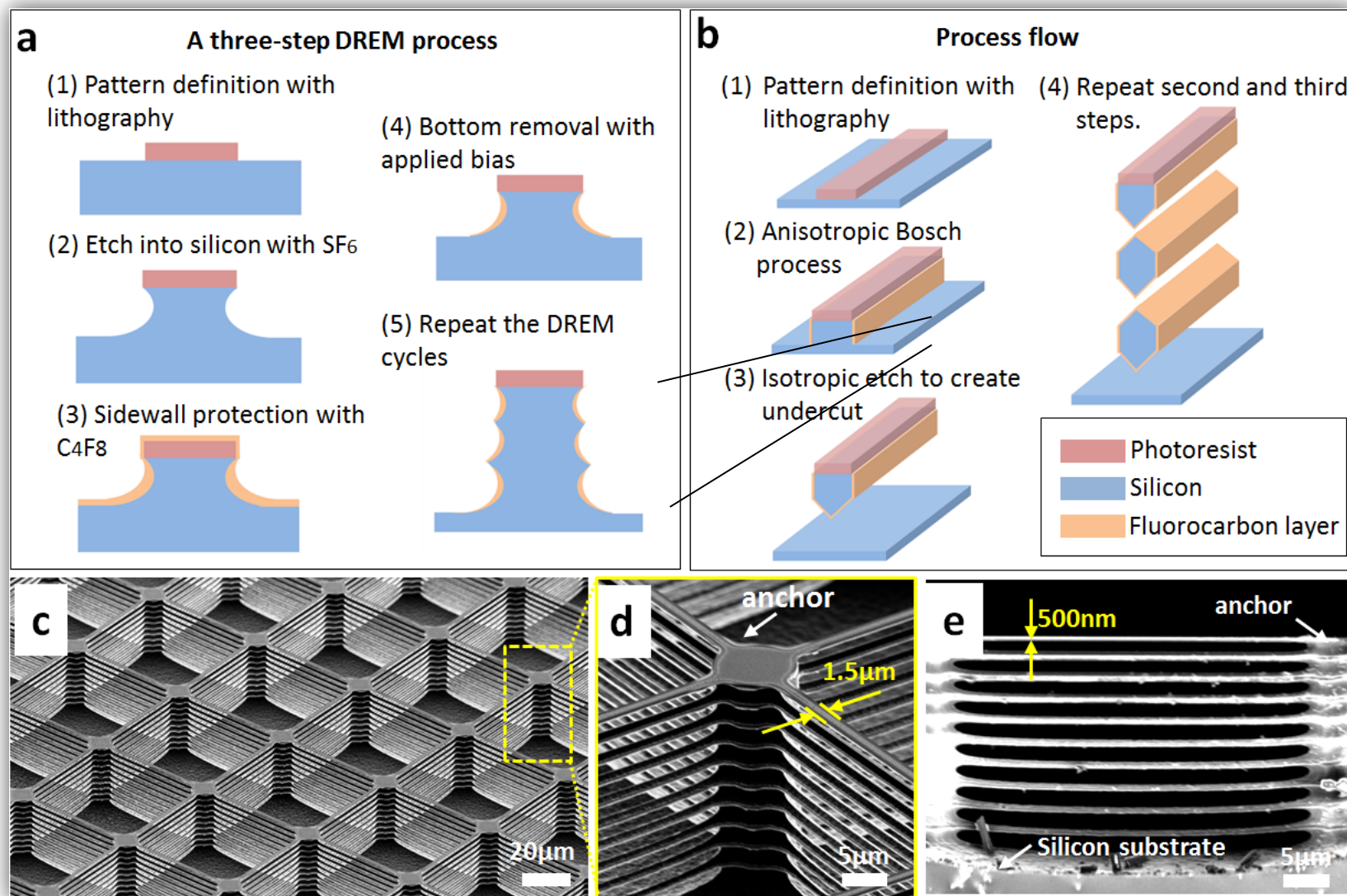
Beyond DREM

4-steps and 3D

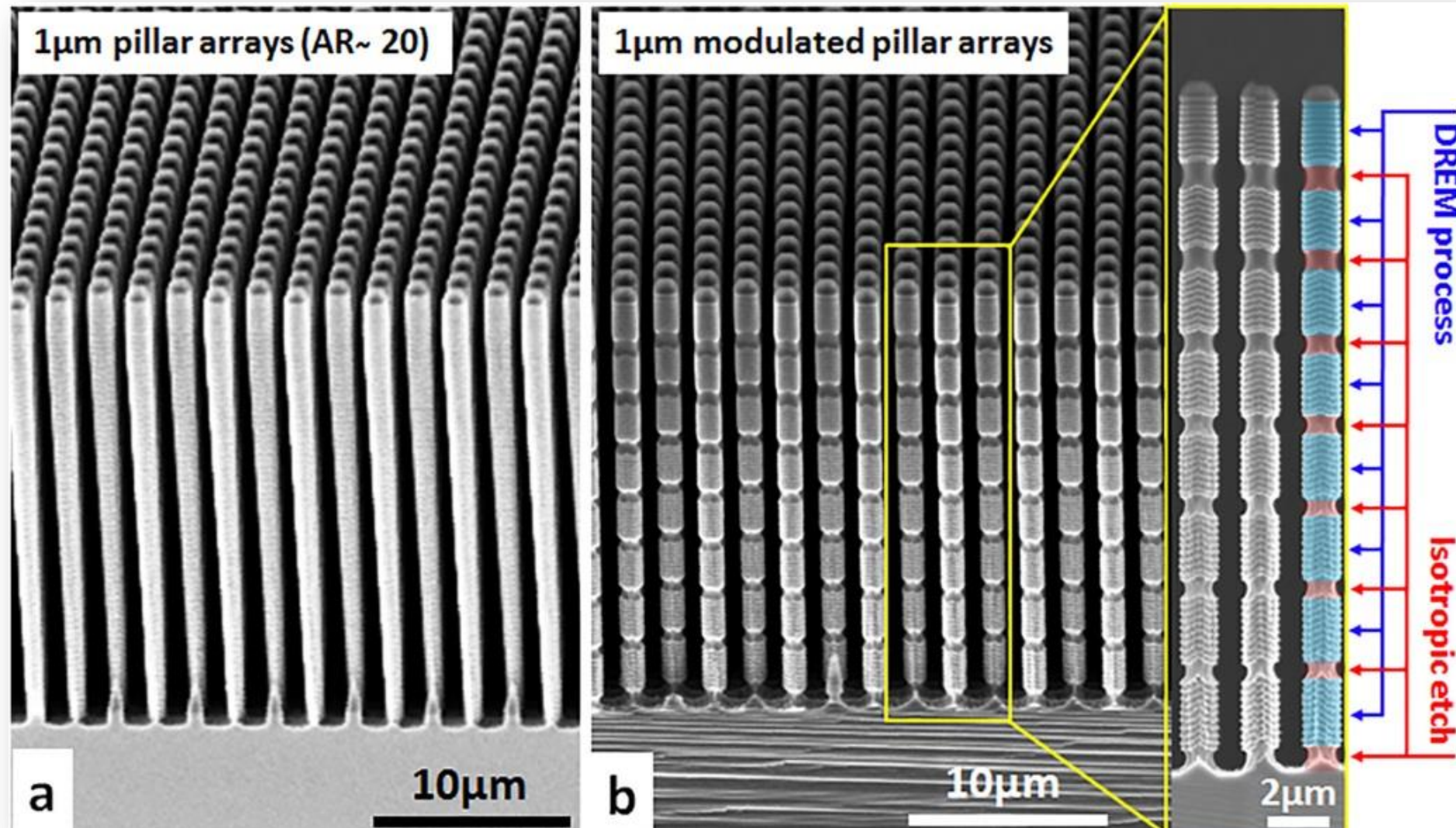
The DREAM process (A for Ash)



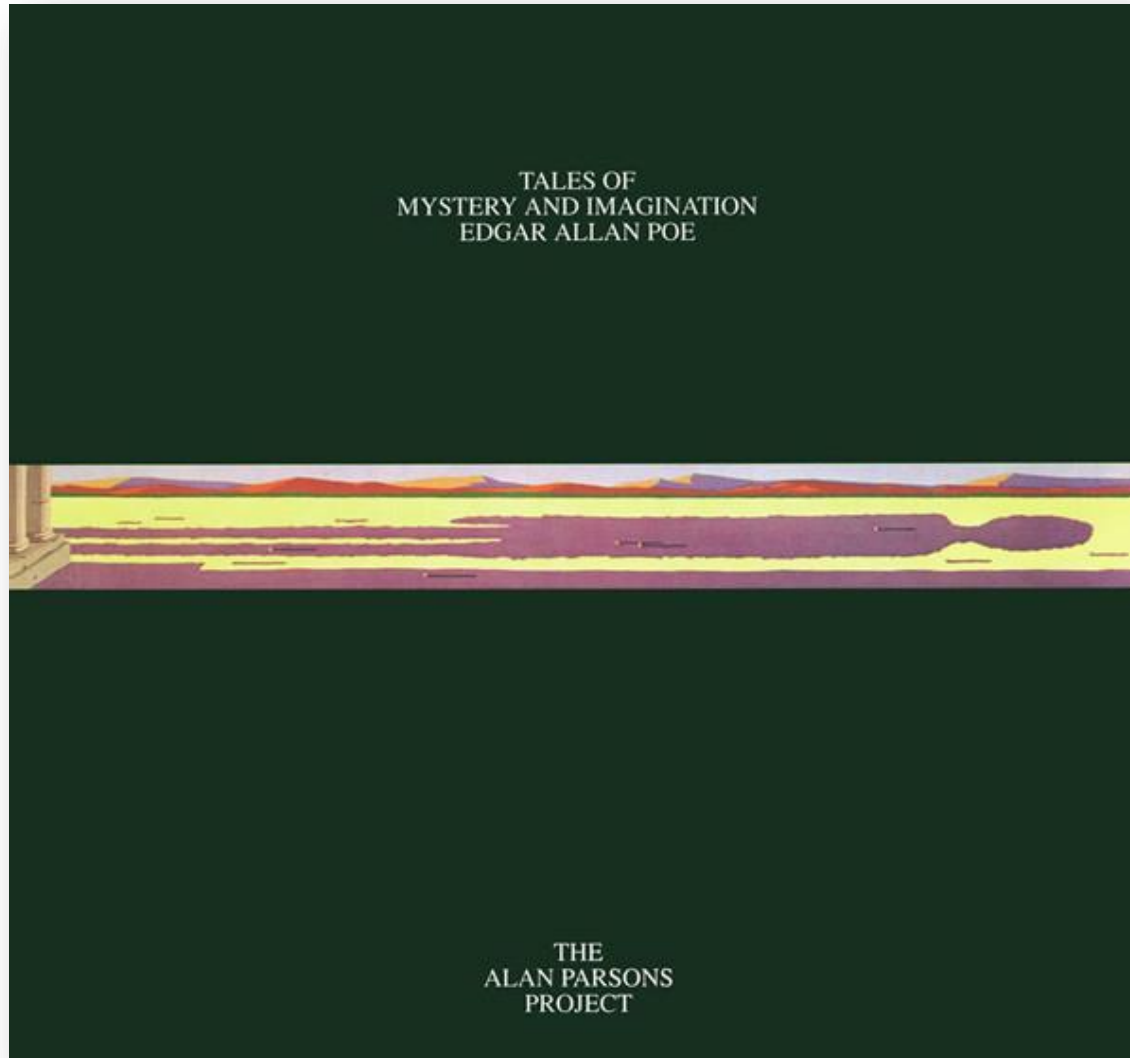
3D silicon nanosculpturing: DREM within a DREM



3D silicon nanosculpturing: DREM within a DREM



A DREAM Within a DREAM by Edgar Allan Poe

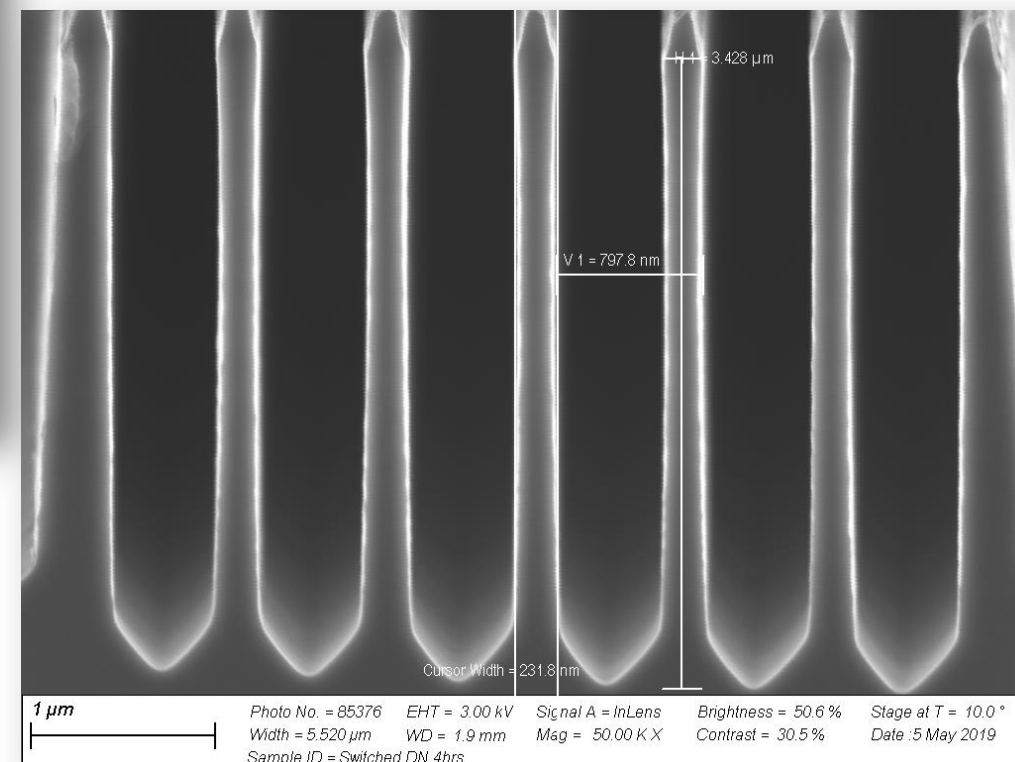
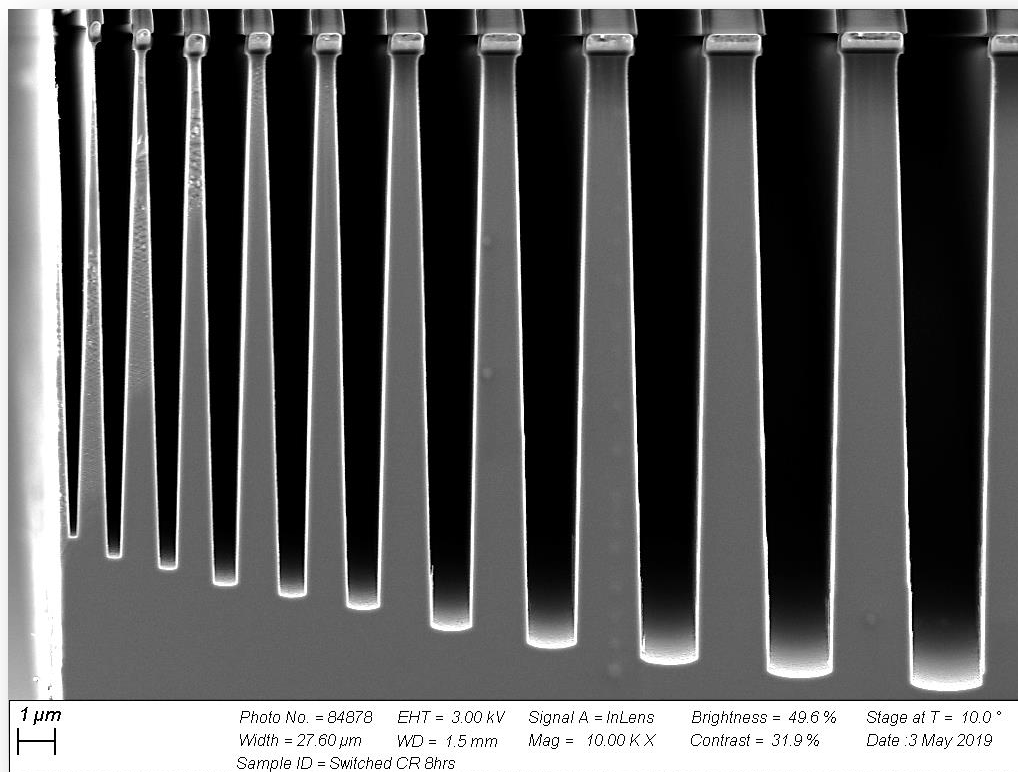


*I stand amid the roar
Of a surf-tormented shore,
And I hold within my hand
Grains of the golden sand —
How few! yet how they creep
Through my fingers to the deep,
While I weep — while I weep!
O God! Can I not grasp
Them with a tighter clasp?
O God! can I not save
One from the pitiless wave?
Is all that we see or seem
But a dream within a dream?*

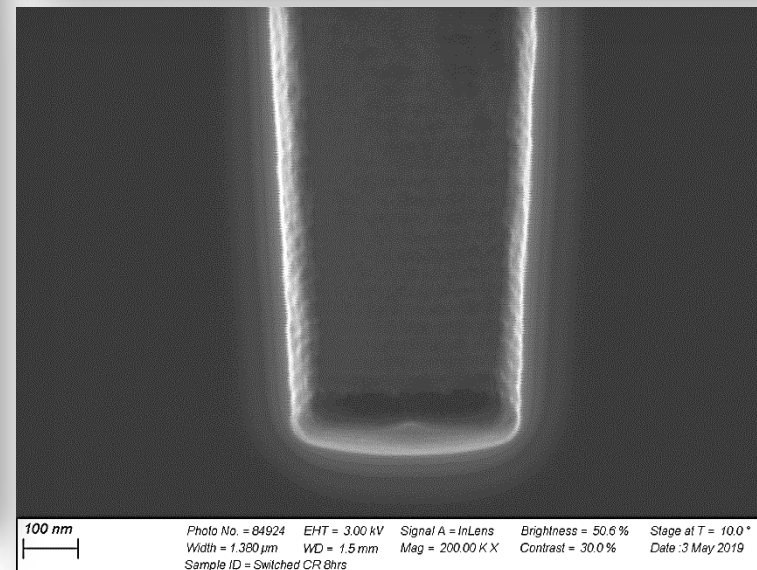
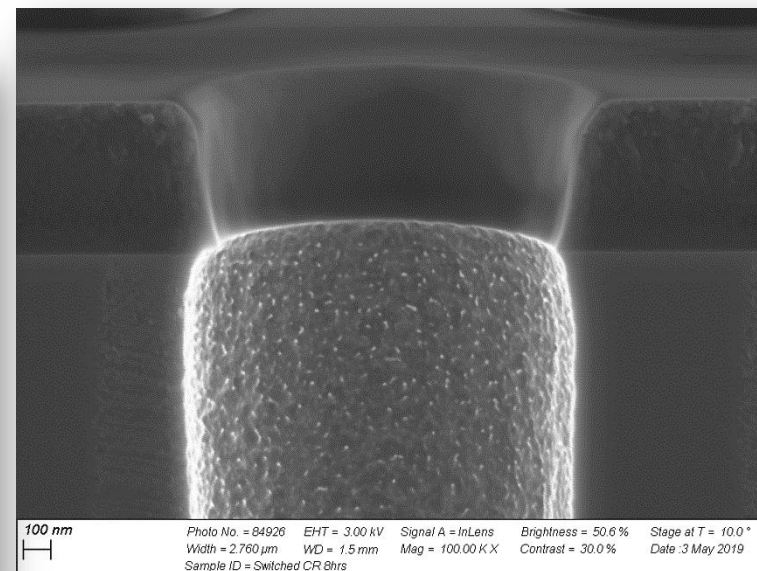
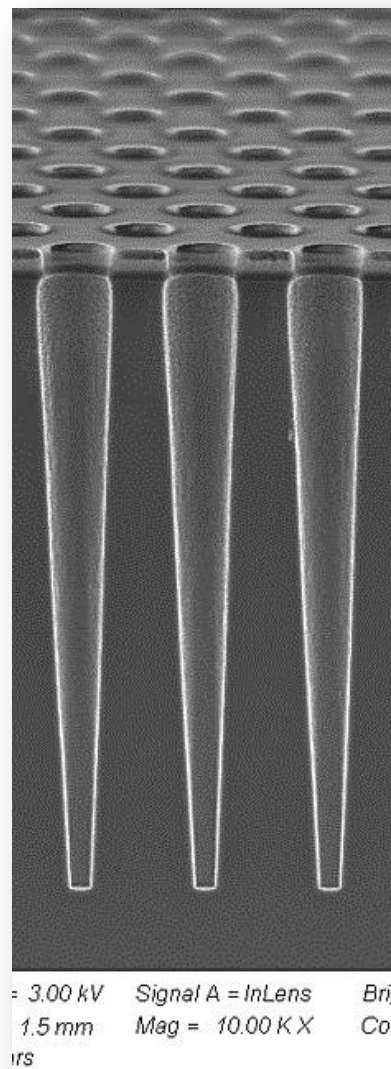
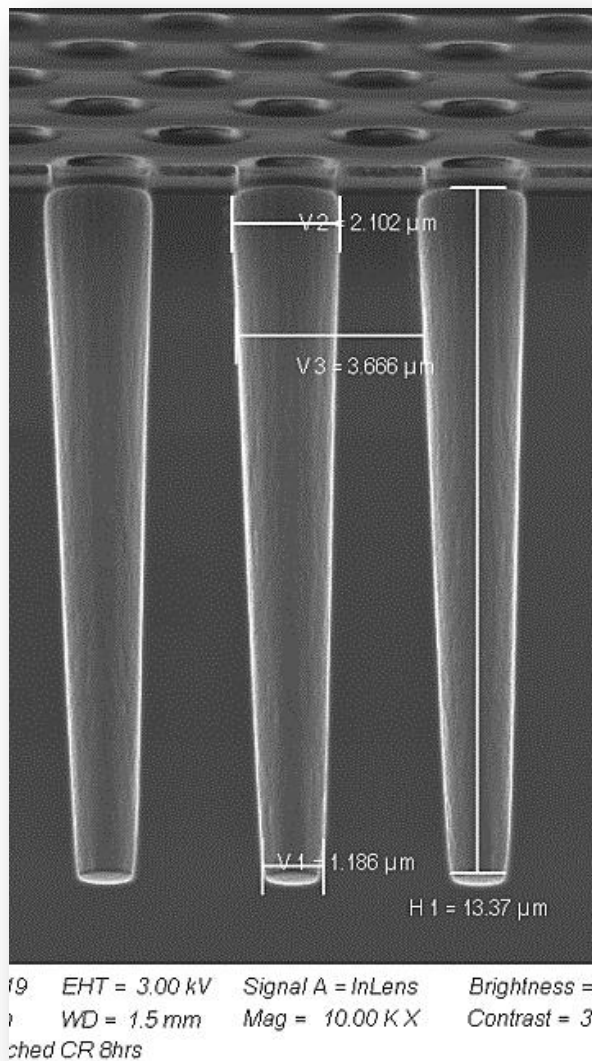
Switched O₂ mode

4-steps CORE

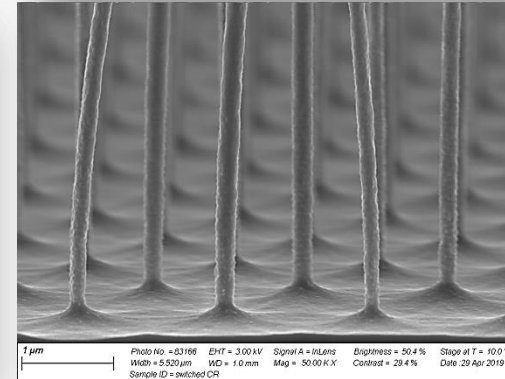
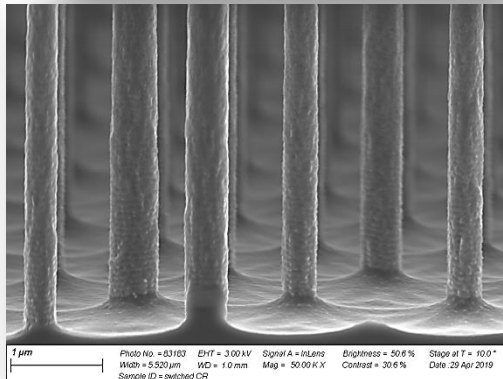
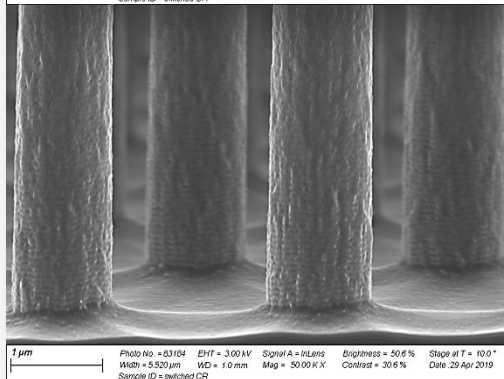
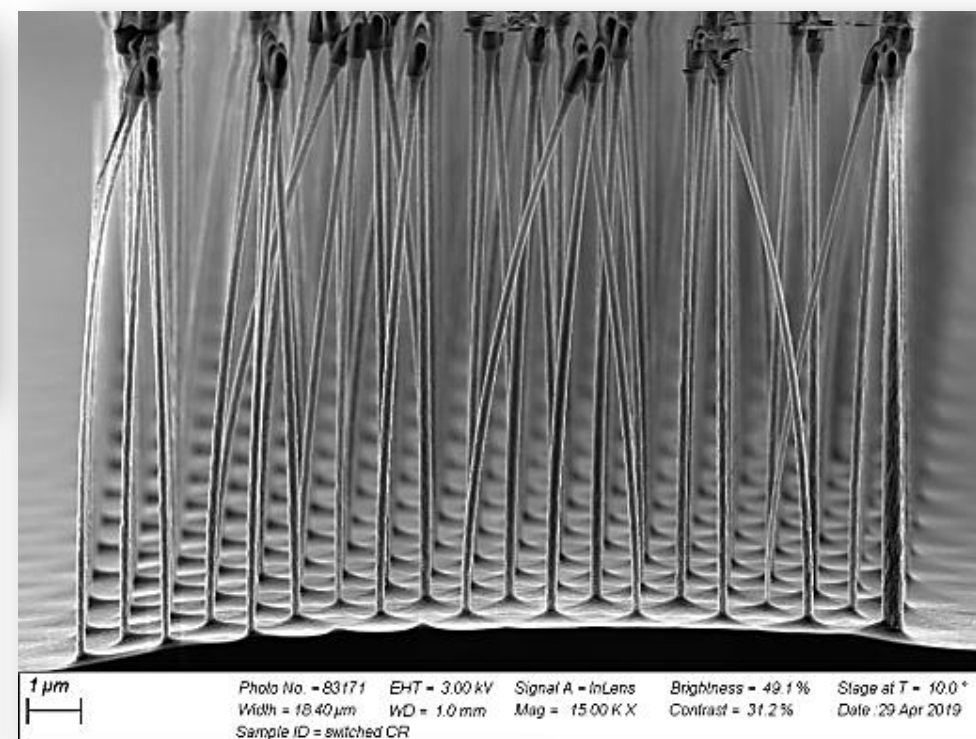
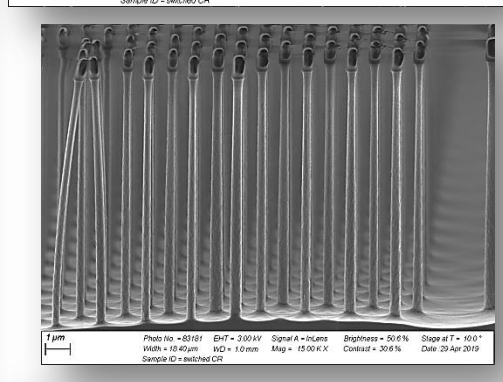
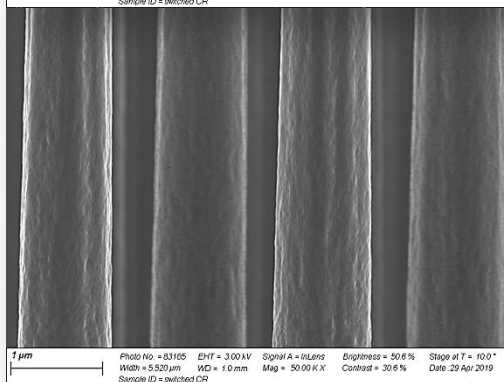
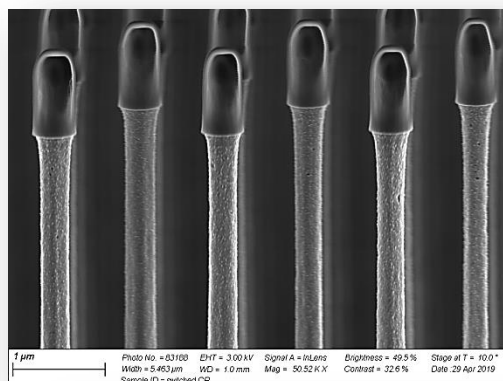
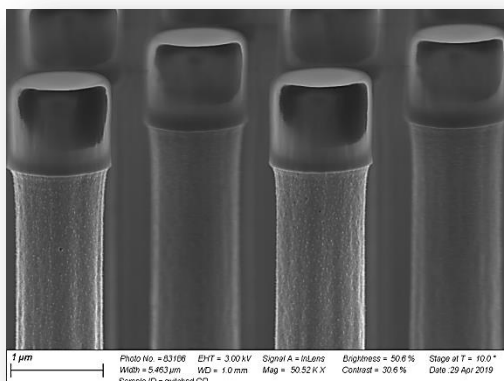
Switched O₂ and trenches, lines, or gratings



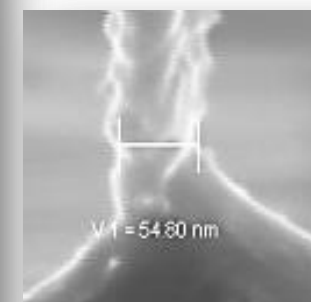
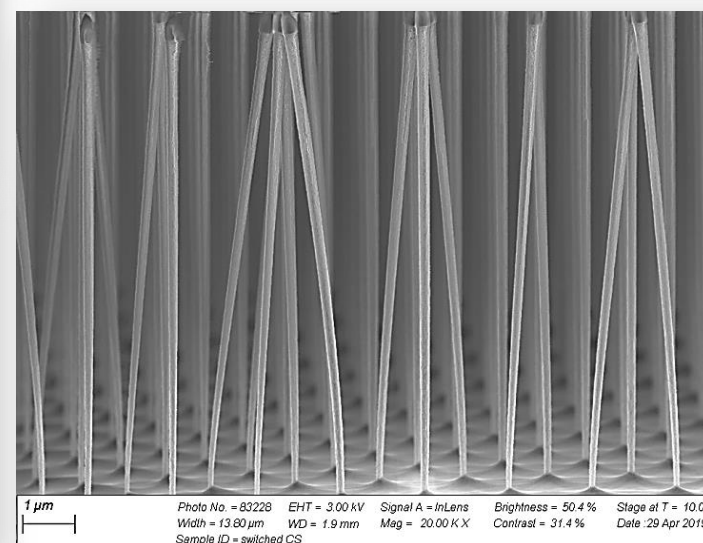
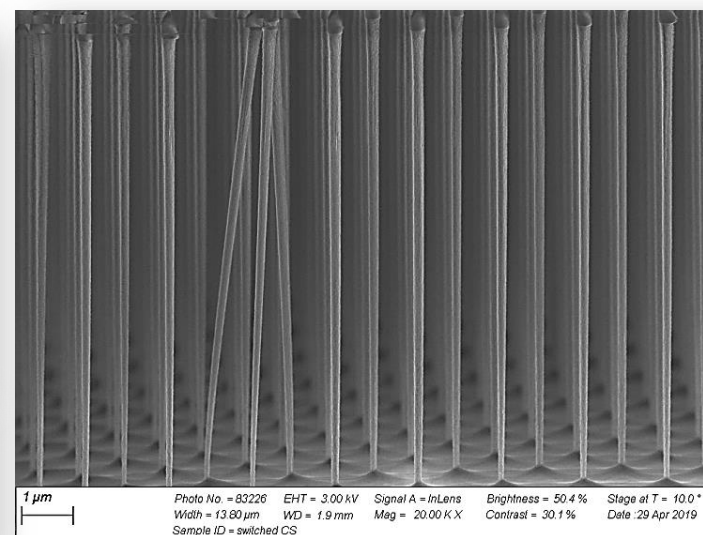
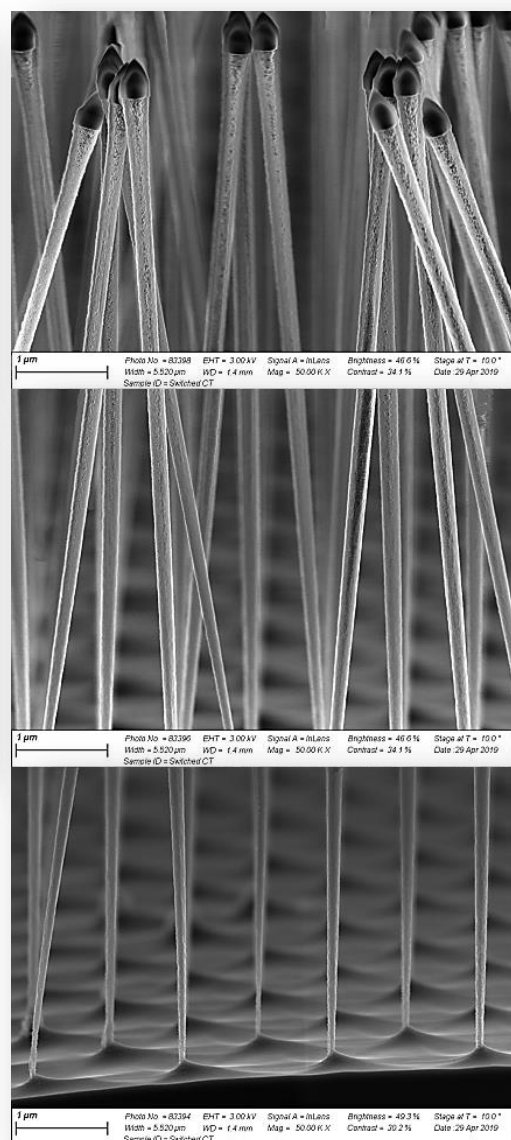
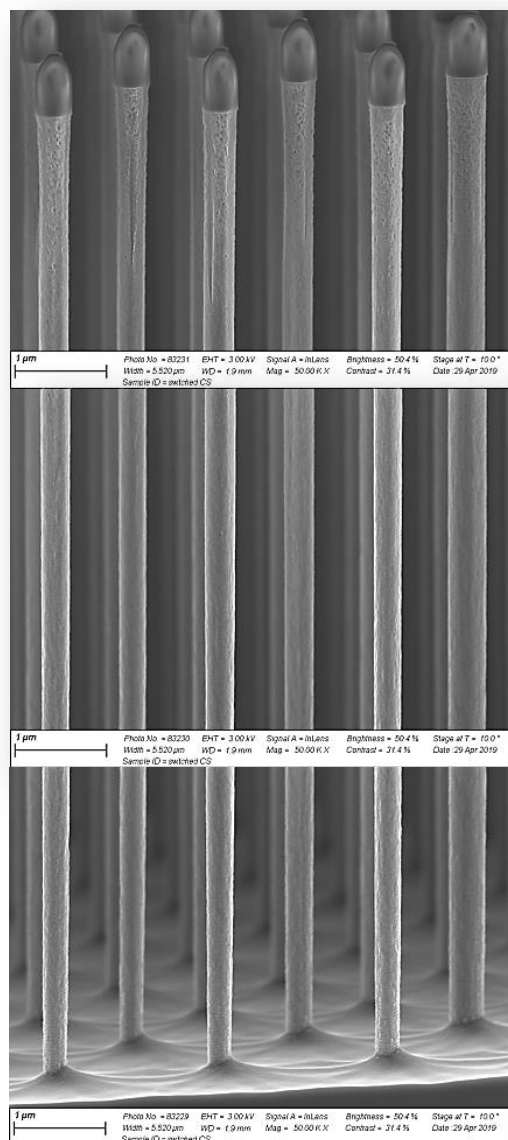
Switched O₂ and holes



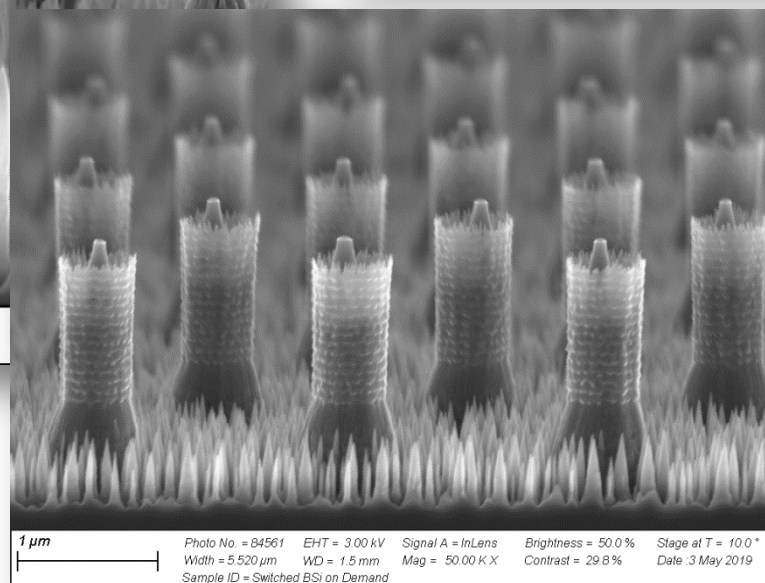
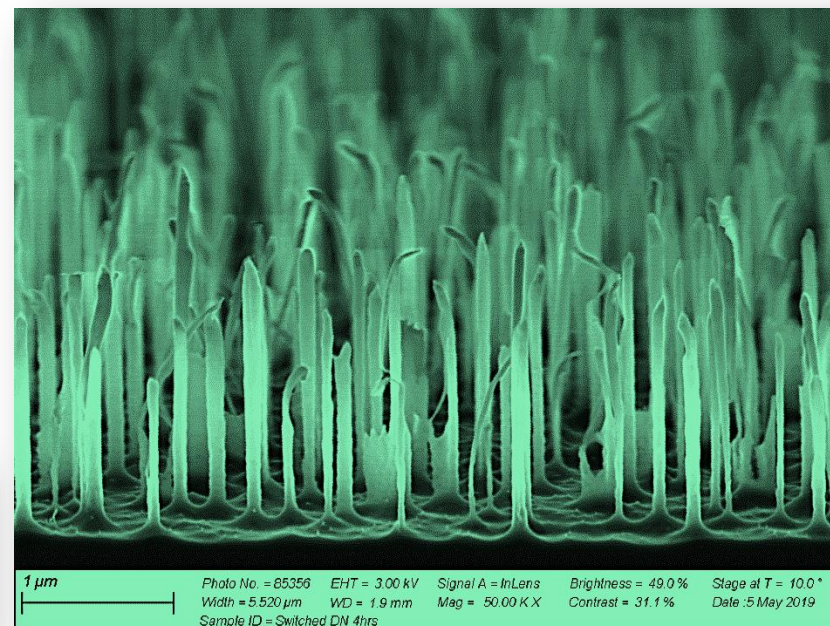
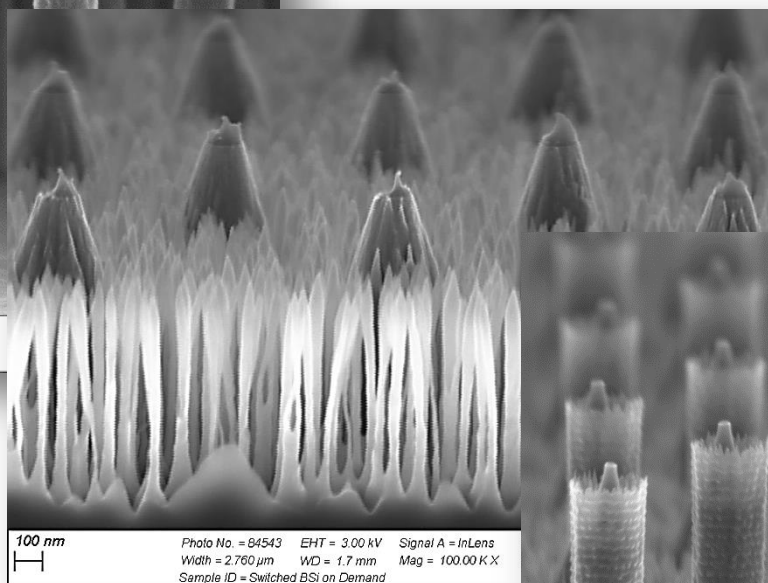
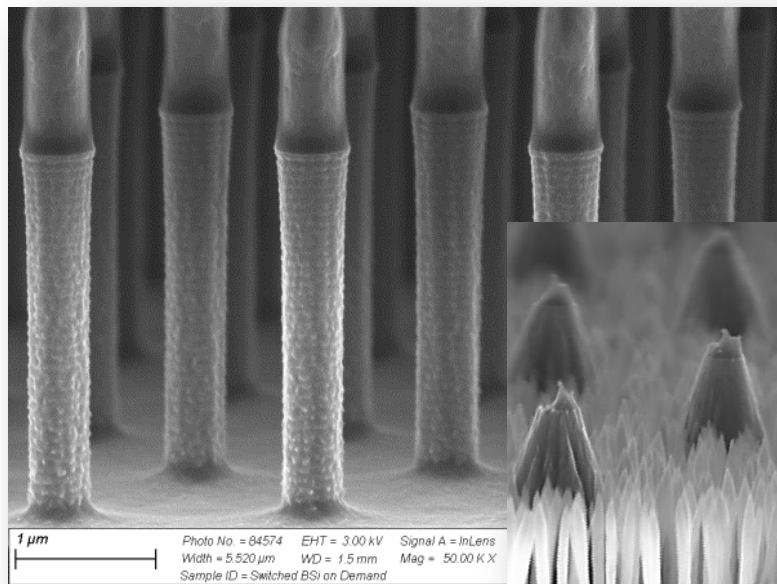
Switched O₂ and pillars



Switched O₂ and pillars



Switched O₂ and Black Silicon on Demand

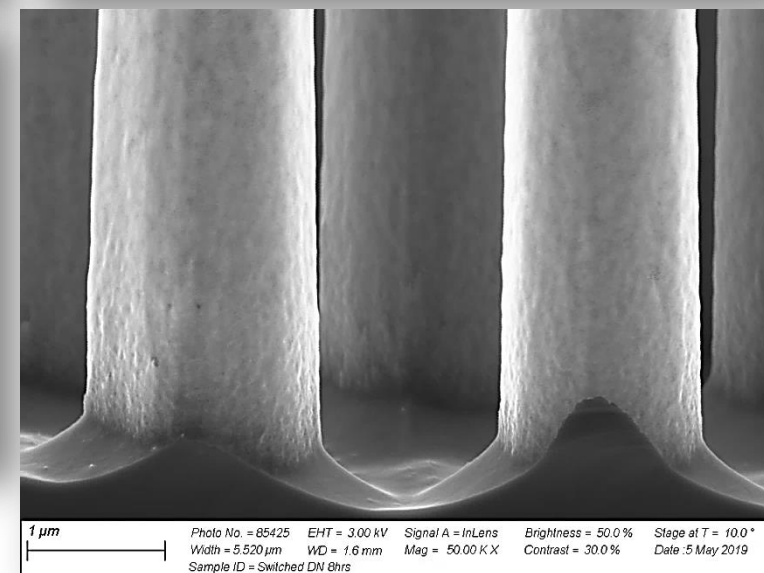
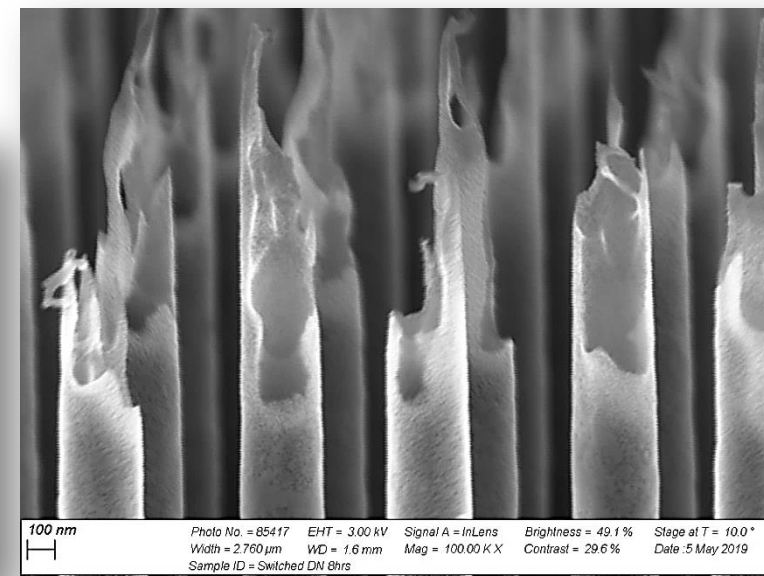
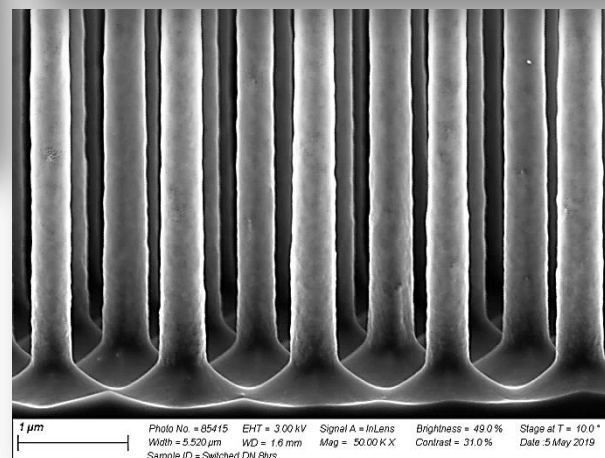
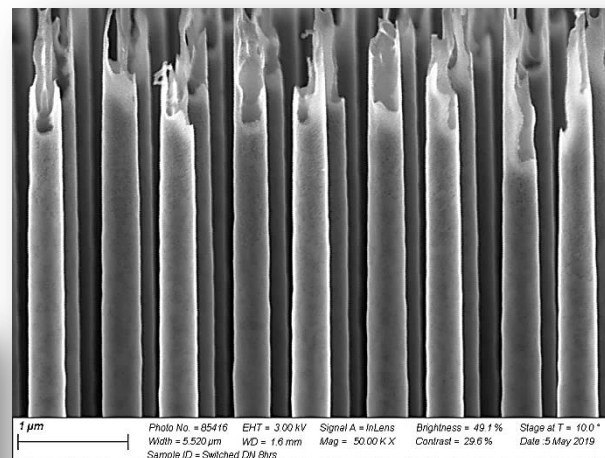
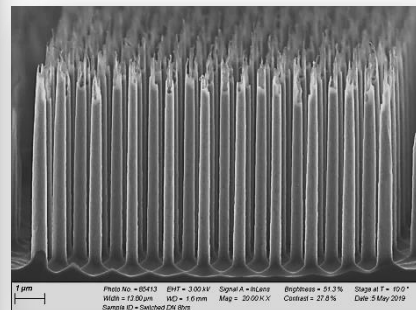
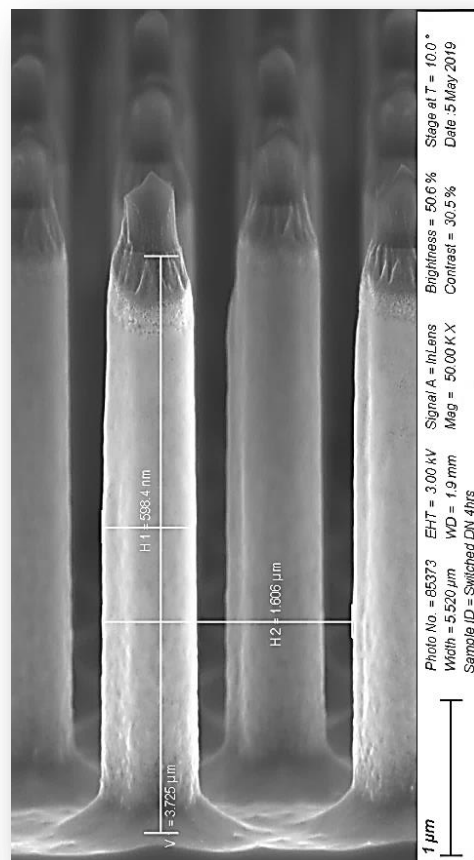


*To be presented at MNE2019
by Vy*

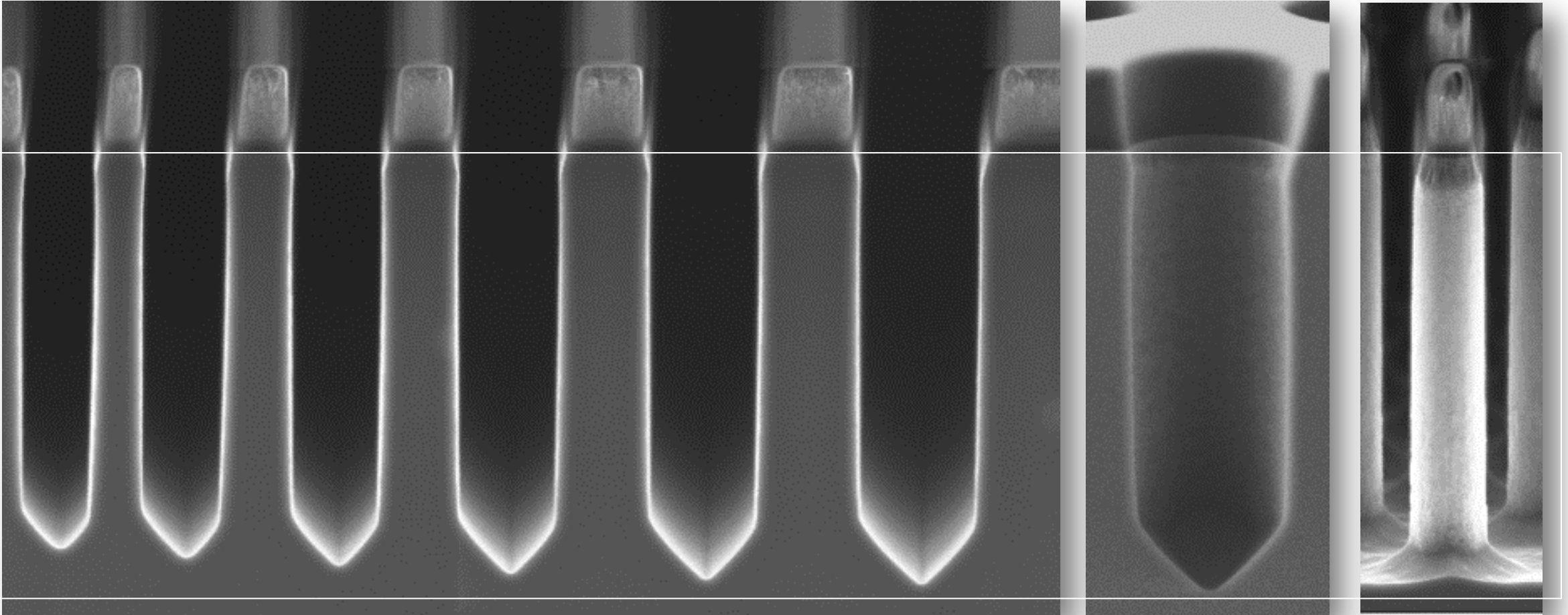
Combined O₂ mode

4-steps

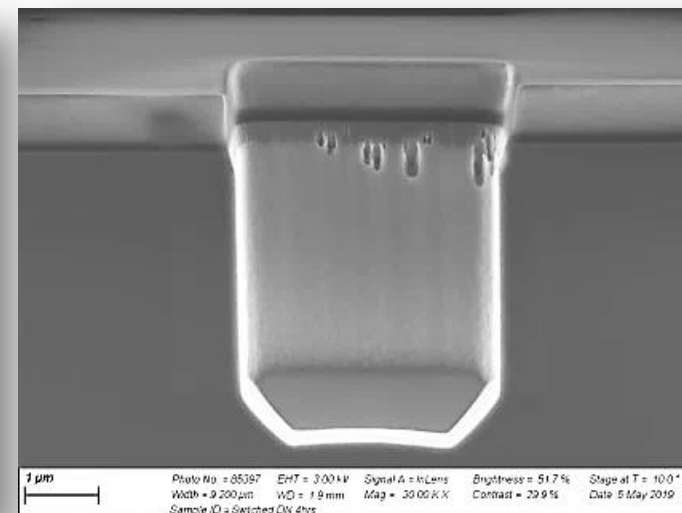
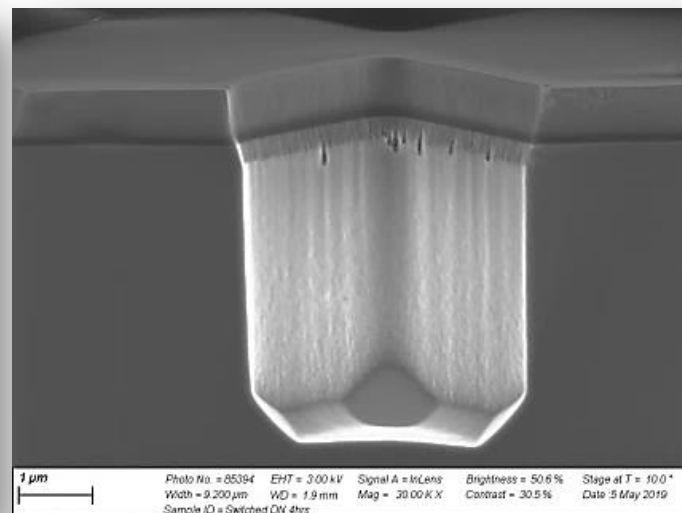
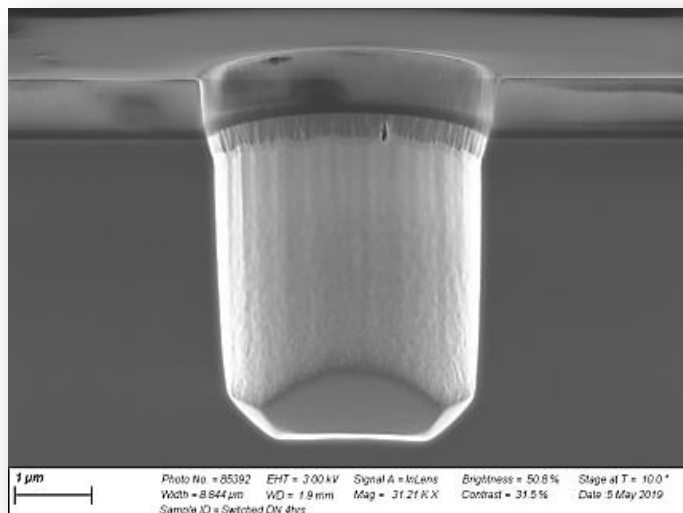
Combined O₂ and pillars: reducing scallops



Combined O_2 and pattern dependency



Combined O_2 and crystal plane dependency



Switched O₂ and 3D

