

New plasma technologies for atomic scale precision etching

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Journées des réseaux plasma froids
17-20 octobre 2016, La Rochelle

Outline

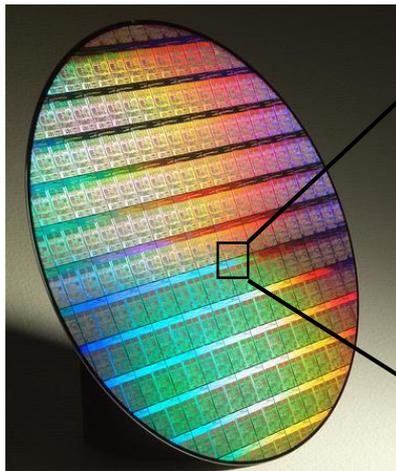
I. Introduction

II. Limitations of current plasma technologies

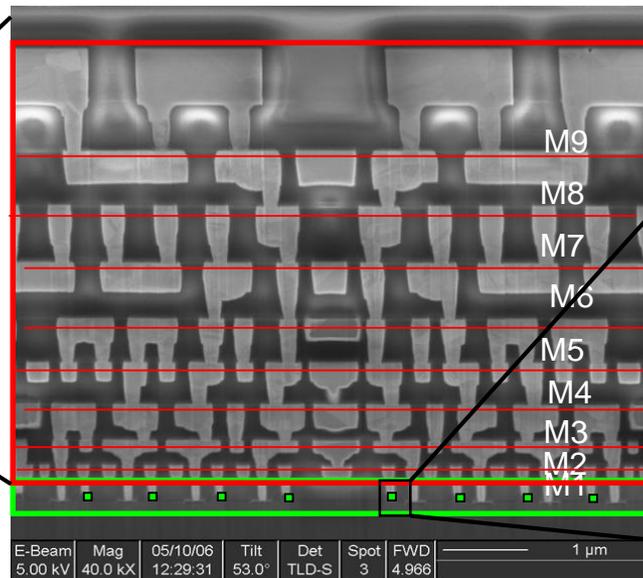
III. Atomic layer etching concept : ALE

IV. From lab to fab

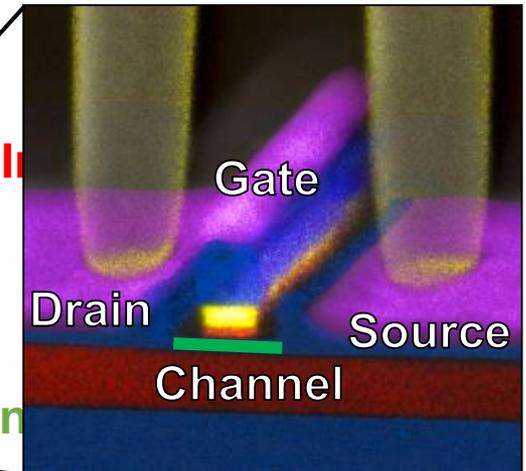
From consumer devices to CMOS technologies



300mm Si wafer

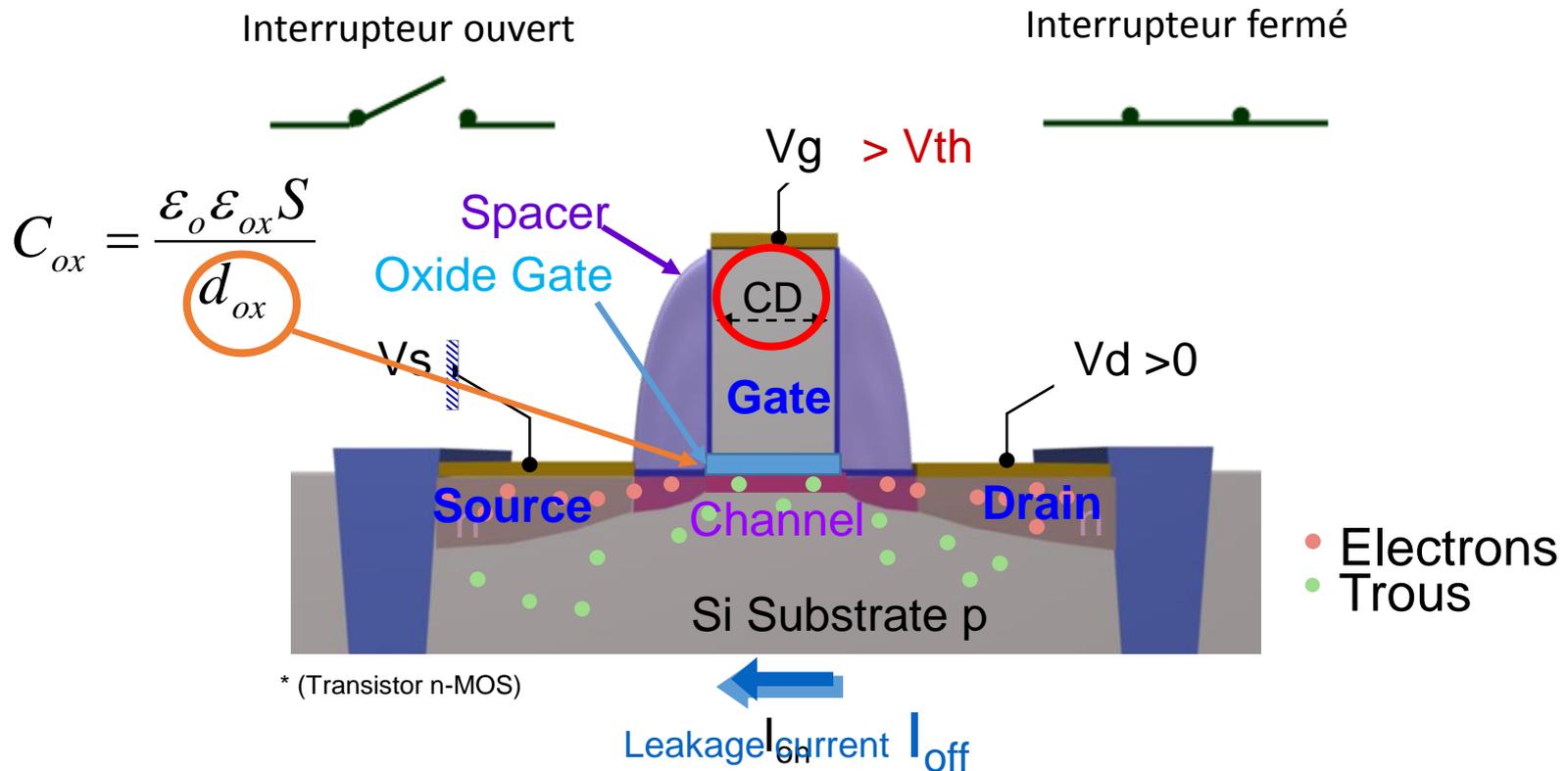


Cross section observation of an Integrated circuit



MOS transistor

MOS transistor: architecture and principle



$$I_{on} = \frac{W}{CD} \mu C_{ox} \frac{(V_g - V_{th})^2}{2}$$

CD: critical dimension (channel length)

W: channel width

μ : carrier mobility

C_{ox} : oxide gate capacitance

V_g : Gate voltage

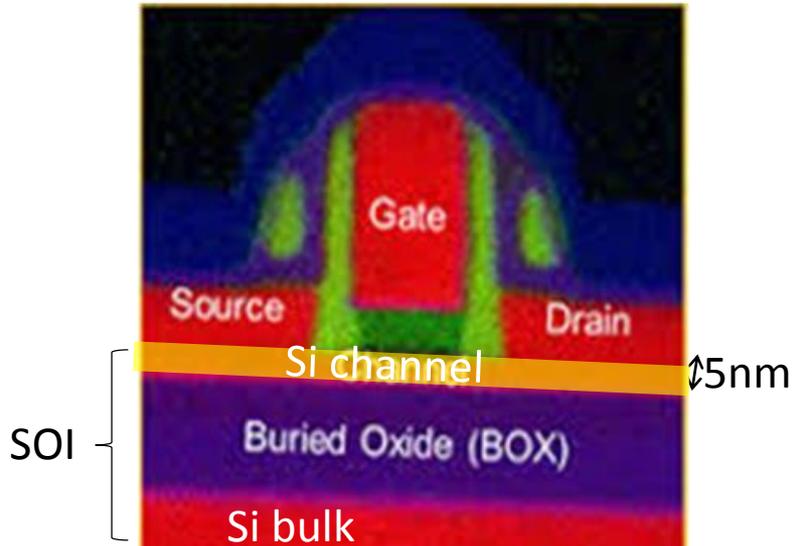
V_{th} : threshold voltage

Increase MOS performance
relies on our ability to
decrease its dimension

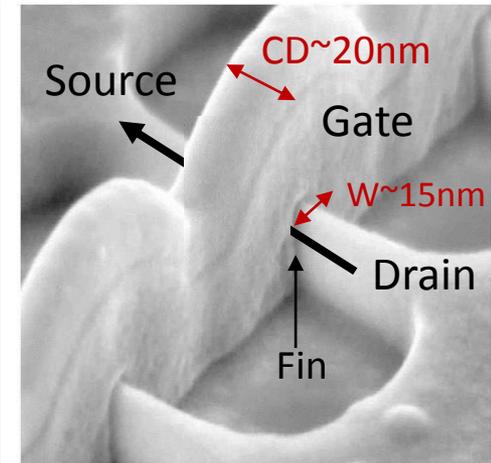
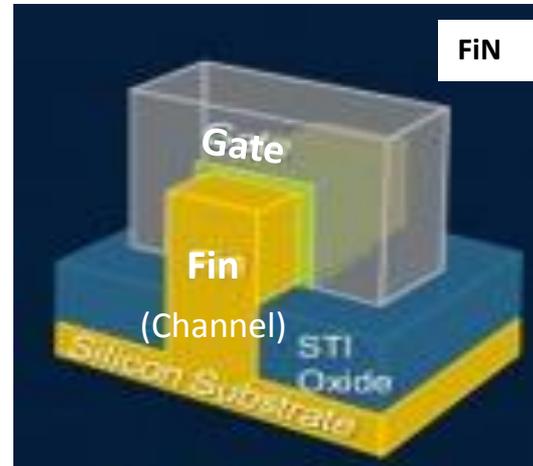
The need for atomic precision etching for today's devices

- ❑ Plasma Technologies must allow the patterning of ultra-thin layers of materials integrated in complex 2D or 3D architectures with atomic precision etching.

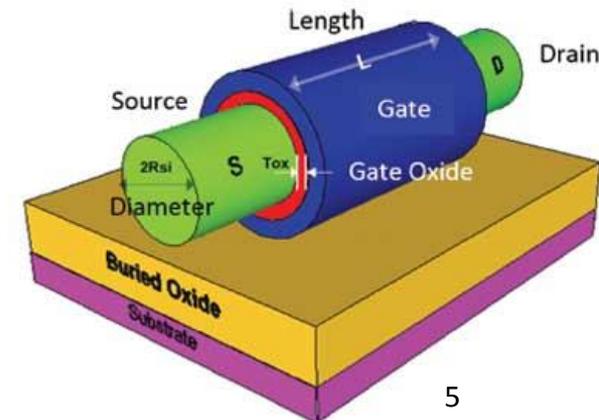
FD SOI devices (2D) (Node sub-20nm)



Fin FET devices (3D) (Node sub-20nm)



Gate all around (Node 5-3nm)



- ❑ Main challenges:

- Ability to control the profile of the patterns: anisotropy (**CD control requirement < 1 nm !**)
- Good selectivity between layers
- No plasma induced damage

Outline

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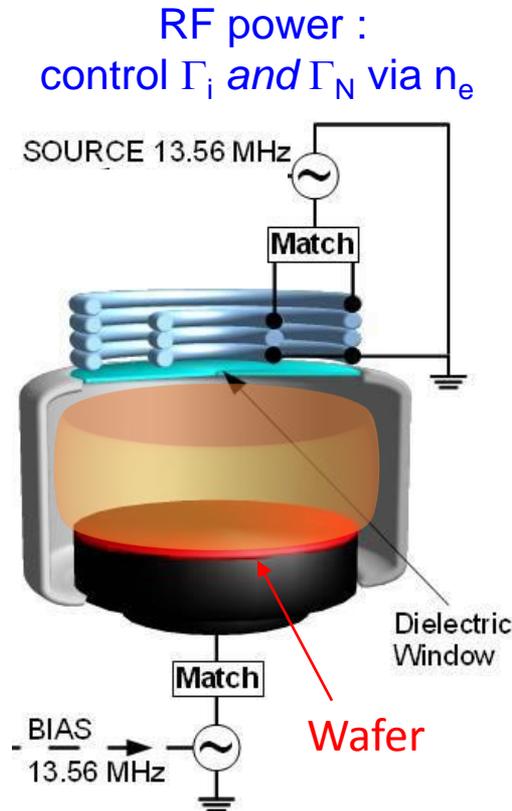
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Inductive Coupled Plasma reactor (ICP)

Semiconductor/metal etching are typically achieved in high-density ICP reactor



RF power 2
(Control ion energy E_i)

→ Independent control of ion energy and ion flux

BUT:

- Impossible to control the Γ_N / Γ_i ratio !
- Ion energy range is *restricted*: 15 → 200 eV

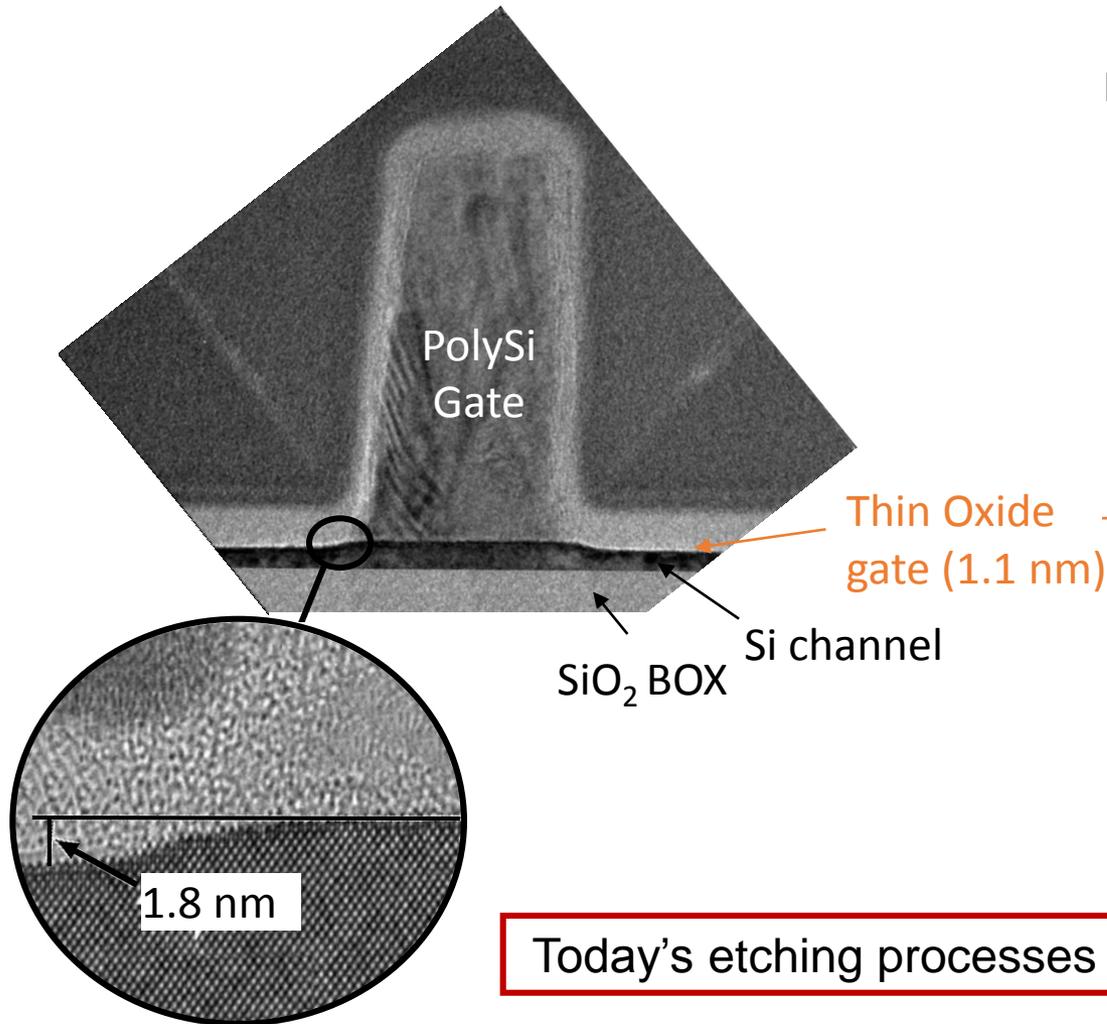
$$V_p = T_e / 2 * \log(M_i / 2\pi m_e) \sim 5kT_e$$

→ About 15 eV for $T_e = 3\text{eV}$

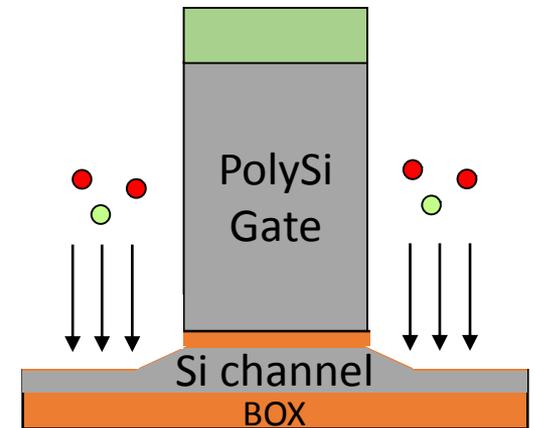
→ Conventional plasma reach their intrinsic limits
→ Need of a major breakthrough

Limitation of typical ICP plasmas in terms of selectivity: ion induced damages

Typical issue: Si-recess in FDSOI transistors during gate etching



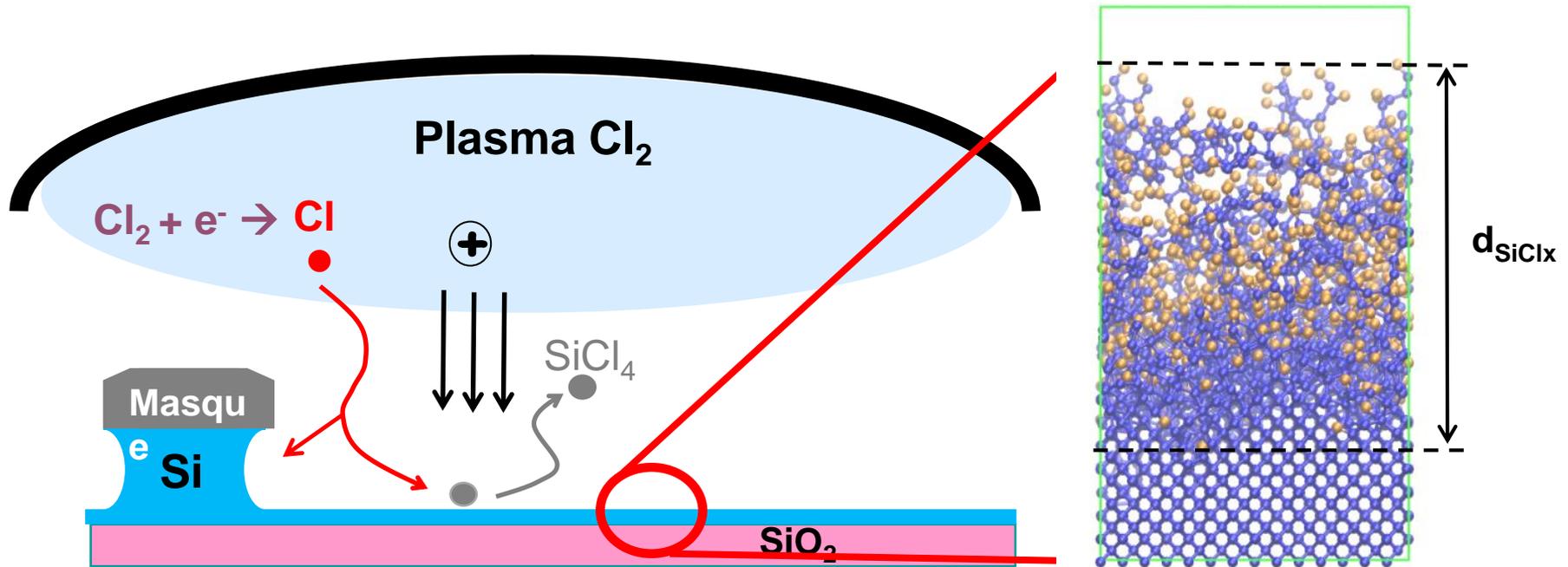
PolySi Gate etching in HBr/O₂ plasma



- Highly selective over SiO₂ oxide gate
- But H⁺ and O⁺ penetration through the oxide gate leads to Si channel oxidation

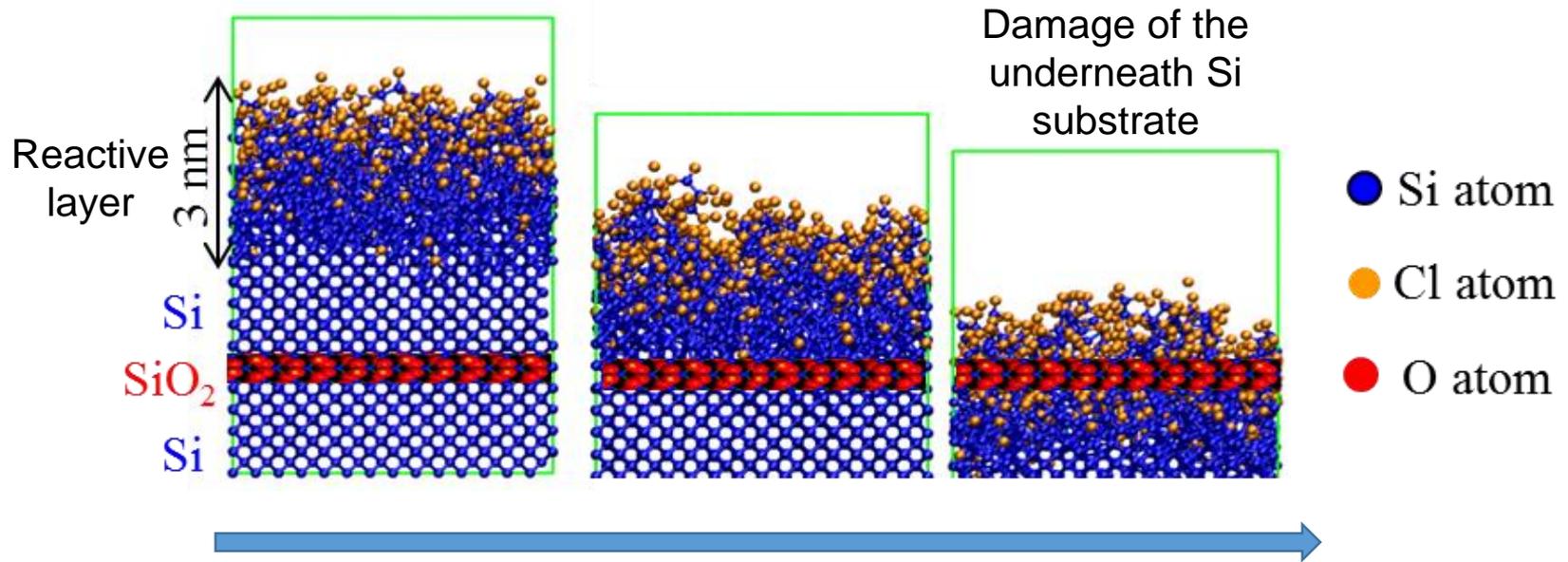
Today's etching processes are not adapted to ultrathin layers

The ion/radical synergy: a limitation for atomic precision etching



- During plasma etching, the surface is bombarded **simultaneously** and **continuously** by fluxes of radicals and energetic ions.
- Incoming ions and neutral species blur the surface forming a **thick mixed reactive layer**.
- In this way, energetic ions work in synergy with neutral chemical species from the plasma to remove film from the wafer surface.

Importance of reactive layer thickness for atomic precision etching

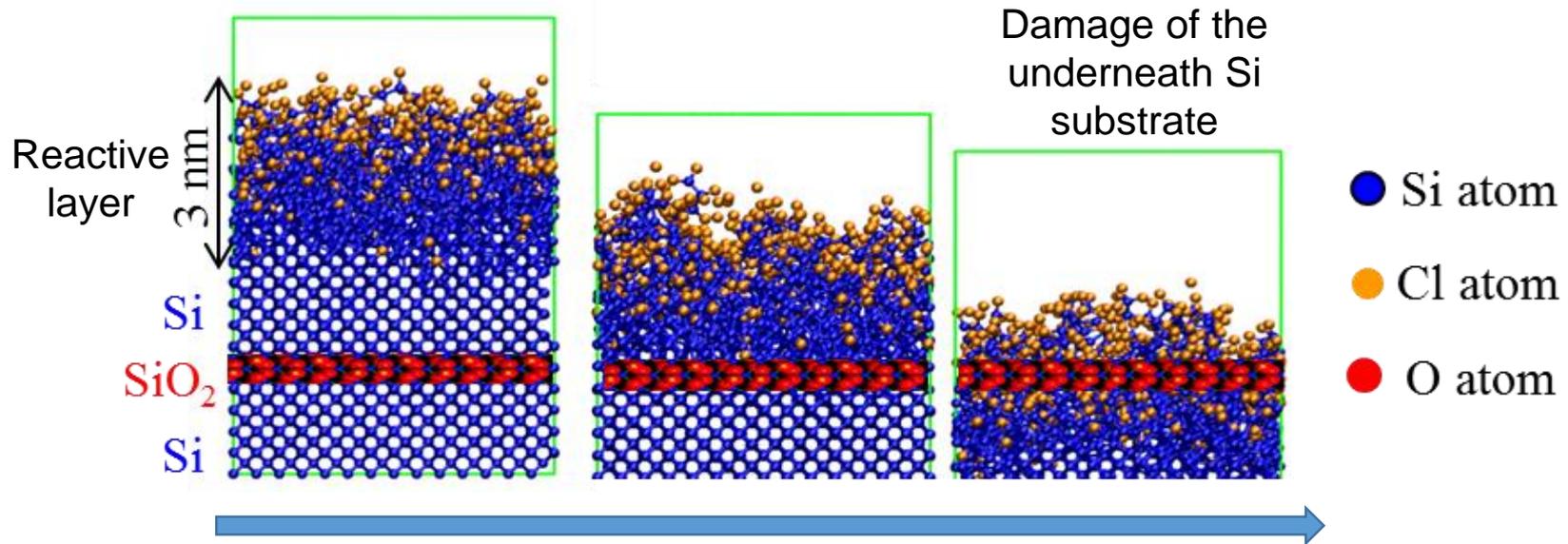


Silicon etching proceeds through the reactive layer propagation

Even if the etch selectivity between materials is high, etch precision can be lost if the ion induced mixed layer (reactive layer SiCl_x layer in this example) is thicker than etch stop layer (thin oxide layer).

Damage and etching are convoluted

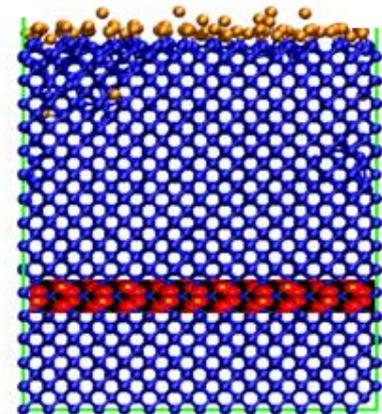
Importance of reactive layer thickness for atomic precision etching



Silicon etching proceeds through the reactive layer propagation

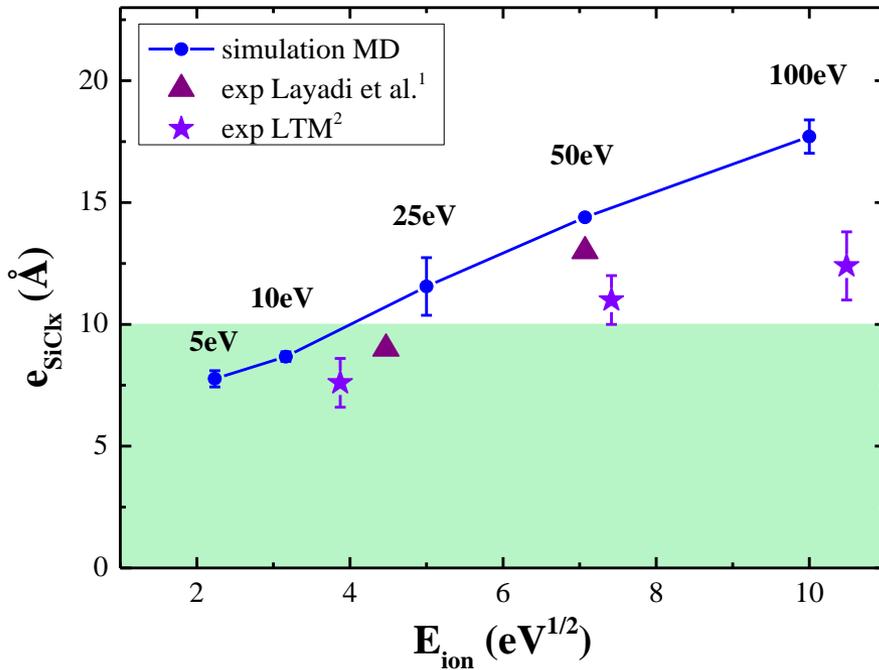
For atomic precision etching: the reactive layer thickness must be minimized and ideally must be thinner than the etch stop layer thickness

Ideal case:
Reactive layer thickness = one atomic layer

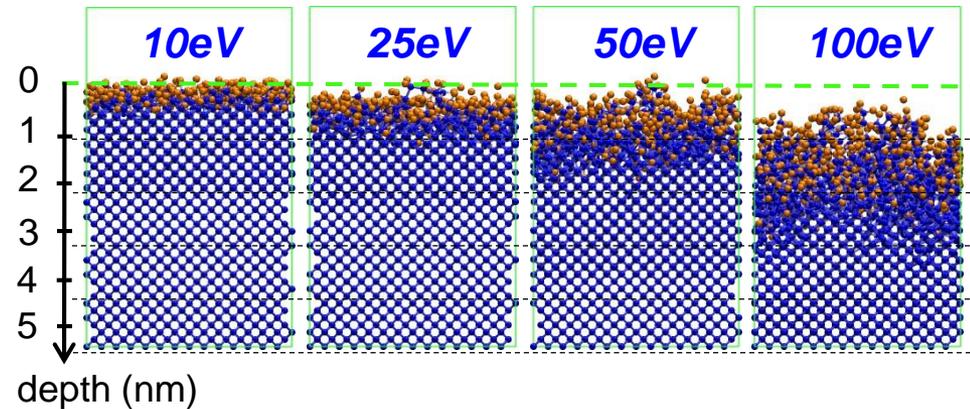


Key parameter for controlling the reactive layer : ion energy

P. Brichon, E. Despiau-Pujo, J. Appl. Phys. 118, 053303 (2015)



Fluence $\text{Cl}^+ = 3,5 \cdot 10^{15} \text{ ions/cm}^2$
 $\text{Cl}/\text{Cl}^+ - \Gamma_n/\Gamma_i = 100$



Experimental conditions:

¹ plasma Cl_2 CW Helicon, 300Ws, 4mTorr

¹ Layadi et al., JAP, **81**, 6738 (1997)

² plasma Cl_2 CW-ICP, 600Ws, 5mTorr

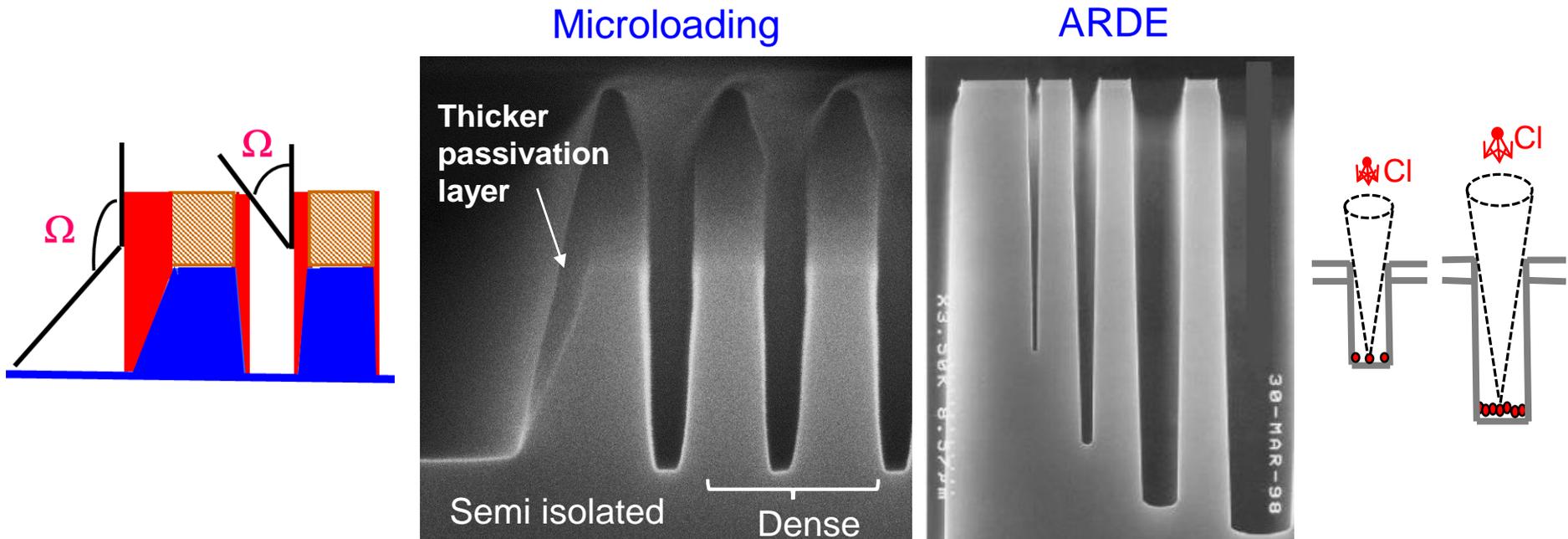
² O. Mourey, thèse en cours au LTM

The reactive layer thickness is driven by the ion energy

→ Necessity to work at very low energy to etch ultrathin layers (<25eV)

Limitation of typical ICP plasmas in terms of CD control and uniformity

- ❑ In conventional plasma etching, etch rates and profiles are strongly dependent on the **fluxes of reactive species and ions** that arrive on the surface
- ❑ A small species **gradient** will generate **local non uniformity** such as ARDE or microloading



→ Such transport-limited phenomena compromise the atomic precision etching

The limitations of current plasma technologies for CD control at the atomic scale originate from the impossibility to **control independently of the fluxes of radicals or ion** bombarding the surface.

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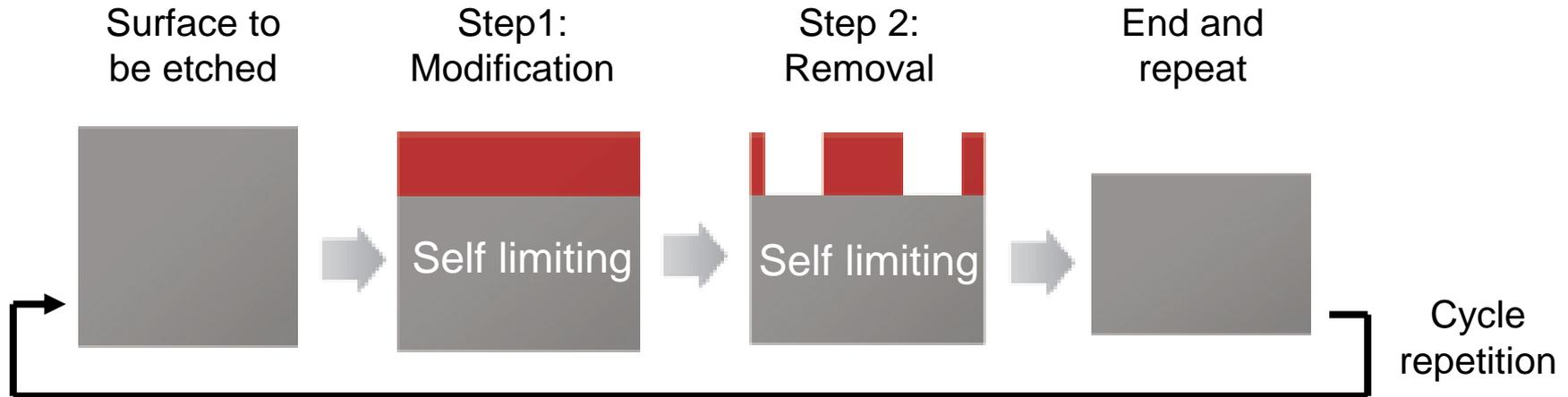
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III. Atomic layer etching concept : ALE

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ALE concept* : a way to achieve atomic precision etching

ALE is a technique that removes thin layers of material using 2 sequential **self-limiting and independent** reactions.



- ❑ **Step 1:** Modification forms a thin reactive surface layer with a well defined thickness

Self-limited reaction: the formation of the modified layer stops when the surface is saturated with reactants

- ❑ **Step 2:** The removal step takes away the modified layer while keeping the underlying substrate intact

Self-limited reaction: the reaction stops when the modified layer is entirely consumed

→ The surface is reset to a pristine or near-pristine state for the next etching cycle.

ALE offers fundamental advantage for atomic precision

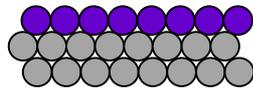
❑ The ALE concept allows to overcome the intrinsic limitations of « plasma etching fundamentals » because of:

1. **Separation** into a sequence of **independent** unit process reactions
2. **Self-limited** reactions

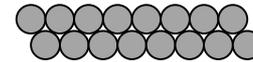
❑ Consequences on :

1. Surface damage

Atomically smooth surface
after modification

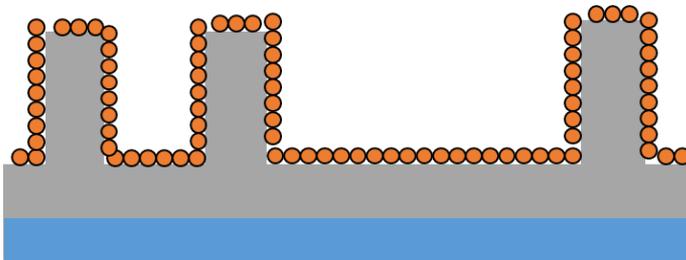


Flat, smooth surface, Same
composition after removal



2. Uniformity, CD control, ARDE

Identical surface coverage at both the wafer
and pattern scale during the modification

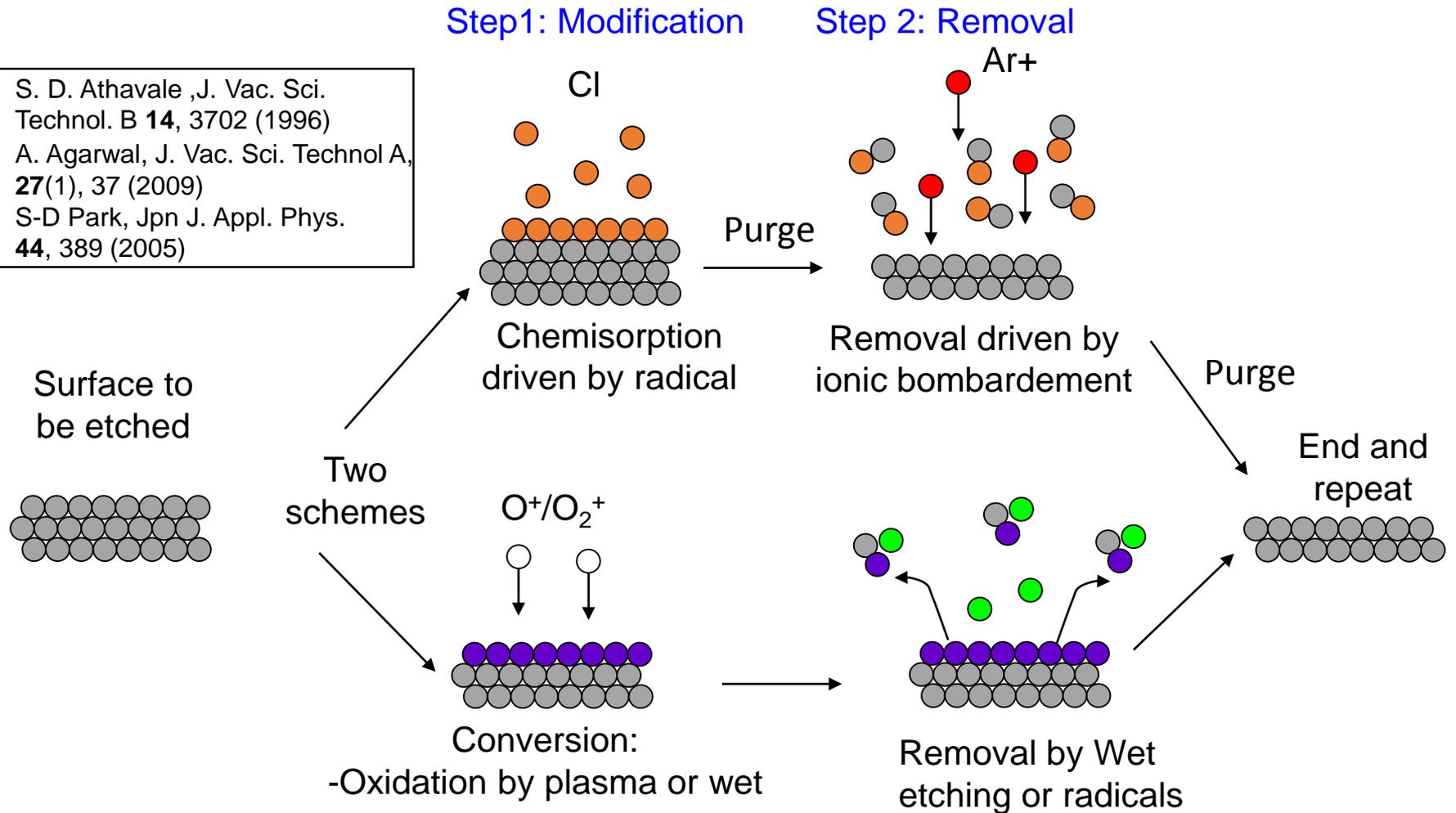


Same etch depth and profile for any
patterns on the wafer



ALE concept : a way to control independently neutral and ion flux

- S. D. Athavale ,J. Vac. Sci. Technol. B **14**, 3702 (1996)
- A. Agarwal, J. Vac. Sci. Technol A, **27**(1), 37 (2009)
- S-D Park, Jpn J. Appl. Phys. **44**, 389 (2005)



- J. Lin, et al., IEEE Elec. Dev. Lett., **35**, 440,(2014)
- X. Cao, Microelectron. Eng., **67**, 333 (2003).

ALE concept : from lab to fab

- ❑ ALE has been studied for over 25 years in laboratory but never implemented into semiconductor high-volume manufacturing because low throughputs and high cost-efficiency

Ex: S-D Park, Jpn J. Appl. Phys. 44, 389 (2005) -ALE of Si with Cl₂ thermal adsorption followed by Ar⁺

ER= 1.36 A/cycle

But 1 cycle = 85s

(20s chemisorption-20s purge-40s removal-5s purge)



14 min to etch 1nm!!

- ❑ Now that the major industrial concern is ATOMIC PRECISION etching, the ALE concept creates renewed interest
- ❑ How to implement ALE concept with industrial constraints?

1nm in 10s acceptable



Develop plasma technologies that allow:

- Low ion energy (<25eV)
- An independent control of radical and ion fluxes

- ❑ Which technologies?

- Low Te plasma reactor
- Pulsed plasmas
- Fast injection pulsed plasma
- Smart etch technology

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1. Low Te

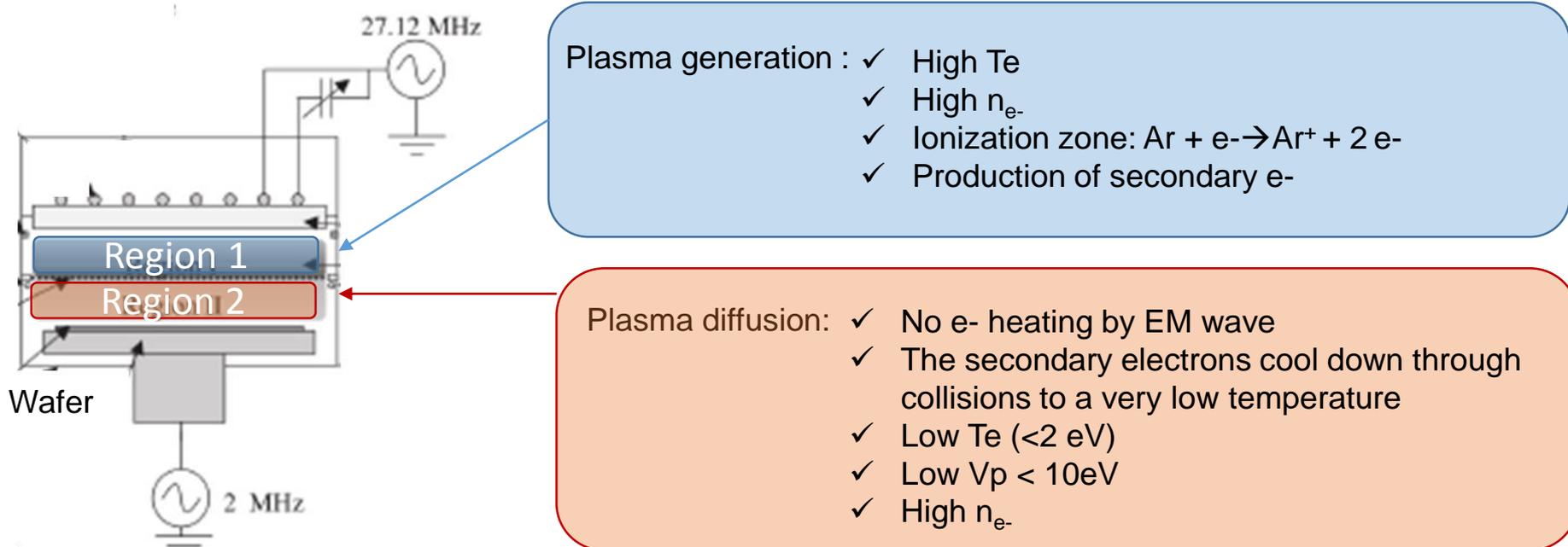
2. Pulsed plasmas

3. Fast gas injection plasma

4. Smart etch technology

“Low T_e ” plasmas

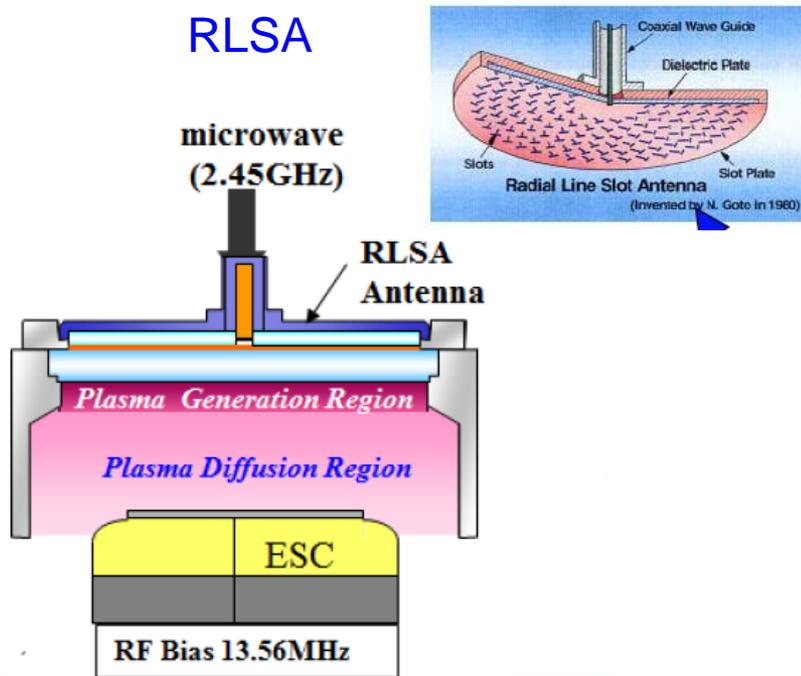
- ❑ Design a reactor chamber capable to provide electrons with low electronic temperature near the wafer surface ($T_e < 1 \text{ eV}$)
 - Very low ion energy achievable : $V_p - V_f \sim 5kT_e < 5 \text{ eV}$
- ❑ How?
 - By separating of the plasma generation region from the wafer plasma region



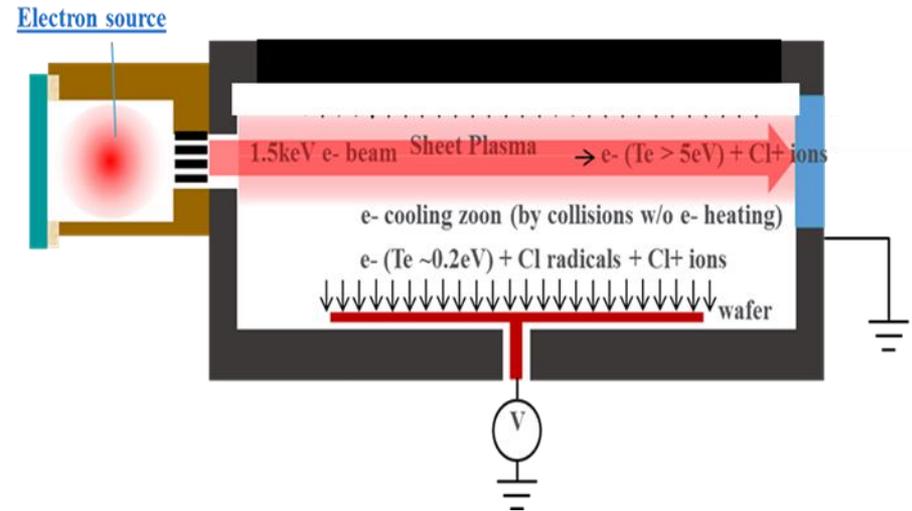
An ideal Low T_e source has a sufficient ionization population with a reduced dissociation population while maintaining a low bulk T_e

"Low T_e " plasma reactors

□ Several designs



Electron beam generated plasma

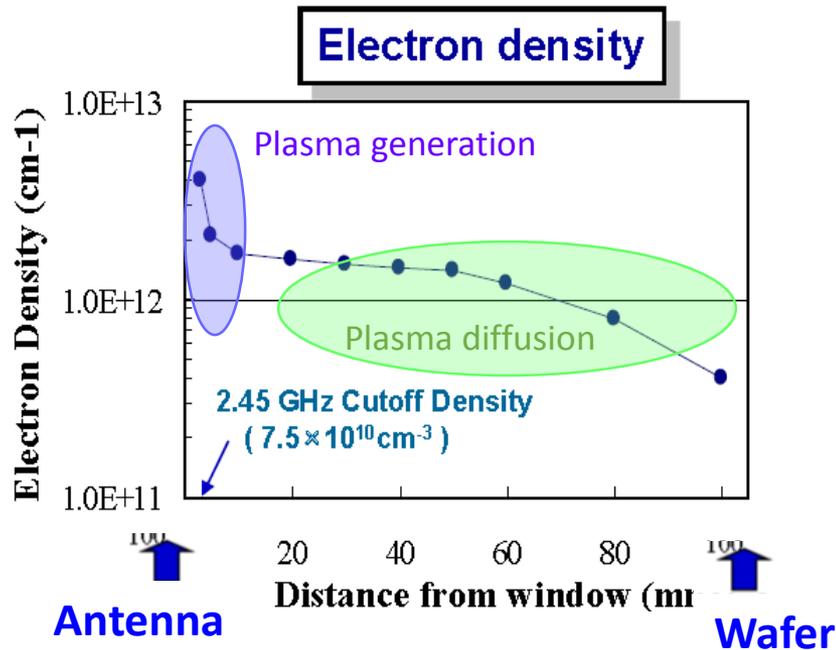


- Surfacar wave Plasma generated by RLSA antenna*
 - *M. Ando, *IEEE Trans. Ant. propag.* **AP-33**, 1347, (1985)
 - Goto et al., *Jpn. J. Appl. Phys.*, **42**, 1887 (2003)
- RLSA technology implemented **in industrial plasma reactor in 2010 by TEL**
 - C. Tian, *J. Vac. Sci. Technol. A* **24**, 1421, (2006)
 - Q. yang, *ECS Transactions*, **52** (1) 275-280 (2013)

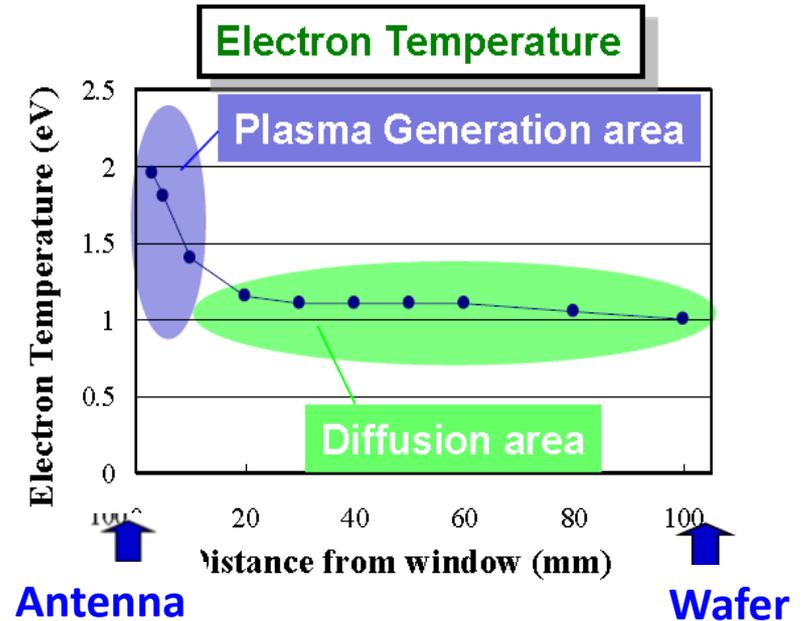
- Concept exists from late 1970's used for deposition
 - R. A. Dugdale, *J. Mat. Sci.* **10**, 896 (1975)
- Naval research laboratory (NRL) is the first to develop a plasma reactor based on this concept
 - R. A. Meger, "Large Area Plasma Processing System (LAPPS)" U. S. Pat. 5,874,807 (1999).
 - S.G. Walton et al, *ECS J. Of Sol. State Sci.Tech.*, **4** (6) N5033 (2015)
- More recently, TEL and AMAT show some interest in this technology. No industrial tool yet
 - L. Chen, *PlasmaSources Sci. Technol.* **22**, 065015 (2013).
 - S. Rauf, *61st AVS Int. Symp. and Exhib., Baltimore* (2014).

“Low T_e ” plasma properties

- Te and Ne in a RLSA reactor



Q. yang, ECS Transactions, **52** (1) 275-280 (2013)



- RLSA can sustain an over-dense high density plasma from a few mTorr to 1torr (ICP<100mT)

- Te and Ne varies only slightly with chamber pressure
→Control of Γ_N independently of Γ_i

“Low T_e ” vs ICP summary

Design Element	ICP	Low T_e
Te	2-4eV	< 2 eV
Minimum ion energy	15-20 eV	<10 eV
VUV flux	high	low
Ion flux	10^{10} - 10^{11}	10^{10} - 10^{12}
Dissociation/Etch byproducts redissociation	high	low
Ions and radical production	coupled	uncoupled

Minimum surface damage

Reduced microloading and ARDE

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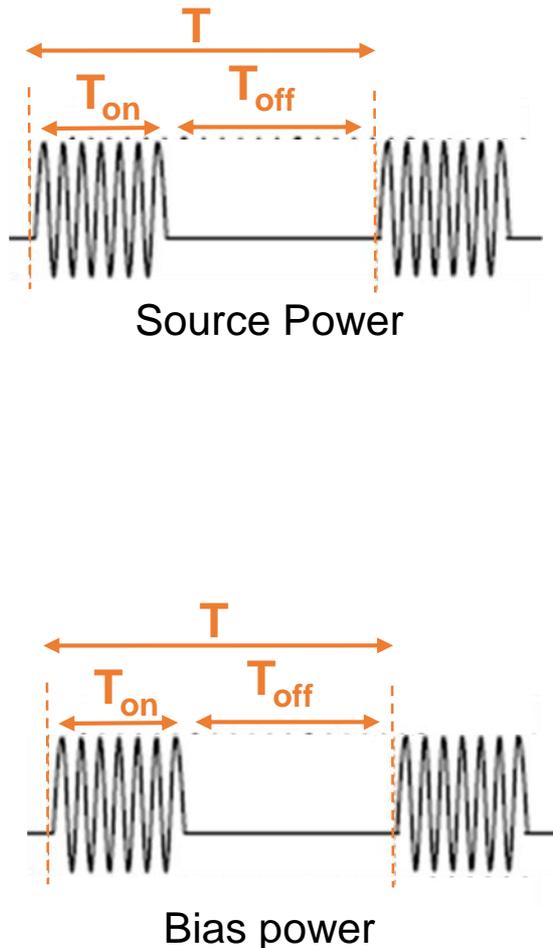
2. Pulsed plasmas

3. Fast gas injection plasma

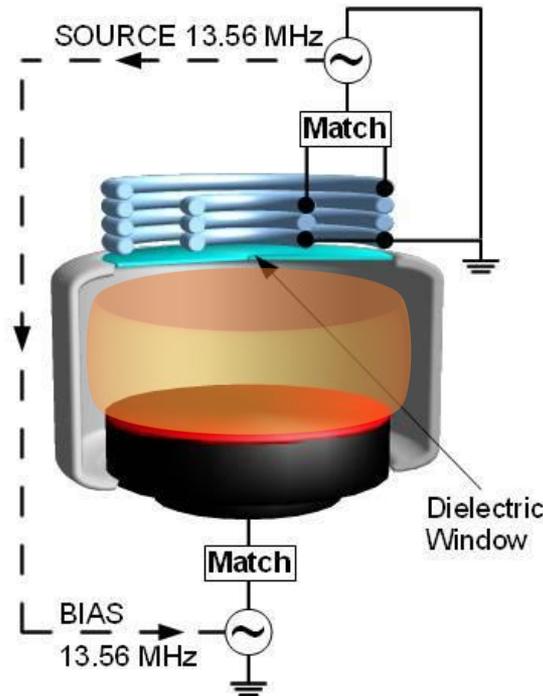
4. Smart etch technology

Pulsed plasma technologies

- ❑ **Principle:** modulation of the plasma power supplies (turned « on » and « off »)
- ❑ First studies in the 90's: source pulsing only (S. Samukawa ,Appl. Phys. Lett. 63 2044 (1993))
- ❑ In 2009, AMAT commercialized an ICP reactor equipped with **Pulsync™**



S. Banna, et al., IEEE Trans. Plasma Sci. 37, 1730 (2009).



Two new knobs:

- Frequency: $f = 1/T$
- Duty cycle: $DC = \frac{T_{on}}{T_{on} + T_{off}}$

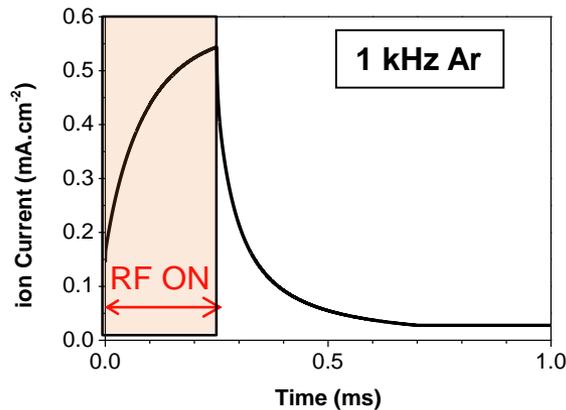
Three new regimes:

- Source pulsing only
- Bias pulsing only
- Synchronized pulsing

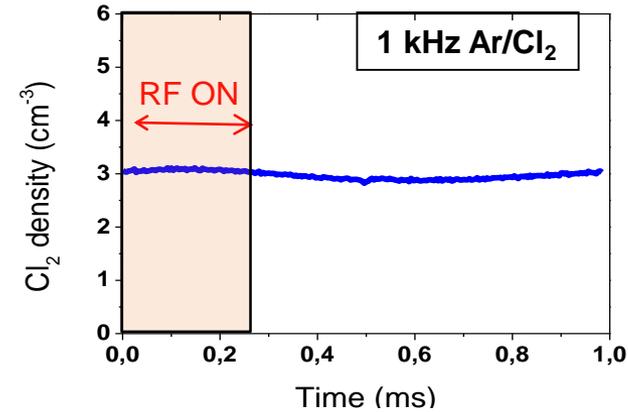
Pulsed plasmas: important timescales

For typical etching applications the pulsing frequency is $> 1\text{kHz}$ ($T < 1\text{ms}$)

Ions kinetics



Radicals kinetics

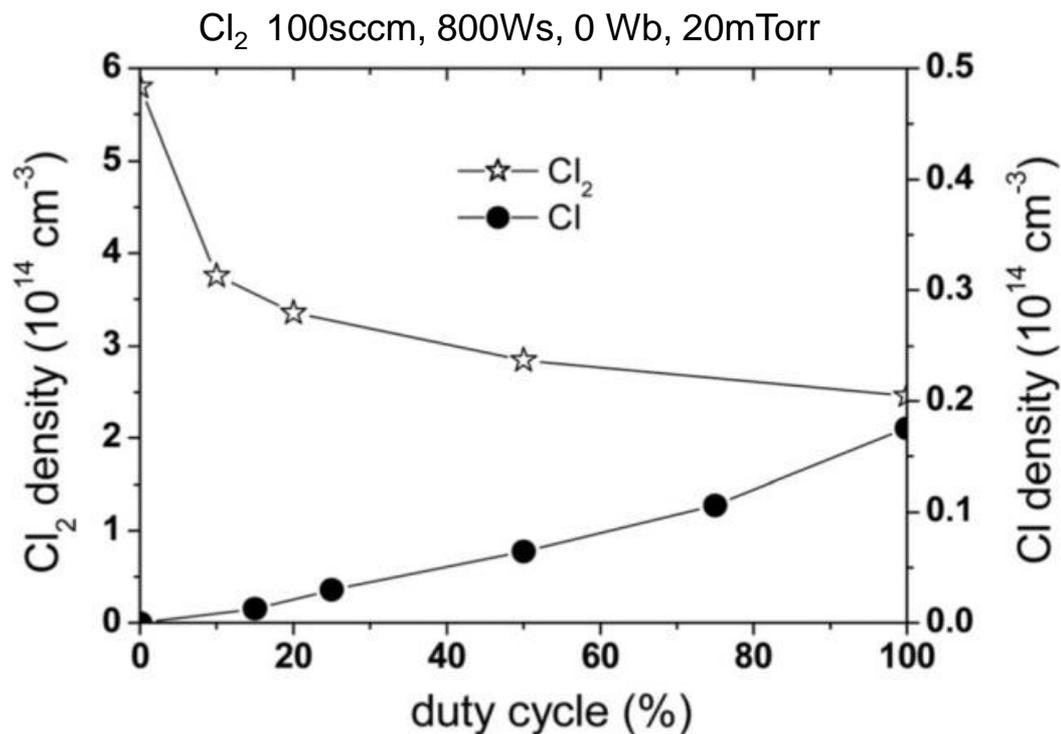


- Ion production: 100-1000 μs
- Ion losses (ambipolar diffusion) $\sim 100\mu\text{s}$
- Radical production: 100-1000 μs
- **Radical losses (diffusion, pumping) $> \text{ms}$**

Radical density is not modulated during plasma pulses
while ion flux is strongly modulated

Pulsing the ICP power allows independent control of the ion flux and radicals flux

Impact of the duty cycle on the plasma chemistry

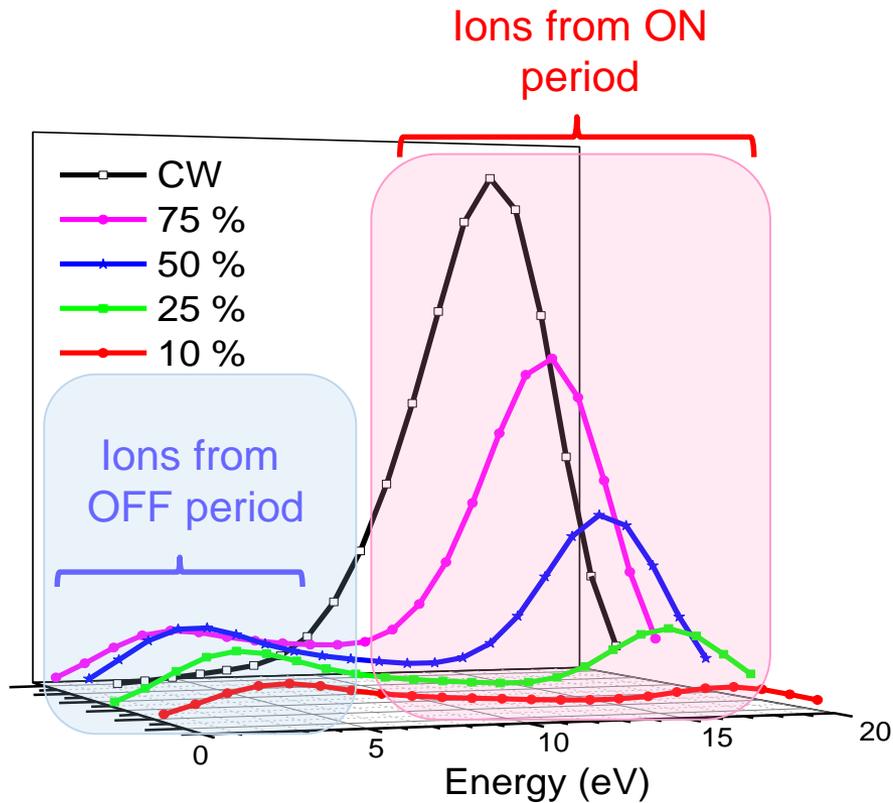


Decreasing Dissociation

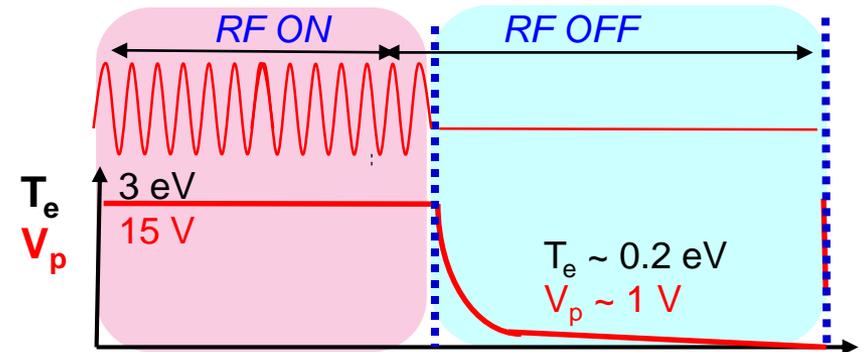
Duty cycle is the major knob and controls dissociation

Pulsed plasmas with small duty cycle = reduced chemical reactivity

Impact of the duty cycle on the ion energy distribution



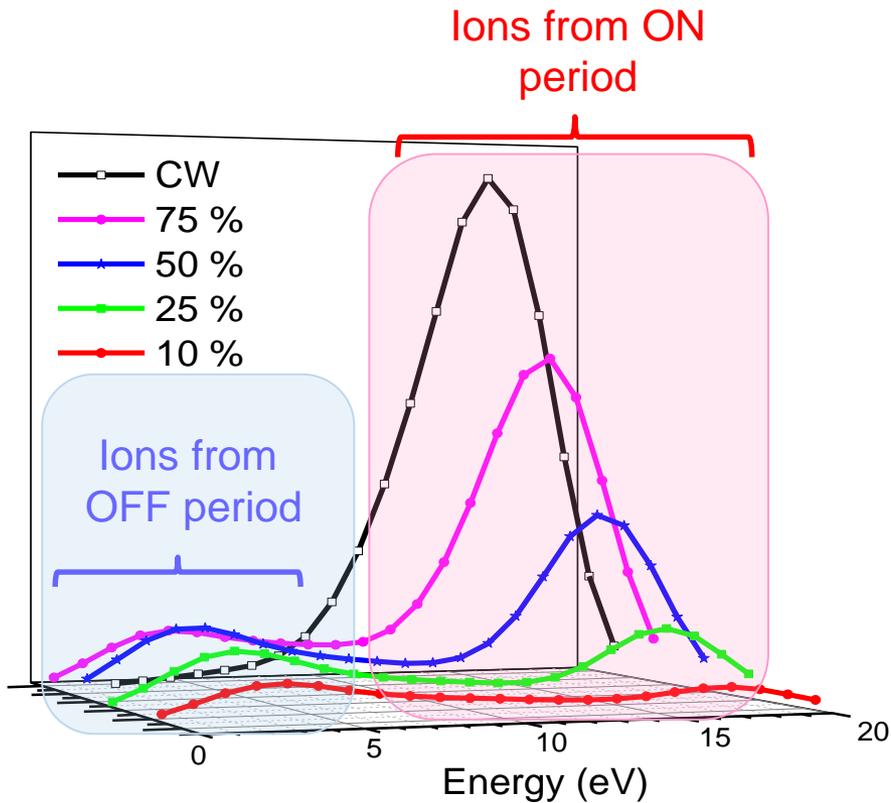
No bias applied to the substrate
(in continuous plasma : $E_i \sim V_p$)



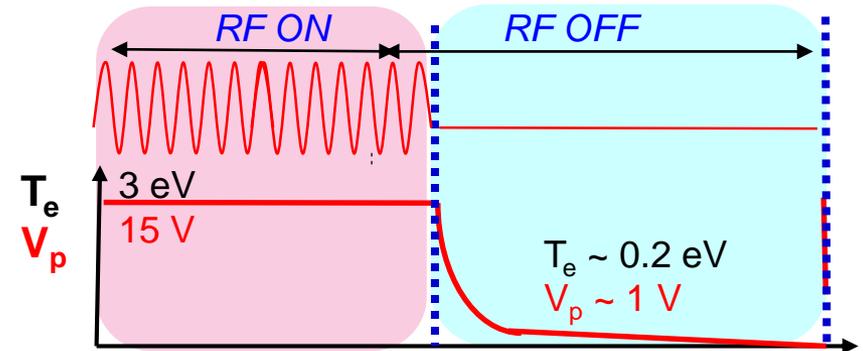
- ❑ When pulsing the plasma, the ion distribution function switches from unimodal to bimodal
- ❑ During the ON period: the ions are accelerated towards the wafer by $V_p \sim 15 \text{ eV}$ (No bias power)
Similar behavior for continuous and pulsed plasma
- ❑ During the OFF period: T_e and consequently V_p decrease \rightarrow low ion energy ($< 10 \text{ eV}$)

By pulsing the plasma, low ion energy regime can be reached

Impact of the duty cycle on the ion energy distribution



No bias applied to the substrate
(in continuous plasma : $E_i \sim V_p$)



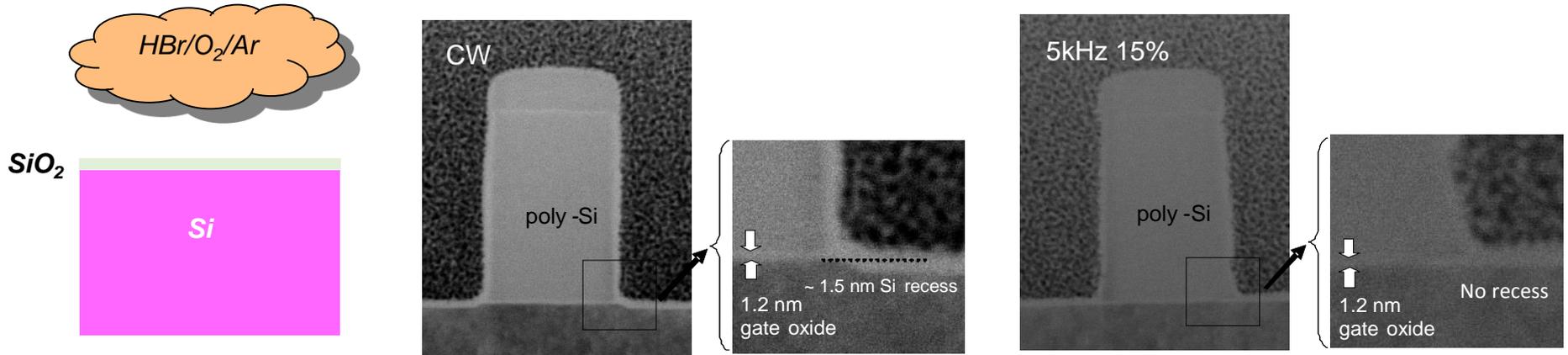
In an ICP plasma pulsed with a small duty cycle the wafer is bombarded by:

- **Low flux of low energy ions**
- **Low flux of reactive radicals**

→ **key point to reduce surface damages and local non uniformity**

Example of application

Minimizing Si recess during the over-etch of gate etching processes



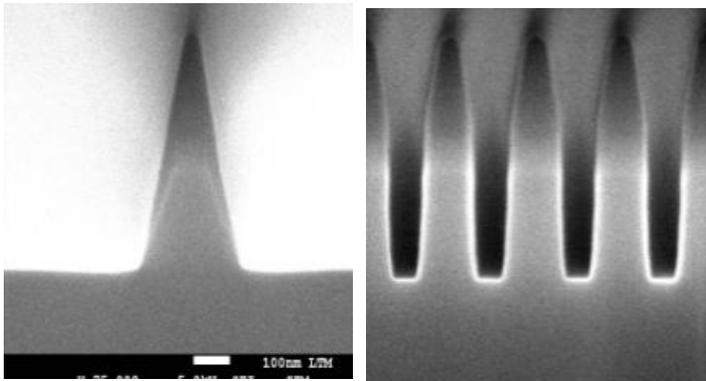
From Petit-Etienne et al. *J. Vac. Sci. Technol B* 30(4), 1071 (2012)

Minimizing microloading effect during PolySi etching in HBr/O_2

Continuous plasma

Isolated

Dense

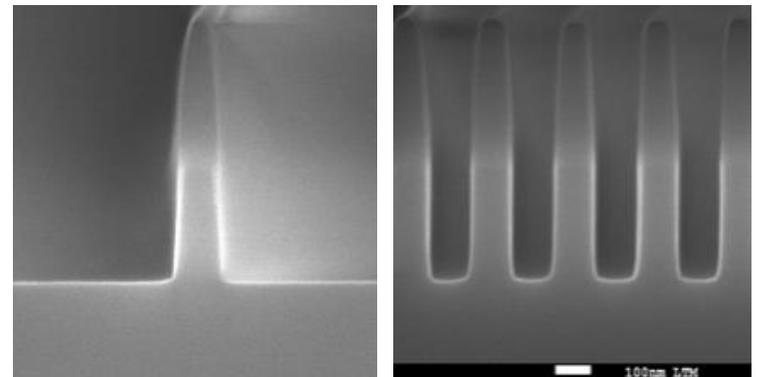


Microloading effect

Pulsed plasma: DC=20%, 1kHz

Isolated

Dense



**Identical iso-dense profile
Better selectivity over HM**

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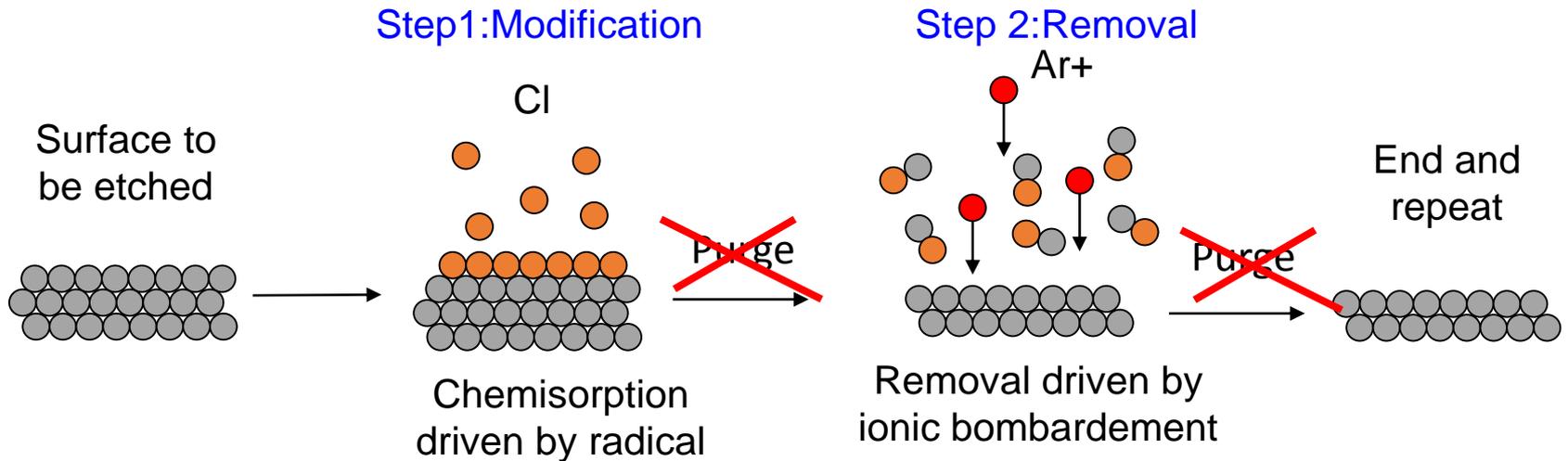
1. Low Te

2. Pulsed plasmas

3. Fast gas injection plasma

4. Smart etch technology

How can we reproduce the two steps of the ALE concept in an industrial reactor with acceptable time constraints?

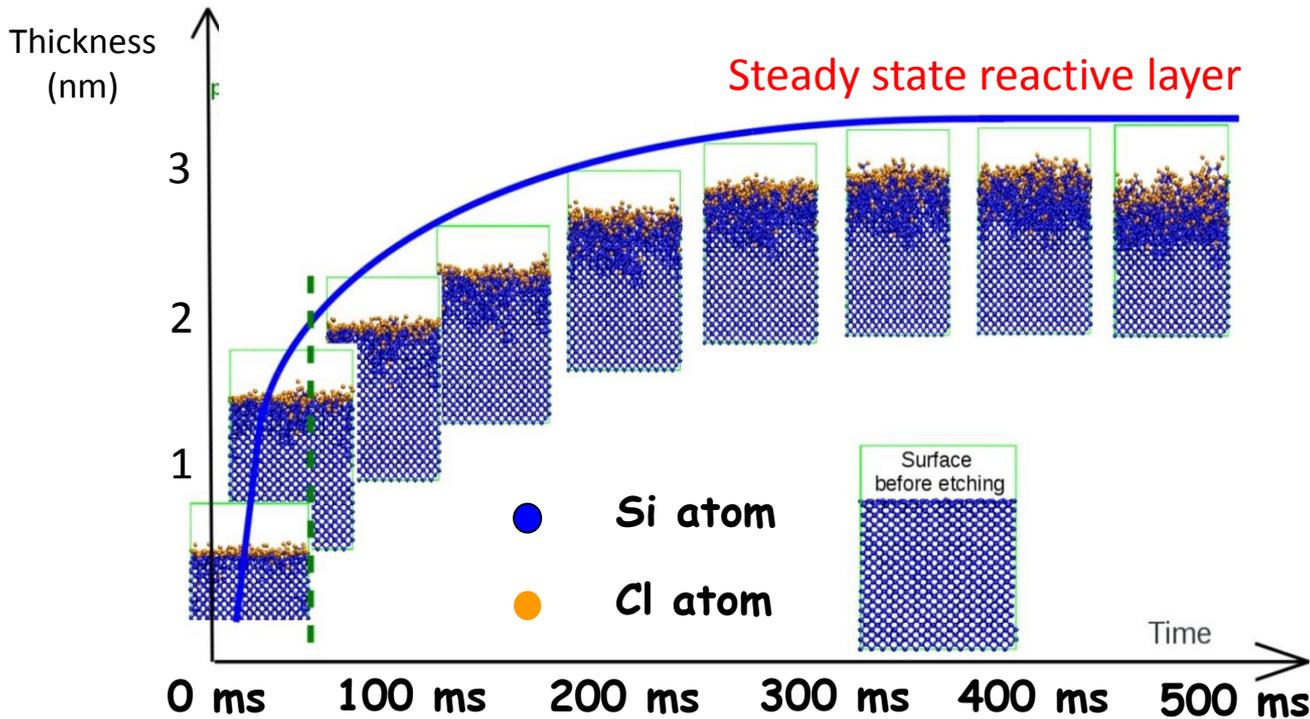


□ Step 1: plasma needs to operate in a regime that forms sub-1nm reactive layer

→ Ion energy <25eV → Hardly achievable with conventional ICP reactor

→ Can we stop the growth of the reactive layer before it reaches 1 nm thickness ?

A dynamic control of the reactive layer thickness

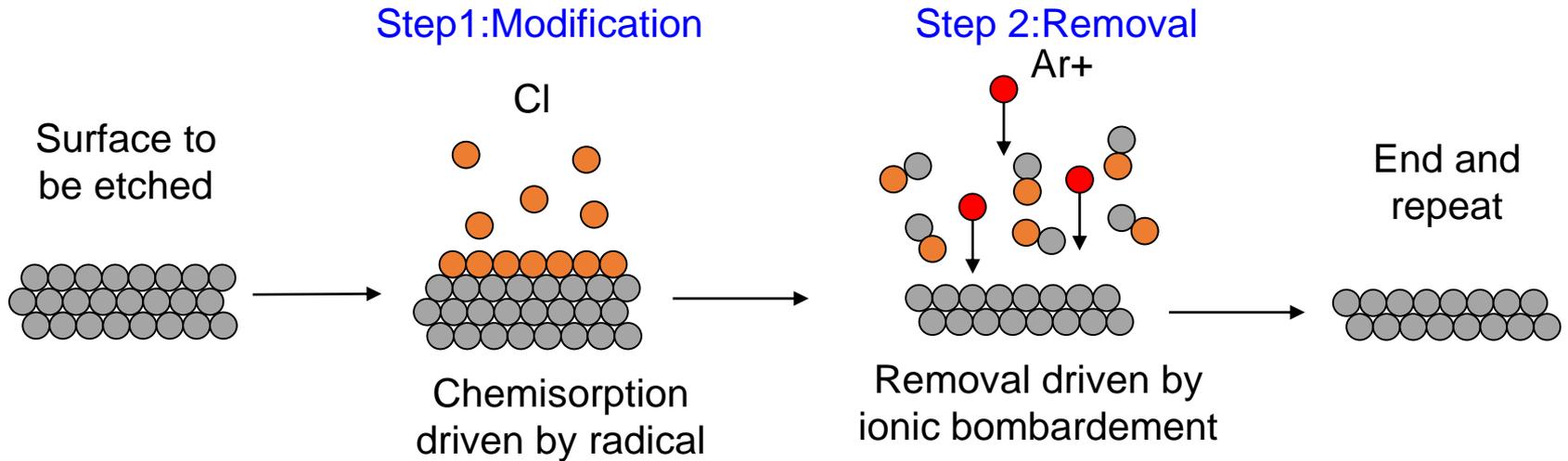


- Typical time to reach 1nm thick reactive layer ~ 100-200 ms
- Sub-1 nm thick reactive layer can be obtained if the reactive gas injection in the plasma chamber is stopped before the reactive layer reaches its steady state thickness



Technically feasible by **fast gas switching technology** (if $t > 100\text{ms}$)
Patent US 8133349 B1 (2012) "Rapid and uniform gas switching for a plasma etch process"

How can we reproduce the two steps of the ALE concept in an industrial reactor with acceptable time constraints?

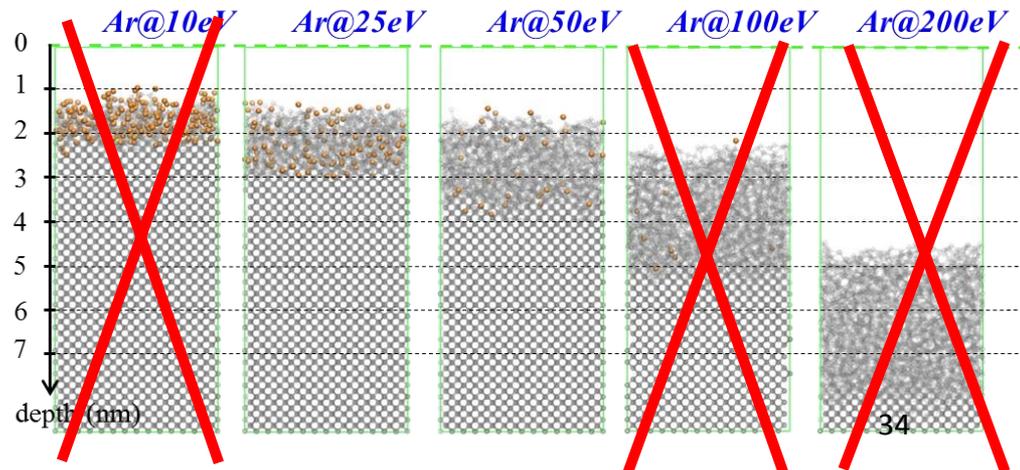


- Step 2: bombarding particles are used to provide enough energy to break the Si-Si bonds that have been weakened by adsorbed chlorine.

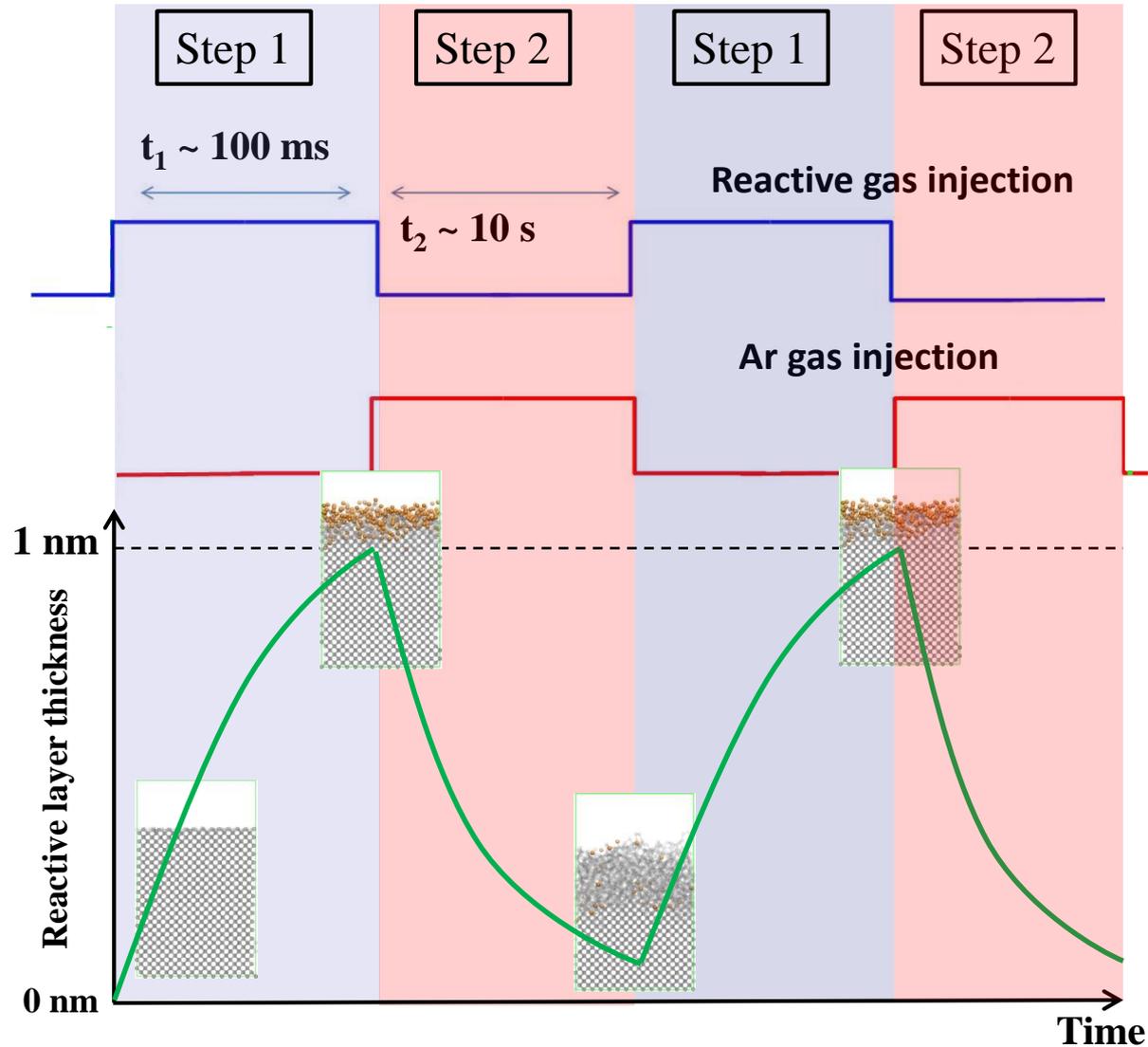
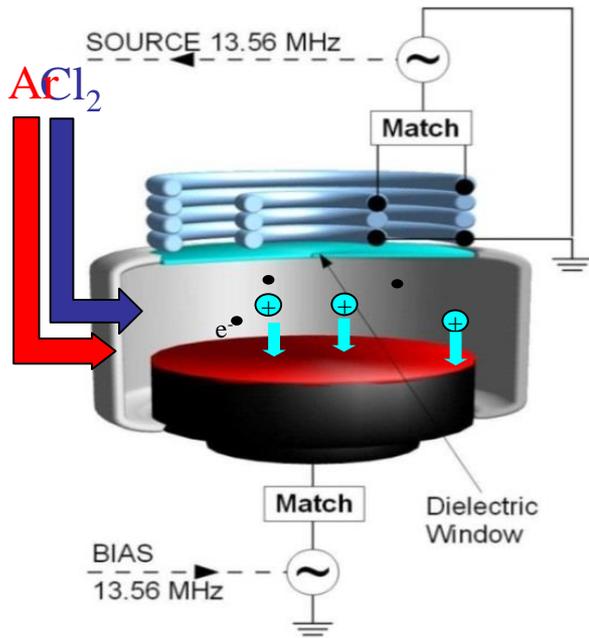
MD simulations show that 25-50eV ion energy range allows

- SiCl removal with acceptable time constraint
- with limited Si amorphization

After 10s plasma for ion flux of 2mA/cm²

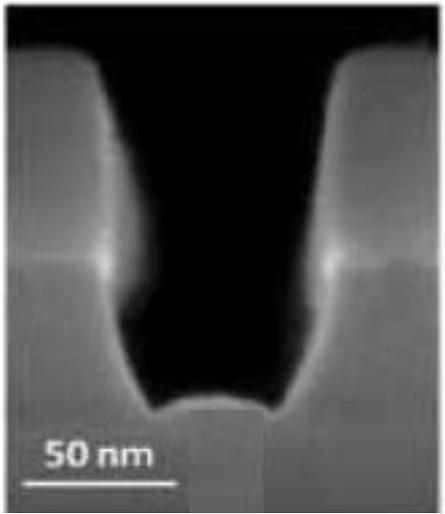


Atomic Precision etching using Fast gas injection

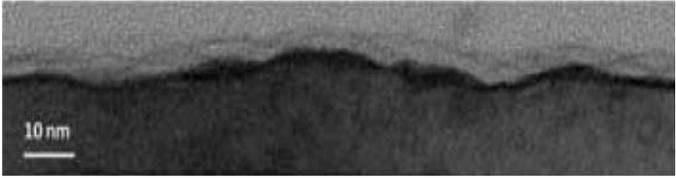


Demonstration of Atomic Precision etching using Fast gas injection

ICP
(Ar/Cl₂ plasma)

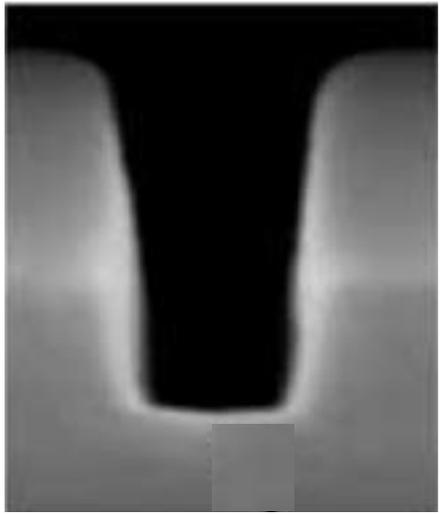


Microtrenching

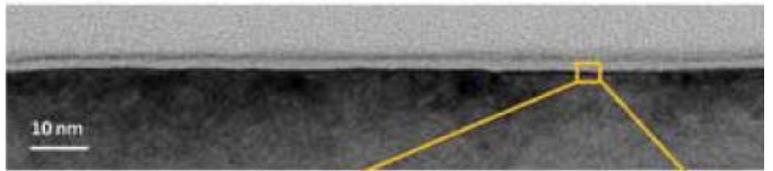


Rough

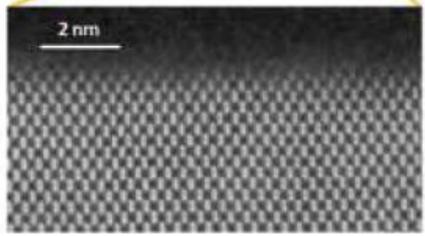
Plasma enhanced ALE
(Cl₂ followed by Ar)



Flat etch front



Smooth



Outline

I. Introduction

II. Limitations of current plasma technologies

III. Atomic layer etching concept : ALE

IV. From lab to fab

1. Low Te

2. Pulsed plasmas

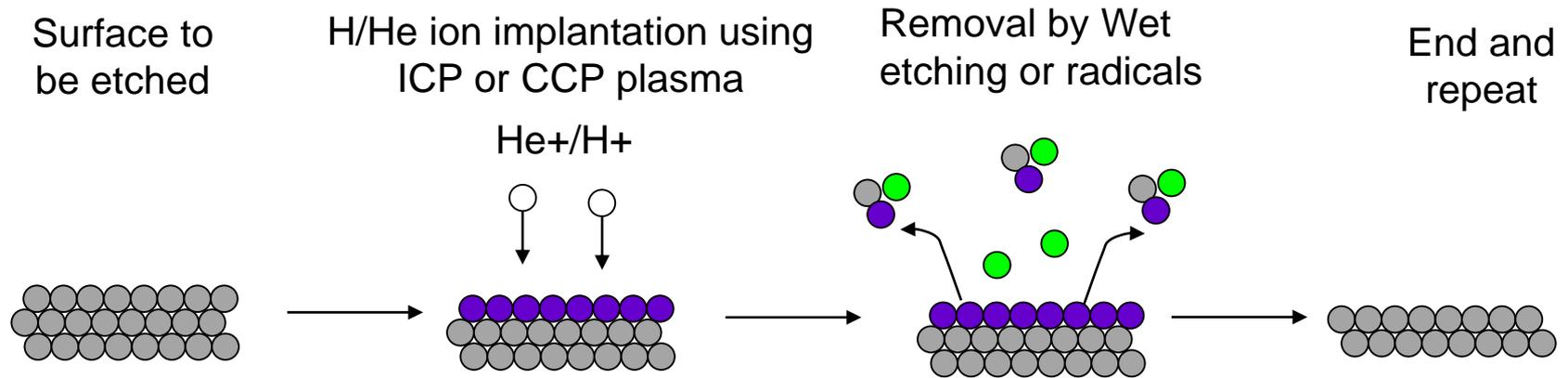
3. Fast gas injection plasma

4. Smart etch technology

Smart etch Technology :

An alternative process for thin layer etching

- ❑ Based on the ALE concept using a « conversion » modification step
- ❑ Developed for SiN or SiO₂ materials

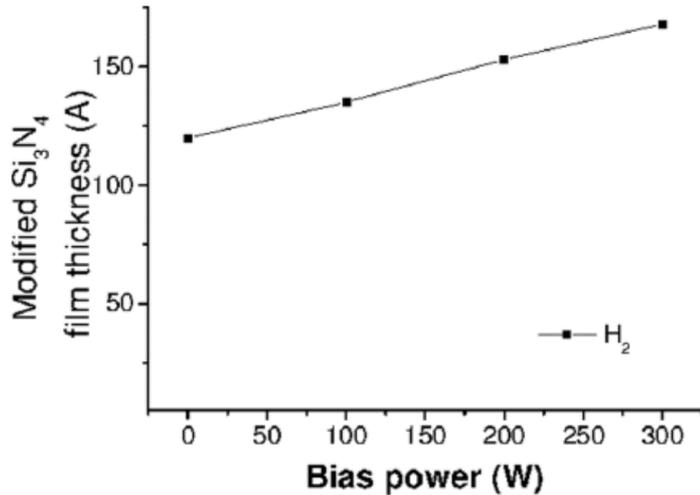


- ❑ **Step 1:** Implantation of light ions (He⁺ or H⁺) to modify the material without sputtering it
→The modification depth is driven by ion flux and energy
- ❑ **Step 2:** Removal of the modified layer by chemical action: Wet etching or radicals produced by downstream plasma
→The chemical step must present high etch selectivity over the non modified layer

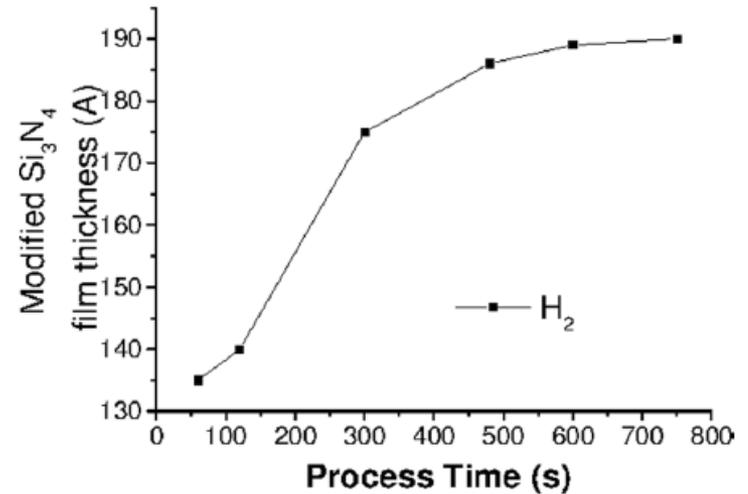
Smart etch Technology: Proof of concept

Step 1: Implantation of light ions

Impact of ion energy



Impact of ion dose (ion flux*time)



N. Posseme *et al*, Appl. Phys. Lett. 105, 051605 (2014)

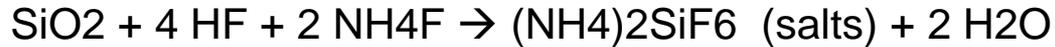
- ❑ The modified layer thickness is driven by the ion energy
- ❑ This step is self-limited: at a given ion energy, the modified layer thickness saturates above a certain ion dose.

→Respect of the ALE criteria

Smart etch Technology: Proof of concept

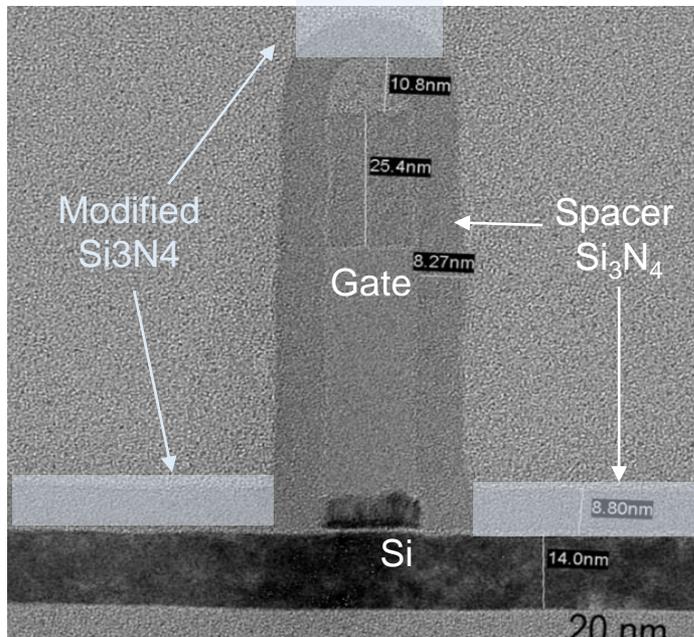
Step 2: removal by NF₃/NH₃ downstream plasma

- ❑ Formation of HF and NH₄F by NH₃ and NF₃ dissociation and subsequent recombination
- ❑ Etching proceeds through the formation of salts that can sublime for T>100°C

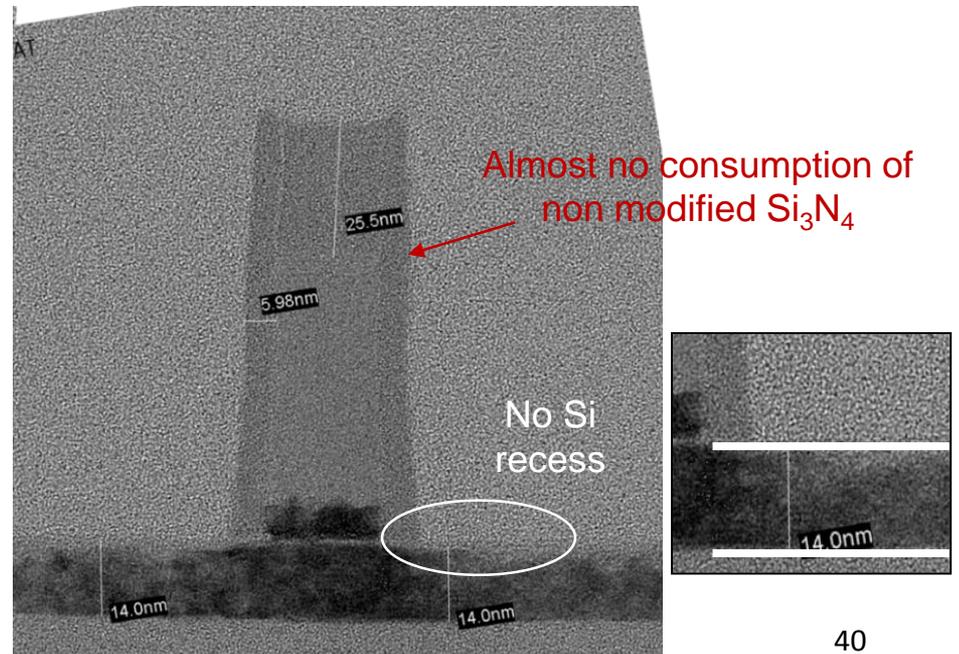


- ❑ Etch mechanisms of the modified Si₃N₄ not well understood
- ❑ However the smart etch technology shows remarkable capability to etch modified Si₃N₄ layer with excellent selectivity over the non modified Si₃N₄

After H⁺ implantation



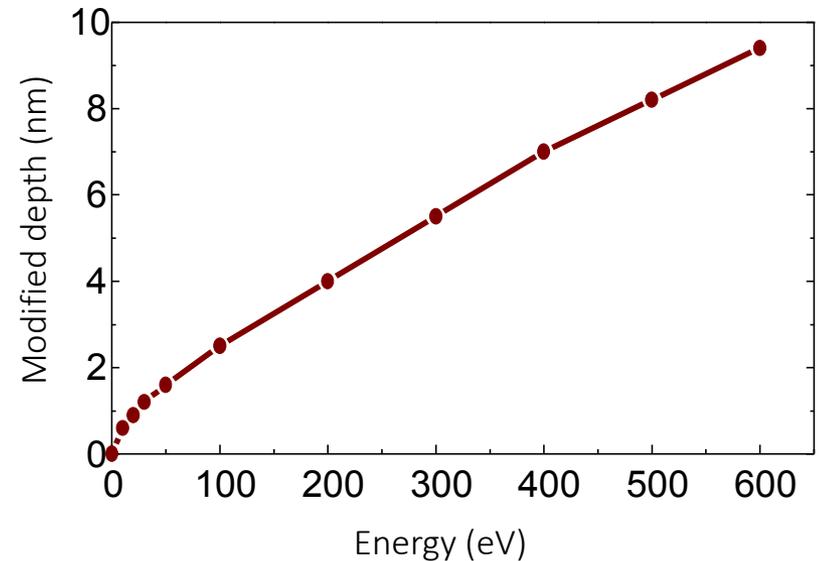
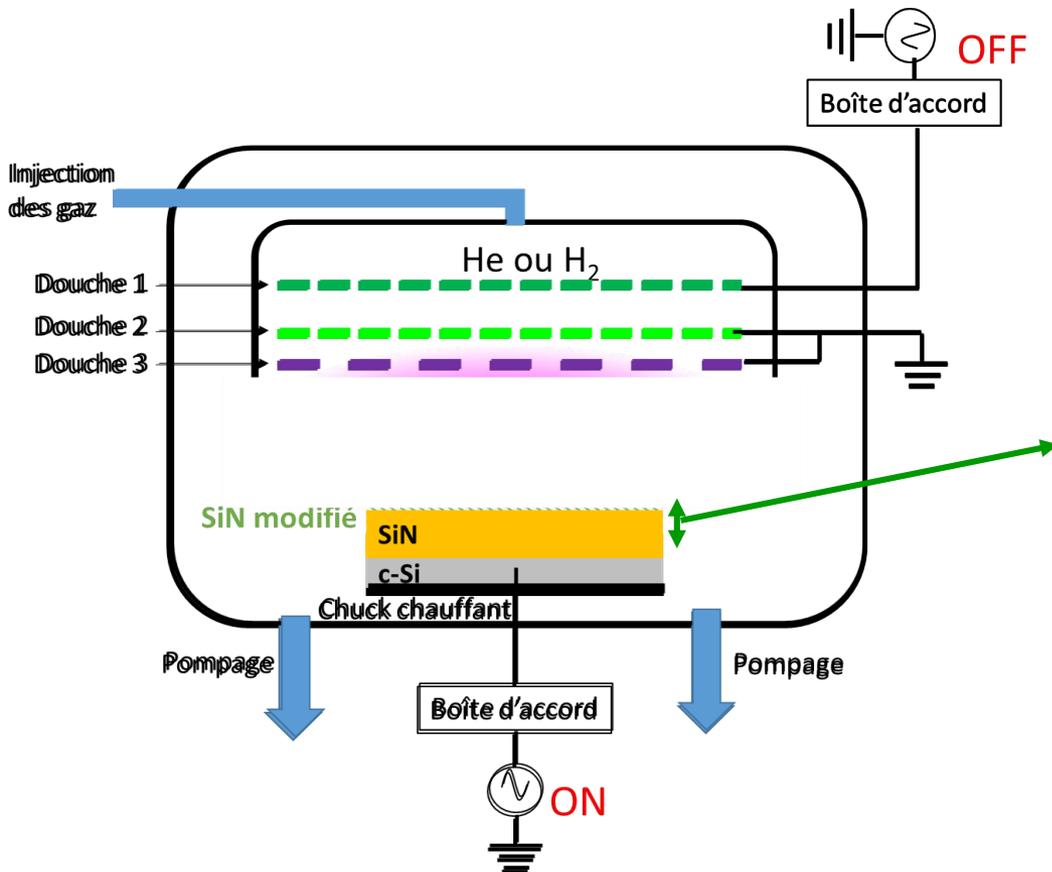
After NH₃/NF₃ downstream plasma



Towards a technological rupture for atomic precision etching

AMAT proposes a new reactor design that allows to achieve the two ALE steps in the same chamber

1. Step1: modification by ion implantation generated by CCP plasma



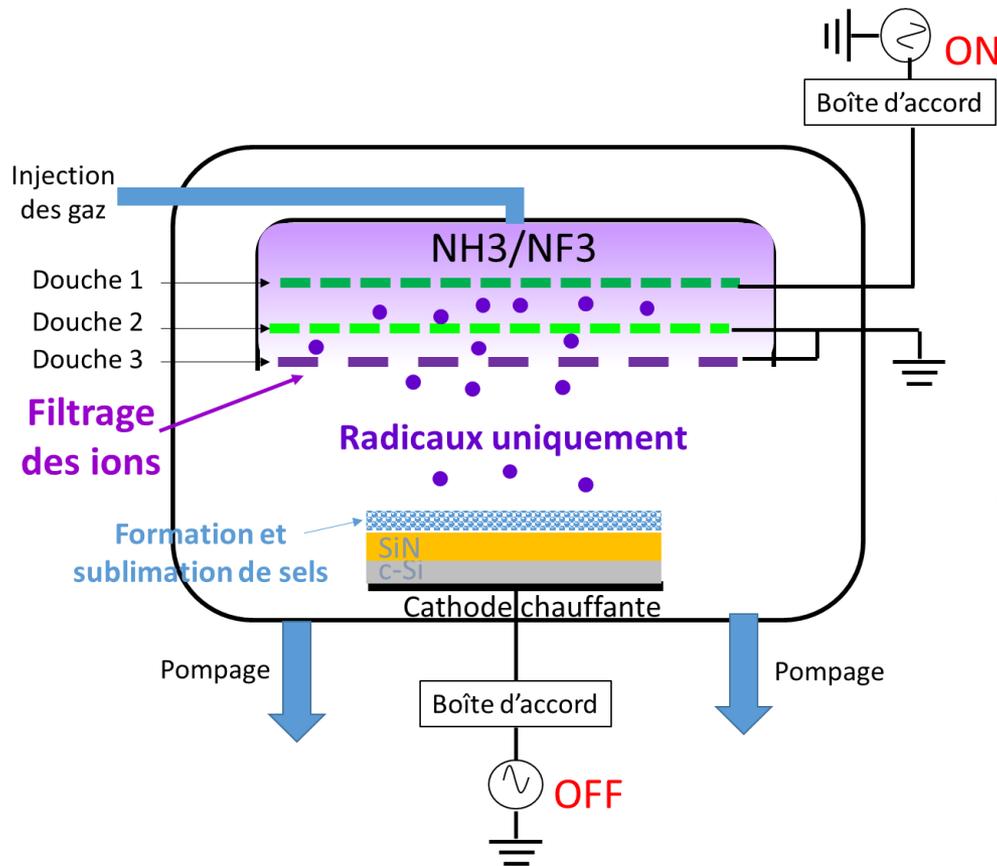
Modification depth driven by ion energy

→ Self limited

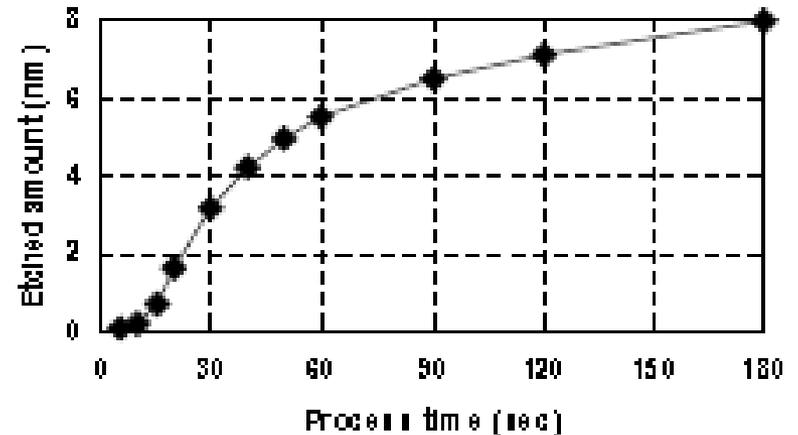
Towards a technological rupture for atomic precision etching

AMAT proposes a new reactor design that allows to achieve the two ALE steps in the same chamber

2. Step2 : removal of the modified layer by radicals generated by down stream plasma



The etching proceeds through the formation of salts



→ Self limited: the etched amount saturates with process time

Conclusion

- ❑ The complexification of MOS transistors architecture imposed by the miniaturization requires atomic precision etching
 - CD control at the nanometer scale
 - Etching of ultra thin layers without introducing plasma damage
- ❑ Conventional ICP reactor reach their intrinsic limits to have an atomic precision etching
 - Impossible to control the Γ_N / Γ_i ratio !
 - Ion energy range is *restricted*: 15 → 200 eV
- ❑ New tool concepts are being introduced to meet the needs of future process technologies
- ❑ The ideal tool does not exist. Each of them have pros and cons. The right tool has to be chosen according to the application targeted

