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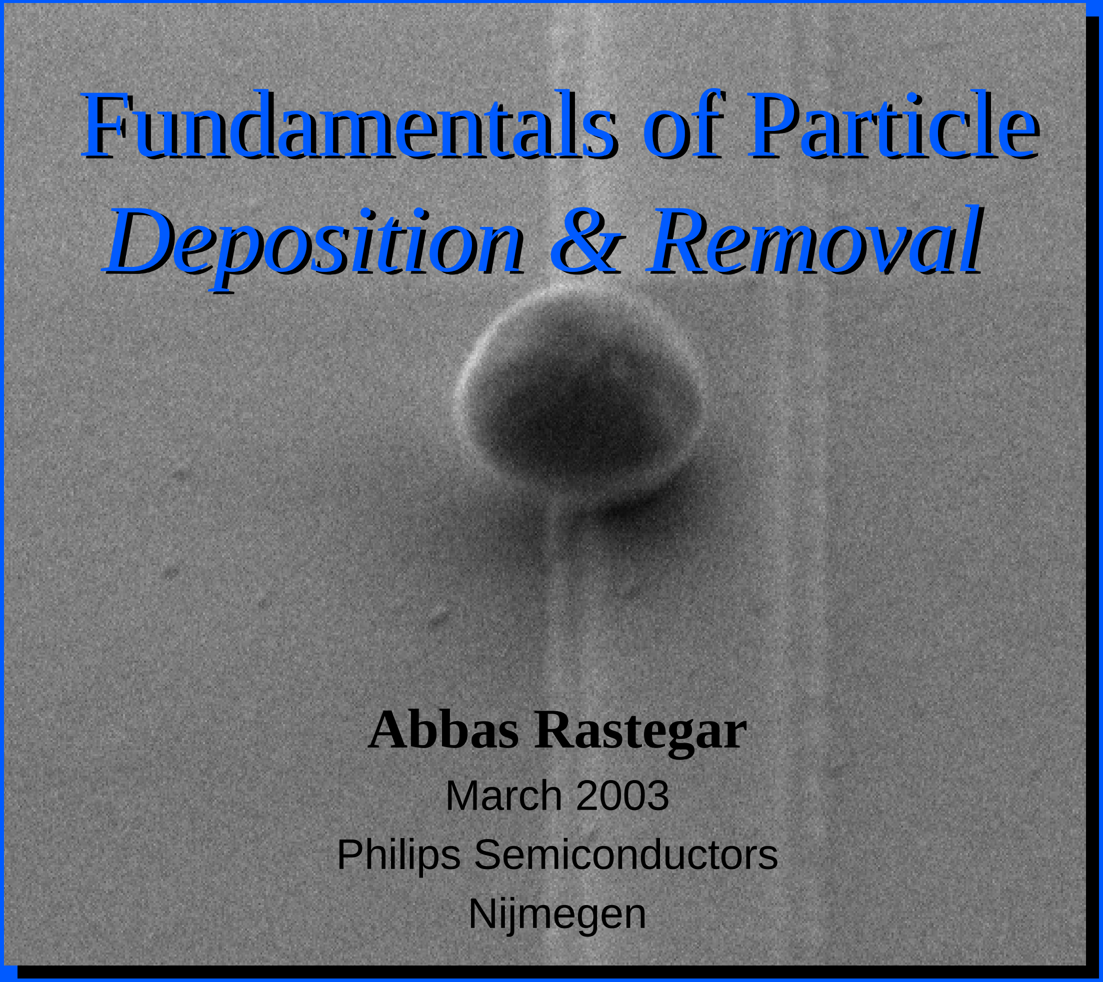


Fundamentals of Particle *Deposition & Removal*

Abbas Rastegar

March 2003

Philips Semiconductors
Nijmegen

Out line

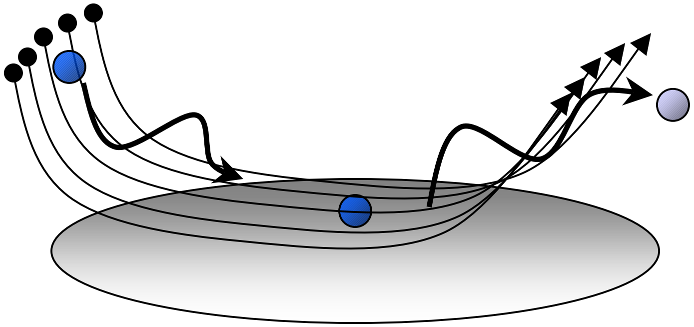
- Particles & surface
- Particle deposition (Air)
- particle adhesion (Air, liquid)
- particle removal
  - Wet cleans
  - Dry cleans
    - O_3 remote plasma
    - Supercritical CO_2 cleaning
    - Cryogenic Aerosol cleaning
  - PLASMAX

Particles & wafer surface

Adhesion

Deposition

Removal



Deposition

- Brownian motion
- Gravity
- Inertial motions
- External fields

Adhesion

- Electrostatic force
- van der Waals force
- Born repulsion

Removal

- Dissolve/decompose
- Detach by under etching
- Detach by collision
- Shear forces

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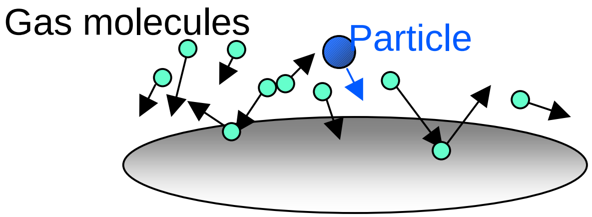
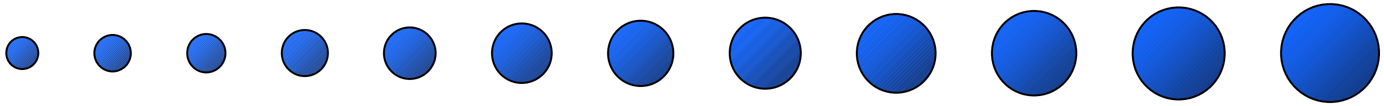
Particle dynamics

- Particle dynamics depends on particle size



$$K_n = \frac{2\lambda_f}{d_p} \propto \frac{Mean\ free\ path_{fluid}}{Particle\ diameter} = Knudsen$$



$K_n >> 1$

Free molecule
regime

$K_n << 1$

Continuous
regime

Mechanism of the particle deposition in the Air

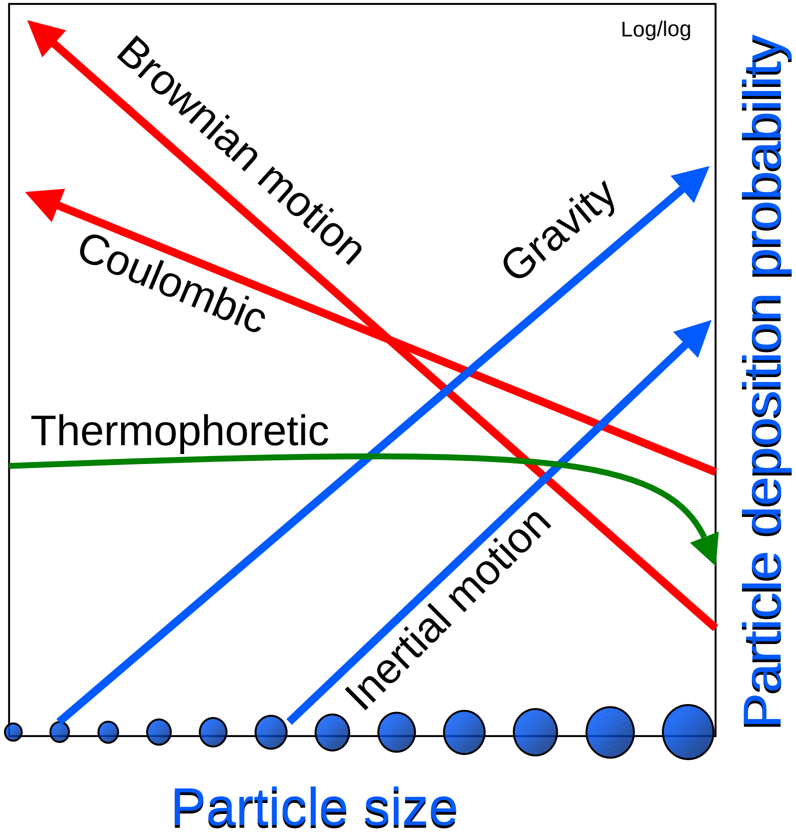
No external field

- Brownian motion $D \propto \frac{1}{d_P}$
- Inertial motion $\tau_g \propto d_P^2$

External field

- Gravity force $v_g \propto d_P^2$
- Coulombic force $v_e \propto \frac{1}{d_P}$
- Thermophoretic force $v_{th} \propto \frac{\nabla T}{T}$
- Diffusiophoretic force

$$m_p \frac{dv_p}{dt} = F_{ext} + \frac{1}{\tau_g} m_p (v_f - v_p)$$



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Notation info
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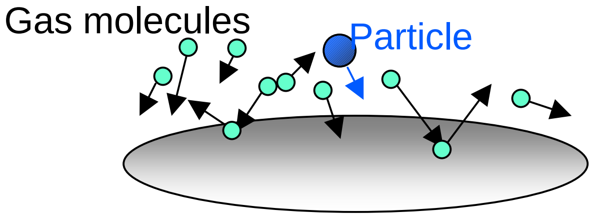
Particle deposition in the Air (no force)



- Brownian motion : random collision of particles due to thermal motion

$$D = \frac{C_c}{3\pi}\frac{k_B T}{\mu\, d_p} \propto \frac{1}{d_p}$$

- Inertial motion : when gas flow direction changes, large particles do not follow the flow and collide with the surface.

  If a particle enters a gas stream, it adopts the velocity of stream after time τ_g

$$\tau_g = \frac{C_c}{18}\frac{\rho_p}{\mu} d_p^2 \propto d_p^2$$

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Notation info last page

Particle deposition in the Air (External forces)

External force ↔ Stokes resisting force

- Gravity force :(m_pg) particles fall on the wafer (important for large particles)

$$v_g = \frac{C_c}{18}\frac{\rho_p}{\mu} g\, d_p^2 \propto d_p^2$$

- Coulombic force :(ZeE) particles accelerate under electric field (important for small particles)

$$v_e = \frac{C_c}{3\pi}\frac{Ze\,E}{\mu\, d_p} \propto \frac{1}{d_p}$$

- Thermophoretic force :(Temperature gradient) particles move from warmer (high KT) to the cooler(low KT) region (independent of size for <1μm particles)

$$v_{th} = -K_r \frac{\mu_{Kinematic}}{T}\nabla T$$

- Diffusophoretic force :(in multi components gas systems) particles move in direction of diffusion flux of the heavier gas component

$$v_{df} = -\frac{\sqrt{m_1}}{\gamma_1\sqrt{m_1}+\gamma_2\sqrt{m_2}}\frac{D_{12}}{\gamma_2}\nabla\gamma_1$$

Notation info
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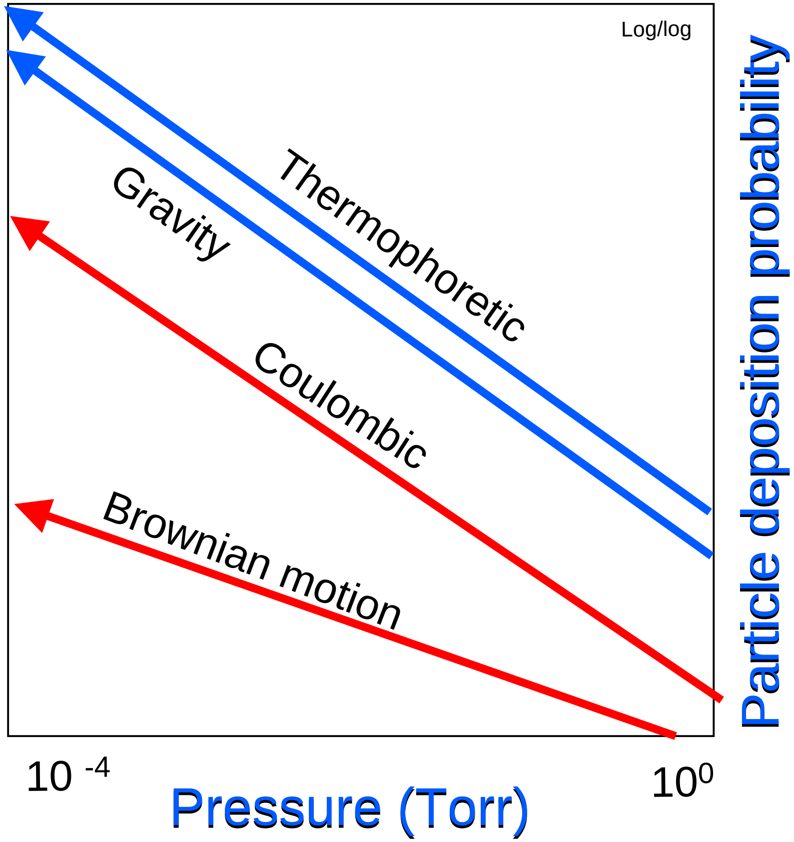
Particle deposition in the plasma

- Pressure : see figure
- Temperature : $v_{th} \propto \nabla T$
- Electric field : due to different ion and electron mobility in plasma
  $$v_e \propto E$$
- RF : particles are suspended in the plasma-sheath boundary (competition between Coulombic and gravitational and/or thermophoretic forces)



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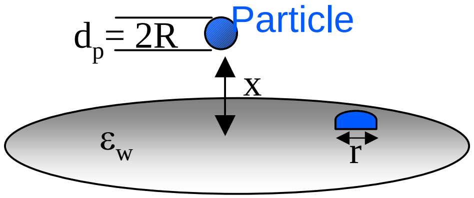
Adhesion Forces in the air



- Electrostatic force : External+ image

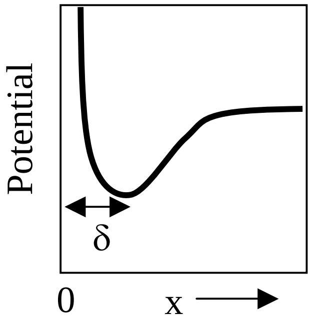
  (between charged particle and induced charge on wafer)

$$F_E(x) = zeE + \frac{(\varepsilon_w - 1)}{(\varepsilon_w + 1)} \frac{z^2 e^2}{4\pi\varepsilon_0 x^2}$$

- Van der Waals force : Short range attractive forces due to charge density fluctuations of the molecules (Surface properties in Hamaker constant)

$$F_{vdW} = \frac{A_H}{6x^2}\left(R + \frac{r^2}{x}\right)$$

- Born repulsion force :due to electronic charge overlap of particle and surface atoms



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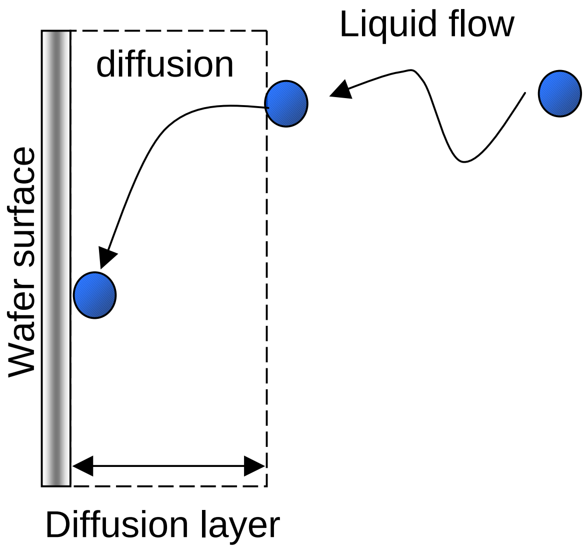
Adhesion Forces in the liquid



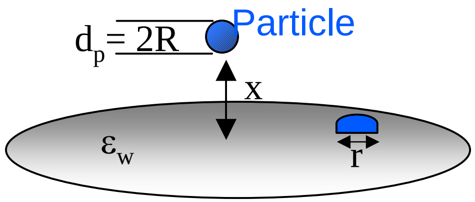
- Van der Waals interaction :(3nm)

$$V_{vdW} = \frac{A_H}{6}\left(\frac{d_p(2x+d_p)}{2x(x+d_p)} + \ln\left(\frac{(x+d_p)}{x}\right)\right)$$

- Electrostatic interaction : (κ^{-1})Debye-Huckle length (thickness of the electrostatic double-layer)

$$V_{el} = \frac{\varepsilon\, d_p}{8}\left(\left(\Psi_p^2 + \Psi_w^2\right)\ln\left(\frac{e^{2\kappa x}-1}{e^{2\kappa x}}\right) + 2\Psi_p\Psi_w \ln\left(\frac{e^{\kappa x}+1}{e^{\kappa x}-1}\right)\right)$$

Ψ : electrostatic surface potential (particle , wafer) $\kappa = \sqrt{\frac{2000e^2 N_A I}{\varepsilon k_B T}}$



- Short range interactions : (1-3 nm) solvation and other types of steric forces (i.g. attractive hydrophobic forces, chemical bond)

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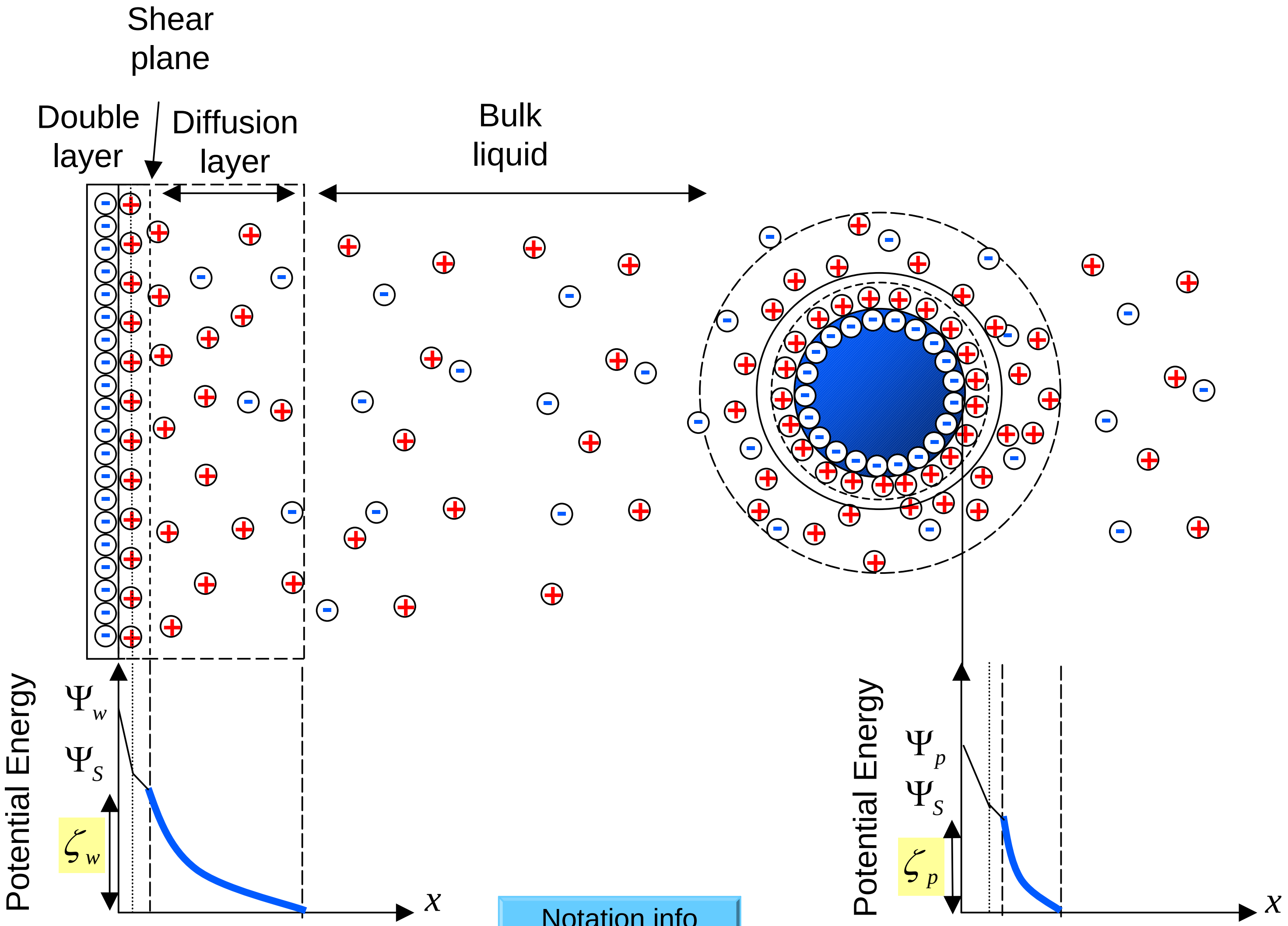
Particle-Surface interactions in the liquids



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Particle-Surface interactions in the liquids

Particle close to surface but not attached

$$U_{\text{interaction}} = V_{vdW} + V_{el}^{w} + V_{el}^{p}$$

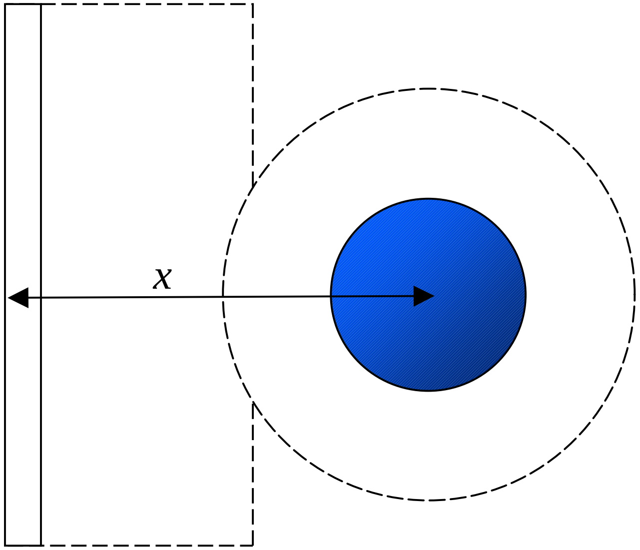
$$U_{\text{interaction}} > 0 \qquad \textit{repulsion}$$

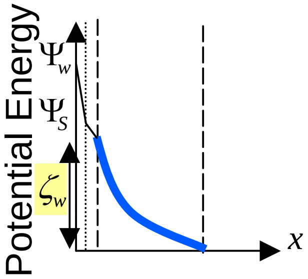
$$U_{\text{interaction}} < 0 \qquad \textit{attraction}$$

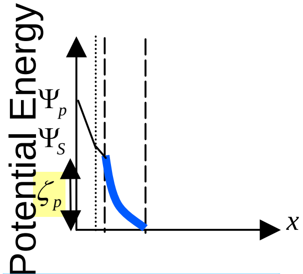
$$V_{el} >> V_{vdW} \longrightarrow U_{\text{interaction}} \approx V_{el}^{w} + V_{el}^{p}$$

$$\left\{\begin{array}{l} \zeta_{\text{p}} < 0 \,, \zeta_{w} < 0 \\ \zeta_{\text{p}} > 0 \,, \zeta_{w} > 0 \end{array}\right. \qquad \text{repulsion}$$

$$\left\{\begin{array}{l} \zeta_{\text{p}} < 0 \,, \zeta_{w} > 0 \\ \zeta_{\text{p}} > 0 \,, \zeta_{w} < 0 \end{array}\right. \qquad \text{deposition}$$







Notation info
last page

ζ potential and pH of solution

- Iso-Electric Point(IEP) (Point of zero charge) positive and negative charges are equal

$$IEP_{SiO_2} \longrightarrow pH \approx 2-3$$

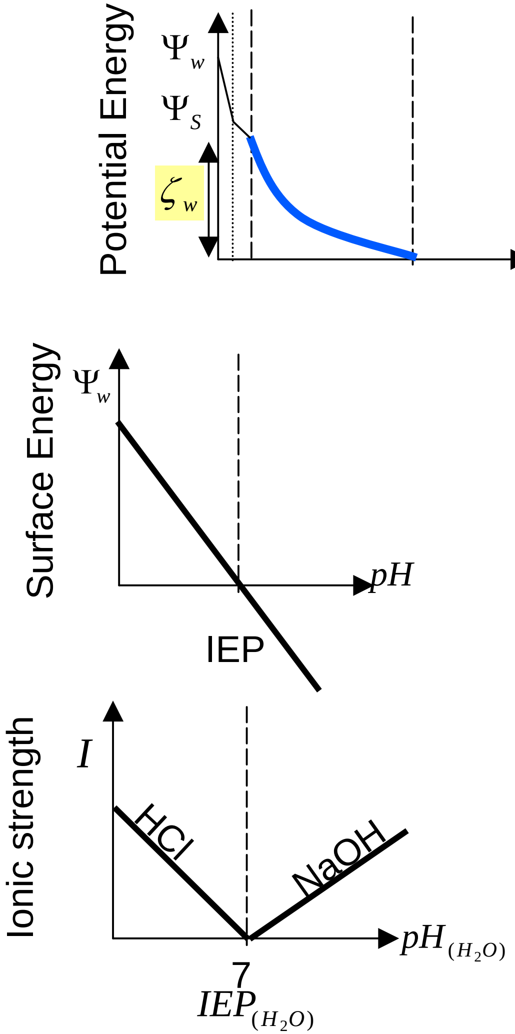
$$IEP_{Si_3N_4} \longrightarrow pH \approx 3-4$$

$$IEP_{Al_2O_3} \longrightarrow pH \approx 8$$

- ζ_w depends on surface electrostatic potential and ionic strength

pH below IEP
$$\begin{cases} pH \downarrow \longrightarrow \Psi_w \uparrow \longrightarrow \zeta_w \uparrow \\ pH \downarrow \longrightarrow I \uparrow \longrightarrow \zeta_w \downarrow \end{cases}$$

pH above IEP
$$\begin{cases} pH \uparrow \longrightarrow \Psi_w \uparrow \longrightarrow \zeta_w \uparrow \\ pH \uparrow \longrightarrow I \uparrow \longrightarrow \zeta_w \downarrow \end{cases}$$



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Adhesion in liquids (summary)

- Ionic strength of liquid(I) :Range of electrostatic interaction

$$I\uparrow \longrightarrow V_{el}\downarrow \longrightarrow V_{vdW} > V_{el} \longrightarrow \text{deposition}$$

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon k_B T}{2000 e^2 N_A I}} \propto \frac{1}{\sqrt{I}}$$

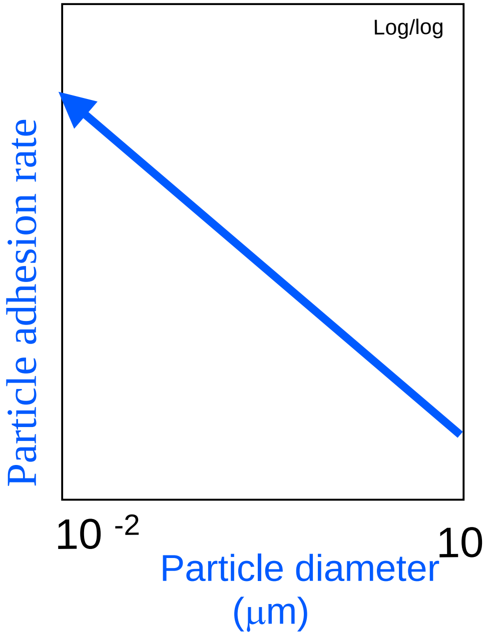
- Zeta potential(ζ) :

ζ_p, ζ_w *the same sign* repulsion

ζ_p, ζ_w *opposite sign* attraction

- Particle size(d_p) :(figure)

Diffusion constant (D) $D \propto \frac{1}{d_p}$



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Controlling of the particle adhesion in liquids

- Deposition ↔ Removal process can be controlled by controlling the Zeta (ζ)potentials
- Zeta potential(ζ) :can be controlled by adding surfactants to acidic solutions
- Surfactants
  - Hydrophobic part
  - Hydrophilic part
    - Anionic (R-SO3$^-$)
    - Cationic (R-NH3$^+$)
    - Nonionic

ζ potential (mV) **(HCL, pH 3.3)**

Surfactant	**No**	**Anionic**	**Cationic**
Si	**-23**	**-32**	**+63**
Si_3N_4	**+43**	**-52**	**+45**
SiO_2	**+7**	**-7**	**+55**
Polystyrene particles	**+39**	**-67**	**+78**
Si-PSL	**d**	**R**	**R**

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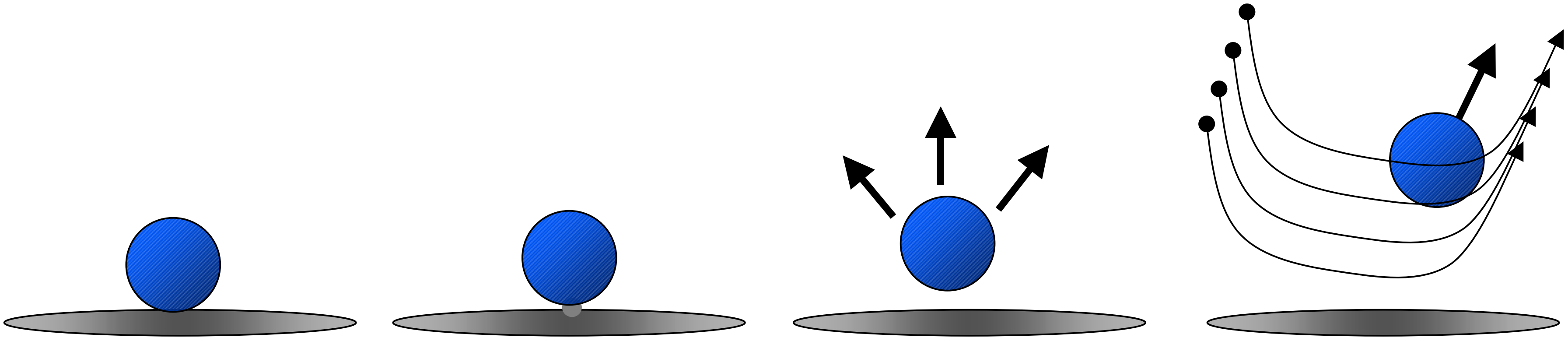
Source: M. Itano et.al. Daikin Industries

Particle Removal



Particle attached to the wafer surface

- Breaking the vdW forces
- under etching

- Lift-off from the surface
- Repulsive forces
- Zeta potential

- Transport away from surface
- Diffusion
- Convection

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Typical Wet Cleans

Object	**Chemical**	**Popular name**
Particles	APM($NH_4OH/H_2O_2/H_2O$)(1:1:5)	RCA (SC-1)
Organics	SPM(H_2SO_4/H_2O_2) (5 or 8:1) APM($NH_4OH/H_2O_2/H_2O$)	Piranha RCA (SC-1)
Metalics	HPM($HCl/H_2O_2/H_2O$) (1:1: >5) SPM(H_2SO_4/H_2O_2) DHF (HF/H_2O)	RCA (SC-2) Piranha
Native Oxides	DHF (HF/H_2O) (1:>50) BHF (NH_4F /HF/H_2O)	Diluted HF Buffered HF

SPM → **DHF** → **APM (SC-1)** → **HPM (SC-2)** → **Dry**

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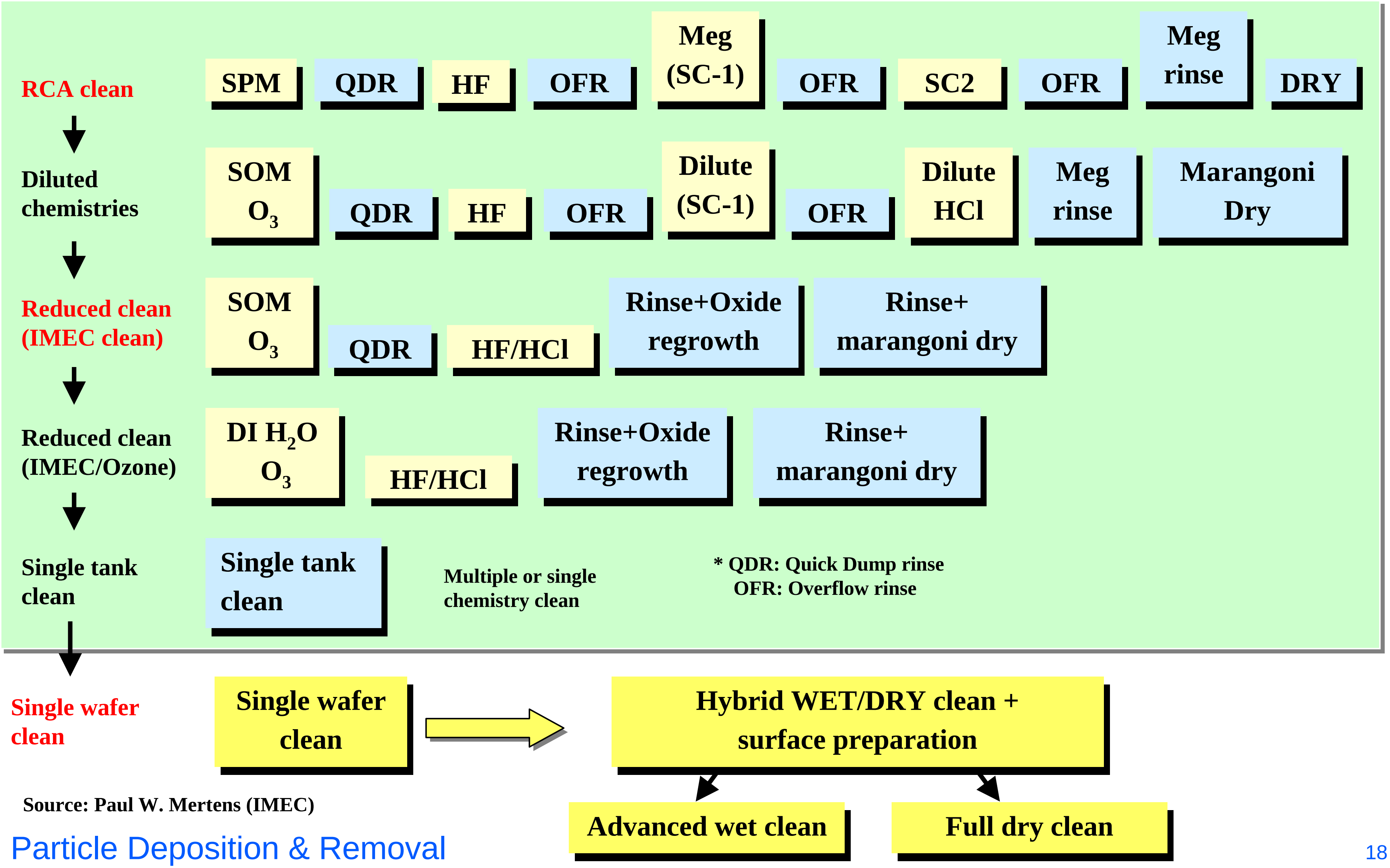
Wet Cleaning Roadmap



RCA clean

SPM → QDR → HF → OFR → Meg (SC-1) → OFR → SC2 → OFR → Meg rinse → DRY

Diluted chemistries

SOM O$_3$ → QDR → HF → OFR → Dilute (SC-1) → OFR → Dilute HCl → Meg rinse → Marangoni Dry

Reduced clean (IMEC clean)

SOM O$_3$ → QDR → HF/HCl → Rinse+Oxide regrowth → Rinse+ marangoni dry

Reduced clean (IMEC/Ozone)

DI H_2O O$_3$ → HF/HCl → Rinse+Oxide regrowth → Rinse+ marangoni dry

Single tank clean

Single tank clean

Multiple or single chemistry clean

* QDR: Quick Dump rinse
OFR: Overflow rinse

Single wafer clean

Single wafer clean → Hybrid WET/DRY clean + surface preparation

Advanced wet clean

Full dry clean

Source: Paul W. Mertens (IMEC)

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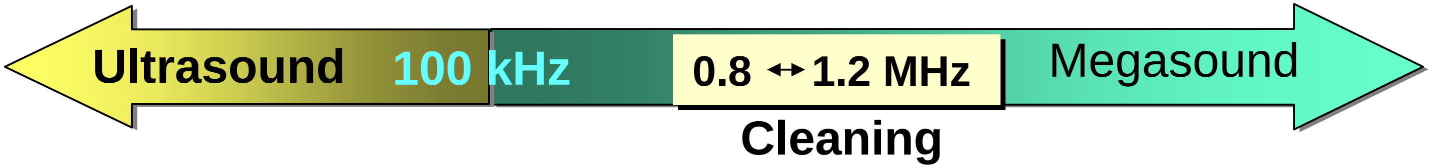
Megasonic & Ultrasonic Cleans

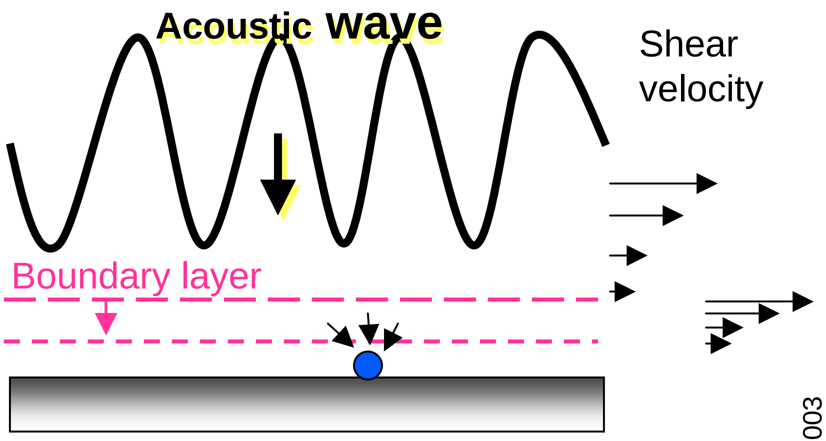


Ultrasound 100 kHz

0.8 ↔ 1.2 MHz

Megasound

Cleaning



Acoustic wave

Shear velocity

Boundary layer

- By reducing the boundary layer increases transport of chemicals
- Physically transfer energy to the particle and helps in removal
- Cavitation
- Higher frequency leads to better removal of small particles and less cavitation
- Less effective to sub 100 nm particles

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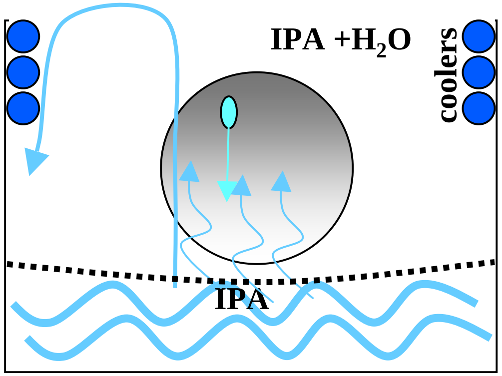
Source: D. M. Knotter ,Cleaning Expertise Center, Philips Semiconductors

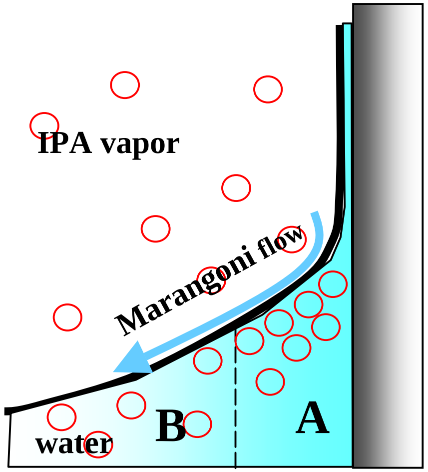
Drying

IPA drying :IPA evaporates and vapor remove water droplets form surface



Marangoni drying

- IPA diffuse into water close to surface (A) than far from surface (B)
- IPA concentration gradient leads to surface tension gradient($\gamma_B > \gamma_A$)
- Marangoni flow goes from low γ_A towards high γ_B
- Marangoni flow can also remove particles



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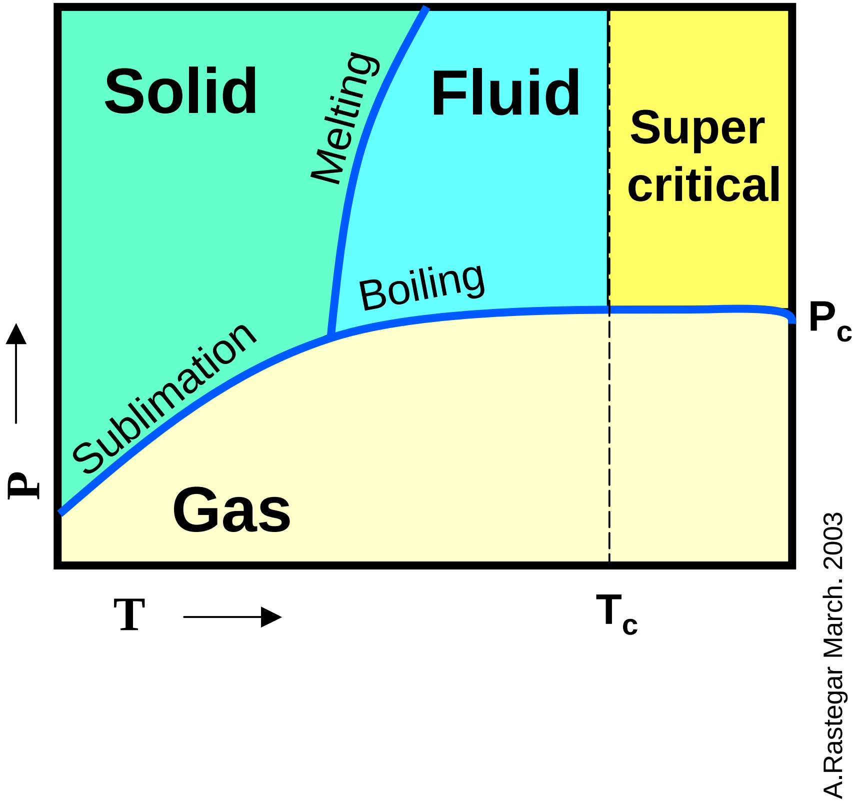
Super critical fluid cleans

SC CO_2 :T_C=31.06 C, P_C=73.8 Bar

No surface tension :Excellent wet-ability to all surfaces- (deep vias)

Co-solvent(1%) :required for cleaning

Compatibility :compatible with low-k



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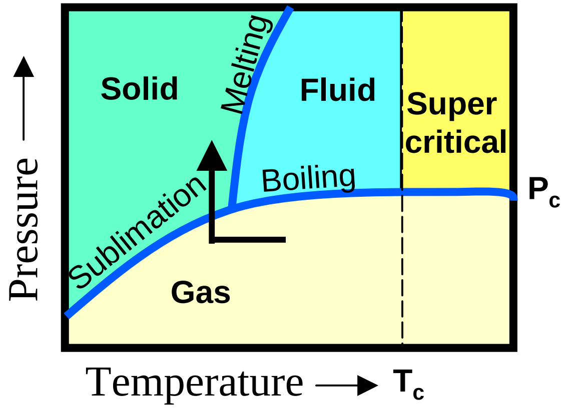
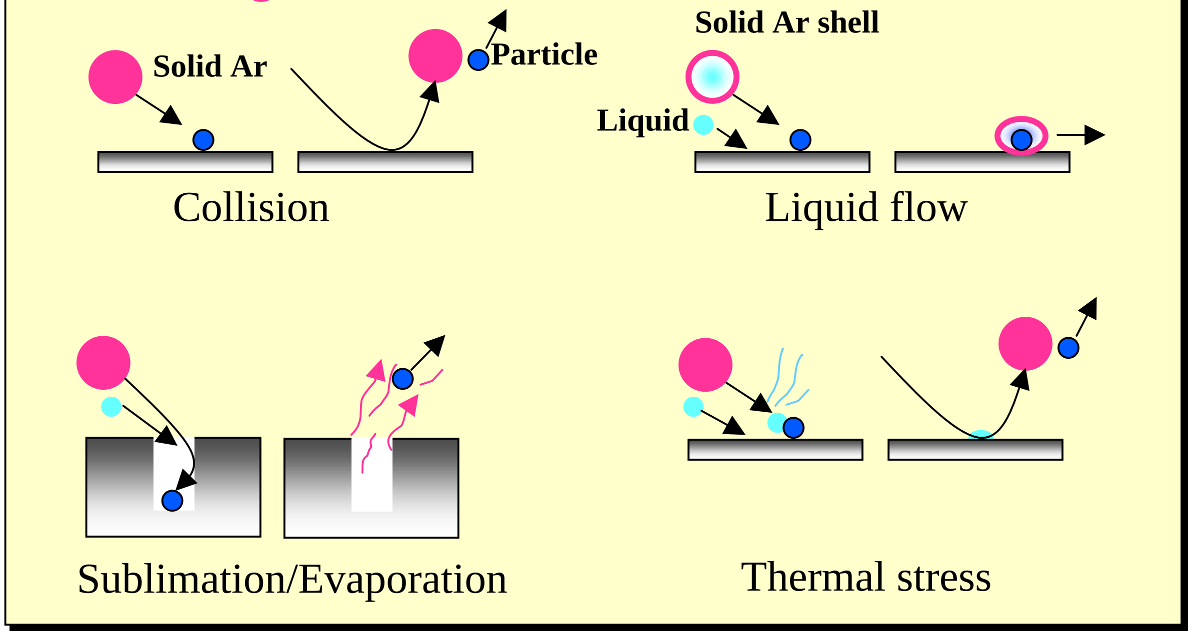
Cryogenic Aerosol Cleaning (Ar, CO_2)

Aerosol :Created by cooling a gas and rapid expansion



Cleaning mechanism



Source: M. Okada et.al. J.Vac. Sci. Technol. B20, 71(2002)

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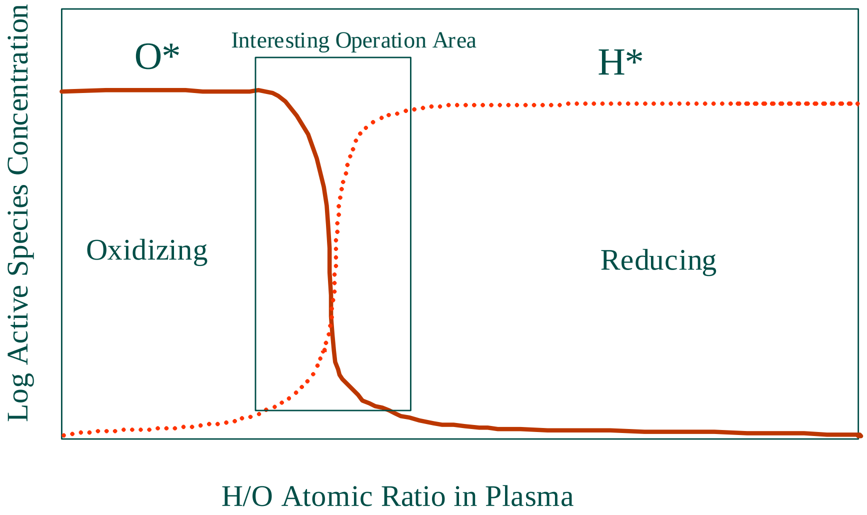
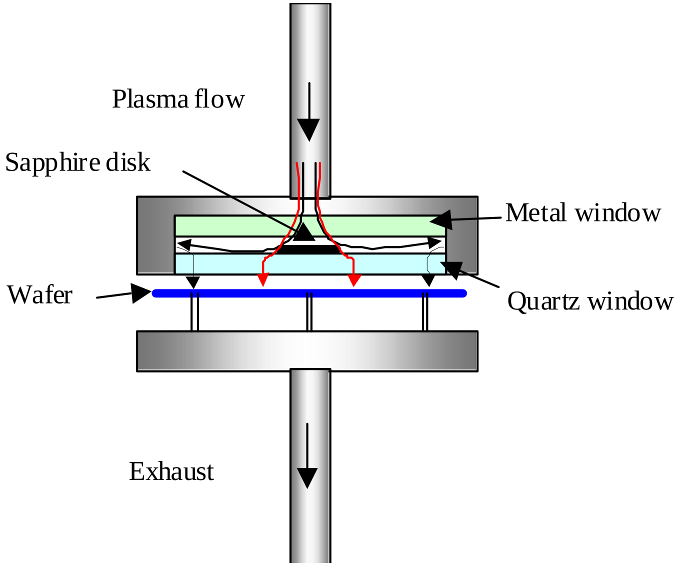
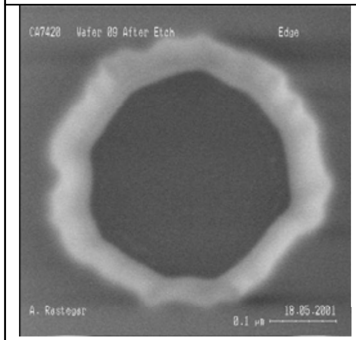
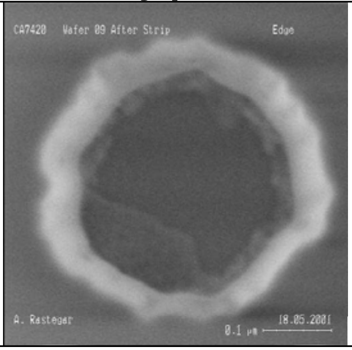
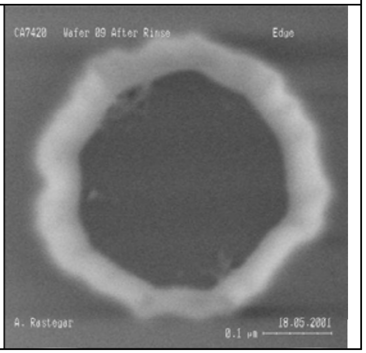
Remote Plasma Cleans





- Oxidation: CHNSO +O* → CO_2 + H_2O+ NO_2 + SO_2
- Reduction: CHNSO +H* → CO_2 + (-C-H_X)+ CN + H_2S

After Etch	**After dry plasma**	**After rinse**
		

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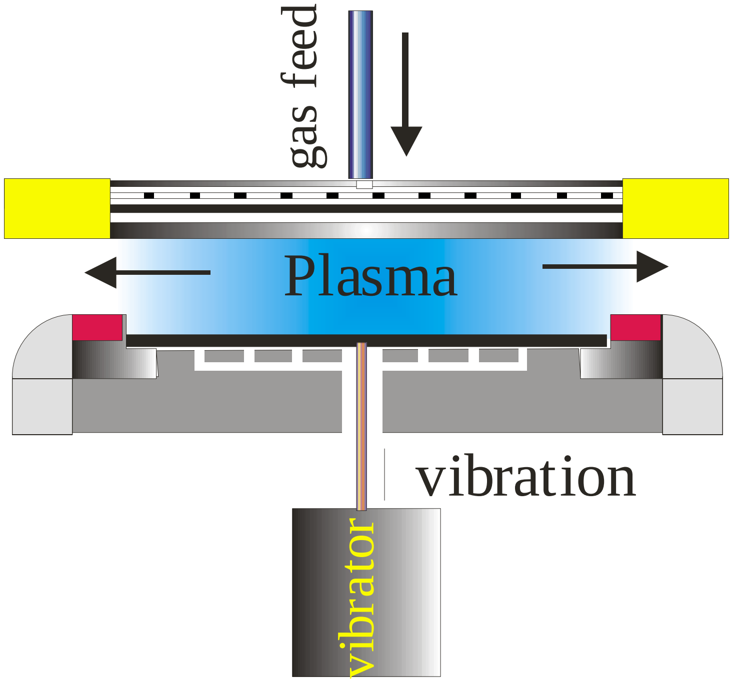
PLASMAX

Working mechanism:

- Mechanical excitation
- Plasma properties
- Surface chemistry
- gas flow

issues:

- acceleration uniformity across the wafer
- mounting conditions



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Source: W. H. Semke et.al. J.Vac. Sci. Technol. B18, 3221(2000)

Summary & Conclusions

Deposition

Air

- Brownian motion, Culombic & Thermophoretic are important
- Thermophoretic forces can be used as pellicle for EUV masks

  (Carmelo Romeo LITH115)

Liquid

- Zeta potentials can be used to control repulsion or adhesion to the surface

Removal

Wet clean is favored

- Easier to remove metals (high solubility) and particles (ζ control)
- Energy gain in separation of particles in liquid compared to gas
- Possibility of megasonication → better energy transfer (30nm particles removal)
- Single chemistry (Ozone based) + Marangoni dry is promising

Other Cleaning Techniques

• **Remote plasma**	+ Etch residues, organics - Plasma damage, particles
• **Supercritical fluids**	+ HAR structures - Require co-solvent
• **Cryogenic Aerosols**	+ Good particle removal, - Substrate damage
• **PLASMAX**	+ Particle removal - Uniformity
• **Liquid Assisted Laser**	+ No aggressive chemistry - Substrate damage

Acknowledgement

thanks to :

- D. Martin Knotter, Cleaning Expertise Center- Philips
- Paul W. Mertens, Advanced Cleaning Technology- IMEC

Notations

v_x : particle velocity

ρ_p : particle density

μ : gas viscosity

d_p : particle diameter

C_c : Cunningham correction factor

K_r : Thermophoretic coefficient

ρ_p : particle density

Z : number of charges

ε_w : dielectric constant of wafer

A_H : Hamaker constant

r : radius of contact area

Ψ_P, Ψ_w : relectrostatic surface potential (particle, wafer)

$m_{1,2}$: gas component's mass

m_P : particle mass

$\gamma_{1,2}$: mole fractions of component

D_{12} : mutual diffusion coefficient

v_f : fluid velocity

v_P : particle velocity

k_B : Bultzmann constant

v_g : particle velocity in gravitational field

v_e : particle velocity in external electric field

v_{th} : particle velocity in thermophoretic field

v_{df} : particle velocity in diffusophoretic field

N_A : Avagadro's number

I : Ionic strength

ζ_p, ζ_w : Zeta potentials

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