Nanometer Scale Patterning and Processing

Spring 2016

Lecture 4
Contamination Control and Substrate Cleaning

Contaminants

- A substance causes uncontrolled variations in the (electrical) performance of the device or in the device fabrication process
  - Contaminants are defects
  - Excessive cleaning may also create defects
    - E.g. excessive etching of the Si surface
- Maybe observed visually or may only be detected with sophisticated analytical equipment during the inspection or final device test
- Balance and tradeoff
  - No excessive cleaning
    - Remove unwanted contamination
    - Not contribute to undesired defects

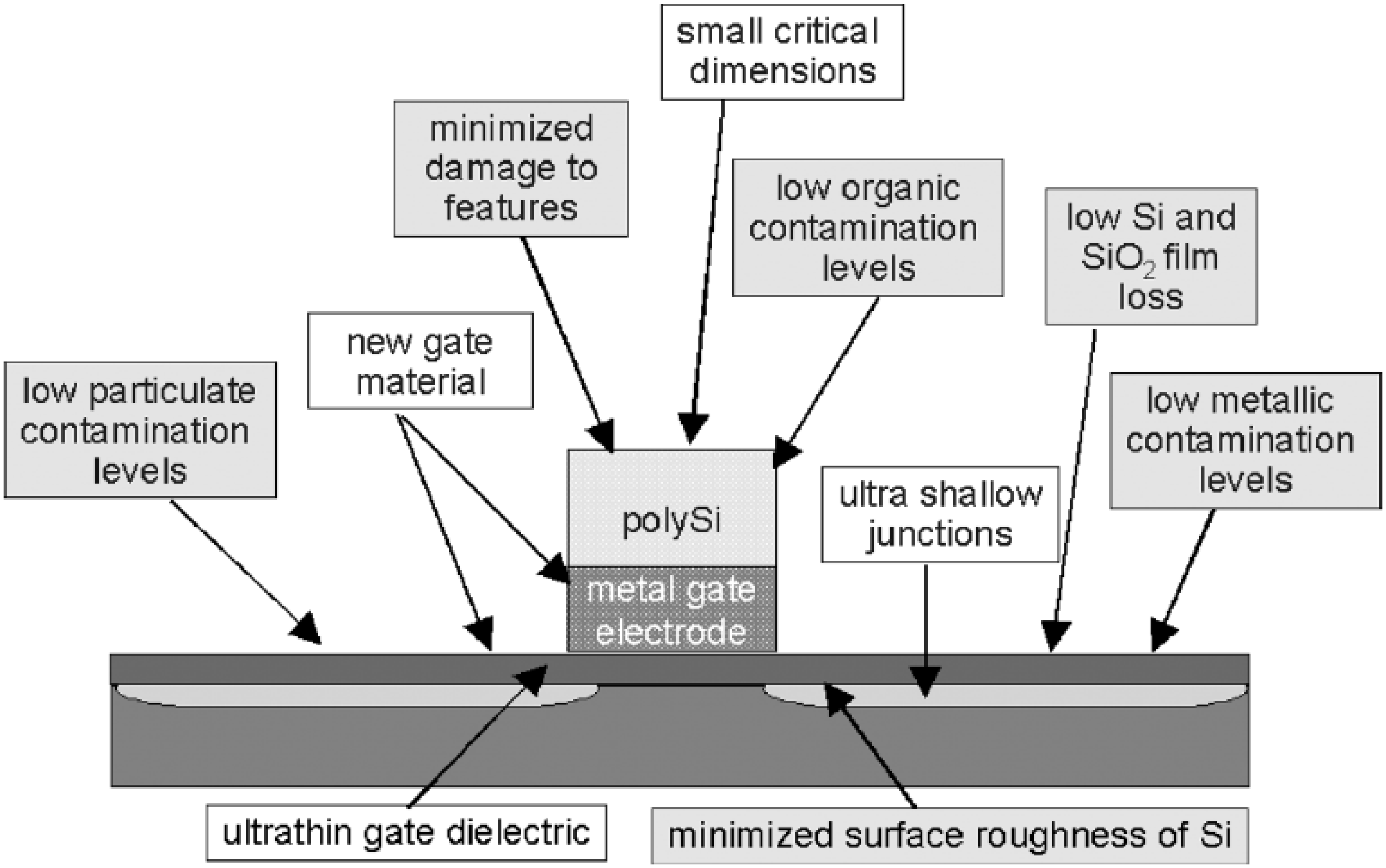
Contaminations & Counter-measures

- Atomic and molecular
  - Adsorbed ions and elements
  - Adsorbed gases
- Microscopic
  - Thin films
  - Particle related
    - Discrete particles
    - Particulates (clusters of particles)
- Particles (number and size)
  - Filtering, brushing and megasonics
- Inorganic contaminants
  - Aqueous cleaning solutions
- Organic contaminants
  - Removed using strong oxidizers
- Impurities
  - Gettering

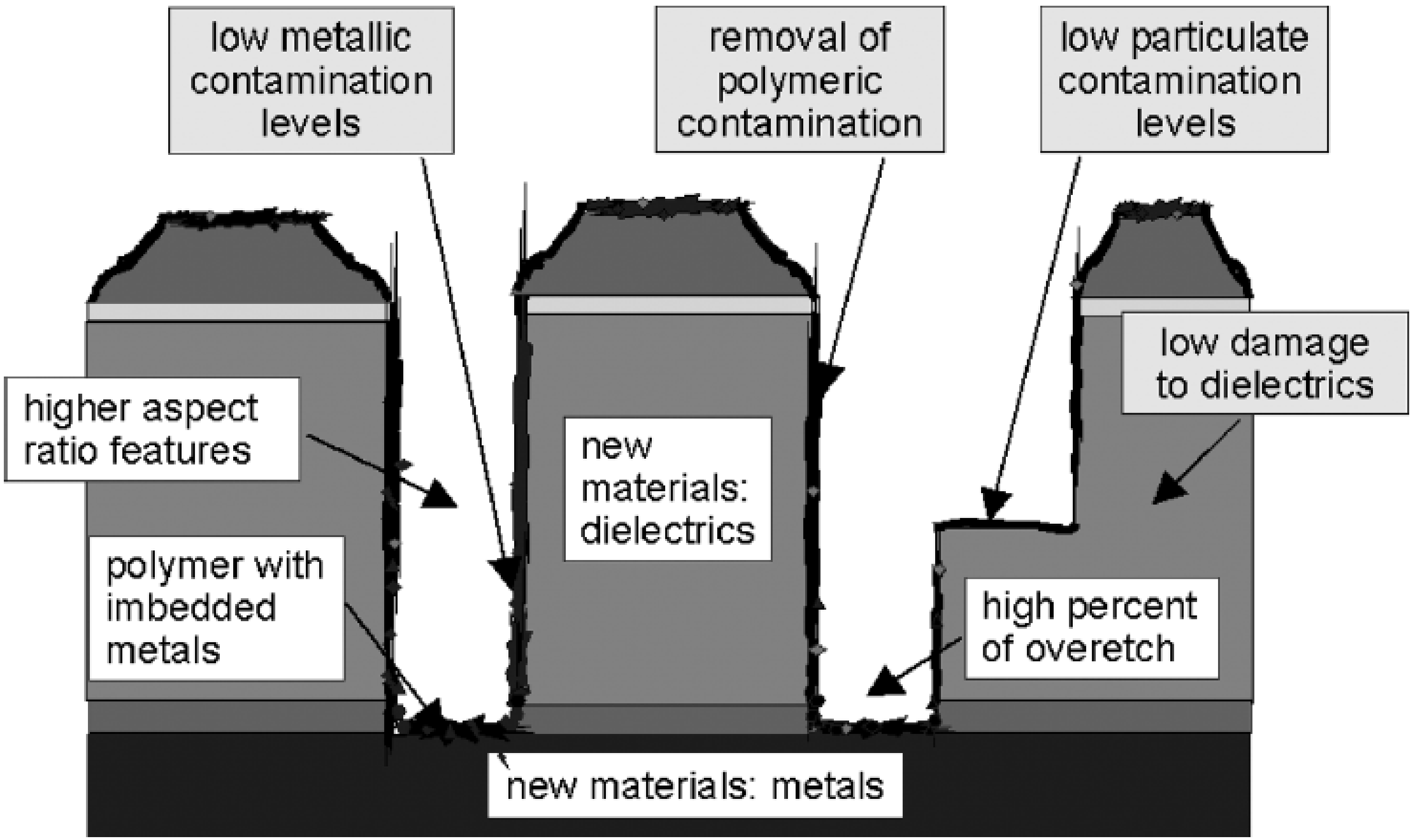
Semiconductor Wafer Cleaning Technology for CMOS Processing

- Critical challenges for front end of line (FEOL)
  - Removal of small particles (< 45 nm)
  - Minimal damage to narrow (<1 nm) gate lines
  - Minimal Si/SiO_2 consumption (<4 micron)
  - Watermark-free drying for hydrophobic/hydrophilic combination surface
- Critical challenges for back end of line (BEOL)
  - Damage-free cleaning to the low-k material
  - Removal of small particles (< 45 nm)
  - Watermark-free drying for hydrophobic/hydrophilic combination surface

Cleaning post-gate features



Critical Components for cleaning of BEOL Structures



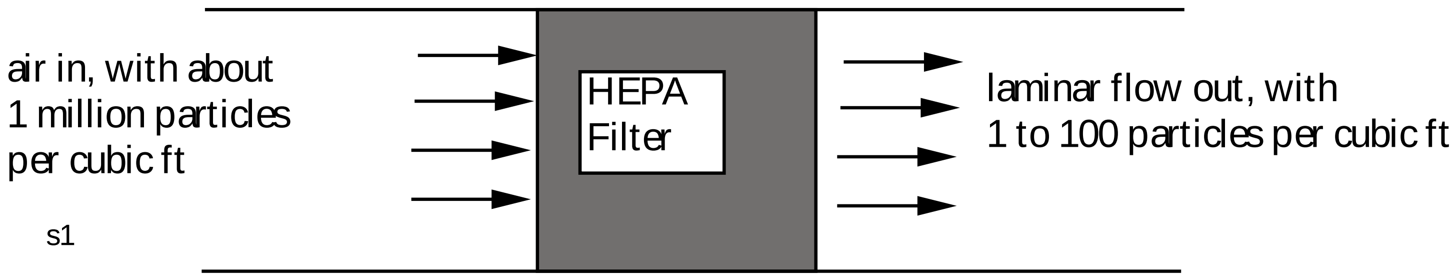
Critical Impurity Elements for Si Devices

- Heavy metals (most critical) Cu, Fe, Ni, Cr, Co, Mo
- Alkali metals (critical) Na, K, Li, Ca
- Other elements (least critical) Al, Mg, C, S, Cl, F

Sources of Contamination

- Humans
  - Emits 10^5 particles (>0.3 μm) per minute
- Chemicals and process gases
- Process equipment
  - Evaporators, Etchers, CVD tools
- Plumbing
- Handling

Air filtering



- Cleanrooms has laminar flow from roof to floor.
- Cleanroom classification: the number of particles per cubic foot that are greater than 0.5 μm in diameter
  - Class 1,000-10,000: clean general purpose lab
  - Class 10-100: very clean lab space, general cleanroom
  - Class 1-10: Commercial Fabs
  - Class 0.1-1: Most advanced IC process lines

Various Standards in Cleanroom Classification

http://en.wikipedia.org/wiki/Cleanroom

US FED STD 209E cleanroom standards

particle/ft³

Class	0.1 µm	0.2 µm	0.3 µm	0.5 µm	5 µm
1	35	7	3	1	
10	350	75	30	10	
100		750	300	100	
1,000				1,000	7
10,000				10,000	70
100,000				100,000	700

ISO 14644-1 cleanroom standards

particle/m³

Class	0.1 µm	0.2 µm	0.3 µm	0.5 µm	1 µm	5 µm
ISO 1	10	2				
ISO 2	100	24	10	4		
ISO 3	1,000	237	102	35	8	
ISO 4	10,000	2,370	1,020	352	83	
ISO 5	100,000	23,700	10,200	3,520	832	29
ISO 6	1,000,000	237,000	102,000	35,200	8,320	293
ISO 7				352,000	83,200	2,930
ISO 8				3,520,000	832,000	29,300
ISO 9				35,200,000	8,320,000	293,000

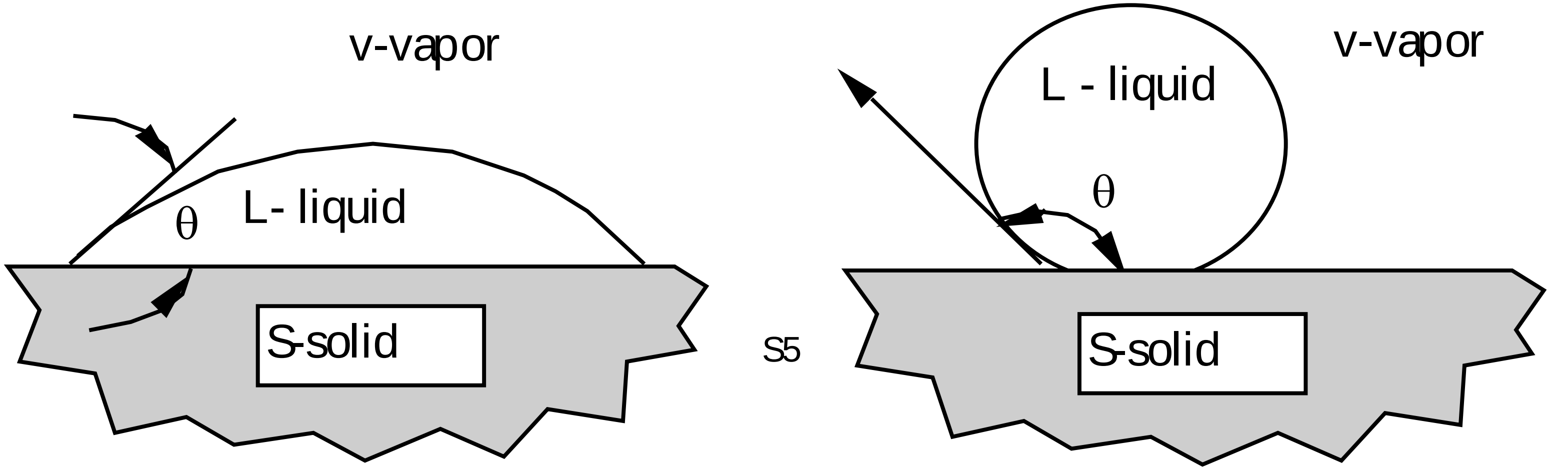
Cleanroom class comparison

ISO 14644-1	FED STD 209E
ISO 3	1
ISO 4	10
ISO 5	100
ISO 6	1,000
ISO 7	10,000
ISO 8	100,000

Detection of Contaminations

- For Particles: Light scattering
  - Gas phase
  - Wafer surface
    - Automation
- For organics:
  - Wetting

Wetting angles



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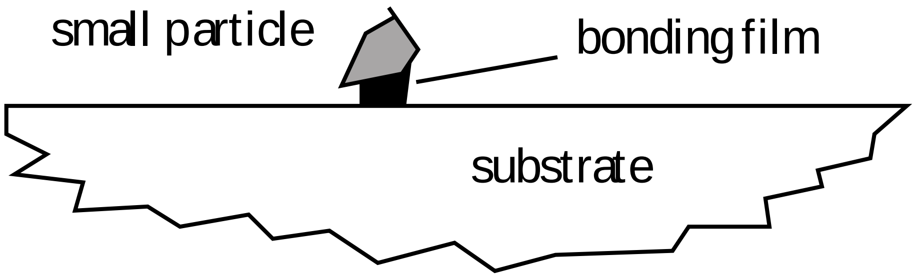
Classification of Contamination and Defects

- Classification according to detection method
  - Metallic contamination
    - Total reflection X-ray fluorescence (TXRF)
    - Atomic absorption spectrometry (AA)
    - Inductively coupled plasma-mass spectrometry (ICP-MS)
  - Particle contamination
    - Detected with light scattering tools
  - Organic contamination
    - Thermal desorption mass spectrometry
    - X-ray photoelectron spectroscopy
    - Auger electron spectroscopy
  - Surface defectivity (roughness of film surface or Line edge roughness)
    - Atomic force microscopy (AFM)
  - Atmospheric molecular contamination (AMC) and moisture
    - Ion mass spectrometry
    - Capillary electrophoresis

Wafer Cleaning and Surface Conditioning Technology



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- Liquid processes
  - Dertergent plus Ultrasonic
  - Megasonic agitation
  - High pressure water jet (300-3000 psi)
- Gas-phase methods
  - High pressure argon or CO_2 jet.
- Wafer rinsing and drying techniques
- Excimer lasers

Liquid Processes and Wafer Drying Techniques

- Diluted HF solutions:
  - 1:50 or 1:100 of 49 wt% HF:DI H_2O
  - To remove 1.0-1.5nm thick native oxide
  - Changes the wafer surface from hydrophilic to hydrophobic
    - Hydrogen passivation of the Si surface
  - Can also desorb metallic particles
- Buffered oxide etch (BOE or BHF)
  - Mixture of 7:1 40 wt% NH_4F and 49 wt% HF
  - More stable rate and prevents loss of photoresit polymer in acidic environment
  - HF_2^- is the enthant

Removal of residual organics (including resists)

- Oxygen plasma etching (ashers)
- H_2O_2 and H_2O, especially at boiling temperature
- Piranha cleaning;
- UV/ozone.
- Acetone→ Methanol → IPA

H_2SO_4/H_2O_2 Mixtures (Piranha Etch)

- 98 wt% H_2SO_4 and 30 wt% H_2O_2
- Volume ratios of 2:1 – 4:1
- Temperature 100 – 130 C
- Time: 10 – 15 minutes
- Destroys organic contaminants by oxidation
- Contaminates Si surface with sulfur residues
- Goggles, face shields, and plastic gloves needed
- Diluted HF dipping of 15 seconds is recommended
- Alternatives:
  - Add $(NH_4)_2SO_4$ (known as SA-80)
  - Add $H_2S_2O_4$ (peroxydisulfuric acid, or Caros acid)
  - Add ozonated H_2O, i.e. DI H_2O/O_3

RCA Standard Cleaning (RCA Cleaning)

- Developed at radio corporation of america
  - Standard Clean 1 (SC-1)
    - 27 wt% NH_4OH: 30 wt% H_2O_2: DI H_2O
    - Volume ratio 1:1:5 (range from 1:1:5 to 1:2:7)
  - Standard Clean 2 (SC-2)
    - 37 wt% HCl: 30 wt% H_2O_2: DI H_2O
    - Volume ratio 1:1:6 (range from 1:1:6 to 1:2:8)
  - Temp: 75-85 C for 10-20 minutes
  - Quench and overflow rinse in running DI water, followed by spun dry
  - Immediately transferred to boxes with pre-filtered N_2 for storage if not immediately processed
  - Exact composition are not critical

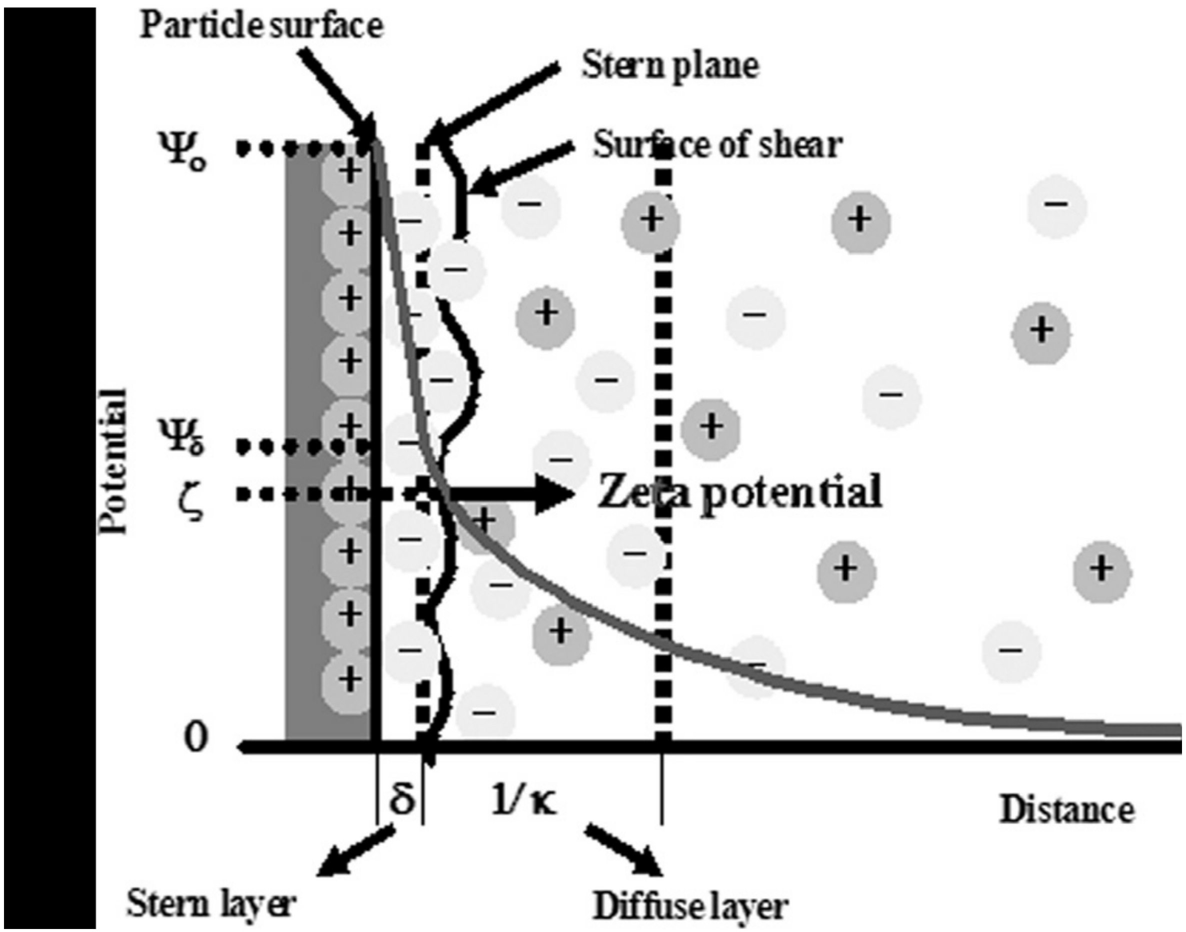
SC-1

- Removes organic contaminants from Si, oxide and quartz
  - NH_4OH
    - Solvating action
    - Provide alkaline environment for H_2O_2
    - Complexing some periodic group IB and IIB metals
      - Cu, Au, Ag, Zn and Cd, as well as Ni, Co and Cr.
  - H_2O_2
    - Oxidizing action in alkaline environment is relatively powerful
  - SC-1 dissolves the thin native oxide of Si at a very low rate and forms a new oxide on the Si surface by oxidation at the same rate
    - Help remove particles and chemical impurities

Mechanism to Remove Particles in SC-1

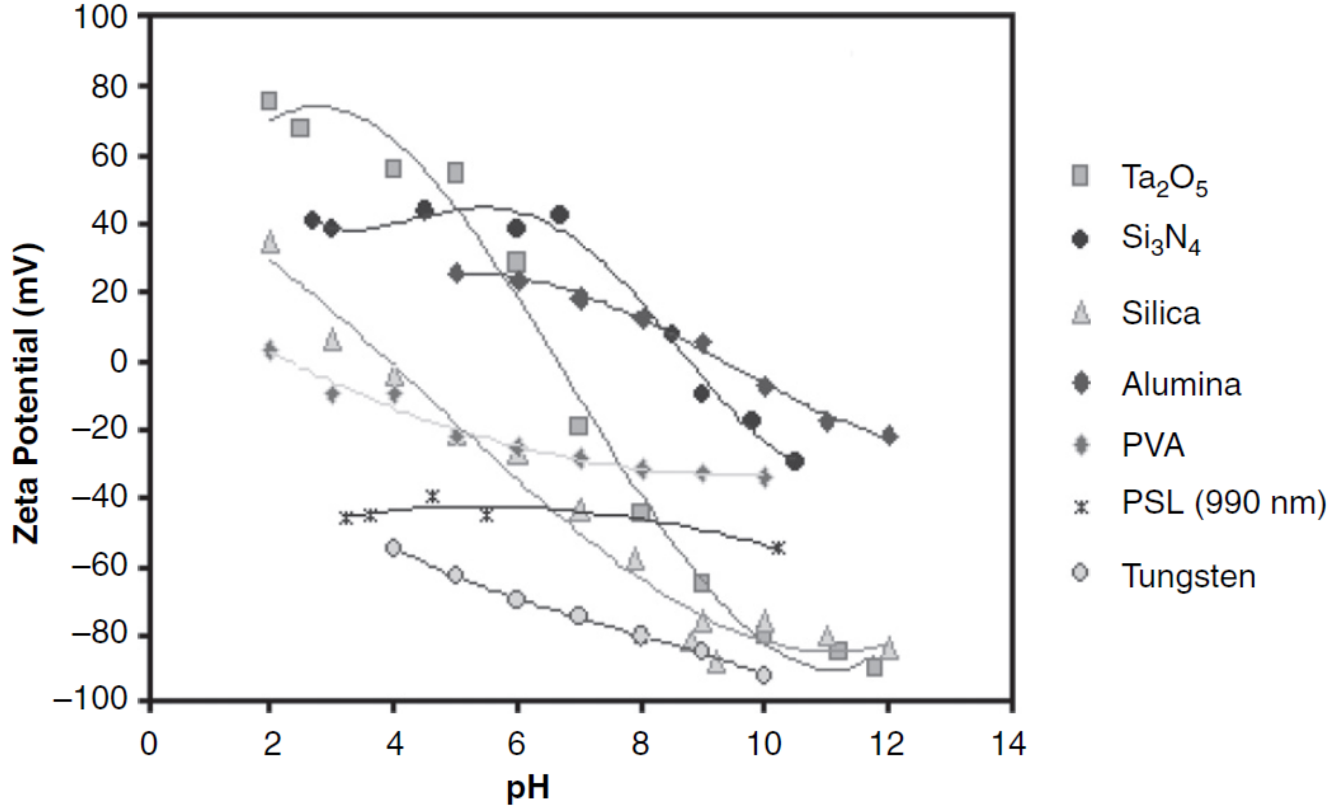
- Micro-etching of Si surface by the NH_4OH
  - Increase Si surface roughness
- Zeta potential of colloids dispersed in a high pH medium is negative, as is the wafer surface
  - Prevents the re-deposition of the dislodged particle
- Magasonic energy decreases the boundary layer of fluid flow over the wafer surface
- Acoustic streaming and the formation of cavitation.

Zeta Potential and the Double Layer



- ζ Affected by pH and ionic strength of a solution

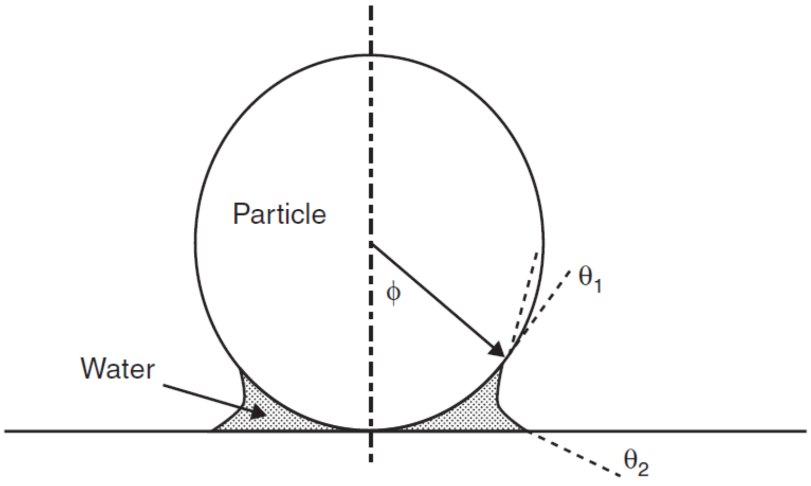
ζ Potential vs pH



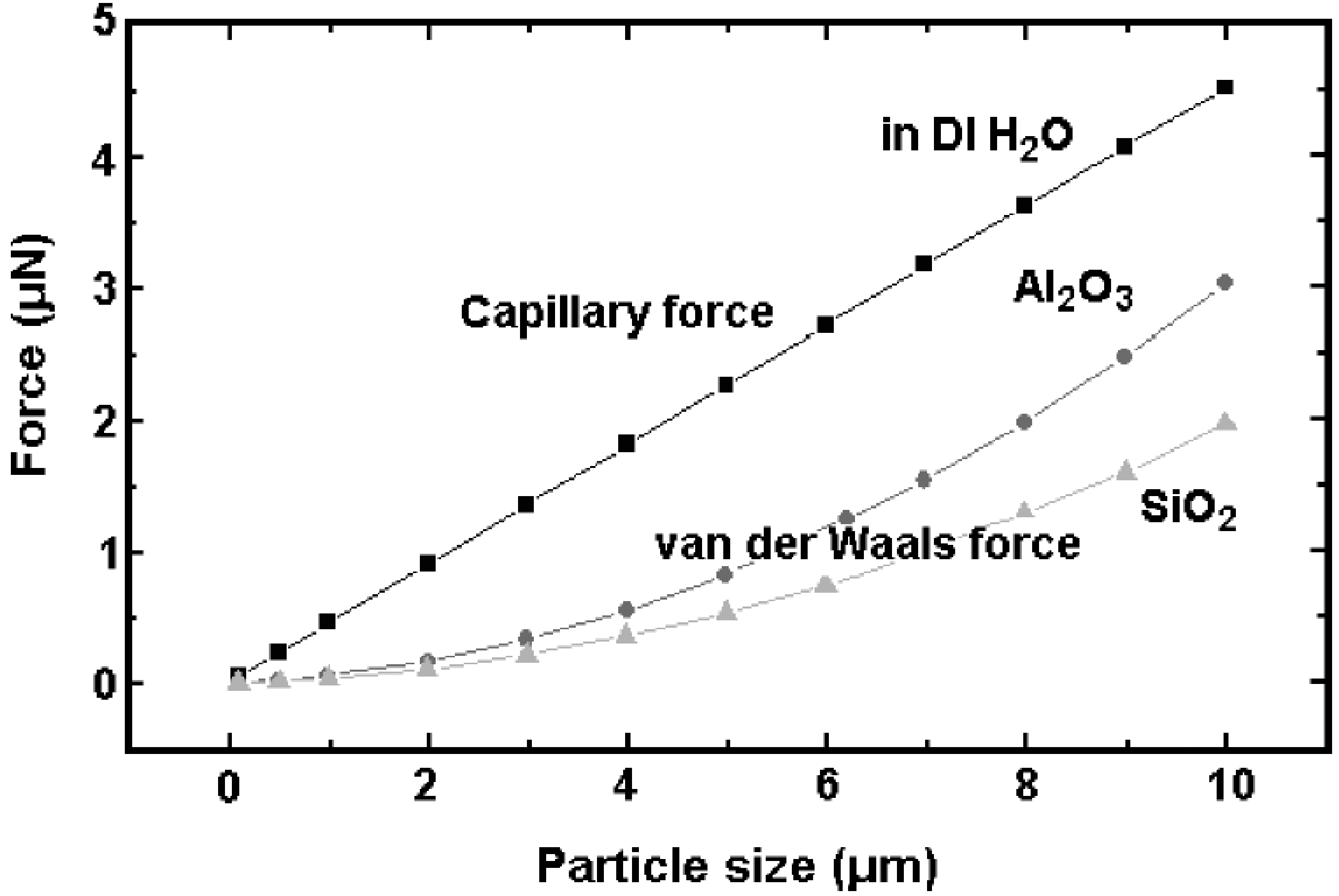
- ζ typically positive in acidic pH due to H^+ adsorption
- Higher pH → more adsorption of OH^- → ζ decreases (move to a more negative value)
- Isoelectric point (IEP): pH value where ζ = 0

Particle Adhesion

- Van der Waals Force
  – Omni-present, regardless whether they have dipoles
- Electrostatic forces
  – Effect of pH and ionic strength on zeta potentials
- Capillary condensation
  – Contact angles
- Measurement
  – AFM
  – Zeta potential



The Capillary and van der Waals force vs particle size



- Silica and alumina particles on a flat surface

SC-2

- Dissolve and remove alkali residues and any residual trace metals or metal hydroxides
  - Au, Ag
  - $Al(OH)_3$, FeOH, $Mg(OH)_2$, or $Zn(OH)_2$
- Dissolved metal ions form metal complexes
  - Prevents replating from solution
- Does not etch Si or SiO_2
  - No surfactant activity or capability to remove particle
- Temperature control is more forgiving

Improvements

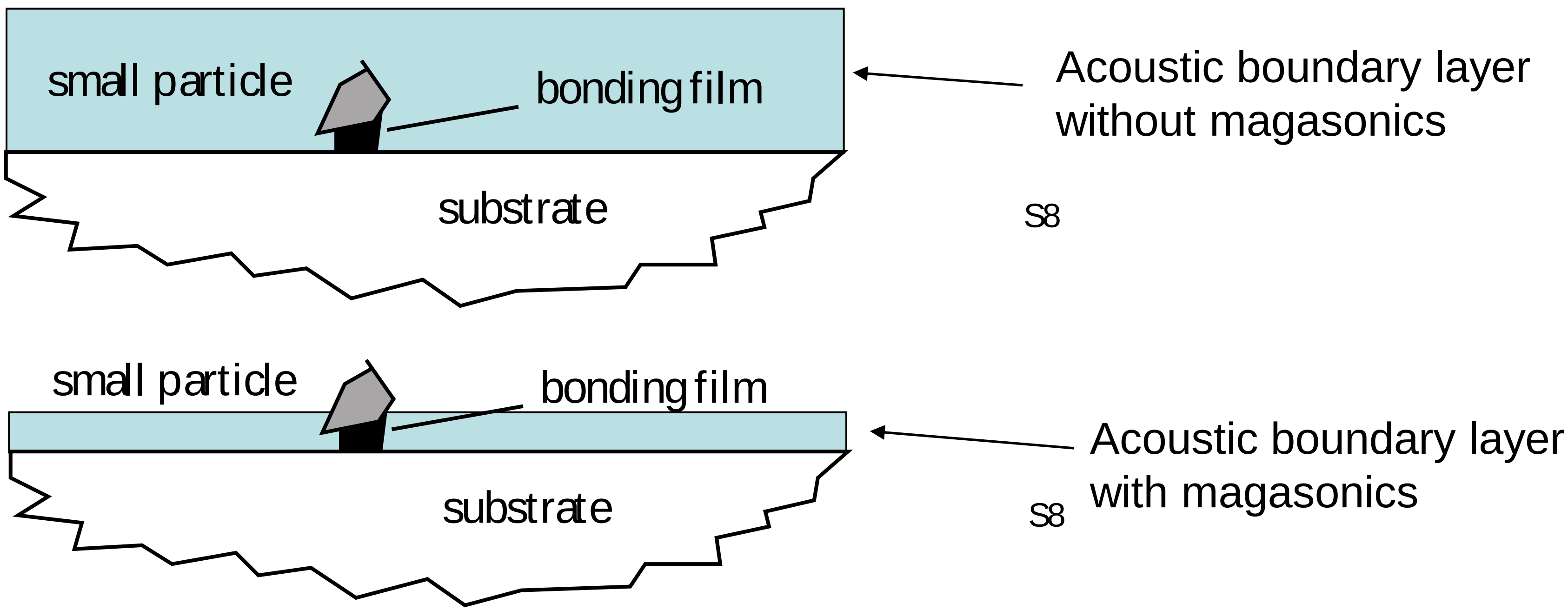
- Introduce a 10 second 1:50 diluted HF dip
  - Between SC-1 and SC-2
  - Re-expose the Si surface for the SC-2 step
- Use fused silica vessels instead of Pyrex
  - Eliminate leached glass components (e.g. sodium)
- Replacement of SC-2 with very dilute, room temperature HCl
  - All metals except Ag and Au are readily soluble in dilute HCl, no need for oxidative desorption
  - Au and Ag contaminants are no longer present in high-purity process chemicals

RCA Megasonic Cleaning System

- Megasonic treatment in SC-1 bath
  - Allows substantial reduction in solution temperature
- Megasonic in rinsing of wafers
  - Much more efficient than immersion tank processing

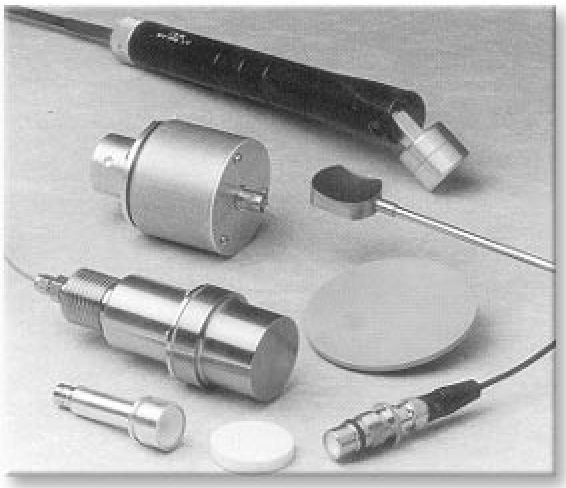
Megasonic Cleaning

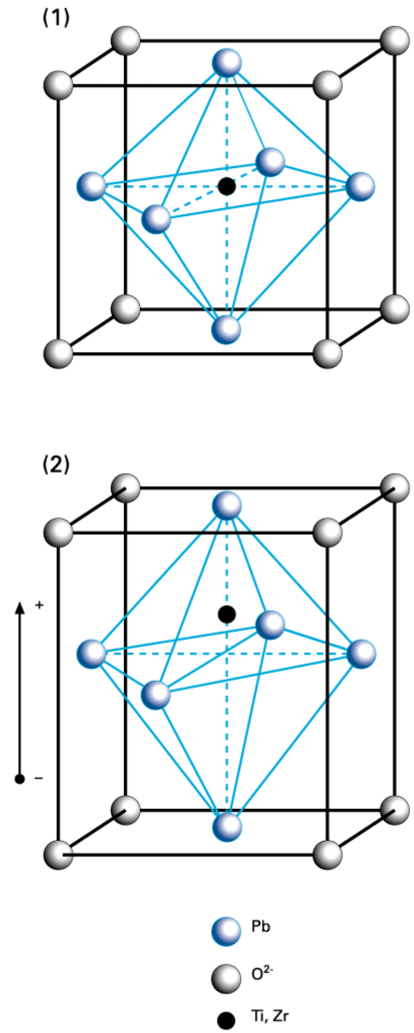
- Ultrasonic energy with frequencies near 1 MHz
- Can be combined with other liquid cleaning solutions
  - SC1 and SC2
- Small acoustic boundary layer.

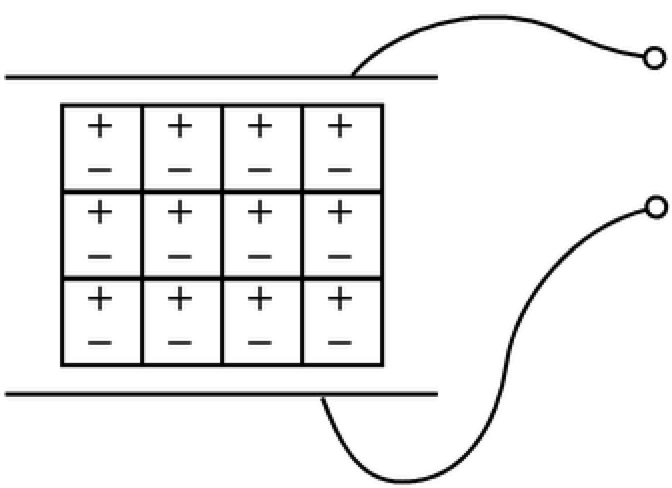


A.A. Busnaina & F. Dai, “Megasonic Cleaning”
Semiconductor International, August, 1997

Megasonic/Ultrasonic Transducers



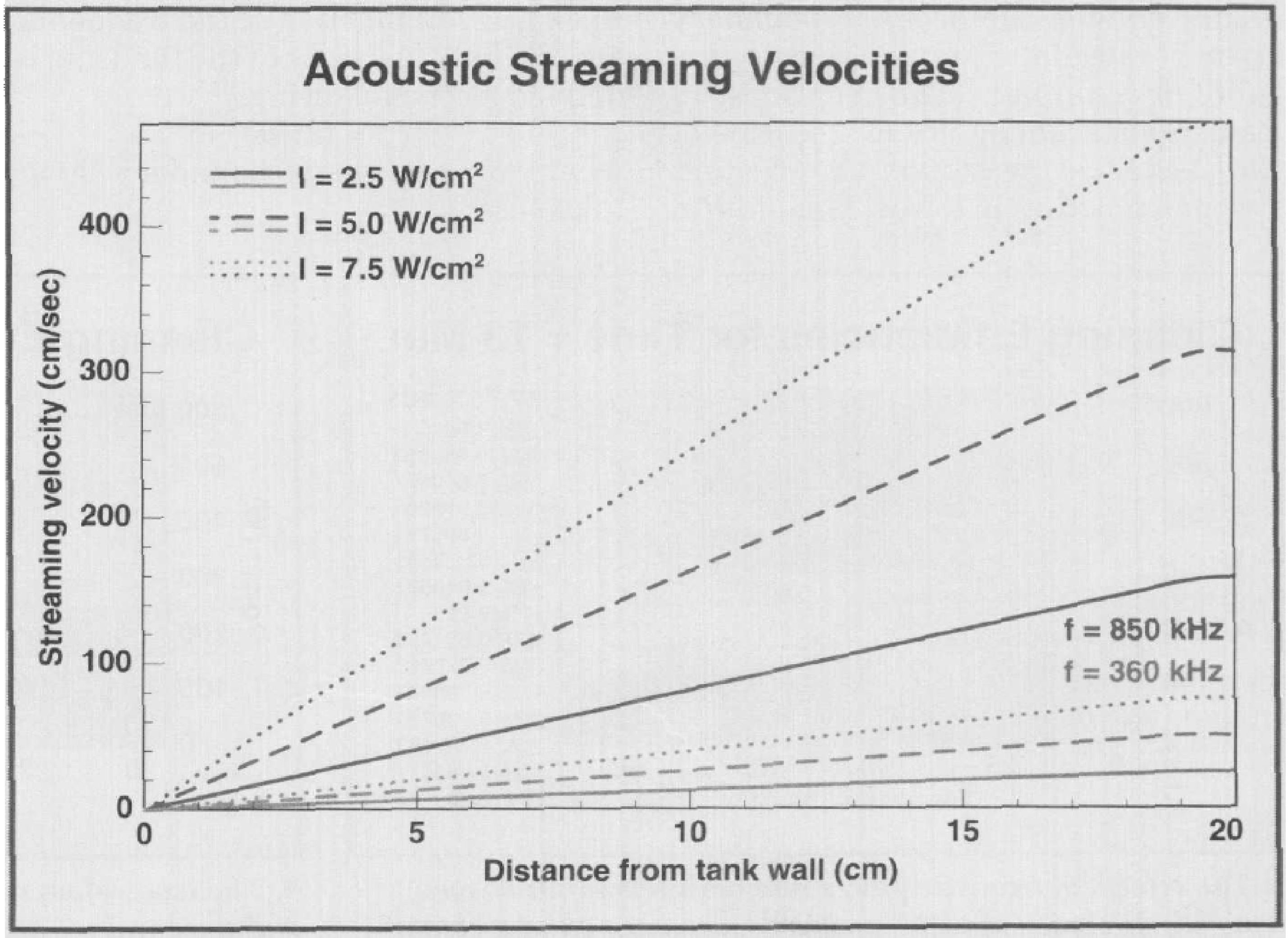




Piezoelectric transducers

ceramic lead and zircon titanite (PZT)

Acoustic Streaming

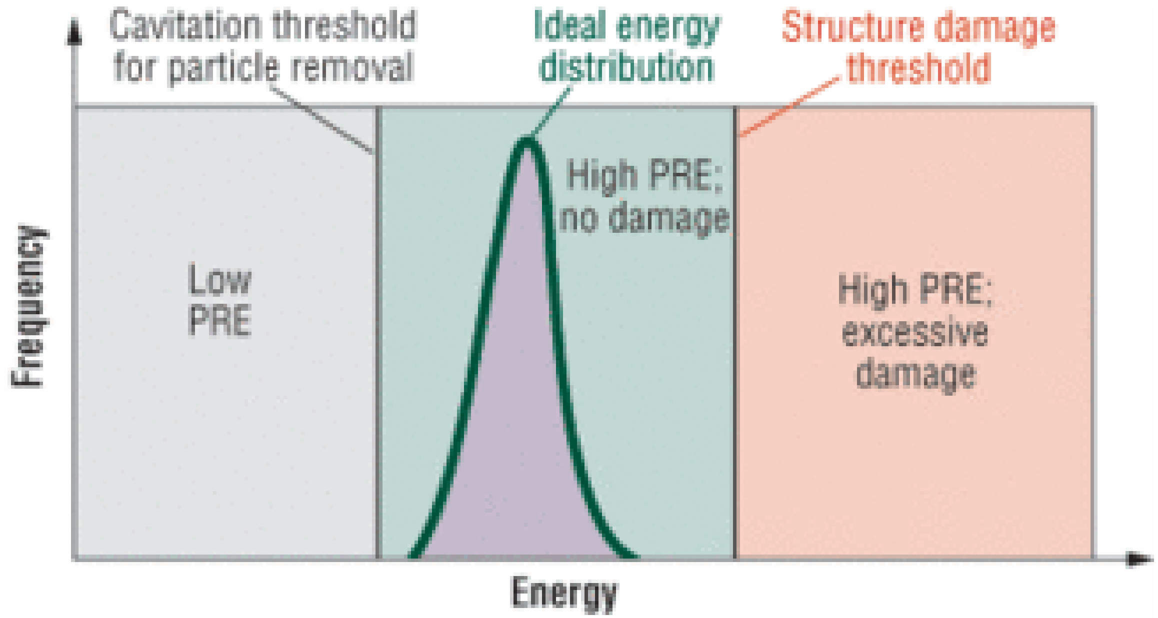


- Eckart-type acoustic streaming

Magasonic Cleaning (II)

- Particle removal efficiency (PRE)
  - Optimal megasonic power (400-500W)
  - Optimal cleaning temperature (28-35 C)
  - Optimal cleaning time (12-15 min)
  - Redeposition

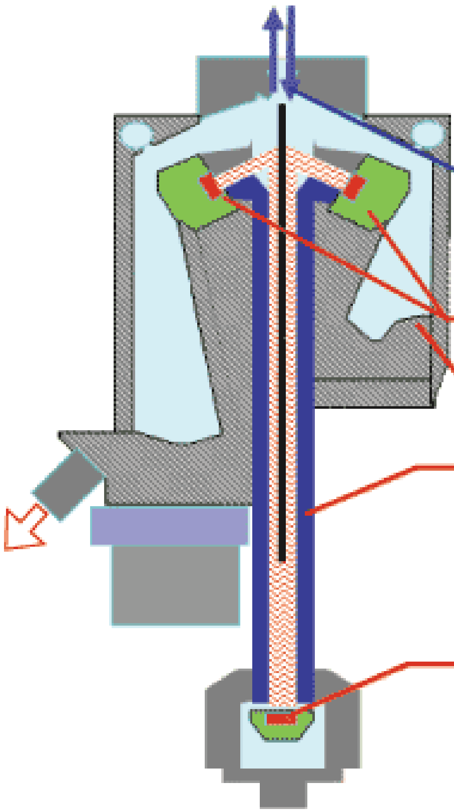
Dilemma between cleaning power and structure damage

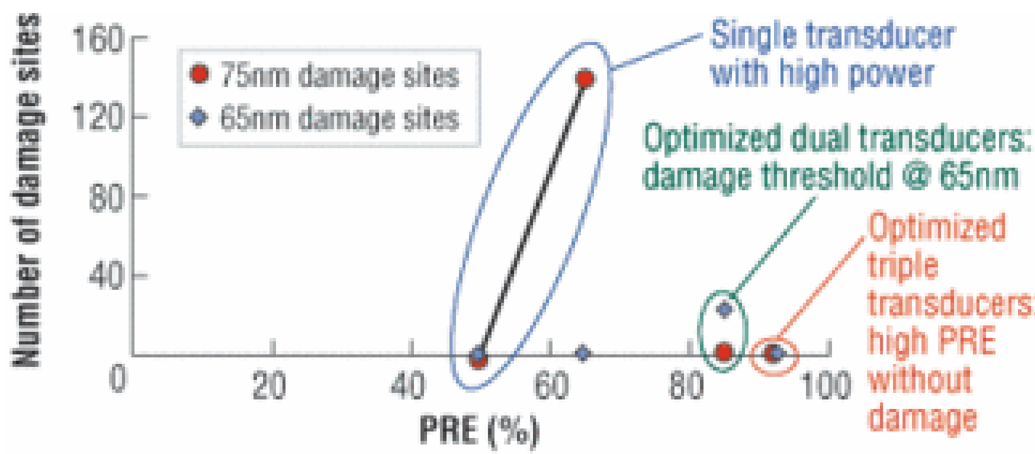


- High particle removal efficiency (PRE)
- No substrate damage
- Low substrate film loss

Film loss comparison (Å)			
Film	Batch tool	Single-wafer Emersion	*ITRS* target
Si	2.5–10	<0.25	0.4
SiO_2	3–6	<0.1	0.4

Dual-Transducer Megasonic Cleaning



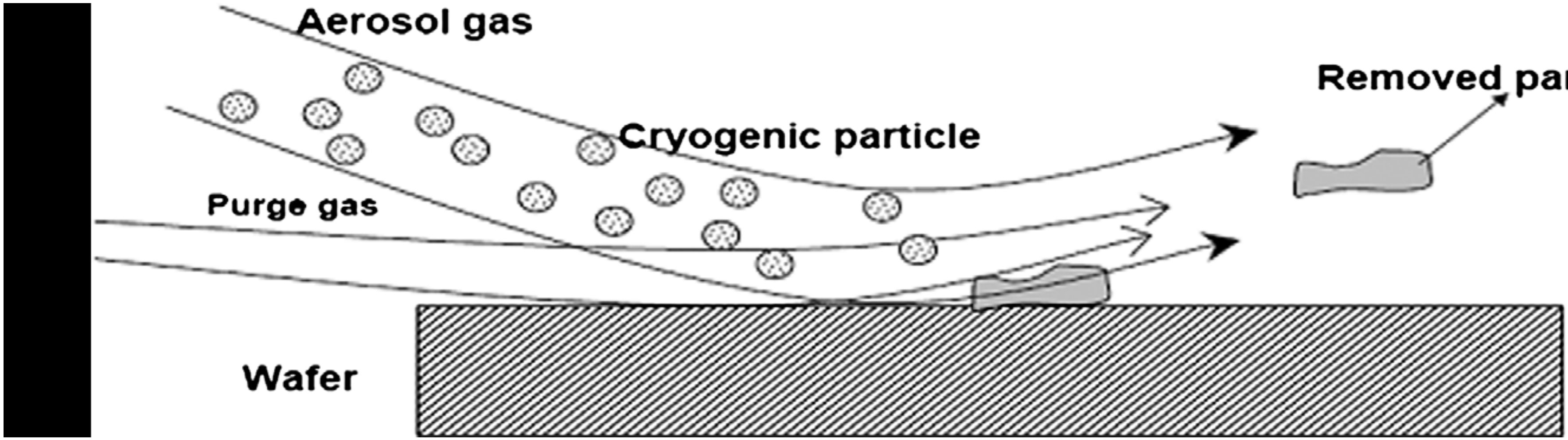


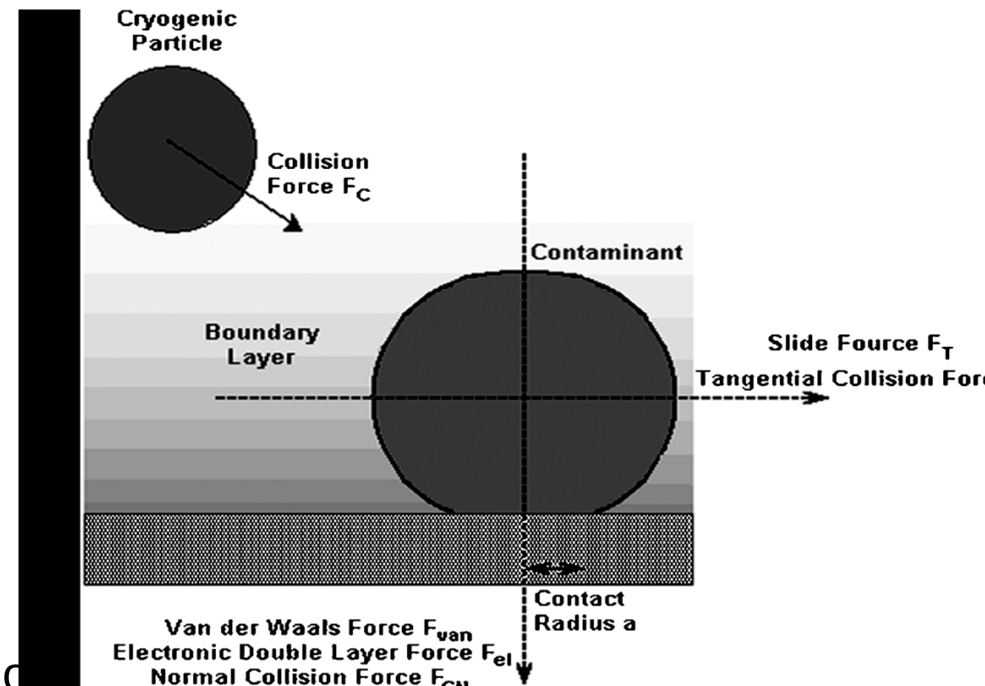
Particle Removal

- Adopted by IC manufacturing
  - RCA cleaning
  - Brush scrubbing
  - Megasonic cleaning

- In development
  - Laser shock wave
  - Supercritical CO_2 cleaning

Cryogenic Cleaning

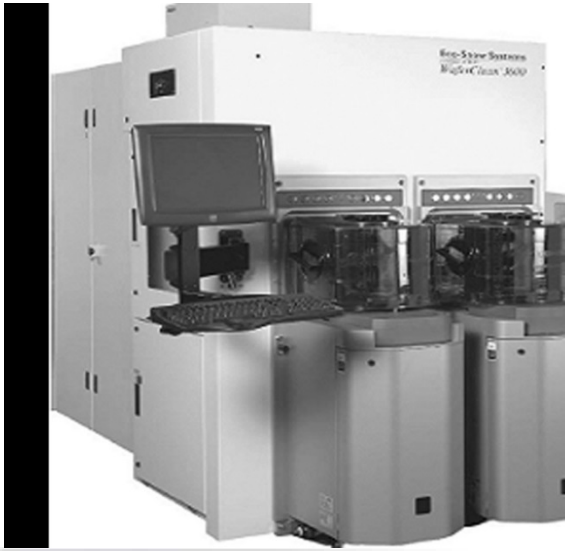




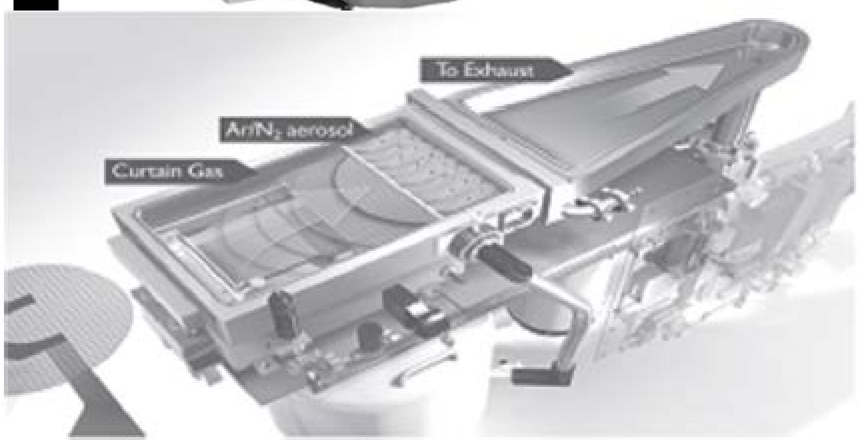
Cryogenic Aerosol Cleaning

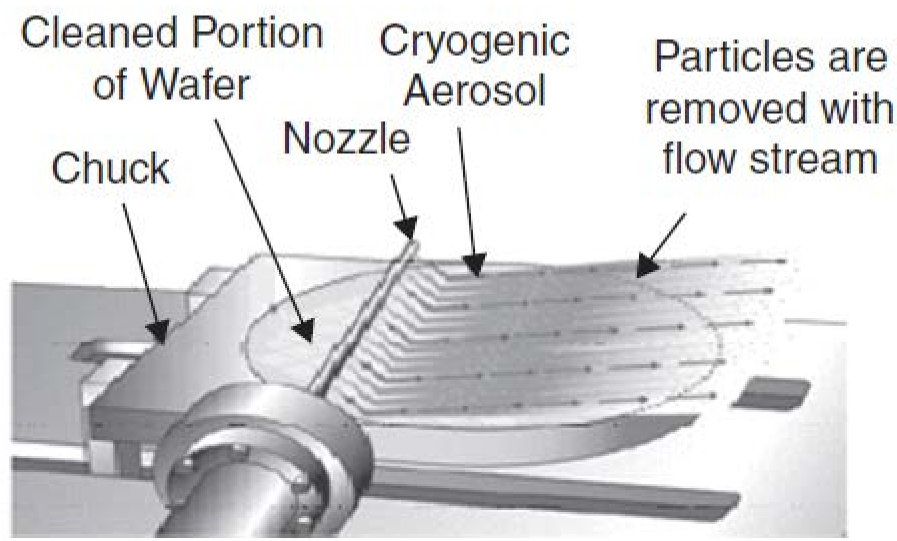
- Dry, non-aqueous, surface conditioning and cleaning method
- Contaminant removal is primarily by physical momentum transfer
  - Does not etch or oxidize surface films
- CO_2, N_2, and Ar/N_2 cryoaerosols
- Particle removals in FEOL transistor gates or high aspect ratio patterns in the BEOL.
- Has been used in MEMS, read/write magnetic moemory heads, photomasks, compound semiconductor devices.

Equipment



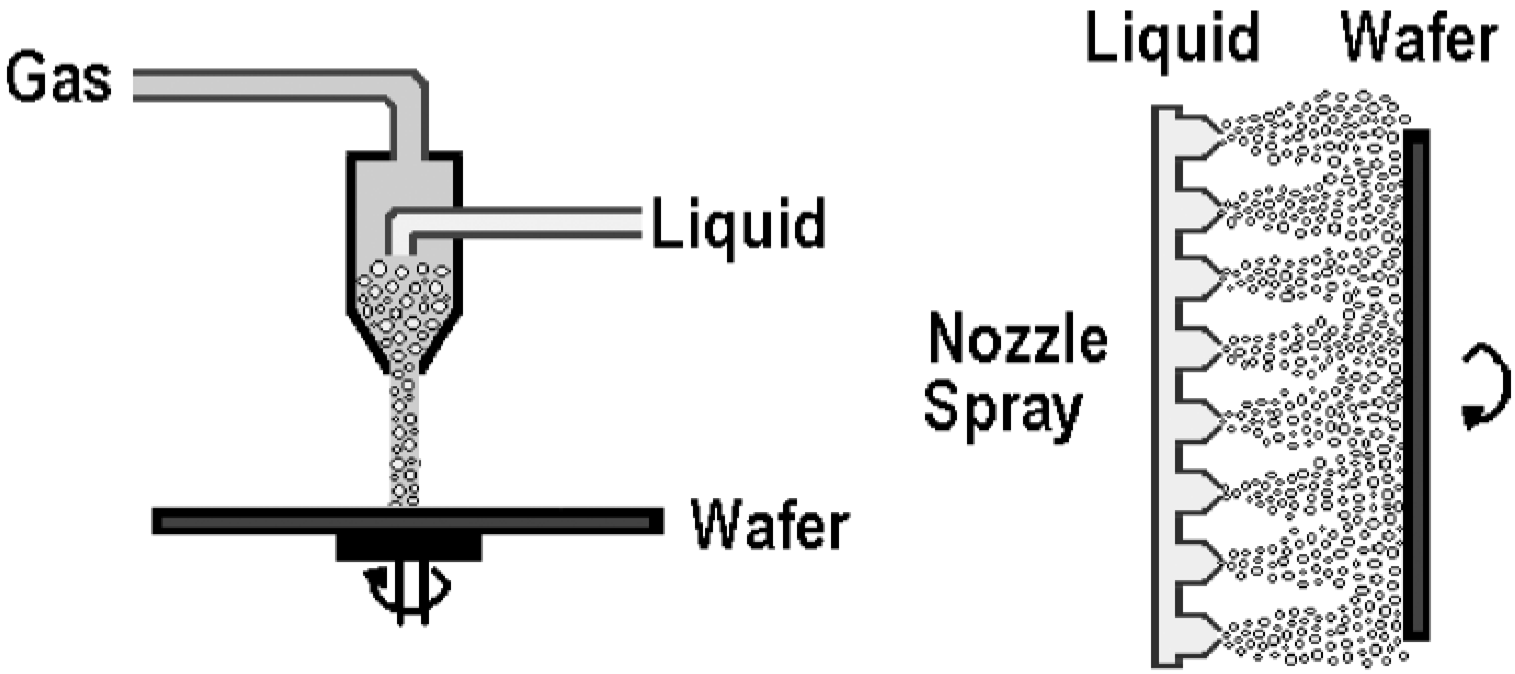
Waferclean™ 3600 manufactured by Eco-Snow Systems.





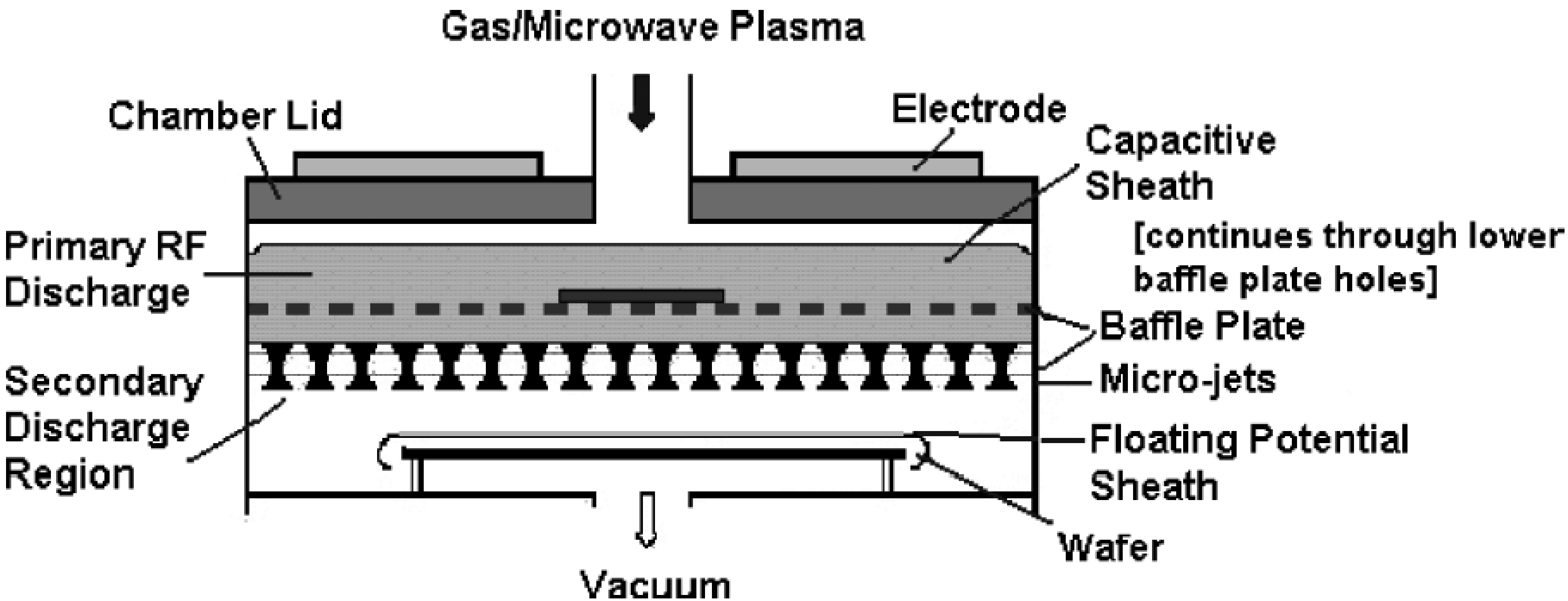
The left-hand side image shows the inside of the process chamber of an ANTARES® CX cleaning system. The right-side hand image depicts the flow pattern and particle transport path during cleaning. Courtesy of FSI International.

Nozzle-based cleaning technology



- Pressurized gas spray, pulsed liquid jet spray

Plasma source for rapid photoresist stripping



- Courtesy of Axcelis Technologies

Brushless post oxide CMP cleaning

- HF:HCl (1:2:200) for 5 min @ 24 C;
- Rinse with Ozone
- SC1 (1:2:30) for 6 min @ 70 C with megasonics
- Rinse with megasonics
- HF:HCl (1:2:200) for 5 min @ 24 C;
- Ozonated rinse, dry