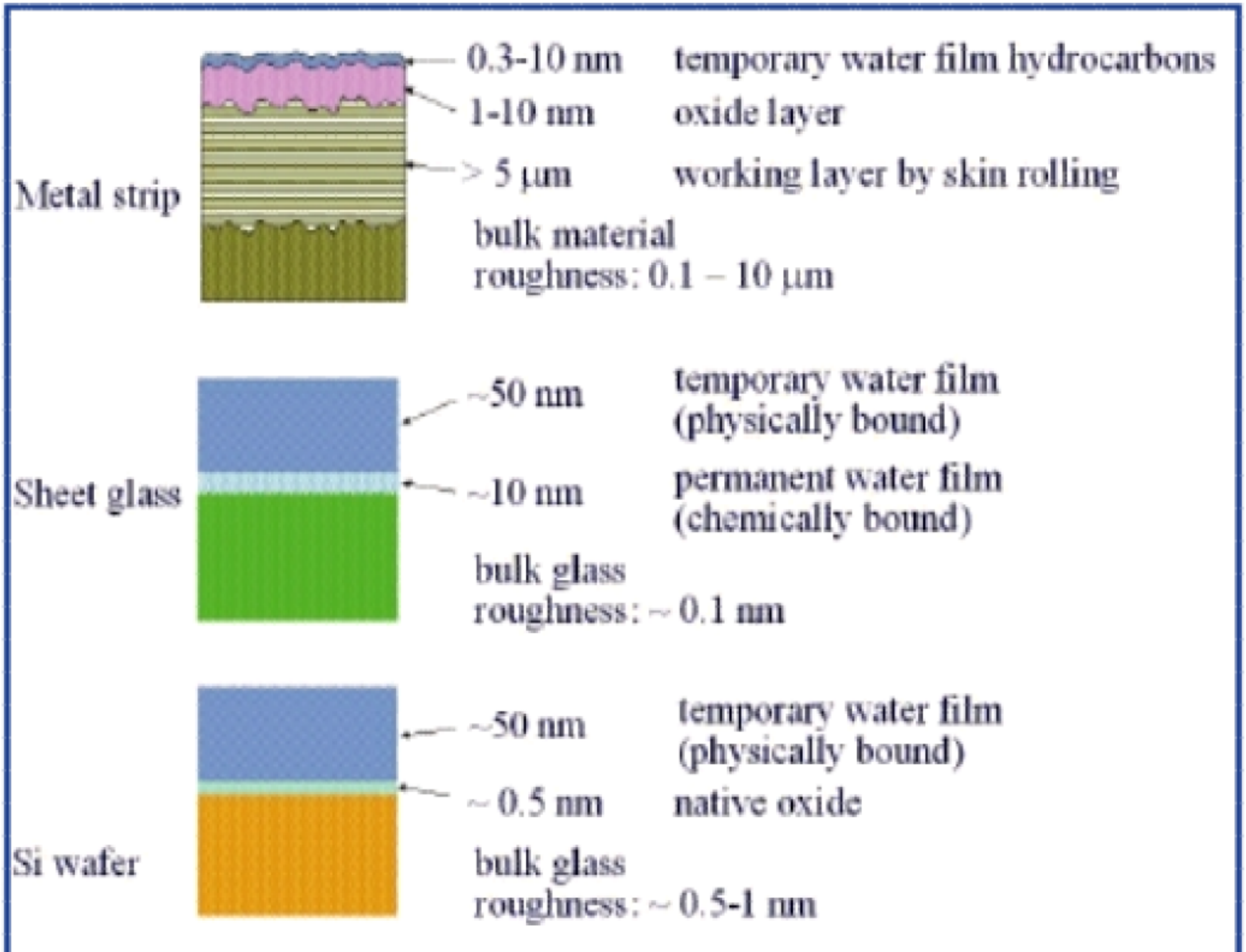
Aalto University

Surface preparation

sami.franssila@aalto.fi

Non-ideal surfaces



Belkind & Gershman; Vacuum Technology and Coatng 2008

Sources of contamination

Gas phase, e.g. water vapor, ammonia, hydro-carbons.

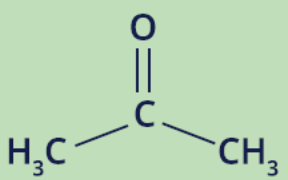
Airborne particles: pollen, smog, viruses,…

Liquid phase, e.g. dissolved oxygen, dissolved metal ions, waterborne particles, residues of cleaning solvents

Solid phase, e.g. packages and boxes, tweezers, spatulas, conveyor belts, robot hands, chucks and holders,…

Liquid phase contamination

- Water purity (18 MΩ-cm; reverse osmosis)
- Cleaning chemicals !!! Never fully pure.



ACETONE

Product:	Acetone
Quality:	ULSI
Bottle size:	2,5L (Unit = 4 x 2,5L)
Parameter	**Specification**
Copper (Cu):	< 20 ppb
Iron (Fe):	< 20 ppb
Lead (Pb):	< 20 ppb
Zinc (Zn):	< 20 ppb

MicroChemical GmbH

Product	**HYDROCHLORIC ACID 37%**
Grade	**ULSI**
Lot Number	"Example"
Manufacturing Date	"Example"
Expiration Date	"Example"

Analysis	Spécifications	Résults
Assay	36.5 % min.	37.9 %
Specific gravity (20°C)	1.19	1.19
Color	10 APHA	<5
Phosphate	0.05 ppm	<0.02 ppm
Sulphate	0.5 ppm	<0.1 ppm
Sulfite	0.8 ppm	<0.5 ppm
Bromide	50 ppm	<5 ppm
Ammonium (NH4)	1 ppm	<0.5 ppm
Free halogens (Cl_2)	Pass test	Pass test
Cations		
Aluminium (Al)	10 ppb	<10 ppb
Antimony (Sb)	10 ppb	<10 ppb
Arsenic (As)	10 ppb	<10 ppb
Barium(Ba)	10 ppb	<10 ppb
Bismuth (Bi)	10 ppb	<10 ppb
Bore (B)	10 ppb	<10 ppb
Cadmium (Cd)	10 ppb	<10 ppb
Calcium (Ca)	10 ppb	<10 ppb
Chromium (Cr)	10 ppb	<10 ppb
Cobalt (Co)	10 ppb	<10 ppb
Copper (Cu)	10 ppb	<10 ppb

0.1 ppm sulphate

If we have 2.5 liters of HCl, how many sulphate groups are there ?

2.5 liters is ca. 2.5 kg, or 70 moles $\approx 4*10^{25}$ molecules.
0.1 ppm means 10^{-7} ➔ $4*10^{18}$ molecules.

If we clean a batch of 25 silicon wafers, 100 mm diameter, total surface area is 4000 cm^2.
If all sulphate from liquid would be deposited on the wafers, that would equal 10^{15} molecules/cm^2.
Silicon surface atom density is $(5*10^{22}\ cm^{-3})^{2/3} = 10^{15} cm^{-2}$.

Solid phase contamination

Objects are stored in boxes, or containers.
Objects are handled by tweezers, hands…
Objects are placed on chucks/holders for processing.

Process chambers are made of solid materials, and the more energetic the process, the more likely it is to kick chamber wall atoms around.

Avoiding solid contamination

- Use inert and hard materials like stainless steel and molybdenum.
- Polish surfaces to minimize sites for foreign atom attachment.
- Clean tweezers/chucks/chambers/boxes (by wet or dry cleaning, or if really dirty, by mechanical cleaning like sand blasting).

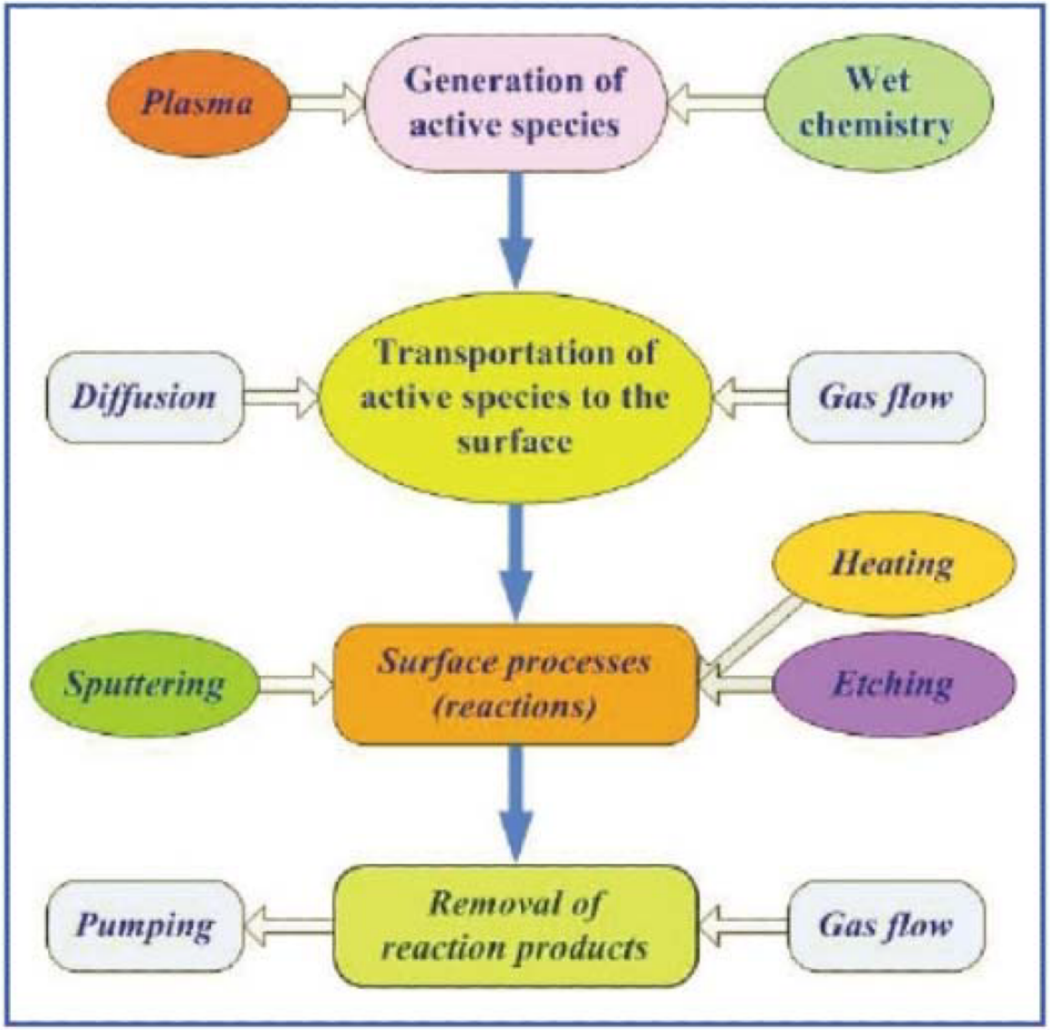
Surface preparation goals

- Removes contamination
- Leaves surface in known condition
- Eliminates previous step peculiarities
- Eliminates waiting time effects

Surface preparation operations

- Cleaning (removal of adherent stuff)
- Etching (removal of surface layers)
- Activation (surface bond modification)
- Passivation (surface bond inactivation)
- Deposition (coating the surface)

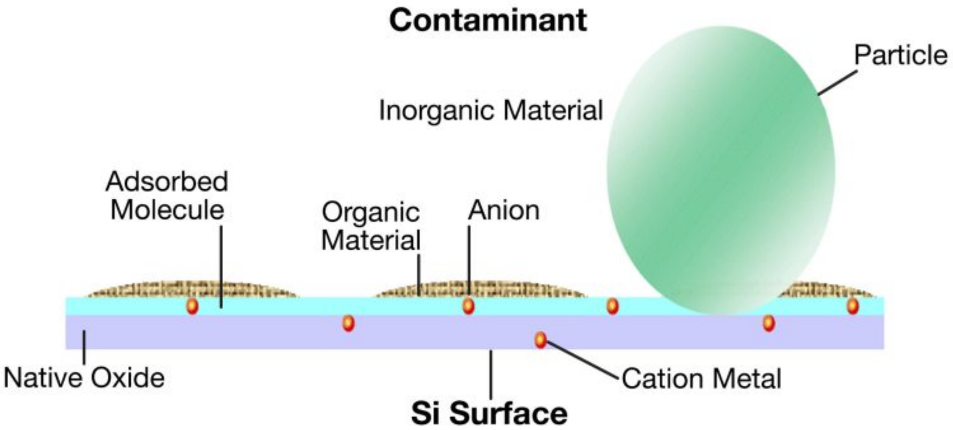
Process steps in cleaning



Belkind & Gershman; Vacuum Technology and Coatng 2008

Cleaning

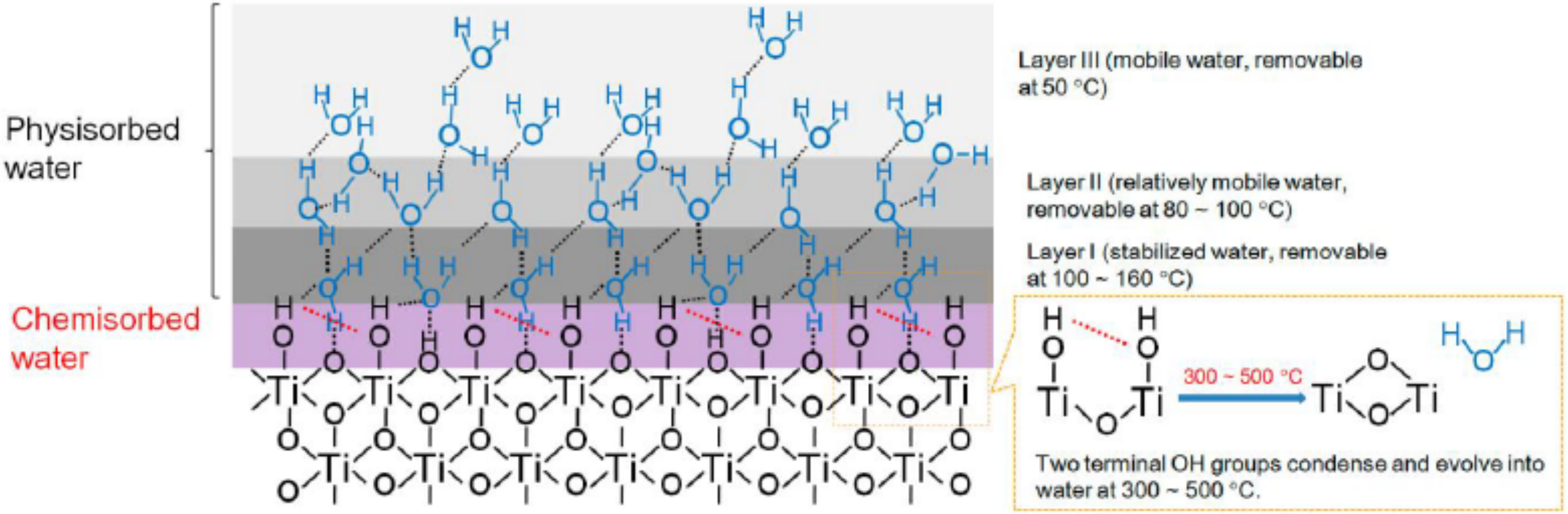
- removal of particles
- removal of native films
- removal of polymeric films
- removal of metals and ions
- removal of adsorbed water



https://www.mksinst.com/n/wafer-surface-cleaning

Surface water

Different kinds of water !
Strongly bonded inner layer (chemisorption, covalent bonds)
Weakly bonded outer layers (physisorption, H-bonds)



C.-Y. Wu et al. Materials 2017, 10, 566

Water removal bake

Water boils at 100^{o}C, in bulk.
But chemisorbed H_2O molecules are tightly bound.

Table 1. Split test matrix

ID	EXSITU WET CLEAN	QUEUE-TIME	WAFER LOADING TEMP.	WAFER BAKE TEMP. AND TIME
<B1>	typical dHF last	1 min.	250°C	650°C for 90s
<B2>	typical dHF last	1 min.	600°C	650°C for 90s
<B3>	typical dHF last	1 min.	800°C	800°C for 180s
<B4>	typical dHF last	3 hrs.	250°C	650°C for 90s
<B5>	typical dHF last	3 hrs.	600°C	650°C for 90s
<B6>	typical dHF last	3 hrs.	800°C	800°C for 180s
<B7>	typical dHF last	8 hrs.	250°C	650°C for 90s
<B8>	typical dHF last	8 hrs.	600°C	650°C for 90s
<C9>	optimized dHF last	1 hr.	250°C	650°C for 90s
<C10>	optimized dHF last	3 hrs.	250°C	650°C for 90s
<C11>	optimized dHF last	8 hrs.	250°C	650°C for 90s

Pagliaro: Surface Preparation for Low Temperature CVD Si Epitaxy Processing, https://www.semiconductor-digest.com/2020/02/03/surface-preparation-for-low-temperature-cvd-si-epitaxy-processing/

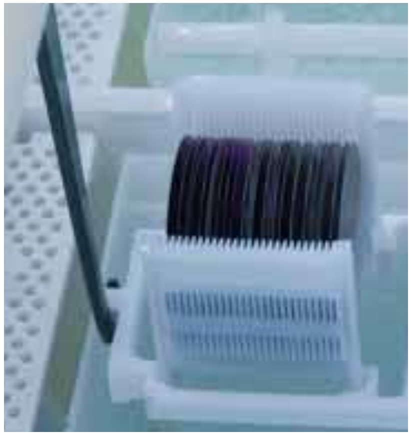
Wet cleaning

Aqueous solutions

Acidic solutions

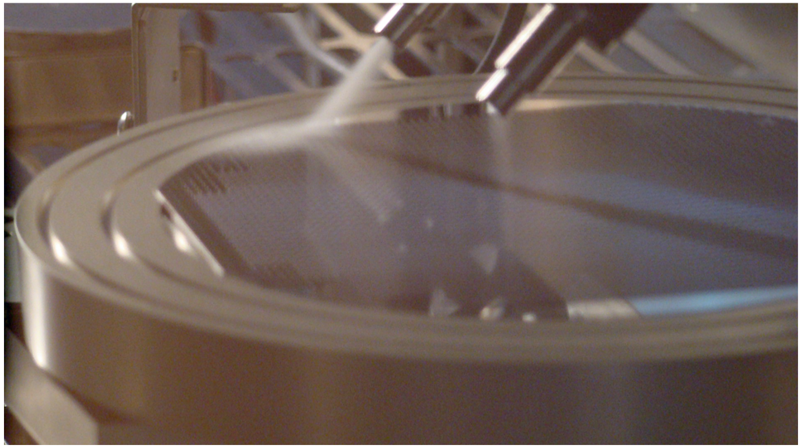
Alkaline solutions

Solvent treatments



immersion

spray/jet



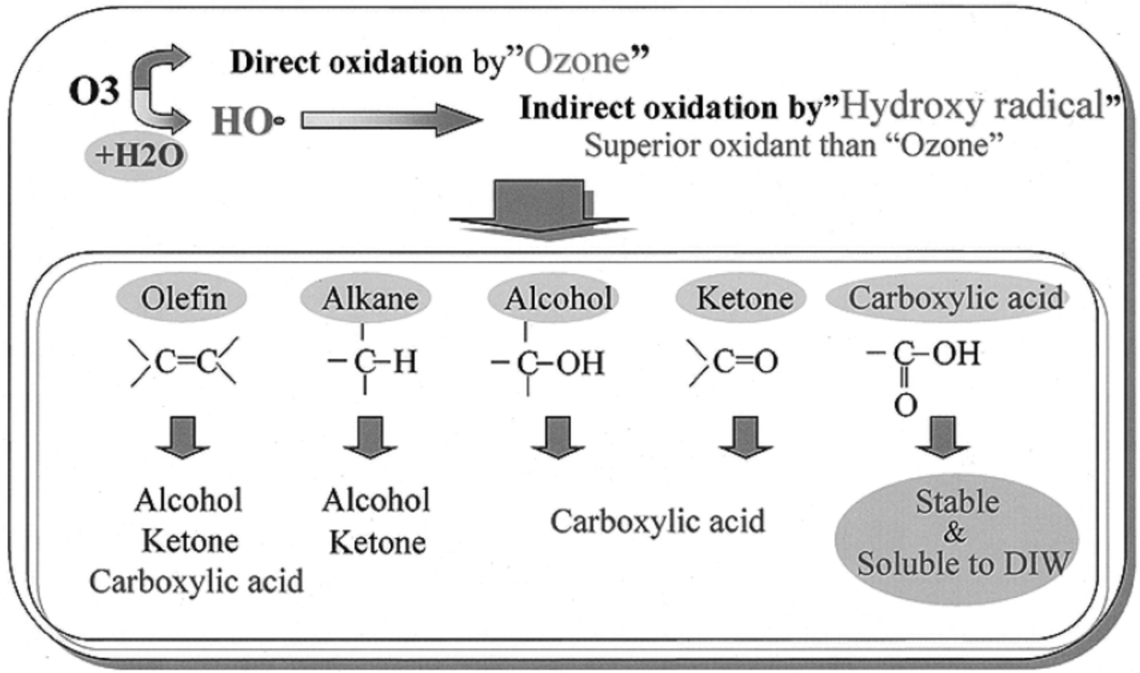
Ozone-spiked water

Ozone, O_3, is very reactive

Ozonated DI-water with 1-100 ppm ozone

Ozone breaks down organic molecules to smaller fragments ➔ water soluble

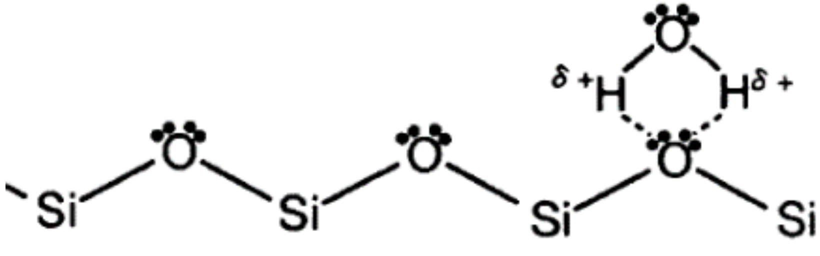
Ozone addition to acidic cleans is also beneficial.



Abe et al: IEEE TRANSACTIONS ON SEMICONDUCTOR MANUFACTURING, VOL. 16, NO. 3, AUGUST 2003 401

Ammonia-peroxide (APM)

- $NH_4OH:H_2O_2:H_2O$ (1:1:5)
- a.k.a. APM, RCA-1 and SC-1 (standard clean)
- operated at 80^{o}C
- removes particles (by undercutting them)
- removes organic materials by oxidation
- leaves surface hydrophilic (OH-terminated)



APM reactions

Ammonia peroxide solution works by oxidizing the silicon surface, and subsequently etching the oxide away.

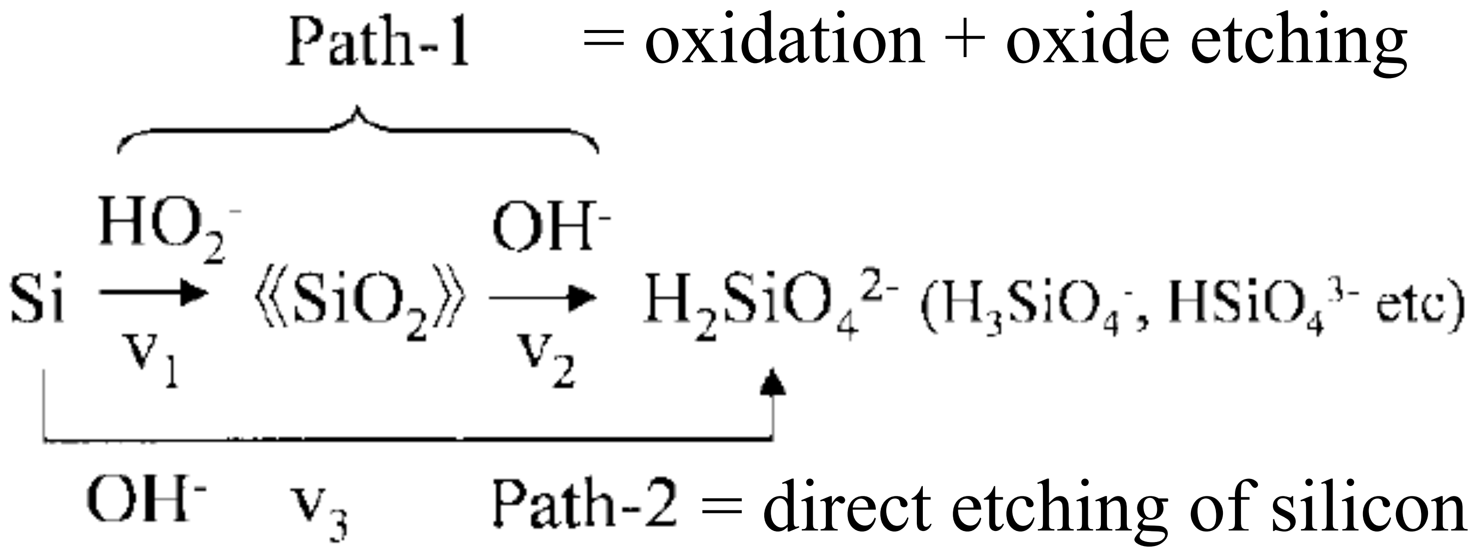
Eq. 12.1	$2\ H_2O_2 \implies 2\ HO_2^- + 2H^+$	peroxide disproportionation
Eq. 12.2	$Si + 2\ HO_2^- \implies SiO_2 + 2\ OH^-$	silicon oxidation

----

Eq. 12.3	$Si + 2\ H_2O_2 \implies SiO_2 + 2\ H_2O$	total reaction for oxidation
Eq. 12.4	$SiO_2 + OH^- \implies HSiO_3^-$ (aq)	oxide etching

Silicon etch rate in ammonia-peroxide is ca. 0.5 nm/min and typical 10 minute clean thus results in ca. 5 nm silicon etching.

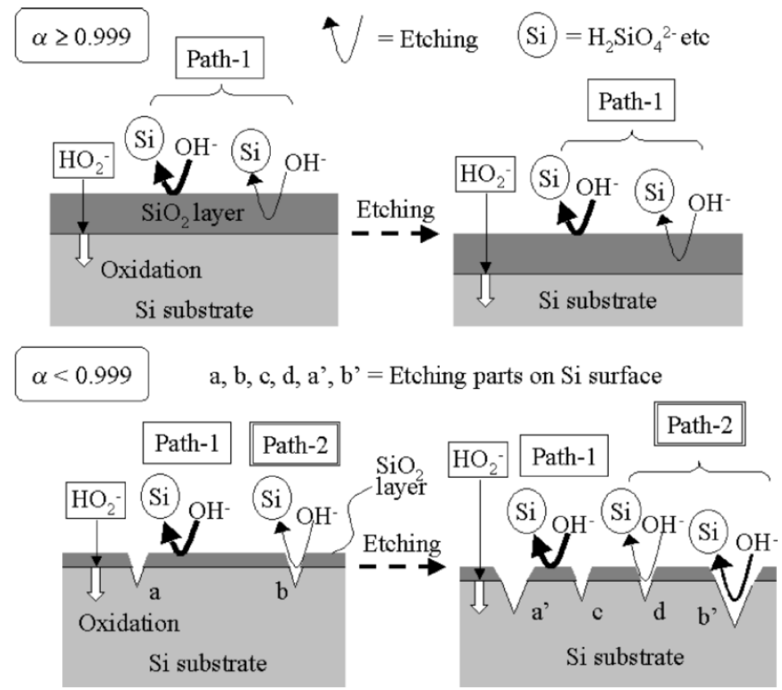
Detail mechanism of APM



α is the ratio of the etching reaction of path-1 to total etching reaction.

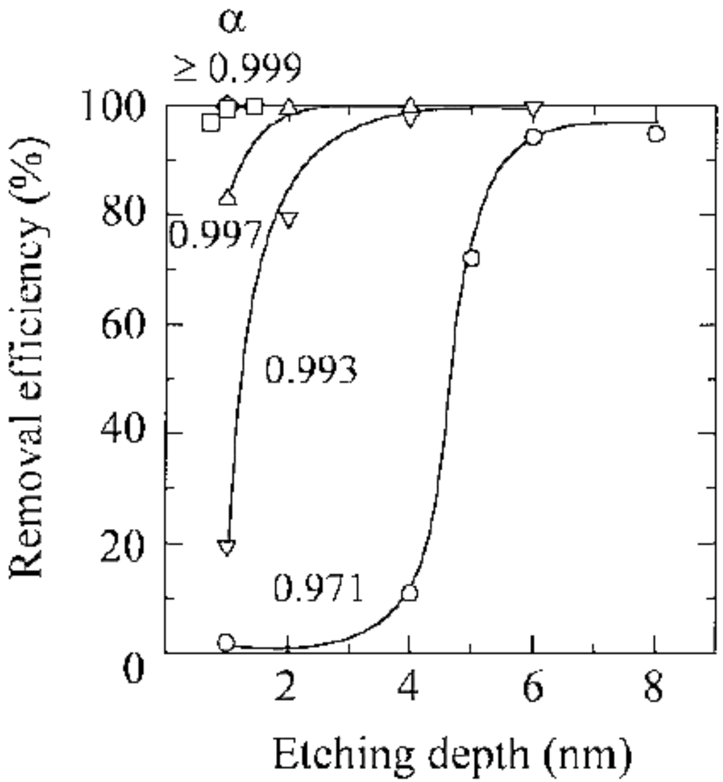
Competing etching reactions

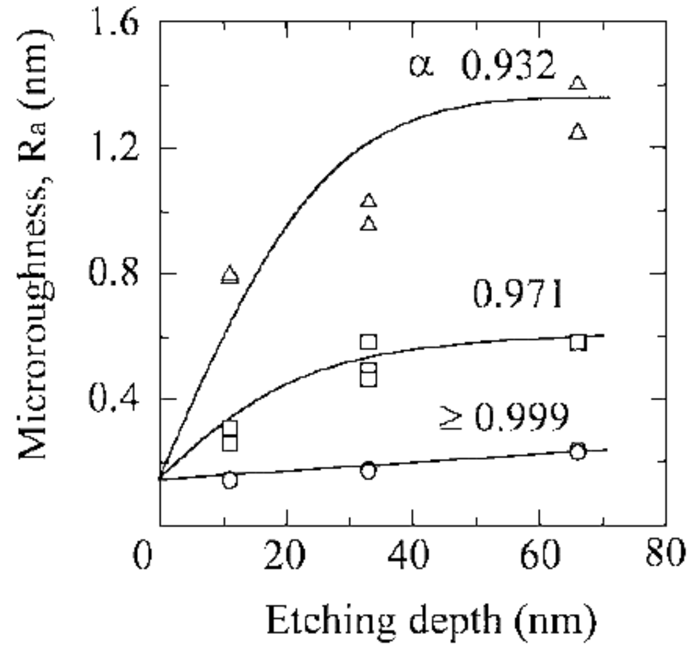
- etching reaction of a Si substrate proceeds along two paths (path-1, path-2) in APM.
- In path-1, the Si surface is oxidized by OH_2^-
- then the SiO_2 layer is etched by OH-.
- In path-2, the Si surface is directly etched by OH-.
- Path-1 is favorable for APM cleaning because path-2 causes some problems, such as too fast etching, an increase in surface microroughness, and a decrease in particle removal efficiency.



Yamamoto et al: IEEE TRANSACTIONS ON SEMICONDUCTOR MANUFACTURING, VOL. 12, NO. 3, 1999

Particle removal by etching



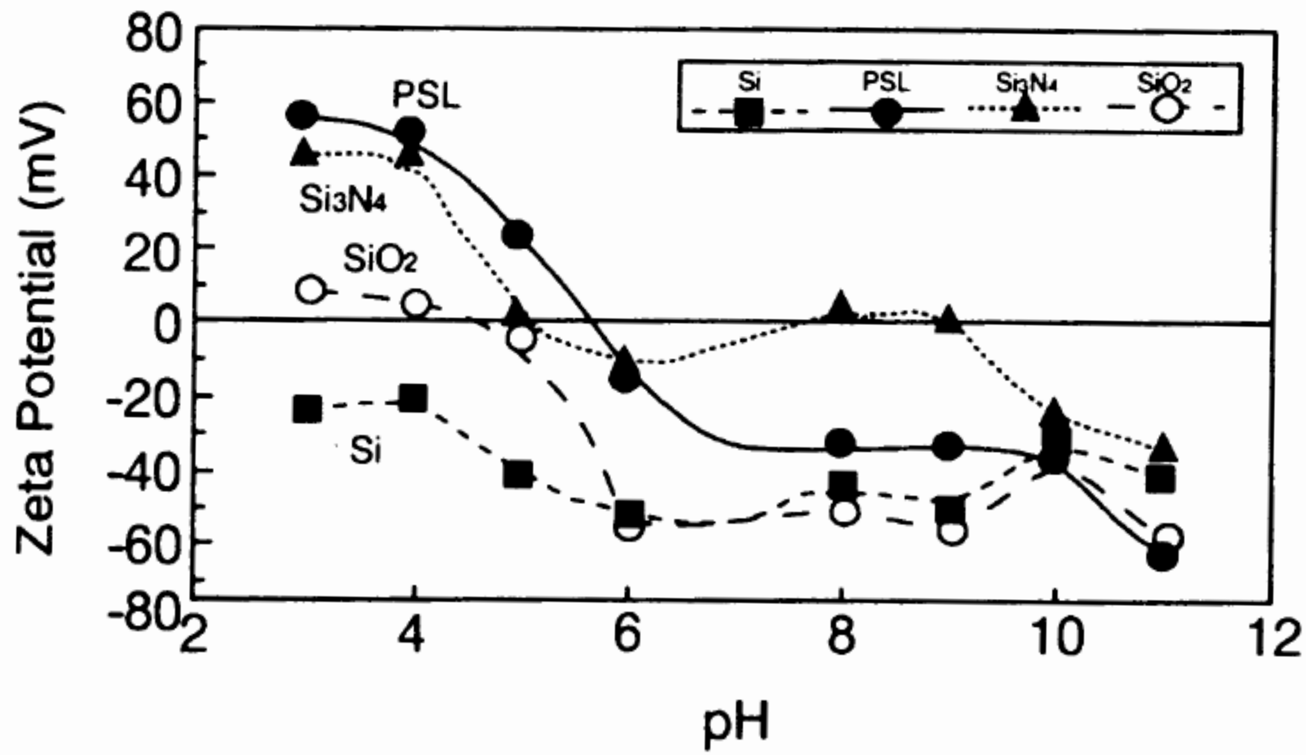


Ammonia-peroxide mixture, etching rate: 1.1 nm/min.

Yamamoto et al: IEEE TRANSACTIONS ON SEMICONDUCTOR MANUFACTURING, VOL. 12, NO. 3, 1999

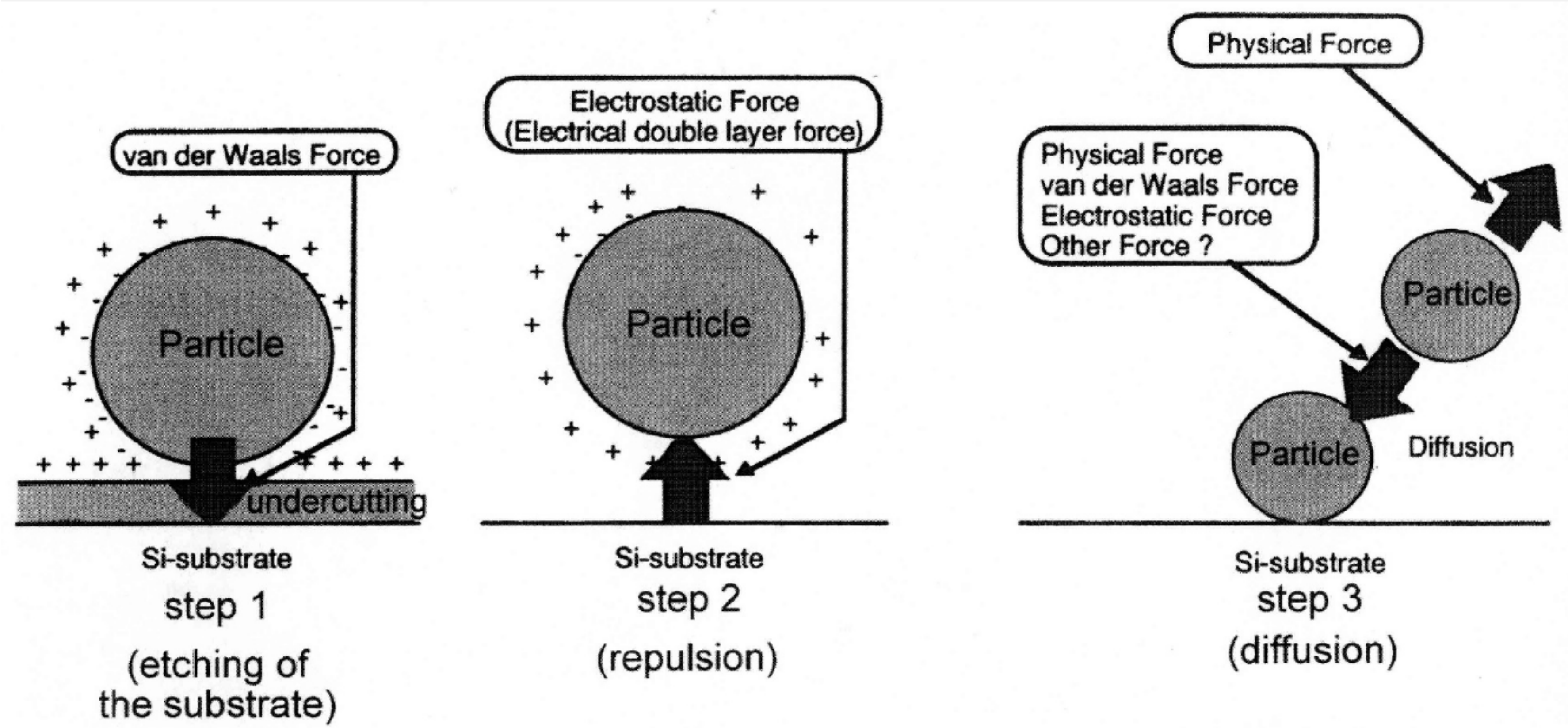
Zeta-potential (surface charge)

If the surface and the particles have opposite charges, they will repel each other ➔ no particle deposition.



Hattori, T. (ed.): *Ultraclean surface processing of silicon wafers,*

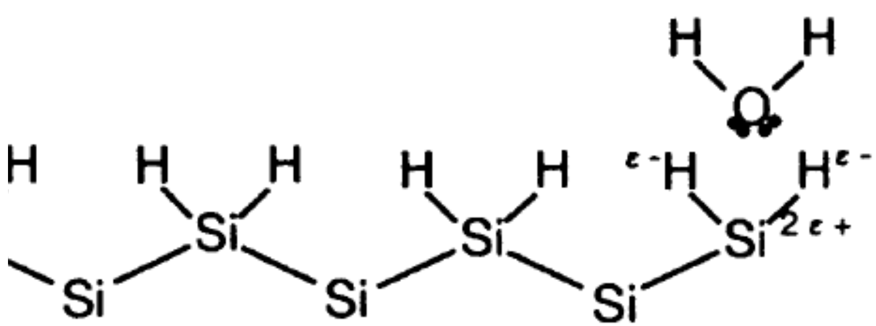
Undercut etching



Hattori, T. (ed.): *Ultraclean surface processing of silicon wafers,*

Hydrogen chloride-peroxide

- $HCl:H_2O_2:H_2O$ (1:1:6)
- a.k.a. RCA-2 and SC-2
- operated at 80^{o}C
- removes metal contamination
- leaves surface hydrophilic (H & F-terminated)



Hattori, T. (ed.): *Ultraclean surface processing of silicon wafers,*

Sulphuric acid

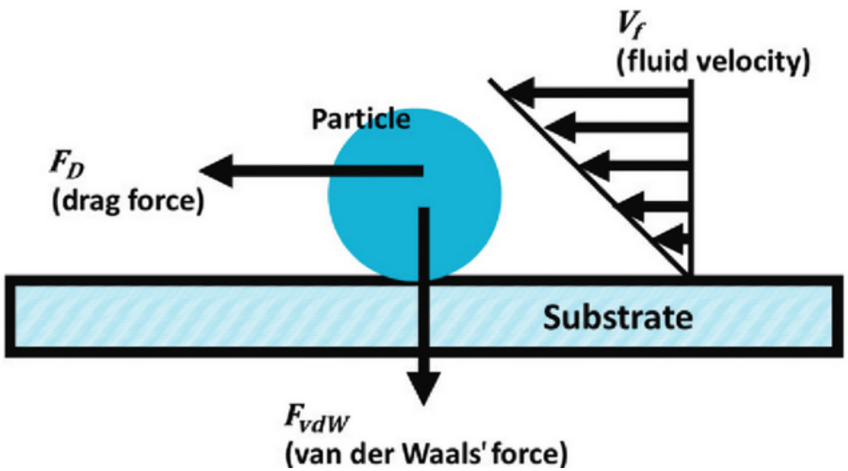
- H_2SO_4 is a strong oxidant
- Organics removal by oxidation
- Metals dissolved
- Oxidation is enhanced by addition of peroxide H_2O_2
- 120^oC operating temperature
- May leave sulphur residue
- Chemical waste

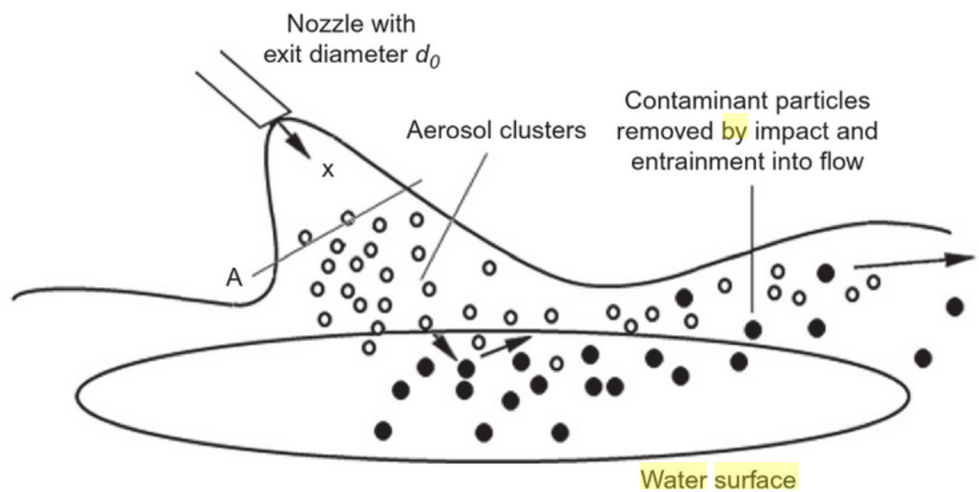
HF, hydrofluoric acid

- removes SiO_2
- comes in many concentrations and formulations:
  - DHF (dilute HF), HF:H_2O (1:100-1:1000) (room temp)
  - BHF (buffered HF, HF:NH_4F 6:1 volume ratio (at 35^oC)
  - strong HF (49%) (room temperature)
- leaves surface hydrophobic

- does not give a burning sensation immediately
- delayed attack on bone after diffusing through the skin
- special gel treatment ! Check this gel before using HF.

Jet cleaning/aerosol cleaning





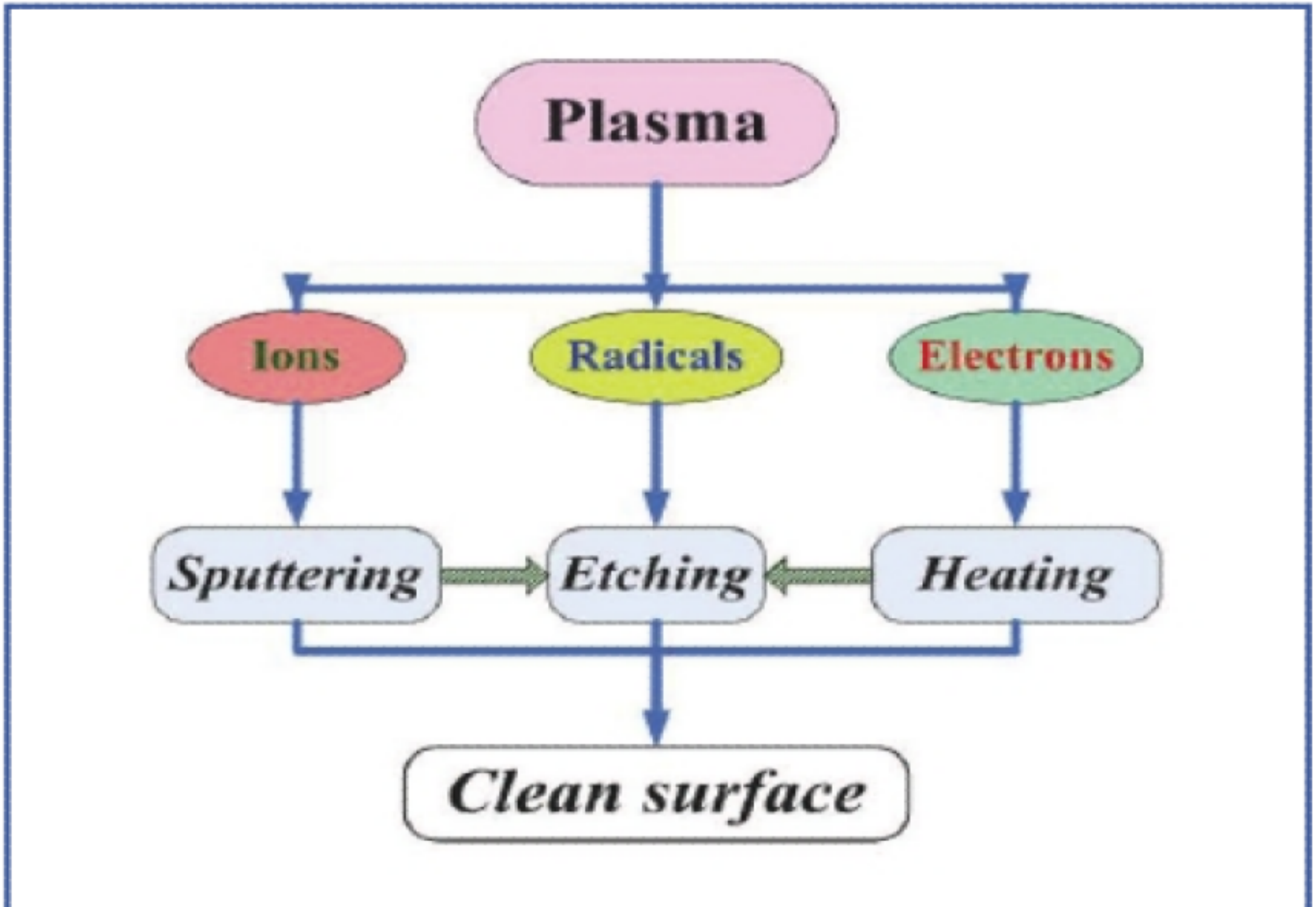
Provides mechanical extra energy.

Kohli & Mittal: Developments in Surface Contamination and Cleaning, Volume 10

Dry cleaning

• Vapors	anhydrous HF
• Gases	O_3, H_2, HCl
• Ions	Ar+
• Atoms	Si
• Photons	UV (with Cl_2 or O_3)
• Plasmas	CF_4
• Aerosols	CO_2
• Thermal bake	

Plasma cleaning mechanisms



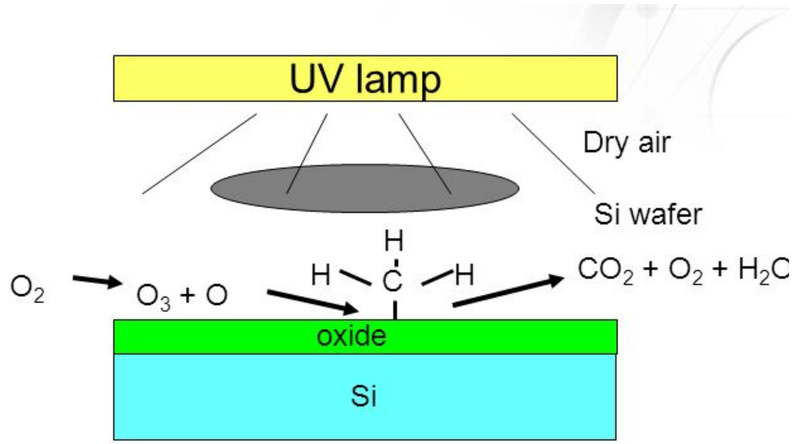
Belkind & Gershman; Vacuum Technology and Coatng 2008

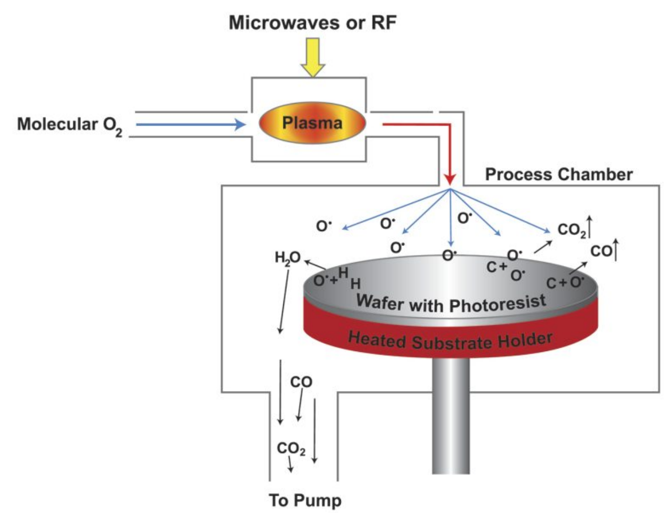
Ozone dry cleaning

UV-ozone cleaning:

Combined effect of UV-induced bond breakage and chemical action by ozone

Downstream plasma cleaner:
ozone diffuses; no UV-exposure

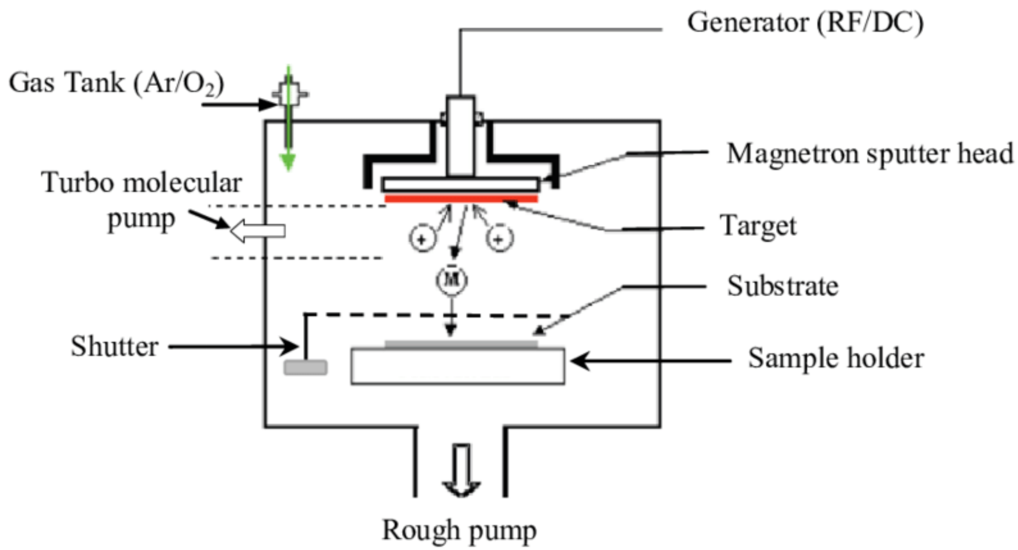




Surfaces will be oxidized in the process (a few nanometers)

https://www.mksinst.com/c/wafer-and-chamber-cleaning

In-situ cleaning in sputtering



1. Sputter clean the target, while substrate is covered by shutter
2. Apply bias to substrate, and argon ions will bombard the substrate, and hit off surface specie

Adel et al: Modeling of magnetic properties of iron thin films deposited by RF magnetron sputtering using Preisach model, 2016

Plasma: sales talk

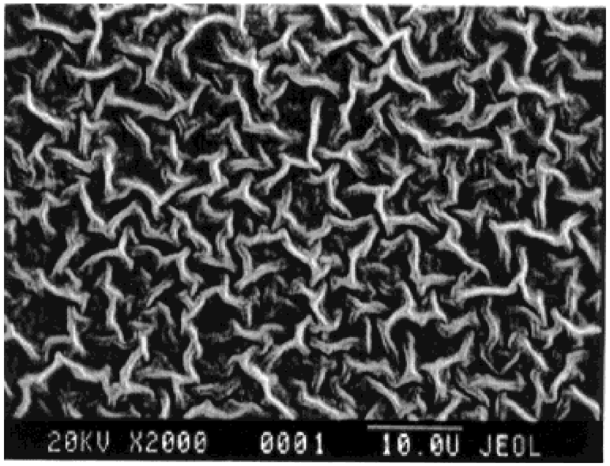
✓ Cleans even in **the smallest cracks** and gaps
✓ Cleans **all component surfaces** in one work step, including the **interior of hollow bodies**
✓ **Residue-free removal** of breakdown products by vacuum extraction
✓ **No damage** to solvent-sensitive surfaces by chemical cleaning agents
✓ **Removal** also of **molecularly fine residues**
✓ **Fit for immediate further processing**. No venting or removal of solvents
✓ **No** storage and **disposal** of hazardous, polluting and harmful **cleaning agents**
✓ Very **low process costs**

https://www.plasma.com/en/cleaning-with-plasma/

Etching

- Etch away any unwanted film/material
- Remove uppermost layers of material itself to reveal hopefully intact material
- Etch and undercut particles ➔ particle removal

Etching easily roughens surface



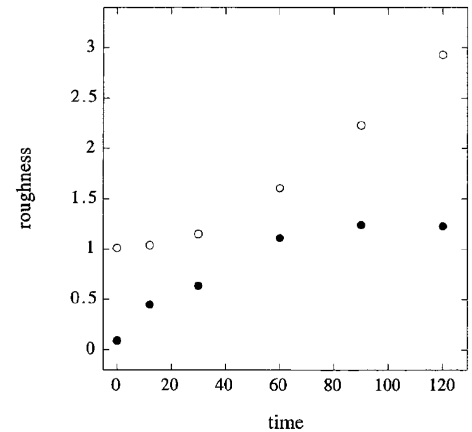
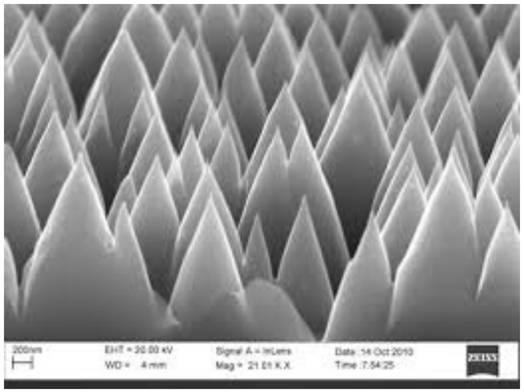


Figure 5. Peak to valley (●, in micrometers) and Wenzel's (○, ratio of surface area to geometric area) roughness values of polypropylene as a function of argon/PTFE plasma reaction time.

- Polypropylene was simultaneously roughened and fluorinated by etching in argon + PTFE plasma.
- Surface is roughened due to the differential rates of crystalline and amorphous regimes.
- Reaction time can be used to control the nature of the surface roughness.

Youngblood & McCarthy: *Macromolecules* **1999,** *32,* 6800-6806

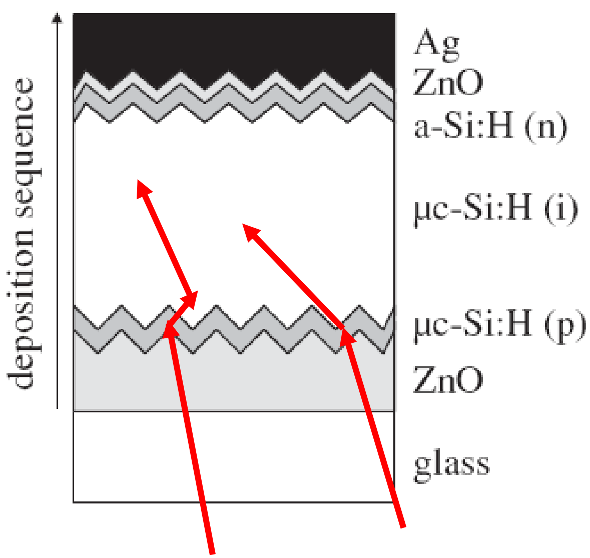
Rough on purpose



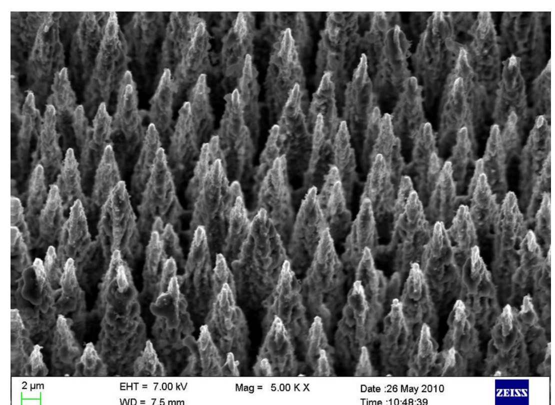
You might want to increase surface area ➔ keep etching…

Trap light by forward scattering in solar cells and photodetectors.

More area for sensing molecules to attach to.



Improved adhesion by increasing mechanical locking.

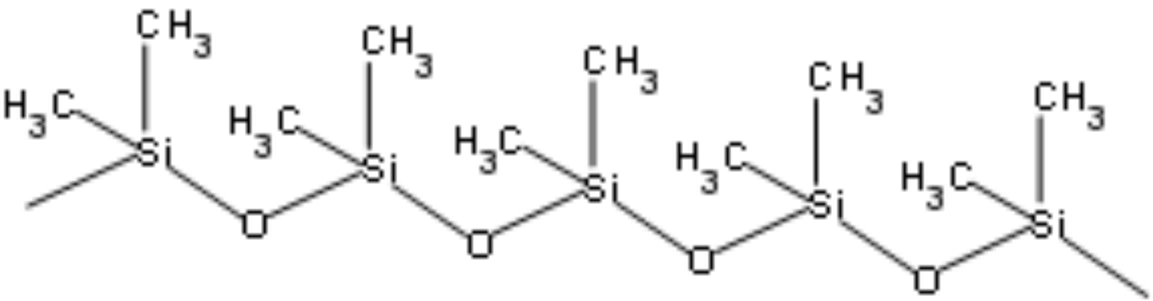


Gimple et al: Study on contact materials for sulfur hyperdoped Black Silicon, 2011

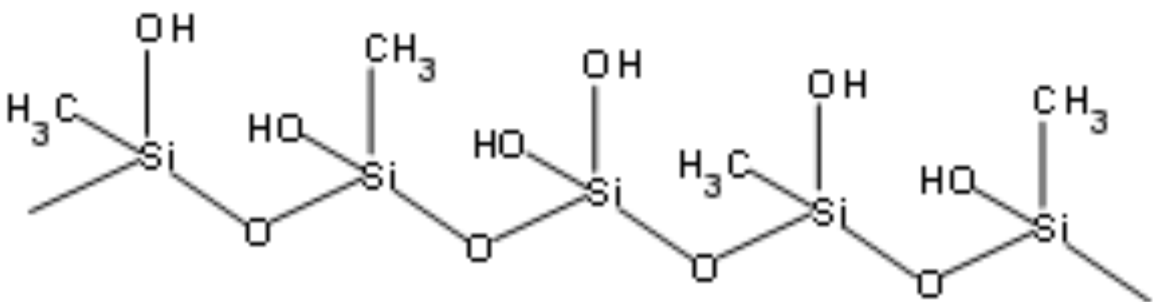
Activation

- Provide surface with bonds that are useful in the next step
- Chemical treatment, e.g. NaOH ➔ hydroxyl-terminated surface
- Physical treatment, e.g. UV, ion bombardment ➔ broken, active bonds
- Biological treatment, e.g. single strand DNA attached, to bind to complementary strand

PDMS in O_2 plasma



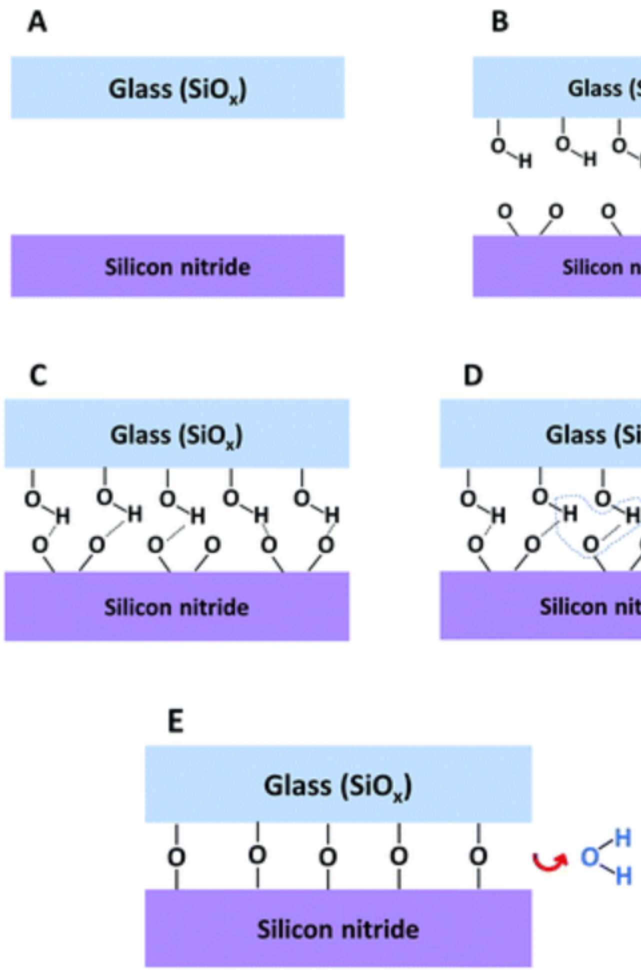
Native PDMS surface with methyl groups (CH_3).



Oxygen plasma treated hydrophilic PDMS surface with hydroxyl and methyl groups.

OH- groups good for bonding with glass/oxides.

Activation can lower bonding temperature



Reactive bonds from activation enable bonding at lower temperature.

One or both wafers may need to be activated.

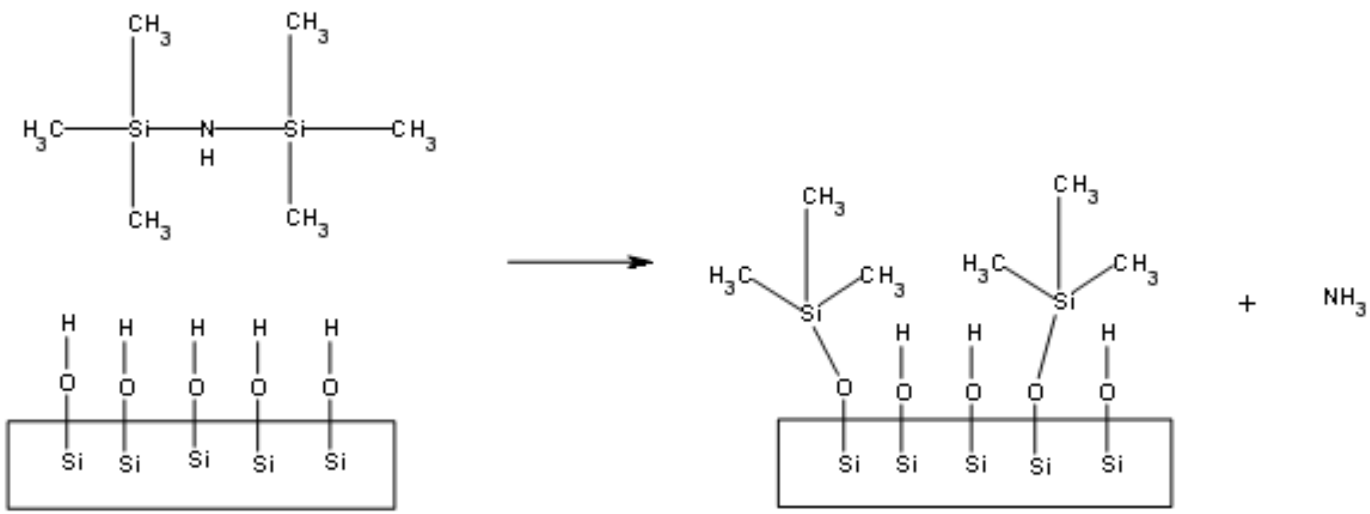
At least we need to start from known condition.

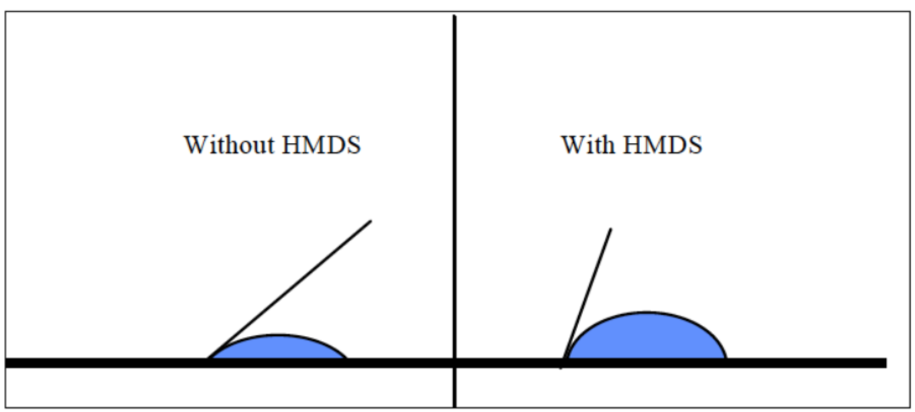
Pasternak et al: RSC Adv., 2018, **8**, 2161-2172

Deposition

- Adding material on surface
- Molecular layers with desired physical properties, e.g. HMDS renders surface mildly hydrophobic ➔ better interaction with hydrophobic material
- Self-assembled monolayers, SAMs
- Oxidation to create native oxide film
- Deposition of real thin films (PVD, CVD, ALD)

HMDS hydrophobization



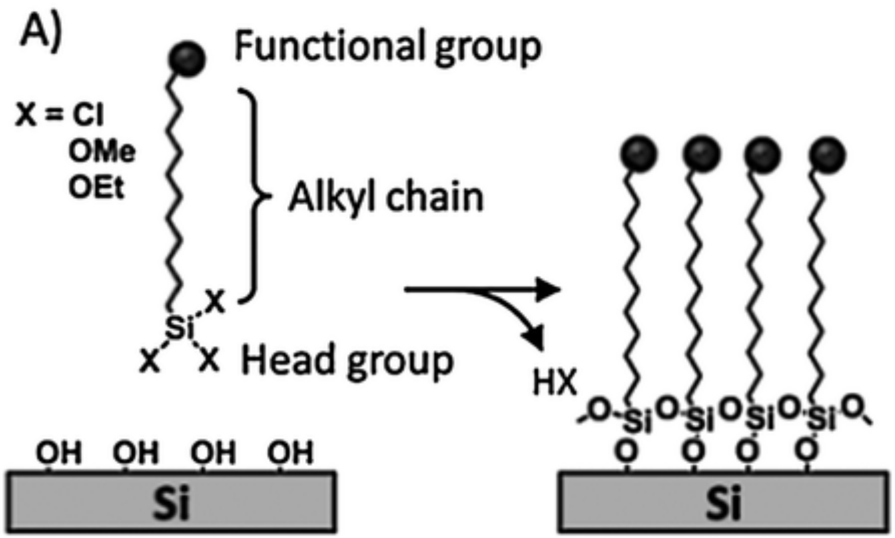


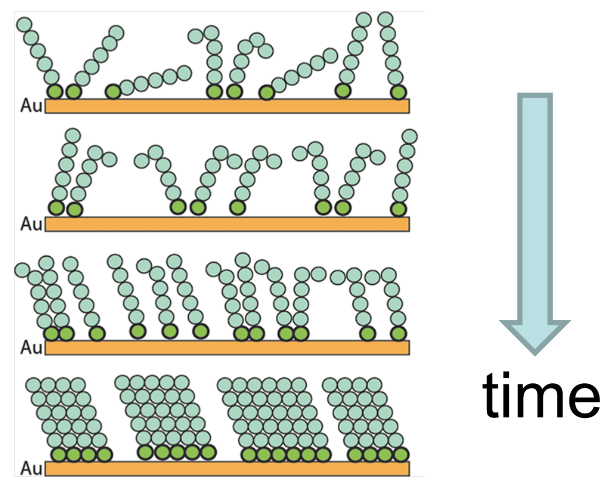
Hexamethyl disilazane (HMDS) vapor phase coating renders silicon surface slightly hydrophobic, CA ca. 70^{o}. Hydrophobic polymer in next step will adhere to it better than to oxidized surface with CA ca. 20^{o}.

SAMs: self-assembled monolayers

A single reaction.
Covalent bond.
Self-terminating.

In liquid or vapor phase.
Slow reaction, hours typically.
Shorter chain ➔ easy assembly
Longer chain ➔ more difficult assembly, but functional group further from surface and effect greater.

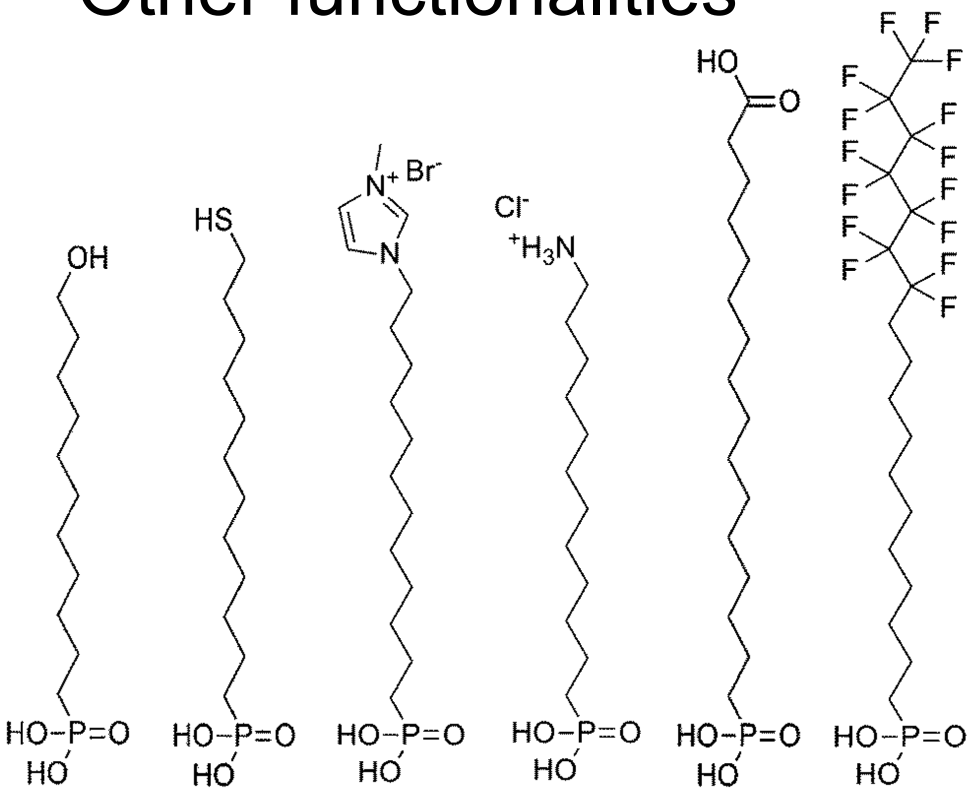




SAM functionalities

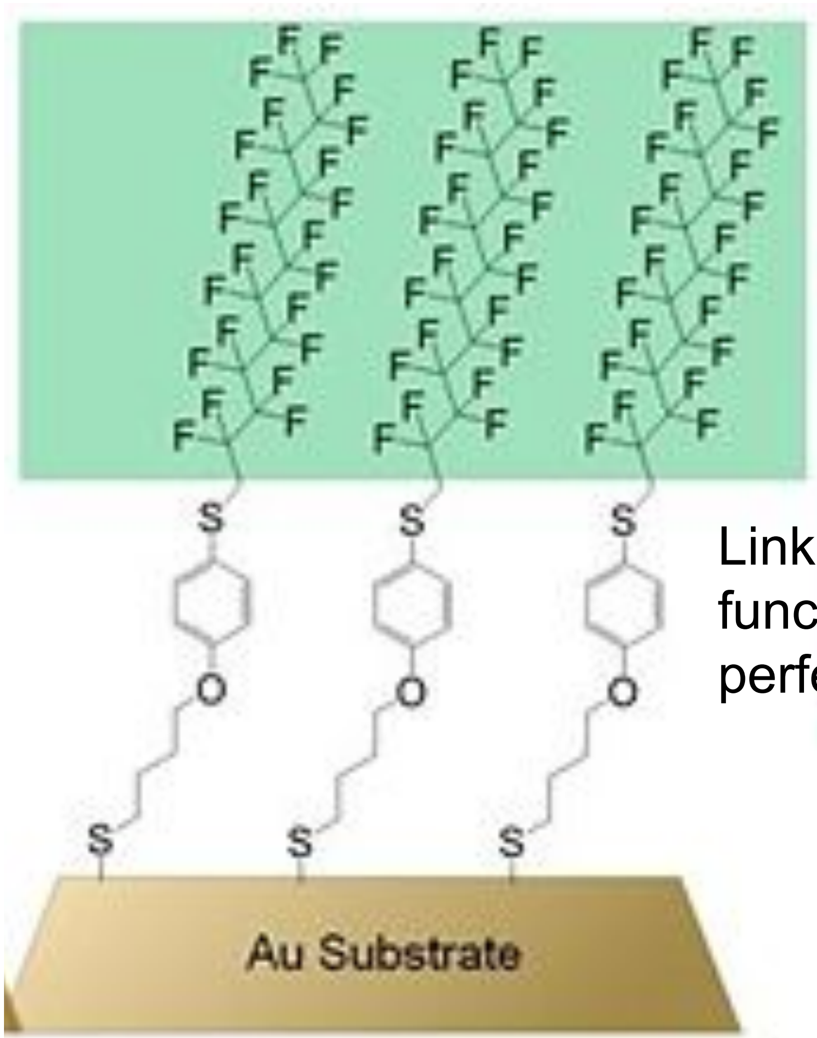
Other functionalities

Hydrophilic, with polar hydroxyl-groups (OH)



Hydrophobic fluorinated surface

Perfluorinated surface



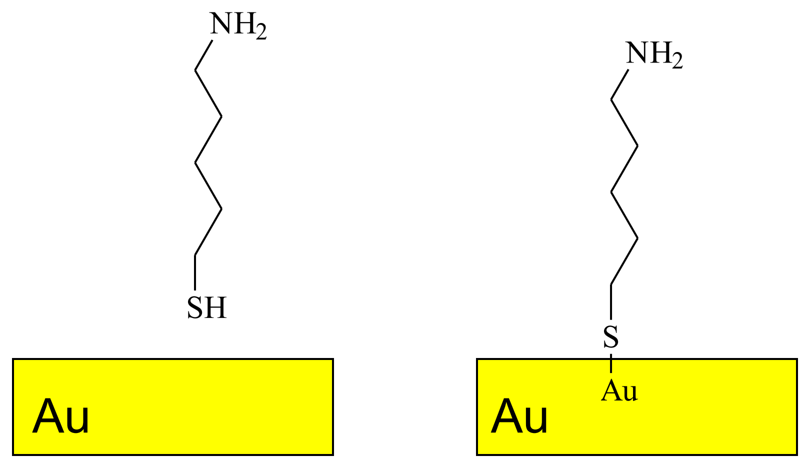
Fluorinated surface the most hydrophobic.

Linker molecule affects distance of functional group from surface, and coating perfection.

Au-S bond (thiol-bond) is very strong (otherwise gold does not readily react; that is why noble metals are called noble)

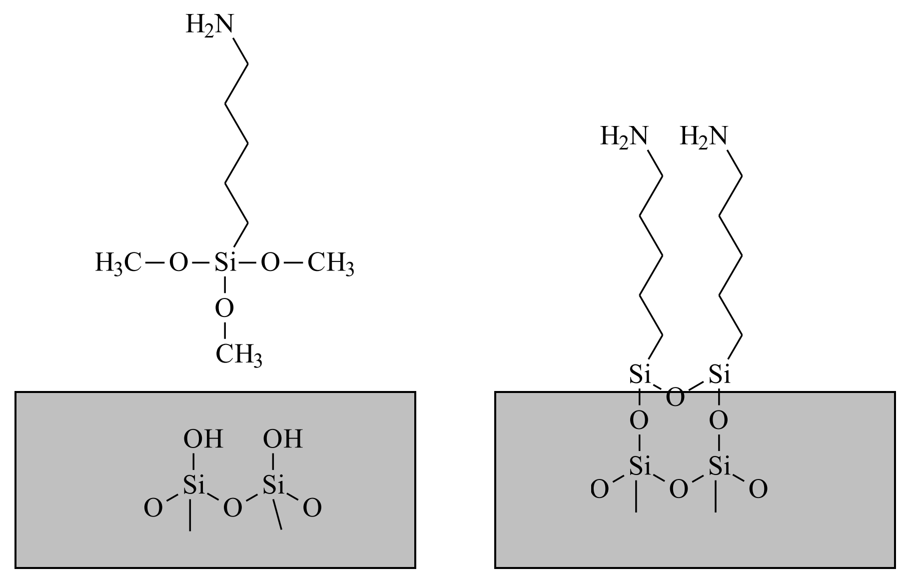
How to make a surface charged

Aminoalkanethiols



Example 1: Self-assembled monolayers (SAM) on gold

- Thiol –SH makes a covalent bond to Au
- Amino $-NH_2$ becomes positively charged $-NH_3^+$ under acidic conditions



Example 2: Silane chemistry on silica, glass, Si-wafer

Native oxides

- Native oxides, e.g. SiO_2, TiO_2, CuO form in room air, self-limited to ~ a few nm
- Thin oxides of slightly better quality can be made by e.g. acid treatment, boiling HNO_3 + Si ➔ SiO_2 film 2-3 nm
- Oxygen plasma and ozone obviously can be used, too

Native oxides are thin !

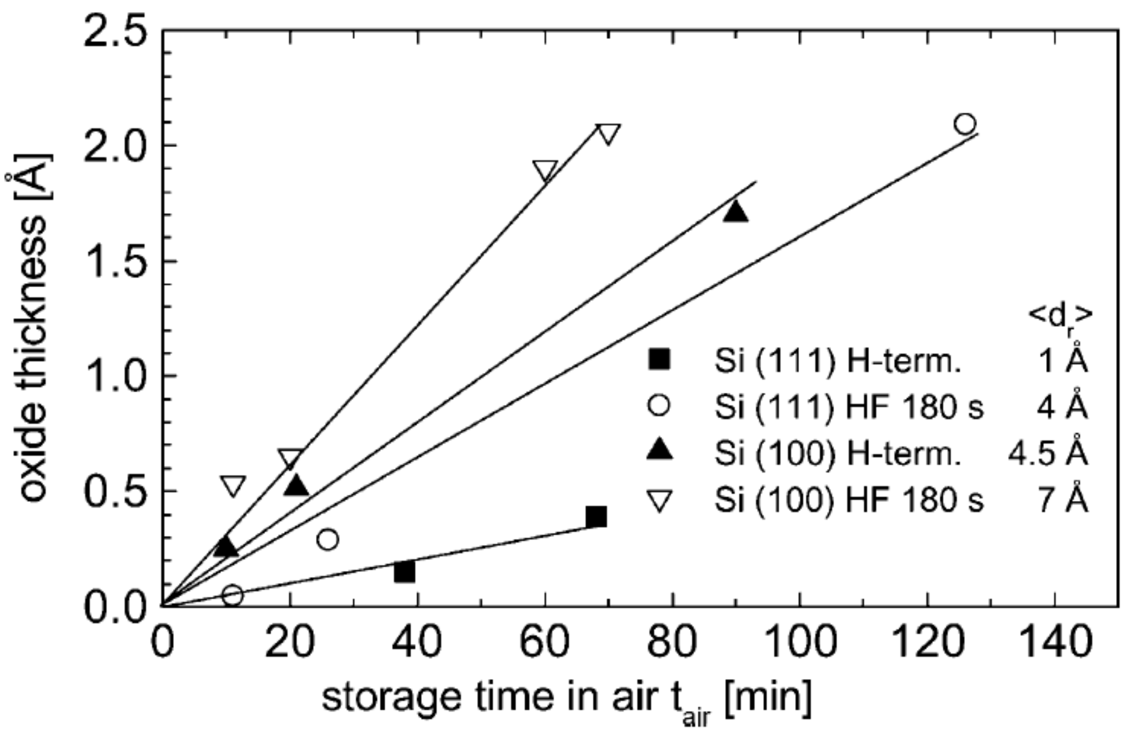


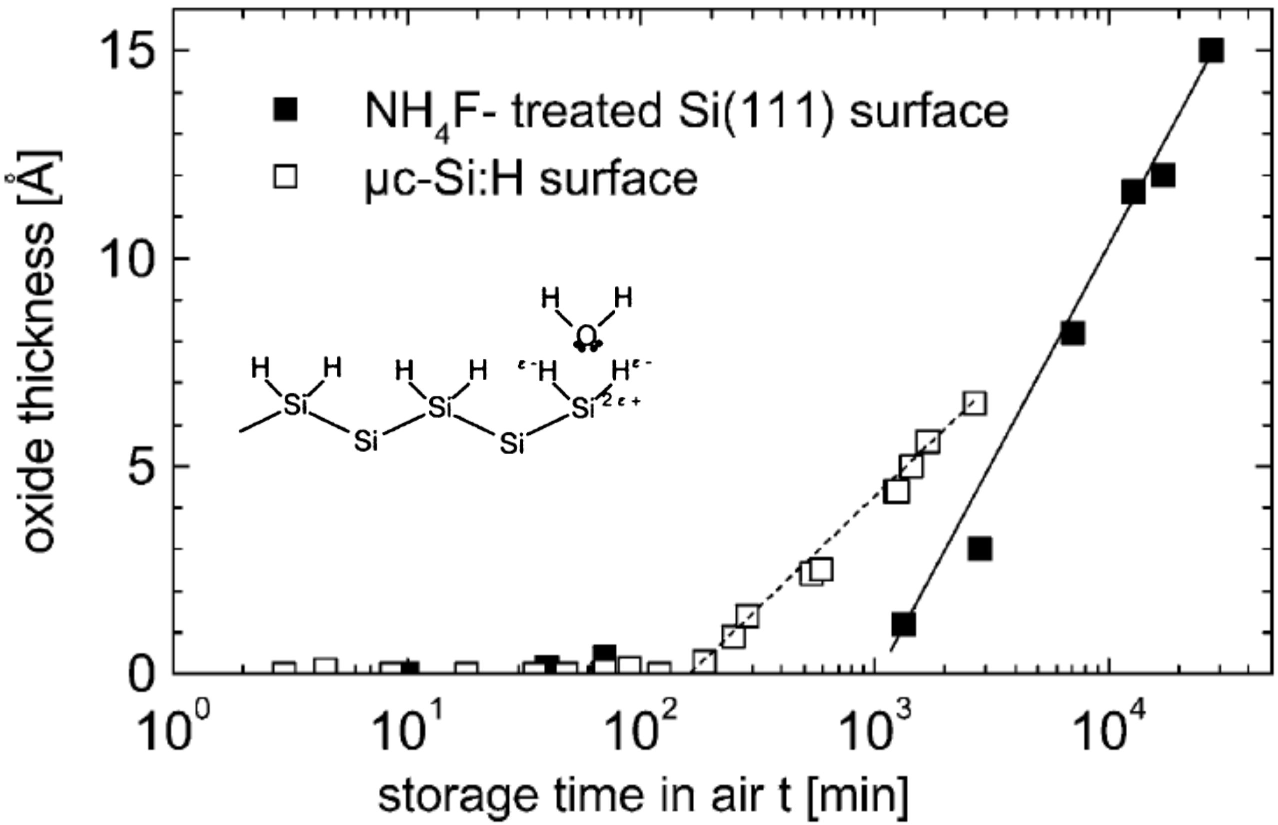
Fig. 4. Native oxide-thickness $<d_{ox}>$ vs. storage time in clean-room air t_{air} on NH_4F- and HF-etched Si(1 1 1) and Si(1 0 0) during the initial phase of oxidation.

W. Henrion et al. / Applied Surface Science 202 (2002) 199–205

Passivation

- Surface specie chosen to be inactive
- Just the outermost atoms sometimes enough
- Sometimes native oxide works
- Sometimes monomolecular layer enough
- But you may need to coat the surface for real

Passivation delays native oxide



”To prepare atomically flat H-terminated surfaces the samples were reoxidized in deionized water of 18 Mohm-cm resistivity at 80^{o}C for 60 min. Afterwards the wafers were placed into NH_4F solution for 6.5 min. To minimize dissolved oxygen, the NH_4F solution was bubbled by nitrogen and the preparation was carried out under dry N_2-atmosphere.”

W. Henrion et al. / Applied Surface Science 202 (2002) 199–205

Aluminum plasma etching

- Done in vacuum
- $2\ Al + 3Cl_2 \rightarrow 2\ AlCl_3$ (moderately volatile product)
- After etching, in room air, residues of $AlCl_3$ react with atmospheric water vapor:
- $AlCl_3 + xH_2O \rightarrow Al + yHCl + zH_2O$
- But: $2Al + 6HCl \rightarrow 2\ AlCl_3 + 3\ H_2$
- This is wet etching reaction of aluminum

Aluminum plasma etching

Solution 1:

- After etching in vacuum, we passivate the surface before atmospheric exposure
- Oxygen plasma ➔ Al_2O_3 formed
- Then take wafer out of the reactor

Solution 2:

- Immediately after taking away from vacuum, wash vigorously in water to remove all $AlCl_3$

Rinsing and drying are essential

Polyallylamine (PA) film was prepared as follows:

- glass slide was rinsed three times with DI water,
- soaked in 70% ethanol for 15 min,
- **rinsed** three times with DI water.

Subsequently,

- the glass was immersed in 6 M nitric acid for 20 min,
- then thoroughly rinsed in DI water.
- the glass was then exposed to oxygen plasma,
- treated with pure GOPTS at 37 °C for 60 min,
- then with 15% PA in water (pH = 11) and left to react at 75 °C for 36 h in a closed container.

Subsequently, the films were

- rinsed with DI water (10 times) to remove unattached polymer
- **dried** with nitrogen

- This is an antiviral coating.

ACS Appl. Mater. Interfaces 2020, 12, 31, 34723–34727

COVID-19 resistant surface

The Cu_2O/PU coating was fabricated as follows.

- A very thin layer of PU was applied to a glass slide using a sponge and then left to dry for approximately 8 min to allow partial curing of the polymer.
- Cu_2O (10%) in ethanol suspension was sonicated for 3 min, and then, 1 mL was applied to the PU film and left to partially dry for about 5 min at room temperature.
- The film was then heated in an oven at 120 °C for 2 h to finish the cure, forcefully blown with compressed nitrogen gas, washed thoroughly with DI water, and dried with a stream of nitrogen gas.
- Each piece was then cleaned with argon plasma to remove excess polyurethane.
- After plasma cleaning, the film was wetted by water, but the advancing water contact angle was recovered after 1 day.

ACS Appl. Mater. Interfaces 2020, 12, 31, 34723–34727